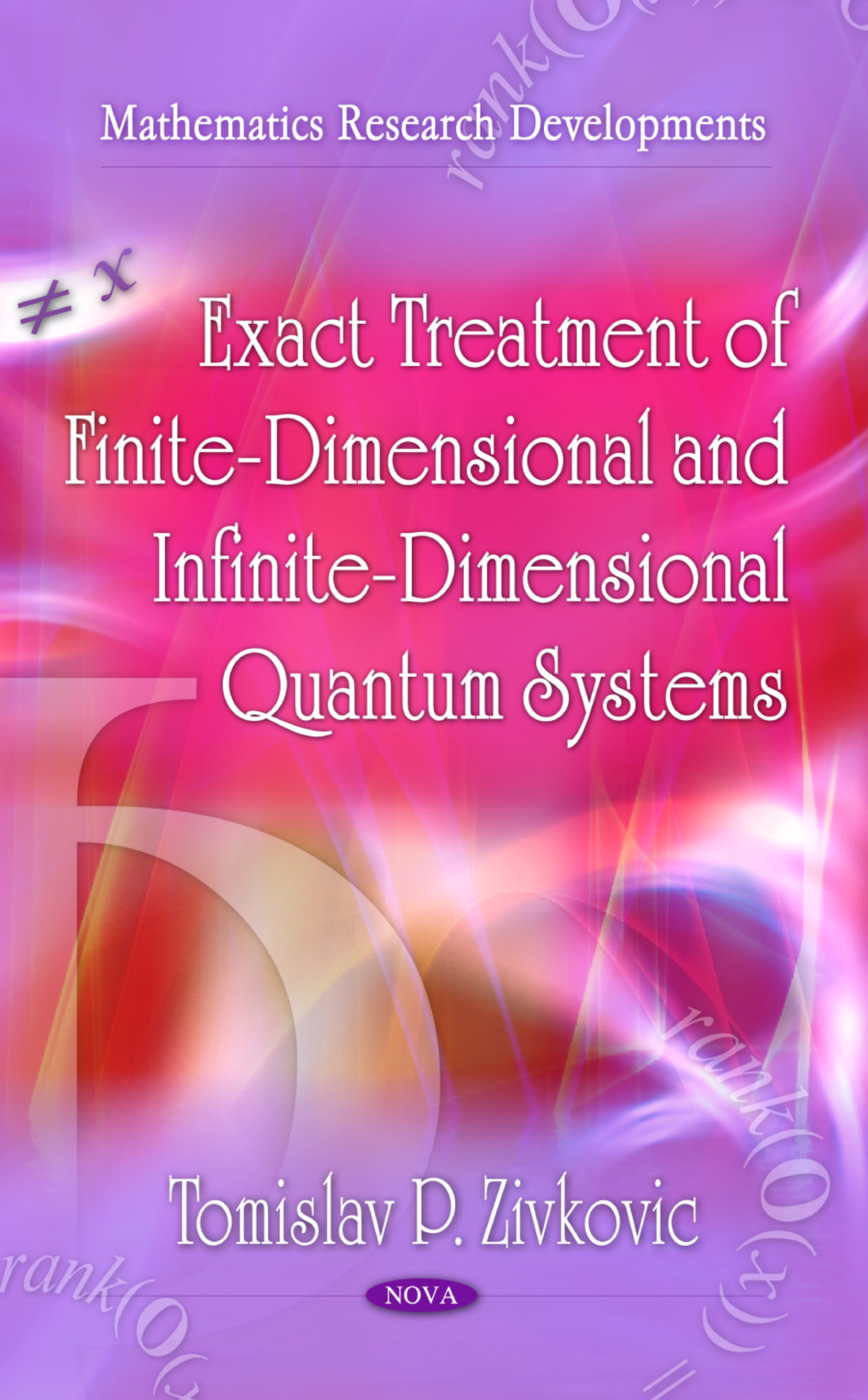

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Exact Treatment of Finite-Dimensional and Infinite-Dimensional Quantum Systems

Tomislav P. Zivkovic

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EXACT TREATMENT OF FINITE-DIMENSIONAL AND INFINITE-DIMENSIONAL QUANTUM SYSTEMS

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Nova Science Publishers, Inc.
New York

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Available upon Request
ISBN: 978-1-61668-890-5 (eBook)

Published by Nova Science Publishers, Inc. ✍ New York

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PREFACE

This book introduces a new method that produces exact solutions of finite- and infinite-dimensional modified systems. In this method, named Low Rank Modification (LRM), eigenvalues and eigenstates of a modified system are expressed in terms of the known eigenvalues and eigenstates of the original system. In this respect LRM is similar to the perturbation approach. However, there are profound differences. Perturbation theory relies on power series expansion, in most cases it produces only an approximate result, and it breaks down if the perturbation is to strong. Advantage of the LRM is that it is exact, regardless of how strong is the perturbation of the original system. Numerical efficiency of LRM depends essentially on the rank of the operators that represent modification of this system, and not on the strength of this modification. LRM applies to almost arbitrary eigenvalue problems. It applies to standard as well to generalized eigenvalue equations. As long as modification of the parent system is represented by finite rank operators, it applies also to infinite-dimensional systems. In addition, it applies to time-independent as well as to time-dependent systems.

LRM is particularly suitable for the treatment of those problems where modification of the original system is too large to be treated efficiently within a standard perturbation expansion approach. The method is illustrated with several examples involving finite-dimensional as well as infinite-dimensional systems. As a particular example, vibrational isotope effect in the harmonic approximation is treated within this formalism.

Low Rank Modification should offer graduate students as well as research workers a new tool for the treatment of many presently intractable eigenvalue problems as well as a new insight into those eigenvalue problems which can be efficiently solved by some other methods.

ACKNOWLEDGMENTS

This book is a result of my efforts to develop a general non-perturbative method in order to replace standard perturbation expansion in the treatment of eigenvalue problems involving finite-rank modifications of finite- and infinite-dimensional systems. My primary goal was to develop such a formalism which will not break down if the perturbation is to strong, and which will provide an exact solution with reasonable computational complexity, however large this perturbation. Accordingly, this method could not be based upon standard perturbation approach which relies on power series expansion and which is limited by radius of convergence of this series. As a result, Low Rank Modification (LRM) was developed in a series of papers. This method produces correct results (eigenvalues and eigenstates of the modified system) however strong perturbation of the original system, as long as this perturbation is represented by finite rank operators.

My thanks are due to Dr. S. Lugomer from the Institute Rudjer Bošković in Zagreb who helped with many valuable suggestions during the preparation of this book.

T. P. Živković

Chapter 1

INTRODUCTION

There are very few quantum systems that can be solved exactly. In most cases one has to use some approximate method. One of the most important approximate methods is perturbation expansion [1-3]. The main idea of this method is simple: if one knows the solution of some parent system $\mathcal{A}$, one can find the solution of the "perturbed" system $\mathbf{C}$. It is assumed that the system $\mathbf{C}$ does not differ from the parent system very much, in which case "perturbation" is small. Next one expresses eigenvalues and eigenstates of the perturbed systems as a power series expansion in terms of the eigenvalues and eigenstates of the parent system. Hence in order to obtain the solution of the perturbed system, one has to know the solution of the parent system.

There are two problems with this approach. First, computation of each successive term in the perturbation expansion is in most cases much more time-consuming than the computation of the preceding term. One is hence usually restricted to the calculation of only few leading terms in this expansion. Hence one obtains only an approximate and not an exact solution of the perturbed system. If the perturbation is not small, in order to obtain an acceptable solution one has to calculate so many terms that the entire approach becomes computationally unacceptable. Second, if the perturbation is large, perturbation expansion may diverge, in which case the solution cannot be obtained in this way. However, the problems which involve large perturbations are in many cases of prime interest. For example, if one knows the solution of some molecule $\mathcal{A}$, one would like to find the solution of the related "perturbed" molecule $\mathbf{C}$ which differs from the original molecule by a single heteroatom substitution or by few such substitutions. However, the replacement of an atom by a heteroatom is by no means a small perturbation. Hence such and similar problems cannot be treated efficiently within the standard perturbation theory.

A new approach, which avoids such problems, was developed some time ago [4,5]. This approach was originally named Low Rank perturbation (LRP). However, the term "perturbation" was misleading suggesting that this approach is a variant of the perturbation expansion, which is not the case. In order to avoid any further misunderstanding, this method was recently renamed Low Rank Modification (LRM) [6].

LRM is a general mathematical method by which one can express the eigenvalues and the eigenstates of the modified system $\mathbf{C}$ in terms of the eigenvalues and the eigenstates of the parent system $\boldsymbol{A}$. In this respect LRM is similar to the perturbation approach. However, there are profound differences. Perturbation method relies on power series expansion, in most cases it produces only an approximate result, and it breaks down if the perturbation is to strong. On the other hand, LRM is exact regardless of how strong is the perturbation of the original system. Hence LRM can successfully treat many systems where standard perturbation expansion fails. LRM applies to almost arbitrary eigenvalue problems. Moreover, it applies to standard as well as to generalized eigenvalue equations. As long as modification of the parent system is represented by finite rank operators, it applies also to infinite-dimensional systems. In addition, it applies to time-independent as well as to time-dependent systems. Numerical efficiency of LRM depends essentially on the rank of the operators that represent modification of the original system, and not on the strength of this modification. This method is hence particularly suitable for those cases when this rank is relatively small. Substitution of an atom by a heteroatom in a large molecule, provided this substitution changes molecular geometry only in the immediate vicinity of this substitution, can be approximated as such a low rank modification. Similar example is a substitution of one or few atoms by isotopes of those atoms. Such substitutions have negligible effect on the molecular wavefunctions and on the corresponding energies. However, they have a significant influence on the molecular vibrations. Accordingly, vibrational isotope effect is another example of the modification of the original system which is not small but which can be represented as a low rank modification.

There are two qualitatively different ways how the original parent system can be modified: One can modify this system either externally and/or internally. In an external modification parent system $\boldsymbol{A}$ interacts with a finite-dimensional base system $\boldsymbol{B}$. Given the solution of the parent system, one has to find the solution of the combined system $\boldsymbol{C}$. In the case of the internal modification, finite-dimensional portion inside the parent system $\boldsymbol{A}$ is affected by the modification to produce modified system $\boldsymbol{C}$. Once again, given the solution of the parent system $\boldsymbol{A}$, one has to find the solution of the modified system $\boldsymbol{C}$. There is also a possibility to have simultaneously both types of modification and to modify parent system $\boldsymbol{A}$ internally as well as externally. Such more general modifications of the parent system will not be considered here.

1.1. GENERAL PLAN OF THE PRESENTATION

Presentation of the LRM approach is organized in the succeeding chapters as follows. In the second chapter finite-dimensional systems are considered. Those systems are treated in a most general form, as represented by the generalized eigenvalue equation. The same applies to the modified systems. In the case of an external modification, n-dimensional parent system $\boldsymbol{A}_n$ interacts with a ρ-dimensional base system $\boldsymbol{B}_\rho$ forming a combined $(n+\rho)-$dimensional modified system $\boldsymbol{C}_{n+\rho}$. In the case of an internal modification, n-dimensional parent system $\boldsymbol{A}_n$ is modified internally. This modification involves σ-dimensional subspace X_σ^{int} of the original n-dimensional space X_n^a. Thus one produces n-dimensional modified system $\boldsymbol{C}_n$. LRM treats external and internal modifications of the original parent system $\boldsymbol{A}_n$ in the similar though not in the identical way. In both cases one has to distinguish two types of eigenvalues and eigenstates of the modified system. If an eigenvalue ε_s of the modified system (either combined system $\boldsymbol{C}_{n+\rho}$ in the case of an external modification or modified system $\boldsymbol{C}_n$ in the case of an internal modification) differs from all the eigenvalues λ_i of the parent system $\boldsymbol{A}_n$, this eigenvalue and the corresponding eigenstate is cardinal, otherwise it is singular. In the case of external modifications all cardinal solutions of the combined system $\boldsymbol{C}_{n+\rho}$ can be obtained as solutions of the $(\rho\times\rho)$ nonlinear matrix eigenvalue equation. In the case of internal modifications all cardinal solutions of the modified system $\boldsymbol{C}_n$ can be obtained as solutions of (another) $(\sigma \times \sigma)$ nonlinear matrix eigenvalue equation. LRM expressions for singular solutions are obtained in the similar way. However, those solutions are usually much less numerous and much less important than cardinal solutions. Operation count of a standard diagonalization of an $n \times n$ matrix is of the order $O(n^3)$ [7,8]. Hence if $\rho << n$ in the case of external modifications or if $\sigma << n$ in the case of internal modifications and if the modification is not small (in which case it cannot be treated efficiently by various perturbation expansion methods), LRM will be numerically superior to other approaches. An example of the LRM treatment of external modifications involving parent system $\mathbf{A}_n$ and base system $\mathbf{B}_\rho$ which are both described by generalized eigenvalue equations and which are subject to the generalized interaction is given. Concerning internal modifications, LRM is applied to the vibrational isotope effect in the harmonic approximation. As an illustration, vibration isotope effect of few selected molecules is treated in this way.

In Chapter 3 finite rank modifications of infinite-dimensional systems are considered. In order to emphasize key points in the transition from the LRM treatment of finite-dimensional systems to the LRM treatment of infinite-dimensional systems, infinite-dimensional parent system $\boldsymbol{A}_\infty$ is described not by a generalized but rather by a standard eigenvalue equation. Most infinite-dimensional systems that are of interest are usually described in this way.

In general, system $\boldsymbol{A}_\infty$ may contain discrete as well as continuous eigenvalues. Continuous eigenvalues of this system can be contained in several eigenvalue bands. The set of all continuous eigenvalues of $\boldsymbol{A}_\infty$ forms a range D. This range can consist of several disconnected intervals. Modified system $\boldsymbol{C}_\infty$ can also contain discrete eigenvalues as well as continuous eigenvalues. One finds that continuous eigenvalues of $\boldsymbol{C}_\infty$ are contained in the same range D where continuous eigenvalues of the parent system $\boldsymbol{A}_\infty$ are contained. In order to maintain clear distinction between the solutions of $\boldsymbol{A}_\infty$ and the solutions of $\boldsymbol{C}_\infty$, discrete solutions of $\boldsymbol{C}_\infty$ are referred to as *isolated solutions*, while continues solutions of $\boldsymbol{C}_\infty$ are referred to as *embedded solutions*. The notion of cardinal and singular solutions which applies to finite-dimensional modified systems can be generalized to infinite-dimensional modified systems. If an isolated eigenvalue ε_s of modified system $\boldsymbol{C}_\infty$ differs from all discrete eigenvalues λ_i of the parent system $\boldsymbol{A}_\infty$, this eigenvalue and the corresponding eigenstate (or eigenstates) is cardinal, otherwise it is singular. This is a natural generalization of the notion of cardinal and singular solutions from finite-dimensional systems to isolated solutions of infinite-dimensional systems. In the LRM approach all isolated cardinal solutions of the modified system are obtained from the *generic* eigenvalue equation. In the case of external modifications this is a $\rho \times \rho$ nonlinear matrix eigenvalue equation, while in the case of internal modifications this is (another) $\sigma \times \sigma$ nonlinear matrix eigenvalue equation. Similar equations are obtained for isolated singular solutions of the modified system.

Concerning embedded solutions, distinction between embedded cardinal and embedded singular solutions is more subtle. Key quantity in this distinction is *fractional shift* $x(\varepsilon,\ldots)$. Fractional shift is defined as the ration of two infinitesimal quantities, and with each embedded eigenstate $\left|\Psi(\varepsilon,\ldots)\right\rangle$ of the modified system is associated the corresponding fractional shift. As far as the eigenstate $\left|\Psi(\varepsilon,\ldots)\right\rangle$ is concerned, fractional shifts that differ by an integer cannot be distinguished. Hence one can confine fractional shift to the interval $[0,1)$. Fractional shift confined to this interval is defined as a *principal value* of a fractional shift. Provided fractional shift is confined to its principal value, fractional shift $x(\varepsilon,\ldots)=0$ is associated with embedded singular solutions of the modified system, while fractional shift $x(\varepsilon,\ldots)\neq 0$ is associated with embedded cardinal solutions of the modified system. Embedded cardinal solutions of the modified system can be obtained from the solution of the *fractional shift eigenvalues equation.* In the case of external modifications, for each $\varepsilon \in D$ fractional shift eigenvalue equation is a $\rho \times \rho$ linear matrix eigenvalues equation. One finds that for each $\varepsilon \in D$ modified system may have at most ρ embedded cardinal eigenstates and at most ρ corresponding fractional shifts. Those eigenstates and fractional shifts can be obtained from the solution of the fractional shift eigenvalue equation. Similar equation can be derived for embedded singular solutions which have fractional shift zero. However, as in the case of isolated solutions, embedded singular solutions are much less important than embedded cardinal solutions.

In conclusion, in the case of infinite-dimensional modified systems most important are cardinal solutions. All those solutions can be obtained from two eigenvalue equations, *generic* eigenvalue equation and *factional shift* eigenvalue equation. Isolated cardinal eigenvalues and eigenstates can be obtained from the solution of the *generic eigenvalue equation,* while embedded cardinal eigenvalues and eigenstates can be obtained from the solution of the *fractional shift* eigenvalue equation. In the case of external modifications generic equation is a $\rho \times \rho$ nonlinear eigenvalues equation, while for each $\varepsilon \in D$ fractional shift eigenvalue equation is a $\rho \times \rho$ linear eigenvalues equation. Similar results are obtained for internal modifications of infinite dimensional parent systems. In this way LRM reduces infinite-dimensional eigenvalue problems which are usually impossible to solve or for which one can at best obtain only an approximate solution, into two finite-dimensional eigenvalue problems. Those finite-dimensional problems can be successfully treated by known mathematical methods. LRM thus provides an exact solution to finite rank modifications of infinite-dimensional systems.

In many cases of interest is not the entire modified system $\boldsymbol{C}_\infty$, but rather only a small portion of this system. For example, in the case of an external modification, base finite-dimensional system $\boldsymbol{B}_\rho$ is usually of prime interest. From the point of view of this system, infinite-dimensional parent system $\boldsymbol{A}_\infty$ plays the role of the surrounding of $\boldsymbol{B}_\rho$. System $\boldsymbol{B}_\rho$ without the interaction with its surrounding is an isolated system. This system, subject to the interaction with $\boldsymbol{A}_\infty$, is an open system. LRM provides an exact description of open quantum systems. It is remarkable that exact solutions to ρ-dimensional open quantum systems are provided by two $\rho \times \rho$ eigenvalue equations, though the corresponding combined systems are infinite-dimensional. It turns out that, as far as properties of open quantum systems are concerned, huge amount of information about infinite-dimensional parent system $\boldsymbol{A}_\infty$ (surrounding of $\boldsymbol{B}_\rho$) is redundant. As an illustration, in the third chapter several examples of the LRM treatment of infinite-dimensional modified systems are given.

In the last chapter finite rank modifications of infinite-dimensional time-dependent systems are considered. If the Hamiltonian of the modified system is time-independent, general time-dependent eigenstate of the modified system can be expressed in terms of the eigenstates and eigenvalues of the corresponding time-independent system. LRM treatment of such time-dependent systems is thus reduced to the LRM treatment of the corresponding time-independent systems. At first sight, restriction to time-independent Hamiltonians seems to be a severe drawback of the LRM approach. However, from a more general point of view, such an approach is entirely acceptable. If namely Hamiltonian of the parent infinite-dimensional system $\mathbf{A}_\infty$ is time-dependent, one can always enlarge this system in such a way that a new (bigger) system is described by a time-independent Hamiltonian. Since the huge amount of information about the parent system $\mathbf{A}_\infty$ is redundant, enlargement of this system is not so critical for the LRM approach. Thus, in principle, each time-dependent system can be described with *some* time-independent Hamiltonian.

1.2. SOME MISSING POINTS

General LRM approach presented in the following chapters needs some additional work in order to be completed. In particular, external and internal modifications of the parent system $\mathbf{A}$ are at present treated separately, and the simultaneous presence of both types of modifications is not considered. However, for the efficient treatment of some problems extension of the LRM approach to such more general modifications is required. For example, if $\mathbf{A}_\infty$ represents an infinite dimensional perfect solid, due to the periodic symmetry one can obtain more or less reliable solution to this system [9]. Hence one can apply LRM formalism to describe internal modifications of this system, such as creation of local defects, influence of various impurities, etc. Creation of the surface can be also approximated in this way. However, if one considers external modifications, such as the interaction of the solid with a molecule situated on the surface of this solid, LRM treatment in the present form is not so reliable. Namely in this case a parent system $\mathbf{A}_\infty$ represents a solid with a surface. The solution of this system is not well known, since the presence of the surface destroys periodic symmetry, and therefore standard methods which rely on periodic symmetry cannot be applied [10]. In order to treat such and similar systems one has to extend present LRM formalism to a general case where internal as well as external modifications are simultaneously present. In the example considered, parent system $\mathbf{A}_\infty$ should represent infinite dimensional perfect solid which formally has no surface and no impurities and defects. Due to the periodic symmetry of such an idealized system, one can obtain more or less reliable solution to this system by many other methods [9]. Modified system contains now external as well as internal modifications. Creation of a surface can be approximated as an internal modification of the parent system $\mathbf{A}_\infty$. Simultaneously, interaction of a molecule (base system $\mathbf{B}_\rho$) with thus created surface can be approximated as an external modification of this system. Applying such a combined modification to the parent system $\mathbf{A}_\infty$ one should obtain reliable LRM description of the interaction of a molecule with the surface of an infinite solid.

Progress along above lines is already partially completed. In particular, general LRM expressions for the simultaneous external and internal modifications of finite-dimensional parent systems $\mathbf{A}_n$ are derived. Those expressions are not included here. Successful generalization of LRM formalism to combined modifications of finite-dimensional systems suggests that analogous generalization to combined modifications of infinite-dimensional systems should be also possible. In addition to the inclusion of such combined modifications into the LRM formalism, present LRM treatment of infinite-dimensional and time-dependent systems also requires some additional work. My conviction is that all those missing parts can be successfully incorporated into the general LRM formalism. LRM is thus likely to be developed into a powerful tool for the efficient mathematical treatment of many important eigenvalue problems involving finite-dimensional as well as infinite-dimensional systems.

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Chapter 2

FINITE-DIMENSIONAL SYSTEMS

Consider a finite-dimensional time-independent quantum system $\boldsymbol{A}_n$ that contains n eigenvalues λ_i and n eigenstates $|\Phi_i\rangle$. Usually those eigenvalues and eigenstates satisfy a standard eigenvalue equation $\mathbf{H}_a|\Phi_i\rangle = \lambda_i|\Phi_i\rangle$ ($i = 1,\cdots,n$) where $\mathbf{H}_a$ is a Hermitean operator, Hamiltonian of a system [1,2]. However, in some cases instead of this simple eigenvalue equation one has to consider a generalized eigenvalue equation

$$\mathbf{H}_a|\Phi_i\rangle = \lambda_i\mathbf{S}_a|\Phi_i\rangle, \qquad i = 1,\cdots,n, \tag{2.1a}$$

where $\mathbf{S}_a$ is positive-definite Hermitean operator. Eigenvalues λ_i of (2.1a) are real and the corresponding eigenstates $|\Phi_i\rangle$ span n-dimensional space X_n^a. Those eigenstates can be orthonormalized according to

$$\langle\Phi_i|\mathbf{S}_a|\Phi_j\rangle = \delta_{ij}, \; i,j = 1,\cdots,n. \tag{2.1b}$$

If $\lambda_i \neq \lambda_j$ eigenstates $|\Phi_i\rangle$ and $|\Phi_j\rangle$ are automatically orthogonal to each other according to (2.1b). However if $\lambda_i = \lambda_j$ one has to enforce this condition by some appropriate orthonormalization procedure such as Gram-Schmidt, QR, or alike [3,4].

Solution of a generalized eigenvalue equation (2.1) is for example required in the treatment of the molecular vibrations in the harmonic approximation. In the Cartesian coordinates this problem leads to the eigenvalue equation $\mathbf{F}|\Phi_i\rangle = \lambda_i \mathbf{M}|\Phi_i\rangle$ where $\mathbf{F}$ and $\mathbf{M}$ are force field and mass operators, respectively [5-8]. Those operators are Hermitean and in addition operator $\mathbf{M}$ is positive definite. As another example, consider various methods for the calculation of molecular electronic structure [2]. Molecular systems are too complicated to be solved exactly. Hence one has to apply an approximate method. One of the most important approximate methods is a Linear Combination of Atomic Orbitals (LCAO). In this approach one expands each molecular wave-function in terms of the finite number of known atomic orbitals. This leads to a matrix eigenvalue equation of a type (2.1a). Matrix $\mathbf{S}_a$ in this expression contains overlaps between various atomic orbitals. Orbitals situated on the same atom are orthogonal to each other. Overlaps between orbitals situated on two atoms that are in a molecule far from each other are usually so small that they can be neglected. However, overlaps between orbitals situated on adjacent atoms are usually not negligible. There are many semi-empirical methods which further simplify LCAO approach [2]. Some of those methods are so extreme as to neglect all overlaps between mutually distinct orbitals [2]. This applies for example to the Hückel molecular orbital theory (HMO) which treats only π-electron conjugated systems. However, in the treatment of general molecular systems involving σ-orbitals more realistic semi-empirical methods are needed [2]. Most of those methods require the solution of the eigenvalue equation (2.1a) where $\mathbf{S}_a$ is a nontrivial positive-definite operator. In conclusion, in order to treat many eigenvalue problems of practical interest, generalized eigenvalue equation (2.1a) should be considered.

LRM is not restricted to generalized eigenvalue equations of a type (2.1a) where $\mathbf{H}_a$ and $\mathbf{S}_a$ are Hermitean operators and where $\mathbf{S}_a$ is in addition positive definite. Within the LRM formalism one may treat more general eigenvalue equations where $\mathbf{H}_a$ and $\mathbf{S}_a$ are arbitrary operators which are not necessarily Hermitean [9]. In such more general cases left and right eigenstates of (2.1a) may differ and eigenvalues λ_i of this expression may be complex. However, in physics and chemistry of prime interest are eigenvalues equations of a type (2.1a) where $\mathbf{H}_a$ and $\mathbf{S}_a$ are Hermitean and where $\mathbf{S}_a$ is in addition positive-definite [1,2]. Restriction to such eigenvalues equations simplifies

LRM approach [10-13]. Therefore only such eigenvalues equations will be considered here. For the sake of reference the system $\boldsymbol{A}_n$ described by the eigenvalue equation (2.1a) will be referred to as a *parent system*.

2.1. INTERNAL AND EXTERNAL MODIFICATIONS OF FINITE-DIMENSIONAL SYSTEMS

One can modify parent system $\boldsymbol{A}_n$ in two different ways. One can modify this system *internally* or *externally*.

In the case of an internal modification, modified system $\mathbf{C}_n$ has the same dimension as the parent system $\boldsymbol{A}_n$. In particular, eigenstates $|\Psi_{\mathbf{s}}\rangle$ of $\mathbf{C}_n$ and eigenstates $|\Phi_i\rangle$ of $\boldsymbol{A}_n$ span the same space X_n^a. In the most general formulation, modification of the parent system is represented by two operators $\mathbf{V}_a$ and $\mathbf{P}_a$. Operator $\mathbf{V}_a$ modifies operator $\mathbf{H}_a$, while operator $\mathbf{P}_a$ modifies operator $\mathbf{S}_a$. Those operators are Hermitean, and they act in the space X_n^a. Both operators are scaled by the same coupling parameter β. This parameter is real and it is introduced for convenience, in order to have a clear insight into the effect of the change of the modification strength. If β is small, LRM expressions reduce to the well known expressions obtained within the formalism of the perturbation expansion. However if β is large, LRM produces qualitatively new results which cannot be obtained within a standard perturbation expansion approach. Those results usually describe qualitatively new features of the modified system which are in most cases not present in the parent system.

In the case of an internal modification, modified system $\mathbf{C}_n$ is described by the generalized eigenvalue equation

$$\mathbf{H}_c\,|\Psi_s\rangle = \varepsilon_s \mathbf{S}_c\,|\Psi_s\rangle, \qquad s = 1,\dots,n, \tag{2.2a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \beta\,\mathbf{V}_a, \qquad \mathbf{S}_c = \mathbf{S}_a + \beta\,\mathbf{P}_a, \tag{2.2b}$$

In order to guarantee reality of the eigenvalues ε_s, operator $\mathbf{S}_c$ is required to be positive-definite in X_n^a. This requirement imposes some restrictions on the modification operator $\mathbf{P}_a$ and on the coupling parameter β. There are no restrictions on the modification operator $\mathbf{V}_a$, except that this operator should be Hermitean. In analogy to (2.1b), eigenstates $\left|\Psi_s\right\rangle$ of (2.2a) can be orthonormalized according to

$$\left\langle\Psi_s\left|\mathbf{S}_c\right|\Psi_p\right\rangle = \delta_{sp}, \; s, p = 1, \ldots, n. \tag{2.2c}$$

The case of an internal modification is shown schematically in figure 2.1.

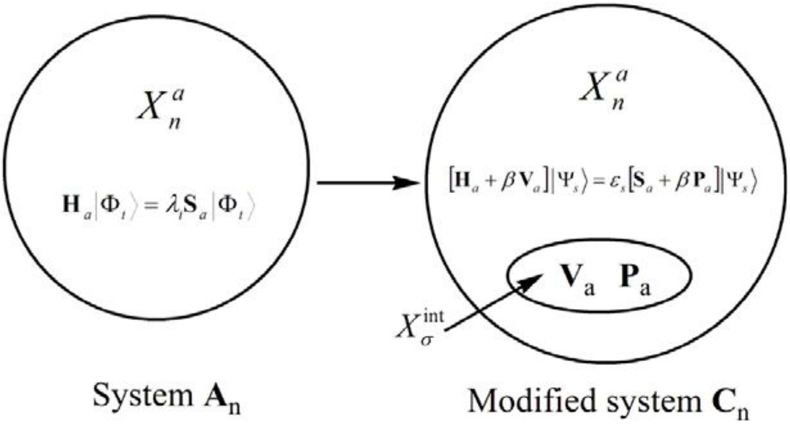

Figure 2.1. Internal modification of a finite-dimensional system. System $\mathbf{A}_n$ is modified internally by a generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. This modification effects interaction space X_σ^{int}.

In the LRM approach, the notion of *rank* and *range* of modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ is important. By definition, *range* of the operator $\mathbf{O}$ that acts in the space X is image of this operator [3,4]. In other words, this is the space spanned by all vectors of the type $\mathbf{O}|\phi\rangle$ where $|\phi\rangle \in X$. Dimension of this space is *rank* of $\mathbf{O}$[3,4]. If operator $\mathbf{O}$ is Hermitean, rank of $\mathbf{O}$ equals the number (counting degeneracies) of nonzero eigenvalues of this operator.

Above definition of rank and range of an operator $\mathbf{O}$ can be generalized in a natural way to the notion of *rank* and *range* of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. By definition, *range* of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$ is the space X_σ^{int} spanned by all states of the type $\mathbf{V}_a|\phi\rangle$ and by all states of the type $\mathbf{P}_a|\phi\rangle$ where $|\phi\rangle \in X_n^a$. Dimension of this space is *rank* of the generalized modification and it is denoted by σ. One easily finds $\sigma \le \sigma_h + \sigma_s$ where σ_h is the rank of the modification operator $\mathbf{V}_a$ while σ_s is the rank of the modification operator $\mathbf{P}_a$. In particular, if $\mathbf{P}_a = 0$ one has $\sigma = \sigma_h$, while if $\mathbf{V}_a = 0$ one has $\sigma = \sigma_s$. One can also consider operator $\mathbf{O}(x) = \mathbf{V}_a + x\mathbf{P}$ which depends on a parameter x and on modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$. One finds that for almost each $x \neq 0$ this operator satisfies $rank(\mathbf{O}(x)) = \sigma$ and $range(\mathbf{O}(x)) = X_\sigma^{\text{int}}$. One can have $rank(\mathbf{O}(x)) < \sigma$ only for some isolated points $x = x_0$. In this case range of the operator $\mathbf{O}(x_0)$ is a subspace of X_σ^{int}. The space X_σ^{int} which is the range of the generalized modification is the *interaction space*. It is that part of the space X_n^a which is modified by the operators $\mathbf{V}_a$ and $\mathbf{P}_a$.

Let $\{|\mu\rangle\}$ be a base in X_σ^{int} orthonormalized in a standard way

$$\langle \mu | \nu \rangle = \delta_{\mu\nu}, \qquad \mu, \nu = 1, \ldots, \sigma, \tag{2.3a}$$

This base can be extended to the orthonormalized base $\{|\alpha\rangle\}$ in the space X_n^a:

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta}, \qquad \alpha, \beta = 1, \ldots, n, \tag{2.3b}$$

For the sake of reference, labels α and β will refer to the entire space X_n^a, while labels μ and ν will refer to the interaction space X_σ^{int}, subspace of X_n^a. Base $\{|\mu\rangle\}$ considered as a set is a subset of the set $\{|\alpha\rangle\}$. In the base $\{|\alpha\rangle\}$ equations (2.1a) and (2.2a) are $n \times n$ matrix eigenvalue equations, while in the base $\{|\mu\rangle\}$ operators $\mathbf{V}_a$ and $\mathbf{P}_a$ are $\sigma \times \sigma$ matrices. Projection operator $\mathbf{I}_\sigma^{\text{int}}$ on the space X_σ^{int} can be expressed in terms of the vectors $|\mu\rangle$ as

$$\mathbf{I}_\sigma^{\text{int}} = \sum_{\mu}^{\sigma} |\mu\rangle\langle\mu|, \tag{2.3c}$$

while unit operator $\mathbf{I}_n^a$ in the space X_n^a can be expressed in terms of vectors $|\alpha\rangle$ as

$$\mathbf{I}_n^a = \sum_{\alpha}^{n} |\alpha\rangle\langle\alpha|. \tag{2.3d}$$

Since modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ are nonzero only over the interaction space $\mathbf{I}_\sigma^{\text{int}}$, those operators satisfy

$$\mathbf{V}_a = \mathbf{I}_\sigma^{\text{int}} \mathbf{V}_a \mathbf{I}_\sigma^{\text{int}}, \quad \mathbf{P}_a = \mathbf{I}_\sigma^{\text{int}} \mathbf{P}_a \mathbf{I}_\sigma^{\text{int}}. \tag{2.4}$$

As an example of the internal modification, consider replacement of one or several atoms in a large molecule with isotopes. To a very good approximation, isotopic substitutions do not change molecular geometry and they have negligible influence on the molecular electronic structure. However, such substitutions have significant influence on molecular vibrations. Given frequencies and normal modes of a parent molecule $\boldsymbol{A}_n$, of interest are frequencies and normal modes of various isotopomers $\mathbf{C}_n$ of this molecule. Similar examples of internal modifications are replacements of one or few selected atoms in a large molecule with heteroatoms, creation and/or destruction of chemical bonds, etc.

In the case of an external modification, system $\boldsymbol{A}_n$ interacts with another ρ-dimensional system $\boldsymbol{B}_\rho$ which is outside the original system $\boldsymbol{A}_n$. With the system $\mathbf{B}_\rho$ is associated ρ-dimensional space X_ρ^b which is orthogonal to the space X_n^a. In analogy to (2.1a), system $\boldsymbol{B}_\rho$ alone is described by the generalized eigenvalue equation

$$\mathbf{H}_b|\Theta_r\rangle = E_r\mathbf{S}_b|\Theta_r\rangle, \qquad r = 1,\cdots,\rho, \tag{2.5a}$$

where $\mathbf{H}_b$ and $\mathbf{S}_b$ are Hermitean operators that act in the space X_ρ^b and where $\mathbf{S}_b$ is in addition positive definite in this space. No other assumption about those operators is made. Hermiticity of those operators and positive definiteness of $\mathbf{S}_b$ ensures that the eigenvalues E_r of (2.5a) are real. In analogy to (2.1b), the corresponding eigenstates $|\Theta_r\rangle$ can be orthonormalized according to:

$$\langle\Theta_r|\mathbf{S}_b|\Theta_t\rangle = \delta_{rt}, \quad r,t = 1,\cdots,\rho. \tag{2.5b}$$

Since the states $|\Theta_r\rangle$ form a complete set in X_ρ^b, this implies

$$\sum_r^\rho |\Theta_r\rangle\langle\Theta_r|\mathbf{S}_b = \mathbf{I}_\rho^b \qquad . \tag{2.5c}$$

where $\mathbf{I}_\rho^b$ is a projection operator on the space X_ρ^b.

Inclusion of the interaction between initially noninteracting systems $\mathbf{B}_\rho$ and $\boldsymbol{A}_n$ creates a combined $(\rho+n)$-dimensional system $\mathbf{C}_{n+\rho}$. Each state in this combined system is contained in the $(\rho+n)$-dimensional space $X_{n+\rho}^c$, orthogonal sum of spaces X_ρ^b and X_n^a. Interaction between subsystems $\mathbf{B}_\rho$ and $\boldsymbol{A}_n$ of the combined system $\mathbf{C}_{n+\rho}$ is described by the modification operators $\mathbf{V}$ and $\mathbf{P}$. Those operators are Hermitean and in analogy to the case of an internal modification, they are scaled by the coupling parameter β. This parameter is again introduced for convenience, in order to have a clear distinction between weak and strong modifications. In the case of an external modification, modification operators connect mutually distinct spaces X_ρ^b and

X_n^a, and those operators vanish over the space X_ρ^b as well as over the space X_n^a. Combined system $\mathbf{C}_{n+\rho}$ that includes this interaction is described by the generalized eigenvalue equation

$$\mathbf{H}_c \left|\Psi_s\right\rangle = \varepsilon_s \mathbf{S}_c \left|\Psi_s\right\rangle, \qquad s = 1,\ldots,n+\rho, \tag{2.6a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \mathbf{H}_b + \beta\mathbf{V}\,,\; \mathbf{S}_c = \mathbf{S}_a + \mathbf{S}_b + \beta\mathbf{P}\,, \tag{2.6b}$$

In order to guarantee reality of the eigenvalues ε_s, operator $\mathbf{S}_c$ is required to be positive-definite in $X_{n+\rho}^c$. In analogy to (2.2c), eigenstates $\left|\Psi_s\right\rangle$ of (2.6a) can be orthonormalized according to

$$\left\langle\Psi_s\left|\mathbf{S}_c\right|\Psi_p\right\rangle = \delta_{sp}\,,\; s,p = 1,\ldots,n+\rho\,. \tag{2.6c}$$

Let $\{|r\rangle\}$ be a base in X_ρ^b orthonormalized in a standard way

$$\langle r|t\rangle = \delta_{rt}\,,\; r,t = 1,\ldots,\rho\,, \tag{2.7a}$$

Let further $\{|\alpha\rangle\}$ be a base in X_n^a orthonormalized according to (2.3b). Projection operator $\mathbf{I}_\rho^b$ on the space X_ρ^b can be expressed in terms of the vectors $|r\rangle$ as

$$\mathbf{I}_\rho^b = \sum_r^\rho |r\rangle\langle r|\,. \tag{2.7b}$$

while projection operator $\mathbf{I}_n^a$ on the space X_n^a is given by (2.3d).

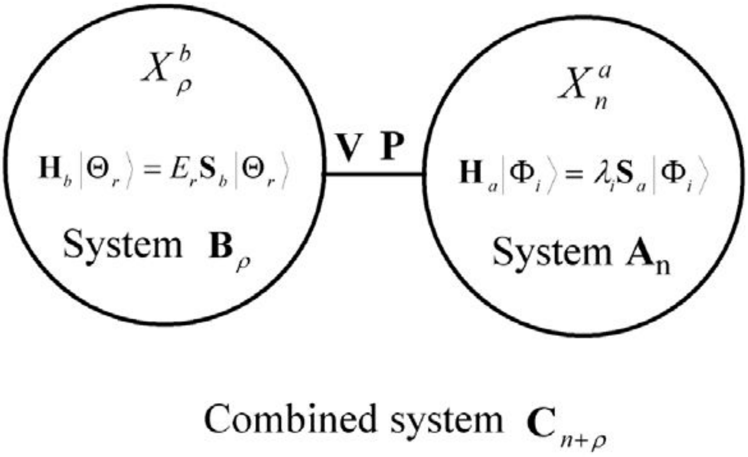

Figure 2.2. External modification of a finite-dimensional system. Finite systems $\mathbf{A}_n$ and $\mathbf{B}_\rho$ interact with generalized interaction $(\mathbf{V},\mathbf{P})$. This forms a combined system $\mathbf{C}_{n+\rho}$. From the point of view of the system $\mathbf{B}_\rho$, this system is modified externally by the interaction with the system $\mathbf{A}_n$.

The case of an external modification is shown schematically in figure 2.2. Note that the role of the mutually interacting systems $\mathbf{B}_\rho$ and $\mathbf{A}_n$ is symmetrical. One can consider system $\mathbf{A}_n$ to be a parent system which is modified by the interaction with a base system $\mathbf{B}_\rho$. One can also consider system $\mathbf{B}_\rho$ to be a parent system which is modified by the interaction with a base system $\mathbf{A}_n$. I will take this first point of view and consider system $\mathbf{B}_\rho$ to be a base system and system $\mathbf{A}_n$ to be a parent system. All expressions to be derived are equally valid if the roles of systems $\mathbf{B}_\rho$ and $\mathbf{A}_n$ are permuted. Essentially what one has is the interaction of two systems that are both subsystems of the larger system $\mathbf{C}_{n+\rho}$. Each of those two systems can be considered to be modified by the interaction with another system.

The role of the base space X_ρ^b in the case of an external modification is similar to the role of the interaction space X_σ^{int} in the case of an internal modification. Note also that operator $\mathbf{I}_n^a$ is in the case of an internal modification a unit operator since X_n^a is the entire space considered, while in the case of an external modification $\mathbf{I}_n^a$ is a projection operator on the space X_n^a, subspace of the space $X_{n+\rho}^c$.

Since in the case of an external modification operators $\mathbf{V}$ and $\mathbf{P}$ that describe interaction between systems $\mathbf{B}_\rho$ and $\boldsymbol{A}_n$ have non-vanishing matrix elements only between spaces X_ρ^b and X_n^a, those operators satisfy

$$\mathbf{V} = \mathbf{I}_\rho^b \mathbf{V} \mathbf{I}_n^a + \mathbf{I}_n^a \mathbf{V} \mathbf{I}_\rho^b, \qquad \mathbf{P} = \mathbf{I}_\rho^b \mathbf{P} \mathbf{I}_n^a + \mathbf{I}_n^a \mathbf{P} \mathbf{I}_\rho^b. \tag{2.8}$$

From the point of view of the base system $\mathbf{B}_\rho$, parent system $\boldsymbol{A}_n$ plays the role of the surrounding of $\mathbf{B}_\rho$. System $\mathbf{B}_\rho$ without the interaction with the system $\boldsymbol{A}_n$ is a closed system. This system alone is described by the eigenvalue equation (2.5a). System $\mathbf{B}_\rho$ subject to the interaction with its surrounding is an open system. If from the solution of the combined system $\mathbf{C}_{n+\rho}$ one extracts only those properties that refer to its subsystem $\mathbf{B}_\rho$, one obtains properties of an open system. Therefore expressions to be derived can be considered to describe an open quantum system.

A comment concerning quantities σ and ρ is in place here. LRM expressions are numerically most efficient if those quantities are small with respect to the dimension n of the space X_n^a, i.e. if $\sigma << n$ in the case of internal modifications and if $\rho << n$ in the case of external modifications. In the case of an internal modification, quantity σ is the rank of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. The corresponding interaction space X_σ^{int} is σ-dimensional and it is a range of this modification. In the case of an external modification, quantity ρ is the dimension of the system $\mathbf{B}_\rho$ that interacts with the n-dimensional parent system $\boldsymbol{A}_n$. By the known theorem of algebra, rank of the $n \times m$ matrix is at most $\min(n,m)$ [3,4]. In matrix form operator $\boldsymbol{V}$ is represented by one (ρ, n) and one (n, ρ) nonzero sub-matrix. The same applies to the operator $\mathbf{P}$. Thus one finds that if $n \geq \rho$ (which is usually the case) rank of the generalized modification $(\mathbf{V},\mathbf{P})$ is at most 2ρ. The quantity ρ is hence intimately connected with the rank of this generalized modification. Hence from the more general point of view, external modifications as well as internal modifications are both low rank modifications.

2.2. LRM TREATMENT OF EXTERNAL MODIFICATIONS

Consider an external modification of a ρ-dimensional base system $\mathbf{B}_\rho$. This system interacts with the n-dimensional parent system $\boldsymbol{A}_n$ through the generalized modification $(\mathbf{V},\mathbf{P})$. Combined system $\mathbf{C}_{n+\rho}$ is described by the generalized eigenvalue equation (2.6a). In analogy to the perturbation expansion, one assumes that eigenvalues λ_i and eigenstates $|\Phi_i\rangle$ of the system $\boldsymbol{A}_n$ are known. From those quantities one can construct Hermitean operator $\overline{\mathbf{\Omega}}(\varepsilon)$ which depends on a real parameter ε:

$$\overline{\mathbf{\Omega}}(\varepsilon)=\sum_{i(\lambda_i\neq\varepsilon)}^{n}\frac{|\Phi_i\rangle\langle\Phi_i|}{\varepsilon-\lambda_i}. \tag{2.9}$$

If ε equals some eigenvalue λ_i of the eigenvalue equation (2.1a) ($\varepsilon=\lambda_i$), the corresponding term or terms is excluded from the summation in (2.9).

Operator $\overline{\mathbf{\Omega}}(\varepsilon)$ is associated with the parent system $\boldsymbol{A}_n$. Since $\{|\Phi_i\rangle\}$ is a complete set in X_n^a, in the case $\varepsilon\notin\{\lambda_i\}$ one has $\overline{\mathbf{\Omega}}(\varepsilon)|\psi\rangle\neq 0$ for each nontrivial state $|\psi\rangle\in X_n^a$. Operator $\overline{\mathbf{\Omega}}(\varepsilon)$ is in this case nonsingular in X_n and hence $rank(\overline{\Omega}(\varepsilon))=n$. However, if $\varepsilon=\lambda_j\in\{\lambda_i\}$ one has $\overline{\mathbf{\Omega}}(\varepsilon)|\Phi_j\rangle=0$ and in this case $rank(\overline{\Omega}(\varepsilon))<n$.

With the base system $\mathbf{B}_\rho$ that interacts with the parent system $\boldsymbol{A}_n$ is associated Hermitean operator $\mathbf{\Omega}_b(\varepsilon)$

$$\mathbf{\Omega}_b(\varepsilon) = (\mathbf{V} - \varepsilon\,\mathbf{P})\overline{\mathbf{\Omega}}(\varepsilon)(\mathbf{V} - \varepsilon\,\mathbf{P}), \tag{2.10a}$$

This operator is a key quantity in the LRM formalism involving external modifications of finite dimensional quantum systems. Due to the expressions (2.8), operator $\mathbf{\Omega}_b(\varepsilon)$ has non-vanishing matrix elements only between the states contained in the base space X_ρ^b. Over the parent space X_n^a this operator vanishes. In the base $\{|r\rangle\}$ of the space X_ρ^b this operator is a $\rho \times \rho$ matrix with matrix elements

$$\Omega_{rt}^b(\varepsilon) \equiv \langle r|\mathbf{\Omega}_b(\varepsilon)|t\rangle = \sum_{i(\lambda_i \neq \varepsilon)}^{n} \frac{\langle r|\mathbf{V} - \varepsilon\,\mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{V} - \varepsilon\,\mathbf{P}|t\rangle}{\varepsilon - \lambda_i},$$
$$r,t = 1,\ldots,\rho\,. \tag{2.10b}$$

In order to construct operator $\mathbf{\Omega}_b(\varepsilon)$ it is not necessary to have complete information about eigenstates $|\Phi_i\rangle$ of $\mathbf{A}_n$. One has to know only $2\rho\,n$ matrix elements $\langle r|\mathbf{V}|\Phi_i\rangle$ and $\langle r|\mathbf{P}|\Phi_i\rangle$ ($r = 1,\ldots,\rho;\ i = 1,\ldots,n$) of the modification operators $\mathbf{V}$ and $\mathbf{P}$ between base vectors $|r\rangle \in X_\rho^a$ of the space X_ρ^a and eigenstates $|\Phi_i\rangle$ of the parent system, as well as n eigenvalues λ_i of this system. This makes a total of $(2\rho + 1)n$ quantities. On the other hand, in order to specify all n eigenstates $|\Phi_i\rangle$ of $\mathbf{A}_n$ one has to know n^2 matrix elements $\langle\alpha|\Phi_i\rangle$ ($\alpha = 1,\ldots,n;\ i = 1,\ldots,n$). Hence if $\rho << n$, construction of the operator $\mathbf{\Omega}_b(\varepsilon)$ requires much less information than exact specification of all eigenstates $|\Phi_i\rangle$ of (2.1a).

For the sake of simplicity, operators that act in spaces X_n^a, X_ρ^b and $X_{n+\rho}^c$ will be identified with their representations in bases $\{|\alpha\rangle\}$, $\{|r\rangle\}$ and $\{|r\rangle,|\alpha\rangle\}$, respectively. For example, representation of the operator $\mathbf{I}_\rho^b$ in the base $\{|r\rangle\}$ is a unit matrix with matrix elements δ_{rt} ($r,t = 1,\ldots,\rho$). Considered as the operator in the space $X_{n+\rho}^c$, $\mathbf{I}_\rho^b$ is a projection operator on the space X_ρ^b, subspace of the space $X_{n+\rho}^c$. Strictly, this identification is not allowed. However, from the context it is usually clear whether $\mathbf{O}$ denotes an operator or a representation of this operator in the space X_n^a, X_ρ^b or $X_{n+\rho}^c$.

In a perturbation approach each eigenvalue $\varepsilon_s = \varepsilon_s(\beta)$ of a perturbed system, considered as a function of a coupling parameter β, can be connected in a continuous way with the unperturbed eigenvalue $\varepsilon_s(0)$ [1,2]. Solutions of the perturbed system that are in this way connected with non-degenerate eigenvalues of the original system are treated differently from those solutions of the perturbed system that are connected with degenerate eigenvalues of the original system. In a perturbation theory one has to distinguish between degenerate and non-degenerate eigenvalues and eigenstates of the original system. In particular, perturbation treatment of degenerate eigenstates differs from the perturbation treatment of non-degenerate eigenstates [1,2,14]. In this respect there are major differences between a standard perturbation approach and a LRM approach. First, if the coupling parameter β is large enough, perturbation expansion may fail. In this case perturbed system may contain some eigenvalues $\varepsilon_s = \varepsilon_s(\beta)$ which cannot be connected in a continuous way with any eigenvalue of the non-perturbed system (see some examples in the following chapter). Since in this case perturbation expansion fails, such solutions of the modified systems cannot be treated by standard perturbation approach. However, LRM provides an exact solution in all cases, irrespective of how large is the coupling parameter. In the LRM the distinction between modifications of the original degenerate and original non-degenerate solutions is not important. In addition, if the modified eigenvalues $\varepsilon_s(\beta)$ cannot be connected in the continuous way with some eigenvalues of the original system, this distinction is even not possible. One finds that in the LRM approach one has to treat in a different way *cardinal* ($\varepsilon_s \notin \{\lambda_i\}$) and *singular* ($\varepsilon_s \in \{\lambda_i\}$) eigenvalues and eigenstates of the combined system [9-13]. This distinction is qualitatively different from the distinction between degenerate and non-degenerate eigenstates in the perturbation theory. In particular in the case of LRM cardinal solutions, all what is required is that modified eigenvalue ε_s should differ from all eigenvalues λ_j of the parent system $\mathbf{A}_n$, though it may coincide with some eigenvalue E_r of a base system $\mathbf{B}_\rho$. It is not important whether or not $\varepsilon_s = \varepsilon_s(\beta)$ can be continuously connected with some parent eigenvalue λ_j (or with some base eigenvalue E_r) in such a way that $\varepsilon_s(0) = \lambda_j$ (or $\varepsilon_s(0) = E_r$). On the other hand, each singular eigenvalues ε_s of the combined system coincides with some eigenvalue λ_j of the parent system. Singular solutions are thus rather special solutions of the combined system.

In addition to LRM expressions that provide exact values for the modified eigenvalues ε_s and for the corresponding eigenstates $|\Psi_s\rangle$, qualitative distribution of modified eigenvalues ε_s relative to the parent eigenvalues λ_i is also of interest. Due to the interaction, modified eigenvalues ε_s of the combined system shift relative to the parent eigenvalues λ_i. One finds that maximum possible shift of those eigenvalues is not arbitrary, and that this shift is mainly determined by the dimension ρ of the base space X_ρ^b. Let me first consider in qualitative terms how eigenvalues ε_s of the combined system $\mathbf{C}_{n+\rho}$ are related to the eigenvalues λ_i of the parent system $\boldsymbol{A}_n$. This is given by the *interlacing rule* [10].

2.2.1. Interlacing of Modified Eigenvalues with Parent Eigenvalues

Eigenvalues ε_s of the combined system $\mathbf{C}_{n+\rho}$ and eigenvalues λ_i of the parent system $\boldsymbol{A}_n$ satisfy [10]:

Interlacing rule I (external modifications):

Arrange eigenvalues λ_i ($i = 1,\cdots,n$) of $\boldsymbol{A}_n$ in a nondecreasing order and arrange also eigenvalues ε_s ($s = 1,\cdots,n+\rho$) of $\mathbf{C}_{n+\rho}$ in a non-decreasing order. These eigenvalues thus arranged satisfy

$$\varepsilon_i \le \lambda_i \le \varepsilon_{i+\rho}, \qquad i = 1,\cdots,n. \tag{2.11}$$

In particular, condition $\lambda_1 \le \varepsilon_{1+\rho}$ implies that at most ρ modified eigenvalues $\varepsilon_1, \dots, \varepsilon_\rho$ can be smaller than the first parent eigenvalue λ_1. Similarly, condition $\varepsilon_n \le \lambda_n$ implies that at most ρ modified eigenvalues $\varepsilon_{n+1}, \dots, \varepsilon_{n+\rho}$ can be larger than the last parent eigenvalue λ_n. Hence at least $n - \rho$ modified eigenvalues ε_s are confined to the interval $[\lambda_1, \lambda_n]$.

As a consequence of the above rule one has:

Corollary 1:

Let eigenvalue λ_j of $\boldsymbol{A}_n$ be η_j-degenerate. In this case at most $\eta_j + \rho$ modified eigenvalues ε_s of $\mathbf{C}_{n+\rho}$ can be equal to λ_j. In addition if $\eta_j > \rho$ at least $\eta_j - \rho$ modified eigenvalues ε_s of $\mathbf{C}_{\boldsymbol{n}+\rho}$ are equal to λ_j.

This corollary directly follows from the above interlacing rule. Namely if λ_j is η_j-degenerate, one has

$$\lambda_{j-1} < \lambda_j = \lambda_{j+1} = \dots = \lambda_{j+\eta_j-1} < \lambda_{j+\eta_j}.$$

Interlacing rule now implies $\varepsilon_{j-1} \le \lambda_{j-1} < \lambda_j$ and $\lambda_{j+\eta_j-1} < \lambda_{j+\eta_j} \le \varepsilon_{j+\eta_j+\rho}$. Hence only $\eta_j + \rho$ modified eigenvalues $\varepsilon_j, \varepsilon_{j+1}, \dots, \varepsilon_{j+\eta_j+\rho-1}$ can be equal to the parent eigenvalue λ_j. This proves first part of the above corollary. Similarly one derives second part of this corollary.

According to the above corollary, in the case of an external modification operators $\mathbf{V}$ and $\mathbf{P}$ can change (increase or decrease) degeneracy of each particular eigenvalue λ_j of $\boldsymbol{A}_n$ at most by ρ.

Let me now consider cardinal and singular solutions of the combined system $\mathbf{C}_{n+\rho}$ in more details.

2.2.2. Cardinal Solutions of the Combined System

Concerning cardinal solutions of $\mathbf{C}_{n+\rho}$ one has [10]:

Theorem I: (cardinal eigenvalues and eigenstates):

Let eigenstates $|\Phi_i\rangle$ of (2.1a) be orthonormalized according to (2.1b). Than

a) $\varepsilon_s \notin \{\lambda_i\}$ is a cardinal eigenvalue of the combined eigenvalue equation (2.6a) if and only if it satisfies

$$[\beta^2\mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b]|\theta_s\rangle = \varepsilon_s\mathbf{S}_b|\theta_s\rangle, \qquad |\theta_s\rangle \in X_\rho^b, \qquad (2.12a)$$

In the base $\{|r\rangle\}$ operator $\mathbf{\Omega}_b(\varepsilon)$ is a $\rho \times \rho$ matrix with matrix elements (2.10b) and above expression is a $\rho \times \rho$ matrix equation. Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of (2.6a) is hence a root of the $\rho \times \rho$ determinant $h(\varepsilon)$

$$h(\varepsilon) \equiv |\beta^2\mathbf{\Omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon\mathbf{S}_b| = 0. \qquad (2.12b)$$

b) $|\Psi_s\rangle$ is an eigenstate of the eigenvalue equation (2.6a) that has cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ if and only if it is a linear combination

$$|\Psi_s\rangle = \beta\sum_i^n \frac{\langle\Phi_i|\mathbf{V} - \varepsilon_s\mathbf{P}|\theta_s\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle + |\theta_s\rangle. \qquad (2.13a)$$

where $|\theta_s\rangle \in X_\rho^b$ is an eigenstate of (2.12a) that corresponds to the eigenvalue $\varepsilon = \varepsilon_s$.

c) Degeneracy of cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of the combined system $\mathbf{C}_{n+\rho}$ equals nullity of the matrix $\beta^2\mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s\mathbf{S}_b$. Since this is a $\rho \times \rho$ matrix, each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ can be at most ρ-degenerate.

Note that according to (2.13a) projection of the cardinal eigenstate (2.13a) on the space X_ρ^b equals $|\theta_s\rangle \in X_\rho^b$:

$$\mathbf{I}_\rho^b|\Psi_s\rangle = |\theta_s\rangle \in X_\rho^b. \qquad (2.13b)$$

Cardinal eigenstates (2.13a) can be orthonormalised according to (2.6c). If $\varepsilon_s \neq \varepsilon_p$ eigenstates $\left|\Psi_s\right\rangle$ and $\left|\Psi_p\right\rangle$ automatically satisfy $\left\langle\Psi_s\left|\mathbf{S}_c\right|\Psi_p\right\rangle = 0$ [10]. However, if $\varepsilon_s = \varepsilon_p$ one has to enforce orthogonality of those eigenstates by some standard orthonormalization procedure [3,4].

There is a strong formal similarity between the LRM equation (2.12a) and standard equations that describe perturbation of the base system $\mathbf{B}_\rho$. Equation (2.12a) formally describes ρ-dimensional system $\mathbf{B}_\rho$ described by the eigenvalue equation (2.5a) that is perturbed by the perturbation $\beta^2\mathbf{\Omega}_b(\varepsilon_s)$. This perturbation depends on the eigenvalue ε_s, and LRM equation (2.12a) is hence a nonlinear eigenvalue equation. According to (2.13b), eigenstate $\left|\theta_s\right\rangle$ of this equation equals projection of the modified eigenstate $\left|\Psi_s\right\rangle$ on the space X_ρ^b. In conclusion, equation (2.12a) is a $\rho \times \rho$ nonlinear eigenvalue equation, it acts entirely in the base space X_ρ^b, and the solution to this equation describes system $\mathbf{B}_\rho$ subject to the interaction $(\mathbf{V},\mathbf{P})$ with the external system $\mathbf{A}_n$. In addition, according to the expression (2.13a), this equation also determines complete cardinal eigenstate $\left|\Psi_s\right\rangle$ of the combined system $\mathbf{C}_{n+\rho}$.

Unlike LRM equation (2.12a) which is a $\rho \times \rho$ nonlinear eigenvalue equation, original eigenvalue equation (2.6a) that describes combined system $\mathbf{C}_{n+\rho}$ is a $(\rho+n)\times(\rho+n)$ linear eigenvalue equation. However large dimension n of the parent system $\mathbf{A}_n$, dimension of the corresponding LRM equation (2.12a) is still only ρ. Nevertheless, this LRM equation produces exact solutions of the $(\rho+n)\times(\rho+n)$ eigenvalue equation (2.6a). Hence if the system $\mathbf{A}_n$ is much larger than the system $\mathbf{B}_\rho$, LRM treatment will be numerically much faster than any other standard treatment of the eigenvalue equation (2.6a).

2.2.3. Singular Solutions of the Combined System

Concerning singular eigenvalues and eigenstates of the combined system $\mathbf{C}_{n+\rho}$ one has [10]

Theorem 2 (singular solutions): Let λ_j be a η_j-degenerate eigenvalue of the eigenvalue equation (2.1a) and let $X_{\eta j}^{\lambda j}$ be the corresponding η_j-dimensional space spanned by η_j degenerate eigenstates $\left|\Phi_{jl}\right\rangle$ ($l = 1,\ldots,\eta_j$) of (2.1a). Let further $\mathbf{I}_{\eta j}^{\lambda j}$ be the projection on the space $X_{\eta j}^{\lambda j}$. Then:

Each singular eigenstate $\left|\Psi_s\right\rangle$ of the combined system $\mathbf{C}_{n+\rho}$ that has eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ is a linear combination

$$\left|\Psi_s\right\rangle = \beta \sum_{i(\lambda_i \neq \varepsilon_s)}^{n} \frac{\left\langle\Phi_i\left|\mathbf{V} - \varepsilon_s\mathbf{P}\right|\theta_s\right\rangle}{\varepsilon_s - \lambda_i}\left|\Phi_i\right\rangle + \left|\theta_s\right\rangle + \left|\chi_s\right\rangle, \tag{2.14a}$$

where

$$\left|\theta_s\right\rangle \in X_\rho^b, \ \left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j} \subseteq X_n^a. \tag{2.14b}$$

and where those two states satisfy

$$\left[\beta^2\,\mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s\mathbf{S}_b\right]\left|\theta_s\right\rangle + \beta\left(\mathbf{V} - \varepsilon_s\mathbf{P}\right)\mathbf{I}_{\eta j}^{\lambda j}\left|\chi_s\right\rangle = 0, \tag{2.15a}$$

$$\beta\,\mathbf{I}_{\eta j}^{\lambda j}\left(\mathbf{V} - \varepsilon_s\mathbf{P}\right)\left|\theta_s\right\rangle = 0. \tag{2.15b}$$

In a matrix form, expressions (2.15) form a set of $(\rho + \eta_j)$ homogenous linear equations in $(\rho + \eta_j)$ unknowns, ρ unknown coefficients $C_r^{(s)}$ that determine the state $\left|\theta_s\right\rangle \in X_\rho^b$ and η_j unknown coefficients $D_l^{(s)}$ that determine the state $\left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j}$:

$$\left|\theta_s\right\rangle = \sum_r^{\rho} C_r^{(s)} \left|r\right\rangle, \quad \left|\chi_s\right\rangle = \sum_l^{\eta j} D_l^{(s)} \left|\Phi_{jl}\right\rangle . \tag{2.16}$$

Combined system $\mathbf{C}_{n+\rho}$ has a singular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ if and only if determinant of the system (2.15) vanishes. If λ_j is η_j-degenerate, this system may have at most $(\rho+\eta_j)$ linearly independent eigenstates $\left|\Psi_s\right\rangle$ with the eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$. Further, since $\left|\Phi_i\right\rangle \in X_n^a$ and $\left|\chi_s\right\rangle \in X_n^a$, X_ρ^b-component of the modified eigenstate (2.14a) satisfies (2.13b). Thus in the case of cardinal eigenstates as well as in the case of singular eigenstates, in both cases the state $\left|\theta_s\right\rangle \in X_\rho^b$ is the X_ρ^b-component of the corresponding modified eigenstate $\left|\Psi_s\right\rangle$ as given by expressions (2.13a) and (2.14a). Concerning the state $\left|\chi_s\right\rangle$ one finds

$$\mathbf{O}_{\eta_j}^{\lambda_j} \left|\Psi_s\right\rangle = \left|\chi_s\right\rangle \in X_{\eta_j}^{\lambda_j} . \tag{2.17a}$$

where operator $\mathbf{O}_{\eta_j}^{\lambda_j}$ is given by

$$\mathbf{O}_{\eta_j}^{\lambda_j} = \sum_l^{\eta j} \left|\Phi_{jl}\right\rangle \left\langle\Phi_{jl}\right| \mathbf{S}_a , \tag{2.17b}$$

Due to (2.1b) this operator satisfies

$$(\mathbf{O}_{\eta_j}^{\lambda_j})^2 = \mathbf{O}_{\eta_j}^{\lambda_j} . \tag{2.17c}$$

In addition, each state $\left|\Psi\right\rangle$ satisfies $\mathbf{O}_{\eta_j}^{\lambda_j} \left|\Psi\right\rangle \in X_{\eta j}^{\lambda j}$. The same properties has operator $\mathbf{I}_{\eta j}^{\lambda j}$ which is a projection operator on the space $X_{\eta_j}^{\lambda_j}$. However, operator $\mathbf{O}_{\eta_j}^{\lambda_j}$ is in general not Hermitean and hence in general $\mathbf{O}_{\eta_j}^{\lambda_j} \neq \mathbf{I}_{\eta j}^{\lambda j}$. In a special and most important case when $\mathbf{S}_a = \mathbf{I}_a$ is a unit operator in X_n^a, operator $\mathbf{O}_{\eta_j}^{\lambda_j}$ is Hermitean and in this case one has $\mathbf{O}_{\eta_j}^{\lambda_j} = \mathbf{I}_{\eta j}^{\lambda j}$.

It is convenient to distinguish *strongly singular* and *weakly singular* eigenstates of the modified system. By definition, strongly singular eigenstate $|\Psi_s\rangle$ of the eigenvalue equation (2.6a) has no component in the base space X_ρ^b, *i.e.* it satisfies $\mathbf{I}_\rho^b|\Psi_s\rangle = 0$. On the other hand, each weakly singular eigenstate $|\Psi_s\rangle$ satisfies $\mathbf{I}_\rho^b|\Psi_s\rangle \neq 0$. In addition, each weakly singular eigenstate should be orthogonal to all strongly singular eigenstates.

Theorem 2 implies:

Theorem 2a:

$|\Psi_s\rangle$ is *strongly singular* eigenstate of the eigenvalue equation (2.6a) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if this state satisfies:

$$|\Psi_s\rangle \equiv |\chi_s\rangle \in X_{\eta j}^{\lambda j}, \qquad (\mathbf{V} - \varepsilon_s \mathbf{P})\mathbf{I}_{\eta j}^{\lambda j}|\chi_s\rangle = 0. \tag{2.18}$$

This state is hence a linear combination

$$|\Psi_s\rangle = \sum_l^{\eta j} D_l^{(s)}|\Phi_{jl}\rangle, \tag{2.19a}$$

where the coefficients $D_l^{(s)}$ satisfy

$$\sum_l^{\eta_j} \langle r|\mathbf{V} - \varepsilon_s \mathbf{P}|\Phi_{jl}\rangle D_l^{(s)} = 0, \qquad r = 1,\ldots,\rho. \tag{2.19b}$$

The set of all strongly singular eigenstates associated with the eigenvalue $\varepsilon_s = \lambda_j$ spans some r_j-dimensional space $X_{rj}^{\lambda j-}$, subspace of the space $X_{\eta j}^{\lambda j}$. Since the space $X_{\eta j}^{\lambda j}$ is η_j-dimensional while the space X_ρ^b is ρ-dimensional, expression (2.19b) implies

$$\eta_j - \rho \le r_j \le \eta_j. \tag{2.20}$$

$\left|\Psi_s\right\rangle$ is weakly singular eigenstate of the generalized eigenvalue equation (2.6a) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if it is a linear combination (2.14a) where the states $\left|\theta_s\right\rangle$ and $\left|\chi_s\right\rangle$ satisfy expressions (2 .15) and where $\left|\theta_s\right\rangle \neq 0$. In addition, each weakly singular eigenstate should be orthogonal to all strongly singular eigenstates.

If $\left|\Psi_s\right\rangle$ is weakly singular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j$, the state $\left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j}$ in the expression (2.14a) is uniquely determined by the state $\left|\theta_s\right\rangle \in X_\rho^b$ in this expression. Since the space X_ρ^b is $\rho-$dimensional, this implies that one may have at most ρ linearly independent weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$, however large degeneracy η_j of the parent eigenvalue λ_j. Note that this condition is stronger than the condition implied by the inequality (2.20). Namely this inequality implies that one may have at most 2ρ such linearly independent eigenstates.

According to the above Theorem, there is a substantial qualitative difference between strongly and weakly singular eigenstates of the combined system. If degeneracy η_j of the eigenvalue λ_j of the parent system $\boldsymbol{A}_n$ satisfies $\eta_j > \rho$, combined system $\mathbf{C}_{n+\rho}$ has at least $\eta_j - \rho$ strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. If this degeneracy is very large, one may have very many strongly singular eigenstates with this eigenvalue. Those eigenstates do not depend on the coupling parameter β, and they exist for each value of this parameter. Further, each strongly singular eigenstate $\left|\Psi_s\right\rangle$ of the modified system $\mathbf{C}_{n+\rho}$ is at the same time an eigenstate of the parent system $\boldsymbol{A}_n$ with the same eigenvalue. Accordingly, modification operators $\mathbf{V}$ and $\mathbf{P}$ have no influence on strongly singular eigenstates. On the other hand, each weakly singular eigenstate $\left|\Psi_s\right\rangle$ depends on a coupling parameter β as well as on the modification operators $\mathbf{V}$ and $\mathbf{P}$. Unlike strongly singular eigenstates of the combined system, each weakly singular eigenstate of this system differs from all eigenstates of the parent system $\boldsymbol{A}_n$. In addition, modified system may have at most ρ weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$, however large degeneracy η_j of the eigenvalue λ_j. Since expressions (2.15) represent the set of $(\rho + \eta_j)$ homogenous linear equations in $(\rho + \eta_j)$ unknowns, and since each weakly singular eigenstate is required to satisfy $\left|\theta_s\right\rangle \neq 0$, and since in addition this state is required to be orthogonal to all strongly singular eigenstates, in the case of weakly singular eigenstates those expressions are highly overdetermined. Hence, unless there is some special reason, combined system contains no weakly singular eigenstate. This special reason is usually due to symmetry. According to the inequality (2.20), inclusion of the generalized interaction $(\mathbf{V}, \mathbf{P})$ between the parent system $\boldsymbol{A}_n$ and the base system $\boldsymbol{B}_\rho$ can increase degeneracy η_j of the parent eigenvalue λ_j only if this combined system has some weakly singular eigenstate $\varepsilon_s \equiv \lambda_j$ with this eigenvalue. One finds that combined system $\mathbf{C}_{n+\rho}$ may have such an eigenstates only if this system is more symmetrical than original systems $\boldsymbol{A}_n$ and $\mathbf{B}_\rho$. In general, only in the case when the modification operators $\mathbf{V}$ and $\mathbf{P}$ increase the symmetry of the initially non-interacting systems $\boldsymbol{A}_n$ and $\mathbf{B}_\rho$, combined system $\mathbf{C}_{n+\rho}$ may have some weakly singular eigenstates. Otherwise combined system has no such eigenstates.

Above two theorems produce all solutions of the combined system $\mathbf{C}_{n+\rho}$. All cardinal eigenvalues $\varepsilon_s \notin \{\lambda_i\}$ of the combined eigenvalue equation are roots of the function $h(\varepsilon)$. Once a particular root ε_s of $h(\varepsilon)$ is found, the corresponding eigenstate (or eigenstates) is given by eq. (2.13a) where the state $\left|\theta_s\right\rangle \in X_\rho^b$ satisfies (2.12a). Concerning remaining singular eigenvalues $\varepsilon_s \in \{\lambda_i\}$, each such eigenvalue coincides with some eigenvalue λ_j of a parent system, and all one has to do is to verify conditions (2.15). This verification is highly simplified by the expressions (2.19b) which produce all strongly singular eigenstates. If all modified solutions are required, in the numerical implementation of LRM one has first to calculate all cardinal solutions using expressions (2.12). If there are $(n+\rho)$ such solutions LRM calculation is completed, since combined system has exactly $(n+\rho)$

solutions. However if there are less than $(n+\rho)$ cardinal solutions, one has to calculate strongly singular solutions. This can be done using expressions (2.19). Only if the total number of all cardinal plus all strongly singular solutions is still less than $(n+\rho)$, one has to look for weakly singular solutions.

2.2.4. How Efficient Is a Finite-Dimensional LRM Approach?

In the computer implementation of the above method, most important and most time-consuming is the solution of the equation (2.12b) which produces cardinal eigenvalues of the combined system. Operation count required to obtain singular solutions of the combined system is usually negligible with respect to the operation count required to obtain cardinal solutions of this system. In order to find a particular eigenvalue ε_s of the equation (2.12b), one has to recalculate in an iterative way function $h(\varepsilon)$ for many different values of ε. Each recalculation of this function requires calculation of matrix elements (2.10b) of the operator $\mathbf{\Omega}_b(\varepsilon)$. Operation count for the calculation of those matrix elements is of the order $O(\rho^2 n)$. Operation count for a single calculation of the function $h(\varepsilon)$ is dominated by the operation count for this operator. This operation count is hence also of the order $O(\rho^2 n)$. Though one has to recalculate this function many times, the number of those calculations is independent on ρ and on n [10]. Operation count for a single modified eigenvalue is hence still of the order $O(\rho^2 n)$. Accordingly, operation count for all eigenvalues is of the order $O(\rho^2 n^2)$. On the other hand, operation count of a standard diagonalization which produces all eigenvalues of the eigenvalue equation (2.6a) is of the order $O((n+\rho)^3) > O\left(n^3\right)$ [3,4]. Hence if all modified eigenvalues are needed, LRM will be numerically more efficient if $\rho << \sqrt{n}$. If a single or only a few selected eigenvalues are required, LRM is comparatively even more efficient since it requires only $O(\rho^2 n)$ operations per eigenvalue, while all known numerical methods require substantially more than $O((n+\rho)^2) \approx O(n^2)$ operations per eigenvalue.

Once an eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ is obtained, calculation of the corresponding eigenstate or eigenstates $|\Psi_s\rangle$ requires the solution of the expression (2.12a). Since ε_s is known, this calculation is of the order $O(\rho^3)$. Since $\rho << \sqrt{n} < n$ this operation count is negligible with respect to the operation count required to obtain the eigenvalue ε_s in the first place.

One finds that multiple recalculation of the function $h(\varepsilon)$ is more time-consuming in the case $\mathbf{P} \neq 0$ than in the case $\mathbf{P} = 0$ [10]. If $\mathbf{P} = 0$ one can devise much faster algorithm for this recalculation. This is due to the fact than in the case $\mathbf{P} \neq 0$ the unknown ε is in the nominator as well as in the denominator of the matrix elements (2.10b) of the operator $\mathbf{\Omega}_b(\varepsilon)$. One can express matrix $\mathbf{\Omega}_b(\varepsilon)$ in an equivalent form where this unknown is eliminated from the nominator of those matrix elements [10]:

$$\mathbf{\Omega}_b(\varepsilon) = \Omega'_b(\varepsilon) + \mathbf{K} + \varepsilon\,\mathbf{\Lambda}\,, \tag{2.21a}$$

where

$$\Omega'_b(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)}^{n} \frac{(\mathbf{V} - \lambda_i \mathbf{P})|\Phi_i\rangle\langle\Phi_i|(\mathbf{V} - \lambda_i \mathbf{P})}{\varepsilon - \lambda_i}\,, \tag{2.21b}$$

$$\mathbf{K} = \sum_i^n \left[\lambda_i \mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{P} - \mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{V} - \mathbf{V}|\Phi_i\rangle\langle\Phi_i|\mathbf{P}\right], \tag{2.21c}$$

$$\mathbf{\Lambda} = \sum_i^n \mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{P}\,. \tag{2.21d}$$

Expressions (2.12) can be written in terms of the above operators as [10]

$$\left[\beta^2\left(\mathbf{\Omega}'_b(\varepsilon_s) + \mathbf{K}\right) + \mathbf{H}_b\right]|\theta_s\rangle = \varepsilon_s\left(\mathbf{S}_b - \beta^2\mathbf{\Lambda}\right)|\theta_s\rangle\,, |\theta_s\rangle \in X_\rho^b, \tag{2.22a}$$

$$h(\varepsilon) \equiv \left|\beta^2\left(\mathbf{\Omega}'_b(\varepsilon) + \mathbf{K}\right) + \mathbf{H}_b - \varepsilon\left(\mathbf{S}_b - \beta^2\mathbf{\Lambda}\right)\right| = 0\,. \tag{2.22b}$$

Expression (2.22b) seems to be more complicated than the equivalent expression (2.12b). However, it is numerically easier to obtain roots of the expression (2.22b) than roots of the expression (2.12b). This is due to the fact that according to (2.21b) operator $\mathbf{\Omega}'_b(\varepsilon)$ has unknown variable ε only in its denominator. Concerning operators $\mathbf{K}$ and $\mathbf{\Lambda}$, those operators do not depend on ε, and hence matrix elements of those operators can be calculated only once, i.e. there is no need to recalculate those matrix elements in each iteration cycle. Using expression (2.22b) instead of the expression (2.12b) one can substantially speed up LRM calculation of each particular eigenvalue of (2.12a) [10].

2.2.5. Normalization of Modified Eigenstates

Cardinal eigenstate $|\Psi_s\rangle$ as given by the expression (2.13a) is not normalized. This can be easily done once this expression is known. Eigenstate (2.13a) can be normalized according to

$$|\Psi_s\rangle \rightarrow |\Psi_s'\rangle = \frac{1}{\sqrt{N_s}}|\Psi_s\rangle . \tag{2.23a}$$

where $|\Psi_s\rangle$ is given by (2.13a) while normalization constant N_s equals [10]

$$\begin{aligned} N_s \equiv \langle\Psi_s|\mathbf{S}_c|\Psi_s\rangle = \beta^2\sum_i^n \frac{\langle\theta_s|\mathbf{V}-\varepsilon_s\mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{V}-\varepsilon_s\mathbf{P}|\theta_s\rangle}{(\varepsilon_s-\lambda_i)^2} + \langle\theta_s|\mathbf{S}_b|\theta_s\rangle + \\ +\beta^2\sum_i^n \frac{\langle\theta_s|\mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{V}-\varepsilon_s\mathbf{P}|\theta_s\rangle + \langle\theta_s|\mathbf{V}-\varepsilon_s\mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{P}|\theta_s\rangle}{\varepsilon_s-\lambda_i} \end{aligned} \tag{2.23b}$$

This expression can be written in a compact form [10]

$$N_s = \beta^2\sum_i^n \frac{\langle\theta_s|\mathbf{V}-\lambda_i\mathbf{P}|\Phi_i\rangle\langle\Phi_i|\mathbf{V}-\lambda_i\mathbf{P}|\theta_s\rangle}{(\varepsilon_s-\lambda_i)^2} - \beta^2\langle\theta_s|\mathbf{\Lambda}|\theta_s\rangle + \langle\theta_s|\mathbf{S}_b|\theta_s\rangle, \tag{2.23c}$$

In particular if $\mathbf{P} = 0$ (the most important case) one has

$$N_s = \beta^2 \sum_i^n \frac{\langle \theta_s | \mathbf{V} | \Phi_i \rangle \langle \Phi_i | \mathbf{V} | \theta_s \rangle}{(\varepsilon_s - \lambda_i)^2} + \langle \theta_s | \mathbf{S}_b | \theta_s \rangle . \tag{2.23d}$$

It is remarkable that normalization constant N_s involves only calculations within the space X_ρ^b associated with a base system $\mathbf{B}_\rho$, and no calculation within the parent space X_n^a. In order to normalize cardinal eigenstate $|\Psi_s\rangle \in X_{n+\rho}^c$ it is not necessary to know X_n^a-component $|\Psi_s^a\rangle$ of this eigenstate. LRM eigenvalue equation (2.12a) produces the state $|\theta_s\rangle$ and the corresponding eigenvalue ε_s. In connection with known eigenvalues λ_i and known matrix elements $\langle r|\mathbf{V}|\Phi_i\rangle$ and $\langle r|\mathbf{P}|\Phi_i\rangle$ that describe the interaction of the eigenstates $|\Phi_i\rangle$ of the parent system with the base system $\mathbf{B}_\rho$, those quantities determine normalization constant N_s. Hence, though cardinal eigenstate $|\Psi_s\rangle$ extends over the entire space $X_{n+\rho}^c$, one can normalize this eigenstate using only its projection on the much smaller space X_ρ^b in conjuncture with key information about the interaction of the base system $\mathbf{B}_\rho$ with its surrounding (parent system $\mathbf{A}_n$). The projection $\mathbf{I}_n^a|\Psi_s\rangle \in X_n^a$ of this eigenstate on the space X_n^a is not explicitly required and it does not affect the normalization constant N_s. This independence of the normalization constant N_s on the space X_n^a is an important feature of the LRM approach.

Concerning normalization of singular eigenstates (2.14a), particularly simple is the normalization of strongly singular eigenstates (2.19a). As implied by this expression, in order to normalize a strongly singular eigenstate $|\Psi_s\rangle$, one has to know the state (2.19a) which is contained in the subspace $X_{nj}^{\lambda j}$ of the space X_n^a. This differs from the normalization of cardinal eigenstate $|\Psi_s\rangle$ which does not require the knowledge of the X_n^a component of this eigenstate. Concerning normalization of the weakly singular eigenstates, this normalization can be also obtained in an explicit form. However as explained above, in most cases combined system has no such eigenstates.

Above theorems apply to generalized eigenvalue equations (2.1a), (2.5a) and (2.6a). All the corresponding relations substantially simplify if those equations are not completely generalized. The most important special case is $\mathbf{P} = 0$. This allows for the unperturbed eigenvalue equations (2.1a) and (2.5a) to be still of the most general type. Only the modified equation (2.6a) is slightly restricted with this requirement. This eigenvalue equation is still a generalized eigenvalue equation, though not of a most general type. If $\mathbf{P} = 0$ operators $\mathbf{K}$ and $\mathbf{\Lambda}$ in the expressions (2.21,2.22) vanish ($\mathbf{K} = 0$, $\mathbf{\Lambda} = 0$), and hence one has $\mathbf{\Omega}(\varepsilon) = \mathbf{\Omega'}(\varepsilon)$. One has $\mathbf{P} = 0$ in a special but highly important case when instead of generalized eigenvalue equations (2.1a), (2.5a) and (2.6a) one has standard eigenvalue equations $\mathbf{H}_a|\Phi_i\rangle = \lambda_i|\Phi_i\rangle$, $\mathbf{H}_b|\Theta_r\rangle = E_r|\Theta_r\rangle$ and $(\mathbf{H}_a + \mathbf{H}_b + \beta\mathbf{V})|\Psi_s\rangle = \varepsilon_s|\Psi_s\rangle$, respectively.

2.2.6. An Example of the LRM Solution of an Externally Modified System

In order to illustrate LRM treatment of external modification, consider as an example the interaction of a two-dimensional system $\mathbf{B}_2$ with a known three-dimensional system $\boldsymbol{A}_3$.

Let the base system $\mathbf{B}_2$ be described by the generalized eigenvalue equation (2.5a) where in a base $\{|r\rangle\}$ one has

$$\mathbf{H}_b = \begin{bmatrix} 1 & -0.5 \\ -0.5 & 0 \end{bmatrix},$$

$$\mathbf{S}_b = \begin{bmatrix} 1 & 0.3 \\ 0.3 & 1 \end{bmatrix}. \qquad (2.24)$$

Let the parent system $\boldsymbol{A}_3$ be described by the generalized eigenvalue equation (2.1a) where in a base $\{|\alpha\rangle\}$ one has

$$\mathbf{H}_a = \begin{bmatrix} 1 & 2 & 3 \\ 2 & 2 & 1 \\ 3 & 1 & 5 \end{bmatrix}, \ \mathbf{S}_a = \begin{bmatrix} 1 & 0.5 & 0.2 \\ 0.5 & 1.2 & 0.5 \\ 0.2 & 0.5 & 1.3 \end{bmatrix}. \tag{2.25}$$

Let further the combined system $\mathbf{C}_5$ that includes the interaction between systems $\mathbf{B}_2$ and $\boldsymbol{A}_3$ be described by the generalized eigenvalue equation (2.6a) where in a base $\{|\alpha\rangle, |r\rangle\}$

$$\mathbf{H}_c = \begin{bmatrix} \mathbf{H}_a & \mathbf{V}_{ab} \\ \mathbf{V}_{ba} & \mathbf{H}_b \end{bmatrix}, \mathbf{S}_c = \begin{bmatrix} \mathbf{S}_a & \mathbf{P}_{ab} \\ \mathbf{P}_{ba} & \mathbf{S}_b \end{bmatrix}, \tag{2.26a}$$

In this base generalized interaction $(\mathbf{V}, \mathbf{P})$ is given by

$$\mathbf{V} = \begin{bmatrix} 0 & \mathbf{V}_{ab} \\ \mathbf{V}_{ba} & 0 \end{bmatrix}, \ \mathbf{P} = \begin{bmatrix} 0 & \mathbf{P}_{ab} \\ \mathbf{P}_{ba} & 0 \end{bmatrix}, \tag{2.26b}$$

Let this interaction be determined by matrices

$$\mathbf{V}_{ba} = \begin{bmatrix} 1 & 2 & -1 \\ 1 & 2 & 3 \end{bmatrix}, \qquad \mathbf{P}_{ba} = \begin{bmatrix} 0.3 & -0.5 & 0.2 \\ 0.3 & 0.1 & -0.4 \end{bmatrix}. \tag{2.26c}$$

In the above expressions $\mathbf{V}_{ab}$ is a transpose of $\mathbf{V}_{ba}$, $\mathbf{P}_{ab}$ is a transpose of $\mathbf{P}_{ba}$, and parameter β is chosen to equal unity. One finds that combined system $\mathbf{C}_5$ has eigenvalues [10]

$$\begin{aligned} &\varepsilon_1 = -2.32918, \quad \varepsilon_2 = -1.50057, \quad \varepsilon_3 = 0.06038, \\ &\varepsilon_4 = 4.35986, \quad \varepsilon_5 = 60.42988, \end{aligned} \tag{2.27a}$$

The corresponding normalized eigenstates are

$$|\Psi_1\rangle = \begin{pmatrix} 1.11912 \\ -0.49548 \\ -0.39826 \\ -0.51397 \\ 0.05630 \end{pmatrix}, \qquad |\Psi_2\rangle = \begin{pmatrix} 0.35630 \\ 0.29638 \\ -0.02665 \\ -0.37694 \\ -0.73890 \end{pmatrix},$$

$$|\Psi_3\rangle = \begin{pmatrix} 0.53374 \\ -0.49000 \\ 0.20859 \\ 0.40996 \\ -0.57247 \end{pmatrix},$$

$$|\Psi_4\rangle = \begin{pmatrix} 0.07052 \\ 0.63770 \\ 0.27950 \\ 0.44679 \\ 0.34263 \end{pmatrix}, |\Psi_5\rangle = \begin{pmatrix} 1.17903 \\ -2.38652 \\ 1.73945 \\ -2.44302 \\ 1.36072 \end{pmatrix}. \tag{2.27b}$$

This can be verified by inserting those eigenvalues and eigenstates in the eigenvalue equation (2.6a) with matrices $\mathbf{H}_c$ and $\mathbf{S}_c$ as given by expression (2.26a). One can also verify that eigenstates (2.27b) are orthonormalized according to (2.6c), as required.

One can solve the same eigenvalue equation by the LRM approach. In LRM, in order to solve combined eigenvalue equation, one has to know the solution of the eigenvalue equation (2.1a) that describes parent system $\boldsymbol{A}_3$. This system has three eigenvalues and three corresponding eigenstates. One finds

$$\lambda_1 = -1.66138, \qquad \lambda_2 = 1.89610, \; \lambda_3 = 5.20405, \tag{2.28a}$$

$$|\Phi_1\rangle = \begin{pmatrix} 0.99832 \\ -0.56029 \\ -0.32137 \end{pmatrix}, \qquad |\Phi_2\rangle = \begin{pmatrix} 0.23961 \\ 0.86544 \\ -0.26545 \end{pmatrix},$$

$$\left|\Phi_3\right\rangle = \begin{pmatrix} 0.45738 \\ -0.39004 \\ 0.86160 \end{pmatrix}. \qquad (2.28b)$$

Eigenstates (2.28b) are orthonormalized according to (2.1b) where matrix $\mathbf{S}_a$ is given by the expression (2.25).

From (2.26c) and (2.28b) one derives matrix elements $\left\langle r\middle|\mathbf{V}\middle|\Phi_i\right\rangle \equiv \Delta H_{r,i}$ and $\left\langle r\middle|\mathbf{P}\middle|\Phi_i\right\rangle \equiv \Delta S_{r,i}$ [10]:

$\Delta H_{1,1} = 0.19912$ $\Delta H_{2,1} = -1.08638$ $\Delta S_{1,1} = 0.51537$

$\Delta S_{2,1} = 0.37202$

$\Delta H_{1,2} = 2.23594$ $\Delta H_{2,2} = 1.17415$ $\Delta S_{1,2} = -0.41393$

$\Delta S_{2,2} = 0.26461$

$\Delta H_{1,3} = -1.18430$ $\Delta H_{2,3} = 2.26211$ $\Delta S_{1,3} = 0.50456$

$\Delta S_{2,3} = -0.24643$ (2.29)

In order to obtain cardinal eigenvalues of the combined system $\mathbf{C}_5$, one can use either expression (2.12b) or expression (2.22b). Let me use this latter expression. Using expressions (2.21), (2.28a) and (2.29) one obtains matrix elements $\mathbf{\Omega}'_{rt}(\varepsilon)$ of the operator $\mathbf{\Omega}'_b(\varepsilon)$:

$$\Omega'_{11}(\varepsilon) = \frac{1.11373}{\varepsilon - \lambda_1} + \frac{9.12516}{\varepsilon - \lambda_2} + \frac{14.51632}{\varepsilon - \lambda_3},$$

$$\Omega'_{22}(\varepsilon) = \frac{0.21932}{\varepsilon - \lambda_1} + \frac{0.45215}{\varepsilon - \lambda_2} + \frac{12.56382}{\varepsilon - \lambda_3},$$

$$\Omega'_{12}(\varepsilon) \equiv \Omega'_{21}(\varepsilon) = \frac{-0.49423}{\varepsilon - \lambda_1} + \frac{2.03125}{\varepsilon - \lambda_2} - \frac{13.50483}{\varepsilon - \lambda_3}, \qquad (2.30a)$$

as well as matrices $\mathbf{K}$ and $\mathbf{\Lambda}$

$$\mathbf{K} = \begin{bmatrix} 4.04931 & -2.22630 \\ -2.22630 & 1.52069 \end{bmatrix},$$

$$\mathbf{\Lambda} = \begin{bmatrix} 0.69151 & -0.04214 \\ -0.04214 & 0.26914 \end{bmatrix}. \tag{2.30b}$$

Inserting above expressions into (2.22b) one obtains [10]

$$h(\varepsilon) \equiv \begin{vmatrix} \Omega'_{11}(\varepsilon) + 5.04931 - 0.30849\varepsilon & \Omega'_{12}(\varepsilon) - 2.72630 - 0.34214\varepsilon \\ \Omega'_{21}(\varepsilon) - 2.72630 - 0.34214\varepsilon & \Omega'_{22}(\varepsilon) + 1.52069 - 0.73086\varepsilon \end{vmatrix} = 0 \tag{2.31}$$

Roots of this equation are cardinal eigenvalues of the combined system $\mathbf{C}_5$. One easily verifies that eigenvalues (2.27a) satisfy (2.31). In addition, one finds that there are no other solutions to (2.31). This shows that expression (2.12b) as well as equivalent expression (2.22b) produces correct cardinal eigenvalues of the combined system. Moreover, in this particular example the function $h(\varepsilon)$ has exactly five roots. Since the combined system is five-dimensional, those are all eigenvalues of this system, and there are no singular solutions.

Once a particular eigenvalue ε_s is found as a root of $h(\varepsilon)$, the corresponding cardinal eigenstate (2.13a) is determined by the state $|\theta_s\rangle$, nontrivial solution of (2.22a):

$$\begin{bmatrix} \Omega'_{11}(\varepsilon_s) + 5.04931 & \Omega'_{12}(\varepsilon_s) - 2.72630 \\ \Omega'_{21}(\varepsilon_s) - 2.72640 & \Omega'_{22}(\varepsilon_s) + 1.52069 \end{bmatrix} |\theta_s\rangle = \varepsilon_s \begin{bmatrix} 0.30849 & 0.34214 \\ 0.34214 & 0.73086 \end{bmatrix} |\theta_s\rangle . \tag{2.32}$$

Using eigenvalues ε_s which were obtained as roots of (2.31) one finds [10]:

$$|\theta_1\rangle = \begin{pmatrix} 1 \\ -0.10954 \end{pmatrix}, \qquad |\theta_2\rangle = \begin{pmatrix} 1 \\ 1.96028 \end{pmatrix},$$

$$|\theta_3\rangle = \begin{pmatrix} 1 \\ -1.39639 \end{pmatrix},$$

$$|\theta_4\rangle = \begin{pmatrix} 1 \\ 0.76687 \end{pmatrix}, \qquad |\theta_5\rangle = \begin{pmatrix} 1 \\ -0.55698 \end{pmatrix}. \tag{2.33}$$

Inserting above states into the expression (2.13a) one obtains, up to the norm and phase, eigenstates (2.27b) of the combined system. If one normalizes those eigenstates according to (2.23), one reproduces eigenstates (2.27b) up to the phase. This shows that suggested method produces correct cardinal eigenstates of the combined system. Since above system has no singular eigenstates, LRM calculation is completed.

From a numerical point of view, above example is not very interesting. It can be solved more efficiently by many other methods, in particular by direct diagonalization. However, it illustrates main features of the LRM approach, its advantageous and possible drawbacks.

Eigenvalue equation (2.32) that describes base system $\mathbf{B}_2$ subject to the interaction (2.26b) with the parent system $\boldsymbol{A}_3$ is a 2×2 eigenvalue equation. In this example, system $\boldsymbol{A}_3$ is relatively small three-dimensional system. However, dimension n of this system can be arbitrary large. All cardinal solutions of the combined system will be still the solutions of the 2×2 eigenvalue equation that is similar to the eigenvalue equation (2.32). Thus if the dimension n of the system $\boldsymbol{A}_n$ is large enough, LRM approach will be numerically more efficient than any other known method.

2.3. LRM TREATMENT OF INTERNAL MODIFICATIONS

Consider now internal modifications of finite-dimensional systems (see figure 2.1). Let again $\boldsymbol{A}_n$ be n-dimensional parent system described by the eigenvalue equation (2.1a), and let the corresponding eigenstates $|\Phi_i\rangle$ be orthonormalised according to (2.1b). Let further $\mathbf{C}_n$ be a modified system described by the eigenvalue equation (2.2a) where $\mathbf{V}_a$ and $\mathbf{P}_a$ are Hermitean operators which represent internal modification of the parent system $\boldsymbol{A}_n$ and where β is a coupling parameter. Let σ be the rank of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. As shown in section 2.1, range of this modification is σ-dimensional interaction space X_σ^{int}. This space is spanned by all vectors of a type $\mathbf{V}_a|\psi\rangle$ and all vectors of a type $\mathbf{P}_a|\psi\rangle$ where $|\psi\rangle \in X_n^a$.

Let $\{|\mu\rangle\}$ be a base in X_σ^{int} orthonormalized according to (2.3a) and let $\{|\alpha\rangle\}$ be the base in X_n^a orthonormalized according to (2.3b). Projection operator $\mathbf{I}_\sigma^{\text{int}}$ on the interaction space X_σ^{int} can be expressed in terms of the states $|\mu\rangle$ according to (2.3c), while modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ satisfy (2.4).

In analogy to the case of external modifications, in the case of internal modifications one considers operator $\mathbf{\Omega}_a(\varepsilon)$ defined as

$$\mathbf{\Omega}_a(\varepsilon) = \left(\mathbf{V}_a - \varepsilon\,\mathbf{P}_a\right)\overline{\mathbf{\Omega}}(\varepsilon)\left(\mathbf{V}_a - \varepsilon\,\mathbf{P}_a\right), \tag{2.34a}$$

In the base $\{|\mu\rangle\}$ of the interaction space operator $\mathbf{\Omega}_a(\varepsilon)$ is a $\sigma \times \sigma$ matrix with matrix elements

$$\Omega_{\mu\nu}^a(\varepsilon) \equiv \langle\mu|\mathbf{\Omega}_a(\varepsilon)|\nu\rangle = \sum_{i(\lambda_i \neq \varepsilon)}^{n} \frac{\langle\mu|\mathbf{V}_a - \varepsilon\,\mathbf{P}_a|\Phi_i\rangle\langle\Phi_i|\mathbf{V}_a - \varepsilon\,\mathbf{P}_a|\nu\rangle}{\varepsilon - \lambda_i},$$
$$\mu,\nu = 1,\ldots,\sigma. \tag{2.34b}$$

Expressions (2.34) are formally identical to the expressions (2.10). However, in the case of an internal modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ satisfy expressions (2.4), while in the case of an external modification operators $\mathbf{V}$ and $\mathbf{P}$ satisfy expressions (2.8). Hence operator $\mathbf{\Omega}_a(\varepsilon)$ has non-vanishing matrix elements in the interaction space X_σ^{int}, while operator $\mathbf{\Omega}_b(\varepsilon)$ has non-vanishing matrix elements in the base space X_ρ^b.

In analogy to the interlacing rule that applies to external modifications, there is an interlacing rule that applies to internal modifications.

2.3.1. Interlacing of Modified Eigenvalues with Parent Eigenvalues

Eigenvalues ε_s of the modified system $\mathbf{C}_n$ and eigenvalues λ_i of the parent system $\boldsymbol{A}_n$ satisfy [13]:

Interlacing rule 2 (internal modifications):

Let ranks of modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ be σ_h and σ_s, respectively. Let further r_h nonzero eigenvalues of $\mathbf{V}_a$ be positive, the remaining $\sigma_h - r_h$ nonzero eigenvalues of $\mathbf{V}_a$ being negative. Arrange eigenvalues λ_i ($i = 1, \cdots, n$) of the parent system $\mathbf{A}_n$ in the non-decreasing order and arrange also eigenvalues ε_s ($s = 1, \cdots, n$) of the modified system $\mathbf{C}_n$ in the non-decreasing order. These eigenvalues thus arranged satisfy

$$\lambda_{s+r_h-\sigma_s-\sigma_h} \leq \varepsilon_s \leq \lambda_{s+r_h+\sigma_s} . \tag{2.35}$$

2.3.2. Cardinal Solutions of the Modified System

Let me now consider solutions of the modified system $\mathbf{C}_n$ in more details. In analogy to the external modifications, in the case of internal modifications one can also have cardinal ($\varepsilon_s \notin \{\lambda_i\}$) and singular ($\varepsilon_s \in \{\lambda_i\}$) solutions of this system. Concerning cardinal solutions of $\mathbf{C}_n$, one has [13]:

Theorem 3 (cardinal solutions): Let the system $\boldsymbol{A}_n$ be described by the eigenvalue equation (2.1a) and let eigenstates $|\Phi_i\rangle$ of this system be orthonormalized according to (2.1b). Then:

a) $\varepsilon_s \notin \{\lambda_i\}$ is cardinal eigenvalue of the eigenvalue equation (2.2a) if and only if it satisfies

$$\left[\beta\mathbf{\Omega}_a(\varepsilon_s) - \mathbf{V}_a + \varepsilon_s\mathbf{P}_a\right]|\varphi_s\rangle = 0, \quad |\varphi_s\rangle \in X_\sigma^{\text{int}}, \tag{2.36a}$$

where operator $\mathbf{\Omega}_a(\varepsilon)$ is given by expressions (2.34).

In the base $\{|\mu\rangle\}$ expression (2.36a) is a $\sigma \times \sigma$ matrix equation. In particular, operator $\mathbf{\Omega}_a(\varepsilon)$ is in this base $\sigma \times \sigma$ matrix with matrix elements (2.34b). Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of (2.2a) is hence a root of the $\sigma \times \sigma$ determinant $g(\varepsilon)$:

$$g(\varepsilon) \equiv \left|\beta \mathbf{\Omega}_a(\varepsilon) - \mathbf{V}_a + \varepsilon \mathbf{P}_a\right| = 0. \tag{2.36b}$$

b) $|\Psi_s\rangle$ is an eigenstate of the eigenvalue equation (2.2a) that has cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ if and only if it is a linear combination

$$|\Psi_s\rangle = \beta \sum_i^n \frac{\langle \Phi_i | \mathbf{V}_a - \varepsilon_s \mathbf{P}_a | \varphi_s \rangle}{\varepsilon_s - \lambda_i} |\Phi_i\rangle, \tag{2.37a}$$

where $|\varphi_s\rangle \in X_\rho^{\text{int}}$ is an eigenstate of (2.36a) corresponding to the eigenvalue $\varepsilon = \varepsilon_s$.

Degeneracy of the cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of the modified system $\mathbf{C}_n$ equals number of linearly independent eigenstates $|\varphi_s\rangle$ of (2.36a) that correspond to this eigenvalue. In other words, this degeneracy equals nullity of the matrix $\beta \mathbf{\Omega}_a(\varepsilon_s) - \mathbf{V}_a + \varepsilon_s \mathbf{P}_a$. Since this is a $\sigma \times \sigma$ matrix, each cardinal eigenvalue of a modified system can be at most σ-degenerate.

X_σ^{int}-component of the cardinal eigenstate (2.37a) equals eigenstate $|\varphi_s\rangle$ of (2.36a):

$$\mathbf{I}_\sigma^{\text{int}} |\Psi_s\rangle = |\varphi_s\rangle \in X_\sigma^{\text{int}}, \tag{2.37b}$$

This expression is analogous to the expression (2.13b) in the case of external modifications.

Eigenstates $|\Psi_s\rangle$ can be orthonormalized according to (2.2c). If $\varepsilon_s \neq \varepsilon_p$ eigenstates $|\Psi_s\rangle$ and $|\Psi_p\rangle$ automatically satisfy (2.2c). However, if

$\varepsilon_s = \varepsilon_p$ one has to enforce this orthogonality by some standard orthonormalization procedure. In particular, using expressions (2.4a) and (2.37a), one finds that cardinal eigenstate (2.37a) can be normalized according to

$$\left|\Psi_s\right\rangle \to \left|\Psi_s^{'}\right\rangle = \frac{1}{\sqrt{N_s}}\left|\Psi_s\right\rangle, \tag{2.37c}$$

where normalization constant N_s equals

$$N_s \equiv \left\langle\Psi_s\right|\mathbf{S}_a + \beta\mathbf{P}_a\left|\Psi_s\right\rangle = \\ \beta^2\sum_i^n \frac{\left\langle\varphi_s\right|\mathbf{V}_a - \varepsilon_s\mathbf{P}_a\left|\Phi_i\right\rangle\left\langle\Phi_i\right|\mathbf{V}_a - \varepsilon_s\mathbf{P}_a\left|\varphi_s\right\rangle}{\left(\varepsilon_s - \lambda_i\right)^2} + \beta\left\langle\varphi_s\right|\mathbf{P}_a\left|\varphi_s\right\rangle \text{,(2.37d)}$$

In the case of standard eigenvalue equations one has $\mathbf{P}_a = 0$ and above expression simplifies to

$$N_s = \beta^2\sum_i^n \frac{\left\langle\varphi_s\right|\mathbf{V}_a\left|\Phi_i\right\rangle\left\langle\Phi_i\right|\mathbf{V}_a\left|\varphi_s\right\rangle}{\left(\varepsilon_s - \lambda_i\right)^2}. \tag{2.37e}$$

In analogy to the case of external modification, calculation of the normalization constant N_s requires only the knowledge of the X_σ^{int}-component $\left|\varphi_s\right\rangle$ of the eigenstate $\left|\Psi_s\right\rangle$. The knowledge of the component of this eigenstate outside the interaction space is not required. Of course, as in the case of external modifications, this is due to the fact that X_σ^{int}-component of the cardinal eigenstate $\left|\Psi_s\right\rangle$ uniquely determines complete eigenstate. Information about the complete cardinal eigenstate $\left|\Psi_s\right\rangle$ is hence implicitly contained in its X_σ^{int}-component. Therefore this component alone should be sufficient to normalize this eigenstate. Nevertheless it is quite remarkable and highly convenient that this normalization can be done by the relatively simple expressions (2.23) and (2.37d).

2.3.3. Singular Solutions of the Modified System

Concerning singular solutions of $\mathbf{C}_n$, one has [13]:

Theorem 4 (singular solutions): Let λ_j be a η_j-degenerate eigenvalue of the eigenvalue equation (2.1a) that describes parent system $\boldsymbol{A}_n$ and let $X_{\eta j}^{\lambda j}$ be the corresponding η_j-dimensional space spanned by η_j degenerate eigenstates $\left|\Phi_{jl}\right\rangle$ ($l = 1,\ldots,\eta_j$) of (2.1a). Let further $\mathbf{I}_{\eta j}^{\lambda j}$ be the projection operator on the space $X_{\eta j}^{\lambda j}$. Then:

Each singular eigenstate $\left|\Psi_s\right\rangle$ of the modified system $\mathbf{C}_n$ that has eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ is a linear combination

$$\left|\Psi_s\right\rangle = \beta \sum_{i(\lambda_i \neq \varepsilon_s)}^{n} \frac{\left\langle \Phi_i \middle| \mathbf{V}_a - \varepsilon_s \mathbf{P}_a \middle| \varphi_s \right\rangle}{\varepsilon_s - \lambda_i} \left|\Phi_i\right\rangle + \left|\chi_s\right\rangle, \tag{2.38a}$$

where

$$\left|\varphi_s\right\rangle \in X_\sigma^{\text{int}}, \qquad \left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j}. \tag{2.38b}$$

and where those two states satisfy

$$\left[\beta \mathbf{\Omega}_a(\varepsilon_s) - \mathbf{V}_a + \varepsilon_s \mathbf{P}_a\right]\left|\varphi_s\right\rangle + \left(\mathbf{V}_a - \varepsilon_s \mathbf{P}_a\right)\mathbf{I}_{\eta_j}^{\lambda_j}\left|\chi_s\right\rangle = 0, \tag{2.39a}$$

$$\beta \mathbf{I}_{\eta j}^{\lambda j}\left(\mathbf{V}_a - \varepsilon_s \mathbf{P}_a\right)\left|\varphi_s\right\rangle = 0. \tag{2.39b}$$

In addition, the state $\left|\varphi_s\right\rangle$ is X_σ^{int}-component of the eigenstate $\left|\Psi_s\right\rangle$ and it satisfies (2.37b). Concerning the state $\left|\chi_s\right\rangle$, according to (2.38b) this state is contained in the space $X_{\eta_j}^{\lambda_j} \subset X_n^a$ and in analogy to the case of external modifications it satisfies:

$$\mathbf{O}_{\eta_j}^{\lambda_j}\left|\Psi_s\right\rangle = \left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j}. \tag{2.40}$$

where operator $\mathbf{O}_{\eta_j}^{\lambda_j}$ is given by (2.17b).

In a matrix form expressions (2.39) form a set of $(\sigma+\eta_j)$ homogenous linear equations in $(\sigma+\eta_j)$ unknowns, σ unknown coefficients $C_\nu^{(s)}$ and η_j unknown coefficients $D_l^{(s)}$ where

$$\left|\varphi_s\right\rangle = \sum_\nu^\sigma C_\nu^{(s)}\left|\nu\right\rangle, \quad \left|\chi_s\right\rangle = \sum_l^{\eta j} D_l^{(s)}\left|\Phi_{jl}\right\rangle. \tag{2.41}$$

Modified system $\mathbf{C}_n$ has a singular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ if and only if determinant of the system (2.39) vanishes. Since this is a $(\sigma+\eta_j)\times(\sigma+\eta_j)$ system, one may have at most $(\sigma+\eta_j)$ linearly independent singular eigenstates with this eigenvalue.

One can again distinguish *strongly singular* and *weakly singular* eigenstates. In analogy to the case of external modifications, in the case of an internal modification strongly singular eigenstate $\left|\Psi_s\right\rangle$ of the eigenvalue equation (2.2a) has no component in the interaction space X_σ^{int}, *i.e.* it satisfies $\mathbf{I}_\sigma^{\text{int}}\left|\Psi_s\right\rangle = 0$ and hence $\left|\varphi_s\right\rangle = 0$. On the other hand, each weakly singular eigenstate $\left|\Psi_s\right\rangle$ satisfies $\mathbf{I}_\sigma^{\text{int}}\left|\Psi_s\right\rangle \neq 0$.

Theorem 4 implies:

Theorem 4a:

$\left|\Psi_s\right\rangle$ is *strongly singular* eigenstate of the eigenvalue equation (2.2a) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if this state satisfies

$$\left|\Psi_s\right\rangle \equiv \left|\chi_s\right\rangle \in X_{\eta j}^{\lambda j}, \qquad (\mathbf{V}_a - \varepsilon_s\mathbf{P}_a)\mathbf{I}_{\eta j}^{\lambda j}\left|\chi_s\right\rangle = 0. \tag{2.42}$$

This state is hence a linear combination

$$\left|\Psi_s\right\rangle = \sum_{l}^{\eta j} D_l^{(s)} \left|\Phi_{jl}\right\rangle, \tag{2.43a}$$

where the coefficients $D_l^{(s)}$ satisfy

$$\sum_{l}^{\eta_j} \left\langle \mu \left| \mathbf{V}_a - \varepsilon_s \mathbf{P}_a \right| \Phi_{jl} \right\rangle D_l^{(s)} = 0, \qquad \mu = 1,\ldots,\sigma \ . \tag{2.43b}$$

$\left|\Psi_s\right\rangle$ is weakly singular eigenstate of the generalized eigenvalue equation (2.2b) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if it is a linear combination (2.38a) where the states $\left|\varphi_s\right\rangle$ and $\left|\chi_s\right\rangle$ satisfy expressions (2.39) and where $\left|\varphi_s\right\rangle \neq 0$. In addition, each weakly singular eigenstate should be orthogonal to all strongly singular eigenstates.

According to the above expressions, the set of all strongly singular eigenstates associated with the eigenvalue $\varepsilon_s = \lambda_j$ spans some r_j-dimensional space $X_{rj}^{\lambda j-}$, subspace of the space $X_{\eta j}^{\lambda j}$. Expression (2.43b) implies

$$\eta_j - \sigma \le r_j \le \eta_j \,. \tag{2.44}$$

Strongly singular eigenstates in the case of internal modifications have essentially the same properties as strongly singular eigenstates in the case of external modifications. In particular, expressions (2.42-2.44) are formally identical to the expressions (2.18-2.20). Thus according to (2.44), if degeneracy η_j of the eigenvalue λ_j of the parent system $\boldsymbol{A}_n$ satisfies $\eta_j > \sigma$, modified system $\mathbf{C}_n$ has at least $\eta_j - \sigma$ linearly independent strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. Those eigenstates do not depend on the coupling parameter β and each strongly singular eigenstate $\left|\Psi_s\right\rangle$ of the modified system $\mathbf{C}_n$ is at the same time an eigenstate of the parent system $\boldsymbol{A}_n$. Weakly singular eigenstates in the case of an internal modification have similar though not identical properties to the weakly singular eigenstates in the case of an external modification. In particular, expressions (2.39) differ from the corresponding expressions (2.15). However in analogy to the case of external modifications, in the case of internal modifications each weakly singular eigenstate $\left|\Psi_s\right\rangle$ depends on a coupling parameter β as well as on the modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$. Further, no weakly singular eigenstate of the modified system can be at the same time an eigenstate of the parent system. Finally, if $\left|\Psi_s\right\rangle$ is weakly singular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j$, the state $\left|\chi_s\right\rangle$ in the expressions (2.39) which produce this eigenstate is uniquely determined by the state $\left|\varphi_s\right\rangle \in X_\sigma^{\text{int}}$ in those expressions. As a consequence and since the space X_σ^{int} is σ-dimensional, one may have at most σ linearly independent weakly singular eigenstates with each particular eigenvalue $\varepsilon_s = \lambda_j$.

Above two theorems produce all solutions of the modified system $\mathbf{C}_n$. All cardinal eigenvalues $\varepsilon_s \notin \{\lambda_i\}$ of the modified eigenvalue equation (2.2a) are roots of the function (2.36b). Once a particular root ε_s of this function is found, the corresponding eigenstate (or eigenstates) is given by eq. (2.37a) where the state $\left|\varphi_s\right\rangle \in X_\sigma^{\text{int}}$ satisfies (2.36a). Concerning singular eigenvalues $\varepsilon_s \in \{\lambda_i\}$, each such eigenvalue coincides with some parent eigenvalue λ_j, and all one has to do is to verify conditions (2.39). This verification is simplified by the expressions (2.43) which produce all strongly singular eigenstates.

In analogy to the case of external modifications, in the case of internal modifications most important and most time-consuming is finding roots of the determinant (2.36b). Roots of this determinant are cardinal eigenvalues of the modified system. Operational count for a single cardinal eigenvalue is of the order $O(\sigma^2 n)$. Once an eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ is obtained, LRM calculation of the corresponding modified eigenstate or eigenstates is of the order $O(\sigma^3)$. Hence if $\sigma << \sqrt{n}$, LRM will be more efficient than any other numerical method in finding eigenvalues and eigenstates of the modified system.

Note that in the case of an internal modification, it is not strictly required that one should use the interaction space X_σ^{int} which is the range of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. Instead of this space one can use any other κ-dimensional space $X_\kappa^{\text{int}} \subset X_n^a$ which contains the interaction space X_σ^{int} as its subspace. Interaction space X_σ^{int} is the smallest space with the property that modification operators $\mathbf{V}_a$ and $\mathbf{P}_a$ vanish in the orthogonal complement of this space. From the LRM point of view, the use of the interaction space X_σ^{int} which is the smallest space with this property is most economical. However, in some cases it might be more practical to use some of those larger spaces instead of the interaction space.

In the original presentation of the LRM treatment of internal modifications described by eigenvalue equations of a general type (2.1a) and (2.2a), corresponding LRM expression were not Hermitean [13]. Key expressions (2.36a) and (2.39) presented here are Hermitean. Those expressions can be easily derived from the original expressions in ref. [13]. It is clearly advantageous to have Hermitean instead of non-Hermitean equations.

There are two special cases of particular interest when above LRM expressions substantially simplify. Those are cases $\mathbf{P}_a = 0$ and $\mathbf{V}_a = 0$. Consider first the case $\mathbf{P}_a = 0$.

2.3.4. Case $\mathbf{P}_a = 0$

If $\mathbf{P}_a = 0$ equation (2.2a) reduces to

$$(\mathbf{H}_a + \beta \mathbf{V}_a) \left| \Psi_s \right\rangle = \varepsilon_s \mathbf{S}_a \left| \Psi_s \right\rangle, \quad s = 1, \dots, n. \qquad (2.45)$$

Define operator $\mathbf{\Omega}^0(\varepsilon)$:

$$\mathbf{\Omega}^0(\varepsilon) = \mathbf{I}_\sigma^{\text{int}} \overline{\Omega}(\varepsilon) \mathbf{I}_\sigma^{\text{int}}, \qquad (2.46a)$$

This operator vanishes outside the interaction space X_σ^{int}, and in the base $\{|\mu\rangle\}$ of this space it has matrix elements

$$\mathbf{\Omega}^0_{\mu\nu}(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)}^{n} \frac{\langle \mu | \Phi_i \rangle \langle \Phi_i | \nu \rangle}{\varepsilon - \lambda_i}, \qquad \mu, \nu = 1, \ldots, \sigma . \tag{2.46b}$$

Theorem 3 now reduces to:

Theorem 3A (cardinal solutions): Let the system $\boldsymbol{A}_n$ be described by the eigenvalue equation (2.1a) and let eigenstates $|\Phi_i\rangle$ of this system be orthonormalized according to (2.1b). Let further modified system $\mathbf{C}_n$ be described by the eigenvalue equation (2.45). Then:

a) $\varepsilon_s \notin \{\lambda_i\}$ is a cardinal eigenvalue of the eigenvalue equation (2.45) if and only if it satisfies

$$\left[\beta \mathbf{\Omega}^0(\varepsilon_s) - \mathbf{V}_a^{-1}\right] |\varphi_s\rangle = 0 \, , |\varphi_s\rangle \in X_\sigma^{\text{int}} , \tag{2.47a}$$

where $\mathbf{V}_a^{-1}$ is Hermitean operator, inverse of $\mathbf{V}_a$ in the interaction space X_σ^{int}.

In the base $\{|\mu\rangle\}$ expression (2.47a) is a $\sigma \times \sigma$ matrix equation. Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of (2.45) is hence a root of a $\sigma \times \sigma$ determinant $f(\varepsilon)$:

$$f(\varepsilon) \equiv \left| \beta \mathbf{\Omega}^0(\varepsilon) - \mathbf{V}_a^{-1} \right| = 0 \, . \tag{2.47b}$$

Note that since σ is the rank of the modification operator $\mathbf{V}_a$, this operator is nonsingular in X_σ^{int} and hence inverse $\mathbf{V}_a^{-1}$ exist.

b) Each normalized cardinal eigenstate $|\Psi_s\rangle$ of the generalized eigenvalue equation (2.45) that has eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ is a linear combination

$$|\Psi_s\rangle = \frac{1}{\sqrt{N_s}} \sum_i^n \frac{\langle \Phi_i | \varphi_s \rangle}{\varepsilon_s - \lambda_i} |\Phi_i\rangle , \tag{2.48a}$$

where $\left|\varphi_s\right\rangle \in X_\rho^{\text{int}}$ is an eigenstate of (2.47a) that corresponds to the eigenvalue ε_s, and where N_s is a normalization constant

$$N_s = \sum_i^n \frac{\left\langle \varphi_s \middle| \Phi_i \right\rangle \left\langle \Phi_i \middle| \varphi_s \right\rangle}{\left(\varepsilon_s - \lambda_i\right)^2} . \tag{2.48b}$$

In addition, cardinal eigenstate (2.48a) is related to the state $\left|\varphi_s\right\rangle \in X_\sigma^{\text{int}}$ according to

$$\left|\varphi_s\right\rangle = \sqrt{N_s}\,\mathbf{V}_a \left|\Psi_s\right\rangle . \tag{2.48c}$$

In a similar way can be treated singular solutions of (2.45).

Of special interest is the case $\sigma = rank(\mathbf{V}) = 1$. In this case the space X_σ^{int} reduces to a single state $\left|\tau\right\rangle$. Hence $\mathbf{V}_a = \Delta h_\tau \left|\tau\right\rangle\left\langle\tau\right|$, $\left|\varphi_s\right\rangle = \left|\tau\right\rangle$, and expression (2.47b) reduces to

$$\beta\,\Omega_{\tau\tau}^0(\varepsilon) = \frac{1}{\Delta h_\tau} . \tag{2.49}$$

where $\Omega_{\tau\tau}^0(\varepsilon)$ is given by (2.46b).

Each root $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of (2.49) is a cardinal eigenvalue of the modified system. The corresponding normalized eigenstate $\left|\Psi_s\right\rangle$ is non-degenerate and one has

$$\left|\Psi_s\right\rangle = \frac{1}{\sqrt{N_s}} \sum_i^n \frac{\left\langle \Phi_i \middle| \tau \right\rangle}{\varepsilon_s - \lambda_i} \left|\Phi_i\right\rangle , \tag{2.50a}$$

where

$$N_s = \sum_i^n \frac{\langle \tau | \Phi_i \rangle \langle \Phi_i | \tau \rangle}{(\varepsilon_s - \lambda_i)^2}. \tag{2.50b}$$

Further, each normalized strongly singular eigenstate $|\Psi_s\rangle$ that has eigenvalue $\varepsilon_s = \lambda_j$ is a linear combination

$$|\Psi_s\rangle = \frac{1}{\sqrt{N_s}} \sum_l^{\eta_j} D_l^{(s)} |\Phi_{jl}\rangle, \tag{2.51a}$$

where normalization constant N_s equals

$$N_s = \sum_l^{\eta_l} D_l^{(s)} D_l^{(s)*}, \tag{2.51b}$$

and where the coefficients $D_l^{(s)}$ satisfy a single condition

$$\sum_l^{\eta_j} \langle \tau | \Phi_{jl} \rangle D_l^{(s)} = 0. \tag{2.51c}$$

In particular, if eigenvalue λ_j is degenerate ($\eta_j > 1$), modified system $\mathbf{C}_n$ has at least $\eta_j - 1$ strongly singular eigenstates with this eigenvalue. Concerning weakly singular eigenstates, one finds that weakly singular eigenstate $|\Psi_s\rangle$ associated with the eigenvalue $\varepsilon_s = \lambda_j$ exists if and only if all matrix elements $\langle \Phi_{jl} | \tau \rangle$ vanish

$$\langle \Phi_{jl} | \tau \rangle = 0, \qquad l = 1, \ldots, \eta_j, \tag{2.52a}$$

and if in addition this eigenvalue satisfies

$$\beta \Omega_{\tau\tau}^{0}(\varepsilon_s) = \frac{1}{\Delta h_\tau}. \qquad (2.52b)$$

If this is the case, the corresponding (normalized) weakly singular eigenstate is a linear combination

$$|\Psi_s\rangle = \frac{1}{\sqrt{N_s}} \sum_{i(\lambda_i \neq \varepsilon_s)} \frac{\langle \Phi_i | \tau \rangle}{\varepsilon_s - \lambda_i} |\Phi_i\rangle, \quad \varepsilon_s = \lambda_j. \qquad (2.53a)$$

where

$$N_s = \sum_{i(\lambda_i \neq \varepsilon_s)}^{n} \frac{\langle \tau | \Phi_i \rangle \langle \Phi_i | \tau \rangle}{(\varepsilon_s - \lambda_i)^2}. \qquad (2.53b)$$

Those expressions are similar to the expressions (2.50) which apply to cardinal eigenstates, except that the term with $\lambda_i = \varepsilon_s$ is excluded from the summations in (2.53a) and (2.53b).

Concerning interlacing rule, in the case $\sigma = 1$ and $\mathbf{P}_a = 0$ expression (2.35) reduces to

$$\lambda_1 \le \varepsilon_1 \le \lambda_2 \le \varepsilon_2 \le \ldots \le \varepsilon_n, \qquad \textit{if} \quad \Delta h_\tau > 0, \qquad (2.54a)$$

$$\varepsilon_1 \le \lambda_1 \le \varepsilon_2 \le \lambda_2 \le \ldots \le \lambda_n, \qquad \textit{if} \quad \Delta h_\tau < 0. \qquad (2.54b)$$

2.3.5. Case $\mathbf{V}_a = 0$

Another special case is $\mathbf{V}_a = 0$. In this case equation (2.2a) describing modified system $\mathbf{C}_n$ reduces to

$$\mathbf{H}_a |\Psi_s\rangle = \varepsilon_s (\mathbf{S}_a + \beta \mathbf{P}_a) |\Psi_s\rangle, \quad s = 1, \ldots, n. \qquad (2.55)$$

while **Theorem 3** reduces to:

Theorem 3B (cardinal solutions): Let the system $\boldsymbol{A}_n$ be described by the eigenvalue equation (2.1a) and let eigenstates $|\Phi_i\rangle$ of this system be orthonormalized according to (2.1b). Let further the system $\mathbf{C}_n$ be described by the eigenvalue equation (2.55). Then:

a) $\varepsilon_s \neq 0$ is a cardinal eigenvalue of the eigenvalue equation (2.55) if and only if it satisfies

$$\left[\beta\mathbf{\Omega}^0(\varepsilon_s) + \frac{\mathbf{P}_a^{-1}}{\varepsilon_s}\right]|\varphi_s\rangle = 0, \qquad |\varphi_s\rangle \in X_\sigma^{\text{int}}, \tag{2.56a}$$

where $\mathbf{P}_a^{-1}$ is a Hermitean operator, inverse of $\mathbf{P}_a$ in the interaction space X_σ^{int}. In the base $\{|\mu\rangle\}$ expression (2.56a) is a $\sigma\times\sigma$ matrix equation. Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of (2.55) that differs from zero is hence a root of a $\sigma\times\sigma$ determinant

$$f(\varepsilon) \equiv \left|\beta\mathbf{\Omega}^0(\varepsilon) + \frac{\mathbf{P}_a^{-1}}{\varepsilon}\right| = 0. \tag{2.56b}$$

Note that since σ is the rank of the modification operator $\mathbf{P}_a$, this operator is nonsingular in X_σ^{int} and hence inverse $\mathbf{P}_a^{-1}$ exist.

b) Each eigenstate $|\Psi_s\rangle$ of the generalized eigenvalue equation (2.55) that has eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ is a linear combination

$$|\Psi_s\rangle = \sum_i^n \frac{\langle\Phi_i|\varphi_s\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle, \tag{2.57a}$$

where $|\varphi_s\rangle \in X_\sigma^{\text{int}}$ is an eigenstate of (2.56a) that corresponds to the eigenvalue ε_s. In addition, one has

$$\left|\varphi_s\right\rangle = -\varepsilon_s \beta \mathbf{P}_a \left|\Psi_s\right\rangle . \tag{2.57b}$$

Above expressions produce all cardinal solutions of the combined system, except of cardinal solutions with the eigenvalue $\varepsilon_s = 0$ (provided such solutions exist). The possibility $\varepsilon_s = 0$ can be easily verified using general expressions (2.36). Inserting $\mathbf{V}_a = 0$ and $\varepsilon_s = 0$ into (2.36b) one derives condition $\left|\mathbf{\Omega}^0(\mathbf{0})\right| = 0$. Accordingly, cardinal eigenvalue $\varepsilon = \varepsilon_s = 0$ exist if and only if $0 \notin \{\lambda_i\}$ (no eigenvalue λ_i of $\mathbf{A}_n$ equals zero) and if in addition determinant of the matrix $\mathbf{\Omega}^0(\mathbf{0})$ vanishes. With the exception of this special case, above expressions produce all cardinal solutions of the modified system. In a similar way can be obtained expressions for the singular solutions of this system.

Concerning the interlacing rule, since $\mathbf{V}_a = 0$ expression (2.35) simplifies to $\lambda_{s-\sigma} \le \varepsilon_s \le \lambda_{s+\sigma}$ where $\sigma = \sigma_s$. This rule can be further tightened in some special but important cases. In particular, if no eigenvalue λ_i of (2.1a) is negative, one has

Interlacing rule 3 (case $\mathbf{V}_a = 0$): Let the rank of the operator $\mathbf{P}_a$ be σ and let all eigenvalues λ_i of the parent system $\boldsymbol{A}_n$ be nonnegative. Let further r nonzero eigenvalues of the operator $\mathbf{P}_a$ be positive, the remaining $\sigma - r$ nonzero eigenvalues being negative. Arrange eigenvalues λ_i of $\boldsymbol{A}_n$ in the non-decreasing order, and arrange also eigenvalues ε_s of the modified system $\mathbf{C}_n$ in the non-decreasing order. Those eigenvalues thus arranged satisfy:

$$\lambda_{s-r} \le \varepsilon_s \le \lambda_{s+\sigma-r} . \tag{2.58}$$

Of special interest is the case $\sigma = rank(\mathbf{P}_a) = 1$. In this case the space X_σ^{int} reduces to a single state $\left|\tau\right\rangle$. Hence $\mathbf{P}_a = \Delta s_\tau \left|\tau\right\rangle\left\langle\tau\right|$, $\left|\varphi_s\right\rangle = \left|\tau\right\rangle$, and expression (2.56b) reduces to

$$\beta\,\Omega^{0}_{\tau\tau}(\varepsilon)+\frac{1}{\varepsilon\,\Delta s_{\tau}}=0\,, \tag{2.59}$$

Each root $\varepsilon=\varepsilon_s\notin\{\lambda_i\}$ of (2.59) is a cardinal eigenvalue of the modified system. The corresponding eigenstate $|\Psi_s\rangle$ is non-degenerate and one has

$$|\Psi_s\rangle=\sum_{i}^{n}\frac{\langle\Phi_i|\tau\rangle}{\varepsilon_s-\lambda_i}|\Phi_i\rangle, \tag{2.60}$$

Further, each strongly singular eigenstate $|\Psi_s\rangle$ that has eigenvalue $\varepsilon_s=\lambda_j$ is a linear combination

$$|\Psi_s\rangle=\sum_{l}^{\eta_j}D_l^{(s)}|\Phi_{jl}\rangle, \tag{2.61a}$$

where the coefficients $D_l^{(s)}$ satisfy a single condition

$$\sum_{l}^{\eta_j}\langle\tau|\Phi_{jl}\rangle D_l^{(s)}=0 \tag{2.61b}$$

Concerning weakly singular eigenstates, one finds that weakly singular eigenstate $|\Psi_s\rangle$ associated with the eigenvalue $\varepsilon_s=\lambda_j$ exists if and only if all matrix elements $\langle\Phi_{jl}|\tau\rangle$ vanish

$$\begin{aligned}&\langle\Phi_{jl}|\tau\rangle=0\,,\\&l=1,\ldots,\eta_j\,,\end{aligned} \tag{2.62a}$$

and if in addition this eigenvalue satisfies

$$\beta\,\Omega^{0}_{\tau\tau}(\varepsilon_s)+\frac{1}{\varepsilon_s\Delta s_{\tau}}=0\,. \tag{2.62b}$$

If this is the case, the corresponding weakly singular eigenstate is a linear combination

$$\left|\Psi_s\right\rangle = \sum_{i(\lambda_i \neq \varepsilon_s)} \frac{\left\langle \Phi_i \middle| \tau \right\rangle}{\varepsilon_s - \lambda_i} \left|\Phi_i\right\rangle,$$

$$\varepsilon_s = \lambda_j . \tag{2.63}$$

According to (2.62a), if modified system has weakly singular eigenstate (2.63), it has in addition η_j strongly singular eigenstates $\left|\Phi_{jl}\right\rangle$ ($l = 1,\ldots,\eta_j$) with the same eigenvalue. Hence in this case modification operator $\mathbf{P}_a$ increases degeneracy of the eigenvalue λ_j of the parent system by one. Note that the expression (2.63) is similar to the expression (2.60) which applies to cardinal eigenstates.

For simplicity in the above expressions normalization constants were not given. Those constants can be easily obtained observing the condition $\left\langle \Psi_s \middle| \mathbf{S}_a + \beta \mathbf{P}_a \middle| \Psi_s \right\rangle = 1$.

2.4. LRM TREATMENT OF THE VIBRATIONAL ISOTOPE EFFECT IN THE HARMONIC APPROXIMATION

Let me now show how one can apply LRM formalism to the concrete problem in quantum chemistry. In particular, I will consider vibrational isotope effect in the harmonic approximation.

Molecular vibrations can be relatively well described within the harmonic approximation where atomic nuclei are represented by mathematical points with masses [5,6]. Displacements of nuclei from equilibrium positions can be described by Cartesian coordinates. If the molecule $\boldsymbol{A}_n$ contains N nuclei, there are $n = 3N$ such coordinates. Mathematical treatment of the molecular system $\boldsymbol{A}_n$ consisting of N masses connected by harmonic forces leads to the generalized eigenvalue equation

$$\mathbf{F}\left|\Phi_i\right\rangle = \lambda_i \mathbf{M}\left|\Phi_i\right\rangle, \; i = 1,\ldots,n, \tag{2.64a}$$

where $\mathbf{F}$ and $\mathbf{M}$ are force field and mass operators, respectively. Eigenstates $\left|\Phi_i\right\rangle$ of (2.64a) describe molecular vibrations, while the corresponding eigenvalues λ_i are connected with the vibrational frequencies ν_i according to [5-8]

$$\lambda_i = 4\pi^2\nu_i^2. \tag{2.64b}$$

In view of the expression (2.1b), eigenstates $\left|\Phi_i\right\rangle$ should be orthonormalized according to

$$\left\langle\Phi_i\middle|\mathbf{M}\middle|\Phi_j\right\rangle = \delta_{ij}, \quad i, j = 1,\ldots,n. \tag{2.64c}$$

Expression (2.64a) is essentially a standard $(\mathbf{F},\mathbf{G})$ formalism [5-8]. In this formalism one usually uses internal coordinates which are suitable for the actual molecular geometry. In the LRM approach it is more appropriate to use Cartesian coordinates. In order to emphasize that Cartesian coordinates are used, the symbol $\mathbf{M}$ is retained.

If in the original molecule $\boldsymbol{A}_n$ some or all atoms are replaced by an isotope, one obtains modified molecule $\mathbf{C}_n$. To a very good approximation, force field is not changed by isotopic substitutions [5-8]. Within the harmonic approximation vibrations of the isotopomer $\mathbf{C}_n$ are hence described by the eigenvalue equation

$$\mathbf{F}\left|\Psi_s\right\rangle = \varepsilon_s(\mathbf{M} + \Delta\mathbf{M})\left|\Psi_s\right\rangle, \qquad s = 1,\ldots,n, \tag{2.65a}$$

where $\Delta\mathbf{M}$ is the operator of the isotope mass changes. Eigenstates $\left|\Psi_s\right\rangle$ of (2.65a) are vibrations of the isotopomer $\mathbf{C}_n$, while the corresponding eigenvalues ε_s are related to the vibrational frequencies ω_s of this isotopomer according to

$$\varepsilon_s = 4\pi^2\omega_s^2 . \tag{2.65b}$$

Apart from different notation, equation (2.64a) is identical to the equation (2.1a), while equation (2.65a) is identical to the equation (2.55) where $\beta = 1$. As required by the LRM formalism, operators $\mathbf{M}$ and $\mathbf{M} + \Delta\mathbf{M}$ are positive definite. According to the LRM treatment of those expressions, if one knows the solution of the eigenvalue equation (2.64a), one can obtain an exact solution of the eigenvalue equation (2.65a) where $\Delta\mathbf{M}$ is an arbitrary isotope mass change. In other words, if one knows frequencies and normal modes of a parent molecule $\boldsymbol{A}_n$, one can obtain frequencies and normal modes of all isotopomers $\mathbf{C}_n$ of this molecule. In the case of each particular isotopomer $\mathbf{C}_n$ all one needs to know are positions (x_μ, y_μ, z_μ) of isotopic substitutions and corresponding mass changes Δm_μ. It is remarkable that in the harmonic approximation normal modes and corresponding frequencies of a parent molecule $\boldsymbol{A}_n$ uniquely determine all normal modes and vibrational frequencies of all possible isotopomers of this molecule.

One further point. In a standard mathematical treatment of molecular vibrations, equations (2.64a) and (2.65a) are expressed in a mass weighted coordinates where dependence on molecular masses is absorbed in the definition of related coordinates [5-8]. In the LRM approach explicit dependence on those masses is retained. Normal modes as defined in a standard treatment hence differ from normal modes as defined in the LRM. In a standard treatment normal modes $\left|\Phi_i^*\right\rangle$ of the parent molecule $\boldsymbol{A}_n$ are orthonormalized according to $\left\langle\Phi_i^*\middle|\Phi_j^*\right\rangle = \delta_{ij}$, while in the LRM approach those normal modes are orthonormalized according to (2.1b) where $\mathbf{S}_a \equiv \mathbf{M}$. Connection between normal modes $\left|\Phi_i^*\right\rangle$ and $\left|\Phi_i\right\rangle$ is $\left|\Phi_i^*\right\rangle = \mathbf{M}^{1/2}\left|\Phi_i\right\rangle$. In similar way normal modes $\left|\Psi_s^*\right\rangle$ and $\left|\Psi_s\right\rangle$ of the modified molecule $\mathbf{C}_n$ are related to each other according to $\left|\Psi_s^*\right\rangle = (\mathbf{M} + \Delta\mathbf{M})^{1/2}\left|\Psi_s\right\rangle$.

If molecules $\boldsymbol{A}_n$ and $\mathbf{C}_n$ are planar, in-plane and out-of-plane vibrations separate and expressions (2.64a) and (2.65a) apply separately to in-plane and separately to out-of-plane vibrations. For the sake of simplicity I will consider here only the LRM treatment of the vibrational isotope effect of out-of-plane vibrations of planar molecules. LRM treatment of in-plane vibrations of planar molecules and of the vibrations of arbitrary (nonplanar) molecules is formally the same, though numerically more involved.

2.4.1. Out-of-Plane Vibrations of Planar Molecules

Let $\boldsymbol{A}_n$ be a planar nonlinear molecule containing n atoms. Put the origin of the coordinate system in the centre of mass of this molecule and let x-, y- and z- axis coincide with principal axis of $\boldsymbol{A}_n$. Let further z-axis be perpendicular to the molecular plane, and let x- and y-axis lie in this plane. With this convention non-proper out-of-plane vibrations, translation $|T_z\rangle$ in the z-direction and rotations $|R_x\rangle$ and $|R_y\rangle$ around x- and y-axis of the parent molecule $\boldsymbol{A}_n$, are [15-17]

$$|T_z\rangle = \frac{1}{\sqrt{M}}\sum_{\alpha}^{n}|\alpha\rangle, \qquad |R_x\rangle = \frac{1}{\sqrt{I_x}}\sum_{\alpha}^{n} y_\alpha|\alpha\rangle,$$

$$|R_y\rangle = \frac{-1}{\sqrt{I_y}}\sum_{\alpha}^{n} x_\alpha|\alpha\rangle. \tag{2.66}$$

where M is molecular mass of the molecule $\boldsymbol{A}_n$, while I_x and I_y are moments of inertia of this molecule around x- and y- axis, respectively. Further, $|\alpha\rangle$ is a unit displacement of the α-*th* atom in the z-direction perpendicular to the molecular plane, while (x_α, y_α) is the position of this atom in this plane. Unit displacements $|\alpha\rangle$ ($\alpha = 1,\dots,n$) are orthonormalized according to (2.3b) and they span n-dimensional space X_n^a. If the origin of the coordinate system is in the centre of mass of molecule $\boldsymbol{A}_n$ and if x- and y-axis coincide with principal axis of this molecule, non-proper vibrations (2.66) are orthonormalized according to (2.64c), as required [15-17].

If one replaces $\sigma \leq n$ atoms in a parent molecule $\boldsymbol{A}_n$ with various isotopes, one obtains an isotopomer $\mathbf{C}_n$. In the harmonic approximation out-of-plane vibrations of this isotopomer are described by the eigenvalue equation (2.65a). In the base $\{|\mu\rangle\}$ ($\mu = 1,\ldots,\sigma$) operator $\Delta\mathbf{M}$ is diagonal and it satisfies $\Delta\mathbf{M}|\mu\rangle = \Delta m_\mu |\mu\rangle$ where the eigenvalue $\Delta m_\mu \neq 0$ is mass change at the substitution site μ. Matrix elements of the corresponding operator $\mathbf{\Omega}^0(\varepsilon)$ are given by expression (2.46b). From this expression one can eliminate non-proper vibrations (2.66) to obtain [15-17].

$$\mathbf{\Omega}^0_{\mu\nu}(\varepsilon) = \frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{x_\mu x_\nu}{I_y} + \frac{y_\mu y_\nu}{I_x}\right] + \sum_{i(\lambda_i \neq \varepsilon)}^{n-3} \frac{\langle\mu|\Phi_i\rangle\langle\Phi_i|\nu\rangle}{\varepsilon - \lambda_i},$$

$$\mu,\nu = 1,\ldots,\sigma, \tag{2.67a}$$

Since $\Delta\mathbf{M}$ is diagonal in the base $\{|\mu\rangle\}$, one has

$$\Delta\mathbf{M}^{-1}_{\mu\nu} = \frac{\delta_{\mu\nu}}{\Delta m_\mu}. \tag{2.67b}$$

In the expression (2.67a) $\langle\mu|\Phi_i\rangle$ is the amplitude of the normalized (out-of-plane) vibration $|\Phi_i\rangle$ of molecule $\boldsymbol{A}_n$ at the position (x_μ, y_μ) of the isotopic substitution, while λ_i is the corresponding eigenvalue. The summation in (2.67a) is performed over all proper vibrations $|\Phi_i\rangle$ that satisfy $\lambda_i \neq \varepsilon$.

According to **Theorem 3B**, each cardinal eigenvalue which differs from zero ($\varepsilon_s \neq 0$) of the isotopomer $\mathbf{C}_n$ satisfies

$$\left[\mathbf{\Omega}^0(\varepsilon_s) + \frac{\Delta\mathbf{M}^{-1}}{\varepsilon_s}\right]|\varphi_s\rangle = 0, \qquad |\varphi_s\rangle \in X^{\text{int}}_\rho, \tag{2.68a}$$

It is hence a root of the $\sigma \times \sigma$ determinant

$$f(\varepsilon) \equiv \left| \mathbf{\Omega}^0(\varepsilon) + \frac{\Delta\mathbf{M}^{-1}}{\varepsilon} \right| = 0 . \tag{2.68b}$$

This eigenvalue is related to the corresponding frequency ω_s according to (2.65b). Once ε_s and $|\varphi_s\rangle$ are known, the corresponding eigenstate is given as a linear combination (2.57a). From this expression one can eliminate the contribution of non-proper vibrations to obtain

$$|\Psi_s\rangle = \frac{1}{\varepsilon_s}\left[T^{(s)}|T_z\rangle + R_x^{(s)}|R_x\rangle + R_y^{(s)}|R_y\rangle\right] + \sum_i^{n-3} \frac{\langle\Phi_i|\varphi_s\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle , \tag{2.69a}$$

where $|\Phi_i\rangle$ are proper out-of-plane vibrations of the parent molecule $\boldsymbol{A}_n$, while $|T_z\rangle$, $|R_x\rangle$ and $|R_y\rangle$ are non-proper vibrations (2.66). Coefficients $T^{(s)}$, $R_x^{(s)}$ and $R_y^{(s)}$ are

$$T^{(s)} = \frac{1}{\sqrt{M}} \sum_\nu^\sigma \langle\nu|\varphi_s\rangle ,$$

$$R_x^{(s)} = \frac{1}{\sqrt{I_x}} \sum_\nu^\sigma y_\nu \langle\nu|\varphi_s\rangle ,$$

$$R_y^{(s)} = \frac{(-1)}{\sqrt{I_y}} \sum_\nu^\sigma x_\nu \langle\nu|\varphi_s\rangle , \tag{2.69b}$$

Due to (2.57b) and (2.65b), coefficients $\langle\nu|\varphi_s\rangle$ are related to the cardinal eigenstate (2.69a) according to

$$\langle\nu|\varphi_s\rangle = -4\pi^2\omega_s^2\Delta m_\nu \langle\nu|\Psi_s\rangle , \qquad \nu = 1,\ldots,\sigma . \tag{2.69c}$$

Vibrations $|\Psi_s\rangle$ can be orthonormalized according to (2.2c) where $\mathbf{S}_c = \mathbf{M} + \mathbf{\Delta M}$. If $\varepsilon_s \neq \varepsilon_p$ this expression is automatically satisfied.

However, if $\varepsilon_s = \varepsilon_p$ one has to enforce this relation by some standard orthonormalization procedure. According to (2.69a), modified vibration $\left|\Psi_s\right\rangle$ is expressed as a linear combination $\left|\Psi_s\right\rangle = \sum_i c_i \left|\Phi_i\right\rangle$. In order to normalize this vibration, matrix elements $\left\langle\Phi_i\right|\mathbf{M}+\Delta\mathbf{M}\left|\Phi_j\right\rangle$ are required. Those matrix elements can be obtained using expression

$$\Delta\mathbf{M} = \sum_{\mu}^{\sigma} \left|\mu\right\rangle \Delta m_\mu \left\langle\mu\right|, \tag{2.70a}$$

where Δm_μ is the change of the mass of atom μ by the isotope substitution. Since $\left|\Psi_s\right\rangle = \sum_i c_i \left|\Phi_i\right\rangle$ one has

$$\left\langle\Psi_s\right|\mathbf{M}+\Delta\mathbf{M}\left|\Psi_s\right\rangle = \sum_i c_i^* c_i + \sum_{i,j} c_i^* c_j \left\langle\Phi_i\right|\Delta\mathbf{M}\left|\Phi_j\right\rangle, \tag{2.70b}$$

where according to (2.70a) matrix elements $\left\langle\Phi_i\right|\Delta\mathbf{M}\left|\Phi_j\right\rangle$ equal

$$\left\langle\Phi_i\right|\Delta\mathbf{M}\left|\Phi_j\right\rangle = \sum_{\mu}^{\sigma} \left\langle\Phi_i\middle|\mu\right\rangle \Delta m_\mu \left\langle\mu\middle|\Phi_i\right\rangle, \tag{2.70c}$$

In particular, in the case of a single isotopic substitution on the atomic site τ, expression (2.70c) reduces to

$$\left\langle\Phi_i\right|\Delta\mathbf{M}\left|\Phi_j\right\rangle = \left\langle\Phi_i\middle|\tau\right\rangle \Delta m_\tau \left\langle\tau\middle|\Phi_i\right\rangle. \qquad . \tag{2.70d}$$

Using above expressions one can normalize each eigenstate $\left|\Psi_s\right\rangle$ of the modified system.

As emphasized in section 2.3.5, expression (2.68) does not produce cardinal solutions with the eigenvalue $\varepsilon_s = 0$. However if $\boldsymbol{A}_n$ is a rigid planar molecule, all proper frequencies ν_i of this molecule are positive, only three non-proper frequencies associated with non-proper vibrations (2.66) are zero. The same applies to the modified molecule $\mathbf{C}_n$. Since $\varepsilon_s = 4\pi^2\omega_s^2$, expression (2.68) produces all proper cardinal vibrations of the modified molecule $\mathbf{C}_n$ and no non-proper vibration of this molecule. Since in the analysis of the vibrational isotope effect one is interested only in the proper vibrations, this is exactly what is needed.

In a similar way can be treated singular vibrations of the isotopomer $\mathbf{C}_n$.

2.4.2. Interlacing Rule for out-of-Plane Vibrations of Planar Molecules

Vibrational spectra provide a large amount of information about a molecule. An efficient study and analysis of experimental frequencies requires correct assignment of those frequencies to various vibrational types and normal modes. Besides vibrational spectra of the original molecule, vibrational spectra of isotopically substituted molecules generate a huge amount of additional experimental data. Those data are important as a valuable source of information for the correct assignment and interpretation of experimental spectra. This assignment is highly facilitated by some simple rules which apply to vibrational frequencies of isotopically related molecules. One such rule is well known order rule [5-8]. If in a mechanical system that exhibits harmonic oscillations one increases the mass of one or few particles without changing the potential energy, the frequencies of normal vibrations do not increase. Those frequencies either decrease or remain the same. In particular, if frequencies ν_i of the parent molecule $\mathbf{A}_n$ are arranged in the increasing order, and if frequencies ω_s of the heavier isotopic molecule $\mathbf{C}_n$ are also arranged in the increasing order, then [7,8]

$$\omega_1 \le \nu_1, \omega_2 \le \nu_2, \ldots, \omega_s \le \nu_s, \ldots \tag{2.71}$$

Order rule involves all frequencies of such isotopic molecules $\mathbf{A}_n$ and $\mathbf{C}_n$ where all substituted isotopes in the molecule $\mathbf{C}_n$ are heavier than the corresponding isotopes in the molecule $\mathbf{A}_n$.

Since the order rule is derived within the harmonic approximation, anharmonicity effects may violate this rule in some cases. However, those effects are usually small and experimental frequencies almost always satisfy this rule.

Some additional types of connections between vibrational frequencies of isotopic molecules can be obtained by various other isotopic rules. Of such rules are known the product rule [18], the sum rule [19] and the complete isotopic rule [20,21]. For example, the complete isotopic rule concerns three isotopic molecules A, B and C. These molecules must be in a special relation: molecule A is a planar molecule in which two definite atoms form a symmetrically equivalent set. B is identical to A except that one of these two atoms is exchanged for an isotope, and C is identical to A and B except that both of these two atoms are exchanged for this isotope [20]. An example is the set of three molecules: ethylene, *d1*-ethylene and *d2-trans*-ethylene. From the known frequencies of the compounds A and C one can now calculate frequencies of the compound B. Unlike order rule which is more general, the complete isotopic rule requires a ruther special arangemet of three related molecules. All other isotopic rules have also rather special and narow application. From all those rules order rule (2.71) is most general and most powerful.

Within the LRM formalism one can derive vibrational interlacing rule [15-17]. According to the expressions (2.64b) and (2.65b) all eigenvalues λ_i of the parent molecule $\boldsymbol{A}_n$ as well as all eigenvalues ε_s of the modified molecule $\mathbf{C}_n$ are nonnegative. Hence to this case applies LRM interlacing rule 3 (expression (2.58)). Due to the expressions (2.64b) and (2.65b), the same rule applies also to the corresponding frequencies ν_i and ω_s. In the case of out-of-plane vibrations, if the modified molecule $\mathbf{C}_n$ differs from the original molecule $\boldsymbol{A}_n$ by σ isotopic substitutions, modification operator $\Delta\mathbf{M}$ has rank σ. In addition, if r out of σ substituted isotopes are heavier in the molecule $\mathbf{C}_n$ and remaining $\sigma - r$ isotopes heavier in the molecule $\boldsymbol{A}_n$, mass change operator $\Delta\mathbf{M}$ has r positive and $\sigma - r$ negative eigenvalues. Hence expression (2.58) implies:

Vibrational interlacing rule (out-of-plane vibrations of planar molecules): Let $\boldsymbol{A}_n$ and $\mathbf{C}_n$ be two planar molecules and let molecule $\mathbf{C}_n$ differ from molecule $\boldsymbol{A}_n$ by σ isotopic substitutions. Let further r

substituted isotopes be heavier in a molecule $\mathbf{C}_n$, and let the remaining $\sigma - r$ isotopes be heavier in a molecule $\boldsymbol{A}_n$. Arrange out-of-plane frequencies ν_i of the parent molecule $\boldsymbol{A}_n$ in the nondecreasing order and arrange also out-of-plane frequencies ω_s of the isotopomer $\mathbf{C}_n$ in the nondecreasing order. If the force field does not change upon isotopic substitutions and in the harmonic approximation, those frequencies satisfy:

$$\nu_{s-r} \le \omega_s \le \nu_{s+\sigma-r}, \tag{2.72}$$

If all substituted isotopes are heavier in the isotopomer $\mathbf{C}_n$ one has $r = \sigma$ and expression (2.72) reduces to $\nu_{s-\sigma} \le \omega_s \le \nu_s$. In particular this implies $\omega_s \le \nu_s$ ($s = 1,\dots,n$). This is well known order rule (2.71) applied to out-of-plane frequencies: If all substituted isotopes are heavier in the isotopomer $\mathbf{C}_n$, modified frequencies ω_s do not increase [7,8]. Order rule is thus a special case of the interlacing rule. Interlacing rule is more general since it applies to arbitrary distribution of heavier and lighter isotopes in the isotopomer $\mathbf{C}_n$. It is also much stronger since it limits each frequency ω_s from both sides, while order rule limits each frequency ω_s only from one side.

Expression (2.72) applies to the vibrational isotope effect of out-of-plane vibrations of planar molecules. In the case of in-plane vibrations this expression is replaced with the expression $\nu_{s-2r} \le \omega_s \le \nu_{s+2\sigma-2r}$, while in the case of arbitrary (non-planar) vibrations it is replaced with the expression $\nu_{s-3r} \le \omega_s \le \nu_{s+3\sigma-3r}$ [17].

2.4.3. Single Isotopic Substitutions

LRM treatment of out-of-plane vibrations of planar molecules $\boldsymbol{A}$ and $\mathbf{C}_\tau$ which differ by a single isotopic substitution at atomic site τ is particularly simple. In the case of such a substitution one has $\sigma = 1$ and expressions (2.67-2.69) simplify to

$$\Omega^0_{\tau\tau}(\varepsilon) = \frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x}\right] + \sum_{i(\lambda_i \neq \varepsilon)}^{n-3} \frac{\langle\tau|\Phi_i\rangle\langle\Phi_i|\tau\rangle}{\varepsilon - \lambda_i}, \tag{2.73a}$$

$$f(\varepsilon) \equiv \Omega^0_{\tau\tau}(\varepsilon) + \frac{1}{\varepsilon\,\Delta m_\tau} = 0, \qquad \varepsilon \notin \{\lambda_i\}, \tag{2.73b}$$

$$|\Psi_s\rangle = \frac{1}{\varepsilon_s}\left[\frac{1}{\sqrt{M}}|T_z\rangle + \frac{y_\tau}{\sqrt{I_x}}|R_x\rangle - \frac{x_\tau}{\sqrt{I_y}}|R_y\rangle\right] + \sum_i^{n-3}\frac{\langle\Phi_i|\tau\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle. \tag{2.73c}$$

Each root $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of (2.73b) is a cardinal out-of-plane eigenvalue of the isotopomer $\mathbf{C}_\tau$. Once $\varepsilon = \varepsilon_s$ is known, the corresponding vibration $|\Psi_s\rangle$ is given by (2.73c). Since $\sigma = 1$, each cardinal vibration $|\Psi_s\rangle$ is nondegenerate.

Consider now singular solutions of $\mathbf{C}_\tau$. Each strongly singular vibration $|\Psi_s\rangle$ that corresponds to the eigenvalue $\varepsilon_s \equiv \lambda_j$ is a linear combination (2.61a) where coefficients $D_l^{(j)}$ satisfy a single condition (2.61b).

Concerning weakly singular vibrations with the eigenvalue $\varepsilon_s = \lambda_j$, expressions (2.62) imply

$$\Omega^0_{\tau\tau}(\varepsilon_s) + \frac{1}{\varepsilon_s \Delta m_\tau} = 0, \tag{2.74a}$$

$$\langle\Phi_{jl}|\tau\rangle = 0, \qquad l = 1,\ldots,\eta_j. \tag{2.74b}$$

Isotopomer $\mathbf{C}_\tau$ has weakly singular vibration $|\Psi_s\rangle$ with the eigenvalue $\varepsilon_s \equiv \lambda_j$ if and only if this eigenvalue satisfies (2.74a) and if in addition all amplitudes $\langle\Phi_{jl}|\tau\rangle$ $(l = 1,\ldots,\eta_j)$ vanish. If this is the case isotopomer $\mathbf{C}_\tau$ has in addition η_j strongly singular vibrations $|\Psi_{sl}\rangle \equiv |\Phi_{jl}\rangle$ $(l = 1,\ldots,\eta_j)$

with this same eigenvalue. Degeneracy of the parent eigenvalue λ_j hence increases by one.

In the case of a single isotopic substitution vibrational interlacing rule (2.72) also substantially simplifies. In particular, if molecule $\mathbf{C}_\tau$ is heavier than molecule $\boldsymbol{A}$ one has $\sigma = r = 1$ and this rule reduces to

$$0 < \omega_1 \le \nu_1 \le \omega_2 \le \nu_2 \le \ldots \le \omega_{n-3} \le \nu_{n-3} . \tag{2.75}$$

Similar expression is obtained if molecule $\boldsymbol{A}$ is heavier than molecule $\mathbf{C}_\tau$.

According to (2.75), each out-of-plane frequency ω_s of the isotopomer $\mathbf{C}_\tau$ is bracketed between exactly two adjacent out-of-plane frequencies ν_i of a parent molecule $\boldsymbol{A}$, and vice-versa. In particular, a single isotopic substitution in a planar molecule can change (increase or decrease) degeneracy of each particular out-of-plane frequency ν_j at most by one. One similarly finds that a single isotopic substitution in a planar molecule can change (increase or decrease) degeneracy of each particular in-plane frequency ν_j at most by two, while a single isotopic substitution in a non-planar molecule can change (increase or decrease) degeneracy of each particular frequency ν_j at most by three [17].

Solution of the vibrational isotope effect in the case of the single isotopic substitution demonstrates efficiency of the LRM approach. In a standard approach one has to diagonalize $n \times n$ eigenvalue equation (2.65a). In the LRM approach this equation is replaced with much simpler expressions (2.73) that produces all cardinal solutions. Calculation of the remaining singular solutions, if any, is numerically trivial.

2.4.4. Inversion Relations

Expressions (2.73) imply *inversion relation* [12,17,22]

$$\mathbf{Y} = \mathbf{G}^{-1}\mathbf{X} , \tag{2.76a}$$

where $\mathbf{G}$ is a square matrix with matrix elements G_{si} while $\mathbf{X}$ and $\mathbf{Y}$ are column vectors with components X_s and Y_i, respectively

$$G_{si} = \frac{1}{\varepsilon_s - \lambda_i}, \qquad X_s = -\frac{1}{\varepsilon_s}\left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau}\right], \tag{2.76b}$$

$$Y_i = \sum_l^{\eta_i} \langle \tau | \Phi_{il} \rangle \langle \Phi_{il} | \tau \rangle . \tag{2.76c}$$

In choosing the set $\{\lambda_i\}$ of parent eigenvalues λ_i and the set $\{\varepsilon_s\}$ of modified eigenvalues ε_s that are required for the construction of the matrix $\mathbf{G}$ and vector $\mathbf{X}$, following rule applies [12,17,22]: The set $\{\lambda_i\}$ should contain all mutually distinct out-of-plane eigenvalues of a parent molecule $\boldsymbol{A}$ that satisfy $Y_i \neq 0$. By definition, each eigenvalue λ_i that satisfies $Y_i = 0$ is *passive* [17,22]. Otherwise it is *active* [17,22]. Passive eigenvalues have no influence on the vibrational isotope effect, and hence those eigenvalues should not be considered. Concerning the set $\{\varepsilon_s\}$, this set should contain all mutually distinct cardinal out-of-plane eigenvalues of the isotopomer $\mathbf{C}_\tau$. One finds that both sets contain the same number of elements, and $\mathbf{G}$ is hence a square matrix. In addition, matrix $\mathbf{G}$ is in almost all cases nonsingular and hence invertible. Expression (2.76a) is hence well defined.

Inversion relation (2.76a) expresses squares of the amplitudes $\langle \tau | \Phi_i \rangle$ at the substitution site τ (or, if λ_i is degenerate, sum Y_i of such squares) in terms of active vibrational frequencies ν_i of the parent molecule $\boldsymbol{A}$, in terms of the cardinal vibrational frequencies $\omega_{s\tau}$ of the isotopomer $\boldsymbol{B}_\tau$, in terms of the position (x_τ, y_τ) of the isotopic substitution in molecule $\boldsymbol{A}$, in terms of mass change Δm_τ of this substitution, and finally in terms of the total mass M and moments of inertia I_x and I_y of the parent molecule $\boldsymbol{A}$. All those quantities are experimental quantities and they can be obtained from the experimental data. Hence inversion relation provides squares of the vibrational amplitudes $\langle \tau | \Phi_i \rangle$ at the selected substitution site τ in terms of experimental data alone. Using several such substitution sites τ, one can derive in this way amplitude squares of all vibrations $|\Phi_i\rangle$ at all substitution sites τ thus selected. Only relative phases between amplitudes of those vibrations at different substitution sites remain to be determined. However, since all proper vibrations $|\Phi_i\rangle$ are orthogonal to non-proper vibrations $|\Phi_T\rangle$, $|\Phi_{Rx}\rangle$ and $|\Phi_{Ry}\rangle$, and since those proper vibrations are mutually orthogonal, those orthogonality requirements in most cases uniquely determine all relative phases of amplitudes $\langle\tau|\Phi_i\rangle$ at various substitution sites τ [12,15-17].

Inversion relations that involve out-of-plane frequencies of planar molecule $\boldsymbol{A}_n$ and out-of-plane frequencies of several mono-substituted isotopomers $\mathbf{C}_{\tau s}$ of this molecule determine amplitudes $\langle\tau_1|\Phi_i\rangle, \langle\tau_2|\Phi_i\rangle, \ldots,$ of the vibrations $|\Phi_i\rangle$ of $\boldsymbol{A}_n$ at all substitution sites τ thus selected. Once those amplitudes are known, one can derive out-of-plane frequencies and corresponding vibrations of all isotopomers $\mathbf{C}$ that contain substituted isotopes at thus selected substitution sites. If a parent molecule $\boldsymbol{A}_n$ has some symmetry (in addition to being planar) amplitudes $\langle\tau|\Phi_i\rangle$ can be partly or completely determined by this symmetry. This reduces the dimension of matrix $\mathbf{G}$ and vectors $\mathbf{Y}$ and $\mathbf{X}$ that are involved in the construction of the inversion relation (2.76a). Quantities $\mathbf{G}$, $\mathbf{X}$ and $\mathbf{Y}$ obtained in this way are accordingly modified, and they differ from their generic form (2.76).

In conclusion, inversion relation provides a systematic method for determining out-of-plane frequencies and normal modes of all isotopomers of a given planar molecule. All one needs to know are out of plane frequencies ν_i of a parent molecule $\mathbf{A}$, and several sets $\{\omega_s\}$ of out-of-plane frequencies of mono-substituted molecules $\mathbf{C}_\tau$.

2.4.5. Interlacing of out-of-Plane Vibrational Frequencies of Thiophene (H,D)-Isotopomers

Let me illustrate the application of the LRM formalism to the vibrational isotope effect with few examples. Consider first vibrational interlacing rule. As an example of the application of this rule consider thiophene molecule

[23]. Thiophene with the corresponding atom numbering is shown in figure 2.3. There are 10 deuteration patterns of thiophene. The interlacing hierarchy of these isotopomers is shown in figure 2.4. This hierarchy is an example of *partial ordering* [24]. One can make as many as 16 comparisons between various pairs of deuterated thiophenes that differ by a single isotopic substitution. Such pairs are in figure 2.4. connected by an arrow. Frequencies of all such pairs should satisfy interlacing Rule (2.75).

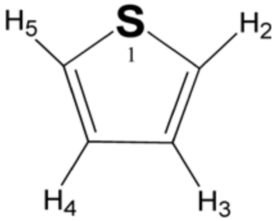

Figure 2.3. Thiophene.

Thiophene has 9 atoms and hence 9 out-of-plane degrees of freedom. One combination of the out-of-plane displacements describes the translation in the z-direction and other two combinations describe rotations around in-plane x- and y-axes, respectively. Hence each thiophene isotopomer has $9\text{-}3=6$ proper out-of-plane vibrations.

Table 1. Experimental [25] out-of-plane vibrational frequencies of thiophene and deuterated thiophenes (all frequencies in cm^{-1})

	1 $\boldsymbol{d_0}$	2 $2\text{-}d_1$	3 $3\text{-}d_1$	4 $2,5\text{-}d_2$	5 $2,3\text{-}d_2$
1	452	433	446	419	427
2	565	533	516	528	511
3	683	567	645	566	553
4	712	701	685	584	668
5	867	839	800	819	744
6	898	896	882	887	882
	6 $2,4\text{-}d_2$	7 $3,4\text{-}d_2$	8 $2,3,5\text{-}d_3$	9 $2,3,4\text{-}d_3$	10 d_4
1	427	442	416	427	414
2	504	488	504	486	484
3	561	587	531	531	531
4	645	671	579	614	531
5	786	775	711	738	684
6	861	811	860	788	750

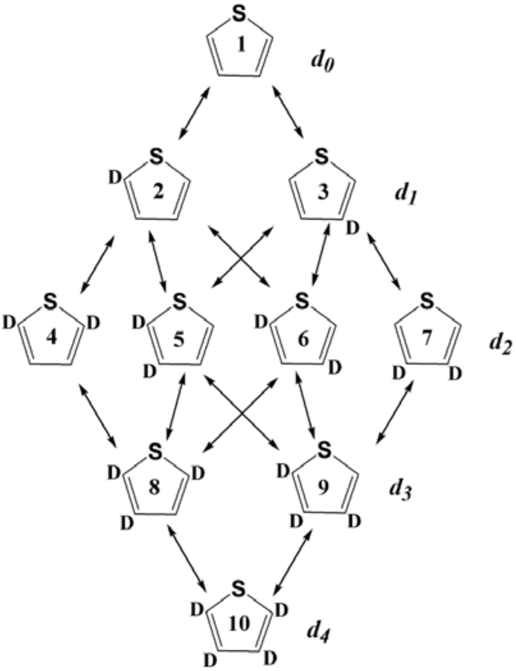

Figure 2.4. Interlacing hierarchy of deuterated thiophenes. Adopted from ref. 23.

Experimental out-of-plane frequencies [25] of thiophene (H,D)-isotopomers are given in Table 1. Using data from this Table one finds that thiophene and two d_1-thiophenes frequencies satisfy (all frequencies are in cm^{-1}).

$$\begin{pmatrix} 433(2) \\ 446(3) \end{pmatrix}_1 < 452(1)_1 < \begin{pmatrix} 533(2) \\ 516(3) \end{pmatrix}_2 < 565(1)_2 < \begin{pmatrix} 567(2) \\ 645(3) \end{pmatrix}_3 < 683(1)_3 <$$

$$< \begin{pmatrix} 701(2) \\ 685(3) \end{pmatrix}_4 < 712(1)_4 < \begin{pmatrix} 839(2) \\ 800(3) \end{pmatrix}_5 < 867(1)_5 < \begin{pmatrix} 896(2) \\ 882(3) \end{pmatrix}_6 < 898(1)_6 \tag{2.77a}$$

In this expression symbols (1), (2) and (3) denote thiophene and deuterated d_1-thiophenes 2-C_4H_3DS and 3-C_4H_3DS, respectively (see figure 2.4). Subscripts 1 through 6 denote corresponding out-of-plane frequencies arranged in the non-decreasing order. As shown in this expression, all out-of-plane frequencies of those isotopomers satisfy interlacing rule (2.75).

Interlacing rule for isotopomer 2 (d_1-thiophene 2-C_4H_3DS) and three d_2-thiophenes is verified in the following expression

$$\begin{pmatrix} 419(4) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 433(2)_1 < \begin{pmatrix} 528(4) \\ 511(5) \\ 504(6) \end{pmatrix}_2 < 533(2)_2 < \begin{pmatrix} 566(4) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < 567(2)_3 <$$

$$< \begin{pmatrix} 584(4) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < 701(2)_4 < \begin{pmatrix} 819(4) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 839(2)_5 < \begin{pmatrix} 887(4) \\ 882(5) \\ 861(6) \end{pmatrix}_6 < 896(2)_6 \tag{2.77b}$$

Compound 4 is isotopomer 2,5-$C_4H_2D_2S$, compound 5 is isotopomer 2,3-$C_4H_2D_2S$, while compound 6 is isotopomer 2,4-$C_4H_2D_2S$ (see figure 2.4). Again, the interlacing rule is satisfied for all out-of-plane frequencies considered.

Comparison of the out-of-plane frequencies of the isotopomer 3 (d_1-thiophene 3-C_4H_3DS) with out-of-plane frequencies of three d_2-thiophenes is shown in the following expression

$$\begin{pmatrix} 427(5) \\ 427(6) \\ 442(7) \end{pmatrix}_1 < 446(3)_1 < \begin{pmatrix} 511(5) \\ 504(6) \\ 488(7) \end{pmatrix}_2 < 516(3)_2 < \begin{pmatrix} 553(5) \\ 561(6) \\ 587(7) \end{pmatrix}_3 < 645(3)_3 \le$$

$$\le \begin{pmatrix} 668(5) \\ 645(6) \\ 671(7) \end{pmatrix}_4 < 685(3)_4 < \begin{pmatrix} 744(5) \\ 786(6) \\ 775(7) \end{pmatrix}_5 < 800(3)_5 < \begin{pmatrix} 882(5) \\ 861(6) \\ 811(7) \end{pmatrix}_6 \le 882(3)_6 \tag{2.77c}$$

Comparison of the out-of-plane frequencies of the isotopomer 8 (d_3-thiophene 2,3,5-$C_4H_1D_3S$) with out-of-plane frequencies of three d_2-thiophenes is shown in the following expression

$$\begin{aligned}
&416(8)_1 < \begin{pmatrix} 419(4) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 504(8)_2 < \begin{pmatrix} 528(4) \\ 511(5) \\ 504(6) \end{pmatrix}_2 < 531(8)_3 < \begin{pmatrix} 566(4) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < \\
&< 579(8)_4 < \begin{pmatrix} 584(4) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < 711(8)_5 < \begin{pmatrix} 819(4) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 860(8)_6 < \begin{pmatrix} 887(4) \\ 882(5) \\ 861(6) \end{pmatrix}_6
\end{aligned} \tag{2.77d}$$

Out-of-plane frequencies of the isotopomer 9 (d_3-thiophene 2,3,4-$C_4H_1D_3S$) are compared with out-of-plane frequencies of three d_2-thiophenes in the following expression

$$\begin{aligned}
&427(9)_1 \le \begin{pmatrix} 427(5) \\ 427(6) \\ 442(7) \end{pmatrix}_1 < 486(9)_2 < \begin{pmatrix} 511(5) \\ 504(6) \\ 488(7) \end{pmatrix}_2 < 531(9)_3 < \begin{pmatrix} 553(5) \\ 561(6) \\ 587(7) \end{pmatrix}_3 < \\
&< 614(9)_4 < \begin{pmatrix} 668(5) \\ 645(6) \\ 671(7) \end{pmatrix}_4 < 738(9)_5 < \begin{pmatrix} 744(5) \\ 786(6) \\ 775(7) \end{pmatrix}_5 < 788(9)_6 < \begin{pmatrix} 882(5) \\ 861(6) \\ 811(7) \end{pmatrix}_6
\end{aligned} \tag{2.77e}$$

One can finally compare out-of-plane frequencies of d_4-thiophene and d_3-thiophenes 2,3,5-$C_4H_1D_3S$ and 2,3,4-$C_4H_1D_3S$:

$$\begin{aligned}
&414(10)_1 < \begin{pmatrix} 427(9) \\ 416(8) \end{pmatrix}_1 < 484(10)_2 < \begin{pmatrix} 486(9) \\ 504(8) \end{pmatrix}_2 < 531(10)_3 \le \begin{pmatrix} 531(9) \\ 531(8) \end{pmatrix}_3 \le \\
&\le 531(10)_4 < \begin{pmatrix} 614(9) \\ 579(8) \end{pmatrix}_4 < 684(10)_5 < \begin{pmatrix} 738(9) \\ 711(8) \end{pmatrix}_5 < 750(10)_6 < \begin{pmatrix} 788(9) \\ 860(8) \end{pmatrix}_6
\end{aligned} \tag{2.77f}$$

As shown in expressions (2.77), all experimental out-of-plane frequencies of deuterated thiophenes satisfy the basic interlacing rule (2.75). This automatically guaranties that the generalized interlacing rule (2.72) is also satisfied. One finds that theoretical DFT scaled vibrational frequencies of thiophene isotopomers as calculated by A.A. El-Azhary and R.H. Hilal [26] also satisfy this rule [23].

2.4.6. Out-of-Plane Vibrations of Ethylene (H,D)-Isotopomers

As another example, consider deuterated ethylenes [12,15]. Ethylene molecule is shown in figure 2.5. This molecule has three out-of-plane vibrations. Those vibrations are shown in figure 2.6. The corresponding experimental frequencies [7] are given in Table 2. Following ref [7], frequency labels $\nu_4(a_{1u})$, $\nu_7(b_{1u})$ and $\nu_8(b_{2g})$ are used in order to denote those frequencies and the corresponding normal modes.

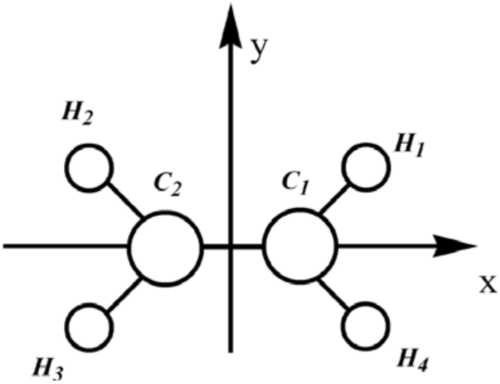

Figure 2.5. Ethylene.

Table 2. Experimental out-of-plane frequencies of ethylene. Data and frequency enumeration (ν_4, ν_7 and ν_8) are from Ref. [7]

	Symmetry	Vibrational type	$\nu(cm^{-1})$
ν_4	a_{1u}	$\chi_{CH_2}^{CH_2}$	(1024) (inactive)
ν_7	b_{1u}	ρ_{CH_2}	949.3 (IR, gas)
ν_8	b_{2g}	ρ_{CH_2}	943 (Raman, liquid)

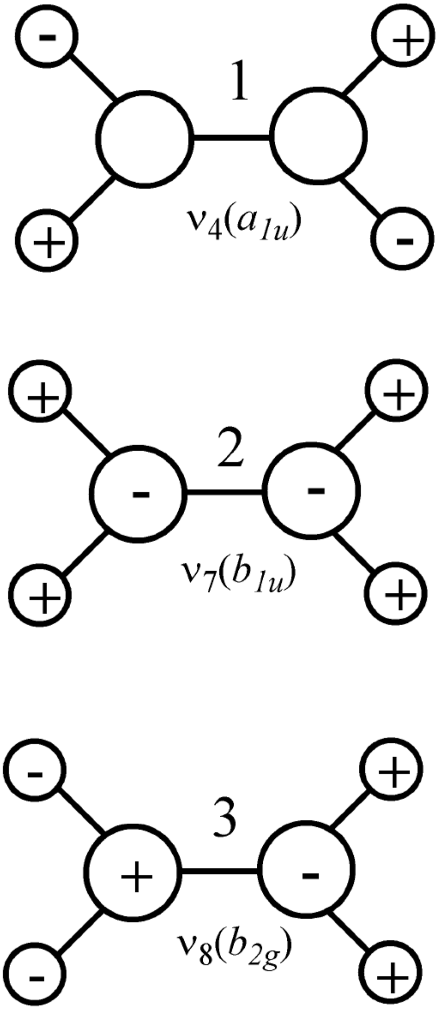

Figure 2.6. Out-of-plane vibrations of ethylene.

Concerning the interlacing rule, note that there are seven deuteration patterns of ethylene. The interlacing hierarchy of these isotopomers is shown in figure 2.7. One can make as many as 8 comparisons between various pairs of deuterated ethylenes that differ by a single isotopic substitution. Frequencies of all such pairs should satisfy interlacing rule (2.75).

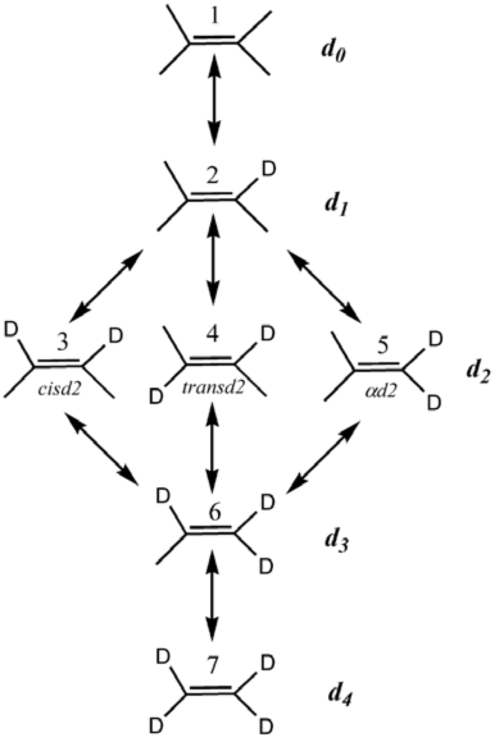

Figure 2.7. Interlacing hierarchy of deuterated ethylenes.

Experimental out-of-plane frequencies of ethylene (H,D)-isotopomers [7] are shown in Table 3. Using data in this Table and in Table 2 one can verify interlacing rule (2.75). In particular, ethylene and d_1-ethylene frequencies satisfy (experimental frequencies in cm^{-1}):

$$807\,(2)_1 < 943\,(1)_1 \le 943\,(2)_2 < 943\,.3(1)_2 < 1001\,(2)_3 < 1024\,(1)_3\,, \tag{2.78a}$$

Similarly d_1-ethylene frequencies and three d_2-ethylenes frequencies satisfy

$$\begin{pmatrix} 763(3) \\ 725(4) \\ 751(5) \end{pmatrix}_1 < 807(2)_1 < \begin{pmatrix} 842(3) \\ 863(4) \\ 892(5) \end{pmatrix}_2 < 943(2)_2 \le \begin{pmatrix} 978(3) \\ 987(4) \\ 943(5) \end{pmatrix}_3 < 1001(2)_3\,, \tag{2.78b}$$

while those three d_2-ethylene frequencies and d_3-ethylene frequencies satisfy

$$724(6)_1 < \begin{pmatrix} 763(3) \\ 725(4) \\ 751(5) \end{pmatrix}_1 < 765(6)_2 < \begin{pmatrix} 842(3) \\ 863(4) \\ 892(5) \end{pmatrix}_2 < 919(6)_3 < \begin{pmatrix} 978(3) \\ 987(4) \\ 943(5) \end{pmatrix}_3 , \qquad (2.78c)$$

Finally, d_3-ethylene and d_4-ethylene out-of-plane frequencies satisfy

$$720(7)_1 < 724(6)_1 < 729(7)_2 < 765(6)_2 < 780(7)_3 < 919(6)_3 . \qquad (2.78d)$$

All those experimental frequencies satisfy interlacing rule (2.75).

For some deuterated ethylenes two experimental frequencies are available. One experimental frequency is obtained in a liquid phase, and another in a gas phase. Whereever possible gas experimental frequencies, as more reliable, should be considered. In a liquid phase there are additional interactions betwen molecules, and those interactions can shift original gas frequencies. Hence some liquid experimental frequencies may violate the interlacing rule. For example, in the comparation of monodeuterated (compound 2) and α-bideuterated (compound 5) ethylenes in the expession (2.78b) one has $943(2)_2 \le 943(5)_3$ in agreement with the interlacing rule (2.75). However, in addition to the gas frequency $\nu = 943\ cm^{-1}$ of d_1-ethylene, there is another liquid frequency of d_1-ethylene: $\nu = 945\ cm^{-1}$ [7]. Clearly this frequency does not satisfy $945(2)_2 \le 943(5)_3$.

Let me now consider in more quantitative terms LRM frequencies and normal modes of ethylene (H,D)-isotopomers. Ethylene parameters determined from the rotational structure of IR and Raman bands are [7]:

$$r_{CH} = 1.086\ A^0, \quad r_{CC} = 1.338\ A^0, \quad \alpha(HCH) = 117^0 30' . \qquad (2.79a)$$

In conjuncture with atomic masses as expressed in atomic units [27]

$$m_H = 1.007825, \quad m_D = 2.014018, \qquad m_C = 12.0107 . \qquad (2.79b)$$

those parameters determine molecular mass, molecular geometry and moments of inertia of ethylene molecule. Atomic mass m_C in (2.79b) is taken to be atomic mass of a natural mixture of 98.93 % of ^{12}C (atomic mass 12.0000 u) and of 1.07 % of ^{13}C (atomic mass $13.00335\ u$ [27]).

Table 3. Theoretical (LRM) and experimental [7] out-of-plane frequencies (*cm*$^{-1}$) for six deuterated ethylenes. LRM frequencies were calculated using ethylene parameters (2.79a) and experimental ethylene frequencies from table 2. *) liquid. Adopted from Ref. [15]

	2 C_2H_3D			3 $cis-C_2H_2D_2$			4 $trans-C_2H_2D_2$		
	Exp.	*LRM*	*Diff.*	*Exp.*	*LRM*	*Diff.*	*Exp.*	*LRM*	*Diff.*
ν_4	1001	*999.4*	*-1.6*	*978*	*980.2*	*2.2*	*987*	*987.7*	*0.7*
ν_7	*943*	*945.7*	*2.7*	*842*	*841.7*	*-0.3*	*725*	*720.7*	*-4.3*
ν_8	*807*	*804.8*	*-2.2*	*763*	*757.4*	*-5.6*	*863**	*864.7*	*1.7*
	5 $\alpha-C_2H_2D_2$			*6* C_2HD_3			*7* C_2D_4		
	Exp.	*LRM*	*Diff.*	*Exp.*	*LRM*	*Diff.*	*Exp.*	*LRM*	*Diff.*
ν_4	*892*	*886.9*	*-5.1*	*724*	*720.6*	*-3.4*	*(729)*	*724.4*	*-4.6*
ν_7	*751* *752*	*749.5*	*-1.5* *-2.5*	*765*	*762.2*	*-2.8*	*720*	*718.1*	*-1.9*
ν_8	*943*	*945.7*	*2.7*	*919*	*918.9*	*-0.1*	*780*	*778.6*	*-1.4*

All three ethylene out-of-plane normal modes are determined by the ethylene geometry and atomic masses of C and H atoms. From symmetry and data (2.79) one obtains amplitudes $\langle H_1|\Phi_i\rangle$ and $\langle C_1|\Phi_i\rangle$ at hydrogen atom 1 and carbon atom 1 [15]:

$$\langle H_1|\nu_4\rangle = 0.49806\,, \qquad \langle H_1|\nu_7\rangle = 0.46088\,,$$

$$\langle H_1|\nu_8\rangle = 0.39756\,, \tag{2.80a}$$

$$\langle C_1|\nu_4\rangle = 0.00000\,, \qquad \langle C_1|\nu_7\rangle = -0.07735\,,$$

$$\langle C_1|\nu_8\rangle = -0.12290\,. \tag{2.80b}$$

Carbon amplitudes (2.80b) are not needed in the calculation of deuterium isotope effects. However they are required for the calculation of carbon isotope effects.

Using hydrogen amplitudes (2.80a) and experimental ethylene out-of-plane frequencies from Table 2, one can obtain out-of-plane frequencies and vibrations for all deuterated ethylenes. In using relations (2.68) one has to observe relative sign of the amplitudes $\langle \tau | \Phi_i \rangle$ on different deuterated sites. Those relative signs are needed in order to construct matrix elements (2.67a) of the operator $\Omega^0_{\mu\nu}(\varepsilon)$. Those relative signes are determined by symmetry alone, and they are obvious from figure 2.6. In Table 3. are given deuterated frequencies which were calculated in this way. The agreement between theoretical (LRM) and experimental frequencies is very good. A standard error for all LRM frequencies in Table 3 is only $\Delta = 2.92\ cm^{-1}$.

In conclusion, LRM frequencies are in excellent agreement with experimental frequencies. The agreement between LRM and experimental frequences seems to be better than expected from the harmonic approximation. Thus it is likely that unharmonicity effects partially cancel in the LRM approach.

LRM approach can be used in yet another way. Experimental deuterated ethylene frequencies can be used in order to improve ethylene out-of-plane frequencies. In particular, ethylene out of plane frequency $\nu_4 = 1024\ cm^{-1}$ is relatively unreliable. The corresponding vibration is of symmetry type a_{1u} and it is inactive both in Raman and in IR. Hence one has to obtain this frequency indirectly, which makes it very prone to errors. One can consider ethylene out of plane frequencies as adjustable parameters, and try to adjust these frequencies in such a way as to minimize standard error of LRM deuterated frequencies. If this is done one obtains $\nu_4 = 1028.2\ cm^{-1}$, $\nu_7 = 950.1\ cm^{-1}$ and $\nu_8 = 942.2\ cm^{-1}$ as optimal ethylene out of plane frequencies [15]. If the LRM calculation is done with these optimal ethylene frequencies, standard error for LRM frequencies of deuterated ethylenes decreases from $\Delta = 2.92\ cm^{-1}$ to $\Delta = 2.35\ cm^{-1}$. These optimal ethylene frequencies that minimize standard error differ from experimental values given in Table 2 by $\Delta\nu_4 = 4.2\ cm^{-1}$, $\Delta\nu_7 = 0.8\ cm^{-1}$ and $\Delta\nu_8 = -0.8\ cm^{-1}$. There is a negligible change of frequencies ν_7 and ν_8. This is in accord with the fact that these frequencies are experimentally quite reliable. Small discrepancies can be attributed to experimental error and/or to unharmonicity effects. However, frequency ν_4 which is inactive changes much more and the error $\Delta\nu_4 = 4.2\ cm^{-1}$ is very likely significant. This indicates that ethylene frequency ν_4 is probably underestimated, and that the true value of this frequency should be closer to $\nu_4 \approx 1028\ cm^{-1}$ than to the reported value of $\nu_4 = 1024\ cm^{-1}$ [15].

Once a particular modified frequency is obtained, one finds the corresponding normal mode using expressions (2.69) where $\left|\varphi_s\right\rangle$ is the corresponding eigenstate of (2.68a). As an example, consider monodeuterated ethylene. In the case of a single isotope substitution, expressions (2.69) simplify to the expression (2.73c). Using LRM frequencies $\nu_4 = 999.4$, $\nu_7 = 945.7$ and $\nu_8 = 804.8$ from Table 3 one finds corresponding normal modes $\left|\Psi_4\right\rangle$, $\left|\Psi_7\right\rangle$ and $\left|\Psi_8\right\rangle$. Once those normal modes are known, they can be easily normalized. With the convention that *x*-axis points in the direction of the CC bond, normalized vibrations $\left|\Psi_4\right\rangle$, $\left|\Psi_7\right\rangle$ and $\left|\Psi_8\right\rangle$ thus obtained are [15]:

$$\begin{aligned}
&\left|\Psi_4\right\rangle = \\
&0.01615\left|T_z\right\rangle + 0.04259\left|R_x\right\rangle + 0.02566\left|R_y\right\rangle - 0.85524\left|\Phi_4\right\rangle + 0.40313\left|\Phi_7\right\rangle + 0.30991\left|\Phi_8\right\rangle \\
&\left|\Psi_7\right\rangle = \\
&0.00204\left|T_z\right\rangle + 0.00539\left|R_x\right\rangle + 0.00325\left|R_y\right\rangle - 0.03125\left|\Phi_4\right\rangle - 0.65185\left|\Phi_7\right\rangle + 0.75760\left|\Phi_8\right\rangle \\
&\left|\Psi_8\right\rangle = \\
&0.08862\left|T_z\right\rangle + 0.23377\left|R_x\right\rangle + 0.14081\left|R_y\right\rangle - 0.37774\left|\Phi_4\right\rangle - 0.55284\left|\Phi_7\right\rangle - 0.50042\left|\Phi_8\right\rangle
\end{aligned} \tag{2.81}$$

These vibrations satisfy orthonormality relation $\left\langle\Psi_s\middle|\mathbf{M}+\Delta\mathbf{M}\middle|\Psi_p\right\rangle = \delta_{sp}$, as required. This is an independent proof that LRM method is consistent and valid.

In the above example six deuterated ethylenes were considered. However, each ethylene hydrogen atom can be substituted either with a deuterium or with a tritium, in all possible combinations. There are 26 such isotopomers. To obtain LRM out-of-plane frequencies and normal modes of all these isotopomers no additional information (except of the mass of tritium atom) is required. To this list one can add various possible combinations with ^{12}C, ^{13}C and ^{14}C isotopes. This increases the number of all possible isotopomers to over two hundreds. Out-of-plane frequencies and the corresponding normal modes of all these isotopomers can be obtained by using only three ethylene out-of-plane frequencies. This relates a huge amount of experimental data to only three experimental quantities, ethylene out-of-plane frequencies ν_4, ν_7 and ν_8 from Table 2.

2.4.7. Out-of-Plane Vibrations of Benzene (H,D)-Isotopomers

In the above example all amplitudes of the out-of-plane vibrations of a parent molecule $\mathbf{A}$ were determined by symmetry. Let me now consider another example where this is not the case. As such an example consider out-of-plane frequencies and normal modes of benzene (H,D)-isotopomers. Symmetry alone is not sufficient to fix all amplitudes of the benzene out-of-plane vibrations. Hence in order to fix those amplitudes one has to use either some independent calculation, or one can use inversion relations. I will demonstrate here how inversion relations can be utilized.

Benzene is a planar molecule with $n = 12$ atoms (see figure 2.8). Three vibrations are non-proper: translation in the z-direction perpendicular to the molecular plane, and rotations around two in-plane axes. Hence benzene has $n - 3 = 9$ proper out-of plane vibrations. Equilibrium benzene geometry [7]

$$r_{CH} = 1.0897\ A^0,$$

$$r_{CC} = 1.4000\ A^0, \qquad (2.82)$$

in conjuncture with atomic masses (2.79b) determines molecular mass and moments of inertia of all (H,D)-benzene isotopomers. Those isotopomers are shown in figure 2.9. Isotopomers connected by an arrow in this Figure differ from each other by a single isotopic substitution. In the harmonic approximation out-of-plane frequencies of all such isotopomer pairs should satisfy interlacing rule (2.75).

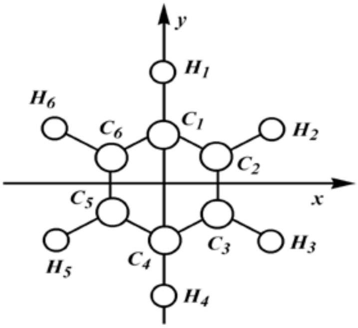

Figure 2.8. Benzene.

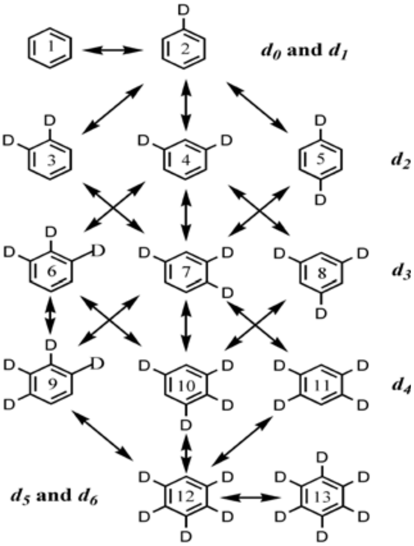

Figure 2.9. Interlacing hierarchy of deuterated benzenes. Adopted from ref. 22.

Benzene out-of-plane vibrations, arranged in the order of non-decreasing frequency, are shown in figure 2.10. In order to simplify presentation, notation in this Figure differs from the standard notation [8]. This standard notation is also shown in this Figure. For example, in a standard notation vibration $\left|\Phi_1\right\rangle$ is vibration $\left|\nu_{16b}\right\rangle$, vibration $\left|\Phi_2\right\rangle$ is vibration $\left|\nu_{16a}\right\rangle$, etc.

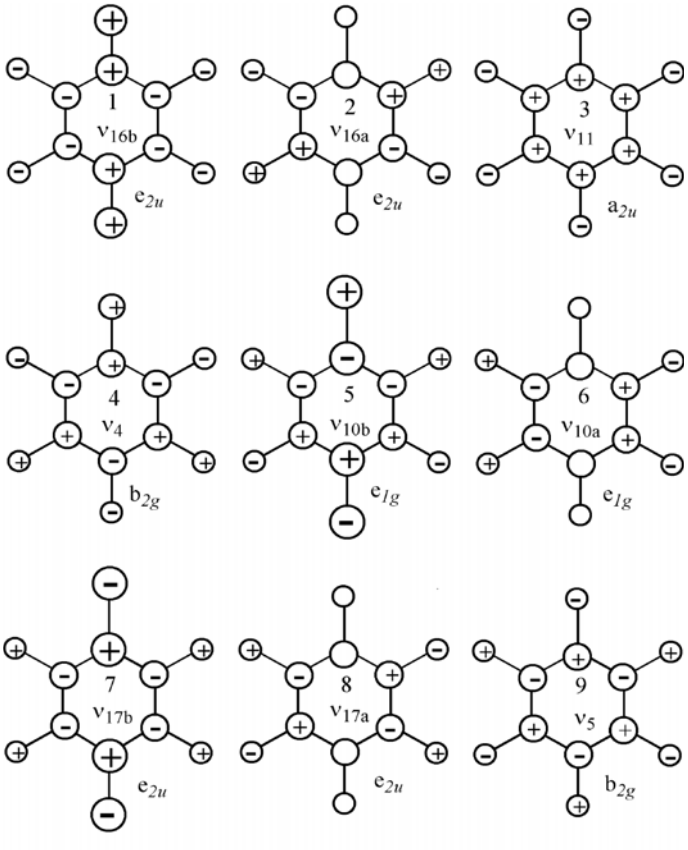

Figure 2.10. Out-of-plane vibrations of benzene. Adopted from ref. 22.

Symmetry constrains partially or complete determine all benzene out-of-plane vibrations. For example, symmetry alone completely determines all amplitudes of benzene vibrations $|\Phi_3\rangle \equiv |\nu_{11}\rangle$, $|\Phi_5\rangle \equiv |\nu_{10b}\rangle$ and $|\Phi_6\rangle \equiv |\nu_{10a}\rangle$. Using data (2.82) and (2.79b) one finds [22]

$$\langle H_1|\Phi_3\rangle = -0.39060\,, \qquad \langle C_1|\Phi_3\rangle = 0.03278\,. \tag{2.83a}$$

$$\langle H_1|\Phi_5\rangle = 0.51126\,, \qquad \langle H_2|\Phi_5\rangle = 0.25563\,,$$

$$\langle C_1|\Phi_5\rangle = -0.07629\,, \qquad \langle C_2|\Phi_5\rangle = -0.03815\,. \tag{2.83b}$$

$$\langle H_1|\Phi_6\rangle = 0\,, \qquad \langle H_2|\Phi_6\rangle = -0.44276\,,$$
$$\langle C_1|\Phi_6\rangle = 0\,, \qquad \langle C_2|\Phi_6\rangle = 0.06607\,. \tag{2.83c}$$

All remaining amplitudes of those vibrations are determined by the symmetry (see figure 2.10).

All amplitudes of vibrations $|\Phi_4\rangle \equiv |\nu_4\rangle$ and $|\Phi_9\rangle \equiv |\nu_5\rangle$ which are of a symmetry type b_{2g} depend on only one amplitude. With the choice of the amplitude $\langle H_1|\Phi_4\rangle$ one finds [22]

$$\langle C_1|\Phi_4\rangle = \sqrt{\frac{1-6m_H\langle H_1|\Phi_4\rangle^2}{6m_C}}\,, \tag{2.84a}$$

$$\langle H_1|\Phi_9\rangle = -\sqrt{\frac{1-6m_H\langle H_1|\Phi_4\rangle^2}{6m_H}}\,,$$
$$\langle C_1|\Phi_9\rangle = \sqrt{\frac{m_H}{m_C}}\langle H_1|\Phi_4\rangle. \tag{2.84b}$$

All amplitudes of vibrations $|\Phi_1\rangle \equiv |\nu_{16b}\rangle$, $|\Phi_2\rangle \equiv |\nu_{16a}\rangle$, $|\Phi_7\rangle \equiv |\nu_{17b}\rangle$ and $|\Phi_8\rangle \equiv |\nu_{17a}\rangle$ which are of a symmetry type e_{2u} depend also on only one amplitude. With the choice of the amplitude $\langle H_1|\Phi_1\rangle$ one has [22]

$$\langle C_1|\Phi_1\rangle = \sqrt{\frac{1-3m_H\langle H_1|\Phi_1\rangle^2}{3m_C}}\,, \quad \langle H_2|\Phi_1\rangle = -0.5\langle H_1|\Phi_1\rangle\,,$$
$$\langle C_2|\Phi_1\rangle = -\frac{1}{2}\sqrt{\frac{1-3m_H\langle H_1|\Phi_1\rangle^2}{3m_C}}\,, \tag{2.85a}$$

$$\langle H_1|\Phi_2\rangle = 0\,, \qquad \langle H_2|\Phi_2\rangle = \frac{\sqrt{3}}{2}\langle H_1|\Phi_1\rangle\,,$$

$$\langle C_1 | \Phi_2 \rangle = 0\,, \qquad \langle C_2 | \Phi_2 \rangle = \sqrt{\frac{1-3m_H \langle H_1 | \Phi_1 \rangle^2}{4m_C}}\,, \tag{2.85b}$$

$$\langle H_1 | \Phi_7 \rangle = -\sqrt{\frac{1-3m_H \langle H_1 | \Phi_1 \rangle^2}{3m_H}}\,,$$

$$\langle H_2 | \Phi_7 \rangle = \frac{1}{2}\sqrt{\frac{1-3m_H \langle H_1 | \Phi_1 \rangle^2}{3m_H}}\,,$$

$$\langle C_1 | \Phi_7 \rangle = \sqrt{\frac{m_H}{m_C}} \langle H_1 | \Phi_1 \rangle\,,$$

$$\langle C_2 | \Phi_7 \rangle = -\frac{1}{2}\sqrt{\frac{m_H}{m_C}} \langle H_1 | \Phi_1 \rangle\,, \tag{2.85c}$$

$$\langle H_1 | \Phi_8 \rangle = 0\,, \qquad \langle H_2 | \Phi_8 \rangle = -\sqrt{\frac{1-3m_H \langle H_1 | \Phi_1 \rangle^2}{4m_H}}\,,$$

$$\langle C_1 | \Phi_8 \rangle = 0\,, \qquad \langle C_2 | \Phi_8 \rangle = \sqrt{\frac{3m_H}{4m_C}} \langle H_1 | \Phi_1 \rangle. \tag{2.85d}$$

Amplitudes of all benzene out-of-plane vibrations are thus expressed in terms of only two amplitudes: amplitude $\langle H_1 | \Phi_4 \rangle$ and amplitude $\langle H_1 | \Phi_1 \rangle$. Those two amplitudes can be obtained from the frequencies of d_0- and d_1-benzene using inversion relation. Since d_0-benzene frequencies $\nu_1 = \nu_2$, $\nu_5 = \nu_6$ and $\nu_7 = \nu_8$ are doubly degenerate, d_1-benzene has three strongly singular vibrations with those frequencies. One can place deuterium at the benzene H$_1$ position. Since $\langle H_1 | \Phi_2 \rangle = \langle H_1 | \Phi_6 \rangle = \langle H_1 | \Phi_8 \rangle = 0$ (see figure 2.10), with this choice d_0-benzene vibrations $|\Phi_2\rangle$, $|\Phi_6\rangle$ and $|\Phi_8\rangle$ are at the same time d_1-benzene strongly singular vibrations (those vibrations are also strongly singular vibrations of the para d_2-benzene). Remaining six out-of-plane d_1-benzene vibrations are cardinal. Since one has to fix only two amplitudes $\langle H_1 | \Phi_4 \rangle$ and $\langle H_1 | \Phi_1 \rangle$, inversion relation (2.75) involving 6×6 matrix $\mathbf{G}$ reduces to the inversion relation involving 2×2 matrix $\mathbf{G}$. One finds [22]

$$\mathbf{Y} = \mathbf{G}^{-1}\mathbf{X}, \tag{2.86a}$$

where 2×2 matrix $\mathbf{G}$and 2-component column vectors $\mathbf{X}$ and $\mathbf{Y}$ have components

$$\begin{aligned}
&G_{i,1} = \frac{1}{\varepsilon_{si} - \lambda_1} - \frac{1}{\varepsilon_{si} - \lambda_7}, \quad G_{i,2} = \frac{1}{\varepsilon_{si} - \lambda_4} - \frac{1}{\varepsilon_{si} - \lambda_9}, \\
&Y_1 = \langle H_1 | \Phi_1 \rangle^2, \qquad Y_2 = \langle H_1 | \Phi_4 \rangle^2, \\
&X_i = g(\varepsilon_{si}), \qquad i = 1,2 .
\end{aligned} \tag{2.86b}$$

and where function $g(\varepsilon)$ is given by

$$\begin{aligned}
g(\varepsilon) = -\frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{y_{H1}^2}{I_x} + \frac{1}{\Delta m_\tau}\right] - \frac{m_C}{m_H M(\varepsilon - \lambda_3)} - \frac{m_C x_{C2}^2}{m_H I_y(\varepsilon - \lambda_5)} - \\
- \frac{1}{3m_H(\varepsilon - \lambda_7)} - \frac{1}{6m_H(\varepsilon - \lambda_9)}
\end{aligned} \tag{2.86c}$$

This function is determined by experimental data alone. $\Delta m_\tau = m_D - m_H = 1.006193$ is isotope mass change at the substitution site $\tau = 1$, y_{H1} is y-coordinate of the hydrogen atom H_1, x_{C2} is x-coordinate of the carbon atom C_2, etc. (see figure 2.8). Matrix $\mathbf{G}$ in (2.86b) is determined by d_0-benzene frequencies ν_1, ν_4, ν_7 and ν_9 as well as by any two mutually distinct cardinal frequencies ω_{s1} and ω_{s2} of d_1-benzene. Since there are six such frequencies, one has 15 possible pairs ($\varepsilon_{s1} = 4\pi^2\omega_{s1}^2$, $\varepsilon_{s2} = 4\pi^2\omega_{s2}^2$) of cardinal eigenvalues ε_{si}. Each such pair determines amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$. According to (2.83-2.85) those two amplitudes determine all remaining amplitudes of all d_0-benzene out-of-plane vibrations. Once those amplitudes are known, expressions (2.67-

2.69) produce out-of-plane normal modes and corresponding vibrational frequencies for all benzene isotopomers. If one considers all possible (H,D) and (^{12}C, ^{13}C) combinations, there are few hundreds of such isotopomers. If in addition one includes isotopomers that may contain ^{3}H and ^{14}C isotopes, one finds almost one hundred thousands of such isotopomers. LRM produces with a single stroke vibrational frequencies and normal modes for all those isotopomers!

LRM can be compared either with some reliable theoretical calculation, or directly with experimental results. Since there are no experimental frequencies for all (H,D)-benzene isotopomers, I will first compare LRM with theoretical out-of-plane vibrations of those isotopomers.

In order to calculate vibrational isotope effect one can use theoretical approaches such as MP2, HF or DFT theory [28-30]. Vibrational analysis by the DFT method, in particular the B3LYP density functional, is superior to alternant approaches [30]. Hence DFT calculation will be considered here. Wu and Cremer [30] derived all vibrational frequencies for all (H,D)-benzene isotopomers using DFT with the hybrid functional B3LYP [31-33] and Pople's 6-31G(d,p) basis set [34]. This calculation is done within the harmonic approximation and under standard assumption that force field does not change upon isotopic substitutions. LRM treatment of the vibrational isotope effect is based on the same assumptions. Hence if in the LRM approach as input data one uses DFT frequencies and DFT normal modes of d_0-benzene, as well as the same molecular geometry as in DFT, one should exactly reproduce DFT frequencies and normal modes for all isotopomers of this molecule.

In ref. [30] only benzene frequencies and not their normal modes are reported. However, amplitudes of those normal modes can be obtained using the inversion relation (2.86). As input to those relations one can use DFT d_0-benzene out-of-plane frequencies and a choice of any two DFT d_1-benzene out-of-plane cardinal frequencies.

DFT d_0- and d_1-benzene out-of-plane frequencies are shown in Table 4. Using inversion relation (2.86) with d_0-benzene frequencies and d_1-benzene frequencies $\omega_1 = 393\ cm^{-1}$ and $\omega_3 = 622\ cm^{-1}$ from this Table, one finds [22]:

$$\langle H_1 | \Phi_1 \rangle = 0.30583\,, \qquad \langle H_1 | \Phi_4 \rangle = 0.17971\,, \tag{2.87a}$$

Table 4. DFT out-of-plane frequencies of d_0- and d_1-benzene. B3LYP/6-31G(d,p) calculation[30]. All frequencies in cm^{-1}

	1 C_6H_6 D_{6h}		2 C_6DH_5 C_{2v}	
1	e_{2u}	414	b_2	393
2	e_{2u}	414	a_2	414
3	a_{2u}	694	b_2	622
4	b_{2g}	718	b_2	714
5	e_{1g}	865	b_2	792
6	e_{1g}	865	a_2	865
7	e_{2u}	974	b_2	934
8	e_{2u}	974	a_2	974
9	b_{2g}	1013	b_2	1003

Expressions (2.84-2.85) now determines all amplitudes of out-of-plane benzene vibrations $|\Phi_1\rangle$, $|\Phi_2\rangle$, $|\Phi_4\rangle$, $|\Phi_7\rangle$, $|\Phi_8\rangle$ and $|\Phi_9\rangle$:

$$\begin{aligned}
&\langle H_2|\Phi_1\rangle = -0.15291, \langle C_1|\Phi_1\rangle = 0.14108, \langle C_2|\Phi_1\rangle = -0.07054,\\
&\langle H_2|\Phi_2\rangle = 0.26485, \langle C_2|\Phi_2\rangle = 0.12218, \langle C_1|\Phi_4\rangle = 0.10567,\\
&\langle H_1|\Phi_7\rangle = -0.48705, \langle H_2|\Phi_7\rangle = 0.24352, \langle C_1|\Phi_7\rangle = 0.08859,\\
&\langle C_2|\Phi_7\rangle = -0.04429, \langle H_2|\Phi_8\rangle = -0.42180, \langle C_2|\Phi_8\rangle = 0.07672\\
&\langle H_1|\Phi_9\rangle = -0.36480, \qquad \langle C_1|\Phi_9\rangle = 0.05206. \qquad (2.87b)
\end{aligned}$$

Amplitudes (2.87) are derived from a particular choice $\omega_1 = 393\ cm^{-1}$ and $\omega_3 = 622\ cm^{-1}$ of two DFT d_1-frequencies and six mutually distinct d_0-benzene DFT frequencies. In an exact calculation, each particular choice of two DFT cardinal d_1-frequencies should produce the same numerical values for those amplitudes. However, DFT frequencies are in ref. [30] reported with the precision of $1\,cm^{-1}$. This introduces an initial uncertainty $\Delta\nu_i = \pm 0.5\ cm^{-1}$ which is reflected in the accuracy of LRM frequencies and corresponding vibrations of benzene isotopomers. Hence each choice of two DFT d_1-frequencies produces slightly different results.

2.4.8. Equality of LRM and DFT out-of-Plane Frequencies of Benzene (H,D)-Isotopomers

LRM and DFT out-of-plane frequencies of 12 deuterated (H,D)-isotopomers are compared in Table 5. Two d_1-frequencies $\omega_1 = 393\,cm^{-1}$ and $\omega_3 = 622\,cm^{-1}$ in this Table serve as input in LRM, while all other LRM frequencies are obtained as the result of the LRM calculation. LRM calculation reproduces DFT frequencies with a standard deviation (on average) $\approx 0.38\,cm^{-1}$. This error is even smaller from the initial uncertainty ($\pm 0.5\,cm^{-1}$) of the input DFT d_0- and d_1-frequencies. LRM produces similar results with all other possible choices of two input DFT d_1-frequencies [22]. Such a high agreement between LRM and DFT frequencies proves that, given identical initial conditions, LRM exactly reproduces the corresponding DFT frequencies. The same applies to DFT normal modes. Since LRM is numerically much faster then DFT, this provides an efficient method to calculate vibrational isotope effect within the harmonic approximation.

Table 5. DFT [30] and LRM [22] frequencies of out-of-plane vibrations of deuterated benzenes. All frequencies in cm^{-1}. LRM reproduces DFT frequencies within approximately $\pm 0.5\,cm^{-1}$. Adopted from Refs. [12] and [22]

	2 C_6DH_5 Δ=0.26			3 1,2-$C_6D_2H_4$ Δ=0.34			4 1,3-$C_6D_2H_4$ Δ=0.23			5 1,4-$C_6D_2H_4$ Δ=0.40		
	C_{2v}	DFT	LRM	C_{2v}	DFT	LRM	C_{2v}	DFT	LRM	D_{2h}	DFT	LRM
1	a_2	393	**393.00**[a]	a_2	384	383.89	a_2	386	386.02	b_{1u}	374	373.30
2	b_2	414	414.00	b_2	403	402.87	b_2	402	401.83	a_u	414	414.00
3	b_2	622	**622.00**[a]	b_2	591	590.81	b_2	582	581.71	b_{1u}	611	611.31
4	a_2	714	714.16	a_2	676	675.96	b_2	714	714.12	b_{3g}	648	647.61
5	a_2	792	792.46	a_2	782	782.58	a_2	719	719.48	b_{3g}	750	749.99
6	b_2	865	865.00	b_2	797	797.12	b_2	830	830.19	b_{2g}	865	865.00
7	a_2	934	933.84	a_2	900	900.25	a_2	934	933.73	b_{1u}	879	878.57
8	b_2	974	974.00	b_2	960	959.57	b_2	934	934.07	a_u	974	974.00
9	a_2	1,003	1,003.11	a_2	998	998.61	b_2	991	990.90	b_{3g}	978	978.16
	6 1,2,3-$C_6D_3H_3$ Δ=0.28			7 1,2,4-$C_6D_3H_3$ Δ=0.53			8 1,3,5-$C_6D_3H_3$ Δ=0.36			9 1,2,3,4-$C_6D_4H_2$ Δ=0.36		
	C_{2v}	DFT	LRM	C_s	DFT	LRM	D_{3h}	DFT	LRM	C_{2h}	DFT	LRM
1	b_2	383	383.05	a''	370	369.24	e''	386	386.02	b_2	368	367.78
2	a_2	386	386.02	a''	400	399.16	e''	386	386.02	a_2	384	383.70
3	b_2	558	558.10	a''	573	573.13	a_2''	545	545.16	b_2	544	544.23
4	b_2	670	669.72	a'	647	646.16	a_2''	714	714.11	a_2	640	639.65
5	a_2	719	719.48	a''	718	718.07	e''	719	719.48	a_2	698	698.13
6	b_2	790	790.16	a''	782	782.61	e''	719	719.48	b_2	746	745.73
7	b_2	840	840.53	a''	873	873.41	e''	934	933.73	a_2	822	822.60
8	a_2	934	933.73	a''	934	934.06	e''	934	933.73	b_2	873	873.61
9	B_2	991	990.88	a'	976	976.13	a_2''	934	934.74	a_2	976	976.07

Table 5. (Continued).

	10 1,2,3,5-$C_6D_4H_2$ Δ=0.38			11 1,2,4,5-$C_6D_4H_2$ Δ=0.62			12 C_6D_5H Δ=0.34			13 C_6D_6 Δ=0.41		
	C_{2v}	*DFT*	*LRM*	D_{2h}	*DFT*	*LRM*	C_{2v}	*DFT*	*LRM*	D_{6h}	*DFT*	*LRM*
1	b_2	*368*	*367.23*	a_u	361	*360.54*	a_2	*361*	*360.54*	e_{2u}	*361*	*360.54*
2	a_2	*386*	*386.02*	b_{1u}	*390*	*389.45*	b_2	*376*	*375.41*	e_{2u}	*361*	*360.54*
3	b_2	*537*	*537.14*	b_{1u}	*560*	*559.63*	b_2	*526*	*525.69*	a_{2u}	*509*	*509.54*
4	b_2	*646*	*645.81*	b_{3g}	*631*	*629.99*	a_2	*628*	*627.43*	b_{2g}	*615*	*614.31*
5	b_2	*718*	*717.73*	b_{2g}	*673*	*672.90*	a_2	*673*	*672.90*	e_{1g}	*673*	*672.90*
6	a_2	*719*	*719.48*	b_{3g}	*779*	*779.90*	b_2	*719*	*718.90*	e_{1g}	*673*	*672.90*
7	b_2	*810*	*810.33*	a_u	*791*	*791.16*	a_2	*791*	*791.16*	e_{2u}	*791*	*791.16*
8	a_2	*934*	*933.73*	b_{1u}	*931*	*931.37*	b_2	*825*	*825.14*	e_{2u}	*791*	*791.16*
9	b_2	*934*	*934.44*	b_{3g}	*936*	*936.87*	a_2	*934*	*934.11*	b_{2g}	*837*	*837.53*

[a] d_1-frequencies $\omega_1 = 393\,cm^{-1}$ and $\omega_3 = 622\ cm^{-1}$ serve as input in the LRM calculation.

2.4.9 Comparison of LRM, Frequency Scaled DFT and Experimental out-of-Plane Frequencies of Benzene (H,D)-Isotopomers

In order to improve the agreement of DFT frequencies with experimental frequencies, one usually applies scaling technique [30,35-39]. One can scale either theoretical force field [35-37], or one can scale theoretical frequencies [30,37-39]. In both approaches one uses one or several individual scaling factors which optimally reproduce frequencies of the parent molecule $\mathbf{A}$. It is assumed that those same factors should improve frequencies of all isotopomers $\mathbf{C}$ of $\mathbf{A}$.

There is a fundamental difference between force field scaling and frequency scaling. In a force field scaling, one replaces one force field with another (scaled) force field. The calculation done with a modified force field is still within the harmonic approximation. Hence one can apply LRM to the scaled force field DFT in the same way as to the initial unscaled DFT.

In a frequency scaling one uses several individual scaling factors in order to scale theoretical frequencies of a parent molecule. The same scaling factors are then applied to theoretical frequencies of all isotopomers of this molecule. Frequency scaling usually violates the assumption that force field does not change under isotopic substitutions and/or the harmonic approximation [22]. This is most drastically evident by the violation of the interlacing rule (2.75). Since this rule is based on the harmonic approximation and on the assumption that force field does not change upon isotopic substitutions, any violation of this rule implies that either of those two assumptions is not valid.

Table 6. Scaled out-of-plane benzene frequencies [30]. Those frequencies equal experimental frequencies. All frequencies in *cm*$^{-1}$

	C_6H_6 D_{6h}	
1	e_{2u}	398
2	e_{2u}	398
3	a_{2u}	673
4	b_{2g}	707
5	e_{1g}	846
6	e_{1g}	846
7	e_{2u}	967
8	e_{2u}	967
9	b_{2g}	990

Scaled DFT frequencies which accurately reproduce all out-of-plane vibrational frequencies of benzene [30] are shown in Table 6. Since benzene has six mutually distinct out-of-plane frequencies, six scaling factors are required in order to reproduce exactly those six frequencies. Those scaling factors are used to obtain DFT scaled frequencies for all benzene (H,D) isotopomers. One finds that those scaled frequencies violate interlacing rule (2.75). For example, if one compares scaled out-of-plane frequencies of (H,D)-benzene isotopomers 7 and 11 as reported in reference [30] , one finds [22]

$$\begin{aligned}&347(11)_1 < 356(7)_1 < 375(11)_2 < 385(7)_2 < 582(11)_3 \,?\, 556(7)_3 < \\ &621(11)_4 < 637(7)_4 < 658(11)_5 < 702(7)_5 < 762(11)_6 < 765(7)_6 < \\ &785(11)_7 < 867(7)_7 < 915(11)_8 < 927(7)_8 \,?\, 924(11)_9 < 954(7)_9\end{aligned} \qquad (2.88)$$

Those isotopomers differ by a single isotopic substitution (see figure 2.9), and hence in the harmonic approximation the corresponding out-of-plane frequencies should satisfy interlacing rule (2.75). However, above frequencies violate this rule in two places. Particularly serious is the violation $582(11)_3 \,?\, 556(7)_3$ which amounts to $26\,cm^{-1}$. It is highly unlikely that violation as large as $26\,cm^{-1}$ is due to the anharmonicity effects. No force field can produce those scaled frequencies, provided harmonic approximation is valid and provided force field does not change under isotopic substitutions.

Since LRM is based on the harmonic approximation and on the assumption that force field does not change upon isotopic substitutions, it cannot reproduce frequency scaled frequencies. However, it should exactly reproduce force field scaled frequencies, provided as input d_0- benzene frequencies one uses d_0- benzene experimental frequencies. In addition to d_0-benzene frequencies one has to know the corresponding vibrational amplitudes. In the case of non-scaled frequencies shown in Tables 4 and 5, those amplitudes were derived using the inversion relation (2.86) with six theoretical DFT frequencies of d_0- benzene and two theoretical DFT frequencies of d_1- benzene. In a consistent approach based on experimental data alone, one should use d_0- benzene out-of-plane experimental frequencies and a choice of any two cardinal d_1-benzene out-of-plane experimental frequencies. In the absence of d_1-benzene experimental frequencies, one can combine d_0- benzene experimental frequencies with the amplitudes obtained in the above way from the DFT theoretical frequencies. This is a hybrid approach which combines experimental data (d_0- experimental frequencies) with theoretical data (DFT vibrational amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$). LRM out-of-plane frequencies of (H,D)-benzene isotopomers obtained in this way differ from frequency scaled DFT frequencies on average by standard deviation $\Delta \approx 4.4\ cm^{-1}$ [22]. In view of the reported precision of the input DFT frequencies ($\pm 0.5\, cm^{-1}$), this difference is significant and it demonstrates that LRM differs qualitatively from frequency scaled DFT. Both approaches can be also compared with available experimental data [22]. This comparison is shown in Table 7. For reliable comparison, experimental data for isotopomer 8 ($C_6(DH)_3$) and isotopomer 13 (C_6D_6) which are reported in ref. [30] are used. In both cases above LRM hybrid approach is superior to frequency scaled DFT. Thus LRM out-of-plane frequencies for the isotopomer (8) ($C_6(DH)_3$) differ from the experimental frequencies by $\Delta_{LRM} = 2.78\, cm^{-1}$, while frequency scaled DFT out-of-plane frequencies differ from the same experimental frequencies by $\Delta_{DFT} = 4.04\, cm^{-1}$. In the case of benzene isotopomer C_6D_6 one finds $\Delta_{LRM} = 3.78\, cm^{-1}$ and $\Delta_{DFT} = 4.69\, cm^{-1}$ [22]. Since LRM is consistent with force field scaling while it is not consistent with frequency scaling, this suggests that force field scaling is preferable to frequency scaling.

Table 7. Comparison of DFT scaled frequencies [30] and LRM frequencies [12] with experimental frequencies [30]. All frequencies in cm^{-1}. Adopted from ref. [12]

	$C_6(DH)_3$			C_6D_6		
	DFT Δ=4.04	LRM Δ=2.78	exp.	DFT Δ=4.69	LRM Δ=3.78	exp.
1	371	371.33	368	347	*346.97*	*345*
2	371	371.33	368	347	*346.97*	*345*
3	528	530.01	531	494	*494.12*	*496*
4	703	701.67	697	606	*603.64*	*599*
5	703	705.81	708	658	*658.12*	*660*
6	703	705.81	708	658	*658.12*	*660*
7	913	913.15	917	785	*784.63*	*787*
8	927	923.65	924	785	*784.63*	*787*
9	927	923.65	924	818	*820.21*	*829*

LRM can in the above way improve numerical efficiency of any theoretical method which is based on the harmonic approximation and on the assumption that force field does not change upon isotopic substitutions.

2.4.10. Symmetry Increase and Emergence of Weakly Singular Solutions

In the case of out-of-plane benzene (H,D)-isotopomers almost all solutions are cardinal with only few solutions which are strongly singular. Emergence of those strongly singular solutions is easy to understand. Since benzene out-of plane vibrations $\left|\Phi_2\right\rangle$, $\left|\Phi_6\right\rangle$ and $\left|\Phi_8\right\rangle$ have zero amplitudes at hydrogen positions H_1 and H_4, replacement of hydrogen at those positions with deuterium (and/or tritium) has no effect on those vibrations. Those vibrations are hence strongly singular vibrations of d_1-benzene and of para d_2-benzene (isotopomers 2 and 5 in figure 2.9). All remaining vibrations of benzene (H,D)-isotopomers shown in figure 2.9 are cardinal and there are no weakly singular solutions. According to the general discussion in section 2.3.3, in order for the modified system to have weakly singular solutions, this system should have some symmetry element which is absent in the parent system. Clearly, no benzene isotopomer is more symmetric than benzene. However, one can consider a following situation. Choose as a parent system d_1-benzene. From a point of view of d_1-benzene as a parent system, benzene itself is a modified system. This modification consists in the replacement of the deuterium atom in d_1-benzene with hydrogen atom. The corresponding interaction space X_σ^{int} is one-dimensional, i.e. $\sigma = 1$. Modified system has now higher symmetry than the parent system. As a result, this modification increases degeneracy of some d_1-benzene vibrations by one. One such vibration is d_1-benzene vibration that has frequency $\omega_2 = 414.00\,cm^{-1}$ and which is non-degenerate. As shown in Table 4, benzene has two singular vibrations with this frequency. Those are benzene vibrations ν_{16b} and ν_{16a} that are of symmetry type e_{2u} (see figure 2.10). Vibration ν_{16a} has no component on the position of the substitution $D \to H$ and hence it is strongly singular vibration of the modified system. Since d_1-benzene vibration with frequency $\omega_2 = 414.00\,cm^{-1}$ is non-degenerate, expression (2.44) implies that modified system can have at most $r_j = \eta_j = 1$ strongly singular eigenstates with this eigenvalue. Another benzene vibration ν_{16b} is hence weakly singular. As required, this vibration has a non-vanishing component at the position of the $D \to H$ substitution (see figure 2.10). Further and as explained in section 2.3.2, modified system may have at most σ linearly independent weakly singular eigenstates with each particular eigenvalue $\varepsilon_s = \lambda_j$. Since in the case considered $\sigma = 1$, one may have at most one weakly singular vibration with this eigenvalue. Analogous conclusions apply to the d_1-benzene vibration corresponding to the frequency $\omega_6 = 865.00\,cm^{-1}$. By isotopic substitution $D_1 \to H_1$ one obtains one strongly singular and one weakly singular benzene vibration with this frequency. Yet another example is d_1-benzene vibration with the frequency $\omega_8 = 974.00\,cm^{-1}$ which by isotopic substitution $D_1 \to H_1$ also produces one strongly singular and one weakly singular vibration with this frequency. In all three cases degeneracy of the parent d_1-benzene vibration increases by one and modified system has weakly singular vibration with this frequency. This increase of the degeneracy of the parent d_1-benzene vibration and the existence of the weakly singular vibrations is due to the fact that benzene, which is in this case treated as a modified system, has higher symmetry then the parent d_1-benzene. This is a general property which is not restricted to the vibrational isotope effect. In general, except for the very unlikely coincidence, modified system $\mathbf{C}_n$ can have weakly singular eigenstates only if this system has higher symmetry from the corresponding parent system $\boldsymbol{A}_n$. Analogous conclusion applies to external modifications. Combined system $\mathbf{C}_{n+\rho}$ can have weakly singular eigenstates only if this system has higher symmetry from its combined non-interacting subsystems $\boldsymbol{A}_n$ and $\boldsymbol{B}_\rho$.

2.5. EXTERNAL MODIFICATION AS A SPECIAL CASE OF INTERNAL MODIFICATION

This completes the LRM treatment of finite-dimensional systems. One final point. I have mentained a strict separation of external and internal modifications. However, from a more general point of view, each external modification can be considered as a special case of an internal modification. In an external modification system $\boldsymbol{A}_n$ interacts with another system $\boldsymbol{B}_\rho$ through the interaction represented by the modification operators $\mathbf{V}$ and $\mathbf{P}$. However, one can consider system $\mathbf{A}_{n+\rho}$ that consists of two non-interacting subsystems $\boldsymbol{A}_n$ and $\mathbf{B}_\rho$ as the initial parent system. From this point of view, interaction between subsystems $\boldsymbol{A}_n$ and $\boldsymbol{B}_\rho$ of $\mathbf{C}_{n+\rho}$ is an internal modification. Parent system $\mathbf{A}_{n+\rho}$ is $(n+\rho)$-dimensional, and it is described by the eigenvalue equation

$$\mathbf{H}_a^{'}\left|\psi_s\right\rangle = x_s \mathbf{S}_a^{'}\left|\psi_s\right\rangle, \qquad s = 1,\cdots,n+\rho, \tag{2.89a}$$

Where

$$\mathbf{H}_a^{'} = \mathbf{H}_a + \mathbf{H}_b, \quad \mathbf{S}_a^{'} = \mathbf{S}_a + \mathbf{S}_b, \tag{2.89b}$$

and where

$$x_s = \begin{cases} E_s & if \quad s = 1,\ldots,\rho \\ \lambda_{s-\rho} & if \quad s = \rho+1,\ldots,\rho+n \end{cases}. \tag{2.89c}$$

Expressions (2.89) incorporate expressions (2.1) and (2.5). Each eigenstate $\left|\psi_s\right\rangle$ of (2.89a) is contained in the $(n+\rho)$-dimensional space $X_{n+\rho}^c$, orthogonal sum of spaces X_n^a and X_ρ^b. Modified system $\boldsymbol{B}_{n+\rho}$ is now created by introducing the interaction between the subsystems $\boldsymbol{A}_n$ and $\mathbf{B}_\rho$ of the system $\mathbf{A}_{n+\rho}$. This interaction is described by the Hermitean operators $\mathbf{V}$ and $\mathbf{P}$ scaled by the coupling parameter β. In the case of an external modification, those operators satisfy expressions (2.8) which are suitable for Theorems 1 and 2 that apply to external modifications. In order to use Theorems 3 and 4 that apply to internal modifications, expressions (2.8) should be transformed into expressions (2.4). This is nontrivial and it requires the construction of the interaction space X_σ^{int}. In order to construct this space one has to solve eigenvalue equations $\mathbf{V}\left|h_s\right\rangle = h_s\left|h_s\right\rangle$ and $\mathbf{P}\left|s_s\right\rangle = s_s\left|s_s\right\rangle$. This can be done. However, it is more convenient to avoid this problem and to have two separate methods for external and internal modifications, as this was done here.

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Chapter 3

INFINITE DIMENSIONAL SYSTEMS

In the previous chapter finite-dimensional systems were considered. Let me now consider infinite-dimensional systems. In order to treat such systems one has to generalize finite-dimensional space X_n^a to an infinite-dimensional space X_∞^a. Concerning finite-dimensional space X_ρ^b in the case of external modifications and finite-dimensional interaction space X_σ^{int} in the case of internal modifications, those spaces will not be generalized to infinite-dimensional spaces. Accordingly, one still considers finite rank modifications of the original infinite-dimensional system.

Is there any need for such a generalization? Following general structure of LRM approach, the system $\boldsymbol{A}_\infty$ associated with the infinite-dimensional space X_∞^a should be known, i.e. one should know eigenvalues and eigenstates of this system. This knowledge is required in order to obtain the solution of the corresponding modified system $\mathbf{C}_\infty$. Are there any infinite-dimensional systems with such a property? In particular, is there any infinite-dimensional system $\boldsymbol{A}_\infty$ with a known solution that interacts externally with a finite-dimensional system $\mathbf{B}_\rho$, and where the solution of the corresponding combined system $\mathbf{C}_\infty$ is of interest?

As one referee commented to a paper submitted to a journal, to consider such problems is ridiculous: what one needs, he claimed, is to consider perturbations of large unknown systems, and not to consider perturbations of large known systems!

However, this is a rather narrow point of view. Consider for example the interaction of an isolated molecule with the electromagnetic field. Of interest are effects such as shifts of molecular energy levels, broadening of those levels, emission and absorption of radiation, etc. All those effects are due to the interaction of the molecular system with the electromagnetic field. Isolated molecule can be approximated with a finite system X_ρ^b which contains a finite number of eigenvalues E_r and eigenstates $|\Theta_r\rangle$. Those eigenstates interact with one-photon states $|\Theta_t,\mathbf{k}\varpi\rangle$ where $|\mathbf{k}\varpi\rangle$ represents a state that contains a single photon with momentum $\mathbf{k}$ and polarization ϖ. States $|\Theta_t,\mathbf{k}\varpi\rangle$ interact with two-photon states $|\Theta_v,\mathbf{k}'\varpi',\mathbf{k}''\varpi''\rangle$, which in turn interact with three photon states, etc [1]. If there is no external electromagnetic field, one can to a very good approximation ignore all states containing multiple photons, and one can associate system $\mathbf{A}_\infty$ with the set of all one-photon states $|\Theta_r,\mathbf{k}\varpi\rangle$ with the corresponding eigenvalues. Those states span an infinite-dimensional space X_∞^a. The solution to this system is known, since the states $|\mathbf{k}\varpi\rangle$ are essentially plane waves, while $|\Theta_r\rangle$ are eigenstates of the isolated molecule which is approximated as a finite system. Hence one has formally the interaction of a finite-dimensional system X_ρ^b with the known infinite-dimensional system X_∞^a. With an appropriate modification, in the similar way can be treated the case when an external electromagnetic field is present.

As another example consider the interaction of the molecule situated on the surface of a solid with this solid. Molecule in isolation can be again approximated with a finite-dimensional system $\mathbf{B}_\rho$. Infinite-dimensional system $\mathbf{A}_\infty$ now represents a solid with a surface. The solution to this system consists of multiple eigenvalue bands $\lambda_s(\mathbf{k})$ with the corresponding eigenstates $|\Phi_s(\mathbf{k})\rangle$ ($s = 1,2,\dots$) [1]. In addition, system $\mathbf{A}_\infty$ may contain some discrete eigenvalues that correspond to the surface states [2,3]. One is usually interested in the properties of the molecule (system $\mathbf{B}_\rho$) subject to the interaction with the solid (system $\mathbf{A}_\infty$). Again one can assume that the solution to the system $\mathbf{A}_\infty$ is known. Usually one knows only an approximate solution to this system [2,3]. Assuming this approximate solution is good enough, one has again the interaction of a finite-dimensional system $\mathbf{B}_\rho$ with a known infinite-dimensional system $\mathbf{A}_\infty$.

Those and similar problems are usually treated either within the formalism of the perturbation expansion approach (where $\mathbf{B}_\rho$ is treated as the unperturbed system), or using some approximate semi-classical model [1, 4]. If the interaction between the molecular system $\mathbf{B}_\rho$ and the infinite system $\mathbf{A}_\infty$ is relatively strong, convergence of the perturbation series may be very slow. In many cases of interest such as the interaction of the molecule with the surface of the solid, this interaction is usually so strong that perturbation expansion diverges and the entire method fails. Concerning various semi-classical models, those models are only approximate, and they can never completely replace exact quantum treatment.

Such and similar problems can be efficiently treated within the LRM formalism of external modifications of quantum systems. Molecular system $\mathbf{B}_\rho$ is a base system which is modified by the interaction with an external infinite-dimensional system $\mathbf{A}_\infty$ with known eigenvalues and eigenstates. In the first example this external system is essentially a free electromagnetic field, while in the second example it is an infinite solid. In both cases emphasize is on the properties of the molecule, and not on the properties of the electromagnetic field or on the properties of a solid. Such LRM treatment of those systems provides a description of open quantum systems: molecular system $\mathbf{B}_\rho$ in isolation is a finite-dimensional closed system. Molecular system $\mathbf{B}_\rho$ subject to the interaction with its “surrounding” (either the electromagnetic field or a solid, or anything else) is an open quantum system. Unlike perturbation expansion which provides only an approximate solution to such systems, LRM provides an exact solution of the infinite-dimensional combined system $\mathbf{C}_\infty$, regardless of how strong is the interaction between its subsystems $\mathbf{B}_\rho$ and $\mathbf{A}_\infty$. In general, LRM formalism of externally modified quantum systems can be applied to all those cases where one has some relatively small finite-dimensional system $\mathbf{B}_\rho$ in the interaction with its surrounding represented by a known infinite-dimensional system $\mathbf{A}_\infty$.

In the similar way can be treated internal modifications of infinite-dimensional systems. As an example of such a modification consider a perfect solid. This solid is an infinite quantum system and in LRM it represents a parent system $\boldsymbol{A}_{\infty}$. Though this system is infinite-dimensional, since effective potential is periodic one can obtain relatively reliable solution to this system [2]. Consider now introduction of various impurities and/or defects in this solid, creation of a surface, etc. Most properties of interest are due to such and similar modifications of a perfect solid. However, all such modifications break periodic symmetry and in addition those modifications are usually not small. Hence such effects cannot be efficiently treated within the standard formalism of the perturbation expansion. On the other hand, introduction of impurities and defects, as long as those modifications do not produce a global change of the crystal structure, can be very well approximated with operators that have finite rank. This is not the case with a creation of a crystal surface, since a surface of a real three-dimensional solid is two-dimensional, and hence such a modification should be represented with Hermitean operators that have infinite rank. However, one can still approximate a real surface with a small finite portion of this surface. Accordingly, the corresponding modification is approximated with finite rank operators. To the extent that this approximation is reliable, all properties associated with the creation of a surface, such as surface states, distortion of few unit cells close to the surface and alike can be also treated within the LRM formalism.

In conclusion, there are many important problems which can be treated within the LRM formalism and which involve either external or internal modifications of known infinite-dimensional systems. LRM can be also generalized to those cases where both types of modification, external and internal, are simultaneously present.

Generalization of the LRM formalism to the infinite-dimensional systems is important for yet another reason. Consider for example LRM description of open quantum systems: finite-dimensional system $\mathbf{B}_{\rho}$ in the interaction with its surrounding, an infinite-dimensional system $\mathbf{A}_{\infty}$. From a point of view of quantum theory, each finite-dimensional system $\mathbf{B}_{\rho}$ is an open quantum system, since there is always *some* interaction of this system with the surrounding. Of course, in most cases one does not know the solution of this surrounding, and hence one cannot predict what will be exact behavior of the system $\mathbf{B}_{\rho}$ subject to the interaction with its surrounding. However, from a broad theoretical point of view, the details of this interaction are not important.

What is important is that each surrounding, however complicated, can be represented as *some* infinite-dimensional system $\mathbf{A}_\infty$. Since LRM formalism produces exact consequences of the interaction of a finite-dimensional system $\mathbf{B}_\rho$ with its surrounding, however complex this surrounding may be, one can obtain a clear idea how this interaction may modify original system $\mathbf{B}_\rho$. All possibilities, however exotic, should be contained in this formalism.

3.1. INFINITE-DIMENSIONAL PARENT SYSTEM

Let me now generalize finite-dimensional parent system $\boldsymbol{A}_n$ to an arbitrary infinite-dimensional parent system $\boldsymbol{A}_\infty$. This generalization should be broad enough in order to include as many various infinite-dimensional systems as possible. Some pathological infinite-dimensional systems might be excluded, which is hopefully of no practical consequences.

Let $\boldsymbol{A}_\infty$ be such an infinite-dimensional quantum system. With this system is associated an infinite-dimensional space X_∞^a. In general, this system may contain several eigenvalue bands and/or several discrete eigenstates. Each of those eigenvalue bands may be one-parameter eigenvalue band (non-degenerate eigenvalue band) or it may be a many-parameter eigenvalue band (degenerate eigenvalue band).

Concerning discrete solutions of $\boldsymbol{A}_\infty$, in the most general formulation those solutions satisfy eigenvalue equation (2.1a) where n can assume any value, including the possibility $n=\infty$. For the sake of simplicity, instead of this generalized eigenvalue equation consider a standard eigenvalue equation

$$\mathbf{H}_a\left|\Phi_i\right\rangle = \lambda_i\left|\Phi_i\right\rangle,\ i=1,2,3,\cdots, \tag{3.1a}$$

where $\mathbf{H}_a$ is Hermitean operator in X_∞^a. Eigenstates $\left|\Phi_i\right\rangle$ of (3.1a) are orthonormalized in a standard way

$$\left\langle\Phi_i\middle|\Phi_j\right\rangle = \delta_{ij}, \qquad i,j=1,2,3,\cdots. \tag{3.1b}$$

In addition to the discrete eigenvalues and eigenstates described by the eigenvalue equation (3.1a), system $\boldsymbol{A}_\infty$ may contain κ eigenvalue bands where κ can assume any integer value. In general, eigenvalues and corresponding eigenstates of those eigenvalue bands satisfy

$$\mathbf{H}_a \left| \Phi_{\tau,m}(k,l) \right\rangle = \lambda_\tau(k) \left| \Phi_{\tau,m}(k,l) \right\rangle,$$

$$k \in \left[k_{a\tau}, k_{b\tau} \right], \tau = 1,2,\ldots,\kappa, \tag{3.2a}$$

Index τ labels different eigenvalue bands. It is assumed that each eigenvalue $\lambda_\tau(k)$ is a continuous and monotonic function of a parameter *k* in the interval $\left[k_{a\tau}, k_{b\tau} \right]$ ($\tau = 1,\ldots,\kappa$). If this is not the case, one can always treat the corresponding eigenvalue band as if this band consists of several smaller eigenvalue bands. Parameters *l* and *m* are optional. Those parameters label possible degeneracy's inside eigenvalue band τ. Parameter *l* represents one or several continuous parameters and parameter *m* represents one or several discrete parameters. With this convention eigenstates $\left| \Phi_{\tau,m}(k,l) \right\rangle$ of (3.2a) can be orthonormalized according to

$$\left\langle \Phi_{\tau,m}(k,l) \middle| \Phi_{\tau',m'}(k',l') \right\rangle = \delta_{\tau,\tau'} \delta_{m,m'} \delta(k-k') \delta(l-l'), \tag{3.2b}$$

Without loss of generality one can assume that each function $\lambda_\tau(k)$ is monotonic increasing. In this case all eigenvalues of the eigenvalue band τ are confined to the interval $I_\tau = \left[a_\tau, b_\tau \right]$ where $a_\tau = \lambda_\tau(k_{a\tau})$ and $b_\tau = \lambda_\tau(k_{b\tau})$ are the smallest and the largest possible eigenvalue, respectively. One may have $b_\tau = \infty$. However, one may not have $a_\tau = -\infty$, since eigenvalues $\lambda_\tau(k)$ of $\mathbf{H}_a$ cannot assume arbitrary large negative values.

Since $\lambda_\tau(k)$ is monotonic, it has well defined inverse

$$\varepsilon = \lambda_\tau(k), \; k = \lambda_\tau^{-1}(\varepsilon), \qquad \varepsilon \in I_\tau \equiv \left[a_\tau, b_\tau \right]. \tag{3.2c}$$

Union of all eigenvalue intervals I_τ forms a range D of the continuous eigenvalues of the infinite system $\boldsymbol{A}_\infty$, $D = \bigcup_\tau I_\tau$. This range may consist of several disconnected intervals D_μ, where each D_μ is a union of one or several eigenvalue intervals I_τ. It is convenient to define a point set $\overline{D}$, a complement of D. Accordingly, $D \cup \overline{D} = R$ is the entire real axis.

In addition to orthonormality expressions (3.1b) and (3.2b), all discrete eigenstates $\left|\Phi_i\right\rangle$ are orthogonal to all continuous eigenstates $\left|\Phi_{\tau,m}(k,l)\right\rangle$

$$\left\langle\Phi_i\middle|\Phi_{\tau,m}(k,l)\right\rangle = 0. \tag{3.3}$$

Eigenvalue equations (3.1a) and (3.2a) can be written in a compact form

$$\mathbf{H}_a\left|\Phi(\ldots)\right\rangle = \lambda(\ldots)\left|\Phi(\ldots)\right\rangle, \tag{3.4a}$$

where

$$\mathbf{H}_a = \sum_i \lambda_i \left|\Phi_i\right\rangle\left\langle\Phi_i\right| + \sum_{\tau,m}\int \lambda_\tau(k)\left|\Phi_{\tau,m}(k,l)\right\rangle\left\langle\Phi_{\tau,m}(k,l)\right| dldk\,. \tag{3.4b}$$

and where dots $(\ldots)$ represent all required continuous and/or discrete parameters. Eigenstates $\left|\Phi_i\right\rangle$ and $\left|\Phi_{\tau,m}(k,l)\right\rangle$ of $\boldsymbol{A}_\infty$ form a complete set in X_∞^a. Hence those eigenstates satisfy completeness relation

$$\sum_\tau\sum_m\int\left|\Phi_{\tau,m}(k,l)\right\rangle\left\langle\Phi_{\tau,m}(k,l)\right|\,dkdl + \sum_i\left|\Phi_i\right\rangle\left\langle\Phi_i\right| = \mathbf{I}_\infty^a. \tag{3.5}$$

where $\mathbf{I}_\infty^a$ is a unit operator in X_∞^a.

Replacement of the generalized eigenvalue equation (2.1a) with the standard eigenvalue equation (3.4a) presents no restriction on generality. However, it may in some cases influence numerical efficiency of the derived LRM expressions. In this and in the following chapter I would like to demonstrate that LRM can be successfully extended to infinite-dimensional systems. It is not my intension to present here a full scale and most efficient LRM treatment of such systems.

In most models used in a solid state physics infinite-dimensional space X_∞^a that describes a solide state has a denumerable base $\{|\alpha\rangle\}$ orthonormalized according to [2]:

$$\langle\alpha|\beta\rangle = \delta_{\alpha\beta}, \qquad \alpha,\beta = 1,\ldots,\infty . \tag{3.6a}$$

The base $\{|\alpha\rangle\}$ can be chosen in such a way that each scalar product $\langle\alpha|\Psi_{\tau,m}(k,l)\rangle$ is a smooth function of parameters k and l for all admissible values of those parameters, with the possible exception of few isolated points. For example, in the tight-binding approximation [4] each eigenstate $|\Phi_{\tau,m}(k,l)\rangle$ of an infinite solid is approximated as a linear combination of atomic orbitals. This eigenstate reflects periodic symmetry of a solid, and the states $|\alpha\rangle$ can be chosen to be atomic orbitals situated at various atoms of this solid. Those orbitals should be orthonormalized according to (3.6a) by some appropriate method. Alternatively those orbitals can be chosen to be Wannier functions which are by definition orthonormalized in this way [2]. One finds that scalar products $\langle\alpha|\Psi_{\tau,m}(k,l)\rangle$ of such orbitals with the eigenstates $|\Phi_{\tau,m}(k,l)\rangle$ are smooth function of parameters k and l for almost all admissible values of those parameters, as required. In addition, each state $|\Psi\rangle \in X_\infty^a$ can be expressed as a linear combination of base orbitals $|\alpha\rangle$, and hence the set $\{|\alpha\rangle\}$ of all such orbitals spans the space X_∞^a. In this case a unit operator $\mathbf{I}_\infty^a$ in the space X_∞^a can be expressed in terms of the states $|\alpha\rangle$ as

$$\mathbf{I}_\infty^a = \sum_\alpha^\infty |\alpha\rangle\langle\alpha| . \tag{3.6b}$$

In the case of the electromagnetic field it is more natural to consider non-denumerable infinite-dimensional bases. For eample, the set of all plane waves forms such a base. However, if the system of particles can be treated non-relativistically and if such a system interacts with the electromagnetic field, high frequency components of this field can be truncated [1]. Those high-frequency field components describe exchange of high energy between the field and the system of particles. Such an exchange is not in accord with the assumption that the system of particles is treated non-relativistically [1]. It can be shown that such a truncation implies nonlocal interactions, i.e. the interaction of the field with a particle is not point-like local interaction, but ruther an interaction involving the value taken by the field in some small domain of a finite extension [1]. This suggests that the corresponding infinite-dimensional space X_∞^a can be very well approximated with the infinite-dimensional space that has a denumerable basis. In conclusion, one can safely assume that in the space X_∞^a one can construct denumerable base $\{|\alpha\rangle\}$ orthonormalized according to (3.6a). Having said this, it should be emphasized that the existence of the denumerable base is not essential for the LRM approach. However, it is more convenient to work in such a basis.

3.1.1. Characteristic and Derived Operators of the Parent System

As shown in section 2.2, with a finite-dimensional system $\mathbf{A}_n$ is associated Hermitean operator $\overline{\mathbf{\Omega}}(\varepsilon)$. This operator depends on the continuous parameter ε and it contains complete information about eigenvalues and corresponding eigenstates of the system $\mathbf{A}_n$. According to (2.10), operator $\overline{\mathbf{\Omega}}(\varepsilon)$ determines operator $\mathbf{\Omega}_b(\varepsilon)$ which acts in the space X_ρ^b and which vanishes outside this space. This operator is crucial in the LRM treatment of externally modified systems. In a similar way, according to (2.34) operator $\overline{\mathbf{\Omega}}(\varepsilon)$ determines operator $\mathbf{\Omega}_a(\varepsilon)$ which acts in the interaction space X_σ^{int} and which vanishes outside this space. This operator is crucial in the LRM treatment of internaly modified systems. In the case of infinite-dimensional systems operators $\overline{\mathbf{\Omega}}(\varepsilon)$, $\mathbf{\Omega}_a(\varepsilon)$ and $\mathbf{\Omega}_b(\varepsilon)$ are derived from the corresponding *characteristic operators* $\overline{\mathbf{f}}(\varepsilon)$, $\mathbf{f}_a(\varepsilon)$ and $\mathbf{f}_b(\varepsilon)$, respectively.

With the infinite-dimensional system $\boldsymbol{A}_\infty$ is associated *characteristic operator* $\bar{\mathbf{f}}(\varepsilon)$ which depends on the continuous parameter ε [5]. This operator is a sum of characteristic operators $\bar{\mathbf{f}}_\tau(\varepsilon)$ that are associated with eigenvalue bands τ of the system $\boldsymbol{A}_\infty$ and of the characteristic operator $\overline{\mathbf{F}}(\varepsilon)$ that is associated with discrete solutions of this system

$$\bar{\mathbf{f}}(\varepsilon) = \sum_\tau \bar{\mathbf{f}}_\tau(\varepsilon) + \overline{\mathbf{F}}(\varepsilon), \tag{3.7a}$$

Operator $\bar{\mathbf{f}}_\tau(\varepsilon)$ contains information about the eigenvalue band τ of the infinite system $\boldsymbol{A}_\infty$. This operator is defined as

$$\bar{\mathbf{f}}_\tau(\varepsilon) = \left.\frac{\sum_m \int \left|\Phi_{\tau,m}(k,l)\right\rangle\left\langle\Phi_{\tau,m}(k,l)\right| dl}{d\lambda_\tau(k)/dk}\right|_{k=\lambda_\tau^{-1}(\varepsilon)} \cdot \begin{cases} 1 & if \quad \varepsilon \in I_\tau \\ 0 & if \quad \varepsilon \notin I_\tau \end{cases}$$

$$\tau = 1,\ldots,\kappa, \tag{3.7b}$$

Operator $\bar{\mathbf{f}}_\tau(\varepsilon)$ associated with the eigenvalue band τ vanishes for each $\varepsilon \notin I_\tau$ and it is positive definite for almost each $\varepsilon \in I_\tau$. Only in some isolated points $\varepsilon_0 \in I_\tau$, if any, one may have $\bar{\mathbf{f}}_\tau(\varepsilon_0) = 0$.

Operator $\overline{\mathbf{F}}(\varepsilon)$ contains information about discrete eigenstates of the system $\boldsymbol{A}_\infty$. This operator is defined as

$$\overline{\mathbf{F}}(\varepsilon) = \sum_i \left|\Phi_i\right\rangle\left\langle\Phi_i\right| \delta(\varepsilon - \lambda_i). \tag{3.7c}$$

Operator $\overline{\mathbf{F}}(\varepsilon)$ vanishes for each $\varepsilon \notin \{\lambda_j\}$ and it is a δ-type operator in each point $\varepsilon \in \{\lambda_j\}$.

Characteristic operators $\bar{\mathbf{f}}_\tau(\varepsilon)$ and $\overline{\mathbf{F}}(\varepsilon)$ determine *derived operators* $\overline{\boldsymbol{\omega}}_\tau(\varepsilon)$ and $\overline{\boldsymbol{\Omega}}(\varepsilon)$, respectively. Unlike operator $\bar{\mathbf{f}}_\tau(\varepsilon)$ that vanishes outside the interval I_τ, the corresponding derived operator $\overline{\boldsymbol{\omega}}_\tau(\varepsilon)$ is nonzero in all points outside I_τ and in almost all points inside I_τ. This operator is expressed in terms of the corresponding characteristic operator $\bar{\mathbf{f}}_\tau(\varepsilon)$ according to

$$\overline{\boldsymbol{\omega}}_\tau(\varepsilon) = P\int \frac{\bar{\mathbf{f}}_\tau(\lambda)}{\varepsilon - \lambda} d\lambda \,, \tag{3.8a}$$

where P denotes principal Cauchy integral value [14]. Hence and due to (3.7b) one has [5]

$$\overline{\omega}_\tau(\varepsilon) = P\int \frac{\sum\limits_m \int \left|\Phi_{\tau,m}(k,l)\right\rangle\left\langle\Phi_{\tau,m}(k,l)\right| dl}{\varepsilon - \lambda_\tau(k)} dk \,,$$

$$\tau = 1,\ldots,\kappa \,, \tag{3.8b}$$

If $\varepsilon \notin I_\tau$ above expression is a standard integral. However, if $\varepsilon \in I_\tau$ sub-integral function on the right-hand side of this expression usually diverges in a point $\lambda_\tau(k) = \varepsilon$. In this case one has to take a principal Cauchy integral value of this expression.

In analogy to (3.8a), derived operator $\overline{\boldsymbol{\Omega}}(\varepsilon)$ is expressed in terms of the corresponding characteristic operator $\overline{\mathbf{F}}(\varepsilon)$ according to

$$\overline{\boldsymbol{\Omega}}(\varepsilon) = P\int \frac{\overline{\mathbf{F}}(\lambda)}{\varepsilon - \lambda} d\lambda \,, \tag{3.8c}$$

Hence and due to (3.7c) one has

$$\overline{\boldsymbol{\Omega}}(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)} \frac{\left|\Phi_i\right\rangle\left\langle\Phi_i\right|}{\varepsilon - \lambda_i} \,. \tag{3.8d}$$

This expression is identical to the expressions (2.9).

In analogy to (3.7a), derived operators $\overline{\boldsymbol{\omega}}_\tau(\varepsilon)$ and $\overline{\boldsymbol{\Omega}}(\varepsilon)$ combine to a global derived operator $\overline{\boldsymbol{\omega}}(\varepsilon)$ according to

$$\overline{\boldsymbol{\omega}}(\varepsilon) = \sum_\tau \overline{\boldsymbol{\omega}}_\tau(\varepsilon) + \overline{\boldsymbol{\Omega}}(\varepsilon) \quad . \qquad (3.9)$$

For each real ε this operator is uniquely determined by the eigenvalues and eigenstates of the parent system $\boldsymbol{A}_\infty$. Above expression generalizes operator $\overline{\boldsymbol{\Omega}}(\varepsilon)$ that applies to finite-dimensional parent system $\boldsymbol{A}_n$ to the derived operator $\overline{\boldsymbol{\omega}}(\varepsilon)$ that applies to infinite-dimensional parent system $\boldsymbol{A}_\infty$. New features in this expression are derived operators $\overline{\boldsymbol{\omega}}_\tau(\varepsilon)$ which are associated with eigenvalue bands τ.

3.2. EXTERNAL MODIFICATIONS OF INFINITE-DIMENSIONAL PARENT SYSTEMS

Consider finite-dimensional system $\mathbf{B}_\rho$ described by the eigenvalue equation (2.5a) which interacts with the infinite-dimensional system $\boldsymbol{A}_\infty$ described by the eigenvalue equation (3.4). With system $\mathbf{B}_\rho$ is associated ρ-dimensional space X_ρ^b while with the system $\boldsymbol{A}_\infty$ is associated ∞-dimensional space X_∞^a. Inclusion of the interaction between initially non-interacting systems $\mathbf{B}_\rho$ and $\boldsymbol{A}_\infty$ creates a combined ∞-dimensional system $\mathbf{C}_\infty$. Each state in this combined system is contained in the ∞-dimensional space X_∞^c, orthogonal sum of spaces X_ρ^b and X_∞^a. Interaction between subsystems $\mathbf{B}_\rho$ and $\boldsymbol{A}_\infty$ of $\mathbf{C}_\infty$ is described by the Hermitean operator $\mathbf{V}$ scaled by the coupling parameter β. This operator connects mutually distinct spaces X_ρ^b and X_∞^a, and it vanish over the space X_ρ^b as well as over the space X_n^a.

Combined system $\mathbf{C}_\infty$ is described by the generalized eigenvalue equation

$$\mathbf{H}_c \left|\Psi(\ldots)\right\rangle = \varepsilon(\ldots)\mathbf{S}_c\left|\Psi(\ldots)\right\rangle, \tag{3.10a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \mathbf{H}_b + \beta\mathbf{V}, \qquad \mathbf{S}_c = \mathbf{I}_\infty^a + \mathbf{S}_b. \tag{3.10b}$$

In analogy to the system $\boldsymbol{A}_\infty$, combined system $\mathbf{C}_\infty$ can also contain continuous as well as discrete eigenvalues and eigenstates. This possibility is indicated by dots $(\ldots)$ in the expression (3.10a). Coupling parameter β is again introduced in order to make manifest dependence on the strength of the modification. If this parameter is small LRM expressions should reduce to the corresponding expressions obtained within the standard perturbation expansion approach. However if this parameter is large, qualitatively new results are obtained. In connection with the expressions (3.10), note that since $\mathbf{S}_b$ is positive-definite in X_ρ^b, operator $\mathbf{S}_c$ is automatically positive-definite in X_∞^c. Eigenvalues $\varepsilon(\ldots)$ of (3.10a) are hence guaranteed to be real.

Expression (3.10a) is still generalized eigenvalue equation, though not of a most general type. In order to avoid technical details which are not essential for the intended generalization of the LRM approach from the finite combined systems $\mathbf{C}_{n+\rho}$ to the infinite combined systems $\mathbf{C}_\infty$, instead of the modification of a general type $(\mathbf{V},\mathbf{P})$ expression (3.10a) contains a simpler modification where $\mathbf{P}=0$. This is in fact the most important case. Once this generalization is obtained, one can consider more general combined systems $\mathbf{C}_\infty$ that contain an arbitrary modification of a general type $(\mathbf{V},\mathbf{P})$.

In analogy to (2.8) one has

$$\mathbf{V} = \mathbf{I}_\rho^b\mathbf{V}\mathbf{I}_\infty^a + \mathbf{I}_\infty^a\mathbf{V}\mathbf{I}_\rho^b. \tag{3.11}$$

Since $\mathbf{P}=0$, there is no analogous expression for the operator $\mathbf{P}$.

From the point of view of the base system $\mathbf{B}_\rho$, system $\boldsymbol{A}_\infty$ plays the role of the surrounding of $\mathbf{B}_\rho$. System $\mathbf{B}_\rho$ without the interaction with the system $\boldsymbol{A}_\infty$ is a closed system. System $\mathbf{B}_\rho$ subject to the interaction with its surrounding represented by the system $\boldsymbol{A}_\infty$ is an open system.

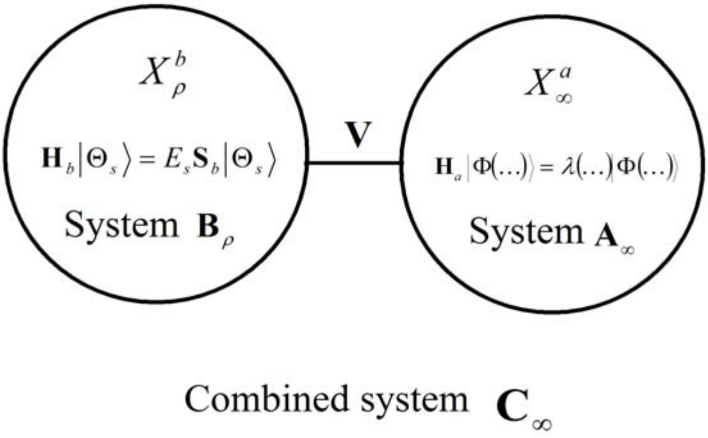

Figure 3.1. External modification of a finite-dimensional system by an infinite-dimensional system. Finite-dimensional system $\mathbf{B}_\rho$ is an open system which is modified externally by the interaction $\mathbf{V}$ with an infinite-dimensional parent system $\mathbf{A}_\infty$. Mutually interacting systems $\mathbf{B}_\rho$ and $\mathbf{A}_\infty$ form infinite-dimensional combined system $\mathbf{C}_\infty$.

The case of an external modification of the finite system $\mathbf{B}_\rho$ by the interaction with an infinite system $\boldsymbol{A}_\infty$ is shown schematically in figure 3.1.

3.3. GENERAL PROPERTIES OF LRM SOLUTIONS TO THE INFINITE-DIMENSIONAL COMBINED SYSTEMS

Expression (3.10a) is an infinite-dimensional eigenvalue equation. A general strategy in the LRM solution of this equation is to approximate infinite-dimensional system $\boldsymbol{A}_\infty$ with a huge but finite-dimensional system

$\boldsymbol{A}_n$ containing n eigenvalues λ_i and n corresponding eigenstates. Infinite-dimensional combined system $\mathbf{C}_\infty$ is accordingly approximated with a huge but finite $(n+\rho)$-dimensional combined system $\mathbf{C}_{n+\rho}$ that has $(n+\rho)$ eigenvalues ε_s and $(n+\rho)$ corresponding eigenstates. As shown in a previous chapter, there are explicit LRM expressions for all eigenvalues and eigenstates of such finite-dimensional systems. Given those expressions, one can derive their $n \to \infty$ limit. Provided the approximation of $\boldsymbol{A}_\infty$ with finite-dimensional systems $\boldsymbol{A}_n$ is done in an appropriate way, this limit is well defined [5,7,8]. One thus derives the required expressions for the infinite-dimensional combined system $\mathbf{C}_\infty$.

Finite-dimensional combined system $\mathbf{C}_{n+\rho}$ has two kinds of eigenvalues and eigenstates: If ε_s differs from all the eigenvalues λ_i of the parent system $\mathbf{A}_n$ ($\varepsilon_s \notin \{\lambda_j\}$) the corresponding solution is *cardinal*, otherwise it is *singular* [9]. In addition, one can have two kinds of singular eigenstates $|\Psi_s\rangle$ associated with the eigenvalue $\varepsilon_s \equiv \lambda_j \in \{\lambda_i\}$: If this eigenstate has no component in the space X_ρ^b ($\mathbf{I}_\rho^b|\Psi_s\rangle = 0$), it is *strongly singular*, otherwise ($\mathbf{I}_\rho^b|\Psi_s\rangle \neq 0$), it is *weakly singular*. As emphasized in section 2.2.3, there is an important difference between strongly and weakly singular eigenstates of finite-dimensional systems: each strongly singular eigenstate $|\Psi_s\rangle$ of the combined system $\mathbf{C}_{\mathbf{n}+\rho}$ is at the same time an eigenstate of the parent system $\mathbf{A}_n$. On the other hand, no weakly singular eigenstate $|\Psi_s\rangle$ of $\mathbf{C}_{n+\rho}$ is an eigenstate of $\mathbf{A}_n$. This distinction between cardinal, strongly singular and weakly singular eigenstates in the case of finite-dimensional systems generalizes to infinite-dimensional systems. In addition and in analogy to the infinite-dimensional parent system $\mathbf{A}_\infty$, combined system $\mathbf{C}_\infty$ may contain discrete and continuous eigenvalues. In order to maintain clear distinction between the solutions of the combined system and the solutions of the parent system, each discrete eigenvalue ε_I of $\mathbf{C}_\infty$ will be referred to as an *isolated* eigenvalue while each continuous eigenvalue ε of $\mathbf{C}_\infty$ will be referred to as an *embedded* eigenvalue [5].

Eigenstates $\left|\Psi_I\right\rangle$ corresponding to isolated eigenvalues ε_I of $\mathbf{C}_\infty$ can be normalized to unity. This normalization is done in accord with the metrics induced by the operator $\mathbf{S}_c$. In particular one has [5]

$$\left\langle\Psi_I\left|\mathbf{S}_c\right|\Psi_J\right\rangle = \delta_{I,J}\,. \tag{3.12}$$

Concerning embedded solutions of $\mathbf{C}_\infty$, one finds that each $\varepsilon \in D$ is an embedded eigenvalue of the combined system [5]. Since embedded eigenvalues are part of a continuous band of eigenvalues, the corresponding embedded eigenstates are with respect to those continuous eigenvalues normalized to a δ-function. Those eigenstates are hence of a general type $\left|\Psi(\varepsilon,\ldots)\right\rangle$ where dots (...) denote additional discrete and/or continuous parameters, if any.

Embedded eigenvalues of the combined system $\mathbf{C}_\infty$ are confined to the same range D as continuous eigenvalues of the parent system $\mathbf{A}_\infty$. This is due to the fact that modification operator $\mathbf{V}$ has a finite rank. One finds that if the rank of this operator is infinite (the case not considered here), embedded eigenvalues of the combined system are not necessarily confined to the same range D as the continuous eigenvalues of the parent system.

One can generalize the notion of cardinal and singular solutions defined for finite combined systems $\mathbf{C}_{n+\rho}$ to all isolated as well as to all embedded solutions of the infinite combined systems $\mathbf{C}_\infty$. By definition, each isolated eigenvalue ε_I of $\mathbf{C}_\infty$ is *cardinal* if it differs from all discrete eigenvalues λ_i of $\mathbf{A}_\infty$ ($\varepsilon_I \notin \{\lambda_j\}$). Otherwise it is *singular*. If ε_I is singular and if the corresponding eigenstate $\left|\Psi_I\right\rangle$ has no component in the space X_ρ^b ($\mathbf{I}_\rho^b\left|\Psi_I\right\rangle = 0$), this eigenstate is *strongly singular*, otherwise ($\mathbf{I}_\rho^b\left|\Psi_I\right\rangle \neq 0$) it is *weakly singular*. This is a natural generalization of the notion of cardinal and singular solutions of finite-dimensional combined systems to isolated cardinal and isolated singular solutions of infinite-dimensional combined systems. Concerning embedded solutions of $\mathbf{C}_\infty$, distinction between cardinal and singular solutions is more subtle. This distinction is provided by the *fractional shift* $x(\varepsilon,\ldots)$ [5, 10-13]. Fractional shift is a key quantity in the LRM treatment of embedded solutions of the combined system $\mathbf{C}_\infty$ [5, 10-13].

3.3.1. Fractional Shift

With each embedded eigenstate $\left|\Psi(\varepsilon,\ldots)\right\rangle$ of $\mathbf{C}_\infty$ is associated a fractional shift $x(\varepsilon,\ldots)$. Fractional shift has the following interpretation: Imagine infinite system $\boldsymbol{A}_\infty$ approximated with a huge but finite system $\boldsymbol{A}_n$ containing n eigenvalues λ_i. The corresponding combined system $\mathbf{C}_\infty$ is accordingly approximated with a huge but finite system $\mathbf{C}_{n+\rho}$ containing $n+\rho$ eigenvalues ε_s. In particular, if the infinite system $\mathbf{A}_\infty$ contains a single eigenvalue band τ with eigenvalues $\lambda_\tau(k)$ in the eigenvalue interval $I_\tau = \left[a_\tau, b_\tau\right]$, this system can be approximated with a huge but finite number of eigenstates with uniformly spaced eigenvalues λ_i inside this eigenvalue interval. Eigenvalue band τ of the infinite modified system $\mathbf{C}_\infty$ is also approximated with huge but finite number of modified eigenstates with eigenvalues ε_s contained in the same interval I_τ. Consider quantities

$$x(\varepsilon_s) = \frac{\varepsilon_s - \lambda_{s-1}}{\lambda_s - \lambda_{s-1}}. \tag{3.13}$$

where $\varepsilon_s \in I_\tau$ are eigenvalues of the combined system $\mathbf{C}_{n+\rho}$ while $\lambda_s, \lambda_{s-1} \in I_\tau$ are eigenvalues of the parent system $\boldsymbol{A}_n$. Each $x(\varepsilon_s)$ is a *fractional shift* of the modified eigenvalue ε_s relative to the parent eigenvalue λ_{s-1} [5, 10-13]. Fractional shift is thus defined as the ratio of two infinitesimal quantities: There is an infinitesimal shift $\Delta\varepsilon_s = \varepsilon_s - \lambda_{s-1}$ of the modified eigenvalue ε_s relative to the corresponding parent eigenvalue λ_{s-1}. Another infinitesimal quantity is the interval $\Delta\lambda_s = \lambda_s - \lambda_{s-1}$ between two adjacent parent eigenvalues $\lambda_s \in I_\tau$. As long as infinite systems $\mathbf{A}_\infty$ and $\mathbf{C}_\infty$ are approximated with finite systems $\boldsymbol{A}_n$ and $\mathbf{C}_{n+\rho}$, there is a clear distinction between cardinal and singular solutions. Due to the interlacing rule (2.11) fractional shift $x(\varepsilon_s)$ is confined to the interval $[1-\rho,1]$, i.e. $x(\varepsilon_s) \in [1-\rho,1]$. Further, if $|\Psi_s\rangle$ is a singular eigenstate of $\mathbf{C}_{n+\rho}$, fractional shift $x(\varepsilon_s)$ equals an integer to the order $O(n^{-1})$. In the limit $n \to \infty$ this is exactly an integer, and hence in an infinite system singular eigenstates are characterized by integer fractional shift. However, if $|\Psi_s\rangle$ is a cardinal eigenstate of $\mathbf{C}_{n+\rho}$, fractional shift $x(\varepsilon_s)$ may assume any non-integer value in the interval $[1-\rho,1]$.

If the infinite system $\mathbf{A}_\infty$ is approximated with finite systems $\mathbf{A}_n$ in an appropriate way and if the base system $\mathbf{B}_\rho$ is one-dimensional ($\rho = 1$), in a limit $n \to \infty$ discrete quantities $x(\varepsilon_s)$ that correspond to cardinal solutions of the combined system converge to a single function $x(\varepsilon)$ of a continuous parameter $\varepsilon \in D$ [10-13]. However, if the base system $\mathbf{B}_\rho$ is ρ-dimensional where $\rho > 1$, in a limit $n \to \infty$ discrete quantities $x(\varepsilon_s)$ that correspond to cardinal solutions of this system usually converge to several nontrivial functions $x_d(\varepsilon)$ [5]. In conclusion, in a limit $n \to \infty$ fractional shifts $x(\varepsilon_s)$ associated with cardinal eigenstates converge to one or several well defined continuous functions $x_d(\varepsilon)$, while fractional shifts associated with singular eigenstates converge to a trivial function $x(\varepsilon,\ldots) \equiv \text{int}$. One finds that for each particular eigenvalue $\varepsilon \in D$ combined system $\mathbf{C}_\infty$ may contain at most $e(\varepsilon) \leq \rho$ embedded cardinal eigenstates and $e(\varepsilon) \leq \rho$ corresponding fractional shifts $x_d(\varepsilon)$. Those embedded eigenstates are hence of the type $|\Psi_d(\varepsilon)\rangle$ ($d = 1,\ldots,e(\varepsilon)$). On the other hand, for each particular eigenvalue $\varepsilon \in D$ combined system $\mathbf{C}_\infty$ may contain anything from zero to an infinite number of singular eigenstates [5]. Accordingly, embedded singular eigenstates of the combined system with the eigenvalue $\varepsilon \in D$ are of the form $|\Psi(\varepsilon,\ldots)\rangle$ where dots (…) indicate additional continuous and/or discrete parameters, if any. Further, as far as properties of embedded eigenstates are concerned, there is no difference between fractional shifts $x_d(\varepsilon)$ and $x_d(\varepsilon)\pm 1$ (see section 3.6.1) [10-13]. Fractional shift can be hence confined to the interval $[0,1)$. By definition, fractional shift confined to this interval is a *principal value* of a fractional shift [5]. Assuming fractional shift to be confined to its principal value, embedded cardinal eigenstates are characterized by fractional shift $x_d(\varepsilon)\neq 0$, while embedded singular eigenstates are characterized by fractional shift $x(\varepsilon,\ldots)=0$.

Above conclusions generalize to the case when the parent system $\mathbf{A}_\infty$ contains several eigenvalue bands as well as several isolated eigenstates. In all cases for each $\varepsilon \in D$ one may have at most $e(\varepsilon)\leq \rho$ embedded cardinal eigenstates, while the number of embedded singular eigenstates can be anything from zero to infinite. Further, each embedded singular solution satisfies $x(\varepsilon,\ldots)=0$, while each embedded cardinal solution satisfies $x_d(\varepsilon)\neq 0$ [5]. This is a natural generalization of the notion of singular and cardinal solutions of the finite-dimensional combined system $\mathbf{C}_{n+\rho}$ to embedded singular and embedded cardinal solutions of the infinite-dimensional combined system $\mathbf{C}_\infty$. Concerning embedded singular solutions, one can again distinguish embedded strongly singular eigenstates and embedded weakly singular eigenstates. For each $\varepsilon \in D$ combined system may have an infinite number of embedded strongly singular eigenstates $|\Psi(\varepsilon,\ldots)\rangle$. Those eigenstates have no X_ρ^b component and hence they do not contribute to the properties of the open system $\mathbf{B}_\rho$. On the other hand, for each $\varepsilon \in D$ combined system may have at most ρ embedded weakly singular eigenstates. One finds that those weakly singular eigenstates exist only if combined system $\mathbf{C}_\infty$ is more symmetrical than non-interacting systems $\mathbf{A}_\infty$ and $\mathbf{B}_\rho$. Such eigenstates are hence quite exceptional.

In addition to embedded singular solutions which are characterized by fractional shift $x(\varepsilon,\ldots)=0$, a special role is played by embedded cardinal solutions with fractional shift $x_d(\varepsilon)=0.5$. This fractional shift corresponds to the modified eigenvalue ε that is exactly in a middle between two adjacent infinitesimally close parent eigenvalues λ. Each embedded solution that satisfies $x_d(\varepsilon)=0.5$ is a *resonant* solution and the point $\varepsilon \in D$ where there is an embedded solution such that $x_d(\varepsilon) = 0.5$ is by definition a *resonant point.* This name is due to the resonant shape of the corresponding embedded cardinal eigenstates in a small neighborhood of this point in the case of the weak coupling [5, 10-13] (see section 3.6.4).

3.3.2. Description of the Open System that Interacts with an Infinite System

Each isolated as well as each embedded eigenstate of the combined system can be written as a linear combination

$$|\Psi\rangle = |\Psi^b\rangle + |\Psi^a\rangle, \tag{3.14a}$$

where $|\Psi^b\rangle \in X_\rho^b$ and $|\Psi^a\rangle \in X_\infty^a$ are components of this eigenstate in spaces X_ρ^b and X_∞^a, respectively. Let $\mathbf{O}$ be an observable that describes some property of the open system $\mathbf{B}_\rho$ that interacts with the infinite system $\boldsymbol{A}_\infty$ and let $|\Psi_1\rangle$ and $|\Psi_2\rangle$ be two eigenstates of the combined system $\mathbf{C}_\infty$. Since operator $\mathbf{O}$ refers to the base system $\boldsymbol{B}_\rho$, it has non-vanishing matrix elements only between the states contained in the space X_ρ^b. This implies

$$\langle\Psi_1|\mathbf{O}|\Psi_2\rangle = \langle\Psi_1^b|\mathbf{O}|\Psi_2^b\rangle. \tag{3.14b}$$

Hence, in order to obtain properties of the open system $\mathbf{B}_\rho$, it is sufficient to know X_ρ^b-components of (properly normalized) eigenstates of the combined system. The knowledge of X_∞^a-components of those eigenstates is not needed.

Consider now isolated and embedded eigenstates of the combined system from a point of view of the open system $\mathbf{B}_\rho$. In the case of a finite combined system $\mathbf{C}_{n+\rho}$, strongly singular eigenstates have no component in the space X_ρ^b. Hence and according to (3.14), those eigenstates do not contribute to the properties of the open system $\mathbf{B}_\rho$. Concerning weakly singular eigenstates of $\mathbf{C}_{n+\rho}$, those eigenstates do have non-vanishing X_ρ^b-component. However, weakly singular eigenstates exist only if the combined system $\mathbf{C}_{n+\rho}$ has some symmetry which is not present in the initial non-interacting systems $\boldsymbol{B}_\rho$ and $\boldsymbol{A}_n$. One finds that the same applies to the infinite combined system $\mathbf{C}_\infty$. Accordingly, if one is interested in the open system $\boldsymbol{B}_\rho$ that interacts with the infinite system $\boldsymbol{A}_\infty$, most important are cardinal solutions of the combined system. In particular, those are X_ρ^b-components of embedded cardinal and X_ρ^b-components of the isolated cardinal eigenstates of the combined system. One finds that those components are described by two key eigenvalue equations. Those are *generic* eigenvalue equation and *fractional shift* eigenvalue equation. Both equations act in the space X_ρ^b and they can be both represented as $\rho \times \rho$ matrix eigenvalue equations. In addition to operators $\mathbf{H}_b$ and $\mathbf{S}_b$ that according to (2.5a) describe isolated system $\boldsymbol{B}_\rho$, those eigenvalue equations involve *characteristic operator* $\mathbf{f}_b(\varepsilon)$ and *derived operator* $\boldsymbol{\omega}_b(\varepsilon)$ [5, 10-13]. Characteristic operator $\mathbf{f}_b(\varepsilon)$ incorporates essential features of the interaction of the base system $\boldsymbol{B}_\rho$ with the infinite-dimensional parent system $\boldsymbol{A}_\infty$. This operator is basic. Derived operator $\boldsymbol{\omega}_b(\varepsilon)$ is uniquely determined by the corresponding characteristic operator $\mathbf{f}_b(\varepsilon)$. This derived operator generalizes to infinite-dimensional systems operator $\boldsymbol{\Omega}_b(\varepsilon)$ defined in section 2.2.

3.4. CHARACTERISTIC AND DERIVED OPERATORS OF THE BASE SYSTEM

Key role in the LRM expressions that replace infinite-dimensional eigenvalue equation (3.10a) is played by the *characteristic* operator $\mathbf{f}_b(\varepsilon)$ which depends on the real parameter ε [5]. This operator is defined in terms of the characteristic operator $\bar{\mathbf{f}}(\varepsilon)$ that is associated with the parent system $\boldsymbol{A}_\infty$ and in terms of the operator $\mathbf{V}$ that describes the interaction between the parent system and the base system

$$\mathbf{f}_b(\varepsilon) = \mathbf{V}\,\bar{\mathbf{f}}(\varepsilon)\mathbf{V}\,, \tag{3.15a}$$

Unlike characteristic operator $\bar{\mathbf{f}}(\varepsilon)$ which acts in the infinite-dimensional space X_∞^a, operator $\mathbf{f}_b(\varepsilon)$ acts in the ρ-dimensional space X_ρ^b and in this space it is represented as a $\rho \times \rho$ Hermitean matrix. Characteristic operator $\mathbf{f}_b(\varepsilon)$ is a sum of characteristic operators $\mathbf{f}_\tau(\varepsilon)$ associated with eigenvalue bands τ of the system $\boldsymbol{A}_\infty$ and of the characteristic operator $\mathbf{F}_b(\varepsilon)$ associated with discrete solutions of this system

$$\mathbf{f}_b(\varepsilon) = \sum_\tau \mathbf{f}_\tau(\varepsilon) + \mathbf{F}_b(\varepsilon)\,, \tag{3.15b}$$

where

$$\mathbf{f}_\tau(\varepsilon) = \mathbf{V}\,\bar{\mathbf{f}}_\tau(\varepsilon)\mathbf{V}\,,\ \ \mathbf{F}_b(\varepsilon) = \mathbf{V}\,\bar{\mathbf{F}}(\varepsilon)\mathbf{V}\,. \tag{3.15c}$$

Operator $\mathbf{f}_\tau(\varepsilon)$ contains information about the interaction of the finite system $\boldsymbol{B}_\rho$ with the eigenvalue band τ of the parent system $\boldsymbol{A}_\infty$. According to (3.7b) and (3.15c) one has

$$\mathbf{f}_\tau(\varepsilon) = \left.\frac{\sum_m \int \mathbf{V}\left|\Phi_{\tau,m}(k,l)\right\rangle\left\langle\Phi_{\tau,m}(k,l)\right|\mathbf{V}dl}{d\lambda_\tau(k)/dk}\right|_{k=\lambda_\tau^{-1}(\varepsilon)} \cdot \begin{cases} 1 & if \quad \varepsilon \in I_\tau \\ 0 & if \quad \varepsilon \notin I_\tau \end{cases}$$

$$\tau = 1,\ldots,\kappa\,, \tag{3.16a}$$

Operator $\mathbf{f}_\tau(\varepsilon)$ vanishes for each $\varepsilon \notin I_\tau$ and it is positive definite for almost each $\varepsilon \in I_\tau$. Only in some isolated points $\varepsilon_0 \in I_\tau$, if any, one may have $\mathbf{f}_\tau(\varepsilon_0) = 0$. Further, operator $\mathbf{f}_\tau(\varepsilon)$ vanishes over the infinite-dimensional space X^a_∞, and it can have non-vanishing matrix elements only over the finite-dimensional space X^b_ρ. In the base $\{|r\rangle\}$ of this space operator $\mathbf{f}_\tau(\varepsilon)$ is a $\rho \times \rho$ matrix with matrix elements:

$$f^{(\tau)}_{rt}(\varepsilon) \equiv \langle r|\mathbf{f}_\tau(\varepsilon)|t\rangle = \left.\frac{\sum_m \int \langle r|\mathbf{V}|\Phi_{\tau,m}(k,l)\rangle\langle\Phi_{\tau,m}(k,l)|\mathbf{V}|t\rangle dl}{d\lambda_\tau(k)/dk}\right|_{k=\lambda_\tau^{-1}(\varepsilon)} \cdot \begin{cases} 1 & if \quad \varepsilon \in I_\tau \\ 0 & if \quad \varepsilon \notin I_\tau \end{cases}$$

$$\tau = 1,\ldots,\kappa, \qquad r,t = 1,\ldots,\rho. \tag{3.16b}$$

Each matrix element $f^{(\tau)}_{rt}(\varepsilon)$ is usually an analytic function of ε inside the interval I_τ. However, it is not analytic for each real ε, since outside this interval $f^{(\tau)}_{rt}(\varepsilon)$ is identically zero. Since $\mathbf{f}_\tau(\varepsilon)$ is positive definite almost everywhere inside the interval I_τ and zero outside this interval, each eigenvalue $f^{(\tau)}_j(\varepsilon)$ ($j = 1,\ldots,\rho$) of this operator is nonnegative inside I_τ and zero outside I_τ. In particular, if τ is one-parameter eigenvalue band, operator $\mathbf{f}_\tau(\varepsilon)$ has rank one for each $\varepsilon \in I_\tau$ with a possible exception of few isolated points where this rank vanishes [5]. In this case each eigenvalue $f^{(\tau)}_j(\varepsilon)$ is identically zero ($f^{(\tau)}_j(\varepsilon) = 0$ for each ε) except for only one eigenvalue (say $f^{(\tau)}_1(\varepsilon)$) which is positive almost everywhere in the interval I_τ and zero outside this interval [5].

Operator $\mathbf{F}_b(\varepsilon)$ contains essential features of the interaction of the finite system $\boldsymbol{B}_\rho$ with discrete eigenstates of the infinite system $\boldsymbol{A}_\infty$. According to (3.7c) and (3.15c) one has

$$\mathbf{F}_b(\varepsilon) = \sum_i \mathbf{V}|\Phi_i\rangle\langle\Phi_i|\mathbf{V}\delta(\varepsilon - \lambda_i), \tag{3.16c}$$

This operator vanishes for each $\varepsilon \notin \{\lambda_j\}$ and it is a δ -type operator in each point $\varepsilon \in \{\lambda_j\}$. Operator $\mathbf{F}_b(\varepsilon)$ is also zero over the entire space X_∞^a, it is also positive definite, and in the base $\{|r\rangle\}$ of the space X_ρ^b this operator is a $\rho \times \rho$ matrix with matrix elements $F_{r,t}(\varepsilon)$

$$F_{rt}(\varepsilon) \equiv \langle r|\mathbf{F}_b(\varepsilon)|t\rangle = \sum_i \langle r|\mathbf{V}|\Phi_i\rangle\langle\Phi_i|\mathbf{V}|t\rangle\delta(\varepsilon-\lambda_i),$$

$$r,t = 1,\ldots,\rho\,. \tag{3.16d}$$

Characteristic operator $\mathbf{f}_b(\varepsilon)$ determines derived operator $\boldsymbol{\omega}_b(\varepsilon)$ according to

$$\boldsymbol{\omega}_b(\varepsilon) = P\int\frac{\mathbf{f}_b(\lambda)}{\varepsilon-\lambda}d\lambda\,, \tag{3.17a}$$

which can be also written as

$$\boldsymbol{\omega}_b(\varepsilon) = \mathbf{V}\overline{\boldsymbol{\varpi}}(\varepsilon)\mathbf{V}\,, \tag{3.17b}$$

Hence

$$\boldsymbol{\omega}_b(\varepsilon) = \sum_\tau \boldsymbol{\omega}_\tau(\varepsilon) + \boldsymbol{\Omega}_b(\varepsilon), \tag{3.17c}$$

where

$$\boldsymbol{\omega}_\tau(\varepsilon) = P\int\frac{\mathbf{f}_\tau(\lambda)}{\varepsilon-\lambda}d\lambda\,, \qquad \boldsymbol{\Omega}_b(\varepsilon) = P\int\frac{\mathbf{F}_b(\lambda)}{\varepsilon-\lambda}d\lambda\,, \tag{3.17d}$$

Unlike operator $\mathbf{f}_\tau(\varepsilon)$ that vanishes outside the interval I_τ, the corresponding derived operator $\boldsymbol{\omega}_\tau(\varepsilon)$ is nonzero in all points outside I_τ and in almost all points inside I_τ. The same applies to the operator $\boldsymbol{\Omega}_b(\varepsilon)$. In the base $\{|r\rangle\}$ of the space X_ρ^b matrix elements of the derived operators $\boldsymbol{\omega}_\tau(\varepsilon)$ $(\tau = 1,2,\ldots)$ are

$$\omega_{rt}^{(\tau)}(\varepsilon) \equiv \left\langle r \middle| \boldsymbol{\omega}_\tau(\varepsilon) \middle| t \right\rangle = P\int \frac{f_{rt}^{(\tau)}(\lambda)}{\varepsilon - \lambda} d\lambda, \quad r,t = 1,\ldots,\rho. \tag{3.17e}$$

while matrix elements of the derived operator $\boldsymbol{\Omega}_b(\varepsilon)$ are

$$\Omega_{rt}(\varepsilon) \equiv \left\langle r \middle| \boldsymbol{\Omega}_b(\varepsilon) \middle| t \right\rangle = \sum_{i(\lambda_i \neq \varepsilon)} \frac{\left\langle r \middle| \mathbf{V} \middle| \Phi_i \right\rangle \left\langle \Phi_i \middle| \mathbf{V} \middle| t \right\rangle}{\varepsilon - \lambda_i},$$

$$r,t = 1,\ldots,\rho. \tag{3.17f}$$

If $\varepsilon \notin I_\tau$, expression (3.17e) is a standard integral. However, if $\varepsilon \in I_\tau$ sub-integral function on the right-hand side of this expression usually diverges in a point $\lambda = \varepsilon$. In this case one has to take a principal Cauchy integral value of this expression.

Note that the expression (3.17f) is identical to the expressions (2.10b) where $\mathbf{P} = 0$.

If the range D and the set $\{\lambda_j\}$ are bounded, each state $\left|\Theta\right\rangle \in X_\rho^a$ satisfies

$$\left\langle \Theta \middle| \boldsymbol{\omega}_b(\pm\infty) \middle| \Theta \right\rangle = 0, \tag{3.18a}$$

This is true also if the range D and/or the set $\{\lambda_j\}$ is not bounded, provided in the limit $\lambda \to \infty$ matrix elements $f_{rt}^b(\lambda)$ satisfy some mild conditions. Further, since $\mathbf{f}_b(\lambda)$ is nonnegative, for each $\varepsilon \notin D$ and $\varepsilon \notin \{\lambda_j\}$ an arbitrary state $\left|\Theta\right\rangle \in X_\rho^b$ satisfies $d\left\langle \Theta \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \Theta \right\rangle / d\varepsilon \leq 0$. This holds true also if $\varepsilon = \varepsilon_0 \in D$, provided the state $\left|\Theta\right\rangle$ satisfies $\mathbf{f}_b(\varepsilon_0)\left|\Theta\right\rangle = 0$. Since $\mathbf{f}_b(\varepsilon)\left|\Theta\right\rangle = 0$ whenever $\varepsilon \notin D$, this can be concisely written as

$$\frac{d}{d\varepsilon}\left\langle \Theta \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \Theta \right\rangle \le 0, \qquad \text{if } \mathbf{f}_b(\varepsilon)\left|\Theta\right\rangle = 0 \text{ and } \qquad \varepsilon \notin \{\lambda_j\} \quad (3.18b)$$

However, if $\varepsilon \in D$ and $\mathbf{f}_b(\varepsilon)\left|\Theta\right\rangle \neq 0$, one may have $d\left\langle \Theta \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \Theta \right\rangle / d\varepsilon \le 0$ as well as $d\left\langle \Theta \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \Theta \right\rangle / d\varepsilon > 0$. The condition $\mathbf{f}_b(\varepsilon)\left|\Theta\right\rangle = 0$ is hence essential. Concerning the condition $\varepsilon \notin \{\lambda_j\}$, in the point $\varepsilon \in \{\lambda_j\}$ derivation of the matrix element $\left\langle \Theta \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \Theta \right\rangle$ is usually not well defined.

As a consequence of expressions (3.18), each eigenvalue $\omega_j(\varepsilon)$ ($j = 1, \ldots \rho$) of the derived operator $\boldsymbol{\omega}_b(\varepsilon)$ is a continuous decreasing function of ε for each ε that satisfies $\varepsilon \notin D$ and $\varepsilon \notin \{\lambda_j\}$. However, if $\varepsilon \in D$ eigenvalue $\omega_j(\varepsilon)$ may be decreasing as well as increasing function of ε, while in each point $\varepsilon = \lambda_i$ this eigenvalue usually diverges [5]. Similar conclusions apply to eigenvalues of operators $\boldsymbol{\omega}_\tau(\varepsilon)$ and $\boldsymbol{\Omega}(\varepsilon)$. In particular, each eigenvalue $\omega_j^{(\tau)}(\varepsilon)$ ($j = 1, \ldots, \rho$) of the operator $\boldsymbol{\omega}_\tau(\varepsilon)$ is a continuous decreasing function for each real ε that satisfies $\varepsilon \notin I_\tau$. However if $\varepsilon \in I_\tau$ this eigenvalue may be decreasing as well as increasing function of ε.

Characteristic operator $\mathbf{f}_b(\varepsilon)$ contains all information necessary for the description of the open system $\boldsymbol{B}_\rho$ subject to the interaction with the infinite parent system $\boldsymbol{A}_\infty$. Since this operator vanishes over the infinite-dimensional space X_∞^a, in order to construct this operator it is not necessary to specify all the details of the infinite-dimensional system $\boldsymbol{A}_\infty$. All what is needed is the knowledge of $\rho \cdot (\rho + 1)/2$ functions (or more precisely distributions [1]) $f_{rt}^b(\varepsilon)$ ($r \le t$). There are an infinite number of possible systems $\boldsymbol{A}_\infty$ that generate the same functions $f_{rt}^b(\varepsilon)$. As far as the properties of the open system $\boldsymbol{B}_\rho$ that interacts with the infinite system $\boldsymbol{A}_\infty$ are concerned, huge amount of information about this system is redundant. Hence if the details of the system $\boldsymbol{A}_\infty$ and of the interaction of this system with the system $\mathbf{B}_\rho$ are not known, one can still model those functions in such a way as to satisfy some required properties and/or some known data of the combined system.

3.4.1. Calculation of the Derived Operators

In the LRM approach in order to find the solution of the combined system one has to know matrix elements of the derived operator $\boldsymbol{\omega}_b(\varepsilon)$. Calculation of those matrix elements involves evaluation of expressions of the types (3.17e) and (3.17f). There is no problem with the expression (3.17f). More problems present calculation of the integrals (3.17e). If $f_{rt}^{(\tau)}(\varepsilon) \equiv q(\varepsilon)$ is an analytic function in the interval I_τ, matrix element $\omega_{rt}^{(\tau)}(\varepsilon)$ can be usually expressed in a closed form as an infinite sum. In particular, if $I_\tau = [a,b]$ is a finite interval ($a \neq -\infty$ and $b \neq \infty$) and if $q(\lambda)$ is analytic in this interval, one has [5, 13]

$$P\int_a^b \frac{q(\lambda)}{\varepsilon - \lambda} d\lambda = q(\varepsilon)\ln\left|\frac{a-\varepsilon}{b-\varepsilon}\right| - g(\varepsilon), \tag{3.19a}$$

where the function $g(\varepsilon)$ equals

$$g(\varepsilon) = \sum_{i=1}^{\infty} \frac{q^{(i)}(\varepsilon)}{i!\,i}\left[(b-\varepsilon)^i - (a-\varepsilon)^i\right], \quad \varepsilon \in (-\infty,\infty). \tag{3.19b}$$

In the above expression $q^{(i)}(\varepsilon)$ is *i*-th derivative of the function $q(\varepsilon)$. If $q(\varepsilon)$ is polynomial, the sum in (3.19b) contains a finite number of terms and $g(\varepsilon)$ is hence also polynomial. More generally, if $q(\varepsilon)$ is an analytic function with the only singularity at infinity, infinite sum in (3.19b) is guaranteed to converge for each finite ε. Function $g(\varepsilon)$ defined with this sum is also analytic with the only singularity at infinity. Note however that principal integral value (3.19a) is not an analytic function of ε in the points

$\varepsilon = a$ and $\varepsilon = b$ on the edgese of the interval I_τ where the function $\ln\left|(a-\varepsilon)/(b-\varepsilon)\right|$ is not analytic.

In addition to the integrals of the general type (3.19a), in some cases one has to evaluate integrals of a general type

$$P\int_a^b \frac{p(\lambda)}{(\varepsilon-\lambda)\sqrt{(\lambda-a)(b-\lambda)}}\,d\lambda\,, \tag{3.20a}$$

where $p(\lambda)$ is a polynomial. With a simple change of variables this integral can be transformed to the integral of a type

$$P\frac{1}{\pi}\int_{-1}^{1} \frac{q(\lambda)}{(\varepsilon-\lambda)\sqrt{1-\lambda^2}}\,d\lambda\,, \tag{3.20b}$$

where $q(\lambda)$ is polynomial. Since each polynomial can be written as a linear combination of Chebyshev polynomials $T_n(\lambda)$ of a first kind [14], integral (3.20b) can be written as a linear combination of integrals $I_n(\varepsilon)$ where

$$I_n(\varepsilon) \equiv P\frac{1}{\pi}\int_{-1}^{1} \frac{T_n(\lambda)}{\left(\varepsilon-\lambda\right)\sqrt{1-\lambda^2}}\,d\lambda\,,\ n = 0,1,2,3,\cdots \tag{3.21}$$

One can obtain an exact solution of the integrals $I_n(\varepsilon)$ [10]

$$I_n(\varepsilon) = -U_{n-1}(\varepsilon) + \frac{T_n(\varepsilon)}{\sqrt{\varepsilon^2-1}}\Theta(\varepsilon)\,, \qquad n = 0,1,2,3,\cdots \tag{3.22a}$$

where

$$\Theta(\varepsilon) = \begin{cases} -1 & \varepsilon < -1 \\ 0 & \varepsilon \in \left[-1,1\right], \\ 1 & \varepsilon > 1 \end{cases} \qquad \varepsilon \in \left(-\infty,\infty\right). \tag{3.22b}$$

and where $T_n(x)$ and $U_n(x)$ are Chebyshev polynomials of the first and of the second kind, respectively. Those polynomials are defined as [14]

$$T_n(\cos\theta) = \cos(n\theta), \qquad U_n(\cos\theta) = \frac{\sin(n+1)\theta}{\sin\theta},$$

$$n = 0,1,2,3,\cdots, \tag{3.23a}$$

and they satisfy recursive relations

$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x), \qquad U_{n+1}(x) = 2xU_n(x) - U_{n-1}(x),$$

$$n = 1,2,3,\cdots, \tag{3.23b}$$

where

$$T_0(x) = U_0(x) = 1, \qquad T_1(x) = x, \qquad U_1(x) = 2x. \tag{3.23c}$$

First few Chebyshev polynomials are [14]

$$\begin{aligned} &T_0(x) = 1, \qquad T_1(x) = x, \qquad T_2(x) = 2x^2 - 1, \\ &T_3(x) = 4x^3 - 3x, \\ &T_4(x) = 8x^4 - 8x^2 + 1, \ldots \end{aligned} \tag{3.24a}$$

$$\begin{aligned} &U_0(x) = 1,\ U_1(x) = 2x,\ U_2(x) = 4x^2 - 1, \\ &U_3(x) = 8x^3 - 4x,\ U_4(x) = 16x^4 - 12x^2 + 1, \ldots \end{aligned} \tag{3.24b}$$

Concerning the above definition of Chebyshev polynomials, two remarks are in place.

First, in view of the definition (3.23a), and since for real θ the value of $\cos\theta$ is confined to the interval $[-1,1]$, those polynomials are usually considered only for argument values $x \in [-1,1]$. However, since $T_n(x)$ and $U_n(x)$ are polynomials, they are well defined for each $x \in (-\infty,\infty)$. In particular, the expression (3.22a) is valid for each $\varepsilon \in (-\infty, \infty)$. Note that this is not a standard way how those polynomials are treated.

Second, Chebyshev polynomial $T_n(x)$ and $U_n(x)$ are defined for $n = 0,1,2,3,\cdots$ [14]. In order for the expression (3.22a) to be valid for each $n \geq 0$ including the case $n = 0$, one has to define polynomial $U_{-1}(x)$. One finds that the proper definition is

$$U_{-1}(x) = 0. \qquad (3.24c)$$

This definition is in accord with expressions (3.23a). It is also in accord with iterative relations (3.23b).

Expressions (3.19) and (3.22) are needed in order to calculate matrix elements $\omega_{rt}(\varepsilon)$ of the derived operator $\boldsymbol{\omega}(\varepsilon)$. Those matrix elements are required in the LRM solution of the eigenvalue equation (3.10) that describes infinite-dimensional combined system $\mathbf{C}_\infty$. Let me now consider LRM solution of this equation.

3.5. ISOLATED SOLUTIONS OF THE COMBINED SYSTEM

Concerning isolated solutions of the combined system $\mathbf{C}_\infty$, most important are isolated cardinal solutions that satisfy $\varepsilon_I \notin \{\lambda_j\}$. Isolated cardinal eigenvalues and the corresponding eigenstates can be obtained as a solution of the *generic* eigenvalue equation [5]

$$\left[\beta^2 \boldsymbol{\omega}_b(\varepsilon_I) + \mathbf{H}_b\right]\left|\theta_I\right\rangle = \varepsilon_I \mathbf{S}_b \left|\theta_I\right\rangle, \qquad \left|\theta_I\right\rangle \in X_\rho^b, \qquad (3.25a)$$

In the base $\{|r\rangle\}$ of the space X_ρ^b above expression is a $\rho \times \rho$ nonlinear eigenvalue equation. Each eigenvalue ε_I of this equation is a root of the $\rho \times \rho$ determinant $h(\varepsilon)$

$$h(\varepsilon) \equiv \left|\beta^2 \boldsymbol{\omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon \mathbf{S}_b\right| = 0. \qquad (3.25b)$$

Expressions (3.25) generalize expressions (2.12) to infinite-dimensional systems. One finds that each solution $\varepsilon = \varepsilon_I \notin D$ of (3.25b) is an isolated eigenvalue of the infinite-dimensional combined system $\mathbf{C}_\infty$. Corresponding eigenstate $\left|\theta_I\right\rangle \in X_\rho^b$ of (3.25a) determines X_ρ^b-component $\left|\Psi_I^b\right\rangle \in X_\rho^b$ of the normalized isolated eigenstate $\left|\Psi_I\right\rangle \in X_\infty^c$ according to

$$\left|\Psi_I^b\right\rangle = \frac{1}{\sqrt{N_I}}\left|\theta_I\right\rangle, \tag{3.26a}$$

where normalization constant N_I equals

$$N_I = \left\langle\theta_I\middle|\mathbf{S}_b\middle|\theta_I\right\rangle - \beta^2 \frac{d}{d\varepsilon_I}\left\langle\theta_I\middle|\boldsymbol{\omega}_b(\varepsilon)\middle|\theta_I\right\rangle, \tag{3.26b}$$

In this expression $d/d\varepsilon_I$ is a shorthand notation for the derivation with respect to the variable ε in a point $\varepsilon = \varepsilon_I$.

X_∞^a-component $\left|\Psi_I^a\right\rangle \in X_\infty^a$ of the isolated eigenstate $\left|\Psi_I\right\rangle$ equals [7]

$$\left|\Psi_I^a\right\rangle = \frac{\beta}{\sqrt{N_I}}\left[\sum_i \frac{\left\langle\Phi_i\middle|\mathbf{V}\middle|\theta_I\right\rangle}{\varepsilon_I - \lambda_i}\left|\Phi_i\right\rangle + \sum_\tau \int \frac{\sum_m \int \left\langle\Phi_{\tau,m}(k,l)\middle|\mathbf{V}\middle|\theta_I\right\rangle dl}{\varepsilon_I - \lambda_\tau(k)}\left|\Phi_{\tau,m}(k,l)\right\rangle dk\right], \tag{3.26c}$$

Since $\varepsilon_I \notin D$ and $\varepsilon_I \notin \{\lambda_i\}$, expression (3.17a) implies

$$\frac{d}{d\varepsilon_I}\left\langle\theta_I\middle|\boldsymbol{\omega}_b(\varepsilon)\middle|\theta_I\right\rangle = -\int \frac{\left\langle\theta_I\middle|\mathbf{f}_b(\lambda)\middle|\theta_I\right\rangle}{(\varepsilon_I - \lambda)^2} d\lambda. \tag{3.26d}$$

In addition one has $\mathbf{f}_b(\varepsilon_I) = 0$. Expression (3.17a) is hence a standard integral, and there is no need to take principal integral value of this expression. As a consequence, one can take derivative of this expression in a standard way. This implies (3.26d). In particular, since $\mathbf{f}_b(\lambda)$ is nonnegative one has $d\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle / d\varepsilon_I < 0$.

Concerning solutions $\varepsilon_I \in D$ of (3.25b), those solutions are *resonant points* [5, 10-13] and they are related to the embedded solutions of the combined system [5] (see section 3.6.4). In general, in a resonant point expression (3.26d) is not valid, and one has to calculate this derivative more carefully. First, one has to calculate matrix element $\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle$ according to the expressions (3.17). This involves taking principal Cauchy integral value of some integrals. Next one has to take derivative of thus obtained expression. As a result, one may have $d\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle / d\varepsilon_I < 0$ as well as $d\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle / d\varepsilon_I \geq 0$. However, if in a point $\varepsilon = \varepsilon_I \in D$ there is an eigenstate $\left|\theta_I\right\rangle$ of (3.25a) that in addition to (3.25a) satisfies

$$\mathbf{f}_b(\varepsilon_I)\left|\theta_I\right\rangle = 0 \qquad (3.27)$$

this point is an *anomal point*. The corresponding integral $\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle$ can be obtained in a standard way, without involving special treatment of the principal integral value. In each anomal point combined system has an isolated solution (see section 3.6.5). Eigenvalue of this isolated solution is eigenvalue ε_I of the generic eigenvalue equation (3.25a). In addition, components $\left|\Psi_I^b\right\rangle$ and $\left|\Psi_I^a\right\rangle$ of the corresponding isolated eigenstate $\left|\Psi_I\right\rangle$ are again given by expressions (3.26) where $\left|\theta_I\right\rangle$ satisfies (3.25a) and (3.27). In particular, since $\left|\theta_I\right\rangle$ satisfies (3.27) there is no divergence in the point $\lambda = \varepsilon_I$. Hence one again derives expression (3.26d).

In conclusion, eigenvalues and eigenstates of the generic eigenvalue equation determine all isolated cardinal eigenvalues $\varepsilon_I \notin \{\lambda_j\}$ of the combined system and all the corresponding eigenstates $\left|\Psi_I\right\rangle$. If $\varepsilon_I \notin D$, this solution is determined by the generic eigenvalue equation (3.25a). However, if

$\varepsilon_I \in D$, the corresponding eigenstate $|\theta_I\rangle$ should satisfy additional condition (3.27).

In a similar way can be derived expressions for isolated singular solutions that satisfy $\varepsilon_I \in \{\lambda_j\}$. Those expressions are almost identical to the expressions (2.15) that apply to finite systems. However, those expressions are not that important. Strongly singular eigenstates have no component in the space X_ρ^b. Hence those eigenstates do not contribute to the properties of the open system $\mathbf{B}_\rho$. Concerning weakly singular eigenstates, those eigenstates exist only if the infinite-dimensional combined system $\mathbf{C}_\infty$ has some symmetry not present in the component subsystems $\mathbf{A}_\infty$ and $\mathbf{B}_\rho$. This is a rather exceptional situation and hence it can be usually neglected.

3.5.1. Isolated Cardinal Eigenvalues and Resonant Points

As emphasized above, each eigenstate $|\theta_I\rangle$ of the generic eigenvalue equation (3.25a) that satisfies (3.27) generates an isolated cardinal eigenstate of the combined system $\mathbf{C}_\infty$. However if $\varepsilon_I \in D$ and if the eigenstate $|\theta_I\rangle$ of (3.25a) does not satisfy (3.27), this is not the case and the eigenvalue ε_I is a resonant point.

One can consider each eigenvalue ε_I of the generic eigenvalue equation (3.25a) as a continuous function of the coupling parameter β, $\varepsilon_I \equiv \varepsilon_I(\beta)$. From this point of view eigenvalue $\varepsilon_I(\beta)$ of (3.25a) may be connected with some eigenvalue E_r of the base system $\mathbf{B}_\rho$, in which case one has $\varepsilon_I(0) = E_r$. It may be also connected with some discrete eigenvalues λ_i of the parent system $\boldsymbol{A}_\infty$, in which case one has $\varepsilon_I(\beta) \to \lambda_i$ in a limit $\beta \to 0$. However, generic eigenvalue equation may contain some additional eigenvalues $\varepsilon_I(\beta)$ that are connected neither to some eigenvalue of $\mathbf{B}_\rho$, nor to some isolated eigenvalue λ_i of $\boldsymbol{A}_\infty$ [5]. In some cases such an additional eigenvalue $\varepsilon_I(\beta)$ may exist for each β however small, as long as $\beta \neq 0$. In some other cases such an additional eigenvalue $\varepsilon_I(\beta)$ exists only if β is large enough, i.e. one must have $\beta > \beta_0$ where $\beta_0 \neq 0$ (see section 3.9 and figures 3.5, 3.12 and 3.17 for some examples).

In order to have a better insight into the dependence of the eigenvalue $\varepsilon_I(\beta)$ on the coupling parameter β, it is convenient to know the rate of change of $\varepsilon_I(\beta)$ with the change of this parameter. One finds [5]

$$\frac{\partial \varepsilon_I(\beta)}{\partial \beta} = \frac{2\beta \left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon_I) \middle| \theta_I \right\rangle}{\left\langle \theta_I \middle| \mathbf{S}_b \middle| \theta_I \right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I} \left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle}, \quad \varepsilon_I \notin \{\lambda_j\} \tag{3.28}$$

As shown in a previous section, if $\varepsilon_I(\beta)$ is an isolated eigenvalue of the combined system one has $d\left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle / d\varepsilon_I \leq 0$. The sign of the derivative $\left(\partial \varepsilon_I / \partial \beta\right)$ in this case equals the sign of the matrix element $\left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon_I) \middle| \theta_I \right\rangle$. However, if $\varepsilon_I(\beta)$ is a resonant point and not an isolated eigenvalue, one may have $d\left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle / d\varepsilon_I \leq 0$ as well as $d\left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle / d\varepsilon_I > 0$ [5]. In particular, in this case one may have $d\varepsilon_I(\beta)/d\beta = \infty$ (see figures 3.5 and 3.12 for some examples).

3.5.2. Probabilities Associated with Isolated Cardinal Eigenstates

Once isolated eigenstate $\left| \Psi_I \right\rangle \in X_\infty^c$ is known, one can find all related properties. In particular, if the emphasize is on the properties of the open system $\mathbf{B}_\rho$ only X_ρ^b-component $\left| \Psi_I^b \right\rangle \in X_\rho^b$ of the eigenstate $\left| \Psi_I \right\rangle$ is required. In a metrics induced by the operator $\mathbf{S}_b$ probability amplitude to find isolated eigenstate $\left| \Psi_I \right\rangle$ in the local state $\left| \Theta_r \right\rangle$ equals $\left\langle \Theta_r \middle| \mathbf{S}_b \middle| \Psi_I \right\rangle$ [5].

Hence and according to (3.26), probability $w_{I,r}$ to find isolated eigenstate $\left|\Psi_I\right\rangle$ in the local state $\left|\Theta_r\right\rangle \in X_\rho^b$ equals

$$w_{I,r} \equiv \left|\left\langle\Theta_r\left|\mathbf{S}_b\right|\Psi_I\right\rangle\right|^2 = \frac{\left\langle\theta_I\left|\mathbf{S}_b\right|\Theta_r\right\rangle\left\langle\Theta_r\left|\mathbf{S}_b\right|\theta_I\right\rangle}{\left\langle\theta_I\left|\mathbf{S}_b\right|\theta_I\right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I}\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle},$$

$$r = 1,\ldots\rho\,, \tag{3.29a}$$

Note that since $\left|\Psi_I\right\rangle$ is an isolated eigenstate, the state $\left|\theta_I\right\rangle$ should satisfy expression (3.27) in addition to the generic eigenvalue equation (3.25a).

Since $\left\{\left|\Theta_r\right\rangle\right\}$ is a complete orthonormalized set in X_ρ^b, probability w_I^b to find isolated eigenstate $\left|\Psi_I\right\rangle$ in the open system $\mathbf{B}_\rho$ equals a sum $\sum_r w_{I,r}$. Hence and due to (2.5c)

$$w_I^b \equiv \sum_r^\rho w_{I,r} = \frac{\left\langle\theta_I\left|\mathbf{S}_b\right|\theta_I\right\rangle}{\left\langle\theta_I\left|\mathbf{S}_b\right|\theta_I\right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I}\left\langle\theta_I\left|\boldsymbol{\omega}_b(\varepsilon)\right|\theta_I\right\rangle}, \tag{3.29b}$$

According to (3.26), this equals norm of the X_ρ^b-component of the isolated eigenstate $\left|\Psi_I\right\rangle$

$$w_I^b = \left\langle\Psi_I^b\left|\mathbf{S}_b\right|\Psi_I^b\right\rangle. \tag{3.29c}$$

All other properties associated with the open system $\mathbf{B}_\rho$ and with the isolated eigenstate $\left|\Psi_I\right\rangle$ can be also expressed in terms of the X_ρ^b-component $\left|\Psi_I^b\right\rangle$ of this eigenstate. In a similar way can be found more general properties of the isolated eigenstate $\left|\Psi_I\right\rangle$ that involve entire combined system $\mathbf{C}_\infty$.

3.5.3. Isolated Singular Eigenstates

Concerning isolated singular solutions of the combined infinite-dimensional systems, those solutions have almost identical properties to singular solutions of the combined finite-dimensional systems. Each isolated singular solution of the combined system $\mathbf{C}_\infty$ has eigenvalue ε_I that coincides with some discrete eigenvalue of the parent system $\boldsymbol{A}_\infty$, $\varepsilon_I \in \{\lambda_i\}$. Further, corresponding singular eigenstate $|\Psi_I\rangle$ can be strongly singular, in which case it has no component in the base space X_ρ^b, and it can be weakly singular, in which case it has such a component. Each strongly singular eigenstate of the combined system is at the same time an eigenstate of the parent system $\boldsymbol{A}_\infty$. Such an eigenstate is not effected by the interaction of the parent system with the base system, and since it has no component in the space X_ρ^b, it does not contribute to the properties of the base system $\mathbf{B}_\rho$. Isolated strongly singular eigenstates are hence not important in the description of the open systems $\mathbf{B}_\rho$. Concerning isolated weakly singular eigenstates, those eigenstates may exist only if the combined system $\mathbf{C}_\infty$ is in some sence more symmetrical than its component subsystems $\boldsymbol{A}_\infty$ and $\mathbf{B}_\rho$.

3.6. EMBEDDED SOLUTIONS OF THE COMBINED SYSTEM

Embedded solutions of the combined system depend on a continuous parameter ε and they exist for each $\varepsilon \in D$, while for $\varepsilon \notin D$ those solutions do not exist. With each embedded solution is associated a fractional shift $x(\varepsilon, \ldots)$ [5]. As explained in section 3.3.1, this quantity is $n \to \infty$ limit of fractional shifts (3.13). Embedded singular solutions satisfy $x(\varepsilon, \ldots) = 0$ while embedded cardinal solutions satisfy $x_d(\varepsilon) \neq 0$ (see section 3.3.1). Most important are embedded cardinal solutions.

3.6.1. Embedded Cardinal Solutions and Fractional Shift Eigenvalue Equation

Embedded cardinal eigenstates of the combined system have non-vanishing fractional shift ($x_d(\varepsilon) \neq 0$) and non-vanishing X_ρ^b component. Hence those eigenstates contribute to the properties of the system $\mathbf{B}_\rho$ that interacts with the infinite system $\boldsymbol{A}_\infty$. Embedded cardinal eigenstates are obtained as a solution of the *fractional shift* eigenvalue equation [5]

$$\mathbf{h}_b(\varepsilon)\left|\theta_d(\varepsilon)\right\rangle = X_d(\varepsilon)\mathbf{f}_b(\varepsilon)\left|\theta_d(\varepsilon)\right\rangle,$$
$$d = 1,2,\ldots,e(\varepsilon) \leq \rho, \tag{3.30a}$$

where

$$\mathbf{h}_b(\varepsilon) = \beta^2\boldsymbol{\omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon\,\mathbf{S}_b, \qquad \varepsilon \in D,\ \left|\theta_d(\varepsilon)\right\rangle \in X_\rho^b, \tag{3.30b}$$

Eigenvalues $X_d(\varepsilon)$ of this equation are related to the corresponding fractional shifts $x_d(\varepsilon)$ according to

$$X_d(\varepsilon) = -\pi\beta^2 \cot(\pi\, x_d(\varepsilon)), \qquad d = 1,2,\ldots,e(\varepsilon) \leq \rho. \tag{3.30c}$$

Each (finite) eigenvalue $X_d(\varepsilon)$ of (3.30a) is hence associated with a nonzero fractional shift $x_d(\varepsilon) \neq 0$ and it corresponds to embedded cardinal solutions. Embedded singular solutions have fractional shift zero, and according to (3.30c) this fractional shift corresponds to the value $X_d(\varepsilon) = \pm\infty$. This value is not an eigenvalue of (3.30a). Hence fractional shift eigenvalue equation produces only embedded cardinal solutions, as required.

For each $\varepsilon \in D$ fractional shift eigenvalue equation is a generalized eigenvalue equation with a nontrivial operator $\mathbf{f}_b(\varepsilon)$ on the right hand side of this equation. In the base $\{|r\rangle\}$ of the space X_ρ^b this equation is represented as a $\rho \times \rho$ matrix eigenvalue equation. For each $\varepsilon = \varepsilon_0 \in D$ eigenvalues

$X_d \equiv X_d(\varepsilon_0)$ of the fractional shift eigenvalue equation are roots of the $\rho \times \rho$ determinant $d(X)$

$$d(X) \equiv \left| \beta^2 \boldsymbol{\omega}_b(\varepsilon_0) + \mathbf{H}_b - \varepsilon_0 \mathbf{S}_b - X \mathbf{f}_b(\varepsilon_0) \right| = 0 . \tag{3.30d}$$

Fractional shift $x_d(\varepsilon)$ in conjuncture with the corresponding eigenstate $\left|\theta_d(\varepsilon)\right\rangle$ of the fractional shift eigenvalue equation determines X_ρ^b-component $\left|\Psi_d^b(\varepsilon)\right\rangle$ of the normalized embedded eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ according to [5]

$$\left|\Psi_d^b(\varepsilon)\right\rangle = \frac{\sin\left(\pi x_d(\varepsilon)\right)}{\pi\beta\sqrt{\left\langle\theta_d(\varepsilon)\middle|\mathbf{f}_b(\varepsilon)\middle|\theta_d(\varepsilon)\right\rangle}}\left|\theta_d(\varepsilon)\right\rangle ,$$

$$d = 1,2,\ldots,e(\varepsilon) \le \rho , \tag{3.31a}$$

Using (3.30c) one can eliminate fractional shift from this expression to obtain

$$\left|\Psi_d^b(\varepsilon)\right\rangle = \frac{\beta}{\sqrt{\pi^2\beta^4 + \left(X_d(\varepsilon)\right)^2}\sqrt{\left\langle\theta_d(\varepsilon)\middle|\mathbf{f}_b(\varepsilon)\middle|\theta_d(\varepsilon)\right\rangle}}\left|\theta_d(\varepsilon)\right\rangle . \tag{3.31b}$$

Fractional shift eigenvalue equation thus produces X_ρ^b-components of embedded cardinal eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ as well as the corresponding fractional shifts $x_d(\varepsilon)$. Since X_ρ^b-component of embedded cardinal eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ uniquely determines X_∞^a-component of this eigenstate, this equation determines complete eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$, not only its X_ρ^b-component. However, from the point of view of the open system $\mathbf{B}_\rho$ of interest is only X_ρ^b-component of this eigenstate.

Index d in (3.31) is used to label multiple fractional shifts associated with degenerate embedded cardinal eigenstates. Fractional shift $x_d(\varepsilon)$ is determined by the eigenvalue $X_d(\varepsilon)$ of the fractional shift eigenvalue equation according to (3.30c) and it is confined to the interval $\left[1-\rho,1\right]$ [5, 10-13].

$$1-\rho \le x_d(\varepsilon) \le 1. \qquad (3.32)$$

Since for each integer m one has $\cot\left(\pi(x_d(\varepsilon)+m)\right)=\cot\left(\pi x_d(\varepsilon)\right)$, expression (3.30c) determines fractional shift up to an additive integer constant. According to the expressions (3.31), X_ρ^b-component of the embedded cardinal eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ does not depend on this additive constant. One finds that neither X_∞^a-component of this eigenstate depends on this constant. Hence one can confine fractional shift $x_d(\varepsilon)$ to the interval $\left[0,1\right)$. This is a rational for the introduction of a notion of a *principal value* of a fractional shift as this was done in section 3.3.1. For all practical purposes one can assume that fractional shift is confined to its principal value. With this convention, fractional shift $x_d(\varepsilon)\neq 0$ corresponds to embedded cardinal eigenstates, while fractional shift $x(\varepsilon,\ldots)=0$ corresponds to embedded singular eigenstates.

Fractional shift eigenvalue equation reduces to the generic eigenvalue equation in the case $X_d(\varepsilon)=0$. In this case fractional shift equals $x_d(\varepsilon)=0.5$. In particular, if $\varepsilon_I\equiv\varepsilon_I(\beta)$ is an eigenvalue of the generic eigenvalue equation (3.25a) and if $\left|\theta_I\right\rangle\equiv\left|\theta_I(\beta)\right\rangle$ is the corresponding eigenstate, than there is an eigenstate $\left|\theta_d(\varepsilon)\right\rangle\equiv\left|\theta_d(\varepsilon,\beta)\right\rangle$ of the fractional shift eigenvalue equation (3.30a) such that $X_d(\varepsilon_I(\beta),\beta)=0$ and (up to the norm and phase) $\left|\theta_I(\beta)\right\rangle\equiv\left|\theta_d(\varepsilon_I(\beta),\beta)\right\rangle$. Each solution to (3.25a) can be hence considered as a special case of solutions to (3.30a). Accordingly, one could obtain both, isolated as well as embedded solutions, using only fractional shift eigenvalue equation. However, it is important to have a clear distinction between isolated eigenstates and embedded eigenstates. Those two types of eigenstates have different properties and hence they should be treated separately.

3.6.2. Basic Properties of the Solutions to the Fractional Shift Eigenvalue Equation

In a base $\left\{|r\rangle\right\} \in X_{\rho}^{b}$ fractional shift equation is a $\rho \times \rho$ matrix eigenvalue equation. Standard $\rho \times \rho$ eigenvalue equation involving Hermitean matrix has ρ eigenvalues and ρ orthonormalized eigenstates. However, fractional shift equation is a generalized eigenvalue equation with Hermitean operator $\mathbf{f}_b(\varepsilon)$ on the right hand side of this equation. Hence for each $\varepsilon \in D$ the number $e(\varepsilon)$ of linearly independent eigenstates $\left|\theta_d(\varepsilon)\right\rangle$ of this equation may be anything from $e(\varepsilon)=0$ to $e(\varepsilon)=\rho$. As a consequence, one may have at most ρ linearly independent embedded cardinal eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ with each particular eigenvalue $\varepsilon \in D$. If $\mathbf{h}_b(\varepsilon)$ is regular, the number of linearly independent solutions to fractional shift equation equals rank of the operator $\mathbf{f}_b(\varepsilon)$, i.e. $e(\varepsilon) = rank(\mathbf{f}_b(\varepsilon))$. In particular, if in some point $\varepsilon = \varepsilon_0 \in D$ this rank vanishes and if $\mathbf{h}_b(\varepsilon_0)$ is regular, there is no solution of the fractional shift eigenvalue equation in this point. This is quite exceptional case and in general fractional shift eigenvalue equation has a solution for each $\varepsilon \in D$, with a possible exception of only few isolated points.

One finds that the number $e(\varepsilon)$ of linearly independent solutions to (3.30a) is mainly determined by the continuous eigenstates of the infinite system $\boldsymbol{A}_{\infty}$ that enter definition of the characteristic operator $\mathbf{f}_b(\varepsilon)$. In particular, if the point $\varepsilon = \varepsilon_0 \in D$ is contained in a single eigenvalue band τ and if $\varepsilon_0 \notin \{\lambda_i\}$, one has $\mathbf{f}_b(\varepsilon_0) = \mathbf{f}_{\tau}(\varepsilon_0)$. If now eigenstates associated with this eigenvalue band are u-degenerate (i.e. if those eigenstates are of a type $\left|\Phi_{\tau,m}(k)\right\rangle$ where $m = 1,\cdots,u$) and if the modification operator $\mathbf{V}$ is nontrivial, one has almost certainly $rank(\mathbf{f}_b(\varepsilon_0)) = rank\left(\mathbf{f}_{\tau}(\varepsilon_0)\right) = \min(\rho, u)$. In particular if degeneracy u of those eigenstates is smaller than ρ, one has $rank(\mathbf{f}_b(\varepsilon_0)) = u$. On the other hand, if $u \geq \rho$ one has $rank(\mathbf{f}_b(\varepsilon_0)) = \rho$. Similarly, if eigenstates associated with this eigenvalue band are of a type $|\Phi_\tau(k,l)\rangle$ where l is a continuous parameter, those eigenstates are ∞-degenerate. In this case fractional shift equation has almost certainly ρ eigenstates $|\theta_d(\varepsilon_0)\rangle$.

In general, eigenstates $|\theta_d(\varepsilon)\rangle$ of the fractional shift eigenvalue equation are not orthogonal to each other. Hence usually $\langle\Psi_d^b(\varepsilon)|\mathbf{S}_b|\Psi_{d'}^b(\varepsilon)\rangle \neq 0$ ($d \neq d'$). Orthogonal to each other are complete embedded eigenstates $|\Psi_d(\varepsilon)\rangle$, not necessarily their X_ρ^b-components. However, those components satisfy [5]

$$\langle\Psi_d^b(\varepsilon)|\mathbf{f}_b(\varepsilon)|\Psi_{d'}^b(\varepsilon)\rangle = 0, \qquad d \neq d'. \tag{3.33}$$

Note further that all $e(\varepsilon)$ embedded eigenstates $|\Psi_d(\varepsilon)\rangle$ ($d = 1,\ldots,e(\varepsilon)$) have the same eigenvalue ε and hence each linear combination of those eigenstates is again an embedded eigenstate of the combined system with this eigenvalue. However, corresponding linear combination of the eigenstates $|\theta_d(\varepsilon)\rangle$ of the fractional shift equation is usually not an eigenstate of this equation. Each eigenstate $|\theta_d(\varepsilon)\rangle$ of (3.30a) has well defined fractional shift $x_d(\varepsilon)$. Hence, unless $x_d(\varepsilon) = x_{d'}(\varepsilon)$, linear combination $a|\theta_d(\varepsilon)\rangle + b|\theta_{d'}(\varepsilon)\rangle$ is not an eigenstate of (3.30a) and it has not well defined fractional shift.

3.6.3. Probabilities Associated with Embedded Cardinal Eigenstates

Once X_ρ^b-component $|\Psi_d^b(\varepsilon)\rangle$ of the embedded cardinal eigenstate $|\Psi_d(\varepsilon)\rangle$ is known, one can obtain all related properties of the open system $\mathbf{B}_\rho$. For example, probability amplitude to find local state $|\Theta_r\rangle$ in this eigenstate equals $\langle\Theta_r|\mathbf{S}_b|\Psi_d(\varepsilon)\rangle$ [5]. Hence and according to (3.31b) probability density $\rho_{d,r}(\varepsilon)$ to find this state in the embedded eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ equals

$$\rho_{d,r}(\varepsilon) \equiv \left|\left\langle\Theta_r\left|\mathbf{S}_b\right|\Psi_d(\varepsilon)\right\rangle\right|^2 = \frac{\beta^2\left\langle\theta_d(\varepsilon)\left|\mathbf{S}_b\right|\Theta_r\right\rangle\left\langle\Theta_r\left|\mathbf{S}_b\right|\theta_d(\varepsilon)\right\rangle}{\left[\pi^2\beta^4 + \left(X_d(\varepsilon)\right)^2\right]\left\langle\theta_d(\varepsilon)\left|\mathbf{f}_b(\varepsilon)\right|\theta_d(\varepsilon)\right\rangle},$$

$$r = 1, \ldots \rho, \tag{3.34}$$

One can also consider probability density $\sigma_r(\varepsilon)$ to find local state $\left|\Theta_r\right\rangle$ in any of the embedded eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ with the eigenvalue ε. One has

$$\sigma_r(\varepsilon) = \sum_d^{e(\varepsilon)} \rho_{d,r}(\varepsilon) = \sum_d \left|\left\langle\Theta_r\left|\mathbf{S}_b\right|\Psi_d(\varepsilon)\right\rangle\right|^2,$$
$$r = 1, \ldots \rho, \tag{3.35a}$$

Of interest is also total probability S_r to find local state $\left|\Theta_r\right\rangle$ in any of the embedded eigenstates of the combined system

$$S_r = \int \sigma_r(\varepsilon)d\varepsilon, \quad r = 1, \ldots \rho. \tag{3.35b}$$

In conjuncture with isolated eigenvalues ε_I and corresponding probabilities $w_{I,r}$, probability density $\sigma_r(\varepsilon)$ determines eigenvalue distribution (or spectral distribution) of the local state $\left|\Theta_r\right\rangle$. If one measures eigenvalue of the state $\left|\Theta_r\right\rangle$ in a closed system $\mathbf{B}_\rho$, one obtains with certainty $E = E_r$. However, if one measures eigenvalue of this state in the open system $\mathbf{B}_\rho$ that interacts with the infinite system $\mathbf{A}_\infty$, one finds each isolated eigenvalue ε_I with the probability $w_{I,r}$ and each embedded eigenvalue $\varepsilon \in D$ with probability density $\sigma_r(\varepsilon)$. Thus instead of a single eigenvalue $E = E_r$, one obtains a spectral distribution which depends on the details of the interaction of the system $\mathbf{B}_\rho$ with its surrounding (system $\mathbf{A}_\infty$).

In analogy to (3.29b), one can also consider probability density $\rho_d^b(\varepsilon)$ to find embedded eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ in the open system $\mathbf{B}_\rho$, i.e. to find this eigenstate in any of the states $\left|\Theta_r\right\rangle$. Due to (2.5c) one has

$$\rho_d^b(\varepsilon) \equiv \sum_r^\rho \rho_{d,r}(\varepsilon) = \frac{\beta^2 \left\langle \theta_d(\varepsilon)\right|\mathbf{S}_b\left|\theta_d(\varepsilon)\right\rangle}{\left[\pi^2\beta^4 + X_d(\varepsilon)^2\right]\left\langle\theta_d(\varepsilon)\right|\mathbf{f}_b(\varepsilon)\left|\theta_d(\varepsilon)\right\rangle}, \quad (3.36a)$$

This probability density equals norm of the X_d^b-component $\left|\Psi_d^b(\varepsilon)\right\rangle$ of the embedded cardinal eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$:

$$\rho_d^b(\varepsilon) = \left\langle \Psi_d^b(\varepsilon)\right|\mathbf{S}_b\left|\Psi_d^b(\varepsilon)\right\rangle, \qquad d = 1,\ldots e(\varepsilon), \quad (3.36b)$$

This expression is similar to the expression (3.29c) which gives probability w_I^b to find isolated eigenstate $\left|\Psi_I\right\rangle$ of the combined system in the base system $\mathbf{B}_\rho$. Total probability density $\rho_b(\varepsilon)$ to find any embedded eigenstate that has eigenvalue ε in the base system $\mathbf{B}_\rho$ can be expressed in terms of the densities $\rho_d^b(\varepsilon)$ as well as in terms of the densities $\sigma_r(\varepsilon)$ and $\rho_{d,r}(\varepsilon)$ as

$$\rho_b(\varepsilon) \equiv \sum_d^{e(\varepsilon)} \rho_d^b(\varepsilon) = \sum_r^\rho \sigma_r(\varepsilon) = \sum_{d,r} \rho_{d,r}(\varepsilon), \quad (3.36c)$$

In particular, if the system $\mathbf{B}_\rho$ is one-dimensional ($\rho = 1$), for each $\varepsilon \in D$ combined system has only one embedded eigenstate $\left|\Psi_1(\varepsilon)\right\rangle \equiv \left|\Psi(\varepsilon)\right\rangle$ and in this case all above densities coincide

$$\rho_b(\varepsilon) \equiv \rho_1^b(\varepsilon) \equiv \sigma_1(\varepsilon) \equiv \rho_{1,1}(\varepsilon). \quad (3.36d)$$

3.6.4. Emergence of Resonance in the Case of the Weak Coupling

If the eigenvalue $X_d(\varepsilon)$ of the fractional shift equation is non-degenerate, one has [5]

$$\frac{\partial X_d(\varepsilon)}{\partial\varepsilon}=\frac{\beta^2\langle\theta_d(\varepsilon)|d\boldsymbol{\omega}_b(\varepsilon)/d\varepsilon|\theta_d(\varepsilon)\rangle-X_d(\varepsilon)\langle\theta_d(\varepsilon)|d\mathbf{f}_b(\varepsilon)/d\varepsilon|\theta_d(\varepsilon)\rangle-\langle\theta_d(\varepsilon)|\mathbf{S}_b|\theta_d(\varepsilon)\rangle}{\langle\theta_d(\varepsilon)|\mathbf{f}_b(\varepsilon)|\theta_d(\varepsilon)\rangle} \quad (3.37a)$$

where $|\theta_d(\varepsilon)\rangle$ is eigenstate of the fractional shift eigenvalue equation that corresponds to this eigenvalue.

Let the eigenvalue E_r of the closed system $\mathbf{B}_\rho$ satisfy $E_r \in D$ and let the corresponding eigenstate $|\Theta_r\rangle$ be non-degenerate. Let further E_r differ from all discrete eigenvalues λ_i of the infinite system $\mathbf{A}_\infty$. In this case there is one and only one isolated eigenvalue $\varepsilon_I \equiv \varepsilon_I(\beta)$ of a generic equation such that for $\beta = 0$ it reduces to E_r: $\varepsilon_I(0) = E_r$. The corresponding eigenstate $|\theta_I\rangle \equiv |\theta_I(\beta)\rangle$ reduces (up to the norm and phase) to $|\Theta_r\rangle$: $|\theta_I(0)\rangle = |\Theta_r\rangle$. In a resonant point $\varepsilon = \varepsilon_I$ fractional shift eigenvalue equation (3.30a) reduces to a generic eigenvalue equation (3.25a), and hence in this point one has (up to the norm and phase) $|\theta_d(\varepsilon_I)\rangle = |\theta_I\rangle$ for some d. In addition, in this point corresponding eigenvalue $X_I(\varepsilon)$ of a fractional shift equation vanishes: $X_I(\varepsilon_I) = 0$. Hence and according to (3.37a), in some small neighboorhood of the point $\varepsilon = \varepsilon_I$ eigenvalue $X_I(\varepsilon)$ of a fractional shift eigenvalue equation can be approximated as

$$X_I(\varepsilon) \approx \frac{\beta^2 \dfrac{d}{d\varepsilon_I}\langle\theta_I|\boldsymbol{\omega}_b(\varepsilon)|\theta_I\rangle-\langle\theta_I|\mathbf{S}_b|\theta_I\rangle}{\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle}(\varepsilon-\varepsilon_I). \quad (3.37b)$$

This approximation is exact in the point $\varepsilon = \varepsilon_I$ and as $|\varepsilon - \varepsilon_I|$ increases it deteriorates. If $\mathbf{f}_b(E_r)|\Theta_r\rangle \neq 0$ and if β is sufficiently small, according to (3.31b) components $|\Psi_d^b(\varepsilon)\rangle \in X_\rho^b$ of embedded eigenstates $|\Psi_d(\varepsilon)\rangle$ can be in some small neighborhood $\Delta(\varepsilon_I)$ of the resonant point $\varepsilon = \varepsilon_I \equiv \varepsilon_I(\beta)$ approximated as [5]

$$|\Psi_d^b(\varepsilon)\rangle \approx$$

$$|\Psi_d^b(\varepsilon)\rangle^\circ = \frac{\beta\sqrt{\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle}}{\sqrt{\pi^2\beta^4\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle^2 + a_I^2(\varepsilon - \varepsilon_I)^2}}|\theta_I\rangle\delta_{I,d} \tag{3.38a}$$

where

$$a_I = \langle\theta_I|\mathbf{S}_b|\theta_I\rangle - \beta^2\frac{d}{d\varepsilon_I}\langle\theta_I|\boldsymbol{\omega}_b(\varepsilon)|\theta_I\rangle,\ \varepsilon \in \Delta(\varepsilon_I). \tag{3.38b}$$

In particular, if $\varepsilon \in \Delta(\varepsilon_I)$ and if $d \neq I$ one has $|\Psi_d^b(\varepsilon)\rangle \approx 0$. According to (3.38a), close to the point $\varepsilon = \varepsilon_I$ probability density $\rho_d^b(\varepsilon) = \langle\Psi_d^b(\varepsilon)|\mathbf{S}_b|\Psi_d^b(\varepsilon)\rangle$ to find embedded cardinal eigenstate $|\Psi_d(\varepsilon)\rangle$ in the open system $\mathbf{B}_\rho$ can be approximated as

$$\rho_d^b(\varepsilon) \approx \rho_d^0(\varepsilon) = \rho_I^0(\varepsilon)\delta_{d,I}, \qquad \varepsilon \in \Delta(\varepsilon_I), \tag{3.39a}$$

where

$$\rho_I^0(\varepsilon) = \frac{\beta^2\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle\langle\theta_I|\mathbf{S}_b|\theta_I\rangle}{\pi^2\beta^4\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle^2 + a_I^2(\varepsilon - \varepsilon_I)^2}. \tag{3.39b}$$

and where a_I is given by (3.38b). Density $\rho_I^0(\varepsilon)$ represents a universal resonance curve [15] centered at the point $\varepsilon = \varepsilon_I$ and with the width $\Delta\varepsilon_I$

$$\Delta\varepsilon_I = \frac{2\pi\beta^2 \left\langle \theta_I \middle| \mathbf{f}_b(\varepsilon_I) \middle| \theta_I \right\rangle}{\left\langle \theta_I \middle| \mathbf{S}_b \middle| \theta_I \right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I} \left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle}, \tag{3.40a}$$

Height of this curve equals $\rho_I^0(\varepsilon_I)$ and it has the area $w_I^0 = \int \rho_I^0(\varepsilon) d\varepsilon$

$$\rho_I^0(\varepsilon_s) = \frac{\left\langle \theta_I \middle| \mathbf{S}_b \middle| \theta_I \right\rangle}{\pi^2 \beta^2 \left\langle \theta_I \middle| \mathbf{f}_b(\varepsilon_I) \middle| \theta_I \right\rangle}, \tag{3.40b}$$

$$w_I^0 = \frac{\left\langle \theta_I \middle| \mathbf{S}_b \middle| \theta_I \right\rangle}{\left\langle \theta_I \middle| \mathbf{S}_b \middle| \theta_I \right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I} \left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle}. \tag{3.40c}$$

Since β is small, this implies $w_I^0 \approx 1$.

The area w_I^0 is an approximation of a total probability to find any of the embedded cardinal eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ where $\varepsilon \in \Delta(\varepsilon_I)$ in the system $\mathbf{B}_\rho$. Expression (3.40c) is formally identical to the expression (3.29b) for the probability to find isolated eigenstate $\left|\Psi_I\right\rangle$ in a local system $\mathbf{B}_\rho$. Similar expression applies to the probability density $\sigma_I(\varepsilon)$ to find the state $\left|\Theta_r\right\rangle \in X_\rho^b$ in any of the embedded cardinal eigenstates with the eigenvalue $\varepsilon \in \Delta(\varepsilon_I)$. In an explicit notation, in order to emphasize dependence on the coupling parameter β, one should write $\left|\theta_I\right\rangle \equiv \left|\theta_I(\beta)\right\rangle$. Since

$\left|\theta_I(0)\right\rangle = \left|\Theta_r\right\rangle$ and since β is small, one has $\left|\theta_I(\beta)\right\rangle \approx \left|\Theta_r\right\rangle$. Hence $\sigma_I(\varepsilon) \approx \rho_I(\varepsilon)$.

In conclusion, if $E_r \in D$ is non-degenerate and if $\mathbf{f}_b(E_r)\left|\Theta_r\right\rangle \neq 0$, for sufficiently small interaction parameter β there is one and only one embedded eigenstate $\left|\Psi_I(\varepsilon)\right\rangle$ with the property that X_ρ^b-component $\left|\Psi_I^b(\varepsilon)\right\rangle$ of this eigenstate exhibits a strong resonance feature in a small neighborhood of the resonant point $\varepsilon = \varepsilon_I(\beta)$, while X_ρ^b-components of all other embedded eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ ($d \neq I$) are negligible in this neighborhood [5]. In particular, probability density $\sigma_I(\varepsilon)$ to find local state $\left|\Theta_r\right\rangle$ with the eigenvalue $\varepsilon \in D$ exhibits a strong resonance feature in the interval $\Delta(\varepsilon_I)$. The same applies to the probability density $\rho_I(\varepsilon)$, and if β is sufficiently small one has $\rho_I(\varepsilon) \approx \sigma_I(\varepsilon)$. This property is a rational for the name "resonant point" [5]. For an example of such a resonance see section 3.9 and figure 3.6.

Similar resonance features are obtained if $E_r \in D$ is degenerate. However, in this case there are several eigenstates $\left|\theta_I(\beta)\right\rangle$ of a generic eigenvalue equation that satisfy $\left|\theta_I(0)\right\rangle = \left|\Theta_r\right\rangle$ and one may have several closed spaced resonant structures corresponding to the degeneracy of E_r [5].

Emergence of resonance in the case of the weak coupling is usually derived within the formalism of the time-independent perturbation expansion approach [1,4]. If a system of particles interacts weakly with the field (such as e.g. electromagnetic field), there are two main effects of such an interaction. First, due to this interaction each eigenvalue E_r of this system shifts to a new position $\varepsilon_I \equiv \varepsilon_I(\beta)$ where $\varepsilon_I(0) = E_r$. Second, this shifted eigenvalue is not sharp and it acquires the shape of the universal resonance curve [1]. As shown above, both effects are correctly described within the small β limit of the LRM approach.

3.6.5. Anomal Points and Emergence of Isolated Cardinal Solutions in the Continuum

As shown in a previous section, if β is sufficiently small the width $\Delta\varepsilon_I(\beta)$ of the universal resonance curve (3.39b), as calculated according to (3.40a), is small. This implies emergence of resonance in the case of small β. However, if $\langle\theta_I|\mathbf{f}_b(\varepsilon_I)|\theta_I\rangle$ is sufficiently small one may have small width $\Delta\varepsilon_I(\beta)$ of a resonant shape even for large β. Hence open system $\mathbf{B}_\rho$ may display a strong resonant feature even in the case of strong interaction with its surrounding. Such an extreme case is the case of anomal point $\beta = \beta_a$ where $\varepsilon_a = \varepsilon_I(\beta_a) \in D$. Anomal point is a special case of a resonant point. In the anomal point there is at least one eigenstate $|\theta_I\rangle$ of the generic eigenvalue equation such that $\mathbf{h}_b(\varepsilon_a)|\theta_I\rangle = 0$ and $\mathbf{f}_b(\varepsilon_a)|\theta_I\rangle = 0$. This implies $\langle\theta_I|\mathbf{f}_b(\varepsilon_a)|\theta_I\rangle = 0$ and hence formally $\Delta\varepsilon_I(\beta) = 0$. Corresponding eigenvalue $X_d(\varepsilon_a)$ of a fractional shift eigenvalue equation can assume any value and fractional shift $x_I(\varepsilon_a)$ is hence not well defined [5]. This case can be analyzed as a $\beta \to \beta_a$ limit of the quantity $\langle\theta_I|\mathbf{f}(\varepsilon_I)|\theta_I\rangle$. Let $\varepsilon_I = \varepsilon_I(\beta)$ be nondegenerate in the point $\beta = \beta_a$. In the process $\beta \to \beta_a$ the width $\Delta\varepsilon_I(\beta)$ of resonance curve (3.39b) decreases, approximate probability (3.40c) improves, and in a limit $\Delta\varepsilon_I(\beta) \to 0$ it is exact. In this limit resonant shape at the anomal point $\varepsilon_a = \varepsilon_I(\beta_a)$ becomes infinitely narrow and infinitely high. Unlike in the case of small β, probability (3.40c) does not approximate to $w_I^0 \approx 1$, and one has to use full expression (3.40c). In the anomal point this expression is exact and it is identical to the expression (3.29b). Formal similarity between expressions (3.40c) and (3.29b) is not accidental. One obtains qualitatively the same result in the case when $\varepsilon_I(\beta)$ is degenerate in the point $\beta = \beta_a$. Such infinitely narrow and infinitely high densities correspond to one or several isolated cardinal eigenstates [5]. Since $\varepsilon_I = \varepsilon_a \in D$ those eigenstates are embedded in the continuum. One finds that those eigenstates are given by expressions (3.26) [5]. Thus all isolated cardinal eigenstates, those with eigenvalues $\varepsilon_I \notin D$ as well as those with eigenvalues $\varepsilon_I \in D$, are described in the same way.

3.6.6. Embedded Singular Solutions

Expressions (2.15) that apply to singular solutions of a finite combined system $\mathbf{C}_{n+\rho}$ imply analogous expressions for the embedded singular solutions of the infinite combined system $\mathbf{C}_\infty$:

$$\left[\beta^2 \boldsymbol{\omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon \mathbf{S}_b\right] \left|\theta(\varepsilon,\ldots)\right\rangle + \beta \mathbf{V}\,\mathbf{I}^a(\varepsilon) \left|\chi(\varepsilon,\ldots)\right\rangle = 0\,, \tag{3.41a}$$

$$\mathbf{I}^a(\varepsilon)\mathbf{V}\left|\theta(\varepsilon,\ldots)\right\rangle = 0\,, \tag{3.41b}$$

where

$$\left|\theta(\varepsilon,\ldots\right\rangle \in X_\rho^b, \qquad \left|\chi(\varepsilon,\ldots\right\rangle \in X^a(\varepsilon)\,. \tag{3.41c}$$

and where $X^a(\varepsilon) \subset X_\infty^a$ is the space spanned by all those continuous eigenstates of the parent system $\mathbf{A}_\infty$ that have eigenvalue ε. Operator $\mathbf{I}^a(\varepsilon)$ is a projection operator on this space.

In analogy to a finite system $\mathbf{C}_{n+\rho}$, infinite system $\mathbf{C}_\infty$ may contain embedded strongly singular eigenstates which satisfy $\left|\theta(\varepsilon,\ldots)\right\rangle = 0$ and which have no X_ρ^b-component, as well as embedded weakly singular eigenstates which satisfy $\left|\theta(\varepsilon,\ldots)\right\rangle \neq 0$ and which have a non-vanishing X_ρ^b-component. In the case of embedded strongly singular eigenstates expressions (3.41) reduce to

$$\mathbf{V}\,\mathbf{I}^a(\varepsilon)\left|\chi(\varepsilon,\ldots)\right\rangle = 0\,, \tag{3.42a}$$

The corresponding normalized strongly singular eigenstate of the infinite-dimensional combined system $\mathbf{C}_\infty$ is

$$\left|\Psi(\varepsilon,\ldots)\right\rangle \equiv \left|\Psi^a(\varepsilon,\ldots)\right\rangle = \frac{1}{\sqrt{\left\langle \chi(\varepsilon,\ldots)\right|\left.\chi(\varepsilon,\ldots)\right\rangle}}\left|\chi(\varepsilon,\ldots)\right\rangle \in X^a(\varepsilon)\,. \quad (3.42b)$$

Combined system may have an infinite number of such eigenstates associated with each $\varepsilon \in D$. For example, if the system $\boldsymbol{A}_\infty$ is described by the eigenvalue equation

$$\mathbf{H}_a\left|\Phi(k,l)\right\rangle = \lambda(k)\left|\Phi(k,l)\right\rangle, \qquad k \in \left[k_a, k_b\right], \qquad (3.43a)$$

where l is a continuous parameter, each eigenvalue $\lambda(k)$ where $k \in \left[k_a, k_b\right]$ is ∞-degenerate. In this case for each $\varepsilon \in D$ the space $X^a(\varepsilon)$ is an ∞-dimensional space spanned by ∞ eigenstates $\left|\Phi(k,l)\right\rangle$ where $k = \lambda^{-1}(\varepsilon)$. Projection $\mathbf{I}^a(\varepsilon)$ on this space can be written as

$$\mathbf{I}^a(\varepsilon) = \int \left|\Phi(k,l)\right\rangle\left\langle\Phi(k,l)\right| dl\,, \qquad k = \lambda^{-1}(\varepsilon)\,, \qquad (3.43b)$$

Each state $\left|\chi(\varepsilon,\ldots)\right\rangle \in X^a(\varepsilon)$ is hence a linear combination

$$\left|\chi(\varepsilon,\ldots)\right\rangle = \int c(l,k)\left|\Phi(k,l)\right\rangle dl\,, \quad k = \lambda^{-1}(\varepsilon)\,, \qquad (3.44a)$$

where unknown function $c(l,k)$ satisfies

$$\int c(l,k)\left\langle r\right|\mathbf{V}\left|\Phi(k,l)\right\rangle dl = 0\,, \qquad r = 1,\ldots,\rho\,,$$

$$k = \lambda^{-1}(\varepsilon)\,. \qquad (3.44b)$$

This generalizes expressions (2.19). For each particular eigenvalue $\varepsilon \in D$ one has an infinite number of the solutions to (3.44b) and hence an infinite number of embedded strongly singular eigenstates (3.42b) of the combined system. All those eigenstates of the combined system $\mathbf{C}_\infty$ are at the same time eigenstates of the parent system $\mathbf{A}_\infty$ with the same eigenvalue ε. Since those strongly singular eigenstates have no X_ρ^b-component, they do not contribute to the properties of the open system $\mathbf{B}_\rho$. One can say that eigenstates do not "see" the base system $\mathbf{B}_\rho$ since according to (3.44) each such eigenstate $\left|\Psi(\varepsilon,\ldots)\right\rangle$ satisfies

$$\left\langle r\middle|\mathbf{V}\middle|\Psi(\varepsilon,\ldots)\right\rangle = 0\,, \qquad r = 1,\ldots,\rho\,. \tag{3.44c}$$

Hence no embedded strongly singular eigenstate $\left|\Psi(\varepsilon,\ldots)\right\rangle$ interacts with any state of the base system $\mathbf{B}_\rho$.

Concerning embedded weakly singular eigenstates, one finds that for each $\varepsilon \in D$ one may have at most ρ such linearly independent eigenstates. This is analogous to the case of finite combined systems (see section 2.2.3). In addition one again finds that, unless the combined system $\mathbf{C}_\infty$ has some symmetry not contained in the mutually noninteracting systems $\mathbf{B}_\rho$ and $\mathbf{A}_\infty$, it contains no weakly-singular eigenstates.

3.7. COMPLETENESS RELATIONS

As emphasized above, non-vanishing X_ρ^b-component have only cardinal and weakly singular eigenstates of the combined system. Strongly singular eigenstates have no X_ρ^b-component. Hence to the properties of the open system $\mathbf{B}_\rho$ that interacts with the infinite system $\mathbf{A}_\infty$ can contribute only cardinal and weakly-singular eigenstates of the combined system. In addition, unless the combined system $\mathbf{C}_\infty$ has some symmetry not contained in its isolated subsystems $\mathbf{B}_\rho$ and $\boldsymbol{A}_\infty$, it has no weakly singular eigenstates. Hence in most cases isolated cardinal and embedded cardinal solutions are sufficient to provide complete description of the open system $\mathbf{B}_\rho$. In particular, if the combined system contains no weakly-singular eigenstate, each state $\left|\Theta_r\right\rangle \in X_\rho^b$ must be found with certainty either in some isolated cardinal eigenstate of the combined system, or in some embedded cardinal eigenstate of this system. Hence and according to (3.29) and (3.35), in this case one has

$$\sum_I w_{I,r} + S_r = 1, \quad r = 1,\ldots,\rho, \tag{3.45a}$$

where

$$w_{I,r} = \left|\left\langle\Theta_r\right|\mathbf{S}_b\left|\Psi_I\right\rangle\right|^2,$$

$$S_r = \sum_d \int \left|\left\langle\Theta_r\right|\mathbf{S}_b\left|\Psi_d(\varepsilon)\right\rangle\right|^2 d\varepsilon = \int \sigma_r(\varepsilon)d\varepsilon, \tag{3.45b}$$

Quantity $w_{I,r}$ is a probability to find local state $\left|\Theta_r\right\rangle$ in the isolated cardinal eigenstate $\left|\Psi_I\right\rangle$ of the combined system, while S_r is a probability to find this state in any of the embedded cardinal eigenstates $\left|\Psi_d(\varepsilon)\right\rangle$ ($d = 1,\ldots e(\varepsilon)$) of this system. Those quantities are given by expressions (3.29a), (3.34) and (3.35). If the combined system contains no weakly singular eigenstates, expressions (3.45a) should be satisfied. However, if combined system contains some weakly singular eigenstates, those expressions should produce result which is less than one for at least one $r = 1,\ldots,\rho$. If this is the case, it indicates that combined system contains some weakly singular eigenstate which should be included in the calculation [5].

Summing expressions (3.45a) over r one finds

$$\sum_I w_I^b + \sum_r^\rho S_r = \rho. \tag{3.45c}$$

where probabilities $w_I^b = \sum_r w_{I,r}$ are given by expression (3.29b).

Expressions (3.45) are *completeness relations*. Those expressions are satisfied for each value of the coupling parameter β, however large. Significance of those expressions is twofold. First, those expressions provide an efficient test for the validity of the LRM approach as applied to infinite-dimensional systems. Second, provided LRM is shown to be correct, those expressions present a simple test to verify whether combined system contains any weakly singular eigenstate [5].

3.8. ONE-DIMENSIONAL OPEN SYSTEMS

A very important special case of open quantum systems is the case $\rho = 1$. In this case system $\mathbf{B}_1$ contains a single state $|\Theta\rangle$ with the eigenvalue E. This state interacts with an infinite-dimensional system $\mathbf{A}_\infty$. This situation is shown schematically in figure 3.2. A large part of problems associated with the interaction of matter with radiation is exactly of this type: one considers for example a single molecular level $|\Theta\rangle$ that interacts with the radiation. Due to this interaction the corresponding eigenvalue is shifted to a new position and it is not sharp, but it acquires some natural width. Of interest are also various transition probabilities associated with time-dependent properties to be discussed in chapter 4. Such and similar problems are usually treated within the perturbation expansion formalism [1, 4].

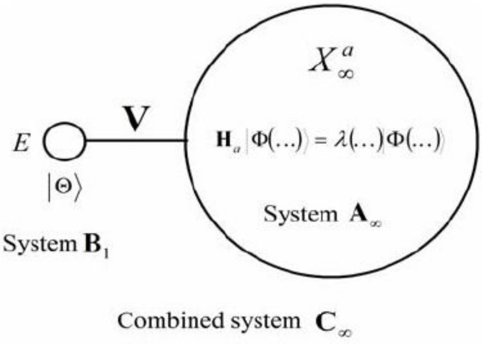

Figure 3.2. External modification of a single state $|\Theta\rangle$ by an infinite-dimensional parent system.

Consider now LRM treatment of such systems. Since the system $\mathbf{B}_1$ is one-dimensional, general LRM expressions substantially simplify. In particular, since $\rho = 1$ characteristic operator $\mathbf{f}_b(\varepsilon)$ reduces to a single matrix element and it becomes a characteristic function $f_b(\varepsilon)$. Similarly, derived operator $\boldsymbol{\omega}_b(\varepsilon)$ becomes derived function $\omega_b(\varepsilon)$. This derived function is expressed in terms of the characteristic function $f_b(\varepsilon)$ according to

$$\omega_b(\varepsilon) = P\int \frac{f_b(\lambda)}{\varepsilon - \lambda} d\lambda . \tag{3.46}$$

Concerning isolated cardinal solutions, generic equation (3.25) reduces to

$$\beta^2 \omega_b(\varepsilon) + E - \varepsilon = 0 , \tag{3.47a}$$

while condition (3.27) translates into

$$f_b(\varepsilon_I) = 0 . \tag{3.47b}$$

Each root $\varepsilon = \varepsilon_I$ of (3.47a) that satisfies (3.47b) is an isolated eigenvalue of the combined system $\mathbf{C}_\infty$. According to (3.26), X_1^b-component of the corresponding eigenstate $|\Psi_I\rangle$ is

$$|\Psi_I^b\rangle = \frac{1}{\sqrt{N_I}} |\Theta\rangle , \tag{3.48a}$$

where

$$N_I = 1 - \beta^2 d\omega_b / d\varepsilon_I , \tag{3.48b}$$

and where $\left|\Theta\right\rangle$ is normalized ($\left\langle\Theta|\Theta\right\rangle = 1$). The corresponding X_∞^a-component $\left|\Psi_I^a\right\rangle$ of the isolated state $\left|\Psi_I\right\rangle$ is given by expression (3.26c) where $\left|\theta_I\right\rangle = \left|\Theta\right\rangle$.

According to (3.48), probability w_I to find isolated cardinal eigenstate $\left|\Psi_I\right\rangle$ in a state $\left|\Theta\right\rangle$ (system $\mathbf{B}_1$) equals

$$w_I^b \equiv \left|\left\langle\Theta|\Psi_I\right\rangle\right|^2 = \frac{1}{1-\beta^2\, d\omega_b(\varepsilon)/d\varepsilon_I}. \tag{3.48c}$$

Consider now embedded eigenstates. Since $\rho = 1$, for each $\varepsilon \in D$ one has only one fractional shift $x(\varepsilon)$. Fractional shift eigenvalue equation (3.30a) hence reduces to

$$h_b(\varepsilon) \equiv \beta^2\omega_b(\varepsilon) + E - \varepsilon = X(\varepsilon) f_b(\varepsilon), \quad \varepsilon \in D. \tag{3.49}$$

where $X(\varepsilon)$ is given by (3.30c). One finds

$$x(\varepsilon) = \frac{1}{\pi}\cot^{-1}\left(\frac{\varepsilon - E - \beta^2\omega_b(\varepsilon)}{\pi\beta^2 f_b(\varepsilon)}\right), \qquad \varepsilon \in D. \tag{3.50}$$

Further, expression (3.31a) reduces to

$$\left|\Psi^b(\varepsilon)\right\rangle = \frac{\sin(\pi x(\varepsilon))}{\pi\beta\sqrt{f_b(\varepsilon)}}\left|\Theta\right\rangle, \qquad \varepsilon \in D, \tag{3.51a}$$

Using (3.50) fractional shift $x(\varepsilon)$ can be eliminated from this expression to obtain

$$\left|\Psi^b(\varepsilon)\right\rangle = \left[\frac{\beta^2 f_b(\varepsilon)}{\pi^2\beta^4 f_b^2(\varepsilon) + \left(\beta^2\omega_b(\varepsilon) + E - \varepsilon\right)^2}\right]^{1/2}\left|\Theta\right\rangle,$$

$$\varepsilon \in D. \tag{3.51b}$$

Probability density $\rho_b(\varepsilon)$ to find embedded eigenstate $|\Psi(\varepsilon)\rangle$ in the state $|\Theta\rangle$ hence equals

$$\rho_b(\varepsilon) \equiv \left|\langle\Theta|\Psi(\varepsilon)\rangle\right|^2 = \frac{\beta^2 f_b(\varepsilon)}{\pi^2\beta^4 f_b^2(\varepsilon) + \left(\beta^2\omega_b(\varepsilon) + E - \varepsilon\right)^2},$$
$$\varepsilon \in D. \qquad (3.52a)$$

This probability density is the same as probability density to find the state $|\Theta\rangle$ with the (embedded) eigenvalue $\varepsilon \in D$. Since $\mathbf{B}_1$ is one-dimensional and since as a consequence for each $\varepsilon \in D$ there is only one embedded cardinal eigenstate $|\Psi(\varepsilon)\rangle$, there is only one probability density $\rho_b(\varepsilon)$ (see expression (3.36d).

Let $\varepsilon = \varepsilon_I \in D$ be a root of (3.47a). Since $\varepsilon_I \in D$ this is a resonant point. According to (3.52a), if $f_b(\varepsilon_I) \neq 0$ one has

$$\rho_b(\varepsilon_I) \equiv \left|\langle\Theta|\Psi(\varepsilon_I)\rangle\right|^2 = \frac{1}{\pi^2\beta^2 f_b(\varepsilon_I)}, \quad \varepsilon_I \in D. \qquad (3.52b)$$

If β is small, this density can be very large. In this case one can approximate density $\rho_b(\varepsilon)$ in a neighborhood of a resonant point $\varepsilon_I \in D$ according to

$$\rho_b(\varepsilon) \approx \rho_I^0(\varepsilon) = \frac{\beta^2 f_b(\varepsilon_I)}{\pi^2\beta^4 f_b^2(\varepsilon_I) + (\varepsilon - \varepsilon_I)^2}, \quad \varepsilon \in D. \qquad (3.53a)$$

This is a universal resonance curve centered at the point $\varepsilon = \varepsilon_I$, with the width

$$\Delta\varepsilon_I = 2\pi\beta^2 f_b(\varepsilon_I), \qquad (3.53b)$$

and with a unit area. If β is small the width $\Delta\varepsilon_I$ is also small. Approximation (3.53a) of the density $\rho_b(\varepsilon)$ in the neighborhood of the resonance point

$\varepsilon = \varepsilon_I$ is hence reliable. The same expression can be obtained from the general discussion in section 3.6.4 and from the expression (3.39b). Since β is small and since X_ρ^b is one-dimensional, one can approximate quantity a_I in this expression with $a_I \approx 1$. In addition one has $\left\langle \theta_I \left| f_b(\varepsilon_I) \right| \theta_I \right\rangle \to f_b(\varepsilon_I)$ and $\left\langle \theta_I \left| \mathbf{S}_b \right| \theta_I \right\rangle \to 1$. Hence (3.39b) implies (3.53a). In addition and according to (3.47a), as a first approximation resonant point $\varepsilon = \varepsilon_I$ equals

$$\varepsilon_I \approx \varepsilon_I^0 = E + \beta^2 \omega_b(E), \tag{3.53c}$$

As a next approximation one has

$$\varepsilon_I \approx \varepsilon_I^1 = E + \beta^2 \omega_b(\varepsilon_I^0). \tag{3.53d}$$

which iteratively produces exact value of ε_I. Above LRM expressions provide a simple quantitative explanation of two main effects of the interaction of a single state with an infinite system: the shift of the original eigenvalue E to a new position ε_I, and the broadening of this eigenvalue to the resonance shape. For this to happen shifted eigenvalue ε_I (resonant point) must be contained inside the eigenvalue range D of the continuous eigenvalues of the infinite system $\mathbf{A}_\infty$ and the width $\Delta\varepsilon_I$ as calculated according to (3.53b) should be relatively small.

3.9. EXAMPLES

Let me illustrate LRM treatment of infinite-dimensional systems with some examples. In order to cover various aspects of open quantum systems, three different quantum systems in the interaction with various surroundings will be considered.

3.9.1. Example 3.1: Interaction of a Base System with an Infinite System that Contains a Single Eigenvalue Band

Consider two-dimensional system $\mathbf{B}_2$ that is in the base $\{|r\rangle\}$ characterized by matrices

$$\mathbf{H}_b = \begin{pmatrix} 0.5 & -0.25 \\ -0.25 & 0.6 \end{pmatrix}, \quad \mathbf{S}_b = \begin{pmatrix} 1.1 & 0.1 \\ 0.1 & 1 \end{pmatrix}, \tag{3.54a}$$

Eigenvalues and eigenstates of this system are

$$E_1 = 0.25474, \qquad E_2 = 0.85536, \tag{3.54b}$$

$$|\Theta_1\rangle = \begin{pmatrix} 0.72621 \\ 0.57942 \end{pmatrix}, |\Theta_2\rangle = \begin{pmatrix} 0.62454 \\ -0.82064 \end{pmatrix}. \tag{3.54c}$$

where $|\Theta_r\rangle$ are orthonormalized according to (2.5b).

Let the surrounding of the system $\boldsymbol{B}_2$ contain a single eigenvalue band in the interval $D \equiv I_1 = [a_1, b_1] = [-1,1]$ and let this surrounding contain no isolated eigenvalues λ_i. Interaction of the system $\mathbf{B}_2$ with this eigenvalue band is described by the characteristic operator $\mathbf{f}_1(\varepsilon)$ which is identically zero outside the interval I_1 and which is nonnegative inside this interval. Let in the base $\{|r\rangle\}$ this operator be given by

$$\mathbf{f}_1(\varepsilon) = \begin{pmatrix} f_{11}^{(1)}(\varepsilon) & f_{12}^{(1)}(\varepsilon) \\ f_{21}^{(1)}(\varepsilon) & f_{22}^{(1)}(\varepsilon) \end{pmatrix} \equiv \begin{pmatrix} q_{11}^{(1)}(\varepsilon) & q_{12}^{(1)}(\varepsilon) \\ q_{21}^{(1)}(\varepsilon) & q_{22}^{(1)}(\varepsilon) \end{pmatrix} \cdot \begin{cases} 1 & if \quad \varepsilon \in I_1 \\ 0 & otherwise \end{cases} \tag{3.55a}$$

where $q_{rt}^{(1)}(\varepsilon)$ are polynomials

$$\begin{aligned} q_{11}^{(1)}(\varepsilon) &= \left(\varepsilon^2 - 1\right)^2 \left(2\varepsilon^2 - 2\varepsilon + 1\right), \\ q_{22}^{(1)}(\varepsilon) &= \left(\varepsilon^2 - 1\right)^2 \left(\varepsilon^2 - 2\varepsilon + 2\right), \end{aligned} \tag{3.55b}$$

$$q_{12}^{(1)}(\varepsilon) \equiv q_{21}^{(1)}(\varepsilon) = \left(\varepsilon^2 - 1\right)^3 .$$

Matrix elements $f_{rt}^{(1)}(\varepsilon)$ of the operator $\mathbf{f}_1(\varepsilon)$ are identical to polynomials $q_{rt}^{(1)}(\varepsilon)$ inside the interval $I_1 = [-1,1]$, and they are identically zero outside this interval. Since $\boldsymbol{A}_\infty$ contains only this single eigenvalue band, one has $\mathbf{f}_b(\varepsilon) \equiv \mathbf{f}_1(\varepsilon)$ and hence $f_{rt}^{b}(\varepsilon) \equiv f_{rt}^{(1)}(\varepsilon)$. In figure 3.3 are shown eigenvalues $f_1(\varepsilon)$ and $f_2(\varepsilon)$ of the characteristic operator $\mathbf{f}_b(\varepsilon)$. Since polynomials $q_{rt}^{(1)}(\varepsilon)$ are zero on both end-points of the interval I_1, those eigenvalues are continuous at those end-points and they vanish outside the range $D \equiv I_1$. As required, eigenvalues $f_1(\varepsilon)$ and $f_2(\varepsilon)$ are nonnegative. Rank of the operator $\mathbf{f}_b(\varepsilon)$ equals two for each interior point $\varepsilon \in D$, except for the critical point $\varepsilon = \varepsilon_c = 0.38197$ where $rank\left(\mathbf{f}_b(\varepsilon_c)\right) = 1$ and where eigenvalue $f_2(\varepsilon)$ of $\mathbf{f}_b(\varepsilon)$ vanishes: $f_2(\varepsilon_c) = 0$.

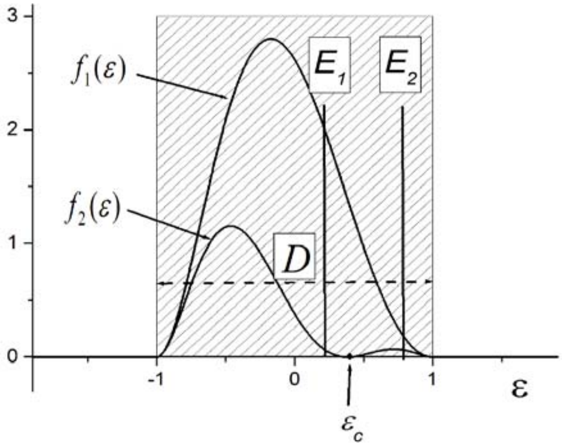

Figure 3.3. Example 3.1. Eigenvalues of the characteristic operator $\mathbf{f}_b(\varepsilon)$. Eigenvalues E_1 and E_2 of the base system $\mathbf{B}_2$ are inside the range D. Adopted from ref. [5].

$$rank(\mathbf{f}_b(\varepsilon)) = \begin{cases} 2 \; if \; \varepsilon \in D \;\&\; \varepsilon \neq \varepsilon_c \\ 1 \; if \; \varepsilon = \varepsilon_c = 0.38197 \\ 0 \; if \; \varepsilon \in \overline{D} \end{cases} \tag{3.56}$$

Since for almost each $\varepsilon \in D$ one has $rank(\mathbf{f}_b(\varepsilon)) > 1$, this characteristic operator corresponds to multi-parameter eigenvalue band. In figure 3.3 are also shown eigenvalues E_1 and E_2 of the base system $\mathbf{B}_2$. Both eigenvalues are contained inside the range $D \equiv I_1$.

Derived operator $\boldsymbol{\omega}_1(\varepsilon)$ that corresponds to the characteristic operator $\mathbf{f}_1(\varepsilon)$ is given by expressions (3.17c) and (3.17d). In particular, since matrix elements of $\mathbf{f}_1(\varepsilon)$ are polynomials inside the interval $D \equiv I_1$, one can use expressions (3.19) to obtain [5]:

$$\begin{aligned} \omega_{11}^{(1)}(\varepsilon) &= q_{11}^{(1)}(\varepsilon)\ln\left|\frac{\varepsilon+1}{\varepsilon-1}\right| - g_{11}^{(1)}(\varepsilon), \\ \omega_{22}^{(1)}(\varepsilon) &= q_{22}^{(1)}(\varepsilon)\ln\left|\frac{\varepsilon+1}{\varepsilon-1}\right| - g_{22}^{(1)}(\varepsilon), \\ \omega_{12}^{(1)}(\varepsilon) \equiv \omega_{21}^{(1)}(\varepsilon) &= q_{12}^{(1)}(\varepsilon)\ln\left|\frac{\varepsilon+1}{\varepsilon-1}\right| - g_{12}^{(1)}(\varepsilon), \end{aligned} \tag{3.57a}$$

where $q_{rt}^{(1)}(\varepsilon)$ are polynomials (3.55b), while $g_{rt}^{(1)}(\varepsilon)$ are polynomials:

$$\begin{aligned} g_{11}^{(1)}(\varepsilon) &= 4\varepsilon^5 - 4\varepsilon^4 - \frac{14}{3}\varepsilon^3 + \frac{20}{3}\varepsilon^2 - \frac{6}{5}\varepsilon - \frac{32}{15}, \\ g_{22}^{(1)}(\varepsilon) &= 2\varepsilon^5 - 4\varepsilon^4 + \frac{2}{3}\varepsilon^3 + \frac{20}{3}\varepsilon^2 - \frac{28}{5}\varepsilon - \frac{32}{15}, \\ g_{12}^{(1)}(\varepsilon) \equiv g_{21}^{(1)}(\varepsilon) &= 2\varepsilon^5 - \frac{16}{3}\varepsilon^3 + \frac{22}{5}\varepsilon. \end{aligned} \tag{3.57b}$$

Since $\mathbf{f}_b(\varepsilon) \equiv \mathbf{f}_1(\varepsilon)$ one has $\boldsymbol{\omega}_b(\varepsilon) \equiv \boldsymbol{\omega}_1(\varepsilon)$. In figure 3.4 are shown eigenvalues $\omega_1(\varepsilon)$ and $\omega_2(\varepsilon)$ of the derived operator $\boldsymbol{\omega}_b(\varepsilon)$. Those eigenvalues are finite and continuous functions of ε for each real ε, including end-points $a_1 = -1$ and $b_1 = 1$ of the interval $I_1 \equiv D$. This follows from the property $\lim_{x \to 0}(x \ln(x)) = 0$ and from the fact that matrix elements of the operator $\mathbf{f}_1(\varepsilon)$ vanish at those end-points [5]. In accord with the expression (3.18b), both eigenvalues are decreasing functions of ε for each $\varepsilon \notin D = [-1,1]$. However, if $\varepsilon \in D$ those eigenvalues may be decreasing as well as increasing functions of ε.

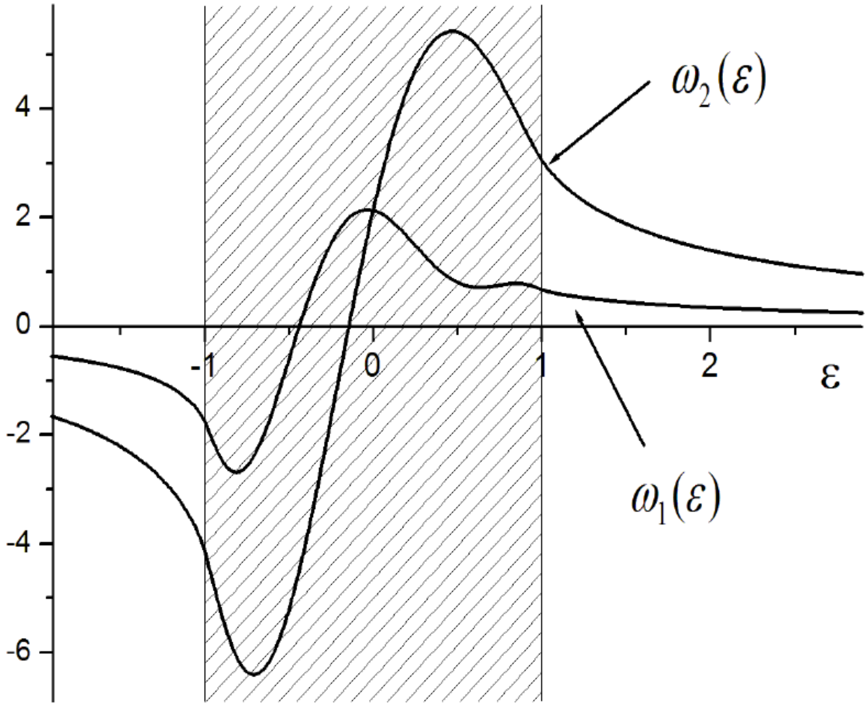

Figure 3.4. Example 3.1. Eigenvalues of the derived operator $\boldsymbol{\omega}_b(\varepsilon)$. Adopted from ref. [5].

Once operator $\boldsymbol{\omega}_b(\varepsilon)$ is known, one can write down generic eigenvalue equation (3.25a). This equation produces all isolated cardinal solutions of the combined system and all resonant points. Solutions of the equation (3.25b) of a type $\varepsilon = \varepsilon(\beta)$ are shown in figure 3.5. There are six such solutions: $\varepsilon_{R1}(\beta)$, $\varepsilon_{R2}(\beta)$, $\varepsilon_1(\beta)$, $\varepsilon_2(\beta)$, $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$. Those solutions are eigenvalues of a generic eigenvalue equation considered as functions of the coupling parameter β. Eigenvalues inside the range D are resonant points, while eigenvalues outside this range are isolated eigenvalues of the combined system.

If there is no interaction ($\beta = 0$) eigenvalues of the generic equation reduce to the eigenvalues E_1 and E_2 of the isolated base system $\mathbf{B}_2$. In particular, one has $\varepsilon_{R1}(0) = E_1$ and $\varepsilon_{R2}(0) = E_2$. Both eigenvalues are contained in the range D. Hence for small β one has $\varepsilon_{R1}(\beta), \varepsilon_{R2}(\beta) \in D$ and those eigenvalues are resonant points. However, if the coupling is as strong as $\beta > \beta_{R2}$ one has $\varepsilon_{R2}(\beta) \notin D$ and this eigenvalue becomes an isolated eigenvalue of the combined system. Also, if $\beta > \beta_{R1}$ one finds $\varepsilon_{R1}(\beta) \notin D$ and this eigenvalue becomes another isolated eigenvalue of the combined system. As $\beta > \beta_{R1}$ further increases, isolated eigenvalues $\varepsilon_{R1}(\beta)$ and $\varepsilon_{R2}(\beta)$ continue to increase. Hence for each $\beta > \beta_{R1}$ combined system has two isolated eigenvalues that satisfy $\varepsilon_I(\beta) > 1$. This is a special case of a general property of combined systems. In general, if discrete eigenvalues λ_i of the parent system $\boldsymbol{A}_\infty$ are bounded from above, combined system $\mathbf{C}_\infty$ has at most ρ extreme right isolated eigenvalues. Since in the example considered one has $\rho = 2$, for each $\beta > \beta_{R1}$ combined system has 2 extreme right isolated eigenvalues.

In the points β_{R1} and β_{R2} one has $\varepsilon = b_1 = 1$. Since $\mathbf{B}_2$ is a two-dimensional system, one can obtain a closed analytic expression for those points [5]. In particular, one obtains a quadratic equation in the unknown $x = \beta^2$. Thus one finds, $\beta_{R2} = 0.21146$ and $\beta_{R1} = 1.12883$.

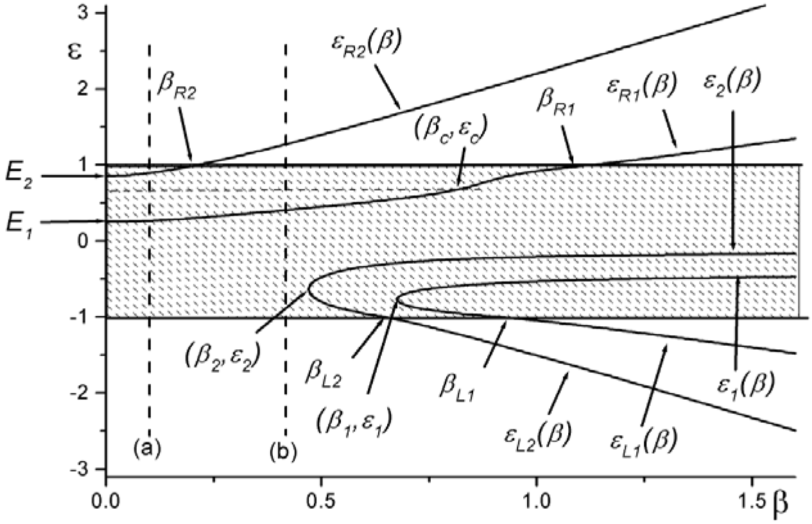

Figure 3.5. Example 3.1. Eigenvalues $\varepsilon_I(\beta)$ of the generic eigenvalue equation considered as functions of a coupling parameter β. Eigenvalues $\varepsilon_I(\beta)$ outside the range $D=[-1,1]$ are isolated eigenvalues of the combined system $\mathbf{C}_\infty$. Eigenvalues $\varepsilon_I(\beta)$ inside this range are resonant points. Eigenvalue distributions of local states $|\Theta_1\rangle$ and $|\Theta_2\rangle$ for the coupling $\beta = 0.1$ corresponding to the line (a) are shown in figure 3.6. Eigenvalue distribution of a local state $|\Theta_1\rangle$ for the coupling $\beta = 0.4$ corresponding to the line (b) is shown in figure 3.7. Adopted from ref. [5].

Consider now remaining four eigenvalues $\varepsilon_{L1}(\beta)$, $\varepsilon_{L2}(\beta)$, $\varepsilon_1(\beta)$ and $\varepsilon_2(\beta)$. Note that $\varepsilon_{L1}(\beta)$ and $\varepsilon_1(\beta)$ are two branches of a single function $\beta=\beta_1(\varepsilon)$, while $\varepsilon_{L2}(\beta)$ and $\varepsilon_2(\beta)$ are two branches of another function $\beta=\beta_2(\varepsilon)$. It is more convenient to analyze those functions in a form $\beta=\beta_1(\varepsilon)$ and $\beta=\beta_2(\varepsilon)$. Since $\mathbf{B}_2$ is two-dimensional, this can be done in a closed form [5]. One thus finds exact positions of critical points $(\beta_1,\varepsilon_1)=(0.67519,-0.76673)$ and $(\beta_2,\varepsilon_2)=(0.47058,-0.63563)$. Eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_1(\beta)$ exist only if $\beta \ge \beta_1$ while eigenvalues $\varepsilon_{L2}(\beta)$ and $\varepsilon_2(\varepsilon)$ exist only if $\beta \ge \beta_2$. For each β (where defined) eigenvalues $\varepsilon_1(\beta)$ and $\varepsilon_2(\beta)$ are inside the range D and hence these eigenvalues are resonant points. Concerning eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$, as β increases one has at first $\varepsilon_{L1}(\beta), \varepsilon_{L2}(\beta) \in D$ and those eigenvalues are resonant points. However, if the coupling is as strong as $\beta > \beta_{L2}$ one has $\varepsilon_{L2}(\beta) \notin D$ and this eigenvalue becomes an isolated eigenvalue of the combined system. Also, if $\beta > \beta_{L1}$ one finds $\varepsilon_{L1}(\beta) \notin D$ and this eigenvalue becomes another isolated eigenvalue of the combined system. As $\beta > \beta_{L1}$ further increases, isolated eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$ continue to decrease. Hence for each $\beta > \beta_{L1}$ combined system has two isolated eigenvalues $\varepsilon_I(\beta)$ that satisfy $\varepsilon_I(\beta) < -1$. This is maximum number of left extreme isolated eigenvalues that combined system with $\rho = 2$ may have.

The position of the points β_{L1} and β_{L2} can be also obtained in the closed analytic form, and one finds $\beta_{L2} = 0.64717$ and $\beta_{L1} = 0.91845$ [5].

Figure 3.5 provides detailed interaction landscape of the open system $\mathbf{B}_2$ that interacts with its surrounding (system $\boldsymbol{A}_\infty$). Note that isolated eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$ cannot be derived by any standard perturbation expansion method. Those eigenvalues do not exist in the point $\beta = 0$ and hence no perturbation expansion in this point can reproduce those eigenvalues. Note also that in a point (β_1, ε_1) one has $d\varepsilon_I(\beta)/d\beta = \infty$. Hence according to the expression (3.28), in this point one has $\langle \theta_I | \mathbf{S}_b | \theta_I \rangle = \beta^2 d \langle \theta_I | \boldsymbol{\omega}_b(\varepsilon) | \theta_I \rangle / d\varepsilon_I$. The same applies to the point (β_2, ε_2). Concerning isolated eigenvalues $\varepsilon_{R1}(\beta)$ and $\varepsilon_{R2}(\beta)$, those eigenvalues can be also not obtained within the standard perturbation expansion formalism. Though functions $\varepsilon_{R1}(\beta)$ and $\varepsilon_{R2}(\beta)$ are continuous for each $\beta > 0$, due to (3.57a) those solutions of the generic eigenvalue equation are not analytic in the points $\beta = \beta_{R1}$ and $\beta = \beta_{R2}$, respectively. Hence no power series expansion of $\varepsilon_{R1}(\beta)$ in the point $\beta = 0$ can extend to those values of β that satisfy $\beta > \beta_{R1}$ where combined system has right isolated eigenvalue $\varepsilon_{R1}(\beta)$. The same applies to right isolated eigenvalue $\varepsilon_{R2}(\beta)$.

Once eigenvalues $\varepsilon_{R1}(\beta)$, $\varepsilon_{R2}(\beta)$, $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$ are known, one can derive all the corresponding isolated eigenstates. Those eigenstates can be also obtained in the closed analytic form [5]. They determine all related properties of the combined system. In particular, probabilities $w_{I,r}$ to find isolated eigenstate $\left|\Psi_I\right\rangle$ in local states $\left|\Theta_r\right\rangle$ as well as probability $w_I = w_{I,1} + w_{I,2}$ to find this eigenstate in the base system $\mathbf{B}_2$ are given by expressions (3.29). For example, isolated eigenstate $\left|\Psi_{R1}(\beta)\right\rangle$ that has eigenvalue $\varepsilon_{R1}(\beta)$ exists only if $\beta > \beta_{R1} = 1.12883$. Hence probabilities $w_{R1,1}(\beta)$ and $w_{R1,2}(\beta)$ to find this eigenstate in the local states $\left|\Theta_1\right\rangle$ and $\left|\Theta_2\right\rangle$, respectively, equal zero if $\beta < \beta_{R1}$. The same of course applies for total probability $w_{R1}(\beta) = w_{R1,1}(\beta) + w_{R1,2}(\beta)$ to find this eigenstate in the system $\mathbf{B}_2$. At the point $\beta = \beta_{R1}$ those probabilities discontinuously jump from zero to $w_{R1}(\beta_{R1}+) = 0.44324$, $w_{R1,1}(\beta_{R1}+) = 0.43952$ and $w_{R1,2}(\beta_{R1}+) = 0.00372$, respectively [5]. Similarly one derives all other probabilities associated with isolated solutions of the combined system.

It remains to determine whether the combined system contains any anomal point where this system could have an isolated eigenstate in addition to isolated eigenstates contained outside the range $D \equiv I_1$. Each anomal point $\varepsilon = \varepsilon_a$ is an interior point of a range D, and in this point one must have a nontrivial state $\left|\theta_I\right\rangle$ that satisfies $\mathbf{f}_b(\varepsilon_a)\left|\theta_I\right\rangle = 0$ in addition to $\mathbf{h}_b(\varepsilon_a)\left|\theta_I\right\rangle = 0$. First condition implies that in this point rank of a characteristic matrix $\mathbf{f}_b(\varepsilon)$ must be smaller than the dimension ρ of the space X_ρ^b. In the example considered expression (3.56) implies that only a point $\varepsilon = \varepsilon_c = 0.38197$ has such a property. Second condition implies that an anomal point must be a resonant point. The only candidate for the anomal point is hence the point (β_c, ε_c) on the intersection of the line $\varepsilon = \varepsilon_c$ and the function $\varepsilon = \varepsilon_{R1}(\beta)$ (see figure 3.5). One finds $\beta_c = 0.32611$ [5]. One also finds that the state $|\theta_I\rangle$ which satisfies $\mathbf{h}_b(\varepsilon_c)|\theta_I\rangle = 0$ does not satisfy $\mathbf{f}_b(\varepsilon_c)|\theta_I\rangle$. The point $\varepsilon = \varepsilon_c$ is hence not an anomal point. In conclusion, the system $\mathbf{C}_\infty$ contains no anomal point and hence no isolated eigenstate inside the range D.

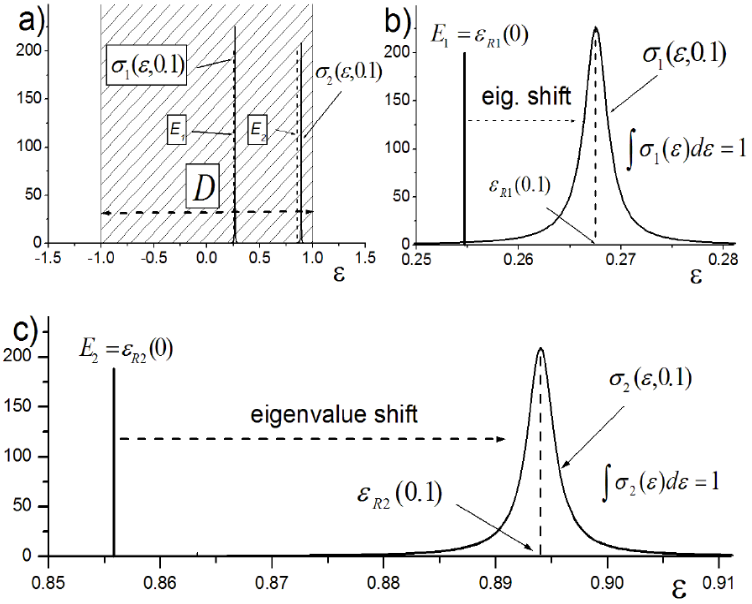

Figure 3.6. Eigenvalue distributions of local states $|\Theta_1\rangle$ and $|\Theta_2\rangle$ in the case $\beta = 0.1$ (line (a) in figure 3.5). a) Probability densities $\sigma_1(\varepsilon,0.1)$ and $\sigma_2(\varepsilon,0.1)$ are sharply localized inside the range D at positions $\varepsilon_{R1}(0.1)$ and $\varepsilon_{R2}(0.1)$, respectively. (b) Probability density $\sigma_1(\varepsilon,0.1)$ highly magnified. This probability density is almost identical to the universal resonance curve $\rho_1^0(\varepsilon,0.1)$ centered at the position $\varepsilon_{R1}(0.1)$. (c) Probability density $\sigma_2(\varepsilon,0.1)$ highly magnified. This probability density is almost identical to the universal resonance curve $\rho_2^0(\varepsilon,0.1)$ centered at the position $\varepsilon_{R2}(0.1)$. Adopted from ref. [5].

Consider now embedded cardinal solutions of the combined system. Fractional shift eigenvalue equation (3.30a) produces all such solutions. In a 2×2 case the solution of this equation can be obtained in the closed analytic form [5]. In particular, eigenvalues $X = X_{1,2}(\varepsilon)$ of a fractional shift eigenvalue equation are roots of the 2×2 determinant (3.30d). Those eigenvalues can be hence explicitly written as roots of a quadratic equation [5]. This determines eigenvalues $X_d(\varepsilon)$ of a fractional shift equation for each $\varepsilon \in D$. Once this eigenvalue is known, the corresponding X_ρ^b-component $\left|\Psi_d^b(\varepsilon)\right\rangle$ of the embedded eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ is given by the expressions (3.31) where $\left|\theta_d(\varepsilon)\right\rangle$ can be obtained in a closed form as a solution to (3.30a). This determines all related properties of the open system $\mathbf{B}_\rho$.

As an example, in figure 3.6 are shown eigenvalue distributions of local states $\left|\Theta_1\right\rangle$ and $\left|\Theta_2\right\rangle$ calculated in this way for the case $\beta = 0.1$. Those distributions correspond to the line (a) in figure 3.5. For this value of β combined system has no isolated eigenstate and those distributions are hence completely determined by probability densities $\sigma_r(\varepsilon,0.1) = \rho_{1,r}(\varepsilon,0.1) + \rho_{2,r}(\varepsilon,0.1)$ to find local state $\left|\Theta_r\right\rangle$ with the eigenvalue $\varepsilon \in D$ (see expressions (3.34) and (3.35)). Since coupling parameter $\beta = 0.1$ is relatively small, interaction of the system $\mathbf{B}_2$ with its surrounding is relatively weak. Initial unperturbed eigenvalues $E_r \in D$ of $\mathbf{B}_2$ are hence only slightly shifted to the new positions $\varepsilon_r(0.1)$ (see figure 3.6(a)). Since in both cases $\varepsilon_r(0.1) \in D$, those shifted eigenvalues are not sharp and they acquire the shape of the universal resonance curves $\rho_r^0(\varepsilon,0.1)$ as given by expression (3.39b). The widths of those two resonant curves calculated according to (3.40a) are[1] $\Delta\varepsilon_1(0.1) = 0.00274$ and $\Delta\varepsilon_2(0.1) = 0.00286$, respectively [5]. Those widths are quite small and densities $\sigma_r(\varepsilon,0.1)$ are hence well approximated with the corresponding universal resonance curves $\rho_r^0(\varepsilon,0.1)$. In particular, density $\sigma_1(\varepsilon,0.1)$ has a

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[1] In ref. [5] half-width instead of width is given.

prominent resonant shape centered at the point $\varepsilon = \varepsilon_{R1}(0.1) = 0.26749$, while density $\sigma_2(\varepsilon,0.1)$ has a prominent resonant shape centered at the point $\varepsilon = \varepsilon_{R2}(0.1) = 0.89403$. In figure 3.6(b) is shown density $\sigma_1(\varepsilon,0.1)$ magnified. This density is almost identical to the universal resonance curve $\rho_1^0(\varepsilon,0.1)$ [5]. On this scale there is virtually no difference between exact density $\sigma_1(\varepsilon,0.1)$ and approximate density $\rho_1^0(\varepsilon,0.1)$. In figure 3.6(c) is in the same way shown density $\sigma_2(\varepsilon,0.1)$ which is also almost identical to the corresponding approximate density $\rho_2^0(\varepsilon,0.1)$. Further, one finds $S_1(0.1) = \int \sigma_1(\varepsilon,0.1)d\varepsilon = 1$ and $S_2(0.1) = \int \sigma_2(\varepsilon,0.1)d\varepsilon = 1$. Probability to find the state $\left|\Theta_1\right\rangle$ with the eigenvalue ε inside the resonance shape $\sigma_1(\varepsilon,0.1)$ equals one, and probability to find the state $\left|\Theta_2\right\rangle$ with the eigenvalue ε inside the resonance shape $\sigma_2(\varepsilon,0.1)$ also equals one. The state $\left|\Theta_1\right\rangle$ subject to the interaction with the infinite system $\boldsymbol{A}_\infty$ is hence completely associated with the resonant shape $\sigma_1(\varepsilon,0.1)$, while the state $\left|\Theta_2\right\rangle$ subject to the interaction with this infinite system is completely associated with the resonance shape $\sigma_2(\varepsilon,0.1)$. Concerning component probabilities $C_{d,r}(0.1) = \int \rho_{d,r}(\varepsilon,0.1)d\varepsilon$, one has $C_{1,1}(0.1) = 0.94312$ and $C_{2,1}(0.1) = 0.05688$. Density $\sigma_1(\varepsilon,0.1)$ is hence mainly associated with the embedded cardinal eigenstate $\left|\Psi_1(\varepsilon)\right\rangle$ of the combined system. Similarly one finds $C_{1,2}(0.1) = 0.02387$ and $C_{2,2}(0.1) = 0.97613$. Density $\sigma_2(\varepsilon,0.1)$ is hence mainly associated with the embedded cardinal eigenstate $\left|\Psi_2(\varepsilon)\right\rangle$ of this system.

As another example, in figure 3.7 is shown a spectral distribution of a local state $\left|\Theta_1\right\rangle$ for the value $\beta = 0.4$. This value corresponds to the line (b) in figure 3.5. This is relatively strong coupling and probability density $\sigma_1(\varepsilon,0.4)$ does not resemble universal resonance curve centered at corresponding resonance point. For this value of β standard perturbation expansion fails. Fractional shift eigenvalue equation produces $S_1(0.4)=\int\sigma_1(\varepsilon,0.4)d\varepsilon=0.99897$ [5]. Unlike in the case $\beta=0.1$, this probability is less than one. In the case $\beta=0.4$ in addition to embedded eigenstates combined system contains an isolated eigenstate $\left|\Psi_{R2}\right\rangle$ with the eigenvalue $\varepsilon_{R2}(0.4)=1.24735$ (see figure 3.5). Missing probability is due to this eigenstate. Using expression (3.29a) one finds $w_{R2,1}(0.4)=0.00103$. As required by the completeness relation (3.45a), those probabilities satisfy $S_1(0.4)+w_{R2,1}(0.4)=1$. In a similar way can be analyzed spectral distribution of another isolated eigenstate $\left|\Theta_2\right\rangle$ in the case $\beta=0.4$ [5].

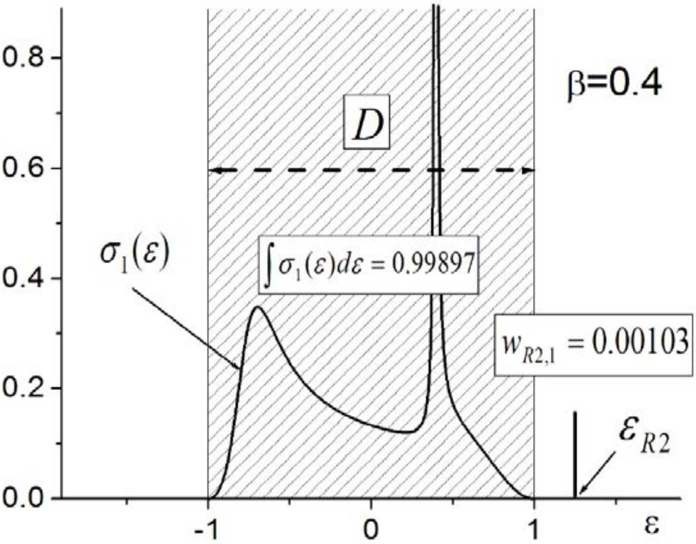

Figure 3.7. Eigenvalue distribution of local state $\left|\Theta_1\right\rangle$ in the case $\beta=0.4$ (line (b) in figure 3.5. In addition to embedded eigenstates, combined system contains an isolated eigenstate $\left|\Psi_{R2}(0.4)\right\rangle$ with the eigenvalue $\varepsilon_{R2}(0.4)=1.24735$. Interaction is strong and this eigenvalue distribution has no resemblance to the universal resonance curve. Adopted from ref. [5].

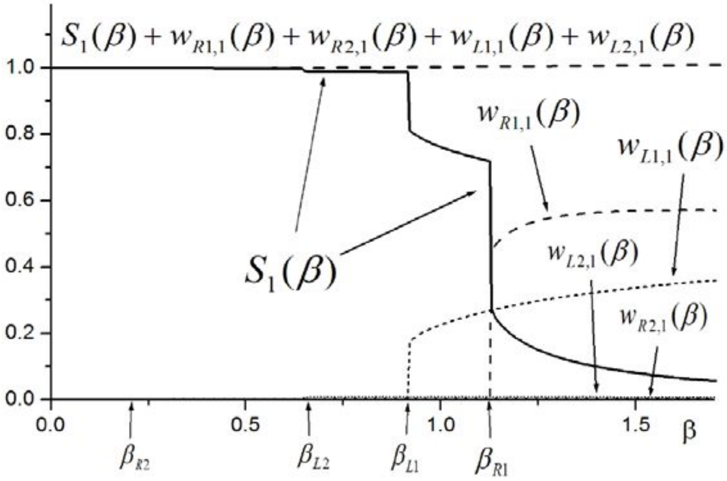

Figure 3.8. Verification of the completeness relation for the eigenvalue distribution of a local state $\left|\Theta_1\right\rangle$. Adopted from ref. [5].

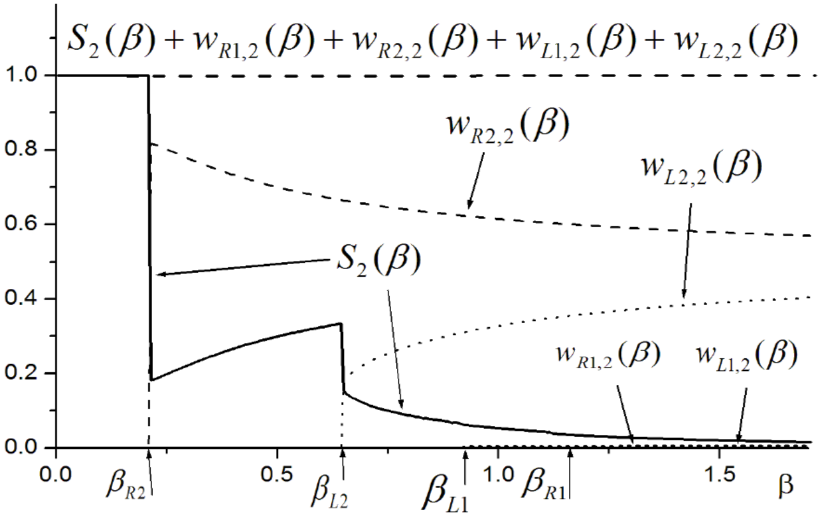

Figure 3.9. Verification of the completeness relation for the eigenvalue distribution of a local state $\left|\Theta_2\right\rangle$. Adopted from ref. [5].

Completeness relations are verified in a systematic way in figures 3.8 and 3.9, respectively. In figure 3.8 probability $S_1(\beta)$ to find local state $\left|\Theta_1\right\rangle$ in any of the embedded eigenstates of the combined system as well as probabilities $w_{R1,1}(\beta)$, $w_{R2,1}(\beta)$, $w_{L1,1}(\beta)$ and $w_{L2,1}(\beta)$ to find this state in the corresponding isolated eigenstates of the combined system are plotted as functions of a coupling parameter β. A sum of all those probabilities is also shown. As required by the completeness relation, this sum equals one for each value of β. In figure 3.9 are in the same way plotted probabilities $S_2(\beta)$, $w_{R1,2}(\beta)$, $w_{R2,2}(\beta)$, $w_{L1,2}(\beta)$ and $w_{L2,2}(\beta)$ that correspond to the local state $\left|\Theta_2\right\rangle$. The sum of those probabilities also equals one for each value of β. Complete agreement of those probabilities with the requirements of the completeness relations (3.45) provides a strong verification of the suggested method. It also shows that in the example considered combined system $\mathbf{B}_\infty$ has no weakly singular eigenstates.

3.9.2. Example 3.2: Interaction of a Base System with an Infinite System that Contains Two Eigenvalue Bands and One Isolated Eigenstate

As another example consider the system $\mathbf{B}_2$ characterized by matrices

$$\mathbf{H}_b = \begin{pmatrix} 0.5 & -0.25 \\ -0.25 & 1.6 \end{pmatrix}, \quad \mathbf{S}_b = \begin{pmatrix} 1.1 & 0.1 \\ 0.1 & 1 \end{pmatrix}, \tag{3.58a}$$

Those matrices are identical to matrices (3.54a) of the previous example, except for a single matrix element of the matrix $\mathbf{H}_b$. Eigenvalues and corresponding eigenstates of the system $\mathbf{B}_2$ are now

$$E_1 = 0.39164, \qquad E_2 = 1.72763, \tag{3.58b}$$

$$\left|\Theta_1\right\rangle = \begin{pmatrix} 0.91093 \\ 0.21799 \end{pmatrix}, \left|\Theta_2\right\rangle = \begin{pmatrix} 0.29604 \\ -0.98064 \end{pmatrix}. \tag{3.58c}$$

where $\left|\Theta_r\right\rangle$ are orthonormalized according to (2.5b).

Let the infinite system $\boldsymbol{A}_\infty$ that interacts with the system $\mathbf{B}_2$ contain two eigenvalue bands in the intervals $I_1 \equiv [a_1, b_1] = [-1,1]$ and $I_2 \equiv [a_2, b_2] = [2,3]$, respectively. Let further this system contain an isolated eigenstate $\left|\Phi_0\right\rangle$ with the eigenvalue $\lambda_0 = 1.2$. Assume that the characteristic operator $\mathbf{f}_1(\varepsilon)$ which describes the interaction of the system $\mathbf{B}_2$ with the first eigenvalue band is given by matrix elements (3.55), while the characteristic operator $\mathbf{f}_2(\varepsilon)$ which describes the interaction of this system with the second eigenvalue band is given by matrix elements

$$\mathbf{f}_2(\varepsilon) = \begin{pmatrix} f_{11}^{(2)}(\varepsilon) & f_{12}^{(2)}(\varepsilon) \\ f_{21}^{(2)}(\varepsilon) & f_{22}^{(2)}(\varepsilon) \end{pmatrix} \equiv \begin{pmatrix} q_{11}^{(2)}(\varepsilon) & q_{12}^{(2)}(\varepsilon) \\ q_{21}^{(2)}(\varepsilon) & q_{22}^{(2)}(\varepsilon) \end{pmatrix} \cdot \begin{cases} 1 & if \quad \varepsilon \in I_2 \\ 0 & otherwis \end{cases} \tag{3.59a}$$

where

$$\begin{aligned} q_{11}^{(2)}(\varepsilon) &= (\varepsilon - 2)^2 \left(2\varepsilon^2 - 14\varepsilon + 25\right), \\ q_{22}^{(2)}(\varepsilon) &= (\varepsilon - 2)^2 \left(\varepsilon^2 - 8\varepsilon + 17\right), \\ q_{12}^{(2)}(\varepsilon) &\equiv q_{21}^{(2)}(\varepsilon) = (\varepsilon - 2)^3 (\varepsilon - 4). \end{aligned} \tag{3.59b}$$

Let further the characteristic operator $\mathbf{F}_b(x)$ which describes the interaction of the system $\mathbf{B}_2$ with the eigenstate $\left|\Phi_0\right\rangle$ be given by

$$\mathbf{F}_b(\varepsilon) = \begin{pmatrix} 0.5 & -0.3 \\ -0.3 & 0.2 \end{pmatrix} \cdot \delta(\varepsilon - \lambda_0). \tag{3.60}$$

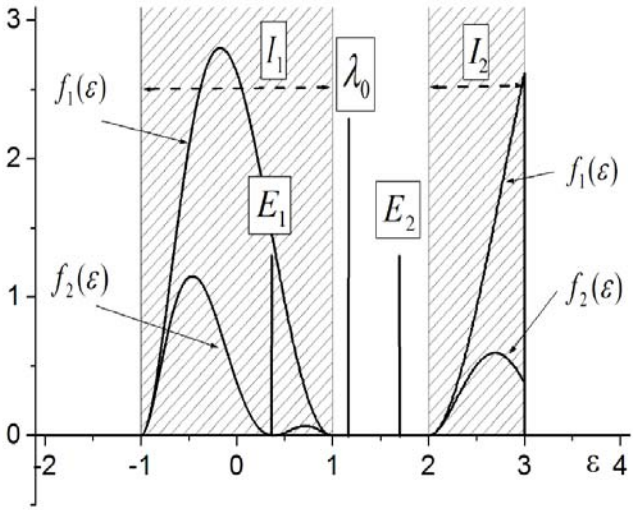

Figure 3.10. Example 3.2. Eigenvalues of the characteristic operator $\mathbf{f}_b(\varepsilon)$. Eigenvalue E_1 of the base system $\mathbf{B}_\rho$ is inside the range D, while another eigenvalue E_2 of this system is outside this range. Adopted from ref. [5].

In figure 3.10 are shown eigenvalues $f_1(\varepsilon)$ and $f_2(\varepsilon)$ of the global characteristic operator $\mathbf{f}_b(\varepsilon) = \mathbf{f}_1(\varepsilon) + \mathbf{f}_2(\varepsilon) + \mathbf{F}_b(\varepsilon)$. As required, those eigenvalues are nonnegative and they vanish outside the range D and outside the point $\varepsilon = \lambda_0$. Interaction of the base system $\mathbf{B}_2$ with the system $\boldsymbol{A}_\infty$ described by this characteristic operator is much more complex than in the previous example. There are several new features. First, the system $\boldsymbol{A}_\infty$ has two non-overlapping eigenvalue bands in the intervals I_1 and I_2, respectively. Second, characteristic operator $\mathbf{f}_b(\varepsilon)$ is not continuous in the point $\varepsilon = b_2 = 3$ on the right edge of the interval I_2. Third, local eigenvalue $E_2 \notin D$ is outside the range $D = I_1 \cup I_2$, while in the previous example both eigenvalues of the base system $\mathbf{B}_2$ were contained inside the range D. Finally, the system $\boldsymbol{A}_\infty$ contains an isolated eigenvalue at the point $\varepsilon = \lambda_0 = 1.2 \notin D$ and in this point characteristic operator $\mathbf{f}_b(\varepsilon)$ diverges.

Rank of this operator equals two for each interior point $\varepsilon \in D$, except for the critical point $\varepsilon_c = 0.38197 \in D$ where $rank(\mathbf{f}_b(\varepsilon_c)) = 1$. This is the same critical point as in the example 3.1**.** In addition, this rank equals two in the point $\varepsilon = \lambda_0$.

Consider now global derived operator $\boldsymbol{\omega}_b(\varepsilon) = \boldsymbol{\omega}_1(\varepsilon) + \boldsymbol{\omega}_2(\varepsilon) + \boldsymbol{\Omega}_b(\varepsilon)$. Matrix elements of the derived operator $\boldsymbol{\omega}_1(\varepsilon)$ associated with the eigenvalue band $\tau = 1$ are given by expressions (3.57). Concerning characteristic operator $\mathbf{f}_2(\varepsilon)$, expressions (3.19) imply:

$$\omega_{11}^{(2)}(\varepsilon) = q_{11}^{(2)}(\varepsilon)\ln\left|\frac{\varepsilon-2}{\varepsilon-3}\right| - g_{11}^{(2)}(\varepsilon),$$

$$\omega_{22}^{(2)}(\varepsilon) = q_{22}^{(2)}(\varepsilon)\ln\left|\frac{\varepsilon-2}{\varepsilon-3}\right| - g_{22}^{(2)}(\varepsilon), \qquad (3.61a)$$

$$\omega_{12}^{(2)}(\varepsilon) \equiv \omega_{21}^{(2)} = q_{12}^{(2)}(\varepsilon)\ln\left|\frac{\varepsilon-2}{\varepsilon-3}\right| - g_{12}^{(2)}(\varepsilon),$$

where $q_{sp}^{(2)}(\varepsilon)$ are polynomials (3.59b), while $g_{sp}^{(2)}(\varepsilon)$ are polynomials:

$$g_{11}^{(2)}(\varepsilon) = 2\varepsilon^3 - 17\varepsilon^2 + \frac{140}{3}\varepsilon - \frac{121}{3},$$

$$g_{22}^{(2)}(\varepsilon) = \varepsilon^3 - \frac{19}{2}\varepsilon^2 + \frac{88}{3}\varepsilon - \frac{109}{4}, \qquad (3.61b)$$

$$g_{12}^{(2)}(\varepsilon) \equiv g_{21}^{(2)}(\varepsilon) = \varepsilon^3 - \frac{15}{2}\varepsilon^2 + \frac{52}{3}\varepsilon - \frac{157}{12}.$$

Since $\mathbf{f}_2(\varepsilon)$ is nonzero in the point $\varepsilon = b_2 = 3$ on the right edge of the interval I_2, those matrix elements diverges in this point [5]. Finally, using (3.17c) and (3.60) one finds derived operator $\boldsymbol{\Omega}_b(\varepsilon)$

$$\mathbf{\Omega}_b(\varepsilon) = \begin{pmatrix} 0.5 & -0.3 \\ -0.3 & 0.2 \end{pmatrix} \cdot \frac{1}{\varepsilon - \lambda_0} \begin{cases} if \ \varepsilon \neq \lambda_0 \\ 0 \ if \ \varepsilon = \lambda_0 \end{cases} \tag{3.62}$$

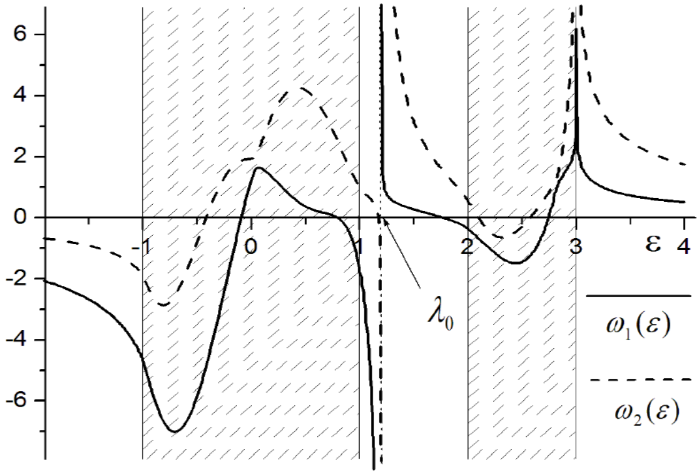

Figure 3.11. Example 3.2. Eigenvalues of the derived operator $\boldsymbol{\omega}_b(\varepsilon)$. Adopted from ref. [5].

In figure 3.11 are shown eigenvalues $\omega_1(\varepsilon)$ and $\omega_2(\varepsilon)$ of the global derived operator $\boldsymbol{\omega}_b(\varepsilon) = \boldsymbol{\omega}_1(\varepsilon) + \boldsymbol{\omega}_2(\varepsilon) + \mathbf{\Omega}_b(\varepsilon)$. In accord with the requirement (3.18b), those eigenvalues are decreasing functions of ε for each $\varepsilon \notin D = I_1 \bigcup I_2$ and $\varepsilon \neq \lambda_0$. However, in the interval I_1 as well as in the interval I_2 those eigenvalues are decreasing as well as increasing functions of ε. In the point $\varepsilon = \lambda_0$ those eigenvalues are not continuous, but they have a finite value in this point [5]. However, the $\varepsilon \to \lambda_0$ limits of those eigenvalues diverge. In addition, since characteristic operator $\mathbf{f}_b(\varepsilon)$ is discontinuous in the point $\varepsilon = b_2 = 3$, both eigenvalues of $\boldsymbol{\omega}_b(\varepsilon)$ also diverge in the point $\varepsilon = 3$.

Consider now generic eigenvalue equation (3.25a). Solutions of the equation (3.25b) of a type $\varepsilon = \varepsilon(\beta)$ are shown in figure 3.12. There are 12 such solutions: $\varepsilon_{R1}(\beta)$, $\varepsilon_{R2}(\beta)$, $\varepsilon_1(\beta)$, $\varepsilon_2(\beta)$, $\varepsilon_{L1}(\beta)$, $\varepsilon_{L2}(\beta)$, $\lambda_1(\beta)$,

$\lambda_2(\beta)$, $E_1(\beta)$, $E_2(\beta)$, $d_1(\beta)$ and $d_2(\beta)$. If $\beta = 0$ eigenvalues of the generic equation coincide with local eigenvalues. In particular, one has $E_1(0) = E_1$ and $E_2(0) = E_2$. In addition, generic equation has two eigenvalues that in a $\beta \to 0$ limit coincide with isolated eigenvalue λ_0 of the parent system $\boldsymbol{A}_\infty$. Those are eigenvalues $\lambda_1(\beta)$ and $\lambda_2(\beta)$:

$$\lim_{\beta\to 0} \lambda_1(\beta) = \lim_{\beta\to 0} \lambda_2(\beta) = \lambda_0 \tag{3.63}$$

Consider eigenvalues $E_1(\beta)$ and $E_2(\beta)$ in more details. Since $E_1(0) \in D$, for small β eigenvalue $E_1(\beta)$ is contained in the range D. It is hence a resonant point. One finds that this is true for each β, however large [5]. On the other hand, since $E_2(0) \notin D$ for small β one has $E_2(\beta) \notin D$. This eigenvalue is hence an isolated eigenvalue of the combined system. However, if the coupling β is as strong as $\beta > \beta_{E2}$ one has $E_2(\beta) \in D$ and this eigenvalue becomes a resonant point. One finds $\beta_{E2} = 0.92203$ [5].

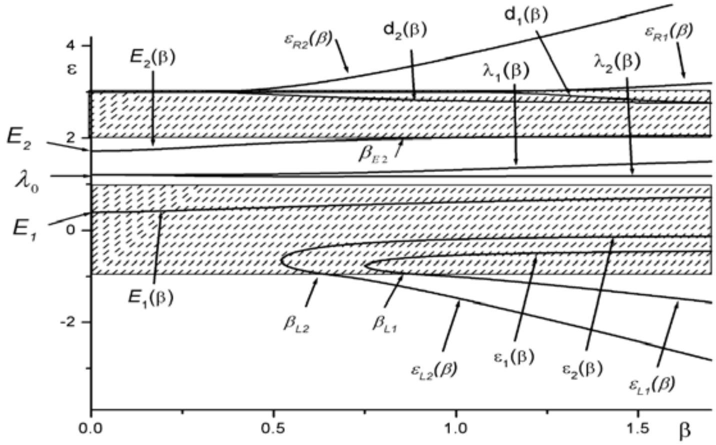

Figure 3.12. Example 3.2. Eigenvalues $\varepsilon_I(\beta)$ of the generic eigenvalue equation considered as functions of a coupling parameter β. Adopted from ref. [5].

Consider now eigenvalues $\varepsilon_{L1}(\beta)$, $\varepsilon_{L2}(\beta)$, $\varepsilon_1(\beta)$ and $\varepsilon_2(\beta)$. Eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_1(\beta)$ are two branches of one and the same function $\beta = \beta_1(\varepsilon)$, while $\varepsilon_{L2}(\beta)$ and $\varepsilon_2(\beta)$ are two branches of another function $\beta = \beta_2(\varepsilon)$. For each β (where defined) eigenvalues $\varepsilon_1(\beta)$ and $\varepsilon_2(\varepsilon)$ are inside the range D and hence these eigenvalues are resonant points. Concerning eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$, for small β those eigenvalues are (where defined) resonant points. However, if the coupling is as strong as $\beta > \beta_{L2}$ eigenvalue $\varepsilon_{L2}(\beta)$ becomes an isolated eigenvalue of the combined system, while if $\beta > \beta_{L1}$ eigenvalue $\varepsilon_{L1}(\beta)$ becomes another isolated eigenvalue of the combined system. As $\beta > \beta_{L1}$ further increases, isolated eigenvalues $\varepsilon_{L1}(\beta)$ and $\varepsilon_{L2}(\beta)$ continue to decrease. Hence for each $\beta > \beta_{L1}$ combined system has two left isolated eigenvalues. In the points β_{L1} and β_{L2} one has $\varepsilon = a_1 = -1$. One finds $\beta_{L2} = 0.69110$ and $\beta_{L1} = 0.98637$.

Concerning eigenvalues $\varepsilon_{R1}(\beta)$, $\varepsilon_{R2}(\beta)$, $d_1(\beta)$ and $d_2(\beta)$, for each $\beta > 0$ eigenvalue $\varepsilon_{R1}(\beta)$ and $\varepsilon_{R2}(\beta)$ are isolated eigenvalues of the combined system, while eigenvalues $d_1(\beta)$ and $d_2(\beta)$ are resonant points of this system. In the limit $\beta \to 0$ those four eigenvalues converge to the point $\varepsilon = 3$ where characteristic operator $\mathbf{f}_b(\varepsilon)$ is discontinuous and where derived operator $\boldsymbol{\omega}_b(\varepsilon)$ diverges. Due to this property, as $\beta > 0$ decreases those eigenvalues approach the value $\varepsilon = b_2 = 3$ asymptotically [5]. For example, if $\beta \approx 0.94$ one has $\varepsilon_{R1}(\beta) \approx 3.001$ and $d_1(\beta) \approx 2.999$, while if β decreases to $\beta = 0.70167$ one finds $\varepsilon_{R1}(\beta) \approx 3.000001$ and $d_1(\beta) \approx 2.999999$. Similarly, if $\beta \approx 0.278$ one has $\varepsilon_{R2}(\beta) \approx 3.001$ and $d_2(\beta) \approx 2.999$, while if β decreases to $\beta = 0.19069$ one finds $\varepsilon_{R2}(\beta) \approx 3.000001$ and $d_2(\beta) \approx 2.999999$. This is extremely close to the value $\varepsilon = 3$. As $\beta > 0$ further decreases it approaches this value even more. This asymptotic behavior is due to the fact that matrix elements of the characteristic operator $\mathbf{f}_b(\varepsilon)$ are discontinuous in the point $\varepsilon = b_2 = 3$ [5].

Consider finally eigenvalues $\lambda_1(\beta)$ and $\lambda_2(\beta)$. According to (3.63), in a limit $\beta \to 0$ those eigenvalues converge to the isolated eigenvalue $\lambda_0 = 1.2$ of the infinite-dimensional parent system $\boldsymbol{A}_\infty$. Since $\lambda_0 \notin D$, for sufficiently small β those eigenvalues are isolated eigenvalues of the combined system. One finds that this is true for each β, however large [5].

In conclusion, for sufficiently big β combined system has 6 isolated eigenvalues, $\varepsilon_{R1}(\beta)$, $\varepsilon_{R2}(\beta)$, $\varepsilon_{L1}(\beta), \varepsilon_{L2}(\beta)$, $\lambda_1(\beta)$ and $\lambda_2(\beta)$. In addition, for each $\beta < \beta_{E2}$ it has an isolated eigenvalue $E_2(\beta)$.

Once above eigenvalues are obtained as roots of (3.25b), one can derive corresponding isolated eigenstates $\left|\Psi_I\right\rangle$ using expressions (3.25a) and (3.26). In particular, those expressions determine X_2^b-components $\left|\Psi_I^b\right\rangle \in X_2^b$ of those eigenstates. In analogy to the previous example, components $\left|\Psi_I^b\right\rangle$ determine all related properties of the open system $\mathbf{B}_2$. In particular, probabilities $w_{L1,r}(\beta) = \left|\left\langle\Theta_r\left|\mathbf{S}\right|\Psi_{L1}\right\rangle\right|^2$ associated with the eigenvalue $\varepsilon_{L1}(\beta)$ are zero if $\beta < \beta_{L1} = 0.98637$. In a point $\beta = \beta_{L1}$ those probabilities discontinuously jump from zero to a finite nonzero values [5]. The same applies to the probabilities $w_{L2,r}(\beta) = \left|\left\langle\Theta_r\left|\mathbf{S}\right|\Psi_{L2}\right\rangle\right|^2$ associated with the eigenvalue $\varepsilon_{L2}(\beta)$. Those probabilities are zero as long as $\beta < \beta_{L2} = 0.69110$, while at this point those probabilities discontinuously jump from zero to finite nonzero values [5]. However, probabilities $w_{R1,r} \equiv \left|\left\langle\Theta_r\left|\mathbf{S}\right|\Psi_{R1}\right\rangle\right|^2$ and $w_{R2,r} = \left|\left\langle\Theta_r\left|\mathbf{S}\right|\Psi_{R2}\right\rangle\right|^2$ associated with discrete eigenvalues $\varepsilon_{R1}(\beta)$ and $\varepsilon_{R2}(\beta)$ have different behavior. For each $\beta \neq 0$ those probabilities are different from zero. However, if $\beta \neq 0$ is small enough, those probabilities are so extremely small that they are zero for all practical purposes. In the case of the probabilities $w_{R1,r}$ and $w_{R2,r}$ there is no discontinuous jump from zero to a finite nonzero value. This behavior is due to the fact that the characteristic operator $\mathbf{f}_b(\varepsilon)$ is discontinuous in the point $\varepsilon = 3$ [5].

Consider now embedded cardinal solutions of the combined system. As emphasized in the previous example, in a 2×2 case the solution of the fractional shift eigenvalue equation (3.30a) can be obtained in the closed form. In particular, eigenvalues $X = X_{1,2}(\varepsilon)$ of this equation are roots of the 2×2 determinant (3.30d) and one obtains those eigenvalues in an explicit form as roots of a quadratic equation [5]. The same applies to the corresponding embedded eigenstates. One can thus obtain all related properties of the open system $\mathbf{B}_2$ in a closed analytic form [5].

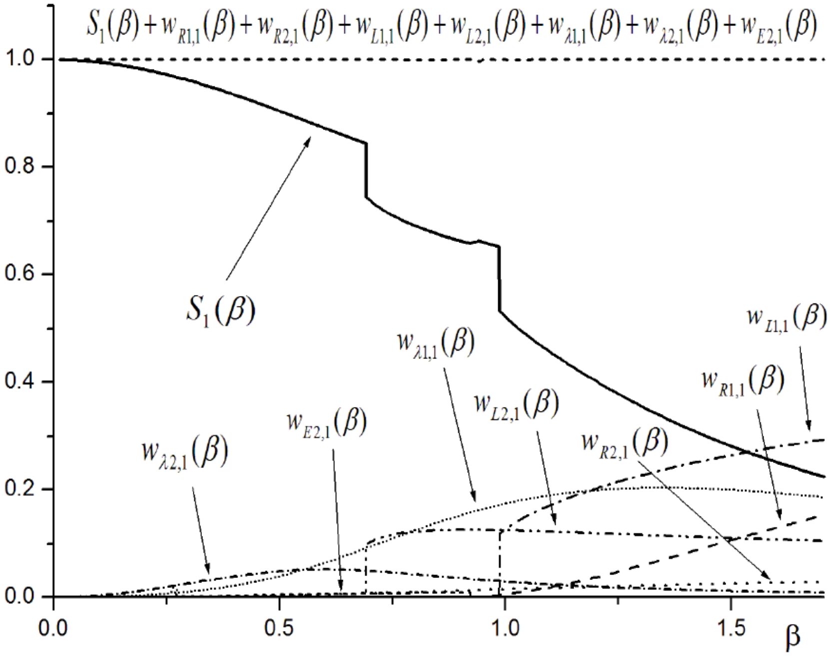

Figure 3.13. Example 3.2. Verification of the completeness relation for the eigenvalue distribution of a local state $|\Theta_1\rangle$. Adopted from ref. [5].

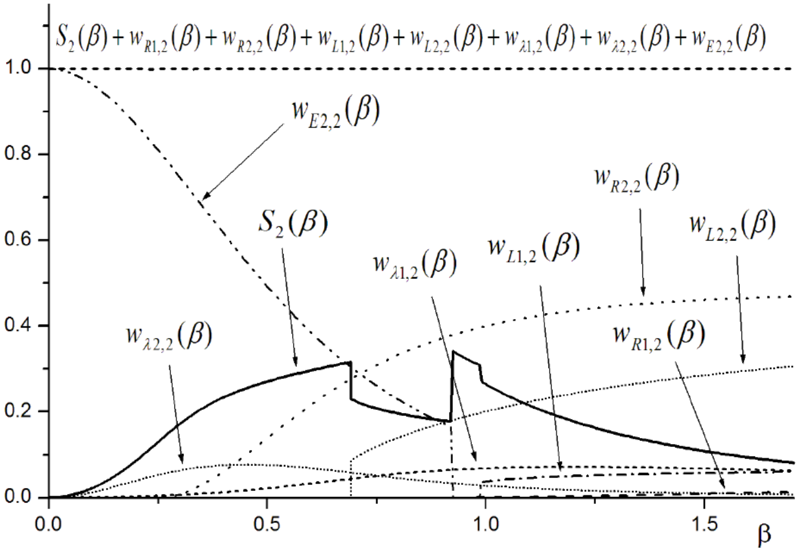

Figure 3.14. Example 3.2. Verification of the completeness relation for the eigenvalue distribution of a local state $\left|\Theta_2\right\rangle$. Adopted from ref. [5].

In order not to be lost with detailed analyze of this example, let me consider only the final result. A powerful test for the LRM approach is given by completeness relations (3.45). Those relations are verified in a systematic way in figures 3.13 and 3.14. In figure 3.13 probabilities $S_1(\beta)$, $w_{R1,1}(\beta)$, $w_{R2,1}(\beta)$, $w_{L1,1}(\beta)$, $w_{L2,1}(\beta)$, $w_{\lambda1,1}(\beta)$, $w_{\lambda2,1}(\beta)$ and $w_{E2,1}(\beta)$ associated with a local state $\left|\Theta_1\right\rangle$ are plotted as functions of a coupling parameter β. A sum of all those probabilities is also shown. As required by the completeness relation, this sum equals one for each value of β. In figure 3.14 are in the same way analyzed probabilities associated with the local state $\left|\Theta_2\right\rangle$. The complete agreement of LRM probabilities and probability densities with completeness relations (3.45) provides a strong support in favor of the LRM expressions. It also shows that in the example considered combined system has no weakly singular solution.

3.9.3. Example 2.3: Interaction of a Single State with One-Dimensional Solid in the Nearest-Neighbor Tight-Binding Approximation

Above two examples are rather artificial. Those examples are intended to illustrate various mathematical aspects of the LRM approach and to emphasize inner consistency of this approach. As a final example consider a very simple model of a molecule situated on the surface of a solid that interacts with this solid. Infinite system $\mathbf{A}_\infty$ is one-dimensional solid in the nearest-neighbor tight-binding approximation [4,16]. With each site of this solid is associated a single state $|j\rangle$ ($j = 1, 2, \cdots$). In this approximation all matrix elements $\langle i|\mathbf{H}_a|i\rangle$ between states on the same atomic site equal α, while matrix elements $\langle i|\mathbf{H}_a|j\rangle$ between states on the adjacent atomic sites equal γ. All remaining matrix elements are zero. This model is widely used in chemistry where it is known as a Hückel approximation [4]. Without loss of generality one can assume $\alpha = 0$ and $\gamma = 1$. The only effect of this assumption is the redefinition of zero eigenvalue and of eigenvalue rescaling. Eigenvalues λ_i and eigenstates $|\Phi_i\rangle$ of such one-dimensional solid containing n atoms are [4]:

$$\lambda_i = 2\cos\left(\frac{\pi}{n+1} i\right), \qquad |\Phi_i\rangle = \sqrt{\frac{2}{n+1}}\sum_{j=1}^{n} \sin\left(\frac{\pi}{n+1} ij\right)|j\rangle,$$
$$i = 1, \cdots, n. \tag{3.64}$$

One can refer to such a solid as a Hückel chain. System $\mathbf{A}_\infty$ is an infinite Hückel chain, which is obtained in the limit $n \to \infty$. In this limit eigenvalues λ_i are replaced with a continuous function $\lambda(k) = 2\cos(k)$ of a parameter k ($0 < k < \pi$), and discrete eigenstates $|\Phi_i\rangle$ are replaced with continuous eigenstates $|\Phi(k)\rangle$:

$$\lambda(k) = 2\cos(k), \quad \left|\Phi(k)\right\rangle = \sqrt{\frac{2}{\pi}}\sum_{j=1}^{\infty}\sin(jk)\left|j\right\rangle,$$
$$0 < k < \pi . \tag{3.65}$$

Relations (3.65) give all necessary information for the parent system $\mathbf{A}_\infty$. This system contains a single eigenvalue band with eigenvalues $\lambda(k)$ in the interval $D = [-2,2]$.

As a base system $\mathbf{B}_\rho$ consider a molecule situated on the surface of this solid. In general, this molecule can be approximated as a finite dimensional system containing ρ eigenvalues and ρ corresponding eigenstates. If a particular eigenvalue E of this molecule is non-degenerate and if it is well separated from all other eigenvalues of this molecule, to a very good approximation one can consider in isolation the interaction of the corresponding molecular eigenstate $\left|\Theta\right\rangle$ with the infinite system $\mathbf{A}_\infty$. In this approximation system $\mathbf{B}_\rho$ is one-dimensional system $\mathbf{B}_1$ and it contains a single state $\left|\Theta\right\rangle$ with the eigenvalue E. An arbitrary interaction between the systems $\mathbf{B}_1$ and $\mathbf{A}_\infty$ can be written in the form $\beta\,\mathbf{V}$ ($\beta \ge 0$) where matrix element of the Hermitean operator $\mathbf{V}$ between the state $\left|\Theta\right\rangle$ and j-th state of the Hückel chain is $\left\langle\Theta\right|\mathbf{V}\left|j\right\rangle = \beta_j$, and where this operator is normalized according to $\left\langle\Theta\right|\mathbf{V}^2\left|\Theta\right\rangle = 1$. This normalization is equivalent to the condition $\sum_j \beta_j^2 = 1$. Hence and from (3.65) one obtains

$$\left\langle\Theta\right|\mathbf{V}\left|\Phi(k)\right\rangle = \sqrt{\frac{2}{\pi}}\sum_{j=1}^{\infty}\beta_j \sin(kj), \quad 0 < k < \pi , \tag{3.66a}$$

$$\sum_j \beta_j^2 = 1. \tag{3.66b}$$

Relations (3.66) describe an arbitrary interaction of a single state $|\Theta\rangle$ with the infinite Hückel chain. In this general form the state $|\Theta\rangle$ is allowed to interact with each state $|j\rangle$ of the Hückel chain. Usually this interaction is confined to few states close to the surface of a solid. For the sake of simplicity assume that the state $|\Theta\rangle$ interacts only with the first state $|1\rangle$ of the infinite Hückel chain. In this case one has $\langle\Theta|\mathbf{V}|1\rangle = \beta_1 = 1$ and expressions (3.66) reduces to

$$\langle\Theta|\mathbf{V}|\Phi(k)\rangle = \sqrt{\frac{2}{\pi}}\sin(k),\; 0 < k < \pi . \tag{3.67}$$

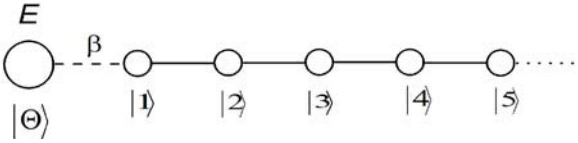

Figure 3.15. Example 3.3. Interaction of one-dimensional system $\mathbf{B}_1$ with infinite-dimensional system $\mathbf{A}_\infty$. System $\mathbf{B}_1$ contains a single eigenstate $|\Theta\rangle$ with the eigenvalue E. System $\mathbf{A}_\infty$ is an infinite one-dimensional solid (Hückel chain) in the nearest-neighbor tight-binding approximation. State $|\Theta\rangle$ interacts with a first atom of the one-dimensional solid. Coupling parameter is β. Adopted from ref. [9].

This situation is shown in figure 3.15. One has one-dimensional solid approximated as an infinite Hückel chain. Surface of this solid is at the state $|1\rangle$, and with this surface interacts a single state $|\Theta\rangle$ that has eigenvalue E. Since the space X_1^b is one-dimensional, characteristic operator $\mathbf{f}_b(\varepsilon)$ reduces to a single function $f_b(\varepsilon)$, and derived operator $\boldsymbol{\omega}_b(\varepsilon)$ also reduces to a single function $\omega_b(\varepsilon)$. Eigenvalue function $\lambda(k)$ as defined in (3.65) is non-increasing in the interval $[\lambda_a, \lambda_b] \equiv [-2,2]$, while it was assumed in the theoretical considerations that $\lambda(k)$ is non-decreasing. This can be corrected by a formal replacement of a parameter k with a parameter $k' = \pi - k$. As another solution, in the definition (3.16b) of the matrix elements of the characteristic operator $\mathbf{f}_b(\varepsilon)$ one can take the absolute value of the derivative $d\lambda/dk$ in order to enforce the non-negativity of this operator. Using expressions (3.16b), (3.65) and (3.67) one finds [10]

$$f_b(\varepsilon) = \left.\frac{\sin(k)}{\pi}\right|_{\varepsilon=2\cos(k)} = \frac{1}{\pi}\sqrt{1-\frac{\varepsilon^2}{4}}\cdot\begin{cases}1 & if \quad \varepsilon \in D \equiv [-2,2] \\ 0 & otherwise\end{cases}. \quad (3.68)$$

Hence and according to (3.46)

$$\omega_b(\varepsilon) = \frac{1}{\pi}P\int_{-2}^{2}\frac{\sqrt{1-\lambda^2/4}}{\varepsilon-\lambda}d\lambda, \qquad \varepsilon \in (-\infty,\infty). \quad (3.69)$$

One can integrate this expression using relations (3.21) and (3.22) to obtain

$$\omega_b(\varepsilon) = \frac{1}{2}\begin{cases}\left(\varepsilon+\sqrt{\varepsilon^2-4}\right) & if \quad \varepsilon < -2 \\ \varepsilon \quad if \quad \varepsilon \in D \equiv [-2,2] & \\ \left(\varepsilon-\sqrt{\varepsilon^2-4}\right) & if \quad \varepsilon > 2\end{cases}. \quad (3.70)$$

Derived function $\omega_b(\varepsilon)$ is shown in figure 3.16. One has now all necessary information for the description of the combined system $\mathbf{C}_\infty$.

Let me first consider isolated solutions of this system. Since $\mathbf{B}_1$ is one-dimensional, generic equation reduces to the expression (3.47a). Using (3.70) one finds

$$\frac{\beta^2}{2}\left(\varepsilon+\sqrt{\varepsilon^2-4}\right)+E-\varepsilon=0, \qquad \varepsilon<-2, \quad (3.71a)$$

$$\frac{\beta^2}{2}\varepsilon+E-\varepsilon=0, \quad \varepsilon \in [-2,2], \quad (3.71b)$$

$$\frac{\beta^2}{2}\left(\varepsilon-\sqrt{\varepsilon^2-4}\right)+E-\varepsilon=0, \qquad \varepsilon>2. \quad (3.71c)$$

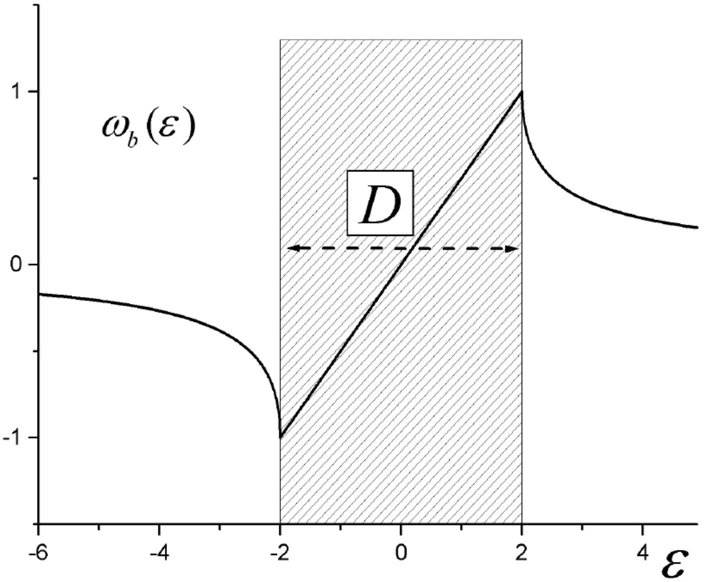

Figure 3.16. Example 3.3. Derived function $\omega_b(\varepsilon)$.

Roots $\varepsilon = \varepsilon_I \notin D$ of (3.71) are isolated eigenvalues of the combined system, while roots $\varepsilon = \varepsilon_0 \in D$ are resonant points. Since the system $\mathbf{A}_\infty$ contains only one eigenvalue band in the interval $D = [-2,2]$ and since $\rho = 1$, for each β combined system $\mathbf{C}_\infty$ has at most one right ($\varepsilon_R > 2$) and at most one left ($\varepsilon_L < -2$) isolated eigenvalue.

Expressions (3.71) have a solution [10,11]

$$\varepsilon_R = \frac{E(\beta^2 - 2) + \beta^2\sqrt{E^2 + 4(\beta^2 - 1)}}{2(\beta^2 - 1)} > 2 \qquad \text{if}$$

$$\beta^2 > 2 - E, \tag{3.72a}$$

$$\varepsilon_L = \frac{E(\beta^2 - 2) - \beta^2\sqrt{E^2 + 4(\beta^2 - 1)}}{2(\beta^2 - 1)} > -2 \qquad \text{if}$$

$$\beta^2 > 2 + E, \tag{3.72b}$$

$$\varepsilon_0 = \frac{2E}{2-\beta^2} \in [-2,2], \qquad \text{if} \qquad \beta^2 < 2 - |E| \qquad \text{or if}$$

$$\beta^2 > 2 + |E|. \tag{3.72c}$$

Eigenvalues ε_R and ε_L are right and left isolated eigenvalues of the combined system, while ε_0 is a resonant point of this system. According to the above expressions, right isolated eigenstate that has eigenvalue $\varepsilon_R > 2$ exist if and only if $\beta^2 > \beta_R^2 = 2 - E$, left isolated eigenstate that has eigenvalue $\varepsilon_L < -2$ exist if and only if $\beta^2 > \beta_L^2 = 2 + E$, while resonant point $\varepsilon_0 \in [-2,2]$ exist if and only if $\beta^2 < 2 - |E|$ or if $\beta^2 > 2 + |E|$. In particular, if $|E| > 2$ eigenvalue E is outside the eigenvalue band D, and in this case there is no resonant point for small β.

In figure 3.17 are shown eigenvalues (3.72) of the generic eigenvalue equation as functions of the coupling parameter β and for the case $E = 1.5$. Since $E \in D$, for small β combined system has a resonant point at $\varepsilon_0 \equiv \varepsilon_0(\beta) \in D$. However, if the coupling is as strong as $\beta > \beta_R = 0.707107$ (where $\beta_R^2 = 2 - E = 0.5$) combined system acquires right isolated eigenstate with he eigenvalue $\varepsilon_R(\beta) > 2$. If the coupling becomes as strong as $\beta > \beta_L = 1.870829$ (where $\beta_L^2 = 2 + E = 3.5$) combined system acquires left isolated eigenstate with the eigenvalue $\varepsilon_L(\beta) < -2$. In addition, resonant points $\varepsilon_0 \equiv \varepsilon_0(\beta) \in D$ exist if $\beta < \beta_R$ and also if $\beta > \beta_L$. Interaction landscape for the case $E = 1.5$ is shown in figure 3.17 . Note that neither isolated eigenvalue $\varepsilon_R(\beta)$ nor isolated eigenvalue $\varepsilon_L(\beta)$ extends to the point $\beta = 0$. In particular, right isolated eigenvalue $\varepsilon_R(\beta)$ is not an analitic continuation of resonant points $\varepsilon_0(\beta)$ (see expressions (3.72) and figure 3.17). Accordingly, isolated eigenvalues and the corresponding eigenstates can not be obtained by a standard perturbation expansion approach. Compare with previous two examples (figures 3.5 and 3.12).

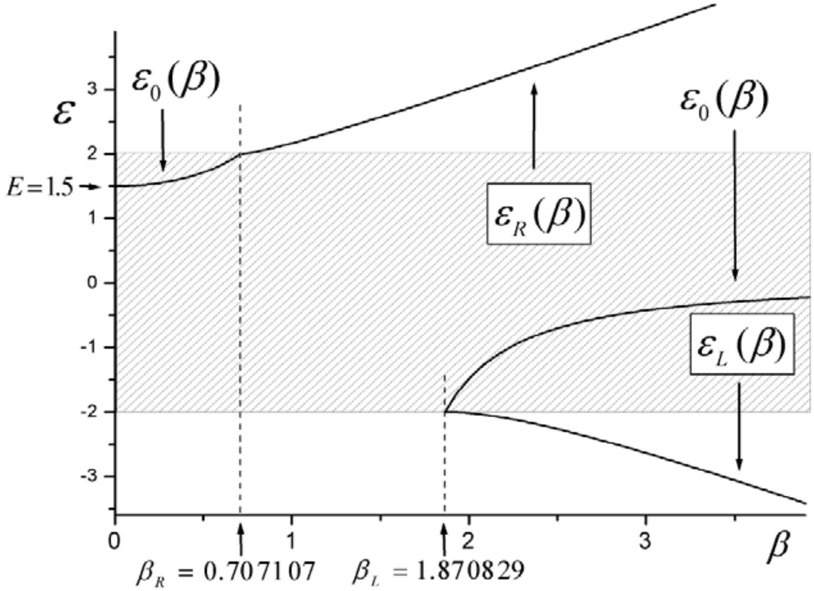

Figure 3.17. Example 3.3. Eigenvalues of the generic eigenvalue equation in the case $E = 1.5$.

Once isolated eigenvalue ε_I is known, one easily finds the corresponding eigenstate $|\Psi_I\rangle$. Expressions (3.26), (3.65) and (3.67) imply [10]

$$|\Psi_I\rangle = \frac{1}{\sqrt{N_I}}\left[|\Theta\rangle + \beta\sqrt{\frac{2}{\pi}}\int_0^{\pi}\frac{\sin(k)}{\varepsilon_I - 2\cos(k)}|\Phi(k)\rangle dk\right], \tag{3.73a}$$

where

$$N_I = 1 - \beta^2\frac{d\omega_b(\varepsilon_I)}{d\varepsilon_I} = 1 + \beta^2\frac{|\varepsilon_I| - \sqrt{\varepsilon_I^2 - 4}}{2\sqrt{\varepsilon_I^2 - 4}},$$

$$\varepsilon_I^2 > 4. \tag{3.73b}$$

and where $\varepsilon_I = \varepsilon_R$ or $\varepsilon_I = \varepsilon_L$, as given by (3.72). Hence the probability $w_I = \left|\left\langle \Theta \middle| \Psi_I \right\rangle\right|^2$ to find the corresponding isolated eigenstate $\left|\Psi_I\right\rangle$ in a local state $\left|\Theta\right\rangle \in X_1^b$ and the probability density $\rho_I(k) = \left|\left\langle \Phi(k) \middle| \Psi_I \right\rangle\right|^2$ to find this eigenstate in the state $\left|\Phi(k)\right\rangle \in X_\infty^a$ are [10]

$$w_I = \frac{1}{1+\beta^2 \dfrac{\left|\varepsilon_I\right| - \sqrt{\varepsilon_I^2 - 4}}{2\sqrt{\varepsilon_I^2 - 4}}},$$

$$\varepsilon_I^2 > 4, \qquad (3.74a)$$

$$\rho_I(k) = \frac{2\beta^2}{\pi\left[\varepsilon_I - 2\cos(k)\right]^2} \frac{\sin^2(k)}{1+\beta^2 \dfrac{\left|\varepsilon_I\right| - \sqrt{\varepsilon_I^2 - 4}}{2\sqrt{\varepsilon_I^2 - 4}}}, \qquad k \in [0,\pi] \quad (3.74b)$$

In particular, if the coupling β between the state $\left|\Theta\right\rangle$ and the infinite Hückel chain is small and if $E > 2 - \beta^2$, one has $w_I = w_R \approx 1$ and $\rho_I(k) = \rho_R(k) \approx 0$. In this case modified eigenstate $\left|\Psi_R\right\rangle$ is essentially original eigenstate $\left|\Theta\right\rangle$ slightly perturbed by the interaction with this infinite chain.

One similarly obtains probabilities $w_I^j = \left|\left\langle j \middle| \Psi_I \right\rangle\right|^2$ to find isolated eigenstate $\left|\Psi_I\right\rangle$ in the states $\left|j\right\rangle$ ($j = 1,2,\ldots$) of the infinite Hückel chain:

$$w_I^j = \frac{4\beta^2}{\pi^2} \frac{I_j^2(\varepsilon_R)}{1+\beta^2 \dfrac{\left|\varepsilon_I\right| - \sqrt{\varepsilon_I^2 - 4}}{2\sqrt{\varepsilon_I^2 - 4}}}, \qquad (3.75a)$$

where integrals $I_j(\varepsilon_I)\,(j=1,2,\dots)$ equal

$$I_j(\varepsilon_I)=\int_0^{\pi}\frac{\sin(k)\sin(jk)}{\varepsilon_I-2\cos(k)}dk\,,\qquad \varepsilon_I^2>4\ . \tag{3.75b}$$

There is an exact analytic expression for those integrals. However, it is sufficient to realize that due to the oscillatory factor $\sin(jk)$ in a sub-integral function of $I_j(\varepsilon_I)$, those integrals decrease with the increase of j. Probabilities w_I^j hence decrease as j increases. Isolated state $\left|\Psi_I\right\rangle$ is hence mainly localized close to the surface of the infinite Hückel chain (position $j=1$).

Consider now embedded eigenstates of the combined system. Since $\mathbf{B}_1$ is one-dimensional, one can use expressions (3.49-3.52). In particular, probability density $\rho_b(\varepsilon)=\left|\left\langle\Theta\middle|\Psi(\varepsilon)\right\rangle\right|^2$ to find embedded eigenstate $\left|\Psi(\varepsilon)\right\rangle$ in a system $\mathbf{B}_1$ that contains a single state $\left|\Theta\right\rangle$ is given by the expression (3.52a). Using expressions (3.68) and (3.70) for characteristic and derived functions, one finds

$$\rho_b(\varepsilon)\equiv\left|\left\langle\Theta\middle|\Psi(\varepsilon)\right\rangle\right|^2=\frac{\beta^2\sqrt{1-\varepsilon^2/4}}{\pi\beta^4\left(1-\varepsilon^2/4\right)+\pi\left(\beta^2\varepsilon/2+E-\varepsilon\right)^2}\,,$$
$$\varepsilon\in\left[-2,2\right]. \tag{3.76}$$

Using expressions (3.74a) for probabilities w_I and expression (3.76) for the probability density $\rho_b(\varepsilon)$ one can verify completeness relations (3.45). This is done in figure 3.18 for the case $E=1.5$. In this figure probabilities $w_R\equiv w_R(\beta)$ and $w_L\equiv w_R(\beta)$ as well as total probability $S_b(\beta)=\int\rho_b(\varepsilon)d\varepsilon\equiv\int\rho_b(\varepsilon,\beta)d\varepsilon$ are shown as functions of a coupling parameter β. A sum of all those probabilities is also shown. As β increases from the initial value $\beta=0$, the combined system at first has no isolated eigenstates and hence $S_b(\beta)=1$. However, if $\beta>\beta_R$ combined system has right isolated eigenstate which contributes probability $w_R \equiv w_R(\beta)$. If the coupling β is as strong as $\beta > \beta_L$, in addition to this right isolated eigenstate combined system has also left isolated eigenstate. This eigenstate contributes probability $w_L \equiv w_L(\beta)$ to the total probability of one. As required by the completeness relation, the sum of all those probabilities equals one for each value of β.

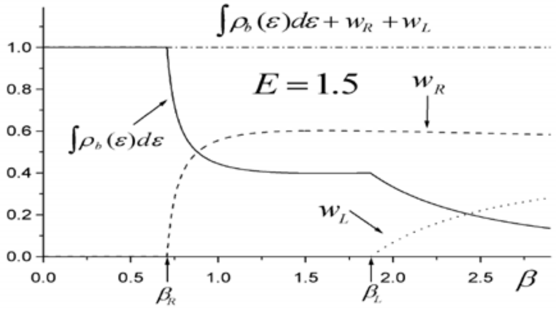

Figure 3.18. Example 3.3. Verification of the completeness relation. Adopted from ref. [9].

As a more detailed verification of the LRM approach, one can compare LRM probability density (3.76) that applies to an infinite combined system $\mathbf{C}_\infty$ with probabilities $w_s^n = \left|\langle \Theta | \Psi_s \rangle\right|^2$ that apply to the case of the finite combined system $\mathbf{C}_{n+1}$. Those later probabilities can be obtained in a standard way. Since in the limit $n \to \infty$ probabilities w_s^n are replaced with $\rho_b(\varepsilon)d\varepsilon$, one should compare LRM density $\rho_b(\varepsilon_s)$ with discrete probability w_s^n normalized per unit interval, i.e. one should compare $\rho_b(\varepsilon_s)$ with the ratio $w_s^n / \Delta\varepsilon_s$ where $\Delta\varepsilon_s = \varepsilon_s - \varepsilon_{s-1}$. Slightly better choice is to use the average of the intervals $\Delta\varepsilon_{s+1}$ and $\Delta\varepsilon_s$ on both sides of the eigenvalue ε_s instead of the interval $\Delta\varepsilon_s$ alone. From this comparison isolated eigenstates, if any, should be excluded. In addition, the smallest and the largest eigenvalue that in a limit $n \to \infty$ converge to some point inside the band $[\lambda_a, \lambda_b]$ should be separately normalized, since for the purpose of normalization only the intervals $\Delta\varepsilon_r$ that are inside the band $[\lambda_a, \lambda_b]$ can be utilized. Extreme eigenvalues ε_1 and ε_{n+1} of $\mathbf{C}_{n+1}$ should be hence normalized according to $W_1^n = w_1^n / \Delta\varepsilon_2$ and $W_{n+1}^n = w_{n+1}^n / \Delta\varepsilon_{n+1}$, respectively [10].

In figure 3.19 is compared in this way LRM probability density $\rho_b(\varepsilon)$ that corresponds to an infinite combined system $\mathbf{C}_\infty$ (expression (3.76) - dashed line), with normalized discrete probabilities W_s^{100} ($s = 1,\ldots,101$) that correspond to a finite combined system $\mathbf{C}_{n+1}$ with $n = 100$ (vertical columns). Those probabilities are sampled at the points ε_s of this finite system. The case $E = 0.5$ and $\beta = 0.9$ is considered. The agreement between probabilities W_s^{100} and corresponding densities $\rho_b(\varepsilon_s)$ ($s = 1,\ldots,101$) is excellent. Standard deviation of normalized probabilities W_s^{100} from those densities is $\Delta \approx 0.00056$ [10]. If one excludes points ε_1 and ε_{101} that are least reliable and that are close to the edge of the interval $[-2,2]$, standard deviation drops to $\Delta \approx 0.00004$. With further increase of n, results for a finite system $\mathbf{C}_{n+1}$ rapidly converge to the theoretical value $\rho_b(\varepsilon)$ as given by the expression (3.76).

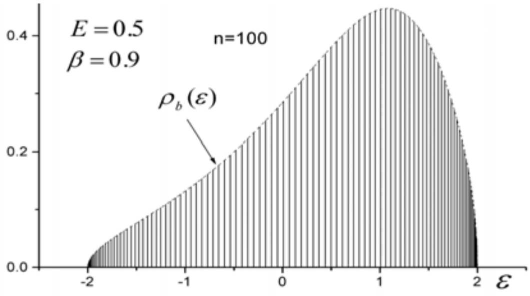

Figure 3.19. Example 3.3. Comparison of LRM density distribution $\rho_b(\varepsilon)$ of an infinite system $\mathbf{C}_\infty$ (dashed line) with normalized probabilities W_r^a of the corresponding finite combined system $\mathbf{C}_{n+1}$ (vertical columns) in the case $E = 0.5$ and $\beta = 0.9$. Finite combined system $\mathbf{C}_{n+1}$ contains a Hückel chain with $n = 100$ atoms. Adopted from ref. [9].

3.9.4. The Case of the Weak Coupling

In the case when the coupling parameter β is small, above results reduce to the well known results which can be obtained within the formalism of the perturbation expansion approach [1, 4].

Consider first isolated solutions of the combined system in the case of small β. According to the expressions (3.72), if β is small isolated eigenvalue ε_I may exist only if the eigenvalue E of the base system is either outside the range $D = [-2,2]$, or if E is inside this range it must be very close either to the boundary point $a = -2$ or to the boundary point $b = 2$. If this is the case, combined system has exactly one isolated eigenvalue which is close to the parent eigenvalue E and one corresponding eigenstate. For example, if $E > 2 - \beta^2$ and if β is small combined system has one right isolated eigenstate with the eigenvalue $\varepsilon_R > 2$ as given by the expression (3.72a). This eigenvalue is close to the eigenvalue E. The corresponding eigenstate is given by expressions (3.73). Since β is small, this modified eigenstate is virtually identical to the (normalized) state $|\Theta\rangle$. Similarly, if $E < \beta^2 - 2$, combined system has exactly one left isolated eigenstate with the eigenvalue $\varepsilon_L < -2$. However, if the eigenvalue E is sufficiently deep inside the band $[-2,2]$ so that $\beta^2 - 2 < E < 2 - \beta^2$, combined system contains no isolated eigenstate.

Consider now embedded solutions. If β is small and if the eigenvalue E satisfies $\beta^2 - 2 < E < 2 - \beta^2$, combined system has the resonant point $\varepsilon_0 \in D$, as given by the expression (3.72c). In this case density (3.76) reduces to the universal resonance curve $\rho_b^0(\varepsilon)$

$$\rho_b(\varepsilon) \approx \rho_b^0(\varepsilon) = \frac{\beta^2 \sqrt{1 - \varepsilon_0^2/4}}{\pi\beta^4\left(1 - \varepsilon_0^2/4\right) + \pi(\varepsilon - \varepsilon_0)^2},$$
$$\varepsilon \in [-2,2]. \qquad (3.77)$$

where resonant point $\varepsilon_0 \in D$ is given by (3.72c). The effect of the weak interaction of the eigenstate $|\Theta\rangle$ with an infinite Hückel chain is a) shift of the eigenvalue E to a new position $\varepsilon_0 \approx E\left(1+\beta^2/2\right)$ and b) broadening of this eigenvalue to a universal resonance curve (3.77).

3.10. INTERNAL MODIFICATIONS OF INFINITE-DIMENSIONAL SYSTEMS

Untill now external modifications of the infinite dimensional parent system $\boldsymbol{A}_\infty$ were considered. In the similar way can be treated internal modifications of this system. In analogy to the expressions (3.10) that describe an externally modified system, internally modified system $\mathbf{C}_\infty$ can be described by the standard eigenvalue equation

$$\mathbf{H}_c\left|\Psi(\ldots)\right\rangle = \varepsilon(\ldots)\left|\Psi(\ldots)\right\rangle, \tag{3.78a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \beta\mathbf{V}_a. \tag{3.78b}$$

and where the parent system $\boldsymbol{A}_\infty$ is described by the eigenvalue equation (3.4).

Expression (3.78a) is a standard eigenvalue equation. In particular, instead of the modification of a general type $(\mathbf{V}_a, \mathbf{P}_a)$ it contains a simpler modification where $\mathbf{P}_a = 0$. This is the most important case to be considered.

In the LRM approach it is assumed that the perturbation $\mathbf{V}_a$ has finite rank. According to (2.4) one has

$$\mathbf{V}_a = \mathbf{I}_\sigma^{\text{int}}\mathbf{V}_a\mathbf{I}_\sigma^{\text{int}}. \tag{3.79}$$

where $\mathbf{I}_\sigma^{\mathrm{int}}$ is the projection on the σ-dimensional interaction space X_σ^{int}, subspace of the infinite-dimensional space X_∞^a. Operator $\mathbf{V}_a$ has non-vanishing matrix elements only over the interaction space, and rank of this operator equals dimension of this space.

Modified system $\mathbf{C}_\infty$ can contain embedded as well as isolated eigenvalues and eigenstates. This possibility is indicated by dots $(\ldots)$ in the expression (3.78a).

Equations of a general type (3.78a) that describe internal modifications of infinite-dimensional systems are needed for example in the mathematical treatment of infinite-dimensional solids. A perfect infinite-dimensional solid is an ideal system and it can be described by the eigenvalue equation (3.4a). Due to the periodicity of the effective potential, one can obtain more or less reliable solution to this eigenvalue equation with various standard mathematical methods [2]. However, most interesting are properties of real solids that usually contain impurities and/or defects. In addition and unlike ideal infinite-dimensional solids, real solids always contain surfaces. Such and similar modifications of the initial perfect system can be described by the operator $\mathbf{V}_a$. However, all such modifications break periodic symmetry which is crucial in deriving reliable solutions to the initial parent system $\boldsymbol{A}_\infty$. Due to the lack of periodic symmetry one cannot reduce mathematical treatment of such systems to the equations that involve only a unit cell, which is a standard mathematical treatment of infinite-dimensional perfect solids [2]. On the other hand, those modifications are usually quite large. Therefore such systems cannot be efficiently treated within the standard formalism of the perturbation expansion. However, introduction of impurities and defects, as long as those modifications do not produce a global change of the crystal structure, can be very well approximated with operators that have finite rank. Hence such modifications can be efficiently treated within the LRM formalism. A special problem represents creation of a surface. Since a surface of a real three-dimensional solid is two-dimensional, creation of such a surface should be represented with Hermitean operator that has an infinite rank. Such a modification can not be treated within the LRM formalism as presented here. Nevertheless, one can still approximate a real surface with a small finite portion of such an infinite surface. Modifications that describe creation of such finite surfaces are represented by finite rank operators. If such a finite portion of an infinite surface is large enough, it should provide reliable approximation of a real infinite-dimensional surface. Hence all problems associated with the creation of a surface, such as existence of surface states, distortion of few unit cells close to the surface and alike can be also treated within the LRM formalism.

3.11. LRM TREATMENT OF INTERNALLY MODIFIED SYSTEMS

LRM treatment of infinite-dimensional (internally) modified systems is similar to the LRM treatment of infinite-dimensional combined systems. Both types of systems can contain isolated as well as embedded solutions. Isolated eigenvalues ε_I can assume any value, while embedded eigenvalues ε are confined to the range D and, with a possible exception of few discrete points, each $\varepsilon \in D$ is an embedded eigenvalue of the modified system. Further, both types of solutions can be cardinal as well as singular. In addition, one can distinguish strongly singular and weakly singular eigenstates of internally modified systems. Strongly singular eigenstates of those systems have no component in the interaction space X_σ^{int}, while weakly singular eigenstates have a non-vanishing component in this space. Thus the role of the base space X_ρ^b in the case of externally modified systems is in the case of internally modified systems assumed by the interaction space X_σ^{int}.

In the LRM treatment of internally modified infinite-dimensional systems crucial role is played by the characteristic operator $\mathbf{f}_a(\varepsilon)$ and by the corresponding derived operator $\boldsymbol{\omega}_a(\varepsilon)$. Those operators play analogous role to the characteristic operator $\mathbf{f}_b(\varepsilon)$ and derived operator $\boldsymbol{\omega}_b(\varepsilon)$ in the case of externally modified infinite-dimensional systems. In analogy to (3.15a) and (3.17b), those operators are defined according to

$$\mathbf{f}_a(\varepsilon) = \mathbf{V}_a \bar{\mathbf{f}}(\varepsilon)\mathbf{V}_a, \, \boldsymbol{\omega}_a(\varepsilon) = \mathbf{V}_a \overline{\boldsymbol{\omega}}(\varepsilon)\mathbf{V}_a, \tag{3.80a}$$

Derived operator $\boldsymbol{\omega}_a(\varepsilon)$ can be expressed in terms of the corresponding characteristic operator $\mathbf{f}_a(\varepsilon)$ according to

$$\boldsymbol{\omega}_a(\varepsilon) = P\int \frac{\mathbf{f}_a(\lambda)}{\varepsilon - \lambda} d\lambda . \tag{3.80b}$$

Operators $\mathbf{f}_a(\varepsilon)$ and $\boldsymbol{\omega}_a(\varepsilon)$ act in the σ-dimensional interaction space X_σ^{int} and outside this space those operators are zero. In the space X_σ^{int} operators $\mathbf{f}_a(\varepsilon)$ and $\boldsymbol{\omega}_a(\varepsilon)$ are represented as $\sigma \times \sigma$ matrices.

3.11.1. Isolated Solutions of Modified Systems

Concerning isolated solutions of the infinite-dimensional modified system $\mathbf{C}_\infty$, most important are isolated cardinal solutions that satisfy $\varepsilon_I \notin \{\lambda_j\}$. Isolated cardinal eigenvalues and the corresponding eigenstates can be obtained as a solution of the *generic* eigenvalue equation

$$[\beta\,\boldsymbol{\omega}_a(\varepsilon_I) - \mathbf{V}_a]|\varphi_I\rangle = 0, \; |\varphi_I\rangle \in X_\sigma^{\text{int}}, \tag{3.81a}$$

In the base $\{|\mu\rangle\}$ of the interaction space X_σ^{int} above expression is a $\sigma \times \sigma$ nonlinear eigenvalue equation. Each eigenvalue ε_I of this equation is hence a root of the $\sigma \times \sigma$ determinant $h(\varepsilon)$

$$h(\varepsilon) \equiv |\beta\,\boldsymbol{\omega}_a(\varepsilon) - \mathbf{V}_a| = 0 . \tag{3.81b}$$

Expressions (3.81) generalize expressions (2.36) (in the case $\mathbf{P}_a = 0$) to infinite-dimensional systems. Each solution $\varepsilon = \varepsilon_I \notin D$ of (3.81b) is an isolated eigenvalue of the infinite-dimensional modified system $\mathbf{C}_\infty$. Corresponding eigenstate $|\varphi_I\rangle \in X_\rho^{\text{int}}$ of (3.81a) determines isolated eigenstate $|\Psi_I\rangle \in X_\infty^a$ according to

$$\left|\Psi_I\right\rangle = \frac{1}{\sqrt{N_I}}\left[\sum_i \frac{\left\langle \Phi_i \left| \mathbf{V} \right| \varphi_I \right\rangle}{\varepsilon_I - \lambda_i}\left|\Phi_i\right\rangle + \sum_\tau \int \frac{\sum_m \int \left\langle \Phi_{\tau,m}(k,l) \left| \mathbf{V} \right| \varphi_I \right\rangle dl}{\varepsilon_I - \lambda_\tau(k)}\left|\Phi_{\tau,m}(k,l)\right\rangle dk\right], \quad (3.82a)$$

where normalization constant N_I equals

$$N_I = -\frac{d}{d\varepsilon_I}\left\langle \varphi_I \left| \boldsymbol{\omega}_a(\varepsilon) \right| \varphi_I \right\rangle, \quad (3.82b)$$

In particular, X_σ^{int}-component of the (normalized) eigenstate $\left|\Psi_I\right\rangle$ equals

$$\left|\Psi_I^{\text{int}}\right\rangle \equiv \mathbf{I}_\sigma^{\text{int}}\left|\Psi_I\right\rangle = \frac{1}{\beta\sqrt{N_I}}\left|\varphi_I\right\rangle. \quad (3.82c)$$

In a point $\lambda = \varepsilon_I \notin D$ one has $\mathbf{f}_a(\lambda) = 0$. Expression (3.80b) is hence a standard integral. As a consequence, one can take derivative of this expression in a standard way. Hence

$$\frac{d}{d\varepsilon_I}\left\langle \varphi_I \left| \boldsymbol{\omega}_a(\varepsilon) \right| \varphi_I \right\rangle = -\int \frac{\left\langle \varphi_I \left| \mathbf{f}_a(\lambda) \right| \varphi_I \right\rangle}{(\varepsilon_I - \lambda)^2} d\lambda. \quad (3.82d)$$

In particular, one has $d\left\langle \varphi_I \left| \boldsymbol{\omega}_a(\varepsilon) \right| \varphi_I \right\rangle / d\varepsilon_I < 0$.

Above expressions produce all isolated cardinal solutions that satisfy $\varepsilon_I \notin D$. Consider now solutions of the generic eigenvalue equation (3.81) that satisfy $\varepsilon_I \in D$. By definition, each solution $\varepsilon = \varepsilon_I \in D$ of (3.81b) is a resonant point. If the corresponding eigenvalue $\left|\varphi_I\right\rangle$ in addition to the generic eigenvalue equation (3.81a) satisfies also

$$\mathbf{f}_a(\varepsilon_I)\left|\varphi_I\right\rangle = 0. \quad (3.83)$$

the point $\varepsilon_I \in D$ is an *anomal point.* In the anomal point modified system has an isolated solution. Eigenvalue of this isolated solution is eigenvalue ε_I of the generic eigenvalue equation (3.81a) and the corresponding isolated eigenstate is again given by the above expressions. In conclusion, eigenvalues and eigenstates of the generic eigenvalue equation (3.81a) determine all isolated cardinal eigenvalues $\varepsilon_I \notin \{\lambda_j\}$ of the modified system and all the corresponding eigenstates $|\Psi_I\rangle$. If $\varepsilon_I \notin D$, this solution is determined by the generic eigenvalue equation (3.81a). However, if $\varepsilon_I \in D$, the corresponding eigenstate $|\varphi_I\rangle$ should satisfy additional condition (3.83). Expressions (3.81-3.83) that produce isolated cardinal solutions in the case of (internally) modified systems are analogous (though not identical) to the expressions (3.25-3.27) that produce isolated cardinal solutions in the case of combined (externally modified) systems.

3.11.2. Embedded Solutions of the Modified System

Concerning embedded solutions of modified systems, most important are embedded cardinal solutions. Those solutions can be obtained from the fractional shift eigenvalue equation

$$\mathbf{h}_a(\varepsilon)|\varphi_d(\varepsilon)\rangle = X_d(\varepsilon)\mathbf{f}_a(\varepsilon)|\varphi_d(\varepsilon)\rangle,$$
$$d = 1,2,\ldots,e(\varepsilon) \le \rho, \qquad (3.84a)$$

Where

$$\mathbf{h}_a(\varepsilon) = \beta^2\boldsymbol{\omega}_a(\varepsilon) - \mathbf{V}_a, \quad \varepsilon \in D, \ |\varphi_d(\varepsilon)\rangle \in X_\sigma^{\text{int}}. \qquad (3.84b)$$

Eigenvalues $X_d(\varepsilon)$ of this equation are related to the corresponding fractional shifts $x_d(\varepsilon)$ according to

$$X_d(\varepsilon) = -\pi\beta\cot(\pi x_d(\varepsilon)), \qquad d = 1,2,\ldots,e(\varepsilon) \le \rho. \quad (3.84c)$$

Fractional shift eigenvalue equation (3.84a) that applies to internal modification of the parent system $\mathbf{A}_{\infty}$ is analogous to the fractional shift eigenvalue equation (3.30a) that applies to the external modification of this system. Basic properties of those two equations are similar and they both determine corresponding embedded cardinal eigenstates. Note that the role of the space X_{ρ}^{b} in the case of an external modification is in the case of an internal modification assumed by the interaction space X_{σ}^{int} .

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Chapter 4

TIME-DEPENDENT SYSTEMS

In the previous two chapters time-independent systems were considered. Let me now consider time-dependent systems. LRM approach can be generalized to those systems in a rather straightforward way.

Consider an external modification of a finite-dimensional system $\mathbf{B}_\rho$ by the interaction $\mathbf{V}$ with an infinite-dimensional system $\mathbf{A}_\infty$. For the sake of simplicity, let the system $\mathbf{B}_\rho$ be described by the standard eigenvalue equation

$$\mathbf{H}_b\left|\Theta_r\right\rangle = E_r\left|\Theta_r\right\rangle, \qquad r = 1,\ldots,\rho, \tag{4.1a}$$

instead of by the generalized eigenvalue equation (2.5a). Orthonormalization (2.5b) in this case reduces to

$$\left\langle\Theta_r\middle|\Theta_t\right\rangle = \delta_{rt}. \qquad r,t = 1,\ldots,\rho. \tag{4.1b}$$

Let the system $\mathbf{A}_\infty$ be again described by the eigenvalue equations (3.4), and let the combined system be described by the eigenvalue equation

$$\mathbf{H}_c\left|\Psi(\ldots)\right\rangle = \varepsilon(\ldots)\left|\Psi(\ldots)\right\rangle, \tag{4.2a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \mathbf{H}_b + \beta\mathbf{V}\,. \tag{4.2b}$$

This differs from the eigenvalue equation (3.10) considered in section 3.2 in that $\mathbf{S}_b \equiv \mathbf{I}_b$ is now a unit operator in the space X_ρ^b.

Equation (4.2a) is time-independent and it describes time-independent combined system. If (4.2a) represents a standard time-independent Schrödinger equation, the corresponding time-dependent equation is

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \mathbf{H}_c\left|\Psi(t)\right\rangle. \tag{4.3}$$

General solution to this equation can be expressed in terms of the solutions to the time-independent equation (4.2)

$$\left|\Psi(t)\right\rangle = \sum_I c_I\left|\Psi_I\right\rangle \exp(-i\varepsilon_I t/\hbar) + \sum_{(\ldots)}\int c(\varepsilon,\ldots)\left|\Psi(\varepsilon,\ldots)\right\rangle \exp\left(-i\varepsilon t/\hbar\right)d\varepsilon\ldots \tag{4.4}$$

where first term contains summation over all isolated solutions of the eigenvalue equation (4.2), while second term contains summation and integration over all embedded solutions of this equation. Dots $(\ldots)$ represent any additional discrete and/or continuous parameters which are needed. Coefficients c_I and functions $c(\varepsilon,\ldots)$ are unknown quantities to be determined from the initial conditions.

Let at time $t = 0$ the combined system $\mathbf{C}_\infty$ be prepared in the system $\mathbf{B}_\rho$. In this case

$$\left|\Psi(0)\right\rangle = \left|\Theta\right\rangle \in X_\rho^b. \tag{4.5}$$

Since isolated and embedded eigenstates of the combined system $\mathbf{C}_\infty$ form a complete set in X_∞^c, each state $\left|\Psi\right\rangle \in X_\infty^c$ can be written as a linear combination of those eigenstates. In particular, each state $\left|\Theta\right\rangle \in X_\rho^b$ can be written in this way. Since strongly singular eigenstates of $\mathbf{C}_\infty$ have no X_ρ^a-component, the state $\left|\Theta\right\rangle$ contains no such eigenstates. As explained in the previous chapter, unless the system $\mathbf{C}_\infty$ has some symmetry not contained in the isolated systems $\mathbf{A}_\infty$ and $\mathbf{B}_\rho$, almost certainly it has no weakly singular eigenstates. The state $|\Theta\rangle \in X_\rho^b$ is hence a linear combination of isolated cardinal and embedded cardinal eigenstates of the combined system. In this case

$$|\Theta\rangle = \sum_I |\Psi_I\rangle\langle\Psi_I|\Theta\rangle + \sum_d \int |\Psi_d(\varepsilon)\rangle\langle\Psi_d(\varepsilon)|\Theta\rangle d\varepsilon , \qquad (4.6)$$

where the first term contains summation over all isolated cardinal eigenstates, while the second term contains summation and integration over all embedded cardinal eigenstates of the combined system. Expressions (3.26) and (3.31b) now imply

$$|\Theta\rangle = \sum_I c_I(\Theta)|\Psi_I\rangle + \sum_d \int c_d(\varepsilon,\Theta)|\Psi_d(\varepsilon)\rangle d\varepsilon , \qquad (4.7a)$$

where

$$c_I(\Theta) \equiv \langle\Psi_I|\Theta\rangle = \frac{\langle\theta_I|\Theta\rangle}{\sqrt{\langle\theta_I|\theta_I\rangle - \beta^2 \dfrac{d}{d\varepsilon_I}\langle\theta_I|\boldsymbol{\omega}_b(\varepsilon)|\theta_I\rangle}} , \qquad (4.7b)$$

$$c_d(\varepsilon,\Theta) \equiv \langle\Psi_d(\varepsilon)|\Theta\rangle = \frac{\beta\langle\theta_d(\varepsilon)|\Theta\rangle}{\sqrt{\pi^2\beta^4 + X_d(\varepsilon)^2}\sqrt{\langle\theta_d(\varepsilon)|\mathbf{f}_b(\varepsilon)|\theta_d(\varepsilon)\rangle}} . \qquad (4.7c)$$

Hence

$$|\Psi(t)\rangle = \sum_I c_I(\Theta)|\Psi_I\rangle \exp(-\frac{i\varepsilon_I t}{\hbar}) + \sum_d \int c_d(\varepsilon,\Theta)|\Psi_d(\varepsilon)\rangle \exp\left(-\frac{i\varepsilon t}{\hbar}\right) d\varepsilon , \qquad (4.8)$$

This is the required time-evolution of the state $\left|\Psi(t)\right\rangle$ which is at time $t = 0$ prepared in the system $\mathbf{B}_\rho$. Probability amplitude to find this state at time t in another state $\left|\Theta'\right\rangle \in X_\rho^b$ of this system equals

$$\left\langle\Theta'\middle|\Psi(t)\right\rangle = \sum_I w_I(\Theta',\Theta)\exp(-\frac{i\varepsilon_I t}{\hbar}) + \sum_d \int \rho_d(\varepsilon,\Theta',\Theta)\exp\left(-\frac{i\varepsilon t}{\hbar}\right)d\varepsilon \text{ ,(4.9a)}$$

Where

$$w_I(\Theta',\Theta) \equiv \left\langle\Theta'\middle|\Psi_I\right\rangle\left\langle\Psi_I\middle|\Theta\right\rangle = \frac{\left\langle\Theta'\middle|\theta_I\right\rangle\left\langle\theta_I\middle|\Theta\right\rangle}{\left\langle\theta_I\middle|\theta_I\right\rangle - \beta^2\dfrac{d}{d\varepsilon_I}\left\langle\theta_I\middle|\boldsymbol{\omega}_b(\varepsilon)\middle|\theta_I\right\rangle} \text{, (4.9b)}$$

$$\rho_d(\varepsilon,\Theta',\Theta) \equiv \left\langle\Theta'\middle|\Psi_d(\varepsilon)\right\rangle\left\langle\Psi_d(\varepsilon)\middle|\Theta\right\rangle = \frac{\beta^2\left\langle\Theta'\middle|\theta_d(\varepsilon)\right\rangle\left\langle\theta_d(\varepsilon)\middle|\Theta\right\rangle}{\left[\pi^2\beta^4 + X_d(\varepsilon)^2\right]\left\langle\theta_d(\varepsilon)\middle|\mathbf{f}_b(\varepsilon)\middle|\theta_d(\varepsilon)\right\rangle} \text{.(4.9c)}$$

Probability to find the state $\left|\Psi(t)\right\rangle$ which is at time $t = 0$ prepared in the state $\left|\Psi(0)\right\rangle \equiv \left|\Theta\right\rangle$ at some later time t in another state $\left|\Theta'\right\rangle$ equals square $\left|\left\langle\Theta'\middle|\Psi(t)\right\rangle\right|^2$ of the amplitude (4.9a).

Probability amplitude (4.9a) for the transition between arbitrary states $\left|\Psi(t)\right\rangle$ and $\left|\Theta'\right\rangle \in X_\rho^b$ can be expressed in terms of the probability amplitudes $\left\langle\Theta_p\middle|\Psi_r(t)\right\rangle$ ($r, p = 1,\dots\rho$) where the states $\left|\Psi_r(t)\right\rangle$ are at time $t = 0$ prepared in the eigenstates $\left|\Theta_r\right\rangle \in X_\rho^b$ of the closed system $\mathbf{B}_\rho$ ($\left|\Psi_r(0)\right\rangle = \left|\Theta_r\right\rangle$). One has:

$$\left\langle\Theta_p\middle|\Psi_r(t)\right\rangle = \sum_I w_{pr}^I \exp(-\frac{i\varepsilon_I t}{\hbar}) + \sum_d \int \rho_{pr}^d(\varepsilon)\exp\left(-\frac{i\varepsilon t}{\hbar}\right)d\varepsilon\text{ ,}$$

$$r, p = 1,\dots\rho\text{ ,} \qquad \text{(4.10a)}$$

where according to (4.7) matrix elements w_{rp}^{I} and $\rho_{rp}^{d}(\varepsilon)$ are

$$w_{rp}^{I} \equiv \left\langle \Theta_r \middle| \Psi_I \right\rangle \left\langle \Psi_I \middle| \Theta_p \right\rangle = \frac{\left\langle \Theta_r \middle| \theta_I \right\rangle \left\langle \theta_I \middle| \Theta_p \right\rangle}{\left\langle \theta_I \middle| \theta_I \right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I} \left\langle \theta_I \middle| \boldsymbol{\omega}_b(\varepsilon) \middle| \theta_I \right\rangle}, \quad (4.10b)$$

$$\rho_{rp}^{d}(\varepsilon) \equiv \left\langle \Theta_r \middle| \Psi_d(\varepsilon) \right\rangle \left\langle \Psi_d(\varepsilon) \middle| \Theta_p \right\rangle = \frac{\beta^2 \left\langle \Theta_r \middle| \theta_d(\varepsilon) \right\rangle \left\langle \theta_d(\varepsilon) \middle| \Theta_p \right\rangle}{\left[\pi^2 \beta^4 + X_d(\varepsilon)^2\right] \left\langle \theta_d(\varepsilon) \middle| \mathbf{f}_b(\varepsilon) \middle| \theta_d(\varepsilon) \right\rangle}. \quad (4.10c)$$

Those matrix elements are determined by the solutions of the generic eigenvalue equation and fractional shift eigenvalue equation, respectively. Expressions (4.9) and (4.10) provide a complete description of the X_ρ^b-component $\left|\Psi^b(t)\right\rangle$ of the time-dependent state $\left|\Psi(t)\right\rangle$ which is at time $t = 0$ prepared in the system $\mathbf{B}_\rho$. Note that diagonal matrix element $w_{rr}^{I} = w_{I,r} = \left|\left\langle \Theta_r \middle| \Psi_I \right\rangle\right|^2$ is a probability to find the state $\left|\Theta_r\right\rangle$ in the isolated cardinal eigenstate $\left|\Psi_I\right\rangle$ of the combined system, while diagonal matrix element $\rho_{rr}^{d}(\varepsilon) = \rho_{d,r}(\varepsilon) = \left|\left\langle \Theta_r \middle| \Psi_d(\varepsilon) \right\rangle\right|^2$ is a probability density to find this state in the embedded cardinal eigenstate $\left|\Psi_d(\varepsilon)\right\rangle$ of the combined system (see expressions (3.29a) and (3.34)).

Of particular interest is the probability $w^b(t)$ to find the state $\left|\Psi(t)\right\rangle$ at some later time in the base system $\mathbf{B}_\rho$. This probability represents decay of the state $\left|\Psi(t)\right\rangle$. Due to the interaction with the parent system $\mathbf{A}_\infty$, the state which is originally prepared in the system $\mathbf{B}_\rho$ after long enough time partially or completely decays to the system $\mathbf{A}_\infty$. Since the probability to find the state $\left|\Psi(t)\right\rangle$ in the eigenstate $\left|\Theta_r\right\rangle$ of the base system $\mathbf{B}_\rho$ equals $\left|\left\langle \Theta_r \middle| \Psi(t) \right\rangle\right|^2$, the probability $w^b(t)$ to find this state at time *t* anywhere in the system $\mathbf{B}_\rho$ equals

$$w^b(t) = \sum_r^{\rho} \langle \Psi(t) | \Theta_r \rangle \langle \Theta_r | \Psi(t) \rangle = \langle \Psi^b(t) | \Psi^b(t) \rangle . \qquad (4.11)$$

where $|\Psi^b(t)\rangle$ is X_ρ^b-component of the state $|\Psi(t)\rangle$. Probability to find the state $|\Psi(t)\rangle$ which is at time $t = 0$ prepared in the base system $\mathbf{B}_\rho$ ($|\Psi(0)\rangle \in X_\rho^b$) at some later time in this system hence equals norm of the X_ρ^b-component $|\Psi^b(t)\rangle$ of the state $|\Psi(t)\rangle$.

Consider the $t \to \infty$ limit of the above probabilities. For sufficiently big times the second term on the right hand side of the expression (4.10a) becomes negligibly small. Hence

$$\lim_{t\to\infty} \langle \Theta_p | \Psi_r(t) \rangle = \sum_I w_{pr}^I \exp(-i\varepsilon_I t/\hbar), \qquad (4.12a)$$

If all quantities w_{pr}^I are real, probability $w_{pr}^b(t)$ to find the state $|\Psi_r(t)\rangle$ which is at time $t = 0$ prepared in the state $|\Psi_r(0)\rangle = |\Theta_r\rangle \in X_\rho^b$ at large enough time in another state $|\Theta_p\rangle \in X_\rho^b$ of the same system $\mathbf{B}_\rho$ equals

$$w_{pr}^b(\infty) \equiv \left| \langle \Theta_p | \Psi_r(\infty) \rangle \right|^2 = \sum_I \left(w_{pr}^I \right)^2 + 2 \sum_{I<J} w_{pr}^I w_{pr}^J \cos\left(\frac{(\varepsilon_I - \varepsilon_J)t}{\hbar} \right) . (4.12b)$$

If the combined system contains no isolated eigenstate, after long enough time there is a complete decay of a state $|\Psi_r(t)\rangle$ and hence $w_{pr}^b(\infty) = 0$ for each *r* and each *p*. In this case the state $|\Psi_r(\infty)\rangle$ has no X_ρ^b-component and there is a complete decay of this state in the system $\mathbf{A}_\infty$. This is a usual case that can be also obtained within the formalism of the perturbation expansion [1, 2]. However, if the combined system contains some isolated eigenstates $|\Psi_I\rangle$, the situation is different. For example, if this system contains a single isolated eigenstate $|\Psi_I\rangle$, one usually has $w_{pr}^b(\infty) = \left(w_{pr}^I \right)^2 \neq 0$. In this case at infinite time the state $|\Psi_r(\infty)\rangle$ will be found with a finite probability $\left(w_{pr}^I \right)^2$

in the state $\left|\Theta_p\right\rangle \in X_\rho^b$. In particular, the state $\left|\Psi_r(\infty)\right\rangle$ will be found with finite probability $W_r^b = \sum_p \left(w_{pr}^I\right)^2$ in the system $\mathbf{B}_\rho$. Expressions (4.10b) imply

$$W_r^b = \frac{\left\langle\theta_I\middle|\theta_I\right\rangle\left\langle\Theta_r\middle|\theta_I\right\rangle\left\langle\theta_I\middle|\Theta_r\right\rangle}{\left[\left\langle\theta_I\middle|\theta_I\right\rangle - \beta^2 \dfrac{d}{d\varepsilon_I}\left\langle\theta_I\middle|\omega_b(\varepsilon)\middle|\theta_I\right\rangle\right]^2}, \tag{4.12c}$$

According to (4.12c) at infinite time decay of the initial state $\left|\Psi_r(0)\right\rangle = \left|\Theta_r\right\rangle$ to the system $\mathbf{A}_\infty$ will not be complete and there will be finite probability W_r^b to find the state $\left|\Psi_r(\infty)\right\rangle$ in the base system $\mathbf{B}_\rho$. Note that this probability will have its maximum value $W_{\max}^b$ if the initial state $\left|\Psi_r(0)\right\rangle = \left|\Theta_r\right\rangle$ is chosen to coincide with the eigenstate $\left|\theta_I\right\rangle$ of the generic equation, i.e. if $\left|\Psi_r(0)\right\rangle = \left|\theta_I\right\rangle$. In this case (4.12c) reduces to

$$W_{\max}^b = \frac{1}{\left[1 - \beta^2 \dfrac{d}{d\varepsilon_I}\left\langle\theta_I\middle|\omega_b(\varepsilon)\middle|\theta_I\right\rangle\right]^2}, \qquad \left\langle\theta_I\middle|\theta_I\right\rangle = 1\ , \tag{4.12d}$$

where the state $\left|\theta_I\right\rangle$ is normalized ($\left\langle\theta_I\middle|\theta_I\right\rangle = 1$).

The situation is more complex if the combined system contains several isolated eigenstates. In this case one has to use a general expression (4.12b). According to this expression, after long enough time the state $\left|\Psi_r(t)\right\rangle$ will only partially decay, and in a limit $t \to \infty$ there will be an oscillatory probability to find this state in any of the eigenstates $\left|\Theta_p\right\rangle$ of the base system $\mathbf{B}_\rho$. However, if the quantities $\left(\varepsilon_I - \varepsilon_J\right)$ ($\varepsilon_I \neq \varepsilon_J$) are large, those oscillations will be extremely fast. It is quite difficult to detect such fast oscillations experimentally. Instead one should detect a time-average $\overline{w}_{pr}^b(\infty)$

of those oscillations. Time average of a second term in (4.12b) equals zero, and hence

$$\overline{w}_{pr}^{b}(\infty) = \sum_{I} \left(w_{pr}^{I}\right)^{2}. \qquad (4.12e).$$

Similar results are obtained if quantities w_{pr}^{I} are not real. Since an arbitrary state $\left|\Psi(t)\right\rangle$ that satisfies $\left|\Psi(0)\right\rangle \in X_{\rho}^{b}$ is a linear combination of the states $\left|\Psi_{r}(t)\right\rangle$ considered above, all obtained results generalize in a natural way to such an arbitrary state.

4.1. ONE DIMENSIONAL TIME-DEPENDENT OPEN SYSTEMS

Of particular interest is the case $\rho = 1$. In this case base system $\mathbf{B}_{1}$ contains a single state $\left|\Theta\right\rangle$ with the eigenvalue E. In section 3.8 time-independent one-dimensional open systems were considered. Let me now consider time-dependent one-dimensional open systems.

Since $\rho = 1$, for each $\varepsilon \in D$ there is only one embedded cardinal eigenstate $\left|\Psi(\varepsilon)\right\rangle$ of the combined system. Hence expression (4.8) reduces to

$$\left|\Psi(t)\right\rangle = \sum_{I} c_{I}\left|\Psi_{I}\right\rangle \exp(-i\varepsilon_{I}t/\hbar) + \int c(\varepsilon)\left|\Psi(\varepsilon)\right\rangle \exp\left(-i\varepsilon t/\hbar\right)d\varepsilon \,. \qquad (4.13a)$$

where according to (3.48) and (3.51b)

$$c_{I} \equiv \left\langle \Psi_{I} \middle| \Theta \right\rangle = \sqrt{w_{I}} = \frac{1}{\sqrt{1-\beta^{2}\, d\omega_{b}(\varepsilon)/d\varepsilon_{I}}}, \qquad (4.13b)$$

$$c(\varepsilon) \equiv \left\langle \Psi(\varepsilon) \middle| \Theta \right\rangle = \sqrt{\rho_{b}(\varepsilon)} = \beta\left[\frac{f_{b}(\varepsilon)}{\pi^{2}\beta^{4}f_{b}^{2}(\varepsilon) + \left(\beta^{2}\omega_{b}(\varepsilon) + E - \varepsilon\right)^{2}}\right]^{\frac{1}{2}}. \qquad (4.13c)$$

Consider now probability $w^b(t)$ to find the state $\left|\Psi(t)\right\rangle$ at time t in the initial state $\left|\Psi(0)\right\rangle = \left|\Theta\right\rangle$. This probability is a square of the amplitude $\left\langle\Theta\middle|\Psi(t)\right\rangle$

$$w^b(t) = \left|\left\langle\Theta\middle|\Psi(t)\right\rangle\right|^2, \tag{4.14a}$$

Above expressions imply

$$\left\langle\Theta\middle|\Psi(t)\right\rangle = \sum_I w_I^b \exp\left(-i\,\varepsilon_I t/\hbar\right) + \int \rho_b(\varepsilon)\exp\left(-i\varepsilon t/\hbar\right) d\varepsilon\,. \tag{4.14b}$$

where density $\rho_b(\varepsilon)$ is given by (3.52a), eigenstates ε_I are roots of (3.47a), while probabilities w_I^b are given by (3.48c).

Consider now the $t \to \infty$ limit of the above amplitude. Since $\rho = 1$ expressions (4.12) that apply to this limit reduce to

$$\lim_{t\to\infty}\left\langle\Theta\middle|\Psi(t)\right\rangle = \sum_I w_I^b \exp\left(-i\varepsilon_I t/\hbar\right), \tag{4.15a}$$

$$\lim_{t\to\infty} w^b(t) = \sum_I \left(w_I^b\right)^2 + 2\sum_{I<J} w_I^b w_J^b \cos\left(\frac{(\varepsilon_I - \varepsilon_J)t}{\hbar}\right), \tag{4.15b}$$

Since $\mathbf{B}_1$ is one dimensional, in each interval $\left(a,b\right) \subseteq \overline{D}$ that contains no eigenvalue λ_i of the parent system $\mathbf{A}_\infty$ there can be at most two isolated eigenstates. All quantities $\left(\varepsilon_I - \varepsilon_J\right)$ ($\varepsilon_I \neq \varepsilon_J$) are hence usually relatively large. Hence, If the system $\mathbf{C}_\infty$ contains several isolated eigenstates $\left|\Psi_I(t)\right\rangle$, almost certainly one has to use time-average of the expression (4.15b). According to (4.12c) one has

$$\overline{w}^b(\infty) = \sum_I \left(w_I^b\right)^2 \tag{4.15c}$$

4.1.1. Decay of a Local State in the Weak Coupling Limit

If the coupling between the local state $\left|\Theta\right\rangle$ and the infinite system $\mathbf{A}_\infty$ is weak one can distinguish two qualitatively different cases, the case $E \in \overline{D}$ and the case $E \in D$. There are also small intermediate regions close to the boundaries between D and $\overline{D}$.

Most important is the case when eigenvalue E differs from all isolated eigenvalues λ_i of the parent system, $E \notin \{\lambda_i\}$. In this case if $E \in \overline{D}$ is an interior point in $\overline{D}$ and if β is sufficiently small, there is one and only one isolated eigenvalue $\varepsilon_I \equiv \varepsilon_I(\beta)$ of the combined system that satisfies $\varepsilon_I(0) = E$. For small β the corresponding isolated eigenstate $\left|\Psi_I\right\rangle \equiv \left|\Psi_I(\beta)\right\rangle$ satisfies (up to the norm and phase) $\left|\Psi_I(\beta)\right\rangle \approx \left|\Theta\right\rangle$ and hence $w_I^b \approx 1$. In addition, one has $\rho_b(\varepsilon) \approx 0$. Relations (4.14) hence imply $w^b(t) \approx 1$. In conclusion, If $E \in \overline{D}$ is an interior point in $\overline{D}$ and if β is sufficiently small, the state $\left|\Theta\right\rangle$ is only slightly effected by the interaction with the system $\mathbf{A}_\infty$ and essentially it does not change with time, i.e. $\left|\Psi(t)\right\rangle \approx \left|\Theta\right\rangle$.

Another possibility is $E \in D$ where E is an interior point in D. If the coupling β is sufficiently small, resonant point $\varepsilon_I \equiv \varepsilon_I(\beta)$ that satisfies $\varepsilon_I(0) = E$ is close to E. If $\varepsilon_I \equiv \varepsilon_I(\beta)$ is not an anomal point (i.e. if $f_b(\varepsilon_I) \neq 0$), the combined system contains no isolated eigenstate. In this case density $\rho_b(\varepsilon)$ is well approximated with the universal resonance curve $\rho_I^0(\varepsilon)$ given by the expression (3.53a). Hence and due to (4.14b) amplitude $\left\langle\Theta\middle|\Psi(t)\right\rangle$ can be approximated as [3-5]

$$\left\langle\Theta\middle|\Psi(t)\right\rangle \approx \int \rho_I^0(\varepsilon)\exp\left(-i\frac{\varepsilon t}{\hbar}\right)d\varepsilon = \exp\left(-i\frac{\varepsilon_I t}{\hbar}\right)\exp\left(-\frac{\pi\beta^2 f_b(\varepsilon_I)}{\hbar}t\right), \quad (4.16a)$$

where $\varepsilon_I \in D$ is a root of (3.47a). Probability $w^b(t)$ to find the state $\left|\Psi(t)\right\rangle$ at time t in the initial state $\left|\Theta\right\rangle$ hence equals

$$w^b(t) \approx w^{b0}(t) = \exp\left(-\frac{2\pi\beta^2 f_b(\varepsilon_I)}{\hbar} t \right). \tag{4.16b}$$

This expression describes well-known exponential decay of the state $\left|\Theta\right\rangle$.

If the coupling β is not small, instead of the above approximate expressions one has to use exact expressions (4.14).

4.1.2. Transition of the Local State to the Eigenstates of the Parent System

In the previous section X_1^b-component of the time-dependent state $\left|\Psi(t)\right\rangle$ was analyzed. In LRM one can also obtain X_∞^a-component of this state [3-6]. This component determines probabilities to find the state $\left|\Psi(t)\right\rangle$ at time t in continuous eigenstates $\left|\Phi_{\tau,m}(k,l)\right\rangle \in X_\infty^a$ of the infinite system $\mathbf{A}_\infty$, as well as probabilities to find this state at time t in discrete eigenstates $\left|\Phi_i\right\rangle \in X_\infty^a$ of this system. Most important is the transition to the continuous eigenstates. Let $\rho_\tau^a(\varepsilon,t)$ be probability density to find the state $\left|\Psi(t)\right\rangle$ at time t in any of the eigenstates $\left|\Phi_{\tau,m}(k,l)\right\rangle \in X_\infty^a$ of the eigenvalue band τ that have eigenvalue $\varepsilon = \lambda_\tau(k)$. Probability to find those eigenstates in the eigenvalue interval $d\varepsilon$ hence equals $\rho_\tau^a(\varepsilon,t)d\varepsilon$. This probability density is a square of the corresponding amplitude $u_\tau^a(\varepsilon,t)$:

$$\rho_\tau^a(\varepsilon,t) = \left|u_\tau^a(\varepsilon,t)\right|^2, \tag{4.17a}$$

If the system $\mathbf{A}_\infty$ contains several eigenvalue bands, the state $|\Psi(t)\rangle$ may decay via different channels $|\Psi(t)\rangle \to |\Phi_{\tau,m}(k,l)\rangle$ ($\tau = 1,\cdots,\kappa$). For example, one can consider the decay of some molecular state $|\Psi(t)\rangle$. In principle, this state may decay to each molecular state $|\Theta_f\rangle$ that has energy E_f lower than the energy E of the original state $|\Theta\rangle \equiv |\Psi(0)\rangle$. This decay is accompanied by the emission of a photon in the state $|\mathbf{k}\varpi\rangle$ where $\mathbf{k}$ denotes wavevector, while ϖ denotes photon polarization [1]. Hence one has the transition $|\Psi(t)\rangle \to |\Theta_f \mathbf{k}\varpi\rangle$. In the above notation $|\Phi_{\tau,m}(k,l)\rangle \equiv |\Theta_f \mathbf{k}\varpi\rangle$ is the state contained in the parent system $\mathbf{A}_\infty$. Transitions to various finale states $|\Theta_f\rangle$ are physically very different, they are usually well separated, and it is quite important to know relative probabilities of those transitions.

One finds that the amplitude $u_\tau^a(\varepsilon,t)$ can be expressed in terms of the probabilities w_I^b and in terms of the probability density $\rho_b(\varepsilon)$ according to [3,4,6]

$$u_\tau^a(\varepsilon,t) = \beta\sqrt{f_\tau(\varepsilon)}\left[\int \frac{\rho_b(\lambda)\left[e^{-i(\lambda-\varepsilon)t/\hbar} - 1\right]}{\lambda-\varepsilon}d\lambda + \sum_I w_I^b \frac{\left[e^{-i(\varepsilon_I-\varepsilon)t/\hbar} - 1\right]}{\varepsilon_I - \varepsilon}\right],\text{(4.17b)}$$

Using (4.14b) this amplitude can be expressed in terms of the amplitude $\langle\Theta|\Psi(t)\rangle$ according to [4,5]

$$u_\tau^a(\varepsilon,t) = -i\frac{\beta}{\hbar}\sqrt{f_\tau(\varepsilon)}\int_0^t \langle\Theta|\Psi(t)\rangle \exp\left(i\frac{\varepsilon t}{\hbar}\right)dt\,,$$
$$\tau = 1,\ldots,\kappa\,. \qquad \text{(4.17c)}$$

This expression provides a connection between the amplitude $\langle\Theta|\Psi(t)\rangle$ that determines probability $w^b(t)$ to find the state $|\Psi(t)\rangle$ at time *t* in the base system $\mathbf{B}_1$ (the state $|\Theta\rangle$) with the amplitudes $u_\tau^a(\varepsilon,t)$ that determine probability densities $\rho_\tau^a(\varepsilon,t)$ to find this state at time t in those eigenstates $|\Phi_{\tau,m}(k,l)\rangle$ of the eigenvalue band τ of the parent system $\mathbf{A}_\infty$ that satisfy $\varepsilon = \lambda_\tau(k)$.

At $t = 0$ one has $u_\tau^a(\varepsilon,0) = 0$ and hence $\rho_\tau^a(\varepsilon,0) = 0$. Probability density to find the state $|\Psi(t)\rangle$ at initial time $t = 0$ in any of the eigenstates $|\Phi_{\tau,m}(k,l)\rangle$ of the infinite system $\mathbf{A}_\infty$ equals zero. This is obvious and trivial, since at $t = 0$ the state $|\Psi(t)\rangle$ is prepared in the system $\mathbf{B}_1$ and hence it has no X_∞^a-component. As t increases, one obtains non-vanishing probability densities $\rho_\tau^a(\lambda,t)$ to find this state in various continuous eigenstates $|\Phi_{\tau,m}(k,l)\rangle$ of the system $\mathbf{A}_\infty$. Above expressions imply

$$\frac{\rho_\nu^a(\varepsilon,t)}{\rho_\mu^a(\varepsilon,t)} = \frac{f_\nu(\varepsilon)}{f_\mu(\varepsilon)}. \tag{4.18}$$

For each eigenvalue ε the ratio of the probability densities to decay to different eigenvalue bands τ is independent on time.

If the combined system contains no isolated eigenstate, there is a well-defined $t \to \infty$ limit of the probability densities $\rho_\tau^a(\varepsilon,t)$ $(\tau = 1,2,\ldots)$. Otherwise for large times those probability densities exhibit fast oscillations. This is similar and complementary to the analogous behavior of the probability $w^b(t)$ discussed above.

Probability $w_\tau^a(t)$ to find the state $|\Psi(t)\rangle$ at time t anywhere in the eigenvalue band τ equals

$$w_\tau^a(t) = \int \rho_\tau^a(\varepsilon,t)d\varepsilon\,, \tag{4.19}$$

Unlike the ratio (4.18) that involves probability densities and that does not depend on time, the ratio $w_\mu^a(t)\big/w_\nu^a(t)$ of total probabilities to decay via two different channels μ and ν usually depends on time.

Above expressions provide probability amplitudes and corresponding probabilities to find the state $\left|\Psi(t)\right\rangle$ at time t in continuous eigenstates $\left|\Phi_{\tau,m}(k,l)\right\rangle \in X_\infty^a$ of the parent system $\mathbf{A}_\infty$. In a similar way can be expressed probability amplitudes $u_j(t)$ to find this state at time t in the discrete eigenstates $\left|\Phi_j\right\rangle$ of this system. For simplicity those expressions are omitted here. If the system $\mathbf{A}_\infty$ contains no discrete eigenstates $\left|\Phi_i\right\rangle$, at each time $t \geq 0$ the state $\left|\Psi(t)\right\rangle$ must be found with certainty either in the original state $\left|\Theta\right\rangle \in X_1^b$ or in some state $\left|\Phi_{\tau,m}(k,l)\right\rangle \in X_\infty^a$. In this case

$$w^b(t) + \sum_\tau^\kappa w_\tau^a(t) = 1\,. \tag{4.20}$$

where probability $w^b(t)$ is given by the expressions (4.14), while probabilities $w_\tau^a(t)$ are given by the expressions (4.17) and (4.19). Relation (4.20) is a key completeness relation for time-dependent systems in the case when the parent system $\mathbf{A}_\infty$ contains no discrete eigenstates. This relation can be used as an efficient test for the validity of the LRM treatment of such systems.

4.1.3. Transition of the Local State to the Eigenstates of the Parent System in the Weak Coupling Limit

If the coupling parameter β is small, probability densities $\rho_\tau^a(\varepsilon,t)$ can be approximated as [3,4]

$$\rho_\tau^a(\varepsilon,t) \approx \rho_\tau^{a0}(\varepsilon,t) = \\ = \frac{f_\tau(\varepsilon_I)}{f_b(\varepsilon_I)} \rho_I^0(\varepsilon) \left[\exp\left(-\frac{2\pi\beta^2 f_b(\varepsilon_I)}{\hbar} t \right) - 2\exp\left(-\frac{\pi\beta^2 f_b(\varepsilon_I)}{\hbar} t \right) \cos\left((\varepsilon_I - \varepsilon) t/\hbar \right) + 1 \right]. \quad (4.21)$$

This expression is a product of three terms. First term is a ratio $f_\tau(\varepsilon_I)/f_b(\varepsilon_I)$ that determines relative probabilities of a transition via different channels τ. In particular, if $\varepsilon_I \notin I_\tau$ one has $f_\tau(\varepsilon_I) = 0$ and there is no transition to the channel τ. Second term is universal resonant curve (3.53a) that has a sharp peak in the resonant point $\varepsilon = \varepsilon_I$ and that satisfies $\int \rho_I^0(\varepsilon) d\varepsilon = 1$. Last term describes an exponential approach to the $t = \infty$ limit modified in an oscillatory way by the *cos()* term. This oscillatory modification is absent in the resonant point $\varepsilon = \varepsilon_I$ where density $\rho_I^0(\varepsilon)$ has a maximum. As one departs from this point, frequency of those oscillations increases, while probability $\rho_\tau^{a0}(\varepsilon,t)$ sharply decreases.

One finds that total probability $w_\tau^a(t)$ for the decay to the eigenvalue band τ can be approximated as [4-6]

$$w_\tau^a(t) \approx w_\tau^{a0}(t) = \int \rho_\tau^{a0}(\varepsilon,t) d\varepsilon = \frac{f_\tau(\varepsilon_I)}{f_b(\varepsilon_I)} \left[1 - \exp\left(-\frac{2\pi\beta^2 f_b(\varepsilon_I)}{\hbar} t \right) \right]. \quad (4.22)$$

Relations (4.16b) and (4.22) satisfy $w^{b0}(t) + \sum_\tau w_\tau^{a0}(t) = 1$ in accord with the completeness requirement (4.20). In addition one has

$$\frac{w_\nu^{a0}(t)}{w_\mu^{a0}(t)} = \frac{f_\nu(\varepsilon_I)}{f_\mu(\varepsilon_I)}. \quad (4.23)$$

which is similar to (4.18). Thus in the case of small β and if $\varepsilon_I(0) = E \in D$, ratios of the probabilities to decay via different channels are independent of time. Unlike exact expression (4.18) this result is only approximate, and it depends on the validity of the above approximations. One has also

$$w^a(t) \approx w^{a0}(t) \equiv \sum_\tau w_\tau^{a0}(t) = 1 - \exp\left(-\frac{2\pi\beta^2 f_b(\varepsilon_l)}{\hbar} t \right). \qquad (4.24)$$

After long enough time the state $|\Theta\rangle$ completely decays into the system $\boldsymbol{A}_\infty$. Hence $w^{a0}(\infty) = 1$.

Above results are in accord with the well-known results obtained in a standard way within the formalism of the perturbation expansion approach [1, 2].

4.1.4. Example 4.1

Let me illustrate LRM treatment of time-dependent systems with a simple example. Consider the interaction of a single state with one-dimensional solid in the nearest-neighbor tight-binding approximation [7]. Time-independent properties of this system were discussed in the previous chapter (section 3.9.3). Let me now consider time-dependent properties of this system.

Consider first probability $w^b(t)$ to find the state $|\Psi(t)\rangle$ which is at time $t = 0$ prepared in the state $|\Psi(0)\rangle = |\Theta\rangle$ at some later time in the same state $|\Theta\rangle$. This probability is given by the expressions (4.14). In order to verify those expressions one can compare probability $w^b(t)$ as given by those expressions with corresponding probabilities for a finite combined system $\mathbf{C}_{n+1}$ [6]. Those probabilities for a finite system $\mathbf{C}_{n+1}$ can be obtained in a standard way since they involve diagonalization of finite $(n+1)\times(n+1)$ matrices. This comparison is shown in figures 4.1 and 4.2. In figure 4.1 combined system $\mathbf{C}_\infty$ with local eigenvalue $E = 1.5$ and with the coupling $\beta = 0.6$ is considered. In this figure probability $w^b(t)$ (solid line) is compared with corresponding probabilities $w_n^b(t)$ for finite combined systems $\mathbf{C}_{n+1}$. Those probabilities are given as functions of time t. Time is expressed in units $\hbar$. This is a natural time unit for a model considered. In the case $\beta = 0.6$ infinite system $\mathbf{C}_\infty$ contains no isolated eigenstate (see figure 3.17), and hence after long enough time the state $|\Psi(t)\rangle$ which is at time $t = 0$

prepared in the state $\left|\Theta\right\rangle$ makes a complete decay to the infinite Hückel chain (system $\boldsymbol{A}_\infty$), hence $\lim_{t\to\infty} w^b(t) = 0$. In order to illustrate the convergence of $w_n^b(t)$ to $w^b(t)$ as n increases, probability $w^b(t)$ is compared with two finite-chain probabilities $w_{10}^b(t)$ and $w_{20}^b(t)$. Those finite Hückel chains contain $n = 10$ and $n = 20$ atoms, respectively. For small times t both probabilities $w_n^b(t)$ follow theoretical curve $w^b(t)$ almost exactly. However, each curve $w_n^b(t)$ at some large enough time t' separates from $w^b(t)$. As n increases separation point t' also increases.

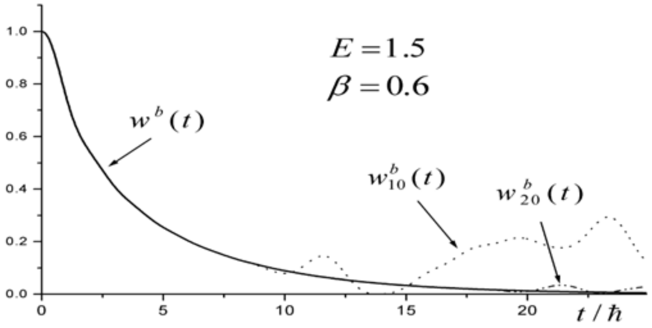

Figure 4.1. Example 4.1. Decay of a state $\left|\Psi(t)\right\rangle$ in the case $\beta = 0.6$ and $E = 1.5$. Probability $w^b(t)$ to find the state $\left|\Psi(t)\right\rangle$ at time t in the base system $\mathbf{B}_1$ (solid line) is compared with corresponding probabilities for finite combined systems $\mathbf{C}_{10+1}$ and $\mathbf{C}_{20+1}$ (other two lines). Since this interaction is relatively weak, combined system contains no isolated eigenstate. There is hence a complete decay of the eigenstate $\left|\Psi(t)\right\rangle$. Adopted from ref. [6].

In figure 4.2 the case $\beta = 1.5$ is considered. In this case combined system $\mathbf{C}_\infty$ contains right isolated eigenstate $\left|\Psi_R\right\rangle$ (see figure 3.17) and the state $\left|\Psi(t)\right\rangle$ only partially decays to the system $\boldsymbol{A}_\infty$. This decay exhibits damped oscillations, and for large times probability $w^b(t)$ converges to $\left(w_R^b\right)^2 = 0.36165$ [6]. This probability is compared with probabilities $w_{10}^b(t)$

and $w_{20}^b(t)$. For small times probabilities $w_n^b(t)$ again follow theoretical curve $w^b(t)$, while at some large enough time t' each curve $w_n^b(t)$ separates from $w^b(t)$. As n increases this point of separation again shifts towards higher values of t.

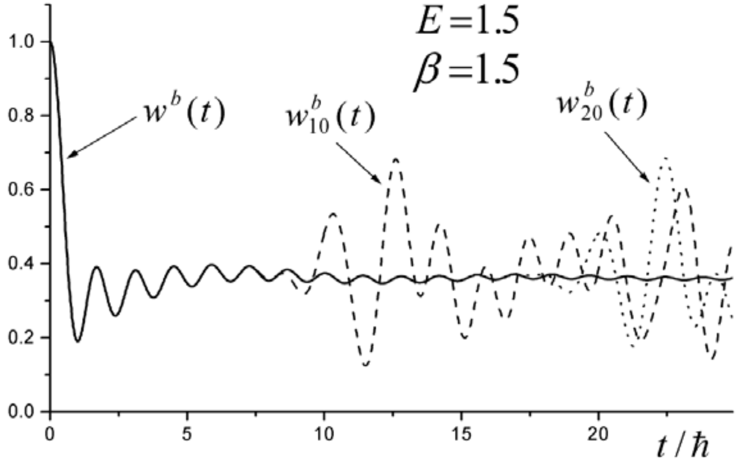

Figure 4.2. Example 4.1. Decay of a state $\left|\Psi(t)\right\rangle$ in the case $\beta = 1.5$ and $E = 1.5$. Probability $w^b(t)$ (solid line) is compared with corresponding probabilities for finite combined systems $\mathbf{C}_{10+1}$ and $\mathbf{C}_{20+1}$ (other two lines). This interaction is relatively strong and combined system contains a single isolated eigenstate. Decay of the state $\left|\Psi(t)\right\rangle$ is not complete. Adopted from ref. [6].

Above property is general. Each probability $w_n^b(t)$ of a finite system $\mathbf{C}_{n+1}$ reproduces theoretical probability $w^b(t)$ of the corresponding infinite system $\mathbf{C}_\infty$ up to some point $t = t'$. If $t < t'$ probability $w_n^b(t)$ is virtually identical to the theoretical probability $w^b(t)$ for an infinite system $\mathbf{A}_\infty$. However, if $t > t'$ probability $w_n^b(t)$ deviates significantly from $w_n^b(t)$. As n increases the point $t = t'$ increases approximately linearly with n. In addition, the agreement between $w_n^b(t)$ and $w_n^b(t)$ for small values of t also improves [4,6]. One finds that probabilities $w_n^b(t)$ converge to the probability $w^b(t)$ for an infinite system $\mathbf{C}_\infty$, i.e. one has $\lim_{n\to\infty} w_n^b(t) = w^b(t)$.

4.1.5. Example 4.2

In the previous example system $\mathbf{B}_1$ interacts with the infinite-dimensional system $\boldsymbol{A}_\infty$ that contains a single one-parameter eigenvalue band. In the example shown in figures (4.3-4.6), system $\mathbf{B}_1$ that contains a single eigenstate $|\Theta\rangle$ with the eigenvalue $E = 1$ interacts with the infinite-dimensional system $\boldsymbol{A}_\infty$ that contains two eigenvalue bands $\tau = 1$ and $\tau = 2$ in the intervals $I_1 = [-2,2]$ and $I_2 = [-0.5,1.5]$, respectively. The details of this example are given elsewhere [4]. I will report here only main results.

In figure 4.3 the case $\beta = 0.9$ is considered. In this figure probability $w^b(t)$ to find the state $|\Psi(t)\rangle$ at time *t* in the initial state $|\Theta\rangle$ as well as probabilities $w_1^a(t)$ and $w_2^a(t)$ to find this state at time *t* in the two eigenvalue bands are shown. Since $\beta = 0.9$ is relatively weak coupling, combined system $\mathbf{C}_\infty$ contains no isolated eigenstate and hence in a limit $t \to \infty$ one has $w^b(\infty) = 0$. Probability $w^b(t)$ is calculated according to the expressions (4.14), while probabilities $w_\tau^a(t)$ are calculated according to the expressions (4.17) and (4.19). The sum $w^b(t) + w_1^a(t) + w_2^a(t)$ of those probabilities is also shown. As required by the completeness relation (4.20), for each time *t* this sum equals unity.

In figure 4.4 the same system is considered, but this time coupling β is as strong as $\beta = 1.5$. In this case combined system $\mathbf{C}_\infty$ has a single isolate eigenstate $|\Psi_I\rangle$ with the eigenvalue $\varepsilon_R = 2.3186$ [4]. Hence in a limit $t \to \infty$ one has $w^b(\infty) = 0.2523 \neq 0$ [4]. As shown in this figure, completeness relation (4.20) is again satisfied.

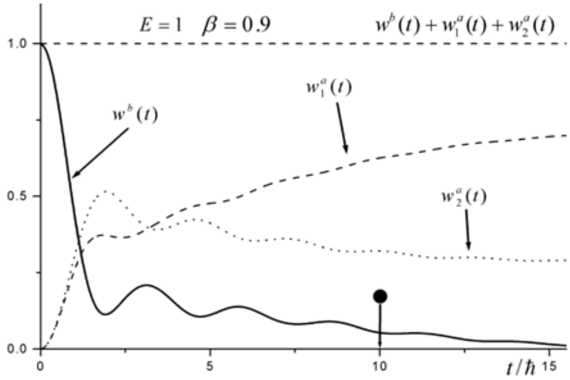

Figure 4.3. Example 4.2. In this example the system $\mathbf{A}_\infty$ contains two eigenvalue bands. The case $\beta = 0.9$ and $E = 1$ is considered. Probabilities $w^b(t)$ (solid line) and probabilities $w_1^a(t)$ and $w_2^a(t)$ to find the state $|\Psi(t)\rangle$ at time t in the corresponding eigenvalue bands $\nu = 1$ and $\nu = 2$ (dashed and dotted line) are shown as functions of time t. In accord with the completeness relation (4.20), for each time t the sum of those probabilities equals unity. In the case $\beta = 0.9$ combined system contains no isolated eigenstate and hence $\lim_{t\to\infty} w^b(t) = 0$. Detailed probability densities $\rho_1^a(\varepsilon,t)$ and $\rho_2^a(\varepsilon,t)$ at time $t/\hbar = 10$ (position •) are shown in figures 4.5 and 4.6, respectively . Adopted from ref. [4].

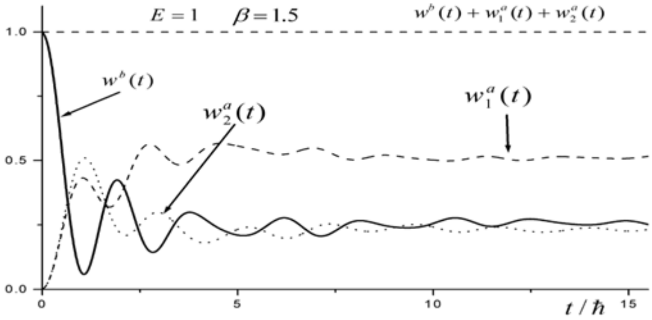

Figure 4.4. The same as figure 4.3, but for the coupling $\beta = 1.5$. In this case combined system contains an isolated eigenstate and hence $\lim_{t\to\infty} w^b(t) \neq 0$. In accord with the completeness relation, the sum of probabilities $w^b(t)$, $w_1^a(t)$ and $w_2^a(t)$ equals unity. Adopted from ref. [4].

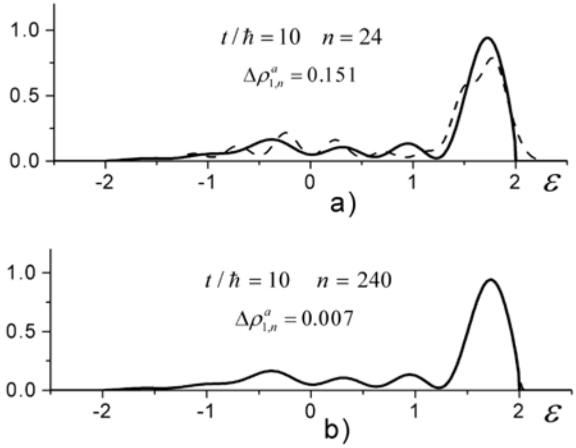

Figure 4.5. Probability density $\rho_1^a(\varepsilon,t)$ to find the state $|\Psi(t)\rangle$ at time $t/\hbar = 10$ in the eigenvalue band $\nu = 1$ and with the eigenvalue ε. This time corresponds to the position ● in figure 4.3. a) Probability density $\rho_1^a(\varepsilon,t)$ (solid line) compared with the result for the corresponding finite system $\mathbf{A}_{24}$ (dashed line). Average standard deviation between those two curves is $\Delta\rho_{1,24}^a = 0.151$. b) The same as a) but this time the corresponding finite system is $\mathbf{A}_{240}$. Average standard deviation drops to $\Delta\rho_{1,240}^a = 0.007$. Adopted form ref. [4].

In figures 4.5 and 4.6 are analyzed details of the probability densities $\rho_\tau^a(\varepsilon,t)$ ($\tau = 1,2$). Those probability densities correspond to the case $\beta = 0.9$ and to the time $t/\hbar = 10$. This time is shown in figure 4.3 with symbol ●. In figure 4.5 probability density $\rho_1^a(\varepsilon,t)$ derived from the expressions (4.17) (solid lines) is compared with the corresponding results obtained in a standard way for finite systems $\mathbf{A}_n$. Systems $\mathbf{A}_n$ containing $n = 24$ atoms (figure 4.5a) and $n = 240$ atoms (figure 4.5b) are considered (dashed lines). Standard deviations $\Delta\rho_{1,n}^a$ between exact (combined system $\mathbf{C}_\infty$) and approximate (combined systems $\mathbf{C}_{n+1}$) results are also shown. Those standard deviations decrease from $\Delta\rho_{1,24}^a = 0.151$ to $\Delta\rho_{1,240}^a = 0.007$ with the increase of *n* from $n = 24$ to $n = 240$, respectively. In figure 4.5b) there is no noticeable difference between exact ($n = \infty$) and approximate ($n = 240$) calculation. In figure 4.6 the same is shown for probability density

$\rho_2^a(\varepsilon,t)$ associated with the eigenvalue band $\tau = 2$. As shown in those Figures, as n increases approximate results obtained for finite systems converge to the exact LRM result.

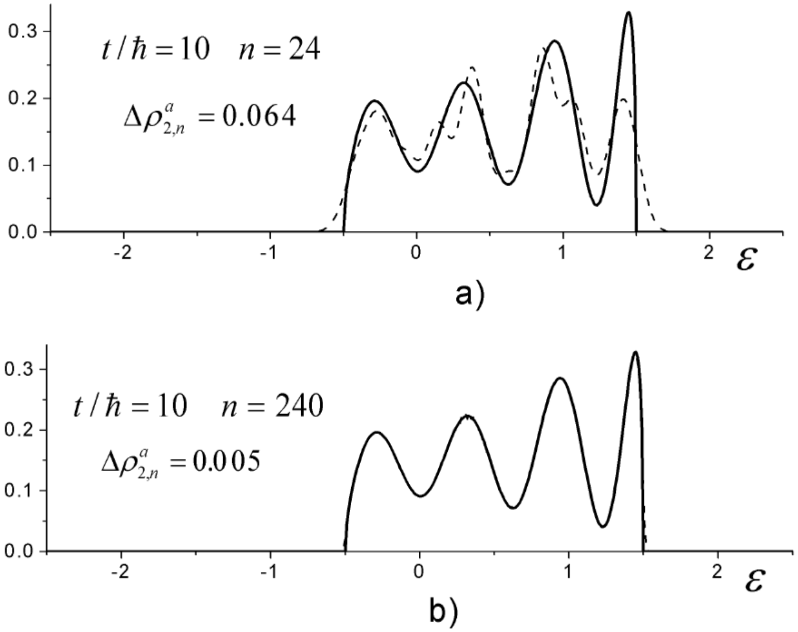

Figure 4.6. The same as figure 4.5, but for the eigenvalue band $\nu = 2$. a) Comparison of the probability density $\rho_2^a(\varepsilon,t)$ with the result obtained for the approximate finite system $\mathbf{A}_{24}$. Average standard deviation between the exact and approximate calculation is $\Delta\rho_{2,24}^a = 0.064$. b) The same as a), but this time the corresponding finite system is $\mathbf{A}_{240}$. Average standard deviation drops to $\Delta\rho_{2,240}^a = 0.005$. Adopted form ref. [4].

Example 4.2 demonstrated that LRM correctly predicts all the fine details of the time-dependent systems, however strong the coupling β between the base system $\mathbf{B}$ and the infinite system $\mathbf{A}_\infty$. The case $\beta = 0.9$ as well as the case $\beta = 1.5$ is an example of a rather strong coupling. As shown in figure 4.3, even in the case $\beta = 0.9$ small coupling approximation (4.16b), which predicts exponential decay of the state $\left|\Psi(t)\right\rangle$, breaks down. In particular, as time *t* increases exact probability $w^b(t)$ at first decreases, but at some point it starts to increase. This behavior is contrary to the exponential decay approximation and it is not reproducible by the standard perturbation expansion. Deviation from this small coupling approximation is even more drastical in the case $\beta = 1.5$ (figure 4.4).

Note that in a standard experimental set up one usually measures $t \to \infty$ limit of above probabilities and probability densities. Also standard perturbation formalism gives only those limit results. Of course, LRM provides information about those limit quantities as well. However, LRM provides in addition detailed information about probabilities $w_\tau^a(t)$ to find the state $\left|\Psi(t)\right\rangle$ at each particular time t in the eigenvalue band τ, as well as detailed probability densities $\rho_\tau^a(\varepsilon, t)$ to find this state in the eigenvalue band τ at each particular time t and with each particular eigenvalue ε. This additional information could be utilized, with an appropriate experimental set up, in order to enhance as much as possible transition probabilities into the appropriately selected final states.

CONCLUSION

In the previous chapters Low Rank Modification (LRM) was described. This approach is a general mathematical method by which one can express the eigenvalues and the eigenstates of the modified system $\mathbf{C}$ in terms of the eigenvalues and the eigenstates of the parent system $\boldsymbol{A}$. Unlike perturbation expansion, LRM is exact however large “modification” of the original system $\boldsymbol{A}$. The only requirement on this method is that the operators which represent modification of the parent system $\boldsymbol{A}$ have finite rank. Numerical complexity of LRM depends essentially on the rank of those operators.

LRM was originally developed for finite-dimensional time-independent systems [8]. Those systems are represented by generalized matrix eigenvalue equations that may contain arbitrary matrices of any type, not necessarily Hermitean [8]. In such a general formulation, left and right eigenstates may differ. However, in physics and chemistry most important are Hermitean eigenvalue equations. Hence only such equations are treated here.

In LRM it is convenient to distinguish “internal” and “external” modifications of the parent system $\boldsymbol{A}$. In an internal modification modified system $\mathbf{C}$ has the same dimension as the parent system $\boldsymbol{A}$. An example of internal modification of a finite-dimensional system is replacement of one or several atoms in a large molecule with various isotopes. Such a modification of the original system has a strong influence on molecular vibrations. In addition, provided relatively few isotopes are substituted, Such a modification is represented by operators that have relatively low rank. Hence vibrational isotope effect can be efficiently treated within the LRM formalism. In the similar way can be treated internal modifications of infinite-dimensional systems. As an example consider a perfect infinite-dimensional solid. Due to the periodicity of the effective potential one can obtain more or less reliable solution to this system [9]. However such perfect solid is an ideal approximation of a real solid, and most important and most interesting properties of real solids are due to various impurities and/or defects, existence of a surface which may generate surface states, etc. [7,9,10]. All such modifications of the original system break periodicity of this system and in addition those modifications are usually not small. Hence such modifications cannot be efficiently treated within the standard perturbation formalism. However, introduction of impurities and defects, as long as those modifications do not produce a global change of the crystal structure, can be very well approximated with operators that have finite rank. Though the creation of a crystal surface is not a low rank modification, it can still be approximated as such a modification. One can, for example, approximate a real two-dimensional crystal surface which is infinite-dimensional with a finite portion of this surface. This is of course an approximation. Nevertheless, to the extent this approximation is acceptable, all problems associated with the creation of a surface, such as surface states, distortion of few unit cells close to the surface and alike can be treated within the LRM formalism.

In an external modification parent system $\boldsymbol{A}$ interacts with an external finite-dimensional system $\boldsymbol{B}$ that is outside this parent system. Systems $\boldsymbol{A}$ and $\boldsymbol{B}$ that interact with each other form a combined system $\mathbf{C}$. An example of such a modification involving infinite-dimensional systems is the interaction of a molecule with a radiation. Molecule in isolation can be approximated with a finite-dimensional system $\boldsymbol{B}$. Radiation in isolation can be approximated with an infinite dimensional system $\mathbf{A}$. Reliable approximate solution to this system is known since this system essentially represents a free electromagnetic field. LRM provides (within the given approximations) an exact solution of the combined system $\mathbf{C}$. Within the LRM formalism one can describe time-independent effects such as shift of molecular eigenvalues due to the interaction with radiation as well as broadening of those levels due to this interaction. One can also describe time-dependent properties such as probabilities and probability densities for the transitions between various eigenstates of this molecule. Since the coupling with the radiation is very weak, all those effects can be efficiently described within the standard perturbation expansion [1, 2]. Nevertheless, LRM provides a new way of describing all such effects.

As another example of the external modification consider the interaction of a molecule situated on a surface of a solid with this solid. Unlike the interaction of a molecule with radiation, this interaction is usually so strong that standard perturbation expansion fails. Here LRM offers a possibility for completely new and innovative approach to such problems.

In conclusion, there are many important problems which can be treated within the LRM formalism and which involve either external or internal modifications of known finite and infinite-dimensional systems. LRM can be also generalized to those cases where both types of modifications, external and internal, are simultaneously present. Even in the case of those systems that can be efficiently treated by some other known method (such as interaction of matter with radiation), LRM offers a new insight and a new way of thinking about such systems. As Sir William Brag remarked: “The most important thing in science is not so much to obtain new facts, as to discover new ways of thinking about them”. LRM hopefully offers a new way of thinking about many old problems.

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