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Exact treatment of generalized modifications of finite-dimensional systems by the LRM approach

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Abstract   LRM (Low Rank Modification) is a mathematical method that produces eigenvalues and eigenstates of generalized eigenvalue equations. It is similar to the perturbation expansion in that it assumes the knowledge of the eigenvalues and eigenstates of some related (unperturbed) system. However, unlike perturbation expansion, LRM produces correct results however large the modification of the original system. LRM of finite-dimensional systems is here generalized to the combined (external and internal) modifications. Parent n-dimensional system $\mathbf{A}_n$ containing n eigenvalues λ_i and n eigenstates $|\Phi_i\rangle$ is described by the generalized $n \times n$ eigenvalue equation. In an external modification system $\mathbf{A}_n$ interacts with another ρ-dimensional system $\mathbf{B}_\rho$ which is situated outside the system $\mathbf{A}_n$. In an internal modification relatively small σ-dimensional subsystem of the parent system $\mathbf{A}_n$ is modified. Modified system $\mathbf{C}_{n+\rho}$ that contains external as well as internal modifications is described by the generalized $(n + \rho) \times (n + \rho)$ eigenvalue equation. This system has $(n + \rho)$ eigenvalues ε_s and $(n + \rho)$ corresponding eigenstates $|\Psi_s\rangle$. In LRM this generalized $(\rho + n) \times (\rho + n)$ eigenvalue equation is replaced with a (nonlinear) $(\rho + \sigma) \times (\rho + \sigma)$ equation which produces all eigenvalues $\varepsilon_s \notin \{\lambda_i\}$ and all the corresponding eigenstates $|\Psi_s\rangle$ of $\mathbf{C}_{n+\rho}$. Another equation produces remaining solutions (if any) that satisfy $\varepsilon_s \in \{\lambda_i\}$. Those two equations produce exact solution of the modified system $\mathbf{C}_{n+\rho}$. If $(\rho + \sigma)$ is small with respect to n, this approach is numerically much more efficient than a standard diagonalization of the original generalized eigenvalue equation. Unlike perturbation expansion, LRM produces exact results, however large modification of the parent system $\mathbf{A}_n$.

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1 Introduction

Low Rank Modification (LRM) is a general mathematical method by which one can
obtain eigenvalues and eigenstates of a modified quantum system if eigenvalues and
eigenstates of some related parent system are known [1–3]. In this respect this method
is similar to the perturbation expansion which also produces a solution of a perturbed
system if the solution of some related unperturbed system is known [4,5]. However,
there are profound differences between those two methods. Perturbation approach
relies on power series expansion and it is numerically efficient only if the perturba-
tion of the original system is relatively small [4–7]. In addition, if this perturbation is
sufficiently large, power series may diverge and in this case perturbation expansion
fails. However, in many cases of interest are exactly such modifications of the original
system which represent a large perturbation. For example, in a study of the vibrational
isotope effect in the harmonic approximation replacement of an atom by an isotope is
a large perturbation. Similarly, replacement of an atom in a large molecule by a het-
eroatom is also a large perturbation. The same applies to a local defects and impurities
of an infinite solid, etc. Such and similar modifications of the original system cannot
be efficiently treated by the perturbation expansion. Unlike perturbation approach,
LRM produces exact solution (eigenvalues and eigenstates of the modified system),
however large modification of the original parent system. Numerical efficiency of
LRM depends mainly on the rank of the operators that represent modification of this
system, and not on the magnitude of those operators. In addition, LRM applies to
finite-dimensional [1,2] as well as to infinite dimensional systems [3]. It also applies
to time-dependent systems [8,9]. Present paper is restricted to the generalization of
the original LRM approach to the most general modifications of finite-dimensional
systems.

Parent system **A** can be modified in two different ways. This system can be modi-
fied externally as well as internally. In an external modification system **A** is modified
by the interaction with another external system **B**. In an internal modification rela-
tively small portion inside the system **A** is modified. Previous development of LRM
approach was restricted either to external or to internal modifications of the parent
system. The aim of this paper is to generalize LRM approach to the case when the
finite-dimensional parent system **A** is simultaneously modified by an arbitrary exter-
nal as well as by an arbitrary internal modification. Generalization of LRM approach
to such combined modifications enables efficient treatment of arbitrary Hermitean
modifications of finite-dimensional systems.

2 Parent system

Consider a finite-dimensional time-independent quantum system $\mathbf{A}_n$ that contains
n eigenvalues λ_i and n eigenstates $|\Phi_i\rangle$. Usually those eigenvalues and eigenstates

satisfy a standard eigenvalue equation $\mathbf{H}_a|\Phi_i\rangle = \lambda_i|\Phi_i\rangle$ $(i = 1, \ldots, n)$ where $\mathbf{H}_a$ is a Hermitean operator, Hamiltonian of a system. However, in some cases instead of this standard eigenvalue equation one has to consider a generalized eigenvalue equation

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

where $\mathbf{S}_a$ is positive-definite Hermitean operator. Eigenvalues λ_i of (1a) are real and the corresponding eigenstates $|\Phi_i\rangle$ span n-dimensional space X_n^a. Those eigenstates can be orthonormalized according to (see Appendix)

$$\langle\Phi_i|\mathbf{S}_a|\Phi_j\rangle = \delta_{ij}, \qquad i, j = 1, \ldots, n, \tag{1b}$$

Since the states $|\Phi_i\rangle$ form a complete set in X_n^a, expression (1b) implies

$$\mathbf{I}_a = \sum_i^n |\Phi_i\rangle\langle\Phi_i|\mathbf{S}_a = \sum_i^n \mathbf{S}_a|\Phi_i\rangle\langle\Phi_i|. \tag{1c}$$

where $\mathbf{I}_a$ is a unit operator in the space X_n^a.

Solution of a generalized eigenvalue Eq. (1a) is for example required in the treatment of 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 [10,11]. Those operators are Hermitean and in addition operator $\mathbf{M}$ is positive definite.

The system $\mathbf{A}_n$ described by the eigenvalue Eq. (1a) will be referred to as a *parent system*.

2.1 Internal and external modifications of a parent system

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

In the case of an internal modification and in the absence of the external modification, modified system $\mathbf{C}_n$ has the same dimension as the parent system $\mathbf{A}_n$. In particular, eigenstates $|\Psi_s\rangle$ of $\mathbf{C}_n$ and eigenstates $|\Phi_i\rangle$ of $\mathbf{A}_n$ span the same space X_n^a. In the most general formulation, internal modification of the parent system is represented by two operators $\mathbf{V}_a$ and $\mathbf{P}_a$. Operator $\mathbf{V}_a$ modifies operator $\mathbf{H}_a$ of a parent system, while operator $\mathbf{P}_a$ modifies operator $\mathbf{S}_a$ of this system. Those operators are Hermitean, and they act in the space X_n^a. System $\mathbf{C}_n$ which is modified by an internal modification is hence described by the generalized eigenvalue equation

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

where β is a coupling parameter. This parameter controls the strength of the internal modification.

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 [12,13]. 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 $\mathbf{O}$ [12,13]. 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 a single operator $\mathbf{O}$ can be generalized to the notion of *rank* and *range* of the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$. By definition, *range* of this modification 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 $\sigma \leq \sigma_h + \sigma_s$ 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 internal 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/or $\mathbf{P}_a$.

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

$$\langle \mu|\nu\rangle = \delta_{\mu\nu}, \qquad \mu, \nu = 1, \ldots, \sigma, \tag{2a}$$

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

$$\langle \alpha|\beta\rangle = \delta_{\alpha\beta}, \qquad \alpha, \beta = 1, \ldots, n, \tag{2b}$$

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 $\{|\alpha\rangle\}$ Eq. (1a) is an $n \times n$ matrix eigenvalue equations, while in the base $\{|\mu\rangle\}$ operators $\mathbf{V}_a$ and $\mathbf{P}_a$ are $\sigma \times \sigma$ matrices. Projection operator $\mathbf{I}_{\text{int}}$ on the space X_σ^{int} can be expressed in terms of the vectors $|\mu\rangle$ as

$$\mathbf{I}_{\text{int}} = \sum_{\mu}^{\sigma} |\mu\rangle\langle\mu|, \tag{2c}$$

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

$$\mathbf{I}_a = \sum_{\alpha}^{n} |\alpha\rangle\langle\alpha|. \tag{2d}$$

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

$$\mathbf{V}_a = \mathbf{I}_{\text{int}} \mathbf{V}_a \mathbf{I}_{\text{int}}, \qquad \mathbf{P}_a = \mathbf{I}_{\text{int}} \mathbf{P}_a \mathbf{I}_{\text{int}}. \qquad (3)$$

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 [10,11]. However, such substitutions have significant influence on molecular vibrations [10,11]. Given frequencies and normal modes of a parent molecule $\mathbf{A}_n$, of interest are frequencies and normal modes of various isotopomers $\mathbf{C}_n$ of this molecule. If in a large molecule relatively few atoms are substitute with an isotope, dimension of the corresponding interaction space is relatively small and in this case LRM is numerically very efficient [14]. 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 $\mathbf{A}_n$ interacts with another ρ-dimensional system $\mathbf{B}_\rho$ which is outside the system $\mathbf{A}_n$. 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 (1a), system $\mathbf{B}_\rho$ alone is described by the generalized eigenvalue equation

$$\mathbf{H}_b|\Theta_r\rangle = E_r \mathbf{S}_b|\Theta_r\rangle, \qquad r = 1, \ldots, \rho, \qquad (4a)$$

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 (4a) are real. In analogy to (1b), the corresponding eigenstates $|\Theta_r\rangle$ can be orthonormalized according to:

$$\langle\Theta_r|\mathbf{S}_b|\Theta_t\rangle = \delta_{rt}, \qquad r, t = 1, \ldots, \rho. \qquad (4b)$$

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

$$\mathbf{I}_b = \sum_r^\rho |\Theta_r\rangle\langle\Theta_r|\mathbf{S}_b = \sum_r^\rho \mathbf{S}_b|\Theta_r\rangle\langle\Theta_r|. \qquad (4c)$$

where $\mathbf{I}_b$ is a projection operator on the space X_ρ^b. The system $\mathbf{B}_\rho$ described by the eigenvalue Eq. (4a) will be referred to as a *base system*.

Inclusion of the interaction between initially non-interacting systems $\mathbf{B}_\rho$ and $\mathbf{A}_n$ 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 $\mathbf{A}_n$ of the combined system $\mathbf{C}_{n+\rho}$ is described by the modification operators $\mathbf{V}$ and $\mathbf{P}$. Those operators connect mutually distinct spaces X_ρ^b and X_n^a, and they vanish over the space X_ρ^b as well as over the space X_n^a.

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

$$\langle r|t\rangle = \delta_{rt}, \qquad r, t = 1, \ldots, \rho, \tag{5a}$$

Projection operator $\mathbf{I}_b$ on the space X_ρ^b can be expressed in terms of the vectors $|r\rangle$ as

$$\mathbf{I}_b = \sum_r^\rho |r\rangle\langle r|. \tag{5b}$$

as well as in terms of the eigenstates $|\Theta_r\rangle$ of the system $\mathbf{B}_\rho$ according to (4c).

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 in the absence of the external modification operator $\mathbf{I}_a$ is a unit operator since X_n^a is the entire space considered, while in the presence of the external modification $\mathbf{I}_a$ is a projection operator on the space X_n^a, subspace of the space $X_{n+\rho}^c$.

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

$$\mathbf{V} = \mathbf{I}_b\mathbf{V}\mathbf{I}_a + \mathbf{I}_a\mathbf{V}\mathbf{I}_b, \qquad \mathbf{P} = \mathbf{I}_b\mathbf{P}\mathbf{I}_a + \mathbf{I}_a\mathbf{P}\mathbf{I}_b. \tag{6}$$

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 $(\sigma + \rho) << n$. By definition, quantity σ is the rank of the generalized internal modification $(\mathbf{V}_a, \mathbf{P}_a)$. The corresponding interaction space X_σ^{int} is a range of this modification. On the other hand, quantity ρ is the dimension of the base system $\mathbf{B}_\rho$ that interacts with the n-dimensional parent system $\mathbf{A}_n$. By the known theorem of algebra, rank of the $n \times m$ matrix is at most $\min(n, m)$ [12,13]. In a matrix form operator $\mathbf{V}$ is represented by one (ρ, n) and one (n, ρ) nonzero sub-matrix. The same applies to the operator $\mathbf{P}$. One finds that if $n \geq \rho$ (which is required in order for LRM to be numerically efficient) rank of the generalized external modification $(\mathbf{V}, \mathbf{P})$ is at most 2ρ. Dimension ρ of the space X_ρ^b is hence intimately connected with the rank of this modification. Hence from the more general point of view, external modifications as well as internal modifications are both low rank modifications.

2.2 Combined modifications of finite-dimensional systems

Modified system $\mathbf{C}_{n+\rho}$ that contains both, internal as well as external modifications of the parent system, is described by the generalized eigenvalue equation

$$\mathbf{H}_c |\Psi_s\rangle = \varepsilon_s \mathbf{S}_c |\Psi_s\rangle, \qquad s = 1, \ldots, n + \rho, \tag{7a}$$

where

$$\mathbf{H}_c = \mathbf{H}_a + \mathbf{H}_b + \beta\,(\mathbf{V} + \mathbf{V}_a), \qquad \mathbf{S}_c = \mathbf{S}_a + \mathbf{S}_b + \beta\,(\mathbf{P} + \mathbf{P}_a), \tag{7b}$$

Fig. 1 Combined modifications of a parent system. **a** Parent system $\mathbf{A}_n$ and base system $\mathbf{B}_\rho$. **b** Modified system $\mathbf{C}_{n+\rho}$. Parent system $\mathbf{A}_n$ is modified externally by the interaction $(\mathbf{V}, \mathbf{P})$ with the base system $\mathbf{B}_\rho$, and internally by modification operators $(\mathbf{V}_a, \mathbf{P}_a)$
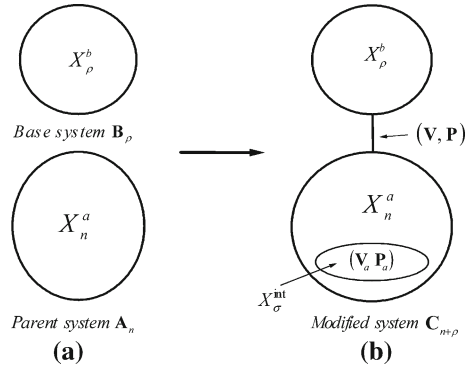
and where β is a coupling parameter. This parameter is introduced for convenience, in order to have more direct control over the strength of the modification. In particular, if $\beta = 0$ expression (7a) reduces to the expressions (1a) and (4a) that describe parent system $\mathbf{A}_n$ and base system $\mathbf{B}_\rho$ in isolation, i.e. without mutual interaction. If β is small one has a small perturbation of the original system and in this case LRM expressions should 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 [2,3].

Operators $\mathbf{H}_c$ and $\mathbf{S}_c$ in expressions (7b) are by construction Hermitean. In addition, in order to guarantee the reality of the modified eigenvalues ε_s, operator $\mathbf{S}_c$ is required to be positive definite in the $(n + \rho)$-dimensional combined space $X^c_{n+\rho}$. Eigenstates $|\Psi_s\rangle$ of (7a) can be hence orthonormalised according to

$$\langle\Psi_s|\mathbf{S}_s|\Psi_p\rangle = \delta_{sp}, \qquad s, p = 1, \ldots, n + \rho. \qquad (7c)$$

Since operators $\mathbf{S}_a$ and $\mathbf{S}_b$ are positive-definite in spaces X^a_n and X^b_ρ, respectively, if β is sufficiently small operator $\mathbf{S}_c$ is guaranteed to be positive definite in the combined space $X^c_{n+\rho}$. However, depending on the modification operators $\mathbf{P}$ and $\mathbf{P}_a$, as β increases for some sufficiently large β this may be not the case. Condition that operator $\mathbf{S}_c$ should be positive definite hence imposes some restrictions on the operators $\mathbf{P}$ and $\mathbf{P}_a$, as well as on the parameter β. For example, if $\mathbf{P} = \mathbf{P}_a = 0$ operator $\mathbf{S}_c$ is positive definite for each β, however large. However, if $\mathbf{P} \neq 0$ and/or $\mathbf{P}_a \neq 0$, this is not necessarily so. Concerning modification operators $\mathbf{V}$ and $\mathbf{V}_a$, there are no restrictions on those operators, except that they should be Hermitean and that they should satisfy expressions (6) and (3), respectively.

Combined modification of a parent system $\mathbf{A}_n$ is shown schematically in Fig. 1

Each eigenstate $|\Psi_s\rangle$ of (7a) can be written as a linear combination

$$|\Psi_s\rangle = |\Psi^a_s\rangle + |\theta_s\rangle, \qquad (8a)$$

where

$$|\Psi^a_s\rangle = \mathbf{I}_a|\Psi_s\rangle \in X^a_n, \qquad |\theta_s\rangle = \mathbf{I}_b|\Psi_s\rangle \in X^b_\rho, \qquad (8b)$$

are projections of this eigenstate on subspaces X_n^a and X_ρ^b, respectively. One can consider also the state $|\varphi_s\rangle$

$$|\varphi_s\rangle = \mathbf{I}_{\text{int}}|\Psi_s\rangle \in X_\sigma^{\text{int}}. \tag{8c}$$

which is a projection of the eigenstate $|\Psi_s\rangle$ on the interaction space X_σ^{int}. In bases $\{|\mu\rangle\}$ and $\{|r\rangle\}$ components $|\varphi_s\rangle$ and $|\theta_s\rangle$ of the modified eigenstate $|\Psi_s\rangle$ can be written as

$$|\varphi_s\rangle = \sum_\mu^\sigma C_\mu^{(s)}|\mu\rangle, \qquad |\theta_s\rangle = \sum_r^\rho B_r^{(s)}|r\rangle. \tag{9}$$

3 LRM treatment of the combined modification

Consider combined modification of the n-dimensional parent system $\mathbf{A}_n$ described by the generalized eigenvalue Eq. (1a). This system is modified externally with the generalized modification $(\mathbf{V}, \mathbf{P})$ that satisfies expressions (6) and internally with the generalized modification $(\mathbf{V}_a, \mathbf{P}_a)$ that satisfies expressions (3). Combined system $\mathbf{C}_{n+\rho}$ is described by the generalized eigenvalue Eq. (7a). In analogy to the perturbation expansion, one assumes that eigenvalues λ_i and eigenstates $|\Phi_i\rangle$ of the system $\mathbf{A}_n$ are known. From those quantities one can construct Hermitean operator $\overline{\mathbf{\Omega}}(\varepsilon)$ which depends on a real parameter ε:

$$\overline{\mathbf{\Omega}}(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)}^n \frac{|\Phi_i\rangle\langle\Phi_i|}{\varepsilon - \lambda_i}. \tag{10}$$

If ε equals some eigenvalue λ_i of the eigenvalue Eq. (1a) ($\varepsilon = \lambda_i$), the corresponding term or terms is excluded from the summation in (10).

Operator $\overline{\mathbf{\Omega}}(\varepsilon)$ is associated with the parent system $\mathbf{A}_n$ and it acts in the space X_n^a of this system. 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 nonzero state $|\psi\rangle \in X_n^a$. Operator $\overline{\mathbf{\Omega}}(\varepsilon)$ is in this case nonsingular in X_n^a and hence $rank\left(\overline{\mathbf{\Omega}}(\varepsilon)\right) = n$. However, if $\varepsilon = \lambda_j \in \{\lambda_i\}$ one has $\overline{\mathbf{\Omega}}(\varepsilon)|\Phi_j\rangle = 0$ and in this case $rank\left(\overline{\mathbf{\Omega}}(\varepsilon)\right) < n$.

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

$$\mathbf{\Omega}_b(\varepsilon) = (\mathbf{V} - \varepsilon\mathbf{P})\overline{\mathbf{\Omega}}(\varepsilon)(\mathbf{V} - \varepsilon\mathbf{P}), \tag{11a}$$

This operator is a key quantity in the LRM formalism involving external modifications of finite dimensional quantum systems. Due to the expressions (6), 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

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

(11b)

In analogy to (11), with the internal modification of the parent system $\mathbf{A}_n$ is associated Hermitean operator $\boldsymbol{\Omega}_a(\varepsilon)$

$$\boldsymbol{\Omega}_a(\varepsilon) = (\mathbf{V}_a - \varepsilon\mathbf{P}_a)\overline{\boldsymbol{\Omega}}(\varepsilon)(\mathbf{V}_a - \varepsilon\mathbf{P}_a),$$

(12a)

This operator is a key quantity in the LRM formalism involving internal modifications of finite dimensional quantum systems. Due to the expressions (3), operator $\boldsymbol{\Omega}_a(\varepsilon)$ has non-vanishing matrix elements only between the states contained in the interaction space X_σ^{int}. In the base $\{|\mu\rangle\}$ of this space this operator is a $\sigma \times \sigma$ matrix with matrix elements

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

(12b)

Finally in the case of the combined modification, in addition to the operators $\boldsymbol{\Omega}_a(\varepsilon)$ and $\boldsymbol{\Omega}_b(\varepsilon)$ one has to consider operators $\boldsymbol{\Omega}_{ab}(\varepsilon)$ and $\boldsymbol{\Omega}_{ba}(\varepsilon)$. Operator $\boldsymbol{\Omega}_{ab}(\varepsilon)$ is defined as

$$\boldsymbol{\Omega}_{ab}(\varepsilon) = (\mathbf{V}_a - \varepsilon\mathbf{P}_a)\overline{\boldsymbol{\Omega}}(\varepsilon)(\mathbf{V} - \varepsilon\mathbf{P}),$$

(13a)

This operator connects σ-dimensional interaction space X_σ^{int} with the ρ-dimensional space X_ρ^{b} of the base system $\mathbf{B}_\rho$. It has matrix elements

$$\Omega_{\mu r}^{ab}(\varepsilon) \equiv \langle\mu|\boldsymbol{\Omega}_{ab}(\varepsilon)|r\rangle = \sum_{i(\lambda_i \neq \varepsilon)}^{n} \frac{\langle\mu|\mathbf{V}_a - \varepsilon\mathbf{P}_a|\Phi_i\rangle\langle\Phi_i|\mathbf{V} - \varepsilon\mathbf{P}|r\rangle}{\varepsilon - \lambda_i},$$
$$\mu = 1,\ldots,\sigma, \quad r = 1,\ldots,\rho.$$

(13b)

Operator $\boldsymbol{\Omega}_{ba}(\varepsilon)$ is a complex conjugate of the operator $\boldsymbol{\Omega}_{ab}(\varepsilon)$:

$$\boldsymbol{\Omega}_{ba}(\varepsilon) = \Omega_{ab}(\varepsilon)^{*} = (\mathbf{V} - \varepsilon\mathbf{P})\overline{\boldsymbol{\Omega}}(\varepsilon)(\mathbf{V}_a - \varepsilon\mathbf{P}_a).$$

(13c)

Note that operators $\boldsymbol{\Omega}_{ab}(\varepsilon)$ and $\boldsymbol{\Omega}_{ba}(\varepsilon)$ are not Hermitean. However, the sum $\boldsymbol{\Omega}_{ab}(\varepsilon) + \boldsymbol{\Omega}_{ba}(\varepsilon)$ of those operators is Hermitian.

In order to construct operator $\overline{\boldsymbol{\Omega}}(\varepsilon)$ according to the expression (10), one has to know all n eigenvalues λ_i of a parent system and in addition one should have a complete knowledge about all the corresponding eigenstates $|\Phi_i\rangle$. However, in order to construct operators $\boldsymbol{\Omega}_a(\varepsilon)$, $\boldsymbol{\Omega}_b(\varepsilon)$ and $\boldsymbol{\Omega}_{ab}(\varepsilon)$ it is not necessary to have complete

information about eigenstates $|\Phi_i\rangle$ of $\mathbf{A}_n$. In particular, in order to construct operator $\mathbf{\Omega}_b(\varepsilon)$ associated with a base system $\mathbf{B}_\rho$ one has to know $2\rho n$ matrix elements $\langle r|\mathbf{V}|\Phi_i\rangle$ and $\langle r|\mathbf{P}|\Phi_i\rangle (r = 1, \ldots, \rho; \ i = 1, \ldots, n)$ as well as n eigenvalues λ_i of the parent system. This makes a total of $(2\rho + 1)n$ quantities. Similarly, in order to construct operator $\mathbf{\Omega}_a(\varepsilon)$ associated with the interaction space X_σ^{int} one has to know $2\sigma n$ matrix elements $\langle \mu|\mathbf{V}_a|\Phi_i\rangle$ and $\langle \mu|\mathbf{P}_a|\Phi_i\rangle (\mu = 1, \ldots, \sigma; \ i = 1, \ldots, n)$ as well as the same n eigenvalues λ_i of the parent system. In order to construct operator $\mathbf{\Omega}_{ab}(\varepsilon)$ in addition to operators $\mathbf{\Omega}_a(\varepsilon)$ and $\mathbf{\Omega}_b(\varepsilon)$, no new quantities are required. Hence in order to construct all three operators one has to know only $(2\rho + 2\sigma + 1)n$ 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 $(\rho + \sigma) << n$, construction of the operators $\mathbf{\Omega}_a(\varepsilon)$, $\mathbf{\Omega}_b(\varepsilon)$ and $\mathbf{\Omega}_{ab}(\varepsilon)$ requires much less information than exact specification of all eigenstates $|\Phi_i\rangle$ of (1a).

For the sake of simplicity, operators that act in spaces X_n^a, X_ρ^b, X_σ^{int} and $X_{n+\rho}^c$ will be identified with their representations in bases, $\{|\alpha\rangle\}$, $\{|r\rangle\}$, $\{|\mu\rangle\}$ and $\{|r\rangle, |\alpha\rangle\}$, respectively. For example, representation of the operator $\mathbf{I}_b$ in the base $\{|r\rangle\}$ is a unit matrix with matrix elements $\delta_{rt}(r, t = 1, \ldots, \rho)$. Considered as the operator in the space $X_{n+\rho}^c$, $\mathbf{I}_b$ 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, X_σ^{int} or $X_{n+\rho}^c$.

In the case of finite-dimensional systems 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 some unperturbed eigenvalue $\varepsilon_s(0)$. This unperturbed eigenvalue coincides either with some eigenvalue λ_i of a parent system $\mathbf{A}_n$, and/or with some eigenvalue E_r of a base system $\mathbf{B}_\rho$. 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. Hence perturbation treatment of degenerate eigenstates differs from the perturbation treatment of non-degenerate eigenstates [4–7]. In this respect there are major differences between a perturbation approach and a LRM approach. In the LRM approach one treats in a different way *cardinal* $(\varepsilon_s \notin \{\lambda_i\})$ and *singular* $(\varepsilon_s \in \{\lambda_i\})$ eigenvalues and corresponding eigenstates of the modified system [2,3,14,15]. This distinction is qualitatively different from the distinction between degenerate and non-degenerate eigenstates in the perturbation theory. 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 $\mathbf{B}_\rho$. On the other hand, each singular eigenvalue ε_s of the modified system coincides with some eigenvalue λ_j of the parent system. Singular solutions are thus rather special solutions of the modified system.

3.1 Cardinal solutions of the modified system

As shown in the Appendix, concerning cardinal solutions of $\mathbf{C}_{n+\rho}$ one has:

Theorem 1 (cardinal eigenvalues and eigenstates)
Let eigenstates $|\Phi_i\rangle$ *of (1a) be orthonormalized according to (1b) and let* $\beta \neq 0$. *Then*
(a) $\varepsilon_s \notin \{\lambda_i\}$ *is a cardinal eigenvalue of the modified eigenvalue Eq. (7a) if and only if it satisfies*

$$\left[\begin{array}{cc} \beta^2 \mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s \mathbf{S}_b & \beta^2 \mathbf{\Omega}_{ba}(\varepsilon_s) \\ \beta^2 \mathbf{\Omega}_{ab}(\varepsilon_s) & \beta^2 \mathbf{\Omega}_a(\varepsilon_s) + \beta (\varepsilon_s \mathbf{P}_a - \mathbf{V}_a) \end{array} \right] \left| \begin{array}{c} \theta_s \\ \varphi_s \end{array} \right| = 0, \quad (14a)$$

where

$$|\theta_s\rangle \in X_\rho^b, \qquad |\varphi_s\rangle \in X_\sigma^{\text{int}}, \quad (14b)$$

and where the eigenstate $|\Xi_s\rangle \equiv |\theta_s\rangle + |\varphi_s\rangle$ *of (14a) is not zero. In other words, either* $|\theta_s\rangle \neq 0$ *and/or* $|\varphi_s\rangle \neq 0$.
   In the base $\{|r\rangle, |\mu\rangle\}$ *expression (14a) is a* $(\rho + \sigma) \times (\rho + \sigma)$ *matrix equation. Each cardinal eigenvalue* $\varepsilon_s \notin \{\lambda_i\}$ *of (7a) is hence a root of the* $(\rho + \sigma) \times (\rho + \sigma)$ *determinant* $h(\varepsilon)$

$$h(\varepsilon) \equiv \left| \begin{array}{cc} \beta^2 \mathbf{\Omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon \mathbf{S}_b & \beta^2 \mathbf{\Omega}_{ba}(\varepsilon) \\ \beta^2 \mathbf{\Omega}_{ab}(\varepsilon) & \beta^2 \mathbf{\Omega}_a(\varepsilon) + \beta (\varepsilon \mathbf{P}_a - \mathbf{V}_a) \end{array} \right| = 0. \quad (14c)$$

   (b) $|\Psi_s\rangle$ *is an eigenstate of the eigenvalue Eq. (7a) with the eigenvalue* $\varepsilon_s \notin \{\lambda_i\}$ *if and only if it is a linear combination*

$$|\Psi_s\rangle = \beta \sum_i^n \frac{\langle \Phi_i | \mathbf{V} - \varepsilon_s \mathbf{P} | \theta_s \rangle + \langle \Phi_i | \mathbf{V}_a - \varepsilon_s \mathbf{P}_a | \varphi_s \rangle}{\varepsilon_s - \lambda_i} |\Phi_i\rangle + |\theta_s\rangle, \quad (15a)$$

where the states $|\theta_s\rangle$ *and* $|\varphi_s\rangle$ *are obtained as a solution to (14a) that corresponds to the eigenvalue* $\varepsilon = \varepsilon_s$.
   (c) Projection of the cardinal eigenstate (15a) on the base space X_ρ^b *equals* $|\theta_s\rangle$, *while projection of this eigenstate on the interaction space* X_σ^{int} *equals* $|\varphi_s\rangle$:

$$\mathbf{I}_b |\Psi_s\rangle = |\theta_s\rangle \in X_\rho^b, \qquad \mathbf{I}_{\text{int}} |\Psi_s\rangle = |\varphi_s\rangle \in X_\sigma^{\text{int}}. \quad (15b)$$

   Above theorem produces all cardinal eigenvalues and eigenstates of the modified system. Note that the key LRM Eq. (14a) which produces those solutions is manifestly Hermitean.
   Concerning degenerate cardinal solutions, as shown in the Appendix one has

Lemma 1 *Let* $|\Psi_{sk}\rangle (k = 1, \ldots \kappa)$ *be* κ *degenerate cardinal eigenstates of the modified system that have eigenvalue* $\varepsilon_s \notin \{\lambda_i\}$. *Those eigenstates are linearly independent if and only if the corresponding eigenstates* $|\Xi_{sk}\rangle = |\theta_{sk}\rangle + |\varphi_{sk}\rangle (k = 1, \ldots \kappa)$ *of the LRM Eq. (14a) are linearly independent.*

According to this lemma, degeneracy of cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of the modified system $\mathbf{C}_{n+\rho}$ equals nullity of the matrix that determines LRM Eq. (14a). Since this is a $(\rho + \sigma) \times (\rho + \sigma)$ matrix, each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of the modified system $\mathbf{C}_{n+\rho}$ can be at most $(\rho + \sigma)$-degenerate.

Since operators $\mathbf{\Omega}_a(\varepsilon)$, $\mathbf{\Omega}_b(\varepsilon)$ and $\mathbf{\Omega}_{ab}(\varepsilon)$ depend on the parameter ε, LRM expression (14a) is a nonlinear eigenvalue equation. According to (15b), eigenstate $|\Xi_s\rangle = |\theta_s\rangle + |\varphi_s\rangle$ of this equation determines projections of the corresponding cardinal eigenstate $|\Psi_s\rangle$ of the modified system on spaces X_ρ^b and X_σ^{int}, respectively. In conclusion, Eq. (14a) is a $(\rho + \sigma) \times (\rho + \sigma)$ nonlinear equation that acts entirely in the base space X_ρ^b and in the interaction space X_σ^{int}. However, though this equation acts only in those two spaces, it determines according to (15a) complete cardinal eigenstate $|\Psi_s\rangle \in X_{n+\rho}^c$ of the modified system $\mathbf{C}_{n+\rho}$.

Unlike LRM Eq. (14a) which is a $(\rho + \sigma) \times (\rho + \sigma)$ nonlinear equation, original eigenvalue Eq. (7a) that describes modified 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 Eq. (14a) is still only $(\rho + \sigma)$. Nevertheless, this LRM equation produces exact solutions of the $(\rho + n) \times (\rho + n)$ eigenvalue Eq. (7a).

Theorem 1 produces all cardinal eigenstates of the modified system in the case $\beta \neq 0$. In the trivial case $\beta = 0$ LRM formalism implies that cardinal eigenstates of the modified system $\mathbf{C}_{n+\rho}$ are those eigenstates $|\Theta_s\rangle$ of $\mathbf{B}_\rho$ that have eigenvalue $E_s \notin \{\lambda_j\}$ (see Appendix). This is in complete agreement with the definition of cardinal solutions. Namely if $\beta = 0$ all eigenstates $|\Phi_j\rangle$ of $\mathbf{A}_n$ as well as all eigenstates $|\Theta_s\rangle$ of $\mathbf{B}_\rho$ are at the same time eigenstates of $\mathbf{C}_{n+\rho}$ with the same eigenvalues. Since by definition cardinal eigenstates of modified system are those eigenstates of this system that have eigenvalue $\varepsilon_s \notin \{\lambda_j\}$, it follows that in the case $\beta = 0$ cardinal eigenstates of the modified system are those and only those eigenstates $|\Theta_s\rangle$ of $\mathbf{B}_\rho$ that have eigenvalue $E_s \notin \{\lambda_j\}$.

3.2 Singular solutions of the modified system

By definition, each singular eigenvalue ε_s of the modified system $\mathbf{C}_{n+\rho}$ coincides with some eigenvalue λ_j of the parent system $\mathbf{A}_n$: $\varepsilon_s \equiv \lambda_j \in \{\lambda_i\}$. Concerning singular eigenvalues and eigenstates of the modified system, as shown in the Appendix one has:

Theorem 2 (singular solutions)
Let λ_j be a η_j-degenerate eigenvalue of the eigenvalue Eq. (1a) and let $X_{\eta_j}^j$ be the corresponding η_j-dimensional space spanned by η_j degenerate eigenstates $|\Phi_{jm}\rangle (m = 1, \ldots, \eta_j)$ of (1a). Let further $\mathbf{I}_j$ be the projection operator on the space $X_{\eta_j}^j$ and let $\beta \neq 0$. Then:

(a) $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ is a singular eigenvalue of the modified eigenvalue Eq. (7a) if and only if it satisfies

$$
\begin{bmatrix}
\beta^2\boldsymbol{\Omega}_b(\lambda_j) + \mathbf{H}_b - \lambda_j\mathbf{S}_b & \beta^2\boldsymbol{\Omega}_{ba}(\lambda_j) & \beta\left(\mathbf{V} - \lambda_j\mathbf{P}\right)\mathbf{I}_j \\
\beta^2\boldsymbol{\Omega}_{ab}(\lambda_j) & \beta^2\boldsymbol{\Omega}_a(\lambda_j) + \beta\left(\lambda_j\mathbf{P}_a - \mathbf{V}_a\right) & \beta\left(\mathbf{V}_a - \lambda_j\mathbf{P}_a\right)\mathbf{I}_j \\
\beta\mathbf{I}_j\left(\mathbf{V} - \lambda_j\mathbf{P}\right) & \beta\mathbf{I}_j(\mathbf{V}_a - \lambda_j\mathbf{P}_a) & 0
\end{bmatrix}
$$

$$
\times \begin{bmatrix} \theta_s \\ \varphi_s \\ \chi_s^j \end{bmatrix} = 0, \tag{16a}
$$

where

$$
|\theta_s\rangle \in X_\rho^b, \qquad |\varphi_s\rangle \in X_\sigma^{\mathrm{int}}, \qquad |\chi_s^j\rangle \in X_{\eta_j}^j. \tag{16b}
$$

and where the eigenstate $|\Xi_s\rangle \equiv |\theta_s\rangle + |\varphi_s\rangle + |\chi_s^j\rangle$ of (16a) is not zero.

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

$$
|\Psi_s\rangle = \beta \sum_{i(\lambda_i \neq \lambda_j)} \frac{\langle\Phi_i|\mathbf{V} - \lambda_j\mathbf{P}|\theta_s\rangle + \langle\Phi_i|\mathbf{V}_a - \lambda_j\mathbf{P}_a|\varphi_s\rangle}{\lambda_j - \lambda_i}|\Phi_i\rangle + |\chi_s^j\rangle + |\theta_s\rangle. \tag{16c}
$$

where the states $|\theta_s\rangle$, $|\varphi_s\rangle$ and $|\chi_s^j\rangle$ satisfy (16a) and (16b).

(c) Projection of the singular eigenstate (16c) on the space X_ρ^b equals $|\theta_s\rangle$, while projection of this eigenstate on the interaction space X_σ^{int} equals $|\varphi_s\rangle$:

$$
\mathbf{I}_b|\Psi_s\rangle = |\theta_s\rangle \in X_\rho^b, \qquad \mathbf{I}_{\mathrm{int}}|\Psi_s\rangle = |\varphi_s\rangle \in X_\sigma^{\mathrm{int}}, \tag{17a}
$$

In addition, the state $|\chi_s^j\rangle \in X_{\eta_j}^j$ in (16c) is a linear combination

$$
|\chi_s^j\rangle = \sum_m^{\eta_j} |\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a|\Psi_s\rangle \equiv \mathbf{O}_j|\Psi_s\rangle \in X_{\eta_j}^j, \tag{17b}
$$

where operator $\mathbf{O}_j$ satisfies

$$
\mathbf{O}_j = \sum_m^{\eta j} |\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a, \qquad (\mathbf{O}_j)^2 = \mathbf{O}_j. \tag{17c}
$$

In the special and most important case when $\mathbf{S}_a = \mathbf{I}_a$ is a unit operator in the space X_n^a, operator $\mathbf{O}_j$ equals projection operator $\mathbf{I}_j$. In this case the state $|\chi_s^j\rangle$ equals projection of the singular eigenstate $|\Psi_s\rangle$ on the space $X_{\eta_j}^j$. However, in a general case operator $\mathbf{O}_j$ is not necessarily Hermitean and one has $\mathbf{O}_j \neq \mathbf{I}_j$, though for each state $|\Psi\rangle \in X_{\eta_j}^j$ those two operators still satisfy $\mathbf{I}_j|\Psi\rangle = \mathbf{O}_j|\Psi\rangle = |\Psi\rangle$.

Note that the key LRM expression (16a) which produces singular solutions is manifestly Hermitean. In a matrix form, this expression forms a set of $(\rho + \sigma + \eta_j)$ homogenous linear equations in $(\rho + \sigma + \eta_j)$ unknowns, ρ unknown coefficients $B_r^{(s)}$ that determine the state $|\theta_s\rangle \in X_\rho^b$, σ unknown coefficients $C_\mu^{(s)}$ that determine the state $|\varphi_s\rangle \in X_\sigma^{\text{int}}$, and η_j unknown coefficients $D_m^{(s)}$ that determine the state $|\chi_s^j\rangle \in X_{\eta_j}^j$:

$$|\theta_s\rangle = \sum_r^\rho B_r^{(s)}|r\rangle, \qquad |\varphi_s\rangle = \sum_\mu^\sigma C_\mu^{(s)}|\mu\rangle, \qquad |\chi_s^j\rangle = \sum_m^{\eta_j} D_m^{(s)}|\Phi_{jm}\rangle. \quad (18)$$

As shown in the Appendix, linearly independent solutions of (16a) produce linearly independent eigenstates $|\Psi_s\rangle$ of $\mathbf{C}_{n+\rho}$, and vice versa. Hence:

Lemma 2 *Let $|\Psi_{sk}\rangle (k = 1, \ldots \kappa)$ be κ degenerate singular eigenstates of the modified system that have eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$. Those eigenstates are linearly independent if and only if the corresponding eigenstates $|\Xi_{sk}\rangle \equiv |\theta_{sk}\rangle + |\varphi_{sk}\rangle + |\chi_{sk}^j\rangle$ $(k = 1, \ldots \kappa)$ of the LRM Eq. (16a) are linearly independent.*

According to this lemma, degeneracy of singular eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ of the modified system $\mathbf{C}_{n+\rho}$ equals nullity of the matrix that determines eigenvalue Eq. (16a). Since this is a $(\rho + \sigma + \eta_j) \times (\rho + \sigma + \eta_j)$ matrix, singular eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ can be at most $(\rho + \sigma + \eta_j)$-degenerate.

Theorem 2 produces all singular eigenstates of the modified system in the case $\beta \neq 0$. In the trivial case $\beta = 0$ LRM formalism implies that each eigenstate $|\Phi_j\rangle$ of a parent system $\mathbf{A}_n$ is a singular eigenstate of a modified system $\mathbf{C}_{n+\rho}$. In addition, if eigenvalue E_s of a base system $\mathbf{B}_\rho$ coincides with some eigenvalue λ_j of a parent system, the corresponding eigenstate $|\Theta_s\rangle$ of $\mathbf{B}_\rho$ is also singular eigenstate of the modified system $\mathbf{C}_{n+\rho}$. This is in complete agreement with the definition of singular solutions. Namely if $\beta = 0$ all eigenstates $|\Phi_j\rangle$ of $\mathbf{A}_n$ are at the same time eigenstates of $\mathbf{C}_{n+\rho}$ with the same eigenvalue. Hence by definition those solutions of $\mathbf{C}_{n+\rho}$ are singular. The same applies to each eigenstates $|\Theta_s\rangle$ of $\mathbf{B}_\rho$, provided the corresponding eigenvalue E_s satisfies $E_s \in \{\lambda_j\}$.

Treatment of singular solutions of the modified system is highly simplified by the clear distinction between *strongly singular* and *weakly singular* eigenstates of this system. By definition, strongly singular eigenstate $|\Psi_s\rangle$ of the eigenvalue Eq. (7a) has no component in the base space X_ρ^b and no component in the interaction space X_σ^{int}. Hence this eigenstate satisfies $\mathbf{I}_b|\Psi_s\rangle = \mathbf{I}_{\text{int}}|\Psi_s\rangle = 0$. On the other hand, each weakly singular eigenstate $|\Psi_s\rangle$ of the modified system satisfies either $\mathbf{I}_b|\Psi_s\rangle \neq 0$ and/or $\mathbf{I}_{\text{int}}|\Psi_s\rangle \neq 0$. In addition, each weakly singular eigenstate of this system is required to be orthogonal to all strongly singular eigenstates.

As shown in the Appendix, weakly singular eigenstates satisfy:

Lemma 3 *Let $|\Psi_s\rangle$ be weakly singular eigenstate of the modified system with the eigenvalue $\varepsilon_s = \lambda_j$. Component $|\chi_s^j\rangle \in X_{\eta_j}^j$ of this eigenstate is uniquely determined by components $\mathbf{I}_b|\Psi_s\rangle = |\theta_s\rangle \in X_\rho^b$ and $\mathbf{I}_{\text{int}}|\Psi_s\rangle = |\varphi_s\rangle \in X_\sigma^{\text{int}}$ of this eigenstate.*

Since X_ρ^b is ρ-dimensional while X_σ^{int} is σ-dimensional, Lemmas 2 and 3 imply that the space spanned by all weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$ is at most $(\rho + \sigma)$-dimensional. In addition, Lemma 3 and Theorem 2 imply:

Theorem 2a *Let λ_j be a η_j-degenerate eigenvalue of the eigenvalue Eq. (1a) and let $X_{\eta_j}^j$ be the corresponding η_j-dimensional space spanned by η_j degenerate eigenstates $|\Phi_{jm}\rangle (m = 1, \dots, \eta_j)$ of (1a). Let further $\mathbf{I}_j$ be the projection operator on the space $X_{\eta_j}^j$ and let $\beta \neq 0$. Then:*

(a) $|\Psi_s\rangle$ is strongly singular eigenstate of the eigenvalue Eq. (7a) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if it is contained in the space $X_{\eta_j}^j$

$$|\Psi_s\rangle \equiv |\chi_s^j\rangle \in X_{\eta_j}^j, \tag{19a}$$

and if in addition it satisfies

$$(\mathbf{V} - \varepsilon_s \mathbf{P})\mathbf{I}_j|\chi_s^j\rangle = 0, \qquad (\mathbf{V}_a - \varepsilon_s \mathbf{P}_a)\mathbf{I}_j|\chi_s^j\rangle = 0. \tag{19b}$$

This state is hence a linear combination

$$|\Psi_s\rangle = \sum_m^{\eta_j} |\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a|\Psi_s\rangle = \sum_m^{\eta_j} D_m^{(s)}|\Phi_{jm}\rangle, \tag{20a}$$

where the coefficients $D_m^{(s)}$ satisfy $(\rho + \sigma)$ linear conditions

$$\begin{aligned} \sum_m^{\eta_j} \langle r|\mathbf{V} - \varepsilon_s\mathbf{P}|\Phi_{jm}\rangle D_m^{(s)} = 0, \qquad r = 1, \dots, \rho, \\ \sum_m^{\eta_j} \langle \mu|\mathbf{V}_a - \varepsilon_s\mathbf{P}_a|\Phi_{jm}\rangle D_m^{(s)} = 0, \qquad \mu = 1, \dots, \sigma. \end{aligned} \tag{20b}$$

The set of all strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$ spans some r_j-dimensional space $X_{r_j}^{j-}$, subspace of the space $X_{\eta_j}^j$. Since the space $X_{\eta_j}^j$ is η_j-dimensional, expressions (20b) imply

$$\eta_j - \rho - \sigma \leq r_j \leq \eta_j. \tag{21}$$

In particular, one may have at most η_j linearly independent strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$.

(b) $|\Psi_s\rangle$ is weakly singular eigenstate of the generalized eigenvalue Eq. (7a) with the eigenvalue $\varepsilon_s = \lambda_j$ if and only if it is a linear combination (16c) where the states $|\theta_s\rangle, |\varphi_s\rangle$ and $|\chi_s^j\rangle$ satisfy (16a) and where either $|\theta_s\rangle \neq 0$ and/or $|\varphi_s\rangle \neq 0$. In addition, each weakly singular eigenstate is required to be orthogonal to all strongly singular eigenstates. Due to Lemma 3, one can have at most $\rho + \sigma$ linearly independent weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$.

According to the above Theorem, there is a substantial qualitative difference between strongly and weakly singular eigenstates of the modified system. Inequalities (21) imply that if degeneracy η_j of the eigenvalue λ_j of the parent system $\mathbf{A}_n$ satisfies $\eta_j > \rho + \sigma$, modified system $\mathbf{C}_{n+\rho}$ has at least $\eta_j - \rho - \sigma$ linearly independent strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. If this degeneracy is large, one may have very many strongly singular eigenstates with this eigenvalue. According to the expressions (20), those eigenstates do not depend on the coupling parameter β, and they exist for each value of this parameter. Further, each strongly singular eigenstate $|\Psi_s\rangle$ of the modified system $\mathbf{C}_{n+\rho}$ is at the same time an eigenstate of the parent system $\mathbf{A}_n$ with the same eigenvalue. Accordingly, modification operators $\mathbf{V}$, $\mathbf{P}$, $\mathbf{V}_a$ and $\mathbf{P}_a$ have no influence on strongly singular eigenstates. On the other hand, each weakly singular eigenstate $|\Psi_s\rangle$ depends on a coupling parameter β as well as on those modification operators. Unlike strongly singular eigenstates of the modified system, each weakly singular eigenstate of this system differs from all eigenstates of the parent system $\mathbf{A}_n$. In addition, modified system may have at most $\rho + \sigma$ weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$, however large degeneracy η_j of the eigenvalue λ_j.

Weakly singular eigenstates are rather special eigenstates of the modified system. Each such eigenstate is obtained as a solution to (16a) where either $|\theta_s\rangle \neq 0$ and/or $|\varphi_s\rangle \neq 0$. Expression (16a) is a set of $(\rho + \sigma + \eta_j)$ homogenous linear equations in $(\rho + \sigma + \eta_j)$ unknowns that determine the states $|\theta_s\rangle$, $|\varphi_s\rangle$ and $|\chi_s^j\rangle$. However, in the case of weakly singular eigenstates, the state $|\chi_s^j\rangle$ is completely determined by the states $|\theta_s\rangle$ and $|\varphi_s\rangle$. As a consequence, expression (16a) provides $(\rho + \sigma + \eta_j)$ conditions in only $(\rho + \sigma)$ unknowns. This expression is hence highly over-determined, especially if degeneracy η_j of the parent eigenvalue λ_j is large. Only by chance or due to some special reason this expression can have a nontrivial solution. This latter possibility implies that modified system $\mathbf{C}_{n+\rho}$ should posses some symmetry elements not contained in the set of its two non-interacting subsystems $\mathbf{A}_n$ and $\mathbf{B}_\rho$. Unless this is the case, modified system $\mathbf{C}_{n+\rho}$ can only by pure accident (which is very unlikely) have some weakly singular eigenstates.

Above two theorems produce all solutions of the modified system $\mathbf{C}_{n+\rho}$ in the nontrivial case $\beta \neq 0$. All cardinal eigenvalues $\varepsilon_s \notin \{\lambda_i\}$ of the modified eigenvalue Eq. (7a) are roots of the function $h(\varepsilon)$ (expression 14c). Once a particular root ε_s of $h(\varepsilon)$ is found, the corresponding eigenstate (or eigenstates) is given by the expression (15a) where the states $|\theta_s\rangle \in X_\rho^b$ and $|\varphi_s\rangle \in X_\sigma^{\text{int}}$ satisfy (14a). Concerning remaining singular eigenvalues $\varepsilon_s \in \{\lambda_i\}$ and corresponding eigenstates, it is rather straightforward to verify expressions (20) which produce all strongly singular eigenstates with this eigenvalue. If all solutions of the modified system $\mathbf{C}_{n+\rho}$ are required, in the numerical implementation of LRM approach one has first to calculate all cardinal solutions of this system. This can be done using expressions (14) and (15). If there are $(n + \rho)$ such solutions LRM calculation is completed, since modified system has exactly $(n + \rho)$ solutions. However if there are less than $(n + \rho)$ linearly independent cardinal solutions, one has to calculate strongly singular solutions using expressions (20). 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.

3.3 Normalization of modified eigenstates

Cardinal eigenstate $|\Psi_s\rangle$ as given by the expression (15a) is not normalized. This can be easily done according to

$$|\Psi_s\rangle \rightarrow |\Psi_s'\rangle = \frac{1}{\sqrt{N_s}}|\Psi_s\rangle, \tag{22a}$$

where

$$N_s = \langle\Psi_s|\mathbf{S}_c|\Psi_s\rangle. \tag{22b}$$

and where $|\Psi_s\rangle$ is given by (15a). Using (15a) and (7b) one finds that normalization constant N_s equals

$$N_s = \langle\Psi_s^a|\mathbf{S}_a|\Psi_s^a\rangle + \langle\theta_s|\mathbf{S}_b|\theta_s\rangle + \beta\left\{\langle\varphi_s|\mathbf{P}_a|\varphi_s\rangle + \langle\Psi_s^a|\mathbf{P}|\theta_s\rangle + \langle\theta_s|\mathbf{P}|\Psi_s^a\rangle\right\}, \tag{23a}$$

As shown in the Appendix, matrix elements $\langle\Psi_s^a|\mathbf{S}_a|\Psi_s^a\rangle$ and $\langle\Psi_s^a|\mathbf{P}|\theta_s\rangle$ which involve X_n^a component $|\Psi_s^a\rangle$ of the cardinal eigenstate $|\Psi_s\rangle$ can be expressed in terms of matrix elements involving only the states $|\theta_s\rangle$ and $|\varphi_s\rangle$:

$$\langle\Psi_s^a|\mathbf{S}_a|\Psi_s^a\rangle = -\beta^2\left[\langle\theta_s|(\mathbf{V}-\varepsilon_s\mathbf{P}) + \langle\varphi_s|(\mathbf{V}_a-\varepsilon_s\mathbf{P}_a)\right]$$
$$\times\frac{d\overline{\mathbf{\Omega}}(\varepsilon_s)}{d\varepsilon}\left[(\mathbf{V}-\varepsilon_s\mathbf{P})|\theta_s\rangle + (\mathbf{V}_a-\varepsilon_s\mathbf{P}_a)|\varphi_s\rangle\right] \tag{23b}$$

$$\langle\Psi_s^a|\mathbf{P}|\theta_s\rangle = \beta\left[\langle\theta_s|(\mathbf{V}-\varepsilon_s\mathbf{P}) + \langle\varphi_s|(\mathbf{V}_a-\varepsilon_s\mathbf{P}_a)\right]\overline{\mathbf{\Omega}}(\varepsilon_s)\mathbf{P}|\theta_s\rangle. \tag{23c}$$

This can be written in the explicit form

$$\langle\Psi_s^a|\mathbf{S}_a|\Psi_s^a\rangle = \beta^2\sum_i^n\frac{|\langle\Phi_i|\mathbf{V}-\varepsilon_s\mathbf{P}|\theta_s\rangle + \langle\Phi_i|\mathbf{V}_a-\varepsilon_s\mathbf{P}_a|\varphi_s\rangle|^2}{(\varepsilon_s-\lambda_i)^2}, \tag{24a}$$

$$\langle\Psi_s^a|\mathbf{P}|\theta_s\rangle = \beta\sum_i^n\frac{\langle\theta_s|\mathbf{V}-\varepsilon_s\mathbf{P}|\Phi_i\rangle + \langle\varphi_s|\mathbf{V}_a-\varepsilon_s\mathbf{P}_a|\Phi_i\rangle}{\varepsilon_s-\lambda_i}\langle\Phi_i|\mathbf{P}|\theta_s\rangle. \tag{24b}$$

According to the above expressions, in order to normalize cardinal eigenstate $|\Psi_s\rangle \in X_{n+\rho}^c$ it is not necessary to know all fine details of this eigenstate. LRM expression (14a) produces the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ as well as the corresponding eigenvalue ε_s. In connection with known eigenvalues λ_i of $\mathbf{A}_n$ and known matrix elements $\langle r|\mathbf{V}|\Phi_i\rangle$, $\langle r|\mathbf{P}|\Phi_i\rangle$, $\langle\mu|\mathbf{V}_a|\Phi_i\rangle$ and $\langle\mu|\mathbf{P}_a|\Phi_i\rangle$, those quantities uniquely determine normalization constant N_s. Hence, though cardinal eigenstate $|\Psi_s\rangle$ extends over the entire $(n+\rho)$-dimensional space $X_{n+\rho}^c$, one can normalize this eigenstate using only projections of this eigenstate on much smaller spaces X_ρ^b and X_σ^{int}. This independence of the normalization constant N_s on the details of the space X_n^a is an important feature of the LRM approach.

Expressions (23) and (24) apply to a most general case when all modification operators differ from zero. In many special but important cases those expressions substantially simplify. Most important is the case when modification operators $\mathbf{P}_a$ and $\mathbf{P}$ vanish. If $\mathbf{P}_a = \mathbf{P} = 0$ expressions (23) and (24) reduce to

$$N_s = \beta^2 \sum_i^n \frac{|\langle \Phi_i | \mathbf{V} | \theta_s \rangle + \langle \Phi_i | \mathbf{V}_a | \varphi_s \rangle|^2}{(\varepsilon_s - \lambda_i)^2} + \langle \theta_s | \mathbf{S}_b | \theta_s \rangle. \tag{24$'$}$$

Consider now strongly singular eigenstates (20). In the case of those eigenstates normalization constant N_s equals

$$N_s \equiv \langle \Psi_s | \mathbf{S}_a + \beta \mathbf{P}_a | \Psi_s \rangle = \sum_m^{\eta_j} |D_m^{(s)}|^2 + \beta \sum_{m,m'} D_m^{(s)} D_{m'}^{(s)} \langle \Phi_{jm'} | \mathbf{P}_a | \Phi_{jm} \rangle, \tag{25a}$$

where strongly singular eigenstate $|\Psi_s\rangle$ is given by (20a).

Normalization of strongly singular eigenstates also simplifies in some special cases. In particular, if modification operator $\mathbf{P}_a$ vanishes, expression (25a) reduces to

$$N_s = \sum_m^{\eta_j} |D_m^{(s)}|^2. \tag{25b}$$

Note that strongly singular eigenstate $|\Psi_s\rangle$ with the eigenvalue $\varepsilon_s = \lambda_j$ is contained in the subspace $X_{\eta_j}^j$ of the space X_n^a and it has no X_σ^{int} and no X_ρ^b components. There is hence substantial qualitative difference between normalization of cardinal eigenstates and normalization of strongly singular eigenstates of the modified system. Normalization of cardinal eigenstate $|\Psi_s\rangle$ depends on the X_σ^{int} and X_ρ^b projections of this eigenstate. On the other hand, normalization of strongly singular eigenstate $|\Psi_s\rangle$ does not depend on those projections, since in the case of strongly singular eigenstates those projections are zero.

Concerning weakly singular eigenstates, those eigenstates can be normalized in a similar way as cardinal eigenstates, and normalization of those eigenstates again depends on their X_σ^{int} and X_ρ^b components.

3.4 Numerical considerations

Consider now efficiency of the LRM approach from the numerical point of view. In order to obtain a single cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ of the modified system $\mathbf{C}_{n+\rho}$, one has to derive this eigenvalue as a root of the $(\rho + \sigma)(\rho + \sigma)$ determinant (14c). Assume that $(\rho + \sigma)$ is relatively small with respect to n. Operation count for the calculation of the determinant (14c) is dominated by the calculation of the matrix elements of the operators $\mathbf{\Omega}_b(\varepsilon)$, $\mathbf{\Omega}_a(\varepsilon)$ and $\mathbf{\Omega}_{ab}(\varepsilon)$. There are $(\rho + \sigma)^2$ such matrix elements and according to the expressions (11b), (12b) and (13b), calculation of each of those matrix element is of the order $O(n)$. A single calculation of the determinant

(14c) is hence of the order $O\left(n\left(\rho+\sigma\right)^2\right)$. In order to obtain a single root of (14c) one has to perform several calculations of this determinant. However, the number of those calculations is on average independent on the size of the problem, i.e. it is independent on n, on ρ and on σ. Operation count required to obtain a single LRM cardinal eigenvalue is hence of the order $O\left(n\left(\rho+\sigma\right)^2\right)$. Once cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ is known, operational count required to derive the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ using the expression (14a) is of the order $O\left((\rho+\sigma)^3\right)$. There is also an additional operation count of the order $O\left(n\left(\rho+\sigma\right)\right)$ required to construct the eigenstate $|\Psi_s\rangle$ according to (15a), once the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ are known. Since by assumption $(\rho+\sigma) << n$, those operation counts are negligible with respect to the operational count required to obtain cardinal eigenvalue $\varepsilon_s \notin \{\lambda_i\}$ in the first place. Concerning strongly singular eigenstates, operation count required to obtain all strongly singular eigenstate with a particular eigenvalue λ_j is of the order $O\left(\eta_j^3\right)$. Since in almost all cases $\eta_j << n$, this is usually negligible relative to the operation count required to derive a single cardinal eigenstate. Concerning weakly singular eigenstates, there are usually only very few such eigenstates, if any. Operation count required to obtain all solutions of the modified system is hence dominated by the operation count required to obtain all cardinal solutions, which is of the order $O\left(n^2(\rho+\sigma)^2\right)$. In comparison, standard diagonalization of the eigenvalue Eq. (7a) has operation count $O\left((n+\rho)^3\right) \approx O(n^3)$ [12,13]. Hence if $(\rho+\sigma) << \sqrt{n}$, LRM will be numerically more efficient than standard diagonalization. Additional advantage of LRM is that it can produce selected solutions with the operational count $O\left(n(\rho+\sigma)^2\right)$ which is $\approx n$ times smaller, while no known diagonalization method produces selected solutions of (7a) with the operational count as low as $O(n^2)$. Hence if only few selected solutions of the eigenvalue Eq. (7a) are required, LRM will be even more efficient in comparison with other possible approaches. Concerning various perturbation methods, those methods are only approximate and they are efficient only if the coupling parameter β is relatively small. Hence if the modification of the parent system is not small and if $(\rho+\sigma) << \sqrt{n}$, LRM approach will be numerically superior to standard diagonalization methods as well as to various perturbation expansion approaches.

4 Numerical examples

Let me illustrate LRM treatment of a combined modification of a parent system with two examples. In order to emphasize essential features of this approach, those examples are necessarily simple. They are intended to illustrate LRM approach, and not to obtain particularly realistic solution of a given problem.

4.1 Combined modification of benzene molecule in the Hückel approximation

As a first example consider combined modification of a benzene molecule within a Hückel approximation (See Fig. 2). Within this approximation, parent system $\mathbf{A}_6$ that represents benzene is six-dimensional. This system is described by a standard eigenvalue equation
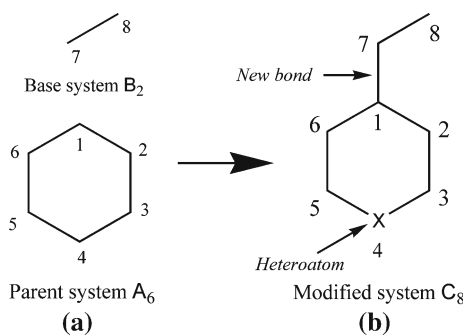
Fig. 2 Modification of the benzene molecule in the Hückel approximation. **a** Benzene molecule is a six-dimensional parent system $\mathbf{A}_6$ and ethylene molecule is a two-dimensional base system $\mathbf{B}_2$. **b** Modified system $\mathbf{C}_8$. Parent system $\mathbf{A}_6$ is modified externally by the interaction with the base system $\mathbf{B}_2$ (creation of the bond 1–7), and internally by the heteroatom $\mathbf{X}$ introduce at the position of the carbon atom C_4

$$\mathbf{H}_a|\Phi_i\rangle = \lambda_i\mathbf{I}_a|\Phi_i\rangle, \tag{26a}$$

where $\mathbf{S}_a = \mathbf{I}_a$ is a unit operator in X_6^a. Without loss of generality one can assume Hückel Coulomb integral to equal zero, while the corresponding eigenvalues λ_i can be expressed in units of the Hückel resonant integral. In this case those eigenvalues are

$$\lambda_1 = -2, \quad \lambda_2 = \lambda_3 = -1, \quad \lambda_4 = \lambda_5 = 1, \quad \lambda_6 = 2, \tag{26b}$$

The states $|\alpha\rangle(\alpha = 1, \ldots, 6)$ situated at respective atomic sites of the system $\mathbf{A}_6$ form an orthonormalized base $\{|\alpha\rangle\}$ in the space X_6^a (see Fig. 2a):

$$\langle\alpha|\beta\rangle = \delta_{\alpha\beta}, \qquad \alpha, \beta = 1, \ldots, 6. \tag{26c}$$

System $\mathbf{A}_6$ can be modified internally as well as externally. As an internal modification consider replacement of the carbon atom C_4 with a heteroatom X. Without loss of generality one can assume that coupling parameter equals one, $\beta = 1$. Replacement of the carbon atom C_4 with a heteroatom can be approximated by the change of the corresponding Coulomb integral from zero to $\alpha_X \neq 0$. The interaction space X_1^{int} is in this case one-dimensional and it is spanned by a single state $|\mu\rangle \equiv |4\rangle$ situated at the carbon atom 4. The projection operator on this interaction space is $\mathbf{I}_1^{\text{int}} = |\mu\rangle\langle\mu| \equiv |4\rangle\langle4|$. The corresponding modification operators are

$$\mathbf{V}_a = \alpha_X|4\rangle\langle4|, \qquad \mathbf{P}_a = 0. \tag{27}$$

As an external modification of the benzene molecule, consider attachment of the ethylene structure to the carbon atom C_1. In LRM and within the Hückel approximation, this structure represents a two-dimensional base system $\mathbf{B}_2$ with eigenvalues $E_1 = -1$ and $E_2 = 1$:

$$\mathbf{H}_b|\Theta_r\rangle = E_r\mathbf{I}_b|\Theta_r\rangle, \tag{28a}$$

where

$$E_1 = -1, \qquad E_2 = 1, \tag{28b}$$

and where $\mathbf{S}_b = \mathbf{I}_b$ is a unit operator in the base space X_2^b.

The states $|r_1\rangle \equiv |7\rangle$ and $|r_2\rangle \equiv |8\rangle$ situated at respective atomic sites of the system $\mathbf{B}_2$ form an orthonormalized base $\{|r\rangle\}$ in the space X_2^b (see Fig. 2a):

$$\langle r_i | r_j \rangle = \delta_{ij}, \qquad r_i, r_j = 7, 8. \tag{28c}$$

In this base Hamiltonian $\mathbf{H}_b$ and projection operator $\mathbf{I}_b$ can be expressed as

$$\mathbf{H}_b = |7\rangle\langle 8| + |8\rangle\langle 7|, \qquad \mathbf{I}_b = |7\rangle\langle 7| + |8\rangle\langle 8|, \tag{29a}$$

In the base $\{|1\rangle, \ldots, |8\rangle\}$ of the combined space X_8^c modification operators $\mathbf{V}$ and $\mathbf{P}$ that describe external interaction between benzene (system $\mathbf{A}_6$) and ethylene (system $\mathbf{B}_2$) can be expressed as

$$\mathbf{V} = |1\rangle\langle 7| + |7\rangle\langle 1|, \qquad \mathbf{P} = 0. \tag{29b}$$

Modified system $\mathbf{C}_8$ that contains above external as well as above internal modifications is shown in Fig. 2b). This system is eight-dimensional, and the states situated at respective atomic sites of this system form orthonormalized base $\{|1\rangle, \ldots, |8\rangle\}$ in the space X_8^c.

Consider now LRM cardinal solutions of this system. Since $\mathbf{S}_b = \mathbf{I}_b$ is a unit operator in X_2^b while modification operators $\mathbf{P}$ and $\mathbf{P}_a$ are zero and since $\beta = 1$, LRM expression (14a) reduces to

$$\left[\begin{matrix} \mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s \mathbf{I}_b & \mathbf{\Omega}_{ba}(\varepsilon_s) \\ \mathbf{\Omega}_{ab}(\varepsilon_s) & \mathbf{\Omega}_a(\varepsilon_s) - \mathbf{V}_a \end{matrix} \right] \left| \begin{matrix} \theta_s \\ \varphi_s \end{matrix} \right. = 0, \tag{30a}$$

where

$$|\theta_s\rangle = \langle 7|\theta_s\rangle|7\rangle + \langle 8|\theta_s\rangle|8\rangle \in X_2^b, \qquad |\varphi_s\rangle = \langle 4|\varphi_s\rangle|4\rangle \in X_1^{\text{int}}, \tag{30b}$$

Each root $\varepsilon_s \notin \{\lambda_i\}$ of the determinant

$$h(\varepsilon) \equiv \left| \begin{matrix} \mathbf{\Omega}_b(\varepsilon) + \mathbf{H}_b - \varepsilon \mathbf{I}_b & \mathbf{\Omega}_{ba}(\varepsilon) \\ \mathbf{\Omega}_{ab}(\varepsilon) & \mathbf{\Omega}_a(\varepsilon) - \mathbf{V}_a \end{matrix} \right| = 0. \tag{30c}$$

is a cardinal eigenvalue of the modified system. According to (15a), the corresponding eigenstate $|\Psi_s\rangle$ is a linear combination

$$|\Psi_s\rangle = \sum_i^6 \frac{\langle \Phi_i | \mathbf{V} | \theta_s \rangle + \langle \Phi_i | \mathbf{V}_a | \varphi_s \rangle}{\varepsilon_s - \lambda_i} |\Phi_i\rangle + |\theta_s\rangle. \tag{31}$$

where $|\Xi_s\rangle \equiv |\theta_s\rangle + |\varphi_s\rangle$ is an eigenstate of (30a) that corresponds to the eigenvalue ε_s.

Expressions (11–13), (27) and (29b) imply

$$
\begin{aligned}
\mathbf{\Omega}_a(\varepsilon) &= \alpha_X^2 |4\rangle\langle 4|\Omega_{44}(\varepsilon), \qquad \mathbf{\Omega}_b(\varepsilon) = |7\rangle\langle 7|\Omega_{11}(\varepsilon),\\
\mathbf{\Omega}_{ab}(\varepsilon) &= \alpha_X |4\rangle\langle 7|\Omega_{41}(\varepsilon),
\end{aligned}
\tag{32a}
$$

where

$$
\mathbf{\Omega}_{\alpha\beta}(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)}^{6} \frac{\langle\alpha|\Phi_i\rangle\langle\Phi_i|\beta\rangle}{\varepsilon - \lambda_i}, \qquad \alpha, \beta = 1, \ldots, 6.
\tag{32b}
$$

and where $\langle\alpha|\Phi_i\rangle$ are amplitudes of the benzene eigenstate $|\Phi_i\rangle$ on the atomic sites α. Using (32), (27) and (29a) expression (30a) can be written in the base $\{|7\rangle, |8\rangle, |4\rangle\}$ as

$$
\begin{bmatrix}
\Omega_{11}(\varepsilon_s) - \varepsilon_s & 1 & \alpha_X \cdot \Omega_{14}(\varepsilon_s) \\
1 & -\varepsilon_s & 0 \\
\alpha_X \cdot \Omega_{41}(\varepsilon_s) & 0 & \alpha_X^2 \cdot \Omega_{44}(\varepsilon_s) - \alpha_X
\end{bmatrix}
\begin{vmatrix}
\langle 7|\theta_s\rangle \\
\langle 8|\theta_s\rangle \\
\langle 4|\varphi_s\rangle
\end{vmatrix}
= 0,
\tag{33a}
$$

Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_j\}$ of the modified system is hence a root of a determinant $h(\varepsilon)$

$$
h(\varepsilon) \equiv
\begin{vmatrix}
\Omega_{11}(\varepsilon) - \varepsilon & 1 & \alpha_X \cdot \Omega_{14}(\varepsilon) \\
1 & -\varepsilon & 0 \\
\alpha_X \cdot \Omega_{41}(\varepsilon) & 0 & \alpha_X^2 \cdot \Omega_{44}(\varepsilon) - \alpha_X
\end{vmatrix}
= 0.
\tag{33b}
$$

Expression (33a) involves only the states $|7\rangle$, $|8\rangle$ and $|4\rangle$ which span base space X_2^b and interaction space X_1^{int}. No other state $|\alpha\rangle$ (except of the state $|\alpha\rangle = |4\rangle$) contained in the parent benzene system is explicitly present in this expression.

Once a particular cardinal eigenvalue $\varepsilon_s \notin \{\lambda_j\}$ is obtained as a root of (33b), the corresponding eigenstate is given by the expression (31) where the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ are given by (30b) and where the amplitudes $\langle 7|\theta_s\rangle$, $\langle 8|\theta_s\rangle$ and $\langle 4|\varphi_s\rangle$ are obtained as a solution to (33a).

As a particular example consider the case $\alpha_X = 0.5$. If $\alpha_X = 0.5$ function $h(\varepsilon)$ given by the expression (33b) has six roots

$$
\begin{aligned}
\varepsilon_1 &= -2.0996751, \quad \varepsilon_2 = -1.3066889, \quad \varepsilon_3 = -0.5814234,\\
\varepsilon_4 &= 0.7335911, \qquad \varepsilon_5 = 1.5525022, \qquad \varepsilon_6 = 2.2016941.
\end{aligned}
\tag{34}
$$

Those roots are cardinal eigenvalues of the modified system. Once a particular eigenvalue ε_s is known, the corresponding eigenstate $|\Psi_s\rangle$ is determined by the solution of (33a). For example, inserting cardinal eigenvalue $\varepsilon_1 = -2.0996751$ into (33a) and since $\alpha_X = 0.5$ one obtains

$$
\begin{bmatrix}
-0.0237358 & 1 & -0.7179320 \\
1 & 2.0996751 & 0 \\
-0.7179320 & 0 & -1.0308527
\end{bmatrix}
\begin{vmatrix}
\langle 7|\theta_1\rangle \\
\langle 8|\theta_1\rangle \\
\langle 4|\varphi_1\rangle
\end{vmatrix}
= 0,
\tag{35a}
$$

This equation has a nontrivial solution

$$\langle 7|\theta_1\rangle = 0.7643029, \qquad \langle 8|\theta_1\rangle = -0.3640101, \qquad \langle 4|\varphi_1\rangle = 0.5322948. \quad (35b)$$

Inserting those values into (31) where $\varepsilon_s \equiv \varepsilon_1$ and normalizing according to (24′), one finds modified eigenstate $|\Psi_1\rangle$. In particular, in the base $\{|1\rangle, \ldots, |8\rangle\}$ one has

$$|\Psi_1\rangle = \begin{pmatrix} 0.5445634 \\ -0.4039812 \\ 0.3036657 \\ -0.2336182 \\ 0.3036657 \\ -0.4039812 \\ -0.3354440 \\ 0.1597599 \end{pmatrix}. \qquad (35c)$$

In a similar way, inserting cardinal eigenvalue $\varepsilon_2 = -1.3066889$ into (33a) one finds

$$\begin{bmatrix} -0.2652931 & 1 & -0.6165829 \\ 1 & 1.3066889 & 0 \\ -0.6165829 & 0 & -0.7603489 \end{bmatrix} \begin{vmatrix} \langle 7|\theta_2\rangle \\ \langle 8|\theta_2\rangle \\ \langle 4|\varphi_2\rangle \end{vmatrix} = 0, \qquad (36a)$$

This equation has a nontrivial solution

$$\langle 7|\theta_1\rangle = -0.6676665, \qquad \langle 8|\theta_1\rangle = 0.5109606, \qquad \langle 4|\varphi_1\rangle = 0.5414248. \quad (36b)$$

Inserting into (31) and normalizing, one finds modified eigenstate $|\Psi_2\rangle$

$$|\Psi_2\rangle = \begin{pmatrix} -0.2832862 \\ -0.0765423 \\ 0.3833032 \\ -0.4243157 \\ 0.3833032 \\ -0.0765423 \\ 0.5232516 \\ -0.4004408 \end{pmatrix}. \qquad (36c)$$

In this way one can derive all remaining cardinal solutions of the modified system. Since there are six cardinal solutions, while the system $\mathbf{C}_8$ is 8-dimensional, this system must have two singular solutions.

Consider now those singular solutions. According to the expressions (20), (27) and (29b), each strongly sigular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j$ is a linear combination

$$|\Psi_s\rangle = \sum_m^{\eta_j} D_m^{(s)} |\Phi_{jm}\rangle, \qquad (37a)$$

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

$$\sum_m^{\eta_j} \langle 1|\Phi_{jm}\rangle D_m^{(s)} = 0, \qquad \sum_m^{\eta_j} \langle 4|\Phi_{jm}\rangle D_m^{(s)} = 0. \tag{37b}$$

and where η_j is degeneracy of the corresponding parent eigenvalue λ_j. In particular, if the eigenvalue λ_j is non-degenerate, conditions (37b) reduce to $\langle 1|\Phi_j\rangle D_1^{(s)} = 0$ and $\langle 4|\Phi_j\rangle D_1^{(s)} = 0$. Since no non-degenerate eigenstate $|\Phi_j\rangle$ has zero amplitude at sites 1 and 4, non-degenerate eigenvalues $\lambda_1 = -2$ and $\lambda_6 = 2$ cannot be singular eigenvalues of $\mathbf{C}_8$. Consider next doubly degenerate eigenvalues $\lambda_2 = \lambda_3 = -1$ and $\lambda_4 = \lambda_5 = 1$ of $\mathbf{A}_6$. Expressions (37b) in conjuncture with expressions for the corresponding benzene eigenstates $|\Phi_j\rangle$ imply that there is only one strongly singular eigenstate $|\Psi_7\rangle$ with the eigenvalue $\varepsilon_7 = -1$

$$|\Psi_7\rangle = \frac{1}{2}\left(|2\rangle - |3\rangle + |5\rangle - |6\rangle\right), \tag{38a}$$

and only one strongly singular eigenstate $|\Psi_8\rangle$ with the eigenvalue $\varepsilon_8 = 1$

$$|\Psi_8\rangle = \frac{1}{2}\left(|2\rangle + |3\rangle - |5\rangle - |6\rangle\right). \tag{38b}$$

Both eigenstates of the modified system $\mathbf{C}_8$ are at the same time eigenstates of the parent benzene system. This is trivially obvious. For example, eigenstate $|\Psi_7\rangle$ of $\mathbf{C}_8$ is a linear combination of the degenerate benzene eigenstates $|\Phi_2\rangle$ and $|\Phi_3\rangle$ with the eigenvalue $\lambda_2 = \lambda_3 = -1$. This eigenstate is hence also benzene eigenstate with the same eigenvalue. Further, according to the expression (38a), this eigenstate has amplitude zero at atomic sites 1 and 4 which are subject to the modification of the parent system. This eigenstate is hence not modified by the inclusion of external and internal modifications, and hence it is also an eigenstate of the modified system with the same eigenvalue. The same applies to the strongly singular eigenstate $|\Psi_8\rangle$. Since the modified system is 8-dimensional, and since it contains six cardinal eigenstates and two strongly singular eigenstates, this system contains no weakly singular eigenstate.

This completes LRM treatment of the modified system $\mathbf{C}_8$. One can verify this LRM calculation with a standard diagonalization of this system. One finds that above LRM calculation produces correct eigenvalues and eigenstates of this system.

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

4.2 Combined modification of the one-dimensional solid in the tight-binding approximation

As another example, consider a simple combined modification of a finite one-dimensional solid in the tight-binding approximation. In order to maintain translational
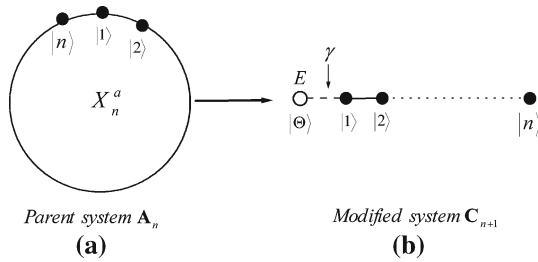
Fig. 3 Modification of the finite one-dimensional solid in the tight-binding approximation. **a** Parent system $\mathbf{A}_n$ is circular chain containing n atoms. **b** Modified system $\mathbf{C}_{n+1}$. Internal modification is destruction of the connection between the states $|1\rangle$ and $|n\rangle$ in the parent system. External modification is the interaction of the state $|1\rangle$ with the external state $|\Theta\rangle$

invariance of such a solid, one has to supply appropriate boundary conditions. The most convenient choice is the Born-von Karman periodic boundary condition [16]. In the case of linear chain containing n atoms, we simply join atom number 1 with atom number n, thus forming a circular chain of n atoms (see Fig. 3a). For simplicity, assume that each atomic site α contains only one orbital $|\alpha\rangle$ ($\alpha = 1, \ldots, n$). Those orbitals form a base in the corresponding n-dimensional space X_n^a. Assume further that orbitals $|\alpha\rangle$ situated at adjacent atomic sites are orthogonal to each other. In this case those orbitals can be orthonormalized according to

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta}, \qquad \alpha, \beta = 1, \ldots, n. \tag{39}$$

Since by assumption each atomic site contains only one atomic orbital, one can without loss of generality assume that all matrix elements $\mathbf{H}_{\alpha\beta}^a$ of the Hamiltonian $\mathbf{H}_a$ between adjacent atomic sites equal 1, while all remaining matrix elements equal zero. Since atom number n is connected to the atom number 1, one can use a cyclic convention

$$|n + 1\rangle \equiv |1\rangle, \qquad |n\rangle \equiv |0\rangle, \tag{40a}$$

With this convention matrix elements $\mathbf{H}_{\alpha\beta}^a$ of the tight-binding Hamiltonian $\mathbf{H}_a$ can be expressed in a compact form:

$$\mathbf{H}_{\alpha\beta}^a \equiv \langle \alpha | \mathbf{H}_a | \beta \rangle = \begin{cases} 1 & if \ \beta = \alpha + 1 \ or \ if \ \beta = \alpha - 1 \\ 0 & otherwise \end{cases}, \ \alpha = 1, \ldots, n. \tag{40b}$$

Hamiltonian $\mathbf{H}_a$ hence equals

$$\mathbf{H}_a = \sum_{\alpha}^{n} [|\alpha\rangle\langle \alpha + 1| + |\alpha + 1\rangle\langle \alpha|]. \tag{41a}$$

and it satisfies

$$\mathbf{H}_a|\Phi_j\rangle = \lambda_j \mathbf{I}_a|\Phi_j\rangle, \tag{41b}$$

where $\mathbf{I}_a$ is a unit operator in X_n^a. This Hamiltonian has eigenvalues λ_j and eigenstates $|\Phi_j\rangle$

$$\lambda_j = 2 \cdot \cos\left(\frac{2\pi j}{n}\right), \qquad |\Phi_j\rangle = \frac{1}{\sqrt{n}} \sum_\alpha^n \exp\left(i\frac{2\pi j\alpha}{n}\right)|\alpha\rangle, \qquad (41c)$$

Let n be even. In this case one can choose index j in the above expressions to assume n values

$$j = -n/2, \ldots, n/2 - 1. \qquad (41d)$$

Since $\lambda_j = \lambda_{-j}(j = 1, \ldots, n/2 - 1)$, corresponding eigenstates $|\Phi_j\rangle$ and $|\Phi_{-j}\rangle$ of the parent system $\mathbf{A}_n$ are degenerate. There are in addition two non-degenerate eigenstates of this system

$$|\Phi_0\rangle = \frac{1}{\sqrt{n}} \sum_\alpha^n |\alpha\rangle, \qquad |\Phi_{-n/2}\rangle = \frac{1}{\sqrt{n}} \sum_\alpha^n (-)^\alpha |\alpha\rangle, \qquad (42a)$$

with eigenvalues

$$\lambda_0 = 2, \qquad \lambda_{-n/2} = -2. \qquad (42b)$$

Above expressions describe parent system $\mathbf{A}_n$. As an internal modification of this system consider destruction of the interaction between atomic sites $|1\rangle$ and $|n\rangle$. This modification of a parent system transforms circular chain containing n atoms into linear chain containing n atoms. With the choice of the coupling parameter $\beta = 1$, this modification is given by the operators

$$\mathbf{V}_a = -\left[|1\rangle\langle n| + |n\rangle\langle 1|\right], \qquad \mathbf{P}_a = 0, \qquad (43a)$$

Since $\beta = 1$, modification operator $\mathbf{V}_a$ transforms Hamiltonian $\mathbf{H}_a$ into the Hamiltonian $\mathbf{H}_a'$

$$\mathbf{H}_a' = \mathbf{H}_a + \mathbf{V}_a = \sum_\alpha^{n-1} \left[|\alpha\rangle\langle\alpha + 1| + |\alpha + 1\rangle\langle\alpha|\right]. \qquad (43b)$$

Hamiltonian $\mathbf{H}_a'$ describes a linear chain containing n atoms. Modification operator $\mathbf{V}_a$ thus destroys translational invariance of the parent system $\mathbf{A}_n$ and creates two "surfaces" at atomic sites $\alpha = 1$ and $\alpha = n$. In the LRM approach interaction space X_2^{int} that corresponds to the modification operator $\mathbf{V}_a$ is two-dimensional, and it is spanned by the base states $|\mu\rangle \equiv |1\rangle$ and $|\nu\rangle \equiv |n\rangle$. Denote linear chain described by the Hamiltonian $\mathbf{H}_a'$ with $\mathbf{A}_n'$.

Once the surface at the atomic site $\alpha = 1$ (and also at the atomic site $\alpha = n$) is created by the modification operator $\mathbf{V}_a$, one can introduce interaction of thus created

surface with some molecule $\mathbf{B}_\rho$. Such an interaction represents an external modification of the parent system $\mathbf{A}_n$. For simplicity, consider the interaction of the linear chain $\mathbf{A}'_n$ with a single eigenstate $|\Theta\rangle$ of this molecule. Let this eigenstate correspond to the eigenvalue E. Base system $\mathbf{B}_1$ is in this case one-dimensional and it is described by the eigenvalue equation

$$\mathbf{H}_b|\Theta\rangle = E\mathbf{I}_b|\Theta\rangle, \tag{44a}$$

where $\mathbf{I}_b$ is a unit operator in X_1^b and where

$$\mathbf{H}_b = E|\Theta\rangle\langle\Theta|, \qquad \langle\Theta|\Theta\rangle = 1. \tag{44b}$$

In general, the state $|\Theta\rangle$ which is connected to the first state $|1\rangle$ of the linear chain (system $\mathbf{A}'_n$) can interact with several states of this chain. The strength of this interaction should rapidly decrease as one penetrates inside the chain. Assume for simplicity that the state $|\Theta\rangle$ interacts only with the first state $|1\rangle$ of this chain, and let the strength of this interaction be γ. Modification operators $\mathbf{V}$ and $\mathbf{P}$ that describe such interaction are

$$\mathbf{V} = \gamma\left[|1\rangle\langle\Theta| + |\Theta\rangle\langle 1|\right], \qquad \mathbf{P} = 0. \tag{45}$$

Modified system $\mathbf{C}_{n+1}$ that includes above internal as well as above external modification is $(n+1)$-dimensional, and it is described by the eigenvalue equation

$$\mathbf{H}|\Psi_s\rangle = \varepsilon_s\mathbf{I}_c|\Psi_s\rangle, \qquad s = 1,\ldots,n+1, \tag{46a}$$

where

$$\mathbf{H} = \mathbf{H}_a + \mathbf{H}_b + \mathbf{V}_a + \mathbf{V}. \tag{46b}$$

and where $\mathbf{I}_c$ is a unit operator in the combined space X_{n+1}^c. Modified system $\mathbf{C}_{n+1}$ is shown schematically in Fig. 3b.

Consider now LRM treatment of the above system. In the LRM formalism one has to consider operator $\overline{\mathbf{\Omega}}(\varepsilon)$

$$\overline{\mathbf{\Omega}}(\varepsilon) = \sum_{j(\lambda_j \neq \varepsilon)} \frac{|\Phi_j\rangle\langle\Phi_j|}{\varepsilon - \lambda_j}. \tag{47}$$

where eigenvalues λ_j and eigenstates $|\Phi_j\rangle$ of the parent system $\mathbf{A}_n$ are given by the expressions (41c). Next one has to construct operators $\mathbf{\Omega}_a(\varepsilon)$, $\mathbf{\Omega}_b(\varepsilon)$ and $\mathbf{\Omega}_{ab}(\varepsilon)$. Using (41c), (43a) and (45) one finds

$$\boldsymbol{\Omega}_a(\varepsilon) \equiv \mathbf{V}_a\overline{\boldsymbol{\Omega}}(\varepsilon)\mathbf{V}_a = \frac{1}{n}\sum_{j(\lambda_j\neq\varepsilon)}\frac{\left[|1\rangle + \exp\left(i\frac{2\pi j}{n}\right)|n\rangle\right]\left[\langle 1| + \exp\left(-i\frac{2\pi j}{n}\right)\langle n|\right]}{\varepsilon - \lambda_j},$$

$$(48a)$$

$$\boldsymbol{\Omega}_b(\varepsilon) \equiv \mathbf{V}\overline{\boldsymbol{\Omega}}(\varepsilon)\mathbf{V} = \frac{\gamma^2}{n}\sum_{j(\lambda_j\neq\varepsilon)}\frac{|\Theta\rangle\langle\Theta|}{\varepsilon - \lambda_j}, \qquad (48b)$$

$$\boldsymbol{\Omega}_{ab}(\varepsilon) \equiv \mathbf{V}_a\overline{\boldsymbol{\Omega}}(\varepsilon)\mathbf{V} = -\frac{\gamma}{n}\sum_{j(\lambda_j\neq\varepsilon)}\frac{\left[|1\rangle + \exp\left(i\frac{2\pi j}{n}\right)|n\rangle\right]\exp\left(-i\frac{2\pi j}{n}\right)\langle\Theta|}{\varepsilon - \lambda_j}. \quad (48c)$$

Operators $\boldsymbol{\Omega}_a(\varepsilon)$, $\boldsymbol{\Omega}_b(\varepsilon)$ and $\boldsymbol{\Omega}_{ab}(\varepsilon)$ are key operators in the LRM treatment of the modified system $\mathbf{C}_{n+1}$. All matrix elements of those operators can be expressed in terms of the functions $f_1(\varepsilon)$ and $f_2(\varepsilon)$

$$f_1(\varepsilon) = \frac{1}{n}\sum_{j(\lambda_j\neq\varepsilon)}\frac{1}{\varepsilon - \lambda_j}, \qquad f_2(\varepsilon) = \frac{1}{n}\sum_{j(\lambda_j\neq\varepsilon)}\frac{\exp\left(i\frac{2\pi j}{n}\right)}{\varepsilon - \lambda_j}, \qquad (49a)$$

The function $f_2(\varepsilon)$ is apparently complex. However, expressions (41c) imply

$$f_2(\varepsilon) = \frac{2}{n}\sum_{j=1}^{n/2-1}\frac{\cos\left(\frac{2\pi j}{n}\right)}{\varepsilon - \lambda_j} + \frac{1}{n}\left(\frac{1}{\varepsilon - 2} - \frac{1}{\varepsilon + 2}\right), \qquad \varepsilon \notin \{\lambda_i\}. \quad (49b)$$

Both functions $f_1(\varepsilon)$ and $f_2(\varepsilon)$ are hence real.

In the base $\{|\Theta\rangle, |1\rangle, |n\rangle\}$ all matrix elements of the operators (48) can be expressed in terms of above two functions according to

$$\langle 1|\boldsymbol{\Omega}_a(\varepsilon)|1\rangle = \langle n|\boldsymbol{\Omega}_a(\varepsilon)|n\rangle = f_1(\varepsilon), \qquad (50a)$$

$$\langle 1|\boldsymbol{\Omega}_a(\varepsilon)|n\rangle = \langle n|\boldsymbol{\Omega}_a(\varepsilon)|1\rangle = f_2(\varepsilon), \qquad (50b)$$

$$\langle\Theta|\boldsymbol{\Omega}_b(\varepsilon)|\Theta\rangle = \gamma^2 f_1(\varepsilon), \qquad (50c)$$

$$\langle 1|\boldsymbol{\Omega}_{ab}(\varepsilon)|\Theta\rangle = \langle\Theta|\boldsymbol{\Omega}_{ba}(\varepsilon)|1\rangle = -\gamma f_2(\varepsilon), \qquad (50d)$$

$$\langle n|\boldsymbol{\Omega}_{ab}(\varepsilon)|\Theta\rangle = \langle\Theta|\boldsymbol{\Omega}_{ba}(\varepsilon)|n\rangle = -\gamma f_1(\varepsilon). \qquad (50e)$$

All remaining matrix elements of those operators in the base $\{|1\rangle, \ldots, |n\rangle, |\Theta\rangle\}$ of the combined space X_{n+1}^c are zero. Using relations (50), (43a) and (44b), and since $\beta = 1$ and $\mathbf{P} = \mathbf{P}_a = 0$, in the base $\{|\Theta\rangle, |1\rangle, |n\rangle\}$ LRM expression (14a) reduces to

$$\begin{bmatrix} \gamma^2 f_1(\varepsilon_s) + E - \varepsilon_s & -\gamma f_2(\varepsilon_s) & -\gamma f_1(\varepsilon_s) \\ -\gamma f_2(\varepsilon_s) & f_1(\varepsilon_s) & f_2(\varepsilon_s) + 1 \\ -\gamma f_1(\varepsilon_s) & f_2(\varepsilon_s) + 1 & f_1(\varepsilon_s) \end{bmatrix} \begin{vmatrix} \langle\Theta|\theta_s\rangle \\ \langle 1|\varphi_s\rangle \\ \langle n|\varphi_s\rangle \end{vmatrix} = 0, \qquad (51a)$$

where

$$|\theta_s\rangle = \langle\Theta|\theta_s\rangle|\Theta\rangle \in X_1^b, \qquad |\varphi_s\rangle = \langle 1|\varphi_s\rangle|1\rangle + \langle n|\varphi_s\rangle|n\rangle \in X_2^{\text{int}}, \qquad \text{(51b)}$$

Each cardinal eigenvalue $\varepsilon_s \notin \{\lambda_j\}$ of the modified system $\mathbf{C}_{n+1}$ is hence a root of the determinant

$$h(\varepsilon) \equiv \begin{vmatrix} \gamma^2 f_1(\varepsilon) + E - \varepsilon & -\gamma f_2(\varepsilon) & -\gamma f_1(\varepsilon) \\ -\gamma f_2(\varepsilon) & f_1(\varepsilon) & f_2(\varepsilon) + 1 \\ -\gamma f_1(\varepsilon) & f_2(\varepsilon) + 1 & f_1(\varepsilon) \end{vmatrix} = 0, \qquad \text{(51c)}$$

According to (15a), once $\varepsilon_s \notin \{\lambda_j\}$ is obtained as a root of (51c), the corresponding cardinal eigenstate $|\Psi_s\rangle$ is a linear combination

$$|\Psi_s\rangle = \sum_i^n \frac{\langle\Phi_i|\mathbf{V}|\theta_s\rangle + \langle\Phi_i|\mathbf{V}_a|\varphi_s\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle + |\theta_s\rangle. \qquad \text{(51d)}$$

where the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ are given by (51b) and where the corresponding amplitudes $\langle\Theta|\theta_s\rangle$, $\langle 1|\varphi_s\rangle$ and $\langle n|\varphi_s\rangle$ are obtained as a solution to (51a). All cardinal eigenvalues and eigenstates of the modified system are thus obtained as a solution to the 3×3 matrix eigenvalue Eq. (51a), however large the dimension n of the parent system $\mathbf{A}_n$.

Consider now singular solutions of the modified system $\mathbf{C}_{n+1}$. According to the expressions (20), each strongly singular eigenstate $|\Psi_s\rangle$ with the eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ is a linear combination (20a) where the coefficients $D_m^{(s)}$ satisfy (20b). Since $\mathbf{P} = \mathbf{P}_a = 0$, since $\beta \neq 0$, and since all eigenvalues λ_i of the base system are double degenerate except for the eigenvalues λ_0 and $\lambda_{-n/2}$ which are non-degenerate, expressions (20b) reduce to

$$\langle 1|\mathbf{V}_a|\Phi_j\rangle D_j^{(s)} + \langle 1|\mathbf{V}_a|\Phi_{-j}\rangle D_{-j}^{(s)} = 0, \quad \langle n|\mathbf{V}_a|\Phi_j\rangle D_j^{(s)} + \langle n|\mathbf{V}_a|\Phi_{-j}\rangle D_{-j}^{(s)} = 0,$$
$$\langle\Theta|\mathbf{V}|\Phi_j\rangle D_j^{(s)} + \langle\Theta|\mathbf{V}|\Phi_{-j}\rangle D_{-j}^{(s)} = 0, \quad j = 1, \ldots, n/2 - 1. \qquad \text{(52a)}$$

$$\langle\Theta|\mathbf{V}|\Phi_0\rangle D_0^{(s)} = 0, \qquad \langle 1|\mathbf{V}_a|\Phi_0\rangle D_0^{(s)} = 0, \qquad \langle n|\mathbf{V}_a|\Phi_0\rangle D_0^{(s)} = 0$$
$$\langle\Theta|\mathbf{V}|\Phi_{-n/2}\rangle D_{-n/2}^{(s)} = 0, \quad \langle 1|\mathbf{V}_a|\Phi_{-n/2}\rangle D_{-n/2}^{(s)} = 0, \quad \langle n|\mathbf{V}_a|\Phi_{-n/2}\rangle D_{-n/2}^{(s)} = 0. \qquad \text{(52b)}$$

According to (42a), eigenstates $|\Phi_0\rangle$ and $|\Phi_{-n/2}\rangle$ of $\mathbf{A}_n$ have nonzero amplitudes at the states $|1\rangle$ and $|n\rangle$. Hence and due to (43a) expressions (52b) imply $D_0^{(s)} = D_{-n/2}^{(s)} = 0$. There are hence no strongly singular eigenstates with the eigenvalues $\varepsilon_s = \lambda_0 = 2$ and $\varepsilon_s = \lambda_{-n/2} = -2$. Consider now expressions (52a). Using (41c), (43a) and (45) one finds that those expressions imply $D_j^{(s)} = D_{-j}^{(s)} = 0$ $(j = 1, \ldots, n/2 - 1)$.

There are hence no strongly singular eigenstates with the eigenvalues $\varepsilon_s = \lambda_j$ ($j = \pm 1, \ldots, \pm n/2 - 1$). In conclusion, modified system contains no strongly singular solutions. Further, since the introduction of internal and external modifications reduces the symmetry of the parent system $\mathbf{A}_n$, there are also no weakly singular solutions. Expressions (51) hence produce all solutions of the modified system. There are $(n + 1)$ such solutions, and all those solutions are cardinal. This completes LRM treatment of the modified system $\mathbf{C}_{n+1}$.

Consider now some special cases of this system. All cardinal solutions of the modified system $\mathbf{C}_{n+1}$ depend on the interaction γ between the finite chain $\mathbf{A}_n'$ and the state $|\Theta\rangle$. In particular, if there is no interaction between this chain and the state $|\Theta\rangle$, one has $\gamma = 0$. In this case modified system $\mathbf{C}_{n+1}$ reduces to two non-interacting subsystems, system $\mathbf{B}_1$ that contains a single state $|\Theta\rangle$ with the eigenvalue E, and system $\mathbf{A}_n'$ that represents a finite chain in the tight-binding approximation. Since $\gamma = 0$ LRM expression (51c) reduces to

$$h(\varepsilon) \equiv \begin{vmatrix} E - \varepsilon & 0 & 0 \\ 0 & f_1(\varepsilon) & f_2(\varepsilon) + 1 \\ 0 & f_2(\varepsilon) + 1 & f_1(\varepsilon) \end{vmatrix} = 0, \tag{53a}$$

This factorizes into two expressions, expression $\varepsilon = E$ which reproduces eigenvalue E of the base system $\mathbf{B}_1$, and reduced determinant

$$h'(\varepsilon) \equiv \begin{vmatrix} f_1(\varepsilon) & f_2(\varepsilon) + 1 \\ f_2(\varepsilon) + 1 & f_1(\varepsilon) \end{vmatrix} \equiv f_1^2(\varepsilon) - [f_2(\varepsilon) + 1]^2 = 0, \tag{53b}$$

This latter expression can be simplified to

$$f_2(\varepsilon) + 1 = \pm f_1(\varepsilon). \tag{53c}$$

Roots of (53c) produce all cardinal eigenvalues of the finite one-dimensional chain $\mathbf{A}_n'$. There are exact expressions for eigenvalues and eigenstates of such a finite-dimensional chain containing n atoms [5]:

$$\varepsilon_s = 2\cos\left(\frac{s\pi}{n+1}\right), \tag{54a}$$

$$|\Psi_s\rangle = \sqrt{\frac{2}{n+1}} \sum_{\alpha}^{n} \sin\left(\frac{\pi}{n+1}\alpha s\right)|\alpha\rangle, \qquad s = 1, \ldots, n. \tag{54b}$$

One can verify that eigenvalues (54a) really satisfy LRM expression (53c). This shows that in the case $\gamma = 0$ LRM expressions produces correct eigenvalues of the modified system. One similarly finds that the corresponding eigenstates (54b) are also correctly reproduced by the LRM expression (51d).

Consider now the case $\gamma \neq 0$ which introduces a nontrivial interaction of the parent system $\mathbf{A}_n$ with a base system $\mathbf{B}_1$. As a particular example consider the case $n = 100$, $\gamma = 0.5$ and $E = 2.1$. Since n is relatively large, eigenvalues λ_i of the parent

system $\mathbf{A}_{100}$ (expression 41c) are relatively dense inside the interval $D = [-2, 2]$. In the limit $n \to \infty$ this interval becomes an eigenvalue band of the parent system. Eigenvalue $E = 2.1$ of the base system $\mathbf{B}_1$ is outside this eigenvalue band, and this system interacts with a parent system with the strength $\gamma = 0.5$. Eigenvalues $\varepsilon_s (s = 1, \ldots, 101)$ of the modified system $\mathbf{C}_{n+1}$ are roots of the LRM expression (51c) where $\gamma = 0.5$. First few and last few roots ε_s of this expression arranged in the decreasing order are:

$$\varepsilon_1 = 2.2520943, \quad \varepsilon_2 = 1.9990188, \quad \varepsilon_3 = 1.9960765, \quad \varepsilon_4 = 1.9911775,$$
$$\varepsilon_5 = 1.9843285, \quad \varepsilon_6 = 1.9755391, \quad \varepsilon_7 = 1.9648208, \quad \varepsilon_8 = 1.9521876, \quad (55)$$
$$\ldots \quad\quad\quad \varepsilon_{99} = -1.9913099, \quad \varepsilon_{100} = -1.9961362, \quad \varepsilon_{101} = -1.9990338.$$

All roots $\varepsilon = \varepsilon_s (s = 2, \ldots, 101)$ of the LRM expression (51c) are contained inside the interval $D = [-2, 2]$. The only exception is the root $\varepsilon_1 = 2.2520943$ which is contained outside this interval.

Consider eigenstate $|\Psi_1\rangle$ that corresponds to the eigenvalue $\varepsilon_1 \notin D$. Inserting LRM eigenvalue ε_1 into (51a) where $\gamma = 0.5$, $E = 2.1$ and $n = 100$ one finds

$$\begin{bmatrix} 0.0893723 & -0.2938055 & -0.4829332 \\ -0.2938055 & 0.9658664 & 1.5876111 \\ -0.4829332 & 1.5876111 & 0.9658664 \end{bmatrix} \begin{vmatrix} \langle\Theta|\theta_1\rangle \\ \langle 1|\varphi_1\rangle \\ \langle 100|\varphi_1\rangle \end{vmatrix} = 0, \quad (56a)$$

This equation has a nontrivial solution

$$\langle\Theta|\theta_1\rangle = 0.9567163, \quad \langle 1|\varphi_1\rangle = 0.2910222, \quad \langle 100|\varphi_1\rangle = 0, \quad (56b)$$

Note that amplitude $\langle 100|\varphi_1\rangle = 0$ is zero. According to (15b) and since the interaction space X_2^{int} is spanned by the states $|1\rangle$ and $|100\rangle$, this amplitude is the projection $\langle 100|\Psi_1\rangle$ of the modified eigenstate $|\Psi_1\rangle$ (expression 51d) on the state $|100\rangle$. Since eigenvalue $\varepsilon_1 \notin [-2, 2]$ of $|\Psi_1\rangle$ is outside the range $[-2, 2]$, eigenstate $|\Psi_1\rangle$ is essentially eigenstate $|\Theta\rangle$ of the base system $\mathbf{B}_1$ perturbed by the interaction with the one-dimensional chain $\mathbf{A}'_{100}$. Eigenstate $|\Psi_1\rangle$ is hence localized on the state $|\Theta\rangle$ and on those states $|j\rangle$ of this chain that are close to the state $|1\rangle$ where the system $\mathbf{A}'_{100}$ connects to the state $|\Theta\rangle$. Projection $\langle 100|\Psi_1\rangle$ of the modified eigenstate $|\Psi_1\rangle$ on the state $|100\rangle$ situated at the end of the chain $\mathbf{A}'_{100}$ is hence negligible.

Inserting eigenvalue $\varepsilon_1 = 2.2520943$ and amplitudes (56b) into the expression (51d) and normalizing according to (24′), one finds (see Fig. 4)

$$\langle\Theta|\Psi_1\rangle = 0.9337631, \quad \langle 1|\Psi_1\rangle = 0.2840401, \quad \langle 2|\Psi_1\rangle = 0.1728035,$$
$$\langle 3|\Psi_1\rangle = 0.1051297, \quad \langle 4|\Psi_1\rangle = 0.0639585, \quad \langle 5|\Psi_1\rangle = 0.0389109\ldots \quad (56c)$$
$$\langle 10|\Psi_1\rangle = 0.0032429\ldots \langle 20|\Psi_1\rangle = 0.0000225\ldots \langle 30|\Psi_1\rangle = 0.0000002\ldots$$

where $|\Psi_1\rangle$ is normalized. Eigenstate $|\Psi_1\rangle$ is mainly localized at the state $|\Theta\rangle$ and on few sites $|j\rangle$ close to the beginning of the chain $\mathbf{A}'_{100}$. Probability to find this eigenstate at the state $|\Theta\rangle$ equals $\langle\Theta|\Psi_1\rangle^2 = 0.8719135$. If one include probabilities to find this eigenstate at first five states $|\alpha\rangle(\alpha = 1, \ldots, 5)$ of the one-dimensional chain $\mathbf{A}'_{100}$, one
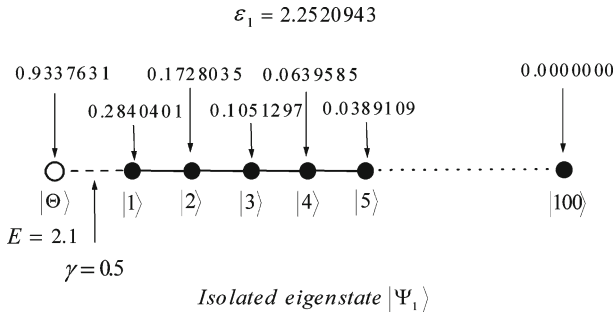
$$\varepsilon_1 = 2.2520943$$

Fig. 4 Modified system shown in Fig. 3b with parameters $n = 100$, $E = 2.1$ and $\gamma = 0.5$ is considered. Shown are amplitudes $\langle \Theta | \Psi_1 \rangle$ and $\langle i | \Psi_1 \rangle$ ($i = 1, \ldots, 100$) of the modified eigenstate $|\Psi_1\rangle$ that has eigenvalue $\varepsilon_1 = 2.2520943$. This eigenvalue is outside the range $D = [-2, 2]$. It is hence localized at the state $|\Theta\rangle$ and at few states $|i\rangle$ close to the state $|i\rangle = |1\rangle$

finds $\langle \Theta | \Psi_1 \rangle^2 + \sum_1^5 \langle \alpha | \Psi_1 \rangle^2 = 0.9991103$. Eigenstate $|\Psi_1\rangle$ is hence essentially base state $|\Theta\rangle$ modified by the interaction of the base system $\mathbf{B}_1$ with the parent system $\mathbf{A}_{100}$. Due to this interaction, initial eigenvalue $E = 2.1$ shifts to $\varepsilon_1 = 2.2520943$.

With the exception of the modified eigenstate $|\Psi_1\rangle$, all other modified eigenstates $|\Psi_s\rangle$ of $\mathbf{C}_{101}$ extend over the entire chain $\mathbf{A}'_{100}$. Consider for example root $\varepsilon_2 = 1.9990188$ of the expression (51c). This root is an eigenvalue of the modified system that is contained inside the range $D = [-2, 2]$. Inserting LRM eigenvalue $\varepsilon_2 = 1.9990188$ into (51a) where $\gamma = 0.5$, $E = 2.1$ and $n = 100$ one finds

$$\begin{bmatrix} 0.0829971 & -0.2859506 & -0.0359682 \\ -0.2859506 & -0.0719365 & 0.4280988 \\ -0.0359682 & 0.4280988 & -0.0719365 \end{bmatrix} \begin{vmatrix} \langle \Theta | \theta_2 \rangle \\ \langle 1 | \varphi_2 \rangle \\ \langle 100 | \varphi_2 \rangle \end{vmatrix} = 0, \qquad (57a)$$

This equation has a nontrivial solution

$$\langle \Theta | \theta_2 \rangle = 0.8075445, \qquad \langle 1 | \varphi_2 \rangle = -0.1630937, \qquad \langle 100 | \varphi_2 \rangle = -0.5668089, \tag{57b}$$

Unlike in the previous case, the amplitude $\langle 100 | \varphi_2 \rangle$ now differs from zero. This amplitude equals projection $\langle 100 | \Psi_2 \rangle$ of the modified eigenstate $|\Psi_2\rangle$ as given by the expression (51d) on the state $|100\rangle$. Unlike modified eigenstate $|\Psi_1\rangle$, modified eigenstate $|\Psi_2\rangle$ extends over the entire chain $\mathbf{A}'_{100}$ and it has a non-vanishing amplitude at the end of this chain.

Inserting eigenvalue $\varepsilon_2 = 1.9990188$ and amplitudes (57b) into (51d) and normalizing according to (24′), one finds (see Fig. 5)

$$\begin{aligned} &\langle \Theta | \Psi_2 \rangle = -0.0063015, \quad \langle 1 | \Psi_2 \rangle = 0.0012727, \quad \langle 2 | \Psi_2 \rangle = 0.0056948, \\ &\langle 3 | \Psi_2 \rangle = 0.0101114, \quad \langle 4 | \Psi_2 \rangle = 0.0145181, \quad \langle 5 | \Psi_2 \rangle = 0.0189105 \ldots \\ &\langle 10 | \Psi_2 \rangle = 0.0405087 \ldots \langle 20 | \Psi_2 \rangle = 0.0802254 \ldots \langle 30 | \Psi_2 \rangle = 0.1121337 \ldots \\ &\langle 98 | \Psi_2 \rangle = 0.0132513, \quad \langle 99 | \Psi_2 \rangle = 0.0088416, \quad \langle 100 | \Psi_2 \rangle = 0.0044230. \end{aligned} \tag{57c}$$

$$\varepsilon_2 = 1.9990188$$

Embedded eigenstate $|\Psi_2\rangle$

Fig. 5 The same as Fig. 4, but this time are shown amplitudes $\langle\Theta|\Psi_2\rangle$ and $\langle i|\Psi_2\rangle$ ($i = 1, \ldots, 100$) of the modified eigenstate $|\Psi_2\rangle$ that has eigenvalue $\varepsilon_2 = 1.9990188$. This eigenvalue is inside the range $D = [-2, 2]$. Eigenstate $|\Psi_2\rangle$ is hence an embedded eigenstate and it extends over the entire one-dimensional chain $\mathbf{A}'_{100}$

The state $|\Psi_2\rangle$ has non-vanishing amplitudes over the entire chain $\mathbf{A}'_{100}$ and one has in particular $\langle100|\Psi_2\rangle \neq 0$.

In a similar way can be obtained all other LRM solutions of the combined system $\mathbf{C}_{101}$. With the exception of the eigenstate $|\Psi_1\rangle$, each other eigenstate $|\Psi_s\rangle$ of the modified system has non-vanishing components $\langle\alpha|\Psi_s\rangle$ for almost each α ($\alpha = 1, \ldots, 100$). One can verify this LRM calculation with a standard diagonalization of this system. One thus finds that above LRM calculation produces correct eigenvalues and eigenstates of the modified system.

4.3 Comment on the example 4.2

Example 4.2 is given in order to illustrate possible application of the LRM approach to some problems in the solid state physics. This example is necessarily simple and hence not particularly useful. In the more realistic tight-binding approach, instead of a single atom α and a single atomic orbital $|\alpha\rangle$ situated at this atom, one should consider a unit cell that may contain several atoms and several atomic orbitals situated at each of those atoms [16]. This generalization presents no problem for the LRM approach. For example, if with each unit cell are associated ξ atomic orbitals and if the parent system contains n unit cells, this system is $n\xi$-dimensional, i.e. parent system is system $\mathbf{A}_{n\xi}$. If in accord with tight-binding approximation one assumes that only those orbitals that are situated at adjacent unit cells can interact with each other, one has 2ξ atomic orbitals that participate in the interaction between adjacent unit cells (1) and (n). In this case, in order to transform a circular chain into a linear chain, destruction of the interaction between those two unit cells involves $\sigma = 2\xi$ dimensional interaction space $X_{2\xi}^{\text{int}}$. The construction of the corresponding modification operator $\mathbf{V}$ that acts in the space $X_{2\xi}^{\text{int}}$ is rather straightforward. Further, one can assume that the parent system $\mathbf{A}_{n\xi}$ interacts with a base system $\mathbf{B}_\rho$ that contains not only one but rather $\rho > 1$ atomic orbitals. In this case base space X_ρ^b is ρ-dimensional. As a result, instead of the 3×3 matrix Eq. (51a) and a 3×3 determinant (51c), one has to consider $(2\xi + \rho) \times (2\xi + \rho)$ matrix equation and $(2\xi + \rho) \times (2\xi + \rho)$ corresponding determinant.

In a similar way can be treated more general cases when atomic orbitals situated at adjacent unit cells are not orthogonal to each other. The only new feature in this case is that modification operators $\mathbf{P}_a$ and $\mathbf{P}$ are no more zero. Otherwise LRM treatment of cardinal solutions of the modified system again results in the $(2\xi + \rho) \times (2\xi + \rho)$ matrix equation. Similar conclusions apply to singular solutions of the modified system.

Above approach can be also generalized to the LRM treatment of three-dimensional solids. In order to maintain translational invariance of a parent system one can again use Born-van Karman periodic boundary condition. In a similar way as above this solid can be modified internally in order to create a surface of such a solid, and externally in order to establish interaction of thus created surface with some molecule (or some other quantum system). However, efficient transition to the three-dimensional case requires generalization of the LRM approach to the treatment of infinite-dimensional parent systems [3].

The main point of the above approach is that due to the translational invariance one can obtain relatively reliable solution of the parent system $\mathbf{A}_n$, though this system may be very large. Once this is done, LRM formalism does the rest.

5 Conclusion

In this paper LRM appropach is generalized to the simultaneous presence of intenal and external modifications of the parent finite-dimensional system $\mathbf{A}_n$. This system is modified externally by the interaction with a ρ-dimensional base system $\mathbf{B}_\rho$ and internally with a modification involving σ-dimensional interaction space X_σ^{int}. Most important feature of this approach is that the LRM expressions that produce cardinal ($\varepsilon_s \notin \{\lambda_i\}$) eigenvalues and eigenstates of the modified $(n + \rho)$-dimensional system $\mathbf{C}_{n+\rho}$ is $(\sigma + \rho) \times (\sigma + \rho)$ matrix equation. In particular, dimension of this LRM equation does not depend on the dimension n of the parent system. The same applies to the LRM expressions that produce singular ($\varepsilon_s = \lambda_j \in \{\lambda_i\}$) eigenvalues and eigenstates of the modified system. LRM approach is hence particularly suitable to those cases when the dimension of the parent system is large with respect to the dimension σ of the interaction space and with respect to the dimension ρ of the base system.

Key point in the LRM treatment of such systems is that in many cases of interest one has relatively reliable solution of the parent system $\mathbf{A}_n$, though this system may be very large. For example if $\mathbf{A}_n$ represents an ideal translationally invariant solid, due to this translational invariance one can obtain relatively reliable solution of such a solid, however large n. Once eigenvalues and eigenstates of $\mathbf{A}_n$ are known, LRM provides a straightforward formalism to derive solutions to various modified systems $\mathbf{C}_{n+\rho}$. Modifications of the parent system $\mathbf{A}_n$ can include creation of surfaces, establishment of the interaction with various molecules with thus created surfaces, creation of impurities and defects in the parent system $\mathbf{A}_n$, etc. All such modifications of a parent system destroy original translational invariance and it is hence usually rather difficult to obtain an exact solution of such modified systems by other standard methods. However LRM provides an exact solution to all such systems. As long as rank of the corresponding modification operators is small with respect to the dimension n of

the original parent system, this approach is numerically very efficient. In addition, it is possible to obtain $n \rightarrow \infty$ limit of the corresponding LRM expressions [3,8,9]. In this way LRM can provide exact solution of the external and internal modifications of infinite-dimensional systems. This extension of LRM to infinite dimensional systems was successfully obtained in the case of external modifications of infinite-dimensional parent systems [3]. It remains to generalize thus obtained results to the simultaneous presence of internal and external modifications of such infinite-dimensional systems.

Appendix A

LRM treatment of finite-dimensional systems is generalized to modified systems that contain both, external as well as internal modifications of the original parent system.

A1. Parent system $\mathbf{A}_n$

Consider the system $\mathbf{A}_n$ described by the generalized eigenvalue Eq. (1a). Operators $\mathbf{H}_a$ and $\mathbf{S}_a$ are Hermitean in the n-dimensional space X_n^a spanned by eigenstates $|\Phi_i\rangle$ of (1a). Operator $\mathbf{S}_a$ is in addition positive definite in this space. Since $\mathbf{S}_a$ is Hermitean and positive definite, operators $\mathbf{S}_a^{1/2}$ and $\mathbf{S}_a^{-1/2}$ are well defined. In addition, those operators are also Hermitean and positive definite in X_n^a. Hence eigenvalue Eq. (1a) can be transformed into a standard eigenvalue equation

$$\mathbf{H}_a'|\Phi_i'\rangle = \lambda_i|\Phi_i'\rangle, \qquad i = 1, \ldots, n, \tag{A1a}$$

where

$$\mathbf{H}_a' = \mathbf{S}_a^{-1/2}\mathbf{H}_a\mathbf{S}_a^{-1/2}, \qquad |\Phi_i'\rangle = \mathbf{S}_a^{1/2}|\Phi_i\rangle. \tag{A1b}$$

Hermiticity of $\mathbf{H}_a$ and $\mathbf{S}_a^{-1/2}$ implies Hermiticity of $\mathbf{H}_a'$. Eigenvalues λ_i of (1a) are hence real. Further, since eigenstates $|\Phi_i'\rangle$ of $\mathbf{H}_a'$ can be orthonormalized in a standard way $\langle\Phi_i'|\Phi_j'\rangle = \delta_{ij}$, eigenstates $|\Phi_i\rangle$ of (1a) can be orthonormalized according to (1b). In a similar way one finds that eigenstates $|\Psi_s\rangle$ of the eigenvalue Eq. (7a) that describes modified system can be orthonormalized according to (7c).

Consider the operator $\mathbf{I}_a$

$$\mathbf{I}_a = \sum_j^n |\Phi_j\rangle\langle\Phi_j|\mathbf{S}_a, \tag{A2a}$$

Expression (1b) implies $\mathbf{I}_a|\Phi_i\rangle = |\Phi_i\rangle$ for each eigenstate $|\Phi_i\rangle$ of (1a). Since those eigenstates form a complete set in X_n^a, operator $\mathbf{I}_a$ is a unit operator in this space. Operator $\mathbf{I}_a$ as given by the expression (A2a) is not manifestly Hermitean. However, since it is a unit operator in X_n^a, it must be Hermitean. Taking Hermitean conjugate of the

expression (A2a) one finds

$$\mathbf{I}_a = \sum_{j}^{n} \mathbf{S}_a |\Phi_j\rangle\langle\Phi_j|. \tag{A2b}$$

This is another possible representation of the unit operator $\mathbf{I}_a$.

Expressions (A2) imply

$$\mathbf{S}_a^{-1} = \sum_{j}^{n} |\Phi_j\rangle\langle\Phi_j|, \tag{A3a}$$

where $\mathbf{S}_a^{-1}$ is inverse of $\mathbf{S}_a$ in the space X_n^a. In a similar way using expression (1b) one finds that the operator $\mathbf{H}_a$ can be written as

$$\mathbf{H}_a = \sum_{j}^{n} \lambda_j \mathbf{S}_a |\Phi_j\rangle\langle\Phi_j| \mathbf{S}_a. \tag{A3b}$$

By definition, system $\mathbf{A}_n$ described by the eigenvalue Eq. (1a) is a *parent system*.

A2. Modifications of a parent system

Parent system $\mathbf{A}_n$ can be modified internally as well as externally.

In an external modification, system $\mathbf{A}_n$ interacts with ρ-dimensional system $\mathbf{B}_\rho$ which is outside the system $\mathbf{A}_n$. System $\mathbf{B}_\rho$ is described by the generalized eigenvalue Eq. (4a). Operators $\mathbf{H}_b$ and $\mathbf{S}_b$ are Hermitean in the ρ-dimensional space X_ρ^b spanned by eigenstates $|\Theta_r\rangle$ of (4a). Operator $\mathbf{S}_b$ is in addition positive definite in this space. In analogy to (1b), eigenstates $|\Theta_r\rangle$ of $\mathbf{B}_\rho$ can be orthonormalized according to (4b) while a unit operator $\mathbf{I}_b$ in the space X_ρ^b can be written in the form

$$\mathbf{I}_b = \sum_{r}^{\rho} |\Theta_r\rangle\langle\Theta_r| \mathbf{S}_b = \sum_{r}^{\rho} \mathbf{S}_b |\Theta_r\rangle\langle\Theta_r|. \tag{A4}$$

By definition, system $\mathbf{B}_\rho$ described by the eigenvalue Eq. (4a) is a *base system*.

Interaction between the parent system $\mathbf{A}_n$ and the base system $\mathbf{B}_\rho$ is described by modification operators $\mathbf{V}$ and $\mathbf{P}$. Those operators are Hermitean, they connect vectors in the parent space X_n^a with vectors in the base space X_ρ^b, and they vanish over spaces X_n^a and X_ρ^b. Hence those operators satisfy

$$\mathbf{V} = \mathbf{I}_b \mathbf{V} \mathbf{I}_a + \mathbf{I}_a \mathbf{V} \mathbf{I}_b, \qquad \mathbf{P} = \mathbf{I}_b \mathbf{P} \mathbf{I}_a + \mathbf{I}_a \mathbf{P} \mathbf{I}_b, \tag{A5a}$$

Operator $\mathbf{V}$ modifies operators $\mathbf{H}_a$ and $\mathbf{H}_b$, while operator $\mathbf{P}$ modifies operators $\mathbf{S}_a$ and $\mathbf{S}_b$. From the point of view of the parent system $\mathbf{A}_n$, base system $\mathbf{B}_\rho$ in conjuncture with the operators $\mathbf{V}$ and $\mathbf{P}$ represents an *external* modification.

In addition to the external modification, parent system $\mathbf{A}_n$ can be modified internally. Internal modification involves Hermitean operators $\mathbf{V}_a$ and $\mathbf{P}_a$ that act in the space X_n^a. Operator $\mathbf{V}_a$ modifies operator $\mathbf{H}_a$, while operator $\mathbf{P}_a$ modifies operator $\mathbf{S}_a$. Those operators are nonzero over a σ-dimensional space X_σ^{int}, subspace of the space X_n^a. By definition, X_σ^{int} is the *interaction space*. This space is a combined image of operators $\mathbf{V}_a$ and $\mathbf{P}_a$. In other words, X_σ^{int} is spanned by all vectors of a type $\mathbf{V}_a|\Psi\rangle$ and by all vectors of a type $\mathbf{P}_a|\Psi\rangle$, where $|\Psi\rangle \in X_n^a$.

Let $\mathbf{I}_{\text{int}}$ be projection operator on the interaction space X_σ^{int}. Since $\mathbf{V}_a$ and $\mathbf{P}_a$ are nonzero only over X_σ^{int}, those operators satisfy

$$\mathbf{V}_a = \mathbf{I}_{\text{int}}\mathbf{V}_a\mathbf{I}_{\text{int}}, \qquad \mathbf{P}_a = \mathbf{I}_{\text{int}}\mathbf{P}_a\mathbf{I}_{\text{int}}. \tag{A5b}$$

Modified system $\mathbf{C}_{n+\rho}$ that contains both, internal and external modifications of the parent system $\mathbf{A}_n$, is described by the generalized eigenvalue Eq. (7a) where β is the coupling parameter. This parameter is introduced for convenience, in order to have a clear distinction between the weak modifications (small β) and strong modifications (large β). Since all operators in the expressions (7b) are Hermitean, operators $\mathbf{H}_c$ and $\mathbf{S}_c$ are also Hermitean. In addition, operator $\mathbf{S}_c$ is required to be positive definite in the $(n + \rho)$-dimensional combined space $X_{n+\rho}^c$ spanned by the eigenstates $|\Psi_s\rangle$ of the modified system $\mathbf{C}_{n+\rho}$. Since $\mathbf{S}_c$ is Hermitean and positive definite in $X_{n+\rho}^c$, eigenstates $|\Psi_s\rangle$ of $\mathbf{C}_{n+\rho}$ can be orthonormalized according to (7c).

Modified system $\mathbf{C}_{n+\rho}$ that contains both, external as well as internal modifications is shown schematically in Fig. 1.

In LRM are treated in a different way *cardinal* and *singular* eigenvalues ε_s and corresponding eigenstates $|\Psi_s\rangle$ of the modified system $\mathbf{C}_{n+\rho}$ [1–3]. By definition, eigenvalue ε_s of $\mathbf{C}_{n+\rho}$ is *cardinal* if it differs from all eigenvalues λ_i of the parent system $\mathbf{A}_n$ ($\varepsilon_s \notin \{\lambda_i\}$), otherwise it is singular ($\varepsilon_s = \lambda_j \in \{\lambda_i\}$). If ε_s is cardinal (singular), the corresponding eigenstate $|\Psi_s\rangle$ (or eigenstates if ε_s is degenerate) is cardinal (singular).

A3. Proof of Theorems 1 and 2

Consider eigenvalue Eq. (1a). Since $\mathbf{H}_a$ and $\mathbf{S}_a$ are Hermitean, this equation implies

$$\langle\Phi_i|\mathbf{H}_a = \lambda_i\langle\Phi_i|\mathbf{S}_a, \qquad i = 1, \ldots, n. \tag{A6}$$

and similarly for eigenvalue Eqs. (4a) and (7a). Multiplying (7a) from left by $\langle\Phi_i|$, using $\langle\Phi_i|\mathbf{H}_b = \langle\Phi_i|\mathbf{S}_b = 0$ and expressions (A5) and (A6), one finds

$$(\varepsilon_s - \lambda_i)\,\langle\Phi_i|\mathbf{S}_a|\Psi_s^a\rangle = \beta\langle\Phi_i|\mathbf{V} - \varepsilon_s\mathbf{P}|\theta_s\rangle$$
$$+ \beta\langle\Phi_i|\mathbf{V}_a - \varepsilon_s\mathbf{P}_a|\varphi_s\rangle, i = 1, \ldots, n, \quad s = 1, \ldots, n+\rho. \tag{A7a}$$

where

$$|\Psi_s^a\rangle = \mathbf{I}_a|\Psi_s\rangle \in X_n^a, \qquad |\theta_s\rangle = \mathbf{I}_b|\Psi_s\rangle \in X_\rho^b, \qquad |\varphi_s\rangle = \mathbf{I}_{\text{int}}|\Psi_s\rangle \in X_\sigma^{\text{int}},$$
(A7b)

are projections of the modified eigenstate $|\Psi_s\rangle$ on spaces X_n^a, X_ρ^b and X_σ^{int}, respectively. In particular, modified eigenstate $|\Psi_s\rangle$ is a linear combination

$$|\Psi_s\rangle = |\Psi_s^a\rangle + |\theta_s\rangle.$$
(A7c)

Since $|\Psi_s\rangle \neq 0$ one must have either $|\Psi_s^a\rangle \neq 0$ and/or $|\theta_s\rangle \neq 0$.

In a similar way, multiplying (7a) from left by $\langle\Theta_r|$ and using (A7b) and $\langle\Theta_r|\mathbf{H}_a = \langle\Theta_r|\mathbf{S}_a = \langle\Theta_r|\mathbf{V}_a = \langle\Theta_r|\mathbf{P}_a = 0$ one finds

$$\langle\Theta_r|\varepsilon_s\mathbf{S}_b - \mathbf{H}_b|\theta_s\rangle = \beta\langle\Theta_r|\mathbf{V} - \varepsilon_s\mathbf{P}|\Psi_s^a\rangle, \qquad r = 1,\dots,\rho, \quad s = 1,\dots,n+\rho,$$
(A8a)

Since $(\varepsilon_s\mathbf{S}_b - \mathbf{H}_b)|\theta_s\rangle \in X_\rho^b$ and $(\mathbf{V} - \varepsilon_s\mathbf{P})|\Psi_s^a\rangle \in X_\rho^b$, and since the states $|\Theta_r\rangle(r = 1,\dots,\rho)$ form a complete set in X_ρ^b, this implies

$$(\varepsilon_s\mathbf{S}_b - \mathbf{H}_b)|\theta_s\rangle = \beta(\mathbf{V} - \varepsilon_s\mathbf{P})|\Psi_s^a\rangle, \qquad s = 1,\dots,n+\rho.$$
(A8b)

Expressions (A7) and (A8) are starting expressions for the LRM treatment of modified systems.

Cardinal solutions (Theorem 1)

Let $\varepsilon_s \notin \{\lambda_i\}$ be a cardinal eigenvalue of the generalized eigenvalue Eq. (7a). Divide (A7a) by $(\varepsilon_s - \lambda_i)$, multiply from left by $|\Phi_i\rangle$, sum over i and use (A2a) to obtain

$$|\Psi_s^a\rangle = \beta\sum_i^n \frac{\langle\Phi_i|\mathbf{V} - \varepsilon_s\mathbf{P}|\theta_s\rangle + \langle\Phi_i|\mathbf{V}_a - \varepsilon_s\mathbf{P}_a|\varphi_s\rangle}{\varepsilon_s - \lambda_i}|\Phi_i\rangle.$$
(A9)

Multiply (A9) from left by $(\mathbf{V} - \varepsilon_s\mathbf{P})$ to obtain

$$(\mathbf{V} - \varepsilon_s\mathbf{P})|\Psi_s^a\rangle = \beta\mathbf{\Omega}_b(\varepsilon_s)|\theta_s\rangle + \beta\mathbf{\Omega}_{ba}(\varepsilon_s)|\varphi_s\rangle.$$
(A10)

where operators $\mathbf{\Omega}_b(\varepsilon)$ and $\mathbf{\Omega}_{ab}(\varepsilon) \equiv (\mathbf{\Omega}_{ba}(\varepsilon))^*$ are given by expressions (11) and (13), respectively. Assume now $\beta \neq 0$. In this case using expression (A8b) one can eliminate component $|\Psi_s^a\rangle$ from the expression (A10) to obtain:

$$\left[\beta^2\mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s\mathbf{S}_b\right]|\theta_s\rangle + \beta^2\mathbf{\Omega}_{ba}(\varepsilon_s)|\varphi_s\rangle = 0,$$
(A11a)

Multiplying (A9) from left by $(\mathbf{V}_a - \varepsilon_s \mathbf{P}_a)$ and using (A7b) one finds

$$[\beta \mathbf{\Omega}_a(\varepsilon_s) + \varepsilon_s \mathbf{P}_a - \mathbf{V}_a]|\varphi_s\rangle + \beta \mathbf{\Omega}_{ab}(\varepsilon_s)|\theta_s\rangle = 0. \tag{A11b}$$

where $\mathbf{\Omega}_a(\varepsilon)$ is given by the expression (12). Since according to (A7c) and (A9) $|\Psi_s\rangle \neq 0$ implies $|\theta_s\rangle \neq 0$ and/or $|\varphi_s\rangle \neq 0$, expressions (A11) must have a nontrivial solution $|\Xi_s\rangle \equiv |\theta_s\rangle + |\varphi_s\rangle \neq 0$.

If $\beta \neq 0$ expressions (A11) can be written in the manifestly Hermitean form (14a). However if $\beta = 0$ expression (A11a) reduces to the expression (4a) which describes isolated system $\mathbf{B}_\rho$, while expression (A11b) reduces to $[\varepsilon_s \mathbf{P}_a - \mathbf{V}_a]|\varphi_s\rangle = 0$. However, as implied by the expressions (A7b) and (A9), if $\beta = 0$ one has $|\Psi_s^a\rangle = |\varphi_s\rangle = 0$. In conclusion, if $\beta = 0$ expressions (A11) reduce to the expression (4a) that describes isolated system $\mathbf{B}_\rho$ and in addition the corresponding cardinal eigenstate $|\Psi_s\rangle$ has no X_n^a-component. This eigenstate is hence an eigenstate of the isolated base system $\mathbf{B}_\rho$. This conclusion is trivially obvious, since in the case $\beta = 0$ there is no interaction between the systems $\mathbf{A}_n$ and $\mathbf{B}_\rho$, and each eigenstate $|\Theta_r\rangle$ of the isolated system $\mathbf{B}_\rho$ that has eigenvalue $E_r \notin \{\lambda_i\}$ is by definition cardinal eigenstate of the combined system $\mathbf{C}_{n+\rho}$ that consists of non-interactions subsystems $\mathbf{A}_n$ and $\mathbf{B}_\rho$.

Let $\{|\mu\rangle\}$ be the base in X_σ^{int} orthonormalized according to (2a), let $\{|r\rangle\}$ be the base in X_ρ^b orthonormalized according to (5a), and let $\beta \neq 0$. Projection operators $\mathbf{I}_{\text{int}}$ and $\mathbf{I}_b$ can be expressed in terms of the base vectors $|\mu\rangle$ and $|r\rangle$ according to (2c) and (5b), respectively. In the base $\{|r\rangle, |\mu\rangle\}$ $(r = 1, \ldots \rho; \mu = 1, \ldots \sigma)$ expressions (A11) can be written in the explicit form

$$\sum_t^\rho \langle r|\beta^2 \mathbf{\Omega}_b(\varepsilon_s) + \mathbf{H}_b - \varepsilon_s \mathbf{S}_b|t\rangle B_t^{(s)}$$

$$+\beta^2 \sum_v^\sigma \langle r|\mathbf{\Omega}_{ba}(\varepsilon_s)|v\rangle C_v^{(s)} = 0. \qquad r = 1, \ldots, \rho, \tag{A12a}$$

$$\beta \sum_t^\rho \langle \mu|\mathbf{\Omega}_{ab}(\varepsilon_s)|t\rangle B_t^{(s)}$$

$$+\sum_v^\sigma \langle \mu|\beta \Omega_a(\varepsilon_s) + \varepsilon_s \mathbf{P}_a - \mathbf{V}_a|v\rangle C_v^{(s)} = 0 \qquad \mu = 1, \ldots, \sigma. \tag{A12b}$$

where

$$\sum_v^\sigma C_v^{(s)}|v\rangle = |\varphi_s\rangle \in X_\sigma^{\text{int}}, \qquad \sum_t^\rho B_t^{(s)}|t\rangle = |\theta_s\rangle \in X_\rho^b. \tag{A12c}$$

Expressions (A12a) and (A12b) form a set of $\rho + \sigma$ homogenous linear equations in $\rho + \sigma$ unknowns, ρ unknown coefficients $B_t^{(s)}$ that determine the state $|\theta_s\rangle$ and σ unknown coefficients $C_v^{(s)}$ that determine the state $|\varphi_s\rangle$. Those equations have a non-trivial solution if and only if the determinant of this system vanishes. Each cardinal

eigenvalue $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of the generalized eigenvalue Eq. (7a) is hence a root of the $(\rho + \sigma) \times (\rho + \sigma)$ determinant (14c).

One finds that the inverse is also true, each root $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of (14c) is an eigenvalue of the generalized eigenvalue Eq. (7a). According to (A8c) and (A9), once $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ is obtained as a root of (14c), the corresponding eigenstate $|\Psi_s\rangle$ is given by the expression (15a) where $|\theta_s\rangle$ and $|\varphi_s\rangle$ are obtained as a solution of (14a). This proves Theorem 1.

Proof of Lemma 1 Let $|\Xi_{sk}\rangle \equiv |\theta_{sk}\rangle + |\varphi_{sk}\rangle$ $(k = 1, \ldots, \kappa)$ be the set of κ linearly dependent eigenstates of (14a) that correspond to the same eigenvalue $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of the modified system. Since those states are linearly dependent, there are coefficients $c_k (k = 1, \ldots, \kappa)$ which are not all zero such that

$$\sum_k^\kappa c_k |\Xi_{sk}\rangle \equiv \sum_k^\kappa c_k \left(|\theta_{sk}\rangle + |\varphi_{sk}\rangle \right) = 0, \tag{A13a}$$

Using this expression one finds that the corresponding eigenstates $|\Psi_{sk}\rangle$ $(k = 1, \ldots, \kappa)$ of the modified system $\mathbf{C}_{n+\rho}$ as given by (15a) satisfy

$$\sum_k^\kappa c_k |\Psi_{sk}\rangle = 0. \tag{A13b}$$

Linear dependence of the eigenstates $|\Xi_{sk}\rangle$ $(k = 1, \ldots \kappa)$ of (14a) hence implies linear dependence of the corresponding eigenstates $|\Psi_{sk}\rangle$ of the modified system $\mathbf{C}_{n+\rho}$. The inverse is also true. Let namely eigenstates $|\Psi_{sk}\rangle$ $(k = 1, \ldots, \kappa)$ of the modified system $\mathbf{C}_{n+\rho}$ correspond to the same eigenvalue ε_s and let those eigenstates be linearly dependent. In this case there are coefficients c_k $(k = 1, \ldots, \kappa)$ which are not all zero and which satisfy (A13b). Multiplying this expression from left by $\mathbf{I}_b$ as well as by $\mathbf{I}_{\text{int}}$ and using (A7b) one derives (A13a). Linear dependence of modified eigenstates $|\Psi_{sk}\rangle$ hence implies linear dependence of the corresponding eigenstates $|\Xi_{sk}\rangle$ of the eigenvalue Eq. (14a). This proves Lemma 1.   □

Since (14a) is a $(\rho + \sigma) \times (\rho + \sigma)$ matrix equation, Lemma 1 implies that each cardinal eigenvalue $\varepsilon = \varepsilon_s \notin \{\lambda_i\}$ of the modified system can be at most $(\rho + \sigma)$ degenerate.

Normalization of cardinal eigenstates

Cardinal eigenstate (15a) of the modified system $\mathbf{C}_{n+\rho}$ can be normalized according to

$$|\Psi_s\rangle \rightarrow |\Psi_s'\rangle = \frac{1}{\sqrt{N_s}} |\Psi_s\rangle, \tag{A14a}$$

where normalization constant N_s is given by

$$N_s = \langle \Psi_s | \mathbf{S}_c | \Psi_s \rangle. \tag{A14b}$$

Expression (7b) implies that normalization constant N_s can be given in the form (23a). Matrix elements $\langle\theta_s|\mathbf{S}_b|\theta_s\rangle$ and $\langle\varphi_s|\mathbf{P}_a|\varphi_s\rangle$ in (23a) involve only the states $|\theta_s\rangle$ and $|\varphi_s\rangle$ which are obtained as a solution to LRM Eq. (14a). Matrix elements $\langle\Psi_s^a|\mathbf{S}_a|\Psi_s^a\rangle$ and $\langle\Psi_s^a|\mathbf{P}|\theta_s\rangle = \langle\theta_s|\mathbf{P}|\Psi_s^a\rangle^*$ in this expression can be expressed in terms of those two states and in terms of the known eigenstates $|\Phi_i\rangle$ and corresponding eigenvalues λ_i of the parent system $\mathbf{A}_n$. Using definition (10) of the operator $\overline{\Omega}(\varepsilon)$ one derives expressions (23) and (24).

Singular solutions (Theorem 2)

Let $\varepsilon_s = \lambda_j \in \{\lambda_i\}$ be a singular eigenvalue of the modified system $\mathbf{C}_{n+\rho}$. Let further λ_j be η_j-degenerate and let $|\Phi_{jm}\rangle(m = 1, \ldots, \eta_j)$ be the corresponding eigenstates of the parent system $\mathbf{A}_n$ orthonormalized according to (1b). Those eigenstates span η_j-dimensional space $X_{\eta_j}^j$, subspace of the space X_n^a.

Divide (A7a) by $(\lambda_j - \lambda_i)$ where $\lambda_i \neq \lambda_j = \varepsilon_s$, multiply from left by $|\Phi_i\rangle$, sum over $i(\lambda_i \neq \varepsilon_s)$, add to both sides $\Sigma_m|\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a|\Psi_s\rangle$ and use (A2a) to obtain

$$|\Psi_s^a\rangle = \beta \sum_{i(\lambda_i \neq \lambda_j)} \frac{\langle\Phi_i|\mathbf{V} - \lambda_j\mathbf{P}|\theta_s\rangle + \langle\Phi_i|\mathbf{V}_a - \lambda_j\mathbf{P}_a|\varphi_s\rangle}{\lambda_j - \lambda_i}|\Phi_i\rangle + |\chi_s^j\rangle. \quad \text{(A15a)}$$

where the states $|\Psi_s^a\rangle$, $|\theta_s\rangle$ and $|\varphi_s\rangle$ satisfy (A7b) and where

$$|\chi_s^j\rangle = \sum_m^{\eta_j} |\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a|\Psi_s\rangle \equiv \sum_m^{\eta_j} D_m^{(s)}|\Phi_{jm}\rangle \in X_{\eta_j}^j. \quad \text{(A15b)}$$

One can write the state $|\chi_s^j\rangle$ as

$$|\chi_s^j\rangle = \mathbf{O}_j|\Psi_s\rangle, \quad \text{(A16a)}$$

where operator $\mathbf{O}_j$ is given by

$$\mathbf{O}_j = \sum_m^{\eta_j} |\Phi_{jm}\rangle\langle\Phi_{jm}|\mathbf{S}_a. \quad \text{(A16b)}$$

Multiply (A15a) from left by $(\mathbf{V} - \lambda_j\mathbf{P})$ and use expressions (11) and (13) to obtain

$$(\mathbf{V} - \lambda_j\mathbf{P})|\Psi_s^a\rangle = \beta\mathbf{\Omega}_b(\lambda_j)|\theta_s\rangle + \beta\mathbf{\Omega}_{ba}(\lambda_j)|\varphi_s\rangle + (\mathbf{V} - \lambda_j\mathbf{P})|\chi_s^j\rangle, \quad \text{(A17)}$$

Assume now $\beta \neq 0$. In this case using expression (A8b) one can eliminate component $|\Psi_s^a\rangle$ from (A17). One thus finds

$$\left[\beta^2\mathbf{\Omega}_b(\lambda_j) + \mathbf{H}_b - \lambda_j\mathbf{S}_b\right]|\theta_s\rangle + \beta^2\mathbf{\Omega}_{ba}(\lambda_j)|\varphi_s\rangle + \beta(\mathbf{V} - \lambda_j\mathbf{P})|\chi_s^j\rangle = 0,$$
$$\text{(A18a)}$$

Multiply (A15a) from left by $\left(\mathbf{V}_a - \lambda_j \mathbf{P}_a\right)$ and use (A5b) and (A7b) to obtain

$$\left[\beta \boldsymbol{\Omega}_a(\lambda_j) + \lambda_j \mathbf{P}_a - \mathbf{V}_a\right] |\varphi_s\rangle + \beta \boldsymbol{\Omega}_{ab}(\lambda_j)|\theta_s\rangle + \left(\mathbf{V}_a - \lambda_j \mathbf{P}_a\right) |\chi_s^j\rangle = 0. \tag{A18b}$$

Further, in the case $\varepsilon_s = \lambda_j$ expression (A7a) implies

$$\beta \langle \Phi_{jm}|\mathbf{V} - \lambda_j \mathbf{P}|\theta_s\rangle + \beta \langle \Phi_{jm}|\mathbf{V}_a - \lambda_j \mathbf{P}_a|\varphi_s\rangle = 0, \qquad m = 1, \ldots, \eta_j;$$

Since the states $|\Phi_{jm}\rangle (m = 1, \ldots, \eta_j)$ form a complete set in the space $X_{\eta_j}^j$, this implies

$$\beta \mathbf{I}_j \left(\mathbf{V} - \lambda_j \mathbf{P}\right) |\theta_s\rangle + \beta \mathbf{I}_j \left(\mathbf{V}_a - \lambda_j \mathbf{P}_a\right) |\varphi_s\rangle = 0. \tag{A18c}$$

where $\mathbf{I}_j$ is a projection operator on the space $X_{\eta_j}^j$.

Since $\beta \neq 0$ expressions (A18) can be written in the manifestly Hermitean form (16a). In the base $\{|r\rangle, |\mu\rangle, |\Phi_{jm}\rangle\}$ $(r = 1, \ldots \rho; \mu = 1, \ldots \sigma; m = 1, \ldots \eta_j)$ those expressions form a set of $(\rho + \sigma + \eta_j)$ homogenous linear equation in $(\rho + \sigma + \eta_j)$ unknowns; ρ unknown coefficients $B_r^{(s)}$ that determine component $|\theta_s\rangle \in X_\rho^b$ of the eigenstate $|\Psi_s\rangle$, σ unknown coefficients $C_\mu^{(s)}$ that determine component $|\varphi_s\rangle \in X_\sigma^{\text{int}}$ of this eigenstate, and finally η_j unknown coefficients $D_m^{(s)}$ that determine the state $|\chi_s^j\rangle \in X_{\eta_j}^j$. Once the states $|\theta_s\rangle$, $|\varphi_s\rangle$ and $|\chi_s^j\rangle$ are obtained as a solution to (16a), the corresponding singular eigenstate is given by (16c). This proves Theorem 2.

For each $\varepsilon_s = \lambda_j$ expression (16a) may have at most $\rho + \sigma + \eta_j$ linearly independent solutions $|\Xi_{sk}\rangle = |\theta_{sk}\rangle + |\varphi_{sk}\rangle + |\chi_{sk}^j\rangle (k = 1, 2, \ldots)$. The set of all such solutions forms a linear space. In analogy to Lemma 1, one can prove Lemma 2. According to this Lemma the set of all singular eigenstates (16c) that have eigenvalue $\varepsilon_s = \lambda_j$ forms a linear space that is isomorphic to the linear space spanned by the set $\{|\Xi_{sk}\rangle\}$ $(k = 1, 2, \ldots)$. Since (16a) is a $(\rho + \sigma + \eta_j) \times (\rho + \sigma + \eta_j)$ matrix equation, one can have at most $\rho + \sigma + \eta_j$ singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$.

In the special case $\beta = 0$ expressions (A18) reduce to

$$\left[\mathbf{H}_b - \lambda_j \mathbf{S}_b\right] |\theta_s\rangle = 0, \tag{A19a}$$

$$\left[\lambda_j \mathbf{P}_a - \mathbf{V}_a\right] |\varphi_s\rangle + \left(\mathbf{V}_a - \lambda_j \mathbf{P}_a\right) |\chi_s^j\rangle = 0. \tag{A19b}$$

Equation (A19a) is Eq. (4a) that describes isolated base system $\mathbf{B}_\rho$ with the condition that parent system $\mathbf{A}_n$ should contain eigenvalue λ_j which coincides with an eigenvalue E_r of $\mathbf{B}_\rho$. By definition, such a solution of a base system is a singular solution of a combined system $\mathbf{C}_{n+\rho}$ that consists of mutually non-interactions subsystems $\mathbf{A}_n$ and $\mathbf{B}_\rho$. Consider now expression (A19b). As implied by the expression (A15a), if $\beta = 0$ one has $|\varphi_s\rangle = \mathbf{I}_{\text{int}}|\Psi_s^a\rangle = \mathbf{I}_{\text{int}}|\chi_s^j\rangle$. Further, due to expressions (3), one has $\mathbf{V}_a|\chi_s^j\rangle = \mathbf{V}_a \mathbf{I}_{\text{int}}|\chi_s^j\rangle$ and similarly for the operator $\mathbf{P}_a$. Inserting into (A19b) one finds that this expression is satisfied for each state $|\chi_s^j\rangle \in X_{\eta_j}^j$. All such states

are eigenstates of the parent system $\mathbf{A}_n$, and in addition one can chose each eigenstate $|\Phi_j\rangle$ of $\mathbf{A}_n$ to equal some state $|\chi_s^j\rangle$. In conclusion, if $\beta = 0$ each eigenstate $|\Phi_j\rangle$ of a parent system $\mathbf{A}_n$ is a singular eigenstate of the combined system $\mathbf{C}_{n+\rho}$. According to the definition of singular solutions of the modified system this is trivially obvious. If there is no interaction between the subsystems $\mathbf{A}_n$ and $\mathbf{B}_\rho$ of the combined system $\mathbf{C}_{n+\rho}$, each eigenstate $|\Phi_j\rangle$ of the system $\mathbf{A}_n$ is at the same time an eigenstate of the combined system $\mathbf{C}_{n+\rho}$. Moreover this eigenstate has eigenvalue $\varepsilon_s = \lambda_j \in \{\lambda_i\}$, and hence it is by definition singular solution of the combined system.

Consider now Theorem 2a. Each singular eigenstate $|\Psi_s\rangle$ is either strongly singular or weakly singular. By definition, strongly singular eigenstates have no X_ρ^b and no X_σ^{int} component. On the other hand, each weakly singular eigenstate $|\Psi_s\rangle$ satisfies either $\mathbf{I}_b|\Psi_s\rangle \neq 0$ and/or $\mathbf{I}_{\text{int}}|\Psi_s\rangle \neq 0$. In addition, each weakly singular eigenstate should be orthogonal to all strongly singular eigenstates.

Expressions (A18) and (A7b) imply that strongly singular eigenstates satisfy expressions (19). Those expressions can be written in the explicit form (20). This is a set of $(\sigma + \rho)$ homogenous linear equations in η_j unknown coefficients $D_m^{(s)}$. Hence if $\eta_j > \sigma + \rho$ one has at least $\eta_j - \sigma - \rho$ linearly independent strongly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. According to (A15a), each strongly singular eigenstate with the eigenvalue $\varepsilon_s = \lambda_j$ is contained in the space $X_{\eta_j}^j$.

Consider now weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. Each such eigenstate is given by the expression (16c) where the states $|\theta_s\rangle$, $|\varphi_s\rangle$ and $|\chi_s^j\rangle$ satisfy (16a) and where either $|\theta_s\rangle \neq 0$ and/or $|\varphi_s\rangle \neq 0$. In addition, each weakly singular eigenstate must be orthogonal to all strongly singular eigenstates. One finds that the set of all weakly singular eigenstates with the eigenvalue λ_j forms a linear space. Since there are at most $\sigma + \rho + \eta_j$ linearly independent singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$, and since if $\eta_j > \sigma + \rho$ one has at least $\eta_j - \sigma - \rho$ linearly independent strongly singular eigenstates with this eigenvalue, one may have at most $2(\sigma + \rho)$ linearly independent weakly singular eigenstates with this eigenvalue. However, this estimate can be further improved. According to Lemma 3, one may have at most $(\sigma + \rho)$ linearly independent weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$:

Proof of Lemma 3 Let $|\Psi_{s1}\rangle$ and $|\Psi_{s2}\rangle$ be two weakly singular eigenstates that have the same eigenvalue $\varepsilon_s = \lambda_j$. Let further those eigenstates have the same X_ρ^b and X_σ^{int} components, i.e. let $|\theta_{s1}\rangle = |\theta_{s2}\rangle$ and $|\varphi_{s1}\rangle = |\varphi_{s2}\rangle$. According to (16c), difference $|\Psi_s\rangle = |\Psi_{s1}\rangle - |\Psi_{s2}\rangle$ of the corresponding weakly singular eigenstates satisfies $|\Psi_s\rangle = |\chi_{s1}^j\rangle - |\chi_{s2}^j\rangle$. Since the state $|\Psi_s\rangle$ contains no X_ρ^b and no X_σ^{int} component, this state must be strongly singular eigenstate of the modified system. However, since the set of all weakly singular eigenstates associated with the eigenvalue λ_j forms a linear space, linear combination $|\Psi_s\rangle = |\Psi_{s1}\rangle - |\Psi_{s2}\rangle$ of weakly singular eigenstates $|\Psi_{s1}\rangle$ and $|\Psi_{s2}\rangle$ must be weakly singular eigenstate. Those two conditions imply $|\Psi_s\rangle = 0$ and hence $|\chi_{s1}^j\rangle = |\chi_{s2}^j\rangle$. In conclusion, if two weakly singular eigenstates associated with the same eigenvalue λ_j have the same X_ρ^b and the same X_σ^{int} components, they must also have the same $X_{\eta_j}^j$ component. $X_{\eta_j}^j$ component $|\chi_s^j\rangle$ of the weakly singular

eigenstate $|\Psi_s\rangle$ is hence uniquely determined by its X_ρ^b and X_σ^{int} components. This proves Lemma 3. □

Since X_ρ^b is ρ-dimensional while X_σ^{int} is σ-dimensional, above lemma implies that one may have at most $(\rho + \sigma)$ linearly independent weakly singular eigenstates with the eigenvalue $\varepsilon_s = \lambda_j$. This completes the proof of Theorem 2a.

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