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Evaluation of the 3rd order perturbations for the degenerate cases / A. Teleki and T. Obert

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In the calculation of quantum systems in most cases, the perturbation theory is used. Lot of calculation techniques are used for both (nondegenerate and degenerate) cases. In our contribution we evaluate the projection operator technique in such case when the Hamiltonian of the given quantum system has point spectrum with finite degree of degeneracy.

1. Introduction

Let us suppose that $\mathbf{H}_0$ represents Hamiltonian of unperturbed quantum system which is defined on the separable Hilbert space H_0. The set of eigenvalues $\{E_n^0\}_{n\in N_0}$ and set of orthonormal eigenvectors $\{|u_n\rangle\}_{n\in N_0}$ are known and N_0 is a subset of natural numbers $\hbar$ (i.e. $N_0 \subset N$). Let d_k is degree of degeneracy of the kth level of the Hamiltonian $\mathbf{H}_0$ and D_k presents the full set of indices for the kth level (d_k is the number of indices in $D_k \subset N_0$ and $N_0 = \bigcup_{k\in N} D_k$). The Schrödinger equation for the nonperturbed system has the form

$$\mathbf{H}_0\,|u_n\rangle = E_k^0\,|u_n\rangle, \quad n \in D_k,$$

Because of the degeneracy we have also

$$\mathbf{H}_0\,\big|E_n^0\big\rangle = E_k^0\,\big|E_n^0\big\rangle, \quad n \in D_k, \tag{1}$$

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where $|E_n^0\rangle$ for $n \in D_k$ is another set of eigenvectors belonging to the same eigenvalue E_k^0.

Moreover let us suppose that perturbed Hamiltonian $\mathbf{H}$ is defined on the same separable Hilbert space as Hamiltonian $\mathbf{H}_0$ is. The perturbation then is $\mathbf{V} = \mathbf{H} - \mathbf{H}_0$ from which

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}. \tag{2}$$

Furthermore let us suppose that this perturbation is small, i.e. differences between eigenvalues of the unperturbed $\{E_n^0\}$ and perturbed $\{E_n\}$ quantum systems are small. The same is valid for the unperturbed $\{|u_n\rangle\}$ and perturbed $\{|E_n\rangle\}$ orthonormal eigenvectors of given quantum system. It is assumed also that base $\{|u_n\rangle\}$ of the unperturbed quantum system is not given unambiguously.

Explanation of the mathematical bases of the quantum mechanics are given in satisfactory level in books [1–3]. In the following we will use the technique of projection operator formalism from these books.

2. Projection operator formalism

From the introduction follows, that calculation is complicated because of the unambiguous of the orthonormal base $\{|u_n\rangle\}$. In this case the H_k^0 Hilbert space is given, and it is spanned by the orthonormal base $\{|u_n\rangle\}$ where $n \in D_k$. The problem became extraordinary complicated if the degeneracy is not removed in the first order (see [4]). In such cases the projection operator formalism is very useful and very effective.

From the theory of linear operators it is known that each hermitian operator, defined on the separable Hilbert space is diagonalized by its eigenvectors, in our case it means that $\mathbf{H}_0$ is given by the relation

$$\mathbf{H}_0 = \sum_{k \in N_0} E_k^0 \,|u_k\rangle \langle u_k| = \sum_{k \in N} E_k^0 \sum_{n \in D_k} |u_n\rangle \langle u_n| = \sum_{k \in N} E_k^0 \mathbf{P}_k^0,$$

where the operator $\mathbf{P}_k^0$ is given by the relation

$$\mathbf{P}_k^0 = \sum_{n \in D_k} |u_n\rangle \langle u_n| \,. \tag{3}$$

Operator (3) is projection operator (orthogonal projector or projector only). This operator is hermitian and idempotent, i.e.

$$\left(\mathbf{P}_k^0\right)^+ = \mathbf{P}_k^0 \text{ and } \left(\mathbf{P}_k^0\right)^2 = \mathbf{P}_k^0$$

and $\mathbf{P}_k^0 \mathbf{P}_l^0 = \mathbf{P}_l^0 \mathbf{P}_k^0 = 0$ if $l \neq k$. This operator projects into the space H_k^0, i.e.

$$\mathbf{P}_k^0 \,|u_n\rangle = |u_n\rangle \quad \forall n \in D_k \text{ and } \mathbf{P}_k^0 \,|u_n\rangle = 0 \quad \forall n \notin D_k.$$

These equations are equivalent to equations

$$\mathbf{P}_k^0 \,|\varphi\rangle = \varphi\rangle \quad \forall\,|\varphi\rangle \in \mathbf{H}_k^0 \text{ and } \mathbf{P}_k^0\,|\varphi\rangle = 0 \quad \forall|\varphi\rangle \in \mathbf{H}_k^{0\perp},$$

where $\mathbf{H}_k^{0\perp}$ is the orthogonal complement to subspace $\mathbf{H}_k^0$. For these subspaces the following equations are valid

$$\mathbf{H}_0 = \mathbf{H}_k^0 \oplus \mathbf{H}_k^{0\perp} = \bigoplus_{k\in N} \mathbf{H}_k^0 \text{ and } \mathbf{H}_k^{0\perp} = \bigoplus_{l\in N, l\neq k} \mathbf{H}_l^0.$$

From the practical point of view it is convenient to introduce the complement operator

$$\mathbf{Q}_k^0 = \sum_{l\in N, l\neq k} \mathbf{P}_l^0 = \mathbf{1} - \mathbf{P}_k^0, \tag{4}$$

where $\mathbf{1}$ is unit operator (identity operator) on the Hilbert space H_0. The operator $\mathbf{Q}_k^0$ is also projector and it is hermitian and idempotent operator, i.e.

$$\left(\mathbf{Q}_k^0\right)^+ = \mathbf{Q}_k^0 \text{ and } \left(\mathbf{Q}_k^0\right)^2 = \mathbf{Q}_k^0.$$

It is clear that all properties of the operator $\mathbf{P}_k^0$ given above are independent from the given orthonormal base in Hilbert space $\mathbf{H}_k^0$. From this statement follows advantage their use in the case of system with degenerate spectra.

3. Perturbation theory

For the derivation of perturbation formulae of degenerate systems we will use the projection operator technique developed in the book [5].

The goal of perturbation theory is solving – in our case – stationary Schrödinger equation

$$\mathbf{H}\,|E_n\rangle = E_n\,|E_n\rangle, \tag{5}$$

where perturbed Hamiltonian $\mathbf{H}$ is possible write in the form (2) in which $\mathbf{V}$ represents small perturbation. The operator equation (5) is possible expand into the operator-valued series so in this case it is assumed that $\mathbf{H}$ operator is given in the form

$$\mathbf{H}(\lambda) = \mathbf{H}_0 + \lambda\mathbf{V},$$

where λ is perturbation parameter. According this assumption $\mathbf{H}(\lambda)$ is parametrized perturbed Hamiltonian. Eigenvalues and eigenvectors are also parametrized so the equation (5) has parametrized form

$$\mathbf{H}(\lambda)\,|E_n(\lambda)\rangle = E_n(\lambda)\,|E_n(\lambda)\rangle. \tag{6}$$

It is assumed that solutions [i.e. eigenvectors $\{|E_n(\lambda)\rangle\}$ and eigenvalues $E_n(\lambda)$] and projectors $\mathbf{P}_k^0(\lambda)$ (which projects into the corresponding subspaces) is possible to expand into the Taylor series. These series converge to the results of the perturbed Schrödinger equation (5) if $\lambda \to 1$ and converges to the results of the unperturbed Schrödinger equation (1) if $\lambda \to 0$, i.e.

$$E_n(\lambda) \xrightarrow{\lambda\to 0} \text{ and } |E_n(\lambda)\rangle \xrightarrow{\lambda\to 0} |E_n^0\rangle,$$

where $\{|E_n^0\rangle\}_{n\in D_k}$ represents orthonormal base in Hilbert space H_k^0. This base does not necessary is equal to the base $\{|u_n\rangle\}_{n\in D_k}$ which represents solution of the non-perturbed Schrödinger equation $\mathbf{H}_0|u_n\rangle = E_n^0|u_n\rangle$. This base $\{|u_n\rangle\}_{n\in D_k}$ is chosen as the base in H_k^0 without any assumptions.

Eigenvalues of the equation (6) (under the assumption $\lambda = 1$) are roots of the determinantal (or secular) equation

$$\det(\mathbf{H}_k(\lambda) - z\mathbf{K}_k(\lambda)) = 0. \tag{7}$$

Operators $\mathbf{H}_k(\lambda)$ and $\mathbf{K}_k(\lambda)$ are given by the relations

$$\mathbf{H}_k(\lambda) = \mathbf{P}_k^0\mathbf{H}(\lambda)\mathbf{P}_k(\lambda)\mathbf{P}_k^0 \quad \text{resp.} \quad \mathbf{K}_k(\lambda) = \mathbf{P}_k^0\mathbf{P}_k(\lambda)\mathbf{P}_k^0. \tag{8}$$

According to [5] let us introduce a new $\mathbf{A}_j$ – operators as follows, for $j = -1$

$$\mathbf{A}_{-1} = \mathbf{P}_k^0 \tag{9}$$

and for $j \geqslant 0$

$$\mathbf{A}_j = (-1)^j \frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^{j+1}} Q_k^0 = (-1)^j \sum_{n,n\neq k} \frac{\mathbf{P}_n^0}{\left(E_k^0 - E_n^0\right)^{j+1}}. \tag{10}$$

By the help of these operators the parametrized projectors $\mathbf{P}_k(\lambda)$ are

$$\mathbf{P}_k(\lambda) = \sum_{s=0}^{\infty} \lambda^s \Bigg(\sum_{\substack{j_0, j_1, \dots, j_s \\ j_0+j_1+\dots+j_s=-1}} \mathbf{A}_{j_0}\mathbf{V}\mathbf{A}_{j_1}\dots\mathbf{V}\mathbf{A}_{j_s} \Bigg) \stackrel{\text{def}}{=} \sum_{s=0}^{\infty} \lambda^s \mathbf{P}_k^{(s)}. \tag{11}$$

There may be such situation, that perturbation $\mathbf{V}$ does not remove the degeneracy of the given level completely, i.e. secular equation (7) has manifold roots. This problem the projector formalism solves without any problem.

4. Solution of the perturbed Hamiltonian into the 3rd order

In this part we express the projectors $\mathbf{P}_k^{(s)}$ defined by (11) for $s = 1, 2$ and 3 and by them help we set-up secular equation (7). By use of general eigenvalue problem we find its eigenvalues $\{E_n^{(s)}\}$ and its orthonormal eigenvectors $\{|E_n^{(s)}\rangle\}$.

From relations (9), (10) and (11) it is obvious that

$$
\begin{aligned}
\mathbf{P}_k^{(0)} &= \mathbf{P}_k^0 \\
\mathbf{P}_k^{(1)} &= \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0 + \mathbf{A}_0\mathbf{V}\mathbf{A}_{-1} = \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0 + \mathbf{Q}_k^0\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{V}\mathbf{P}_k^0 \\
\mathbf{P}_k^{(2)} &= \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1 + \mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_0 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_{-1} \\
&\quad + \mathbf{A}_0\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_1\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1} \\
&= -\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{(E_k^0 - \mathbf{H}_0)^2}\mathbf{Q}_k^0 + \frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0 \\
&\quad + \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 + \frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0 \\
\mathbf{P}_k^{(3)} &= \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_2 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_1 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1 \\
&\quad + \mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_0 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_0 \\
&\quad + \mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_0 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0 + \mathbf{A}_0\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0 \\
&\quad + \mathbf{A}_1\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0 + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_2\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_{-1} \\
&\quad + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_0\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1} \\
&\quad + \mathbf{A}_1\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_{-1}\mathbf{V}\mathbf{A}_2\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_0\mathbf{V}\mathbf{A}_1\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1} \\
&\quad + \mathbf{A}_1\mathbf{V}\mathbf{A}_0\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1} + \mathbf{A}_2\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1}\mathbf{V}\mathbf{A}_{-1} \\
&= \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^3}\mathbf{Q}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0 \\
&\quad - \frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0
\end{aligned}
$$

$$
\begin{aligned}
&- \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&+ \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&+ \frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&- \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&+ \frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&- \frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0 \\
&+ \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&+ \frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&+ \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&- \frac{1}{\left(E_k^0-\mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0-\mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&+ \frac{1}{\left(E_k^0-\mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0.
\end{aligned}
$$

Above-mentioned relations are rather complicated [above that $\mathbf{Q}_k^0$ operators represent summation according relation (4)], but the situation for secular equation

(7) considerable simplifies owing to projection into the Hilbert space H_k^0 by the help of projectors $\mathbf{P}_k^0$. In equation (8) $\mathbf{H}_k(\lambda)$ is given by the relation

$$\mathbf{H}_k(\lambda) = \sum_{s=0}^{\infty} \lambda^s \mathbf{H}_k^{(s)}.$$

Its $d_k \times d_k$ dimension rectangular matrix elements are given by the relations

$$H_{k,mn}^{(s)} = \left\langle u_m \left| \mathbf{H}_k^{(s)} \right| u_n \right\rangle \quad \text{for} \quad m, n \in D_k,$$

where

$$\mathbf{H}_k^{(0)} = \mathbf{P}_k^0 \mathbf{H}_0 \mathbf{P}_k^0 \text{ and } \mathbf{H}_k^{(s)} = \mathbf{P}_k^0 \left(\mathbf{H}_0 \mathbf{P}_k^{(s)} + \mathbf{V} \mathbf{P}_k^{(s-1)} \right) \mathbf{P}_k^0 \quad \text{for} \quad s \geqslant 1.$$

By the similar manner is defined $\mathbf{K}_k$ operator. It is given also by the rectangular matrices $d_k \times d_k$ with matrix elements

$$K_{k,mn}^{(s)} = \left\langle u_m \left| \mathbf{K}_k^{(s)} \right| u_n \right\rangle \quad \text{for} \quad m, n \in D_k,$$

where

$$\mathbf{K}_k^{(s)} = \mathbf{P}_k^0 \mathbf{P}_k^{(s)} \mathbf{P}_k^0 \quad \text{for} \quad s \geqslant 0.$$

Operators $\mathbf{P}_k^0$, $\mathbf{Q}_k^0$ and $\mathbf{H}_0$ in pairs mutually commute and for $\mathbf{H}_k^{(s)}$ and for $\mathbf{K}_k^{(s)}$ we obtain following relations

$$\begin{aligned}
\mathbf{H}_k^{(0)} &= \mathbf{P}_k^0 \mathbf{H}_0 \mathbf{P}_k^0, \\
\mathbf{K}_k^{(0)} &= \mathbf{P}_k^0 \mathbf{P}_k^{(0)} \mathbf{P}_k^0 = \mathbf{P}_k^0, \\
\mathbf{H}_k^{(1)} &= \mathbf{P}_k^0 \left(\mathbf{H}_0 \mathbf{P}_k^{(1)} + \mathbf{V} \mathbf{P}_k^{(0)} \right) \mathbf{P}_k^0 = \mathbf{P}_k^0 \mathbf{V} \mathbf{P}_k^0, \\
\mathbf{K}_k^{(1)} &= \mathbf{P}_k^0 \mathbf{P}_k^{(1)} \mathbf{P}_k^0 = 0, \\
\mathbf{H}_k^{(2)} &= \mathbf{P}_k^0 \left(\mathbf{H}_0 \mathbf{P}_k^{(2)} + \mathbf{V} \mathbf{P}_k^{(1)} \right) \mathbf{P}_k^0 = -\mathbf{P}_k^0 \mathbf{H}_0 \mathbf{V} \frac{1}{\left(E_k^0 - \mathbf{H}_0 \right)^2} \mathbf{Q}_k^0 \mathbf{V} \mathbf{P}_k^0 \\
&\quad + \mathbf{P}_k^0 \mathbf{V} \mathbf{Q}_k^0 \frac{1}{E_k^0 - \mathbf{H}_0} \mathbf{V} \mathbf{P}_k^0, \\
\mathbf{K}_k^{(2)} &= \mathbf{P}_k^0 \mathbf{P}_k^{(2)} \mathbf{P}_k^0 = -\mathbf{P}_k^0 \mathbf{V} \frac{1}{\left(E_k^0 - \mathbf{H}_0 \right)^2} \mathbf{Q}_k^0 \mathbf{V} \mathbf{P}_k^0,
\end{aligned}$$

$$\begin{aligned}
\mathbf{H}_k^{(3)} &= \mathbf{P}_k^0\left(\mathbf{H}_0\mathbf{P}_k^{(3)} + \mathbf{V}\mathbf{P}_k^{(2)}\right)\mathbf{P}_k^0 \\
&= \mathbf{P}_k^0\mathbf{H}_0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{H}_0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{H}_0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad + \mathbf{P}_k^0\mathbf{H}_0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0, \\
&\quad - \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad + \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0, \\
\mathbf{K}_k^{(3)} = \mathbf{P}_k^0\mathbf{P}_k^{(3)}\mathbf{P}_k^0 &= \mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad - \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^2}\mathbf{Q}_k^0\mathbf{V}\frac{1}{E_k^0 - \mathbf{H}_0}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0 \\
&\quad + \mathbf{P}_k^0\mathbf{V}\frac{1}{\left(E_k^0 - \mathbf{H}_0\right)^3}\mathbf{Q}_k^0\mathbf{V}\mathbf{P}_k^0\mathbf{V}\mathbf{P}_k^0.
\end{aligned}$$

For the sake of completeness we will give all matrix elements $H_{k,mn}^{(s)}$ and $K_{k,mn}^{(s)}$. For the matrix elements of the perturbation operator **V** we will use following designation

$$V_{mn} = \langle u_m \,|\mathbf{V}|\, u_n\rangle$$

for all *m, n* and δ_{mn} for the Kronecker delta. Then

$$\begin{aligned}
H_{k,mn}^{(0)} &= E_k^0\delta_{mn}, \\
K_{k,mn}^{(0)} &= \delta_{mn}, \\
H_{k,mn}^{(1)} &= V_{mn},
\end{aligned}$$

$$K_{k,mn}^{(1)} = 0,$$

$$H_{k,mn}^{(2)} = -E_k^0 \sum_{p,\, p\notin D_k} \frac{V_{mp}V_{pn}}{\left(E_k^0 - E_p^0\right)^2} + \sum_{p,\, p\notin D_k} \frac{V_{mp}V_{pn}}{E_k^0 - E_p^0} = -\sum_{p,\, p\notin D_k} E_p^0 \frac{V_{mp}V_{pn}}{\left(E_k^0 - E_p^0\right)^2},$$

$$K_{k,mn}^{(2)} = -\sum_{p,\, p\notin D_k} \frac{V_{mp}V_{pn}}{\left(E_k^0 - E_p^0\right)^2},$$

$$\begin{aligned}
H_{k,mn}^{(3)} = {} & E_k^0 \sum_{\substack{p,\, p\in D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_r^0\right)^3} - E_k^0 \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)\left(E_k^0 - E_r^0\right)^2} \\
& - E_k^0 \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^2\left(E_k^0 - E_r^0\right)} \\
& + E_k^0 \sum_{\substack{p,\, p\notin D_k\\ r,r\in D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^3} - \sum_{\substack{p,\, p\in D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_r^0\right)^2} \\
& + \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)\left(E_k^0 - E_r^0\right)} - \sum_{\substack{p,\, p\notin D_k\\ r,r\in D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^2} \\
= {} & \sum_{\substack{p,\, p\in D_k\\ r,r\notin D_k}} E_r^0 \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_r^0\right)^3} + \sum_{\substack{p,\, p\notin D_k\\ r,r\in D_k}} E_p^0 \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^3} \\
& - \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \left(\left(E_k^0\right)^2 - E_p^0 E_r^0\right) \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^2\left(E_k^0 - E_r^0\right)^2}.
\end{aligned}$$

$$\begin{aligned}
K_{k,mn}^{(3)} = {} & \sum_{\substack{p,\, p\in D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_r^0\right)^3} - \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)\left(E_k^0 - E_r^0\right)^2} \\
& - \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^2\left(E_k^0 - E_r^0\right)} + \sum_{\substack{p,\, p\notin D_k\\ r,r\in D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^3} \\
= {} & \sum_{\substack{p,\, p\in D_k\\ r,r\notin D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_r^0\right)^3} + \sum_{\substack{p,\, p\notin D_k\\ r,r\in D_k}} \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^3} \\
& - \sum_{\substack{p,\, p\notin D_k\\ r,r\notin D_k}} \left(2E_k^0 - E_p^0 - E_r^0\right) \frac{V_{mp}V_{pr}V_{rn}}{\left(E_k^0 - E_p^0\right)^2\left(E_k^0 - E_r^0\right)^2}.
\end{aligned}$$

The approximate matrix elements of operators **H** and **K** up to the third order of full perturbation ($\lambda = 1$) are

$$\tilde{\mathrm{H}}_{k,mn} = H^{(0)}_{k,mn} + H^{(1)}_{k,mn} + H^{(2)}_{k,mn} + H^{(3)}_{k,mn}$$

and

$$\tilde{\mathrm{K}}_{k,mn} = K^{(0)}_{k,mn} + K^{(1)}_{k,mn} + K^{(2)}_{k,mn} + K^{(3)}_{k,mn}.$$

By substitution of the matrix elements $\tilde{H}_{k,mn}$ and $\tilde{K}_{k,mn}$ into the secular equation we obtain generalized eigenvalue problem

$$\tilde{\mathrm{H}}\,|E_n\rangle = E_n\tilde{\mathrm{K}}\,|E_n\rangle, \tag{12}$$

where both $\tilde{\mathrm{H}}$ and $\tilde{\mathrm{K}}$ are $d_k \times d_k$ matrices and E_n are scalars. These scalars satisfy the equation (12) and they are generalized eigenvalues and the corresponding values $|E_n\rangle$ are generalized right eigenvectors. For the solution of the standard and generalized eigenvalue problem by PC see *eig* procedure given in [6]. By use this procedure one gain all generalized eigenvalues and all generalized eigenvectors.

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