Explicit equations are obtained which define the derivatives with respect to parameters entering in the Hamiltonian of the eigenvalues of the Hamiltonian (through third order in the degenerate and nondegenerate cases). A method is indicated of introducing a basis depending on the parameters. A compact expression is obtained for the correction of arbitrary order to the energy in the Rayleigh–Schrodinger perturbation theory.

The method presented in [1] is developed in the present paper with the object of obtaining explicit equations defining the derivatives with respect to parameters of an isolated eigenvalue of the Hamiltonian. These equations can be used directly in applications. Some alterations in notation for the quantities used are introduced as compared with [1].

Thus, let $A$ be a Hilbert space containing the domain of the Hamiltonian operator $H$. Solution of the eigenvalue problem

$$\left(H - IE_s\right)|s> = 0$$

leads to the decomposition $A = A_s \oplus A'$, where $A_s$ is the eigensubspace (degenerate, in general) of the operator $H$ and $|s>$ is any eigenvector of $A_s$, i.e., $|s> \in A_s$.

As is evident from [1], determination of the derivatives of the degenerate eigenvalues leads to a further decomposition of $A_s$ and to further specification of $|s>$. Thus, in finding the first derivative

$$A_s = \sum \Theta A_{sq} \text{and} |s> \in A_{sq},$$

in determining the second derivative

$$A_{sq} = \sum \Theta A_{sq} \text{and} |s> \in A_{sq},$$

e tc.

The orthoprojectors onto $A_s$, $A_{sq}$, $A_{sqr}$, etc. we shall denote by $P_s$, $P_{sq}$, $P_{sqr}$, etc. respectively, while the orthoprojector onto $A'$ we shall denote for brevity by $Q_s = 1 - P_s$. Hereby both the subspaces $A_s$ and others as well as the orthoprojectors $P$ are always taken for fixed values of the parameters $R = R_0$ without special mention.

The possibility of different normalizations of the eigenvectors leads to an indeterminacy in their derivatives. This does not affect the modulus of the derivatives of the eigenvalues, but it does have an appreciable effect on the compactness of the corresponding formulas. In the case of nondegenerate states two normalizations are most frequently used which, taking into account the dependence of the vectors on the parameters $R$, can be written as follows:

$$<s(R)|s(R)> = 1 \text{ and } <s(R)|s(R)> = 1$$

for any values of $R$. From the second of the normalizations of (4) it follows that

$$P_s|\partial_s> = P_s|\partial_s> = P_s|\partial_s> = \cdots = 0.$$

From the first normalization only $\text{Re}[P_s|\partial_j> = 0$, but $P_s|\partial_k> = 0$, $P_s|\partial_l> = 0$, etc. (Here and below

the operators P and Q act after differentiation and setting \( R = R_0 \). Property (5) of the second normalization makes it more convenient for obtaining general expressions for the derivatives of the eigenvalues.

In the case of a degenerate eigenvalue it can be shown that the analog of (5) is the equations

\[
P_{sq} \left| \partial s q \right\> = P_{sq} \left| \partial s q r \right\> = P_{sq} \left| \partial s q r t \right\> = 0,
\]

but, in general (for \( q' \neq q, r' \neq r, t' \neq t \)),

\[
P_{sq'} \left| \partial s q \right\> \neq 0, \quad P_{sq'} \left| \partial s q r \right\> \neq 0, \quad P_{sq'} \left| \partial s q r t \right\> \neq 0.
\]

The latter projections, and also \( Q_s \left| \partial s q \right\>, Q_s \left| \partial s q r \right\>, \) etc., must be determined from the differentiated Schrödinger equation by the action of the corresponding orthoprojectors. Thus, differentiating (1), using (6), and successively substituting the lower order derivatives of the eigenvectors into the expression for the higher order derivatives of the eigenvalues, we obtain the following equations for the eigenvalues:

\[
\begin{align*}
\{ P, H^{(1)} - \partial_s H \} \left| s \right\> & = 0, \\
\{ P_{sq}, H^{(2)} - \partial_s H \} \left| q r \right\> & = 0, \\
\{ P_{sq}, H^{(3)} - \partial_s H \} \left| q r t \right\> & = 0.
\end{align*}
\]

Here

\[
H^{(1)} = \partial_s H,
\]

\[
H^{(2)} = \partial_s H - \sum_{n} \left[ \partial_s H - \partial_\ell H \right] Q_{sq} R_{\ell} Q_s \left[ \partial_s H - I \partial_s E_{sq} \right];
\]

\[
H^{(3)} = \partial_s H - \sum_{n} \sum_{\ell} \left[ \partial_s H - \partial_\ell H \right] Q_{sq} R_{\ell} Q_s \left[ \partial_s H - I \partial_s E_{sq} \right]
\]

\[
+ \sum_{n} \left[ \partial_s H - I \partial_s E_{sq} \right] Q_s R_{\ell} Q_s \left[ \partial_s H - \partial_s E_{sq} \right] Q_{sq} R_{\ell} Q_s \left[ \partial_s H - I \partial_s E_{sq} \right].
\]

In these formulas the following notation is used: \( \sum \) denotes the sum over all possible permutations of the indices indicated between different square brackets but not inside them; \( \sum \) denotes the sum over all possible permutations of the different order derivatives standing inside the square brackets; \( \sum \) denotes the sum over all \( q' \) with the exception of \( q' = q \). The operator \( R_0 \) is constructed as follows: the operator \( (H - IE_s)^{-1} \) is found which is inverse to \( (H - IE_s)^{-1} \); the latter is generated in \( \Lambda' \) by the operator \( (H - IE_s) \); further, \( (H - IE_s)^{-1} \) is extended as a Hermitian operator to all of \( \Lambda \) which gives \( R_0 \).

The solution of Eqs. (7)-(9) gives the derivatives of the eigenvalues and the eigenvectors which define the decomposition of \( \Lambda_0 \) according to (2), (3). Moreover, as noted in [1], these vectors need not depend on the indices of the differentiation parameters.

For the nondegenerate case at all stages \( \Lambda = \Lambda_0 \oplus \Lambda' \) and correspondingly \( I = P_0 + Q_0 \). Then the derivatives of the eigenvalues and the exterior parts (lying in \( \Lambda' \)) of the derivatives of the eigenvectors can be written as follows:

\[
\begin{align*}
\partial E_x & = \langle s | H_1 | s \rangle, \quad Q_s \partial E_x = -Q_s R_s Q_s H_1 | s \rangle; \\
\partial E_y & = \langle s | H_2 | s \rangle, \quad Q_s \partial E_y = -Q_s R_s Q_s H_2 | s \rangle; \\
\partial E_z & = \langle s | H_3 | s \rangle, \quad Q_s \partial E_z = -Q_s R_s Q_s H_3 | s \rangle.
\end{align*}
\]

where \( H_1, H_2, \) and \( H_3 \) are obtained from \( H^{(0)}, H^{(1)}, \) and \( H^{(2)} \) respectively (see (10), (11), (12)) if it is recalled that for a nondegenerated eigenvalue \( \partial_\ell E_{sq} = \partial_\ell E_{s0}, \partial_\ell E_{sq r} = \partial_\ell E_{s0}, \) and \( P_{sq} = 0 \) \( (q' \neq q) \). In this case it is furthermore not difficult to obtain expressions for the higher order derivatives although they are more complicated. The inner parts of the derivatives of the eigenvectors (lying in \( \Lambda_0 \)) according to (5) are equal to zero.