JOURNAL OF COMPUTATIONAL PHYSICS 4, 411–414 (1969)

NOTES

On Degenerate Rayleigh-Schrödinger Perturbation

ABSTRACT

Degenerate Rayleigh–Schrödinger perturbation theory is treated by expansions in unperturbed eigenfunctions. The results of seventh order perturbation are presented for the cases in which the degeneracy can be totally removed in the first and second orders.

Degenerate Rayleigh-Schrödinger perturbation theory is treated by expansions in unperturbed eigenfunctions. Perturbation energies up to seventh order have been derived for cases in which the degeneracy is removable in the first or second order. The final results are presented in this Note.

We follow the notations of Hirschfelder, Byers Brown, and Epstein [1]. To simplify book-keeping the following ordering of states is introduced. The state of interest is labelled state 1. We consider a total of N states, of which states 1 to M are degenerate in ϵ and states 1 to L degenerate in $\epsilon^{(1)}$. Furthermore, summation limits are implied by the following limits on the indices:

$$1 \leqslant (\alpha \text{ and } \beta) \leqslant N, \quad \text{and} \quad 1 \leqslant (l \text{ and } l') \leqslant L < m \leqslant M < (n \text{ and } n') \leqslant N.$$

To begin, we assume that

$$\Delta_\alpha = \epsilon_\alpha - \epsilon_1 \tag{1}$$

$$P_{\alpha\beta} = \langle \psi_\alpha \mid V \mid \psi_\beta \rangle \tag{2}$$

are known quantities.

The first step is to find the correct zeroth order wavefunctions:

$$\phi_\alpha = \sum \psi_\beta T_{\beta\alpha} \,. \tag{3}$$

To accomplish this, we first diagonalize the $M \times M$ block of the $\mathbf{P}$ matrix:

$$\mathbf{PA} = \mathbf{A\Pi}, (M \times M), \tag{4}$$

where $\mathbf{\Pi}$ is diagonal and $\epsilon^{(1)} = \Pi_{11}$; enlarge the $\mathbf{A}$ matrix to $N \times N$ by adding zero off-diagonal elements and unit diagonal elements; and transform the $\mathbf{P}$ matrix:

$$\mathbf{Q} = \mathbf{A}^\dagger\mathbf{PA}, (N \times N), \tag{5}$$

Next, an $L \times L$ **G** matrix is constructed:

$$G_{ll'} = -\sum_n Q_{ln} \Delta_n^{-1} Q_{nl'} , \tag{6}$$

and diagonalized:

$$\mathbf{GB} = \mathbf{B\Gamma}, (L \times L), \tag{7}$$

where $\mathbf{\Gamma}$ is diagonal and $\epsilon^{(2)} = \Gamma_{11}$. This $L \times L$ **B** matrix is enlarged to $N \times N$ in the same manner in which **A** has been. Then,

$$\mathbf{T} = \mathbf{AB}, (N \times N). \tag{8}$$

The second step involves the simple transformation by **T**:

$$\mathbf{V} = \mathbf{T}^{\dagger}\mathbf{PT}, (N \times N), \tag{9}$$

$$\mathbf{W} = \mathbf{V} - \epsilon^{(1)}\mathbf{1}, (N \times N). \tag{10}$$

Now, we expand the perturbed wavefunctions in the set of $\{\phi\}$:

$$\psi^{(1)} = \sum_\alpha \phi_\alpha a_\alpha , \tag{11}$$

$$\psi^{(2)} = \sum_\alpha \phi_\alpha b_\alpha , \tag{12}$$

$$\psi^{(3)} = \sum_\alpha \phi_\alpha c_\alpha . \tag{13}$$

After some simple but tedious algebra, we find that the expansion coefficients are given by:

$$\left.\begin{aligned} a_n &= -\Delta_n^{-1} W_{n1} , \\ a_m &= -W_{mm}^{-1} \sum_n W_{mn} a_n , \\ a_l &= [\Gamma_{ll} - \epsilon^{(2)}]^{-1} \left\{ \sum_n W_{ln} \Delta_n^{-1} \left[\sum_{n'} W_{nn'} a_{n'} \right.\right. \\ &\quad \left.\left. + \sum_m W_{nm} a_m \right] \right\}, \qquad l \neq 1, \\ a_1 &= 0; \end{aligned}\right\} \tag{14}$$

$$\left.\begin{aligned}
b_n &= -\Delta_n^{-1}\sum_\alpha W_{n\alpha}a_\alpha\,,\\
b_m &= -W_{mm}^{-1}\left\{\sum_n W_{mn}b_n - \epsilon^{(2)}a_m\right\},\\
b_l &= [\Gamma_{ll} - \epsilon^{(2)}]^{-1}\left\{\sum_n W_{ln}\Delta_n^{-1}\left[\sum_{n'} W_{nn'}b_{n'}\right.\right.\\
&\qquad \left.\left. + \sum_m W_{nm}b_m - \epsilon^{(2)}a_n\right] + \epsilon^{(3)}a_l\right\}, \qquad l \neq 1,\\
b_1 &= -(1/2)\sum_\alpha a_\alpha^2;
\end{aligned}\right\} \tag{15}$$

$$\left.\begin{aligned}
c_n &= -\Delta_n^{-1}\left\{\sum_\alpha W_{n\alpha}b_\alpha - \epsilon^{(2)}a_n\right\},\\
c_m &= -W_{mm}^{-1}\left\{\sum_n W_{mn}c_n - \epsilon^{(2)}b_m - \epsilon^{(3)}a_m\right\},\\
c_l &= [\Gamma_{ll} - \epsilon^{(2)}]^{-1}\left\{\sum_n W_{ln}\Delta_n^{-1}\left[\sum_{n'} W_{nn'}c_{n'}\right.\right.\\
&\qquad \left. + \sum_m W_{nm}c_m - \epsilon^{(2)}b_n - \epsilon^{(3)}a_n\right]\\
&\qquad \left. + \epsilon^{(3)}b_l + \epsilon^{(4)}a_l\right\}, \qquad l \neq 1,\\
c_1 &= -\sum_\alpha a_\alpha b_\alpha\,.
\end{aligned}\right\} \tag{16}$$

Finally, Eqs. (II.9) to (II.12) of Hirschfelder, Byers Brown, and Epstein [1] are used to obtain perturbation energies up to $\epsilon^{(7)}$.

For nondegenerate perturbations, $M = L = 1$, $\mathbf{T} = \mathbf{1}$, and $\mathbf{V} = \mathbf{P}$. Examples can easily be found. Seventh order perturbation theory has been applied to the method of solving constrained secular equations [2]. A subroutine, called DPERT0, has been submitted to Quantum Chemistry Program Exchange (QCPE).

Cases in which the degeneracy is removed in first order are fairly common. For $M > L = 1$, $\mathbf{T} = \mathbf{A}$, and $\mathbf{V} = \mathbf{Q}$. An example is the determination of electron spin resonance parameters from observed spectra [3]. A subroutine, called DPERT1, has also been submitted to QCPE.

Cases in which the degeneracy is removed in second or higher order are relatively rare.

ACKNOWLEDGMENT

We are grateful to the National Research Council of Canada for financial support.

REFERENCES

1. J. O. HIRSCHFELDER, W. BYERS BROWN, AND S. T. EPSTEIN, *Adv. Quantum Chem.* **1**, 255 (1964); erratum in D. P. CHONG AND Y. RASIEL, *J. Chem. Phys.* **44**, 1819 (1964), footnote 5.
2. D. P. CHONG, *Theoret. Chim. Acta.* **12**, 337 (1969).
3. C. BYFLEET, Ph.D. Thesis, University of British Columbia, 1969.

RECEIVED: November 21, 1968

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