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The Perturbation Theory for Non-Degenerate States and the Extended Hückel Method

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A formal study of the perturbation theory of the pseudosecular equations and particularly of those within the framework of the EHT method, proposed by Hoffmann, is given. In the case of the first-order perturbation in the hamiltonian matrix, it is shown that the classical and the present formalisms are equivalent. In the other more general cases, the recurrence formulae in the n-th order for the eigenvalues and eigenvectors are also given.

Die Störungsrechnung für Pseudo-Säkulärgleichungen, insbesondere für diejenigen, die in der EHT Methode von Hoffmann auftreten, wird untersucht. Im Falle einer Störung erster Ordnung des Hamiltonoperators sind der klassische und der vorliegende Formalismus gleich. In den allgemeineren Fällen werden die Rekursionsformeln n-ter Ordnung für die Eigenwerte und Eigenvektoren gegeben.

Etude formelle de la théorie perturbative des équations pseudo séculaires, en particulier de celles de la méthode EHT de Hoffmann. Au premier ordre de perturbation de la matrice hamiltonienne, le formalisme classique équivaut à celui proposé ici. Dans les autres cas on donne les formules de récurrence à l'ordre n pour les valeurs et les vecteurs propres.

1. Introduction

Recently, Imamura [6] has treated some particular aspects of the perturbation theory for the pseudosecular equations. The purpose of the present work is to generalize the perturbation treatment of such equations.

If we consider a pseudosecular equation of the type

$$H^0|0;i\rangle = S^0|0;i\rangle\,\lambda_i^0 \qquad (i=1,m) \tag{1}$$

(where H^0 is the unperturbed hamiltonian matrix; S^0, the unperturbed overlap matrix; λ_i^0, the eigenvalues; and $|0;i\rangle$, the corresponding eigenvectors), one may consider three possible cases of perturbation:

1. $H^0 \to H = H^0 + \varepsilon\Delta$ and $S^0 \to S^0$;
2. $H^0 \to H = H^0 + \varepsilon\Delta$ and $S^0 \to S = S^0 + \varepsilon\Sigma$,

Δ and Σ being matrices and ε a sufficiently small scalar.

It is also possible that second order perturbations may be present in H^0, when a first order perturbation in S^0 is made. That is,

3. $H^0 \to H = H^0 + \varepsilon\Delta_1 + \varepsilon^2\Delta_2$ and $S^0 \to S = S^0 + \varepsilon\Sigma$.

The two first cases may appear in any method which used the formalism of Eq. (1). The third one appears only in some empirical formulations.

2. Perturbation in the Hamiltonian Matrix

Following the classical procedure of perturbation theory [1], perturbed eigenvalues and eigenvectors of the equation

$$H|i\rangle = S^0|i\rangle\,\lambda_i\,, \qquad (i=1,m) \tag{2}$$

(where H is the perturbed hamiltonian matrix, and λ_i and $|i\rangle$ the eigenvalues and eigenvectors, respectively), can be expanded in terms of a power series

$$|i\rangle = \sum_{k=0}^{\infty} \varepsilon^k |k; i\rangle , \tag{3}$$

$$\lambda_i = \sum_{k=0}^{\infty} \varepsilon^k \lambda_i^k, \tag{4}$$

where λ_i^k and $|k; i\rangle$ represent the k-th order corrections. Substituting $H = H^0 + \varepsilon \Delta$ in Eq. (2) yields, after collecting the terms with the same power of ε,

$$H^0 |n; i\rangle + \Delta |n-1; i\rangle = \sum_{k=0}^{n} S^0 |n-k; i\rangle \lambda_i^k . \tag{5}$$

The n-th order eigenvalue correction is

$$\lambda_i^n = \langle i; 0 | \Delta | n-1; i\rangle - \sum_{k=1}^{n-1} \lambda_i^k \langle i; 0 | S^0 | n-k; i\rangle, \quad (n \neq 1) . \tag{6}$$

Taking into account the orthonormalization condition in the vector space of basis $\{|0; i\rangle\}$ and metric S^0, one has

$$\langle i; 0 | S^0 | 0; j\rangle = \delta_{ij} ; \tag{7}$$

with

$$|k; i\rangle = \sum_{j \neq i}^{m} a_{ji}^k |0; j\rangle , \tag{8}$$

where a_{ji}^k are some coefficients associated with the k-th order correction, it follows that

$$\langle i; 0 | S^0 | k; i\rangle = \delta_{0k} , \tag{9}$$

and Eq. (6) simplifies to

$$\lambda_i^n = \langle i; 0 | \Delta | n-1; i\rangle, \quad (\forall n) ; \tag{10}$$

the a_{ji}^k coefficients are then given by

$$a_{ji}^k = \langle j; 0 | S^0 | k; i\rangle . \tag{11}$$

Multiplying Eq. (5) on the left by $\langle j; 0|$, we obtain

$$\langle j; 0 | \Delta | n-1; i\rangle = (\lambda_i^0 - \lambda_j^0) \langle j; 0 | S^0 | n; i\rangle + \sum_{k=1}^{n-1} \lambda_i^k a_{ji}^{n-k} , \tag{12}$$

and therefore

$$a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \left[\sum_{l \neq i}^{m} a_{li}^{n-1} \langle j; 0 | \Delta | 0; l\rangle - \sum_{k=1}^{n-1} \lambda_i^k a_{ji}^{n-k} \right] \quad (n \neq 1) , \tag{13}$$

$$a_{ji}^1 = (\lambda_i^0 - \lambda_j^0)^{-1} \langle j; 0 | \Delta | 0; i\rangle . \tag{14}$$

These equations are formally identical to those obtained in a typical perturbation treatment with orthonormal functions.

3. Perturbation in Both Hamiltonian and Overlap Matrices

In this case the perturbed pseudosecular equation is

$$H |i\rangle = S |i\rangle \lambda_i , \quad (i = 1, m) , \tag{15}$$

with $H = H^0 + \varepsilon\Delta$ and $S = S^0 + \varepsilon\Sigma$. Using the same procedure as in Sect. 2. Eq. (5) transforms into

$$H^0|n;i\rangle + \Delta|n-1;i\rangle = \sum_{k=0}^{n} \lambda_i^k S^0|n-k;i\rangle + \sum_{k=0}^{n-1} \lambda_i^k \Sigma|n-k-1;i\rangle . \quad (16)$$

The corrections to the eigenvalues are then

$$\lambda_i^n = \langle i;0|\Delta - \lambda_i^0\Sigma|n-1;i\rangle - \sum_{k=1}^{n-1} \lambda_i^k \langle i;0|\Sigma|n-k-1;i\rangle , \quad (n \neq 1) , \quad (17)$$

$$\lambda_i^1 = \langle i;0|\Delta - \lambda_i^0\Sigma|0;i\rangle , \quad (n=1) , \quad (18)$$

the latter being formally identical to Eq. (10), with $\Delta \to \Delta - \lambda_i^0\Sigma$. The eigenvector correction equivalent to Eq. (12) is

$$\begin{aligned}\langle j;0|\Delta|n-1;i\rangle &= (\lambda_i^0 - \lambda_j^0)\langle j;0|S^0|n;i\rangle \\ &+ \sum_{k=1}^{n-1} \lambda_i^k a_{ji}^{n-k} + \sum_{k=0}^{n-1} \lambda_i^k \langle j;0|\Sigma|n-k-1;i\rangle ,\end{aligned} \quad (19)$$

that leads to

$$\begin{aligned}a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \Big\{ &\langle j;0|\Delta - \lambda_i^0\Sigma|n-1;i\rangle \\ &- \sum_{k=1}^{n-1} \lambda_i^k (a_{ji}^{n-k} + \langle j;0|\Sigma|n-k-1;i\rangle) \Big\} , \quad (n \neq 1) ,\end{aligned} \quad (20)$$

$$a_{ji}^1 = (\lambda_i^0 - \lambda_j^0)^{-1} \langle j;0|\Delta - \lambda_i^0\Sigma|0;i\rangle , \quad (n=1) . \quad (21)$$

An example of the application of the results in this section is given in the Appendix.

4. The EHT Method in the Hoffmann Formulation

Although the conclusions obtained above have general applicability, it is convenient to study the perturbational problems of Hoffmann's method [2–5].

In this approximation the H^0 matrix can be expressed by

$$H^0 = \alpha A^0 + \beta\{A^0, S^0\} , \quad (22)$$

where α and β are scalars, A^0 a diagonal matrix, and $\{A^0, S^0\}$ is the anticonmutator of A^0 and S^0.

Three cases may be considered in conjunction with Eq. (22):

a) First-Order Perturbation in A^0. In this case we can apply the results of Sect. 2; there is only a first-order perturbation in H^0,

$$\Delta = \alpha A^1 + \beta\{A^1, S^0\} , \quad (23)$$

with

$$A^0 \to A = A^0 + \varepsilon A^1 .$$

b) First-Order Perturbation in S^0. This implies a first-order perturbation in H^0,

$$\Delta = \beta\{A^0, \Sigma\} , \quad (24)$$

assuming $S^0 \to S = S^0 + \varepsilon\Sigma$. The formulation given in Sect. 3 applies in this case.

c) First-Order Perturbations in Both A^0 and S^0. In this case the perturbation in H^0 consists of a first-order term

$$\Delta_1 = \alpha A^1 + \beta [\{A^1, S^0\} + \{A^0, \Sigma\}] \tag{25}$$

and a second-order term

$$\Delta_2 = \beta \{A^1, \Sigma\}, \tag{26}$$

with $A^0 \to A = A^0 + \varepsilon A^1$ and $S^0 \to S = S^0 + \varepsilon \Sigma$.

If the term Δ_2 is considered negligible, the problem may be treated as in Sect. 3; otherwise a new formula is needed.

5. Introduction of Second Order Terms in H°

When Δ_2 is not negligible, that is,

$$H^0 \to H = H^0 + \varepsilon \Delta_1 + \varepsilon^2 \Delta_2,$$

the equations equivalent to Eq. (15) and Eq. (16) are[1]

$$H^0 |n; i\rangle + \Delta_1 |n-1; i\rangle + \Delta_2 |n-2; i\rangle = \sum_{k=0}^{n} \lambda_i^k S^0 |n-k; i\rangle + \sum_{k=0}^{n-1} \lambda_i^k \Sigma |n-k-1; i\rangle, \tag{27}$$

and the n-th correction to the eigenvalues is

$$\lambda_i^n = \langle i; 0 | \Delta_1 - \lambda_i^0 \Sigma | n-1; i\rangle - \sum_{k=1}^{n-1} \lambda_i^k \langle i; 0 | \Sigma | n-k-1; i\rangle + \langle i; 0 | \Delta_2 | n-2; i\rangle, \quad (n \neq 1). \tag{28}$$

while the first-order correction remains the same as in Sect. 3, The n-th correction for the eigenvectors is

$$a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \Big[\langle j; 0 | \Delta_1 - \lambda_i^0 \Sigma | n-1; i\rangle + \langle j; 0 | \Delta_2 | n-2; i\rangle - \sum_{k=1}^{n-1} \lambda_i^k \{ a_{ji}^{n-k} + \langle j; 0 | \Sigma | n-k-1; i\rangle \} \Big], \quad (n \neq 1) \tag{29}$$

and the first-order correction is also equivalent to that of the Sect. 3.

6. Generalization

It is now possible to generalize the results to the case

$$H^0 \to H = H^0 + \sum_{g=1}^{p} \varepsilon^g \Delta_g,$$

$$S^\circ \to S = S^0 + \sum_{g=1}^{p} \varepsilon^g \Sigma_g.$$

[1] See Ref. [1] for more details of the treatment.

Eq. (27) becomes

$$H^0|n;i\rangle+\sum_{g=1}^{p}\Delta_g|n-g;i\rangle=\sum_{k=0}^{n}\lambda_i^k S^0|n-k;i\rangle \\ +\sum_{g=1}^{p}\sum_{k=0}^{n-g}\lambda_i^k\Sigma_g|n-k-g;i\rangle\,, \tag{30}$$

that leads to

$$\lambda_i^n=\sum_{g=1}^{p}\left[\langle i;0|\Delta_g|n-g;i\rangle-\sum_{k=0}^{n-g}\lambda_i^k\langle i;0|\Sigma_g|n-k-g;i\rangle\right], \tag{31}$$

and

$$a_{ji}^n=(\lambda_i^0-\lambda_j^0)^{-1}\left\{\sum_{g=1}^{p}\left[\langle j;0|\Delta_g|n-g;i\rangle \\ -\sum_{k=0}^{n-g}\lambda_i^k\langle j;0|\Sigma_g|n-k-g;i\rangle\right]-\sum_{k=1}^{n-1}\lambda_i^k a_{ji}^{n-k},\quad (n>p)\,. \tag{32}$$

Furthermore one can also obtain a general formulation applicable to all the perturbational treatments outlined here. Using the notation

$$\Pi_{ji}^n=\sum_{g=1}^{p}\left[\langle j;0|\Delta_g|n-g;i\rangle-\sum_{k=0}^{n-g}\lambda_i^k\langle j;0|\Sigma_g|n-k-g;i\rangle\right], \tag{33}$$

we can rewrite Eqs. (31) and (32) in the form

$$\lambda_i^n=\Pi_{ii}^n\,, \tag{31a}$$

$$a_{ji}^n=(\lambda_i^0-\lambda_j^0)^{-1}\left[\Pi_{ji}^n-\sum_{k=1}^{n-1}\lambda_i^k a_{ji}^{n-k}\right], \tag{32a}$$

which apply to all the perturbation forms. The only change must be made in the expressions for Π_{ji}^n and Π_{ii}^n.

7. Conclusions

It has been shown that general recursion formulae can be derived for all the possible cases arising in the perturbation treatment of pseudosecular equations.

In some particular cases the formalism can be the same as that used for the secular equations. Within the framework of the EHT method, simultaneous first and second-order equations are obtained when perturbation terms are included in both H and S.

Appendix

Interactions of Two Molecular Systems

If two systems, designated as A and B, are supposed to be non-interacting, the pseudosecular equation can be written as

$$\begin{bmatrix}H_A^0 & 0\\ 0^T & H_B^0\end{bmatrix}\begin{bmatrix}|0;\,iA\rangle\\ |0;\,iB\rangle\end{bmatrix}=\begin{bmatrix}S_A^0 & 0\\ 0^T & S_B^0\end{bmatrix}\begin{bmatrix}|0;\,iA\rangle\\ |0;\,iB\rangle\end{bmatrix}\lambda_i^0\,. \tag{A1}$$

The interaction can be treated as a perturbation, because if A and B interact we can write Eq. (A1) as

$$\begin{bmatrix} H_A^0 & \Delta \\ \Delta^T & H_B^0 \end{bmatrix} \begin{bmatrix} |iA\rangle \\ |iB\rangle \end{bmatrix} = \begin{bmatrix} S_A^0 & \Sigma \\ \Sigma^T & S_B^0 \end{bmatrix} \begin{bmatrix} |iA\rangle \\ |iB\rangle \end{bmatrix} \lambda_i . \tag{A2}$$

Applying Eq. (17) we obtain

$$\begin{aligned} \lambda_i^n = {} & \langle iB;0|\Delta^T - \lambda_i^0 \Sigma^T|n-1;iA\rangle + \langle iA;0|\Delta - \lambda_i^0 \Sigma|n-1;iB\rangle \\ & - \sum_{k=1}^{n-1} \lambda_i^k \{\langle iB;0|\Sigma^T|n-k-1;iA\rangle + \langle iA;0|\Sigma|n-k-1;iB\rangle\} . \end{aligned} \tag{A3}$$

Taking into account the structure of Eq. [A1], we can separate Eq. (A3) in two parts:

a) $\lambda_i^n = \langle iA;0|\Delta - \lambda_i^0 \Sigma|n-1;iB\rangle$
$$- \sum_{k=1}^{n-1} \lambda_i^k \langle iA;0|\Sigma|n-k-1;iB\rangle, \quad \text{if} \quad \lambda_i^0 \varepsilon A;$$

b) $\lambda_i^n = \langle iB;0|\Delta^T - \lambda_i^0 \Sigma^T|n-1;iA\rangle$
$$- \sum_{k=1}^{n-1} \lambda_i^k \langle iB;0|\Sigma^T|n-k-1;iA\rangle, \quad \text{if} \quad \lambda_i^0 \varepsilon B.$$

The eigenvalues have only second- and higher-order corrections (i.e., $\lambda_i^1 = 0$).

A similar result is obtained for the n-th order correction to the eigenvectors,

$$\begin{aligned} a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \Big\{ & \langle jB;0|\Delta^T - \lambda_i^0 \Sigma^T|n-1;iA\rangle + \langle jA;0|\Delta - \lambda_i^0 \Sigma|n-1;iB\rangle \\ & - \sum_{k=1}^{n-1} \lambda_i^k (a_{ji}^{n-k} + \langle jB;0|\Sigma^T|n-k-1;iA\rangle + \langle jA;0|\Sigma|n-k-1;iB\rangle) \Big\} . \end{aligned}$$

It is again possible to distinguish two cases:

a) if $\lambda_j^0 \varepsilon A$,

$$\begin{aligned} a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \Big\{ & \langle jA;0|\Delta - \lambda_i^0 \Sigma|n-1;iB\rangle \\ & - \sum_{k=1}^{n-1} \lambda_i^k (a_{ji}^{n-k} + \langle jA;0|\Sigma|n-k-1;iB\rangle) \Big\} ; \end{aligned}$$

b) if $\lambda_j^0 \varepsilon B$,

$$\begin{aligned} a_{ji}^n = (\lambda_i^0 - \lambda_j^0)^{-1} \Big\{ & \langle jB;0|\Delta^T - \lambda_i^0 \Sigma^T|n-1;iA\rangle \\ & - \sum_{k=1}^{n-1} \lambda_i^k (a_{ji}^{n-k} + \langle jB;0|\Sigma^T|n-k-1;iA\rangle) \Big\} . \end{aligned}$$

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