Theoret. chim. Acta (Berl.) 26, 273—278 (1972)

Perturbation Theory for Excited States. IV

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Received November 26, 1971

Two of the perturbation methods developed in Paper I (CIPT and SCPT) are extended for use with uncoupled Hartree-Fock perturbation theory. Corrections to the uncoupled results are discussed and it is found that it is possible to correct using functions which when applied to ground state calculations are equivalent to the geometric approximation. It is also shown that CIPT and SCPT can be applied to ground state calculations and that when coupled perturbed orbitals are used CIPT and SCPT are equivalent to the usual coupled perturbation theory.

Introduction

Uncoupled Hartree-Fock perturbation theory has been used with some sucess in ground state molecular calculations. For the ground state it is possible to correct the uncoupled function by double perturbation theory [1–4] so that the results obtained are qualitively equivalent to coupled Hartree-Fock perturbation theory. In earlier papers in this series [5–7] coupled Hartree-Fock perturbation theory was applied to excited states of molecules. In this paper uncoupled theory is applied in a similar way. The perturbations used are restricted to perturbations by one electron operators and the methods are illustrated, as in Paper I, by a simple π-electron type calculation on *trans*-butadiene.

In Section 3 of this paper Tuan's interpretation of the geometric approximation is discussed and it is seen how this may be used as a correction to uncoupled perturbation theory applied to excited states.

The perturbation method described (that is CIPT of Paper I) can be used in ground state calculations. The relationship between the usual uncoupled Hartree-Fock perturbation theory and CIPT is discussed in Section 4. As in Paper I by CIPT we mean all possible configurations of correct spin symmetry made up from the ground state and single excitations of the ground state Hartree-Fock function. In the coupled theory presented in Paper I the ground state coupled single determinant had zero contribution with the first singlet excited state. However, as we shall see in Section 2, when we use uncoupled theory this is no longer true.

1. Uncoupled Perturbation Theory

As in coupled theory the starting point for uncoupled theory is the Hartree-Fock single determinant for $2n$ electrons

$$\psi_0 = |u_1^0(1)\,\alpha(1)\,u_1^0(2)\,\beta(2)\dots u_n^0(2n)\,\beta(2n)|\,, \tag{1}$$

where the u_i^0 satisfy the Hartree-Fock equations

$$F^0 u_i^0 = \varepsilon_i^0 u_i^0\,, \tag{2}$$

where

$$F^0 = \boldsymbol{h} + \sum_{i\,\mathrm{occ}} (2[-i^0|-i^0] - [-i^0|i^0-]) \tag{3}$$

in the notation of Ref. [4]. If we now perturb the system by a sum of one electron operators $\lambda \sum_i z(i)$ and neglect the change in the self consistent terms in F^0 we obtain the perturbation equations:

$$F^0 u_i^k + z u_i^{k-1} = \sum_{t=0}^{k} \varepsilon_i^t u_i^{k-t} \tag{4}$$

with the normalisation conditions:

$$\sum_{t=0}^{k} \langle u_i^{*t} | u_j^{k-t} \rangle = \delta_{k0} \delta_{ij} . \tag{5}$$

From these we obtain the expressions:

$$u_i^1 = \sum_{j \neq i} \frac{\langle u_j^{*0} | z | u_i^0 \rangle}{(\varepsilon_i^0 - \varepsilon_j^0)} u_j^0 , \tag{6}$$

$$u_i^2 = \sum_{j \neq i} \frac{\langle u_j^{*0} | z - \varepsilon_i^1 | u_i^1 \rangle}{(\varepsilon_i^0 - \varepsilon_j^0)} u_j^0 - \tfrac{1}{2} \langle u_i^{*1} | u_i^1 \rangle u_i^0 . \tag{7}$$

2. Configuration Interaction Wavefunctions for Excited States

As in Paper I we take our zero order functions for singlet and triplet excited states to be

$$\psi^{0S} = \sum_I c_I^0 \, S(q_i p_i) \psi_0 , \tag{8}$$

$$\psi^{0T} = \sum_I d_I^0 \, T(q_i p_i) \psi_0 , \tag{9}$$

where c_I and d_I are found by diagonalising the matrix elements of the total Hamiltonian between singlet and triplet states denoted by H^{0S} and H^{0T} respectively. We will now make the convention that expressions without superscripts (except for T, S) are quantities obtained through infinite order. For example the quantities H^S and u_i are defined as follows

$$H^S = \sum_{i=0}^{\infty} \lambda^i H^{iS} , \tag{10}$$

$$u_i = \sum_{k=0}^{\infty} \lambda^k u_i^k . \tag{11}$$

With this convention F is now the generalisation of F^0 for the perturbed system. The matrix elements are more complicated in uncoupled theory as the uncoupled infinite order orbitals u_i are not optimised to all orders. In fact we have

$$H_{IJ}^S = X + 2[p_i q_j | q_i p_j] - [p_i q_j | p_j q_i] , \tag{12}$$

$$H_{IJ}^T = X - [p_i q_j | p_j q_i] , \tag{13}$$

where

$$X = \delta_{p_i p_j} \delta_{q_i q_j} E + \delta_{p_i p_j} \langle q_i | F | q_j \rangle - \delta_{q_i q_j} \langle p_i | F | p_j \rangle \tag{14}$$

and E is the single determinant ground state energy for the perturbed system. The theory for the triplet now follows Paper I exactly where we solve the secular equation

$$\boldsymbol{H c} = E \boldsymbol{c} \tag{15}$$

perturbatively. The single configuration function discussed in Papers I and II may be deduced in exactly the same way for both the singlet and the triplet. However, for full CIPT in the singlet case the functions $S(q_i p_i) \psi$ have non zero interaction with ψ with respect to the total hamiltonian for the perturbed system $\mathscr{H} + \lambda \sum_i \boldsymbol{z(i)}$. That is to say when we use uncoupled functions Brillouin's theorem does not hold for the perturbed system. We may, however, take this into account in our perturbation equations by including the ground state determinant in our configurations. Thus

$$\psi^S = \sum_I^N c_I \, S(q_i p_i) \psi + c_0 \psi \,, \tag{16}$$

where $c_0^0 = 0$ and the matrix elements H_{0I}^S are given by

$$H_{0I}^S = \sqrt{2} \langle p_i | F | q_i \rangle \,. \tag{17}$$

Thus expressions for E^1 and E^2 are given by

$$E^1 = \sum_{I,J=0}^N c_I^0 H_{IJ}^{1S} c_J^0 = \sum_{I,J=1}^N c_I^0 H_{IJ}^{1S} c_J^0 \tag{18}$$

and

$$\begin{aligned} E^2 &= \sum_{I,J=0}^N c_I^0 (H_{IJ}^{1S} c_J^1 + H_{IJ}^{2S} c_J^0) \\ &= \sum_{I,J=1}^N c_I^0 (H_{IJ}^{1S} c_J^1 + H_{IJ}^{2S} c_J^0) + \sum_{I=1}^N H_{I0}^{1S} c_I^0 c_0^1 \,. \end{aligned} \tag{19}$$

3. Corrections to the Uncoupled Wavefunctions

The essential feature of the uncoupled approximation is the neglect of changes in the self consistent potential. Suppose we try to allow for the changes by a sum of one electron operators $\boldsymbol{\omega(i)}$ where

$$\boldsymbol{\omega(i)} = k \boldsymbol{z(i)} \tag{20}$$

and the constant k is chosen in some way so that $(k-1) \sum_i \boldsymbol{z(i)}$ approximates to the change in self consistent terms $\boldsymbol{F}^1 - \sum_i \boldsymbol{z(i)}$. With this definition of $\boldsymbol{\omega(i)}$ the first two perturbation equations of (4) become

$$\boldsymbol{F}^0 \hat{u}_i^1 + k \boldsymbol{z} u_i^0 = \varepsilon_i^0 \hat{u}_i^1 + \hat{\varepsilon}_i^1 u_i^0 \,, \tag{21}$$

$$\boldsymbol{F}^0 \hat{u}_i^2 + k \boldsymbol{z} \hat{u}_i^1 = \varepsilon_i^0 \hat{u}_i^2 + \hat{\varepsilon}_i^1 \hat{u}_i^1 + \hat{\varepsilon}_i^2 u_i^0 \tag{22}$$

and the normalisation conditions are the same as defined in Eq. (5) with $\hat{u}_i^k$ replacing u_i^k. It is easy to see from (21) and (22) that the following identities hold:

$$\hat{u}_i^1 = k u_i^1 , \tag{23}$$

$$\hat{u}_i^2 = k^2 u_i^2 , \tag{24}$$

$$\hat{\varepsilon}_i^1 = k^2 \varepsilon_i^1 , \tag{25}$$

$$\hat{\varepsilon}_i^2 = k \varepsilon_i^2 . \tag{26}$$

It is well known that the first order coupled orbitals u_i^c and the second order coupled energy E_c^2 may be obtained by minimising the functional

$$\begin{aligned}\hat{E}_c^2 = 2 \sum_{i=1}^{n} (\langle \hat{u}_i^1 | \boldsymbol{F}^0 - \varepsilon_i^0 | \hat{u}_i^1 \rangle + 2 \langle u_i^1 | z - \varepsilon_i^1 | u_i^0 \rangle \\ + \sum_{j=1}^{n} (4[\hat{u}_i^1 \hat{u}_j^1 | u_i^0 u_j^0] - [\hat{u}_i^1 \hat{u}_j^1 | u_j^0 u_i^0] - [\hat{u}_i^1 u_j^0 | \hat{u}_j^1 u_i^0]))\end{aligned} \tag{27}$$

with respect to variations in $\hat{u}_i$. Tuan [8] has considered the case when $\hat{\mathrm{u}}_i$ are of special form $k u_i^1$ where u_i^1 are the uncoupled functions. With this restriction we have that

$$\hat{E}_c^2 = k^2 (E^{1,2} - E^{0,2}) + 2k E^{0,2} , \tag{28}$$

where

$$E^{0,2} = 2 \sum_{i=1}^{n} \langle u_i^1 | z | u_i^0 \rangle \tag{29}$$

and

$$E^{1,2} = \sum_{i,j}^{n} (8 [u_i^1 u_j^1 | u_i^0 u_j^0] - 2 [u_i^1 u_j^1 | u_j^0 u_i^0] - 2 [u_i^1 u_j^0 | u_j^1 u_i^0]) . \tag{30}$$

Thus the best $\hat{u}_i$ in the restricted form are obtained by choosing k to minimise (28). Following Tuan we see that this choice of k is

$$k = -E^{0,2} / (E^{1,2} - E^{0,2}) \tag{31}$$

and leads to

$$\min(\hat{E}_c^2) = (E^{0,2})^2 / (E^{0,2} - E^{1,2}) \tag{32}$$

which is identical with the usual geometric approximation [8–10] used as a correction to the uncoupled wavefunctions. Thus it would seem that a reasonable choice of k in Eqs. (21) and (22) would be as defined in (31).

4. Relationship with the Ground State

We may apply CIPT to ground state calculations. To do this we consider the ground state wavefunction for the perturbed system to be of the form

$$\psi^G = \sum_{I}^{N} c_I \, S(q_i p_i) \, \psi + c_0 \psi . \tag{33}$$

In the case of the ground state $\psi_0^G = \psi_0$. This means that $c_0^0 = 1$ and $c_I^0 = 0$ for non zero I. Now if we use coupled theory Brillouin's theorem holds for all orders so that $c_I^k = 0$ for non zero I and all k. In addition we have the normalisation condition

$$\sum_{I=0}^{N} c_I^1 c_I^0 = 0 \tag{34}$$

which means that for coupled or uncoupled functions we have $c_0^1 = 0$. However if we use uncoupled functions we have $c_I^k \neq 0$ for non zero I and for all orders k (since the uncoupled functions are not optimised to all orders). Thus for the ground state the first and second order energies are given by

$$E^1 = H_{00}^1 , \tag{35}$$

$$E^2 = H_{00}^2 + \sum_{s=1}^{N} H_{0J}^{1S} c_J^1 , \tag{36}$$

where

$$H_{00}^1 = 2 \sum_{i=1}^{n} \langle u_i^0 | z | u_i^0 \rangle \tag{37}$$

the usual uncoupled first order energy and

$$\begin{aligned} H_{00}^2 = 2 \sum_i \langle u_i^1 | z | u_i^0 \rangle + \sum_{i,j}^{n} (8[u_i^1 u_j^1 | u_i^0 u_j^0] \\ - 2[u_i^1 u_j^1 | u_j^0 u_i^0] - 2[u_i^1 u_j^0 | u_j^1 u_i^0]) \end{aligned} \tag{38}$$

which is the usual uncoupled corrected second order energy [1–4]. In Papers I and II of this series we discussed a single configuration function. In the case of the ground state this corresponds to defining $\psi^G \equiv \psi$; in this case the first and second order energies are H_{00}^1 and H_{00}^2 respectively.

Thus SCPT is equivalent to the usual uncoupled theory plus Dalgarno's correction when uncoupled functions are used whereas if we use coupled functions both SCPT and CIPT are equivalent to the usual coupled theory. Also if we use the geometric functions discussed in Section 3 the SCPT is equivalent to the geometric approximation.

5. Results

In Tables 1 and 2 the results of simple π-electron calculations on *trans*-butadiene are presented. The perturbations used are the point perturbations discussed in Papers I and III of this series. In Table 1 the results of applying CIPT and SCPT

Table 1

Perturbation at atom	1		2	
	E^1	E^2	E^1	E^2
Uncoupled energies	1	−0.046	1	−0.039
Uncoupled with Dalgarno's correction		−0.058		−0.049
Uncoupled with geometric approximation	1	−0.063	1	−0.054
CIPT (uncoupled functions)	1	−0.059	1	−0.050
CIPT (geometric functions)	1	−0.063	1	−0.054
Coupled theory energies	1	−0.063	1	−0.054

Table 2

Perturbation at atom		1		2	
		Singlet	Triplet	Singlet	Triplet
CIPT (coupled)	E^1	1	1	1	1
	E^2	−0.026	−0.070	−0.046	−0.120
CIPT (uncoupled)	E^1	1	1	1	1
	E^2	−0.014	−0.051	−0.032	−0.105
CIPT (geometric)	E^1	1	1	1	1
	E^2	−0.027	−0.071	−0.046	−0.129
SCPT (coupled)	E^1	1	1	1	1
	E^2	−0.031	−0.064	−0.016	−0.113
SCPT (uncoupled)	E^1	1	1	1	1
	E^2	−0.007	−0.050	−0.026	−0.087
SCPT (geometric)	E^1	1	1	1	1
	E^2	−0.039	−0.066	−0.005	−0.122

to ground state calculations are presented whereas in Table 2 the first and second order energies given are for the first singlet and first triplet excited state. In all cases the geometric functions give results which agree remarkably well with the coupled theory results. Thus we may conclude that the use of geometric functions (that is corrected uncoupled theory) in excited state perturbation theory seems to lead to improved results in the same way that the geometric correction improves uncoupled theory ground state calculations.

Acknowledgement. I would like to proffer my appreciation to Dr. A. T. Amos for constant advice and encouragement in the preparation of this paper and to the S.R.C. for the provision of a research grant.

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