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Perturbation Theory for Excited States of Molecules. I

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The problem of perturbations of excited states is discussed and three methods are developed. The first of these uses a zero order wave-function made up of a linear sum of singly excited SCF configurations, whereas the second uses just one of these configurations. The third method is restricted to small π-systems, the zero order wave-function being a linear sum of all possible determinants formed from the basis set used. The perturbations considered here are one-electron operators. Example calculations are performed on the butadiene molecule within the context of the π-electron approximation.

Für das Problem einer Störung von Einelektronen-Operatoren für angeregte Zustände werden drei Verfahren vorgeschlagen: Erstens die Verwendung einer Zustandsfunktion nullter Ordnung, die eine Linearkombination einfach angeregter SCF-Konfigurationen ist, zweitens die entsprechende Verwendung nur einer ausgewählten Konfiguration. Drittens läßt sich, wenn auch nur bei kleinen π-Elektronensystemen, als nullte Näherung eine Linearkombination von allen möglichen angeregten Konfigurationen verwenden. Als Beispiel wird das π-Elektronensystem des Butadiens gewählt.

Discussion du problème de perturbation pour les états excités et développement de trois méthodes. La première utilise une fonction d'ordre zéro combinaison linéaire de configurations SCF monoexcitées, alors que la seconde utilise seulement une de ces configurations. La troisième méthode est restreinte à de petits systèmes π, la fonction d'onde d'ordre zéro étant une combinaison linéaire de tous les déterminants construits dans la base utilisée. Les perturbations envisagées ici sont constituées par des opérateurs monoélectroniques. La molécule de butadiène sert d'exemple dans le cadre de l'approximation à électrons π.

1. Introduction

In recent years there have been many applications of perturbation theory to molecular systems. In almost all of these calculations only the ground state of the molecule has been considered (see however Ref. [1–3]). The rapid progress in experimental technique, particularly in the field of photochemistry, where low lying electronically excited states are important, makes it increasingly necessary to extend perturbation calculations from the ground state to these excited states. The purpose of this paper is to undertake a preliminary investigation into the problems involved.

It turns out that the major difficulty in developing a perturbation expansion is to decide on a zero order wave-function for the excited states. Unlike ground state calculations, where the Hartree-Fock wave-function forms an obvious and acceptable starting point, there is no definitive approximate wave-function for excited states. We have therefore considered two different forms. One is a linear sum of all singly excited configurations which can be built up from the Hartree-

Fock molecular orbitals; the second consists of just one of these. Clearly the development of a perturbation theory depends on which of these two forms is used; the second is in some ways easier to deal with theoretically but the first is probably more accurate and in some cases e.g. where there is near degeneracy, it is certainly the one to use.

To illustrate these points we have made some simple π-electron type calculations on trans-butadiene. There are three reasons for choosing to do such a calculation as a prototype:

(a) being a π-electron calculation it is relatively easy to make and so the theory is not swamped by problems of a numerical nature, as would be the case of an *ab-initio* calculation, (b) if the theory is to be of use to experimentalists it will have to be applied to large conjugated systems where π approximation is the only practical possibility and (c) for trans butadiene it is possible to obtain "exact" answers within the context of π-electron theory and these are available for comparison.

2. Perturbed Molecular Orbitals

Consider a ground state wave function in the form of a Slater determinant

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

where the u_i^0 satisfy the Hartree-Fock equations

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

where

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

and the notation of Ref. [4] has been used in Eq. (3) for Coulomb and exchange operators. Now suppose we perturb the original Hamiltonian by adding to it a sum of one electron operators $\lambda \sum_i z(i)$. Then the orbitals will change and to first and second order we have that

$$(\boldsymbol{F}^0 - \varepsilon_i^0)\,u_i' = (\varepsilon_i' - \boldsymbol{F}')\,u_i^0 \tag{4}$$

and

$$(\boldsymbol{F}^0 - \varepsilon_i^0)\,u_i^2 = (\varepsilon_i' - \boldsymbol{F}')\,u_i' + (\varepsilon_i^2 - \boldsymbol{F}^2)\,u_i^0 \tag{5}$$

with the normalisation conditions:

$$\langle u_i' | u_j^0 \rangle + \langle u_i^0 | u_j' \rangle = 0\,, \tag{6}$$

$$\langle u_i^2 | u_j^0 \rangle + \langle u_i' | u_j' \rangle + \langle u_i^0 | u_j^2 \rangle = 0\,, \tag{7}$$

where

$$\boldsymbol{F}' = z + \sum_{i\,occ} \{2[-i'|-i^0] + 2[-i^0|-i'] - [-i'|i^0-] - [-i^0|i'-]\} \tag{8}$$

and,

$$\begin{aligned}\boldsymbol{F}^2 = \sum_{i\,occ} \{&2[-i^2|-i^0] + 2[-i^0|-i^2] + 2[-i'|-i'] - [-i^2|i^0-] \\ &- [-i^0|i^2-] - [-i'|i'-]\}\,.\end{aligned} \tag{9}$$

Notice that here we use coupled Hartree-Fock perturbation theory and allow for the variation of the Coulomb and exchange terms when the orbitals change [4, 5].

3. Excited States

In general the Hartree-Fock operator has an infinite number of solutions. However, since in practical calculations $\boldsymbol{F}^0$ is usually expressed in terms of a finite set of basis orbitals which has the effect of truncating the operator, only a small number of molecular orbitals are available for use in forming excited states. Let us suppose the basis set consists of m orbitals so that in solving (2) we also obtain m molecular orbitals. The lowest n of these will be used for the ground state wave function so that there are $(m-n)$ virtual orbitals.

Singly excited configurations can be formed from the ground state by removing one of the ground state molecular orbitals and replacing it by a virtual orbital. Using the notation of Ref. [6] where $\boldsymbol{a}_{p_i}$ annihilates an occupied orbital p_i and $\boldsymbol{a}_{q_i}^+$ replaces it by a virtual orbital q_i, both with α spin and similarly $\boldsymbol{b}_{p_i}$ and $\boldsymbol{b}_{q_i}^+$ for β spin we can define operators:

$$\boldsymbol{T}(q_i, p_i) = \frac{1}{\sqrt{2}} (\boldsymbol{a}_{q_i}^+ \boldsymbol{a}_{p_i} - \boldsymbol{b}_{q_i}^+ \boldsymbol{b}_{p_i}), \tag{10}$$

$$\boldsymbol{S}(q_i, p_i) = \frac{1}{\sqrt{2}} (\boldsymbol{a}_{q_i}^+ \boldsymbol{a}_{p_i} + \boldsymbol{b}_{q_i}^+ \boldsymbol{b}_{p_i}) \tag{11}$$

which when acting on the ground state Hartree-Fock function, form singly excited triplet and singlet configurations. We shall use a single, upper case, index I to refer to the pair of integers (p_i, q_i). Since there are n possible values for p_i and $(m-n)$ for q_i, there will be $n(m-n)$ possible singly excited configurations i.e. $1 \leqq I \leqq n(m-n)$.

There are three possibilities to be considered if we are to use these configurations to form wave functions for excited states of molecules. Firstly one singly excited configuration by itself may be a reasonable approximation to an excited state. We shall term this a single configuration wave-function. Normally, however, this will not be satisfactory and we shall have to take a linear combination of the singly excited configurations to get a reasonable wave-function for the excited state. This we shall call a configuration interaction wave-function and to make it definite, we shall assume we have taken a linear combination of all the singly excited functions compatible with the basis used. The third possibility is that neither of these is satisfactory and that doubly excited and higher configurations have to be included. Although it would be possible to develop a perturbation theory which could allow for this we shall not do so here since we believe that the first two possibilities will cover most of the cases we are interested in. Moreover it will be recalled that, for the ground state, perturbation theory is usually based on Hartree-Fock wave-functions; the inclusion of singly excited configurations will not change this since, because of Brillouin's theorem [7], there is no interaction between the ground state and these configurations. However this is not the case when doubly excited configurations are included, so that, to be consistent, if we used these for excited state perturbation theory, we would then have to revise ground state perturbation theory, and at the present time we are not prepared to do this.

Thus there are two types of excited state wave functions we shall consider here: configuration interaction functions and single configuration functions. We now discuss in turn perturbation theories for each of these.

4. Configuration Interaction Wave Functions

The configuration interaction wave function for a singlet state will be

$$\psi^s = \sum_I C_I S(q_i, p_i)\, \psi_0 \tag{12}$$

and for the triplet state

$$\psi^T = \sum_I D_I T(q_i, p_i)\, \psi_0 \,. \tag{13}$$

The coefficients C_I and D_I are found by diagonalising the matrix elements of the total Hamiltonian between the singlet and triplet configurations. Denoting these matrices by $\boldsymbol{H}^S$ and $\boldsymbol{H}^T$ for the singlet and triplet states respectively, we have that

$$\begin{aligned} H^s_{IJ} &= \langle S(q_i, p_i)\, \psi_0 | \mathscr{H} | S(q_j, p_j)\, \psi_0 \rangle \\ &= \delta_{IJ}(E_G + \varepsilon_{q_i} - \varepsilon_{p_i}) \\ &\quad + 2[p_i q_j | q_i p_j] - [p_i q_j | p_j q_i] \,, \end{aligned} \tag{14}$$

$$\begin{aligned} H^T_{IJ} &= \langle T(q_i, p_i)\, \psi_0 | \mathscr{H} | T(q_j, p_j)\, \psi_0 \rangle \\ &= \delta_{IJ}(E_G + \varepsilon_{q_i} - \varepsilon_{p_i}) - [p_i q_j | p_j q_i] \,, \end{aligned} \tag{15}$$

where E_G is the ground state Hartree-Fock energy, and the matrix elements in square brackets are with respect to $1/r_{12}$. Notice that because we are using molecular orbitals the matrix elements of $\boldsymbol{F}$ occur only along the diagonals of $\boldsymbol{H}^s$ and $\boldsymbol{H}^T$. This is why we have used coupled perturbation theory to find the first and second order orbitals since it is only with these that we can use Eqs. (14) and (15).

Now let us subject the molecule to an external perturbation, as in Sect. 2. The first effect of this will be to change the orbitals u_i and hence the singly excited configurations $\boldsymbol{T}(q_i, p_i)\, \psi^0$ and $\boldsymbol{S}(q_i, p_i)\, \psi^0$. Because of this and because the Hamiltonian has changed the matrices $\boldsymbol{H}^S$ and $\boldsymbol{H}^T$ will also change. However, since we were careful to use coupled perturbation theory to find the perturbation corrections to the original molecular orbitals we can make a direct perturbation expansion of Eqs. (14) and (15).

Thus we write

$$\boldsymbol{H}^S = \boldsymbol{H}^{S0} + \lambda \boldsymbol{H}^{S1} + \lambda^2 \boldsymbol{H}^{S2} + - \tag{16}$$

$$\boldsymbol{H}^T = \boldsymbol{H}^{T0} + \boldsymbol{H}^{T1} + \lambda^2 \boldsymbol{H}^{T2} + - \,, \tag{17}$$

where, from (15), for example,

$$\begin{aligned} \boldsymbol{H}^{T1} &= \delta_{IJ}(E^1_G + \varepsilon^1_{q_i} - \varepsilon^1_{p_i}) - [p^0_i q^0_j | p^0_j q^1_i] - [p^0_i q^0_j | p^1_j q^0_i] \\ &\quad - [p^0_i q^1_j | p^0_j q^0_i] - [p^1_i q^0_j | p^0_j q^0_i] \,. \end{aligned} \tag{18}$$

The expressions for $\boldsymbol{H}^{T2}$, $\boldsymbol{H}^{S1}$, $\boldsymbol{H}^{S2}$ can similarly be obtained but they are rather cumbersome so we shall not write them out in full. Because of these changes in $\boldsymbol{H}^S$ and $\boldsymbol{H}^T$ the coefficients $\{C_I\}$ and $\{D_I\}$ will also change. Notice, therefore, that the effect of the perturbation on the excited states according to this theory is compounded of two parts, i.e. both a change of the singly excited configuration basis functions and the coefficients multiplying them.

Dropping the T and S superscript since the final development proceeds the same way for both, we have to solve the secular equation

$$\boldsymbol{H}\boldsymbol{C} = E\boldsymbol{C} \tag{19}$$

to find the energy. The usual perturbation results give us that

$$E^1 = \sum_{IJ} C_I^0 H_{IJ}^1 C_J^0 , \tag{20}$$

$$E^2 = \sum_{IJ} (C_I^0 H_{IJ}^1 C_J^1 + C_I^0 H_{IJ}^2 C_J^0) , \tag{21}$$

where $\{C_I^0\}$ are the zero and first order coefficients in the expansion of ψ^S or ψ^T. The first order coefficients satisfy

$$(\boldsymbol{H}^0 - E^0\boldsymbol{1})\,\boldsymbol{C}^1 = (E^1\boldsymbol{1} - \boldsymbol{H}^1)\,\boldsymbol{C}^0 \tag{22}$$

together with the extra normalisation condition

$$\sum_I C_I^1 C_I^0 = 0 . \tag{23}$$

5. Single Configuration Function

Having developed the theory of configuration interaction function, that for the single configuration function can be deduced quite simply. Let us suppose the single configuration is $\boldsymbol{S}(q, p)\,\psi_0$ or $\boldsymbol{T}(q, p)\,\psi_0$ and that the index I is used for the pair (p, q). The original unperturbed energy for such functions will be just H_{II}^{S0} and H_{II}^{T0}. Thus the first and second order corrections will be H_{II}^{S1}, H_{II}^{S2} and H_{II}^{T1}, H_{II}^{T2} respectively.

In general the zero order energy H_{II}^0 will not be as accurate as zero order energy for the configuration interaction wave function. However the first and second order energies, in the single configuration case, do not depend on the zero order energy, as may be seen by examination of Eqs. (20), (21), and (23). Therefore to obtain an energy to second order, comparable with that energy obtained by the configuration interaction theory, we may redefine H_{II}^0 so that both the single configuration and configuration interaction wave-function have the same zero order energy.

6. Exact Perturbation Solutions for π-Systems

For small π-electron systems it is possible to find exact solutions for the first and second order energies within the context of the π-electron hamiltonian. For a molecular system of $2n$ electrons a wave function Ψ which is an eigenfunction of S^2 with eigenvalue zero and satisfies the Pauli principle may be expanded in the form:

$$\Psi = \Sigma C[i, \ldots i_n | j, \ldots j_n] \, |\omega_i, \alpha \ldots \omega_{in} \alpha \omega_j, \beta \ldots \omega_{jn} \beta| \,, \tag{24}$$

where the sum is over all the set of ordered integers

$$\begin{aligned} i, \ldots i_n, j, \ldots j_n \text{ satisfying } & 1 \leqq i_1 \leqq i_2 \leqq \cdots \leqq i_n \leqq n \,, \\ & 1 \leqq j_1 \leqq j_2 \leqq \cdots \leqq j_n \leqq n \,, \end{aligned}$$

and $\{\omega_i\}$ are the limited basis set of atomic orbitals used [8]. We wish to solve the equation:

$$\mathscr{H} \Psi = \varepsilon \Psi \,. \tag{25}$$

As we have assumed semiempirical values for the integrals $\langle \omega_i(1) | \boldsymbol{h}(1) | \omega_j(1) \rangle$ and $\langle \omega_i(1) \, \omega_j(2) | \dfrac{1}{r_{12}} | \omega_m(1) \, \omega_n(2) \rangle$ [9], the problem reduces to diagonalisation of the hamiltonian matrix with respect to the configurations $|\omega_i, \alpha \ldots \omega_{i_n} \alpha \omega \beta \ldots \omega_{jn} \beta|$.

In this way we obtain first excited singlet (or triplet) Ψ^0 (say). We will denote the physical eigenfunctions of the hamiltonian obtained in this way by $\{\theta_r\}$ where $\Psi^0 = \theta_m$ say. If we now perturb the system by $\boldsymbol{W} = \lambda \sum_i z(i)$ we obtain the following equation

$$\mathscr{H} \Psi^0 = E^0 \Psi^0 \,, \tag{26}$$

$$(\mathscr{H} - E^0) \, \Psi^1 = (E^1 - W) \, \Psi^0 \,, \tag{27}$$

$$(\mathscr{H} - E^0) \, \Psi^2 = (E^1 - W) \, \Psi^1 + E^2 \Psi^2 \,. \tag{28}$$

From these are obtained

$$E^1 = \langle \Psi^0 | W | \Psi^0 \rangle \tag{29}$$

and

$$E^2 = \sum_{r \neq m} \frac{\langle \Psi^0 | W | \theta_r \rangle \, \langle \theta_r | W | \Psi^0 \rangle}{(E^0 - \varepsilon_r)} \,, \tag{30}$$

where

$$\mathscr{H} \, \theta_r = \varepsilon_r \theta_r \,. \tag{31}$$

7. Results and Discussion

For butadiene we have computed the values of E^1 and E^2 using the various methods described in the paper. We have assumed that the perturbation is such that the only non zero elements are of the form $\langle \omega_i | z | \omega_i \rangle = \lambda \beta (\beta = -4.78 \text{ eV})$ and thus correspond to the perturbation acting at atom i. This is the type of perturbation considered in the calculation of atom-atom polarisabilities for ground state systems [10]. We have considered the cases when the perturbation is confined to one atom (i.e. atom 1 or atom 2) and also where it affects two different atoms (all possible pairs). The results are given in Table 1 and the energies are in electron volts. Because butadiene is an alternant hydrocarbon it follows automatically that E^1 is either 1 or 2 depending on the number of carbon sites affected by the perturbation.

If, first, we consider the CI and single configuration results we see that on the whole they agree but there are some poor values. To some extent we believe that the agreement is a special property of the butadiene molecule, for in this particular case $C_1^0 = C_4^0 = 0$, and C_3^0 is approximately unity for both the triplet and singlet functions. Also if we consider the last five entries in Table 1, where the agreement is most pronounced, in these cases $C_I^1 = 0$ for all I. Thus the configuration interaction functions and single configuration functions are almost the same. However in the case of the seventh entry in Table 1, there is considerable mixing of states and the single configuration function is not a good approximation to the CI function. Thus we consider that the configuration interaction method is the safest one to use although, for large systems, one may have to use the simpler method.

A comparison between the CI and single configuration results and the exact values shows poor agreement indeed. The same sort of result has been found previously in calculations for the ground state of butadiene [11]. This, however, does not invalidate the non-exact values. It will be recalled that the semi-empirical integrals were originally obtained from a comparison between the experimental

Table 1

Perturbation at atom	Singlet or triplet	CIPT E^1	CIPT E^2	Single E^1	CIPT E^2	Exact E^1	PT E^2
1	T	1	-0.026	1	-0.031	1	-0.019
1	S	1	-0.070	1	-0.064	1	-0.016
2	T	1	-0.046	1	-0.016	1	-0.042
2	S	1	-0.120	1	-0.113	1	-0.131
1, 2	T	2	-0.053	2	-0.042	2	-0.048
1, 2	S	2	-0.158	2	-0.130	2	-0.099
2, 4	T	2	-0.047	2	-0.004	2	-0.043
2, 4	S	2	-0.133	2	-0.132	2	-0.164
1, 4	T	2	-0.047	2	-0.049	2	-0.032
1, 4	S	2	-0.091	2	-0.091	2	-0.030
2, 3	T	2	-0.047	2	-0.049	2	-0.032
2, 3	S	2	-0.091	2	-0.091	2	-0.030

Table 2

Perturbation at atom	Singlet or triplet	E(CI)	E^P
1	S	-36.325	-36.326
1	T	-39.720	-39.719
2	S	-36.375	-36.376
2	T	-39.741	-39.739
1, 2	S	-35.404	-35.414
1, 2	T	-38.747	-38.746
1, 4	S	-35.345	-35.347
1, 4	T	-38.738	-38.740
2, 3	S	-35.345	-35.347
2, 3	T	-38.738	-38.746
2, 4	S	-35.387	-35.389
2, 4	T	-38.740	-38.740

spectra of aromatics and excited state energies computed from CI functions. Thus although the CI perturbation results may disagree with the exact ones nevertheless from the point of view of comparison with experiment the former may be better.

Finally to see how well the energy summed through second order agrees with a conventional calculation in Table 2 we give the perturbation energy $E^p = E^0 + E^1 + E^2$ with $\lambda = 1/|\beta| \sim 0.2$. We have also computed the ordinary configuration interaction energy, E(CI) for the Hamiltonian $\mathscr{H} + \boldsymbol{W}$, with singly excited SCF configurations. The agreement between the perturbation calculation and the straightforward configuration interaction calculation is very good.

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