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Unrestricted Hartree Fock Perturbation Theory

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The coupled and uncoupled Hartree Fock perturbation theories are generalised using unrestricted Hartree Fock theory. The variational approach to coupled theory is discussed and various corrections to the uncoupled theory are considered. Trial calculations are carried out to obtain atom-atom polarizabilities for Allyl and the first excited triplet state of *cis*-Butadiene, and to obtain estimates of spin and charge densities for various heterocyclics.

Die gekoppelte and die ungekoppelte Hartree-Fock Störungstheorie werden mit Hilfe der uneingeschränkten Hartree-Fock-Theorie verallgemeinert. Das Variationsverfahren für die gekoppelte Theorie wird diskutiert und verschiedene Korrekturen für die ungekoppelte Theorie werden untersucht. Es werden Testrechnungen durchgeführt, um die Atom-Atom-Polarisierbarkeiten des Allylradikals und des ersten angeregten Tripletzustandes von *cis*-Butadien, und um die Spin- und Ladungsdichten verschiedener Heterozyklen abzuschätzen.

1. Introduction

For many years there has been considerable interest in perturbation theoretic treatments of molecules (see Refs. [1–10]). Almost all of these have been restricted to the ground state, or the excited states, of the most common type of molecule that is those molecules with an even number of electrons. For these molecules the ground state wavefunction is a singlet and may be approximated by a single determinant of $2m$ functions of space and spin coordinates (spin orbitals) where $2m$ is the number of electrons. The purpose of this paper is to extend these calculations to calculations applied to molecules with an odd number of electrons, and to triplet excited states of molecules with an even number of electrons, using unrestricted Hartree-Fock perturbation theory. That is to say the zero order approximation for the perturbation theory is taken to be the unrestricted Hartree-Fock single determinant. This function is a determinant of spin orbitals v_i^0 which are products of a space function u_i^0 and a spin function α or β. The single determinant is constrained to be an eigenfunction of $\hat{S}_z$ and this is done by assuming that p spin orbitals are associated with α spin and q with β spin so that

$$\frac{1}{2}(p-q)=M \tag{1}$$

where M is the chosen eigenvalue of $\hat{S}_z$. For a molecule with an even number of electrons, if we choose $M=1$ the single determinant is an approximation to the wavefunction for the first triplet excited state so that unrestricted perturbation theory becomes an excited state perturbation theory. A full discussion of the relevent theory for the most general single determinant has been given by Amos and Hall [18] and Amos [19].

The two particular theories discussed in this chapter are the coupled and uncoupled Hartree-Fock theories for perturbations by one electron operators (see Refs. [1–10]). The coupled theory takes into account, to all orders of the perturbation theory, the change in the Hartree-Fock operator due to changes in the spin orbitals (i.e. the change in the self consistency conditions), whereas these are ignored in uncoupled theory. These theories are discussed in Sections 2 and 4 of this paper. Recently there has been interest in a variational principle for the first order spin orbitals in coupled theory (see Refs. [3, 6]). A discussion of this, with regard to the unrestricted perturbation theory presented in this paper, is given in Section 3. In general the single determinant is not an eigenfunction of the total spin operator $\hat{S}^2$. It is possible to correct for this perturbatively in both the coupled and uncoupled theories. In the case of uncoupled theory it is also possible to correct the first and second order total energies by double perturbation theory as shown by Tuan *et al.* [1]. Both of these corrections are discussed in Section 5.

Finally in Section 6 two applications of this theory are discussed. The spin and charge densities of various hetromolecules are considered. The theory is also appropriate for a discussion of chemical reactivity which is related to the atom-atom polarizabilities for alternant hydrocarbons. The atom-atom polarizabilities for various ions and triplet excited states are calculated.

2. Coupled Perturbation Theory

Consider the best single determinant wavefunction, for an approximation to the ground state of a general molecule with n electrons, in the form

$$\Psi_0 = (n!)^{-\frac{1}{2}} \det \{\psi_1^0(1)\alpha(1) \ldots \psi_p^0(p)\alpha(p)\phi_1^0(p+1)\beta(p+1) \ldots \phi_q^0(p+q)\beta(p+q)\} \quad (2)$$

where $p+q=n$ and without loss in generality we may choose the sets of functions $\{\psi_i^0\}$, $\{\phi_i^0\}$ to be separately orthonormal and $p \geqq q$. The functions $\{\psi_i^0\}$ and $\{\phi_i^0\}$ are determined by minimising the functional

$$\langle \Psi_0 | \mathscr{H} | \Psi_0 \rangle / \langle \Psi_0 | \Psi_0 \rangle \quad (3)$$

with respect to variations $\delta\psi_i^0$ and $\delta\phi_i^0$ in ψ_i^0 and ϕ_i^0 where

$$\mathscr{H} = \sum_{i=1}^{n} h(i) + \sum_{i<j} \frac{1}{r_{ij}} \quad (4)$$

is the total hamiltonian for the molecule. The molecular orbitals $\{\psi_i^0\}$ and $\{\phi_i^0\}$ obtained in this way satisfy equations of the form

$$F^{\alpha_0}(1)\psi_i^0(1) = E_{\alpha_i}^0 \psi_i^0(1), \quad (5)$$

$$F^{\beta_0}(1)\phi_i^0(1) = E_{\beta_i}^0 \phi_i^0(1) \quad (6)$$

where $E^0_{\alpha_i}$ and $E^0_{\beta_i}$ are the orbital energies,

$$F^{\alpha o}(1)=h(1)+G^{\alpha o}(1)=h(1)+\sum_{j=1}^{p}\left([-\psi_j^0|-\psi_j^0]-[-\psi_j^0|\psi_j^0-]\right)+\sum_{j=1}^{q}[-\phi_j^0|-\phi_j^0] \tag{7}$$

and

$$F^{\beta o}(1)=h(1)+G^{\beta o}(1)=h(1)+\sum_{j=1}^{p}[-\psi_j^0|-\psi_j^0]+\sum_{j=1}^{q}\left([-\phi_j^0|-\phi_j^0]-[-\phi_j^0|\phi_j^0-]\right) \tag{8}$$

in the notation of Amos and Musher [8] for the coulomb and exchange operators. The total single determinant wavefunction Ψ_0 satisfies the eigenvalue equation

$$\hat{H}_0\Psi_0=E_0\Psi_0 \tag{9}$$

where

$$\hat{H}_0=\sum_{i=1}^{n}\left(h(i)+G^{\alpha o}(i)|\alpha\rangle\langle\alpha|+G^{\beta o}(i)|\beta\rangle\langle\beta|\right)+C^0 \tag{10}$$

and C^0 is chosen so that

$$E_0=\langle\Psi_0|\mathscr{H}|\Psi_0\rangle/\langle\Psi_0|\Psi_0\rangle\,. \tag{11}$$

In principle Eqs. (5) and (6) have an infinite number of solutions in practice however the functions $\{\psi_i^0\}$ and $\{\phi_i^0\}$ are expanded as a linear combination of m (say) basis functions $\{\omega_r\}$ so that the operators $F^{\alpha o}$ and $F^{\beta o}$ are truncated.

If we now change the one-electron operators in the hamiltonian by an amount $W=\sum_i z(i)$ and denote the changes to the k^{th} order in the Hartree Fock operators $F^{\alpha o}$ and $F^{\beta o}$ by F^{α_k} and F^{β_k} we obtain the following set of perturbation equations:

$$\sum_{s=1}^{m}\left(F^{\alpha o}_{rs}-S_{rs}E^0_{\alpha_i}\right)a^k_{is}=(1-\delta_{k0})\sum_{s=1}^{m}\sum_{j=1}^{k}\left(E^j_{\alpha i}S_{rs}-F^{\alpha_j}_{rs}\right)a^{k-j}_{is}\,, \tag{12}$$

$$\sum_{s=1}^{m}\left(F^{\beta o}_{rs}-S_{rs}E^0_{\beta_i}\right)b^k_{is}=(1-\delta_{k0})\sum_{s=1}^{m}\sum_{j=1}^{k}\left(E^j_{\beta_i}S_{rs}-F^{\beta_j}_{rs}\right)b^{k-j}_{is} \tag{13}$$

where

$$S_{rs}=\int\omega_r^*(1)\omega_s(1)d\tau \tag{14}$$

$$F^{\alpha_j}_{rs}=\int\omega_r^*(1)F^{\alpha_j}(1)\omega_s(1)\,d\tau\,, \tag{15}$$

$$F^{\beta_j}_{rs}=\int\omega_r^*(1)F^{\beta_j}(1)\omega_s(1)\,d\tau\,, \tag{16}$$

$$\psi_i^k=\sum_{r=1}^{m}a^k_{ir}\omega_r\,, \tag{17}$$

and

$$\phi_i^k=\sum_{r=1}^{m}b^k_{ir}\omega_r\,. \tag{18}$$

It is easy to see that if we define

$$P^k_{uv} = \sum_{i=1}^{p} \sum_{j=0}^{k} a^{k-j}_{iu} a^{*j}_{iv} \tag{19}$$

and

$$Q^k_{uv} = \sum_{i=1}^{q} \sum_{j=0}^{k} b^{k-j}_{iu} b^{*j}_{iv} \tag{20}$$

then we may express $F^{\alpha_k}_{rs}$ and $F^{\beta_k}_{rs}$ in the form

$$F^{\alpha_k}_{rs} = h_{rs}\delta_{k0} + z_{rs}\delta_{k1} + \sum_{uv}^{m} P^k_{uv}([rv|su] - [rv|us]) + \sum_{uv}^{m} Q^k_{uv}[rv|su] \tag{21}$$

and

$$F^{\beta_k}_{rs} = h_{rs}\delta_{k0} + z_{rs}\delta_{k1} + \sum_{uv}^{m} P^k_{uv}[rv|su] + \sum_{uv}^{m} Q^k_{uv}([rv|su] - [rv|us]) \tag{22}$$

where

$$h_{rs} = \int \omega^*_r(1) h(1) \omega_s(1) d\tau \,, \tag{23}$$

$$z_{rs} = = \int \omega^*_r(1) z(1) \omega_s(1) d\tau \tag{24}$$

and

$$[rv|us] = \int \omega^*_r(1) \omega^*_v(2) \frac{1}{r_{12}} \omega_u(1) \omega_s(2) d\tau \,. \tag{25}$$

The additional conditions that the orbitals remain orthonormal are given by the following set of equations:

$$\sum_{rs}^{m} \sum_{j=0}^{k} b^{*j}_{ir} b^{k-j}_{ls} S_{rs} = \delta_{k0}\delta_{il} \,, \tag{26}$$

$$\sum_{rs}^{m} \sum_{j=0}^{k} a^{*j}_{ir} a^{k-j}_{ls} S_{rs} = \delta_{k0}\delta_{il} \,. \tag{27}$$

The first and second order changes in the total energy of the molecule are given by

$$E_1 = \sum_{rs}^{m} (P^0_{sr} + Q^0_{sr}) z_{rs} \tag{28}$$

$$2E_2 = \sum_{rs}^{m} (P^1_{sr} + Q^1_{sr}) z_{rs} \,. \tag{29}$$

For a pi-electron system the Pariser-Parr-Pople schemes enables F^{α_k} to be considerably simplified:

$$F^{\alpha_k}_{rs} = h_{rs}\delta_{k0} + z_{rs}\delta_{k1} + \delta_{rs}\Big(\sum_{v}^{m} (P^k_{vv} + Q^k_{vv})\gamma_{rv}\Big) - \frac{1}{2} P^k_{rs}\gamma_{rs} \tag{30}$$

where γ_{rs} is the electron repulsion integral and the functions $\{\omega_r\}$ are orthonormal so that $S_{rs} = \delta_{rs}$. Expressions for $F^{\beta k}$ are similar in form with P^k_{uv} and Q^k_{uv} interchanged.

3. Variational Principle

It is possible to calculate the first order coupled wavefunction making use of a variational principle. This is sometimes to be prefered to the more conventional perturbation method where Eqs. (12) and (13) are solved iteratively. The variational procedure for the coupled functions was developed by Langhoff, Karplus and Hurst [3]. In order to examine this procedure as applied to unrestricted perturbation theory we will use a result established by Epstein and Johnson [6]. Consider any single determinant approximation to the perturbed system $\hat{\Psi}$ such that

$$\hat{\Psi} = \sum_{k=0}^{\infty} \lambda^k \hat{\psi}_k \tag{31}$$

and $\hat{\psi}_0 = \Psi_0$ the Hartree-Fock wavefunction for the unperturbed system. Let Ψ^c be the coupled single determinant approximation to the perturbed system so that

$$\Psi^c = \sum_{k=0}^{\infty} \lambda^k \psi_k^c . \tag{32}$$

As Ψ^c is the best single determinant for the perturbed system we have the following inequality:

$$E\,(\text{exact}) \leqq \frac{\langle \Psi^c | \mathscr{H} + \lambda W | \Psi^c \rangle}{\langle \Psi^c | \Psi^c \rangle} \leqq \frac{\langle \hat{\Psi} | \mathscr{H} + \lambda W | \hat{\Psi} \rangle}{\langle \hat{\Psi} | \hat{\Psi} \rangle} . \tag{33}$$

This may be written as

$$E\,(\text{exact}) \leqq \sum_{k=0}^{\infty} E_k^c \lambda^k \leqq \sum_{k=0}^{\infty} \hat{E}_k \lambda^k . \tag{34}$$

Now by Brillouin's theorem

$$\langle \hat{\psi}_1 | \mathscr{H} | \Psi_0 \rangle + \langle \Psi_0 | \mathscr{H} | \hat{\psi}_1 \rangle = 0 \tag{35}$$

so that

$$E_0^c + \lambda E_1^c = \hat{E}_0 + \lambda \hat{E}_1 . \tag{36}$$

Consequently we may cancel these terms in (34) and obtain the following inequality

$$\sum_{k=2}^{\infty} E_k^c \lambda^k \leqq \sum_{k=2}^{\infty} \hat{E}_k \lambda^k \tag{37}$$

for all values of λ in the range [0, 1]. If we consider the limit as $\lambda \to 0$ we see that

$$E_2^c \leqq \hat{E}_2 \tag{38}$$

which is the result of Epstein and Johnson. Now if we assume all wavefunctions are real

$$\begin{aligned} \hat{E}_2 = {} & 2E_0 \langle \Psi_0 | \hat{\psi}_2 \rangle + \langle \hat{\psi}_1 | \hat{H}_0 | \hat{\psi}_1 \rangle + 2 \langle \Psi_0 | W | \hat{\psi}_1 \rangle \\ & + \left\langle \hat{\Psi} \,\middle|\, \sum_{i<j} \frac{1}{r_{ij}} - \sum_i (G^{\alpha_0}(i) | \alpha \rangle \langle \alpha | + G^{\beta_0}(i) | \beta \rangle \langle \beta |) - C^0 \,\middle|\, \hat{\Psi} \right\rangle_2 \end{aligned} \tag{39}$$

where

$$E_0 = \sum_{i=1}^{p} E_{\alpha_i}^0 + \sum_{i=1}^{q} E_{\beta_i}^0 + C^0 . \tag{40}$$

The single determinant $\hat{\Psi}$ may be written in the form of Eq. (2) that is

$$\hat{\Psi} = (n\,!)^{-\frac{1}{2}} \det \{ \hat{\psi}_1(1) \alpha(1) \ldots \hat{\phi}_1(p+1) \beta(p+1) \ldots \hat{\phi}_q(p+q)\, \beta(p+q) \} \tag{41}$$

where

$$\hat{\psi}_i = \sum_{k=0}^{\infty} \hat{\psi}_i^k \lambda^k \tag{42}$$

$$\hat{\phi}_i = \sum_{k=0}^{\infty} \hat{\phi}_i^k \lambda^k , \tag{43}$$

and without loss of generality the sets of functions $\{\hat{\psi}_i\}$ and $\{\hat{\phi}_i\}$ are chosen separately orthonormal. Expressing $\hat{\Psi}$ in this way it is easy to verify that

$$\begin{aligned}\hat{E}_2 = & \sum_{i=1}^{p} \langle \hat{\psi}_i^1(1) | F^{\alpha_0}(1) - E_{\alpha_i}^0 | \hat{\psi}_i^1(1) \rangle \\ & + \sum_{i=1}^{q} \langle \hat{\phi}_i^1(1) | F^{\beta_0}(1) - E_{\beta_i}^0 | \hat{\phi}_i^1(1) \rangle + 2 \sum_{i=1}^{p} \langle \hat{\psi}_i^1(1) | z(1) | \psi_i^0(1) \rangle \\ & + 2 \sum_{i=1}^{q} \langle \hat{\phi}_i^1(1) | z(1) | \phi_i^0(1) \rangle + \sum_{i=1}^{p} \sum_{j=1}^{p} (2[\hat{\psi}_i^1 \hat{\psi}_j^1 | \psi_i^0 \psi_j^0] \\ & - [\hat{\psi}_i^1 \hat{\psi}_j^1 | \psi_j^0 \psi_i^0] - [\hat{\psi}_i^1 \psi_j^0 | \hat{\psi}_j^1 \psi_i^0]) + \sum_{i=1}^{q} \sum_{j=1}^{q} (2[\hat{\phi}_i^1 \hat{\phi}_j^1 | \phi_i^0 \phi_j^0] \\ & - [\hat{\phi}_i^1 \hat{\phi}_j^1 | \phi_j^0 \phi_i^0] - [\hat{\phi}_i^1 \phi_j^0 | \hat{\phi}_j^1 \phi_i^0]) + \sum_{i=1}^{p} \sum_{j=1}^{q} 4[\hat{\psi}_i^1 \hat{\phi}_j^1 | \psi_i^0 \phi_j^0] .\end{aligned} \tag{44}$$

We note that $\hat{E}_2$ depends only on zero and first order orbitals. Also since $\hat{E}_2$ is always greater or equal to the coupled second order energy E_2^c and idential with E_2^c when $\hat{\Psi} = \Psi^c$ we may calculate the first order orbitals $\{\psi_i^{c1}\}$ and $\{\phi_i^{c1}\}$ by minimising (44) with respect to variations in $\{\hat{\psi}_i^1\}$ and $\{\hat{\phi}_i^1\}$ subject to the conditions:

$$\langle \hat{\phi}_i^1 | \phi_j^0 \rangle + \langle \phi_i^0 | \hat{\phi}_j^1 \rangle = 0 , \tag{45}$$

$$\langle \hat{\psi}_i^1 | \psi_j^0 \rangle + \langle \psi_i^0 | \hat{\psi}_j^1 \rangle = 0 . \tag{46}$$

4. Uncoupled Perturbation Theory

The complexity of the equations of coupled perturbation theory has led to considerable interest in the simpler uncoupled perturbation theory. In his original paper Dalgarno [2] showed that it is possible to correct the energies obtained from the simpler uncoupled theory; this theory is discussed in the next section. The zero order equation is identical with that of coupled theory (Eqs. (5) and (6)).

If we now perturb the system by a sum of one electron operators $\lambda W = \lambda \sum_i z(i)$ as in Section 2 we obtain the perturbation equations

$$(\hat{H}_0 - E_0) \Psi_k = (E_1 - W) \Psi_{k-1} + \sum_{i=2}^{k} E_i \Psi_{k-i} \delta_{k_1} \tag{47}$$

for $k \geqq 1$. These equations differ from those of coupled theory in that they neglect the change of the self consistent terms due to the perturbation. Expanding the orbitals $\{\psi_i\}$ and $\{\phi_i\}$ in terms of a basis set $\{\omega_r\}$ as in Section 2 we obtain the equations:

$$\sum_{s=1}^{m} (F_{rs}^{\alpha_0} - E_{\alpha_i}^0 S_{rs}) a_{is}^k = \sum_{s=1}^{m} \left((E_{\alpha_i}^1 S_{rs} - z_{rs}) a_{is}^{k-1} + \delta_{k_1} \sum_{j=2}^{k} E_{\alpha i}^j S_{rs} a_{is}^{k-j} \right) \tag{48}$$

$$\sum_{s=1}^{m} (F_{rs}^{\beta_0} - E_{\beta_i}^0 S_{rs}) b_{is}^k = \sum_{s=1}^{m} \left((E_{\beta_i}^1 S_{rs} - z_{rs}) b_{is}^{k-1} + \delta_{k_1} \sum_{j=2}^{k} E_{\beta_i}^j S_{rs} b_{is}^{k-j} \right) \tag{49}$$

for all orders $k \geqq 1$. The first and second order energies are given by

$$E_1 = \langle \Psi_0 | W | \Psi_0 \rangle = \sum_{rs} (P_{sr}^0 + Q_{sr}^0)\, z_{rs} \tag{50}$$

$$E_2 = \langle \Psi_1 | W | \Psi_0 \rangle = \frac{1}{2} \sum_{rs} (P_{sr}^1 + Q_{sr}^1)\, z_{rs} \tag{51}$$

where the charge and bond order matrices of the k^{th} order are defined analogously to Eqs. (19) and (20).

5. Corrections

Uncoupled theory usually gives poor energies compared with coupled theory. It has been found, however that it is possible to correct the uncoupled results so that their accuracy is comparable. This was first introduced by Dalgarno [2] and has been developed by Tuan *et al.* [1] and Amos and Musher [8]. In order to correct the uncoupled energies we define V such that

$$V = \mathscr{H} - \hat{H}_0 . \tag{52}$$

Suppose we have solved the uncoupled equations to infinite order so that we obtain the uncoupled wavefunctions and energy defined as follows:

$$\Psi^0 = \sum_{k=0}^{\infty} \lambda^k \Psi_k , \tag{53}$$

$$E^0 = \sum_{k=0}^{\infty} \lambda^k E_k . \tag{54}$$

Let

$$\hat{H} = \hat{H}_0 + \lambda W \tag{55}$$

then

$$\hat{H} \Psi^0 = E^0 \Psi^0 . \tag{56}$$

Consider the perturbation equation

$$(\hat{H} + \mu V) \left(\sum_{k=0}^{\infty} \mu^k \Psi^k \right) = \left(\sum_{k=0}^{\infty} \mu^k \Psi^k \right) \left(\sum_{j=0}^{\infty} \mu^j E^j \right) \tag{57}$$

then the first order correction to the energy is given by

$$E^1 = \langle \Psi^0 | V | \Psi^0 \rangle . \tag{58}$$

If we assume that the wavefunctions are real and expand in powers of we can obtain corrections for the first and second order uncoupled energies:

$$E_1^1 = 0 \tag{59}$$

$$\begin{aligned} E_2^1 = & \sum_{i=1}^{p} \sum_{j=1}^{p} (2[\psi_i^1 \psi_j^1 | \psi_i^0 \psi_j^0] - [\psi_i^1 \psi_j^1 | \psi_j^0 \psi_i^0] - [\psi_i^1 \psi_j^0 | \psi_j^1 \psi_i^0]) \\ & + \sum_{i=1}^{q} \sum_{j=1}^{q} (2[\phi_i^1 \phi_j^1 | \phi_i^0 \phi_j^0] - [\phi_i^1 \phi_j^1 | \phi_j^0 \phi_i^0] - [\phi_i^1 \phi_j^0 | \phi_j^1 \phi_i^0]) \\ & + 4 \sum_{i=1}^{p} \sum_{j=1}^{q} [\psi_i^1 \phi_j^1 | \psi_i^0 \phi_j^0] . \end{aligned} \tag{60}$$

In the case of coupled theory we define $\hat{H}$ such that

$$\hat{H} = \hat{H}_0 + \lambda W + \sum_{k=0}^{\infty} \left(\sum_i \left(G^{\alpha_k}(i) |\alpha\rangle\langle\alpha| + G^{\beta_k}(i) |\beta\rangle\langle\beta| \right) + C^k \right) \tag{61}$$

where the C^k are chosen so that to all orders of λ

$$\langle \Psi^0 | \mathscr{H} + \lambda W | \Psi^0 \rangle = \langle \Psi^0 | \hat{H} | \Psi^0 \rangle . \tag{62}$$

If we define V so that

$$V = \mathscr{H} - \hat{H} + \lambda W \tag{63}$$

and proceed with the double perturbation procedure as in the uncoupled case we obtain

$$E^1 = \langle \Psi^0 | V | \Psi^0 \rangle = 0 . \tag{64}$$

This result is usually summarised by stating that coupled theory is correct to first order although as V is a different operator in the uncoupled case, this is perhaps not a fair comparison.

One of the most significant differences between the single determinant approximation for a molecule with an even number of electrons and one with an odd number is that the former is an eigenfunction of $\hat{S}^2$ whereas the latter is not. The single determinant for an odd number of electrons may be expanded in pure spin states. To obtain a better approximation to the ground state wavefunction Amos and Hall have suggested the use of an annihilator of the largest unwanted component spin state [18]. If the ground state is an eigenfunction of $\hat{S}^2$ with eigenvalue s then the annihilator of the next component A_{s+1} is given by

$$A_{s+1} = \hat{S}^2 - (s+1)(s+2) . \tag{65}$$

The operator $\hat{S}^2$ can be taken as

$$\hat{S}^2 = \frac{1}{2}(p+q) + \frac{1}{4}(p-q)^2 + \sum_{i^\alpha j^\beta} P^\delta_{i_\alpha j_\beta} \tag{66}$$

where $P^\delta_{i_\alpha j_\beta}$ exchanges the spin function associated with the i^{th} orbital with α spin and the j^{th} orbital with β spin so that for example

$$P^\delta_{i_\alpha j_\beta} \Psi_0 = -(n!)^{\frac{1}{2}} \det \{ \psi_1^0(1)\alpha(1) \ldots \phi_j^0(i)\alpha(i) \ldots \psi_i^0(j)\beta(j) \ldots \phi_q^0(p+q)\beta(p+q) \} . \tag{67}$$

In both coupled and uncoupled theory we may correct the single determinant wavefunction by annihilating the highest unwanted spin component perturbatively. To do this we will use Amos-Musher perturbation theory [11]. As before we assume that we have solved the coupled or uncoupled equations to infinite order. The theory will be developed in terms of the operator $\hat{H}$ which has been defined earlier and which is different depending on whether we are using coupled or uncoupled theory. In either case we have

$$\hat{H} \Psi^0 = E^0 \Psi^0 \tag{68}$$

where Ψ^0 and E^0 are defined by Eqs. (53) and (54). Define

$$V = \mathscr{H} - \hat{H} + \lambda W . \tag{69}$$

From (68) we have

$$A_{s+1}\hat{H}\Psi^0 = E^0 A_{s+1}\Psi^0 . \tag{70}$$

Consider the perturbation equations

$$\begin{aligned} A_{s+1}(\hat{H}+\mu V)\Psi^0 + (\hat{H}+\mu V)\left(\sum_{k=1}^{\infty} \mu^k \Psi^k\right) \\ = \left(A_{s+1}\Psi^0 + \sum_{k=1}^{\infty} \mu^k \Psi^k\right)\left(\sum_{k=0}^{\infty} \mu^k E^k\right). \end{aligned} \tag{71}$$

From these we obtain

$$E^1 = \langle \Psi^0 | A_{s+1} V | \Psi^0 \rangle / \langle \Psi^0 | A_{s+1} | \Psi^0 \rangle \tag{72}$$

Expanding in powers of λ where

$$\langle \Psi^0 | A_{s+1} V | \Psi^0 \rangle = \sum_{k=0}^{\infty} \lambda^k Y^k , \tag{73}$$

$$\langle \Psi^0 | A_{s+1} | \Psi^0 \rangle = \sum_{k=0}^{\infty} \lambda^k X^k \tag{74}$$

and

$$E^1 = \sum_{k=0}^{\infty} E_k^1 \lambda^k \tag{75}$$

we may obtain terms through first order in μ and k^{th} order in λ.

6. Results and Discussion

Trial calculations have been carried out on a number of alternants. The perturbations used were point perturbations of the form

$$z_{rs} = \delta_{ru}\delta_{su} \qquad \text{for some } u . \tag{76}$$

In Table 1 the second order energies obtained by the various methods that have been outlined in the previous sections are listed. The term correction 1 refers to the ordinary correction discussed in Section 5 whereas correction 2 is taken to mean correction by Amos-Musher perturbation theory. The geometric approximation, first introduced by Musher and Schulman [7] (see also references [12, 13]), has also been used and the results are given in Table 1.

The perturbation theory developed is suitable for the treatment of aza substituted benzene ions. We assume that the Nitrogen atoms may be represented by a change in the one electron operators so that

$$\begin{aligned} z_{rs} &= v\delta_{rs} \quad \text{if } r \text{ is a Nitrogen site} \\ &= 0 \quad \text{otherwise} . \end{aligned} \tag{77}$$

The value of the parameter v has been discussed by Amos and in this work his parameter will be used namely $v = -1.73$ eV [14].

Table 1

Molecule	Allyl		*Cis*-butadiene triplet	
Perturbation at atom	1	2	1	2
Uncoupled E	−0.024	−0.032	−0.017	−0.039
Uncoupled E + Correction 1	−0.033	−0.043	−0.023	−0.052
Geometric approx.	−0.039	−0.048	−0.026	−0.058
Uncoupled E + Correction 2	−0.034	−0.043	−0.022	−0.052
Coupled E	−0.039	−0.048	−0.029	−0.058
Coupled E + Correction 2	−0.034	−0.045	−0.030	−0.058

Table 2

Molecule	Atom	UBS	UAS	CBS	CAS
Pyridazine −	2	0.320	0.288	0.347	0.317
2/3	4	−0.123	−0.053	−0.109	−0.043
substituted	5	0.302	0.264	0.262	0.227
Pyrimidine −	6	0.273	0.237	0.174	0.160
2/6	1	−0.125	−0.055	−0.039	−0.015
substituted	3	0.352	0.316	0.451	0.399
	4	−0.126	−0.056	−0.209	−0.093
Pyridine −	1	0.394	0.356	0.330	0.306
1	2	0.060	0.076	0.160	0.136
substituted	3	0.023	0.045	−0.053	0.007
	4	0.440	0.400	0.457	0.413
Pyrazine −	1	0.402	0.366	0.364	0.338
1/4 substituted	2	0.049	0.067	0.068	0.082
Pyridine +	1	−0.121	−0.025	−0.095	−0.020
1	2	0.313	0.265	0.289	0.245
substituted	3	0.313	0.264	0.335	0.279
	4	−0.130	−0.028	−0.155	−0.033
Pyrazine +	1	−0.126	−0.026	−0.129	−0.029
1/4 substituted	2	0.313	0.263	0.314	0.262
Pyrimidine +	6	0.031	0.061	0.052	0.062
2/6	1	0.383	0.322	0.259	0.211
substituted	3	0.050	0.076	0.050	0.078
	4	0.457	0.409	0.537	0.507
Pyridazine +	2	0.059	0.081	0.078	0.094
2/3	4	0.418	0.362	0.403	0.353
substituted	5	0.023	0.057	0.019	0.055

UBS	Uncoupled spin densities before annihilation.
UAS	Uncoupled spin densities after annihilation.
CBS	Coupled spin densities before annihilation.
CAS	Coupled spin densities.

Table 3

Molecule	Atom	UBC	UAC	CBC	CAC
Pyrazine –	1	1.388	1.412	1.437	1.439
1/4 substituted	2	1.056	1.057	1.032	1.032
Pyridine –	1	1.407	1.411	1.494	1.492
1	2	1.066	1.066	1.025	1.021
substituted	3	1.085	1.083	1.101	1.101
	4	1.292	1.294	1.254	1.256
Pyrimidine –	6	1.342	1.342	1.442	1.440
2/6	1	0.897	0.897	0.810	0.812
substituted	3	1.204	1.202	1.134	1.134
	4	1.010	1.011	1.037	1.037
Pyridazine –	2	1.332	1.332	1.363	1.363
2/3	4	0.959	0.961	0.937	0.939
substituted	5	1.210	1.208	1.200	1.198
Pyrimidine +	6	1.044	1.046	1.135	1.137
2/6	1	0.629	0.627	0.546	0.544
substituted	3	0.808	0.810	0.743	0.743
	4	0.668	0.664	0.698	0.696
Pyridazine +	2	0.958	0.960	0.984	0.980
2/3	4	0.652	0.648	0.630	0.626
substituted	5	0.890	0.892	0.886	0.890
Pyridine +	1	1.122	1.122	1.192	1.192
1	2	0.699	0.701	0.656	0.656
substituted	3	0.755	0.757	0.769	0.771
	4	0.971	0.967	0.958	0.956
Pyrazine +	1	1.101	1.101	1.156	1.156
1/4 substituted	2	0.700	0.700	0.672	0.672

UBC	Uncoupled charge densities before annihilation.
UAC	Uncoupled charge densities after annihilation.
CBC	Coupled charge densities before annihilation.
CAC	Coupled charge densities after annihilation.

If we define

$$\bar{P}_{rs} = P^0_{rs} + P^1_{rs} + P^2_{rs} \tag{78}$$

and

$$\bar{Q}_{rs} = Q^0_{rs} + Q^1_{rs} + Q^2_{rs} \tag{79}$$

then approximations to the spin and charge densities at atom r are given by

$$\bar{P}_{rr} - \bar{Q}_{rr} \tag{80}$$

and

$$\bar{P}_{rr} + \bar{Q}_{rr} \tag{81}$$

respectively. These are calculated for various aza substituted benzene ions and the results are given in Tables 2 and 3. Approximations are also given to the spin and charge densities after the highest unwanted spin components has been annihilated. The theory of this has been developed by Snyder and Amos [15]. The approximations to the spin and charge densities are of the form

$$\bar{R}_{rr} - \bar{S}_{rr} \tag{82}$$

and

$$\bar{R}_{rr} + \bar{S}_{rr} \tag{83}$$

where

$$\bar{R}_{rs} = \bar{P}_{rs} + (\underline{\bar{P}}\,\underline{\bar{Q}}\,\underline{\bar{P}}_{rs} - \tfrac{1}{2}\underline{\bar{P}}\,\underline{\bar{Q}}_{rs} - \tfrac{1}{2}\underline{\bar{Q}}\,\underline{\bar{P}}_{rs})2/\chi\,, \tag{84}$$

$$\bar{S}_{rs} = \bar{Q}_{rs} + (\underline{\bar{Q}}\,\underline{\bar{P}}\,\underline{\bar{Q}}_{rs} - \tfrac{1}{2}\underline{\bar{Q}}\,\underline{\bar{P}}_{rs} - \tfrac{1}{2}\underline{\bar{P}}\,\underline{\bar{Q}}_{rs})2/\chi \tag{85}$$

and

$$\chi = \tfrac{1}{2}(p+q) + \tfrac{1}{4}(p-q)^2 - (s+1)(s+2) - \sum_{rs} \bar{P}_{sr}\bar{Q}_{rs}\,. \tag{86}$$

As the ground state wavefunctions of the benzene ions are degenerate it is necessary to choose the correct zero order wavefunction for the perturbation. It is possible to choose the two degenerate wavefunctions for the benzene anion (or the cation) so that one of the functions is symmetric with respect to reflection about a plane perpendicular to the molecular plane through atoms 1 and 4 (numbering sequentually from any atom) and the other antisymmetric. This choice imposes a constraint on the Hartree-Fock solution. As $G^{\alpha o}$ and $G^{\beta o}$ depend on the spin orbitals the numerical procedure used was an iterative procedure. If the initial approximation is chosen symmetric (antisymmetric) then at each stage of the iteration the wavefunction will be symmetric (antisymmetric). Wavefunctions obtained this way are not actually energetically equivalent (see Amos and Snyder [16]). However this procedure enables a zero order wavefunction of the correct symmetry to be obtained. For a discussion of which zero order function to choose for a particular aza substitution see Ref. [17].

On examination of Table 1 we see that the results for the geometric approximation are very close to those for coupled theory. This is in line with previous calculations using the geometric approximation [7, 12, 13]. The corrections for the pure spin state (correction 2) may be seen to be smaller than the differences between the uncoupled and coupled theory results.

From Tables 2 and 3 it may be seen that although the correction of Snyder and Amos has only a small effect on the coupled and uncoupled charge densities it has a significant effect on the spin densities. Thus it appears that for charge density calculations the annihilation of the highest unwanted spin state may be unnecessary. For spin density calculations, which involve differences between quantities, and are consequently of a different order of magnitude to the charge densities, it may be necessary to carry out the perturbative calculations to higher orders or to annihilate other unwanted spin states. However the spin densities so obtained are usually related to experimental results using one of several empirical formulae. Considering the inaccuracies inherent in these formulae the accuracy obtained in the calculations presented here is probably sufficient for comparison with experiment.

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