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Commentationes

On Open Shell Hartree-Fock Calculations

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The errors in open shell Hartree-Fock calculations are discussed. Various hamiltonians for single eigenvalue methods are considered, and it is shown that a better energy is obtained with those hamiltonians that correctly account for the open shell/closed shell interactions.

Die Fehler des Hartree-Fock-Verfahrens bei offenen Schalen werden diskutiert, indem verschiedene Hamilton-Operatoren für das Gesamtsystem betrachtet werden. Dabei zeigt sich, daß diejenigen Hamilton-Operatoren, die die Wechselwirkung zwischen offenen und abgeschlossenen Schalen am besten wiedergeben, auch die besten Energien liefern.

Discussion des erreurs dans les calculs Hartree-Fock à couche ouverte. On considère divers hamiltoniens pour les méthodes à valeur propre unique, et l'on montre qu'une meilleure énergie est obtenue avec les hamiltoniens qui rendent compte correctement de l'interaction couche ouverte-couche fermée.

1. Introduction

Although the Hartree-Fock equations for a closed shell atom or molecule may be solved fairly easily in principle, it is not so for open shell systems. This is due to the problem of the off-diagonal multipliers, which cannot be eliminated. Many authors have considered this [1, 2], and have developed methods which involve two coupled eigenvalue equations, one for the open and one for the closed shells. This approach has been successfully applied to many systems, but there are certain difficulties, namely lengthy computing time, and problems related to which sets of orbitals should be chosen for configuration interaction calculations.

An alternative method has been proposed by Roothaan [1], and also by Nesbet [3], which simplifies the Hartree-Fock equations to a single eigenvalue problem. This eliminates the off-diagonal multipliers, either by putting them equal to zero, or by incorporating them partially into the hamiltonian. These procedures are only strictly possible when the open shell orbitals are the only ones of their symmetry. Except for these particular cases, neglect of off-diagonal multipliers implies that the correct hamiltonian is not being used, and the energy obtained from the approximate Hartree-Fock equations is then corrected to allow for this [1].

A recent paper [4] has pointed out some consequences of this neglect of off-diagonal multipliers. The Fock matrix is no longer invariant to a unitary

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transformation of the orbitals, and one is not necessarily at liberty to choose the set of orbitals that diagonalises the matrix of lagrangian multipliers. This has resulted in calculations that give different total energies when different symmetry orbitals are used (even after correcting the energies as above), and discontinuous potential curves have been obtained when the symmetry changes with variation of normal coordinate [5]. Walker demonstrated [4] that the magnitude of the error depended on the number of closed shell orbitals with the same symmetry as the open shell, and on their type. Core closed shell orbitals gave rise to larger errors than valence orbitals, (in fact the error is roughly proportional to the orbital energy) and this was borne out by the results of some Hartree-Fock calculations.

As has already been mentioned, single eigenvalue methods are much more convenient to use than those involving two eigenvalue equations, and it is of interest to investigate these errors in case they can be avoided in the future.

2. Theory

The total hamiltonian for an N-electron system is

$$\sum_{i=1}^{N} T_i + \sum_{i>j=1}^{N} v_{ij} \tag{2.1}$$

where T_i represents the terms due to kinetic energy and the attraction by the nucleus, and v_{ij} the interaction between electrons $(1/r_{ij})$. The Hartree-Fock method approximates this hamiltonian by replacing the two-body interaction v_{ij} by a single particle potential V, that is

$$H_0 = \sum_{i=1}^{n} (T_i + V_i) \tag{2.2}$$

with the eigenvalue equation $H_0 \Phi_0 = E_0 \Phi_0$, where Φ_0 is the determinant formed from the N lowest solutions of the eigenvalue equation

$$(T + V)\,\varphi_n = \varepsilon_n \varphi_n \,. \tag{2.3}$$

(Note that this equation is only obtained after choosing the set of orbitals that diagonalises the matrix corresponding to ε.) The Hartree-Fock potential is then defined by

$$\langle a|V|b\rangle = \sum_{n=1}^{N} \{\langle an|v|bn\rangle - \langle an|v|nb\rangle\} \tag{2.4}$$

with n denoting an occupied spinorbital.

Hence to first order the energy obtained from a Hartree-Fock calculation is

$$E_0 = \sum_{i=1}^{N} \varepsilon_i + \left\{\frac{1}{2} \sum_{i,j}^{N} [\langle ij|v|ij\rangle - \langle ij|v|ji\rangle] - \sum_{i=1}^{N} \langle i|V|i\rangle\right\} \tag{2.5}$$

$$= \sum_{i=1}^{N} \left[\langle n|T|n\rangle + \frac{1}{2} \langle n|V|n\rangle\right] = \frac{1}{2} \sum_{i=1}^{N} (\varepsilon_i^N + \varepsilon_i) \,. \tag{2.6}$$

This is not so for a single eigenvalue equation, because V' (we shall use primes systematically to refer to single eigenvalue calculations) is not defined as in (2.3). In this case, the bracketed part of (2.5) is not equal to $-\frac{1}{2}\sum_{i=1}^{N}\langle i|V|i\rangle$, but includes other terms. To determine these, we must consider the possible hamiltonians.

In the restricted Hartree-Fock method, orbitals with different spins, or those belonging to different degenerate components of the same representation – such as π^+, π^- in linear molecules – are constrained to have the same radial dependence. The hamiltonian is therefore the same for all electrons contained in the same space orbital. This is quite legitimate if there are only closed shells present, but not if there is one or more unpaired electron. Because exchange terms only arise between electrons of parallel spin, the hamiltonian for those electrons with the same spin as the unpaired electron should be different from that for those with opposite spin.

The restricted Hartree-Fock potential, V', for a single eigenvalue calculation is defined so as to be the same for all electrons in spinorbitals of the same symmetry. If we consider a diatomic molecule with one unpaired σ electron in orbital x, possible hamiltonians are

$$\langle a_\sigma|V_1'|b_\sigma\rangle = \sum_{n=1}^{N-1}\{\langle an|v|bn\rangle - \langle an|v|nb\rangle\} + \langle ax|v|bx\rangle - \langle ax|v|xb\rangle\,, \tag{2.7a}$$

$$\langle a_\sigma|V_2'|b_\sigma\rangle = \sum_{n=1}^{N-1}\{\langle an|v|bn\rangle - \langle an|v|nb\rangle\} + \langle ax|v|bx\rangle - \frac{1}{2}\langle ax|v|xb\rangle \tag{2.7b}$$

and for both of these

$$\langle a_\pi|V'|b_\pi\rangle = \sum_{i=1}^{N}\{\langle an|v|bn\rangle - \langle an|v|nb\rangle\}\,. \tag{2.8}$$

The operators V_1', V_2' can also be written in the familiar J and K notation as

$$V_1' = \sum_{n=1}^{N-1}\left(J_n - \frac{1}{2}K_n\right) + J_x - K_x\,, \tag{2.9a}$$

$$V_2' = \sum_{n=1}^{N-1}\left(J_n - \frac{1}{2}K_n\right) + J_x - \frac{1}{2}K_x\,. \tag{2.9b}$$

The energy E' through first order from these hamiltonians is

$$E_1' = \frac{1}{2}\sum_{i=1}^{N}(\varepsilon_i^N + \varepsilon_i) + \frac{1}{2}\sum_{i=\sigma}\langle ix|v|xi\rangle\,, \tag{2.10a}$$

$$E_2' = \frac{1}{2}\sum_{i=1}^{N}(\varepsilon_i^N + \varepsilon_i) - \frac{1}{2}\langle xx|v|xx\rangle \tag{2.10b}$$

and it is immediately clear that the extra integrals needed in the energy expression involve the open shell electron, either with itself or with the closed shell electrons of the same symmetry.

These two different choices of hamiltonian introduce different errors into the energy. V_1' allows exactly for the interaction of the unpaired electron with itself, since $\langle ix|v|ix\rangle - \langle ix|v|xi\rangle = 0$ if $i = x$, but not for the interaction with closed shell electrons. The reverse is true for V_2', which accounts correctly for the closed shells but introduces a spurious contribution for the interaction of the open shell electron with itself. Although these errors are partially corrected by including the extra molecular integrals in the energy expression, there will still be residual terms corresponding to higher orders of perturbation theory.

Until recently it has always been assumed that these terms could be neglected. Kelly [6] included them in his many-body perturbation theory work on the oxygen atom, and showed that they were indeed small. However the large errors reported by Walker [4] and Dixon [5], when single eigenvalue methods were employed for polyatomic molecules, arise from second and higher orders, and this paper contains some further examples. Both the true Hartree-Fock hamiltonian, $\boldsymbol{H}$, and the restricted hamiltonians, $\boldsymbol{H}'$, used in the single eigenvalue approximation are derived from one-body potentials. Thus if one was to write the Hartree-Fock wavefunction as a linear combination of determinants constructed from orbitals obtained from the restricted hamiltonian, only singly excited states contribute. We may then employ perturbation theory with the hamiltonian $\boldsymbol{H}'' = \boldsymbol{V} - \boldsymbol{V}'$ to obtain the Hartree-Fock energy from the restricted wavefunctions.

Two kinds of restriction are involved in these calculations. The first, the requirement that the hamiltonian be the same for electrons with different spins, is common to both single and double eigenvalue methods. It corresponds to the neglect of spin polarisation. The second restriction is that the hamiltonian be the same for electrons in open and closed shells of the same symmetry. It is this second restriction that differentiates the single and double eigenvalue methods and introduces the molecular integrals into the energy expression.

3. Perturbation Calculations

The first order correction due to the perturbation $\boldsymbol{H}'' = \boldsymbol{V} - \boldsymbol{V}'$ has already been discussed. An idea of its magnitude can be obtained from Table 1, where the results of some single eigenvalue calculations are given. The correction is much larger for the hamiltonian V_2', because the integrals $\langle xx|v|xx\rangle$ are larger than the exchange integrals $\langle ix|v|xi\rangle$ involved in the calculation for V_1'. The results for AlO, the only case in which both hamiltonians were used for a

Table 1. First order correction from $\boldsymbol{H}'' = \boldsymbol{V} - \boldsymbol{V}'$ (a.u.)

Molecule	E_0'	E_1'	Total	Hamiltonian
BeH: $X^2\Sigma^+\ 1\sigma^2\,2\sigma^2\,3\sigma$	-15.1759042	0.0260388	-15.1498654	V_1'
CH_3: $^2A_1\ 1a_1^2\,2a_1^2\,3a_1\,1b_1^2\,1b_2^2$	-39.1525820	0.0760063	-39.0765757	V_1'
AlO: $X^2\Sigma^+\ (1-6\sigma)^2\,(1-2\pi)^4\,7\sigma$	-316.8417385	0.0909992	-316.7507392	V_1'
AlO: $X^2\Sigma^+$	-316.6672300	-0.1694578	-316.8366878	V_2'

calculation on the same molecule, are particularly noticeable. Although the correction is much larger for V_2' than for V_1', the final energy is better, and we shall show that this is due to quicker convergence of the perturbation series. However the AlO results give quite a dramatic demonstration of the errors that can occur when single eigenvalue methods are used.

The second order contribution to the energy is

$$\Delta E^2 = \sum_i \frac{\langle \Phi_0 | H'' | \Phi_i \rangle \langle \Phi_i | H'' | \Phi_0 \rangle}{E_0 - E_i} \tag{3.1}$$

where all singly excited states are to be included. If a non-restricted hamiltonian is employed these matrix elements are zero. Two different types of excitation can be distinguished, those in which the electron excited from an occupied spinorbital (q) to an unoccupied spinorbital (k) has spin parallel or antiparallel to the unpaired electron. These can be further subdivided into different symmetries of q. Table 2 gives the matrix elements $\langle \Phi_q^k | H'' | \Phi_0 \rangle$, where Φ_q^k represents the determinant formed by replacing an electron in q with one in k, and we have assumed one unpaired σ electron.

Table 3 shows the results for the second order energy for three molecules, whose wavefunctions were obtained with the hamiltonian V_1'. In the cases of BeH and AlO, only excitations to the first four unoccupied σ orbitals and first three π orbitals were considered, and these corrections would no doubt be increased if all single excitations were included. In CH_3, where only a minimum basis set was used, all excitations were included. To check the convergence, two further calculations were carried out. In BeH, the matrix of all excited states included in the second order calculation was diagonalised and the energy lowering found to be 0.003696 a.u., 97% of which was given by the second order term. In CH_3, the third order contribution was found to be +0.00014 compared to the second order −0.00659 a.u.

Table 2. Matrix elements of H''

Excitation	Spin	$V - V_1'$	$V - V_2'$
$q\sigma \rightarrow k\sigma$	α	0	$-\frac{1}{2}\langle qx\|v\|xk\rangle$
$q\sigma \rightarrow k\sigma$	β	$\langle qx\|v\|xk\rangle$	$+\frac{1}{2}\langle qx\|v\|xk\rangle$
$q\pi \rightarrow k\pi$	α	$-\frac{1}{2}\langle qx\|v\|xk\rangle$	$-\frac{1}{2}\langle qx\|v\|xk\rangle$
$q\pi \rightarrow k\pi$	β	$+\frac{1}{2}\langle qx\|v\|xk\rangle$	$+\frac{1}{2}\langle qx\|v\|xk\rangle$

Table 3. Second order correction from H'' (a.u.)

Molecule	ΔE^2	Hamiltonian
BeH	−0.0036	V_1'
CH_3	−0.0065	V_1'
AlO	−0.0058	V_1'
AlO	−0.0044	V_2'

There is also another means of checking the size of the total error introduced by using a single eigenvalue method. Cade and Huo [7] have reported calculations for BeH using the double eigenvalue method, and their energy was -15.15312 a.u. Our results with the same basis set was -15.14987 a.u., an error of 0.00325 a.u., which agrees well with the partial second order contribution of Table 3. (This error is not due to the different programmes, since a similar calculation on the $A^2\Pi$ state of BeH($|\sigma^2\, 2\sigma^2|\pi$) when the single eigenvalue hamiltonian is identical to that used in the eigenvalue method, gave results which agreed to five decimal places.) The difference, 0.00045 a.u. which remains, and which would be increased if all excited states were included, is due to the effect of using a restricted hamiltonian in the double eigenvalue method, that is of not including spin polarisation.

The error in the CH_3 single eigenvalue calculation was estimated in a previous paper [4] as 0.01 a.u. The fact that the second and third order contributions give slightly less than 70% of this is partially due to a minimum basis set being a bad approximation to the complete set of orbitals.

The calculations for AlO also allow a comparison of the two restricted hamiltonians. The difference between the two values of the total energy is 0.0859 a.u. (=2.3 eV), which is large enough to be of importance when calculating excitation or ionization energies. The second order contributions only make up part of this difference, although they would be larger if all excitations were included. However it is possible to draw some general conclusions about the relative magnitudes of successive terms in the perturbation series.

If we write the energy denominator in Eq. (3.1) as $\Delta E(q,k,s)$ for the excitation of an electron in orbital q to orbital k with spin s (α or β), the second order energy becomes, using the matrix elements in Table 2.

$$\text{For } V_1' \quad \Delta E_1^2 = \sum_{q \neq x} \frac{|\langle qx|v|xk\rangle|^2}{\Delta E_1(q,k,\beta)}, \tag{3.2a}$$

$$\text{for } V_2' \quad \Delta E_2^2 = \frac{1}{4} \sum_{k \neq x} \frac{|\langle qx|v|xk\rangle|^2}{\Delta E_2(q,k,\alpha)} + \frac{1}{4} \sum_{q \neq x} \frac{|\langle qx|v|xk\rangle|^2}{\Delta E_2(q,x,\beta)} \tag{3.2b}$$

where we have assumed the unpaired electron has α spin. The summations over k include $k=x$ (with spin β) unless specifically excluded. To compare these two second order energies, some assumptions must be made about the relative magnitudes of the integrals and energy denominators in the two different calculations.

Since $\Delta E_2(q,k,\beta) = \Delta E_2(q,k,\alpha) + \langle qx|v|xq\rangle - \langle kx|v|xk\rangle$, the difference between the excitation energies will be small, and we can assume $\Delta E_2(q,k,\alpha) = \Delta E_2(q,k,\beta)$ in (3.2b). The expressions for ΔE^2 can then be written

$$\Delta E_1^2 = \sum_{k,q \neq x} \frac{|\langle qx|v|xk\rangle|^2}{\Delta E_1^2(q,k,\beta)} + \sum_{q \neq x} \frac{|\langle qx|v|xx\rangle|^2}{\Delta E_1^2(q,x,\beta)}, \tag{3.3a}$$

$$\begin{aligned} \Delta E_2^2 = {} & \frac{1}{2} \sum_{k,q \neq x} \frac{|\langle qx|v|xk\rangle|^2}{\Delta E_2^2(q,k,\beta)} + \frac{1}{4} \sum_{q \neq x} \frac{|\langle qx|v|xx\rangle|^2}{\Delta E_2^2(q,k,\beta)} \\ & + \frac{1}{4} \sum_{k \neq x} \frac{|\langle xx|v|xk\rangle|^2}{\Delta E_2(x,k,\alpha)}. \end{aligned} \tag{3.3b}$$

Table 4. Comparison of molecular integrals for different calculations on AlO (a.u.)

Integral $\langle qx\vert v\vert xk\rangle$		Calc. 1	Calc. 2
q	k		
6	8	−0.026809	−0.028206
5	8	−0.009270	−0.009658
4	8	−0.002473	−0.002066
3	8	−0.001855	−0.001784
2	8	0.001556	0.001458
1	8	−0.000157	−0.000161
6	7	0.011644	0.007808
5	7	−0.011294	−0.011482
4	7	−0.001809	−0.001421
3	7	−0.002088	−0.001690
2	7	0.001106	0.001145
1	7	0.000581	0.000471

Calc. 1 is with V_1', Calc. 2 with V_2'

Table 5. Comparison of energy denominators for different calculations on AlO (a.u.)

$\Delta E(q,k,\beta)$		Calc. 1	Calc. 2
q	k		
6	8	0.3704	0.3409
5	8	1.1006	1.0669
4	8	3.1471	3.1138
3	8	4.8411	4.8009
2	8	20.3853	20.3459
1	8	58.4207	58.4096
6	7	0.2274	0.1507
5	7	0.8899	0.8182
4	7	2.8484	2.7646
3	7	4.5401	4.3358
2	7	20.1146	19.9078
1	7	58.0943	57.8964

Calc. 1 is with V_1'; Calc. 2 with V_2'

Tables 4 and 5 give some representative values for the integrals and energy denominators for the two hamiltonians, and suggest that in most cases they are the same within about fifteen percent for both calculations. Hence we can deduce that $\Delta E_1^2 > \Delta E_2^2$ provided that

$$\frac{1}{2}\sum_{q,k\neq x}\frac{|\langle qx|v|xk\rangle|^2}{\Delta E_2(q,k,\beta)}+\frac{3}{4}\sum_{q\neq x}\frac{|\langle qx|v|xk\rangle|^2}{\Delta E_2(x,k,\beta)}>\frac{1}{4}\sum_{k\neq x}\frac{|\langle xx|v|xk\rangle|^2}{\Delta E_2(x,k,\alpha)}. \tag{3.4}$$

One would expect this inequality to hold except for light atoms or molecules, when the summation over all q will contain very few terms. Table 6 shows the results for the two calculations on AlO in more detail. It confirms the arguments above, showing that $\Delta E_1^2 > \Delta E_2^2$, and that about half of ΔE_2^2 arises from the term

Table 6. Contributions to ΔE_1^2 and ΔE_2^2 for AlO (a.u.)

	ΔE_1^2	ΔE_2^2
Excitation $7\sigma \rightarrow k\sigma$	0	−0.002041
Total from other σ excitation	−0.005709	−0.002263
Total from π excitation	−0.000109	−0.000101
Grand total	−0.005818	−0.004405

$\frac{1}{4}\sum_{k\neq x}\frac{|\langle xx|v|xk\rangle|^2}{\Delta E(x,k,\alpha)}$. It is this term in light molecules that could invalidate the inequality (3.4). The assumptions about relative sizes of molecular integrals and energy denominators in the two calculations appear to be partially justified by the close agreement between the contributions from Π excitations.

However the difference between the limited second order contributions does not explain the discrepancy between the energies obtained for the two calculations, and higher order terms should be considered. While an actual calculation would be very tedious, there are two factors which suggest that $\sum_{n=3}^{\infty}\Delta E_1^n > \sum_{n=3}^{\infty}\Delta E_2^n$. Firstly, the matrix elements involved in the calculation of ΔE_2^n are a factor two smaller than the nonzero elements for ΔE_1^n. Secondly, although there are twice as many terms, because excitations of both spins contribute, they occur with opposite sign. There will therefore be some degree of cancellation in the higher orders of perturbation theory.

4. Conclusions

These results demonstrate the large errors that can occur when single eigenvalue methods are used, that is the hamiltonian is chosen to be the same for electrons in open and closed shells of the same symmetry. Moreover, these errors are the larger the more closed shells there are of the same symmetry as the open shell [4]. The same conclusions can be drawn from the behaviour of the Fock matrix under a unitary transformation of the orbitals, but the consideration of the second and higher order corrections may allow the errors to be minimised.

This work suggests that of the two hamiltonians considered here, V_2', which accounts correctly for the open shell/closed shell interactions, gives a better energy than V_1'. Although the two hamiltonians dealt with in this paper are the intuitively obvious ones, there are many others which could be used. It would be possible to employ as the Hartree-Fock potential V_3' defined by

$$\langle a_\sigma|V_3'|b_\sigma\rangle = \sum_{n=1}^{N-1}\{\langle an|v|bn\rangle - \langle an|v|nb\rangle\} + \langle ax|v|bx\rangle - \lambda\langle ax|v|xb\rangle$$

where λ is a variational parameter, chosen to minimise the total energy as given by $E_0' + E_1'$. Presumably this choice of λ would also minimise the magnitude of the second order correction to the energy.

The factors dealt with here are another aspect of the symmetry problems first raised by Löwdin [8]. He investigated the relationships between the symmetry orbitals used and the total energy for closed shell molecules, and showed that it was sometimes possible to obtain a lower energy by employing a lower symmetry. Cizek and Paldus [9, 10] and Hibbert and Coulson [11] have investigated the stability of the Hartree-Fock equations for both open and closed shell systems, and the former showed that for cyclic polyenes in the PPP approximation, the equations were always unstable to changes in symmetry. They were able to differentiate two types of instability for molecules with one unpaired electron, doublet and multiplet instability. The latter corresponds to spin polarisation and is always present, that is to say a lower energy will always be obtained if the restriction that electrons in the same orbitals have the same spatial dependence is lifted. Their doublet instability is formally related to the errors introduced by the single eigenvalue methods.

There is an interesting distinction between their work and this paper. They showed that the energy could be lowered by lowering the symmetry, but the reverse can be true for the errors discussed here. This follows because the open shell orbital may be the only one of its symmetry type in a high symmetry, but not in a lower one. For example, the $^2E'$ state in CH_3 has the configuration $(1a_1')^2\,(2a_1')^2\,(1e')^3\,(1a_2'')^2$, but in C_{2v} one component becomes $^2A_1$ with configuration $(1a_1)^2\,(2a_1)^2\,(1b_2)^2\,3a_1(1b_1)^2$. The off-diagonal multipliers connecting closed and open shells will be zero in D_{3h} but not in C_{2v}; thus in D_{3h} the single eigenvalue hamiltonian is exactly the same as the one in the double eigenvalue method.

In this paper we have only considered the energy, but other molecular properties may also be affected. Again singly excited states will contribute to the expectation value unless the correct Hartree-Fock hamiltonian is used. It is only likely that this will be important if the property is very dependent on the unpaired electron, or if contributions from spin polarisation are important.

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