

An average Fock operator technique of approximate open-shell LCAO-MO-SCF calculation

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Abstract. The exchange part of the usual Hartree-Fock potential in the unrestricted Hartree-Fock (UHF) theory is suitably *averaged* to construct an average one-electron model Hamiltonian which generates a set of spin-restricted one-electron orbitals in a self-consistent manner. These orbitals are then used to calculate the electronic energy of the open-shell system by using the proper functional form for the energy which handles the exchange terms correctly. The eigenvalues of F^{av} can be used for calculating either the spin-polarised or spin-averaged ionisation potentials of different orbitals at the *Koopmans' theorem level of approximation*. Comparison of E^{ac} with the UHF-energy shows that $E_{UHF} < E^{ac}$ in each case revealing some kind of an upper bound nature of E^{ac} . An approximate variational argument is given. Relationship of our model with the hyper-Hartree-Fock theory of Slater is explored and the general problem of eliminating 'self-interaction' terms in average Fock-operator based theories is discussed.

Keywords. Average Fock operator ; approximate open-shell theories ; half-electron method ; hyper-Hartree Fock model, etc.

1. Introduction

Open-shell LCAO-MO-SCF calculations are now-a-days performed either by means of the restricted open-shell (ROS) method (Roothaan 1960) or by the spin-unrestricted Hartree-Fock (UHF) formalism (Pople and Nesbet 1954). The coupling operator method of Roothaan, however, frequently experiences convergence difficulties and almost invariably needs the adoption of an appropriate level shifting procedure (Guest and Saunders 1974; Faegri and Manne 1971) for achieving convergence. Even then, convergence is tediously slow and the method is rather too time-consuming to warrant its use in large scale open-shell SCF calculations. The UHF method, on the other hand, requires the formation and diagonalisation of two $n \times n$ matrices (n = dimension of the basis set) at each iteration and leads to a wavefunction that is not an eigenfunction of the S^2 operator (broken-symmetry solutions) in general, unless forced by symmetry. From time to time, therefore

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approximate procedures for performing open-shell SCF calculations have been suggested and used with a fair degree of success. The half-electron method (Dewar *et al* 1968) is a technique of this kind. The symmetry and equivalence restricted method (Nesbet 1955) and the method suggested by Nesbet and Watson (1960) also belong to the same category. Despite many successful applications of these methods they have been customarily regarded as just expedient means of calculating electronic structures of open-shell molecules and little seems to have been done to assess the quality of the results compared to the variationally exact open-shell SCF counterparts. The nature of F^{av} operator also has not been analysed in a way that makes its status fully transparent.

The purpose of the present paper has been to generalise the model of Nesbet and Watson in a form that makes it specially suitable for open-shell-LCAO-MO SCF calculations on molecules and critically examine its utility through actual analysis of the results of numerical calculations. In that process, we have tried to focus attention on certain subtle features of the model, viz., the question of eliminating self-interaction terms, connection of the present model with hyper-Hartree-Fock (HHF) theory, problem of relating F^{av} to a variational potential, etc. We would like to call our method an average hamiltonian model (AHM). As we shall see in §§ 3 and 4, the AHM is quite useful in many ways and has an approximate variational rationale.

2. Theory

Let us suppose that we have an N electron system containing n_1 doubly and m_1 single occupied orbitals (in the restricted Hartree-Fock language) and that the system is in an orbitally non-degenerate electronic state (this is *not* an essential constraint and is assumed only for the sake of simplicity). Let n_α and n_β be the number of electrons having α ($+\frac{1}{2}$) and β ($-\frac{1}{2}$) spins, respectively. Clearly, $n_\alpha = n_1 + m_1$ and $n_\beta = n_1$. Our AHM is executed in the following steps:

(i) For a given stomic orbital basis set (χ), a suitable coefficient matrix (C^0) is guessed.

(ii) The first order spinless density matrices R^α and R^β in the χ basis for the α and β -spin electrons are computed by using (1)

$$R = CC^\dagger. \quad (1)$$

(iii) The Hartree-Fock matrices F^α and F^β for the α and β -spin electrons respectively are computed by using

$$F^\alpha = h + J^\alpha + J^\beta - K^\alpha, \quad (2)$$

$$\text{and } F^\beta = h + J^\alpha + J^\beta - K^\beta. \quad (3)$$

(iv) Instead of solving the two eigenvalue equations, viz., $F^\alpha C^\alpha = C^\alpha \epsilon^\alpha$ and $F^\beta C^\beta = C^\beta \epsilon^\beta$ as done in UHF method we combine the two equations generating a single eigenvalue equation (equation (4)) ($S = I$ has been assumed)

$$F^{av} C^{av} = C^{av} \epsilon^{av}, \quad (4)$$

where F^{av} denotes a model Hamiltonian, the average Hamiltonian, which describes an average of the potentials seen by the α and β -spin electrons. The averaging needed to generate F^{av} is done in the following way :

$$\begin{aligned} F^{\text{av}} &= f_{\alpha}F^{\alpha} + f_{\beta}F^{\beta} \quad \text{where } f_{\alpha} = n_{\alpha}/(n_{\alpha} + n_{\beta}) \text{ and } f_{\beta} = n_{\beta}/(n_{\alpha} + n_{\beta}), \\ &= h + J^{\alpha} + J^{\beta} - f_{\alpha}K^{\alpha} - f_{\beta}K^{\beta}, \\ &= h + J^{\alpha} + J^{\beta} - f_{\alpha}K^{\alpha} - (1 - f_{\alpha})K^{\beta}. \end{aligned} \quad (5)$$

Let us note that

$$K^{\alpha} = \sum_{i=1}^{n_{\alpha}} K_i^{\alpha} \quad \text{and} \quad K^{\beta} = \sum_{j=1}^{n_{\beta}} K_j^{\beta}$$

and similar expressions hold also for J^{α} and J^{β} . Now we impose a spin-restriction in that the first n orbitals are doubly occupied enabling us to write

$$J^{\alpha} = J + \sum_{m=n_{\beta}+1}^{n_{\alpha}} J_m, \quad J = J^{\beta} \quad \text{and}$$

$$K^{\alpha} = K + \sum_{m=n_{\beta}+1}^{n_{\alpha}} K_m, \quad K = K^{\beta},$$

where we have, for obvious reason, dropped the spin-labels. Using these considerations (5) becomes

$$F^{\text{av}} = h + (2J - K) + \sum_{m=n_{\beta}+1}^{n_{\alpha}} J_m - f_{\alpha} \sum_{m=n_{\beta}+1}^{n_{\alpha}} K_m \quad (6)$$

(v) F^{av} is now diagonalised leading to a new approximation to the C -matrix (C^{av}) which can be fed back to step (i). The iteration is then continued to self-consistency. The self-consistent C^{av} matrix defines a set of one-electron orbitals (ϕ^{av}) selected to the basis functions (χ) by the transformation

$$\phi^{\text{av}} = \chi C^{\text{av}}. \quad (7)$$

These orbitals $\{\phi_i^{\text{av}}\}$, and their eigenvalue can be used to determine various molecular properties (e.g., electronic energy, ionisation energies, spin densities, etc.).

We now address ourselves to the problem of providing some rationale for the form of the average Hamiltonian (AH) operator. Admitting that the choice of F^{av} is intuitive, a formal (though not rigorous) justification can be provided. The operators F^{α} and F^{β} in UHF formalism (2, 3) clearly show that the non-equivalence of the potentials seen by the α and β -spin electrons in an open-shell systems stems from the non-equivalence of exchange interactions seen by the electrons of different spins. In the restricted HF theory, a similar difference occurs between the closed and the open-shell Hamiltonians (F° and F°) through the inequality of the exchange interactions felt by the electrons in the doubly- and singly-occupied orbital. This non-equivalence of the two one-electron Hamiltonians ultimately leads to the difficulty of eliminating the off-diagonal Lagrangian multipliers connecting the orbitals spanning the two different

occupied subspaces. In the UHF technique, this problem is tackled by neglecting the off-diagonal multipliers altogether while the orthogonality constraints are indirectly satisfied through the use of spin functions. The spatial functions for different spin types, however, cease to be orthogonal. The restricted open-shell theory of Roothaan, on the other hand, tackles the problem through the use of projection operators in the construction of the one electron Hamiltonian (Roothaan 1960). In AHM we adopt an alternative approach. Keeping in mind that we want to work within the open-shell RHF formalism but avoid the problem of non-zero off-diagonal Lagrangian multipliers we average out the exchange interactions seen by the closed and open-shell electrons, thus generate a common exchange averaged Hartree-Fock type of potential for both the shells (F^{av}) and seek a set of orbitals (ϕ_i^{av}) that renders F^{av} diagonal. This way, the off-diagonal Lagrangian multipliers coupling the two different shells are eliminated, but the orthonormality constraints are automatically satisfied as the orbitals spanning the doubly- or singly- or unoccupied subspaces are all solutions of a single pseudo-eigenvalue equation [cf. eqn. (4)]. As to the specific form of averaging to be adopted, quite a number of choices are open. In the present work we have adopted a form of averaging that depends on the relative abundances of the two types of electrons. One may also try to relate F^{av} to some variational potential derived from an exchange averaged energy functional. For this, let us define an approximate energy functionale $E^{av}(\psi_{av})$ containing partially scaled exchange interactions. The energy correct to first order $E^{actual}(\psi_{av})$ can then be generated from $E^{av}(\psi_{av})$ by the inclusion of the first order correction terms (ΔE^1): Thus, with $(K_{aa} + K_{\beta\beta})$ representing full exchange contribution to the Hartree-Fock energy of the open-shell system, the approximate energy functionale $\bar{E}E^{av}(\psi_{av})$ is given by

$$\bar{E} = E(1) + J_T - f_a K_{aa} - f_\beta K_{\beta\beta}, \quad (8)$$

where $E(1)$ is the kinetic plus electron nuclear interaction energy, J_T is the total Coulomb repulsion energy of the electrons. Then a first order correct estimate of energy is recovered through $E = \bar{E} + \Delta E^1 = \bar{E} - f_\beta K_{aa} - f_a K_{\beta\beta}$ where,

$$K_{aa} = \sum_{p=1}^{n_a} \sum_{i=p}^{n_a} \langle \psi_i | K_p | \psi_i \rangle, \quad (9a)$$

$$K_{\beta\beta} = \sum_{q=1}^{n_\beta} \sum_{m=q}^{n_\beta} \langle \phi_m | K_q | \phi_m \rangle, \quad (9b)$$

clearly then

$$\begin{aligned} E^{actual}(\psi_{av}) = \bar{E} - \{ & f_\beta \sum_{p=1}^{n_a} \sum_{i=p}^{n_a} \langle \psi_i | K_p | \psi_i \rangle \\ & + f_a \sum_{q=1}^{n_\beta} \sum_{m=q}^{n_\beta} \langle \phi_m | K_q | \phi_m \rangle \} \end{aligned} \quad (10)$$

We first note here that we are using a spin-restricted formalism so that the space part of the α and β -spin orbitals are constrained to be identical and then look for

a set of one-electron orbitals (ϕ_i) such that \bar{E} is stationary, i.e., $\delta\bar{E} = 0$ for any first order variation ($\delta\phi_i^{\text{av}}$) of the basis set $\{\phi_i^{\text{av}}\}$ spanning the relevant one-electron space (the space of F^{av}) subject to the usual orthonormality constraints,

$$\langle \phi_i^{\text{av}} | \phi_j^{\text{av}} \rangle = \delta_{ij}.$$

This leads us to the pseudo-eigenvalue equation

$$F^{\text{av}} \phi_i^{\text{av}} = \phi_i^{\text{av}} \epsilon_{ii}^{\text{av}}, \quad (11)$$

which can be solved in the usual iterative manner. It should be noted that once the set ϕ_i^{av} is obtained satisfying the criterion of self-consistency, the first order correct estimate of energy given by (10) can be easily computed.

There remains, of course, the question of legitimacy of carrying out the process of extremalisation based on $E^{\text{av}}(\psi_{\text{av}})$ of (8), a truncated pseudo-energy functional. It does not seem possible at this stage to provide an analytical proof that the energy calculated by our model is an upper bound to the variationally exact one-electron energy of the system. But in all the cases the method has so far been employed, the energy has been found to be slightly higher than the energy estimated by the UHF method. The problem of variational collapse, therefore, does not appear to be there, at least from a numerical point of view.

3. Self-interaction problem in AHM and the choice of f_a

Let us consider the specific case of a single electron outside the closed-shell of $2n$ electrons. The first n eigenvalues of F^{av} is then given by

$$\epsilon_{ii}^{\text{av}} (i = 1, n) = h_{ii} + \sum_{j=1}^n (2J_{ij} - K_{ij}) + J_{i, n+1} - f_a K_{i, n+1} \quad (12)$$

Clearly, there is no self-interaction terms in (12) as whenever $j = i$, $J_{ii} = K_{ii}$ and hence $J_{ii} - K_{ii} = 0$. An examination of the functional E also leads to the same conclusion (see equation (8)). For the open-shell electron, however, the situation is different. Thus the $(n + 1)$ th eigenvalue $\epsilon_{ii}^{\text{av}}$ is given by

$$\epsilon_{ii}^{\text{av}} (i = n + 1) = h_{ii} + \sum_{j=1}^n (2J_{ij} - K_{ij}) + J_{n+1, n+1} - f_a K_{n+1, n+1} \quad (13)$$

Unless $f_a = 1$, it is clear from (13) as also from (8) that the self-repulsion of the open-shell electron is only partly removed. The use of $f_a = 1$ corresponds to the use of the symmetry and equivalence restricted one-electron hamiltonian which leads to an overestimation of the exchange interactions for the closed-shell electrons (equation (12)). This may, however, be a good approximation for states with high spin-multiplicity (i.e., $n_a \gg n_p$). On the other hand, if we choose $f_a = 0$, the open-shell electron experiences a full self-repulsion (13) while for its closed-shell counterparts also, exchange interactions are now underestimated. Clearly then, the choice of f_a in AHM has to be constrained so as to satisfy $0 < f_a < 1$. Our choice of $f_a = n_a / (n_a + n_p)$ automatically satisfies this constraint. The question

that remains unsettled at this point is whether such a choice of f_a is optimum. This, in turn, leads us to examine the behaviour of the energy as a function of f_a . Before doing that, let us first consider a similar problem in the hyper-Hartree-Fock theory (Slater 1972, 1974).

Slater based his discussion on an energy functional

$$E(N) = \sum_i q_i I_i + \sum_i q_i (q_i - 1)/2 \langle J_{ii} \rangle + \sum_{i < j} q_i q_j \langle J_{ij} \rangle \quad (14)$$

which he used for the variational determination of the set of one electron-orbitals, $\{\phi_i\}$. The sums in (14) are over shells of electrons, q_i being the occupation number of the i th shell (ϕ_i) and I_i is the one-electron energy of an electron in the i th shell.

If we restrict ourselves to the Hartree-Fock method only, ϕ_i 's refer to HF spin-orbitals so that q_i 's are restricted to unity making the coefficient of each of the self-repulsion term $[q_i(q_i - 1)] = 0$. The moment we switch over to the HHF method, with E in (14) defining the average energy of a multiplet state, ϕ_i represents a shell of $(2l + 1)$ fold degenerate spin orbitals with $\langle J_{ij} \rangle$ or $\langle J_{ii} \rangle$ referring to suitably-averaged repulsion terms. For open-shell configurations, therefore, the HHF method actually resorts to using non-integer q_i 's. It is immediately clear that while for integer q_i , $q_i(q_i - 1)/2$ correctly counts the number of pairwise interactions between q_i identical electrons and completely eliminates self-repulsion, the situation with non-integer q_i 's is far less clear. For example, with $q_i = \frac{1}{2}$, $q_i(q_i - 1)/2 = -0.125 \langle J_{ii} \rangle$. Instead of self-repulsion, there is now self-attraction! A roughly similar situation would crop up in our AHM had we used $f_a > 1$ (see (13)). Recently Gopinathan and Whitehead (1980) discussed the use of an alternative functional (15).

$$E(Q) = \sum_i q_i I_i + \sum_i (n_i(n_i - 1)/2 + n_i f_i) \langle J_{ii} \rangle + \sum_{i < j} q_i q_j \langle J_{ij} \rangle, \quad (15)$$

where one uses n_i for integer, q_i for non-integer, and f_i for fractions of electrons. When $q_i < 1$; $n_i = 0$ and hence the problem of self-attraction is avoided. This again has a parallel in our AHM which leads to the complete elimination of self-interaction for $f_a = 1$. The point to make in this discussion is that $E(Q)$ or $E(N)$ roughly corresponds to some particular choice of \bar{E} in our model. There is, however, the difference that while our \bar{E} takes into account the exchange interactions of electrons in two different shells (i, j), $E(Q)$ or $E(N)$ neglects these terms. The second important point is that the electronic energy computed by *any average Fock operator model must be free from self-interaction of electrons as these terms (Gopinathan and Whitehead 1980) are large in magnitude*. Our calculation of E^{actual} from \bar{E} in (10) merely ensures that. Since the orbitals are determined variationally from the functional E , the spatial dispositions of the orbitals will certainly depend on the specific form of \bar{E} chosen. The magnitude of $\langle K_{ii} \rangle$ or $\langle K_{ij} \rangle$ terms themselves will depend, therefore, on the choice of f_a parameter in our model. A parallel situation is also encountered in the HHF theory. But as Gopinathan and Whitehead (1980) demonstrated this change is very small compared to the error arising from 'incomplete' or 'overcomplete' elimination of self-interaction terms in the functional. This justifies our contention that the term

ΔE^1 given by (8) to (9) may be added to \tilde{E} just as a first order correction (in the language of perturbation theory) and the change in these terms and the other two and one-electron terms already present in \tilde{E} with change in f_α or f_β may be regarded as higher order corrections. E^{actual} , therefore, may be regarded as providing a good estimate of E . Clearly the extent of dependence of the energy on f_α would be dominantly determined by the variation of $\langle J_{ij} \rangle$ or $\langle K_{ij} \rangle$ with changes in f_α . As we have already seen that the form of F^{av} is such that the elimination of self-interaction is incomplete (for $0 < f_\alpha < 1$) only for the open-shell electron, the variation of $K_{n+1, n+1}$ itself with f_α may be particularly important in determining the behaviour of the energy as a function of f_α .

4. Eigenvalues in AHM and the calculation of ionisation potential

It is well-known that unlike the closed shell case Koopmans' theorem (Koopmans 1933) cannot be applied directly to calculate the unrelaxed ionisation potential of atoms or molecules having open-shell electronic configurations. On the other hand, Koopmans' theorem holds in the UHF framework and can be invoked to compute spin-polarised ionisation potentials directly from the UHF eigenvalues. The structure of F^{av} in our AHM suggests that it may be instructive to try to relate the eigenvalues of F^{av} to the eigenvalues of the corresponding UHF hamiltonians (F^α and F^β). Obviously such a relationship can be developed at various orders of approximations. But we shall restrict ourselves to the analysis at the first order level since the higher order effects on the eigenvalues are expected to be small. Further, we would consider only the doublet ions or radicals.

A little analysis of the form of the energy coupled with the fact that the one-electron orbitals belonging either to the closed or the open-shells are determined by the eigenvectors of one and the same operator would suggest that the first order estimate of the ionisation potential of the open-shell electron (ϕ_m) (in a frozen-orbital approximation) would be given by (this however, is not strictly comparable to the Koopmans' theorem values for closed-shell systems)

$$I_{mm}^{(1)}(\text{AHM}) = -\epsilon_{mm}^{\text{av}} + (1 - f_\alpha) K_{mm}. \quad (16)$$

Comparing with the UHF description of the same system we get for the highest occupied α -spin orbital (ϕ_m^α)

$$I_{mm}^{(1)}(\text{UHF}) = -\epsilon_{mm}^\alpha \approx I_{mm}^{(1)}(\text{AHM}) \quad (17)$$

For the ionisation of an electron from the closed-shell orbitals $\{\phi_i^{\text{av}}\}$, however, one must take care to note that following the ionisation of an electron from one of the closed shell orbitals in the doublet ground state of the molecule, the ionised species may be formed either in the triplet or singlet spin state. One must, therefore, assign two types of ionisation potentials for the inner-shell electrons in a doublet parent: (i) the triplet ionisation potential ($I_i(T)$) and (ii) the singlet ionisation potential ($I_i(S)$). If we are using the UHF model, the former corresponds to the removal of an electron from the orbital ϕ_i^β and the latter from the α -spin counterpart (ϕ_i^α) so that in a frozen-orbital approximation we may write,

$$I_i^{(1)}(T) \approx -\epsilon_{ii}^\beta \quad (18a)$$

$$\text{and } I_i^{(1)}(S) \approx -\epsilon_{ii}^{\alpha}. \quad (18b)$$

The structure of the closed shell eigenvalues in the AHM (viz., (12)) suggests that to a first order approximation

$$\epsilon_{ii}^{\alpha} \approx \epsilon_{ii}^{\text{av}} - f_{\beta} K_{im},$$

$$\text{and } \epsilon_{ii}^{\beta} \approx \epsilon_{ii}^{\text{av}} + f_{\alpha} K_{im}. \quad (19)$$

Thus it is possible to write (approximately)

$$I_i^{(1)}(T) \approx -\epsilon_{ii}^{\text{av}} - f_{\alpha} K_{im} \approx -\epsilon_{ii}^{\beta} \text{ (UHF)}, \quad (20a)$$

$$\text{and } I_i^{(1)}(S) \approx -\epsilon_{ii}^{\text{av}} + f_{\beta} K_{im} \approx -\epsilon_{ii}^{\alpha} \text{ (UHF)} \quad (20b)$$

Hence the singlet triplet splitting of the ionisation potential is given by

$$(\Delta ST)_i^{\text{AHM}} \approx K_{im} \quad (21)$$

and this roughly corresponds to $(\Delta ST)_i^{\text{UHF}}$ which is given by

$$(\Delta ST)_i^{\text{UHF}} = \epsilon_{ii}^{\beta} - \epsilon_{ii}^{\alpha}. \quad (22)$$

Although equations (19)–(22) no doubt show the approximate relationship between the average hamiltonian and UHF ionisation energies, the singlet-type ionisation potential calculated by using $\epsilon_{ii}^{\text{av}}$ and (19) would be in error by an additive factor of K_{im} . This is because in a spin-restricted model like AHM a correct singlet coupling of the spins must be ensured for the wavefunction of the ionised species formed in the singlet state. This leads to the following expression for the singlet type ionisation potential for the closed shell electrons

$$I_i^{(1)}(S) \approx -\epsilon_{ii}^{\text{av}} + (1 + f_{\alpha}) K_{im}. \quad (23)$$

Thus, the spin-restricted estimate of the singlet-triplet splitting $(\Delta ST)_i^R$ of the inner shell ionisation potentials in doublet parents should be given by

$$(\Delta ST)_i^R = 2K_{im}. \quad (24)$$

Since however, the spatial disposition of the average hamiltonian eigenvectors (ϕ_i^{av}) are not expected to vary strongly with changes in the averaging parameter (f_{α}, f_{β}) we anticipate a fair degree of invariance of the ionisation potentials computed by equations (16)–(21) with respect the choice of averaging parameter (see § 5.2).

5. Results and discussion

There are several aspects of the results that need separate attention. We, therefore, proceed to discuss the results under four separate headings.

5.1. AHM and UHF energies

To assess the reliability of AHM energies, we have performed a number of UHF and AHM calculations on the first $\pi\pi^*$ triplet state of a few 6π electron hydrocarbons at the PPP level of approximation (I'Haya 1964). In each we have used $f_a = n_a/(n_a + n_\beta)$. One can clearly see that the AHM energy lies slightly above the corresponding UHF energy (table 1). In the same table we have also reported the per cent error in AHM energies relative to the UHF counterparts. Table 1 also displays similar comparative features of AHM and UHF energies of the anions of these conjugated hydrocarbons (spin-doublet). In general, the per cent error is seen to be quite low.

At this point one naturally gets interested in examining the behaviour of $E^{\text{actual}} \psi_{av}$ as a function of f_a . Table 2 displays this aspect of the problem for two representative cases, viz., dimethylene cyclobutene and methylene cyclopentadiene in the lowest $^3\pi\pi^*$ state (6π electrons) and the singly-ionised species of the same molecule corresponding to the ionisation from the highest occupied MO (5π electrons). Although in each case, the energy shows up a minimum around $f_a = 0.45$ to 0.6 , the variation noted in E^{ac} with changes in f_a is very small and for all practical purposes any value of f_a in the above range can be used. From a theoretical point of view, however, this leads one to note with interest that E^{ac} turns out to be a quadratic function of f ($E^{\text{ac}} \approx a + bf_a + cf_a^2$). Immediately one recalls that in the HHF theory of Slater, the functional $E(Q)$ is similarly regarded as a quadratic function of Q , the fractional occupation number of the degenerate open-shell (viz., $E(Q) = a + bQ^2 + cQ$) so that minimisation with respect to Q may be carried out meaningfully. This result strengthens our speculation in the preceding section that the AHM has similarity with the HHF theory.

5.2. AHM and self-repulsion of electron

As we have already pointed out the open-shell electron in AHM experiences a part of the self-repulsion. For the doublet radicals or ions, this is given by $R(f_a) = (1 - f_a) K_{ii}$; clearly $R(f_a)$ would be a linear function of f_a had K_{ii} been independent of f_a . Unfortunately, variation of f_a introduces variation in the orbitals and as such K_{ii} must also vary with f_a . We, therefore, plan to investigate first the variation of K_{ii} itself with f_a and then the variation of $R(f_a)$. For this we have chosen CN radical at $R_{\text{CN}} = 1.14 \text{ \AA}$ as the model system and performed AHM calculations for different values of f_a at the CNDO/2 level of approximation (Pople *et al* 1965). The switch over from the PPP to CNDO/2 model is effected because the self-repulsion terms in CNDO/2 model is expected to be much larger than the PPP counterparts as the latter uses much reduced values of the basic two-electron integrals compared to those evaluated over the Slater atomic orbital basis so that variation of K_{ii} with changes in f_a is more prominent and detectable.

Table 3 displays K_{ii} , $(1 - f_a) K_{ii}$ and E^{ac} of our system for different values of f_a (from 0 to 1). It is clearly seen that K_{ii} and $(1 - f_a) K_{ii}$ decreases monotonically as f_a increases while E^{ac} passes through a clear minimum at some intermediate value of f_a revealing once again the quadratic nature of the functional dependence of E^{ac} on f_a . The very slow but monotonic decrease of K_{ii} with the

Table 1. Comparison of electronic energies computed by the average hamiltonian model and the unrestricted Hartree-Fock technique at the PPP level of approximation ($f_a = n_a/n_a + n_\beta$ has been used).

Molecule/Ion	Number of π electrons	State	f_a value	AHM energy (a.u)	UHF energy (a.u)	% error in AHM energy
Dimethylene cyclobutene	6	$^3\pi\pi^*$	2/3	-5.63938	-5.66103	0.3826
Methylene butadiene	6	$^3\pi\pi^*$	2/3	-5.54958	-5.57006	0.3678
Triafulvalene	6	$^3\pi\pi^*$	2/3	-5.67955	-5.68113	0.0279
Fulvalene	6	$^3\pi\pi^*$	2/3	-5.71992	-5.73490	0.2717
Dimethylene cyclobutene ion	7	Ground (doublet)	4/7	-5.87065	-5.87374	0.0525
Methylene butadiene ion	7	do	4/7	-5.77629	-5.78286	0.1135
Triafulvalene ion	7	do	4/7	-5.77433	-5.77691	0.0445
Fulvalene ion	7	do	4/7	-5.96257	-5.97046	0.1322

Table 2. Variation of AHM energy with as a function of the exchange-averaging parameter (f_a) in some model systems.

Value of f_a used	$E(f_a)$ of dimethylene cyclobutene (eV) in $^2\pi\pi^*$ state	$E(f_a)$ of singly ionised dimethylene cyclobutene (eV) in the ground state
0.1	-153.35504	-144.14636
0.2	-153.40508	-144.15747
0.3	-153.44567	-144.16834
0.4	-153.46217	-144.17411
0.5	-153.46940	-144.17878
0.6	-153.46230	-144.18023
0.7	-153.44077	-144.17793
0.8	-153.40506	-144.17096
0.9	-153.35437	-144.15859

Table 3. Dependence of the average hamiltonian eigenvalue, the self-interaction and ionisation energy of the open-shell electron of CN radical ($R_{CN} = 1.15 \text{ \AA}$), on the magnitude of f_a .

f_a	$-\epsilon_{ii}^{av} (i=5)$ (a.u.)	K_{ii} (a.u.)	$(1 - f_a) K_{ii}$ (a.u.)	$I_i^{av} (i=5)$ (a.u.)	I_i (UHF) (a.u.)
0.0	0.0454	0.5295	0.5295	0.5749	0.5796
0.2	0.1523	0.5294	0.4235	0.5758	
0.4	0.2592	0.5292	0.3175	0.5767	
0.5	0.3124	0.5291	0.2647	0.5771	
0.6	0.3927	0.5290	0.1852	0.5779	
0.7	0.4194	0.5290	0.1587	0.5781	
0.9	0.5261	0.5289	0.0529	0.5791	
1.0	0.5795	0.5889	0.0	0.5795	

increase of f_a indicates that larger the value of f_a the more the orbital ϕ_i gets delocalised or 'diffuse'. It would be of interest, therefore, to examine the binding energy of ionisation energy of the open-shell electron and its dependence on f_a .

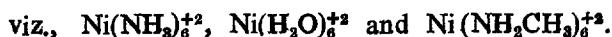
5.3. Ionisation potential in AHM

A first order estimate of the ionisation energy of the open-shell electron in AHM is obtained from (16). The variation of IP for the CN-radical, with f_a has also been displayed in table 3 along with the UHF estimate of the same quantity. The variation observed is clearly very small emphasising that the major error due to the incomplete elimination of the self-repulsion of the open-shell electron is removed by the inclusion of the first order correction term in (16) and the higher

order effects are definitely quite small as far as the particular orbital is concerned. It would be worthwhile to inquire how far do the ionisation energies of the inner shell (closed) electrons get affected by changes in the exchange averaging parameter (f_a). To have an idea of this, we have displayed in table 4 the first order estimate of singlet and triplet ionisation energies of the inner or closed-shell orbitals of the CN radical computed with different values of f_a using (20). For comparison, the UHF estimates of these quantities are also included. Since we have adopted the CNDO/2 approximations, K_{im} in (17) is zero unless ϕ_i and ϕ_m are of the same symmetry which explains why the computed ionisation energies of the inner π_o orbitals do not show any singlet-triplet splitting (table 4). Actually, the ionisation energy of the π_o electrons is remarkably invariant to changes in the exchange averaging parameter. This is quite expected as the first order correction to the π_o electron ionisation energy at the frozen orbital level of approximation is zero in the present model. Similarly, the ionisation energy of the closed-shell σ_u electron also does not show any singlet-triplet splitting or significant variation with the change in the exchange averaging parameter as the open-shell orbital is of σ_g symmetry. The closed-shell σ_g orbital shows fairly large singlet-triplet splitting in the ionisation energy. The singlet ionisation energy of the $1\sigma_g$ (closed) electron computed by (20b) shows a small increase as f_a increases from 0 to 1. The corresponding 'triplet' ionisation energy, however, decreases as f_a increases from 0 to 1. Side by side, the singlet-triplet splitting of the ionisation energy of the $1\sigma_g$ electron given by (21) also increases somewhat. The agreement with the UHF estimate of the same singlet-triplet splitting (22) is best at intermediate values of f_a (0.5 to 0.7) (see table 4). The spin-restricted estimate of the singlet-triplet splitting of the ionisation energy of the $1\sigma_g$ electron (i.e., $(\Delta ST)_i^R$ given by equation (24)), has also been included in table 4. This also increases as f_a increases from 0 to 1. We are at present investigating the effects of higher order corrections on the computed $(\Delta ST)_i^{\text{AHM}}$ within the framework of AHM. The fairly large magnitude of $(\Delta ST)_i$ indicates that the potential surfaces for the singlet and triplet inner-shell ionised species may be significantly different (Banerjee and Bhattacharyya 1981a).

5.4. Molecular geometry and the AHM

To test the performance level of our AHM *vis-a-vis* the UHF method in the calculation of molecular geometry we carried out a series of calculations on the ground states of some octahedral Ni^{II} complexes



All the calculations have been performed using the CNDO type of method developed by us (Bhattacharyya and Chowdhury 1977; Bhattacharyya 1979). The results obtained have been summarised in table 5. It is seen that the agreement between the optimum bond lengths predicted by the two methods is quite good in each case. As expected, the AHM energy at equilibrium bond length lies above the UHF counter part although the error is quite small and remains fairly constant over the whole range of bond lengths studied so that the profile of the potential energy curve or the position of the minimum is not affected.

Table 4. Dependence of ionisation energies of different closed-shell orbitals of CN radical ($R_{CN} = 1.15 \text{ \AA}$) on the magnitude of f_a parameter.

Symmetry of the orbital involved in ionisation	Spin-symmetry of the Ionised state	AHM ionisation energies $I_1(S)$ and $I_1(T)$ of different closed-shell orbitals for different values of f (a.u.)									UHF values of Ionisation energies (a.u.)
		$f_a = 0.0$	0.1	0.2	0.3	0.5	0.7	0.9	1.0		
$1\sigma_g$	Singlet $I_1(S)$	0.8068	0.8073	0.8079	0.8084	0.8091	0.8099	0.8103	0.8104	0.8100	
	Triplet $I_1(T)$	0.7342	0.7342	0.7335	0.7336	0.7333	0.7322	0.7306	0.7283		
	(ΔST) [*]	0.0726	0.0731	0.0744	0.0748	0.0758	0.0777	0.0797	0.0821	0.076 [†]	
	(ΔST) _R ^{**}	0.1452	0.1462	0.1488	0.1496	0.1516	0.1554	0.1594	0.1642	(ΔST) _{UHF}	
π_g $1\sigma_g$	singlet/triplet	0.712	0.712	0.712	0.712	0.712	0.712	0.712	0.712	0.711	
	singlet/triplet	1.476	1.475	1.474	1.474	1.472	1.472	1.471	1.471	1.471	

* See equation (21) † See equation (22) ** See equation (23)

Table 5. Comparison of optimum bond lengths and energies calculated by UHF and AH methods in some transition metal complexes†.

Molecule and electronic state	Optimum bond lengths		Optimum energy (not) predicted by		% error relative to UHF energy
	UHF method (Å)	AH method (Å)	UHF method (eV)	AH method (eV)	
$\text{Ni}(\text{NH}_3)_6^{+2} ({}^3A_{1g})$	1.750	1.725	-821.8472	-821.6112	
${}^2\text{Ni}(\text{H}_2\text{O})_6^{+2} ({}^3A_{1g})$	1.550	1.550	-868.0291	-867.7102	
$\text{Ni}(\text{CH}_3\text{NH}_2)_6^{+2} ({}^3A_{1g})$	1.760	1.760	-807.7178	-807.3990	

* In this case the possibility of π -bonding was neglected. The sigma-bonding by water molecule is assumed to occur through the σ -lone pair (supposed to be SP^2 hybrid). The ionisation energy of this σ -lone pair of H_2O was taken from Al-Joubury and Turner (1964)

† For details of the parametrisation used see (Bhattacharyya 1979b).

6. Conclusion

The results discussed so far seem to indicate that the AHM would be a quite useful tool for obtaining a variety of information (e.g., molecular geometry, ionisation potential, potential surface, etc.) about the open-shell molecules at an approximate level. The results indicate that the method would be specially suitable for the calculation IP of radicals. The basic advantages of the method are its organisational and operational simplicity, absence of convergence difficulty (the restricted open-shell method of Roothaan seldom converges unless one resorts to a some level-shift procedure and is far more time-consuming). The applicability of the method to inner-hole states and excited states of various molecules are being evaluated at present in our laboratory. The results obtained so far seem to indicate that the method would be quite useful for these purposes also. From a theoretical point of view, the AHM can also be regarded as providing some *scaled one-electron hamiltonian* with enough freedom for the choice of the scaling parameter (Bhattacharyya 1981). This aspect of the AHM and its comparison with the open-shell formalism of Roothaan are under investigation (Banerjee and Bhattacharyya (1981).

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