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On The Transferability of Fock Matrix Elements

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The transferability of Fock matrix elements in the linear combination of atomic orbitals molecular orbital scheme is analysed using localized orbitals. It is shown that this transferability is dependent on the transferability of these localized orbitals and the neglect of long-range contributions from partially cancelling Coulomb nuclear attraction and electron repulsion terms. A theoretical basis is thus provided for the simulated ab initio molecular orbital and related methods. Various corrections previously introduced in an ad hoc manner are shown to be justified. Transferability in both the closed shell and open shell schemes is analysed.

Key words: Fock matrix elements – Transferability – SAMO – Molecular orbital theory – Closed shells – Open shells.

1. Introduction

The last two decades or so have witnessed the development of a number of transferability methods for approximating molecular orbital wave functions. A number of these methods utilize the transferability of matrix elements over the Fock operator from a small "pattern" molecule to a "target" molecule. For π-electron systems there is the study by Orloff and Fitts [1] and whilst the Non-Empirical Molecular Orbital (NEMO) method of Newton et al. [2] utilizes the transferability of only on-diagonal elements, the Simulated *Ab initio* Molecular Orbital (SAMO) method introduced by Eilers and Whitman [3] involves the transferability of both on- and off-diagonal Fock matrix elements. Deplus et al. [4] have proposed a related method which uses orthogonalized

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hybrid orbitals whilst Leroy and Peeters [5] have used a basis of localized orbitals. Each of these methods was extensively reviewed in 1975 [6]. The programs are available through Q.C.P.E. [7].

The SAMO method has been applied to hydrocarbons [3], polymers [8], benzenoid aromatic hydrocarbons [9], cyclohexanes [10], polar groups, ionic molecules and orthogonalized basis sets [11], open shell radicals [12, 13], polynuclear aromatic hydrocarbons [14], second row elements [15] and pyrazine [16]. A resolvent technique has also been developed for the SAMO method [17] and a combination of SAMO and semi-empirical methods [18] have been used to evaluate ionization energies.

In addition to these developments the transferability method using a basis set of localized orbitals has been further developed with applications to heteroatom derivatives [19] and polyethylene [20]. A method involving the transferability of atomic potentials has been shown to give similar results [21]. The transferability of Fick matrix elements within semi-empirical methods has also been demonstrated and a semi-empirical version of SAMO developed [22].

The common feature of all methods based on transferability has, up to now, been their reliance upon the use of minimum basis sets occasionally improved with polarization functions. However, the use of SAMO with more extended basis sets has recently been reported [23] and further work in this area is in progress.

In spite of its wide use, and the fact that the necessary approach was outlined many years ago by Hall [24], to date, no attempt has been made to justify this transferability of Fock matrix elements.

2. A Justification of Transferability for Closed Shell Systems

Justification of the transferability of Fock matrix elements necessitates analysis of the error arising in the transferred element i.e. the difference between the correct *ab initio* value for the Fock matrix elements $F^T_{\mu\nu}$ for the target molecule T and its simulated value $F^P_{\mu\nu}$ obtained by transference from a pattern molecule P.

For both the target and pattern molecule the wave equation is given by Eq. (1)

$$\psi = A\{\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\cdots\phi_{m/2}(m-1)\alpha(m-1)\phi_{m/2}(m)\beta(m)\} \qquad (1)$$

where the one-electron molecular orbitals ϕ_i are expanded in the usual "linear combination of atomic orbitals" (L.C.A.O.) approach.

$$\phi_i = \sum_{\mu=1}^{n} C_{\mu i}\chi_\mu \qquad (2)$$

and A is the antisymmetrizer. The energy of P is minimized using the usual molecular Hamiltonian

$$\hat{H} = \sum_{i=1}^{m} \hat{h}(i) + \sum_{i>j} 1/r_{ij} \qquad (3)$$

where $1/r_{ij}$ is the electron repulsion term and $\hat{h}(i)$ is the one electron term given by

$$\hat{h}(i)=-\tfrac{1}{2}\nabla_i^2-\sum_A \frac{z_A}{r_{Ai}}. \tag{4}$$

Here, the first term represents kinetic energy and the second term is the sum of nuclear attraction terms over the nuclei labelled A. The coefficients $C_{\mu i}$ in the expansion of ϕ_i are given by the matrix eigenvalue equation (Roothaan (25) - Hall (26) equation)

$$\boldsymbol{FC}=\boldsymbol{SC\lambda} \tag{5}$$

$$S_{\mu\nu}=\langle\mu\,|\,\nu\rangle. \tag{6}$$

Here, the elements of $\boldsymbol{F}$ are given by

$$F_{\mu\nu}=T_{\mu\nu}-\sum_A\langle\mu|\frac{z_A}{r_A}|\nu\rangle+2\sum_i\langle\mu\nu\,|\,\phi_i\phi_i\rangle-\sum_i\langle\mu\phi_i\,|\,\nu\phi_i\rangle \tag{7}$$

where we make the usual definitions

$$\langle\mu\,|\,\nu\rangle=\int \mathrm{d}\tau_1\chi_\mu(1)\chi_\nu(1) \tag{8}$$

$$T_{\mu\nu}=\langle\chi_\mu|-\tfrac{1}{2}\nabla_1^2|\chi_\nu\rangle=-\tfrac{1}{2}\int \mathrm{d}\tau_1\,\chi_\mu(1)\nabla_1^2\chi_\nu(1) \tag{9}$$

$$\langle\mu|\frac{z_A}{r_A}|\nu\rangle=\int \mathrm{d}\tau_i\,\chi_\mu(i)\frac{z_A}{r_A}\chi_\nu(i) \tag{10}$$

$$\langle ab\,|\,cd\rangle=\int d\tau_1\,d\tau_2\,a(1)c(2)\frac{1}{r_{12}}b(1)\,d(2). \tag{11}$$

It is just this $F_{\mu\nu}$ of Eq. (7) that we are concerned with transferring. However, any direct comparison of $F^P_{\nu\mu}$ with $F^T_{\nu\mu}$, the Fock elements arising from the pattern and target molecules respectively, is difficult because all of the orbitals ϕ_i in Eq. (7) will be delocalized over very different molecular frameworks. For this reason it is desirable to consider the Fock matrix elements in terms of some more localized functions.

The molecular wave function of Eq. (1) can readily be transferred into localized orbitals θ_i such that

$$\psi=A\{\theta_1\alpha(1)\theta_1\beta(2)\cdots\theta_{m/2}\alpha(m-1)\theta_{m/2}\beta(m)\}. \tag{12}$$

The orbitals θ_i can be obtained by a variety of techniques (6) and may or may not be mutually orthogonal. In our case they are chosen in such a way as to be orthogonal, the specific technique being unimportant

$$\langle\theta_i\,|\,\theta_j\rangle=\delta_{ij}. \tag{13}$$

Under this unitary transformation of molecular orbitals only, the expression for $F_{\mu\nu}$ becomes

$$F_{\mu\nu} = T_{\mu\nu} - \sum_A \langle\mu|\frac{Z_A}{r_A}|\nu\rangle + 2\sum \langle\mu\nu|\theta_i\theta_i\rangle - \sum_i \langle\mu\theta_i|\nu\theta_i\rangle. \tag{14}$$

A proof of the equivalence of expressions (7) and (14) is given in Appendix A.

It should be stressed that we introduce localized orbitals merely to facilitate the comparison of $F^P_{\mu\nu}$ and $F^T_{\mu\nu}$. It is not our purpose here to generate the eigenvalue equation whose solutions are localized orbitals.

In Fig. 1, where the simulation of octane from butane is illustrated, a particular matrix element $F_{\mu\nu}$ is shown. To simulate $F^T_{\mu\nu}$ we select $F^P_{\mu\nu}$ from a specific pattern molecule, in this case always butane, with a geometry chosen to exactly match the configuration found in the target molecule. This choice defines a segment S of atoms and bonds common to both target and pattern molecule.

Although the expressions for $F^P_{\mu\nu}$ and $F^T_{\mu\nu}$ are similar, the sums over A and i will be over different atoms and localized orbitals. These sums are now split into those which are inside and those which are outside the common segment S. The following equations are the Fock matrix elements for the pattern and target where integrals and orbitals have been labelled P and T respectively.

$$\begin{aligned} F^P_{\mu\nu} = T^P_{\mu\nu} &- \sum_{A\in S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P + 2\sum_{i\in S} l_i\langle\mu\nu|\theta_i^P\theta_i^P\rangle - \sum_{i\in S} l_i\langle\mu\theta_i^P|\nu\theta_i^P\rangle \\ &- \sum_{A\notin S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P + 2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^P\theta_i^P\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^P|\nu\theta_i^P\rangle \end{aligned} \tag{15}$$

$$\begin{aligned} F^T_{\mu\nu} = T^T_{\mu\nu} &- \sum_{A\in S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T + 2\sum_{i\in S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle - \sum_{i\in S} l_i\langle\mu\theta_i^T|\nu\theta_i^T\rangle \\ &- \sum_{A\notin S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T + 2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^T|\nu\theta_i^T\rangle. \end{aligned} \tag{16}$$

Here, summation $\in S$ and $\notin S$ indicates summation over atoms and localized orbitals which are respectively inside and outside the segment S. Where orbitals lie across the S boundary the appropriate term must be split between the two summations. This is covered by the introduction of the term l_i which is an

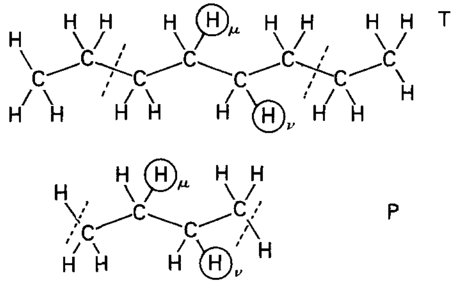


Fig. 1. Illustration of a common segment S for transferability of $F_{\mu\nu}$ from pattern P to target T

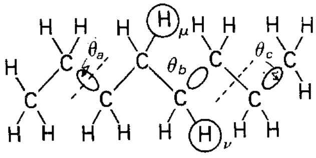


Fig. 2. Illustration of the use of the l_i term associated with a given θ_i

occupation number representing the number of electrons counted in a localized orbital. When θ_i lies completely inside or completely outside the segment S, $l_i = 1$. However, when θ_i lies across the segment boundary $l_i = \frac{1}{2}$. This usage is illustrated in Fig. 2.

In the sum inside the segment $l_b = 1$ and for θ_a, which spans the segment boundary, $l_a = \frac{1}{2}$. In the sum outside the segment $l_c = 1$ and $l_a = \frac{1}{2}$.

Choosing identical geometries and basis sets for P and T and selecting the segment S such that the atoms it contains are common to both the pattern and target (the same atoms A appearing in the same positions in both P and T) results in the following equalities

$$T^P_{\mu\nu} = T^T_{\mu\nu} \tag{17}$$

$$\sum_{A \in S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P = \sum_{A \in S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T. \tag{18}$$

Further, since localized orbitals are localized in bond or core regions and are themselves transferable for similar chemical environments (6), a condition likely to be met to a high degree of accuracy within the SAMO method, we have

$$\theta^P_i \approx \theta^T_i \in S \tag{19}$$

and thus:

$$2 \sum_{i \in S} l_i \langle\mu\nu|\theta^P_i\theta^P_i\rangle \approx 2 \sum_{i \in S} l_i \langle\mu\nu|\theta^T_i\theta^T_i\rangle \tag{20}$$

$$\sum_{i \in S} l_i \langle\mu\theta^P_i|\nu\theta^P_i\rangle \approx \sum_{i \in S} l_i \langle\mu\theta^T_i|\nu\theta^T_i\rangle. \tag{21}$$

These relationships are also based on the choice of an identical basis set for both pattern and target molecule.

Use of Eqs. (17) to (21) with Eqs. (15) and (16) results in the considerably simplified expression for the difference between $F^T_{\mu\nu}$ and $F^P_{\mu\nu}$:

$$\begin{aligned} F^T_{\mu\nu} - F^P_{\mu\nu} = {} & 2 \sum_{i \notin S} l_i \langle\mu\nu|\theta^T_i\theta^T_i\rangle - \sum_{A \notin S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T \\ & -2 \sum_{i \notin S} l_i \langle\mu\nu|\theta^P_i\theta^P_i\rangle + \sum_{A \notin S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P \\ & - \sum_{i \notin S} l_i \langle\mu\theta^T_i|\nu\theta^T_i\rangle + \sum_{i \notin S} l_i \langle\mu\theta^P_i|\nu\theta^P_i\rangle. \end{aligned} \tag{22}$$

The exchange terms occurring in Eq. (22) are small since such sums converge rapidly with increasing distance of θ_i from the orbital pair χ_μ and χ_ν. From the Mulliken approximation (27) we have

$$\langle \mu\theta_i \mid \nu\theta_i \rangle \; \alpha \; S_{\mu\theta_i} S_{\nu\theta_i} \tag{23}$$

and both these terms are small. All θ_i are outside S so the exchange terms can be more readily neglected if the pattern molecule for $F_{\mu\nu}$ is selected such that χ_μ and χ_ν are distant from the boundary of S. This has always been part of the SAMO methodology. Hence

$$\sum_{i \notin S} l_i \langle \mu\theta_i^P \mid \nu\theta_i^P \rangle - \sum_{i \notin S} l_i \langle \mu\theta_i^T \mid \mu\theta_i^T \rangle \approx 0. \tag{24}$$

The nuclear attraction terms appearing in Eq. (22) are slow to converge with increasing distance of atom A from the orbitals χ_μ and χ_ν. Hence, their sums for the target and pattern molecule will not cancel; a similar situation holds for the Coulomb terms. However, the orbital pair χ_μ and χ_ν, since they are inside the segment, will be at some distance from θ_i^T or θ_i^P which are located outside the segment, hence the following approximate equalities are likely to hold:

$$\sum_{A \notin S} \langle \mu | \frac{z_A}{r_A} | \nu \rangle^T \approx 2 \sum_{i \notin S} l_i \langle \mu\nu \mid \theta_i^T \theta_i^T \rangle \tag{25}$$

$$\sum_{A \notin S} \langle \mu | \frac{z_A}{r_A} | \nu \rangle^P \approx 2 \sum_{i \notin S} l_i \langle \mu\nu \mid \theta_i^P \theta_i^P \rangle. \tag{26}$$

These equations themselves arise from the approximate equalities of each nuclear attraction term with a sum of electron repulsion terms for the electron surrounding each atom

$$z_A \langle \mu | \frac{1}{r_A} | \nu \rangle \approx 2 \sum_{i \in A} l_i \langle \mu\nu \mid \theta_i \theta_i \rangle. \tag{27}$$

We illustrate this point by means of Fig. 3.

As can be seen from Figure 3, the l_1 terms of Eq. (27) arise from the division of the localized orbitals between atoms. Since the orbitals θ_2 to θ_5 are localized

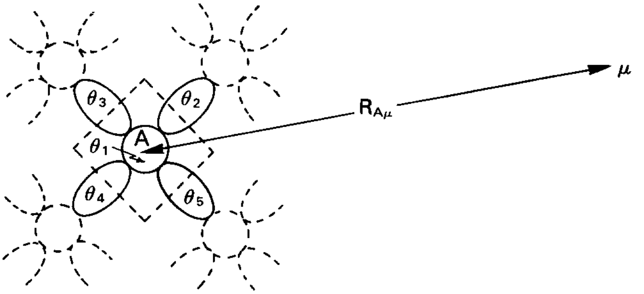


Fig. 3. Illustration of the division of localized orbitals surrounding atom A in a hydrocarbon

in bonds with their respective electron repulsion terms being divided between A and the appropriate neighbouring atom, their associated l_i values are

$$l_2 = l_3 = l_4 = l_5 = \tfrac{1}{2}.$$

The orbital θ_1 since it is localized in the core on atom A will have

$$l_1 = 1.$$

If A is approximately electrically neutral the number of electron repulsion terms counted in Eq. (27) will be equal to z_A.

For a diagonal term, if r_A is large, both the electron attraction term and the sum of electron repulsion terms will approach the classical limit. That is

$$z_A\langle\mu|\frac{1}{r_A}|\mu\rangle \approx 2\sum_{i\in A} l_i\langle\mu\mu\,|\,\theta_i\theta_i\rangle \approx \frac{z_A}{R_{A\mu}} \tag{28}$$

where $R_{A\mu}$ is the distance from atom A to the centre of orbital μ. Similarly, the off diagonal terms can be reduced to the classical limit using the Mulliken approximation

$$\chi_\mu\chi_\nu \approx \frac{S_{\mu\nu}}{2}\{\chi_\mu\chi_\mu + \chi_\nu\chi_\nu\} \tag{29}$$

$$\begin{aligned}\sum_{i\in A}\langle\mu\nu\,|\,\theta_i\theta_i\rangle &\approx \frac{S_{\mu\nu}}{2}2\sum_{i\in A} l_i\{\langle\mu\mu\,|\,\theta_i\theta_i\rangle + \langle\nu\nu\,|\,\theta_i\theta_i\rangle\}\\ &\approx \frac{z_A}{2}S_{\mu\nu}\left\{\frac{1}{R_{A\mu}}+\frac{1}{R_{A\nu}}\right\}\end{aligned} \tag{30}$$

$$\begin{aligned}z_A\langle\mu|\frac{1}{r_A}|\nu\rangle &\approx \frac{z_A}{2}S_{\mu\nu}\left\{\langle\mu|\frac{1}{r_A}|\mu\rangle + \langle\nu|\frac{1}{r_A}|\nu\rangle\right\}\\ &\approx \frac{z_A}{2}S_{\mu\nu}\left\{\frac{1}{R_{A\mu}}+\frac{1}{R_{A\nu}}\right\}.\end{aligned} \tag{31}$$

The equalities in Eqs. (28) and (30) only hold if the "number of electrons" or atomic population around A, N_A is approximately equal to z_A. However, some cancellation will occur in the term by term errors in the sums occurring in Eqs. (25) and (26) for those cases where atomic charges alternate along a chain going away from the segment S.

From the above analysis it is clear that direct transferability for ionic molecules is not possible where a neutral pattern molecule is used for Fock matrix elements distant from the ionic charge. In this case the ionic charge will affect the terms outside the segment. This situation was studied previously (11) and an empirical correction term introduced.

$$F^T_{\mu\nu} = F^P_{\mu\nu} - \sum_A q^P_A\langle\chi_\mu|\frac{1}{r_A}|\chi_\nu\rangle. \tag{32}$$

Here, q_A^P is a Mulliken charge transferred from the ionic pattern to the region of the target outside the segment defined for $F_{\mu\nu}^T$. It can now be seen that this correction follows from the present analysis.

For an atom A outside the segment

$$2\sum l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle \approx N_A\langle\mu|\frac{1}{r_A}|\nu\rangle \tag{33}$$

where N_A is a Mulliken population. Thus we have:

$$\begin{aligned} F_{\mu\nu}^T - F_{\mu\nu}^P &\approx 2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle - \sum_{A\notin S}\langle\mu|\frac{z_A}{r_A}|\nu\rangle^T \\ &\approx \sum_{A\notin S}(N_A - z_A)\langle\mu|\frac{1}{r_A}|\nu\rangle^T \\ &= -\sum q_A^T\langle\mu|\frac{1}{r_A}|\nu\rangle^T \end{aligned} \tag{34}$$

where we define q_A, the Mulliken atomic charge as

$$q_A = (z_A - N_A). \tag{35}$$

3. A Justification of Transferability for Open Shell Systems

The SAMO method has been applied to open shell systems using the spin unrestricted – Unrestricted Hartree–Fock (UHF) or Different Orbitals for Different Spins (DODS) [12, 28] – and the spin restricted – Restricted Hartree Fock (RHF) [13, 29] formalisms. In each case the chosen radical was rather specialized in that its odd electron was localized in one region of the target molecule. With this constraint it is possible to transfer the matrix elements for the radical region of the target from a similar open shell calculation on a small pattern radical; the more distant matrix elements are transferred from a closed shell calculation. We analyse the approach in terms of each of the above formalisms as follows:

3.1. Spin Unrestricted

In the spin unrestricted formalism, the wave function is given by

$$\psi = A\{\phi_1^\alpha(1)\phi_2^\alpha(2)\cdots\phi_{m_\alpha}^\alpha(m_\alpha)\phi_1^\beta(m_\alpha+1)\phi_2^\beta(m_\alpha+2)\cdots\phi_{m_\beta}^\beta(m_\alpha+m_\beta) \tag{36}$$

where there are m_α electrons with α spin and m_β electrons of β spin. In the specialized cases studied

$$m_\alpha = m_\beta + 1. \tag{37}$$

The set of orbitals ϕ_i^α are different from the set ϕ_i^β and are given by

$$\phi_i^\alpha = \sum_{\mu=1}^{n} C_{\mu i}^\alpha \chi_\mu \tag{38}$$

$$\phi_i^\beta = \sum_{\mu=1}^{n} C_{\mu i}^\beta \chi_\mu. \tag{39}$$

The coefficients at the *ab initio* level are given by the solutions of the coupled matrix equations

$$\boldsymbol{F}^\alpha \boldsymbol{C}^\alpha = \boldsymbol{S}\boldsymbol{C}^\beta \boldsymbol{\lambda}^\alpha \tag{40}$$

$$\boldsymbol{F}^\beta \boldsymbol{C}^\beta = \boldsymbol{S}\boldsymbol{C}^\beta \boldsymbol{\lambda}^\beta \tag{41}$$

where $\boldsymbol{S}$ is defined by equation (6), $\boldsymbol{\lambda}^\alpha$ and $\boldsymbol{\lambda}^\beta$ are diagonal matrices of orbital energies for the two sets of orbitals and

$$F_{\mu\nu}^\alpha = T_{\mu\nu} - \sum \langle \mu | \frac{Z_A}{r_A} | \nu \rangle + \sum_{i=1}^{m_\alpha} \langle \mu\nu | \phi_i^\alpha \phi_i^\alpha \rangle + \sum_{i=1}^{m_\beta} \langle \mu\nu | \phi_i^\beta \phi_i^\beta \rangle - \sum_{i=1}^{m_\alpha} \langle \mu \phi_i^\alpha | \nu \phi_i^\alpha \rangle. \tag{42}$$

The element $F_{\mu\nu}^\beta$ is defined similarly to Eq. (42), the difference being that α is replaced by β and β by α throughout the equation. All terms in Eq. (42) are defined previously by Eqs. (9)–(11).

The two sets ϕ_i^α and ϕ_i^β can be independently transferred into the localized orbital sets θ_i^α and θ_i^β by means of the transformations

$$\boldsymbol{\theta}^\alpha = \boldsymbol{L}^\alpha \boldsymbol{\phi}^\alpha \tag{43}$$

$$\boldsymbol{\theta}^\beta = \boldsymbol{L}^\beta \boldsymbol{\phi}^\beta \tag{44}$$

respectively, where, as before, $\boldsymbol{L}^\alpha$ and $\boldsymbol{L}^\beta$ are unitary. Under these transformations Eqs. (36) and (42) become

$$\psi = A\{\theta_1^\theta(1)\theta_2^\alpha \cdots \theta_{m_\alpha}^\alpha(m_\alpha)\theta_1^\beta(m_\alpha+1) \cdots \theta_{m_\beta}^\beta(m_\alpha+m_\beta) \tag{45}$$

$$F_{\mu\nu}^\alpha = T_{\mu\nu} - \sum_A \langle \mu | \frac{Z_A}{r_A} | \nu \rangle + \sum_{i=1}^{m_\alpha} \langle \mu\nu | \theta_i^\alpha \theta_i^\alpha \rangle + \sum_{i=1}^{m_\beta} \langle \mu\nu | \theta_i^\beta \theta_i^\beta \rangle - \sum_{i=1}^{m_\alpha} \langle \mu \theta_i^\alpha | \nu \theta_i^\alpha \rangle. \tag{46}$$

The transference of matrix elements is shown in Fig. 4.

From Fig. 4 we see that since the odd electron is localized at the right of the target molecule, the localized pattern orbitals θ_P^α and θ_P^β will only differ significantly in this region. For matrix elements not obtainable from the open-shell *P*, it was assumed that

$$F_{\mu\nu}^{\alpha T} = F_{\mu\nu}^{\beta T} \tag{47}$$

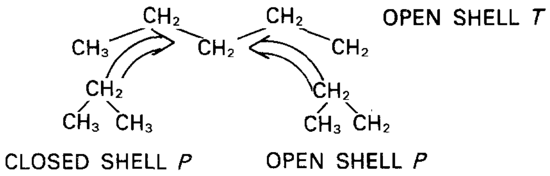


Fig. 4. Illustration of the transfer of matrix elements for open-shell systems

and that each could be obtained by transference from a closed shell P. The two cases are now dealt with separately.

3.1.1. Open shell P

A pair of matrix elements $F^{\alpha T}_{\mu\nu}$ and $F^{\beta T}_{\mu\nu}$ are obtained from $F^{\alpha P}_{\mu\nu}$ and $F^{\beta T}_{\mu\nu}$. This choice defines a common segment S entirely similar to the closed shell cases. Eq. (46) for $F^{\alpha T}_{\mu\nu}$ and $F^{\beta P}_{\mu\nu}$ can be separated with terms inside and outside S. As was the case for closed shell systems, the terms $T_{\mu\nu}$ and summations inside S are now either identical or approximately equal for $F^{\alpha T}_{\mu\nu}$ and $F^{\beta P}_{\mu\nu}$ since

$$\theta_i^{\alpha P} \approx \theta_i^{\alpha P}. \tag{48}$$

The remaining error, analogous to Eq. (22) for the closed shell case, is

$$\begin{aligned} F^{\alpha T}_{\mu\nu} - F^{\alpha P}_{\mu\nu} = {} & \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\alpha T} \theta_i^{\alpha T} \rangle + \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\beta T} \theta_i^{\beta T} \rangle - \sum_{A \notin S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^T \\ & - \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\alpha P} \theta_i^{\alpha P} \rangle - \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\beta T} \theta_i^{\beta T} \rangle + \sum_{A \notin S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^P \\ & - \sum_{i \notin S} l_i \langle \mu \theta_i^{\alpha T} | \nu \theta_i^{\alpha T} \rangle + \sum_{i \notin S} l_i \langle \mu \theta_i^{\alpha P} | \nu \theta_i^{\alpha P} \rangle. \end{aligned} \tag{49}$$

As with the closed shell case, $l_i = 1$ when θ_i lies completely inside or completely outside the segment S. However, when θ_i lies across the segment boundary $l_i = \frac{1}{2}$. Since the odd electron is inside S the extra term in the summation over θ_i^{α} compared with the summation over θ_i^{β} is already taken care of in the sums within S. The sums over i in Eq. (49) will thus all have the same number of electrons. By an argument entirely analogous to the closed shell case – exchange terms are small and Coulomb terms cancel nuclear attraction terms atom by atom. Thus, Eq. (49) reduces to

$$F^{\alpha T}_{\mu\nu} - F^{\alpha P}_{\mu\nu} \approx 0. \tag{50}$$

3.1.2. Closed shell P

The choice of $F^{P}_{\mu\nu}$ for both $F^{\alpha T}_{\mu\nu}$ and $F^{\beta T}_{\mu\nu}$ again defines a common segment S. Sums can be defined inside and outside S as follows:

$$\begin{aligned} F^{\alpha T}_{\mu\nu} = {} & T_{\mu\nu} - \sum_{A \in S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^T + \sum_{i \in S} l_i \langle \mu\nu | \theta_i^{\alpha T} \theta_i^{\alpha T} \rangle \\ & + \sum_{i \in S} l_i \langle \mu\nu | \theta_i^{\beta T} \theta_i^{\beta T} \rangle - \sum_{i \in S} l_i \langle \mu \theta_i^{\alpha T} | \nu \theta_i^{\alpha T} \rangle \\ & - \sum_{A \notin S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^T + \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\alpha T} \theta_i^{\alpha T} \rangle \\ & + \sum_{i \notin S} l_i \langle \mu\nu | \theta_i^{\beta T} \theta_i^{\beta T} \rangle - \sum_{i \notin S} l_i \langle \mu \theta_i^{\alpha T} | \nu \theta_i^{\alpha T} \rangle \end{aligned} \tag{51}$$

$$\begin{aligned} F^{\beta T}_{\mu\nu} = T_{\mu\nu} &- \sum_{A\in S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T + \sum_{i\in S} l_i\langle\mu\nu|\theta_i^{\alpha T}\theta_i^{\alpha T}\rangle \\ &+ \sum_{i\in S} l_i\langle\mu\nu|\theta_i^{\beta T}\theta_i^{\beta T}\rangle - \sum_{i\in S} l_i\langle\mu\theta_i^{\beta T}|\nu\theta_i^{\beta T}\rangle \\ &- \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T + \sum_{i\notin S} l_i\langle\mu\nu|\theta_i^{\alpha T}\theta_i^{\alpha T}\rangle \\ &+ \sum_{i\notin s} l_i\langle\mu\nu|\theta_i^{\beta T}\theta_i^{\beta T}\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^{\beta T}|\nu\theta_i^{\beta T}\rangle \end{aligned} \tag{52}$$

$$\begin{aligned} F^{P}_{\mu\nu} = T_{\mu\nu} &- \sum_{A\in S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P + 2\sum_{i\in S} l_i\langle\mu\nu|\theta_i^{P}\theta_i^{P}\rangle \\ &- \sum_{i\in S} l_i\langle\mu\theta_i^{P}|\nu\theta_i^{P}\rangle - \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_a}|\nu\rangle^P \\ &+ \sum_{i\notin S} l_i\langle\mu\nu|\theta_i^{P}\theta_i^{P}\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^{P}|\nu\theta_i^{P}\rangle. \end{aligned} \tag{53}$$

Eqs. (51) and (52) give

$$\begin{aligned} F^{\alpha T}_{\mu\nu} - F^{\beta T}_{\mu\nu} = &\sum_{i\in S} l_i\langle\mu\theta_i^{\beta T}|\nu\theta_i^{\beta T}\rangle - \sum_{i\in S} l_i\langle\mu\theta_i^{\alpha T}|\nu\theta_i^{\alpha t}\rangle \\ &+ \sum_{i\notin S} l_i\langle\mu\theta_i^{\beta T}|\nu\theta_i^{\beta T}\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^{\alpha T}|\nu\theta_i^{\alpha T}\rangle. \end{aligned} \tag{54}$$

The orbitals θ_i^α and $\theta_i^\beta \in S$ will be very similar and the exchange terms for $\theta_i \notin S$ will be small and also practically cancel. Hence

$$F^{\alpha T}_{\mu\nu} \approx F^{\beta T}_{\mu\nu}. \tag{55}$$

Furthermore, the orbitals θ_i^α and $\theta_i^\beta \in S$ will be transferable from the pattern closed shell molecule

$$\theta_i^{\alpha T} \approx \theta_i^{\beta T} \approx \theta_i^{P}. \tag{56}$$

By an argument entirely analogous to the closed shell case, $T_{\mu\nu}$ and all sums $\in S$ cancel giving

$$\begin{aligned} F^{\alpha T}_{\mu\nu} - F^{P}_{\mu\nu} \approx &\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^{\alpha T}\theta_i^{\alpha T}\rangle + \sum_{i\notin S} l_i\langle\mu\nu|\theta_i^{\beta T}\theta_i^{\beta T}\rangle - \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^T \\ &-2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^{P}\theta_i^{P}\rangle - \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^P \\ &- \sum_{i\notin S} l_i\langle\mu\theta_i^{\alpha T}|\nu\theta_i^{\alpha T}\rangle + \sum_{i\notin S} l_i\langle\mu\theta_i^{P}|\nu\theta_i^{P}\rangle. \end{aligned} \tag{57}$$

The terms for P have already been considered in the closed shell case. The exchange term for T is similarly small. For the Coulomb terms the number of terms over θ_i^α differs from that over θ_i^β as the extra α spin electron is included in the former. However, just as for the closed shell case, each atom $\notin S$ is formally neutral and the number of electrons in θ_i^α and θ_i^β around each atom A balances z_A. Thus

$$F_{\mu\nu}^{\alpha T} - F_{\mu\nu}^{P} \approx 0. \tag{58}$$

3.2. *Spin Restricted*

In the spin restricted formalism, the wave function is given by

$$\psi = A\{\phi_1(1)\alpha\phi_1(2)\beta \cdots \phi_m(2m-1)\alpha\phi_m(2m)\beta\phi_s\alpha(2m+1)\} \tag{59}$$

where the number of electrons is $2m+1$, m orbitals are doubly occupied and one orbital ϕ_s is singly occupied. The orbitals are expanded in the usual way over the basis χ_μ. The solution of the usual variation problem is not unique; it can, as described in Ref. [13], be carried out in matrix form where the associated Hamiltonian matrices are defined in several ways. All these matrices can be defined in terms of the two matrices $\boldsymbol{F}$ and $\boldsymbol{\Delta F}$ and it is elements of these that are transferred in the SAMO method. They are defined as:

$$\begin{aligned} F_{\mu\nu} = T_{\mu\nu} - \sum_A \langle\mu|\frac{z_A}{r_A}|\nu\rangle + \sum_{i=1}^{m} 2\langle\mu\nu|\phi_i\phi_i\rangle \\ - \sum_{i=1}^{m} \langle\mu\phi_i|\nu\phi_i\rangle + \langle\mu\nu|\phi_s\phi_s\rangle - \tfrac{1}{2}\langle\mu\phi_s|\nu\phi_s\rangle \end{aligned} \tag{60}$$

$$\Delta F_{\mu\nu} = \tfrac{1}{2}\langle\mu\phi_s|\nu\phi_s\rangle. \tag{61}$$

The sets of delocalized orbitals, ϕ_i and ϕ_s can be localized separately. Since ϕ_s is a single orbital already well localized no localization is necessary. The set ϕ_i is transferred into a localized set θ_i by means of some unitary transformation $\boldsymbol{L}$

$$\boldsymbol{\theta} = \boldsymbol{L}\boldsymbol{\phi} \tag{62}$$

giving

$$\psi = A\{\theta_1(1)\alpha_1(2)\beta \cdots \theta_m(2m-1)\alpha\theta_m(2m)\beta\phi_s\alpha(2m+1)\} \tag{63}$$

$$\begin{aligned} F_{\mu\nu} = T_{\mu\nu} - \sum \langle\mu|\frac{z_A}{r_A}|\nu\rangle + \sum_{i=1}^{m} 2\langle\mu\nu|\theta_i\theta_i\rangle \\ - \sum_{i=1}^{m} \langle\mu\theta_i|\nu\theta_i\rangle + \langle\mu\nu|\phi_s\phi_s\rangle - \tfrac{1}{2}\langle\mu\phi_s|\nu\phi_s\rangle. \end{aligned} \tag{64}$$

The actual transference of Fock matrix elements is carried out in a manner identical to that used in the spin unrestricted case. Thus both an open and a closed shell pattern molecule is used, and again we deal with the two cases separately.

3.2.1. Open shell P

Elements of both $\boldsymbol{F}$ and $\boldsymbol{\Delta F}$ are transferred. For both target and pattern molecule the matrix element can be divided into sums inside and outside the common area S.

$$\begin{aligned}F_{\mu\nu}^{T} = T_{\mu\nu} - \sum_{A\in S} \langle\mu|\frac{Z_A}{r_A}|\nu\rangle^{T} + 2\sum_{i\in S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle \\ - \sum_{i\in S} l_i\langle\mu\theta_i^T|\nu\theta_i^T\rangle + \langle\mu\nu|\phi_s^T\phi_s^T\rangle - \tfrac{1}{2}\langle\mu\phi_s^T|\nu\phi_s^T\rangle - \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^{T} \\ + 2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle - \sum_{i\notin S} l_i\langle\mu\theta_i^T|\nu\theta_i^T\rangle. \qquad (65)\end{aligned}$$

A similar expression can be written for the element $F_{\mu\nu}^{P}$. Those terms involving ϕ_s can be considered along with all other terms $\in S$ in both $F_{\mu\nu}^{T}$ and $F_{\mu\nu}^{P}$ and, as was the case previously, all terms $\in S$ cancel in the difference $F_{\mu\nu}^{T} - F_{\mu\nu}^{P}$ since

$$\theta_i^T \approx \theta_i^P \qquad (66)$$

$$\phi_s^T \approx \phi_s^P. \qquad (67)$$

Thus

$$\begin{aligned}F_{\mu\nu}^{T} - F_{\mu\nu}^{P} \approx 2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^T\theta_i^T\rangle - \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^{T} \\ -2\sum_{i\notin S} l_i\langle\mu\nu|\theta_i^P\theta_i^P\rangle + \sum_{A\notin S}\langle\mu|\frac{Z_A}{r_A}|\nu\rangle^{P} \\ - \sum_{i\notin S} l_i\langle\mu\theta_i^T|\nu\theta_i^T\rangle + \sum_{i\notin S} l_i\langle\mu\theta_i^P|\nu\theta_i^P\rangle. \qquad (68)\end{aligned}$$

Since Eq. (68) is identical to Eq. (22) we have, using the same reasoning as was used for Eq. (22),

$$F_{\mu\nu}^{T} - F_{\mu\nu}^{P} \approx 0. \qquad (69)$$

The term in $\Delta F_{\mu\nu}$ lies inside the common segment S so, using Eq. (67) we have

$$\Delta F_{\mu\nu}^{T} - \Delta F_{\mu\nu}^{P} \approx 0. \qquad (70)$$

3.2.2. Closed shell P

Here, $F_{\mu\nu}^{T}$ is transferrred from $F_{\mu\nu}^{P}$ using a closed shell calculation for P while $\Delta F_{\mu\nu}^{T}$ is neglected. The element $F_{\mu\nu}^{T}$ is split over terms inside and outside S to give Eq. (65). Now, however, terms involving ϕ_s are grouped with terms outside S.

The element $F^P_{\mu\nu}$ is given by Eq. (53). Again, the terms $T_{\mu\nu}$ and those sums over atoms and θ_i inside S cancel giving

$$\begin{aligned} F^T_{\mu\nu} - F^P_{\mu\nu} \approx {} & 2 \sum_{i \notin S} l_i \langle \mu\nu | \theta^T_i \theta^T_i \rangle - \sum_{A \in S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^T \\ & -2 \sum_{i \notin S} l_i \langle \mu\nu | \theta^P_i \theta^P_i \rangle + \sum_{A \notin S} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle^P \\ & + \langle \mu\nu | \phi^T_s \phi^T_s \rangle - \tfrac{1}{2} \langle \mu \phi^T_s | \nu \phi^T_s \rangle \\ & - \sum_{i \notin S} l_i \langle \mu \theta^T_i | \nu \theta^T_i \rangle + \sum_{i \notin S} l_i \langle \mu \theta^P_i | \nu \theta^P_i \rangle. \end{aligned} \tag{71}$$

Eq. (71) is similar in form to Eq. (23). The Coulomb term in ϕ^T_s is grouped with terms θ^T_i around the terminal carbon atom to balance out the nuclear attraction term. Thus

$$F^T_{\mu\nu} - F^P_{\mu\nu} \approx 0. \tag{72}$$

The term $\Delta F^T_{\mu\nu}$ is given by Eq. (61). Since ϕ_s lies outside S this exchange term, along with all the other exchange terms, is small, so

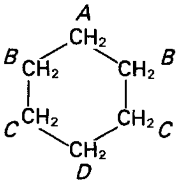
$$\Delta F^T_{\mu\nu} \approx 0. \tag{73}$$

4. Two Difficult Cases

Studies on cyclohexane [10], benzene [9] and pyrazine [16] as target molecules have shown that larger errors arise with SAMO calculations on ring compounds built from chain pattern molecules than arise in other applications of the method. For cyclohexane [10] an empirical correction was introduced using the concept of splitting the Fock matrix element into "through bond" and "through space" contributions. We now show that the present analysis justifies this correction and that the large errors in benzene and pyrazine are to be expected.

4.1. Cyclohexane

In the simulation of an ab initio calculation on cyclohexane using butane as the pattern molecule an empirical correction was introduced for the Fock matrix element $f = F_{\mu\nu}$ where the atoms of cyclohexane are labelled as shown below with $\chi_\mu \in A$ and $\chi_\mu \in D$.



Since there are two bonding pathways from A to D we may write f as

$$f = 2b + s. \tag{74}$$

where b is a bonding pathway contribution and s a direct space contribution. For butane we have

$$f = b + s. \tag{75}$$

The direct space contribution was estimated from a pair of methane molecules positioned to mirror the groups A and D. The resulting empirical correction was thus

$$f^C = 2f^B - f^M \tag{76}$$

where f^C, f^B and f^M are the matrix elements for cyclohexane, butane, and the methane pair respectively.

Although it results in corrections that work well, this approach is unsatisfactory. In order to analyse this problem in terms of our present study we introduce the three systems illustrated in Fig. 5.

Each system in Fig. 5 is divided into labelled common segments. For simplicity we chose a symmetric f where

$$f^C = F_{\mu\nu} \qquad \chi_\mu \in A; \qquad \chi_\nu \in B \tag{77}$$

$$\text{e.g. } \chi_\mu = 2s \text{ on } C_A$$
$$\chi_\nu = 2s \text{ on } C_B.$$

In a non symmetric case, i.e. where χ_μ and χ_ν are not symmetric on the plane AB, the butane pattern positioned to the left of the $A'B'$ plane must also be considered. In each case the molecular orbitals are transferred into localized orbitals. For a segment X we now define

$$Y_X = -\sum_{A \in X} \langle \mu | \frac{Z_A}{r_A} | \nu \rangle + 2 \sum_{i \in X} l_i \langle \mu\nu | \theta_i \theta_i \rangle - \sum_{i \in X} l_i \langle \mu\theta_i | v\theta_i \rangle. \tag{78}$$

Here l_i is 1 if θ_i is entirely inside X and $\frac{1}{2}$ if θ_i crosses the segment boundary. Using this simplified nomenclature the three relevant Fock elements become

$$f^C = T^C + Y_A + Y_B + Y_C + Y_D \tag{79}$$

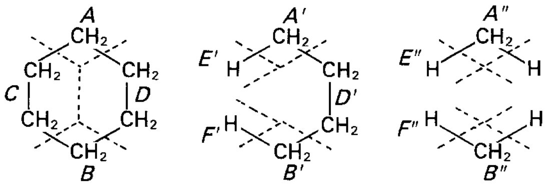


Fig. 5. Illustration of systems used in the analysis of the cyclohexane problem

$$f^B = T^B + Y_{A'} + Y_{B'} + Y_{D'} + Y_{E'} + Y_{F'} \tag{80}$$

$$f^M = T^M + Y_{A''} + Y_{B''} + Y_{E''} + Y_{F''} + Y_{G''} + Y_{H''} \tag{81}$$

where the kinetic energy term for a general system U is

$$T^U = T_{\mu\nu} \tag{82}$$

If localized orbitals are transferable between the three systems and, where appropriate, the geometries are identical, the three kinetic energy terms T^C, T^B and T^M are equal and

$$Y_A \approx Y_{A'} \approx Y_{A''} \tag{83}$$

$$Y_B \approx Y_{B'} \approx Y_{B''} \tag{84}$$

$$Y_D \approx Y_{D''} = Y_C \tag{85}$$

$$Y_{E'} \approx Y_{E''} = Y_{C''} \tag{86}$$

$$Y_F \approx Y_{F''} = Y_{H''} \tag{87}$$

(exact equalities arise from symmetry).

Thus

$$f^C \approx 2f^B - f^M. \tag{88}$$

Hence, the empirical term introduced previously is correct if localized orbitals are transferable. A similar analysis holds for the non symmetrical matrix element.

4.2. Benzene

Benzene [9] and other aromatic hydrocarbons [9, 14] have been simulated from butadiene having a benzene-like geometry. Localized orbitals can be formed for benzene, the π orbitals being localized in either Kekule structure. The transference of a 1,4 symmetric matrix element is illustrated in Fig. 6, where a grouping similar to that in cyclohexane is used.

Defining the Fock matrix element for benzene as f^Z and for butadiene as f^D, we have

$$f^Z = T^Z + Y_A + Y_B + Y_C + Y_D \tag{89}$$

$$f^D = T^B + Y_{A'} + Y_{B'} + Y_{D'} + Y_{E'} + Y_{F'}. \tag{90}$$

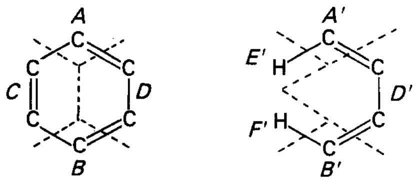


Fig. 6. Illustration of the transference of a 1,4 symmetric matrix element in benzene

If localized orbitals are transferable

$$\left.\begin{aligned} Y_A &\approx Y_{A'} \\ Y_B &\approx Y_{B'} \\ Y_D &\approx Y_{D'} \end{aligned}\right\} \tag{91}$$

and

$$f^Z - f^D = Y_C - Y_{E'} + Y_{F'}. \tag{92}$$

Although all the Y terms are comparable to terms outside the common segment discussed above, in the case of a compact ring system such as benzene they are not likely to be negligible. Here, in contrast to the situation for cyclohexane, no correction for the "through space" contribution appears possible since no suitable pattern system can be formulated. Thus, the increased errors arising with ring systems are to be expected. The error given by Eq. (89), although fairly small, will be larger than corresponding terms for more open systems.

5. Conclusion

We simplify the equations arising from our discussion of the closed shell case by using the Y_X term defined above for cyclohexane. Thus, where the region $\neg S$ is the complement of S, i.e. the atoms and localized orbitals not contained in the common segment S, the Fock matrix element $F_{\mu\nu}$ may be expressed as

$$F_{\mu\nu} = T_{\mu\nu} + (Y_S)_{\mu\nu} + (Y_{\neg S}))_{\mu\nu}. \tag{93}$$

This gives the error $F^T_{\mu\nu} - F^P_{\mu\nu}$ as a sum of short and long range terms

$$F^T_{\mu\nu} - F^P_{\mu\nu} = [(Y^T_S)_{\mu\nu} - (Y^P_S)_{\mu\nu}] + [(Y^T_{\neg S})_{\mu\nu} - (Y^P_{\neg S})_{\mu\nu}]. \tag{94}$$

In light of this, the SAMO approximations may be summarized as

1) The use of identical geometries and bases sets in the common segment S defined for each matrix element $F_{\mu\nu}$. This results in an exact cancellation of kinetic energy integrals and nuclear attraction integrals over atoms within the common segment.

2) An assumption of transferability of localized orbitals within the common segment arising from the selection of a pattern molecule with a chemical and bonding environment closely similar to that found within this segment of the target molecule. This completes the cancellation of terms within the first bracket of Eq. (94).

3) The neglect of long range terms by separate cancellations within each of the terms in the second bracket of Eq. (94).

4) The neglect of matrix elements $F_{\mu\nu}$ where the orbitals χ_μ and χ_μ are at a sufficiently large distance as to render them unobtainable from the pattern molecules.

This point is not covered by the present analyses as it is dependent on the choice of the pattern molecule. The size of pattern molecule is thus crucial in determining the number of neglected matrix elements as well as the size of the error in transferred matrix elements.

An analysis entirely similar to that for the molecular case can be used to justify the application of the SAMO method to infinite polymers. The main difference here being that the term $Y^{T}_{\rightarrow S}$ now contains infinite sums and, where χ_μ and χ_ν are distant, an infinite number of $F_{\mu\nu}$ terms are neglected. As, however, we shall see, these SAMO approximations now have counterparts in the *ab initio* case.

For polymers with translational symmetry using Block orbitals we solve

$$\boldsymbol{F}(k)\boldsymbol{C}(k)=\boldsymbol{S}(k)\boldsymbol{C}(k)\boldsymbol{\lambda}(k) \tag{95}$$

in both the ab initio and SAMO methods. Here the $\boldsymbol{C}(k)$ elements are defined by the expansion of the crystal orbitals

$$\phi_i(k)=(2\mathcal{N}+1)^{-1/2}\sum_{j=-\mathcal{N}}^{+\mathcal{N}}\sum_{\mu=1}^{n}C_{ip}(k)e^{ikjr}\chi^{j}_{\mu} \tag{96}$$

where the translational cells labelled j each contain a basis of n orbitals χ^{j}_{μ}.

$$\boldsymbol{F}_{\mu\nu}(k)=\sum_{j=-\mathcal{N}}^{+\mathcal{N}}e^{ikjr}\boldsymbol{F}^{j}_{\mu\nu} \tag{97}$$

where

$$F^{j}_{\mu\nu}=\langle\chi^{0}_{\mu}|\hat{F}|\chi^{j}_{\nu}\rangle \tag{98}$$

$$\boldsymbol{S}_{\mu\nu}(k)=\sum_{j=-\mathcal{N}}^{+\mathcal{N}}e^{ikjr}\boldsymbol{S}^{j}_{\mu\nu} \tag{99}$$

where

$$\boldsymbol{S}^{j}_{\mu\nu}=\langle\chi^{0}_{\mu}|\chi^{j}_{\nu}\rangle. \tag{100}$$

While in theory $\mathcal{N}$ should be allowed to increase to infinity, in practice the sums have to be truncated at N. Indeed, in the many *ab initio* cases where N is only 1 or 2 the order of the neglected matrix elements $F^{j}_{\mu\nu}$ ($j<-N$ or $j>N$) is similar to that of the SAMO method. Thus approximation (4) is a feature of both *ab initio* and SAMO polymer calculations.

Using a nomenclature similar to that of Piela et al. (3) we express the retained terms F^{j}_{pq} as

$$\begin{aligned}F^{j}_{\mu\nu}&=T^{j}_{\nu}-\sum_{h=-\mathcal{N}}^{\mathcal{N}}\sum_{A}z_A V_\mu(h,A)\\&\quad+\sum_{h=-\mathcal{N}}^{\mathcal{N}}\sum_{l=-\mathcal{N}}^{\mathcal{N}}\sum_{\lambda}\sum_{\sigma}D^{hl}_{\lambda\sigma}\Big[2\Big({}^{oj}_{\mu\nu}\Big|{}^{hl}_{\lambda\sigma}\Big)-\Big({}^{oh}_{\mu\lambda}\Big|{}^{j}_{\nu\sigma}\Big)\Big].\end{aligned} \tag{101}$$

Again, these sums must be truncated by a partition

$$F^j_{\mu\nu} = F^j_{\mu\nu}(\leq N) + F^j_{\mu\nu}(>N). \tag{102}$$

Here, $F^j_{\mu\nu}(\leq N)$ is the term left after truncation to N cells either side of the reference cell 0 and $F^j_{\mu\nu}(>N)$ is the error term. We note that Piela et al. [30] and other workers use $C^j_{\mu\nu}$ for $F^j_{\mu\nu}(>N)$ in Eq. (102), a term that has, until recently, been neglected. Truncation and hence partitioning can be carried out in a number of ways fully described by Karpfen [31] and Kertesz et al. [32]. Eq. (102) with its division between short range and long range terms is entirely analogous to Eq. (93); $T_{\mu\nu}$ in Eq. (93) is, of course, included in the short range term. Evaluation of the long range term using multipole expansions has recently been proposed by Delhalle et al. [33] and extended by Piela et al. [30]. Approximation [3] of the SAMO method is thus equivalent to the neglect of multipole terms. Work is in progress to include these in the SAMO method, particularly for polymers. As a consequence of this analysis it is clear that, at least for many of the published *ab initio* polymer calculations, the SAMO method is closer to the *ab initio* method for polymers than it is to the *ab initio* method for molecules.

Analysis of the open shell cases, while apparently more complex, involves essentially the same approximations as discussed for the closed shell system. Additional but minor approximations arise only from the particular nature of the molecular systems studied. Our present study serves to clarify the rather limited application of the SAMO method to open shell systems. One particularly pleasing aspect of our analysis is that previous *ad hoc* approximations introduced for ionic molecules and cyclic systems, since they are now seen to be justified by the same analysis used for more normal systems, are no longer *ad hoc.*

Finally, while the present analysis is expressed in terms of the SAMO method, it is equally applicable to other related methods involving the transferability of Fock matrix elements. The poor performance of the NEMO method [2] can be readily explained when it is realized that the common segment for transfer of the diagonal matrix elements is often as small as a single atom. The method using a basis set of localized orbitals developed by Peeters, Leroy and Clarisse [5, 19, 20] and recently extended by them [34] can be analysed in an identical manner. The molecular orbitals are expressed as a linear combination of localized orbitals which are transferable from a pattern to a target. The basis set thus has the same properties for this analysis as the SAMO basis and the matrix elements $F_{\mu\nu}$ over this basis can be partitioned as in Eq. (93). The localized orbitals introduced in the definitions of Y_S and $Y_{\neg S}$ are now, in principle, distinct from the localized orbitals used as the working basis and may be assumed to have been generated by a different localization technique. In practice, of course, the two sets of localized orbitals may be similar but this is not required. Leroy et al. [34] experience the same problems in obtaining a good simulation for polynuclear hydrocarbons as are found with SAMO in spite of using naphthalene as pattern molecule.

This analysis provides an understanding of the transferability of Fock matrix elements and methods of calculation based upon the transferability. It also provides guides for the development of improvements to such methods.

Appendix A

Occupied localized orbitals θ_p are formed from occupied molecular orbitals ϕ_i by

$$\theta_p = \sum_i L_{pi}\phi_i \tag{1a}$$

with

$$\langle \theta_p \mid \theta_q \rangle = \delta_{pq}\,;\ \langle \phi_i \mid \phi_j \rangle = \delta_{ij} \tag{2a}$$

$$\begin{aligned}\delta_{pq} &= \langle \theta_p \mid \theta_q \rangle = \left\langle \sum_i L_{pi}\phi_i \,\middle|\, \sum_j L_{qj}\phi_j \right\rangle \\ &= \sum_i \sum_j L_{pi}L_{qj}\langle \phi_i \mid \phi_j \rangle \\ &= \sum_i L_{pi}L_{qi}.\end{aligned} \tag{3a}$$

$$\therefore\quad \boldsymbol{L}\boldsymbol{L}^T = \mathbf{1} \qquad \boldsymbol{L} \text{ is unitary}$$

$$\therefore\quad \text{since } \boldsymbol{\theta} = \boldsymbol{L}\boldsymbol{\phi}, \qquad \boldsymbol{\phi} = \boldsymbol{L}^T\boldsymbol{\theta}$$

$$\phi_i = \sum_p L_{pi}\theta_p. \tag{4a}$$

The Fock matrix element in terms of the ϕ bases is

$$F_{\mu\nu} = H_{\mu\nu} + \sum_i \{2\langle \mu\nu \mid \phi_i\phi_i \rangle\langle \mu\phi_i \mid \nu\phi_i \rangle\}.$$

Using Eq. (4a)

$$\begin{aligned}F_{\mu\nu} &= H_{\mu\nu} + \sum_i \sum_p \sum_q L_{pi}L_{qi}\{2\langle \mu\nu \mid \theta_p\theta_q \rangle - \langle \mu\theta_p \mid \nu\theta_q \rangle\} \\ &= H_{\mu\nu} + \sum_p \sum_q \left\{\sum_i L_{pi}L_{qi}\right\}\{2\langle \mu\nu \mid \theta_p\theta_q \rangle - \langle \mu\theta_p \mid \nu\theta_q \rangle\} \\ &= H_{\mu\nu} + \sum_p \sum_q \delta_{pq}\{2\langle \mu\nu \mid \theta_p\theta_q \rangle - \langle \mu\theta_p \mid \nu\theta_q \rangle\} \\ &= H_{\mu\nu} + \sum_p \{2\langle \mu\nu \mid \theta_p\theta_p \rangle - \langle \mu\theta_p \mid \theta_p \rangle\}.\end{aligned}$$

Therefore the Fock matrix element in terms of the $\boldsymbol{\theta}$ basis takes exactly the same form as in the $\boldsymbol{\phi}$ basis.

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