QUANTUM THEORY PROJECT
FOR RESEARCH IN ATOMIC, MOLECULAR AND SOLID-STATE
CHEMISTRY AND PHYSICS
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA
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ABSTRACT

A molecular orbital method is described which can be applied to molecules where the restrictions of π-electron theory are not fulfilled. It has the following main characteristics: 1) Atomic SCF functions are used as a basis, 2) Core-valence interactions are treated by means of perturbation theory, 3) Mulliken type approximations are used for many-center integrals.

1. Introduction

Molecular quantum mechanics has made great advances in recent years with the help of electronic computers. Ab initio calculations of the electronic structure of many diatomic and some simple polyatomic molecules are now available and will be of increasing importance in the future. However, the amount of labor involved for such a treatment of many chemically interesting molecules is forbidding and makes simplifications necessary. In many cases even very crude approximations can give satisfactory answers to the chemist. For π-electron systems the semiempirical molecular orbital methods named after Hückel[1] and Pariser, Parr, and Pople[2] have been especially fruitful, and several attempts have been made to develop similar schemes for molecules of a more general type.

The extended Hückel or Wolfsberg-Helmholz approach[3] is particularly simple and has given important contributions to the theory of transition metal complexes. However, its theoretical foundation is rather weak and when a more accurate method is needed it seems desirable to base it on the self-consistent field method. Even this method in its non-empirical form has severe limitations, i.e. the neglect of electron correlation and the often very restricted set of basis orbitals employed. In spite of this we will make the MO-LCAO-SCF approximation our starting point and make further approximations and simplifications from there on leading to a scheme analogous to the Pariser-Parr-Pople method for π-electron systems. Since we want to be able to treat all kinds of molecules we cannot however make use of all simplifying assumptions in π-electron theory. Therefore our method is slightly more complex than the Pariser-Parr-Pople method. Several other authors have followed similar lines of thought. Two electron systems have been recently considered by Pohl and coworkers,[4] Klopman,[5] and Jenkins and Pedley.[6] Hart, Robin, and Kuebler[7] have used an approximate MO-LCAO-SCF method including overlap on the P_4 molecule, but with some approximations which are difficult to carry over to more general systems. Finally Pople and coworkers[8] and Kaufman[9] have developed methods making use of the zero-differential-overlap approximation.

The method presented here differs from previous work in several ways. The general principle has been to avoid adjustable parameters as far as possible. Atomic SCF-orbitals are used as basis functions and the eigenvalue relations fulfilled by these are used to simplify matrix elements of the Fock operators. This is an approach similar to the Goeppert-Mayer-Sklar approximation,[10] which is obtained if empirical ionization potentials are introduced for atomic orbital energies. The distinction between core and valence orbitals is explicitly made and core-valence interactions are discussed in terms of Löwdin's partitioning approach to perturbation theory. Since we keep track of the inner shells, we are able to deal with elements belonging to the same group of the periodic table on an equivalent basis, and thereby retain more of classical chemical concepts. For the application of the method to large molecules, integral approximations of the Mulliken type are introduced and their invariance properties discussed.

2. Basis orbitals

We choose as our atomic orbital basis analytical Hartree-Fock orbitals which, thanks to Clementi's calculations,[11] are now available for all atoms and positive ions with $Z \leqslant 36$. In this way we have restricted our basis to only those orbitals which are occupied in the atomic ground states. Compared to a minimal basis of Slater orbitals, analytical atomic Hartree-Fock orbitals are more diffuse and give a better energy in ab initio calculations.[12] The optimum orbitals obtained from molecular Hartree-Fock calculations seem to lie in between these two choices. Another advantage of Hartree-Fock orbitals over simple exponentials is that orbitals on one center are orthogonal to each other and are eigenfunctions to an effective Hamiltonian. Molecular integrals are however more difficult to calculate, a disadvantage which can partly be balanced by means of integral approximations.

3. Formal development of theory.

For a single determinant wavefunction all physical properties can be derived from the first-order or Fock-Dirac density matrix $\rho(1',1) = \sum_i \phi_i^*(1')\,\phi_i(1)$ where the summation extends over all occupied spinorbitals in the determinant. The total energy is given by

$$E = \sum_{g<h} Z_g Z_h / R_{gh} + \int h_1\, \rho_M(1',1)\, dx_1 + \frac{1}{2}\int \frac{1}{r_{12}} \{\rho_M(1,1)\rho_M(2,2) - \rho_M(1,2)\rho_M(2,1)\}\, dx_1\, dx_2 \tag{1}$$

and the effective Hamiltonian or Fock operator by

$$F_M = h_1 + \int dx_2\, \frac{1}{r_{12}} (1 - P_{12})\, \rho_M(2',2). \tag{2}$$

Here $h_1 = T_1 - \sum_g Z_g/r_{g1}$ is the sum of the one-particle kinetic energy operator T_1 and nuclear attractions Z_g/r_{g1}. We write the molecular Fock-Dirac density matrix ρ_M formally as

$$\rho_M = \rho_0 + \rho' = \sum_g \rho_g + \rho' , \tag{3}$$

where ρ_g is a density function associated with the isolated atom $\underline{g}$ and ρ' a correction term. For closed shell atoms, ρ_g will be the atomic Fock-Dirac density matrix, and for open shell atoms, a suitable average which will be discussed further in Sec. 5. It is further convenient to introduce the total atomic effective potentials

$$U_g = -Z_g/r_{g1} + \int dx_2 \frac{1}{r_{12}} (1-P_{12})\, \rho_g(2',2) \tag{4}$$

which permits us to write the Fock operator

$$\begin{aligned} F_M &= T_1 + \sum_g U_g + \int dx_2 \frac{1}{r_{12}} (1-P_{12})\, \rho'(2',2) \\ &= h_M + \int dx_2 \frac{1}{r_{12}} (1-P_{12})\, \rho'(2',2) . \end{aligned} \tag{5}$$

For the total energy we first split ρ_M into ρ_0 and ρ' and write

$$E = E_0 + E' \tag{6}$$

where E_0 contains all terms independent of ρ', thus

$$\begin{aligned} E_0 = {} & \sum_{g<h} Z_g Z_h / R_{gh} + \int h_1 \rho_0(1',1)\, dx_1 \\ & + \frac{1}{2} \int \frac{1}{r_{12}} \left\{ \rho_0(1,1)\, \rho_0(2,2) - \rho_0(1,2)\, \rho_0(2,1) \right\} dx_1\, dx_2 \end{aligned} \tag{7}$$

and

$$\begin{aligned} E' &= \int h_1 \rho'(1',1)\,dx_1 + \int \frac{1}{r_{12}} \{ \rho_0(1,1)\rho'(2,2) - \rho_0(1,2)\rho'(2,1) \} dx_1 dx_2 \\ &\quad + \frac{1}{2} \int \frac{1}{r_{12}} \{ \rho'(1,1)\rho'(2,2) - \rho'(1,2)\rho'(2,1) \} dx_1 dx_2 \\ &= \int h_M \rho'(1',1)\,dx_1 + \frac{1}{2}\int \frac{1}{r_{12}} \{ \rho'(1,1)\rho'(2,2) - \rho'(1,2)\rho'(2,1) \} dx_1 dx_2 \qquad (8) \\ &= \frac{1}{2} \int (h_M + F_M)\, \rho'(1',1)\,dx_1 . \end{aligned}$$

To the atomic densities ρ_g we associate atomic energies

$$\begin{aligned} E_g &= \int (T - Z_g/r_{g1})\, \rho_g(1',1)\,dx_1 \qquad (9) \\ &\quad + \frac{1}{2} \int \frac{1}{r_{12}} \{ \rho_g(1,1)\rho_g(2,2) - \rho_g(1,2)\rho_g(2,1) \} dx_1 dx_2 \end{aligned}$$

and obtain

$$\begin{aligned} E_0 &= \sum_g E_g + \sum_{g<h} \Big[Z_g Z_h / R_{gh} - \int \frac{Z_g}{r_{g1}} \rho_h(1,1)\,dx_1 \\ &\quad - \int \frac{Z_h}{r_{h1}} \rho_g(1,1)\,dx_1 + \int \frac{1}{r_{12}} \{ \rho_g(1,1)\rho_h(2,2) - \rho_g(1,2)\rho_h(2,2)\, dx_1 dx_2 \Big] \qquad (10) \\ &= \sum_g E_g + \sum_{g<h} Z_g \Big[Z_h/R_{gh} - \int \frac{1}{r_{g1}} \rho_h(1,1)\,dx_1 \Big] \\ &\quad + \sum_{g<h} \int U_h \rho_g(1',1)\,dx_1 . \end{aligned}$$

The various terms in these expressions can be given the following physical interpretation. E_g can be thought of as the energy of an atom in a "valence state" with the density matrix ρ_g. The difference between E_g and the Hartree-Fock atomic ground state can either be calculated rigorously or estimated from the atomic spectrum. Since E_g is independent of other atoms it can be neglected in calculations of bond angles and distances. The remaining terms in E_o give the interactions between unperturbed atoms while E' is the energy associated with the electron redistribution which gives the main contribution to the molecular binding energy.

4. Matrix representation of the Fock operator.

As mentioned above, for closed shell atoms the atomic density function ρ_g is chosen to be the Fock-Dirac density matrix of the atom in its ground state. With $|ig\rangle$ denoting an atomic SCF orbital i on center g we have the eigenvalue relation

$$(T_1 + U_g)|ig\rangle = \epsilon_{ig}|ig\rangle \tag{11}$$

where ϵ_{ig} is the orbital energy. For open shell atoms a single determinant does not in general fulfill the symmetry relations of the true wave function. The SCF ground state is therefore in this case represented by a sum of determinants with given coefficients. The Fock operator is different for closed and open shells and contains further coupling terms between open and closed shell orbitals of the same symmetry. All these correction terms are here taken together into an operator W_g defined by

$$(T_1 + U_g)|ig\rangle = (\epsilon_{ig} + W_g)|ig\rangle \tag{12}$$

where ϵ_{ig} is the open or closed shell orbital energy.

Let us now consider the matrix representation of F_M. In the chosen basis system, which is now treated as spin independent, we represent ϱ' by the matrix $\mathbb{R}' = \{R'_{k\ell}\}$ and introduce the Mulliken notation for electron interaction integrals

$$(ij|k\ell) \doteq \int i^*(1)\,j(1)\,\frac{1}{r_{12}}\,k^*(2)\,\ell(2)\,d\tau_{12} \tag{13}$$

where now the atomic indices have been surpressed. Using (12) we write the diagonal elements of the Fock operator as

$$\begin{aligned}\langle ig|F_M|ig\rangle = \epsilon_{ig} + \langle ig|W|ig\rangle + \sum_{f\neq g}\langle ig|U_f|ig\rangle \\ + \sum_{k\ell} R'_{kl}\{(ii|kl) - \tfrac{1}{2}(ik|\ell i)\}.\end{aligned} \tag{14}$$

The off-diagonal elements $\langle ig|F_M|jh\rangle$ are divided into two groups, g = h, and g ≠ h. For g = h we get

$$\begin{aligned}\langle ig|F_M|jg\rangle = \langle ig|W_g|jg\rangle + \sum_{f\neq g}\langle ig|U_f|jg\rangle \\ + \sum_{k\ell} R'_{k\ell}\{(ij|kL) - \tfrac{1}{2}(ik|\ell j)\}\end{aligned} \tag{15}$$

and for g ≠ h

$$\begin{aligned}\langle ig|F_M|jh\rangle = \Delta_{ij}(\epsilon_{ig} + \epsilon_{jh}) + \langle ig|W_g + W_h|jh\rangle \\ - \langle ig|T_1|jh\rangle + \sum_{f\neq g,h}\langle ig|U_f|jh\rangle \\ + \sum_{k,\ell} R'_{kl}\{(ij|k\ell) - \tfrac{1}{2}(ik|\ell j)\}\end{aligned} \tag{16}$$

where Δ_{ij} is the overlap integral $\langle ig|jh\rangle$.

The molecular orbitals are written in LCAO form as

$$\Phi_\lambda = \sum_j |j\rangle\, c_{j\lambda} \tag{17}$$

and the Hartree-Fock equations in matrix notation

$$(\mathbb{F}_M - \Delta\, \epsilon_\lambda)\, \mathbb{C}_\lambda = 0 \; ; \; \lambda = 1, 2, 3 \ldots \qquad (18)$$

where $\mathbb{C}_\lambda$ is the column matrix $\{c_{j\lambda}\}$. The index $\underline{\lambda}$ will frequently be suppressed in future sections.

5. Approximate relations for open shell atoms.

It is convenient to let ρ_g for an open shell atom be the ground state charge distribution averaged over degenerate orbitals. Thus every orbital in an open shell is occupied by the same fractional number of electrons with α and β spin. Neglecting coupling terms which in general are small we have, following Roothaan,[13] for the closed shell Fock operator

$$\begin{aligned} F^c &= T_1 - \frac{Z_g}{r_{g1}} + \int dx_2 \frac{1}{r_{12}} (1 - P_{12}) \sum_i p_i \phi_i^*(2) \phi_i(2) \\ &= T_1 + U_g \end{aligned} \qquad (19)$$

where the summation over $\underline{i}$ is over spin orbitals and p_i denotes the spin orbital average population. In this approximation the W-operator is clearly given by $W = F^c - F^o$. If $|m\rangle$ and $|k\rangle$ are open and closed shell SCF orbitals with the eigenvalue relations

$$F^c |k\rangle = \epsilon_k |k\rangle \; ; \quad F^o |m\rangle = \epsilon_m |m\rangle \qquad (20)$$

we have since $\langle m|k\rangle = 0$

$$\langle m | W | k \rangle = \langle m | k \rangle (\epsilon_k - \epsilon_m) = 0 \qquad (21)$$

The open shell Fock operator is under the same assumptions

$$F^{o} = T_1 - \frac{Z_g}{r_{1g}} + \int dx_2 \frac{1}{r_{12}} \sum_i p_i a_i \phi_i^*(2) \phi_i(2) - \int dx_2 \frac{1}{r_{12}} \sum_i p_i b_i \phi_i^*(2) \phi_i(1) P_{12} \tag{22}$$

where a_i and b_i are constants which are equal to unity for closed shell orbitals and depend on the atomic state for the open shell. A table of these constants for open s and p shells is given in Roothaan's paper.[13] The matrix element of the W_g-operator between an arbitrary orbital i and an open shell orbital on atom g is thus given by

$$\langle i | W_g | mg \rangle = \sum_j R^g_{jj} \left\{ (1-a_j)(im|jj) - \frac{1}{2}(1-b_j)(ij|jm) \right\} \tag{23}$$

where the summation is over open shell space orbitals on atom g and $\{R^g_{jj}\}$ is the (diagonal) matrix representation of ρ_g. However, since the coupling terms have been neglected the relation (22) is not necessarily fulfilled and will have to be imposed a priori.

An alternative to this treatment is to use eigenfunctions of the operators $T_1 + U_g$ as basis orbitals. The Hartree-Fock-Slater functions calculated by Herman and Skillman[14] belong to this category. They are however given in numerical form and will have to be approximated by analytical expressions if conventional molecular integral programs are to be used.

6. Separation of core and valence orbitals.

A solution of the full secular equation (12) can always be achieved. However, it is well known that the inner orbitals do not change very much when going from atom to molecule. We will make use of this fact and make a full variational calculation only for the outer or valence orbitals while we treat the core orbitals and the core-valence interactions by means of perturbation theory.

The core orbitals are localized near the nuclei, and interactions between cores on adjacent orbitals can be neglected in the first approximation due to small overlap integrals. The valence electrons are much more spread out and interact strongly with each other. One-center core-valence interactions are quite small owing to the orthogonality of basis orbitals on the same center, but two-center interactions might be of some importance. Core orbital energies may however be quite different in atoms and molecules. Chemical effects in X-ray spectra are quite small relatively speaking, but represent nevertheless shifts of core orbital energies, sometimes of the order of 10eV.[15] That these facts agree with our model can be seen in the following way. Of terms perturbing the core orbital energies (14) the coulomb interactions $\sum R'_{k\ell}(ii|k\ell)$ are the most important. Since ϱ' contains contributions almost exclusively from valence electrons, and the potential of a uniformly charged spherical shell is constant inside the shell, the spherical component of the perturbation will be more or less constant inside the core, i.e. it will not affect the form of the orbitals as much as their energies. The non-spherical components will cause a first order electrostatic splitting or broadening of innershell p-states in cases of low molecular symmetry; as long as this effect is small second order angular effects in s-orbitals may safely be ignored. Another consequence of a model with a core unaffected by other than first order perturbations is that if there is more than one inner shell the K shell energy changes most, a situation which is also confirmed by experimental evidence in the form of X-ray emission spectra.[16]

In the expression for the total energy, the core-valence electrostatic interactions can be attributed to either the core or the valence orbital energies. Therefore, if second and higher order core effects are neglected, only valence electron energies and wave functions need *to be considered in a discussion of the chemical bond.*

7. Core-valence non-orthogonality and higher-order interactions.

With the atomic orbital basis system employed here there is a non-orthogonality between core and valence orbitals on different centers. This problem does not appear in π-electron theory and has usually been ignored in previous approximate MO-LCAO theories. Here we will make use of a perturbation method leading to results similar to the pseudopotential introduced by Phillips and Kleinman[17] for the orthogonalized plane wave method of band calculations in solids. The scheme is quite general and can be applied even if the requirements *are not fulfilled for a first-order perturbation treatment of the* core electrons.

Following Löwdin[18] we start from a system of linear equations written in matrix form

$$\mathbb{M}\,\mathbb{C} = 0. \tag{24}$$

In our case $\mathbb{M} = \mathbb{F} - \Delta E$ where $\mathbb{F}$ is the matrix representation of the Fock operator and Δ the overlap matrix. Dividing the basis functions into two groups a and b we write

$$\left\{ \begin{array}{l} \mathbb{M}_{aa}\mathbb{C}_a + \mathbb{M}_{ab}\mathbb{C}_b = 0 \\ \mathbb{M}_{ba}\mathbb{C}_a + \mathbb{M}_{bb}\mathbb{C}_b = 0. \end{array} \right. \tag{25}$$

From the second of these equations we solve for $\mathbf{C}_b = -\mathbf{M}_{bb}^{-1}\mathbf{M}_{ba}\mathbf{C}_a$ and obtain the first equation as

$$(\mathbf{M}_{aa} - \mathbf{M}_{ab}\mathbf{M}_{bb}^{-1}\mathbf{M}_{ba})\,\mathbf{C}_a = 0. \tag{26}$$

We now let a be the valence orbitals, b the core orbitals. $\mathbf{V}_{aa} = -\mathbf{M}_{ab}\mathbf{M}_{bb}^{-1}\mathbf{M}_{ba}$ is now the matrix representation of a pseudopotential V from the core orbitals. Its elements are

$$V_{ij} = -\sum_{k,l}(F_{ik} - \Delta_{ik}E)\{(\mathbf{F}_{bb} - \boldsymbol{\Delta}_{bb}E)^{-1}\}_{kl}(F_{lj} - \Delta_{lj}E) \tag{27}$$

where i and j go over the valence orbitals and k and l over the core orbitals. This index convention will be used in the remaining part of this section and will also be referred to in later sections.

A solution of the reduced secular equations

$$(\mathbf{F}_{aa} - \mathbf{V}_{aa} - \boldsymbol{\Delta}_{aa}E)\,\mathbf{C}_a = 0 \tag{28}$$

is rather cumbersome since $\mathbf{V}_{aa}$ is dependent on E, not to mention the fact that $\mathbf{F}$ is dependent on $\mathbf{C}$ through the density matrix. If a solution of arbitrarily high accuracy were desired it would probably be easier to solve the original secular equations directly. However, the matrix $\mathbf{M}_{bb} = \mathbf{F}_{bb} - \boldsymbol{\Delta}_{bb}E$ is almost diagonal due to the smallness of core-core interactions and we can evaluate its inverse by means of a series expansion

$$\mathbf{M}_{bb}^{-1} = A^{-1} - A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} - . \tag{29}$$

where $\mathbf{A} = \mathbf{M}_{bb} - \mathbf{B}$ is diagonal. Furthermore, as discussed in the previous section the core atomic orbitals are close approximations to the core molecular orbitals. We therefore introduce the notation

$$F_{ik} = \Delta_{ik} F_{kk} + G_{ik} \tag{30}$$

where $G_{ik} = 0$ if

$$F^M \chi_k = \epsilon_k \chi_k . \tag{31}$$

We will here treat only the lowest orders of the Brillouin type perturbation expansion one gets from the series expansion of the matrix inverse (29). Again, if the series is slowly convergent it would be better to go back to the original secular equations. We obtain after some simple manipulations

$$\begin{aligned} V^{(1)}_{ij} &= -(M_{ab}\, A\, M_{ba})_{ij} \\ &= -\sum_k \{\Delta_{ik}(F_{kk}-E)\Delta_{kj} + G_{ik}\Delta_{kj} + \Delta_{ik}G_{kj} \\ &\quad + G_{ik}G_{kj}/(F_{kk}-E)\} ; \end{aligned} \tag{32}$$

$$\begin{aligned} V^{(2)}_{ij} &= (M_{ab}\, A^{-1} B A^{-1} M_{ba})_{ij} \\ = \sum_{k,\ell}{}' &\{\Delta_{ik}(F_{k\ell}-\Delta_{k\ell}E)\Delta_{\ell j} \\ &+ G_{ik}(F_{k\ell}-\Delta_{k\ell}E)\Delta_{\ell j}/(F_{kk}-E) \\ &+ \Delta_{ik}(F_{k\ell}-\Delta_{k\ell}E)\, G_{\ell j}/(F_{\ell\ell}-E) \\ &+ G_{ik}(F_{k\ell}-\Delta_{k\ell}E)\, G_{\ell j}/(F_{kk}-E)(F_{\ell\ell}-E)\} \end{aligned} \tag{33}$$

where the double sum $\sum'_{k,\ell}$ excludes $k=\ell$. The term $-\sum_k \Delta_{ik}(F_{kk}-E)\Delta_{kj}$ is the Phillips and Kleinman pseudopotential.[17] If the eigenvalue relation (31) is fulfilled it is the only non-vanishing term. From the computational point of view it is important to have the pseudopotential as insensitive to errors in E as possible. For that purpose we can collect all terms linear in E and include them in the overlap matrix. With the notation

$$\tilde{V}^{(1)}_{ij} = V^{(1)}_{ij} - E \sum_k \Delta_{ik}\Delta_{kj}$$
$$\tilde{V}^{(2)}_{ij} = V^{(2)}_{ij} + E \sum_{k,\ell}{}' \Delta_{ik}\Delta_{k\ell}\Delta_{\ell j} \tag{34}$$

and

$$\tilde{\Delta}_{ij} = \Delta_{ij} - \sum_k \Delta_{ik}\Delta_{kj} + \sum_{k,\ell}{}' \Delta_{ik}\Delta_{k\ell}\Delta_{\ell j} \tag{35}$$

the secular equations (28) now become

$$(\mathbb{F}_{aa} + \mathbb{V}_{aa} - \mathbb{\Delta}_{aa} E)\, \mathbb{C}_a = 0 \tag{36}$$

$\mathbb{\Delta}_{aa}$ is the overlap matrix for the projected valence orbitals $\{\tilde{\chi}_i\}$ with

$$\tilde{\chi}_i = \chi_i - \sum_k \Delta_{ik}\chi_k \text{ and } \langle\tilde{\chi}_i|\chi_k\rangle = 0. \tag{37}$$

An equivalent procedure would be to start by orthogonalizing $\{\chi_i\}$ against $\{\chi_k\}$ and to partition subsequently. In that case integrals over the Fock operator are given by

$$\langle\tilde{\chi}_i|F|\tilde{\chi}_j\rangle = \langle\chi_i - \sum_k \Delta_{ik}\chi_k|F|\chi_j - \sum_\ell \chi_\ell\Delta_{\ell j}\rangle$$
$$= F_{ij} - \sum_k (\Delta_{ik}F_{kk}\Delta_{kj} + \Delta_{ik}G_{kj} + G_{ik}\Delta_{kj}) \tag{38}$$
$$+ \sum_{k,\ell}{}' \Delta_{ik}F_{k\ell}\Delta_{\ell j}$$

and

$$\langle\tilde{\chi}_i|F|\chi_\ell\rangle = \langle\chi_i - \sum_k \Delta_{ik}\chi_k|F|\chi_\ell\rangle$$
$$= G_{i\ell} - \sum_{k\neq\ell} \Delta_{ik}F_{k\ell}. \tag{39}$$

If one uses the inverse expansion (29) all terms with the same denominator will be of the same order.

The operator $\tilde{V}$ is still a function of E. We are however interested in E values only in the range of valence orbital energies. In the denominators $(F_{kk}-E)$, E is thus a numerically small quantity compared to F_{kk} which is essentially a core orbital energy. It is also clear that $\Delta_{k\ell}E$ is numerically small compared to $F_{k\ell}$ where the leading terms are $F_{k\ell} \approx \Delta_{k\ell}(\epsilon_k+\epsilon_\ell) \approx \Delta_{k\ell}(F_{kk}+F_{\ell\ell})$.

The Fock-Dirac density matrix formed from the occupied molecular orbitals in the partitioned representation becomes rather unwieldy if a higher accuracy is desired. The expansion of a set of normalized orbitals $\{\phi_i\}$ in the AO basis $\{\chi_j\}$ will be denoted

$$\phi_i = \sum_j \chi_j c_{ji} \tag{38}$$

with the orthonormalization condition

$$\langle\phi_i|\phi_j\rangle = \sum_{k,\ell} c^*_{ki} c_{\ell j} \langle\chi_k|\chi_\ell\rangle = \mathbb{C}^\dagger_i \Delta \mathbb{C}_j = \delta_{ij} \tag{39}$$

where $\mathbb{C}_i$ stands for the column vector $\{c_{ki}\}$, k = 1, 2,... . The Fock-Dirac density matrix is given by

$$\begin{aligned} \rho(1,1') &= 2\sum_{i\ occ.} \phi_i \phi^*_i \\ &= 2\sum_{i\ occ.}\sum_{j,k} \chi_{j} c_{ji} \chi^*_k c^*_{ki} = \sum_{j,k} \chi_j R_{jk} \chi^*_k \end{aligned} \tag{40}$$

or in matrix notation

$$\mathbb{R} = 2\sum_{i\ occ.} \mathbb{C}_i \mathbb{C}^\dagger_i . \tag{41}$$

The summation over i extends over all doubly occupied space orbitals. Since some of these belong to the core and others to the valence shell and since orbitals calculated from the partitioned secular equations (28) or (36) are in general not normalized to unity, the density matrix becomes quite difficult to evaluate.

The summation over core orbitals can be eliminated in the following way. Let the space formed by the M linearly independent basis functions $\{\chi_i\}$ be occupied by 2M electrons. An arbitrary orthonormal set of orbitals $\{\varphi_i\}$ can be constructed from $\{\chi_i\}$ by means of the relation[17]

$$\varphi = \chi \Delta^{-1/2} U . \tag{42}$$

Here φ and χ are the row matrices $\{\varphi_1, \varphi_2, \ldots \varphi_M\}$ and $\{\chi_1, \chi_2 \ldots \chi_M\}$ respectively, and U is an arbitray unitary matrix. $\Delta^{-1/2}$ fulfills $\Delta^{-1/2} \cdot \Delta^{-1/2} = \Delta^{-1}$, and is assumed to be Hermitian. The density matrix formed from φ is

$$2\sum_i \varphi_i \varphi_i^* = 2\varphi\varphi^+ = 2\chi\Delta^{-1/2} U U^+ \Delta^{-1/2} \chi = 2\chi\Delta^{-1}\chi^+ \tag{43}$$

or

$$R_M = 2\Delta^{-1} \tag{44}$$

The Fock-Dirac density matrix for the system can now be obtained by means of subtraction of the unoccupied orbitals from R_M giving the result

$$R_M = 2(\Delta^{-1} - \sum_{i\ \text{unocc.}} c_i c_i^+). \tag{45}$$

The summation over unoccupied orbitals is clearly not over core orbitals. For the further development we consider a basis of projected valence orbitals. In this case Δ^{-1} is given by

$$\Delta^{-1} = \begin{pmatrix} \Delta_{aa}^{-1} & O_{ab} \\ O_{ba} & \Delta_{bb}^{-1} \end{pmatrix} \tag{46}$$

without any terms linking core and valence orbitals. We write

$$C_i = \begin{pmatrix} C_{ia} \\ C_{ib} \end{pmatrix} \tag{47}$$

where

$$C_{ib} = -M_{bb}^{-1} M_{ba} C_{ia} \tag{48}$$

in accordance with (25). The normalization integral becomes

$$\begin{aligned} C^{+}\Delta C &= C_a^{+}\Delta_{aa} C_a + C_b^{+}\Delta_{bb} C_b \\ &= 1 + C_a^{+} M_{ab} M_{bb}^{-1} \Delta_{bb} M_{bb}^{-1} M_{ba} C_a \end{aligned} \tag{49}$$

if C_a is normalized by $C_a^{+}\Delta_{aa}C_a = 1$. This normalization comes naturally from the solution of the partitioned secular equation by conventional matrix diagonalization methods and is identical to the intermediate normalization common in perturbation theory.

As done previously for the Fock operator we can expand the matrix inverse M_{bb}^{-1} as a power series and insert the result in the density matrix. These results seem however not to offer much simplification of the computations and will therefore be omitted here.

8. Approximate multicenter integrals

Several approximation methods have been proposed for reducing time-consuming many-center integrals to simple one- and two-center coulomb type integrals. In π-electron theory the zero-differential-overlap (ZDO) has been widely applied and Pople[8] has recently discussed some of its consequences for more general systems. The success of this approximation is usually coupled with the success of the Mulliken approximation[20]

$$\chi_i^g \chi_j^h = \Delta_{ij} (\chi_i^g \chi_i^g + \chi_j^h \chi_j^h)/2. \tag{50}$$

In a symmetrically orthogonalized basis $\boldsymbol{\varphi} = \boldsymbol{\chi} \boldsymbol{\Delta}^{-1/2}$ one sees by expanding

$$\boldsymbol{\Delta}^{-1/2} = (\mathbf{1} + \mathbf{S})^{-1/2} = \mathbf{1} - \tfrac{1}{2}\mathbf{S} + \tfrac{3}{4}\mathbf{S}^2 \ldots \tag{51}$$

that the ZDO approximation $\varphi_i \varphi_j = \delta_{ij} \chi_i \chi_j$ is fulfilled to the first order of Δ_{ij}. For large overlap integrals, however, higher order terms in the expansion (51) might be of importance and it is doubtful how well the ZDO approximation works in such cases. In this connection we will therefore discuss some approximations of the Mulliken type.

Pople[8] found that the ZDO approximation as customarily applied is not invariant under transformations of the basis. Thus the calculated energy may depend on how one chooses p_x, p_y, and p_z orbitals. The same holds true for the Mulliken approximation. Consider integrals of an operator V, which might be the potential from a nucleus or some kind of electronic charge distribution. The Mulliken approximation gives

$$\langle \chi_i^g | V | \chi_i^h \rangle = (V|ij) = \Delta_{ij} [(V|ii) + (V|jj)]/2. \tag{52}$$

Let U be a unitary transformation of the orbitals on center h, thus

$$\chi_k'^h = \sum_j \chi_j^h U_{jk} \tag{53}$$

The condition for invariance of the Mulliken approximation is

$$\begin{aligned} &(V|ik') = \Delta_{ik'} [(V|ii) + (V|kk)] \quad \text{where} \\ &\Delta_{ik'} = \sum_j \Delta_{ij} U_{jk} \end{aligned} \tag{54}$$

From (52) and (53) we get however

$$\begin{aligned} (V|ik') &= \sum_j (V|ij) U_{jk} \\ &= \tfrac{1}{2} \sum_j \Delta_{ij} [(V|ii) + (V|jj)] U_{jk} \\ &= \tfrac{1}{2} [\Delta_{ik'} (V|ii) + \sum_j \Delta_{ij} U_{jk} (V|jj)]. \end{aligned} \tag{55}$$

In order to restore the invariance we therefore have to make a further approximation, $(V|ii)$ = constant for all χ_i^h . This is equivalent to Pople's theory with complete neglect of differential overlap. (CNDO).

An approximation which is closely related to the Mulliken approximation and which is invariant under transformations of atomic orbitals on a particular center has been discussed by Ruedenberg.[22] With a complete set of orthonormal orbitals on each center one can write without approximation

$$\begin{aligned} \chi_i^g \chi_j^h &= \chi_i^g \sum_l \chi_l^g \Delta_{lj} = \sum_k \Delta_{ik} \chi_k^h \chi_j^h \\ &= [\sum_l \chi_i^g \chi_l^g \Delta_{lj} + \sum_k \Delta_{ik} \chi_k^h \chi_j^h]/2. \end{aligned} \tag{56}$$

Since the expressions are exact no invariance properties are destroyed so far. With truncated sets $\{\chi_\ell^g\}$ and $\{\chi_k^h\}$ invariance is kept for transformations within the truncated sets. The most extreme truncation keeping only χ_i^g of $\{\chi_\ell^g\}$ and χ_j^h of $\{\chi_k^h\}$ gives the Mulliken approximation.

With the Ruedenberg approximation electrostatic integrals are reduced to integrals of the type $(V|i^g j^g)$, where i and j may be different orbitals located on atom g . This approximation is clearly analogous to Pople's neglect of diatomic differential overlap (NDDO) approximation.

A generalization of the Mulliken and Ruedenberg approximations has been given by Löwdin.[23, 24] Instead of the arithmetic mean of terms from both centers, a weighted mean can be employed to give the correct dipole moment of $\chi_i^g \chi_j^h$, along the internuclear axis,

$$\chi_i^g \chi_j^h = \lambda \sum_\ell \chi_i^g \chi_\ell^g \Delta_{\ell j} + (1-\lambda) \sum_k \Delta_{ik} \chi_k^h \chi_j^h . \qquad (57)$$

It is to be noted, however, that invariance is preserved only if λ is a constant independent of the choice of a particular pair of orbitals on the two centers.

With the Mulliken approximation several simplifications can be made in the calculation of matrix elements to the Fock operator. For the Coulomb integrals one gets

$$\sum_{k,\ell} R_{k\ell} (ij|k\ell) = \frac{1}{2} \Delta_{ij} \left[\sum_k P_k G_{ki} + \sum_k P_k G_{kj} \right] \qquad (58)$$

where $P_K = \sum_\ell R_{k\ell} \Delta_{\ell k}$ is the Mulliken gross population of χ_k

and $G_{ij} = (ii/jj)$.

Exchange integrals give the following expressions

$$\sum_{k,l} R_{kl}(il|kj) = \frac{1}{4}\Big[(\mathbf{\Delta R \Delta})_{ij} G_{ij} + \sum_k (\mathbf{\Delta R})_{ik} G_{ik} \Delta_{kj} + \sum_k \Delta_{ik} G_{kj} (\mathbf{R\Delta})_{kj} + (\mathbf{\Delta Q \Delta})_{ij}\Big] \tag{59}$$

where $Q_{ij} = R_{ij}G_{ij}$. From the computational standpoint formulas like these are very convenient.[24] By calculating and storing matrices $\mathbf{\Delta R}, \mathbf{\Delta R \Delta}, \mathbf{\Delta Q \Delta}$ and the vector $\sum_k P_k G_{kj}$ first, and then evaluating the contributions to $\mathbf{F}$ one gets in the computer program a maximum of three instead of four nested loops and a considerable time saving.

The Mulliken approximation has another interesting feature in connection with the partitioning approach. If core-core overlap integrals are neglected there are no contributions from core orbitals to electron distributions formed from projected valence orbitals. With the notation of section 7 we have

$$\begin{aligned} \tilde{\chi}_i \tilde{\chi}_j &= (\chi_i - \sum_k \Delta_{ik} \chi_k)(\chi_j - \sum_l \chi_l \Delta_{lj}) \\ &= \frac{1}{2}(\Delta_{ij} - \sum_k \Delta_{ik}\Delta_{kj})(\chi_i\chi_i + \chi_j\chi_j) \\ &= \frac{1}{2}\tilde{\Delta}_{ij}(\chi_i\chi_i + \chi_j\chi_j) \end{aligned} \tag{60}$$

In particular, for i = j we get

$$\tilde{\chi}_i \tilde{\chi}_i = \tilde{\Delta}_{ii} \chi_i \chi_i \tag{61}$$

which thus takes into account the different normalizations for the two sets of orbitals.

9. Discussion

A quantum mechanical approximation may be judged under the following criteria: 1) mathematical rigor, 2) computational simplicity, and 3) agreement with experiment. The method presented here is a compromise between 1) and 2) while no emphasis has been placed on 3) in the derivation of formula here. How to balance 1) and 2) is to some extent a matter of personal taste and several alternative approaches are possible on the basis of present results.

An excellent agreement with experiment could always be obtained if various quantitites in the Pariser-Parr-Pople theory of conjugated hydrocarbons. However, in that way some of the physical content of the Schrodinger equation is lost and difficulties arise when totally different systems are to be treated. With no or few parameters, our method seems to be of greatest importance where the experimental information is scarce and ab initio calculations are too laborious.

Applications are in progress to inorganic ions and molecules with sulfur or chlorine as the central atom. Promising results have been obtained for ground state properties such as bond angles and charge distributions. A detailed account will be given in forthcoming papers.

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