Hartree-Fock Approximation with Pseudowavefunctions

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By the introduction of pseudopotentials the Hartee-Fock equations for all electrons of an atom or molecule are exactly transformed into equations yielding orbitals which are non-orthogonal to the lower lying states.

One of the most successful approximations of the Quantum Mechanics is the Hartree-Fock (HF) approximation. In this method it is generally assumed that the one-electron orbitals $\varphi_1, \varphi_2, \ldots, \varphi_N$ are orthonormal:

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} . \tag{1}$$

Since this assumption, which is introduced for mathematical convinience, is not compulsory according to the basic principles of Quantum Mechanics one might ask the following question: Is it possible to formulate an independent particle model in terms of one-electron orbitals which are *not* orthogonal [1], e.i. for which

$$\langle \psi_i | \psi_j \rangle \neq 0 \quad (i, j = 1, 2, \ldots, N) , \tag{2}$$

and especially one might ask the question: What are the equations for the best such orbitals?

In a recent publication [2] we discussed this problem and clarified some aspects of it. The purpose of this note is to show that it is possible to formulate the HF method in terms of nonorthogonal orbitals with the same exactness as in terms of the orthonormal set.

Let us consider an atom or molecule with N electrons in closed shells. The HF equations are

$$H_{\mathrm{F}} \varphi_i = \varepsilon_i \varphi_i \quad (i = 1, \ldots, N) , \tag{3}$$

where H_{F} is the HF Hamiltonian operator

$$H_{\mathrm{F}} = t + U . \tag{4}$$

Here t is the kinetic energy plus nuclear attraction and U is the HF potential

$$U = \sum_{s=1}^{N} U_s , \tag{5}$$

with U_s representing the non-local HF potential associated with the orbital φ_s. After the Eqs. (3) are solved the total energy of the system may be computed from the formula

$$E_{\mathrm{F}} = \sum_{i=1}^{N} \varepsilon_i - \tfrac{1}{2} \sum_{i,j=1}^{N} \langle \varphi_i | U_j | \varphi_i \rangle . \tag{6}$$

We assume that the HF equations were solved for a particular atom or molecule. Consider now the equation

$$(H_{\mathrm{F}} + V_i) \psi_i = E_i \psi_i \quad (i = 1, 2, \ldots, N) , \tag{7}$$

where H_{F} and V_i *are formed from the given HF orbitals*, the operator H_{F} according to (4) and V_i according to the formula

$$V_i = \sum_{s=1}^{i-1} | \varphi_s \rangle \langle F_s | , \tag{8}$$

where φ_s is one of the given HF orbitals and F_s is an arbitrary function with the correct atomic or molecular symmetry. V_i is a pseudopotential which is the generalization of the potential introduced by Austin Heine and Sham for valence electrons; here it is generalized to all electrons (core and valence) of an atom or molecule.

It is easy to show that the lowest eigenvalue of (7) will be

$$E_i = \varepsilon_i , \tag{9}$$

and the corresponding eigenfunction will be

$$\psi_i = \varphi_i + \sum_{s=1}^{i-1} \alpha_{is} \varphi_s , \tag{10}$$

with

$$\alpha_{is} = \langle \varphi_s | \psi_i \rangle . \tag{11}$$

We assume that the pseudopotential V_i is chosen in such a way that we obtain a unique set of α_{is} parameters from (7). Since the HF orbitals are unique for any atom or molecule, (10) shows that we have obtained a unique set of non-orthogonal orbitals ψ_i. These orbitals are also self-consistent: From the set ψ_i we can reconstruct the HF orbitals by Schmidt-orthogonalization i.e. by forming the orbitals

$$\hat{\varphi}_i = \psi_i - \sum_{s=1}^{i-1} \hat{\alpha}_{is} \hat{\varphi}_s \tag{12}$$

where $\hat{\alpha}_{is} = \langle \hat{\varphi}_s | \psi_i \rangle$ and it is clear from (10) and (12) that $\hat{\varphi}_i = \varphi_i$.

Now consider the Eqs. (7) *without the prior knowledge of the HF orbitals*. Let $\tilde{\psi}_1, \tilde{\psi}_2, \ldots, \tilde{\psi}_N$ be a set of self-consistent solutions of these equations. The orthonormal orbitals which occur in the operators H_{F} and V_i are formed, at each stage of the self-consistent procedure, by Schmidt orthogonalization, i.e. they are related to the set $\tilde{\psi}_i$ through the formulas

$$\tilde{\varphi}_i = \tilde{\psi}_i - \sum_{s=1}^{i-1} \tilde{\alpha}_{is}\, \tilde{\varphi}_i \,, \tag{13}$$

where $\tilde{\alpha}_{is} = \langle \tilde{\psi}_s | \tilde{\varphi}_i \rangle$. Here again we have assumed that the pseudopotentials in (7) are chosen in such a way that we get a uniquely determined set of non-orthogonal orbitals $\tilde{\psi}_i$. Since these orbitals are self-consistent in the same sense as those which we obtained using the previously computed HF orbitals, it is clear that the two sets must be identical i.e.

$$\tilde{\psi}_i = \psi_i \,. \tag{14}$$

But then the orthogonalized orbitals $\tilde{\varphi}_i$ must be identical with the HF orbitals since we have shown that the orbitals obtained by the orthogonalization of the ψ_i are identical with the HF functions. In other words, we have exactly recovered the HF orbitals from the self-consistent solutions of (7).

Our result is that the unique, self-consistent solutions of (7) are forming a set of non-orthogonal orbitals which are the "best" in the sense that we can obtain all the relevant quantities from these equations with the same exactness as from the HF equations. The exact solutions of (7) yield the HF orbital parameters ε_i; from the non-orthogonal orbitals we obtain the HF functions by Schmidt orthogonalization; using the orbital parameters and the orthogonalized orbitals we get the HF total energy from (6).

From the discussion it is clear that the pseudopotentials V_i must be determined in such a way as to yield unique solutions for (7). One of the possible choices is

$$V_i = -\sum_{s=1}^{i-1} | \varphi_s \rangle \langle \varphi_s | (h + U) \,, \tag{15}$$

where h is the nuclear attraction and U is the HF potential (5). This choice leads to (almost) the smoothest non-orthogonal orbitals [3] ψ_i.

In the publication mentioned above [2] we wrote down (7) but did not recognize its equivalence to the HF approximation. We note that *for the valence electrons of atoms numerous* solutions of (7) had been computed [4], i.e. self-consistent solutions of this equation can be obtained in a straightforward fashion. Generalization of the procedure from valence electrons to all electrons will be straightforward. It is clear that the Eqs. (7) possess considerable advantages over the original HF equations in that the solutions of (7) do not need to be orthogonal to the lower lying orbitals; the presence of the pseudopotentials V_i are preventing the electrons from "failling down" into the lower lying energy levels.

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[1] Generally such functions are called pseudowavefunctions. We shall avoid this designation because it implies approximations and the point of this note is that we transform the Hartree-Fock orbitals into such functions exactly. We shall call these functions non-orthogonal orbitals.

[2] L. Szasz, J. Chem. Phys. **64**, 492 (1976).

[3] B. Austin, V. Heine, and L. Sham, Phys. Rev. **127**, 276 (1962).

[4] L. Szasz and G. McGinn, J. Chem. Phys. **47**, 3495 (1967).