

# On solutions to the Hartree-Fock problem for atoms and molecules

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In recent years, the questions of proving that the Hartree (H) and the Hartree-Fock (HF) equations for an atom or a molecule have a solution have received attention.<sup>1-5,14</sup> One would also like to know that among the solutions there is one that actually minimizes the HF (or H) energy and is not merely an extremum. The purpose of this note is to announce that both questions have been solved affirmatively, thus providing a secure foundation for the assertion that HF solutions found on a computer actually can be minima. Details of the proof will be given elsewhere.

Despite the strong physical intuition that such a solution must exist, the problem is nontrivial from several points of view. Given  $N$ , orthonormal wave functions of space and spin,  $\Psi = (\phi_1, \dots, \phi_N)$ , for  $N$  electrons, one forms the single particle HF operator,  $\hat{H}_\Psi$  (defined below), and seeks  $N$  bound state eigenfunctions of  $\hat{H}_\Psi$ . Owing to the screening it is not clear that  $\hat{H}_\Psi$  will have even one bound state in the neutral case; in fact it will not if  $\phi_1, \dots, \phi_N$  are concentrated sufficiently close to the origin in the atomic case. Moreover, for a self-consistent solution, one demands that the  $N$  lowest eigenfunctions of  $\hat{H}_\Psi$  be  $\Psi$  itself, and this leads to a highly nonlinear problem. From the energetic point of view, the existence of an energy minimizing solution,  $\Psi$ , implies among other things, that the  $N$  electron system has a lower HF energy than the  $N - 1$  electron system.

For the exact ground state it is known<sup>6,7,8</sup> that the  $N$  electron system does indeed have a lower energy than the  $N - 1$  electron system, but this is not directly relevant to HF theory since, in general, the HF energies are larger than the true energies. As in the exact problem, it is the long range nature of the Coulomb tail which, by guaranteeing an infinite number of bound states, assures that it is always energetically favorable to add an electron in the subneutral case. We rely on this fact heavily in our proof.

In units such that  $\hbar^2/2m = 1 = |e|$ , the  $N$  electron Hamiltonians we consider are of the form

$$H = \sum_{i=1}^N [-\Delta_i + V(r_i)] + \sum_{i < j}^N |r_i - r_j|^{-1},$$

$$V(r) = - \sum_{j=1}^k z_j |r - R_j|^{-1}$$

where  $\Delta$  is the Laplacian and  $z_1, \dots, z_k$  are  $k$  positive charges located at positions  $R_1, \dots, R_k$ . Let  $F$  be the set of single particle functions of space and spin which are bounded in the norm  $\|\phi\|^2 = \langle \phi | \phi \rangle + \langle \nabla \phi | \nabla \phi \rangle$ , where  $\nabla$  is the gradient. Given  $N$  orthonormal functions  $\Psi$  as

above, with  $\phi_i$  in  $F$ , one can form the  $N$  particle Slater determinantal function  $D_\Psi$  and define

$$E(\Psi) = \langle D_\Psi | H | D_\Psi \rangle$$

and

$$E_N = \text{glb} \{ E(\Psi) | \phi_1, \dots, \phi_N \text{ are orthonormal and in } F \}.$$

The HF Hamiltonian is

$$\hat{H}_\Psi = -\Delta + V(r) + U(r) - K.$$

$U$  is the direct interaction:

$$U(r) = \sum_{i=1}^N \int (\phi_i, \phi_i)(R) |R - r|^{-1} d^3R,$$

where  $(\psi, \phi)(R)$  means that the inner product is taken over the spin part of the wave functions.  $K$  is the exchange interaction:

$$(K\phi)(r, \sigma) = \sum_{i=1}^N \left[ \int (\phi_i, \phi)(R) |R - r|^{-1} d^3R \right] \phi_i(r, \sigma).$$

The HF equation is

$$\hat{H}_\Psi \phi_j = \epsilon_j \phi_j, \quad j = 1, \dots, N. \quad (1)$$

and the question to be answered is whether or not it has solutions.

*Theorem 1:* Let  $Z = \sum_{i=1}^k z_i$  and  $N < Z + 1$  (the inequality is important for mathematical reasons and restricts our proof to neutral and positively charged molecules). Then there exists an orthonormal set  $\Psi$  with  $\phi_i$  in  $F$  such that  $E_N = E(\Psi)$ . The ionization potential is positive, i.e.,  $E_N < E_{N-1}$ . Moreover,  $\hat{H}_\Psi$  has at least  $N$  negative energy eigenfunctions among which are  $\phi_1, \dots, \phi_N$ , and these are the  $N$  eigenfunctions of  $\hat{H}_\Psi$  of lowest energy. The  $\phi_i$  have exponential decay at infinity,  $|\phi_i| < c_i \exp(-\lambda r)$  for any  $\lambda < [\min(-\epsilon_1, \dots, -\epsilon_N)]^{1/2}$ .

*Remarks:* (1) Theorem 1 is about unrestricted HF theory. The functions in  $F$  are complex valued and are not restricted to being products of space and spin functions. They need not have any definite rotational symmetry type in the atomic case. That means that a single function has four independent real pieces,  $\phi = [R_+(r) + iI_+(r)]^\dagger + [R_-(r) + iI_-(r)]^\ddagger$ . In practical applications it is usually assumed that the functions are real and/or that they are products, but we can see no reason to believe that the true minimum lies in either of these restricted classes. The fact that the HF equation is nonlinear precludes the usual argument that if  $\phi$  is a solution then  $\phi + \phi^*$  is a solution, which is true for the Schrodinger equation. Concerning restricted HF theory, we are able to state

**Theorem 2:** Let  $C$  be the union of a finite family of real linear subspaces of  $F$ , each of which is closed in the topology on  $F$  and such that (a)  $\hat{H}_\Psi\phi$  is in  $C$  for all  $\phi_1, \dots, \phi_N$  and  $\phi$  in  $C$ ; (b)  $-\Delta + \epsilon V(r)$  has an infinite number of bound states in  $C$  for all  $\epsilon > 0$ . Then Theorem 1 remains true with  $F$  replaced by  $C$ .

Thus,  $C$  could be the set of real functions and/or product functions of the form either  $f(r)\dagger$  or  $f(r)\ddagger$ . It might also be restricted by certain geometric symmetries, e.g.,  $C$  could be the subspace of  $S$ -wave functions in the atomic ( $k=1$ ) case.

(2) Unless there is some miraculous cancellation, all the  $\phi_i$  will decay at the same rate as given by  $\lambda$  in Theorem 1. We thank Professor J. K. Percus for drawing our attention to this fact. To prove the exponential fall-off, we use the methods of Combes and Thomas<sup>9</sup> and of Simon.<sup>10</sup>

(3) Theorems 1 and 2 state that  $N+1$  electrons can be bound when  $Z=N+\epsilon$ ,  $\epsilon > 0$ . It has been conjectured by Kaplan<sup>11</sup> that this remains true when  $Z=N$ , and one wonders whether or not this is so. For binding, it would be sufficient, but not necessary, that  $\hat{H}_\Psi$  have  $N+1$  bound states for the  $\Psi$  which solves the  $Z=N$  problem.

(4) Theorems 1 and 2 are also true, *mutatis mutandis*, for Hartree theory, i.e., when the condition that the  $\phi_i$  be orthogonal is omitted, and the exchange operator,  $K$ , is omitted.

(5) There is another variational procedure, which is also called Hartree-Fock, but which is much simpler mathematically. One chooses an  $M$ -dimensional subspace  $F_M \subset F$  with  $N \leq M < \infty$  and restricts the  $\phi_i$  to be in  $F_M$ . Each  $\phi_i$  is then given in terms of  $M$  bounded parameters  $a_j^i$ ,  $j=1, \dots, M$  and  $E(\Psi)$  is then a function of these

$NM$  parameters. As  $E$  is continuous in the  $a_j^i$ , it is easy to prove it has a minimum and the minimizing  $\Psi$ , if an interior point, will satisfy a HF equation, but in the sense of matrix elements *only*. Upper and lower bounds to the number of such solutions have been found by Fukutome.<sup>12</sup>

(6) The question of how good the HF energy is in comparison to the exact energy lies outside the scope of this work. As  $Z$  tends to infinity, however,  $E$  becomes exact to leading order ( $Z^{7/3}$ ) in  $Z$ . It was by means of HF estimates, in fact, that we were previously<sup>13</sup> able to prove that the Thomas-Fermi energy is asymptotically exact as  $Z \rightarrow \infty$ .

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<sup>14</sup>We have recently received a paper of M. Reeken [*Proc. R. Acad. Edinburgh* (to be published)] with results on solutions of the HF equations.

## Internal conversion in isolated aromatic molecules

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Far-ultraviolet excitation of dilute vapors of aromatic molecules under collision-free conditions leads to a rapid radiationless transition whose rate increases sharply with increasing photon energies.<sup>1,2</sup> On the basis of the excitation energy and the deuteration dependence of its decay rate this radiationless transition was proposed<sup>1-3</sup> to be internal conversion from the lowest excited singlet state ( $S_1$ ) to the ground electronic state ( $S_0$ ). In this communication we report an excitation energy dependence of triplet yield in naphthalene vapor which confirms that the internal conversion to the ground state is indeed the dominant pathway of radiationless singlet deactivation for aromatic molecules with very large excess vibrational energies (the energy difference between the exciting photon and the zero-point level of  $S_1$ ).

The excitation energy dependence of the triplet formation was determined by measuring phosphorescence of biacetyl sensitized by energy transfer from triplet state of naphthalene. Experiments were carried out at room temperatures using a mixture of 0.07 torr of naphthalene with approximately 0.1 torr of biacetyl. Under these conditions the mixture displayed fluorescence of naphthalene whose spectral shape and lifetime were the same as those of naphthalene vapor (0.07 torr) without added biacetyl. This indicates that singlet-singlet energy transfer does not make a measurable contribution to the intensity of the sensitized phosphorescence in biacetyl.

Figure 1 shows the relative quantum yield of the sensitized phosphorescence (defined as the ratio of the num-