The Hartree-Fock Theory for Coulomb Systems

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Abstract. For neutral atoms and molecules and positive ions and radicals, we prove the existence of solutions of the Hartree-Fock equations which minimize the Hartree-Fock energy. We establish some properties of the solutions including exponential falloff.

§ 1. Introduction

In this paper we discuss the Hartree (H) and Hartree-Fock (HF) theories associated with the purely Coulombic Hamiltonian of electrons interacting with static nucleii. Our purpose will be to prove that these theories exist (in the sense that the equations have solutions which minimize the H or HF energy) whenever the system has an excess positive charge after the removal of one electron. An announcement of these results was given in [22] and an outline of the proof was given in [19].

The precise quantum system is described by the Hamiltonian

$$H = - \sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} V(x_i) + \sum_{i<j} |x_i - x_j|^{-1} , \tag{1}$$

where

$$V(x) = - \sum_{j=1}^{k} z_j |x - R_j|^{-1} \tag{2}$$

acting on the Hilbert space $\mathcal{H} = L_a^2 (\mathbb{R}^{3N} ; \mathbb{C}^{2N})$. We assume $z_j > 0$, all j. The subscript a on L^2 indicates that we are to consider functions in L^2 as $\Psi(x_1, \sigma_1 ; \dots ; x_N, \sigma_N)$ with $x_i \in \mathbb{R}^3$, $\sigma_i \in \pm 1/2$ and only allow those Ψ antisymmetric under interchanges of i and j. The particles have two spin states, but we could allow q spin states in our analysis below with only notational changes. The physically correct Fermi statistics

(antisymmetric functions) which we impose turns out to be the most difficult; our method would apply equally well to any other kind of statistics.

In (2), the z_j are the charges of the nucleii at positions R_j. By a famous theorem of Kato [16], H is essentially self-adjoint on $C_0^\infty(\mathbb{R}^{3N}; \mathbb{C}^{2N})_a = \mathscr{D}_{\text{phys}}$, the C^∞ functions of compact support.

We set:

$$E_N^Q(z_i, R_i) \equiv \inf\{(\Psi, H\Psi)| \Psi \in \mathscr{D}_{\text{phys}}; \|\Psi\| = 1\} \tag{3}$$

which is defined to be the quantum ground state energy.

In 1928, Hartree [14] introduced an approximate method for finding E_N^Q. He apriori ignored the spin variables and the Pauli principle and considered product wave functions.

$$\Psi(x_1, \ldots, x_N) = \prod_{i=1}^N u_i(x_i) . \tag{4a}$$

Minimization of the functional

$$\mathscr{E}_{\text{H}}(u_1, \ldots, u_N) = (\Psi, H\Psi) \tag{4b}$$

with the constraint $\|u_i\| = 1$ then leads to the Euler-Lagrange equation

$$\tilde{h}_i u_i = \varepsilon_i u_i , \tag{5a}$$

where the ε_i are Lagrange multipliers and

$$(\tilde{h}_i w)(x) = (-\Delta w)(x) + V(x)w(x) + R_\Psi^i(x)w(x) , \tag{5b}$$

$$R_\Psi^i(x) = \sum_{j \neq i} \int |x - y|^{-1} |u_j(y)|^2 d^3 y . \tag{5c}$$

Note that in the H equations, (5), the h_i depend non-trivially on i. This is to be contrasted with the HF equations (7) where h is independent of i. Of course, the equations (5) formally only correspond to stationary points of $\mathscr{E}_{\text{H}}$ so there should be solutions corresponding to u's that do not minimize $\mathscr{E}_{\text{H}}$. Hartree attempted to take the Pauli principle into account by seeking solutions with $u_1 = u_2$ and u_3 "approximately orthogonal to u_1", $u_3 = u_4$ etc. [We should also mention that Hartree's derivation of (5) did not go through a minimization in the variational principle–this is a refinement due to Slater [30] which led him to the HF equations.] A more systematic and satisfactory way to take the Pauli principle into account was discovered in 1930 independently by Fock [10] and Slater [30] yielding equations now called Hartree-Fock (HF) equations. One considers trial functions $u_i(x_i, \sigma_i)$; $i = 1, \ldots, N$ with $(u_i, u_j) = \delta_{ij}$ and the Slater determinant

$$\Psi(x_1, \sigma_1, \ldots, x_N, \sigma_N) = (N!)^{-1/2} \det(u_i(x_j, \sigma_j)) \tag{6a}$$

and minimizes

$$\mathscr{E}_{\text{HF}}(u_1, \ldots, u_N) = (\Psi, H\Psi) \tag{6b}$$

with the constraint $(u_i, u_j) = \delta_{ij}$. The corresponding Euler-Lagrange equations are:

$$hu_i = \varepsilon_i u_i \, , \tag{7a}$$

$$(hw)(x) = (-\Delta w)(x) + V(x)w(x) + U_\Psi(x)w(x) - (K_\Psi w)(x) \, , \tag{7b}$$

$$U_\Psi(x) = \sum_{j=1}^{N} \int |x - y|^{-1} |u_j(y)|^2 d^3 y \, , \tag{7c}$$

$$(K_\Psi w)(x) = \sum_{j=1}^{N} u_j(x) \int |x - y|^{-1} \overline{u_j(y)} w(y) d^3 y \, . \tag{7d}$$

U_Ψ is the "direct" interaction and K_Ψ is the "exchange" interaction. We will show that minimizing solutions of (7a) exist whenever $N < Z + 1$ where Z is the nuclear charge

$$Z = \sum_{j=1}^{k} z_j \, .$$

We make the convention that when u's depending on spin are involved, as in (7c) and (7d) the symbol $\int - d^3 y$ indicates also a sum over the spin variable attached to y. [We note that the naive Euler-Lagrange equations are more complicated than (7) but after a unitary change, $u_i^{New} = \sum a_{ij} u_j^{Old}$ with a_{ij} a unitary $N \times N$ matrix, (7) results. The Slater determinant (6a) is unaffected by the change so that (6b) is unaffected. This is proved in Lemma 2.3 and is further discussed in many texts, e.g. Bethe-Jackiw [6]; it plays an important role in §2 below.]

Irrespective of the physical content of the H and HF equations, (5), (7), it is far from evident that there exist any solutions of them, let alone minimizing solutions, for they are clearly complicated non-linear equations. Because the full N-body Schrödinger equation is, at present, virtually inaccessible to computer calculation while the HF equation, especially in the spherical approximation [6], is ideal for computer iterative solution, the HF equations are extensively used in quantum chemistry [27].

Before our work, the only existing theorems were for the Hartree equation (5) as follows: Reeken [26] considered the *restricted* Hartree equations for Helium, i.e. he considered (5) with $k = 1$, $z_1 = 2$ and the additional restriction $u_1 = u_2$. He found a solution for this case with $u_i \geq 0$ pointwise; his method works for any $z > 1$. Independently Gustafson and Sather [12] found solutions for the restricted two electron problems for sufficiently large z (they state their results for $z = 2$ but with $\|u_i\|$ sufficiently small rather than 1. Since we insist on the normalization condition $\|u_i\| = 1$, we scale coordinates to translate their result into a large z, $\|u_i\| = 1$ result). These authors all use a bifurcation analysis further discussed in Stuart [32], and depend on the fact that they seek spherically symmetric solutions so that methods of ordinary differential equations are available. Properties of their solutions are further discussed in [3, 4]. Relations between the restricted Hartree two electron problem and the unrestricted problem appear to present some interesting mathematical phenomena and we hope to return to them in a future publication.

Using a Schauder-Tychonoff theorem, Wolkowisky [34] found ground state and excited solutions of the Hartree equation in the spherical approximation (see e.g. Bethe-Jackiw [6] for a discussion of the approximation).

All these authors attack the equations directly as fixed point equations in some sense. The reason we are able to go further is that we exploit the form of the equations as gradient maps, i.e. as Euler-Lagrange equations and directly attempt to find solutions by finding minimizing u's for $\mathscr{E}_\mathrm{H}$ and $\mathscr{E}_\mathrm{HF}$. (This method has already been used successfully in [23] to find solutions of another of the non-linear equations of atomic physics: the Thomas-Fermi [9, 33] model.)

These results for the H and HF equations, which we give in § 2 were announced in [22] and sketched in [19]; seemingly unaware of our work, Bader [2] has recently presented a similar method to obtain similar results for the H (but not HF) equations. We note that prior to our work, solutions of the HF equations for a class of potentials *excluding* Coulomb potentials were found by Fonte et al. [11]. Recently, several authors [7, 8] have proved existence of the time-dependent HF equations.

In § 3, we establish various "regularity" properties of any u's (not necessarily minimizing ones), which solve the H and HF equation. Among these is the exponential falloff of the u's announced in [22]; after our announcement, similar results *for the* H *equations* were obtained by [5].

In § 4, we repeat the remark already made in [23] that our proof that HF theory is "exact" in the $Z \to \infty$ limit implies the same result for HF theory.

§ 2. Solutions of the H and HF Equations

While one could present the existence theory for the H and HF equations as two cases of one general result, we present the two theories in sequence to illustrate the extra difficulties in the HF case. The basic strategy is (cf. [23]) to introduce a weak topology on the trial functions in which the trial functions are precompact and then to prove that the functional one wishes to minimize is lower semicontinuous. This establishes that the functional is minimized at some point in the closure of the trial functions. In many cases, additional arguments are then available to prove that the minimizing point belongs to the original trial functions rather than merely to the closure.

Theorem 2.1 (H Theory). *Fix* N, k; $z_1, \ldots, z_k$, $R_1, \ldots, R_k$. *There exist functions* $u_1, \ldots, u_N \in L^2(\mathbb{R}^3; \mathbb{C}^2)$ *with* $u_i \in Q(-\varDelta)$, *the quadratic form domain of* $-\varDelta$, *such that the* u_i *minimize*

$$\tilde{\mathscr{E}}_\mathrm{H}(u_1, \ldots, u_N) = \sum_{i=1}^{N} (u_i, (-\varDelta + V)u_i)$$
$$+ \sum_{i<j} \int |u_i(x)|^2 |u_j(y)|^2 |x-y|^{-1} d^3x d^3y \tag{8}$$

with the subsidiary conditions, $u_i \in Q(-\varDelta)$ *and*

$$\|u_i\| \leq 1 .$$

The u_i's *satisfy* (5a) *with the additional condition, that for each* i, *either* $\varepsilon_i \leq 0$ *or* $u_i = 0$. *In either event* $\varepsilon_i = \inf \mathrm{spec}(\tilde{h}_i)$ *and if* $\varepsilon_i < 0$, $\|u_i\| = 1$. *If, moreover,* $N < Z + 1$, *then all* $\varepsilon_i < 0$ *and each* $\|u_i\| = 1$. *In all cases*

$$E_\mathrm{H} \equiv \min \{\tilde{\mathscr{E}}_\mathrm{H}(u_1, \ldots, u_N) \,|\, \|u_i\| \leq 1, u_i \in Q(-\varDelta)\}$$

is finite.

Remark. We have introduced the function $\tilde{\mathscr{E}}_H$ which agrees with $\mathscr{E}_H$ *only* when all $\|u_i\| = 1$. Theorem 2.1 says that $\tilde{\mathscr{E}}_H$ always has a minimum if we only impose $\|u_i\| \leq 1$. When the minimum of $\tilde{\mathscr{E}}_H$ occurs for $\|u_i\| = 1$, all i, as we assert it does if $Z + 1 > N$, then, of course, these u_i also minimize $\mathscr{E}_H$ subject to $\|u_i\| = 1$.

Proof. By a well-known result of Kato [18], for any $\varepsilon > 0$,

$$(u, Vu) \leq \varepsilon(u, -\Delta u) + C_\varepsilon(u, u)$$

from which it follows that

$$E_H = \inf\{\tilde{\mathscr{E}}_H(u_1, \ldots, u_N) \mid \|u_i\| \leq 1, u_i \in Q(-\Delta)\}$$

is finite and that for some K:

$$\tilde{\mathscr{E}}_H(u_1, \ldots, u_N) \leq E_H + 1 \; ; \|u_i\| \leq 1 \Rightarrow \|Vu_i\| \leq K \; . \tag{9}$$

Now pick sets $u_i^{(n)}$, $1 \leq i \leq N$, $n = 1, \ldots$ so that $\tilde{\mathscr{E}}_H(u_i^{(n)}) \leq E_H + 1/n$. By (9), the $u_i^{(n)}$'s lie in a fixed ball in the Sobolev space [1], $H^1 = \{u \mid \|\|u\|\| \equiv (\|u\|^2 + \|Vu\|^2)^{1/2} < \infty\}$. Thus, by the Banach-Alaoglu theorem, there exists a subsequence such that $u_i^{(n)} \to u_i^{(\infty)}$ in the weak-H^1 topology. Clearly $\|u_i^{(\infty)}\| \leq 1$. We claim that $\tilde{\mathscr{E}}_H(u_i^{(\infty)}) \leq \varliminf \tilde{\mathscr{E}}_H(u_i^{(n)}) = E_H$, whence it follows that the $u_i^{(\infty)}$ minimize $\tilde{\mathscr{E}}_H$. Positive definite quadratic forms are always non-increasing under weak-limits (see e.g. [23]) so that

$$(u_i^{(\infty)}, -\Delta u_i^{(\infty)}) \leq \varliminf (u_i^{(n)}, -\Delta u_i^{(n)})$$

$$(u_i^{(\infty)} u_j^{(\infty)}, |x_i - x_j|^{-1} u_i^{(\infty)} u_j^{(\infty)}) \leq \varliminf (u_i^{(n)} u_j^{(n)}, |x_i - x_j|^{-1} u_i^{(n)} u_j^{(n)})$$

since $u_i^{(n)} u_j^{(n)} \xrightarrow{w} u_i^{(\infty)} u_j^{(\infty)}$ in $L^2(R^6)$. Finally, because [18, 25] V is relatively $-\Delta$ form *compact* [i.e. $(\Delta + 1)^{-1/2} V(-\Delta + 1)^{-1/2}$ is compact] $(u_i^{(n)}, Vu_i^{(n)}) \to (u_i^{(\infty)}, Vu_i^{(\infty)})$. It follows that $\varliminf \tilde{\mathscr{E}}_H(u_i^{(n)}) \geq \tilde{\mathscr{E}}_H(u_i^{(\infty)})$. Henceforth, u_i is used to denote this $u_i^{(\infty)}$.

To see that the u_i's satisfy (5a), fix $u_1, \ldots, u_{i-1}, u_{i+1}, \ldots, u_N$ and let

$$f(u) = \tilde{\mathscr{E}}_H(u_1, \ldots, u_{i-1}, u, u_{i+1}, \ldots, u_N)$$
$$= \text{const} + (u, \tilde{h}_i u) \; .$$

Since $f(u)$ is minimized by $u = u_i$ subject to $\|u\| \leq 1$, we conclude that either $\tilde{h}_i \geq 0$, $u_i = 0$, or $\tilde{h}_i u_i = \varepsilon_i u_i$ with $\varepsilon_i = \inf \text{spec} \, \tilde{h}_i \leq 0$.

Now suppose that $N < Z + 1$. Let v be a spherically symmetric function on $\mathbb{R}^3$. Then $(v, \tilde{h}_i v) = (v, -\Delta v) + (v, Kv)$, where

$$K(r) = -\sum_{j=1}^k z_j (\max(r, |R_j|))^{-1} + \sum_{j \neq i} \int |u_j(k)|^2 (\max(x, r))^{-1} dx \; .$$

Since $\|u_j\| \leq 1$, we have that

$$K(r) \leq -[Z - (N-1)]|r|^{-1} \quad \text{when} \quad r > \max(|R_j|) \; .$$

It is easy to see (use explicit hydrogenic wave functions, or a scaling argument [28]), that $(v, h_i v) < 0$ for suitable v's. It follows that $\varepsilon_i < 0$ so that $\|u_i\| = 1$. $\quad \square$

Remark. 1) In particular, in the neutral case $\sum z_j = N$, a solution of the H equation exists.

2) Notice that no assertion is made about uniqueness.

3) In the above proof, we used $|x_i - x_j|^{-1} \geq 0$ pointwise. In distinction, at the

analogous point in the TF theory we used the fact that $|x|^{-1}$ is positive definite.

4) The above method fails for the Hartree-like Choquard functional $\mathscr{E}(u,v) = \|\nabla u\|^2 + \|\nabla v\|^2 - \int |u(x)|^2 |v(y)|^2 |x-y|^{-1} dxdy$, because the last term is negative instead of positive. Nevertheless, alternate methods involving rearrangement inequalities can be used to prove that minimizing u and v exist, see Lieb [21].

5) Since the u_i's are ground states of h_i, they are pointwise positive [25].

To prove the existence of solutions of the HF equation, we must extend $\mathscr{E}_{HF}$ in a manner analogous to (8); we define:

$$\tilde{\mathscr{E}}_{HF}(u_1,\ldots,u_N) = \sum_{i=1}^{N} (u_i, (-\Delta + V)u_i) + \sum_{1 \leq i < j \leq N} ((ij)_2, |x_i - x_j|(ij)_2), \tag{10}$$

where

$$(ij)_2(x_i, x_j) = 2^{-1/2}[u_i(x_i)u_j(x_j) - u_j(x_i)u_i(x_j)] .$$

For future reference we note that

$$((ij)_2, |x_i - x_j|^{-1}(ij)_2) = D_{ij} - E_{ij}$$

$$D_{ij} = \int |x-y|^{-2}|u_i(x)|^2|u_j(y)|^2 dxdy$$

$$E_{ij} = \int |x-y|^{-1}\overline{\varrho(x)}\varrho(y)dxdy \tag{11}$$

$$\varrho(x) = u_i(x)\overline{u_j(x)} .$$

The critical element in the extension will be to locate the weak closure of $\{(u_1,\ldots,u_N)|(u_i,u_j) = \delta_{ij}\}$:

Lemma 2.2. *Let* $u_i^{(n)} \to u_i (i=1,\ldots,N)$ *weakly with* $(u_i^{(n)}, u_j^{(n)}) = \delta_{ij}$. *Then* $(u_i, u_j) = M_{ij}$ *is an* $N \times N$ *matrix with* $0 \leq M \leq 1$. *More generally the conclusion remains true if the weaker hypothesis* $(u_i^{(n)}, u_j^{(n)}) = M_{ij}^{(n)}$ *with* $0 \leq M^{(n)} \leq 1$ *is imposed.*

Remark. The point is that it is easy to see that every $(u_1,\ldots,u_N)$ with M_{ij} obeying $0 \leq M \leq 1$ arises as a weak limit of orthonormal N-tuples. Since we do not need this below, we do not give the easy proof of this converse which is based on diagonalizing M.

Proof. Let $z \in \mathbb{C}^N$. Then $(z, Mz) \equiv \sum \bar{z}_i M_{ij} z_j = (u(z), u(z)) = (\text{w-}\lim u^{(n)}(z), \text{w-}\lim u^{(n)}(z)) \leq \sum |z_i|^2$ where $u^{(n)}(z) = \sum z_i u_i^{(n)}$. The last inequality follows from the fact that balls are weakly closed and the calculation $(u^{(n)}(z), u^{(n)}(z)) = \sum |z_i|^2$. Thus $M \leq 1$. $M \geq 0$ is trivial. $\square$

We will also need the elementary observation:

Lemma 2.3. *Let* $\tilde{u}_i = \sum_j a_{ij}u_j$ *where* $A = \{a_{ij}\}_{1 \leq i,j \leq N}$ *is a unitary* $N \times N$ *matrix then*

$$\tilde{\mathscr{E}}_{HF}(\tilde{u}_i) = \tilde{\mathscr{E}}_{HF}(u_i) .$$

Proof. Let $K_{ij} = (u_i, (-\Delta + V)u_j)$, $\tilde{K}_{ij} = (\tilde{u}_i, (-\Delta + V)\tilde{u}_j)$, $R_{i_1 i_2 j_1 j_2} = ((i_1 j_2)_2, |x-y|^{-1}(j_1 j_2)_2)$, etc. Then $\tilde{K} = A^* K A$ so $\sum \tilde{K}_{ii} = \text{Tr}(\tilde{K}) = \text{Tr}(K) = \sum K_{ii}$. Similarly, by taking traces on the antisymmetric tensor product of $\mathbb{C}^N$ with itself

$$\sum_{i<j} \tilde{R}_{ij,ij} = \sum_{i<j} R_{ij,ij} . \quad \square$$

Theorem 2.4 (HF Theory). *Fix $N, k; z_1, \ldots, z_k, R_1, \ldots, R_k$. There exist functions $u_1, \ldots, u_N \in L^2(\mathbb{R}^3; \mathbb{C}^2)$ such that $u_i \in Q(-\Delta)$, the quadratic form domain of $-\Delta$, and such that the u_i minimize $\tilde{\mathscr{E}}_{HF}$ (given by (10)) with the subsidiary condition.*

$$M_{ij} \equiv (u_i, u_j) \quad obeys \quad 0 \leqq M \leqq 1 \ .$$

Moreover, the u's obey $(u_i, u_j) = \lambda_i \delta_{ij}$ and satisfy the HF equations (7) with the additional condition that either $\varepsilon_i \leqq 0$ or $u_i = 0$ for each i. $\varepsilon_i, \ldots, \varepsilon_N$ are the N lowest points of the spectrum of h and if $\varepsilon_i < 0$, $\lambda_i = 1$. If moreover, $N < Z + 1$, then all $\varepsilon_i < 0$ and $(u_i, u_j) = \delta_{ij}$.

Proof. By mimicking the proof of Theorem 2.1, we find $u_i^{(\infty)}$ obeying $0 \leqq M^{(\infty)} \leqq 1$ which minimize $\tilde{\mathscr{E}}_{HF}$. In this proof, we use Lemma 2.2 to be sure that $0 \leqq M^{(\infty)} \leqq 1$ and the fact that $(ij)^{(n)} \to (ij)^{(\infty)}$ if $u_i^{(n)} \to u_i^{(\infty)}$.

Choose a unitary $N \times N$ matrix A so that $A^* M A$ is diagonal and let $u_i = \sum_j a_{ij} u_j^{(\infty)}$. By Lemma 2.3, $\{u_i\}$ minimizes $\tilde{\mathscr{E}}_{HF}$ also, and clearly $(u_i, u_j) = \lambda_i \delta_{ij}$. Now $F(u) \equiv \tilde{\mathscr{E}}_{HF}(u_1, \ldots, u_{i-1}, u, u_{i+1}, \ldots, u_N) = \text{const} + (u, hu)$ so since $u = u_i$ minimizes $F(u)$ subject to $(u, u_j) = 0 (j \neq i)$, $(u, u) \leqq 1$, u_i must be a linear combination of the N smallest eigenvectors of h with only eigenvalues $\leqq 0$ allowed. Since each u_i has this property, by further unitary change, the u_i's can be made to obey $h u_i = \varepsilon_i u_i$.

To complete the proof we need only show that if $N - 1 < Z$, then h has N points of its spectrum below zero, i.e. $\dim P_{(-\infty, 0)}(h) \geqq N$. Now write $h = h_0 - K_\psi$ with K_ψ given by (7d). By the positive definitness of $|x|^{-1}$, K_ψ is a positive operator, so we need only show that h_0 has N negative eigenvalues. This follows, as in the proof of Theorem 2.1 by considering spherically symmetric trial functions. $\quad\square$

As already remarked in [22], the above method also yields solutions of *modified* HF equations in which we restrict the u's to lie in certain sets with suitable properties. Because of the spin independence of the assumed Hamiltonian, H, we can obtain several solutions of the actual HF equation by taking each u_i to be a product of a space and spin function, for example, and demanding a particular symmetry of the spinor functions. We emphasize that the "true" minimum of Theorem 2.4 is *not known* to come from a set of u's which are product functions. An additional restriction which is often made and for which our method applies, is to demand the spatial functions be real.

§ 3. Properties of Solutions

Theorem 3.1. *The solutions of the H equation (5) constructed in Theorem 2.1 obey:*
  a) *The u_i are globally Lipschitz and lie in $D(\tilde{h}_i) = D(-\Delta)$.*
  b) *Away from the points $r = R_j$, the u_i are infinitely differentiable.*
  c) *Exponential falloff: For any $\alpha < |\varepsilon_i|^{1/2}$ there exists a C_α so that*

$$|u_i(x)| \leqq C_\alpha \exp(-\alpha|x|) \ .$$

Proof. $\tilde{h}_i = -\Delta + \tilde{V}_i$, with $\tilde{V}_i = V + R_\psi^i$. Since $u_j \in L^2 \cap Q(-\Delta)$, by a Sobolov estimate [31] (for a simple discussion of this point, see [20]) it follows that $u_j^2 \in L^1 \cap L^{3/2 - \varepsilon}$, so by Young's inequality, $R_\psi^i \in L^\infty$. Thus $D(\tilde{h}_i) = D(-\Delta)$. Since $u_i \in D(\tilde{h}_i)$, we have u_i

continuous so that R^i_ψ is continuous. a) Now follows by a result of Kato [17] and c) by a result of Simon [29] (both specialized to the two-body case; see the original papers for other references including earlier results for the two body case). b) Follows by a bootstrap argument reminiscent of our argument in [23]: We exploit the following facts (see e.g. [24], Section IX.6):

a) Let Ω be a bounded open set. If $u \in L^2(\Omega)$; $-\Delta u = Wu$ and $W \in C^k(\Omega)$, then $D^\alpha u \in L^2$ for all multiindices α with $|\alpha| \leq k+2$.

b) If $D^\alpha u \in L^2(\Omega)$ for all α, then u is C^∞ on Ω.

The additional fact which we need is that if $u \in L^2(\mathbb{R}^3)$ and if $D^\alpha u \in L^2(\Omega)$, $|\alpha| \leq m$, then $g(x) = \int |u(y)|^2 |x-y|^{-1} dy$ is C^m on Ω. This follows by writing $|x|^{-1} = \varphi_1 + \varphi_2$ with $\varphi_2 \in C^\infty$ with support outside a ball of radius $\varepsilon/2$ and φ_1 supported in a ball of radius ε. Then $g(x) = \int |u(y)|^2 \varphi_1(x-y) dy + \int |u(y)|^2 \varphi_2(x-y) dy \equiv g_1 + g_2$. The g_2 term is C^∞ on all of $\mathbb{R}^3$. The g_1 term is easily seen to be C^m on those x such that $\{y \mid |x - y| < \varepsilon\} \subset \Omega$.

With a), b), and the above fact, u_j is C^∞ away from the R_j by an obvious inductive argument. $\square$

At first sight, the methods of Theorem 3.1 appear to be inapplicable to the HF case because of the non-local term. However, an elementary trick allows one to write the HF equations in local form; namely we consider the operator A on $\bigoplus_{j=1}^{N} L^2(R^3; \mathbb{C}^2)$ given by:

$$A_{ij} = \delta_{ij}(-\Delta + V(x) + R(x) - \varepsilon_i) + Q_{ij}(x)$$

with

$$Q_{ij}(x) = -\int |x-y|^{-1} \overline{u_j(y)} u_i(y) dy \ .$$

Then $A\Psi = 0$ where Ψ is the vector with $\Psi_i(x) = u_i(x)$. With this remark, the following can be proven by following the proof of Theorem 3.1:

Theorem 3.2. *The solutions of the* HF *equation* (7) *constructed in Theorem* 2.4 *obey:*
   a) *The u_i are globally Lipschitz and lie in $\mathscr{D}(h) = D(-\Delta)$.*
   b) *Away from the points $r = R_j$, the u_i are C^∞.*

   c) *Let $k_0 = \min_i |\varepsilon_i|^{1/2}$. Then for any $\alpha < k_0$:*

$$|u_i(x)| \leq C_\alpha \exp(-\alpha|x|), \quad all \ i \ .$$

Remarks. 1) The common exponential rate of falloff which was obtained comes about because we have written the HF equation as a single multicomponent equation. However, it is evident that barring some miraculous cancellation, the u_i's should have the same rate of falloff because in the HF equations $[(-\Delta + V)u_i](x)$ is a sum of terms containing all the $u_j(x)$'s in them. After making this remark in [22], we learned that it had already been made in the chemical physics literature [13].

2) By following the method of Kato [17] (or an alternative of Jensen [15]) one can give the precise singularity in the first derivatives of the u_i at the points R_j.

3) We believe that the u_i's are real analytic away from the R_j's.

4) In both Theorems 3.1 and 3.2, only the form of the equations and $u_i \in Q(-\Delta) \cap L^2$ is used. *Any* solutions satisfying this $Q(-\Delta)$ condition will obey the conclusions of the theorems.

§4. Connection with the Quantum Theory

We make explicit a remark of ours in [23]:

Theorem 4.1. *Let $E_N^Q(z_i, R_i)$ be given by (3) and define*

$$E_N^{HF}(z_i, R_i) \equiv \inf\{(\Psi, H\Psi) | \Psi \in \mathscr{D}_{phys}; \|\Psi\| = 1; \Psi \text{ a Slater determinant}\} .$$

Let R_i, z_i be N dependent in the following manner:
   a) $z_i/N \to \lambda_i$.
   b) $R_1 = 0; R_j N^{-1/3} \to r_j$ or to ∞.

Then

$$\lim_{N \to \infty} E_N^{HF}(z_i, R_i)/E_N^Q(z_i, R_i) = 1 .$$

Proof. $E_N^Q \leq E_N^{HF} < 0$ by the variational principle so clearly the $\overline{\lim}$ is ≤ 1. In our proof that *TF* theory is asymptotically correct (§ III of [23]) we constructed an explicit Slater determinant so that as $N \to \infty$, $(\Psi, H\Psi)/E_N^{TF} \to 1$ (where E^{TF} is the Thomas-Fermi energy). Since $E_N^Q/E_N^{TF} \to 1$ by [23], and $E_N^{HF} \leq (\Psi, H\Psi)$, the $\underline{\lim} \geq 1$. $\square$

Remarks. 1) As explained in [23], we expect $E_N^{HF} - E_N^Q = o(N^{5/3})$ and $E_N^Q = aN^{7/3} + bN^2 + cN^{5/3} + o(N^{5/3})$. The proof of these facts seems to us to be an important problem in understanding the bulk properties of large Z atoms and molecules. All we were able to obtain rigorously is the leading term $aN^{7/3}$. In [23], a conjecture, due to Scott, is made about the next term bN^2 (see [20] for more details).

2) We emphasize that Theorem 4.1 is only a limit theorem about total binding energy. It is physically more important to prove that HF theory gives asymptotically correct ionization energies.

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