THERE ARE NO UNFILLED SHELLS IN HARTREE-FOCK THEORY

Volker Bach[(1),*], Elliott H. Lieb[(1),(2)], Michael Loss[(3)] and Jan Philip Solovej[(2)]

[(1)] *Department of Physics, Jadwin Hall, Princeton University, P.O. Box 708, Princeton, NJ, 08544*

[(2)] *Department of Mathematics, Fine Hall, Princeton University, Princeton, NJ, 08544*

[(3)] *School of Mathematics, Georgia Institute of Technology, Atlanta, GA 30332*

Abstract: Hartree-Fock theory is supposed to yield a picture of atomic shells which may or may not be filled according to the atom's position in the periodic table. We prove that shells are always completely filled in an exact Hartree-Fock calculation. Our theorem generalizes to any system having a two-body interaction that, like the Coulomb potential, is repulsive.

The Hartree-Fock (HF) variational calculation provides an approximate determination of ground states and ground state energies of quantum mechanical systems such as atoms and molecules, and is widely used in physics and chemistry.

The picture of atoms it is supposed to yield is one of "shells" (or degenerate eigenvalues of the HF operator) which may or may not be filled according to the position of the atom in the periodic table. (Indeed, the concept of shells stems from HF theory itself, for shells are not overwhelmingly evident, or even precisely defined in the exact many-body wave function.) Despite years of attention to this subject, it is surprising that this notion of

* Current address: FB Mathematik MA 7-2, Technische Universität Berlin, Strasse des 17 Juni 136, D-W-1000 Berlin, Germany

unfilled shells has gone unchallenged. A very simple proof, which we give here, shows that *shells are always filled in HF theory.* In other words, the degeneracy of the highest filled level of the HF operator is always exactly what is needed to accommodate the assumed number of electrons.

The theorem and its proof given below obviously generalize to any system in which the two-body interaction V is repulsive, i.e., positive definite as an operator on the two-particle Hilbert space. In particular, V is allowed to be spin dependent and to contain projection operators, as in the nuclear physics setting. The electronic Coulomb repulsion, for example, satisfies this positivity condition. The one-body part of the Hamiltonian can be arbitrary. For convenience and because of its familiarity, we use the atomic Hamiltonian as an illustration.

Thus, we consider a Hamiltonian

$$H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m}\Delta_i + U(\mathbf{r}_i) \right) + \tfrac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i, \mathbf{r}_j)$$

acting on N-electron wave functions, i.e. wave functions $\Psi(\mathbf{r}_1, \sigma_1; \ldots; \mathbf{r}_N, \sigma_N)$ that are antisymmetric with respect to interchanging $(\mathbf{r}_i, \sigma_i)$ with $(\mathbf{r}_j, \sigma_j)$. In the example of an atom with nuclear charge Ze, U and V would be given by $U(\mathbf{r}) = -Ze^2/r$ and $V(\mathbf{r}, \mathbf{r}') = e^2|\mathbf{r} - \mathbf{r}'|^{-1}$.

To obtain an approximate value for the ground state energy, $E_Q = \min\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$, the HF calculation restricts attention to Slater determinants, i.e., wave functions of the form

$$\Phi(\mathbf{r}_1, \sigma_1; \ldots; \mathbf{r}_N, \sigma_N) = (N!)^{-1/2} \mathrm{Det}\{f_i(\mathbf{r}_j, \sigma_j)\} \tag{1}$$

in which $f_1, \ldots, f_N$ are orthonormal functions of space and spin: $\langle f_i|f_j\rangle = \delta_{ij}$. The approximate ground state energy is then given by the HF-energy, which is defined to be

$$E_{\mathrm{HF}} = \min\langle\Phi|H|\Phi\rangle, \quad \Phi \text{ has the form (1).} \tag{2}$$

Any minimizer, $\Phi_{\rm HF}$, i.e., a determinantal function satisfying $E_{\rm HF} = \langle\Phi_{\rm HF}|H|\Phi_{\rm HF}\rangle$, is a HF ground state. It may not be unique. We remark that mathematical precision actually requires an "infimum" rather than "minimum" in (2) because a HF ground state may not exist. This will be the case, e.g., for an atom with $N > 2Z + 1$, i.e., a very negative ion [1]. For neutral or positively ionized atoms and molecules, however, it was proved in [2] that a HF ground state does exist and, at least in this case, the word "minimum" in (2) is justified.

If a HF ground state does exist, it necessarily obeys the HF (or self-consistent field) eigenfunction equations

$$h_\Phi \varphi_k = \varepsilon_k \varphi_k \tag{3}$$

for all $1 \le k \le N$, where h_Φ is the one-body operator defined by its action on an arbitrary function of one space-spin variable by

$$\begin{aligned}(h_\Phi f)(\mathbf{r},\sigma) = &\left(-\frac{\hbar^2}{2m}\Delta + U(\mathbf{r}) + \int \sum_{\tau=\pm1}\sum_{j=1}^{N} |\varphi_j(\mathbf{r}',\tau)|^2 V(\mathbf{r},\mathbf{r}')d^3\mathbf{r}'\right) f(\mathbf{r},\sigma) \\ &- \sum_{\tau=\pm1}\sum_{j=1}^{N} \varphi_j(\mathbf{r},\sigma)\int \overline{\varphi}_j(\mathbf{r}',\tau) f(\mathbf{r}',\tau) V(\mathbf{r},\mathbf{r}')d^3\mathbf{r}',\end{aligned} \tag{4}$$

and where $\varphi_1,\ldots,\varphi_N$ denote the special N orthonormal functions comprising the energy minimizing Slater determinant $\Phi_{\rm HF}$. The eigenvalues, ε_k, of h_Φ give us some insight into the possible energy levels for binding an extra electron, but that is not our concern here.

Theorem: *Assume that V is positive definite, i.e., for every nonzero function ψ of two space-spin variables*

$$\sum_{\sigma_1,\sigma_2=\pm1} \int |\psi(\mathbf{r},\sigma;\mathbf{r}',\sigma')|^2 V(\mathbf{r},\mathbf{r}')d^3r d^3r' > 0.$$

Let φ be an eigenfunction of h_Φ with eigenvalue ε (i.e., $h_\Phi\varphi = \varepsilon\varphi$) that is orthogonal to the minimizing set $\varphi_1,\ldots,\varphi_N$, i.e., $\langle\varphi|\varphi_k\rangle = 0$ for all $1 \le k \le N$. Then $\varepsilon > \varepsilon_k$ for all $1 \le k \le N$.

Before proving this theorem let us point out its main corollaries. First, it implies that the functions $\varphi_1, \ldots, \varphi_N$ comprising $\Phi_{\rm HF}$ occupy the N *lowest* energy levels of h_Φ; the reader may or may not find this surprising, but we point out that there is no proof of this assertion without the assumption that $V \geq 0$. *Our main point, however, is the second implication which, indeed, is surprising:* $\Phi_{\rm HF}$ *does not leave any degenerate level unfilled. There is a gap because* $\varepsilon > \varepsilon_k$ *for all* $k = 1, 2, \ldots, N$.

Proof of the theorem: Assume $\varepsilon_1 \leq \varepsilon_2 \leq \ldots \leq \varepsilon_N$. We shall derive a contradiction to the assumption that $\varepsilon \leq \varepsilon_N$. First, we introduce some more notation. Denote ε by ε_{N+1} and φ by φ_{N+1}. Further for all $1 \leq k \leq N+1$ and $1 \leq l \leq N+1$, we define

$$
\begin{aligned}
h_k &= \left\langle \varphi_k \middle| -\frac{\hbar^2}{2m}\Delta - U(\mathbf{r}) \middle| \varphi_k \right\rangle \quad \text{and} \\
V_{k,l} &= \sum_{\sigma,\sigma'=\pm 1} \int \tfrac{1}{2} \left| \varphi_k(\mathbf{r},\sigma)\varphi_l(\mathbf{r}',\sigma') - \varphi_l(\mathbf{r},\sigma)\varphi_k(\mathbf{r}',\sigma') \right|^2 V(\mathbf{r},\mathbf{r}') d^3r d^3r'.
\end{aligned}
$$

Notice that $V_{k,k} = 0$ and $V_{k,l} > 0$ if $k \neq l$ since V is positive definite.

Now let $\widetilde{\Phi}$ be the Slater determinant built from $\varphi_1, \ldots \varphi_{N-1}, \varphi_{N+1}$, as in (1). One easily checks that

$$
\begin{aligned}
\langle \Phi_{\rm HF} | H | \Phi_{\rm HF} \rangle &= \sum_{k=1}^{N} h_k + \tfrac{1}{2} \sum_{k,l=1}^{N} V_{k,l} \quad , \\
\langle \widetilde{\Phi} | H | \widetilde{\Phi} \rangle &= \sum_{k=1}^{N-1} h_k + \tfrac{1}{2} \sum_{k,l=1}^{N-1} V_{k,l} + h_{N+1} + \sum_{l=1}^{N-1} V_{l,N+1} \quad ,
\end{aligned}
$$

and, for $1 \leq k \leq N+1$,

$$
h_k + \sum_{l=1}^{N} V_{k,l} = \langle \varphi_k | h_{\rm HF} | \varphi_k \rangle = \varepsilon_k. \tag{5}
$$

Notice that the term $l = k$ in the sum in (5) does not contribute since $V_{k,k} = 0$.

Since Φ_{HF} is the HF ground state it follows that $\langle\Phi_{\mathrm{HF}}|H|\Phi_{\mathrm{HF}}\rangle \leq \langle\widetilde{\Phi}|H|\widetilde{\Phi}\rangle$ and, thus,

$$\begin{aligned} 0 &\leq \langle\widetilde{\Phi}|H|\widetilde{\Phi}\rangle - \langle\Phi_{\mathrm{HF}}|H|\Phi_{\mathrm{HF}}\rangle \\ &= h_{N+1} - h_N + \sum_{l=1}^{N-1}(V_{l,N+1} - V_{l,N}) \\ &= \varepsilon_{N+1} - \varepsilon_N - V_{N,N+1} \leq -V_{N,N+1}. \end{aligned}$$

The last inequality uses the assumption $\varepsilon_{N+1} \leq \varepsilon_N$, but we then have the contradiction $0 \leq -V_{N,N+1} < 0$. QED

The proof does not give a rigorous estimate of the gap $\varepsilon_{N+1} - \varepsilon_N$, but it does show that the gap is at least $V_{N,N+1}$, which is usually not a tiny quantity. Thus, even an "approximate" degeneracy is unlikely.

This work was supported by the U.S. National Science Foundation through the following grants: PHY90-19433 A02 [VB and EHL]; DMS92-07703 [ML]; DMS92-03829 [JPS].

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