Unique Solutions to Hartree-Fock Equations for Closed-Shell Atoms

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In this talk, for all $x = (x_1, x_2, x_3) \in \mathbb{R}^3$:

$$|x| := \frac{1}{2}\sqrt{x_1^2 + x_2^2 + x_3^2}$$

Atoms

Hilbert space

$$\mathcal{H} = \bigwedge^N L^2(\mathbb{R}^3 \times \{1, \ldots, q\})$$

Atomic Hamiltonian

$$H_N = \sum_{k=1}^N (-\Delta_{x_k} - \frac{Z}{|x_k|}) + \sum_{j<k} \frac{1}{|x_j - x_k|}$$

Slater determinants

$$\varphi_1 \wedge \ldots \wedge \varphi_N = \frac{1}{\sqrt{N!}} \sum_\sigma \mathrm{sgn}(\sigma) \varphi_{\sigma 1} \otimes \ldots \otimes \varphi_{\sigma N}$$

Normalization:

$$\langle \varphi_j, \varphi_k \rangle := \int \overline{\varphi_j} \varphi_k \, dx = \delta_{jk}.$$

Hartree-Fock Functional and Hartree-Fock Equations

$$\mathcal{E}_N^{HF}(\varphi_1, \ldots, \varphi_N) = \big\langle (\varphi_1 \wedge \ldots \wedge \varphi_N), H_N(\varphi_1 \wedge \ldots \wedge \varphi_N) \big\rangle$$

$$= \sum_{k=1}^{N} \int |\nabla \varphi_k|^2 - \frac{Z}{|x|}|\varphi_k|^2 \, dx + \sum_{j<k} \int \frac{|\varphi_j(x)|^2 |\varphi_k(y)|^2}{|x-y|} \, dxdy$$

$$- \sum_{j<k} \int \frac{\overline{\varphi_j(x)}\varphi_k(x)\overline{\varphi_k(y)}\varphi_j(y)}{|x-y|} \, dxdy$$

Constraints: $\langle \varphi_j, \varphi_k \rangle = \delta_{jk}$. The Euler-Lagrange equations are:

$$\left(-\Delta - \frac{Z}{|x|} + \sum_{j=1}^{N} \int \frac{|\varphi_j(y)|^2}{|x-y|} \, dy \right) \varphi_k(x)$$

$$- \sum_{j=1}^{N} \varphi_j(x) \int \frac{\overline{\varphi_j(y)}\varphi_k(y)}{|x-y|} dy = \varepsilon_k \varphi_k(x), \quad k = 1, \ldots, N.$$

Critical Points of the Hartree-Fock Functional

1977 **Lieb, Simon**: there exists a minimizer if $N < Z + 1$.

1984 **Lieb**: there is no minimizer if $N \geq 2Z + 1$,

1987 **P.L. Lions**: there are ∞ many critical points if $N < Z + 1$

2000 **Cancé, Le Bris**: the level-shift SCF-algorithm converges to a critical point,

2003 **Solovej**: there is no minimizer if $N \geq Z + Q$.

Remark: The eigenvalues $\varepsilon_1, \ldots, \varepsilon_N$ in the HF-equations associated with a minimizer of the HF-functional are the lowest N eigenvalues of the Fock-operator.

Uniqueness of the Minimizer and other Critical Points

Joint work with Fabian Hantsch

Uniqueness in Other, Related Systems

- **Huber, Siedentop**: Solutions of the Dirac-Fock equations ...2007
- **Cancé, Deleurence, Lewin**: ...local defects in crystals: the reduced HF case, 2008.
- **Lenzmann** Uniqueness ....for pseudorelativistic Hartree equations, 2009.
- **Aschbacher, Fröhlich, Graf, Schnee, Troyer**: Symmetry breaking regime in the nonlinear Hartree equations, 2002.
- **Aschbacher, Squassina**: ...two-particle Hartree system, 2009.

Symmetries of the HF-Functional

$\mathcal{E}_N^{HF}(\varphi_1, \ldots, \varphi_N)$ only depends on the projection:

$$P = \sum_{k=1}^{N} |\varphi_k\rangle\langle\varphi_k|,$$

$$P(x,y) = \sum_{k=1}^{N} \varphi_k(x)\overline{\varphi_k(y)}, \qquad \rho(x) = \sum_{k=1}^{N} |\varphi_k(x)|^2.$$

HF-functional in terms of P:

$$\mathcal{E}_N^{HF}(P) = \mathrm{Tr}((-\Delta - \frac{Z}{|x|})P) + \frac{1}{2}\int \frac{\rho(x)\rho(y) - |P(x,y)|^2}{|x-y|} dxdy.$$

Hartree-Fock equations are equivalent to $[H_P, P] = 0$, which is satisfied if for some $\Omega \subset \mathbb{R}$

$$\boxed{P = \chi_\Omega(H_P), \qquad \mathrm{rank}\, \chi_\Omega(H_P) = N}$$

$$H_P = -\Delta - \frac{Z}{|x|} + \rho * \frac{1}{|x|} - K_P$$

Spherical Symmetry

- For all $R \in SO(3)$:

$$\mathcal{E}^{HF}(U(R)PU(P)^*) = \mathcal{E}^{HF}(P)$$
$$U(R)\psi(x) = \psi(R^{-1}x).$$

- Suppose P is unique minimizer

$\Rightarrow$ $U(R)PU(R)^* = P$ for all $R \in SO(3)$,

$\Rightarrow$ There is a basis of $\mathrm{Ran} P$ of the form:

$$\varphi_k(x) = \frac{1}{|x|} f_{n_k \ell_k}(|x|) Y_{\ell_k m}(x), \qquad -\ell_k \leq m \leq \ell_k.$$

$\Rightarrow$ All shells are filled! (noble gas atom.)

- Uniqueness modulo spherical symmetry?
Not addressed in this talk.

Non-Interacting Electrons

The minimizer of the functional

$$\mathrm{Tr}((-\Delta - \frac{Z}{|x|})P)$$

defined in the set of projections P of rank N is unique if and only if N is of the form

$$N = q\sum_{n=1}^{s} n^2, \qquad \text{some } s \in \mathbb{N},$$

I.e. N is the sum of multiplicities of lowest s eigenvalues of $-\Delta - Z/|x|$. Then the minimizer is the spectral projection

$$P = \chi_\Omega(-\Delta - \frac{Z}{|x|}), \qquad \Omega := [-1, -1/s^2]$$

Perturbation Theory

The set of scaled functions $Z^{3/2}\varphi_k(Zx)$, $k = 1, \ldots, N$, satisfy the HF-equations if and only if $\varphi_1, \ldots, \varphi_N$ solve

$$\Big(-\Delta - \frac{1}{|x|}\Big)\varphi_k + \frac{1}{Z}\Big(\rho * \frac{1}{|x|} - K_P\Big)\varphi_k = \frac{\varepsilon_k}{Z^2}\varphi_k.$$

We expect *uniqueness of the minimizer* provided that

$$Z \gg N = \sum_{n=1}^{s} n^2, \qquad \text{some } s \in \mathbb{N}.$$

Can we get uniqueness for existing ions in this way?

Theorem (Uniqueness of the Minimizer)

If the number of electrons, N, is of the form

$$N = q\sum_{n=1}^{s} n^2, \qquad q\text{=number of spin states}$$

and

$$Z > \frac{1}{\Delta_s}\big(12N + 4\sqrt{N} - 4\big), \qquad \Delta_s = s^{-2} - (s+1)^{-2},$$

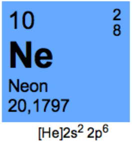
then the HF-functional $\mathcal{E}_N^{HF}$ has a unique minimizing rank N-projection P. Its range is spanned by N orbitals of the form

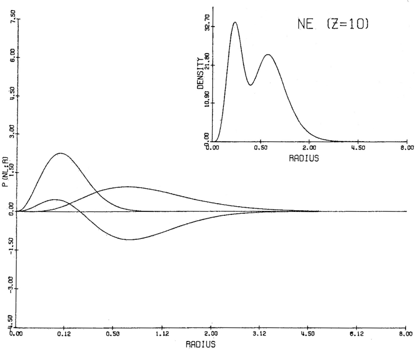
$$\varphi_{n\ell m\sigma}(x,\mu) = \frac{f_{n\ell}(|x|)}{|x|} Y_{\ell m}(x)\delta_{\sigma,\mu} \tag{1}$$

where $n \in \{1,\ldots,s\}$, $0 \le \ell \le n-1$, $-\ell \le m \le \ell$, $\sigma \in \{1,\ldots,q\}$, and each of these quadruples (n,ℓ,m,σ) occurs exactly once. In particular the density is spherically symmetric.

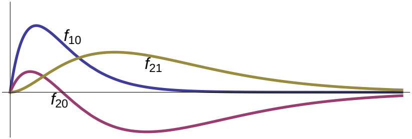
Remark: If $q = 2$, $N = 2$ then $Z \ge 35$ is sufficient.

Hartree-Fock Orbitals of Neon





Hartree–Fock radial functions and radial density function for Ne.



Hydrogen orbitals

Corollary

For $q = N = 2$ and $Z \geq 35$ the minimizer of the HF functional is unique and represented by two orbitals $\varphi_1, \varphi_2 \in L^2(\mathbb{R}^3, \mathbb{C}^2)$ of the form

$$\varphi_1 = \varphi \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \varphi_2 = \varphi \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

where φ is the unique minimizer of the Hartree functional

$$\mathcal{E}^H(\varphi) := \int |\nabla\varphi|^2 - \frac{Z}{|x|}|\varphi|^2 dx + \frac{1}{2}\int \frac{|\varphi(x)|^2|\varphi(y)|^2}{|x-y|} dxdy.$$

Moreover, φ is spherically symmetric.

Counter Example: It is clear that

$$\min_{\varphi_1,\varphi_2} \mathcal{E}^{HF}(\varphi_1, \varphi_2) < -1, \qquad \text{for } Z > 1,$$

but, by Ruskai and Stillinger (1984):

$$\min_{\varphi} \mathcal{E}^H(\varphi) \geq -1 \qquad \text{for } Z \leq 1.0268.$$

Uniqueness for the Hartree Functional: $q = N$

$$\mathcal{E}_N^H(\varphi_1, \ldots, \varphi_N) = \sum_{k=1}^{N} \int |\nabla \varphi_k|^2 - \frac{Z}{|x|} |\varphi_k|^2 dx + \sum_{i<k} \int \frac{|\varphi_i(x)|^2 |\varphi_k(y)|^2}{|x-y|} dx dy.$$

$$\int |\varphi_k|^2 dx = 1, \qquad k = 1 \ldots, N.$$

Theorem

If $Z > 3^{-1}(40N + 16\sqrt{2N} - 8)$ then the minimizer of the Hartree functional is unique, upon phase changes, and of the form $\varphi_1 = \varphi_2 = \ldots = \varphi_N = \varphi$ with a spherically symmetric and positive function φ.

N	2	3	4	5	6	7	8	9
$Z \geq$	35	51	66	81	96	111	126	140

Ingredients of the Proof

For the proof we need to solve:

$$\boxed{P = \chi_\Omega(H_P), \qquad \operatorname{rank} \chi_\Omega(H_P) = N}.$$

$$H_P := -\Delta - \frac{1}{|x|} + \frac{1}{Z}\Big(\rho * \frac{1}{|x|} - K_P\Big).$$

- $\Omega =$ neighborhood of the first N eigenvalues of $-\Delta - 1/|x|$,
- The $N-$th eigenvalue of $-\Delta - 1/|x|$ is separated by a gap of size Δ_s from the rest of the spectrum (by choice of N).
- For $Z \gg N$ the first N eigenvalues of H_P belong to Ω.
  $\rightarrow$ requires good eigenvalue bounds for H_P.
- For $Z \gg N$ the mapping $P \mapsto \chi_\Omega(H_P)$ is a contraction.
  $\rightarrow$ requires good control of $\chi_\Omega(H_P) - \chi_\Omega(H_Q)$ in terms of $P - Q$.

Proposition

Let $A, B : D \subset \mathcal{H} \to \mathcal{H}$ be self-adjoint operators and let $\Omega \subset \mathbb{R}$ be a bounded Borel set for which the spectra of A and B satisfy the gap conditions

$$\operatorname{dist}(\sigma(A) \cap \Omega, \sigma(B) \setminus \Omega) \geq \delta,$$
$$\operatorname{dist}(\sigma(B) \cap \Omega, \sigma(A) \setminus \Omega) \geq \delta,$$

for some $\delta > 0$. Suppose the spectrum of A and B in Ω is pure point. Then

$$\|\chi_\Omega(A) - \chi_\Omega(B)\| \leq \delta^{-1}\Big(\|(A-B)\chi_\Omega(A)\| + \|(A-B)\chi_\Omega(B)\|\Big).$$

where $\|\cdot\|$ denotes the Hilbert-Schmidt norm.

Remark: For Fock operator this implies that:

$$\|\chi_\Omega(H_P) - \chi_\Omega(H_Q)\| \leq \frac{8}{\delta Z}\big(1 + \sqrt{2N}\big)\sqrt{2N}\|P - Q\|.$$

Theorem (Restricted HF Theory)

Given $(n_1, \ell_1), \dots, (n_s, \ell_s)$ *with* $0 \le \ell_k \le n_k - 1$ *and* $0 \le n_k \le n_s$. *Suppose* $N = \sum_{k=1}^{s}(2\ell_k + 1)$.

(i) *If* $Z > 4N/\Delta_{n_s}$ *then there exist normalized functions* $f_1, \dots, f_s \in L^2(\mathbb{R}_+)$ *such that the* N *functions*

$$\varphi_{n\ell m}(x) := \frac{1}{|x|} f_{n\ell}(|x|) Y_{\ell m}(x), \qquad n = 1, \dots s,\ m = -\ell_n \dots \ell_n,$$

solve the Hartree-Fock equations with eigenvalues ε_j *satisfying*

$$-\frac{1}{n_j^2} \le \varepsilon_j \le -\frac{1}{(n_j+1)^2} + \frac{4N}{Z}. \tag{2}$$

(ii) *Assuming that* $Z > (12N + 4\sqrt{2N})/\Delta_s$ *and* (2) *the functions* $f_{n\ell}$ *in (i) are unique up to global phases.*

To solve the restricted Hartree-Fock equations we solve the fix-point equation

$$P = \sum_{j=1}^{s} \chi_{\Omega_j}(H_P)\chi_{\{\ell_j(\ell_j+1)\}}(L^2)$$

where

$$\Omega_j := \Big[-\frac{1}{n_j^2}, -\frac{1}{n_j^2} + \frac{4N}{Z} \Big].$$

We use Schauder-Tychonoff for existence and the contraction principle for uniqueness.