The ground state of the Dirac-Fock energy for molecules and crystals.

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The basic problem in nonrelativistic quantum chemistry

Given a fixed distribution of nuclei, with charge density ν and total charge $Z = \int_{\mathbb{R}^3} \nu \geq 0$, find the ground state of a system of N electrons in the external Coulomb field

$$\varphi = -\frac{1}{|x|} * \nu \ .$$

For $N = 1$ the state of an electron is a wave function $\psi \in L^2(\mathbb{R}^3, \mathbb{C})$ satisfying $\int_{\mathbb{R}^3} |\psi|^2 = 1$. The ground state solves

$$\min_{\int_{\mathbb{R}^3} |\psi|^2 = 1} \left(\psi, (-\frac{\Delta}{2} + \varphi)\psi\right)_{L^2}$$

The minimizer is an eigenstate of $-\frac{\Delta}{2} + \varphi$ with eigenvalue

$$\lambda_1 = \min \sigma(-\frac{\Delta}{2} + \varphi) \ .$$

The nonrelativistic N-body problem

For $N \geq 2$ the state of the system of electrons is a function $\Psi \in L^2((\{+,-\} \times \mathbb{R}^3)^N, \mathbb{C})$, normalized in L^2 and satisfying

$$\Psi(\cdots, \sigma_j, x_j, \cdots, \sigma_i, x_i, \cdots) = -\Psi(\cdots, \sigma_i, x_i, \cdots, \sigma_j, x_j, \cdots) .$$

In other words, $\Psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$. The ground state solves

$$\min_{||\Psi||^2=1} \langle \Psi, \mathcal{H}\Psi \rangle$$

where

$$\mathcal{H} := \sum_{i=1}^{N} \left(-\frac{\Delta_{x_i}}{2} + \varphi(x_i) \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$$

This exact N-body problem is numerically intractable for N large.

The Hartree-Fock approximation

One restricts the quadratic form $\Psi \mapsto \langle \Psi, \mathcal{H}\Psi \rangle$ to the class of the functions Ψ which are a simple (Slater) determinant:

$$\Psi = \sqrt{N!}\, \psi_1 \wedge \cdots \wedge \psi_N = \frac{1}{\sqrt{N!}} \det(\psi_i(x_j))$$

where $(\psi_1, ..., \psi_N)$ is an orthonormal system of $L^2(\mathbb{R}^3, \mathbb{C}^2)$, $\int_{\mathbb{R}^3} \varphi_i^* \varphi_j = \delta_{ij}$.

Since the set of all the Ψ's having this form is not a vector subspace of $\bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}^2)$, one then obtains an energy functional $\mathcal{E}_{HF}$ which is nonlinear in terms of $\psi_1, ..., \psi_N$.

The Hartree-Fock ground state is a minimizer of $\mathcal{E}_{HF}$. Since one has imposed restrictions of the form of Ψ, the ground state energy is overestimated.

The Hartree-Fock functional

$\mathcal{E}_{HF}$ only depends on $\gamma(x,y) = \sum_{k=1}^{N} \psi_k(x)\psi_k^*(y)$, the integral kernel of the projector γ on $\mathrm{Span}\{\psi_1, \cdots, \psi_N\}$. Denoting $\rho_\gamma(x) := \gamma(x,x)$ one finds

$$\mathcal{E}_{HF}(\gamma) = \mathrm{tr}((-\Delta + \varphi)\gamma) + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y) - |\gamma(x,y)|^2}{|x-y|} dx\, dy$$

The ground state minimizes $\mathcal{E}_{HF}(\gamma)$ in the class of operators γ satisfying the *convex* constraints $\gamma = \gamma^*$, $\gamma^2 \leq \gamma$, $\mathrm{tr}(\gamma) \leq N$ (Lieb '81). For $N \leq Z$ the ground state exists, saturates the constraints and solves

$$\gamma = \mathbf{1}_{(-\infty,\mu]}(H_\gamma)$$

where $\quad H_\gamma = -\frac{\Delta}{2} + \varphi + \frac{1}{|x|} * \rho_\gamma - \frac{\gamma(x,y)}{|x-y|}$ is the mean-field Hamiltonian.

μ is a Lagrange multiplier such that H_γ has exactly N eigenvalues below μ.

Relativistic quantum chemistry

When $Z \geq 26$ (Iron) the energies of the core electrons enter in the relativistic regime. As a consequence, models based on the nonrelativistic kinetic operator $-\Delta$ may lead to wrong predictions. For example, nonrelativistic models predict that:

-Gold is white.

-Lead is as hard as Diamond.

-Mercury is solid at room temperature.

Relativistic models give the correct predictions, but their use is much more delicate. They are based on the Dirac operator, which is not bounded below.

The Dirac operator

- Energy of a free electron ($p \longleftrightarrow -i\nabla$)

	non relativistic	relativistic
classical mechanics	$E = p^2/(2m)$	$E^2 = c^2p^2 + m^2c^4$
quantum mechanics	$H = -\Delta/(2m)$	$D^2 = -c^2\Delta + m^2c^4$

- Free Dirac operator ('28):

$$D^0 = -ic\sum_{k=1}^{3}\alpha_k\partial_k + \beta mc^2 = -ic\boldsymbol{\alpha}\cdot\nabla + \beta mc^2$$

$\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and β are 4×4 self-adjoint matrices satisfying

$$\alpha_i\alpha_j + \alpha_j\alpha_i = 2\delta_{ij}, \qquad \alpha_i\beta + \beta\alpha_i = 0.$$

D^0 is defined on $L^2(\mathbb{R}^3, \mathbb{C}^4)$ with domain $H^1(\mathbb{R}^3, \mathbb{C}^4)$ and

$$(D^0)^2 = -c^2\Delta + m^2c^4.$$

It is *unbounded from below*:

$$\sigma(D^0) = (-\infty; -mc^2] \cup [mc^2; +\infty).$$

Dirac's interpretation of the negative spectrum

Dirac (1934): *"We make the assumption that, in the world as we know it, nearly all the states of negative energy for the electrons are occupied, with just one electron in each state, and that a uniform filling of all the negative-energy states is completely unobservable to us."*

$\rightarrow$ **Vacuum = Dirac sea** = infinitely many virtual electrons occupying the negative energies.

Consequence: real electrons can only occupy positive energy states. Moreover, the Dirac sea hypothesis can be tested experimentally:

- The virtual electrons can feel an external field and will react accordingly $\rightarrow$ **Vacuum Polarization.**
- If a photon of high energy is absorbed by a virtual electron, an **electron-positron pair** can be created.

The Dirac-Fock model (Swirles, 1935)

Replacing the Schrödinger operator $-\Delta/2$ by the free Dirac operator D^0 in the Hartree-Fock equations, one gets the Dirac-Fock equations which are widely used in Relativistic Quantum Chemistry:

$$\begin{cases} \gamma = \chi_{[0,\mu]}(D_\gamma) \\ D_\gamma = D^0 + \alpha(\rho_\gamma - \nu) * \dfrac{1}{|\cdot|} - \alpha \dfrac{\gamma(x,y)}{|x-y|} \end{cases} \tag{1}$$

with $\mu \in (0,1)$ such that D_γ has exactly N eigenvalues between 0 and μ.

Units: $\hbar = m = c = 1$, $\alpha = e^2$ (fine structure cst).

The Dirac-Fock energy functional

The Dirac-Fock projector γ is a critical point, under the constraints $\gamma = \gamma^*$, $\gamma^2 = \gamma$, $\mathrm{tr}(\gamma) = N$, of the Dirac-Fock energy functional

$$\mathcal{E}_{\mathrm{DF}}(\gamma) = \mathrm{tr}(D^0\gamma) - \alpha \iint \frac{\nu(x)\rho_\gamma(y)}{|x-y|}dx\,dy + \frac{\alpha}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dx\,dy - \frac{\alpha}{2}\iint \frac{|\gamma(x,y)|^2}{|x-y|}dx\,dy,$$

Here, there is no problem in the definition of the energy. No ultraviolet cutoff is needed. **But** $\mathcal{E}_{\mathrm{DF}}$ is not bounded below. Any of its critical points has an infinite Morse index. The definition and computation of the ground state become problematic.

The case $N = 1$

For $N = 1$, γ is a projector of rank one, so we can equivalently work with a normalized wave function ψ in its range. The DF equation reduces to the linear eigenvalue problem

$$\big(D^0 - \alpha\, \nu * \frac{1}{|\cdot|}\big)\psi = \lambda\, \psi$$

and the ground state ψ_1 corresponds to the choice

$$\lambda_1 = \min\left([0,\infty) \cap \sigma(D^0 - \alpha\nu * \frac{1}{|\cdot|})\right) .$$

However the standard characterization of the ground state as minimizer of the Rayleigh quotient cannot be used, since D^0 is not bounded below. A consequence, in numerical computations, is the existence of "spurious states", i.e. eigenvalues of the discretized problem that do not approximate eigenvalues of the exact problem, even when the discretization is refined.

Talman's principle '86

If ν is a positive measure of total mass Z with $\alpha Z < 1$ then the ground state energy is

$$\lambda_1 = \inf_{\varphi \in C_c^\infty(\mathbb{R}^3, \mathbb{C}^2)\setminus\{0\}} \sup_{\substack{\psi = \binom{\varphi}{\chi} \\ \chi \in C_c^\infty(\mathbb{R}^3, \mathbb{C}^2)}} \frac{(\psi, (H - \alpha\nu * \frac{1}{|\cdot|})\psi)}{(\psi, \psi)}$$

Rigorous proof by Griesemer-Lewis-Siedentop '99 for small densities ν, by Dolbeault-Esteban-S. '00 for $\alpha Z \leq \sqrt{3}/2$, by Esteban-Lewin-S. 19' and Schimmer-Solovej-Tokus 19' when $\alpha Z \leq 1$.

Solutions of DF (Esteban-S. '99, Paturel '00)

Assume that N and $Z = \int_{\mathbb{R}^3} \nu$ are two positive integers satisfying $\alpha Z < \frac{2}{\pi/2+2/\pi}$ and $N \leq Z$. Then, there exists an infinite sequence $(\gamma^j)_{j\geq 0}$ of critical points of the Dirac-Fock functional $\mathcal{E}_{DF}$ on the manifold of projectors of rank N.

Each projector γ^j is solution of the Euler-Lagrange equation

$$[\gamma, D_\gamma] = 0$$

and satisfies the inequality $\gamma^j \leq \chi_{(0,1)}(D_{\gamma^j})$. In other words, γ^j is the projector on a space V^j of dimension N spanned by N eigenvectors of D_{γ^j} with eigenvalues between 0 and 1.

Moreover, for α small enough, $\gamma^1 = \chi_{[0,\mu]}(D_{\gamma^1})$ for a suitable $\mu \in (0,1)$. Its energy level is

$$\mathcal{E}_{\mathrm{DF}}(\gamma^1) \;=\; \min_{\substack{\gamma=\gamma^*=\gamma^2,\, tr(\gamma)=N,\\ \gamma\, \chi_{(-\infty,0)}(D_\gamma)=0}} \mathcal{E}_{\mathrm{DF}}(\gamma)$$

Closed-shell ground state of DF (Huber-Siedentop '07)

Assume that $N = 2, 8, 10, \cdots$, $Z = \int_{\mathbb{R}^3} \nu \geq N$ and $\alpha < \alpha_0(N, Z)$. Then, there exists a solution (γ, μ) of the self-consistent equation

$$\gamma = \mathbf{1}_{[0,\mu]}(D_\gamma) \ , \quad \mathrm{tr}(\bar{\gamma}) = N$$

of smallest energy among the solutions of this equation.

Method: fixed-point, in the spirit of the Roothaan algorithm.

Limitations: closed shells, $\alpha_0(N, Z)$ is very small (less than 3.10^{-3} in the most favorable case $N = 2\,, 60 < Z < 80$; much smaller for other values of Z and N).

Ground state of the relaxed DF energy (S.)

Assume that N and $Z = \int_{\mathbb{R}^3} \nu$ are two positive integers satisfying $N \leq Z$ and

$$\pi\alpha N \ < \ 2(1-2\alpha(N+Z))^{\frac{1}{2}}(1-\alpha Z)^{1/2}\left(1-2\alpha(N+Z)-\frac{\pi}{4}\alpha\, N\right)^{\frac{1}{2}}. \quad (2)$$

Then, there exists an operator $\bar{\gamma}$ solving the minimization problem

$$\mathcal{E}_{\rm DF}(\bar{\gamma}) \ = \min_{\substack{\gamma=\gamma^*,\mathrm{tr}(\gamma)\leq N \\ 0\leq\gamma\leq \mathbf{1}_{(0,+\infty)}(D_\gamma)}} \mathcal{E}_{\rm DF}(\gamma) - \mathrm{tr}(\gamma)\,.$$

This minimizer satisfies the Euler-Lagrange equation

$$\bar{\gamma} = \mathbf{1}_{[0,\mu)}(D_{\bar{\gamma}}) + q \quad \text{with} \quad 0 \leq q \leq \mathbf{1}_{\{\mu\}}(D_{\bar{\gamma}}) \quad \text{and} \quad \mathrm{tr}(\bar{\gamma}) = N\,. \quad (3)$$

Examples with $\alpha = 1/137$: for $N = 2$, one can take $2 \leq Z \leq 63$; for $N = Z$ one can take $Z \leq 22$.

Proof I: a retraction

Assume that N and $Z = \int_{\mathbb{R}^3} \nu$ are two positive integers satisfying (2) and $N \leq Z$. Let

$$\mathcal{G}(N) := \{\gamma = \gamma^* : \ 0 \leq \gamma \leq 1; \ \mathrm{tr}(\gamma) \leq N \, ; \ |D^0|\gamma \in \sigma_1\}$$

For $\gamma \in \mathcal{G}(N)$, let $P_\gamma^+ := \mathbf{1}_{(0,+\infty)}(D_\gamma)$. Let

$$\mathcal{G}_+(N) := \{\gamma \in \mathcal{G}(N) : \ \gamma \ \leq \ P_\gamma^+\}.$$

Then there is a neighborhood U of $\mathcal{G}_+(N)$ in $\mathcal{G}(N)$ such that, if $\gamma_0 \in U$ then the sequence defined by $\gamma_{n+1} = P_{\gamma_n}^+ \gamma_n P_{\gamma_n}^+$ converges geometrically to an operator $\theta(\gamma) \in \mathcal{G}_+(N)$. Moreover, if $\gamma_0 \in \mathcal{G}_+(N)$ then $\theta(\gamma_0) = \gamma_0$.

Proof II: Euler-Lagrange equation

Let $\overline{\gamma}$ be a minimizer of $(\mathcal{E}_{\rm DF} - {\rm tr})$ on $\mathcal{G}_+(N)$. Assume that $\overline{\gamma}$ does *not* satisfy the Euler-Lagrange equation (5). Let γ' be an *aufbau* projector on the N first positive eigenvalues of $D_{\overline{\gamma}}$. Let $\tilde{\gamma} := \theta\big((1-s_0)\overline{\gamma} + s_0\gamma'\big)$ where

$$s_0 = {\rm ArgMin}\{(\mathcal{E}_{\rm DF} - {\rm tr})\big[\theta\big((1-s)\overline{\gamma} + s\gamma'\big)\big]\,,\ s \in [0,1]\}.$$

Then $\tilde{\gamma} \in \mathcal{G}_+(N)$, $(\mathcal{E}_{\rm DF} - {\rm tr})(\tilde{\gamma}) < (\mathcal{E}_{\rm DF} - {\rm tr})(\overline{\gamma})$. This is a contradiction.

A relativistic ODA algorithm

This proof can be transformed into a relativistic version of the ODA algorithm of Cances-Lebris.

Given γ_n in $\mathcal{G}_+(N)$, let g_n be an *aufbau* projector on the N first positive eigenvalues of D_{γ_n}. Let $\gamma_{n+1} := \theta\big((1-s_n)\gamma_n + s_n g_n\big)$ where

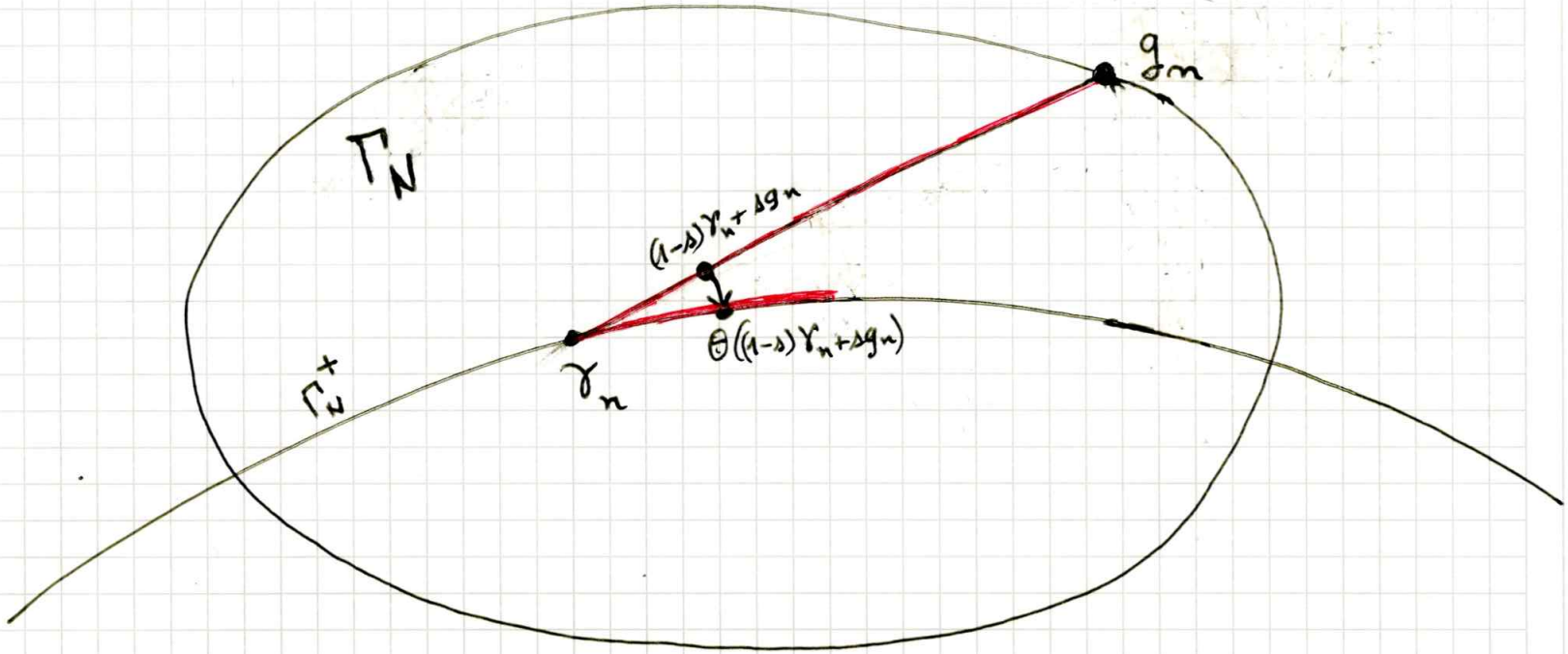
$$s_n = \mathrm{ArgMin}\{(\mathcal{E}_{\mathrm{DF}} - \mathrm{tr})\big[\theta\big((1-s)\gamma_p + s g_n\big)\big]\,,\ s \in [0,1]\}.$$

Then $\gamma_{n+1} \in \mathcal{G}_+(N)$, $(\mathcal{E}_{\mathrm{DF}} - \mathrm{tr})(\gamma_{n+1}) \leq (\mathcal{E}_{\mathrm{DF}} - \mathrm{tr})(\gamma_n)$ and

$$|D^0|^{1/2}(\gamma_{n+1} - \gamma_n) \to 0 \quad \text{in the Hilbert-Schmidt norm.}$$

As a consequence, there is a connected set S of solutions of the DF equations such that the distance of γ_n to S converges to zero as $n \to \infty$.

Maxime Chupin, Guillaume Legendre and Antoine Levitt have implemented this algorithm, and we are now testing it (work in progress).


g_n
Γ_N
$(1-\delta)\gamma_n + \delta g_n$
$\Theta((1-\delta)\gamma_n + \delta g_n)$
γ_n
Γ_N^+

The Dirac-Fock ground state for crystals (Catto, Meng, Paturel, S.)

Consider the case of a cubic crystal with elementary cell is $Q_\ell = (-\frac{\ell}{2}, \frac{\ell}{2}]^3$ and a single point-like nucleus per unit cell, located at the centre of the cell.

The electrons are treated quantum mechanically through a periodic density matrix $\Gamma = \int_{Q_\ell^*}^{\oplus} \gamma_\xi \, d\xi$ where each operator γ_ξ acts on the space of Bloch functions

$$L^2_\xi := \{\psi \in L^2_{loc}(\mathbb{R}^3, \mathbb{C}^4) \, : \, \psi(x + lm) = e^{i\xi}\psi(x) \, , \, \forall m \in \mathbb{Z}^3\}$$

and satisfies

$$\gamma_\xi = \gamma_\xi^* \, , \quad 0 \leq \gamma_\xi \leq \mathbf{1} \, , \quad \mathrm{tr}\, \gamma_\xi \leq q \, .$$

The periodic Dirac–Fock functional

For Γ in a suitable functional space one defines an energy of the form

$$\begin{aligned}\mathcal{E}^{DF}_{per}(\Gamma) = &\int_{Q^*_\ell} \mathrm{tr}_{L^2_\xi}[D_\xi \gamma_\xi]\, d\xi - \alpha z \int_{Q_\ell} G_\ell(x)\rho_\gamma(x)\, dx \\ &+ \frac{\alpha}{2} \iint_{Q_\ell \times Q_\ell} \rho_\gamma(x) G_\ell(x-y)\rho_\gamma(y)\, dxdy \qquad (4) \\ &- \frac{\alpha}{2} \iint_{Q^*_\ell \times Q^*_\ell} d\xi d\xi' \iint_{Q_\ell \times Q_\ell} \mathrm{tr}_4\left[\gamma_\xi(x,y)\gamma_{\xi'}(y,x)\right] W^\infty_\ell(\xi-\xi', x-y)\, dxdy.\end{aligned}$$

Existence of a ground state for relativistic crystals

Assume that q and z satisfy a certain condition that holds, in particular, for $\ell \geq 200$ and $\alpha = 1/137$ $q = z \leq 18$.

Then, there exists an operator $\bar{\Gamma}$ solving the minimization problem

$$\mathcal{E}^{DF}_{per}(\bar{\Gamma}) \;=\; \min_{\substack{\Gamma=\Gamma^*,\mathrm{tr}(\gamma_\xi)\leq q\,(\text{for a.e. }\xi)\\ 0\leq\gamma_\xi\leq \mathbf{1}_{(0,+\infty)}(D_{\Gamma,\xi})\,(\text{for a.e. }\xi)}} \mathcal{E}_{\mathrm{DF}}(\Gamma) - \mathrm{tr}(\Gamma)\,.$$

This minimizer satisfies the Euler-Lagrange equations

$$\bar{\gamma}_\xi = \mathbf{1}_{[0,\mu)}(D_{\bar{\Gamma},\xi}) + q_\xi \quad \text{with} \quad 0 \leq q_\xi \leq \mathbf{1}_{\{\mu\}}(D_{\bar{\Gamma},\xi})\,, \quad \mathrm{tr}(\bar{\gamma}_\xi) = q\,. \quad (5)$$

Here, $D_{\Gamma,\xi}$ is the mean-field operator generated by the periodic nuclear density and the electronic density matrix Γ in the Block waves subspace L^2_ξ.

THANK YOU!