The Hartree-Fock Model

An upper bound for the quantum ground state energy

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Outline

Why does this matter?

The goal

We want to compute the **ground state energy**

$$E^{\mathrm{qu}} = \min_{\Psi \in \mathcal{W}_N} \langle \Psi, H_N \Psi \rangle$$

of a system of N quantum particles.

The obstacle

Ψ depends on dN variables. For a water molecule ($N = 10$, $d = 3$): 30 variables, at least $\sim 10^9$ values just to store Ψ on a coarse grid.

The strategy

The linear problem is intractable (in fact **QMA-hard**). We approximate E^{qu} by simpler, computable models:

$$\underbrace{E^{\mathrm{qu}}}_{\text{exact}} \leq \underbrace{E_N^{\mathrm{HF}}}_{\text{Hartree-Fock}} .$$

Restricting the minimisation set makes **nonlinearities emerge**.

This talk: derive the Hartree-Fock upper bound, and study the resulting nonlinear model.

From classical to quantum mechanics

Three levels of description

Classical
(X, P)
$E^{\mathrm{cl}}(X, P)$

→ *uncertainty* →

Statistical
$\mathrm{d}\mu_X, \mathrm{d}\mu_P$
$+$ entropy

→ *measure correlation* →

Quantum
$\Psi \in L^2((\mathbb{R}^d)^N)$
$\langle \Psi, H_N \Psi \rangle$

$\inf E^{\mathrm{cl}} = -\infty$

same problem

$E^{\mathrm{qu}} > -\infty$

Classical mechanics. N particles with positions x_i, momenta p_i:

$$E^{\mathrm{cl}}(X, P) = \sum_{i=1}^{N} \frac{|p_i|^2}{2} + \sum_{i=1}^{N} V(x_i) + \sum_{i<j} W(x_i - x_j).$$

Minimising gives $p_i = 0$; and for $V(x) = -Z/|x|$ one finds $E^{\mathrm{cl}} = -\infty$: *any atom would be an infinite source of energy.*

Statistical mechanics and entropy

Statistical description. Positions and momenta are known only through probability measures $\mathrm{d}\mu_X \geq 0$, $\mathrm{d}\mu_P \geq 0$ with total mass 1:

$$E_0^{\mathrm{stat}}(\mu) = \iint E^{\mathrm{cl}}(X,P)\,\mathrm{d}\mu_X(X)\,\mathrm{d}\mu_P(P).$$

Indistinguishable particles ⇒ entropy

Particles are indistinguishable: the measures are symmetric, $\mathrm{d}\mu(X_\sigma) = \mathrm{d}\mu(X)$ for all $\sigma \in \mathfrak{S}_N$. This makes some configurations far more likely than others. The Shannon entropy of a distribution $(p_1,\dots,p_M)$ is

$$S(p_1,\dots,p_M) = -\sum_{j=1}^{M} p_j \log p_j.$$

At temperature $T > 0$, one minimises the **free energy** $E_T^{\mathrm{stat}}(\mu) = E_0^{\mathrm{stat}}(\mu) + T\,S(\mu)$. Raising T *convexifies* the problem — but does not yet cure the collapse $E = -\infty$.

The quantum postulate

Wave function

A system of N indistinguishable particles is described by $\Psi \in L^2((\mathbb{R}^d)^N, \mathbb{C})$, $\|\Psi\|_{L^2} = 1$, with

$$|\Psi|^2(X) = \mu_X(X) \quad \text{(position)}, \qquad |\widehat{\Psi}|^2(P) = \mu_P(P) \quad \text{(momentum)},$$

where $\widehat{\Psi} = \mathcal{F}\Psi$ is the Fourier transform (an isometry, by Parseval).

Using $\widehat{\nabla_i \Psi}(P) = -i\, p_i \widehat{\Psi}(P)$ and Parseval, $\int |p_i|^2 |\widehat{\Psi}|^2 = \|\nabla_i \Psi\|_{L^2}^2$, the energy becomes

$$E^{\rm qu}(\Psi) = \langle \Psi, H_N \Psi \rangle, \qquad H_N = \sum_{i=1}^N \Big(-\tfrac{1}{2}\Delta_i + V(x_i) \Big) + \sum_{i<j} W(x_i - x_j).$$

The kinetic energy saves the day

The correlation between the measures in position and momentum forbids a particle from being both localised *and* at rest: this is the uncertainty principle, and it gives $E^{\rm qu} > -\infty$.

Bosons, fermions and the Pauli principle

Indistinguishability forces $|\Psi|(X_\sigma) = |\Psi|(X)$. Removing the modulus leaves two possibilities:

Bosons

$$\Psi(X_\sigma) \;=\; \Psi(X)$$

(symmetric)

Fermions

$$\Psi(X_\sigma) \;=\; \varepsilon(\sigma)\Psi(X)$$

(antisymmetric)

electrons live here

For fermions, swapping two particles produces a sign -1. The set of admissible fermionic wave functions is

$$\mathcal{W}_N = \left\{\Psi \in L^2((\mathbb{R}^d)^N) : \; \|\Psi\|_{L^2} = 1, \; \Psi(X_\sigma) = \varepsilon(\sigma)\Psi(X) \; \forall \sigma \in \mathfrak{S}_N\right\}.$$

ground state energy = first eigenvalue

By the Courant-Fischer (min-max) principle,

$$\inf_{\Psi \in \mathcal{W}_N} \langle \Psi, H_N \Psi \rangle = \lambda_1(H_N).$$

Density matrices

Reduced density matrices

Definition

For $\Psi \in \mathcal{W}_N$ and $1 \le k \le N$, the k-**body density matrix** is

$$\gamma_\Psi^{(k)}(x_1, \ldots, x_k; y_1, \ldots, y_k) = \binom{N}{k} \int_{(\mathbb{R}^d)^{N-k}} \Psi(x_1, \ldots, x_k, z)\, \overline{\Psi(y_1, \ldots, y_k, z)}\, \mathrm{d}z.$$

Its diagonal is the k-body density $\rho_\Psi^{(k)}$; $\rho_\Psi := \rho_\Psi^{(1)}$ is the **electron density**, with $\int \rho_\Psi = N$.

The 1-body matrix $\gamma_\Psi := \gamma_\Psi^{(1)}$ seen as an operator on $L^2(\mathbb{R}^d)$:

$$(\gamma_\Psi f)(x) = \int_{\mathbb{R}^d} \gamma_\Psi(x, y)\, f(y)\, \mathrm{d}y.$$

It satisfies $\mathrm{Tr}(\gamma_\Psi) = N$, $0 \le \gamma_\Psi \le 1$.

Key fact

The full energy $E^{\mathrm{qu}}(\Psi)$ depends on Ψ *only* through $\gamma_\Psi^{(1)}$ and $\rho_\Psi^{(2)}$ — objects of **fixed** dimension, independent of N.

The energy in terms of density matrices

Theorem

For every $\Psi \in \mathcal{W}_N$,

$$E^{\mathrm{qu}}(\Psi) = \frac{1}{2}\mathrm{Tr}(-\Delta\,\gamma_\Psi^{(1)}) + \int_{\mathbb{R}^d} V(x)\,\rho_\Psi(x)\,\mathrm{d}x + \frac{1}{2}\iint_{\mathbb{R}^d\times\mathbb{R}^d} W(x-y)\,\rho_\Psi^{(2)}(x,y)\,\mathrm{d}x\,\mathrm{d}y.$$

Curse of dimensionality, again

One could minimise over $\gamma^{(2)}$ alone (4 variables). But the set of *representable* $\gamma^{(2)}$ has exponentially many constraints in N: the difficulty is conserved.

The Hartree-Fock energy

Slater determinants

Idea. Restrict the minimisation to a simpler subset of $\mathcal{W}_N$.

Definition

Given an orthonormal family $\varphi_1, \ldots, \varphi_N \in L^2(\mathbb{R}^d)$, set

$$\Phi(X) = \frac{1}{\sqrt{N!}} \det\big[\varphi_i(x_j)\big]_{1 \le i,j \le N}.$$

Then $\Phi \in \mathcal{W}_N$ (Pauli from the determinant; $\|\Phi\| = 1$ from orthonormality). Such Φ is a **Slater determinant**; write $\mathcal{S}_N \subset \mathcal{W}_N$ for their set.

Density matrices of a Slater determinant (Theorem)

$$\gamma_\Phi^{(1)}(x,y) = \sum_{j=1}^{N} \varphi_j(x)\overline{\varphi_j(y)}, \qquad \rho_\Phi^{(2)}(x,y) = \tfrac{1}{2}\Big(\rho(x)\rho(y) - |\gamma_\Phi^{(1)}(x,y)|^2\Big).$$

All three quantities depend only on $\gamma_\Phi^{(1)}$. The cross term $-|\gamma|^2$ is the origin of **exchange**.

The Hartree-Fock energy functional

Inserting $\rho_\Phi^{(2)}(x,y) = \frac{1}{2}(\rho(x)\rho(y) - |\gamma|^2(x,y))$ into the energy gives $E^{\mathrm{qu}}(\Phi) = E^{\mathrm{HF}}(\gamma_\Phi)$ with:

HF energy

$$E^{\mathrm{HF}}(\gamma) = \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int_{\mathbb{R}^d} V\rho_\gamma + \underbrace{\frac{1}{2}\iint W(x-y)\rho_\gamma(x)\rho_\gamma(y)}_{\text{Hartree term}} - \underbrace{\frac{1}{2}\iint W(x-y)|\gamma(x,y)|^2}_{\text{Fock (exchange) term}}$$

where $\rho_\gamma(x) = \gamma(x,x)$.

Hartree term:
classical electrostatic energy of the charge density ρ_γ.

Fock term:
purely quantum, from antisymmetry. For $W \geq 0$ it *lowers* the energy.

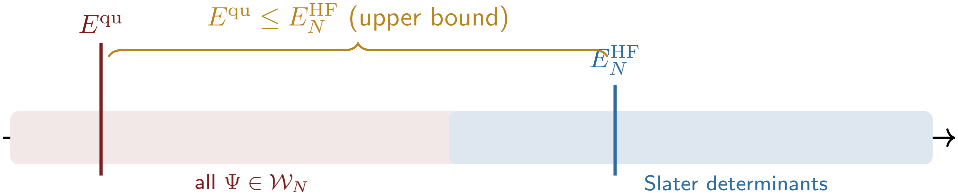
The minimisation set is a set of projectors

Characterisation

Since $\gamma_\Phi = \sum_{j=1}^{N} |\varphi_j\rangle\langle\varphi_j|$ is the orthogonal projector onto $\operatorname{span}\{\varphi_1, \dots, \varphi_N\}$,

$$\mathcal{P}_N^{\text{Slater}} = \left\{\gamma_\Phi : \Phi \in \mathcal{S}_N\right\} = \left\{\gamma = \gamma^* : \ \gamma^2 = \gamma, \ \operatorname{Tr}(\gamma) = N\right\}.$$

The HF energy is then $E_N^{\text{HF}} = \inf\left\{E^{\text{HF}}(\gamma) : \gamma \in \mathcal{P}_N^{\text{Slater}}\right\} \geq E^{\text{qu}}$.



Convexification (Coulomb case)

Neither $\mathcal{W}_N$ nor $\mathcal{P}_N^{\text{Slater}}$ is convex — a source of numerical instability. We pass to the convex hull.

Convex hull of the projectors

A self-adjoint γ is a rank-N projector iff its eigenvalues are 0 or 1 and $\operatorname{Tr}(\gamma) = N$. Relaxing to $0 \leq \gamma \leq 1$ gives the convex set

$$\mathcal{P}_N = \{\gamma = \gamma^* : \ 0 \leq \gamma \leq 1, \ \operatorname{Tr}(\gamma) = N\}, \qquad \widetilde{E}_N^{\text{HF}} = \inf_{\gamma \in \mathcal{P}_N} E^{\text{HF}}(\gamma) \leq E_N^{\text{HF}}.$$

Theorem (Coulomb case: $d = 3$, $W = 1/|x|$, $V = -\sum_i z_i/|x - R_i|$)

If $N \leq Z = \sum_i z_i$, the relaxed problem has minimisers, and *every* minimiser $\gamma \in \mathcal{P}_N$ is in fact a projector: $\gamma \in \mathcal{P}_N^{\text{Slater}}$. Hence $\widetilde{E}_N^{\text{HF}} = E_N^{\text{HF}}$.

The condition $N \leq Z$ (neutral or positive ion) prevents loss of electrons to infinity.

The chain of upper bounds

Since $W = 1/|x| \geq 0$, the Fock term $-\frac{1}{2}\iint W|\gamma|^2$ is negative. Dropping it gives a further (cruder) upper bound: the **Hartree energy**.

Hartree functional

$$E^{\mathrm{H}}(\gamma) = \tfrac{1}{2}\mathrm{Tr}(-\Delta\gamma) + \int V\rho_\gamma + \tfrac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y, \qquad E_N^{\mathrm{H}} = \inf_{\gamma\in\mathcal{P}_N} E^{\mathrm{H}}(\gamma).$$

In the Coulomb case E^{H} is *convex* in γ.

E^{qu} exact $\leq$ $E_N^{\mathrm{HF}} = \widetilde{E}_N^{\mathrm{HF}}$ Hartree-Fock $\leq$ E_N^{H} Hartree

Both E_N^{HF} and E_N^{H} require minimising a *nonlinear* functional over the convex set $\mathcal{P}_N$ — now numerically accessible.

The Fock operator and SCF

Euler-Lagrange equations

Minimise E^{HF} over orthonormal $(\varphi_1, \ldots, \varphi_N)$. With Lagrange multipliers (λ_{jk}) for the constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$, stationarity reads

$$\frac{\delta E^{\mathrm{HF}}}{\delta \overline{\varphi_k}} = \sum_j \lambda_{jk} \varphi_j, \qquad \text{i.e.} \qquad \widehat{F}[\gamma]\, \varphi_k = \sum_j \lambda_{jk} \varphi_j,$$

where $\widehat{F}[\gamma]$ is the **Fock operator**. Diagonalising the Hermitian matrix (λ_{jk}) by a unitary rotation:

Hartree-Fock equations (canonical form)

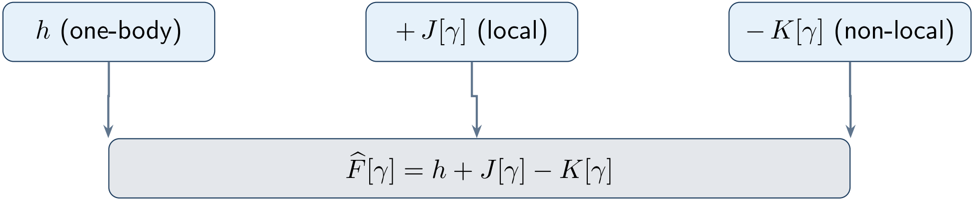
$$\widehat{F}[\gamma]\, \varphi_i = \varepsilon_i\, \varphi_i, \qquad i = 1, \ldots, N,$$

with orbital energies $\varepsilon_i \in \mathbb{R}$, and $\gamma = \sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i|$.

The Fock operator

$\widehat{F}[\gamma] = h + J[\gamma] - K[\gamma]$ with $h = -\frac{1}{2}\Delta + V$

- **Direct (Hartree) potential** — *local*: $\big(J[\gamma]\psi\big)(x) = \big(\int W(x-y)\rho_\gamma(y)\,\mathrm{d}y\big)\psi(x)$
- **Exchange (Fock) potential** — *non-local*: $\big(K[\gamma]\psi\big)(x) = \int W(x-y)\gamma(x,y)\psi(y)\,\mathrm{d}y$

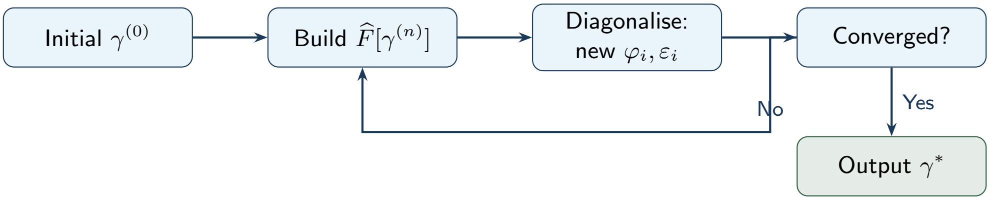


Self-consistency and the SCF algorithm

The nonlinearity

$\widehat{F}[\gamma]$ depends on $\gamma = \sum_i |\varphi_i\rangle\langle\varphi_i|$, yet the φ_i are its own eigenfunctions: a **nonlinear eigenvalue problem**.

Fixed point: find γ with $\gamma = \Pi_{\leq\mu}\big(\widehat{F}[\gamma]\big)$, the projector onto the N lowest eigenvalues.



Summary

Summary

1. **Setting.** $E^{\text{qu}} = \min_{\Psi \in \mathcal{W}_N} \langle \Psi, H_N \Psi \rangle = \lambda_1(H_N)$ — intractable.
2. **Density matrices.** energy depends only on $\gamma_\Psi^{(1)}$ and $\rho_\Psi^{(2)}$.
3. **Ansatz.** Slater determinants $\Leftrightarrow$ rank-N projectors $\gamma^2 = \gamma$.
4. **Energy.** $E^{\text{HF}}(\gamma) = \frac{1}{2}\text{Tr}(-\Delta\gamma) + \int V\rho +$ Hartree − Fock.
5. **Equations.** $\widehat{F}[\gamma]\varphi_i = \varepsilon_i \varphi_i$, solved by SCF; $E^{\text{qu}} \leq E_N^{\text{HF}}$.

Take-home message

Hartree-Fock = best single-determinant upper bound to E^{qu}. Restricting the minimisation set to projectors turns a linear problem in huge dimension into a *nonlinear* one in fixed dimension.

Thank you.

Questions?

Based on the graduate lecture notes *Modèles non linéaires en mécanique quantique* from David GONTIER: *NonLinearModelsInQM.pdf*

The slides were generated using AI.