An introduction to quantum chemistry: the Hartree-Fock model
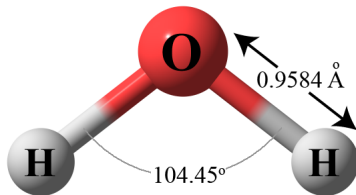
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What is quantum chemistry?

- When working at very small scales (molecules), the world is «quantic»
- Chemistry is about calculating ground state energy of molecules
- Therefore, we need quantum models to predict chemical properties of systems.

Example : geometry of the water molecule

Some numbers

- 30% of the worldwide CPU time.
- The papers in the topic are quoted approximatively 6 times a day.

A simple introduction to quantum mechanics

Let us consider N identical particles of mass $m = 1$, in a potential V, and interacting with W.

The system is entirely described by

- The positions of the particles $\mathbf{x}_i$
- The moments of the particles $\mathbf{p}_i$ (recall that $m\mathbf{v}_i = \mathbf{p}_i$, where $\mathbf{v}_i$ is the speed).

The total energy of the system is

$$\mathcal{E}(\mathbf{x}_1, \ldots, \mathbf{x}_N; \mathbf{p}_1, \ldots \mathbf{p}_N) = \underbrace{\sum_{i=1}^{N} \frac{1}{2}\mathbf{p}_i^2}_{\text{kinetic energy}} + \underbrace{\sum_{i=1}^{N} V(\mathbf{x}_i)}_{\text{external potential energy}} + \underbrace{\sum_{1 \leq i < j \leq N} W(\mathbf{x}_i, \mathbf{x}_j)}_{\text{interaction energy}}.$$

Problem:

With only 1-particle (an electron), and a Coulomb interaction between the electron and a hydrogen nucleus at the origin $V(\mathbf{x}) \approx \dfrac{-1}{|\mathbf{x}|}$, this energy can be arbitrary negative.

With this model, an hydrogen atom is an infinite reservoir of energy!
We need to go to the quantum world to study the ground state of molecules.

Suppose that there is a source of uncertainties in the model.

- $P_x(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ probability that the first particle is in $\mathbf{x}_1$, the second in $\mathbf{x}_2$, ...
- $P_p(\mathbf{p}_1, \ldots \mathbf{p}_N)$ probability that the first particle has momenta $\mathbf{p}_1$, ...

It must hold $P_x \geq 0$, $P_p \geq 0$, and

$$\int_{\mathbb{R}^{3N}} P_p(\mathbf{p}_1, \ldots, \mathbf{p}_N)\mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N = \int_{\mathbb{R}^{3N}} P_x(\mathbf{x}_1, \ldots, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_N = 1.$$

The average total energy is

$$\mathcal{E}(P_x, P_p) = \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^{N} \frac{1}{2}\mathbf{p}_i^2 \right) P_p(\mathbf{p}_1, \ldots, \mathbf{p}_N)\mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N$$

$$+ \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^{N} V(\mathbf{x}_i) + \sum_{1 \leq i,j \leq N} W(\mathbf{x}_i, \mathbf{x}_j) \right) P_x(\mathbf{x}_1, \ldots, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_N.$$

Without other constraints on P_p and P_x, the energy can still be arbitrary negative

Postulate (first postulate of Quantum Mechanics)

There exists a *wave-function* $\Psi : \mathbb{R}^{3N} \to \mathbb{C}$ *such that*

- $|\Psi(\mathbf{x}_1, \ldots \mathbf{x}_N)|^2 = P_x(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ *is the probability that the particles are in* $\mathbf{x}_1$, $\mathbf{x}_2$, ...
- $|\widehat{\Psi}(\mathbf{p}_1, \ldots, \mathbf{p}_2)|^2 = P_p(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ *is the probability that the momenta are* $\mathbf{p}_1$, $\mathbf{p}_2$, ...

Here, $\widehat{\Psi}$ is the normalized Fourier transform of Ψ:

$$\widehat{\Psi}(\mathbf{p}_1, \ldots, \mathbf{p}_N) = \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^{3N}} \Psi(\mathbf{x}_1, \ldots \mathbf{x}_N) e^{-i(\mathbf{p}_1 \cdot \mathbf{x}_1 + \ldots + \mathbf{p}_N \cdot \mathbf{x}_N)} d\mathbf{x}_1 \ldots d\mathbf{x}_N.$$

From the equality $\int P_x = 1$, we deduce that

$$\|\Psi\|^2 := \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \ldots d\mathbf{x}_N = 1,$$

which automatically ensures that $\|\widehat{\Psi}\| = 1$. The total energy is

$$\mathcal{E}(\Psi) = \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^{N} \frac{1}{2} \mathbf{p}_i^2 \right) |\widehat{\Psi}(\mathbf{p}_1, \ldots, \mathbf{p}_N)|^2 d\mathbf{p}_1 \ldots d\mathbf{p}_N$$

$$+ \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^{N} V(\mathbf{x}_i) + \sum_{1 \le i,j \le N} W(\mathbf{x}_i, \mathbf{x}_j) \right) |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \ldots d\mathbf{x}_N.$$

Lemma

For all good choices of V and W (e.g. Coulomb potential), it holds

$$I := \inf \{\mathcal{E}(\Psi), \quad \|\Psi\| = 1\} > -\infty$$

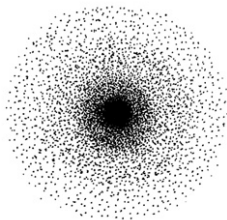I is called the ground state energy of the system, the ground state is the minimizer.

Figure: Electronic cloud ($= |\Psi|^2$) of the ground state of the Hydrogen atom.

Because the particles are indistinguishable, it must hold, for any permutation $p \in \mathfrak{S}_N$,

$$P_x(x_{p(1)}, \ldots, x_{p(N)}) = P_x(x_1, \ldots, x_N) \quad \text{hence} \quad |\Psi(x_{p(1)}, \ldots, x_{p(N)})|^2 = |\Psi(x_1, \ldots, x_N)|^2.$$

Fact. There are only two possibilities:

- Either $\Psi(x_{p(1)}, \ldots, x_{p(N)}) = \Psi(x_1, \ldots, x_N)$ for all $p \in \mathfrak{S}_N \implies$ Bosons
- Either $\Psi(x_{p(1)}, \ldots, x_{p(N)}) = \varepsilon(p)\Psi(x_1, \ldots, x_N)$ for all $p \in \mathfrak{S}_N \implies$ Fermions

We are working with electrons, which are fermions. We introduce the fermionic space

$$\bigwedge_{i=1}^{N} L^2(\mathbb{R}^3) = \left\{ \Psi \in L^2(\mathbb{R}^{3N}), \quad \Psi(x_{p(1)}, \ldots, x_{p(N)}) = \varepsilon(p)\Psi(x_1, \ldots, x_N) \right\}$$

The electronic problem to solve is

$$I = \inf \left\{ \mathcal{E}(\Psi), \quad \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \quad \|\Psi\| = 1 \right\}$$

with

$$\mathcal{E}(\Psi) = \int_{\mathbb{R}^{3N}} \overline{\Psi(\vec{x})} \left(\sum_{i=1}^{N} -\frac{1}{2}\Delta_i + \sum_{i=1}^{N} V(x_i) + \sum_{1 \leq i < j \leq N} W(x_i - x_j) \right) \Psi(\vec{x}) d\vec{x}.$$

How to find the ground state energy with a computer?

This model is extremely accurate!

- Example: ionization of Helium. Calc. 5 945 262 288 Mhz, Exp. 5 945 204 356 Mhz

Problem:
We have a minimization problem for $\Psi \in L^2(\mathbb{R}^{3N})$.
10 degrees of freedom per direction $\implies 10^{3N}$ degrees of freedom in total.

- Ok for small system (Helium)
- Impossible for large systems. ex: Water molecule (N=10), Uranium (N= 92),...

«Curse of dimensionality»

It is necessary to make approximations!
Chemical accuracy:

- energy of a C atom: ≈ 100 Ha
- energy of a H atom: ≈ 0.5 Ha
- energy of a covalent bond: ≈ 0.15 Ha

We need precision up to 4-digits to predict the dissociation of the methane CH_4.

Recall that we want

$$I = \inf \left\{ \mathcal{E}(\Psi), \quad \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \quad \|\Psi\| = 1 \right\}$$

Idea: minimize on a smaller set $\mathcal{M} \subset \left\{ \Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3), \quad \|\Psi\| = 1 \right\} \implies I_{\mathcal{M}}$.

Facts

- It obviously holds $I \leq I_{\mathcal{M}}$
- If $\mathcal{M}$ is large enough, $I_{\mathcal{M}}$ is a good approximation of I.
- The energy $\mathcal{E}$ can have much simpler expression on $\mathcal{M}$ for a correct choice of $\mathcal{M}$.

The Hartree-Fock model

Choose

$$\mathcal{M} = \left\{ \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = (N!)^{-1/2} \det \left(\phi_k(\mathbf{x}_l) \right)_{1 \leq k, l \leq N} \quad \text{with} \quad \int \phi_k \phi_l = \delta_{kl} \right\}.$$

$$\mathcal{M} = \left\{ \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = (N!)^{-1/2} \det \left(\phi_k(\mathbf{x}_l) \right)_{1 \le k, l \le N} \quad \text{with} \quad \int \phi_k \phi_l = \delta_{kl} \right\}.$$

Any element of $\mathcal{M}$ is characterized by the N functions $\phi_k \in L^2(\mathbb{R}^3)$.
In particular, 10 degrees of freedom $\implies 3N \times 10$ degrees of freedom in total.

Introducing

$$\gamma(\mathbf{x}, \mathbf{y}) = \sum_{i=1}^{N} \overline{\phi_i(\mathbf{x})} \phi_i(\mathbf{y}) \quad \text{and} \quad \rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x}) = \sum_{i=1}^{N} \overline{\phi_i(\mathbf{x})} \phi_i(\mathbf{x}),$$

it holds

$$\mathcal{E}(\Psi) = \sum_{i=1}^{N} \int |\nabla \phi_i|^2 + \int V \rho + \frac{1}{2} \iint W(\mathbf{x}, \mathbf{y}) \Big(\rho(\mathbf{x}) \rho(\mathbf{y}) - |\gamma(\mathbf{x}, \mathbf{y})|^2 \Big) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{y}.$$

- We have a simple characterization of $\mathcal{M}$, computationally tractable.
- On this set, the energy can be easily computed.
- But,...

$$\mathcal{E}(\Psi) = \sum_{i=1}^{N} \int |\nabla \phi_i|^2 + \int V \rho + \frac{1}{2} \iint W(\mathbf{x}, \mathbf{y}) \Big(\rho(\mathbf{x})\rho(\mathbf{y}) - |\gamma(\mathbf{x}, \mathbf{y})|^2 \Big) \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}.$$

- The new problem is non linear and non convex!
- Does a minimizer exists on $\mathcal{M}$? (YES)
- Is there an efficient algorithm to find such a minimizer? (YES)
- Does such a minimizer similar properties than the real ground state? (usually NO)
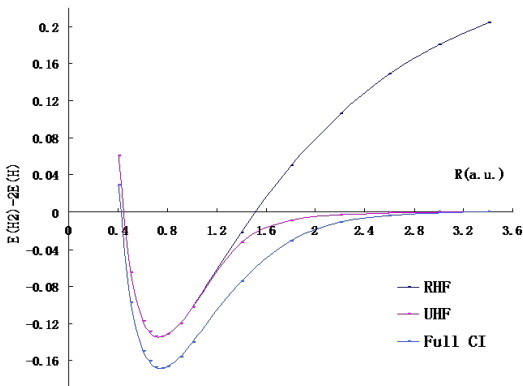
Concluding remarks

As we saw with the Hartree-Fock approximation, the usual scheme is

- The full problem is impossible to solve due to the curse of dimensionality
- We make some kind of approximation (hopefully better than Hartree-Fock)
- We obtain a new minimization problem on a different set, with a different expression.

Then, the mathematical questions raised are

- Can we characterize the new set of minimization?
- Can we prove the existence of minimizer on this set?
- Can we design algorithms to find such a minimizer?
- Can we prove the efficiency of the new model?

In my thesis, I consider those types of questions when we include a magnetic field.