Some (important) problems in Quantum Chemistry

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What is Quantum Chemistry?

Apply quantum theory to problems in chemistry (Schrödinger, Slater, Löwdin ...)

► Optical properties of molecules (spectroscopy)
► What is a chemical bond?
► Determine molecular structure (optimization)
► Chemical reaction mechanisms and rates
► Dynamical properties of electrons and atoms
Structure determination
Electron dynamics and Photochemistry

Photosystem II:

How can photosynthesis be so efficient? Quantum energy transport. $10^5$ atoms..
What do we know?

➤ We know the relevant laws of physics, very very well (too well). Schrödinger equation with Hamiltonian

\[ H = \sum_k -\frac{\nabla^2}{2m_k} + \sum_{i \neq k} \frac{q_i q_k}{r_{ik}} \]

➤ We can easily solve the problem for one particle:

\[ H\Psi = \left[ -\frac{\nabla^2}{2m} + V(r) \right] \Psi = E\Psi \]
Problem One

Space and Time

$10^1 - 10^5$ particles
Times $10^{-15} - 10^{-12}$ s

$10^{23}$ particles
Times $10^{-3} - 10^6$ s

Brute force is impossible. We need clever connections between micro and macro.
Problem Two

Electron Correlation

- Quantum N-body problem
- Quantum calms down chaos, but
- Wave function complexity $N^N$

$$\Psi = \Psi(r_1, r_2, \ldots r_N)$$

- Nevertheless, chemistry is full of concepts: Atoms, bonds, functional groups
- Suggests approximate theories!
- (Counter-example: Spin glasses)
Density Functional Theory (DFT)

- Kohn and {Hohenberg, Sham}: “Ψ(\(r_1, r_2, \ldots\)) is too much”
- Observable properties come from the electron density \(\rho(r)\)!
- Proof that \(E = E[\rho]\), but no closed form.

<table>
<thead>
<tr>
<th></th>
<th>WFT</th>
<th>DFT</th>
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<tbody>
<tr>
<td>Variable</td>
<td>(\Psi(r_1, r_2, \ldots r_N))</td>
<td>(\rho(r))</td>
</tr>
<tr>
<td>Energy</td>
<td>Trivial</td>
<td>Complicated Unknown (kernel trick?)</td>
</tr>
<tr>
<td>Formal Scaling</td>
<td>(N^N)</td>
<td>(N)</td>
</tr>
<tr>
<td>Practical Scaling</td>
<td>(N^6-N^8)</td>
<td>(N^2-N^3)</td>
</tr>
<tr>
<td>Nr atoms</td>
<td>(1-20)</td>
<td>(100-1000)</td>
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</table>

Approximate DFT consumes a majority of Swedish supercomputer time!
Density Functional Theory in practice

DFT Energy:

\[ E_{\text{DFT}} = E_{\text{Kinetic}} + E_{\text{Electrostatic}} + \int_{\mathbb{R}^3} \epsilon_{XC}(\rho(r))dV \]

Only approximate \( \epsilon_{XC}(\rho) \) are known.

Leads to a *one particle* eigenvalue problem

\[ H_{KS}\psi_i = \left[ -\frac{\nabla^2}{2m} + V(r) \right] \psi_i = E_i \psi_i \]

Reduction from \( \Theta(N^N) \) to \( \Theta(N) \)! But \( \epsilon_{XC} \) is very difficult to work with.
Introducing a Basis

To solve

\[ H_{KS}\psi_i = \left[ -\frac{\nabla^2}{2m} + V(r) \right] \psi_i = E_i \psi_i \]

don’t discretize in real space! Use a problem specific basis!

Atom centered Gaussian Type Orbitals.
Generating functions

We can generate a basis

with derivatives!

\[ \varphi_n(r) = \frac{\partial^n}{\partial R^n} e^{-\alpha(r-R)^2} \]

Perfect for AD! Here \( e^{-\alpha(r-R)^2} \) is the Generating Function.

Generating functions are very powerful for combinatorics (look it up)