Many quantum electrons

Lecture 6
2/14/18
Atom with 2 electrons

Two electrons in a Coulomb potential

\[ \hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \]

The problem does not have an analytic solution because electrons see each other (correlated)

Variational approach is to introduce many terms and minimize with respect to a set of parameters

Much more difficult for more electrons (one nucleus)

\[ \left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \ldots, \vec{r}_n) = E_{el} \psi(\vec{r}_1, \ldots, \vec{r}_n) \]
Many atoms with many electrons

The full system interacting Hamiltonian

\[ \hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i \neq j}^{N} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{i \neq j}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \]

constant

\( \hbar \) Planck’s constant / \( 2\pi \)
\( m \) electron mass
\( M_i \) mass of \( i \)th ion
\( e \) charge on electron
\( Z_I \) atomic number of \( i \)th ion
\( r_i \) position of \( i \)th electron
\( R_I \) position of \( i \)th ion
\( n \) number of electrons
\( N \) number of ions

\[ \hat{H} = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{int} + E_{II} \]
Many body wavefunction

\[ \hat{H} \psi(\vec{r}_1, \ldots, \vec{r}_n, \vec{R}_1, \ldots, \vec{R}_N) = E_{\text{tot}} \psi(\vec{r}_1, \ldots, \vec{r}_n, \vec{R}_1, \ldots, \vec{R}_N) \]

**Adiabatic approximation:** We treat only the electrons as quantum particles, in the field of the fixed nuclei

Probability density of particles is given by

\[ n(\mathbf{r}) = \int d^3r_2 \ldots d^3r_N |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)|^2 \]
Many body problem

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

*P.A.M. Dirac, 1929*
Big Data

Consider \( n \) electrons in 3D space
Divide the space into \( N \times N \times N \) grid points
How many points needed to represent the wavefunction?
Answer: \( N^{3n} \)
If \( N=2 \) and only 10 electrons
this is already \( 2^{30} = 1 \) Gigabyte

How can we reduce the number of degrees of freedom?
Atomistic modeling zoo

Accuracy, transferability

Large systems

Small systems

Computation speed

Classical pair potentials
Many-body potentials
Reactive force fields

DFT
Hartree-Fock
TD-DFT
GW
Correlated wavefunction

Quantum Monte Carlo

10^5-10^8 atoms

10^2-10^3 atoms

10 atoms

"empirical, classical"

"first-principles, ab-initio"
Hartree approach

Suppose that eigenfunctions can be written as a simple product of single particle states:

$$\Psi(r_1, \cdots, r_n) = \psi_1(r_1)\psi_2(r_2)\cdots\psi_n(r_n)$$

Probability to find all electrons in a certain configuration is a product of probabilities of finding individual electrons.

Varying states to minimize the expectation value of the total energy leads these equations

$$\begin{cases}
-\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(r_i) + \sum_{j \neq i}^{n} \int d\mathbf{r}_i \frac{\left| \psi_j(\mathbf{r}) \right|^2}{\left| \mathbf{r}_j - \mathbf{r}_i \right|} \psi_i(r_i) = \varepsilon_i \psi_i(r_i)
\end{cases}$$
Mean field

These look like single-particle Schrödinger equations!

N-body Schrödinger equation in 3N dimensions has become a system of N single-particle differential equations, each in 3D. These are coupled integral-differential equations.

Each electron interacts electrostatically only with the charge density due to all other electrons.

Individual electrons are assumed to move as independent particles in the mean field (effective potential) due to all electrons and the nuclei.
How to solve the system of equations

Mechanical differential analyzer

Douglas Hartree

Vannevar Bush
Solving the equation for each one-electron orbital, in a mean field of all electrons, results in a new wavefunction, thus causing a change in the electron density and therefore in the potential we don’t know these solutions \textit{a priori} must be solved iteratively:

- guess form for \( \{ \psi_i^{\text{in}}(r) \} \)
- compute single particle Hamiltonians
- generate \( \{ \psi_i^{\text{out}}(r) \} \)
- compare with old
  - if different set \( \{ \psi_i^{\text{in}}(r) \} \rightarrow \{ \psi_i^{\text{out}}(r) \} \) and repeat
  - if same, you are done

obtain the self-consistent solution
Total energy

\[
\left\{ -\frac{1}{2}\nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) + \sum_{j \neq i}^{n} \int d\mathbf{r}_i \frac{\psi_j(\mathbf{r})^2}{|\mathbf{r}_j - \mathbf{r}_i|} \right\} \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i)
\]

\[
E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{T}_e \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3 r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{II}
\]
What is missing?

**Correlation**
One electron only sees the average density of another, not its instantaneous position
Too much electrostatic repulsion on average

**Exchange**
The wavefunction is not anti-symmetric (particle exchange)
Wrong particle statistics, i.e. no exclusion principle
Spin statistics of elementary particles

All elementary particles are either fermions (half-integer spins) or bosons (integer spins)

This is a result of making QM compatible with relativity

A set of identical (indistinguishable) fermions has a wavefunction that is anti-symmetric by exchange

\[ \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_j, \ldots, \vec{r}_k, \ldots, \vec{r}_n) = -\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_k, \ldots, \vec{r}_j, \ldots, \vec{r}_n) \]

This implies Pauli exclusion principle

For bosons the wavefunction is symmetric under exchange
Spin

\[ \Psi(r_1\alpha, r_2\beta) = -\Psi(r_2\beta, r_1\alpha) \]

2-electron wave function with the same space and spin coordinate will vanish

\[ \Psi(r_1\alpha, r_1\alpha) = -\Psi(r_1\alpha, r_1\alpha) = 0 \]

But a wave function with same space and different spin will not

\[ \Psi(r_1\alpha, r_1\beta) = -\Psi(r_1\beta, r_1\alpha) \]

\[ \Psi(r_1\alpha, r_1\beta) = \frac{1}{\sqrt{2}} \left[ \phi_1(1)\alpha(1)\phi_1(2)\beta(2) - \phi_1(2)\alpha(2)\phi_1(1)\beta(1) \right] = -\Psi(r_1\beta, r_1\alpha) \]
Determinant trial wavefunction

An anti-symmetric wavefunction is constructed via a Slater determinant of the individual orbitals instead of just a product, as in the Hartree approach.

\[ \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{vmatrix} \]
Hartree-Fock equations

Performing variation minimization with respect to the orbitals:

\[
\begin{align*}
\text{Kinetic and potential energy} & \quad -\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I, -\vec{r}_i) \phi_\lambda(\vec{r}_i) + \\
\text{Hartree electrostatics} & \quad \sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) \, d\vec{r}_j \phi_\lambda(\vec{r}_i) - \\
\text{Exchange term} & \quad \sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) \, d\vec{r}_j \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)
\end{align*}
\]
Total energy

\[ E_{\text{Hartree}} = \frac{1}{2} \int d^3r \, d^3r' \frac{n(r)n(r')}{|r - r'|} \]

\[ E = \langle \hat{T}_e \rangle + \int d^3r V_{\text{ext}}(r)n(r) + E_{II} + E_{\text{Hartree}} + E_{\text{exch}} \]
Meet self-interaction

The Hartree operator sums over all orbital densities
The second term in HF has an electron interacting with its own charge density: **self-interaction**
The **non-local** exchange term arises from anti-symmetry of the trial wavefunction
Note that the second term exactly cancels the self-interaction of each electron
HF is a **self-interaction free** method
Self-interaction is a big problem in DFT
Dealing with electron spin

Each orbital in HF actually contains a spatial part times a spin part.
For each spatial orbital, there are two spin orbitals.
A system is **open shell** if it contains one or more unpaired electrons.
There are two ways to handle open shell systems:

**Restricted Hartree-Fock (RHF)**
This approach uses combinations of singly and doubly occupied molecular orbitals. Doubly occupied orbitals use the same spatial functions for electrons of both spins.

**Unrestricted Hartree-Fock (UHF)**
Here, two distinct sets of orbitals are used: one for electrons of up spin and one for electrons of down spin. As a result, effectively two densities are used, one for each spin.
Restricted and unrestricted

Which will be lower energy?
The UHF approach is more general than RHF

\[ \psi_i^\alpha (r) \neq \psi_i^\beta (r) \]
H$_2$ molecule dissociation energy

UHF gives lower energy in general
RHF fails to describe dissociation
RHF doubly occupies the same bonding orbital
Unphysical at far separation
Need some anti-bonding character
RHF fails for spin-dependent effects
UHF is better for bond breaking
Self consistent iterative solution

1. Input 3D Coordinates of atomic nuclei
2. Initial Guess Molecular Orbitals (1-electron vectors)
3. Fock Matrix Formation
4. Fock Matrix Diagonalization
5. SCF Converged?
   - Yes: Calculate Properties, End
   - No: Repeat

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Practical aspects of HF

Iteration does not always converge to self-consistency
Smooth updates of the orbitals are helpful
Scaling of HF is in principle \(~O(N^4)\) to compute all the integrals
In practice it scales better if not all integrals are computed
Good for atomic properties
Self-interaction free
Exchange is included, correlation still not
  \textbf{Dynamical correlations:} the electrons repel each other too much
  \textbf{Static correlations:} a single determinant variational class in not enough
HF accuracy

HF energy accounts for ~99% of the total energy of atoms. Equilibrium bond lengths, bond angles, forces, thermochemistry, can generally be predicted qualitatively. But the missing correlation energy is not negligible. HF tends to underbind nearly all systems, bonds are weak.

<table>
<thead>
<tr>
<th>Energy (Eh)</th>
<th>H₂O</th>
<th>2H + O</th>
<th>dE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-76.058</td>
<td>-75.811</td>
<td>0.246</td>
</tr>
<tr>
<td>CCSD</td>
<td>-76.338</td>
<td>-75.982</td>
<td>0.356</td>
</tr>
</tbody>
</table>

Missing correlation causes a 30% error.
Key aspects of HF

The Hartree-Fock method is the foundation of molecular orbital theory and computational chemistry

It is based upon a choice of wavefunction, a Slater determinant, which is the simplest way to write an anti-symmetrized wavefunction

The Hartree-Fock equations arise from minimizing the energy with respect to that particular trial wavefunction, for a given Hamiltonian

Note that the Hartree-Fock method begins with an exact Hamiltonian, one which includes many-body interactions

Upon introducing the Slater determinant as an approximation to the wavefunction, the picture becomes single-particle in nature
Beyond Hartree-Fock

In HF we use 1 determinant of lowest energy orbitals $\Phi_0$
Can systematically improve HF by generalizing the starting guess
Explore a larger variational space to get a more exact solution

Slater determinants are configurations of occupied orbitals
   Ground-state electron configuration $\Phi_0$ contains orbitals $1s^22s^22p^6$
   A possible excited configuration $\Phi_1$ is a determinant with $1s^22s^22p^53s^1$
Configuration Interaction (CI)

Linear combination of excited Slater determinants
Variationally optimize coefficients $d_i$
Much more accurate
Computationally very expensive
CI scales as $\sim N^{6-10}$
depending on type of excitations

$$
\psi_{el} = d_0 \Phi_{HF} + \sum_{i=1}^{i} d_i \Phi_i \\
\propto \left(1 + \hat{T}_1 + \hat{T}_2 + \ldots\right) \Phi_{HF}
$$
Variants of CI

**Full CI**: all possible configurations included in the expansion. This is the most complete treatment possible for a given set of basis functions.

Full-CI scales like N! and is only feasible for molecules with ~15 electrons and small basis sets

**Truncated CI** methods limit the types of included excitations:

- CIS includes only single excitations
- CID includes only double excitations
- CISD adds single and double excitations
- CISDT adds single, double and triple excitations
Coupled Cluster (CC) method

An exponential operator is used to construct the determinants

\[ |\Psi\rangle = e^T |\Phi_0\rangle = \left(1 + T + T^2 / 2 + \ldots\right) |\Phi_0\rangle \]

Leads to accurate and compact wave function expansions yielding accurate electronic energies for small molecules

Common Variants:

- **CCD**: only double excitations in \( T = T_2 \)
- **CCSD**: excitations limited to singles and doubles \( T = T_1 + T_2 \)
- **CCSD(T)**: CCSD with perturbative treatment of triple excitations. This method, when used with large basis sets, has high accuracy
  
  Scales like \( O(N^7) \), limited to ~15 atom molecules
- Recently **DLPNO-CCSD(T)**: much faster scaling
Møller-Plesset Perturbation Theory

Assume that the solution (correlated \( \psi \) and \( E \)) differs only slightly from the approximate one (HF \( \psi \) and \( E \))

\[
\hat{H} = \hat{H}_0 + \lambda \hat{V}
\]

The energy is calculated to various orders of approximation.
- Second order MP2; Third order MP3; Fourth order MP4...
- Computational cost is \( O(N^{m+3}) \) for MP-\( m \) computations

At infinite order the energy is the exact solution of the M.B.S.E. but no guarantee the series converges

This method is not variational, can get lower energies than \( E_0 \)

MP2 (typically recommended) recovers 80-90% of correlation energy, includes all single and double excitations
Machine Learning again

Add machine learning corrections to computationally inexpensive approximate quantum methods

After training, highly accurate predictions of enthalpies, free energies, and electron correlation energies are possible, for significantly larger molecular sets than used for training.

Can predict electron correlation energy in post Hartree-Fock methods, at the computational cost of Hartree-Fock.

Electronic structure landscape

- Post-HF
- Hybrid DFT
- DFT
- SCF
- HF
- $E_c$
- $\psi$

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**Time is precious**

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{coh}$ % error</th>
<th>Scaling with # electrons</th>
<th>Time for 1 atom</th>
<th>Total time for 100 atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>50%</td>
<td>$N^3$-$N^4$</td>
<td>0.1 sec</td>
<td>3.8 months</td>
</tr>
<tr>
<td>MP2</td>
<td>25%</td>
<td>$N^5$</td>
<td>0.1 sec</td>
<td>32 years</td>
</tr>
<tr>
<td>CCSD(T)</td>
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<td>$N^7$</td>
<td>0.1 sec</td>
<td>320,000 years</td>
</tr>
<tr>
<td>DFT-LDA</td>
<td>15-25%</td>
<td>$N^2$-$N^3$</td>
<td>0.1 sec</td>
<td>27 hrs</td>
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