Electron Correlation
Levels of QM Theory

\[ H\Psi = E\Psi \]

Born-Oppenheimer approximation

Electronic equation: \[ H_e \Psi_e = E_e \Psi_e \]

Single determinant SCF

Semi-empirical methods

Correlation approaches:
1. WF based. Multi-determinantal methods
   - variational (MCSCF, CI)
   - non-variational (MBPT, CC)
2. DFT: “orbital free” (\( \rho \) - based)
   - Single determinantal (Kohn-Sham)

Nuclear equation: \[ H_n \Psi_n = E_n \Psi_n \]
Why “correlation”? 

The Hartree Product

\[ \Phi^{HP}(x_1; x_2; \ldots; x_n) = \varphi_1(x_1) \varphi_2(x_2) \ldots \varphi_n(x_n) \]

is completely uncorrelated, in the sense that the probability of simultaneously finding electron 1 at \(x_1\), electron 2 at \(x_2\), etc., is given by:

\[ |\Phi^{HP}(x_1; x_2; \ldots; x_n)|^2 dx_1 dx_2 \ldots dx_n = |\varphi_1(x_1)|^2 |\varphi_2(x_2)|^2 \ldots |\varphi_n(x_n)|^2 dx_1 dx_2 \ldots dx_n \]

which is the probability of finding electron 1 at \(x_1\) times the probability of finding electron 2 at \(x_2\), etc... the product of the probabilities. This makes the Hartree Product an independent particle model. Electrons move independently; their motion is uncorrelated.
The Hartree-Fock approximation

- The n-electronic wave function $\psi$ in the case of Hartree-Fock (HF) approximation:

$$
\Psi_{HF}(1, 2, ... n) = \det \begin{pmatrix}
\phi_1(1) & \phi_2(1) & ... & \phi_n(1) \\
\phi_1(2) & \phi_2(2) & ... & \phi_n(2) \\
... & ... & ... & ...
\end{pmatrix}

- One-electron density:

$$
\rho_{HF}(x, y, z) = \sum n_j |\phi_j|^2
$$

- $n_j$ is the “occupation number” ($n_j = 0, 1, 2$)
Hartree-Fock Energy

\[ E = \sum_{i=1}^{n} h_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} (J_{ij} - K_{ij}) \]

Sums run over occupied orbitals. \( h_i \) is the one-electron integral, \( J_{ij} \) is the Coulomb integral, and \( K_{ij} \) is the exchange integral.

\[ h_i = \int dr \phi_i^*(r) \left[ -\frac{1}{2} \Delta - \sum_l \frac{Z_l e^2}{R_{l-e}} \right] \phi_i(r) = -(\int dr \left[ \frac{1}{2} \phi_i^*(r) \Delta \phi_i(r) + \frac{Z_l e^2}{R_{l-e}} \rho_i(r) \right] \]

\[ J_{ij} = \int \int dr_1 dr_2 \phi_i^*(r_1) \phi_i(r_1) \frac{1}{r_{12}} \phi_j^*(r_2) \phi_j(r_2) = \int \int dr_1 dr_2 \rho_i(r_1) \frac{1}{r_{12}} \rho_j(r_2) \]

\[ K_{ij} = \int \int dr_1 dr_2 \phi_i^*(r_1) \phi_j(r_1) \frac{1}{r_{12}} \phi_j^*(r_2) \phi_i(r_2) \]
 WF approaches beyond the SCF.

Correlated Methods (CM)

• Include more explicit interaction of electrons than HF: \( E_{\text{corr}} = E - E_{\text{HF}} \), where \( E\Psi = H\Psi \)

• Most CMs begin with HF wavefunction, then incorporate varying amounts of electron-electron interaction by mixing in excited state determinants with ground state HF determinant

• The limit of infinite basis set & complete electron correlation is the exact solution of Schrödinger equation (which is still an approximation)
The N-electron Basis

- A collection of atom-centered Gaussian functions can be used as a basis set for expanding one-electron functions (molecular orbitals).

\[
\phi_j = \sum_{s=1}^{b} c_{sj} \chi_s = c_{1j} \chi_1 + c_{2j} \chi_2 + \ldots + c_{bj} \chi_b
\]

- We need to solve the electronic Schrodinger equation to get \( \Psi_e(r_1; r_2; \ldots; r_n) \), a function of \( n \) electrons.

What can we use as a basis for expanding \( \Psi_e \)?
- Slater determinants are proper \( n \)-electron basis functions: they are functions which can be used to expand any antisymmetric \( n \)-electron function.
- In the limit of an infinite number of Slater determinants, any \( n \)-electron function can be expanded exactly.
Configuration Interaction (CI) and other correlation methods

- CI method for many-electron WF

\[ \Psi_e (r_1, r_2, ..., r_n) = c_0 \Phi_0^{HF} (r_1, r_2, ..., r_n) + \sum_{I=1}^{N} c_I \Phi_I (r_1, r_2, ..., r_n) \]

where \( N \) is the number of “excited” determinants

Ways of Coefficients \( c_I \) definition:

1. Variations - CI
2. Perturbation expansions - MBPT
3. SCF-like iterations - Coupled Cluster
Classification of CI methods

- The Hartree-Fock "reference" determinant $\Phi_0$ should be the leading term. Expect the importance of other configurations to drop off rapidly as they substitute more orbitals.

Let denote a determinant $\Phi_{ij \ldots k}^{ab \ldots c}$ which differs from $\Phi_0$ by replacing occupied orbitals $ij \ldots k$ with virtual orbitals $ab \ldots c$.

$$\Psi = c_0 \Phi_0^{HF} + \sum c_i^a \Phi_i^a + \sum c_{ij}^{ab} \Phi_{ij}^{ab} + \sum c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots$$

Reference  | Singles  | Doubles  | Triples
---|---|---|---
CIS  | CISD  | CISDT
Example of CI calculation: $H_2$ molecule

\[ \Psi_{CI} = c_0 \ket{\psi_{\sigma g} \psi_{\sigma g}} + c_1 \ket{\psi_{\sigma u} \psi_{\sigma u}} + c_2 \ket{\psi_{3\sigma} \psi_{3\sigma}} + c_3 \ket{\psi_{\pi} \psi_{\pi}} + \ldots \]
WF methodology:

- Infinite basis set
- 6-311++G**
- 6-311G**
- 6-311G*
- 3-21G*
- 3-21G
- STO-3G
- STO

Increasing size of basis set:
- Increasing level of theory:
  - HF
  - CI
  - QCISD
  - QCISDT
  - MP2
  - MP3
  - MP4
  - ... full e⁻ correlation

Increasing accuracy, increasing cpu time:
- Schrödinger
Density Functional Theory

- 1998 Nobel Prize in Chemistry (Kohn and Pople) recognized work in this area.
- **Main idea:** Use the density instead of complicated many electron wavefunctions.
- **Basic approach:** minimize the energy with respect to the density.
  
  Relationship of energy to density is the “functional” $E[\rho]$ (true form of this functional is unknown: use approx.)
One-electronic density

The probability density $\rho$ of finding an electron (ANY!!!) in the neighborhood of point $(x,y,z)$ is

$$\rho(x, y, z) = n \sum_{m_s} \int \cdots \int |\psi(x, y, z, x_2, \ldots, z_n, m_{s_1}, \ldots, m_{s_n})|^2 \, dx_2 \ldots dz_n$$

In most cases - knowing the $\rho$ is knowing the system!

$$\langle \hat{A} \rangle = \iiint A(x, y, z) \rho(x, y, z) \, dxdydz$$

$$Z = \sum_{m_s} \iiint e \rho(x, y, z) \, dxdydz = en$$

Main question – How does $\rho$ look like?
The energy functional = density functional (W. Kohn)

• Model Hamiltonian: \( H_\lambda = T + (1-\lambda)V_{\text{ext}}(\lambda) + \lambda V_{\text{ee}} \)
  \( 0 \leq \lambda \leq 1 \); \( \rho_{\lambda=1} = \rho_{\lambda=0} = \rho \)

• \( H_{\lambda=1} = H \quad H_{\lambda=0} = T + V_{\text{ext}}(0) \) - single-e-H

• Kohn - Sham : \( E = E[\Psi] = \int \Psi^* \hat{H} \Psi \, dV = E[\rho] = ? \)

• HF: \( E^{HF}[\rho] = T[\rho(\phi)] + E_{\text{ne}}[\rho] + (J[\rho] + K[\rho(\phi)]) \)

• DFT: \( E[\rho] = T[\rho] + E_{\text{ne}}[\rho] + (J[\rho] + K[\rho] + E_{\text{cor}}[\rho]) \) - single-electron theory including correlation!

\[ \rho(x, y, z) = \sum_j n_j |\phi_j|^2 \]

Alternatives:

I \hspace{2cm} II
Orbital-free DFT


- In the HF method \( E_{corr}[\rho] \) is missed

- General case:
  \[
  E_{ne}[\rho] = - \sum_{a}^{N_{\text{nuclei}}} \int \frac{Z_{a}(R_{a})\rho(r)}{|R_{a} - r|} \, dr
  \]
  \[
  J[\rho] = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} \, dr \, dr'
  \]

- Homogenous e-gas (Tomas-Fermi-Dirac) - simplest case:
  \[
  \]
  \[
  T_{TF}[\rho] = C_{F} \int \rho^{5/3}(r) \, dr
  \]
  \[
  K_{D}[\rho] = -C_{x} \int \rho^{4/3}(r) \, dr
  \]
Kinetic and exchange functionals' corrections

• Kinetic functional:

\[ T[\rho] = T_{TF}[\rho] + T_2[\rho] + T_4[\rho] + T_6[\rho] + \ldots \]

\[ T_2[\rho] = \lambda \tau_w[\rho]; \quad \tau_w[\rho] = \int \frac{[\nabla \rho(\mathbf{r})]^2}{8 \rho(\mathbf{r})} d\mathbf{r} \]

\[ T_4[\rho] = \left( \frac{540 (3\pi)^{2/3}}{5} \right)^{-1} \int \rho^{1/3}(\mathbf{r}) \left\{ \left( \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 - \frac{9}{8} \left( \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right) \left( \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 + \frac{1}{3} \left( \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^4 \right\} d\mathbf{r} \]

• Exchange functional:

\[ K[\rho] = K_D[\rho] + K_2[\rho] + K_4[\rho] + \ldots \]

\[ K_2[\rho] = -\frac{5}{216} (3\pi^5)^{-1/3} \int \frac{[\nabla \rho(\mathbf{r})]^2}{\rho^{4/3}(\mathbf{r})} d\mathbf{r} \]
Correlation functionals

- An example Lee, Parr, Yang (LYP) $E_{\text{corr}}[\rho])$:

$$
E_{\text{LYP}}^{\text{LYP}} = -4a \frac{\rho_\alpha \rho_\beta}{\rho^2(1 + d\rho^{-1/3})} - \\
abla \omega \left[ \frac{\rho_\alpha \rho_\beta}{18} \left[ 144(2^{2/3})C_F(\rho_\alpha^{8/3} + \rho_\beta^{8/3}) + (47 - 7\delta)|\nabla \rho|^2 - \\
(45 - \delta)|\nabla \rho_\sigma|^2 + |\nabla \rho_\beta|^2 \right] + 2\rho^{-1}(11 - \delta)(\rho_\sigma|\nabla \rho_\sigma|^2 + \rho_\beta|\nabla \rho_\beta|^2) \right] \\
+ \frac{2}{3} \rho^2 \left( |\nabla \rho_\sigma|^2 + |\nabla \rho_\beta|^2 - |\nabla \rho|^2 \right) - (\rho_\alpha^2|\nabla \rho_\beta|^2 + \rho_\beta^2|\nabla \rho_\alpha|^2)
\right] \\
\omega = \frac{e^{-c\rho^{-1/3}}}{\rho^{14/3}(1 + d\rho^{-1/3})}
$$

$$
\delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{1 + d\rho^{-1/3}}
$$
Kohn-Sham theory (DFT with orbitals)

- **Exact WF:**
  \[ \rho(x, y, z) = \sum_j n_j |\phi_j|^2 \]

  - \( n_j \) is the “generalized occupation number” \((n_j \equiv 0 \text{ or } 1)\);
  - \( \phi_j \) - natural orbitals \( j=1,\ldots,\infty \)

- **Kohn-Sham (KS) WF:**
  \[ \Psi_{KS}(1, 2, \ldots n) = \det \begin{pmatrix}
  \phi_1(1) & \phi_2(1) & \cdots & \phi_n(1) \\
  \phi_1(2) & \phi_2(2) & \cdots & \phi_n(2) \\
  \vdots & \vdots & \ddots & \vdots \\
  \phi_1(n) & \phi_2(n) & \cdots & \phi_n(n)
\end{pmatrix} \]

- **Exact exchange + KS kinetic functional** - very precise
  \[ T_S = \sum_{i=1}^{N_{\text{elec}}} \langle \phi_i \mid -\frac{1}{2} \nabla^2 \mid \phi_i \rangle \]

  \[ T[\rho_{\text{exact}}] = \sum_{i=1}^{\infty} n_i \langle \phi_i^{\text{NO}} \mid -\frac{1}{2} \nabla^2 \mid \phi_i^{\text{NO}} \rangle \]
# Jacob's Ladder

<table>
<thead>
<tr>
<th>Level</th>
<th>Name</th>
<th>Variables</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Local density</td>
<td>$\rho$</td>
<td>LDA, LSDA, $X_\alpha$</td>
</tr>
<tr>
<td>2</td>
<td>GGA</td>
<td>$\rho, \nabla \rho$</td>
<td>BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH</td>
</tr>
<tr>
<td>3</td>
<td>Meta-GGA</td>
<td>$\rho, \nabla \rho, \nabla^2 \rho$ or $\tau$</td>
<td>BR, B95, VSXC, PKZB, TPSS, $\tau$-HCTH</td>
</tr>
<tr>
<td>4</td>
<td>Hyper-GGA</td>
<td>$\rho, \nabla \rho, \nabla^2 \rho$ or $\tau$</td>
<td>H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, $\tau$-HCTH-hybrid</td>
</tr>
<tr>
<td>5</td>
<td>Generalized RPA</td>
<td>$\rho, \nabla \rho, \nabla^2 \rho$ or $\tau$</td>
<td>OEP2</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>HF exchange</em></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Virtual orbitals</em></td>
<td></td>
</tr>
</tbody>
</table>