Hartree-Fock Theory

Shao Group Meeting

University of Oklahoma

September 2017

Schrödinger equation for a molecular system

- The Schrödinger equation is

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

- The Hamiltonian is

$$\hat{H} = \sum_i \left(-\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{\left|\vec{r}_i - \vec{R}_A\right|} \right) + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

which includes

- kinetic energy, $-\frac{1}{2}\nabla_i^2$, of each electron

- nuclear attraction $-\sum_A \frac{Z_A}{\left|\vec{r}_i - \vec{R}_A\right|}$

- electron-electron repulsion, $\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$

Hartree-Fock wavefunction: Slater determinants

- For N electrons in N molecular orbitals, the Slater determinant is

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{\sqrt{(N)!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

- Each molecular orbital is a linear combination of basis functions

$$\psi_i(\vec{r}) = \sum_\mu C_{\mu i} \phi_\mu(\vec{r})$$

- In most quantum chemistry calculations, we use Gaussian functions

$$\phi_\mu(\mathbf{a}; \vec{r}) = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \sum_k D_k exp\left(-\alpha_k |\vec{r} - \vec{A}|^2\right)$$

  with α_k are called exponents, and D_k contraction coefficients.

- Plane-wave basis functions can be used in QM calns on solid/surface systems.

Why Gaussian Basis Sets?

- Gaussian Product Theorem for 1-D Functions

$$
\begin{aligned}
e^{-\alpha(x-A_x)^2}e^{-\beta(x-B_x)^2} &= e^{-(\alpha+\beta)x^2+2(\alpha A_x+\beta B_x)x-(\alpha A_x^2+\beta B_x^2)} \\
&= e^{-(\alpha+\beta)(x-\frac{\alpha A_x+\beta B_x}{\alpha+\beta})^2+\frac{(\alpha A_x+\beta B_x)^2}{\alpha+\beta}-(\alpha A_x^2+\beta B_x^2)} \\
&= e^{-(\alpha+\beta)(x-\frac{\alpha A_x+\beta B_x}{\alpha+\beta})^2-\frac{\alpha\beta}{\alpha+\beta}(A_x-B_x)^2}
\end{aligned}
$$

- Gaussian Product Theorem for 3-D Functions

$$
\begin{aligned}
e^{-\alpha(r-A)^2}e^{-\beta(r-B)^2} &= e^{-\alpha\left[(x-A_x)^2+(y-A_y)^2+(z-A_z)^2\right]} \\
&\quad \times e^{-\beta\left[(x-B_x)^2+(y-B_y)^2+(z-B_z)^2\right]} \\
&= e^{-(\alpha+\beta)\left[(x-P_x)^2+(y-P_y)^2+(z-P_z)^2\right]} \\
&\quad \times e^{-\frac{\alpha\beta}{\alpha+\beta}\left[(A_x-B_x)^2+(A_y-B_y)^2+(A_z-B_z)^2\right]} \\
&= e^{-(\alpha+\beta)\left|\vec{r}-\vec{P}\right|^2}e^{-\frac{\alpha\beta}{\alpha+\beta}\left|\vec{A}-\vec{B}\right|^2}
\end{aligned}
$$

where $\vec{P} = \dfrac{\alpha\vec{A}+\beta\vec{B}}{\alpha+\beta}$. This means that we can convert 4-center 2-electron integrals $(ab|cd)$ into 2-center 2-electron integrals $(p|q)$.

6-31G Basis Functions for Helium Atom

- The basis set specification is

```
He    0
S   3   1.00
    38.4216340              0.0237660
     5.7780300              0.1546790
     1.2417740              0.4696300
S   1   1.00
     0.2979640              1.0000000
****
```
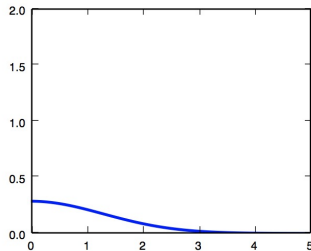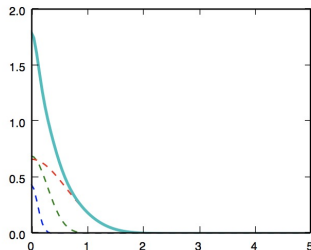
- 1st function has 3 Gaussians

$$\phi_1 = N_t(0.023766 * N_1 * e^{-38.421634r^2}$$
$$+0.154679 * N_2 * e^{-5.77803r^2}$$
$$+0.46963 * N_3 * e^{-1.241774r^2})$$

- 2nd function has 1 Gaussian

$$\phi_2 = N_4 e^{-0.2927640r^2}$$

Pople Gaussian Basis Sets

basis		H, He	Li, Be, B, C, N, O, F, Ne	Comment
STO-3G	core		$3s \rightarrow 1s$	Too small
	valence	$3s \rightarrow 1s$	$3s3p \rightarrow 1s1p$	
6-31G*	core		$6s \rightarrow 1s$	
	valence	$4s \rightarrow 2s$	$4s4p1d \rightarrow 2s2p1d$	
6-31++G**	core		$6s \rightarrow 1s$	medium
	valence	$5s1p \rightarrow 3s1p$	$5s5p1d \rightarrow 3s3p1d$	
6-311++G**	core		$6s \rightarrow 1s$	large
	valence	$6s1p \rightarrow 4s1p$	$6s6p1d \rightarrow 4s4p1d$	
6-311++G(3df,3pd)	core		$6s \rightarrow 1s$	largest
	valence	$6s3p1d \rightarrow 4s3p1d$	$6s6p3d1f \rightarrow 4s4p3d1f$	

- See https://bse.pnl.gov/bse/portal for details
- Dunning basis set (cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, cc-pVQZ, aug-cc-pVQZ) are equally (if not more) popular

Hartree-Fock Energy for a Slater Determinant

- For N electrons in N molecular orbitals, the Slater determinant is

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{\sqrt{(N)!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

The energy of this Slater determinant is

$$E_{HF} = \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} \left[(ii|jj) - (ij|ij) \right]$$

where

$$h_i = \int d\vec{r} \, \psi_i^*(\vec{r}) \left[-\frac{1}{2} \, \nabla^2 - \sum_A \frac{Z_A}{\left| \vec{r} - \vec{R}_A \right|} \right] \psi_i(\vec{r})$$

$$(ii|jj) = \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1) \psi_i^*(\vec{r}_1) \frac{1}{r_{12}} \psi_j(\vec{r}_2) \psi_j(\vec{r}_2)$$

$$(ij|ij) = \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_1) \frac{1}{r_{12}} \psi_i(\vec{r}_2) \psi_j(\vec{r}_2)$$

- Hartree-Fock energy (of a Slater determinant) is

$$
\begin{aligned}
E_{HF} &= \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} [(ii|jj) - (ij|ij)] \\
&= \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} [(ii|jj) - (ij|ij)]
\end{aligned}
$$

- We search for an optimal set of occupied molecule orbitals, $\psi_i(\vec{r})$, to minimize this energy. In practice, this is done through the self-consistent field (SCF) procedure.
- In DFT calculations, the $i = j$ term of Coulomb energy is no longer cancelled by its Hartree Fock exchange counterpart. This is called the self-interaction error.

Electron Density and Density Matrix

- Given a set of orthonormal occupied molecular orbitals, $\psi_i(\vec{r})$, we can write the electron density as

$$
\begin{aligned}
\rho(\vec{r}) &= \sum_{i=1}^{N} (\psi_i(\vec{r}))^2 \\
&= \sum_{i=1}^{N} \left[\sum_{\mu} C_{\mu i} \phi_\mu(\vec{r}) \right] \left[\sum_{\nu} C_{\nu i} \phi_\nu(\vec{r}) \right] \\
&= \sum_{\mu,\nu} \left[\sum_{i} C_{\mu i} C_{\nu i} \right] \phi_\mu(\vec{r}) \phi_\nu(\vec{r}) \\
&= \sum_{\mu,\nu} P^{\mu\nu} \phi_\mu(\vec{r}) \phi_\nu(\vec{r})
\end{aligned}
$$

- (One-Particle) Density matrix is

$$
P^{\mu\nu} = \sum_{i} C_{\mu i} C_{\nu i} \qquad P = C_o C_o^{\dagger}
$$

Hartree-Fock Energy in AO Representation

- The Hartree-Fock energy

$$E_{HF} = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} [(ii|jj) - (ij|ij)]$$

- can be rewritten as

$$E_{HF} = \sum_{\mu\nu} P^{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} (\mu\nu|\lambda\sigma) P^{\lambda\sigma} - \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} (\mu\lambda|\nu\sigma) P^{\lambda\sigma}$$

  This is the Hartree-Fock energy expression in the atomic orbital (AO) representation.

- This requires one-electron and two-electron integrals

$$
\begin{aligned}
h_{\mu\nu} &= \int d\vec{r} \, \phi_\mu(\vec{r}) \left[-\frac{1}{2} \bigtriangledown^2 - \sum_A \frac{Z_A}{\left| \vec{r} - \vec{R}_A \right|} \right] \phi_\nu(\vec{r}) \\
(\mu\nu|\lambda\sigma) &= \int \int d\vec{r_1} d\vec{r_2} \phi_\mu(\vec{r}) \phi_\nu(\vec{r}) \frac{1}{r_{12}} \phi_\lambda(\vec{r}) \phi_\sigma(\vec{r})
\end{aligned}
$$

Concise Notation for Hartree-Fock Energy

- Hartree-Fock energy is

$$
\begin{aligned}
E_{HF} &= \sum_{\mu\nu} P^{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} (\mu\nu|\lambda\sigma) P^{\lambda\sigma} - \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} (\mu\lambda|\nu\sigma) P^{\lambda\sigma} \\
&= \sum_{\mu\nu} P^{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} \left[(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma) \right] P^{\lambda\sigma} \\
&= \sum_{\mu\nu} P^{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu,\lambda\sigma} P^{\mu\nu} (\mu\nu||\lambda\sigma) P^{\lambda\sigma} \\
&= P \cdot h + \frac{1}{2} P \cdot \Pi \cdot P
\end{aligned}
$$

where

$$
\Pi_{\mu\nu,\lambda\sigma} = (\mu\nu||\lambda\sigma) = (\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)
$$

Fock Matrix

- The general definition of Fock matrix (for both Hartree-Fock and DFT) is

$$F_{\mu\nu} = \frac{\partial E}{\partial P^{\mu\nu}}$$

which will be shown to be equal to be $(\phi_\mu|\hat{f}|\phi_\nu)$, namely an AO representation of the Fock operator (one-electron effective Hamiltonian).

- From the energy expression,

$$E_{HF} = \sum_{\mu\nu} P^{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu, \lambda\sigma} P^{\mu\nu} (\mu\nu||\lambda\sigma) P^{\lambda\sigma}$$

we can derive

$$
\begin{aligned}
F_{\mu\nu} = \frac{\partial E}{\partial P^{\mu\nu}} &= h_{\mu\nu} + \sum_{\lambda\sigma} (\mu\nu||\lambda\sigma) P^{\lambda\sigma} \\
&= h_{\mu\nu} + \sum_{\lambda\sigma} (\mu\nu|\lambda\sigma) P^{\lambda\sigma} - \sum_{\lambda\sigma} (\mu\lambda|\nu\sigma) P^{\lambda\sigma} \\
&= h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu}
\end{aligned}
$$

where $J_{\mu\nu}$ is the Coulomb matrix, and $K_{\mu\nu}$ the exchange matrix.

- In concise notation,

$$F = h + \Pi \cdot P = h + J - K$$