Computational Chemistry Course

- introduction to modeling
- lectures are aimed at providing a conceptual understanding of what different modeling methods do and what their physical foundation is.

We will begin with the Hartree-Fock (HF) theory of quantum mechanics.

TDSE \[ i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x) \Psi \quad \text{for} \quad \Psi(x,t) \]

\[ \alpha \cdot i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(t) \Psi \quad \text{for} \quad \Psi(x,y,z,t) \]

Define \[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \text{the Hamiltonian, as the operator corresponding to energy,} \]

where \[ \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad \text{and} \quad \hat{x} = x. \]

We can then write \[ i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (=\hat{H} \Psi \text{ if we are lazy}) \]

Physical interpretation of \[ \Psi : |\Psi|^2 = \Psi^* \Psi \text{ is prob. density, namely prob. of finding particle in volume element } dx dy dz \text{ at time } t \quad \Rightarrow |\Psi(x,y,z,t)|^2 dx dy dz. \]
General solution for $\Psi(x, y, z, t)$:

Try separation of variables $\Psi(x, y, z, t) = \Phi_n(x, y, z) \Theta_n(t)$

Arrive at the pair of linked equations:

\[ \Theta_n(t) = e^{-i\delta_n t} \quad \text{and} \quad \hat{H} \Phi_n = E_n \Phi_n. \]

Let us look at this from a molecular orbital (MO) theory viewpoint.

MO theory makes 2 big assumptions:

i) Born-Opennheimer approx.
ii) Independent electron (orbital) approx.

States were $\{x\} = (x, y, z)$ for spatial variables and $\{x, \alpha\} = \{x, \beta\}$ for $\alpha$ (up) and $\beta$ (down) spin of an electron.

Hartree product (define) does not satisfy indistinguishability, so it is physically wrong.

- basis presentation
- Hartree approximation
Slater Determinants

The Hartree product does not satisfy the antisymmetry (indistinguishability) principle.

We can fix this. Consider a 2-electron system with spin orbitals \( \chi_i \) and \( \chi_j \).

Now, if we put electron \#1 in \( \chi_i \) and electron \#2 in \( \chi_j \) we get the Hartree product \( \Phi_{12}^{\text{HP}}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2) \).

If we swap the electrons we get \( \Phi_{21}^{\text{HP}}(x_1, x_2) = \chi_i(x_2)\chi_j(x_1) \).

Let us combine these \( \Phi(x_1, x_2) = \frac{1}{\sqrt{2L}} \left[ \chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2) \right] \).

Then \( \Phi(x_1, x_2) = -\Phi(x_2, x_1) \).

Also, if \( i = j \), namely if we try to put both electrons in the same spin orbital, we get \( \Phi = 0 \) which is the Pauli exclusion principle.

We can write this \( \Phi \) as \( \Phi(x_1, x_2) = \frac{1}{\sqrt{2L}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} \),

that is, as a determinant with the orbitals each occupying a column and each electron a row.

This generalizes to \( \Phi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{L^N}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_N) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \).
The properties of the det. guarantee us antisymmetry.  

One can define the det recursively as follows:

\[
\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11} a_{22} - a_{21} a_{12}
\]

\[
\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}
\]

\[
= -a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{22} \begin{vmatrix} a_{11} & a_{13} \\ a_{31} & a_{33} \end{vmatrix} - a_{32} \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{23} \end{vmatrix}
\]

(Can use any row or column)

\[
\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} & a_{24} \\ a_{31} & a_{33} & a_{34} \\ a_{41} & a_{43} & a_{44} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} & a_{24} \\ a_{31} & a_{32} & a_{34} \\ a_{41} & a_{42} & a_{44} \end{vmatrix} - a_{14} \begin{vmatrix} a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \end{vmatrix}
\]

How many terms are there?  

\[2 \times 2 = 2! \]

\[3 \times 3 = 3 (2 \times 2) = 3 \cdot 2 = 3! \]

\[4 \times 4 = 4 (3 \times 3) = 4 \cdot 3! = 4! \]

\[N \times N = N! \]

Properties:  

i) if any two rows or columns are interchanged,  
the det changes sign. \( \rightarrow \) antisymmetry.

ii) if any two rows or columns are identical,  
the det is zero. \( \rightarrow \) Pauli exclusion.
The Slater determinant has \( N \) electrons occupying \( N \) spin orbitals without specifying which electron is in which orbital.

We introduce a shorthand notation for a normalized Slater determinant:

\[
\Psi (x_1, x_2, \ldots, x_N) \equiv |\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)\rangle
\]

\[
\equiv |\chi_i\chi_j\cdots\chi_k\rangle
\]

where we only show the diagonal elements of \( \Psi \), and we choose the electron labels to always be in the order \( x_1, x_2, \ldots, x_N \).

The Hartree product is truly an independent-electron wavefunction because

\[
|\Psi_{\text{HP}}(x_1, x_2, \ldots, x_N)|^2 = |\chi_i(x_1)|^2 |\chi_j(x_2)|^2 \cdots |\chi_k(x_N)|^2
\]

or more clearly,

\[
|\Psi|^2 \, dx_1 \cdots dx_N = |\chi_i(x_1)|^2 dx_1 |\chi_j(x_2)|^2 dx_2 \cdots |\chi_k(x_N)|^2 dx_N
\]

Did antisymmetrizing the Hartree product to obtain a Slater determinant change this? YES!

It introduces exchange correlation which means that the motion of two electrons with parallel spins is correlated.

Consider a two-electron Slater determinant \( \Psi (x_1, x_2) = |\chi_1(x_1)\chi_2(x_2)\rangle \).

If the two electrons have opposite spins and occupy different spatial orbitals,

\[
\chi_1(x_1) = \psi_1(r_1) \alpha(\omega_1)
\]

\[
\chi_2(x_2) = \psi_2(r_2) \beta(\omega_2)
\]

then \( \Psi (x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\alpha(\omega_2)\psi_2(r_1)\beta(\omega_1) \right] \).
Define $P(r_1, r_2)$ as the probability density in space (not caring about spin).

$$P(r_1, r_2) = \int \frac{d\omega_1}{\text{spin}} \frac{d\omega_2}{\text{spin}} \left| \Psi(r_1, r_2) \right|^2$$

The rules for these are:

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = \int d\omega \beta^*(\omega) \beta(\omega) = 1$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\int d\omega \alpha^*(\omega) \beta(\omega) = \int d\omega \beta^*(\omega) \alpha(\omega) = 0$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

$$P(r_1, r_2) = \frac{1}{2} \left[ |\Psi_1(r_1)\Psi_2(r_2)|^2 + |\Psi_2(r_1)\Psi_2(r_2)|^2 \right]$$

which, keeping in mind indistinguishability, shows that the motion of these two electrons is uncorrelated.

In particular, if $\Psi_1 = \Psi_2$ (same spatial orbital)

$$P(r_1, r_2) = |\Psi_1(r_1)|^2 |\Psi_2(r_2)|^2$$

However, if the two spins are the same, we have

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left[ \Psi_1(r_1) \beta(\omega) \Psi_2(r_2) \beta(\omega_2) - \Psi_1(r_2) \beta(\omega) \Psi_2(r_1) \beta(\omega_2) \right]$$

and

$$P(r_1, r_2) = \frac{1}{2} \left[ |\Psi_1(r_1)\Psi_2(r_2)|^2 + |\Psi_2(r_1)\Psi_2(r_2)|^2 \right]$$

$$- \Psi_1^*(r_1) \Psi_2(r_2) \Psi_2^*(r_2) \Psi_2(r_2) - \Psi_2^*(r_1) \Psi_2^*(r_1) \Psi_2(r_2) \Psi_2^*(r_2)$$

where the cross terms introduce correlation.

Note that $P(r_1, r_1) = 0$ and therefore the prob. of finding two electrons with parallel spins at the same point in space is zero.

We say a "Fermi hole" exists around an electron.
The Hartree–Fock method finds the best Slater determinant [using the orbitals you provide] to represent the ground (Roothaan-Oppenheimer) state of an N-electron system.

It does this by making use of the variational principle which says that the best wavefunction \( |\Psi_0\rangle = |\chi_1 \chi_2 \cdots \chi_N\rangle \) we can choose is the one which minimizes the energy \( E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \) where \( H \) is the full electronic Hamiltonian.

Why? The eigenfunctions of the full electronic Hamiltonian form a basis for multi-electron wavefunctions, and we can order these eigenfunctions by their eigenvalues (energies) with the smallest one corresponding to the ground state (all this is guaranteed to us by Sturm-Liouville theory)

\[
H |\Phi_i\rangle = E_i |\Phi_i\rangle , \quad E_0 \leq E_1 \leq E_2 \leq \cdots
\]

Imagine writing \( |\Psi_0\rangle \) in the \( \Phi_i \) basis, \( |\Psi_0\rangle = \sum_i c_i |\Phi_i\rangle \)

The less \( |\Psi_0\rangle \) looks like \( |\Phi_0\rangle \), the higher \( E_0 \) the energy will be, which lets us measure how well we are doing.

Namely, \( E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_{ij} c_i^* c_j \langle \Phi_i | H | \Phi_j \rangle = \sum_i c_i^* c_j E_j \delta_{ij} = \sum_j |c_j|^2 E_j \geq E_0 \sum_j |c_j|^2 = E_0 \)
So what is varied in the Hartree Fock method to minimize $E_0$?

The spin orbitals which are used in the $N$-electron Slater determinant. Namely, you give the Hartree Fock method more than $N$ spin orbitals, and it decides which ones should be occupied and which ones should be unoccupied to best approximate the ground state $\Phi_0$.

This minimization procedure can be written as an eigenvalue equation $f(i) \chi(x_i) = \varepsilon \chi(x_i)$ where $f(i)$ is the one-electron Fock operator

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_{i\alpha}} + V_{HF}(i)$$

- electron kinetic energy
- electron-nucleus attraction
- average potential felt by $i$th electron due to other electrons

The key idea is to replace the many-electron problem with $N$ one-electron problems.

Each one-electron problem depends on already having the solution for the other electrons. This means the equations are implicit; they all depend on each other is where do you start?

The procedure to solve the HF equations is called the self-consistent-field method (SCF).

The idea is to start with an initial guess and iterate.
We label the occupied spin orbitals with $a, b, c, \ldots : X_a, X_b, X_c, \ldots$

Misspelled hole orbitals.

Label the unoccupied, a virtual particle spin orbitals with $r, s, t, \ldots : X_r, X_s, X_t, \ldots$

Given $K$ spatial basis functions $\phi_1(r), \phi_2(r), \ldots, \phi_K(r)$ we can form $2K$ spin orbitals ($\uparrow, \downarrow$ spin).

If there are occupied and $2K - N$ are unoccupied the Slater determinant formed from the $N$ occupied spin orbitals is the Hartree-Fock ground state $|\Psi_0\rangle$.

In the limit of $K \to \infty$ we approach the best solution possible in the HF theory, called the Hartree-Fock limit.

(Excited State Det!

We write the HF ground state as $|\Psi_0\rangle = |X_a X_b \cdots X_a X_b \cdots X_N\rangle$.

We can also form other Slater determinants using the unoccupied orbitals in $(2K) = \frac{(2K)!}{N! (2K-N)!}$ different ways.

We will keep track of these by how they differ from $|\Psi_0\rangle$.

In a singly excited det one electron moves from $X_a$ to $X_r$.

In a doubly excited det two electrons move from $X_a, X_b$ to $X_r, X_s$.
Exact Wavefunction and CI

Suppose we have a basis for one-electron wavefunctions \( \{ \chi_i(x) \} \). This could happen if \( K \to \infty \) in the orbitals we use for HF.

Then, any one-electron wavefunction \( \Phi(x) \) can be written \( \Phi(x) = \sum_i \alpha_i \chi_i(x) \) where \( \alpha_i = \langle \chi_i | \Phi \rangle \).

What about a function of two electrons \( \Phi(x_1,x_2) \)?

If we imagine fixing \( x_2 \), we have \( \Phi(x_1,x_2) = \sum_i \alpha_i(x_2) \chi_i(x_1) \) since for each different (fixed) value of \( x_2 \) the expansion coefficients change.

But then \( \alpha_i(x_2) = \sum_j b_{ij} \chi_j(x_2) \) so \( \Phi(x_1,x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2) \).

We also need \( \Phi(x_1,x_2) = -\Phi(x_2,x_1) \Rightarrow b_{ij} = -b_{ji} \) and \( b_{ii} = 0 \), so that \( \Phi(x_1,x_2) = \sum_{ij} b_{ij} \left[ \chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2) \right] \)

\[ = \sum_{i<j} \sqrt{2} b_{ij} \chi_i \chi_j \]

Hence any antisymmetric function of two electrons can be written in terms of all possible determinants from one-electron wavefunctions. This argument extends to N-electron wavefunctions.

Since any N-electron Slater determinant can be expressed by how it differs from the HF ground state, we can express the exact N-electron wavefunction as

\[ \Phi = c_0 | \Phi_0 \rangle + \sum_{\alpha} c_\alpha | \Psi_\alpha \rangle + \sum_{\alpha<\beta} c_{\alpha\beta} | \Psi_{\alpha\beta} \rangle + \sum_{\alpha<\beta<\gamma} c_{\alpha\beta\gamma} | \Psi_{\alpha\beta\gamma} \rangle + \ldots \]
This procedure is called CI "configuration interaction". In principle it gives the exact non-relativistic ground state of the electronic Hamiltonian in the Born–Oppenheimer approx.

The difference between this exact energy $E_0$, and the HF limit $E_0$ is called the correlation energy $E_{\text{corr}} = E_0 - E_0$.

Since the motion of electrons with opposite spin is not correlated at the HF level.

Fig 2.9 of S. Nak.

\[ H_0 \rightarrow \text{HF limit} \rightarrow \text{exact result} \rightarrow \text{full CI} \]
\[ H = H^0 + \lambda V \]  

"turn on" perturbation from \( \lambda = 0 \)

"fill" electronic Hamiltonian

Hartree-Fock Hamiltonian when \( \lambda = 1 \).

For \( \lambda = 0 \) we just have the HF problem,

\[ H^0 | \phi^{(0)}_n \rangle = E^{(0)}_n | \phi^{(0)}_n \rangle \]

\[ \rightarrow \text{N-electron Slater det.,} \ | \phi^{(0)}_n \rangle = | \Psi_0 \rangle \ ; \ | \phi^{(1)}_n \rangle = | \Psi_a \rangle \ etc \]

\[ \rightarrow E^{(0)}_n = \sum_{\alpha} \langle \alpha | h | \alpha \rangle + \frac{1}{2} \sum_{\alpha \beta} \langle \alpha b || ab \rangle \ etc \]

Recall that the set of solutions \( \{ \phi^{(0)}_n \}_{n=0}^{\infty} \) forms a basis for any N-electron wavefunction.

Denote by \( \phi_n, E_n \) the perturbed eigenfunctions, eigenvalues.

\[ H \phi_n = E_n \phi_n \]

We seek a perturbative expansion (power series approach)

\[ E_n = E^{(0)}_n + \lambda E^{(1)}_n + \lambda^2 E^{(2)}_n + \ldots \]

\[ \phi_n = \phi^{(0)}_n + \lambda \phi^{(1)}_n + \lambda^2 \phi^{(2)}_n + \ldots \]
Substitute these power series into $H \phi_n = E_n \phi_n$.

$$(H_0 + \lambda V \phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \ldots \phi_n^{(0)} + \lambda \phi_n^{(1)} + \ldots)$$

Equate like powers of $\lambda$. Why?

Set $\lambda = 0$ (zeroth powers)

Take $\frac{d}{d\lambda}$ on both sides and evaluate at $\lambda = 0$ (first powers)

Take $\frac{d^2}{d\lambda^2}$ on both sides and set $\lambda = 0$ (second powers)

$$\lambda^0 \quad H_0 \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)} \quad \text{unperturbed problem}$$

$$\lambda^1 \quad H_0 \phi_n^{(1)} + V \phi_n^{(0)} = E_n^{(0)} \phi_n^{(1)} + E_n^{(1)} \phi_n^{(0)}$$

To proceed we expand $\phi_n^{(1)} = \sum_l \alpha_l \phi_l^{(0)}$

This gives $$H_0 \sum_l \alpha_l \phi_l^{(0)} + V \phi_n^{(0)} = E_n^{(0)} \sum_l \alpha_l \phi_l^{(0)} + E_n^{(1)} \phi_n^{(0)}$$

$$\sum_l \alpha_l E_l^{(0)} \phi_l^{(0)}$$

Apply $\langle \phi_s^{(0)} \rangle$ to obtain

$$\sum_l \alpha_l E_l^{(0)} S_{sl} + V_{sn} = E_n^{(0)} \sum_l \alpha_l S_{sl} + E_n^{(1)} S_{sn}$$

$$\Rightarrow \alpha_s E_s^{(0)} + V_{sn} = \alpha_s E_n^{(0)} + E_n^{(1)} S_{sn}$$
For $s = n$ we have $a_n E_n^{(0)} + V_{nn} = a_n E_n^{(0)} + E_n^{(1)} \Rightarrow E_n^{(1)} = V_{nn}$

For $s \neq n$ we have $a_s E_s^{(0)} + V_{sn} = a_s E_n^{(0)} \Rightarrow a_s = \frac{V_{sn}}{E_n^{(0)} - E_s^{(0)}} \quad (\text{non-degenerate case})$

$\Rightarrow \phi_n = \phi_n^{(0)} + \lambda \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \phi_k^{(0)} + \ldots$

Szabo works out the higher order energies; for example

$E_n^{(2)} = \sum_{i \neq n} \frac{|V_{in}|^2}{E_i^{(0)} - E_n^{(0)}}$

A few comments:

i) $\alpha_n = 0$ in the $\phi_n^{(1)} = \sum \alpha_k \phi_k^{(0)}$ expansion

ii) degeneracy: suppose $E_l^{(0)} = E_n^{(0)}$ for some $l \neq n$.

Go back to $a_s E_s^{(0)} + V_{sn} = a_s E_n^{(0)} + E_n^{(1)} S_{sn}$ and rewrite as

$\Rightarrow a_s [E_n^{(0)} - E_s^{(0)}] + E_n^{(1)} S_{sn} = V_{sn}$

Consider $E_n^{(0)} = E_s^{(0)}$ for $n \neq s$. Get $V_{sn} = 0$.

This says the perturbation can't connect the zeroth order degenerate states. We must impose this condition by diagonalizing $V_{ij}$ in the degenerate subspace, which corresponds to "rotating" the degenerate subspace basis vectors. Still have $E_n^{(1)} = V_{nn}$ in new basis.