Introduction to Hartree-Fock Molecular Orbital Theory

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Preceding Material

- These notes pick up from "General Introduction to Electronic Structure Theory" by the author.

What Hartree-Fock is for

- A way to approximately solve the Electronic Schrödinger equation

$$\hat{H}_{el}(\mathbf{r};\mathbf{R})\Psi(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\Psi(\mathbf{r};\mathbf{R})$$

- This gives us the electronic wavefunction, from which we can extract dipole moment, polarizability, etc!
- The electronic energy $E_{el}(\mathbf{R})$ is the potential energy surface: gives equilibrium geometries, reaction paths, etc.

The Slater Determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

John Slater

Shorthand: $|\chi_i \chi_j \cdots \chi_k\rangle$ or $|ij \cdots k\rangle$

We will assume the electronic wavefunction can be written as a single Slater Detrminant (this is an approximation). This enforces an antisymmetric wavefunction. The Hartree-Fock procedure will give us the orbitals.

Images from Wikipedia

Hartree-Fock Molecular Orbital Theory

- 1. Invoke the Born-Oppenheimer approximation
- 2. Express the electronic wavefunction as a single Slater Determinant
- 3. Solve for those orbitals which minimize the electronic energy (variational method)
- This winds up being mathematically equivalent to assuming *each electron interacts only with the average charge cloud of the other electrons*

Douglas Hartree

V. A. Fock

Images from Wikipedia

The Operators

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

One-electron operator: for electron *i*, its KE and its attraction to all nuclei

$$v(i,j) = \frac{1}{r_{ij}}$$

Two-electron operator: for electrons *i* and *j*, their Coulomb repulsion

Electronic Hamiltonian in terms of these operators:

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} v(i,j) + V_{NN}$$

The Hartree-Fock Energy

- If the variational theorem says to minimize the energy, *what is* the energy of a Slater determinant?

$$
\begin{aligned}
E_{el}(\mathbf{R}) &= \langle \Psi(\mathbf{r};\mathbf{R}) | \hat{H}_{el} | \Psi(\mathbf{r};\mathbf{R}) \rangle \\
&= \int_{-\infty}^{\infty} d\mathbf{r} \Psi^*(\mathbf{r};\mathbf{R}) \hat{H}_{el} \Psi(\mathbf{r};\mathbf{R})
\end{aligned}
$$

- Slater's Rules tell us how to get the matrix elements of the electronic Hamiltonian using Slater Determinants

The Hartree-Fock Energy

$$E_{HF} = \sum_{i}^{\text{elec}} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{\text{elec}} [ii|jj] - [ij|ji]$$

One-electron integral (4-dimensional):

$$\langle i|\hat{h}|j\rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{x}_1)$$

Two-electron integral (8-dimensional):

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2)$$

Physical Meaning of the Terms

- Each electron contributes a one-electron integral

$$\langle i|\hat{h}|i\rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\hat{h}(\mathbf{r}_1)\chi_i(\mathbf{x}_1)$$

- This looks like the expectation (average) value of the operator $\hat{h}$ for an electron in orbital χ, so long as the orbital is normalized
- Recall $\hat{h}$ contains electron KE and potential of attraction to all the nuclei
- Sum over all orbitals *i* to get total electron KE and attraction to nuclei

Physical Meaning of the Terms

- Each pair of electrons (in orbitals *i* and *j*) has a "Coulomb integral":

$$[ii|jj] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)$$

Probability electron 1 in orbital *i* is located at x_1

Probability electron 2 in orbital *j* is located at x_2

Integrate over all possible locations for the electrons

Coulomb repulsion between electron at x_1 and electron at x_2

Overall this integral represents the Coulomb repulsion between electron 1 in orbital *i* and electron 2 in orbital *j*

Physical Meaning of the Terms

- Each pair of electrons (in orbitals *i* and *j*) has also has an "Exchange integral":

$$[ij|ji] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)$$

- This is like the Coulomb integral

$$[ii|jj] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)$$

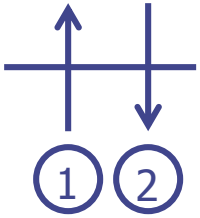
Except two of the orbital indices have been "exchanged"!

No direct physical meaning .. consequence of Slater Determinant

Hartree-Fock Energy Example

$$E_{HF} = \sum_{i}^{\text{elec}} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{\text{elec}} [ii|jj] - [ij|ji]$$

- Simple example: He atom
- 2 electrons, 1sα, 1sβ
- Number the spin orbitals 1=1sα, 2=1sβ



$$E_{HF} = \langle 1|\hat{h}|1\rangle + \langle 2|\hat{h}|2\rangle + [22|11] - [21|12]$$

- We (typically) need a computer to evaluate these integrals
- Is this as simple as we can get it?
- No! The last integral is zero. Why?

Spin Factorization and Spatial Orbitals

- Recall each spin orbital $\chi(\mathbf{x})$ is a function of 4 coordinates: $\chi(x,y,z,\omega)$
- We normally write each spatial orbital as a product of a spatial part $\phi(\mathbf{r})$ and a spin part, which we might call $\sigma(\omega)$, i.e., $\chi(\mathbf{x}) = \phi(\mathbf{r})\,\sigma(\omega)$ [recall $\mathbf{r} = \{x,y,z\}$]
- The operators in Hartree-Fock theory, $\hat{h}$ and $1/r_{12}$, do not depend on the spin coordinate
- That means an integral over $\mathbf{x}$ can be factored into a simple integral over the spin coordinate ω (no operators) times a more complicated integral (involving operators) over the spatial coordinates $\mathbf{r}$, e.g.,

$$\langle i|\hat{h}|j\rangle = \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_j(\mathbf{x})$$

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$$\begin{aligned}\langle i|\hat{h}|j\rangle &= \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_j(\mathbf{x}) \\ &= \int d\mathbf{r}d\omega\phi_i^*(\mathbf{r})\sigma_i^*(\omega)\hat{h}(\mathbf{r})\phi_j(\mathbf{r})\sigma_j(\omega)\end{aligned}$$

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$$
\begin{aligned}
\langle i|\hat{h}|j\rangle &= \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_j(\mathbf{x}) \\
&= \int d\mathbf{r}d\omega\phi_i^*(\mathbf{r})\sigma_i^*(\omega)\hat{h}(\mathbf{r})\phi_j(\mathbf{r})\sigma_j(\omega) \\
&= \int d\omega\sigma_i^*(\omega)\sigma_j(\omega)\int d\mathbf{r}\phi_i^*(\mathbf{r})\hat{h}(\mathbf{r})\phi_j(\mathbf{r})
\end{aligned}
$$

Spin Factorization and Spatial Orbitals

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- We normally write each spatial orbital as a product of a spatial part $\phi(\mathbf{r})$ and a spin part, which we might call $\sigma(\omega)$, i.e., $\chi(\mathbf{x}) = \phi(\mathbf{r})\,\sigma(\omega)$ [recall $\mathbf{r} = \{x,y,z\}$]
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- That means an integral over $\mathbf{x}$ can be factored into a simple integral over the spin coordinate ω (no operators) times a more complicated integral (involving operators) over the spatial coordinates $\mathbf{r}$, e.g.,

$$
\begin{aligned}
\langle i|\hat{h}|j\rangle &= \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_j(\mathbf{x}) \\
&= \int d\mathbf{r}d\omega\phi_i^*(\mathbf{r})\sigma_i^*(\omega)\hat{h}(\mathbf{r})\phi_j(\mathbf{r})\sigma_j(\omega) \\
&= \int d\omega\sigma_i^*(\omega)\sigma_j(\omega)\int \underline{d\mathbf{r}\phi_i^*(\mathbf{r})\hat{h}(\mathbf{r})\phi_j(\mathbf{r})} \\
&\equiv \left[\int d\omega\sigma_i^*(\omega)\sigma_j(\omega)\right] \times \underline{(i|\hat{h}|j)}
\end{aligned}
$$

Spin Factorization of 2-elec Integrals

- We can also factorize out the spin functions in two-electron integrals

$$[ij|kl] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2)$$

Spin Factorization of 2-elec Integrals

- We can also factorize out the spin functions in two-electron integrals

$$
\begin{aligned}
[ij|kl] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) \\
&= \int d\mathbf{r}_1 \int d\omega_1 \int d\mathbf{r}_2 \int d\omega_2 \\
&\quad \phi_i^*(\mathbf{r}_1)\sigma_i^*(\omega_1)\phi_j(\mathbf{r}_1)\sigma_j(\omega_1)\frac{1}{r_{12}}\phi_k^*(\mathbf{r}_2)\sigma_k^*(\omega_2)\phi_l(\mathbf{r}_2)\sigma_l(\omega_2) \\
&= \int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1) \int d\omega_2 \sigma_k^*(\omega_2)\sigma_l(\omega_2) \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\frac{1}{r_{12}}\phi_k^*(\mathbf{r}_2)\phi_l(\mathbf{r}_2) \\
&\equiv \left[\int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1)\right]\left[\int d\omega_2 \sigma_k^*(\omega_2)\sigma_l(\omega_2)\right] \times (ij|kl)
\end{aligned}
$$

Spin Integration

- Integrals over spin coordinates are usually easy to do because the spin function $\sigma(\omega)$ is usually just $\alpha(\omega)$ or $\beta(\omega)$
- The spin integration rules for $\alpha(\omega)$ and $\beta(\omega)$ are very easy and result in 1 or 0

$$\begin{aligned}
\int d\omega \alpha^*(\omega)\alpha(\omega) &= 1, \\
\int d\omega \beta^*(\omega)\beta(\omega) &= 1, \\
\int d\omega \alpha^*(\omega)\beta(\omega) &= 0, \\
\int d\omega \beta^*(\omega)\alpha(\omega) &= 0.
\end{aligned}$$

Spin Integration General Results

$$\langle i|\hat{h}|j\rangle = \left[\int d\omega \sigma_i^*(\omega)\sigma_j(\omega)\right] \times (i|\hat{h}|j)$$

$$= \begin{cases} (i|\hat{h}|j) & \sigma_i = \sigma_j \\ 0 & \sigma_i \neq \sigma_j \end{cases}$$

- One-electron integrals survive if both spin-orbitals have the same spin

$$[ij|kl] = \left[\int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1)\right]\left[\int d\omega_2 \sigma_k^*(\omega_2)\sigma_l(\omega_2)\right] \times (ij|kl)$$

$$= \begin{cases} (ij|kl) & \sigma_i = \sigma_j \text{ and } \sigma_k = \sigma_l \\ 0 & \sigma_i \neq \sigma_j \text{ or } \sigma_k \neq \sigma_l \end{cases}$$

- Two-electron integrals survive if spins *i,j* match on the left and spins *k,l* match on the right

Spin Integration in Hartree-Fock

- We just did the generic one- and two-electron integrals; the ones in Hartree-Fock are specific types

$$E_{HF} = \sum_{i}^{\text{elec}} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{\text{elec}} [ii|jj] - [ij|ji]$$

same index both sides

each index appears twice
(although in different places)

- How do these repeats affect spin integration?

Spin Integration in Hartree-Fock One-electron Integrals

$$\langle i|\hat{h}|i\rangle = \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_i(\mathbf{x})$$

Spin Integration in Hartree-Fock One-electron Integrals

$$\begin{aligned}
\langle i|\hat{h}|i\rangle &= \int d\mathbf{x}\chi_i^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_i(\mathbf{x}) \\
&= \int d\omega\sigma_i^*(\omega)\sigma_i(\omega)\int d\mathbf{r}\phi_i^*(\mathbf{r})\hat{h}(\mathbf{r})\phi_i(\mathbf{r}) \\
&= \left[\cancel{\int d\omega\sigma_i^*(\omega)\sigma_i(\omega)}\right] \times (i|\hat{h}|i)
\end{aligned}$$

Factor in brackets
is always = 1
(same spin function)

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

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

Spin Integration in Hartree-Fock Coulomb Integrals

$$[ii|jj] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)$$

Spin Integration in Hartree-Fock Coulomb Integrals

$$
\begin{aligned}
[ii|jj] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2) \\
&= \int \cancelto{1}{d\omega_1 \sigma_i^*(\omega_1)\sigma_i(\omega_1)} \int \cancelto{1}{d\omega_2 \sigma_j^*(\omega_2)\sigma_j(\omega_2)} \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)
\end{aligned}
$$

Spin Integration in Hartree-Fock Coulomb Integrals

$$
\begin{aligned}
[ii|jj] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2) \\
&= \int \cancelto{1}{d\omega_1 \sigma_i^*(\omega_1)\sigma_i(\omega_1)} \int \cancelto{1}{d\omega_2 \sigma_j^*(\omega_2)\sigma_j(\omega_2)} \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2) \\
&= (ii|jj)
\end{aligned}
$$

Coulomb integrals *always* survive spin integration!

Spin Integration in Hartree-Fock Exchange Integrals

$$[ij|ji] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)$$

Spin Integration in Hartree-Fock Exchange Integrals

$$
\begin{aligned}
[ij|ji] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2) \\
&= \int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1) \int d\omega_2 \sigma_j^*(\omega_2)\sigma_i(\omega_2) \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)
\end{aligned}
$$

Spin Integration in Hartree-Fock Exchange Integrals

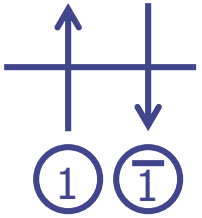
$$
\begin{aligned}
[ij|ji] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2) \\
&= \int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1) \int d\omega_2 \sigma_j^*(\omega_2)\sigma_i(\omega_2) \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\
&= \int d\omega_1 \sigma_i^*(\omega_1)\sigma_j(\omega_1) \int d\omega_2 \sigma_j^*(\omega_2)\sigma_i(\omega_2) \times (ij|ji)
\end{aligned}
$$

Exchange integrals *sometimes* survive spin integration!
Need spin orbitals *i* and *j* to have same spin

Back to our Hartree-Fock Energy Example

$$E_{HF} = \sum_{i}^{\text{elec}} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{\text{elec}} [ii|jj] - [ij|ji]$$

- Simple example: He atom
- 2 electrons, 1sa, 1sβ
- Renumber the spin orbitals: 1=1sα, $\bar{1}$=1sβ



$$E_{HF} = \langle 1|\hat{h}|1\rangle + \langle \bar{1}|\hat{h}|\bar{1}\rangle + [\bar{1}\bar{1}|11] - \cancel{[\bar{1}1|1\bar{1}]}$$

0

Exchange integrals must have same spin on *i* and *j*

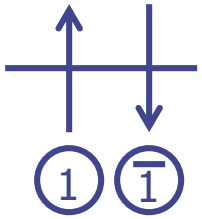
$$E_{HF} = (1|\hat{h}|1) + (\bar{1}|\hat{h}|\bar{1}) + (\bar{1}\bar{1}|11)$$

Can we simplify this result? Yes! (normally)

Simplifying Spatial Integrals

Helium atom example

$$E_{HF} = \langle 1|\hat{h}|1\rangle + \langle \overline{1}|\hat{h}|\overline{1}\rangle + [\overline{1}\overline{1}|11]$$



$$\begin{aligned}
\chi_1(\mathbf{x}) &= \chi_{1s\alpha}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\alpha(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\alpha(\omega) \\
\chi_{\overline{1}}(\mathbf{x}) &= \chi_{1s\beta}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\beta(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\beta(\omega)
\end{aligned}$$

Spatial part is *the same.* Therefore after spin integration, spatial integrals in terms of these two orbitals must be the same. Let's check.

Simplifying Spatial Integrals

$$\chi_1(\mathbf{x}) = \chi_{1s\alpha}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\alpha(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\alpha(\omega)$$

$$\chi_{\overline{1}}(\mathbf{x}) = \chi_{1s\beta}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\beta(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\beta(\omega)$$

$$\begin{aligned}
\langle 1|\hat{h}|1\rangle &= \int d\mathbf{x}\chi_1^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_1(\mathbf{x}) \\
&= \int d\omega\alpha^*(\omega)\alpha(\omega)\int d\mathbf{r}\phi_1^*(\mathbf{r})\hat{h}(\mathbf{r})\phi_1(\mathbf{r}) \\
&= (1|\hat{h}|1) \\
\langle \overline{1}|\hat{h}|\overline{1}\rangle &= \int d\mathbf{x}\chi_{\overline{1}}^*(\mathbf{x})\hat{h}(\mathbf{r})\chi_{\overline{1}}(\mathbf{x}) \\
&= \int d\omega\beta^*(\omega)\beta(\omega)\int d\mathbf{r}\phi_1^*(\mathbf{r})\hat{h}(\mathbf{r})\phi_1(\mathbf{r}) \\
&= (1|\hat{h}|1)
\end{aligned}$$

Simplifying Spatial Integrals

$$\chi_1(\mathbf{x}) = \chi_{1s\alpha}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\alpha(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\alpha(\omega)$$

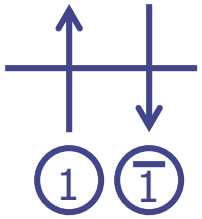
$$\chi_{\overline{1}}(\mathbf{x}) = \chi_{1s\beta}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\beta(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\beta(\omega)$$

$$\begin{aligned}
[\overline{11}|11] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2\, \chi^*_{\overline{1}}(\mathbf{x}_1)\chi_{\overline{1}}(\mathbf{x}_1)\frac{1}{r_{12}}\chi^*_1(\mathbf{x}_2)\chi_1(\mathbf{x}_2) \\
&= \int d\omega_1 \beta^*(\omega_1)\beta(\omega_1) \int d\omega_2 \alpha^*(\omega_2)\alpha(\omega_2) \times \\
&\quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi^*_1(\mathbf{r}_1)\phi_1(\mathbf{r}_1)\frac{1}{r_{12}}\phi^*_1(\mathbf{r}_2)\phi_1(\mathbf{r}_2) \\
&= (11|11)
\end{aligned}$$

Conclusion: if spin orbitals come in α,β pairs with the same spatial part ϕ, then after spin integration we can remove the overbar labels on the spatial orbital integrals

Simplifying Spatial Integrals

Helium atom example



$$E_{HF} = \langle 1|\hat{h}|1\rangle + \langle \overline{1}|\hat{h}|\overline{1}\rangle + [\overline{1}\overline{1}|11]$$

$$\begin{aligned}
\chi_1(\mathbf{x}) &= \chi_{1s\alpha}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\alpha(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\alpha(\omega) \\
\chi_{\overline{1}}(\mathbf{x}) &= \chi_{1s\beta}(\mathbf{x}) = \boxed{\phi_{1s}(\mathbf{r})}\beta(\omega) \equiv \boxed{\phi_1(\mathbf{r})}\beta(\omega)
\end{aligned}$$

$$E_{HF} = 2(1|\hat{h}|1) + (11|11)$$

Restricted Orbitals (Restricted Hartree-Fock, RHF)

- Spin orbitals always come in (α,β) pairs that share the same spatial orbital ϕ

$$\begin{aligned} \chi_n(\mathbf{x}) &= \phi_n(\mathbf{r})\alpha(\omega) \\ \chi_{\overline{n}}(\mathbf{x}) &= \phi_n(\mathbf{r})\beta(\omega) \end{aligned}$$

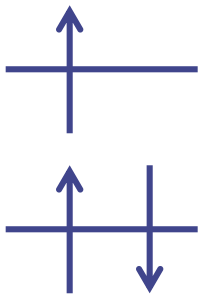
- This is how we normally think about orbitals in chemistry
- There's no reason not to use such "restricted" orbitals in normal molecules in which all electrons are paired ("closed shell" molecules)

Unrestricted Orbitals (Unrestricted Hartree-Fock, UHF)

- When not all electrons are paired ("open-shell" molecules), we can sometimes get a lower energy solution if we "unrestrict" the orbitals: allow the spatial part to be different for the α spin than for the β spin:

$$\chi_n(\mathbf{x}) = \phi_n(\mathbf{r})\alpha(\omega)$$

$$\chi_{\overline{n}}(\mathbf{x}) = \phi_{\overline{n}}(\mathbf{r})\beta(\omega)$$



- Introduces "spin contamination" (e.g., mix singlet and triplet); can *sometimes* cause severe errors in properties
- Can be easier to converge

Pseudo-Classical Interpretation of Hartree-Fock Energies

$$E_{HF} = \sum_{i}^{\text{elec}} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{\text{elec}} [ii|jj] - [ij|ji]$$

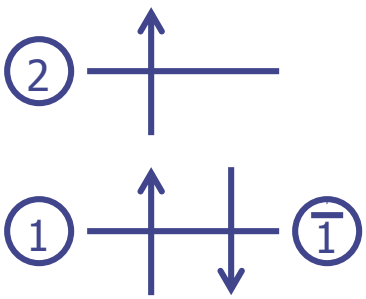
Always survive spin integration

Nonzero only if *i* and *j* have same spin

- Each electron contributes a term $(i|\hat{h}|j) = h_{ij}$
- Each unique pair of electrons contributes a Coulomb repulsion $(ii|jj) = J_{ij}$
- Each unique pair of *same spin* electrons contributes an exchange term $-(ij|ji) = -K_{ij}$

Hartree-Fock Energy Example: Li atom

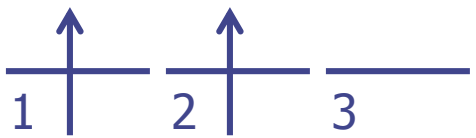
3 electrons: 1=1sα, $\bar{1}$=1sβ, 2=2sα



$$
\begin{aligned}
E_{\mathrm{UHF}} &= h_{11} + h_{\bar{1}\bar{1}} + h_{22} + J_{\bar{1}1} + J_{21} + J_{2\bar{1}} - K_{12} \\
E_{\mathrm{RHF}} &= 2h_{11} + h_{22} + J_{11} + 2J_{21} - K_{12}
\end{aligned}
$$

Connection to Hund's Rules

- Why do Hund's rules say a high-spin state is more stable than a low-spin state for a given electron configuration?
- We can use Hartree-Fock theory to understand this
- As an example, consider the p^2 electron configuration



vs

$E_{HF} = h_{11} + h_{22} + J_{12} - K_{12}$

$E_{HF} = 2h_{11} + J_{11}$

Energy lower because exchange integral is subtracted!

Hartree-Fock Equations

- Minimizing the Hartree-Fock energy with respect to the orbitals leads to the Hartree-Fock equations for the orbitals:

$$h(\mathbf{x}_1)\chi_i(\mathbf{x}_1) + \sum_{j\neq i}\left[\int d\mathbf{x}_2|\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}\right]\chi_i(\mathbf{x}_1) - \sum_{j\neq i}\left[\int d\mathbf{x}_2\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)r_{12}^{-1}\right]\chi_j(\mathbf{x}_1) = \sum_j \epsilon_{ij}\chi_j(\mathbf{x}_1)$$

$$f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_j J_j(\mathbf{x}_1) - K_j(\mathbf{x}_1)$$

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i\chi_i(\mathbf{x}_1)$$

- Problem: This is a very complicated integro-differential equation!

Roothan to the Rescue!

- If we introduce a basis set, we convert the equation into a much simpler linear algebra problem

Clemens C. J. Roothan

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

$$\chi_i = \sum_{\mu=1}^{K} C_{\mu i}\tilde{\chi}_\mu$$

$$S_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1),$$

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}C_{\nu i} \qquad F_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}^*_\mu(\mathbf{x}_1) f(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1)$$

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

Images from Wikipedia

Summary of Hartree-Fock-Roothan Equations

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

$$\begin{aligned} S_{\mu\nu} &= \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1), \\ F_{\mu\nu} &= \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1) f(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1) \end{aligned}$$

- Pseudo-eigenvalue equation
- C collects the expansion coefficients for each orbital expressed as a linear combination of the basis functions (each column of C is a molecular orbital)
- Note: C depends on F, which depends on… C!

Self-consistent-field procedure

- 1. Specify molecule, basis functions, *and electronic state of interest* (i.e., singlet, triplet, etc)
- 2. Form overlap matrix S
- 3. Guess initial MO coefficients C
- 4. Form Fock matrix F
- 5. Solve $FC=SC\varepsilon$
- 6. Use new MO coefficients C to build new Fock matrix F
- 7. Go to step 5; repeat until C no longer changes from one iteration to the next

Forming the Fock Matrix

$$\hat{f}(\mathbf{r}) = \hat{h}(\mathbf{r}) + \sum_{i}^{N/2} 2\hat{J}_i(\mathbf{r}) - \hat{K}_i(\mathbf{r})$$

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{i}^{N/2} 2(\mu\nu|ii) - (\mu i|i\nu)$$

For closed-shell RHF

$$\phi_i(\mathbf{r}) = \sum_{\mu}^{K} C_{\mu i}\tilde{\phi}_\mu$$

$$\begin{aligned} f_{\mu\nu} &= h_{\mu\nu} + \sum_{i}^{N/2}\sum_{\lambda\sigma}^{K} C^*_{\lambda i}C_{\sigma i}\left(2[\mu\nu|\lambda\sigma] - [\mu\sigma|\lambda\nu]\right) \\ &= h_{\mu\nu} + \sum_{\lambda\sigma}^{K} D_{\sigma\lambda}\left([\mu\nu|\lambda\sigma] - \frac{1}{2}[\mu\sigma|\lambda\nu]\right), \end{aligned}$$

Computational Cost

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma}^{K} D_{\sigma\lambda} \left([\mu\nu|\lambda\sigma] - \frac{1}{2}[\mu\sigma|\lambda\nu] \right)$$

- Rate determining step normally computation of $O(n^4)$ integrals
- Integrals very small if basis functions centered on atoms far from each other; can use screening techniques to reduce to $O(n^2)$ significant integrals
- Fast multipole methods, etc., can reduce cost further to "linear scaling"
- Alternatively, can replace 4-index integrals by 3-index integrals using "density fitting"

So What Did We Get?

- The electronic energy (one point on the potential energy surface; PES can give equilibrium geometry, reaction paths, etc.)
- The electronic wave function (can get dipole moment, polarizability, electrostatic potential, other properties)
- Orbitals (can give insight into bonding)
- Orbital energies

Orbital Energies

- Occupied orbital energy (usually negative) approximately gives negative of energy required to remove an electron from that orbital
- Unoccupied orbital energy (usually positive) very approximately gives energy required to put an electron in that orbital
- Orbital energies do *not* sum to the Hartree-Fock energy

Energy Units

- Atomic unit of energy is the Hartree (sometimes abbreviated au or E_h)
- H atom energy in the Born-Oppenheimer approximation (use electron mass not reduced mass) defined as -1/2 Hartree
- It's a big unit! 1 Hartree = 627.509 kcal/mol

Example of Orbital Energies

Comparison of Hartree-Fock to Experiment for Cu^+ (atomic units = Hartree)

Orbital	Hartree-Fock	Experiment
1s	658.4	661.4
2s	82.3	81.0
2p	71.8	68.9

Data from McQuarrie, Quantum Chemistry

Practical considerations

- Hartree-Fock self-consistent-field (HF SCF) usually converges fairly well with a good initial guess
- Stretched bonds, diradicals, transition metals, high-spin states, etc., can cause problems for convergence
- In high-symmetry cases, the program can guess the wrong orbital occupations, and then have trouble recovering from this to get the desired solution
- Not guaranteed to land on a local minimum in C space; can check by running a Hartree-Fock stability analysis (useful but not commonly done). However, even this doesn't guarantee you're not in some other local minimum (esp. for high-symmetry cases)
- User is responsible for making sure the orbital occupations are reasonable and the spin state is correct. Many students don't know that the ground state of O_2 is a triplet, not a singlet. The programs don't know about this!

Improving Convergence

- Most codes use “direct inversion of the iterative subspace” (DIIS) to improve convergence (improves guess for the next step)
- The quality of the guess density makes a big difference. Core Hamiltonian (no initial density) is quite poor. Hückel and GWH ok; superposition of atomic densities (SAD) seems best when available
- Using MO's from one geometry as guesses for a nearby geometry (or neutral orbitals as a guess for a cation or anion, or singlet orbitals as a guess for a triplet) works well