Electronic Structure Theory
TSTC Session 2

1. Born-Oppenheimer approx.- energy surfaces
2. **Mean-field (Hartree-Fock) theory- orbitals**
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. MPn, MCSCF, CI, CC, DFT
8. Gradients and Hessians
9. Special topics: accuracy, metastable states

Jack Simons Henry Eyring Scientist and Professor
Chemistry Department
University of Utah

Digression into atomic units.

Often, we use so-called atomic units.

We let each (e and nuc.) coordinate be represented in terms of a parameter a_0 having units of length and a dimensionless quantity: $\mathbf{r}_j \rightarrow a_0 \, \mathbf{r}_j$; $\mathbf{R}_j \rightarrow a_0 \, \mathbf{R}_j$

The kinetic and potential energies in terms of the new dimensionless variables:

$$T = -(\hbar^2/2m_e)(1/a_0)^2 \, \nabla_j^2 \, , \, V_{en} = - Z_K e^2(1/a_0) \, 1/r_{j,K}, \, V_{ee} = e^2(1/a_0) \, 1/r_{i,j}$$

Factoring e^2/a_0 out from both the kinetic and potential energies gives

$$T = e^2/a_0\{-(\hbar^2/2m_e)(1/e^2 a_0) \, \nabla_j^2\} \text{ and } V = e^2/a_0 \, \{-Z_K/r_{j,K} + 1/r_{j,i}\}$$

Choosing $a_0 = \hbar^2/(e^2 m_e) = 0.529 \text{ Å} = 1 \text{ Bohr}$,

where m_e is the electron mass, allows T and V to be written in terms of

$e^2/a_0 = 1 \text{ Hartree} = 27.21 \text{ eV}$ in a simple manner:

$$T = -1/2 \, \nabla_j^2 \text{ while } V_{en} = - Z_K/r_{j,K} \text{ and } V_{ee} = 1/r_{i,j}$$

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Let's now look into how we go about solving the electronic SE

$$H^0 \, \psi_K(\mathbf{r}|\mathbf{R}) = E_K(\mathbf{R}) \, \psi_K(\mathbf{r}|\mathbf{R})$$

for one electronic state (K) at some specified geometry $\mathbf{R}$.

There are *major difficulties* in solving the electronic SE. The potential terms

$$V_{ee} = \Sigma_{j<k=1,N} e^2/r_{j,k}$$

make the SE equation **not separable**- this means $\psi_K(\mathbf{r}|\mathbf{R})$ is not a product of functions of individual electron coordinates.

$$\psi_K(\mathbf{r}|\mathbf{R}) \neq \phi_1(\mathbf{r_1})\, \phi_2(\mathbf{r_2})\, \ldots \phi_N(\mathbf{r_N})$$

(e.g., $\neq$ 1sα(1) 1sβ(2) 2sα(3) 2sβ(4) 2p1α(5) for Boron).

This means that our desire to use spin-orbitals to describe $\psi_K(\mathbf{r}|\mathbf{R})$ is not really correct. We need to make further progress before we can think in terms of spin-orbitals, orbital energies, orbital symmetries, and the like.

The correct $\psi_K(\mathbf{r}|\mathbf{R})$ have certain properties that we need to know about so that, when we try to create good approximations to $\psi_K(\mathbf{r}|\mathbf{R})$, we can build these properties into our approximate functions.

1. Because $P_{i,j} H^0 = H^0 P_{i,j}$, the $\psi_K(\mathbf{r}|\mathbf{R})$ must obey $P_{i,j} \psi_K(\mathbf{r}|\mathbf{R})$ $= \pm \psi_K(\mathbf{r}|\mathbf{R})$ [-1 for electrons].

2. Usually $\psi_K(\mathbf{r}|\mathbf{R})$ is an eigenfunction of S^2 (spin) and S_z

3. $\psi_K(\mathbf{r}|\mathbf{R})$ **has cusps near nuclei** and when **two electrons get close**

a. Near nuclei, the factors $(-\hbar^2/m_e \, 1/r_k \, \partial/\partial r_k - Z_A e^2/|r_k - R_A|) \, \psi_K(\mathbf{r}|\mathbf{R})$

will blow up unless $\partial/\partial r_k \, \psi = -m_e Z_A e^2 / \hbar^2 \, \psi$ (as $r_k \to R_A$).
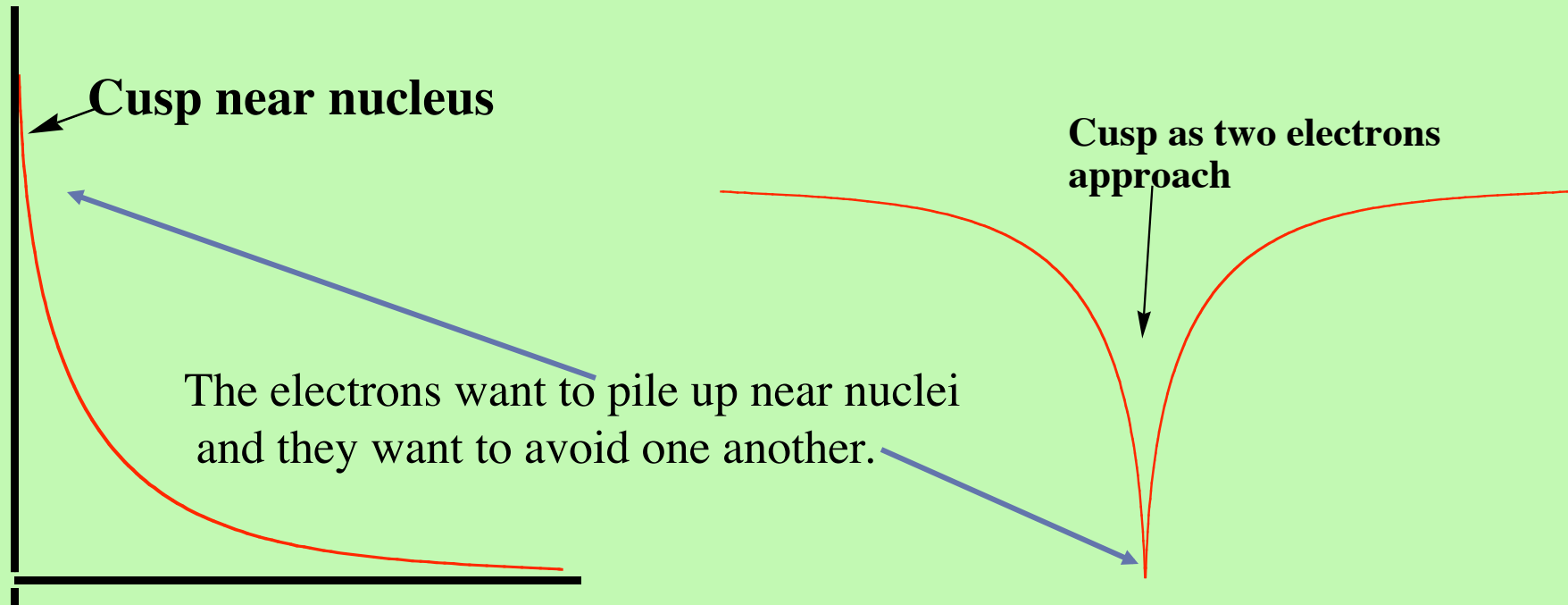
b. As electrons k and l approach, $(-2\hbar^2/m_e \, 1/r_{k,l} \, \partial/\partial r_{k,l} + e^2/r_{k,l}) \, \psi_K(\mathbf{r}|\mathbf{R})$

will blow up unless $\partial/\partial r_{k,l} \, \psi = 1/2 \, m_e e^2 / \hbar^2 \psi$ (as $r_{k,l} \to 0$)

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Cusps

$$\partial/\partial r_k \, \psi = -m_e Z_A e^2/\hbar^2 \, \psi \, (\text{as } r_k \rightarrow R_A) \text{ and}$$

$$\partial/\partial r_{k,l} \, \psi = 1/2 m_e e^2/\hbar^2 \, \psi \, (\text{as } r_{k,l} \rightarrow 0).$$

Cusp near nucleus

Cusp as two electrons approach

The electrons want to pile up near nuclei
and they want to avoid one another.

In the electronic kinetic energy, in addition to the terms like

$$(-\hbar^2/m_e \, 1/r_k \, \partial/\partial r_k - Z_A e^2/r_k) \, \psi_K(\mathbf{r}|\mathbf{R})$$

there are terms involving angular derivatives

$$L^2/2m_e r^2 \, \psi_K(\mathbf{r}|\mathbf{R})$$

$$= -\hbar^2/(2m_e r^2) \, \{(1/\sin\theta)\partial/\partial\theta(\sin\theta\,\partial/\partial\theta + (1/\sin\theta)^2\partial^2/\partial\phi^2\} \, \psi_K(\mathbf{r}|\mathbf{R})$$

These terms will also blow up (for any state with $L > 0$) unless $\psi_K(\mathbf{r}|\mathbf{R})$
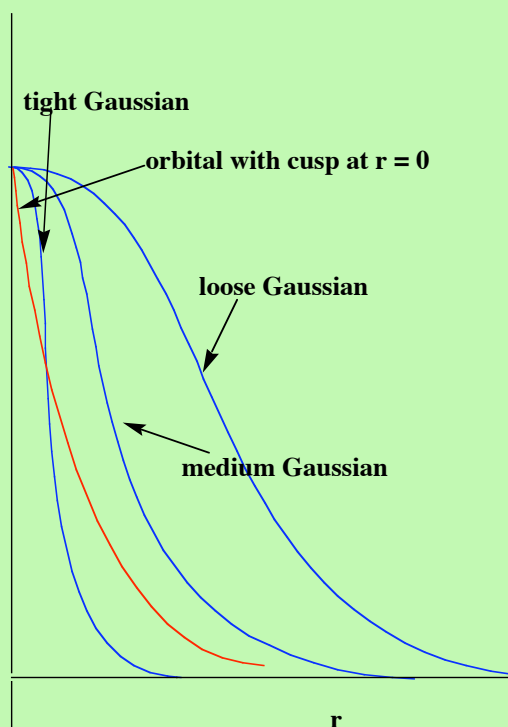
$$\psi_K(\mathbf{r}|\mathbf{R}) \to 0 \text{ (as } r_k \to R_A).$$

So, for $L = 0$ states, one has $\partial/\partial r_k \, \psi = -m_e Z_A e^2/\hbar^2 \, \psi$ (as $r_k \to R_A$),

and for $L > 0$ states, both $\psi_K(\mathbf{r}|\mathbf{R}) \to 0$ (as $r_k \to R_A$) and $\partial/\partial r_k \, \psi = -m_e Z_A e^2/\hbar^2$ ψ (as $r_k \to R_A$) hold, but the latter is "useless" because $\psi_K(\mathbf{r}|\mathbf{R}) \to 0$ anyway.

This is why the cusp condition $\partial/\partial r_k \, \psi = -m_e Z_A e^2/\hbar^2 \, \psi$ (as $r_k \to R_A$) is useful only for ground states.

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This means when we try to approximately solve the electronic SE, we should use "trial functions" that have such cusps. Slater-type orbitals ($exp(-\zeta r_k)$) have cusps at nuclei, but Gaussians ($exp(-\alpha r_k^2)$) do not.

tight Gaussian

orbital with cusp at r = 0

loose Gaussian

medium Gaussian

r

$$d/dr(exp(-\alpha r_k^2) = -2\alpha r_k(exp(-\alpha r_k^2) = 0$$
at $r_k = 0$,

$$d/dr(exp(-\zeta r_k) = -\zeta (exp(-\zeta r_k) = -\zeta$$
at $r_k = 0$.

So, sometimes we try to fit STOs by a linear combination of GTOs, but this can not fix the nuclear cusp problem of GTOs

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It is very difficult to describe the ee cusp (Coulomb hole) accurately. Doing so is important because electrons avoid one another. We call this dynamical correlation. We rarely use functions with e-e cusps, but we should (this is called using explicit e-e correlation).
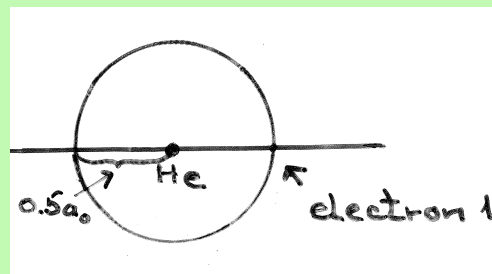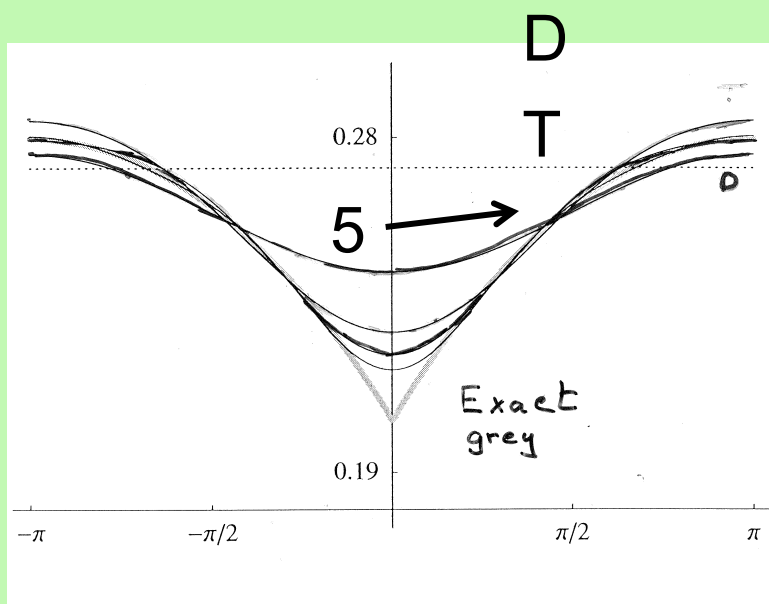
The coulomb hole for He in cc-pVXZ (X=D,T,Q,5) basis sets with one electron fixed at 0.5 a_0

The nuclear cusps $\partial/\partial r_j \psi_K = -m_e Z_A e^2/\hbar^2 \psi_K$ (as $r_j \to R_A$) depend on Z.

Given a wave function $\psi_K(\mathbf{r}|\mathbf{R})$, one can compute the electron density

$$\rho(\mathbf{r}) = N \int \psi^*_K(r, r_2, r_3 ... r_N | R) \psi_K(r, r_2, r_3 ... r_N | R) dr_2 dr_3 ... dr_N$$

Using the cusp condition that ψ_K obeys, one can show that

$\partial/\partial r \rho(\mathbf{r}) = -2m_e Z_A e^2/\hbar^2 \rho(\mathbf{r})$ (as $r \to R_A$) .

So, if we knew the ground-state $\rho(\mathbf{r})$ and could find the locations of its cusps, we would know where the nuclei are located. If we also could measure the "strength" $-2m_e Z e^2/\hbar^2$ of the cusps, we would know

the nuclear charges. If were to integrate $\rho(\mathbf{r})$ over all values of $\mathbf{r}$, we could compute N, the number of electrons.
This observation that the exact ground-state $\rho(\mathbf{r})$ can be used to find $\mathbf{R}$, N, and the $\{Z_K\}$ and thus the Hamiltonian H^0 shows the origins of densityfunctional theory.

Addressing the non-separability problem and the permutational and spin symmetries:

If V_{ee} could be replaced (or approximated) by a one-electron additive potential

$$V_{MF} = \Sigma_{j=1,N} \, V_{MF}(\mathbf{r}_j|R)$$

each of the solutions $\psi_K(\mathbf{r}|\mathbf{R})$ would be a product (an antisymmetrized product called a Slater determinant) of functions of individual electron coordinates (spin-orbitals) $\phi_j(\mathbf{r}|\mathbf{R})$:

$$\psi(r_1, r_2, ..., r_n) =$$

$$\frac{1}{\sqrt{n!}} \sum_P (-1)^{p(P)} P\left\{\varphi_{1\alpha}(1)\varphi_{2\alpha}(2)...\varphi_{n\beta}(n)\right\} = O\left\{\varphi_{1\alpha}\varphi_{2\alpha}...\varphi_{n\beta}\right\}$$

A spinorbital is product of spin-and spatial function

$$\varphi_{k\alpha}(r_j) = \varphi_k(r_j)\alpha_j$$

$$\varphi_{k\beta}(r_j) = \varphi_k(r_j)\beta_j$$

$$\left\langle \varphi_{k\alpha} \middle| \varphi_{k\beta} \right\rangle = \int dv \varphi_k^*(r)\varphi_k(r)\left\langle \alpha \middle| \beta \right\rangle$$

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Is there any optimal way to define $V_{MF} = \Sigma_{j=1,N} V_{MF}(\mathbf{r}_j | R)$?

Does such a definition then lead to equations to determine the optimal spin-orbitals?

Yes! It is the Hartree-Fock definition of V_{MF} .

Before we can find potential V_{MF} and the Hartree-Fock (HF) spin-orbitals $\phi_j(\mathbf{r})(\alpha$ or $\beta)$, we need to review some background about spin and permutational symmetry.

A brief refresher on spin

$$S_Z\alpha = 1/2\hbar\alpha$$

$$S_Z\beta = -1/2\hbar\beta$$

$$<\alpha|\alpha>=1$$

$$<\alpha|\beta>=0$$

$$<\beta|\beta>=1$$

$$S^2\alpha = \hbar^2 1/2(1/2+1)\alpha = 3/4\hbar^2\alpha$$

$$S^2\beta = \hbar^2 1/2(1/2+1)\beta = 3/4\hbar^2\beta$$

Special case of

$$J^2|j,m>= \hbar^2 j(j+1)|j,m>$$

$$S_-\alpha = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)}\beta = \hbar\beta$$

$$S_-\beta = 0$$

Special case of

$$J_\pm|j,m>= \hbar\sqrt{j(j+1)-m(m\pm1)}|j,m\pm1>$$

For acting on a product of spin-orbitals, one uses

$$S_Z = \sum_j S_Z(j) \qquad S_- = \sum_j S_-(j) \qquad S^2 = S_-S_+ + S_Z^2 + \hbar S_Z$$

Examples:

$$S_Z\alpha(1)\alpha(2) = 1/2\hbar\alpha(1)\alpha(2) + 1/2\hbar\alpha(1)\alpha(2) = \hbar\alpha(1)\alpha(2)$$

$$S_-\alpha(1)\alpha(2) = \hbar\beta(1)\alpha(2) + \hbar\alpha(1)\beta(2)$$

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Let's practice forming triplet and singlet spin functions for 2 e's.
We always begin with the highest M_S function because it is "pure".

$$\alpha(1)\alpha(2)$$

$$S_z\alpha(1)\alpha(2) = 1/2\hbar\alpha(1)\alpha(2) + 1/2\hbar\alpha(1)\alpha(2) = \hbar\alpha(1)\alpha(2)$$

So, $M_S = 1$; has to be triplet

$$S_z\beta(1)\beta(2) = -1/2\hbar\beta(1)\beta(2) - 1/2\hbar\beta(1)\beta(2) = -\hbar\beta(1)\beta(2)$$

So, $M_S = -1$; has to be triplet

$$S_-\alpha(1)\alpha(2) = \hbar\beta(1)\alpha(2) + \hbar\alpha(1)\beta(2)$$

So, $|1,0> = \dfrac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

$$= \hbar\sqrt{1(1+1) - 1(1-1)}\,|S = 1, M_S = 0>$$

This is the $M_S = 0$ triplet

How do we get the singlet? It has to have $M_S = 0$ and be orthogonal to the $M_S = 0$ triplet. So, the singlet is

$$|0,0> = \dfrac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

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Slater determinants ($P_{i,j}$) in several notations. First, for two electrons.

$$\psi(r_1,r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_\alpha(r_1) & \varphi_\beta(r_1) \\ \varphi_\alpha(r_2) & \varphi_\beta(r_2) \end{vmatrix}$$

Shorthand

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi(r_1)\alpha(1) & \varphi(r_1)\beta(1) \\ \varphi(r_2)\alpha(2) & \varphi(r_2)\beta(2) \end{vmatrix}$$

$$\psi(r_1,r_2) = \left| \varphi_\alpha \varphi_\beta \right|$$

$$\psi(r_1,r_2) = \frac{1}{\sqrt{2}}\left(\varphi(r_1)\alpha(1)\varphi(r_2)\beta(2) - \varphi(r_1)\beta(1)\varphi(r_2)\alpha(2) \right)$$

Symmetric space; antisymmetric spin (singlet)

$$= \varphi(r_1)\varphi_2(r_2)\frac{1}{\sqrt{2}}\left\{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right\}$$

$$|\phi_1\alpha\phi_2\alpha| = \frac{1}{\sqrt{2}}[\phi_1\alpha(1)\phi_2\alpha(2) - \phi_1\alpha(2)\phi_2\alpha(1)] = \frac{1}{\sqrt{2}}[\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)]\alpha(1)\alpha(2)$$

Antisymmetric space; symmetric spin (triplet)

$$\psi(r_1,r_2) = -\psi(r_2,r_1)$$

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_\alpha(r_1) & \varphi_\beta(r_1) \\ \varphi_\alpha(r_2) & \varphi_\beta(r_2) \end{vmatrix} = -\frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_\alpha(r_2) & \varphi_\beta(r_2) \\ \varphi_\alpha(r_1) & \varphi_\beta(r_1) \end{vmatrix}$$

Notice the $P_{i,j}$ antisymmetry

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More practice with Slater determinants

$$\psi(r_1, r_2, ..., r_n) = \left| \varphi_{1\alpha}, \varphi_{2\alpha} ....., \varphi_{n\beta} \right|$$

Shorthand notation for general case

$$\psi(r_1, r_2, ..., r_n) = \begin{vmatrix} \varphi_{1\alpha}(1) & \varphi_{2\alpha}(1) & \dots & \varphi_{n\beta}(1) \\ \varphi_{1\alpha}(2) & \varphi_{2\alpha}(2) & \cdots & \varphi_{n\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{1\alpha}(n) & \varphi_{2\alpha}(n) & \cdots & \varphi_{n\beta}(n) \end{vmatrix}$$

Odd under interchange of any two rows or columns

The dfn. of the Slater determinant contains a $N^{-1/2}$ normalization.

$$\psi(r_1, r_2, ..., r_n) =$$

$$\frac{1}{\sqrt{n!}} \sum_P (-1)^{p(P)} P \left\{ \varphi_{1\alpha}(1) \varphi_{2\alpha}(2) ... \varphi_{n\beta}(n) \right\} = O \left\{ \varphi_{1\alpha} \varphi_{2\alpha} ... \varphi_{n\beta} \right\}$$

P permutation operator

$(-1)^{p(P)}$ parity ($p(P)$ least number of transpositions that brings the indices back to original order)

$$O = \frac{1}{\sqrt{n!}} \sum_P (-1)^{p(P)} P \quad antisymmetrizer$$

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Example : **Determinant for 3-electron system**

$$O\left\{\varphi_1\,\varphi_2\,\varphi_3\right\} = \frac{1}{\sqrt{6}}\left(1 - \sum_{i,j}P_{ij} + \sum_{i,j,k}P_{ijk}\right)\left\{\varphi_1\,\varphi_2\,\varphi_3\right\}$$

$$= \frac{1}{\sqrt{6}}\left\{\begin{array}{l}\varphi_1(1)\varphi_2(2)\varphi_3(3) - \varphi_2(1)\varphi_1(2)\varphi_3(3)\\ -\varphi_3(1)\varphi_2(2)\varphi_1(3) - \varphi_1(1)\varphi_3(2)\varphi_2(3)\\ +\varphi_2(1)\varphi_3(2)\varphi_1(3) + \varphi_3(1)\varphi_1(2)\varphi_2(3)\end{array}\right\}$$

permutations	1,	P_{12},	P_{13},	P_{23},	P_{231},	P_{312}
transposition*s*	0	1	3	1	2	2
parity	+	–	–	–	+	+

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The good news is that one does not have to deal with most of these complications. Consider two Slater determinants (SD).

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{p^P} P \varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N)$$

$$\psi_B = \frac{1}{\sqrt{N!}} \sum_Q (-1)^{q^Q} Q \varphi'_1(1)\varphi'_2(2)\varphi'_3(3)..\varphi'_N(N)$$

Assume that you have taken t permutations[1] to bring the two SDs into maximal coincidence. Now, consider evaluating the integral

$$\int d1d2d3...dN \psi_A^* [\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)] \psi_B$$

where f(i) is any one-electron operator (e.g., $-Z_A/|\mathbf{r}_j - \mathbf{R}_A|$) and g(i.j) is any two-electron operator (e.g., $1/|\mathbf{r}_j - \mathbf{r}_k|$). This looks like a horrible task ($N! \times (N + N^2) \times N!$ terms).

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1. A factor of $(-1)^t$ will then multiply the final integral I

$$I = \int d1d2d3...dN\psi_A^*[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)]\psi_B$$

$$\psi_A = \frac{1}{\sqrt{N!}}\sum_P (-1)^{p^P} P\varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N) \qquad \psi_B = \frac{1}{\sqrt{N!}}\sum_Q (-1)^{q^Q} Q\varphi'_1(1)\varphi'_2(2)\varphi'_3(3)..\varphi'_N(N)$$

1. The permutation P commutes with the f + g sums, so

$$I = \frac{1}{\sqrt{N!}}\int d\tau \sum_P (-1)^{p^P} \varphi^*_1(1)\varphi^*_2(2)\varphi^*_3(3)..\varphi^*_N(N)[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)]P\psi_B$$

2. $\quad P\psi_B = (-1)^{p^P}\psi_B \quad$ and $\quad \sum_P (-1)^{p^P}(-1)^{p^P} = N! \quad$ so

$$I = \frac{N!}{\sqrt{N!}}\int d\tau \sum_P \varphi^*_1(1)\varphi^*_2(2)\varphi^*_3(3)..\varphi^*_N(N)[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)]\psi_B$$

$$= \int d\tau \varphi^*_1(1)\varphi^*_2(2)\varphi^*_3(3)..\varphi^*_N(N)[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)]\sum_Q (-1)^{q^Q} Q\varphi'_1(1)\varphi'_2(2)\varphi'_3(3)..\varphi'_N(N)$$

Now what?

$$I = \int d\tau \varphi *_1 (1)\varphi *_2 (2)\varphi *_3 (3)..\varphi *_N (N)[\sum_{j=1,N} f(j) + \sum_{j<k=1,N} g(i,j)]\sum_Q (-1)^{q^Q} Q\varphi'_1 (1)\varphi'_2 (2)\varphi'_3 (3)..\varphi'_N (N)$$

Four cases: the Slater-Condon rules – you should memorize.
Recall to multiply the final I by $(-1)^t$

ψ_A and ψ_B differ by three or more spin-orbitals: $I = 0$

ψ_A and ψ_B differ by two spin-orbitals-$\phi_{Ak}\phi_{Al};\phi_{Bk}\phi_{Bl}$

$$I = \int dkdl\varphi *_{Ak} (k)\varphi *_{Al} (l)g(k,l)[\varphi_{Bk}(k)\varphi_{Bl}(l) - \varphi_{Bl}(k)\varphi_{Bk}(l)]$$

ψ_A and ψ_B differ by one spin-orbital-$\phi_{Ak};\phi_{Bk}$

$$I = \sum_{j\in A,B} \int dkdj\varphi *_{Ak} (k)\varphi *_j (j)g(k,j)[\varphi_{Bk}(k)\varphi_j(j) - \varphi_j(k)\varphi_{Bk}(j)]$$

$$+ \int dk\varphi *_{Ak} (k) f(k)\varphi_{Bk}(k)$$

ψ_A and ψ_B are identical

$$I = \sum_{k<j\in A} \int dkdj\varphi *_k (k)\varphi *_j (j)g(k,j)[\varphi_k(k)\varphi_j(j) - \varphi_j(k)\varphi_k(j)]$$

$$+ \sum_{k\in A} \int dk\varphi *_k (k) f(k)\varphi_k(k)$$

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In HF theory, we approximate the true $\psi(\mathbf{r}|\mathbf{R})$ in terms of a single Slater determinant. We then use the variational method to minimize the energy of this determinant with respect to the spin-orbitals appearing in the determinant. Doing so, gives us equations for the optimal spin-orbitals to use in this HF determinant. They are called the HF equations.

A single Slater determinant

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{p^P} P \varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N) = |\varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N)|$$

can be shown to have a density $\rho(\mathbf{r})$ equal to the sum of the densities of the spin-orbitals in the determinant $\rho(r) = \sum_j |\varphi^*_j(r)\varphi_j(r)|$

The fourth of the Slater-Condon rules allows us to write the expectation value of H^0 for a single-determinant wave function

$$\psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^{p^P} P\varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N) = |\varphi_1(1)\varphi_2(2)\varphi_3(3)..\varphi_N(N)|$$

$$< \psi_A^* H^0 \psi_A > = \sum_{k<j\in A} \int dk dj \varphi^*_k(k)\varphi^*_j(j)\frac{1}{r_{k,j}}[\varphi_k(k)\varphi_j(j) - \varphi_j(k)\varphi_k(j)]$$

$$+ \sum_{k\in A} \int dk \varphi^*_k(k)[-1/2\nabla^2(k) - \sum_M \frac{Z_M}{|r_k - R_M|}]\varphi_k(k)$$

$$= \sum_{k\in A} < \varphi^*_k |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r - R_M|}]|\varphi_k >$$

$$+ \sum_{k<j\in A} < \varphi^*_k \varphi^*_j \frac{1}{r_{1,2}}[\varphi_k\varphi_j - \varphi_j\varphi_k] >$$

$$E = \sum_{k \in A} <\varphi *_k |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r - R_M|}]| \varphi_k > \quad + \sum_{k < j \in A} <\varphi *_k \varphi *_j \frac{1}{r_{1,2}} [\varphi_k \varphi_j - \varphi_j \varphi_k] >$$

The integrals appearing here are often written in shorthand as

$$<\varphi *_k |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r - R_M|}]| \varphi_k > = < k | f | k >$$

$$<\varphi *_k \varphi *_j \frac{1}{r_{1,2}} [\varphi_k \varphi_j - \varphi_j \varphi_k] > = < k,j | k,j > - < k,j | j,k > \, (Dirac)$$

$$<\varphi *_k \varphi *_j \frac{1}{r_{1,2}} [\varphi_k \varphi_j - \varphi_j \varphi_k] > = (k,k | j,j) - (k,j | j,k)(Mulliken)$$

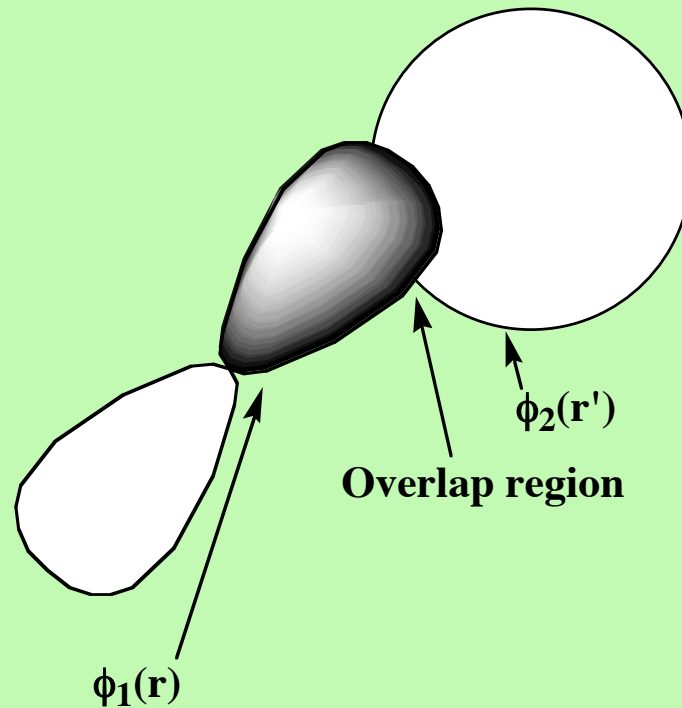When we minimize E keeping the constraints $<\phi_k|\phi_j>=\delta_{k,j}$,
we obtain the Hartree-Fock equations

$$f\phi_k(1) + \sum_{j=1,N} [\int \phi_j^*(2) \frac{1}{r_{1,2}} \phi_j(2) d2\phi_k(1) - \int \phi_j^*(2) \frac{1}{r_{1,2}} \phi_k(2) d2\phi_j(1)] = \varepsilon_k \phi_k(1) = h_{HF}\phi_k(1)$$

$$= f\phi_k(1) + \sum_{j=1,N}[J_j - K_j]\phi_k(1) = f\phi_k(1) + V_{HF}\phi_k(1)$$

Physical meaning of Coulomb and exchange operators and
integrals:

$$J_{1,2} = \int \phi^*_1(r) J_2 \phi_1(r) dr = \int |\phi_1(r)|^2 \, e^2/|r-r'| |\phi_2(r')|^2 \, dr \, dr'$$

$$K_{1,2} = \int \phi^*_1(r) K_2 \phi_1(r) dr = \int \phi_1(r) \, \phi_2(r') \, e^2/|r-r'| \phi_2(r) \, \phi_1(r') dr \, dr'$$

$\phi_2(r')$

Overlap region

$\phi_1(r)$

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What is good about Hartee-Fock ?

It is by making a mean-field model that our (chemists') concepts of orbitals and of electronic configurations (e.g., 1s α1s β 2s α 2s β 2p$_1$ α) arise.

Another good thing about HF orbitals is that their energies ε_K give approximate ionization potentials and electron affinities (**Koopmans' theorem**). IP $\approx$ -$\varepsilon_{occupied}$; EA $\approx$ -$\varepsilon_{unoccupied}$

Koopmans' theorem- what orbital energies mean.

N-electrons' energy

$$E_{HF} = \sum_{k=1,N} <\varphi^*_k |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r-R_M|}]|\varphi_k > \quad + \sum_{k<j=1,N} <\varphi^*_k \varphi^*_j \frac{1}{r_{1,2}}[\varphi_k\varphi_j - \varphi_j\varphi_k] >$$

N+1-electrons' energy

$$E_{HF} = \sum_{k=1,N+1} <\varphi^*_k |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r-R_M|}]|\varphi_k > + \sum_{k<j=1,N+1} <\varphi^*_k \varphi^*_j \frac{1}{r_{1,2}}[\varphi_k\varphi_j - \varphi_j\varphi_k] >$$

Energy difference (neutral minus anion) if spin-orbital m is the N+1st electron's

$$\Delta E = - <\varphi^*_m |[-1/2\nabla^2 - \sum_M \frac{Z_M}{|r-R_M|}]|\varphi_m > \quad - \sum_{k=1,N} <\varphi^*_m \varphi^*_j \frac{1}{r_{1,2}}[\varphi_m\varphi_j - \varphi_j\varphi_m] >$$

But, this is just minus the expression for the HF orbital energy

$$\varepsilon_m = <\phi_m |h_{HF}|\phi_m > = <\phi_{mk}|f|\phi_m > + \sum_{j=1,N} <\phi_m[J_j - K_j]\phi_m >$$

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The sum of the orbital energies is not equal to the HF energy:

$$h_{HF}\phi_k(1) = f\phi_k(1) + \sum_{j=1,N}[J_j - K_j]\phi_k(1) = \varepsilon_k \phi_k$$

So

$$\varepsilon_k = <\phi_k \mid h_{HF} \mid \phi_k> = <\phi_k \mid f \mid \phi_k> + \sum_{j=1,N}<\phi_k[J_j - K_j]\phi_k>$$

$$= <\phi_k \mid f \mid \phi_k> + \sum_{j=1,N}[<k,j \mid k,j> - <k,j \mid j,k>]$$

So

$$\sum_{k=1,N}\varepsilon_k = \sum_{k=1,N}\{<\phi_k \mid f \mid \phi_k> + \sum_{j=1,N}[<k,j \mid k,j> - <k,j \mid j,k>]\}$$

But

$$E_{HF} = \sum_{k=1,N}<\varphi*_k \mid [-1/2\nabla^2 - \sum_M \frac{Z_M}{\mid r - R_M \mid}] \mid \varphi_k> + \sum_{k<j=1,N}<\varphi*_k \varphi*_j \frac{1}{r_{1,2}}[\varphi_k\varphi_j - \varphi_j\varphi_k]>$$

So, the sum of orbital energies double counts the J-K terms. So, we can compute the HF energy by taking

$$E_{HF} = 1/2 \sum_{k=1,N}\varepsilon_k + 1/2 \sum_{k=1,N}<\phi_k \mid f \mid \phi_k>$$

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Orbital energies depend upon which state one is studying. So a π* orbital in the ground state is not the same as a π* in the ππ* state.

$$\varepsilon_k = <\phi_k \mid h_{HF} \mid \phi_k> = <\phi_k \mid f \mid \phi_k> + \sum_{j=1,N} <\phi_k[J_j - K_j]\phi_k>$$

ε_p "feels" 6 J and 3 K interactions
ε_a "feels" 5 J and 2 K interactions

Occupied orbitals feel N-1 others; virtual orbitals feel N others.

p
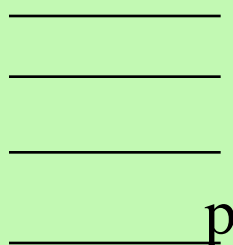
$\downarrow\varepsilon_p$ "feels" 5 J and 2 K interactions
$\uparrow\varepsilon_p$ "feels" 6 J and 3 K interactions
ε_q "feels" 6 J and 3 K interactions
$\uparrow\varepsilon_a$ "feels" 5 J and 2 K interactions
$\uparrow\varepsilon_b$ "feels" 5 J and 2 K interactions
$\downarrow\varepsilon_b$ "feels" 6 J and 3 K interactions

a

p

q

a

b
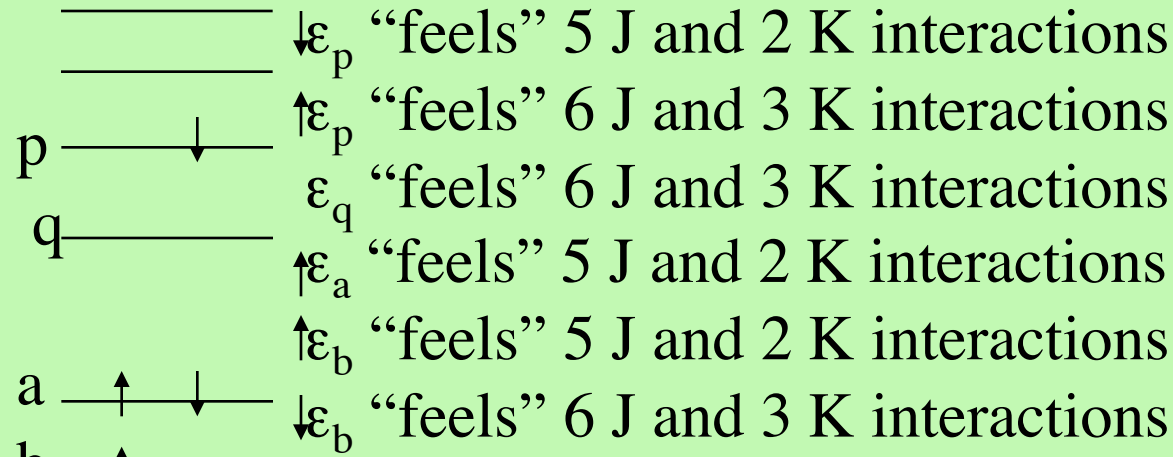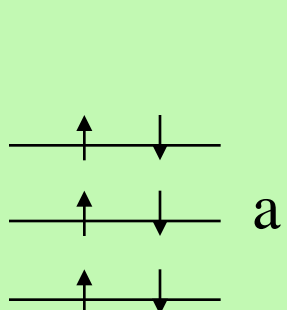
Occupied orbitals feel N-1 others; virtual orbitals feel N others.

This is why occupied orbitals (for the state of interest) relate to IPs and virtual orbitals (for the state of interest) relate to EAs.

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In summary, the true electronic wave functions have $P_{i,j}$ symmetry, nuclear and Coulomb cusps, and are not spin-orbital products or Slater determinants.

However, HF theory attempts to approximate $\psi(\mathbf{r}|\mathbf{R})$ as a single Slater determinant and, in so doing, to obtain a mean-field approximation to $\Sigma_{j<k=1,N} 1/r_{j,k}$ in the form $\quad V_{HF} = \sum_{j=1,N} [J_j - K_j]$

To further progress, we need to study the good and bad of the HF approximation, learn in more detail how the HF equations are solved, and learn how one moves beyond HF to come closer and closer to the correct $\psi(\mathbf{r}|\mathbf{R})$.