Lecture 7 Hartree-Fock Calculations

Basis sets; matrix form of Hartree-Fock equation; solution workflow

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Hartree-Fock results from applying the variational principle to a Slater-determinant wavefunction

• The unknowns are the atomic orbitals, $\phi_{i,\sigma}$

 $\hat{F}^{\sigma}\phi_{i,\sigma}=\phi_{i,\sigma}\epsilon_{i,\sigma}$ Spin-dependent Hartree-Fock equation



- Coupled set of integro-differential equations for each orbital
 - self-consistent solution is needed
 - explicit solution for $\phi_{i,\sigma}(\mathbf{r})$ is not possible

Representation of the orbitals using basis functions leads to a set of algebraic equations

• Each orbital has its own representation

$$\phi_{i,\sigma}({f r}) = \sum \chi_\mu({f r}) C_{\mu,i,\sigma}$$

Point about notation: *i*, *j*, *k*, $l \rightarrow$ orbital function $\mu, \nu, \kappa, \lambda \rightarrow$ basis function

- The basis functions χ_{μ} are specified a priori
 - Their design and selection is a bit of an art
 - Choice affects ease of calculations and accuracy of result
- In this manner, rather than solve for the functions $\phi_{i,\sigma}$, we instead solve for the set of variables $C_{\mu,i,\sigma}$

Any complete basis set can be effective in describing a vector (or function)

- Consider a vector in 2 dimensions
 - Any 2 independent vectors form a complete set



$$\mathbf{r}=a_1oldsymbol{\phi}_1+a_2oldsymbol{\phi}_2$$

apply $\langle \phi_i |$ to both sides

 $\langle \boldsymbol{\phi}_1 | \mathbf{r}
angle = a_1 \langle \boldsymbol{\phi}_1 | \boldsymbol{\phi}_1
angle + a_2 \langle \boldsymbol{\phi}_1 | \boldsymbol{\phi}_2
angle$ $\langle oldsymbol{\phi}_2 | \mathbf{r}
angle = a_1 \langle oldsymbol{\phi}_2 | oldsymbol{\phi}_1
angle + a_2 \langle oldsymbol{\phi}_2 | oldsymbol{\phi}_2
angle$

orthonormal $\left< oldsymbol{\phi}_i \middle| oldsymbol{\phi}_i \right> = \delta_{ij}$

- $a_1 = \langle oldsymbol{\phi}_1 | {f r}
 angle$ $a_2=\langle oldsymbol{\phi}_2 | {f r}
 angle$

When using an incomplete basis, the most effective sets are similar to the target

- Consider a vector in 2 dimensions
 - A 1-vector basis is incomplete, and its choice matters



An infinite set of functions is needed to form a basis set to represent another function

• The Fourier transform is an example of an infinite set of functions providing a new representation of a function $F(k) = \int_{-\infty}^{+\infty} f(x)e^{-2\pi i k x} dx = \langle f | \phi(k) \rangle$

Basis functions indexed by continuous variable k $\phi(x)(k)$

- Electronic structure calculations use a different, finite set of basis functions
 - Use of a finite set introduces another approximation

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When treating functions, the adequacy of the basis set may not be obvious

• Note that all of these basis functions are orthogonal to their target, and would present a bad incomplete set



A natural choice for basis functions starts from the 1-electron atomic orbitals

Orbital

1.0

0.8

0.6

0.4

0.2

• Slater-type orbitals (STO)

 $\chi_{\mu}({f r})=R^{
m STO}_{\mu}(r)Y^m_l(heta,\phi)$

 $R^{
m STO}_{\mu}(r) \propto r^{n-1} e^{-\zeta_{\mu} |{f r}-{f R}_{\mu}|}$ atom center

- Radial component is nodeless
 - Nodes complicate HF calculation
 - STO orbitals are not orthogonal
- Combinations of STO orbitals can mimic true atomic orbitals

Compare to H atomic orbital

$$R_{n,\ell}(r) = r^\ell P_{n,\ell}(r) e^{-(Z/na)r}$$

polynomial of degree n-l-1

- Hydrogen 2s
- STO, n=1, *ζ=*0.95
- STO, n=2, ζ=0.4
- Combination

Gaussian-type orbitals (GTO) have advantages and are most-often used now

$$\chi_{\zeta,l_x,l_y,l_z}(x,y,z) \propto x^{l_x}y^{l_y}z^{l_z}e^{-\zeta(x^2+y^2+z^2)}$$

- Products of Gaussians with different centers are still Gaussians, at a new center
 - 4- or 3-center integrals become 2-center integrals
- Almost always centered at nucleus, but sometimes put elsewhere

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 Center of a bond, or between nonbonded atoms to improve vdW interactions



Gaussians have the wrong shape at the origin. *Contracted sets* are used to mimic STO

- They also decay too fast for $r \rightarrow \infty$
- Several Gaussians added in a fixed way define a new basis function
 Orbital
- These are called contracted basis functions



Inserting basis-set expansion for orbitals in HF equation yields the *Roothaan-Hall* equation

$$\hat{F}^{\sigma}\phi_{i,\sigma}=\phi_{i,\sigma}\epsilon_{i,\sigma}$$
 $\square \longrightarrow$ $F^{\sigma}C^{\sigma}=SC^{\sigma}arepsilon^{\sigma}$

• This is a generalized eigenvalue equation

• F is the Fock matrix

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Coefficient matrix, *C* $\chi_1 \begin{pmatrix} C_{1,1} & C_{1,2} & \cdots \\ C_{2,1} & C_{2,2} & \cdots \\ \vdots & C_{\mu,i} & \cdots \end{pmatrix}$ $\psi_1 & \psi_2 & \cdots & \psi_N$

$$F_{\mu,
u} = \Big\langle \chi_\mu | \hat{F} | \chi_
u \Big
angle = h_{\mu,
u} + \sum_{\kappa,\lambda} [\mu
u|\kappa\lambda] \Big(P^lpha_{\lambda,\kappa} + P^eta_{\lambda,\kappa} \Big) - \sum_{\kappa,\lambda} [\mu\lambda|\kappa
u] P^\sigma_{\lambda,\kappa}$$

ERIs

- P^{σ} is the spin- σ density matrix $P^{\sigma} = C^{\sigma} n^{\sigma} C^{\sigma\dagger} = \sum_{i} n_{i} C_{\mu,i,\sigma} C^{*}_{\nu,i,\sigma}$
- *S* is the overlap matrix, $S_{\mu,\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$

The Roothaan-Hall equation FC=SCε can be solved by finding the zeros of a determinant

$iggle iggle \chi_1 \hat{F} \chi_1 iggree$ $iggle \chi_2 \hat{F} \chi_1 iggree$	$igg \langle \chi_1 \hat{F} \chi_2 ig angle \ \left\langle \chi_2 \hat{F} \chi_2 ight angle$	F	$egin{array}{c} \left\langle \chi_1 \hat{F} \chi_N ight angle \ \left\langle \chi_2 \hat{F} \chi_N ight angle \end{array} ight angle$	$egin{array}{c} C_{1,1} \ C_{2,1} \end{array}$	$C_{1,2} \ C_{2,2}$	C	$egin{array}{cc} C_{1,N} \ C_{2,N} \end{array}$		$egin{array}{l} \langle \chi_1 \chi_1 angle \ \langle \chi_2 \chi_1 angle \end{array}$	$egin{aligned} &\langle \chi_1 \chi_2 angle \ &\langle \chi_2 \chi_2 angle \end{aligned}$	S	$egin{array}{c} \langle \chi_1 \chi_N angle \ \langle \chi_2 \chi_N angle \end{array} \$	$C_{1,1} \ C_{2,1}$	$egin{array}{ccc} C_{1,2} \ C_{2,2} \end{array}$	\mathbf{C}	$\begin{bmatrix} C_{1,N} \\ C_{2,N} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ 0 \end{bmatrix}$	$0 \ arepsilon_2$	3	0 :
:	:	$\left\langle \chi_{\mu} \hat{F} \chi_{ u} ight angle$		÷	÷	$C_{\mu,i}$:	=	:	÷	$\langle \chi_{\mu} \chi_{ u} angle$	÷	÷	÷	$C_{\mu,i}$: :	۰.	·	0
$\left< \chi_N \hat{F} \chi_1 ight>$	$\left\langle \chi_{N} \hat{F} \chi_{2} ight angle$		$\left< \chi_N \hat{F} \chi_N ight> ight floor$	$C_{N,1}$	$C_{N,2}$	•••	$C_{N,N}$		$\langle \chi_N \chi_1 angle$	$\langle \chi_N \chi_2 angle$	•••	$\langle \chi_N \chi_N angle$	$C_{N,1}$	$C_{N,2}$	•••	$C_{N,N} \rfloor \lfloor 0$		0	ε_N

One column of C with one ε represents all

$$\begin{bmatrix} F_{1,1} & F_{1,2} & \dots & F_{1,N} \\ F_{2,1} & F_{2,2} & \dots & F_{2,N} \\ \vdots & \vdots & F_{\mu,\nu} & \vdots \\ F_{N,1} & F_{N,2} & \dots & F_{N,N} \end{bmatrix} \begin{bmatrix} C_{1,i} \\ C_{2,i} \\ \vdots \\ C_{N,i} \end{bmatrix} = \begin{bmatrix} 1 & S_{1,2} & \dots & S_{1,N} \\ S_{2,1} & 1 & \dots & S_{2,N} \\ \vdots & \vdots & S_{\mu,\nu} & \vdots \\ S_{N,1} & S_{N,2} & \dots & 1 \end{bmatrix} \begin{bmatrix} C_{1,i} \\ C_{2,i} \\ \vdots \\ C_{N,i} \end{bmatrix} \boldsymbol{\varepsilon}_{i}$$

Gather terms to left-hand side

 $\begin{bmatrix} F_{1,1} - \varepsilon_i & F_{1,2} - S_{1,2}\varepsilon_i & \dots & F_{1,N} - S_{1,N}\varepsilon_i \\ F_{2,1} - S_{2,1}\varepsilon_i & F_{2,2} - \varepsilon_i & \dots & F_{2,N} - S_{2,N}\varepsilon_i \\ \vdots & \vdots & F_{\mu,\nu} - S_{\mu,\nu}\varepsilon_i & \vdots \\ F_{N,1} - S_{N,1}\varepsilon_i & F_{N,2} - S_{N,2}\varepsilon_i & \dots & F_{N,N} - \varepsilon \end{bmatrix} \begin{bmatrix} C_{1,i} \\ C_{2,i} \\ \vdots \\ C_{N,i} \end{bmatrix} = 0$ 12 $\begin{bmatrix} F_{1,1} - \varepsilon_i & F_{1,2} - S_{1,2}\varepsilon_i & \dots & F_{2,N} - \varepsilon_i \\ \vdots \\ C_{N,i} \end{bmatrix} = 0$

Nontrivial solution requires determinant of this matrix is zero

Presents an N^{th} -order polynomial in ε , solution yields the *N* energies

For each ε_i , basis coefficients are found by setting $C_{N,i} = 1$ and solving *N*-1 equations, then normalizing

N basis functions yields up to *N* orbitals

Procedure to solve for the optimal orbitals in Hartree-Fock self-consistent field treatment

 $P^{\sigma}=C^{\sigma}n^{\sigma}C^{\sigma\dagger}=\sum_{i}n_{i}C_{\mu,i,\sigma}C^{*}_{
u,i,\sigma}$

 $F_{\mu,
u} = h_{\mu,
u} + \sum_{\kappa,\lambda} [\mu
u|\kappa\lambda] \Big(P^lpha_{\lambda,\kappa} + P^eta_{\lambda,\kappa} \Big) - \sum [\mu\lambda|\kappa
u] P^\sigma_{\lambda,\kappa}$

- Specify molecule and basis: $\{\mathbf{R}_A\}, \{Z_A\}, \{\chi_\mu\}, N$
- Calculate integrals: $S_{\mu,\nu}, h_{\mu,\nu}, [\mu\nu|\kappa\lambda]$
- Guess coefficients, C_r , compute P and F
- Solve for *C* from HF matrix equation $F^{\sigma}C^{\sigma} = SC^{\sigma}\varepsilon^{\sigma}$
- Compare to previous iteration, repeat to convergence
- Energy is given by

$$E = \sum_{\mu,
u,\sigma} h_{\mu,
u} P^{\sigma}_{
u,\mu} + rac{1}{2} \sum_{\mu,
u,\sigma} \sum_{\kappa,\lambda} \Big[[\mu
u \mid \kappa\lambda] P^{\sigma}_{
u,\mu} \Big(P^{lpha}_{
u,\kappa} + P^{eta}_{\lambda,\kappa} \Big) - [\mu\lambda \mid \kappa
u] P^{\sigma}_{
u,\mu} P^{\sigma}_{\lambda,\kappa} \Big]$$

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Suggested Reading/Viewing

- Autschbach Secs. 9.2, 9.3, 9.4, 9.5
- <u>TMP Chem</u>, Lectures 4.23, 4.24, 4.25, 4.26, 4.27