Lecture 6 Calculating Energies

Spin-dependent Hartree-Fock equation; calculating Coulomb and exchange integrals

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We developed Hartree-Fock theory in terms of spin-orbitals

- $\hat{F} arphi_i = arphi_i arepsilon_i$ Hartree-Fock equation
- $\hat{F} = \hat{h} + \hat{C} \hat{X}$ Fock operator

$$egin{aligned} \hat{C}oldsymbol{arphi}_{i}(au_{1}) =& \sum_{j}\intrac{1}{r_{12}}oldsymbol{arphi}_{j}^{*}(au_{2})oldsymbol{arphi}_{j}(au_{2})oldsymbol{arphi}_{i}(au_{1})d au_{2} \ \hat{X}oldsymbol{arphi}_{i}(au_{1}) =& \sum_{j}\intrac{1}{r_{12}}oldsymbol{arphi}_{j}(au_{1})oldsymbol{arphi}_{j}^{*}(au_{2})oldsymbol{arphi}_{i}(au_{2})d au_{2} \end{aligned}$$

$$\langle E
angle = \sum_i \langle arphi_i | \hat{h} | arphi_i
angle + rac{1}{2} \sum_i \langle arphi_i | \hat{C} - \hat{X} | arphi_i
angle$$

Coulomb operator

Exchange operator

Expectation energy

Hartree-Fock can instead be developed using spatial orbitals, with spin handled explicitly

• The spatial orbitals may be different for spin states α and β

 $arphi_i({f r},s)=\phi_{i,\sigma}({f r})\sigma(s)$

 $egin{array}{lll} \phi_{i,lpha}({f r}), \ i=1\dots,N_lpha \ \phi_{i,eta}({f r}), \ i=1\dots,N_eta \end{array}$

 $\alpha,\,\beta$ super/subscripts simply indicate which spatial-orbital set is used

- Open-shell systems, different spatial orbitals → *spin-unrestricted* Closed-shell systems, same spatial orbitals → *spin-restricted*
- Spatial orbitals from different sets not necessarily orthogonal
 - But spin-orbitals will be, because of different spins

We end up with coupled Hartree-Fock formulas for each spin state

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

$${\hat F}^{\sigma}={\hat h}+{\hat J}^{lpha}+{\hat J}^{eta}-{\hat K}^{\sigma}$$
 Spin-dependent Fock operator

$$\widehat{J}^{\sigma}\phi_{i, au}(oldsymbol{r}_1) = \sum_j \int \phi_{i, au}(oldsymbol{r}_1) rac{1}{r_{1,2}} \phi^*_{j,\sigma}(oldsymbol{r}_2) \phi_{j,\sigma}(oldsymbol{r}_2) d\mathbf{r}_2$$

$$\widehat{K}^{\sigma}\phi_{i, au}(oldsymbol{r}_1) = \delta_{\sigma, au}\sum_j \int \phi_{j,\sigma}(oldsymbol{r}_1) rac{1}{r_{1,2}} \phi^*_{j,\sigma}(oldsymbol{r}_2) \phi_{i, au}(oldsymbol{r}_2) d\mathbf{r}_2$$

Results from spin-variable sum

Expectation energy

$$E^{ ext{HF}} = \sum_{\sigma=lpha,eta}\sum_{i} \left\langle \phi_{i,\sigma} | \hat{h} | \phi_{i,\sigma}
ight
angle + rac{1}{2}\sum_{\sigma=lpha,eta}\sum_{i} \left(\left\langle \left\langle \phi_{i,\sigma} \Big| \widehat{J}^{lpha} \Big| \phi_{i,\sigma}
ight
angle + \left\langle \left\langle \phi_{i,\sigma} \Big| \widehat{J}^{eta} \Big| \phi_{i,\sigma}
ight
angle - \left\langle \left\langle \phi_{i,\sigma} \Big| \widehat{K}^{\sigma} \Big| \phi_{i,\sigma}
ight
angle
ight
angle
ight
angle$$

 $\sigma, au = lpha \ ext{ or } \ eta$

Coulomb

operator

Exchange

operator

 $J_{i,i}$ \leftarrow Electron repulsion integrals $\rightarrow K_{i,i}$

The electron-repulsion integrals are defined in terms of the spatial orbitals

$$egin{split} J_{i,j} &= \int \phi_i^*(m{r}_1) \phi_i(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_j(m{r}_2) d \mathbf{r}_1 d \mathbf{r}_2 \ K_{i,j} &= \int \phi_i^*(m{r}_1) \phi_j(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_i(m{r}_2) d \mathbf{r}_1 d \mathbf{r}_2 \end{split}$$

• Compare to Mulliken notation for the spin-orbital ERIs

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Let's do a calculation of the electronrepulsion integrals

• Use the *Slater-type orbitals* (STO) as a basis

$$\phi_{n,l,m}(r, heta,\phi)\equiv rac{1}{\sqrt{(2n)!}}(2\zeta)^{n+rac{1}{2}}r^{n-1}e^{-\zeta r}Y_l^m(heta,\phi)$$

- Compute the integrals $J_{i,i}, K_{i,i}$
- Use one center for both orbitals
- Compare to literature for some set of orbitals

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Atoms	Orbital ^a	Present value (a.u)	From literature (a.u.)	Approx. time (sec)	
Li	(2s2s 2s2s)	0-289615078125	0-289615078125*	3	
н	(1s1s 1s1s)	0.554843750000	0.554843750000	1	
F	$(2p_z 2p_z 2p_z 2p_z)$	$0.241301953125 \times 10^{1}$	$0.241301953125 \times 10^{16}$	3	
Be	(1s1s 1s1s)	$0.386647500000 \times 10^{12}$	0-386647500000 × 101°	1	
Na	(1s1s 1s1s)	$0.954725000000 \times 10^{1}$	$0.954725000000 \times 10^{16}$	1	
Н	(1s1s 1s1s)	0.487687500000	0·487687500000 ^b	1	
F	(1s1s 1s1s)	$0.494868750000 \times 10^{1}$	0.494868750000 × 101b	1	
Sc	(1s1s 1s1s)	$0.108062500000 \times 10^{2}$	0.108062500000 × 10 ^{2b}	1	
Н	(1s1s 1s1s)	0.62500000000	0.62500000000°	1	1 Kumar A &
F	$(2p_2 2p_2 2p_2 2p_3)$	0.101765625000 × 101	1.01766°	3	Mishra D C
F	(1s2s 2s1s)	0.146328213305	0·14633°	1	Misira, P. C.
F	$(2p_2p_1)(2p_2p_2)$	0.054843750000	0.05484	3	Evaluation of one-
F	$(2s2p_z 2s2p_z)$	0.208767361111	0·20877	3	centre electron
^a x con ^b From $a_{12s} = 0.7$ $a_{1s} = 15$	aponent corresponds (Yasui and Saika 19 9722 (in LiH), ξ_{Be} (2756 (in NaH), $\xi_{H_{13}}$.	to $m_i = 1$ while z component 182) using the following ξ value $m_i = 6\cdot18636$ (in BeF ⁺), $\xi_{H_{1,i}}$ $= 0\cdot7803$ (in NaH), $\xi_{Se_{1,i}} = 17\cdot2$	corresponds to $m_l = 0$. 108. 108. 108. 10. 10. 10. 10. 10. 10. 10. 10	165 (in BeF ⁺) F).	 interaction integrals over slater type atomic orbitals. <i>Pramana</i> 29, 385–390 (1987).

Table 1. One-centre repulsion integrals.

Here are the formulas

$$\phi_{n,l,m}(r, heta,\phi)\equiv rac{1}{\sqrt{(2n)!}}(2\zeta)^{n+rac{1}{2}}r^{n-1}e^{-\zeta r}Y_l^m(heta,\phi)$$

$$egin{split} J_{i,j} &= \int \phi_i^*(m{r}_1) \phi_i(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_j(m{r}_2) dm{r}_1 dm{r}_2 \ K_{i,j} &= \int \phi_i^*(m{r}_1) \phi_j(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_i(m{r}_2) dm{r}_1 dm{r}_2 \end{split}$$

Atoms	Orbital ^a	Present value (a.u)	From literature (a.u.)	Approx. time (sec)
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н	(1s1s 1s1s)	0.554843750000	0.554843750000*	1
F	$(2p_2 2p_2 2p_2 2p_2)$	$0.241301953125 \times 10^{12}$	0-241301953125 × 101b	3
Be	(1s1s 1s1s)	$0.386647500000 \times 10^{1}$	0.386647500000 × 1016	1
Na	(1s1s 1s1s)	$0.954725000000 \times 10^{1}$	$0.954725000000 \times 10^{1^{b}}$	1
Н	(1s1s 1s1s)	0.487687500000	0.487687500000	1
F	(1s1s 1s1s)	$0.494868750000 \times 10^{1}$	0.494868750000 × 101b	1
Sc	(1s1s 1s1s)	$0.108062500000 \times 10^{2}$	$0.108062500000 \times 10^{2^{b}}$	1
н	(1s1s 1s1s)	0.62500000000	0.62500000000°	1
F	$(2p_2p_2)(2p_22p_3)$	0.101765625000 × 101	1·01766°	3
F	(1s2s 2s1s)	0.146328213305	0·14633°	1
F	$(2p_2p_1)(2p_2p_2)$	0.054843750000	0.05484	3
F	$(2s2p_{2} 2s2p_{2})$	0.208767361111	0·20877°	3

^a x component corresponds to $m_l = 1$ while z component corresponds to $m_l = 0$.

^b From (Yasui and Saika 1982) using the following ξ values.

T-11-1 Origination models

 $\begin{aligned} \xi_{L_{22}} = 0.79722 \quad (\text{in LiH}), \quad \xi_{Be_{12}} = 6\cdot18636 \quad (\text{in BeF}^+), \quad \xi_{H_{13}} = 0\cdot88775 \quad (\text{in LiH}), \quad \xi_{F_{22}} = 6\cdot165 \quad (\text{in BeF}^+), \\ \xi_{Na_{13}} = 15\cdot2756 \quad (\text{in NaH}), \quad \xi_{H_{13}} = 0\cdot7803 \quad (\text{in NaH}), \quad \xi_{Se_{13}} = 17\cdot29 \quad (\text{in ScF}), \quad \xi_{F_{13}} = 7\cdot9179 \quad (\text{in ScF}). \\ \epsilon^{*} \text{From (Pople and Beveridge 1970) using } \quad \xi_{H_{13}} = 1\cdot0, \quad \xi_{F_{22}} = 2\cdot6, \quad \xi_{F_{23}} = 2\cdot6, \quad \xi_{F_{13}} = 8\cdot7 \quad (\text{in HF}). \end{aligned}$

Here are some hints

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$$\phi_{n,l,m}(r, heta,\phi)\equiv rac{1}{\sqrt{(2n)!}}(2\zeta)^{n+rac{1}{2}}r^{n-1}e^{-\zeta r}Y_l^m(heta,\phi)$$

$$egin{split} J_{i,j} &= \int \phi_i^*(m{r}_1) \phi_i(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_j(m{r}_2) dm{r}_1 dm{r}_2 \ K_{i,j} &= \int \phi_i^*(m{r}_1) \phi_j(m{r}_1) rac{1}{r_{1,2}} \phi_j^*(m{r}_2) \phi_i(m{r}_2) dm{r}_1 dm{r}_2 \end{split}$$

- Use spherical coordinates $r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2(\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) + \cos\theta_1\cos\theta_2)$
- Use NIntegrate, with Method -> "MonteCarlo"

Suggested Reading/Viewing

- Autschbach Secs. 8.3., 8.4, 8.5
- <u>TMP Chem</u>, Lectures 4.22