

Lecture 5

Hartree-Fock Theory

Spin; variation principle; Coulomb and exchange operators;
Hartree-Fock theory; an in-class exercise

Prof. David A. Kofke

CE 500 – Modeling Potential-Energy Surfaces

Department of Chemical & Biological Engineering

University at Buffalo

This would be a good time to outline what we've learned so far

- Time-independent Schrödinger equation governs the behavior of atoms and molecules: $\hat{H}\psi = E\psi$ $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r)$
- Our aim is to quantify the PES
 - expectation energy as a function of nuclear positions: $\langle E \rangle(Q^{(M)})$
- Pauli principle requires antisymmetric ψ : $\psi(\tau_1, \tau_2) = -\psi(\tau_2, \tau_1)$
 - Slater determinant is one way to do this
- Energy expectation for Slater determinant is a sum over orbitals of 1- and 2-electron (and NN) terms

Electron spin is a 4th quantity that enters as a wavefunction parameter and state

- Wavefunction parameter, $\tau = (x, y, z, s) = (\mathbf{r}, s)$
 - Electron spin is discrete and has two possible values, $\pm \frac{1}{2}$
 - Physically represents an angular-momentum projection, but (non-relativistic, no magnetic field) Hamiltonian does not depend upon it
- Wavefunction state
 - Full wavefunction comprises coordinate and spin components
 - Spin quantum number is labeled $m_s = \pm \frac{1}{2}$
 - Spin quantum states are labeled α and β
 - Most important in connection to the Pauli principle

Take care to distinguish between spin parameter and spin state

- Spin parameter $s = \pm 1/2$ (or \uparrow, \downarrow) is akin to spatial coordinate \mathbf{r}
- Full electron state combines spatial and spin components

$$\varphi(\tau) = \phi(\mathbf{r})\sigma(s) \quad \text{where } \sigma = \alpha \text{ or } \beta$$

- $\alpha(+1/2) = 1; \alpha(-1/2) = 0; \beta(+1/2) = 0; \beta(-1/2) = 1$
- φ is a “spin orbital”

Separation of orbital into product of spatial and spin wavefunctions is an excellent approximation

- Bracket includes sum over spins if spin orbitals are averaged

$$\langle \varphi_i | \varphi_j \rangle = \sum_{s=\pm 1/2} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \sigma_i(s) \sigma_j(s) = \langle \phi_i | \phi_j \rangle \delta_{\sigma_i \sigma_j}$$

- Wavefunctions are orthogonal if spin states are different

For a $2n$ -electron system: n spatial orbitals, each with 2 spin states, provides a full set of orbitals

Introduce spin

```
aβ[x_] := MatchQ[x, α | β]
Naβ[x_] := ! aβ[x]
BraCKet[{f_? (Naβ)[x_] q_}, {A_[x_], {g_? (Naβ)[x_] r_}}] :=
  BraCKet[{f[x]}, A[x], {g[x]}] × BraCKet[{q}, {r}]
BraCKet[{f_? (Naβ)[x_] i_? (Naβ)[y_] q_}, {A_[x_], y_}, {g_? (Naβ)[x_] h_? (Naβ)[y_] r_}] :=
  BraCKet[{f[x] × i[y]}, A[x, y], {g[x] × h[y]}] × BraCKet[{q}, {r}]
```

Add to MyBraKet.nb

Slater determinant

```
[1598]:= Clear[ψ, M]
nM = 2; (* number of electrons; this should be even,
to ensure it equals the number of spin-orbitals *)
tauList = Range[nM]
M =
Transpose[
Flatten[Table[φ[i][tauList[[j]]] σ[tauList[[j]]],
{σ, {α, β}}, {i, nM/2}, {j, nM}], 1]];
MatrixForm@M (* Just to see what M looks like *)
ψ =  $\frac{1}{\sqrt{nM}}$  Det[M] // Expand
BraKet[ψ, ψ] // . orthonormalRule
```

```
it[1600]=
Spin-orbital #1      #2
↓                         ↓

$$\begin{pmatrix} \alpha[1] \phi_1[1] & \beta[1] \phi_1[1] \\ \alpha[2] \phi_1[2] & \beta[2] \phi_1[2] \end{pmatrix}$$
   electron #1

$$\begin{pmatrix} \alpha[1] \phi_1[1] & \alpha[1] \phi_2[1] & \beta[1] \phi_1[1] & \beta[1] \phi_2[1] \\ \alpha[2] \phi_1[2] & \alpha[2] \phi_2[2] & \beta[2] \phi_1[2] & \beta[2] \phi_2[2] \\ \alpha[3] \phi_1[3] & \alpha[3] \phi_2[3] & \beta[3] \phi_1[3] & \beta[3] \phi_2[3] \\ \alpha[4] \phi_1[4] & \alpha[4] \phi_2[4] & \beta[4] \phi_1[4] & \beta[4] \phi_2[4] \end{pmatrix}$$
 #2
```

```
it[1603]=

$$\Psi = \frac{\alpha[2] \times \beta[1] \phi_1[1] \phi_1[2]}{\sqrt{2}} + \frac{\alpha[1] \times \beta[2] \phi_1[1] \phi_1[2]}{\sqrt{2}}$$

```

1 ← normalized

Energy expectation

```
[1605]:= Φ[tau_List] :=
With[{n = Length[tau]},  $\frac{1}{\sqrt{n!}}$  Det@Transpose@Flatten[Table[φ[i][tau[[j]]] σ[tau[[j]]], {σ, {α, β}}, {i, nM/2}, {j, nM}], 1]]
```

1-electron contribution

```
nM = 4; 4 electrons
tauList = Range[nM]
M =
Transpose@Flatten[Table[φ[i][tauList[[j]]] σ[tauList[[j]]], {σ, {α, β}}, {i, nM/2}, {j, nM}], 1];
MatrixForm@M (* Just to see what M looks like *)
ψ = Φ[tauList];
BraKet[ψ, ψ] // . orthonormalRule
(* do just one term in Hamiltonian *)
BraKet[ψ, h[1], {ψ}];
//. orthonormalRule
//. noDummiesRule // Simplify
```

{1, 2, 3, 4}

$$\begin{pmatrix} \alpha[1] \phi_1[1] & \alpha[1] \phi_2[1] & \beta[1] \phi_1[1] & \beta[1] \phi_2[1] \\ \alpha[2] \phi_1[2] & \alpha[2] \phi_2[2] & \beta[2] \phi_1[2] & \beta[2] \phi_2[2] \\ \alpha[3] \phi_1[3] & \alpha[3] \phi_2[3] & \beta[3] \phi_1[3] & \beta[3] \phi_2[3] \\ \alpha[4] \phi_1[4] & \alpha[4] \phi_2[4] & \beta[4] \phi_1[4] & \beta[4] \phi_2[4] \end{pmatrix}$$

1

$$\frac{1}{24} (12 \langle \phi_1[1] | h[1] | \phi_1[1] \rangle + 12 \langle \phi_2[1] | h[1] | \phi_2[1] \rangle)$$

$$\frac{1}{2} (\langle \phi_1 | h | \phi_1 \rangle + \langle \phi_2 | h | \phi_2 \rangle)$$

2-electron contribution

```
nM = 4;
tauList = Range[nM];
(* do just one term in Hamiltonian *)
BraKet[{Φ[tauList]},  $\frac{1}{r}[1, 2], \{Φ[tauList]\}]$ ;
//. orthonormalRule // Simplify
//. mullikenFormRule
```

$$\frac{1}{6} \left(\langle \phi_1[1] \phi_1[2] | \frac{1}{r}[1, 2] | \phi_1[1] \phi_1[2] \rangle + 2 \langle \phi_1[2] \phi_2[1] | \frac{1}{r}[1, 2] | \phi_1[2] \phi_2[1] \rangle - \langle \phi_1[2] \phi_2[1] | \frac{1}{r}[1, 2] | \phi_1[1] \phi_2[2] \rangle - \langle \phi_1[1] \phi_2[2] | \frac{1}{r}[1, 2] | \phi_1[2] \phi_2[1] \rangle + 2 \langle \phi_1[1] \phi_2[2] | \frac{1}{r}[1, 2] | \phi_1[1] \phi_2[2] \rangle + \langle \phi_2[1] \phi_2[2] | \frac{1}{r}[1, 2] | \phi_2[1] \phi_2[2] \rangle \right)$$

$$\frac{1}{6} ([11|11] + 4 [11|22] - 2 [12|21] + [22|22])$$

Considering spin state, up to two electrons can occupy the same spatial orbital

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18					
1	IA 1s ²	II A 2s ²	III A 3s ²	IV A 1s ² 2s ² 3s ²	V A 1s ² 2s ² 3s ² 4s ²	VIA 1s ² 2s ² 3s ² 3p ⁶	VIIA 1s ² 2s ² 3s ² 3p ⁵										VIII A 1s ²						
2				1 2 3 4	5d ¹ 6 7 8 9 10		2p ⁶		1 2 3p ⁴ 4 5 6														
3					4d ² 5 6 7 8 9	5d ¹ 6 7 8 9 10		3p ⁶		1 2 3p ⁴ 4 5 6													
4						4d ³ 5 6 7 8 9	5d ² 6 7 8 9 10		4p ⁶		1 2 3p ⁴ 4 5 6												
5							4d ⁵ 5 6 7 8 9	5d ³ 6 7 8 9 10		5p ⁶		1 2 3p ⁴ 4 5 6											
6								4d ⁸ 5 6 7 8 9	5d ⁴ 6 7 8 9 10		6p ⁶		1 2 3p ⁴ 4 5 6										
7									4d ¹⁰ 5 6 7 8 9	5d ⁵ 6 7 8 9 10		7p ⁶		1 2 3p ⁴ 4 5 6									
										4f ⁷ 5 6 7 8 9 10	5d ⁶ 6 7 8 9 10		8p ⁶		1 2 3p ⁴ 4 5 6								
											6d ¹⁰ 7 8 9 10	7d ⁵ 8 9 10		9p ⁶		1 2 3p ⁴ 4 5 6							
												8d ¹⁰ 9 10	9d ⁵ 10		10p ⁶		1 2 3p ⁴ 4 5 6						
													10d ¹⁰ 11 12	11d ⁵ 12		12p ⁶		1 2 3p ⁴ 4 5 6					
														11d ¹⁰ 12	12d ⁵ 13		13p ⁶		1 2 3p ⁴ 4 5 6				
															12d ¹⁰ 13	13d ⁵ 14		14p ⁶		1 2 3p ⁴ 4 5 6			

Energy expectation for Slater wavefunction is sum of 1-e terms and electron repulsion integrals

$$\langle E \rangle = \left\langle \Phi \left| \sum_i \hat{h}_i \right| \Phi \right\rangle + \left\langle \Phi \left| \sum_{i < j} \hat{h}_{i,j} \right| \Phi \right\rangle$$

- ERIs include Coulomb and exchange

$$\langle E \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji])$$

Mulliken form

Spin orbitals

$\tau = (\mathbf{r}, s)$

$$\sum_{i,j} [ii|jj] = \sum_i \sum_j \int \varphi_i^*(1) \varphi_i(1) \frac{1}{|\mathbf{r}_{12}|} \varphi_j^*(2) \varphi_j(2) d\tau_2 d\tau_1 \text{ Coulomb}$$

$$[12|21] = \int \phi_1^*(\mathbf{r}_1) \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \text{ Exchange}$$

- Total energy obtained by adding NN Coulomb sum V_{NN}^{Coul}

The *variational principle* provides a powerful tool for estimating the wavefunction

$$\hat{H}(\tau)\psi(\tau) = \psi(\tau)E$$

- The lowest eigenvalue of the Hamiltonian defines the *ground-state energy*, E_0
- The variational principle says that the expectation value of E for *any* normalized wavefunction f is bounded from below by E_0 :

$$\langle E \rangle = \langle f | \hat{H} | f \rangle \geq E_0$$

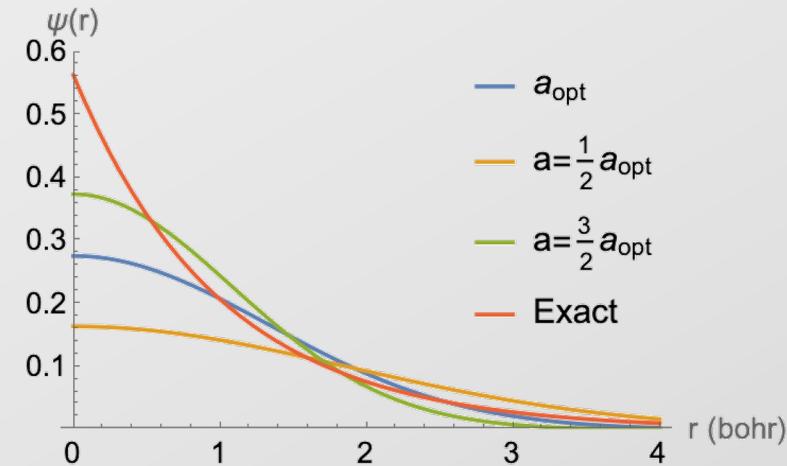
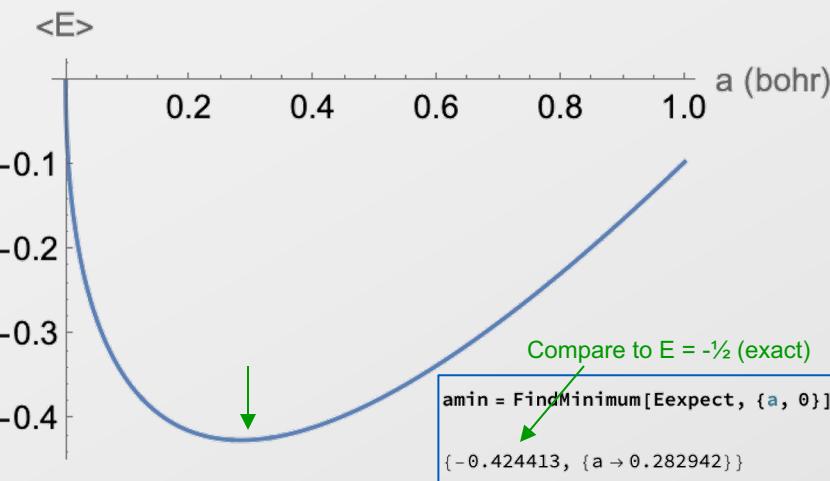
equality achieved when $f \equiv \psi$

- We can guide estimation of the true wavefunction ψ by using any degrees of freedom in f to minimize $\langle E \rangle$

An example of the variational principle, use a Gaussian to estimate the 1s hydrogen orbital

- Normalized wavefunction estimate: $f(r, \theta, \phi; a) = \left(\frac{2a}{\pi}\right)^{3/4} e^{-ar^2}$
- Hamiltonian: $\hat{H}f = -\frac{1}{2}\nabla^2 f - \frac{1}{r}f$
atomic units
- Expectation energy: $\langle E \rangle = \frac{3}{2}a - \left(\frac{8}{\pi}\right)^{\frac{1}{2}}\sqrt{a}$

$$\text{Expect} = \langle f | \hat{H} | f \rangle \approx \frac{3a}{2} - 2\sqrt{a} \sqrt{\frac{2}{\pi}}$$



Another demonstration of the variational principle arose in HW1 application to PiaB

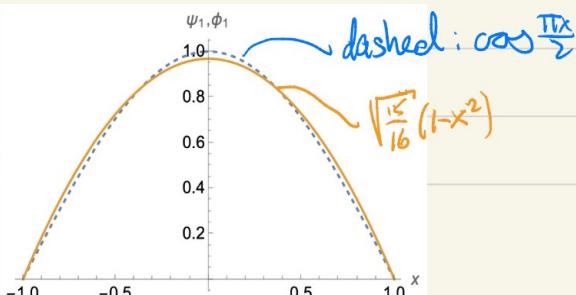
2. An electron is trapped in a one-dimensional box described by the potential (recall 1 bohr = 0.529177 Å, is the atomic unit of length):

$$V(x) = \begin{cases} 0, & -1 < x < 1 \text{ bohr} \\ \infty, & x \leq -1 \text{ or } x \geq 1 \text{ bohr} \end{cases}$$

$a_0 = \text{Bohr radius (1)}$

- (a) Using the energy expression given in class, calculate the ground state ($n = 1$) energy of the electron, in Hartree (the atomic unit of energy), in eV, and in kJ mol⁻¹.
 (b) The ground-state wavefunction for this electron is $\psi_1(x) = \cos(\pi x/2)$ (accounting for the fact that we centered the box on the origin). Plot this wavefunction and show that it obeys the proper boundary conditions, has zero nodes, and is normalized.
 (c) Calculate the expectation value of the energy (i.e., the Hamiltonian) in Hartree for the wavefunction ψ_1 .
 (d) Suppose you approximate the true ground-state wavefunction by $\phi_1(x) = 1 - x^2$. Calculate the expectation value of the energy for this approximation. How does your answer compare to the energies you calculated in (a) and (c)?

(b)



$$\textcircled{a} \quad E_n = \frac{n^2 \hbar^2}{8m L^2} = \frac{n^2 (\pi)^2 \hbar^2}{8m (2a_0)^2} = \frac{n^2 \pi^2 \hbar^2}{8ma_0^2}$$

$L = 2a_0$

Using atomic units, $\hbar = 1$, $m = 1$, $a_0 = 1$
and energy is given in Hartrees

$$E_n = \frac{(1)^2 \pi^2 (1)^2}{8(1)(1)^2} = 1.2357 \text{ Hartrees.}$$

\downarrow
 $\{x27,2114\}$

$$= 33.571 \text{ eV}$$

\downarrow
 $\times (4.5597 \times 10^{-21}) \text{ J/bo}$

$$= 3239.1 \text{ kJ/mol}$$

$= -1, 1$
se (no nodes)

Normalized

continued →

$$\text{Integrate}[\cos^2[\frac{\pi x}{2}], \{x, -1, 1\}]$$

1

$$\textcircled{d} \quad \phi_1(x) = 1 - x^2$$

First, normalize

$$\phi_1(x) = \left(\frac{15}{16}\right)^{1/2} (1 - x^2)$$

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\hat{H}|\phi_1\rangle = +\frac{\sqrt{15}}{4m} \hbar^2 \text{ (constant)}$$

$$\phi_1[x_] := \left(\frac{15}{16}\right)^{1/2} (1 - x^2)$$

$$H\phi_1[x_] := \text{Release}\left[-\frac{1}{2} D[\phi_1[x], x, x]\right]$$

$$H\phi_1[x]$$

$$\text{Integrate}[\phi_1[x] H\phi_1[x], \{x, -1, 1\}] // N$$

\downarrow

$$\sqrt{\frac{15}{16}} \hbar^2 \text{ (constant)}$$

$$\langle \phi_1 | H | \phi_1 \rangle$$

\downarrow

$$1.25 \text{ Hartrees}$$

-1.0

Hartree-Fock theory applies the variational principle to the Slater-determinant energy

- Express energy in terms of 1- and 2-electron integrals

$$\langle E \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji])$$

- Introduce Coulomb and exchange operators to isolate dependence on orbitals
- Minimize $\langle E \rangle$ wrt orbitals with orthonormality constraint
- Form as a new eigenvalue expression
- Solve numerically to obtain self-consistent result

The Coulomb operator averages interaction with the electron density of all orbitals

$$\langle E \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji])$$

$$\begin{aligned}\sum_j [ii|jj] &= \sum_j \int \int \varphi_i^*(\tau_1) \varphi_i(\tau_1) \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_j(\tau_2) d\tau_1 d\tau_2 \\ &= \int \varphi_i^*(\tau_1) \underbrace{\sum_j \int \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_j(\tau_2) d\tau_2}_{\text{Coulomb operator acting on } \varphi_i, (\hat{C}\varphi_i)(\tau_1)} \varphi_i(\tau_1) d\tau_1 \quad \begin{matrix} \text{Function of } \tau_1 \\ \downarrow \end{matrix} \\ &= \int \varphi_i^*(\tau_1) (\hat{C}\varphi_i)(\tau_1) d\tau_1 \\ &= \langle \varphi_i | \hat{C} | \varphi_i \rangle \quad \begin{matrix} \text{Functional of } \varphi_i \\ \uparrow \end{matrix}\end{aligned}$$

The exchange operator is defined in a similar fashion

$$\langle E \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji])$$

$$\begin{aligned}\sum_j [ij|ji] &= \sum_j \int \int \varphi_i^*(\tau_1) \varphi_j(\tau_1) \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_i(\tau_2) d\tau_1 d\tau_2 \\ &= \int \varphi_i^*(\tau_1) \underbrace{\sum_j \int \frac{1}{r_{12}}}_{\text{Function of } \tau_1} \varphi_j(\tau_1) \varphi_j^*(\tau_2) \varphi_i(\tau_2) d\tau_2 d\tau_1 \\ &= \int \varphi_i^*(\tau_1) \left(\hat{X} \varphi_i \right)(\tau_1) d\tau_1 \\ &= \langle \varphi_i | \hat{X} | \varphi_i \rangle\end{aligned}$$

Exchange operator acting on φ_i , $\left(\hat{X} \varphi_i \right)(\tau_1)$

Functional of φ_i

The next step is to express the energy in terms of these operators, and minimize it

$$\langle E \rangle = \sum_i h_{i,i} + \frac{1}{2} \sum_i \langle \varphi_i | \hat{C} - \hat{X} | \varphi_i \rangle$$

- Find set of φ_i that minimize this energy
- But we need to do this while keeping the φ_i orthonormal
- *Constrained* functional minimization w.r.t. φ_i
- Use Lagrange multiplier
 - *Unconstrained* minimization of Lagrange function

$$\Omega \equiv \sum_i \langle \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \langle \varphi_i | \hat{C} - \hat{X} | \varphi_i \rangle - \sum_{i,j} \Lambda_{i,j} (\underbrace{\langle \varphi_i | \varphi_j \rangle - \delta_{i,j}}_{\text{Lagrange multipliers; additional optimization variables}})$$

Orthonormality constraint;
this equal to zero

Lagrange multipliers; additional optimization variables

Constrained functional minimization of the energy yields the *Hartree-Fock equation*

- HF equation: $\hat{F}\varphi_i = \varphi_i\varepsilon_i$
- \hat{F} is the *Fock operator*

$$\hat{F} = \hat{h} + (\hat{C} - \hat{X})$$

- The eigenfunctions of φ_i provide the minimum expectation energy via $\langle E \rangle = \sum_i \langle \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \langle \varphi_i | \hat{C} - \hat{X} | \varphi_i \rangle$
- Remember though that \hat{C} and \hat{X} both depend on the φ_i

$$\hat{C}\varphi_i(\tau_1) = \sum_j \int \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_j(\tau_2) \varphi_i(\tau_1) d\tau_2 \quad \hat{X}\varphi_i(\tau_1) = \sum_j \int \frac{1}{r_{12}} \varphi_j(\tau_1) \varphi_j^*(\tau_2) \varphi_i(\tau_2) d\tau_2$$

- Requires self-consistent solution

Let's do a calculation of the electron-repulsion integrals

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

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

- Compute the integrals

$$\langle \varphi_i | \hat{C} | \varphi_j \rangle \quad \langle \varphi_i | \hat{X} | \varphi_j \rangle$$

- Compare to literature for some set of orbitals
- More in next class...

Table 1. One-centre repulsion integrals.

Atoms	Orbital ^a	Present value (a.u.)	From literature (a.u.)	Approx. time (sec)
Li	(2s2s 2s2s)	0.289615078125	0.289615078125 ^b	3
H	(1s1s 1s1s)	0.554843750000	0.554843750000 ^b	1
F	(2p _z 2p _z 2p _z 2p _z)	0.241301953125 × 10 ¹	0.241301953125 × 10 ¹ ^b	3
Be	(1s1s 1s1s)	0.386647500000 × 10 ¹	0.386647500000 × 10 ¹ ^b	1
Na	(1s1s 1s1s)	0.954725000000 × 10 ¹	0.954725000000 × 10 ¹ ^b	1
H	(1s1s 1s1s)	0.487687500000	0.487687500000 ^b	1
F	(1s1s 1s1s)	0.494868750000 × 10 ¹	0.494868750000 × 10 ¹ ^b	1
Sc	(1s1s 1s1s)	0.108062500000 × 10 ²	0.108062500000 × 10 ² ^b	1
H	(1s1s 1s1s)	0.625000000000	0.625000000000 ^b	1
F	(2p _x 2p _x 2p _x 2p _x)	0.101765625000 × 10 ¹	1.01766 ^c	3
F	(1s2s 2s1s)	0.146328213305	0.14633 ^c	1
F	(2p _z 2p _z 2p _z 2p _z)	0.054843750000	0.05484 ^c	3
F	(2s2p _z 2s2p _z)	0.208767361111	0.20877 ^c	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.

$\xi_{Li_{1s}} = 0.79722$ (in LiH), $\xi_{Be_{1s}} = 6.18636$ (in BeF⁺), $\xi_{H_{1s}} = 0.88775$ (in LiH), $\xi_{F_{2p}} = 6.165$ (in BeF⁺), $\xi_{Na_{1s}} = 15.2756$ (in NaH), $\xi_{H_{1s}} = 0.7803$ (in NaH), $\xi_{Sc_{1s}} = 17.29$ (in ScF), $\xi_{F_{1s}} = 7.9179$ (in ScF).

^c From (Pople and Beveridge 1970) using $\xi_{H_{1s}} = 1.0$, $\xi_{F_{2p}} = 2.6$, $\xi_{F_{2s}} = 2.6$, $\xi_{F_{1s}} = 8.7$ (in HF).

1.Kumar, A. &
Mishra, P. C.
Evaluation of one-
centre electron
interaction integrals
over slater type
atomic orbitals.
Pramana **29**, 385–
390 (1987).

Suggested Reading/Viewing

- Autschbach Sec. 3.4, 8.1, 8.2