

Lecture 5

Hartree-Fock Theory

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

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CE 500 – Modeling Potential-Energy Surfaces

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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

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

Add to MyBraKet.nb

Slater determinant

Energy expectation

it[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 *)

$$\psi = \frac{1}{\sqrt{nM}} \text{Det}[M] \text{ // Expand}$$

BraKet[{ψ}, {ψ}] // . orthonormalRule

it[1600]=

Spin-orbital #1

#2

it[1602]:=MatrixForm=

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

electron #1
#2

it[1603]=

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

it[1604]=

1 ← normalized

it[1605]= S[tauList] :=

With[{n = Length[tauList]}, $\frac{1}{\sqrt{n!}}$ Det@Transpose@Flatten[Table[φ_i[tauList[[j]]] σ[tauList[[j]]], {σ, {α, β}}, {i, nM/2}, {j, nM}], 1]]

nM = 4; 4 electrons

tauList = Range[nM]

1-electron contribution

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 = S[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

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

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

nM = 4;

tauList = Range[nM];

2-electron contribution

(* do just one term in Hamiltonian *)

BraKet[{S[tauList]}, $\frac{1}{r}$ [1, 2], {S[tauList]}];

% /. orthonormalRule // Simplify

% /. mulikenFormRule

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

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

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

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

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

Period

I A II A III A IV A V A VI A VII A VIII A

1 1 **1s** 2 **2s** 3 **3s** 4 **4s** 5 **5s** 6 **6s** 7 **7s**

2 3 **1s** 4 **2s** 5 **3s** 6 **4s** 7 **5s** 8 **6s** 9 **7s**

3 11 **3s** 12 **4s** 13 **5s** 14 **6s** 15 **7s** 16 **8s** 17 **9s** 18 **10s**

4 1 **1s** 2 **2s** 3 **3s** 4 **4s** 5 **5s** 6 **6s** 7 **7s** 8 **8s** 9 **9s** 10 **10s**

5 37 **5s** 38 **6s** 39 **7s** 40 **8s** 41 **9s** 42 **10s** 43 **11s** 44 **12s** 45 **13s** 46 **14s** 47 **15s** 48 **16s** 49 **17s** 50 **18s**

6 55 **6s** 56 **7s** 57 **8s** 58 **9s** 59 **10s** 60 **11s** 61 **12s** 62 **13s** 63 **14s** 64 **15s** 65 **16s** 66 **17s** 67 **18s** 68 **19s** 69 **20s**

7 87 **7s** 88 **8s** 89 **9s** 90 **10s** 91 **11s** 92 **12s** 93 **13s** 94 **14s** 95 **15s** 96 **16s** 97 **17s** 98 **18s** 99 **19s** 100 **20s**

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1 **1s** 2 **2s** 3 **3s** 4 **4s** 5 **5s</**

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

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

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

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

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

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 $f \equiv \psi$

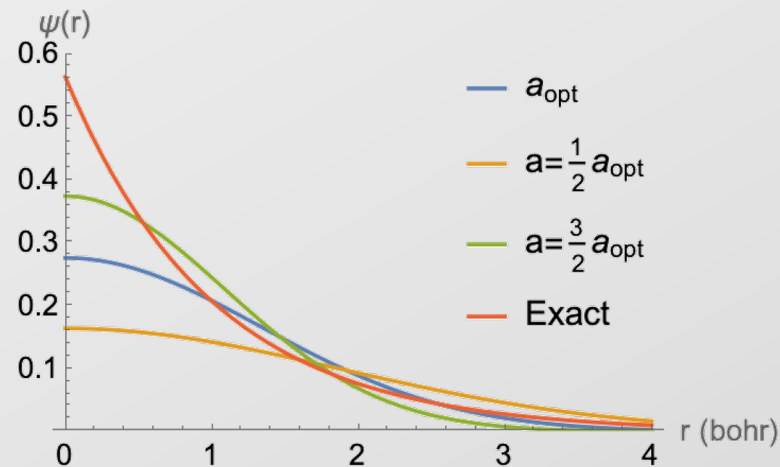
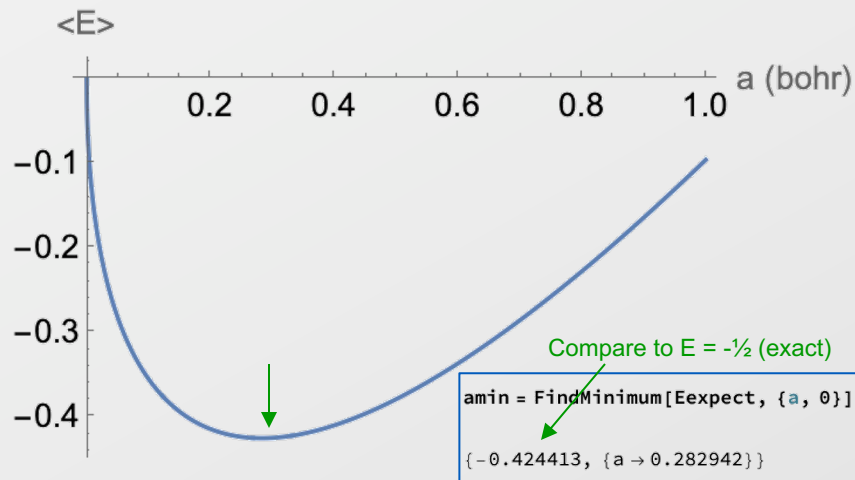
- We can guide estimation of the true wavefunction ψ by using any degrees of freedom in f to minimize $\langle E \rangle$

An 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: $\langle E \rangle = \frac{3}{2}a - \left(\frac{8}{\pi}\right)^{\frac{1}{2}}\sqrt{a}$

$$\text{Eexpect} = \langle f | \text{Hhat}[f] \rangle$$

$$\frac{3a}{2} - 2\sqrt{a}\sqrt{\frac{2}{\pi}}$$



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

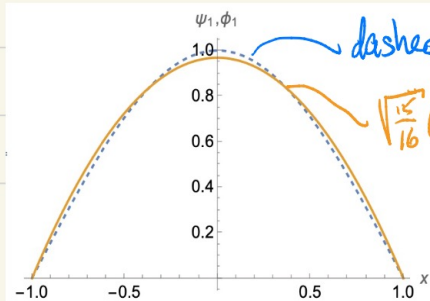
2. An electron is trapped in a one-dimensional box described by the potential (recall 1 bohr = 0.529 177 Å, is the atomic unit of length):

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

$a_0 = \text{Bohr radius}$

- 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.
- 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.
- Calculate the expectation value of the energy (i.e., the Hamiltonian) (in Hartree) for the wavefunction ψ_1 .
- 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)?

6



$$E_n = \frac{n^2 \hbar^2}{8mL^2} = \frac{n^2 (\hbar^2) k^2}{8m(2a_0)^2} = \frac{n^2 \pi^2 \hbar^2}{8ma_0^2}$$

$L = 2a_0$

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

$$E_n = \frac{(1)^2 \pi^2 (1)^2}{8(1)(1)^2} = 1.2337 \text{ Hartrees}$$

$$\begin{aligned} &= 33.571 \text{ eV} \\ &= 3234.1 \text{ kJ/mol} \end{aligned}$$

$\times (27.2114)$ $\times (4.3597 \times 10^{-21}) / \text{Hartree}$

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

Normalized continued \rightarrow

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

1

d) $\phi_1(x) = 1 - x^2$

First, normalize

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

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

Integrate $[(1 - x^2)^2, \{x, -1, 1\}]$ = $\frac{16}{15}$

$\hat{H}|\phi_1\rangle := \left(\frac{15}{16}\right)^{1/2} (1 - x^2)$

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

$H\phi_1[x]$

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

$\frac{\sqrt{15} \hbar^2}{4m} \int \phi_1 |H| \phi_1$

1.25 1.25 Hartrees

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

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

$$\sum_j [ii|jj] = \sum_j \int \int \varphi_i^*(\tau_1) \varphi_i(\tau_1) \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_j(\tau_2) d\tau_1 d\tau_2$$

$$= \int \varphi_i^*(\tau_1) \underbrace{\sum_j \int \frac{1}{r_{12}} \varphi_j^*(\tau_2) \varphi_j(\tau_2) d\tau_2}_{\text{Coulomb operator acting on } \varphi_i} \varphi_i(\tau_1) d\tau_1$$

$$= \int \varphi_i^*(\tau_1) \left(\hat{C} \varphi_i \right) (\tau_1) d\tau_1$$

$$= \langle \varphi_i | \hat{C} | \varphi_i \rangle$$

Function of τ_1

Functional of φ_i

The exchange operator is defined in a similar fashion

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

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

Function of τ_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

$$\Omega \equiv \sum_i \langle \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \langle \varphi_i | \hat{C} - \hat{X} | \varphi_i \rangle - \sum_{i,j} \Lambda_{i,j} (\underbrace{\langle \varphi_i | \varphi_j \rangle - \delta_{i,j}}_{\text{Orthonormality constraint; this equal to zero}})$$

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 ^{1b}	3
Be	(1s1s 1s1s)	0.386647500000 × 10 ¹	0.386647500000 × 10 ^{1b}	1
Na	(1s1s 1s1s)	0.954725000000 × 10 ¹	0.954725000000 × 10 ^{1b}	1
H	(1s1s 1s1s)	0.487687500000	0.487687500000 ^b	1
F	(1s1s 1s1s)	0.494868750000 × 10 ¹	0.494868750000 × 10 ^{1b}	1
Sc	(1s1s 1s1s)	0.108062500000 × 10 ²	0.108062500000 × 10 ^{2b}	1
H	(1s1s 1s1s)	0.625000000000	0.625000000000 ^c	1
F	(2p _z 2p _z 2p _z 2p _z)	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 ζ values.

$\zeta_{Li,2s} = 0.79722$ (in LiH), $\zeta_{Be,1s} = 6.18636$ (in BeF⁺), $\zeta_{H,1s} = 0.88775$ (in LiH), $\zeta_{F,2p} = 6.165$ (in BeF⁺), $\zeta_{Na,1s} = 15.2756$ (in NaH), $\zeta_{H,1s} = 0.7803$ (in NaH), $\zeta_{Sc,1s} = 17.29$ (in ScF), $\zeta_{F,1s} = 7.9179$ (in ScF).

^c From (Pople and Beveridge 1970) using $\zeta_{H,1s} = 1.0$, $\zeta_{F,2p} = 2.6$, $\zeta_{F,2s} = 2.6$, $\zeta_{F,1s} = 8.7$ (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