

Chapter 7

Multielectron Atoms

Homework Solutions

PART A: The Variational Principle and the Helium Atom

1. This problem is worked out in Chap. 3: HW #5.

As shown in the #3.5 (part d) solution, $\langle E \rangle = \frac{7}{4\pi^2} \frac{h^2}{ma^2} = 0.177 \frac{h^2}{ma^2}$

Note that this computed energy is significantly higher than that of other approximate wavefunction, as shown in the PP presentation. Thus, This trial wavefunction is a poorer approximation to the PIB ground state wavefunction.

2. (a) **Lithium Atom Hamiltonian**

$$H = -\frac{\hbar^2}{2m} \nabla_1^2(\vec{r}_1) - \frac{\hbar^2}{2m} \nabla_2^2(\vec{r}_2) - \frac{\hbar^2}{2m} \nabla_3^2(\vec{r}_3)$$

SI Units:

$$-\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} - \frac{Ze^2}{4\pi\epsilon_0 r_3} \\ + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{23}}$$

$$H = -\frac{1}{2} \nabla_1^2(\vec{r}_1) - \frac{1}{2} \nabla_2^2(\vec{r}_2) - \frac{1}{2} \nabla_3^2(\vec{r}_3)$$

Atomic Units:

$$-\frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_3} \\ + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

(b) "Independent Particle Model" Energy

For Li, Z = 3: Electron Configuration = 1s²2s¹

$$E = E_1 + E_2 + E_3 = -\frac{Z^2}{2(1)^2} - \frac{Z^2}{2(1)^2} - \frac{Z^2}{2(2)^2} = -\frac{9}{8} Z^2 \\ = -\frac{9}{8} (3)^2 = -10.13 a.u.$$

(c) Variational Principle

The energy computed from the Independent Particle Model (-10.13 a.u.) is lower than the experimental energy (-7.48 a.u.).

However, it is **NOT** a violation of the Variational Principle because the inter-electron repulsions were excluded from the Hamiltonian. The Variational Principle is valid only when the **complete** Hamiltonian is used in the calculation.

3. (a) Comparison of the two trial wavefunctions:

$$(1) \quad \phi = A \left[e^{-Z(r_1+r_2)} (1 + b \cdot r_{12}) \right]$$

$$(2) \quad \phi = A e^{-Z(r_1+r_2)}$$

The first wavefunction above cannot possibly give a higher energy than the second one because, it reduces to the second equation in the limit, $b \rightarrow 0$

One would expect that wavefunction (1) would give a lower energy than wavefunction (2) because of the additional parameter, b , which can aid in a better description of the electron density.

(b) The purpose of the term, $(1 + b \cdot r_{12})$, is to incorporate the correlation of electrons into the wavefunction. Because of the repulsion of the two electrons, one would expect the probability to be higher when the electrons are further apart, and this is accomplished by the additive term, which increases with increasing r_{12} .

4.

$$E = \frac{3\alpha}{2} - \frac{4\alpha^{1/2}}{\sqrt{2\pi}} \text{ a.u.}$$

Let's take the derivative and set it equal to 0 to find $\alpha_{\min}$

$$\begin{aligned} \frac{dE}{d\alpha} = 0 &= \frac{3}{2} - \frac{4}{\sqrt{2\pi}} (1/2) \alpha^{-1/2} = \frac{3}{2} - \frac{2}{\sqrt{2\pi} \cdot \alpha^{1/2}} \\ \frac{2}{\sqrt{2\pi} \cdot \alpha_{\min}^{1/2}} &= \frac{3}{2} \rightarrow \alpha_{\min}^{1/2} = \frac{4}{3\sqrt{2\pi}} \rightarrow \alpha_{\min} = \frac{16}{18\pi} = 0.293 \end{aligned}$$

$$E = \frac{3\alpha_{\min}}{2} - \frac{4\alpha_{\min}^{1/2}}{\sqrt{2\pi}} = \frac{3}{2} (0.293) - \frac{4(0.293)^{1/2}}{\sqrt{2\pi}} = -0.424 \text{ a.u.}$$

As expected, this approximate energy is higher than the exact Hydrogen Ground State Energy: $E_{\text{exact}} = -0.500 \text{ a.u.}$

5.
$$E = \frac{5\hbar^2}{4\mu\delta^2} + \frac{k\delta^2}{14} = \frac{5\hbar^2}{4\mu\Delta} + \frac{k\Delta}{14}$$

Let's take the derivative with respect to $\Delta (= \delta^2)$ to find $\Delta_{\min}$

$$\frac{dE}{d\Delta} = 0 = -\frac{5\hbar^2}{4\mu\Delta^2} + \frac{k}{14} \rightarrow \frac{5\hbar^2}{4\mu\Delta_{\min}^2} = \frac{k}{14} \rightarrow \frac{5\hbar^2}{4\mu\Delta_{\min}^2} = \frac{k}{14}$$

$$\Delta_{\min}^2 = \frac{14}{k} \frac{5\hbar^2}{4\mu} = \frac{35}{2} \frac{\hbar^2}{k\mu} \rightarrow \Delta_{\min} = \left(\frac{35}{2}\right)^{1/2} \frac{\hbar}{(k\mu)^{1/2}}$$

$$\begin{aligned} E &= \frac{5\hbar^2}{4\mu\Delta_{\min}} + \frac{k\Delta_{\min}}{14} = \left(\frac{5\hbar^2}{4\mu}\right) \left[\left(\frac{2}{35}\right)^{1/2} \frac{(k\mu)^{1/2}}{\hbar}\right] + \frac{k}{14} \left[\left(\frac{35}{2}\right)^{1/2} \frac{\hbar}{(k\mu)^{1/2}}\right] \\ &= \left[\frac{5}{4} \left(\frac{2}{35}\right)^{1/2}\right] \hbar \sqrt{\frac{k}{\mu}} + \left[\frac{1}{14} \left(\frac{35}{2}\right)^{1/2}\right] \hbar \sqrt{\frac{k}{\mu}} = 0.299 \cdot \hbar \sqrt{\frac{k}{\mu}} + 0.299 \cdot \hbar \sqrt{\frac{k}{\mu}} = 0.60 \hbar \sqrt{\frac{k}{\mu}} \\ &= 0.60 \hbar \omega \end{aligned}$$

As expected, this approximate energy is higher than the exact Harmonic Oscillator

Ground State Energy: $E_{\text{exact}} = \frac{1}{2} \hbar \omega$

PART B: Electron Spin and the Pauli Principle

6. (a) $f(1)f(2)\alpha_1\alpha_2$: Symmetric

(b) $f(1)g(2)\alpha_1\alpha_2$: Neither symmetric nor antisymmetric

(c) $f(1)f(2)[\alpha_1\beta_2 - \beta_1\alpha_2]$: Antisymmetric

(d) $[f(1)g(2) + g(1)f(2)]\beta_1\beta_2$: Symmetric

(e) $[f(1)g(2) - g(1)f(2)][\alpha_1\beta_2 + \beta_1\alpha_2]$: Antisymmetric

7. (a) $1s(1)2s(2)(\alpha_1\beta_2 - \beta_1\alpha_2)$: **No**. Spin Function is antisymmetric wrt exchange, but spatial function is neither symmetric nor antisymmetric wrt exchange

- (b) $[1s(1)2s(1) - 2s(1)1s(1)]\alpha_1\beta_2$: **No.** There is no spatial function for electron #2.
- (c) $[1s(1)2s(2) - 2s(1)1s(2)](\alpha_1\beta_2 - \beta_1\alpha_2)$: **No.** Both spatial and spin functions are antisymmetric wrt exchange. Thus, the overall wavefunction is symmetric, rather than antisymmetric.
- (d) $1s(1)2s(2)\alpha_1\beta_2 - 2s(1)1s(2)\beta_1\alpha_2 + 1s(1)2s(2)\beta_1\alpha_2 - 2s(1)1s(2)\alpha_1\beta_2$: **Yes.**
 $P_{12}(\text{term } 1) = -\text{term } 2$; $P_{12}(\text{term } 2) = -\text{term } 4$;
 $P_{12}(\text{term } 3) = -\text{term } 1$; $P_{12}(\text{term } 4) = -\text{term } 3$
 Thus, the overall 4 term wavefunction is antisymmetric wrt electron exchange.

8. $\psi = N(\alpha + c\beta)$

(a) Normalization

$$1 = \langle \psi | \psi \rangle = \langle N(\alpha + c\beta) | N(\alpha + c\beta) \rangle = N^2 [\langle \alpha | \alpha \rangle + c \langle \alpha | \beta \rangle + c \langle \beta | \alpha \rangle + c^2 \langle \beta | \beta \rangle]$$

$$= N^2 [1 + 0 + 0 + c^2] = N^2 [1 + c^2]$$

Therefore, $N = \sqrt{\frac{1}{1 + c^2}}$

(b) $\langle S_z \rangle$

$$\langle S_z \rangle = \langle \psi | \hat{S}_z | \psi \rangle = \langle N(\alpha + c\beta) | \hat{S}_z | N(\alpha + c\beta) \rangle$$

$$= N^2 [\langle \alpha | \hat{S}_z | \alpha \rangle + c \langle \alpha | \hat{S}_z | \beta \rangle + c \langle \beta | \hat{S}_z | \alpha \rangle + c^2 \langle \beta | \hat{S}_z | \beta \rangle]$$

$$= N^2 \left[\frac{1}{2} \hbar \langle \alpha | \alpha \rangle + c \left(-\frac{1}{2} \hbar \right) \langle \alpha | \beta \rangle + c \left(\frac{1}{2} \hbar \right) \langle \beta | \alpha \rangle + c^2 \left(-\frac{1}{2} \hbar \right) \langle \beta | \beta \rangle \right]$$

$$= N^2 \left[\frac{1}{2} \hbar + 0 + 0 - \frac{1}{2} \hbar c^2 \right] = N^2 \frac{1}{2} \hbar (1 - c^2)$$

$$= \left(\sqrt{\frac{1}{1 + c^2}} \right)^2 \frac{1}{2} \hbar (1 - c^2) = \frac{1}{2} \hbar \left(\frac{1 - c^2}{1 + c^2} \right)$$

9. Coulomb Integral [J_{1s2p}]

$$J_{1s2s} = \iint \frac{1s(1)^2 2p(2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 = \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 1s(1)2p(2) \rangle$$

Exchange Integral [K_{1s2p}]

$$J_{1s2s} = \iint \frac{[1s(1)2p(1)] \cdot [1s(2)2p(2)]}{r_{12}} d\vec{r}_1 d\vec{r}_2 = \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 2p(1)1s(2) \rangle$$

10.
$$\psi_{\text{Sing}} = \left[\frac{1}{\sqrt{2}} (1s(1)2p(2) + 2p(1)1s(2)) \right] \cdot \left[\frac{1}{\sqrt{2}} (\alpha_1\beta_2 - \beta_1\alpha_2) \right] = \psi_{\text{spatial}} \cdot \psi_{\text{spin}}$$

(a) S_zψ_{spin}

$$\begin{aligned} \hat{S}_z \psi_{\text{Spin}} &= (\hat{S}_{1z} + \hat{S}_{2z}) \left(\frac{1}{\sqrt{2}} \right) (\alpha_1\beta_2 - \beta_1\alpha_2) = \left(\frac{1}{\sqrt{2}} \right) \left[\hat{S}_{1z} (\alpha_1\beta_2 - \beta_1\alpha_2) \right] + \left[\hat{S}_{2z} (\alpha_1\beta_2 - \beta_1\alpha_2) \right] \\ &= \left(\frac{1}{\sqrt{2}} \right) \left[\left\{ \left(\frac{1}{2} \hbar \right) \alpha_1\beta_2 - \left(-\frac{1}{2} \hbar \right) \beta_1\alpha_2 \right\} + \left\{ \left(-\frac{1}{2} \hbar \right) \alpha_1\beta_2 - \left(\frac{1}{2} \hbar \right) \beta_1\alpha_2 \right\} \right] \\ &= \left(\frac{1}{\sqrt{2}} \right) \left(\frac{1}{2} \hbar \right) [\{ \alpha_1\beta_2 + \beta_1\alpha_2 \} + \{ -\alpha_1\beta_2 - \beta_1\alpha_2 \}] = 0 \end{aligned}$$

This result shouldn't be surprising because the spin function corresponds to a triplet function with L_z = 0

(b) Verify Normalization of ψ_{Spin} and ψ_{Spatial}

$$\begin{aligned} \langle \psi_{\text{Spatial}} | \psi_{\text{Spatial}} \rangle &= \left\langle \frac{1}{\sqrt{2}} [1s(1)2p(2) + 2p(1)1s(2)] \middle| \frac{1}{\sqrt{2}} [1s(1)2p(2) + 2p(1)1s(2)] \right\rangle \\ &= \frac{1}{2} \left[\langle 1s(1)2p(2) | 1s(1)2p(2) \rangle + \langle 1s(1)2p(2) | 2p(1)1s(2) \rangle \right. \\ &\quad \left. + \langle 2p(1)1s(2) | 1s(1)2p(2) \rangle + \langle 2p(1)1s(2) | 2p(1)1s(2) \rangle \right] \\ &= \frac{1}{2} \left[\langle 1s(1) | 1s(1) \rangle \langle 2p(2) | 2p(2) \rangle + \langle 1s(1) | 2p(1) \rangle \langle 2p(2) | 1s(2) \rangle \right. \\ &\quad \left. + \langle 2p(1) | 1s(1) \rangle \langle 2p(2) | 1s(2) \rangle + \langle 2p(1) | 2p(1) \rangle \langle 1s(2) | 1s(2) \rangle \right] \\ &= \frac{1}{2} \{ 1 + 0 + 0 + 1 \} = \frac{1}{2} \cdot 2 = 1 \end{aligned}$$

$$\begin{aligned}
\langle \psi_{Spin} | \psi_{Spin} \rangle &= \left\langle \frac{1}{\sqrt{2}} [\alpha_1 \beta_2 - \beta_1 \alpha_2] \left| \frac{1}{\sqrt{2}} [\alpha_1 \beta_2 - \beta_1 \alpha_2] \right. \right\rangle \\
&= \frac{1}{2} \{ \langle \alpha_1 \beta_2 | \alpha_1 \beta_2 \rangle - \langle \alpha_1 \beta_2 | \beta_1 \alpha_2 \rangle - \langle \beta_1 \alpha_2 | \alpha_1 \beta_2 \rangle + \langle \beta_1 \alpha_2 | \beta_1 \alpha_2 \rangle \} \\
&= \frac{1}{2} \{ \langle \alpha_1 | \alpha_1 \rangle \langle \beta_2 | \beta_2 \rangle - \langle \alpha_1 | \beta_1 \rangle \langle \beta_2 | \alpha_2 \rangle - \langle \beta_1 | \alpha_1 \rangle \langle \alpha_2 | \beta_2 \rangle + \langle \beta_1 | \beta_1 \rangle \langle \alpha_2 | \alpha_2 \rangle \} \\
&= \frac{1}{2} \{ 1 - 0 - 0 + 1 \} = \frac{1}{2} \{ 2 \} = 1
\end{aligned}$$

(c) $\langle E \rangle_{\text{Sing}}$

$$\begin{aligned}
\langle E \rangle &= \left\langle \frac{1}{\sqrt{2}} (1s(1)2p(2) + 2p(1)1s(2)) \left| H \right| \frac{1}{\sqrt{2}} (1s(1)2p(2) + 2p(1)1s(2)) \right\rangle \\
&= \frac{1}{2} \langle 1s(1)2p(2) | H | 1s(1)2p(2) \rangle + \frac{1}{2} \langle 2p(1)1s(2) | H | 2p(1)1s(2) \rangle \\
&\quad + \frac{1}{2} \langle 1s(1)2p(2) | H | 2p(1)1s(2) \rangle + \frac{1}{2} \langle 2p(1)1s(2) | H | 1s(1)2p(2) \rangle \\
&= I_1 + I_2 + I_3 + I_4
\end{aligned}$$

$$\begin{aligned}
I_1 &= \frac{1}{2} \langle 1s(1)2p(2) | H | 1s(1)2p(2) \rangle = \frac{1}{2} \langle 1s(1)2p(2) | H_1 + H_2 + \frac{1}{r_{12}} | 1s(1)2p(2) \rangle \\
I_2 &= \frac{1}{2} \langle 1s(1)2p(2) | H_1 | 1s(1)2p(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | H_2 | 1s(1)2p(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 1s(1)2p(2) \rangle \\
I_3 &= \frac{1}{2} \langle 2p(2) | 2p(2) \rangle \langle 1s(1) | H_1 | 1s(1) \rangle + \frac{1}{2} \langle 1s(1) | 1s(1) \rangle \langle 2p(2) | H_2 | 2p(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 1s(1)2p(2) \rangle \\
&= \frac{1}{2} \langle 1s(1) | H_1 | 1s(1) \rangle + \frac{1}{2} \langle 2p(2) | H_2 | 2p(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 1s(1)2p(2) \rangle \\
&= \frac{1}{2} \mathcal{E}_{1s} + \frac{1}{2} \mathcal{E}_{2p} + \frac{1}{2} J_{1s2p}
\end{aligned}$$

Similarly:

$$\begin{aligned}
I_2 &= \frac{1}{2} \langle 2p(1)1s(2) | H | 2p(1)1s(2) \rangle = \frac{1}{2} \langle 2p(1)1s(2) | H_1 + H_2 + \frac{1}{r_{12}} | 2p(1)1s(2) \rangle \\
&= \frac{1}{2} \mathcal{E}_{2p} + \frac{1}{2} \mathcal{E}_{1s} + \frac{1}{2} J_{1s2p}
\end{aligned}$$

$$\begin{aligned}
I_3 &= \frac{1}{2} \langle 1s(1)2p(2) | H | 2p(1)1s(2) \rangle = \frac{1}{2} \langle 1s(1)2p(2) | H_1 + H_2 + \frac{1}{r_{12}} | 2p(1)1s(2) \rangle \\
&= \frac{1}{2} \langle 1s(1)2p(2) | H_1 | 2p(1)1s(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | H_2 | 2p(1)1s(2) \rangle + \frac{1}{2} \langle 1s(1)2p(2) | \frac{1}{r_{12}} | 2p(1)1s(2) \rangle
\end{aligned}$$

$$I_3 = \frac{1}{2} \langle 2p(2) | 1s(2) \rangle \langle 1s(1) | H_1 | 2p(1) \rangle + \frac{1}{2} \langle 1s(1) | 2p(1) \rangle \langle 2p(2) | H_2 | 1s(2) \rangle + \frac{1}{2} \langle 1s(1) 2p(2) | \frac{1}{r_{12}} | 2p(1) 1s(2) \rangle$$

$$= 0 + 0 + \frac{1}{2} \langle 1s(1) 2p(2) | \frac{1}{r_{12}} | 2p(1) 1s(2) \rangle = \frac{1}{2} K_{1s2p}$$

Similarly:

$$I_4 = \frac{1}{2} \langle 1s(1) 2p(2) | H | 2p(1) 1s(2) \rangle = \frac{1}{2} \langle 1s(1) 2p(2) | H_1 + H_2 + \frac{1}{r_{12}} | 2p(1) 1s(2) \rangle$$

$$= K_{1s2p}$$

Therefore:

$$\langle E \rangle = I_1 + I_2 + I_3 + I_4 = \left(\frac{1}{2} \epsilon_{1s} + \frac{1}{2} \epsilon_{2p} + \frac{1}{2} J_{1s2p} \right) + \left(\frac{1}{2} \epsilon_{2p} + \frac{1}{2} \epsilon_{1s} + \frac{1}{2} J_{1s2p} \right) + \frac{1}{2} K_{1s2p} + \frac{1}{2} K_{1s2p}$$

$$= \epsilon_{1s} + \epsilon_{2p} + J_{1s2p} + K_{1s2p}$$

- Notes:**
1. The methods used in the above calculation are identical to those employed in the calculation of the Triplet (and Singlet) state energies for the $1s^1 2s^1$ configuration of excited He (last section in Chapter 8 PowerPoint presentation).
 2. You would **not** be asked to perform the complete 4 step calculation on a test. Rather, you would be given one of the four integrals and asked to evaluate it (as above).

PART C: Many Electron Atoms

11. Please see the PowerPoint slides and class notes for answers to these qualitative questions.

12. (a)
$$\begin{vmatrix} 9 & 7 & 2 \\ 5 & 8 & 3 \\ 1 & 6 & 4 \end{vmatrix} = 9 \begin{vmatrix} 8 & 3 \\ 6 & 4 \end{vmatrix} - 7 \begin{vmatrix} 5 & 3 \\ 1 & 4 \end{vmatrix} + 2 \begin{vmatrix} 5 & 8 \\ 1 & 6 \end{vmatrix}$$

$$= 9(32 - 18) - 7(20 - 3) + 2(30 - 8) = 51$$

(b)
$$\begin{vmatrix} 6 & -3 & 4 \\ 2 & 4 & -3 \\ 1 & 6 & 4 \end{vmatrix} = 6 \begin{vmatrix} 4 & -3 \\ 6 & 4 \end{vmatrix} - (-3) \begin{vmatrix} 2 & -3 \\ 1 & 4 \end{vmatrix} + 4 \begin{vmatrix} 2 & 4 \\ 1 & 6 \end{vmatrix}$$

$$= 6(16 - (-18)) + 3(8 - (-3)) + 4(12 - 4) = 269$$

13. Be: $Z = 4$, Ground State Configuration: $1s^2 2s^2$

(a) Hamiltonian

$$H = H(KE) + H(\text{Electron / Nucleus Attraction}) + H(\text{Electron / Electron Repulsion})$$

SI Units

$$H = -\frac{\hbar^2}{2m}\nabla_1^2(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2(\vec{r}_2) - \frac{\hbar^2}{2m}\nabla_3^2(\vec{r}_3) - \frac{\hbar^2}{2m}\nabla_4^2(\vec{r}_4) \\ - \frac{4e^2}{4\pi\epsilon_0 r_1} - \frac{4e^2}{4\pi\epsilon_0 r_2} - \frac{4e^2}{4\pi\epsilon_0 r_3} - \frac{4e^2}{4\pi\epsilon_0 r_4} \\ + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}$$

Atomic Units

$$H = -\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{1}{2}\nabla_3^2(\vec{r}_3) - \frac{1}{2}\nabla_4^2(\vec{r}_4) \\ - \frac{4}{r_1} - \frac{4}{r_2} - \frac{4}{r_3} - \frac{4}{r_4} \\ + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}}$$

(b) Ground State Slater Determinant

$$\psi = \frac{1}{\sqrt{24}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 2s(1)\alpha_1 & 2s(1)\beta_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 2s(2)\alpha_2 & 2s(2)\beta_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 2s(3)\alpha_3 & 2s(3)\beta_3 \\ 1s(4)\alpha_4 & 1s(4)\beta_4 & 2s(4)\alpha_4 & 2s(4)\beta_4 \end{vmatrix}$$

14. (a) Correlation Energy of Lithium

$$E_{HF} = -7.432 \text{ au}$$

$$E_{\text{exact}} = E_{\text{exp}} = -\sum_{n=1}^3 IE_n = -(IE_1 + IE_2 + IE_3) = -(5.39 + 75.66 + 122.43) \text{ eV} \\ = -203.48 \text{ eV} \cdot \frac{1 \text{ au}}{27.21 \text{ eV}} = -7.478 \text{ au}$$

$$E_{\text{corr}} = E_{\text{exact}} - E_{HF} = -7.478 \text{ au} - (-7.432 \text{ au}) \\ = -0.046 \text{ au} \cdot \frac{2625 \text{ kJ}}{1 \text{ au}} = -120.75 \text{ kJ / mol} \approx -121 \text{ kJ / mol}$$

(b) Ionization Energy and Electron Affinity

(i) Ionization Energy (IE₁): Li → Li⁺ + e⁻

$$IE_1(\text{HF}) = E_{\text{HF}}(\text{Li}^+) - E_{\text{HF}}(\text{Li}) = -7.236 \text{ au} - (-7.432 \text{ au}) = 0.196 \text{ au} \times 27.21 \text{ eV/au} = 5.33 \text{ eV}$$

The experimental First Ionization Energy of Li is IE₁(exp) = 5.39 eV

A more accurate QM treatment which includes correlation energy would yield a result very near to experiment.

(ii) Electron Affinity (EA): Li + e⁻ → Li⁻

$$\begin{aligned} EA(\text{HF}) &= E_{\text{HF}}(\text{Li}^-) - E_{\text{HF}}(\text{Li}) = -7.427 \text{ au} - (-7.432 \text{ au}) = +0.005 \text{ au} \times 27.21 \text{ eV/au} \\ &= +0.14 \text{ eV} \end{aligned}$$

15. Koopman's Theorem: The Ionization Energy is:

$$\begin{aligned} IE_1 &\approx -\epsilon_{\text{HOMO}} = -(-0.616 \text{ au}) = +0.616 \text{ au} \times 2625 \text{ kJ/mol} / 1 \text{ eV} = +1617 \text{ kJ/mol} \\ \text{vs. } IE_1(\text{exp}) &= +1314 \text{ kJ/mol.} \end{aligned}$$

The reasons for the deviation from experiment are:

- (i) Koopman's Theorem neglects relaxation of the remaining n-1 electrons in the ion.
- (ii) Differences in the Correlation Energy in the ion and neutral atom are neglected.

16. (a) The energy expectation value does NOT depend directly upon ψ_{spin} because the (non-relativistic) Hamiltonian does not contain any spin operators.

(b) Energy Expectation Value, $\langle E \rangle$

For clarity, let's deal with the six terms separately

$$\begin{aligned} \langle E \rangle &= \langle \psi_{\text{spat}} | H | \psi_{\text{spat}} \rangle = \langle 1s(1)1s(2)2s(3) | H_1 + H_2 + H_3 + \frac{1}{r_{12}} + \frac{1}{r_{12}} + \frac{1}{r_{23}} | 1s(1)1s(2)2s(3) \rangle \\ &= E_1 + E_2 + E_3 + E_4 + E_5 + E_6 \end{aligned}$$

$$E_1 = \langle 1s(1)1s(2)2s(3) | H_1 | 1s(1)1s(2)2s(3) \rangle = \langle 1s(2) | 1s(2) \rangle \langle 2s(3) | 2s(3) \rangle \langle 1s(1) | H_1 | 1s(1) \rangle = \epsilon_{1s}$$

$$E_2 = \langle 1s(1)1s(2)2s(3) | H_2 | 1s(1)1s(2)2s(3) \rangle = \langle 1s(1) | 1s(1) \rangle \langle 2s(3) | 2s(3) \rangle \langle 1s(2) | H_2 | 1s(2) \rangle = \epsilon_{1s}$$

$$E_3 = \langle 1s(1)1s(2)1s(3) | H_3 | 1s(1)1s(2)2s(3) \rangle = \langle 1s(1) | 1s(1) \rangle \langle 1s(2) | 1s(2) \rangle \langle 2s(3) | H_3 | 2s(3) \rangle = \epsilon_{2s}$$

$$E_4 = \langle 1s(1)1s(2)2s(3) | \frac{1}{r_{12}} | 1s(1)1s(2)2s(3) \rangle = \langle 2s(3) | 2s(3) \rangle \langle 1s(1)1s(2) | \frac{1}{r_{12}} | 1s(1)1s(2) \rangle$$

$$= \langle 1s(1)1s(2) | \frac{1}{r_{12}} | 1s(1)1s(2) \rangle = J_{1s1s}$$

$$\begin{aligned}
E_5 &= \langle 1s(1)1s(2)2s(3) | \frac{1}{r_{13}} | 1s(1)1s(2)2s(3) \rangle = \langle 1s(2) | 1s(2) \rangle \langle 1s(1)2s(3) | \frac{1}{r_{13}} | 1s(1)2s(3) \rangle \\
&= \langle 1s(1)2s(3) | \frac{1}{r_{13}} | 1s(1)2s(3) \rangle = J_{1s2s}
\end{aligned}$$

$$\begin{aligned}
E_6 &= \langle 1s(1)1s(2)2s(3) | \frac{1}{r_{23}} | 1s(1)1s(2)2s(3) \rangle = \langle 1s(1) | 1s(1) \rangle \langle 1s(2)2s(3) | \frac{1}{r_{23}} | 1s(2)2s(3) \rangle \\
&= \langle 1s(2)2s(3) | \frac{1}{r_{23}} | 1s(2)2s(3) \rangle = J_{1s2s}
\end{aligned}$$

Therefore:

$$\begin{aligned}
\langle E \rangle &= \langle \psi_{Spat} | H | \psi_{Spat} \rangle = E_1 + E_2 + E_3 + E_4 + E_5 + E_6 \\
&= \mathcal{E}_{1s} + \mathcal{E}_{1s} + \mathcal{E}_{2s} + J_{1s1s} + J_{1s2s} + J_{1s2s} \\
&= 2\mathcal{E}_{1s} + \mathcal{E}_{2s} + J_{1s1s} + 2J_{1s2s}
\end{aligned}$$

(c) The Exchange Integral arises only when one uses antisymmetric wavefunctions.