# HW #6 Solutions (221B)

Since the Hamiltonian is spin independent, we can choose any spin state for the $n = 2$ electon, and our results will be the same. I take spin up. Likewise, the Hamiltonian is rotationally symmetric so we can choose any value for the $n = 2$ $m$ value. I will leave $m$ a free variable.

## a)

Since we are not using coordinates $\vec{x}_1$, $\vec{x}_2$, $\vec{x}_3$ to label our electrons, we need another scheme, e.g. subscripts on the ket vectors:

$$\psi(1s^2 2s) = \frac{1}{\sqrt{3!}} \begin{vmatrix} |1s^\uparrow\rangle_1 & |1s^\uparrow\rangle_2 & |1s^\uparrow\rangle_3 \\ |1s^\downarrow\rangle_1 & |1s^\downarrow\rangle_2 & |1s^\downarrow\rangle_3 \\ |2s^\uparrow\rangle_1 & |2s^\uparrow\rangle_2 & |2s^\uparrow\rangle_3 \end{vmatrix},$$

and likewise for $\psi(1s^2 2p)$.

## b)

We presuppose when we write down a wavefunction out of products of single-particle wavefunctions that $H_0$ splits into a sum of single-particle Hamiltonians. For the record, the energy in atomic units (ref. solutions to HW #5) is

$$E_0 = 2E_{n=1} + E_{n=2} = 2(-\frac{Z^2}{2}) - \frac{Z^2}{8} = -\frac{9Z^2}{8} = -\frac{81}{8},$$

the last equality holding for Lithium ($Z = 3$).

## c)

By antisymmetry of the wavefunction,

$$\langle \Delta H \rangle = \langle \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \rangle = 3\langle \frac{e^2}{r_{12}} \rangle.$$

(E.g.

$$\langle 123|\frac{e^2}{r_{12}}|123\rangle = -\langle 132|\frac{e^2}{r_{12}}(-|132\rangle) = \langle 123|\frac{e^2}{r_{13}}|123\rangle,$$

the first equality following by antisymmetry, the second by relabeling.) Therefore only cross terms with identical third-particle states are nonzero, and since everything is normalized, we can drop third-particle states in our notation.

$$\begin{aligned}
\langle \Delta H \rangle &= 3\langle \tfrac{e^2}{r_{12}} \rangle \\
&= 3 \times \tfrac{1}{6} \quad \Big( \langle 1s^\uparrow 1s^\downarrow | \tfrac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle - \langle 1s^\uparrow 1s^\downarrow | \tfrac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \\
&\quad + \langle 1s^\uparrow 2s^\uparrow | \tfrac{e^2}{r_{12}} | 1s^\uparrow 2s^\uparrow \rangle - \langle 1s^\uparrow 2s^\uparrow | \tfrac{e^2}{r_{12}} | 2s^\uparrow 1s^\uparrow \rangle \\
&\quad + \langle 1s^\downarrow 1s^\uparrow | \tfrac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle - \langle 1s^\downarrow 1s^\uparrow | \tfrac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle \\
&\quad + \langle 2s^\uparrow 1s^\uparrow | \tfrac{e^2}{r_{12}} | 2s^\uparrow 1s^\uparrow \rangle - \langle 2s^\uparrow 1s^\uparrow | \tfrac{e^2}{r_{12}} | 1s^\uparrow 2s^\uparrow \rangle \\
&\quad + \langle 1s^\downarrow 2s^\uparrow | \tfrac{e^2}{r_{12}} | 1s^\downarrow 2s^\uparrow \rangle - \langle 1s^\downarrow 2s^\uparrow | \tfrac{e^2}{r_{12}} | 2s^\uparrow 1s^\downarrow \rangle \\
&\quad + \langle 2s^\uparrow 1s^\downarrow | \tfrac{e^2}{r_{12}} | 2s^\uparrow 1s^\downarrow \rangle - \langle 2s^\uparrow 1s^\downarrow | \tfrac{e^2}{r_{12}} | 1s^\downarrow 2s^\uparrow \rangle \Big).
\end{aligned}$$

Since $r_{12} = r_{21}$ there are exactly two of every term.

## d)

The 2nd, 6th, 10th, and 12th terms vanish by orthogonality of spin wavefunctions. The 3rd, 7th, 9th, and 11th terms are equal. Thus

$$\langle \Delta H \rangle = \langle 1s1s | \frac{e^2}{r_{12}} | 1s1s \rangle + 2 \, \langle 1s2s | \frac{e^2}{r_{12}} | 1s2s \rangle - \langle 1s2s | \frac{e^2}{r_{12}} | 2s1s \rangle,$$

and likewise for $p$ states.

## e)

In part ($f$), we will have to distinguish between a variational parameter $\lambda$ and the charge $Z$ in the Hamiltonian which isn't varied, so I will use $\lambda$ in the wavefunctions in this calculation. I use atomic units. We need to calculate the 3 terms in part (d) for both $2s$ and $2p$ cases. I'll do one example and quote results for the others.

Using the expression in the lecture notes

$$\frac{1}{r_{12}} = \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(1) Y_{lm}(2),$$

where the argument 1 in the spherical harmonics means $(\theta_1, \phi_1)$,

$$\begin{aligned}
\langle 1s2p | \tfrac{1}{r_{12}} | 1s2p \rangle &= \int d^3\vec{r}_1 d^3\vec{r}_2 \quad \textstyle\sum_{l,m} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(1) Y_{lm}(2) \\
&\quad \times (2\lambda^{3/2} e^{-\lambda r_1} Y_{00}^*(1)) \times (\tfrac{\sqrt{6}}{12} \lambda^{3/2} \lambda r_2 \, e^{-\lambda r_2/2} Y_{1m'}^*(2)) \\
&\quad \times (2\lambda^{3/2} e^{-\lambda r_1} Y_{00}(1)) \times (\tfrac{\sqrt{6}}{12} \lambda^{3/2} \lambda r_2 \, e^{-\lambda r_2/2} Y_{1m'}(2)).
\end{aligned}$$

We want to evaluate this by using the orthogonality relations for spherical harmonics, but they don't hold if there is other angular dependence (e.g. a third spherical harmonic) in the integral. However, note that $Y^*_{00} = \frac{1}{\sqrt{4\pi}}$ is actually independent of angle, so we can pull it outside the integral. Then we can evaluate the remaining $\theta_1, \phi_1$ angular dependence,

$$\int d\cos\theta_1 d\phi_1 \, Y^*_{lm}(1) Y_{00}(1) = \delta_{l0}\delta_{m0}.$$

We then use the delta functions to cancel the sum and fix $l = 0, m = 0$ elsewhere. That is good because then $Y_{lm}(2) \to Y_{00}(2) = \frac{1}{\sqrt{4\pi}}$, and then there are only two remaining $\theta_2, \phi_2$ spherical harmonics:

$$\int d\cos\theta_2 d\phi_2 \, Y^*_{1m'}(2) Y_{1m'}(2) = 1.$$

We are left with

$$\begin{aligned}
\langle 1s2p|\tfrac{1}{r_{12}}|1s2p\rangle &= \textstyle\int r_1^2 dr_1 \, r_2^2 dr_2 \, \frac{1}{r_>} \times (2\lambda^{3/2} e^{-\lambda r_1}) \times (\frac{\sqrt{6}}{12}\lambda^{3/2}\lambda r_2 \, e^{-\lambda r_2/2}) \\
&\quad \times (2\lambda^{3/2} e^{-\lambda r_1}) \times (\tfrac{\sqrt{6}}{12}\lambda^{3/2}\lambda r_2 \, e^{-\lambda r_2/2}) \\
&= \tfrac{\lambda^8}{6} \textstyle\int dr_1 \, dr_2 \, \frac{1}{r_>} \, r_1^2 \, r_2^4 \, e^{-2\lambda r_1} \, e^{-\lambda r_2}.
\end{aligned}$$

Because of the $1/r_>$ we need to split the integral into two parts,

$$= \frac{\lambda^8}{6} \int dr_1 \, r_1^2 \, e^{-2\lambda r_1} \Big\{ \int_0^{r_1} dr_2 \, \frac{1}{r_1} \, r_2^4 \, e^{-\lambda r_2} + \int_{r_1}^{\infty} dr_2 \, \frac{1}{r_2} \, r_2^4 \, e^{-\lambda r_2} \Big\}.$$

Mathematica does these integrals nicely, giving $\frac{\lambda^8}{6} \times \frac{118}{81\lambda^7}$. Following analagous procedures, I find

$$\begin{aligned}
\langle 1s1s|\tfrac{1}{r_{12}}|1s1s\rangle &= \tfrac{5\lambda}{8} \\
\langle 1s2s|\tfrac{1}{r_{12}}|1s2s\rangle &= \tfrac{17\lambda}{3^4} \\
\langle 1s2s|\tfrac{1}{r_{12}}|2s1s\rangle &= \tfrac{2^4\lambda}{3^6} \\
\langle 1s2p|\tfrac{1}{r_{12}}|1s2p\rangle &= \tfrac{59\lambda}{3^5} \\
\langle 1s2p|\tfrac{1}{r_{12}}|2p1s\rangle &= \tfrac{7\cdot 2^4\lambda}{3^8}.
\end{aligned}$$

Setting $\lambda \to Z$, and then using $Z = 3$,

$$\Delta E_{1s^2 2s} = \frac{5Z}{8} + 2\,\frac{17Z}{3^4} - \frac{2^4 Z}{3^6} \approx 1.022Z \approx 3.068.$$

This contribution raises the energy, as one would expect for electron repulsion, and is a significant offset to the zeroth-order result $E_0 = -\frac{9Z^2}{8} = -\frac{81}{8}$. When we have a $2p$ electron instead,

$$\Delta E_{1s^2 2p} = \frac{5Z}{8} + 2\,\frac{59Z}{3^5} - \frac{7 \cdot 2^4 Z}{3^8} \approx 1.094Z \approx 3.282.$$

In total,

$$\begin{aligned}(E_0 + \Delta E)_{1s^2 2s} &\approx -7.057 \\ (E_0 + \Delta E)_{1s^2 2p} &\approx -6.843.\end{aligned}$$

Confirming our intuition, the total $E_0 + \Delta E$ has smaller magnitude for the $2p$ than the $2s$ case: The $2p$ electron is in a more 'circular' orbit, so it sees less of the nuclear charge (i.e. it is screened more by the inner electrons).

## f)

In our trial wavefunctions we replace $Z$ with $\lambda$ as above. The zeroth-order single-particle contributions to the energy with this wavefunction are

$$\langle 1s|\tfrac{p^2}{2m}|1s\rangle = \tfrac{\lambda^2}{2}, \qquad \langle 2s|\tfrac{p^2}{2m}|2s\rangle = \langle 2p|\tfrac{p^2}{2m}|2p\rangle = \tfrac{\lambda^2}{8},$$

$$\langle 1s|\tfrac{-Z}{r}|1s\rangle = -Z\lambda, \qquad \langle 2s|\tfrac{-Z}{r}|2s\rangle = \langle 2p|\tfrac{-Z}{r}|2p\rangle = -\tfrac{Z\lambda}{4},$$

as you can easily compute. Thus

$$\langle \psi_{var}(1s^2 2s)|H|\psi_{var}(1s^2 2s)\rangle = 2\frac{\lambda^2}{2} + \frac{\lambda^2}{8} - 2Z\lambda - \frac{Z\lambda}{4} + 1.022\lambda,$$

the last being the $\Delta E$ contribution. Minimizing with respect to $\lambda$ (and taking Z=3) gives

$$\begin{aligned}\lambda &\approx Z - \tfrac{4}{9} \cdot 1.022 \approx 2.545, \\ E_{var} &\approx -7.289\end{aligned} \qquad (1s^2 2s).$$

We find $\lambda < Z$, properly reflecting the screening effect of the electrons. As with Helium, the variational energy counters the over-correction from perturbation theory. Repeating for the $1s^2 2p$ case,

$$\begin{aligned}\lambda &\approx 2.514, \\ E_{var} &\approx -7.110\end{aligned} \qquad (1s^2 2p).$$