Physics 221B: Solution to HW #5
The Lithium-like Atom

The ground state will be composed of two electrons in $1s$ with spins up and down and a third electron in an $n = 2$ state. When choosing a state for this third electron we needn't worry about its spin, since the Hamiltonian does not act is spin-space. So lets just say it has spin up. If we choose the $2p$ state we won't specify m, the eigenvalue L_z, since the Hamiltonian is rotationally invariant (i.e. choosing an m will not change anything in our results).

a)

Lets start with notation. $|2s^{\uparrow}\rangle_1$ for example, means a particle in the state $2s$ which is a function of $\vec{x}_1$, with spin $\uparrow$. We can form a Slater determinant

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

and likewise for $|1s^2 2p\rangle$.

b)

The unperturbed Hamiltonian is a sum of three single particle Hamiltonians. Therefore our single particle states are eigenstates of H_0 with their usual energies. Every term in $|1s^2 2s\rangle$ contains the three different single particle states. So,

$$\langle 1s^2 2s|H_0|1s^2 2s\rangle = (2E_{n=1} + E_{n=2})\langle 1s^2|1s^2 2s\rangle = (2E_{n=1} + E_{n=2}),$$

and likewise for $|1s^2 2p\rangle$.

c)

Some more notation— $|\psi_1\rangle_1 \otimes |\psi_2\rangle_2 \otimes |\psi_3\rangle_3 \equiv |\psi_1\psi_2\psi_3\rangle$. The expectation value $\langle \Delta H\rangle$ potentially contains 108 terms because our wave function consists of 6 permutations, and ΔH is the sum of three $1/rij$s. We can reduce this number by using the anti-symmetry of the wavefunction and the orthogonality of single particle states as follows. For example

$$\langle \psi_1\psi_2\psi_3|\frac{1}{r_{12}}|\psi_1\psi_2\psi_3\rangle = -\langle \psi_1\psi_3\psi_2|\frac{1}{r_{12}} - (|\psi_1\psi_3\psi_2\rangle) = \langle \psi_1\psi_2\psi_3|\frac{1}{r_{13}}|\psi_1\psi_2\psi_3\rangle.$$

In the last step we simply switched the labels of particles 2 and 3. Following this we can simplify $\langle \Delta H \rangle$ to

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

We are down to 36 terms.

The operator $1/r_12$ acts only on the particles at $\vec{x}_1$ and $\vec{x}_2$. In other words,

$$\langle \psi_i \psi_j \psi_k | \frac{1}{r_{12}} | \psi_l \psi_m \psi_n \rangle = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_l \psi_m \rangle \langle \psi_k | \psi_n \rangle.$$

By orthogonality, only terms with the same third state in the bra and the ket will survive. This leaves us with the following twelve terms.[1]

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

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

$$\begin{aligned}
\langle \Delta H \rangle &= \langle 1s^{\uparrow} 1s^{\downarrow} | \frac{e^2}{r_{12}} | 1s^{\uparrow} 1s^{\downarrow} \rangle - \langle 1s^{\uparrow} 1s^{\downarrow} | \frac{e^2}{r_{12}} | 1s^{\downarrow} 1s^{\uparrow} \rangle \\
&+ \langle 1s^{\uparrow} 2s^{\uparrow} | \frac{e^2}{r_{12}} | 1s^{\uparrow} 2s^{\uparrow} \rangle - \langle 1s^{\uparrow} 2s^{\uparrow} | \frac{e^2}{r_{12}} | 2s^{\uparrow} 1s^{\uparrow} \rangle \\
&+ \langle 1s^{\downarrow} 2s^{\uparrow} | \frac{e^2}{r_{12}} | 1s^{\downarrow} 2s^{\uparrow} \rangle - \langle 1s^{\downarrow} 2s^{\uparrow} | \frac{e^2}{r_{12}} | 2s^{\uparrow} 1s^{\downarrow} \rangle,
\end{aligned}$$

and likewise for the p states.

[1] Sounds a bit like a beauty contest, doesn't it? we are down to the 12 finalists...

d)

The 2nd and 6th terms vanish by orthogonality of spin wavefunctions. The 3rd and 5th 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 the p states.

e) Perturbation Theory Calculation[2]

In part (f), we will have to distinguish between a variational parameter λ and the charge Z in the Hamiltonian which isn't varied, so I will use λ in the wavefunctions in this calculation. I use atomic units (in these units $e^2/a \equiv 1$. To get an energy in eV, multiply the results by 27.2 eV). 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 (θ_1, ϕ_1),

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

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 θ_1, ϕ_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

[2] I thank Ed Boyda for TEXing the following sections.

there are only two remaining θ_2, ϕ_2 spherical harmonics:

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

We are left with

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

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 analogous 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,

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

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) Variational Calculation

In our trial wavefunctions we replace Z with λ 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 ΔE contribution. Minimizing with respect to λ (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,

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