HW #5 (221B), due March 1, 4pm

1. Consider an atom with three electrons, such as Li, Be^+, B^{++}. The Hamiltonian is

$$\begin{aligned} H &= H_0 + \Delta H && (1) \\ H_0 &= \sum_{i=1}^{3} \left(\frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) && (2) \\ \Delta H &= +\sum_{i<j} \frac{e^2}{r_{ij}}. && (3) \end{aligned}$$

The unperturbed Hamiltonian is the same as in the hydrogen-like atoms and hence solvable. The states $2s$ and $2p$ remain degenerate at this point. Therefore we should consider both the electron configurations $1s^2 2s$ and $1s^2 2p$. Answer the following questions.

(a) Write down the totally anti-symmetric wave function of three electrons for the unperturbed case. Do not use the explcit forms of the wave functions, but rather use symbolic labels $|1s^\uparrow\rangle$, $|2p^\downarrow\rangle$, etc.

(b) Show that the expectation value of H_0 is simply a sum of three single-particle energies.

(c) Show that the expectation value of $\Delta E = \langle 1s^2 2s^\uparrow | \Delta H | 1s^2 2s^\uparrow \rangle$ is given by

$$\begin{aligned} \Delta E &= \langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle - \langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \\ &+ \langle 1s^\uparrow 2s^\uparrow | \frac{e^2}{r_{12}} | 1s^\uparrow 2s^\uparrow \rangle - \langle 1s^\uparrow 2s^\uparrow | \frac{e^2}{r_{12}} | 2s^\uparrow 1s^\uparrow \rangle \\ &+ \langle 1s^\downarrow 2s^\uparrow | \frac{e^2}{r_{12}} | 1s^\downarrow 2s^\uparrow \rangle - \langle 1s^\downarrow 2s^\uparrow | \frac{e^2}{r_{12}} | 2s^\uparrow 1s^\downarrow \rangle \quad (4) \end{aligned}$$

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

(d) The perturbation e^2/r_{12} does not affect the spin. Because of that, some of the terms in the above equation trivially vanish, and some of them are equal. Which one are they?

(e) Calculate ΔE for both $1s^2 2s$ and $1s^2 2p$ configurations.

(f) Further improve the calculation using the variational method, by varying Z in the wave function (not in the Hamiltonian).

Note According to the table Dan Haxton found for me, the ionization potentials for Li are 5.39172, 75.64018, 122.45429 eV for Li, Li^+, and Li^{++}.