

## HW #6 (221B), due Feb 25, 4pm

1. Consider an atom with three electrons, such as Li, Be<sup>+</sup>, B<sup>++</sup>. The Hamiltonian is

$$H = H_0 + \Delta H \quad (1)$$

$$H_0 = \sum_{i=1}^3 \left( \frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) \quad (2)$$

$$\Delta H = + \sum_{i < j} \frac{e^2}{r_{ij}}. \quad (3)$$

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 explicit 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

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

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  $\Delta E$  for both  $1s^2 2s$  and  $1s^2 2p$  configurations. Which one is the ground state?
- (f) Further improve the calculation using the variational method, by varying  $Z$  in the wave function (not in the Hamiltonian).

- (g) The ionization potentials for Li are 5.39172, 75.64018, 122.45429 eV for Li, Li<sup>+</sup>, and Li<sup>2+</sup>. Compare your result with the observed values.