

1. In the table below, circle the orbital with the *lowest* energy in each row (i.e., the *most stable* orbital).

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|----|---|--|---|---|
| a. | He 1s | U 1s | Li 1s | U has highest Z value; shielding doesn't much affect the core electrons |
| b. | Fe 3d | Fe 4s | Fe 4p | The expected ordering, and can be verified from Fe ground state config. |
| c. | F 1s | F⁺ 1s | F ⁻ 1s | F ⁺ will have lower electron-electron repulsion because fewer electrons |
| d. | Li 2s | Na 3s | K 4s | Valence electron is harder to ionize so more stable at lower n |
| e. | O 2p | F 2p | Ne 2p | Across a row, orbital gets more stable because each added electron doesn't completely cancel the added proton |

2. The zero-order electronic energy of the Be atom is calculated assuming that each electron interacts with only the nucleus, as though in a one-electron atom.

- (a) Calculate the complete *zero-order* energy (in E_h) of ground state Be. **Solution:** The ground state electron configuration is $1s^2 2s^2$, and $Z = 4$, so

$$E_0 = \sum_{i=1}^4 - \left(\frac{Z^2}{2n_i^2} \right) = -\frac{16}{2} \left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2} + \frac{1}{2^2} \right) = \boxed{-20.00 E_h}.$$

- (b) Calculate the **total** *first-order* energy (in E_h) of ground state Be.

$$\begin{aligned} \iint 1s(1)^2 1s(2)^2 \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) d\tau_1 d\tau_2 &= 2.494 E_h \\ \iint 2s(1)^2 2s(2)^2 \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) d\tau_1 d\tau_2 &= 0.598 E_h \\ \iint 1s(1)^2 2s(2)^2 \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) d\tau_1 d\tau_2 &= 0.839 E_h \end{aligned}$$

Solution: We count the repulsion energy for each pair of electrons once. Because there are two 1s electrons and two 2s electrons, there are four distinct (1s)(2s) interactions, so we count that integral four times to get the first-order correction. To get the total energy to first order, we add that correction to E_0 :

$$\begin{aligned} E_1^{\text{PT}} &= 2.494 + 0.598 + 4(0.839) = 6.448 E_h \\ E_0 + E_1^{\text{PT}} &= -20.00 + 6.448 E_h = \boxed{-13.55 E_h}. \end{aligned}$$

As a check, we see that this value is somewhat higher than the correct total energy $-14.668 E_h$ in Table 3.1, but much closer than the zero-order energy.

3. Two atoms of ${}^3\text{He}$ occupy the ground state of a one-dimensional box of length a . The ${}^3\text{He}$ nucleus has a spin of $1/2$ and the two electrons have canceling spins, so each atom can be treated as a single particle with total spin of $1/2$ and spin wavefunctions α and β (as for a single electron). Write the normalized and symmetrized two-atom wavefunction for this state. **Solution:** The two atoms will have the same spatial wavefunction, the $n = 1$ ground state function for the particle in a one-dimensional box, so $\psi(1, 2) = \psi_{n=1}(x_1)\psi_{n=1}(x_2)$. Because this is a symmetric spatial wavefunction, and because the atoms are spin $1/2$ fermions, the spin wavefunction must be the antisymmetric wavefunction $(\alpha\beta - \beta\alpha)/\sqrt{2}$:

$$\Psi(1, 2) = \psi_{n=1}(x_1)\psi_{n=1}(x_2)(\alpha\beta - \beta\alpha)/\sqrt{2} = \left(\frac{2}{a}\right) \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right) (\alpha\beta - \beta\alpha)/\sqrt{2}.$$

4. Write the Hamiltonian for LiH^+ . **Solution:** We need kinetic energy terms for the two nuclei and the three electrons, and a potential energy term for each of the ten interactions between the five particles:

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{\hbar^2}{2m_{\text{H}}} \nabla_{\text{H}}^2 - \frac{\hbar^2}{2m_{\text{Li}}} \nabla_{\text{Li}}^2 + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}} + \frac{3}{R_{\text{Li-H}}} - \frac{3}{r_{1,\text{Li}}} - \frac{3}{r_{2,\text{Li}}} - \frac{3}{r_{3,\text{Li}}} - \frac{1}{r_{1,\text{H}}} - \frac{1}{r_{2,\text{H}}} - \frac{1}{r_{3,\text{H}}} \right)$$

5. A neutral atom from the second row of the periodic table (Li–Ne) has an excited electron configuration that leads to the term states 2D , 2P , $2S$, and 4P .

- (a) Write these term symbols, including J values, in order of increasing energy.

Solution: Highest S comes first, then for the doublet terms the energy increases as L drops. The correct ordering of the J values actually depends on your answer to the following question. $\boxed{{}^4P_{1/2,3/2,5/2}, {}^2D_{3/2,5/2}, {}^2P_{1/2,3/2}, {}^2S_{1/2}}$.

- (b) Identify the atom and the lowest energy electron configuration that leads to these terms. **Solution:** The term symbols tell us the possible values for the total spin are $S = 3/2$ (but only when $L = 1$) and $S = 1/2$ (when L can be 0, 1, or 2). To get a half-integer value of S , the electron configuration must have an odd number of electrons. To get $S = 3/2$ we would need three electrons, each in a separate orbital and all with the same m_s . The three electrons could be in the $2p$ subshell, but then there's no way to get $L = 1$ at the same time (the m_l values would all cancel). Instead, we can put one electron in the $2s$ orbital, and the other two in the $2p$ orbitals. We check that this also allows $L = 2$ (both $2p$ electrons in the $m_l = 1$ orbital give $M_L = 2$), but only when two of the spins cancel, so $S = 1/2$. So the lowest energy electron configuration with these terms is $\boxed{1s^2 2s 2p^2}$, and with five electrons, that means the neutral atom has $Z = 5$, so it must be $\boxed{\text{B}}$. It turns out that you get the same set of terms with $1s^2 2s 2p^4$ N, but then the higher J values will be the lower energy.