

1. 40 points.

(a) The Hamiltonian for atomic Li can be written

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) - \frac{3e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right).$$

Circle the perturbation and **box** the zero-order Hamiltonian.

(b) Referring to the Hartree-Fock orbital energies for ground state atomic lithium:

i. what is the ionization energy of the 2s electron? $\boxed{0.196 E_h}$ ii. what is the total ionization energy to form Li^{3+} ? $\boxed{7.433 E_h}$ iii. is the total Hartree-Fock energy $\boxed{\text{higher}}$ (less negative) or lower (more negative) in the lowest excited state than in the ground state?iv. is the 1s orbital energy higher (less negative) or $\boxed{\text{lower}}$ (more negative) in the lowest excited state than in the ground state?(c) For the 4F ground state term of atomic iridium,i. what is the value of L ? $\boxed{3}$ ii. what is the value of S ? $\boxed{3/2}$ (d) Write the Hamiltonian for H_3^+ . **Solution:** There are two electrons and three nuclei:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0} \left[-\frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{C1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} - \frac{1}{r_{C2}} \right. \\ & \left. + \frac{1}{r_{12}} + \frac{1}{R_{AB}} + \frac{1}{R_{AC}} + \frac{1}{R_{BC}} \right] - \frac{\hbar^2}{2m_H} (\nabla_A^2 + \nabla_B^2 + \nabla_C^2) \end{aligned} \quad (1)$$

2. The variational method is used to solve the Schrödinger equation for a particle of mass m with potential energy $U(r) = kr$, starting with a variational (normalized) wavefunction $\psi(r) = 2a^{3/2}e^{-ar}$. The variational parameter is a . The expectation value of the energy obeys the equation $\langle E \rangle = \frac{\hbar^2 a^2}{2m} + \frac{3k}{2a}$. Find the optimized wavefunction and its energy. **Solution:** We want to vary a to get the lowest possible value for $\langle E \rangle$, so we take the derivative to find the minimum of $\langle E \rangle$ as a function of a :

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial a} &= \frac{\partial}{\partial a} \left(\frac{\hbar^2 a^2}{2m} + \frac{3k}{2a} \right) = \frac{\hbar^2 a}{m} - \frac{3k}{2a^2} = 0 \\ \frac{\hbar^2 a}{m} &= \frac{3k}{2a^2} \quad a^3 = \frac{3km}{2\hbar^2} \quad a = \left(\frac{3km}{2\hbar^2} \right)^{1/3} \\ \psi(r) &= 2 \left(\frac{3km}{2\hbar^2} \right)^{1/2} \exp \left[- \left(\frac{3km}{2\hbar^2} \right)^{1/3} r \right] \end{aligned}$$

$$\begin{aligned}\langle E \rangle &= \left(\frac{\hbar^2}{2m} \right) \left(\frac{3km}{2\hbar^2} \right)^{2/3} + \left(\frac{3k}{2} \right) \left(\frac{2\hbar^2}{3km} \right)^{1/3} \\ &= \left(\frac{3}{2} \right)^{5/3} \left(\frac{k^2 \hbar^2}{m} \right)^{1/3}\end{aligned}$$

3. What is the one term missing from the following symmetrized wavefunction for the $1s^2 2s 3s$ excited state of Be?

$$\begin{aligned}\Psi = & 1s1s2s3s\alpha\beta\alpha\alpha - 1s1s3s2s\alpha\beta\alpha\alpha - 1s2s1s3s\alpha\alpha\beta\alpha + 1s2s3s1s\alpha\alpha\alpha\beta \\ & + 1s3s1s2s\alpha\alpha\beta\alpha - 1s3s2s1s\alpha\alpha\alpha\beta + 1s1s2s3s\beta\alpha\alpha\alpha - 1s1s3s2s\beta\alpha\alpha\alpha \\ & - 1s2s1s3s\beta\alpha\alpha\alpha + 1s2s3s1s\beta\alpha\alpha\alpha + 1s3s1s2s\beta\alpha\alpha\alpha - 1s3s2s1s\beta\alpha\alpha\alpha \\ & + 2s1s1s3s\alpha\alpha\beta\alpha - 2s1s3s1s\alpha\alpha\alpha\beta - 2s1s1s3s\alpha\beta\alpha\alpha + 2s1s3s1s\alpha\beta\alpha\alpha \\ & + 2s3s1s1s\alpha\alpha\alpha\beta - 3s1s1s2s\alpha\alpha\beta\alpha + 3s1s2s1s\alpha\alpha\alpha\beta + 3s1s1s2s\alpha\beta\alpha\alpha \\ & - 3s1s2s1s\alpha\beta\alpha\alpha - 3s2s1s1s\alpha\alpha\alpha\beta + 3s2s1s1s\alpha\alpha\beta\alpha\end{aligned}$$

Solution: (i) For the electrons to be indistinguishable, each electron must be equally represented in the four states $1s\alpha$, $1s\beta$, $2s\alpha$, and $3s\alpha$. There are 6 terms with electron 1 in the $1s\alpha$ state, 6 terms where it's in the $1s\beta$, and 6 terms with electron 1 in the $3s$ orbital. So we're missing a term with electron 1 in the $2s$ orbital. (ii) If electron 1 is in the $2s$, then electron 2 has an equal chance of being in the $1s\alpha$ state, the $1s\beta$, or the $3s$. There is only one term with $2s(1)3s(2)$, so we need one more. The one we have is $2s3s1s1s\alpha\alpha\alpha\beta$, so the missing term has the other arrangement for electron 3 and 4, and looks like $2s3s1s1s\alpha\alpha\beta\alpha$. (iii) For Ψ to be antisymmetric under exchange of two electron labels, there must be an equal number of terms with and without minus signs in front. Of the 5 terms shown with electron 1 in the $2s$, 2 have minus signs and 3 don't. So the missing term has a leading minus sign. The missing term is $\boxed{-2s3s1s1s\alpha\alpha\beta\alpha}$.

4. Find all the term states, including J values, resulting from the electron configuration $[\text{Kr}]5s4d$ of strontium, and list the term symbols **in order of increasing energy**. Don't worry about the order of the J values. (It is not necessary to work through the whole vector model to find the terms; there are 20 microstates if you do.)

Solution: First, we ignore all the electrons in filled subshells. The overall L value must be 2, because the $5s$ electron has no orbital angular momentum, and the d electron has $l = 2$, so the vector sum of the l 's is 2. The only possible values of S are 0 (if the two electron spins cancel) and 1 (if they add up). So the two terms resulting are the 1D and 3D . For the 1D , the only J value is $|L - S| = L + S = 2$. For the 3D , the possible J values are 1, 2, and 3. The higher-spin 3D state is the lowest in energy: $\boxed{^3D_{1,2,3} < ^1D_2}$.