1. **40 points.**

   (a) Write the Hamiltonian for the electrons in the $C^{3+}$ ion. **Solution:** $C^{3+}$ has 3 electrons and atomic number $Z = 6$, so we have 3 kinetic energy terms, 3 electron-nucleus potential energy terms, and $3(3-1)/2 = 3$ electron-electron repulsion terms:

   $$\hat{H} = -\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right] - \frac{6e^2}{4\pi\epsilon_0}\left[\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right] + \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}\right].$$

   (b) In the circles below, fill in the correct signs ($+$ or $-$) that make the overall wavefunction antisymmetric with respect to exchange of the labels on electrons 1 and 2. **Solution:** The first and second terms have electrons 1 and 2 switched; and the third and fourth terms have electrons 1 and 2 switched. The relative signs of the two terms in each group must be opposite for the function to change sign under $\hat{P}_{21}$:

   $$\Psi(1,2) = \exp(-r_1/a_0)\exp(-2r_2/a_0)\alpha(1)\beta(2) \ominus \exp(-2r_1/a_0)\exp(-r_2/a_0)\beta(1)\alpha(2)$$

   $$\oplus \exp(-r_1/a_0)\exp(-2r_2/a_0)\beta(1)\alpha(2) \ominus \exp(-2r_1/a_0)\exp(-r_2/a_0)\alpha(1)\beta(2)$$

   It is also okay if the third and fourth terms have $-$ and $+$ respectively; it only matters (for this problem) that they have opposite signs.

   (c) Rank the following in order of increasing energy (less negative = higher energy) of the valence electrons: He, Ar, K. **Solution:** The higher energy the orbital, the closer to ionization, so this is the same as asking to put the atoms in order of *decreasing* first ionization energy. Following the periodic trends, we would arrange them as follows: $\boxed{\text{He}<\text{Ar}<\text{K},}$ meaning that helium has the most stable valence electrons (lowest energy, hardest to ionize).

   (d) Rank the following in order of increasing energy (less negative = higher energy) of the $1s$ core electrons: He, Ar, K. **Solution:** The core electrons in a neutral atom have a single trend: the energy becomes more negative as the nuclear charge increases, regardless of what $n$ value the valence electrons have: $\boxed{\text{K}<\text{Ar}<\text{He.}}$
   Both of these trends appear in the Table of HF energies in Table 3.1.

2. The zero-order system is the particle in a 1D box that runs from $x = 0$ to $a$, and the perturbation is $U_a(x) = E_1(1 - \frac{x}{a})$, where $E_1$ is the zero-order ground state energy, and is equal to $0.100\,E_h$.

   (a) Make a graph of the potential energy function below.

   (b) On your graph, draw a line for the zero order energy.

   (c) Calculate the ground state energy to first order.

   (d) On your graph, draw a line for the first order energy.

   (e) Finally, on your line for the first order energy, sketch the first order wavefunction.

   **Solution:**

   (a) $U_a(x)$ is a straight line with negative slope, from energy $E_1$ at $x = 0$ to 0 at $x = a$.

   (b) $E_1$ is a horizontal line from the top of $U_a(x)$.
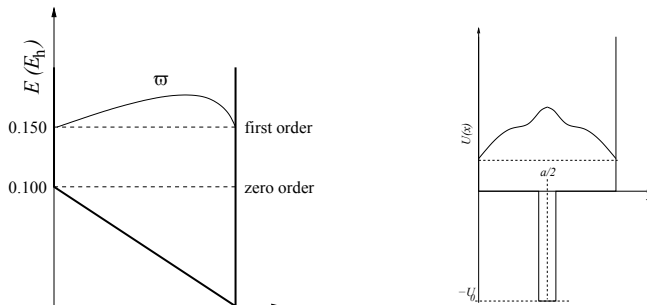
(c) The first order correction is:

$$E_1^{\text{PT}} = \int_0^a \psi(x)^2 \, U_a(x) \, dx = \frac{2E_1}{a} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\left(1 - \frac{x}{a}\right) dx = \frac{2E_1}{a}\frac{a}{4} = \frac{E_1}{2}.$$

We add the first order correction to the zero-order energy to get the first order energy:

$$E_0^{\text{PT}} + E_1^{\text{PT}} = E_1 + frac{E_1}{2} = \frac{3}{2}E_1 = \boxed{0.150 \, E_{\text{h}}.}$$

(d) See below.

(e) The wavefunction, like the case in Example 3.4, leans in the direction of lower energy.



3. We add a well in the middle of a one-dimensional box (see above). Our variational wavefunction is

$$\psi(x)^{\text{var}} = \sum_{n=1}^{3} c_n \sin\left(\frac{n\pi x}{a}\right),$$

where we vary the three parameters $c_1$, $c_2$, and $c_3$. After the variational problem is solved:

(a) Which parameter has the greatest magnitude? **Solution:** $\boxed{c_1}$ The contribution from the $n = 1$ state will still be greatest. The variational ground state function should still have no nodes.

(b) Which parameter is zero? **Solution:** $\boxed{c_2}$ The $n = 2$ state has opposite phase in each half of the box, so adding this in will shift the wavefunction to one side or the other. This is no benefit when the potential looks the same in both halves of the box, so the variational function will not use the $n = 2$ state.

(c) **Sketch the variational wavefunction. Solution:** The ground state function should have no nodes, and will look like a combination of (mostly) $n = 1$ plus some $n = 3$, which will cause it to peak in the middle where the potential energy reaches its minimum value.

4. The hydride ion, $H^-$, has the same number of electrons as atomic helium, He. Write the value of each parameter for $H^-$ if you can, or compare to the value for He with ">" if the value for $H^-$ is *greater* than the value for He, and "<" if it is *less than* the value for He.

| | He | $H^-$ | |
|---|---|---|---|
| $Z$ | 2 | 1 | the atomic number for H is 1 no matter what charge |
| $Z_{\text{eff}}$ | 1.69 | < | take away one proton from He, and $Z_{\text{eff}}$ must decrease |
| $\epsilon_1$ ($E_{\text{h}}$) | $-0.917$ | > | weaker e-nuc attraction, so $H^-$ orbital energy is greater |
| $E_{\text{HF}}$ ($E_{\text{h}}$) | $-2.862$ | > | and so too must the total energy be greater. |
| zero-order energy ($E_{\text{h}}$) | $-4.00$ | $-1.00$ | The zero order energy is the energy of two H electrons, each with energy $-E_{\text{h}}/2$ |
| first-order correction ($E_{\text{h}}$) | $+1.25$ | < | The e-erepulsion is less in $H^-$ because the electrons not so close to the nucleus |

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