1. **40 points.**

(a) Write the perturbation term $\hat{H}'$ in the Hamiltonian for the lithium atom. **Solution:** Lithium has three electrons, and the perturbation Hamiltonian contains the electron-eletron repulsion terms:

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}} \right)$$

(b) Calculate the zero order energy in $E_{\mathrm{h}}$ for the ground state lithium atom. **Solution:** the electron configuration is $1s^2 2s^1$, so there are two $n = 1$ electrons and one $n = 2$ electron. For the zero-order energy, we apply the Bohr energy to each electron:

$$E_0 = -\sum_i^N \frac{Z^2}{2n_i^2} E_{\mathrm{h}} = -\frac{3^2}{2} \left( \frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2} \right) E_{\mathrm{h}} = -\frac{9}{2} \left( \frac{9}{4} \right) E_{\mathrm{h}} = \boxed{ -\frac{81}{8} E_{\mathrm{h}}.}$$

(c) The *binding region* is the region between two nuclei in which the binding force (as we've defined it) is positive, and forces pulling the two nuclei together exceed the forces pulling them apart. Indicate whether each of the following changes, if we could make them, would increase (write "$+$") or decrease (write "$-$") the volume of the binding region:

    i. making the electron charge more negative. $\boxed{+}$ because the opposite charge of the electron is what pulls the nuclei together, overcoming the nuclear-nuclear repulsion.

    ii. making the nuclear charge more positive. $\boxed{-}$ because the repulsion between the nuclei is always a negative contribution to the binding force.

    iii. increasing the separation between the nuclei. $\boxed{+}$ because a greater distance between the nuclei reduces the nuclear-nuclear repulsion. The binding force will also get smaller in magnitude, but will still be positive between the two nuclei (if it was before).

(d) Write the Hamiltonian for the molecule $\mathrm{HeH}^-$. **Solution:** There are two nuclei and four electrons, so six kinetic energy terms, and $6(6-1)/2 = 15$ potential energy terms for each interacting pair of particles (don't forget to use the correct nuclear charges: $e$ for H and $2e$ for He):

$$\hat{H} = -\frac{\hbar^2}{2} \left[ \frac{1}{m_e} \nabla(1)^2 + \frac{1}{m_e} \nabla(2)^2 + \frac{1}{m_{\mathrm{He}}} \nabla(\mathrm{He})^2 + \frac{1}{m_{\mathrm{H}}} \nabla(\mathrm{H})^2 \right]$$

$$+ \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}} + \frac{2}{R} \right.$$

$$\left. -\frac{1}{r_{\mathrm{H}1}} - \frac{1}{r_{\mathrm{H}2}} - \frac{1}{r_{\mathrm{H}3}} - \frac{1}{r_{\mathrm{H}4}} - \frac{2}{r_{\mathrm{He}1}} - \frac{2}{r_{\mathrm{He}2}} - \frac{2}{r_{\mathrm{He}3}} - \frac{2}{r_{\mathrm{He}4}} \right]$$

2. Fill in the electron configurations in table below for the ground state of F and the lowest excited state of $\mathrm{F}^-$. In the other rows of the table, Hartree-Fock energy values for F atom are given. For $\mathrm{F}^-$, write $\uparrow$ if the value is greater than for F atom, $\downarrow$ if it is less than for F atom, and "0" if it is the same.

| | ground state F | lowest excited state F⁻ |
|---|---|---|
| electron configuration | $1s^2 2s^2 2p^5$ | $1s^2 2s^2 2p^5 3s^1$ |
| total energy | $-99.402\,E_{\mathrm{h}}$ | ↓ |
| average energy per electron | $-11.045\,E_{\mathrm{h}}$ | ↑ |
| $1s$ orbital energy | $-26.368\,E_{\mathrm{h}}$ | ↑ |
| total kinetic energy | $99.300\,E_{\mathrm{h}}$ | ↑ |
| average kinetic energy per electron | $11.033\,E_{\mathrm{h}}$ | ↓ |
| total electron-electron repulsion | $39.796\,E_{\mathrm{h}}$ | ↑ |

3. For the $1s^2 2s^2 2p^4 3p^4$ excited electron configuration of atomic calcium:

   (a) **Begin** to apply the vector model to this system by drawing out **any four** distinct, valid microstates for this electron configuration, and give the $M_L$ and $M_S$ values for each. **Solution:** Any microstates that obey Pauli exclusion for four electrons in the $2p$ subshell and four electrons in the $3p$. Some examples:

| $2p$ | | | $3p$ | | | $M_L$ | $M_S$ |
|---|---|---|---|---|---|---|---|
| ↑ | ↑ | ↑↓ | ↑ | ↑ | ↑↓ | $+2$ | $+2$ |
| ↑↓ | ↑ | ↑ | ↑↓ | ↑ | ↓ | $-2$ | $+1$ |
| ↑ | ↑↓ | ↑ | ↑↓ | ↑ | ↓ | $-1$ | $+1$ |
| ↑↓ | ↑↓ | | ↑↓ | ↑ | ↓ | $-3$ | $0$ |
| ↑↓ | ↑↓ | | ↑↓ | ↑↓ | | $+4$ | $0$ |

   (b) In the complete vector model, how many microstates have *all* the electrons paired? **Solution:** To pair all the electrons, we have to fill two of the three orbitals in each of the $2p$ and $3p$ subshells. There are three ways to do that for the $2p$ (fill the $m_l = -1, 0$, or the $-1, +1$, or the $0, +1$ orbitals) and three ways for the $3p$, Altogether, therefore, there are $\boxed{9}$ different microstates in which all the electrons are paired.

   (c) There were 15 microstates for the ground state oxygen atom. What is the total number of microstates in this case? **Solution:** The microstates in oxygen all arise from permutations of the electrons in the $2p$ subshell. Here we would have to look at all combinations of those 15 microstates with the 15 distinct microstates of the $3p^4$ configuration, for a total of $15 \times 15 = \boxed{225.}$

   (d) What is the greatest possible value of $S$ for this configuration? **Solution:** We can have at most two unpaired electrons in each $p$ subshell, which gives a maximum $M_S$ (and therefore a maximum $S$ value) of $\boxed{+2.}$

   (e) What is the greatest possible value of $L$? **Solution:** If we push as many electrons over to the right (maximum $m_l$, the last example in the microstate drawings above), the greatest possible value of $M_L$ (and therefore of $L$) is $\boxed{+4}$.

   (f) What is the greatest possible value of $J$? **Solution:** $L = 4$ is possible only when all electrons are paired (so $S = 0$ for that term), and $M_S = 2$ is possible only for a maximum $M_L$ of $+2$ (see the first microstate drawing above). So the greatest possible value of $L$ for $S = 2$ is $L = 2$. Even if there are terms with $L = 3$, the value of $S$ will have to drop at least to $S = 1$. No matter what, the maximum possible $J$ value is $\boxed{4.}$

4. Consider a set of three $^{16}$O atoms. The nuclear spin of the $^{16}$O nucleus is zero.

   (a) What is the total spin quantum number $S$ of each oxygen atom in its ground electronic term state? **Solution:** From Example 4.4, we know that the maximum possible $S$ value of the electrons in ground state oxygen is $S = 1$. Combined with a nuclear spin of 0, that still gives a total spin of $\boxed{1.}$

(b) Is each oxygen atom (counting all the particles in the atom) a boson or a fermion? **Solution:** Since the spin quantum num,ber is an integer, the complete $^{16}$O atom is a $\boxed{\text{boson.}}$

(c) We place the three atoms in a one-dimensional box with quantum states identified by the quantum number $n$, where for example the $n = 1$ state of oxygen atom 2 may be written $\psi_1(2)$. Write the **three-particle** spatial wavefunction for the lowest energy state of the three atoms in this box. **Solution:** As bosons, all three atoms are not subject to Pauli exclusion and may occupy the lowest energy state simultaneously. (Since the spin is 1, each atom could have a different $M_S$ value and we wouldn't have to worry about Pauli exclusion anyway.) The lowest energy three-particle state is therefore $\boxed{\psi_1(1)\,\psi_1(2)\,\psi_1(3).}$

(d) Let the total spin quantum number of all three atoms be equal to $S_T$, with projection onto the $z$ axis given by the magnetic quantum number $M_{ST}$. What is the maximum value of $S_T$? **Solution:** If all the O atom spins add together, each with $S = 1$, we can get a total spin of $\boxed{3.}$

(e) For that maximum value of $S_T$, give all the possible values of $M_{ST}$. **Solution:** For any angular momentum quantum number $X$, the magnetic quantum number values go from $-X$ to $+X$ in units of one. Here, that would be $\boxed{M_{ST} = -3, -2, -1, 0, 1, 2, 3.}$

(f) Finally, use $\alpha$ to label the spin wavefunction for the maximum value of $M_S$, use $\beta$ for the next lowest $M_S$, and $\gamma$ for the next, and so on. Write one valid spin wavefunction to go with your spatial wavefunction such that $M_{ST} = 0$. **Solution:** We call $M_S = 1$ the $\alpha$ function, $\beta$ is $M_S = 0$, and $\gamma$ is $M_S = -1$. To get $M_{ST} = 0$ we need either all three atoms in the $\beta$ spin state:

$$\beta(1)\beta(2)\beta(3)$$

or one each in $\alpha$, $\beta$, and $\gamma$. But for the second option, we need to make sure that all three electrons are equally represented in each spin state. Writing each term in the order electron 1, 2, and 3:

$$\frac{1}{\sqrt{6}}\left[\alpha\beta\gamma + \alpha\gamma\beta + \beta\alpha\gamma + \beta\gamma\alpha + \gamma\alpha\beta + \gamma\beta\alpha\right].$$

Either of these two solutions is acceptable.