1a) Estimate the lattice energy for CsCl if the Cs-Cl internuclear distance is 356.6 pm.

We can use the Born-Landé equation, with the Madelung constant for CsCl = 1.76267, and the Born exponent = 10.5 (average of Cs\(^+\) and Cl\(^-\)) to get the lattice energy:

\[
U_0 = \frac{(1.76267)(6.022\times10^{23})(1)(-1)(1.60210\times10^{-19})^2}{(4)(3.14159)(8.854185\times10^{-12})(3.566\times10^{-10})}\left(1 - \frac{1}{10.5}\right)
\]

\[
= (-1373.35 \text{ kJ/mol})(0.904762) = -621.5 \text{ kJ/mole}.
\]

b) Now consider a polymorph of CsCl that crystallizes with the NaCl lattice; estimate its lattice energy if the Cs-Cl distance is 347.4 pm.

This simply changes the Madelung constant, as well as the \(r_0\) value:

\[
U_0 = \frac{(1.74756)(6.022\times10^{23})(1)(-1)(1.60210\times10^{-19})^2}{(4)(3.14159)(8.854185\times10^{-12})(3.474\times10^{-10})}\left(1 - \frac{1}{10.5}\right)
\]

\[
= (-1397.64 \text{ kJ/mol})(0.904762) = -632.3 \text{ kJ/mole}.
\]

c) What conclusions can you draw from your answers to parts (a) and (b)?

Crystal structures are based on more than simply lattice energies.

2) ReO\(_3\) is a structure-prototype. Each Re(VI) center is octahedrally sited with respect to the O\(^2-\) centers. The unit cell can be described in terms of a cubic array of Re(VI) centers, with each O\(^2-\) center at the center of each edge of the unit cell. Draw a representation of the unit cell and use your diagram to confirm the stoichiometry of the compound.

Well, here is the picture of the requested compound. Solid spheres represent Re(VI), and open spheres represent O\(^2-\).
If we now carefully look at our structure, we see that in one unit cell we have eight corners (comprising the Re(VI) centers) which are \(1/8\)th “owned” by the unit cell, giving us one Re(VI) atom. Similarly, we have 12 atoms at the center of the sides (representing the O\(^2\-) centers) which are \(1/4\)th “owned” by the unit cell, giving us 3 O\(^2\-) atom. Thus, our ratio is shown to be 1:3 which is what the formula would lead us to conclude.

3) Consider the compound ClF. Using the electronegative values \(a\) and \(b\) derived by Mulliken, at what charge distribution should \(\chi(\text{Cl}) = \chi(\text{F})\)?

Given the compound ClF, we can use the formula \(\chi_X = a + bq\) to calculate the charge at which the electronegativities are equal \(i.e.\ \chi_F = \chi_{\text{Cl}}\). At this point, we need to realize that the charge on F is the negative of the charge on Cl. (since the ClF molecule is neutral), so our equation gets somewhat easier to solve. Choosing the Mulliken-Jaffe electronegativity values for 14% s (approximately sp\(^6.14\) hybridization), we get:

\[
\chi_{\text{Cl}} = 12.15 + 11.55q_{\text{Cl}} = \chi_F = 15.30 + 17.81q_{\text{F}}
\]

which, using our realization from above, can be simplified to:

\[
12.15 - 11.55q_{\text{F}} = 15.30 + 17.81q_{\text{F}}.
\]

Rearranging to solve for \(q_{\text{F}}\), we get: 
\[-3.15 = 29.36q_{\text{F}}\] which gives a \(q_{\text{F}} = -0.107\) and a \(q_{\text{Cl}} = +0.107\).

(Using the values for a p-orbital gives \(q_{\text{F}} = -0.0431\) and \(q_{\text{Cl}} = +0.0431\))

4) The sp\(^2\) hybrid orbitals spoken of in Valence Bond Theory have the form:

(a) \(\frac{1}{\sqrt{3}} \psi_{2s} + \frac{\sqrt{2}}{\sqrt{3}} \psi_{2px}\)

(b) \(\frac{1}{\sqrt{3}} \psi_{2s} - \frac{1}{\sqrt{6}} \psi_{2px} + \frac{1}{\sqrt{2}} \psi_{2py}\)
(c) $\frac{1}{\sqrt{3}} \psi_{2s} - \frac{1}{\sqrt{6}} \psi_{2px} - \frac{1}{\sqrt{2}} \psi_{2py}$

i) Show that (a) and (c) correspond to normalized wavefunctions.

To demonstrate normalization, we need simply to demonstrate that $\Phi^2 = 1$ (more properly, that $<\Phi|\Phi^*>=1$). Before doing so, however, we need to realize that $\psi_{2s}\psi_{2px} = 0$ and $\psi_{2s}\psi_{2s} = \psi_{2px}\psi_{2px} = 1$. More generally, this means that all crossterms go to zero, and all identical terms go to one. Therefore, we have $\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{2}{\sqrt{3}}\right)^2 = (1/3) + (2/3) = 1$.

So (a) is normalized as written. Similarly for (c): $\left(\frac{1}{\sqrt{3}}\right)^2 + (-\frac{1}{\sqrt{6}})^2 + (-\frac{1}{\sqrt{2}})^2 = (1/3) + (1/6) + (1/2) = (2/6) + (1/6) + (3/6) = 6/6 = 1$ and (c) is properly normalized.

ii) Demonstrate that (a) and (c) are orthogonal.

Here we can use the same realizations as we did above, and get: $\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{2}{\sqrt{3}}\right)(-\frac{1}{\sqrt{6}}) = (1/3) - (1/3) = 0$ and thus (a) and (c) are orthogonal.

5) Demonstrate that, in agreement with Pauling’s reasoning about homonuclear diatomics, the form $H^+H^-$ does not make an appreciable contribution to the stability of $H_2$. Recall that here $\chi_a = \chi_b$, and that $\psi = a\phi_{\text{covalent}} + b\phi_{\text{ionic}}$. (Hint: use a Born-Haber type calculation. For $H_2$, $r = 74.1$ pm, and $E = -458$ kJ/mol)

Taking the hint given in the problem, we need to look at the energetics involved in the ionic form, and compare that to the experimental value. We need to look at: (1) ionization of H to $H^+$; (2) electron affinity of H to make $H^-$; and (3) coulombic attraction of $H^+$ to $H^-$ (and vice versa, obviously).

The ionization energy of H is 1312 kJ/mol, and the electron affinity is -72.775 kJ/mol. (Note the change in sign convention given in the text.) This means to get the ions we’ve expended 1239.225 kJ/mol. The coulombic attraction energy between $H^+$ and $H^-$ is given by:

$$E = \frac{Z^+Z^-e^2}{4\pi\varepsilon_0 r}.$$ Substituting the appropriate values, we get: $E = \frac{1(-1)(1.60210 \times 10^{-19})^2}{4\pi(8.854185 \times 10^{-12})(7.41 \times 10^{-11})} = -3.1132 \times 10^{-18}$ J/molecule = -1874.75 kJ/mol. Thus, including everything, we find that the energy (from a Born-Haber type calculation) for forming $H_2$ from $H^+H^-$ is -635.525 kJ/mol. Contrast this with the given value of -458 kJ/mole, and we can see that in this case, Pauling’s reasoning was incorrect, that is, the ionic form does make a significant contribution to the energy.

6) Use a ligand group orbital approach to describe the bonding in [NH₄]$^+$. Draw schematic representations of each of the bonding MOs.
We need to construct LGOs for $H_4$, and interact them with the AOs on N. Then we can put in the electrons, and see what happens. Here it is:

Note that under the $T_d$ scheme, the three orbitals labelled $t_2$ are inseparable. Looking at the nitrogen’s orbitals, we see (happily) that the s, and the three p-orbitals transform under $T_d$ symmetry as $a_1$ and $t_2$, so these are the ones which mix to give the following scheme.
not necessarily to scale.

Now, putting in our eight electrons, we get:
which makes our bonding scheme between the N and the H’s one part s and three parts p, or the classic sp$^3$ hybrid of VBT. Each bonding MO looks something like:

that is, an sp$^3$ hybrid-s orbital overlap.

7) Consider the molecule CH$_3$C≡CH. Applying Bent’s Rule in its classical form, predict whether the bond angles, H-C-H, are greater or less than 109 ½ °.

Considering the arguments on overlap made on p. 228 in the text, predict again. (The experimental result is given by Costain, C.C.; *J. Chem. Phys.* 1958 29 864.)

From our text, we find that the electronegativity of CH$_3$ is 2.34 on the Pauling scale. From organic chemistry, we know two things: (1) CH$_4$ (methane) is not terribly acidic;
(2) C₂H₂ (acetylene) and by extrapolation, alkynes, are quite acidic (as things go.) Therefore, it seems reasonable to believe that the C≡CH fragment is more electronegative than the CH₃ fragment. If this is true, then this fragment will attract orbitals with less s-character from the CH₃ group, leaving more s-character in the C-H bonds. Given this statement, from \( \cos \theta = \frac{S}{S - 1} \), we find that \( \theta \) increases beyond 109.5°.

A counterargument can be made using overlap. Good covalency will happen between similar orbitals. The orbital on the end of the C≡CH fragment is sp, which is 50% p-character. The sp³ hybrid which we might assume CH₃ would use is 75% p-character. In attracting more p-character, one is actually going away from the good covalency desired. This argument would have us increase the s-character of the bonding orbital (moving more towards sp hybridization, which would have the effect of increasing the p-character in the C-H bonds, and decreasing the bond angle below 109.5°.

Going to the reference given, we find that the bond angle has increased slightly from 109.5° to 110.5°. This leads to sp³.5 hybridization in the C-C bond, and sp².86 in the C-H bonds.

8) Consider the MO diagram in Figure 6.16 in the text. Predict, based on this diagram
   a) the geometry of \(^1\text{CH}_2\) (singlet methylene)
   b) the geometry of \(^3\text{CH}_2\) (triplet methylene)
   c) which do you predict to be the ground state, based on lower energy?

Here is a reproduction of Figure 6.16.
a) CH$_2$ (either spin state), we have 6 electrons to distribute. In the $^1$CH$_2$, all electrons would need to be paired, so we get either \((2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2\) or \((2a_1)^2(1b_2)^2(3a_1)^2\). Looking at the ultimate energy, we see that four electrons are stabilized in the bending, and two are destabilized; the highest energy electrons, according to our text, are what more strongly determine the geometry, so for $^1$CH$_2$, we should predict a **bent geometry** (which is in accord with what is currently known.)

b) $^3$CH$_2$, we need two unpaired electrons, so we get either \((2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2\) [with different orbital occupancies] or \((2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1\). Here, one can argue that the highest energy electron(s) are at the same energy in both cases (which they are) so it is the next highest orbitals which should determine the issue. Since unpaired electrons would prefer to occupy degenerate orbitals, the considerably more **linear geometry** would be predicted (also in accord with what is currently known).
c) Here the comparison of energy difference and pairing energy really comes into play. On the singlet side is the lower energy of the electrons (a plus) and the pairing energy (a minus); on the triplet side, the lack of pairing energy, and the degeneracy of the orbitals (a plus), and the higher energy of the electron(s) (a minus). Overall, it seems to me that the pluses outweigh the minuses for the triplet, so I would predict the ground state of CH$_2$ to be the triplet, $^3$CH$_2$ (which, happily, is in accord with experiment.)

9a) ClF$_3$ (C$_{2v}$)

Here is a picture of the molecule:

![ClF3 molecule](image)

From this picture, we have the unique Cl at the center, the unique equitorial fluorine, and the two axial fluorines, which are interconvertible, so we have 3 groups of symmetry-equivalent atoms.

b) Fe(CO)$_5$ (D$_{3h}$)

Here is a picture:

![Fe(CO)$_5$ molecule](image)

Assuming it is not undergoing Berry Pseudorotation, I would say two sets of symmetry equivalent CO’s: 2 axial and 3 equatorial. Obviously, if this molecule undergoes Berry Pseudorotation, then all CO’s are equivalent.

c) B$_2$H$_6$

A picture definitely helps here:

![B$_2$H$_6$ molecule](image)
Here we have **two sets** of symmetry equivalent hydrogens; 4 as terminal hydrogens and two as bridging hydrogens. Note that the terminal and bridging hydrogens can never interconvert. The two borons are also equivalent.

**d) naphthalene, C_{10}H_{10}**

Here’s the picture, for completeness’ sake:

![Naphthalene structure]

Here we have **two sets** of symmetry equivalent hydrogens, both of which sets contain 4 hydrogens. There are also three sets of symmetry equivalent carbons; two sets of 4 each and 1 of 2 carbons. (What is interesting is that these symmetry equivalent hydrogens are not magnetically equivalent under the NMR phenomenon.)

**e) CO_{3}^{2-}**

The requisite picture:

![CO3 structure]

The molecular orbital description of this molecule yields the correct answer: **one set**. All the oxygens are equivalent.