1) Probably this problem is most easily done if we construct a table of Microstates, as shown: (I’ve left it to you to verify the number of ways of obtaining the various microstates.)

Table of Microstates

<table>
<thead>
<tr>
<th>M_M</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
<th>-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3/2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>+1/2</td>
<td>1</td>
<td>4</td>
<td>8</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>-1/2</td>
<td>1</td>
<td>4</td>
<td>8</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>-3/2</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Extracting the term symbols in the usual manner leads to: \( ^4D, ^4P, ^4S, ^2F, ^2D, ^2D, ^2P, ^2P, ^2P, ^2S \) (Contrast this with ground state nitrogen, which we showed had: \( ^4S, ^2D, ^2P \)). You can see we have gained \( ^4D, ^4P, ^2F, \) one \( ^2D \), two \( ^2P \) and a \( ^2S \) state. (As was said in class, the different \( ^2P \) states correspond to different transitions possible. We have developed ‘free-ion’ terms \( i.e. \) no external influences. As we will see in future chapters, when we include external influences, these terms change into differently designated terms.)

2) It is probably a good idea to start out with the electronic configuration, which is: 

\([\text{Rn}]7s^26d^15f^1\), which leads to maximum values of \( M_L \) and \( M_S \) being 5 and 1 respectively. Now we need to construct our table of microstates, which I trust you can do; here are the results (shown on next page):

<table>
<thead>
<tr>
<th>M_L X M_S</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
<th>-3</th>
<th>-4</th>
<th>-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

These give rise to the following term symbols: \( ^3H, ^3G, ^3F, ^3D, ^3P, ^1H, ^1G, ^1F, ^1D, ^1P \). The \( ^3H \) would be the ground state.

Apparently, the textbook gives a different ground state configuration. If you used that one \( ([\text{Rn}]7s^26d^2) \), then you get maximum values of \( M_L \) and \( M_S \) being 4 and 1 respectively. Constructing our table of microstates, we get:

<table>
<thead>
<tr>
<th>M_L X M_S</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
<th>-3</th>
<th>-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
This table of microstates gives rise to the following term symbols: \( ^3F, ^3P, ^1G, ^1D, ^1S \), with \(^3F\) being the ground state.

3) Recall that, for hydrogen-like atoms (which \( \text{Li}^{2+} \) would be), the ionization energy is a good approximation of the energy of the orbital; the converse holds too \textit{i.e.} the energy of the orbital is a good approximation of the ionization energy. For \( \text{Li}^{2+} \), \( Z^* = 3 \). (Remember we are looking at the charge felt by that one last electron, which is not shielded at all!)

The energy of the orbital is:

\[
E_n = -\frac{Z^*^2 2\pi^2 m e^4}{n^2 h^2}
\]

It is important to note at this point that this equation is for the cgs system of units (mass in grams, energies in ergs, charge in electrostatic units; 1 C = 3 x 10^9 esu) For this case, \( Z^* = 3 \), \( m = 9.109 \times 10^{-28} \text{ g} \), \( e = 4.8028 \times 10^{-10} \text{ sC} \), \( n = 1 \), and \( h = 6.6261 \times 10^{-27} \text{ ergs} \cdot \text{s} \). Plugging it all in, we get

\[
E_n = -11.806 \text{ MJ/mol}
\]

(I have to thank Mike Bergman for helping me unpack this one!!)

It is quite interesting that if one tries to do this problem in mks units, one gets values that are totally ridiculous. Doing so yields an orbital energy of \( 1.46 \times 10^{-13} \text{ J/mol} \), which is quite implausible, given that the ionization energy of hydrogen is \( 13.6 \text{ eV} = 1312.4 \text{ kJ/mol} \).

4a) I only see a \( \sigma_v \) in addition to the \( C_1 \), so we have \( C_s \).

b) The three-fold axis is pretty clear, as are the three \( \sigma_v \) planes. A great deal now depends on whether or not this molecule, like benzene, is fully delocalized. If so, then looking carefully, we can find three \( C_2 \) axes perpendicular to the three-fold axis. There is also a \( \sigma_h \), so we appear to have a \( D_{3h} \) molecule. If it is not fully delocalized, and therefore is localized, then we only have the \( \sigma_h \) in addition to the \( C_3 \) and three \( \sigma_v \)'s, so it is \( C_{3h} \).

c) There is a \( C_3 \) axis, plus three \( C_2 \) axes perpendicular to this \( C_3 \); there is also a \( \sigma_h \), so we have a \( D_{3h} \) molecule.

d) There is a \( C_2 \) axis plus a horizontal plane, so we have \( C_{2h} \).

e) There is a \( C_2 \) axis plus two vertical planes, so we have \( C_{2v} \). (Amazing what cis/trans isomerism can do!)

f) This molecule is similar to the one in part c), and therefore is also \( D_{3h} \).

g) Drawing the molecule in a projection-like manner allows one to see more clearly the \( C_5 \) axis. Once that is seen, then looking for (and finding) the five \( C_2 \) axes perpendicular to the \( C_5 \), along with the \( \sigma_v \)'s and \( \sigma_h \) is easier. Thus, we have a molecule with \( D_{5h} \) symmetry.

5) \( \text{SF}_4 \) would have \( C_{2v} \) rather than \( C_{4v} \) symmetry because this molecule does not adopt the pentagonal pyramidal structure but rather a distorted trigonal bipyramidal structure, with the lone pair occupying the preferred equitorial position. The lone pair prefers this position because it is higher in s-character (being an sp\(^2\) hybrid) as opposed to the dp\(^3\) hybrid of the axial positions. That these are distinct sets of orbitals (rather than the dsp\(^3\) hybrid taught in earlier classes) can be shown via group theory.

6a) Remember that the number of irreducible representation \( \Gamma_i = \frac{1}{h} \Sigma \chi^X_i \chi^* X_i \chi^X_i \), we get:

(I’ve done the first one explicitly, then left the rest to you to verify)

\[
\]
\[\frac{(1/12)[5+4+3+3+0+9]}{12} = 24/12 = 2\] so there are 2A1’.

Proceeding a similar manner for the rest, we get a total irreducible representation of: \(2A_1' + E' + A_2''\)

b) Doing the same thing here, we get a total reducible representation of: \(A_{1g} + A_{2g} + B_{2g} + E_{1g} + 2E_{2g} + A_{1u} + B_{1u} + B_{2u} + 2E_{1u} + E_{2u}\)

7) If we look at water, and let vectors represent the bonds in the first instance, and the lone pairs in the second instance, we can get to our answer. The molecule belongs to point group \(C_{2v}\), which gives us the following symmetry elements: E, \(C_2\), \(\sigma_{(xz)}\), \(\sigma_{(yz)}\).

[Recall the principle axis is the z-axis, and that the Cartesian space sets up in accord with the right hand rule i.e.

Therefore, the vectors for the bonds span the reducible representation, \(\Gamma_r: 2, 0, 0, 2\); which reduces to \(A_1 + B_2\) which can be \(s\) (or \(p_z\)) + \(p_y\).

Doing the same vector thing for the lone pairs, we obtain the reducible representation, \(\Gamma_r: 2, 0, 2, 0\); which reduces to \(A_1 + B_1\), which can be \(s\) (or \(p_z\)) + \(p_x\).

Now we need to reconcile experiment with theory. If, as stated, the lone pairs are different, then we know that the lone pairs can not both be \(p\)-orbitals. Therefore, the lone pairs are \(s + p_z\), and the bonds (despite everything we’ve been taught previously) are (essentially) \(p^2\)-hybrids.

The articles cited argue that our conclusion is correct, and that the bond angle observed is due to the hydrogens, at a 90° angle, interfering with each other’s van der Waals space and thereby forcing the bond angle open; in larger Group 16 dihydrides, the bond angle closes, approaching 90°.