Chem 2430: Answers HW #9.

1 p^2 $M_L = 2$

$\psi = p_+(1)\, p_+(2)\, (\alpha\beta - \beta\alpha)$

Yes, this can be expressed as a single Slater determinant.

$p_+ p_+ = (p_x + i p_y)(p_x + i p_y)$

$= (p_x^2 - p_y^2) + i(p_y p_x + p_x p_y)$

Note that either $p_x^2 - p_y^2$ or $p_x p_y + p_y p_x$ will give a correct energy, but individually these are not eigenfunctions of L_z.

2. $pd \to {}^3P_2, {}^3P_1, {}^3P_0, {}^1P_1, {}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2, {}^3F_4, {}^3F_3, {}^3F_2, {}^1F_3$

3. $\langle \psi | H | \psi \rangle = \langle 1s | h | 2s \rangle + \langle 1s | 2J_{1s} - K_{1s} | 2s \rangle$

$= \langle 1s | F | 2s \rangle = 0$

Here h is the standard one-electron core part of the Hamiltonian, and F is the Fock operator, which by design is diagonal.

4. one electron in a p orbital:

-1	0	1	m_L
+	—	—	
—	+	—	
—	—	+	

The only state this can give is ^2P (six arrangements when allowing for spin)

five electrons in p orbitals:

-1	0	1	m_L
++	++	+	
++	+	++	
+	++	++	

Again the only possibility is ^2P.

Similarly p^2 and p^4 can only give ^3P, ^1S, ^1D

p^2:

++ — — ^1D

+ + — ^3P

last state is ^1S

p^4:

— ++ ++ ^1D

+ + ++ ^3P

last state is ^1S

5. The orbitals $1s'$, $1s''$, $2s'$ must be linear combinations of $1s$ and $2s$.

$1s' = c_1 1s + c_2 2s$

$1s'' = c_3 1s + c_4 2s$

$2s' = c_5 1s + c_6 2s$

So
$$|1s'\overline{1s}''2s'| = c_1c_3c_6 |1s\overline{1s}2s| + c_1c_4c_6 |1s\overline{2s}2s| + c_2c_3c_5 |2s\overline{1s}1s| + c_2c_4c_5 |2s\overline{2s}1s|$$

$$= (c_1c_3c_6 - c_2c_3c_5)|1s\overline{1s}2s| + (c_1c_4c_6 - c_2c_4c_5)|1s\overline{2s}2s|$$

$$= c_3(c_1c_6 - c_2c_5)|1s\overline{1s}2s| + c_4(c_1c_6 - c_2c_5)|1s\overline{2s}2s|$$

$$= (c_1c_6 - c_2c_5)\{c_3|1s\overline{1s}2s| + c_4|1s\overline{2s}2s|\}$$

where configurations that violate the Pauli Excl. Princ. have been left out.

We see that the UHF solution for Li includes mixing between the ROHF ground state and an excited configuration.