CH511 Fall 2010 Problem Set 1 - solutions

1. Determine the two values of r for which the RDF of a $3p_z$ orbital is a maximum.

RDF = $R^2 r^2$

for 3p orbitals,

$$\longleftarrow R^2 \longrightarrow \quad r^2$$

$$(RDF)_{3pz} = [(1/9\sqrt{6})\, \rho\, (4 - \rho)\, Z^{3/2} \exp(-\rho/2)]^2\, r^2 \text{ where } \rho = 2Z\, r/na_0 \qquad (1)$$

R_{max} where $d(RDF)_{3pz} / dr = 0$

Finding the derivatives of the above equation and setting $d(RDF)_{3pz} / dr = 0$, yields two values of the r as

na_0/z and $4na_0/Z$

For 3pz where n = 3 and Z = 1, this gives r values of

$3a_0$ and $12a_0$.

As we might expect, the answer will depend inversely on Z.

Alternatively, plotting R as a function of r, and look for the maximum graphically, will give the same answers (but is much easier).

2. Prove that the electron probability function for a ground state P atom has spherical symmetry, i.e. show that the sum of a p_x, p_y and p_z orbital has no angular dependence.

We will consider only the angular part, as the radial part does not have an angular dependence. For p_x, p_y and p_z, l = 1 and $m_l = 0, \underline{+}1$

$$Y_{3px} = (3/2)^{1/2} \sin\theta \exp(i\Phi)$$

$$Y_{3py} = (3/2)^{1/2} \sin\theta \exp(-i\Phi)$$

$$Y_{3pz} = (3)^{1/2} \cos\theta$$

$$YY^* = Y_{3px} Y^*_{3px} + Y_{3py} Y^*_{3py} + Y_{3pz} Y^*_{3pz}$$

$$= (3/2)(\sin^2\theta)(\cos^2\Phi + \sin^2\Phi) + (3/2)(\sin^2\theta)(\cos^2\Phi + \sin^2\Phi) + 3\cos^2\theta = 3$$

YY* is a constant and not a function of θ or Φ and is therefore spherically symmetric.

3. Madelung constants can be derived by calculating a summation of coulombic interactions, each term in the series indicates all the interactions for a specific ion-ion distance. For each term, the sign (from anion or cation), the total number of interactions, and interaction distance needs to be determined. The notes have a simple example for the infinite linear chain.

Derive the first 30 terms (arising from 30 shortest distances) for determining the Madelung constant of CsCl. For each term, indicate the number of interactions, the sign, and the distance in terms of the lattice parameter a. To accomplish this, apply symmetry and permutations to (xyz) coordinates, do not try to use drawings or models.

In the CsCl structure, if we put a Cl at the origin (000), then the lattice generation rules are:

Cl at all sites (n, n, n) and Cs at all sites (n/2, n/2, n/2); where n is any integer (positive or negative)

The distance from the origin is found from the coordinates by: distance = $(x^{2} + y^{2} + z^{2})^{1/2}$

The number of ions at any given distance can be determined from all possible permutations with the same distance, interchanging the coordinates and switching positive and negative values. For example:

(½ ½ ½) has 8 permutations with the same distance: (½ ½ ½), (-½ ½ ½), (½ -½ ½), (½ ½ -½), (-½ -½ ½), (½ -½ -½), (-½ ½ -½), (-½ -½ -½)

(1 0 0) has 6: (1 0 0), (0 1 0), (0 0 1), (-1 0 0), (0 -1 0), (0 0 -1)

Any general coordinates (x y 0) will have 12 permutations if x = y, and 24 if $x \neq y$

At most, the coordinates (x y z) where all are non-zero and $x \neq y \neq z$ has 48 permutations.

The total energy contribution for the interactions at a particular distance will be proportional to the number of interactions / distance.

Finally, note the Madelung constant term is related to d (the closest approach of ions) rather than a (the unit cell edge length). In this cell, d = 0.866 a, so we multiply the total energy contributions by this factor to get the Madelung constant terms.

coordinates	**ion type**	**number of ions**	**distance in a units**	**energy contribution**

½ ½ ½	Cs	8	0.87	-9.1
1 0 0	Cl	6	1.00	+6.0
1 1 0	Cl	12	1.41	+8.5
3/2 ½ ½	Cs	24	1.66	-14.5
1 1 1	Cl	8	1.73	+4.6
2 0 0	Cl	6	2.00	-3.0
3/2 3/2 ½	Cs	24	2.18	-11.0
2 1 0	Cl	24	2.24	-10.7
2 1 1	Cl	24	2.45	+9.8
3/2 3/2 3/2	Cs	8	2.60	-3.1
5/2 ½ ½	Cs	24	2.60	-9.2
2 2 0	Cl	12	2.83	+4.2
5/2 3/2 ½	Cs	48	2.96	-16.2
3 0 0	Cl	6	3.00	+2.0
2 2 1	Cl	24	3.00	+8.0
3 1 0	Cl	24	3.16	+7.6
5/2 3/2 3/2	Cs	24	3.28	-7.3
3 1 1	Cl	24	3.32	+7.2
7/2 ½ ½	Cs	24	3.57	-6.7
3 2 0	Cl	24	3.60	+6.7
3 2 1	Cl	48	3.74	+12.83
7/2 3/2 1/2	Cs	48	3.84	-12.50
7/2 5/2 1/2	Cs	48	4.33	-11.09
7/2 3/2 3/2	Cs	24	4.09	-5.86
7/2 5/2 3/2	Cs	48	4.56	-10.54
7/2 5/2 5/2	Cs	24	4.97	-4.82
7/2 7/2 5/2	Cs	24	5.55	-4.33
7/2 7/2 7/2	Cs	8	6.06	-1.32
3 2 2	Cl	24	4.12	+5.82
3 2 3	Cl	24	4.69	+5.11
Total 30 terms		698		-52.9

4. After solving the above problem, what can you conclude about the convergence of this constant. Are 30 terms sufficient to determine which structures are most stable in terms of lattice enthalpy?

Notice the last few terms (21-25th) change the value of the interaction energy (sum is -26.2 after 20 terms, but -52.9 for 30 terms) significantly. We need more terms to obtain a Madelung constant with useful precision, where the truncation does not effect the result by an amount that is less than the difference in Madelung constants in different structures.

5. Ternary compounds (with 3 elements) often have structures closely related to the common structure types we will discuss for binary compounds. Describe the structure, and its relation to a simple binary structure type, for both K_2PtCl_6 and $NaFeO_2$.

One good resource is Wells, *Structural Inorganic Chemistry*

K_2PtCl_6 has an antifluorite structure, where the $PtCl_6^{2-}$ octahedra form an fcc lattice, with K^+ occupying all Td sites. It is also related to the perovskite structure.

http://www.chemistry.ohio-state.edu/~woodward/ch754/struct/K2PtCl6.htm

$NaFeO_2$ is isostructural with $LiCoO_2$, which has been discussed in class. This is a superlattice of the NaCl structure type, with alternating layers of Na^+ and Fe^{3+} in Oh sites $(AcBaCb)_n$, where the uppercase letters are O^{2-} and lowercase letters are alternately Na^+ and Fe^{3+}. This leads to an anisotropic, layered structure. The strongly bound FeO_2 sheets contain edge-sharing FeO_6 octahedra.

6. Show that the ionic compound CaCl (s), which does not exist, would be thermodynamically unstable with respect to disproportionation.

For the reaction: 2 CaCl (s) -> $CaCl_2$ (s) + Ca (s)

$\Delta H_{rxn} = 2\ \Delta H_L\ (CaCl) - \Delta H_L\ (CaCl_2) - \Delta H_{at}\ (Ca) + I_2\ (Ca) - I_1\ (Ca)$

where I_1 and I_2 refer to the 1st and 2nd ionization energies for Ca

Estimate ΔH_L using the Kapustinskii eqn and the following data:

$r(Ca^{2+}) = 110$ pm, $r(Cl^-) = 167$ pm

$r(Ca^+)$ is not known, however, it must be smaller than r(Ca) = 197 pm, and larger than $r(Ca^{2+})$. Also, we can expect that $r(Ca^+)$ will be larger than $r(K^+) \approx 150$ pm, so let's estimate $r(Ca^+) \approx 160$ pm

then, $\Delta H_L(CaCl) \approx -\ [(2)(+1)(-1) / 3.27\ Å]\ [1 - (0.345\ Å / 3.27\ Å)] \times 1.21\ MJÅ/mol \approx 660$ kJ/mol

and $\Delta H_L(CaCl_2) \approx -\ [(3)(+2)(-1) / 2.77\ Å]\ [1 - (0.345\ Å / 2.77\ Å)] \times 1.21\ MJÅ/mol \approx 2290$ kJ/mol

$\Delta H_{rxn} \approx 2\ (660) - 2290 - 176 + 1145 - 590 \approx -600$ kJ/mol

Even with the assumptions made, it is clear that this disproportionation reaction is exothermic. There should not be any large entropic term at moderate temperature, as all the phases are solids. ΔG_{rxn} should thus be negative, the reaction is favorable and spontaneous. This suggests that it would be difficult to ever isolate CaCl(s). Looking at the energy terms, it is reasonable to state the "driving force" for the reaction is the large lattice enthalpy for $CaCl_2$. If we consider K, where loss of the second electron involves removing a core electron, and $I_2 \approx 3050$ kJ/mol, it becomes clear why we don't see this reaction for group 1 elements.