Chem231B: Assignment #3

February 9, 2020

Problems from Berry, Rice, and Ross

a) Do problems 10, 12, 14, 15, and 18 from BRR. For reference data, use the NIST website, Atomic Spectra Database. (This replaced Moore's tables, and the NBST became NIST). Also check out the Computational Chemistry Comparison and Benchmark DataBase (cccbdb) from which I got some of the basis-set results.

10) Put entries in the following sets of configurations in order of increasing energy. Then check your intuition with experimental results at NIST Spectra Database.

a) Li, $1s^2 2s, 1s^2 2p, 1s2s2p, 1s2s^2$

b) C, $1s^2 2s^2 2p^2, 1s^2 2s 2p^3, 1s^2 2s^2 2p 3s, 1s 2s^2 2p^3$

12) Explain why the second ionization potentail of lithium for the process $\mathrm{Li}^+ \rightarrow \mathrm{Li}^{2+} + e^-$, is less than that predicted for a hydrogenlike atom with $Z = 3$.

The electronic repulsion from the two electrons within lithium ion leads to smaller second ionization potential than predicted by a hydrogenlike atom which only has one electron.

14) The outer electron of an alkali atom may be treated in an approximate way, as if it were in a hydrogenic orbital. Suppose that one takes the quantum number for the outer electron to be 2, 3, 4, 5, and 6, respectively, for Li, Na, K, Rb, and Cs. What values must Z be given to account for the observed first ionization potentials of these atoms? Explain why they differ from unity.

Look up first ionization potential (IP) energy on NIST and solve for Z within the Rydberg equation where the HOMO may be taken as the IP energy from Koopman's Theorem.

For lithium atom, the ionization potential energy is 5.3917eV

$$\frac{13.6Z^2}{2^2} = 5.3917$$
$$Z^2 = \frac{4 * 5.3917}{13.6}$$
$$Z = \{\pm 1.259\}$$

Z value for lithium is 1.259. Repeat for Na, K, Rb, and Cs

Atom	Z
Li	1.259
Na	1.229
K	1.130
Rb	1.108
Cs	1.070

When $Z = 1$, this indicates an unscreened electron from the hydrogen atom. The Z values are differ from unity because the nuclear attraction is increasing while at the same time, the screening effect does not exactly cancel with the attraction.

15) Use the Pauli exclusion principle and Hund's rules to find the number of unpaired electrons and the term of lowest energy for the following atoms.

a) P: $[\mathrm{Ne}]3s^2 3p^3$; $L = 0$ and $S = \frac{3}{2}$ and $J = L + S = \frac{3}{2}$; Term Symbol: ${}^4S_{\frac{3}{2}}$

b) S: $[\mathrm{Ne}]3s^2 3p^4$; $L = 1$ and $S = 1$ and $J = 2$; Term Symbol: ${}^3P_2$

c) Ca: $[\mathrm{Ar}]4s^2$; $L = 0$ and $S = 0$ and $J = 0$; Term Symbol: ${}^1S_0$

d) Br: $[\mathrm{Ar}]4s^2 3d^{10} 4p^5$; $L = 1$ and $S = \frac{1}{2}$ and $J = \frac{3}{2}$; Term Symbol: ${}^2P_{\frac{3}{2}}$

e) Fe: $[\mathrm{Ar}]4s^2 3d^6$; $L = 2$ and $S = 2$ and $J = 4$; Term Symbol: ${}^5D_4$

18) Derive the terms of the configuration $1s^2 2s^2 2p^6 3s^2 3p 3d$, of the silicon atom.

$S = 1$ and $L = 3$ and $J = \{2, 3, 4\}$; Term Symbols: ${}^3F_2, {}^3F_3, {}^3F_4$

b) Deduce formulas for the atomic number of the noble gas atom of the n-th row, and for the width of the n-th row. Ignoring relativity, in what row would the atom with 252 electrons be and what is its ground-state configuration? What would be its lowest energy term?

Keeping with the existence of f-orbitals since g-orbitals have not been discovered yet. After the 6th row, add 32 electrons for the next noble gas atom. This will mean that the 11-th row will be where the atom with 252 electrons is

Row	Width	Atomic Number
1	2	2
2	8	10
3	8	18
4	18	36
5	18	54
6	32	86
7	32	118

placed.

e^- configuration: $[{}^{246}\text{Noble Gas}]11s^2 9f^4$
$S = 2$ and $L = 6$ and $J = 4$; Term Symbol: ${}^5I_4$

c) Repeat (b) but with repulsion between electrons turned off, i.e., purely hydrogenic orbitals and energies.

If there's no electron interactions, lower quantum number orbitals will be filled first e.g. $3d$ orbitals are filled before $4s$ orbitals.

e^- configuration: $[{}^{246}\text{Noble Gas}]9f^6$
$S = 3$ and $L = 3$ and $J = 6$; Term Symbol: ${}^7F_6$