Problem Set 11
Electronic configurations of many-electron atoms

1. An approximate hamiltonian for a the internal energies of an atom is given below: $\mathcal{H} = \sum_{i=1}^{electrons} \{- (\hbar^2/2\mu)\, \nabla^2{}_i - (Z_{eff})_i\, e^2/r_i \}$
where the Laplacian $\nabla^2{}_i = \{\partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2\}$ when transformed to spherical coordinates becomes
$\nabla^2{}_i = \partial^2/\partial r_i^2 + (2/r_i)\, \partial/\partial r_i + \{r_i^2 \sin\theta_i)^{-1} \partial/\partial\theta_i(\sin\theta_i\, \partial/\partial\theta_i) + \{r_i^2 \sin^2\theta_i)^{-1}(\partial^2/\partial\phi_i^2)$
Here, the repulsion between pairs of electrons have been replaced by the average effect, by assuming that the positive energy contribution of the repulsion can be represented by shielding or screening effects, such that the *i*th electron sees an effective charge $+(Z_{eff})_i e$, rather than the full charge +Ze of the nucleus. The effective charge depends on the number of electrons in each s, p, and d subshell in the atom.
(a) Suppose you have a recipe for determining $(Z_{eff})_i$ for each electron in the atom. Then, the problem $\mathcal{H}\Psi = E\Psi$ can be solved for any atom. What would the solutions be? (Use separation of variables to find the eigenfunctions of a general atom with more than one electron, in terms of the known eigenfunctions $\Psi(r,\theta,\phi)$ and eigenvalues $-(Z^2/n^2)e^2/2a_0$ (= 13.56 eV) of the hydrogen-like atom with nuclear charge +Ze on the nucleus.)
(b) Write out the general energy eigenvalues for an atom of 4 electrons under these assumptions. That is, show your eigenvalues in terms of quantities such as $(Z_{eff})_1$, $(Z_{eff})_2$ etc. defined for *i* = 1, 2, 3, 4. Since each electron has spin angular momentum, let us for the moment, ignore the fact that the orbital angular momentum and the spin angular momentum can couple. Introduce the m_s quantum number for each electron, which is either +½ or –½, corrresponding to having z component of the spin angular momentum equal to either $+½\hbar$ or $–½\hbar$. Thus, every one of the electrons can have either one of these m_s values, subject only to the **restriction that no more than one electron may have exactly the same set of quantum numbers n, ℓ, m_ℓ, m_s .** Specifying the set of four quantum numbers n, ℓ, m_ℓ, m_s to each hydrogen-like function $\Psi_{n,\ell,m_\ell,ms}(r_i,\theta_i,\phi_i)$ is sufficient to define the function $\Psi_{n,\ell,m_\ell,ms}(r_i,\theta_i,\phi_i)$ itself. A short-hand for the set n, ℓ, m_ℓ, m_s is usually used: such as $3d_0\uparrow$, where n=3, ℓ=2, m_ℓ=0, and ↑ denotes m_s = + ½ or $3d_{+1}\downarrow$, where ↓ denotes m_s = – ½ . Consider the quantum numbers of the two electrons of He in its lowest (ground) energy level. The product of two hydrogen-like functions $\Psi_{1\,0\,0\uparrow}(r_1,\theta_1,\phi_1) \cdot \Psi_{1\,0\,0\downarrow}(r_2,\theta_2,\phi_2)$ with this set of four quantum

numbers is denoted by the simple notation $1s^2$. This simple notation is called the "*electronic configuration*" of the He atom in its ground state.
Given on the next page is the table of values for $(Z_{eff})_i / n_i$, determined by Clementi and Raimondi. Using this table, it is clear that electrons in the same subshell, say 2p, have the same contribution to the overall energy of the atom, regardless of the values of m_ℓ or m_s. Thus, a short-hand notation to specify the states of an atom that has 5 electrons, corresponding to the quantum numbers of the electrons of the with $n=2$, $\ell=1$, (with $m_\ell=0$, or 1 or -1, $m_s = + ½$ or $– ½$) is the electronic configuration $2p^5$. Specify the quantum numbers of the three electrons of Li in its lowest (ground) energy level. Calculate the energy of the Li atom in its lowest (ground) energy level. The product of three hydrogen-like functions is denoted by what electronic configuration?
What is the electronic configuration of the lowest energy state of Na atom?

From Chemistry 112: "Ionization energy (also called ionization potential for historical reasons) is defined as the energy required to remove an elelctron from an atom or molecule. Electron affinity is defined as the energy released when an electron is added to an atom or molecule. Note that the definitions of ionization energy (*IE*) and *EA* appear to be opposite,

$IE_1 \equiv$ E(+ion) - E(neutral) $\quad EA \equiv$ E(neutral) - E(- ion)

but the energy change is associated with electron detachment process in both cases, *with the energy difference IE and EA being defined for the neutral atom*

$\underline{Na_{(g)}} \rightarrow Na^+_{(g)} + e^-$ $\quad IE_1$ for Na $\equiv$ E(Na^+) - E(Na)

$Cl^-_{(g)} \rightarrow \underline{Cl_{(g)}} + e^-$ $\quad EA$ for Cl $\equiv$ E(Cl) - E(Cl^-)

Note: *EA* of Cl is the *IE* of Cl^-"

(c) Use the $(Z_{eff})_i / n_i$ from the Clementi and Raimondi table on the next page to do the following calculations:

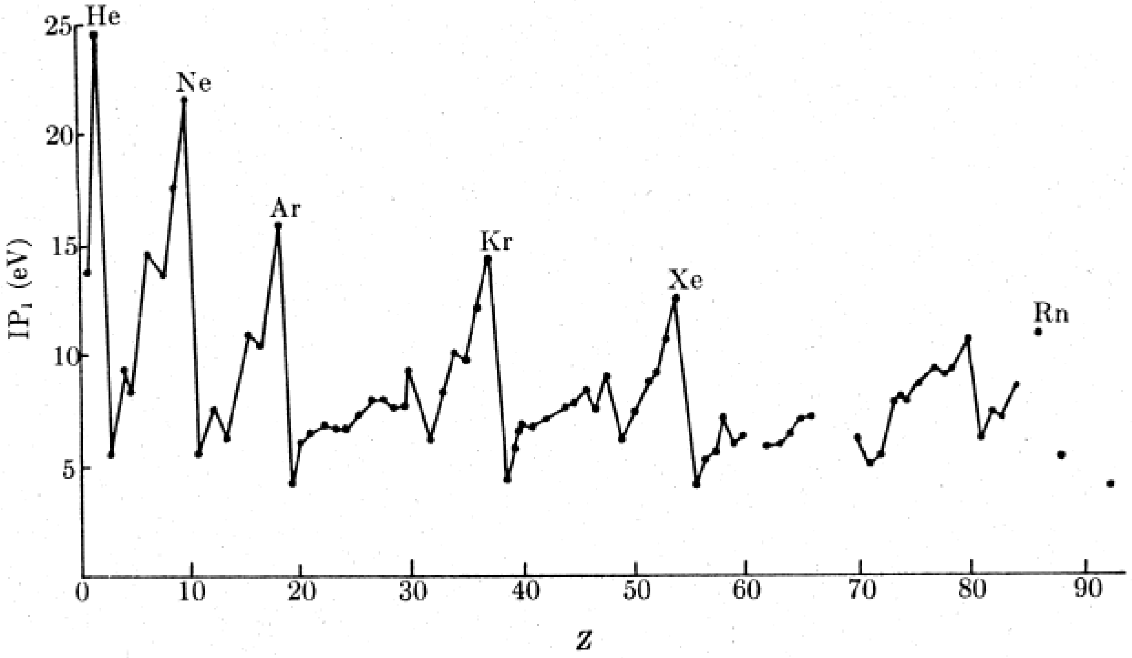
(i) Calculate the energy of the ground state of He atom in units of $(e^2/2a_0)$.

(ii) The energies of the 4 lowest energy states of the Li atom (with 3 electrons) in units of $(e^2/2a_0)$. Draw the energy level scheme for the Li atom and label each energy level with an electronic configuration. Calculate the first ionization potential of Li atom corresponding to the process

Li(ground state) → Li^+ ion (ground state).

Calculate the second ionization potential.

(iii) The first ionization potentials of atoms in the periodic table are shown in the following figure. Explain with examples, why the IPs behave in this periodic fashion.



First ionization potential as a function of atomic number.

(d) The Clementi-Raimondi values of $(Z_{eff})_i / n_i$ are only applicable to the electronic configuration for which the calculations have been done (as shown in the table provided), and does not permit us to find the $(Z_{eff})_i / n_i$ for each electron when other than the ground electronic configuration is being considered. $(Z_{eff})_i$ can be also be approximated by using Slater's rules (attached), which provides the estimate for $(Z_{eff})_i$ for the i<u>th</u> electron in <u>any electronic configuration</u> of an atom or ion.

Calculate the following quantities using Slater's rules:

(i) The energy involved in the transfer of one electron from Na to F. Is the energy absorbed or evolved?

(ii) A common method of producing x-rays is to bombard a piece of metal with electrons of sufficient energy to knock an inner shell electron out of a metal atom. The remaining electrons in the atom rearrange themselves by falling into the "holes" created and emit x radiation. The wavelengths of the x-rays vary with the target substance . Calculate the energy of the x-ray emitted when a 2s electron falls into the hole left in the 1s shell of a Na atom.

(iii) <u>Electronegativity</u> according to R.S. Mulliken's definition is

$$(IP + EA)/2$$

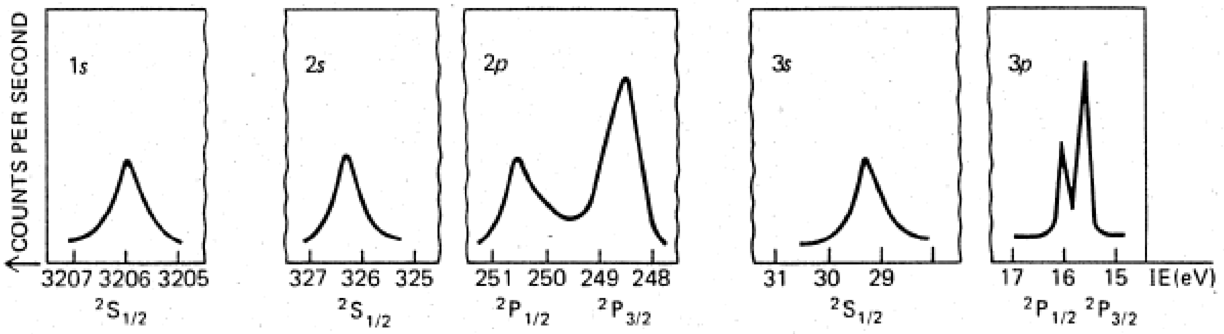
where IP is ionization potential and EA is electron affinity. Using Slater's rules, calculate the electronegativity of these atoms: F, O, N, C, Li, Na, H. You can leave your electronegativity scale in units of ($e^2/2a_0$). Compare with the electronegativity scale from any textbook..

2. "Orbital energies of Atoms"

By photoelectron spectroscopy, XPES or ESCA or variants thereof, a variety of ionization energies are found for the atoms of a sample. In this analytical technique, the sample is irradiated with high-energy radiation and electrons are expelled. Some of the energy of the incident radiation is carried off as kinetic energy of the expelled electrons. The energy required to produce a particular ionization (IE) is equal to the energy of the incident photon ($h\nu$) less the kinetic energy of the expelled electrons (ε_{kin}). We can describe this by

$$IE = h\nu - \varepsilon_{kin} \quad \text{or} \quad \varepsilon_{kin} = h\nu - IE$$

The pattern of electron kinetic energies thus yields a display (spectrum) of the various ionization energies of the atoms or molecules of the sample. Now if we have a model of an atom, such as the Slater model, in which the total energy (not including translation) of the atom for a given electronic configuration can be written in terms of a sum over the one-electron-at-a-time (i.e., 'orbital') energies, it will be possible to use the following language about each measured IE: "Each ionization energy is a measure of the energy required to expel an electron from one of the orbitals of the atom. Or we can think of the measured IE as the energy released when an electron with zero kinetic energy is dropped into the empty orbital of the ion of the atom. Thus the measured ionization energies can be taken to be measures of orbital energies." The ionization spectrum of argon is shown below:



For each frame, the atomic term symbol for the Ar^+ ion formed (e.g., $^2S_{½}$) is the label used under each frame. The orbital of the parent argon atom from which an electron has been expelled (e.g., 1s) in each case is shown as a label within the frame.

Use the Slater rules to calculate

(a) the energy of the Ar atom in its ground electronic state, in eV.

(b) for each of the 5 frames: the energy of the Ar^+ ion with the one electron missing from the orbital indicated, in eV.

(c) for each of the 5 frames: the IE corresponding to the difference: [E(Ar^+ ion) - E (Ar)]. Compare these values with the 5 spectra and *explain* the deficiencies of the Slater model in predicting these IEs.

Slater's rules:

The effective charge seen by the i<u>th</u> electron whose quantum numbers are n ℓ in an atom whose atomic number is Z is given by

$$(Z_{eff})_i = Z - s_{n\ell}$$

Slater provides $s_{n\ell}$ as follows:

1. For i having n ℓ = 1s

$$s_{1s} = 0.30k_{same}$$

where

k_{same} = number of other electrons in the same 1s shell

2. For i having n > 1 and ℓ = 0 or 1

$$s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$$

where

k_{same} = number of other electrons in the same shell as the screened electron of interest

k_{in} = number of electrons in the shell with principal quantum number n-1

k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For the i<u>th</u> electron having quantum numbers n ℓ = 3d

$$s_{3d} = 0.35k_{3d} + 1.00k_{in}$$

where

k_{3d} = number of other electrons in the same 3d shell

k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$

For the purposes of Slater's rules, the "subshells" are taken to be in the order

innermost 1s (2s,2p) (3s,3p) 3d (4s,4p) outermost

ADDITIONAL INFORMATION

$a_0 = (\hbar^2/m_e e^2)$ the "Bohr radius", 0.529177×10^{-10} m

$(e^2/2a_0)$ = 13. 6057 eV one rydberg, a unit of energy = (1/2) hartree

c = frequency•wavelength = 2.997924×10^{10} cm sec^{-1} the speed of light

1 eV = 8065.6 cm^{-1}

The Clementi and Raimondi table can be summarized as follows, applying only to the ground electronic configuration: $(Z_{eff})_i = Z - s_{n\ell}$

$s_{1s} = 0.30[N_{1s} -1] + 0.0072[N_{2s}+N_{2p}] + 0.0158[N_{3s}+N_{3p} +N_{4s} +N_{3d} +N_{4p}]$
$s_{2s} = 0.8604[N_{1s}] + 0.3601[N_{2s}+N_{2p}-1] + 0.2062[N_{3s}+N_{3p} +N_{4s} +N_{3d} +N_{4p}]$
$s_{2p} = 2.5787 + 0.3326[N_{2p}-1] - 0.0773[N_{3s}] - 0.0161[N_{3p} +N_{4s}] - 0.0048[N_{3d}]$
$+ 0.0085[N_{4p}]$
$s_{3s} = 1.0[N_{1s}] +0.8116[N_{2s}+N_{2p}] + 0.2501[N_{3s}+N_{3p}-1] + 0.0778[N_{4s}] + 0.3382[N_{3d}]$
$+ 0.1978[N_{4p}]$
$= 8.4927 +0.2501[N_{3s}+N_{3p}-1] + 0.0778[N_{4s}] + 0.3382[N_{3d}] + 0.1978[N_{4p}]$
$s_{3p} = 9.3345 + 0.3803[N_{3p}-1] + 0.0526[N_{4s}] + 0.3289[N_{3d}] + 0.1558[N_{4p}]$
$s_{4s} = 1.0[N_{1s}] +1.0[N_{2s}+N_{2p}] + 0.6881[N_{3s}+N_{3p}] + 0.8433[N_{3d}] + 0.0971[N_{4s} -1]$
$+ 0.0687[N_{4p}]$
$= 15.505 + 0.8433[N_{3d}] + 0.0971[N_{4s} -1] + 0.0687[N_{4p}]$
$s_{3d} = 13.5894 + 0.2693[N_{3d}-1] - 0.1065[N_{4p}]$
$s_{4p} = 24.7782 + 0.2905[N_{4p}-1]$

where N_{3d} is the number of electrons occupying the 3d subshell, for example. These equations were obtained by fitting to their calculated $(Z_{eff})_i$ for He through Kr atoms.

In comparison:
Using *Slater's rules*, for the ground electronic configuration, we would get
$s_{1s} = 0.30[N_{1s} -1]$
$s_{2s} = 0.85[N_{1s}] + 0.35[N_{2s}+N_{2p}-1]$
$s_{2p} = 0.85[N_{1s}] + 0.35[N_{2s}+N_{2p}-1]$
$= 2.40 + 0.35[N_{2p}-1]$
$s_{3s} = 1.0[N_{1s}] + 0.85[N_{2s}+N_{2p}] + 0.35[N_{3s}+N_{3p}-1]$
$= 8.80 + 0.35[N_{3s}+N_{3p}-1]$
$s_{3p} = 1.0[N_{1s}] + 0.85[N_{2s}+N_{2p}] + 0.35[N_{3s}+N_{3p}-1]$
$= 8.80 + 0.35[N_{3s}+N_{3p}-1]$
$s_{4s} = 1.0[N_{1s}] + 1.0[N_{2s}+N_{2p}] + 0.85[N_{3s}+N_{3p}] + 0.85[N_{3d}] + 0.35[N_{4s} +N_{4p}-1]$
$= 16.8 + 0.85[N_{3d}] + 0.35[N_{4s} +N_{4p}-1]$
$s_{3d} = 1.0[N_{1s}] + 1.0[N_{2s}+N_{2p}] + 1.0[N_{3s}+N_{3p}] + 0.35[N_{3d}-1]$
$= 18.0 + 0.35[N_{3d}-1]$
$s_{4p} = 1.0[N_{1s}] + 1.0[N_{2s}+N_{2p}] + 0.85[N_{3s}+N_{3p}] + 0.85[N_{3d}] + 0.35[N_{4s} +N_{4p}-1]$
$= 26.0 + 0.35[N_{4p}-1]$

TABLE I. Best values of ξ for the ground state of neutral atoms.[a]

Z	$1s$	$2s$	$2p$	$3s$	$3p$	$4s$	$3d$	$4p$
2.	1.6875							
3.	2.6906	0.6396						
4.	3.6848	0.9560						
5.	4.6795	1.2881	1.2107					
6.	5.6727	1.6083	1.5679					
7.	6.6651	1.9237	1.9170					
8.	7.6579	2.2458	2.2266					
9.	8.6501	2.5638	2.5500					
10.	9.6421	2.8792	2.8792					
11.	10.6259	3.2857	3.4009	0.8358				
12.	11.6089	3.6960	3.9129	1.1025				
13.	12.5910	4.1068	4.4817	1.3724	1.3552			
14.	13.5745	4.5100	4.9725	1.6344	1.4284			
15.	14.5578	4.9125	5.4806	1.8806	1.6288			
16.	15.5409	5.3144	5.9885	2.1223	1.8273			
17.	16.5239	5.7152	6.4966	2.3561	2.0387			
18.	17.5075	6.1152	7.0041	2.5856	2.2547			
19.	18.4895	6.5031	7.5136	2.8933	2.5752	0.8738		
20.	19.4730	6.8882	8.0207	3.2005	2.8861	1.0995		
21.	20.4566	7.2868	8.5273	3.4466	3.1354	1.1581	2.3733	
22.	21.4409	7.6883	9.0324	3.6777	3.3679	1.2042	2.7138	
23.	22.4256	8.0907	9.5364	3.9031	3.5950	1.2453	2.9943	
24.	23.4138	8.4919	10.0376	4.1226	3.8220	1.2833	3.2522	
25.	24.3957	8.8969	10.5420	4.3393	4.0364	1.3208	3.5094	
26.	25.3810	9.2995	11.0444	4.5587	4.2593	1.3585	3.7266	
27.	26.3668	9.7025	11.5462	4.7741	4.4782	1.3941	3.9518	
28.	27.3526	10.1063	12.0476	4.9870	4.6950	1.4277	4.1765	
29.	28.3386	10.5099	12.5485	5.1981	4.9102	1.4606	4.4002	
30.	29.3245	10.9140	13.0490	5.4064	5.1231	1.4913	4.6261	
31.	30.3094	11.2995	13.5454	5.6654	5.4012	1.7667	5.0311	1.5554
32.	31.2937	11.6824	14.0411	5.9299	5.6712	2.0109	5.4171	1.6951
33.	32.2783	12.0635	14.5368	6.1985	5.9499	2.2360	5.7928	1.8623
34.	33.2622	12.4442	15.0326	6.4678	6.2350	2.4394	6.1590	2.0718
35.	34.2471	12.8217	15.5282	6.7395	6.5236	2.6382	6.5197	2.2570
36.	35.2316	13.1990	16.0235	7.0109	6.8114	2.8289	6.8753	2.4423

[a] States are the same as given in Table III.