Physics 40—Quantum Physics of Matter

HW 6—Due May 10, 2024

1. Helium energy levels

   (a) In the independent electron approximation, what is the first ionization energy of the He atom (*i.e.*, the energy required to go from the ground state of the He atom to the ground state of the He^+ ion)? What is the second ionization energy (*i.e.*, the energy required to go from the ground state of the He^+ ion to the He^{++} ion)?

   (b) The measured first ionization energy of neutral He is 24.5874 eV. What physical effect has to be included to explain the discrepancy with your result in (a)? Explain the true value 79 eV of the He ground state energy as given in ER (and lecture) in terms of the measured first ionization energy and your calculated second ionization energy. Why is the calculated second ionization energy correct?

2. Fun with the periodic table!

   (a) If atoms could contain electrons with principal quantum numbers up to and including the entire $n = 6$ shell, how many elements would there be?

   (b) Verify that the Madelung rule for filling atomic subshells is equivalent to the rule that subshells are filled first in order of increasing $n + l$, and within a group of $n + l$, in order of increasing n. Point out four exceptions to this rule among the lighter transition metals (periods 4 and 5, columns 3-12 of the periodic table) and explain in what way they violate the rule.

3. Ionization energies

   (a) The measured ionization energy of a sodium atom is 5.14 eV. From this information deduce an empirical value of Z_{eff} for the outer electron in sodium.

   (b) The ionization energies of the elements Li, Na, K, Rb, and Cs (alkali elements)are, respectively, 5.4, 5.1, 4.3, 4.2, and 3.9 eV when rounded to one digit. What is the reason for the decrease in ionization energy with increasing atomic number of these elements?

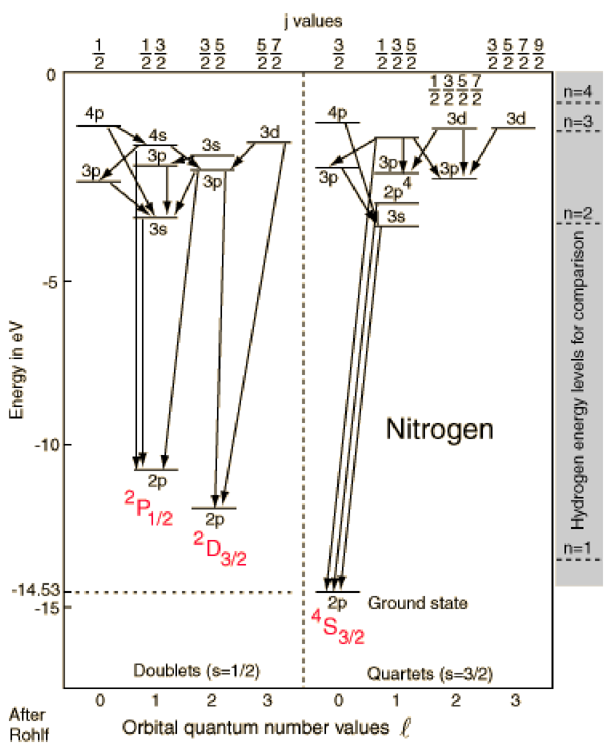
4. (a) The "sodium doublet", a closely spaced pair of spectral lines at wavelengths 588.995 and 589.592 nm, arises from the spin-orbit splitting of the sodium $3p$ level, as a Na atom in the excited $3p$ configuration decays to the ground $3s$ configuration. Show on an energy-level diagram the electronic transitions giving rise to these lines, labeling the participating atomic states with their proper spectroscopic designations.

(b) The size of the spin-orbit coupling can be written as

$$\Delta E_{\mathrm{SO}} = \xi(L,S)[j(j+1) - l(l+1) - s(s+1)].$$

From the doublet spacing, determine the magnitude of the spin-orbit coupling constant $\xi(L,S)$ and the magnitude of the effective magnetic field experienced by the outer electron in the sodium atom. (For the latter, imagine the electron as spin as experiencing a magnetic field from its orbital motion, and find that field value.)

5. With an electron configuration of $1s^2 2s^2 2p^3$, nitrogen has three electrons outside closed shells. The total spin can in this case be either $s = 1/2$, giving rise to doublets (left side of diagram) or $s = 3/2$ giving rise to quartets (right side). For most excited states of nitrogen two of the $2p$ electrons remain in their original shell, and one goes to an $n = 3$ or 4 shell as in the diagram.



Nitrogen atom energy level diagram. The labels with lower case letters specify the shell and orbital angular momentum of the third outer shell electron, assuming the other two remain $2p$. The labels with upper case letters give spectroscopic notation for three possible states of the $2p^3$ configuration.
Source: hyperphysics.phy-astr.gsu.edu/hbase/atomic/nitrogenlev.html

(a) What are all the quantum numbers $(n, l, m_l, m_s, s, l, j)$ for each of the three $2p$ electrons of the ground state given its spectroscopic notation $^4S_{3/2}$? Explain how this state satisfies Pauli exclusion and Hund's first rule.

(b) Explain the energy ordering from low to high of the three states with the $2p^3$ electron configuration in terms of Hund's first rule and the spin-orbit splitting

$$\Delta E_{\mathrm{SO}} = \xi(L,S)[j(j+1) - l(l+1) - s(s+1)].$$

(Ignore any possible variation in $\xi(L,S)$ for this calculation.)

(c) Deduce the possible values of j and l for the two *doublets* with electron configuration $2p^2 3s^1$, and give spectroscopic notation for each. (*Hint*: there are four possibilities. Think first about the possible spin states for the $2p^2$ electrons, and then about possible values for m_l for the $3s$ electron.)

(d) Why is the quadruplet $2p^2 3s^1$ $L = 2$ excited state missing (it exists as a doublet state)?

(e) Why are there no transitions between from any of the quartets to any of the doublets (or vice versa)?

(f) Why are there no transitions between the two $2p^3$ configurations with spectroscopic notation ${}^2P_{1/2}$ and ${}^2D_{3/2}$?