

**Physics 531 Atomic Physics**  
**Problem Set #3**  
 Due Wednesday, Sept. 28, 2011

**Problem 1: Perturbation calculation for two-electron atoms. (10 points)**

Consider the  $1s2p$  configuration, singlet and triplet state ( $^1P_1$  and  $^3P_1$ ) of the helium-like atoms of nuclear charge  $Ze$ . Approximate the one-electron wave functions as hydrogenic, corresponding to charge  $Z$  for  $1s$  electrons and  $Z-1$  for  $2p$  (a variational calculation gives essentially this result).

(a) As a preliminary, we will need an expression for perturbation matrix element:. Show

$$\langle \phi_A(1)\phi_B(2) | \frac{1}{r_{12}} | \phi_C(1)\phi_D(2) \rangle = \delta_{m_A+m_B, m_C+m_D} \sum_k c_{l_A m_A; l_C m_C}^{(k)} c_{l_B m_B; l_D m_D}^{(k)} F^{(k)}(AB, CD),$$

where  $\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \phi)$  is a hydrogenic spatial orbital,

$$c_{lm, l'm'}^{(k)} \equiv \sqrt{\frac{4\pi}{2k+1}} \int d\Omega Y_{lm}^* Y_{k, m-m'} Y_{l'm'}, \quad F^{(k)}(AB, CD) = \int dr_1 dr_2 \frac{r_{\leq}^k}{r_{>}^{k+1}} u_A(1) u_B(2) u_C(1) u_D(2).$$

(b) Compute the necessary integrals in perturbation theory and find the energies of the  $^1P_1$  and  $^3P_1$  states for arbitrary  $Z$ . For helium, compare your results for the ionization energies of the two states with the experimentally measured values,  $27182 \text{ cm}^{-1}$  for singlet and  $29229 \text{ cm}^{-1}$  for triplet.

(c) Data for the energy levels of atoms and ions are now compiled on the web at

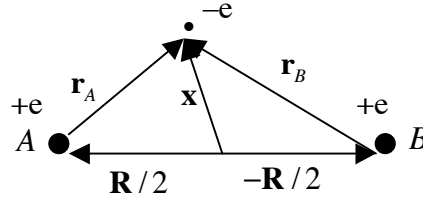
<http://physics.nist.gov/PhysRefData/ASD/index.html>

The different “ionization” stages are listed with roman numerals (for example, neutral Helium is He I; singly ionized Helium is He II).

Find the splitting of the  $1s2p$   $^1P$  and  $^3P$  states (the later averaged over the different  $J$  values) for the two electron spectra of He I (neutral Helium) through F VIII (7 times ionized Fluorine), and compare to this simple theory.

**Problem 2: Diatomic Molecules (20 points)**

The simplest molecule is the hydrogen molecular ion,  $H_2^+$ , consisting of two protons and one electron,



Because the protons are 2000 times heavier than the electrons, it is appropriate to make the *Born-Oppenheimer* approximation: take the nuclei as fixed in space (i.e. treat their position as a classical parameter) and calculate the energy eigenstates of the electrons (here only one electron). The nuclei are then allowed to move in the potential of the resulting electron cloud, with the electrons adjusting adiabatically as a function of  $\mathbf{R}$ .

The B-O Hamiltonian is,

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A} - \frac{e^2}{\hat{r}_B} + \frac{e^2}{R},$$

where  $p$  is the electron momentum,  $m$  its mass, and  $R$  (the internuclear separation) is a parameter.

(a) We seek the ground state electronic levels as a function of  $R$ . The electron wave function is known as a “molecular orbital”. The problem can be solved exactly using elliptical coordinates. We will use here the approximate variational method. The potential presented by the nuclei to the electron is a three dimensional analog of a “double-well” potential in 1D: the electron can be bound to either proton or “tunnel” between them. Thus, we take as our trial ground state wave function,

$$\tilde{\psi}(\mathbf{x}) = c_A \psi_A(\mathbf{x}) + c_B \psi_B(\mathbf{x}),$$

where  $\psi_{A(B)}(\mathbf{x}) = \phi_{1s}(\mathbf{x} \mp \mathbf{R}/2)$  are the hydrogen atom ground states centered at the two nuclei, and the probability amplitudes are real.

Use the variational method to show that there are two possible minima for the ground states according to  $c_A = \pm c_B$ . We of course could have seen this -- these are the symmetric and antisymmetric (gerade/ungerade) solutions of the double well -- the exercise demonstrates the power of the variational method if the right guess is made. Show that the electronic energy level (molecular potential seen by the nuclei) are

$$E(1\sigma_{g(u)}) = E_{g(u)} + \frac{e^2}{R}, \text{ where } E_{g(u)} = E_H(1s) + \frac{I \pm M}{1 \pm P_{AB}}$$

Here  $E_H(1s) = -13.6 eV$  is the hydrogen atom 1s binding energy,

$$I = \int d^3x |\psi_A(\mathbf{x})|^2 \left( -\frac{e^2}{r_B} \right) = \frac{e^2}{a_0} \left( -\frac{1}{\bar{R}} + e^{-2\bar{R}} \left( 1 + \frac{1}{\bar{R}} \right) \right) < 0 \quad (\text{“Coulomb integral”})$$

$$M = \int d^3x \psi_A(\mathbf{x}) \left( -\frac{e^2}{r_B} \right) \psi_B(\mathbf{x}) = -\frac{e^2}{a_0} e^{-\bar{R}} (1 + \bar{R}) < 0 \quad (\text{“Resonance integral”})$$

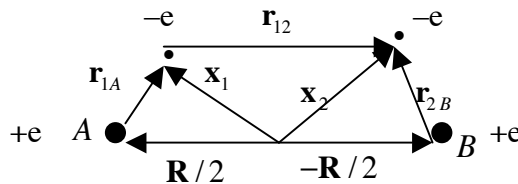
$$P_{AB} = \int d^3x \psi_A(\mathbf{x}) \psi_B(\mathbf{x}) = e^{-\bar{R}} (1 + \bar{R} + \bar{R}^2 / 3), \text{ with } \bar{R} = R / a_0,$$

and I have introduced the molecular orbital spectroscopic notation:  $1\sigma_g \rightarrow$  principal quantum number  $n=1$ , angular momentum  $l_z=0$  about internuclear axis ( $\sigma$  state), and symmetric w.r.t. electron parity (gerade). You need not calculate the integrals above.

(b) Plot the molecular potentials  $E(1\sigma_{g(u)})$  as a function of  $R$ . Show that the  $1\sigma_g$  state allows binding of the two nuclei (i.e. there is a potential well in which the nuclei move). This is simplest example of covalent chemical bond due to the attraction of the nuclei to the shared electron cloud. Estimate the binding energy and equilibrium separation of the nuclei. The exact values are  $E_{bind} = 2.79 eV$ ,  $\Delta R_{eq} = 2.0 a_0$ .

Note: This model underestimates the binding due to the choice of variational wave function. A more sophisticated choice would include the change in the atomic orbitals as the nuclei merge to form a Helium-like charge.

Now consider the simplest *neutral* molecule, diatomic hydrogen  $H_2$ .



The B-O Hamiltonian for this two electron system is

$$\hat{H} = \frac{\hat{p}_1^2}{2m} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} + \frac{\hat{p}_2^2}{2m} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}.$$

(c) One approach to finding the energy levels is to build up single electron “molecular orbitals” in the same way as we can build, e.g. atomic Helium, out of single electron hydrogenic orbitals. An alternative approach (the Heitler-London model) is to consider the problem as two interacting hydrogen *atoms*, and treat everything else (interaction of electron 1 with nucleus B, interaction of electron 2 with nucleus A, and interaction of the two electrons) as a perturbation. We thus take as our trial wave function

$\tilde{\psi}(\mathbf{x}_1, \mathbf{x}_2) = c_1 \psi_A(\mathbf{x}_1) \psi_B(\mathbf{x}_2) + c_2 \psi_A(\mathbf{x}_2) \psi_B(\mathbf{x}_1)$  (state with electron 1 in hydrogen atom at proton A and electron 2 in hydrogen atom at proton B, superposed with  $1 \leftrightarrow 2$ ).

**Show** that the variational methods gives binding and anti-binding molecular potentials arising from the two electrons

$$E_{\Sigma_{g(u)}} = 2E(1s) + \frac{2I + J \pm 2MP_{AB} \pm K}{1 \pm P_{AB}^2} + \frac{e^2}{R},$$

where

$$J = \int d^3x_1 d^3x_2 \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) \frac{e^2}{r_{12}} \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) \text{ is the "direct integral",}$$

$$K = \int d^3x_1 d^3x_2 \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) \frac{e^2}{r_{12}} \psi_A(\mathbf{x}_2)\psi_B(\mathbf{x}_1) \text{ is the "exchange integral",}$$

with two electron wave functions,

$$\tilde{\Psi}_{\Sigma_{g(u)}}(\mathbf{x}_1, \mathbf{x}_2) = \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) \pm \psi_A(\mathbf{x}_2)\psi_B(\mathbf{x}_1) \text{ (unnormalized).}$$

Here I have used the molecular "term notation", where  $\Sigma$  denotes that  $L_z=0$  is the *total* angular momentum of the two electrons. his model gives an equilibrium separation of the bond hydrogen molecule as  $\Delta R_{eq} = 0.73a_0$ , and the binding energy as  $E_{bind} = 9.6eV$

Note: The Heitler-London model assumes as  $R \rightarrow \infty$ , the molecular energy asymptotes to the energy of two free neutral hydrogen atoms. It neglects possibilities of ionic interactions (i.e.  $H_2^+$  + proton). The molecular orbital model treats these equally. Neither is a very good approximation. A better approximation would use the variational method to optimize these two contributions.

(e) The Pauli principle insists on complete antisymmetry of the two-electron wave function. If we write the total electron state, including spin, **argue** that the "binding state" is  $^1\Sigma_g$  (singlet) and the antibinding state is  $^3\Sigma_u$  (triplet). **Further argue** why you expect, *physically*, that the singlet provides a binding potential for the nuclei and the triplet an anti-binding potential.

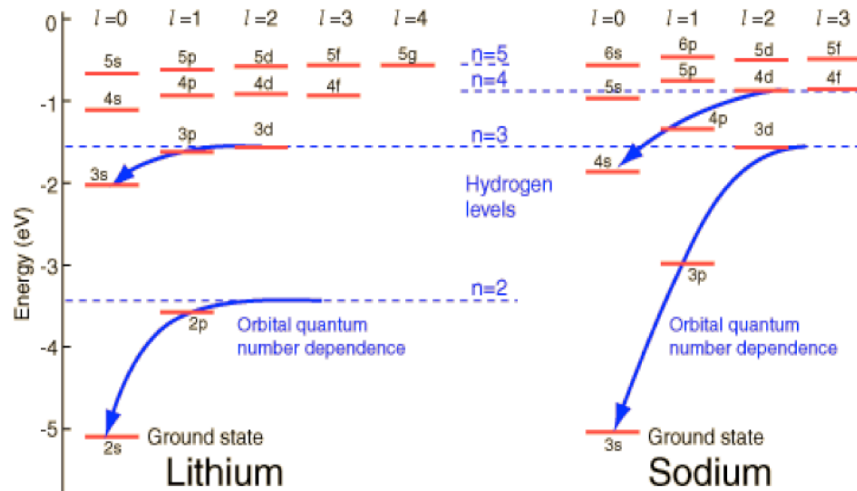
### Problem 3: Spectrum of Alkali Atoms (10 points)

We have seen that the spectrum of hydrogen has an “accidental” degeneracy – states with the same principle quantum number  $n$ , but different angular momentum quantum number  $l$  are degenerate. This was an artifact of the pure  $1/r$  Coulomb potential associated.

In a multielectron atom things are, of course, more complicated. Each electron moves in the combined attractive field of the nucleus and repulsive field of the other electrons. The Pauli principle must also be accounted for. This many-body problem cannot be solved exactly. Much of the middle part of the course will be devoted to solving this.

One coarse approximation is the “mean-field” approximation, whereby every electron moves in the average field of all the other particles. The mean field is spherically symmetric, and thus, the quantum numbers  $n$  and  $l$  are still good. This approximation is especially good for alkalis (group IA in the period table) since they have one valence electron around a stable “noble atom-like core”. They are thus vaguely hydrogenic if the valence electron does not “penetrate” the core.

Consider the spectrum of Li and Na, two alkali atoms, shown below:



Clearly, states with different  $l$  are no longer degenerate.

(a) Using the discussion above and your knowledge of the hydrogenic wave functions, explain the qualitative behavior of these spectra.

(b) Let us take an artificial (but exactly solvable) model of the mean field of the other electrons as having a  $1/r^2$  dependence, so that  $V(r) = -\frac{e^2}{r} + \frac{A}{r^2}$ . Show that wave functions are hydrogenic in form, and the eigenvalues are:

$$E(n_r, l) = -\mathfrak{R} \left[ n_r + \frac{1}{2} \left( 1 + \sqrt{(2l+1)^2 + 8mA/\hbar^2} \right) \right]^2, \text{ where } \mathfrak{R} \text{ is the Rydberg constant.}$$

Hint: Show that the radial equation leads to the same hypergeometric function.

(c) Expand in the  $8mA/\hbar^2 \ll 1$ . Show that you get the correct result to first order perturbation. Sketch an energy-level diagram.