Physics 531, Problem Set #6

Due: Thursday, March 24, 2005

Problem 1: Perturbation calculation for two-electron atoms.

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

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

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

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

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

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

Note: This web site works best with Firefox or IE, not Apple's Safari :-(.

The different "ionization" stages are listed with roman numericals (for example, neutral Helium is He I; singly ionized Helium is He II.

Find the spitting of the 1*s*2*p* ^{1}P and ^{3}P 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: Russell-Saunders description of three equivalent *p*-electrons

Consider a configuration of three identical *p*-electrons (as occurs in Nitrogen).

(a) Construct a "Slater table" listing all possible m_l , m_s and total M_L , M_S values for the three electrons (as in Table 8.7 in the text B&J), together with the possible Terms to which this configuration can contribute.

(b) By considering the state with total spin S=3/2 and projection M_S=3/2 (i.e. the state with three parallel electron spins), show that the only possible *spatial* wave function that is totally antisymmetric under exchange of any two electrons has the form

$$\Psi(1,2,3) = \mathbf{r}_1 \cdot (\mathbf{r}_2 \times \mathbf{r}_3) f(r_1) f(r_2) f(r_3)$$

and is associated with the term ${}^4S_{3/2}$. From the form above, does it make sense that L=0? Write down the four spin states associated with this quadruplet.

(c) Express as a sum of Slater determinants the 3-electron state for the level ${}^2P_{3/2}(M_J = 3/2)$ and show that it can be written as,

$$\Psi(1,2,3) = \sum_p (-1)^p \ \mathbf{r}_1 \cdot \mathbf{r}_2 \ (x_3 + iy_3) \ f(r_1) f(r_2) f(r_3) \left(\left|\uparrow_1\right\rangle \left|\downarrow_2\right\rangle - \left|\downarrow_1\right\rangle \left|\uparrow_2\right\rangle \right) \left|\uparrow_3\right\rangle .$$

where we sum over permutations p.