Chemistry 691, Exam 1, April 6 2017

1. The N atom has the electron occupancy $1s^2 2s^2 2p^3$. There are three possible electronic states: ^2D, ^2P, and ^4S. In terms of definite-m $2p$ orbitals, the Slater determinantal wavefunction for the N atom in the $^2D_{M_L=2,M_S=1/2}$ state is (you can neglect the $1s$ and $2s$ spin-orbitals)

$$\left|{}^2D_{M_L=2,M_S=1/2}\right\rangle = |p_1\bar{p}_1p_0|$$

a. (10 pts) Use the lowering operators (L_- and/or S_-) to generate the normalized Slater determinantal wavefunction for the $^1D_{M_L=1,M_S=1/2}$ state. In writing your answer order your determinants so that the $l = 1$ spin-orbitals appear before the $l = 0$ spin-orbitals and the $l = 0$ before the $l = -1$, and, for a given l, the unbarred spin-orbitals appear before the barred spin-orbitals.

b. (10 pts) Give the Slater determinantal wavefunction for the $^2P_{M_L=1,M_S=1/2}$ state.

c. (5 pts) We know that the relation between the definite-m and the Cartesian p orbitals is

$$p_{\pm 1} = \mp 2^{-1/2}(p_x \pm ip_y), \text{ and } p_0 = p_z$$

Give, in terms of Cartesian p orbitals, a Slater determinantal wavefunctions for the state

$$|{}^2D_+\rangle = 2^{-1/2}\left(|{}^2D_{M_L=2,M_S=1/2}\rangle + |{}^2D_{M_L=-2,M_S=1/2}\rangle\right)$$

Order the determinant so that the x spin-orbitals appear before the y spin-orbitals and then the z spin-orbitals. For a given x, y, or z, the unbarred spin-orbital should be placed before the barred spin-orbital.

d. (10 pts) For this state, what is the expectation value of the electron-electron repulsion between the three $2p$ electrons? Give your answer in terms of the three basic integrals $[p_x^2|p_x^2]$, $[p_x^2|p_y^2]$, and $[p_xp_y|p_yp_x]$.

2. Consider the Na atom ($1s^2 \cdots 2p^6 3s$). In a simple approximation the outermost electron in the alkali metals atom is totally shielded by the inner electrons and thus sees a nuclear charge of +1. This is what is called a "Rydberg" atom, with the outermost electron designated the Rydberg electron. In reality, this shielding is not 100%, since the Rydberg electron is sometimes closer to the nucleus that the outermost non-Rydberg electron. As a consequence the Rydberg electron behaves like a hydrogenic electron with an effective nuclear charge Z_{eff},

which is greater than 1.

a. (10 pts) The $19s \rightarrow 20s$ transition in Na occurs at 36.75 cm^{-1}(1 hartree=219474.6 cm^{-1}). Use this to estimate Z_{eff} for the Rydberg s electrons in Na.

b. (5 pts) In a hydrogenic (one-electron) atom the $19s$ and $19p$ orbitals are degenerate. In the Na atom the $19p$ level (the $1s^2 \cdots 2p^6 19p$ level) lies 19 cm^{-1} **above** the $19s$ level. Why?

3. Consider the simplest approximation of the electronic wavefunction for a two-electron ion

$$\Psi(1,2) = 1s(1)1s(2)$$

where $1s = 1s(r,\theta,\phi) = \sqrt{\zeta^3/\pi}\,\exp(-\zeta r)$. The $1s$ function as written is normalized, so that

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \, 1s^2(r,\theta,\phi) = 1$$

a. (5 pts) We could estimate the size of a two-electron atom by determining the square root of $\langle r_1 r_2 \rangle$, where

$$\langle r_1 r_2 \rangle = \int dV_1 \int dV_2 \, |\psi(1,2)|^2 \, r_1 r_2$$

Knowing that $\int \exp(-ar) r^n dr = n!/(2a)^{n+1}$, what is $\langle r_1 r_2 \rangle^{1/2}$, the average size of the two-electron atom, as a function of ζ?

b. (10 pts) The energy of a two-electron atom with nuclear charge Z is

$$E = \langle \Psi(1,2)|\hat{H}(1,2)|\Psi(1,2)\rangle = \zeta^2 + \zeta(-2Z + 5/8)$$

Predict an expression for the size of the two-electron ions as a function of Z?