

CHEMISTRY 373 – TUTORIAL-9
PRACTICE FOR SPIN AND MANY-ELECTRON ATOMS

March 15, 2000

1. (a) For the ground state of the helium atom, show that within the one-electron approximation (ignores electron-electron repulsion), the wave function for the two electrons is the product of two 1s orbitals, one for electron 1 and the other for electron 2.

(ANS. If we ignore electron-electron repulsion, the Hamiltonian can be written as the sum of two Hamiltonians, one for electron 1 and one for electron 2. Therefore, we have

$$\hat{H} = \hat{H}(1) + \hat{H}(2),$$

where, for the j 'th electron,

$$\hat{H}(j) = -\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_j},$$

which is just the hydrogen atom Hamiltonian for electron j . If we assume that the wave function (excluding spin) can be written as a product of functions, one depending upon the coordinates of electron 1 and the other on the coordinates of electron 2, i.e., $\psi(1,2) = \psi(1)\psi(2)$, then

$$\hat{H}\psi(1,2) = E\psi(1,2),$$

$$\left(\hat{H}(1) + \hat{H}(2)\right)\psi(1)\psi(2) = \psi(2)\hat{H}(1)\psi(1) + \psi(1)\hat{H}(2)\psi(2) = E\psi(1)\psi(2).$$

The Hamiltonian, $H(1)$, for electron 1 operates only on the wave function for electron 1, etc. Dividing by $\psi(1)\psi(2)$ from the left yields

$$\frac{1}{\psi(1)}\hat{H}(1)\psi(1) + \frac{1}{\psi(2)}\hat{H}(2)\psi(2) = E.$$

$$\frac{1}{\psi(1)}\hat{H}(1)\psi(1) = E - \frac{1}{\psi(2)}\hat{H}(2)\psi(2) = E_1.$$

Since $\frac{1}{\psi(1)}\hat{H}(1)\psi(1)$ depends upon electron 1 only and $E - \frac{1}{\psi(2)}\hat{H}(2)\psi(2)$ depends only on electron 2, they can only be equal if they equal a constant, say E_1 . Therefore, we end up with the two equations

$$\hat{H}(1)\psi(1) = E_1\psi(1), \quad \hat{H}(2)\psi(2) = (E - E_1)\psi(2) = E_2\psi(2),$$

where $E = E_1 + E_2$ and E_j is the energy of a hydrogen-like ion:

$$E_j = E_{n_j} = -\frac{2\pi^2 m_e (2)^2 e^4}{(4\pi\epsilon_0)^2 n_j^2 h^2}.$$

The lowest energy state for the two electrons will correspond to the case when $n_1 = n_2 = 1$, that is when each electron occupies a 1s type orbital. In that case, the energy is

$$E = 2 \left(-\frac{2\pi^2 m_e (2)^2 e^4}{(4\pi\epsilon_0)^2 h^2} \right) = -\frac{4\pi^2 m_e (2)^2 e^4}{(4\pi\epsilon_0)^2 h^2}.$$

We write the wave function as

$$\psi(1,2) = \psi_{1,0,0}(1)\psi_{1,0,0}(2) = 1s(1)1s(2).$$

We have ignored spin to this point.)

(b) Show that the total wave function, which is a product of space and spin functions is antisymmetric with respect to an interchange of two electrons. (You may wish to write the total wavefunction as a determinant.)

(ANS. For a 2-electron system, we can still write the wave function as a product of spatial and

spin functions

$$\psi(1,2) = 1s(1)1s(2) \sqrt{\frac{1}{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)).$$

Interchanging the two electrons, we get

$$\begin{aligned} \psi(2,1) &= 1s(2)1s(1) \sqrt{\frac{1}{2}} (\alpha(2)\beta(1) - \beta(2)\alpha(1)), \\ &= 1s(1)1s(2) \sqrt{\frac{1}{2}} (\beta(1)\alpha(2) - \alpha(1)\beta(2)), \\ &= -1s(1)1s(2) \sqrt{\frac{1}{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)), \\ &= -\psi(1,2). \end{aligned}$$

The wave function is antisymmetric with respect to an interchange of two electrons.)

(c) Show that the presence of spin makes no difference to the expression within the one-electron model of the ground state.

(ANS. This follows directly from the fact that the 1-electron Hamiltonians, $\hat{H}(j)$, are independent of spin. Therefore the spin function will simply divide out.)

2. The total spin angular momentum, \vec{S} , for a two-electron system is defined by

$$\vec{S} = \hat{S}_x \tilde{e}_1 + \hat{S}_y \tilde{e}_2 + \hat{S}_z \tilde{e}_3 = \vec{S}_1 + \vec{S}_2$$

where \tilde{e}_1 , \tilde{e}_2 , and \tilde{e}_3 are the three mutually orthogonal unit vectors oriented along the x -, y -, and z -axes, respectively, and \hat{S}_x , \hat{S}_y , and \hat{S}_z are the three components of *total* spin angular momentum. The spin angular momentum for each electron is

$$\vec{S}_j = \hat{S}_{x_j} \tilde{e}_1 + \hat{S}_{y_j} \tilde{e}_2 + \hat{S}_{z_j} \tilde{e}_3, \quad j = 1, 2.$$

(a) Show that

$$\hat{S}_x = \hat{S}_{x_1} + \hat{S}_{x_2}, \quad \hat{S}_y = \hat{S}_{y_1} + \hat{S}_{y_2}, \quad \hat{S}_z = \hat{S}_{z_1} + \hat{S}_{z_2}.$$

(ANS.

$$\vec{S} = \hat{S}_x \tilde{e}_1 + \hat{S}_y \tilde{e}_2 + \hat{S}_z \tilde{e}_3 = \vec{S}_1 + \vec{S}_2 = (\hat{S}_{x_1} + \hat{S}_{x_2}) \tilde{e}_1 + (\hat{S}_{y_1} + \hat{S}_{y_2}) \tilde{e}_2 + (\hat{S}_{z_1} + \hat{S}_{z_2}) \tilde{e}_3.$$

Identifying the coefficients of the unit vectors gives us the result that we want.)

(b) Prove that the square of the total spin angular momentum is

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$$

(ANS.

$$\begin{aligned} \hat{S}^2 &= \vec{S} \cdot \vec{S}, \\ &= (\vec{S}_1 + \vec{S}_2) \cdot (\vec{S}_1 + \vec{S}_2), \\ &= \vec{S}_1 \cdot \vec{S}_1 + \vec{S}_2 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_1, \\ &= \hat{S}_1^2 + \hat{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2. \end{aligned}$$

We have $\vec{S}_1 \cdot \vec{S}_2 = \vec{S}_2 \cdot \vec{S}_1$ since the spin operators for electron 1 commute with the spin operators for electron 2, i.e., $[S_{x_1}, S_{x_2}] = [S_{x_1}, S_{y_2}] = [S_{x_1}, S_{z_2}] = \dots = 0$.)

(c) Show that

$$\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2} (\hat{S}_{1-} \hat{S}_{2+} + \hat{S}_{1+} \hat{S}_{2-}) + \hat{S}_{z_1} \hat{S}_{z_2},$$

where $S_{j\pm} = S_{x_j} \pm iS_{y_j}$, with $j = 1, 2$, and hence

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_{1-}\hat{S}_{2+} + \hat{S}_{1+}\hat{S}_{2-} + 2\hat{S}_{z_1}\hat{S}_{z_2}.$$

(ANS. Since

$$\vec{S}_1 \cdot \vec{S}_2 = \hat{S}_{x_1}\hat{S}_{x_2} + \hat{S}_{y_1}\hat{S}_{y_2} + \hat{S}_{z_1}\hat{S}_{z_2},$$

and from the definition above for $S_{j\pm}$, finding that

$$\hat{S}_{x_j} = \frac{1}{2}(\hat{S}_{j-} + \hat{S}_{j+}), \quad \hat{S}_{y_j} = \frac{i}{2}(\hat{S}_{j-} - \hat{S}_{j+}),$$

we can obtain

$$\begin{aligned} \vec{S}_1 \cdot \vec{S}_2 &= \frac{1}{4}(\hat{S}_{1-} + \hat{S}_{1+})(\hat{S}_{2-} + \hat{S}_{2+}) - \frac{1}{4}(\hat{S}_{1-} - \hat{S}_{1+})(\hat{S}_{2-} - \hat{S}_{2+}) + \hat{S}_{z_1}\hat{S}_{z_2}, \\ &= \frac{1}{2}(\hat{S}_{1-}\hat{S}_{2+} + \hat{S}_{1+}\hat{S}_{2-}) + \hat{S}_{z_1}\hat{S}_{z_2}. \end{aligned}$$

Substituting this expression into that for \hat{S}^2 from part (b), we obtain the desired result.)

3. Using the results from the previous question, determine the eigenvalue of \hat{S}^2 and \hat{S}_z for each of the following two-electron spin functions:

$$\psi_1 = \alpha(1)\alpha(2)$$

$$\psi_2 = \beta(1)\beta(2)$$

$$\psi_3 = \sqrt{\frac{1}{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$$

$$\psi_4 = \sqrt{\frac{1}{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

If the spin quantum number for the two-electron system is denoted by S , then determine values for S and $2S + 1$. Which of these wave functions belong to a triplet state and which to a singlet state.

(Note that a similar procedure may be used to calculate the square of the total orbital angular momentum, \hat{L}^2 , and its z -component \hat{L}_z .)

(ANS. First, for \hat{S}^2 , applying this operator to the first function, we get

$$\hat{S}^2\psi_1 = \left(\hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_{1-}\hat{S}_{2+} + \hat{S}_{1+}\hat{S}_{2-} + 2\hat{S}_{z_1}\hat{S}_{z_2}\right)\alpha(1)\alpha(2) = S(S+1)\hbar^2\psi_1.$$

Keeping in mind that any spin operator for electron j operates only on the spin function for electron j , we get

$$\begin{aligned} \hat{S}^2\psi_1 &= \left(\hat{S}_1^2\alpha(1)\right)\alpha(2) + \alpha(1)\left(\hat{S}_2^2\alpha(2)\right) + \left(\hat{S}_{1-}\alpha(1)\right)\left(\hat{S}_{2+}\alpha(2)\right) \\ &\quad + \left(\hat{S}_{1+}\alpha(1)\right)\left(\hat{S}_{2-}\alpha(2)\right) + 2\left(\hat{S}_{z_1}\alpha(1)\right)\left(\hat{S}_{z_2}\alpha(2)\right), \\ &= \frac{3}{4}\hbar^2\alpha(1)\alpha(2) + \frac{3}{4}\hbar^2\alpha(1)\alpha(2) + 0 + 0 + 2\left(\frac{1}{2}\hbar\alpha(1)\right)\left(\frac{1}{2}\hbar\alpha(2)\right), \\ &= 2\hbar^2\alpha(1)\alpha(2), \\ &= 2\hbar^2\psi_1, \\ &= S(S+1)\hbar^2\psi_1. \end{aligned}$$

This implies that $S(S+1) = 2$ and hence $S = 1$ or -2 . The negative value of S is not possible and hence $S = 1$. This implies that $2S + 1 = 3$, a triplet spin state. Application of \hat{S}^2 to ψ_2 and ψ_3 will yield the same result. Now, from part (a), we have

$$\begin{aligned}
\hat{S}_z \psi_1 &= (\hat{S}_{z_1} + \hat{S}_{z_2}) \alpha(1) \alpha(2), \\
&= (\hat{S}_{z_1} \alpha(1)) \alpha(2) + \alpha(1) (\hat{S}_{z_2} \alpha(2)), \\
&= +\frac{1}{2} \hbar \alpha(1) \alpha(2) + \frac{1}{2} \hbar \alpha(1) \alpha(2), \\
&= +\hbar \alpha(1) \alpha(2), \\
&= +\hbar \psi_1, \\
&= M_S \hbar \psi_1.
\end{aligned}$$

Therefore, we have $M_S = +1$. Similarly, we get

$$\hat{S}_z \psi_2 = -\hbar \psi_2,$$

which implies that $M_S = -1$. Next, we get

$$\hat{S}_z \psi_3 = 0,$$

and so $M_S = 0$. Finally, we can show that

$$\hat{S}^2 \psi_4 = 0,$$

which means that $S = 0$ and $2S + 1 = 1$. Therefore, ψ_4 corresponds to a singlet state. Also, we have

$$\hat{S}_z \psi_4 = 0,$$

and hence, $M_S = 0$. These eigenstates of \hat{S}^2 and \hat{S}_z are the states of two electrons whose spins are coupled. This is an example of the addition of angular momenta for two electrons.)