1 Problem set 10

Handout: 10/31
Due date: 11/7

Problem 1

Produce a totally antisymmetric wavefunction starting from the configuration $1s(1)\alpha(1)2p(2)\beta(2)1s(3)\beta(3)$.

The wavefunction is

$$\psi = 1s(1)\alpha(1)2p(2)\beta(2)1s(3)\beta(3) = 1s2p1s\alpha\beta\beta$$  \hspace{1cm} (1)

Interchange 1 and 3 and subtract gives

$$1s2p1s(\alpha\beta\beta - \beta\beta\alpha)$$ \hspace{1cm} (2)

Interchange 1 and 2 and subtract gives

$$1s2p1s(\alpha\beta\beta - \beta\beta\alpha) - 2p1s1s(\beta\alpha\beta - \beta\beta\alpha)$$ \hspace{1cm} (3)

Interchanges of 2 and 3 and subtract gives

$$1s2p1s(\alpha\beta\beta - \beta\beta\alpha) - 2p1s1s(\beta\alpha\beta - \beta\beta\alpha) - 1s1s2p(\alpha\beta\beta - \beta\alpha\beta)$$ \hspace{1cm} (4)

Therefore, the normalized antisymmetric wavefunction is given by

$$\psi_a = \frac{1}{\sqrt{6}} [1s2p1s(\alpha\beta\beta - \beta\beta\alpha) - 2p1s1s(\beta\alpha\beta - \beta\beta\alpha) - 1s1s2p(\alpha\beta\beta - \beta\alpha\beta)]$$ \hspace{1cm} (5)

Now use a determinant to check the wavefunction. The Slater determinant for the given configuration is

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s & 2p & 1s \\ 1s & 1s & 2p \\ 1s & 1s & 1s \end{vmatrix}$$ \hspace{1cm} (6)

where the bar indicate $\beta$ spin. Expanding the determinant gives

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s & 2p & 1s \\ 2p & 1s & 1s \\ 1s & 1s & 1s \end{vmatrix} - \frac{1}{\sqrt{6}} \begin{vmatrix} 1s & 1s & 2p \\ 1s & 1s & 1s \\ 1s & 1s & 1s \end{vmatrix} + \frac{1}{\sqrt{6}} \begin{vmatrix} 1s & 2p \\ 1s & 1s \\ 1s & 1s \end{vmatrix}$$ \hspace{1cm} (7)
\[
\begin{align*}
\psi &= \frac{1}{\sqrt{6}} \left[ 1s2p1s - 1s1s2p - 2p1s1s + 2p1s1s + 1s1s2p - 1s2p1s \right] \quad (8) \\
\psi &= \frac{1}{\sqrt{6}} \left[ 1s2p1s(\alpha\beta\beta - \beta\beta\alpha) - 2p1s1s(\beta\alpha\beta - \beta\beta\alpha) \\
&\quad - 1s1s2p(\alpha\beta\beta - \beta\alpha\beta) \right] \quad (9)
\end{align*}
\]

which is identical to the wavefunction constructed by electron interchange.

**Problem 2**

1. Write down the Slater determinant for the configuration 1s1s2p_z.

2. Expand the determinant into linear combination of products.

\[
|1s1s2p_z\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & \bar{1}s(1) & 2p_z(1) \\ 1s(2) & \bar{1}s(2) & 2p_z(2) \\ 1s(3) & \bar{1}s(3) & 2p_z(3) \end{vmatrix} 
\]

\[
|1s1s2p_z\rangle = \frac{1}{\sqrt{6}} \left\{ 1s(1) \begin{vmatrix} \bar{1}s(2) & 2p_z(2) \\ \bar{1}s(3) & 2p_z(3) \end{vmatrix} - \bar{1}s(1) \begin{vmatrix} 1s(2) & 2p_z(2) \\ 1s(3) & 2p_z(3) \end{vmatrix} \right\} 
\]

\[
= \frac{1}{\sqrt{6}} \left\{ 1s(1)\bar{1}s(2)2p_z(3) - 1s(1)2p_z(2)\bar{1}s(3) \\
- \bar{1}s(1)1s(2)2p_z(3) + \bar{1}s(1)2p_z(2)1s(3) \\
+ 2p_z(1)1s(2)\bar{1}s(3) - 2p_z(1)\bar{1}s(2)1s(3) \right\} 
\]

**Problem 3**

The following wavefunction is proposed for an excited state of the lithium atom

\[
\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \bar{1}s(1) & 2s(1) & 3s(1) \\ \bar{1}s(2) & 2s(2) & 3s(2) \\ \bar{1}s(3) & 2s(3) & 3s(2) \end{vmatrix} 
\]

where 1s, 2s, and 3s are eigenfunctions for the Li^{2+} Hamiltonian.

1. Does this wavefunction satisfy the Pauli exclusion principle? Explain your reasoning
2. Write the exact Hamiltonian for the lithium atom in atomic units

3. Is \( \psi \) an eigenfunction for the exact Hamiltonian?

4. If interelectronic repulsion terms are neglected in the Hamiltonian, what is the energy associated with the \( \psi \) (in a.u.)?

5. What \( z \) component of spin and orbital angular momentum would you expect from the atom in this state?

Yes, since it is given by a Slater determinant which will ensure that the wavefunction is antisymmetric with respect to interchange of any two electrons. Also, each spin-orbital have only 1 electron.

\[
\hat{H} = \hat{h}(1) + \hat{h}(2) + \hat{h}(3) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \tag{18}
\]

\[
= -\frac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - 3\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \tag{19}
\]

No, since it is product of one-electron orbitals and therefore the solution to the independent electron Hamiltonian. The exact Hamiltonian is not separable due the electron-electron repulsion.

\[
\hat{H}^{\text{approx}} \psi = [\hat{h}(1) + \hat{h}(2) + \hat{h}(3)] \psi = [E_{1s} + E_{2s} + E_{3s}] \psi \tag{20}
\]

Therefore, the energy is

\[
E^{\text{tot}} = E_{1s} + E_{2s} + E_{3s} = -\frac{9}{2} - \frac{9}{8} - \frac{9}{18} = 6.125 \text{ a.u.} \tag{21}
\]

Since all electrons are in space s-orbitals \( L_z = 0 \) and in spin beta orbitals \( s_z = -1/2 \). Therefore, the total momentum is \( S_z = -1/2 -1/2 -1/2 = -3/2 \) a.u.

**Problem 4**

Write the normalized Slater determinant for beryllium in the \( 1s^22s^2 \) configuration. Do not expand the determinant.

\[
\psi_{\text{be}} = \frac{1}{\sqrt{24}} \begin{vmatrix}
1s(1) & \overline{1s}(1) & 2s(1) & \overline{2s}(1) \\
1s(2) & \overline{1s}(2) & 2s(2) & \overline{2s}(2) \\
1s(3) & \overline{1s}(3) & 2s(3) & \overline{2s}(2) \\
1s(4) & \overline{1s}(4) & 2s(4) & \overline{2s}(4)
\end{vmatrix} \tag{22}
\]
Problem 5
Consider the following helium atom wavefunction
\[ \psi = 1s(1)3d_{2+}(2)\alpha(1)\alpha(2) \] (23)
Is this a satisfactory wavefunction? If not, how would you modify it to make it satisfactory.

No, the spin wavefunction is symmetric so the requirement is that the space function is anti-symmetric, which is not the case. Solution write the space part as an antisymmetric linear combination as
\[ \psi = \frac{1}{\sqrt{2}} [1s(1)3d_{2+}(2) - 3d_{2+}(1)1s(2)] \alpha(1)\alpha(2) \] (24)

Problem 6
Given the following space part of an approximate wavefunction for a Li\(^+\) ion
\[ \frac{1}{\sqrt{2}} [1s(1)p_{1}(2) + 2p_{1}(1)s(2)] \] (25)

1. Write a physical acceptable spin part for this wavefunction.

2. If the \(\frac{1}{r_{12}}\) term in the hamiltonian is neglected, what would the energy be (in a.u.)?

Since the space part is symmetric we need an antisymmetric spin part. Therefore, the spin-space wavefunction is
\[ \psi = \frac{1}{\sqrt{2}} [1s(1)p_{1}(2) + 2p_{1}(1)s(2)] \frac{1}{\sqrt{2}} [\alpha\beta - \beta\alpha] \] (26)

If we ignore repulsion we have
\[ E_{approx} = E_{1s} + E_{2p} = -9/2 - 9/8 = -45/8 \] (27)

Problem 7
One way to describe the properties of the spin angular momentum operator \(\hat{S}\) is to represent them using Pauli matrices. The operators are defined as
\[ \hat{S}_x = \frac{1}{2}h\sigma_x, \quad \hat{S}_y = \frac{1}{2}h\sigma_y, \quad \hat{S}_z = \frac{1}{2}h\sigma_z, \] (28)
where the Pauli matrices are given by
\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \] (29)
1. Show that the \( \hat{S} \) operator (using the Pauli matrices) satisfy the usual commutator relations for angular momentum, such as \([\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z\).

2. Find \( \hat{S}^2 \)

3. Show that the diagonal element of \( \hat{S}^2 \) and \( \hat{S}_z \) correspond to angular momentum eigenvalues with spin 1/2.

1. 
\[
[\hat{S}_x, \hat{S}_y] = \frac{1}{4} \hbar^2 (\sigma_x \sigma_y - \sigma_y \sigma_x) \tag{30}
\]
\[
= \frac{1}{4} \hbar^2 \left[ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right] \tag{31}
\]
\[
= \frac{1}{4} \hbar^2 \left[ \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right] \tag{32}
\]
\[
= \frac{i \hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{33}
\]
\[
= i \hbar \frac{1}{2} \sigma_z = i \hbar \hat{S}_z \tag{34}
\]

2. First we need to evaluate
\[
\hat{S}_x \hat{S}_x = \frac{1}{4} \hbar^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{1}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{35}
\]
\[
\hat{S}_y \hat{S}_y = \frac{1}{4} \hbar^2 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{36}
\]
and
\[
\hat{S}_z \hat{S}_z = \frac{1}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{37}
\]
Therefore we have
\[
\hat{S}^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{38}
\]

3. To find the eigenvalues of \( \hat{S}_z \) we have
\[
\hat{S}_z \alpha = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2} \hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{39}
\]
and
\[ \hat{S}_z \beta = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2} \hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix} \] (40)

Similarly for \( \hat{S}_2 \) we have
\[ \hat{S}_z \alpha = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4} \hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix} \] (41)

and
\[ \hat{S}_z \beta = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4} \hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix} \] (42)

which are the expected eigenvalues for a spin-half particle.