1. The quantum mechanical state of a hydrogen atom is described by the following superposition:

\[ \psi = \frac{1}{\sqrt{14}} (2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2}) \]

where \( \psi_{n,l,m} \) are eigenfunctions of the Hamiltonian. The subscripts refer to quantum numbers \( n, l, m \).

(a) What is the probability of finding the hydrogen atom in states \((n = 1, l = 0, m = 0), (n = 2, l = 0, m = 0), (n = 3, l = 2, m = 2)\) or in some other state?

(b) What are the expectation values for energy, \( \hat{L}^2 \) and \( \hat{L}_z \)?

Solution:

First we check that the wavefunctions are normalized. For hydrogen-like atom orbitals we have the following orthonormality condition:

\[ \langle \psi_{n,l,m} | \psi_{n',l',m'} \rangle = \delta_{nn'}\delta_{ll'}\delta_{mm'} \]

The normalization of the given wavefunction can now be evaluated:

\[ \langle \psi | \psi \rangle = \frac{1}{14} \langle 2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2} | 2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2} \rangle \]

\[ = \frac{1}{14} (4 + 9 + 1) = 1 \text{ (due to orthonormality)} \]

(a) The probabilities for the energy eigenstates are given by squaring their coefficients in the wavefunction. The probabilities are then:

\[ P(1,0,0) = \frac{4}{14} = \frac{2}{7}, \quad P(2,0,0) = \frac{9}{14}, \quad P(3,2,2) = \frac{1}{14} \]

(b) The expectation value for energy is:

\[ \langle \psi | \hat{H} | \psi \rangle = \frac{1}{14} \langle 2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2} | \hat{H} | 2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2} \rangle \]

\[ = \frac{1}{14} \left( \frac{4}{E_{1,0,0}} \langle \psi_{1,0,0} | \hat{H} | \psi_{1,0,0} \rangle + \frac{9}{E_{2,0,0}} \langle \psi_{2,0,0} | \hat{H} | \psi_{2,0,0} \rangle + \frac{1}{E_{3,2,2}} \langle \psi_{3,2,2} | \hat{H} | \psi_{3,2,2} \rangle \right) \]

\[ = \frac{2}{7} E_{1,0,0} + \frac{9}{14} E_{2,0,0} + \frac{1}{14} E_{3,2,2} \]
The numerical values for $E_{n,l,m}$’s can be calculated from:

$$E_n = -\frac{hcR}{n^2} = -\frac{13.6 \text{ eV}}{n^2} = E_1 \frac{1}{n^2}$$

Thus the numerical value for $\langle \hat{H} \rangle$ is:

$$\langle \hat{H} \rangle = \left( \frac{2}{7} + \frac{9}{14} \times \frac{1}{4} + \frac{1}{14} \times \frac{1}{9} \right) E_1 = \frac{229}{504} E_1 \approx -6.2 \text{ eV}$$

The expectation value for $\vec{\hat{L}}^2$ is:

$$\vec{\hat{L}}^2 |\psi_{n,l,m}\rangle = l(l+1)\hbar^2 |\psi_{n,l,m}\rangle$$

$$\langle \vec{\hat{L}}^2 \rangle = \frac{\hbar^2}{14} (0 + 0 + 2(2 + 1))) = \frac{3}{7} \hbar^2$$

The expectation value for $\hat{L}_z$ is:

$$\hat{L}_z |\psi_{n,l,m}\rangle = m\hbar |\psi_{n,l,m}\rangle$$

$$\langle \hat{L}_z \rangle = \frac{\hbar}{14} (0 + 0 + 2) = \frac{1}{7} \hbar$$

2. Show that operators $\hat{L}_z$ and $\vec{\hat{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ commute with the hydrogen atom Hamiltonian operator:

$$\left[ -\frac{\hbar^2}{2m} \Delta + \hat{V}, \hat{L}_z \right] = \left[ -\frac{\hbar^2}{2m} \Delta + \hat{V}, \vec{\hat{L}}^2 \right] = 0$$

where $\hat{V}$ is the operator corresponding to electron - nuclear Coulomb interaction. Use spherical coordinates and remember that operators commute, for example, if they depend on different variables. What is the significance of this result?

Solution:

The Hamiltonian consists of the kinetic energy part, which is proportional to the Laplacian operator, and the Coulomb potential. Laplacian in spherical coordinates is (see lecture notes or a tablebook):
\[\Delta \equiv \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2}\]

The Coulomb potential depends on only on spatial coordinate \( r \) (e.g. the distance between the nucleus and the electron). The \( \hat{L}_z \) operator is defined in spherical coordinates as:

\[\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}\]

This clearly commutes with the first two terms in the Laplacian because those terms do not depend on \( \phi \). The third depends on \( \phi \) but both operators consist of differentiation with respect to \( \phi \) and hence they commute. Thus \[\left[ \hat{H}, \hat{L}_z \right] = 0\].

Next we consider \( \vec{\hat{L}}^2 \). This is operator can be written in spherical coordinates as:

\[\vec{\hat{L}}^2 = -\hbar^2 \left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right]\]

This does not depend on \( r \) and therefore it commutes with the Coulomb potential and the first term in the Laplacian, which depends only on \( r \). Apart from \( r \) and some constants \( \vec{\hat{L}}^2 \) is identical to the angular part of the Laplacian. Operators always commute with themselves. Thus \( \left[ \hat{H}, \vec{\hat{L}}^2 \right] \). The significance of these results is that both the energy and the quantum numbers \( l \) and \( m_l \) can be specified simultaneously.

3. Demonstrate that the Cartesian hydrogen like \( p_x \) and \( p_y \) orbitals are not eigenfunctions of \( \hat{L}_z \) but their linear combinations \( p_x \pm ip_y \) are.

Solution:

It is convenient to express the Cartesian orbitals in spherical coordinates (see lecture notes):

\[p_x = \sin(\theta) \cos(\phi) f(r) \text{ where } f(r) \text{ contains all } r \text{ dependency}
\]

\[p_y = \sin(\theta) \sin(\phi) f(r)\]
To simplify calculations, the $\phi$ containing part is rewritten as:

$$\cos(\phi) = \frac{1}{2} (e^{i\phi} + e^{-i\phi})$$

and

$$\sin(\phi) = \frac{1}{2i} (e^{i\phi} - e^{-i\phi})$$

The $\hat{L}_z$ operator in spherical coordinates was already given in the previous problem. Next we operate on $p_x$ and $p_y$ by $\hat{L}_z$:

$$\hat{L}_z p_x = -i \hbar f(r) \sin(\theta) \frac{d}{d\phi} \left( e^{i\phi} + e^{-i\phi} \right) = i \hbar f(r) \sin(\theta) \times \frac{1}{2i} (e^{i\phi} - e^{-i\phi}) = i \hbar p_y$$

Thus the operation does not yield a constant times the original function (e.g. not an eigenfunction). In similar way we can show that $p_y$ is not an eigenfunction of $\hat{L}_z$: $\hat{L}_z p_y = -i \hbar p_x$.

Next we show that the following linear combinations are eigenfunctions of $\hat{L}_z$:

$$p_x + ip_y = f(r) \sin(\theta) e^{i\phi}$$

$$p_x - ip_y = f(r) \sin(\theta) e^{-i\phi}$$

When operating on these by $\hat{L}_z$ we get:

$$\hat{L}_z (p_x + ip_y) = \hbar f(r) \sin(\theta) e^{i\phi} = \hbar (p_x + ip_y)$$

$$\hat{L}_z (p_x - ip_y) = -\hbar f(r) \sin(\theta) e^{i\phi} = -\hbar (p_x - ip_y)$$

These have the right form (e.g. constant $\times$ the original function) and therefore they are eigenfunctions of $\hat{L}_z$.

4. (a) Consider a hydrogenlike atom with one electron on $2s$ orbital. What is the most probable distance from the nucleus? Use the radial wavefunction in your calculation.
(b) Show that the following hydrogenlike atom orbital pairs are orthogonal: \((1s, 2s)\) and \((2p_x, 2p_y)\).

Solution:

(a) The radial part for \(2s\) orbital is (with \(\rho = 2Zr/a_0\) substituted in):

\[
R_{2,0} = \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{a_0}}
\]

The corresponding radial probability density is:

\[
P_{2,0}(r) = r^2 N_{2,0}^2 R_{2,0}^2 = N_{2,0}^2 r^2 \times \frac{1}{8} \left( \frac{Z}{a_0} \right)^3 \left( 2 - \frac{Zr}{a_0} \right)^2 e^{-\frac{Zr}{a_0}}
\]

Next we must find the maximum value for \(P_{2,0}(r)\). To do this, we look for zeros of the first derivative (with respect to \(r\)):

\[
\frac{dP_{2,0}(r)}{dr} = \frac{rZ^3}{8a_0^6} e^{-Zr/a_0} (8a_0^3 - 16a_0^2 rZ + 8a_0r^2Z^2 - r^3Z^3) = 0
\]

The four roots for this equation are: \(r = 0, r = 2a_0/Z\) and \(r = \frac{a_0}{Z} \left( 3 \pm \sqrt{5} \right)\). Next we have to check which root gives the highest probability:

\[
P_{2,0}(0) = 0
\]

\[
P_{2,0}(2a_0/Z) = 0
\]

\[
P_{2,0} \left( \frac{a_0}{Z} \left( 3 + \sqrt{5} \right) \right) / N_{2,0}^2 = \frac{2Z}{a_0} \left( 9 + 4\sqrt{5} \right) e^{-\left(3+\sqrt{5}\right)} \approx 0.191 \times \frac{Z}{a_0}
\]

\[
P_{2,0} \left( \frac{a_0}{Z} \left( 3 - \sqrt{5} \right) \right) / N_{2,0}^2 = \frac{2Z}{a_0} \left( 9 - 4\sqrt{5} \right) e^{-\left(3-\sqrt{5}\right)} \approx 0.0519 \times \frac{Z}{a_0}
\]

Thus the maximum is reached at \(r = \frac{a_0}{Z} \left( 3 + \sqrt{5} \right)\). One could check the second derivatives the further characterize this as a maximum. The most probable radius is therefore \(\frac{a_0}{Z} \left( 3 + \sqrt{5} \right) \approx 5.2 \times \frac{a_0}{Z}\). Note that this is in agreement with the plot given in the lecture notes.
(b) First we show that 1s and 2s orbitals are orthogonal. The wavefunctions are (see lecture notes):

\[ \psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \]

\[ \psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}} \]

These functions depend only on \( r \) and therefore we just need to integrate over \( r \) and may drop the constants:

\[
\int_0^\infty e^{-Zr/a_0} \times \left( 2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}} r^2 dr = \int_0^\infty \left( 2r^2 - \frac{Zr^3}{a_0} \right) e^{-\frac{3Zr}{2a_0}} dr
\]

\[
= 2 \int_0^\infty r^2 e^{-\frac{3Zr}{2a_0}} dr - \frac{Z}{a_0} \int_0^\infty r^3 e^{-\frac{3Zr}{2a_0}} dr
\]

\[
= \frac{32a_0^3}{27Z^3} - \frac{32a_0^3}{27Z^3} = 0
\]

where in the last step the integrals were looked up from a table-book.

Next we show that 2px and 2py are orthogonal. An easy way to see this is to note the angular dependencies of the orbitals:

\[ p_x = \frac{-i}{\sqrt{2}} (p_{+1} - p_{-1}) \propto \sin(\theta) \cos(\phi) \]

\[ p_y = \frac{i}{\sqrt{2}} (p_{+1} + p_{-1}) \propto \sin(\theta) \sin(\phi) \]

The only difference is in the \( \phi \) part. The angular integral over \( \phi \) is:

\[
\int_0^{2\pi} \cos(\phi) \sin(\phi) d\phi = 0 \quad \text{(integrand is odd)}
\]

Because this angular part yields zero, integration over all spherical variables gives also zero. Hence \( p_x \) and \( p_y \) are orthogonal to each other.

6
5. (a) Write the electron configuration for V\(^{2+}\) ion. What quantum numbers for the total electron spin are possible in this configuration?

(b) If two electrons reside on two different orbitals, what are the possible values for total spin and the multiplicity? What values are possible for three electrons on different orbitals?

Solution:

(a) V (vanadium) has 23 electrons and therefore V\(^{2+}\) has 21 electrons. From the lecture notes one can find the electron configuration as: V (Ar3d\(^3\)4s\(^2\)) and V\(^{2+}\) (Ar3d\(^3\)). Two electrons can give either \(S = 1\) or \(S = 0\). However, since we have three electrons we must couple this to the third electron: \(S = 3/2, 1/2\) or \(S = 1/2\). This the possible values for \(S\) are 3/2 and 1/2.

(b) Two electrons on different orbitals: \(s_1 = 1/2\) and \(s_2 = 1/2\). This can give \(S = 1\) or \(S = 0\). The multiplicity \((2S + 1)\) can therefore be either 3 (triplet) or 1 (singlet). Coupling a third electron to this gives: \(S = 3/2, 1/2\) or \(S = 1/2\) (just in previously). The multiplicity can now be either 4 (quartet) or 2 (doublet).

6. (a) What information do the following term symbols provide about a given atom: \(^1D_2\) and \(^3F_4\)?

(b) Consider the emission spectrum of potassium atom, which exhibits lines at \(\lambda_1 = 766.70\) nm and \(\lambda_2 = 770.11\) nm. What is the value of the spin-orbit coupling constant? The emission lines originate from the \(^2P\) excited state (spin-orbit split).

(c) Which of the following atomic transitions are (dipole) allowed: \(5d \rightarrow 2s, 5p \rightarrow 3s, 5p \rightarrow 3f\)?

Solution:

(a) In \(^1D_2\) state there are no unpaired electrons (singlet state) and hence the total spin \(S = 0\). The angular momentum quantum
number $L = 2$, which means that the total angular momentum $\langle \hat{L}^2 \rangle = 2(2+1)\hbar^2 = 6\hbar^2$. The total angular momentum quantum number $J = 2$ (specified by the subscript). In $^3F_4$ state the multiplicity $(2S + 1)$ is 3 which gives $S = 1$ (triplet state) and $F$ term implies $L = 3$. The total angular momentum quantum number is specified as $J = 4$.

(b) The energy level diagram for alkali metal atoms is:

The two emission lines originate from the two $^2P$ states, which are split by the spin-orbit interaction, and terminate to the ground $^2S$ state. Hence the energy difference between the two emission lines gives the energy difference between the spin-orbit split states $^2P_{1/2}$ and $^2P_{3/2}$. The line positions must be converted to energy by relation $E = h\nu = \frac{hc}{\lambda}$ ($h$ is the Planck’s constant and $c$ is the speed of light). To calculate $A$, we have to calculate the energy difference between $^2P_{1/2}$ and $^2P_{3/2}$:

$^2P_{1/2}$: $E_{SO} = \frac{A}{2} [J(J + 1) - L(L + 1) - S(S + 1)] = -A$

$^2P_{3/2}$: $E_{SO} = \frac{A}{2} [J(J + 1) - L(L + 1) - S(S + 1)] = \frac{1}{2}A$

$\Delta E_{SO} = \frac{3}{2}A$

Next we calculate the energies for the observed transitions. For $^2P_{3/2} \rightarrow ^2S_{1/2}$ we have:

$E_1 = h\nu_1 = \frac{hc}{\lambda_1} = (6.6261 \times 10^{-34} \text{ Js}) \times \frac{2.9979 \times 10^8 \text{ m/s}}{766.70 \times 10^{-9} \text{ m}}$

$= 2.5909 \times 10^{-19} \text{ J} = 1.6171 \text{ eV} = 13043 \text{ cm}^{-1}$

For $^2P_{1/2} \rightarrow ^2S_{1/2}$:
\[
E_2 = h\nu_2 = \frac{hc}{\lambda_2} = (6.6261 \times 10^{-34} \text{ Js}) \times \frac{2.9979 \times 10^8 \text{ m/s}}{770.11 \times 10^{-9} \text{ m}} = 2.5794 \times 10^{-19} \text{ J} = 1.6099 \text{ eV} = 12985 \text{ cm}^{-1}
\]

Thus the energy difference is \( \Delta E_{SO} = 39 \text{ cm}^{-1} \) which gives \( A = 2\Delta E_{SO}/3 = 39 \text{ cm}^{-1} \).

(c) The selection rule is \( \Delta l = \pm 1 \). For \( 5d \rightarrow 2s \) we have \( \Delta l = -2 \) and hence it is forbidden. Transition \( 5p \rightarrow 3s \) has \( \Delta l = -1 \) and therefore it is allowed. \( 5p \rightarrow 3f \) has \( \Delta l = +2 \) and it is forbidden.

7. (a) Write all the term symbols that can be obtained from the following electron configurations: \( 2s^12p^1 \), \( 2p^13d^1 \) and \( \text{Ar}4s^23d^{10}4p^5 \) (Br atom).

(b) Write the term symbols for carbon atom (He\(2s^22p^2\)), which has two equivalent \( p \)-electrons. Hint: tabulate all possible \( m_{l_1}, m_{l_2}, m_{s_1} \) and \( m_{s_2} \) values and calculate the total \( L \) and \( S \) values. Remember to exclude the Pauli forbidden states.

Solution:

(a) Consider \( 2s^12p^1 \) electron configuration. The \( s \)-shell has \( l_1 = 0 \) with \( s_1 = 1/2 \) and \( p \)-shell has \( l_2 = 1 \) and \( s_2 = 1/2 \). The total \( L = l_1 + l_2, \ldots, |l_1 - l_2| = 1 \). The total spin \( S = s_1 + s_2, \ldots, |s_1 - s_2| = 1,0 \). Thus the total \( J = L + S, \ldots, |L - S| \) can be 2, 1 or 0 (for \( L = 1, S = 1 \) or 1 \( L = 1, S = 0 \)). This results in the following term symbols: \( ^3P_2, ^3P_1, ^3P_0 \) and \( ^1P_1 \).

For \( 2p^13d^1 \) we can have the following:

\( p \)-electron: \( l_1 = 1, s_1 = 1/2 \).
\( d \)-electron: \( l_2 = 2, s_2 = 1/2 \).

Hence \( L = 3,2,1 \) and \( S = 1,0 \). This gives the following total \( J \) values:

- \( L = 3 \) and \( S = 1 \) results in \( J = 4,3,2 \) (\( ^3F_4, ^3F_3 \) and \( ^3F_2 \) term symbols)
• \( L = 3 \) and \( S = 0 \) results in \( J = 3 \) (\(^1F_3\) term symbol)
• \( L = 2 \) and \( S = 1 \) results in \( J = 3, 2, 1 \) (\(^3D_3, ^3D_2\) and \(^3D_1\) term symbols)
• \( L = 2 \) and \( S = 0 \) results in \( J = 2 \) (\(^1D_2\) term symbol)
• \( L = 1 \) and \( S = 1 \) results in \( J = 2, 1, 0 \) (\(^3P_2, ^3P_1\) and \(^3P_0\) term symbols)
• \( L = 1 \) and \( S = 0 \) results in \( J = 1 \) (\(^1P_1\) term symbol)

For Ar\(s^23d^{10}4p^5\) we have only one unpaired electron which has \( l = 1 \) and \( s = 1/2 \). This gives obviously \( L = 1 \) and \( S = 1/2 \) and the total \( J = 3/2 \) or \( 1/2 \). Hence the two possible term symbols are \(^2P_{3/2}\) and \(^2P_{1/2}\).

(b) Carbon has 2 equivalent \( p\)-electrons: \( l_1 = l_2 = 1 \) and \( s_1 = s_2 = 1/2 \). We should tabulate all the possible states - including \( M_L = m_{l_1} + m_{l_2} \) and \( M_S = m_{s_1} + m_{s_2} \).