Quantum Mechanics in Three Dimensions

8-1 \[ E = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{n_1}{L_x} \right)^2 + \left( \frac{n_2}{L_y} \right)^2 + \left( \frac{n_3}{L_z} \right)^2 \right] \]

\( L_x = L, \quad L_y = L_z = 2L \). Let \( \frac{\hbar^2 \pi^2}{8ml^2} = E_0 \). Then \( E = E_0 \left( 4n_1^2 + n_2^2 + n_3^2 \right) \). Choose the quantum numbers as follows:

<table>
<thead>
<tr>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( n_3 )</th>
<th>( \frac{E}{E_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
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<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>9</td>
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<tr>
<td>1</td>
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<td>2</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>21</td>
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<td>21</td>
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<td>2</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>14</td>
</tr>
</tbody>
</table>

Therefore the first 6 states are \( \psi_{111}, \psi_{121}, \psi_{112}, \psi_{113}, \psi_{131} \) with relative energies \( \frac{E}{E_0} = 6, 9, 9, 12, 14, 14 \). First and third excited states are doubly degenerate.

8-2 (a) \( n_1 = 1, \quad n_2 = 1, \quad n_3 = 1 \)

\[ E_0 = \frac{3\hbar^2 \pi^2}{2ml^2} = \frac{3\hbar^2}{8ml^2} = \frac{3\left(6.626 \times 10^{-34} \text{ Js}\right)^2}{8\left(9.11 \times 10^{-31} \text{ kg}\right)\left(2 \times 10^{-10} \text{ m}\right)^2} = 4.52 \times 10^{-18} \text{ J} = 28.2 \text{ eV} \]

(b) \( n_1 = 2, \quad n_2 = 1, \quad n_3 = 1 \) or \( n_1 = 1, \quad n_2 = 2, \quad n_3 = 1 \) or
\[ n_1 = 1, \ n_2 = 1, \ n_3 = 2 \]
\[ E_1 = \frac{6h^2}{8mL^2} = 2E_0 = 56.4 \text{ eV} \]

8-3 \[ n^2 = 11 \]

(a) \[ E = \left( \frac{\hbar^2 \pi^2}{2mL^2} \right) n^2 = \frac{11}{2} \left( \frac{\hbar^2 \pi^2}{mL^2} \right) \]

(b) \[
\begin{array}{ccc}
1 & 1 & 3 \\
1 & 3 & 1 & 3-fold degenerate \\
3 & 1 & 1 \\
\end{array}
\]

(c) \[
\begin{align*}
\psi_{113} &= A \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{\pi y}{L} \right) \sin \left( \frac{3\pi z}{L} \right) \\
\psi_{131} &= A \sin \left( \frac{\pi x}{L} \right) \sin \left( \frac{3\pi y}{L} \right) \sin \left( \frac{\pi z}{L} \right) \\
\psi_{311} &= A \sin \left( \frac{3\pi x}{L} \right) \sin \left( \frac{\pi y}{L} \right) \sin \left( \frac{\pi z}{L} \right)
\end{align*}
\]

8-4

(a) \[ \psi(x, y) = \psi_1(x)\psi_2(y) \text{. In the two-dimensional case, } \psi = A (\sin k_1 x) (\sin k_2 y) \text{ where } k_1 = \frac{n_1 \pi}{L} \text{ and } k_2 = \frac{n_2 \pi}{L}. \]

(b) \[ E = \frac{\hbar^2 \pi^2 (n_1^2 + n_2^2)}{2mL^2} \]

If we let \[ E_0 = \frac{\hbar^2 \pi^2}{mL^2}, \] then the energy levels are:

\[
\begin{array}{ccc}
n_1 & n_2 & E \\ 
& & \frac{E}{E_0} \\
1 & 1 & 1 & \rightarrow & \psi_{11} \\
1 & 2 & 5 & \rightarrow & \psi_{12} \\
2 & 1 & 5 & \rightarrow & \psi_{21} \quad \text{doubly degenerate} \\
2 & 2 & 4 & \rightarrow & \psi_{22}
\end{array}
\]
The stationary states for a particle in a cubic box are, from Equation 8.10

\[ \Psi(x, y, z, t) = A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) e^{-iEt/\hbar} \quad 0 \leq x, y, z \leq L \]
\[ = 0 \text{ elsewhere} \]

where \( k_1 = \frac{n_1 \pi}{L} \), etc. Since \( \Psi \) is nonzero only for \( 0 < x < L \), and so on, the normalization condition reduces to an integral over the volume of a cube with one corner at the origin:

\[ 1 = \int_0^L \int_0^L \int_0^L |\Psi(r, t)|^2 \, dr \, dy \, dz = A^2 \left\{ \int_0^L \sin^2(k_1 x) \, dx \int_0^L \sin^2(k_2 y) \, dy \int_0^L \sin^2(k_3 z) \, dz \right\} \]

Using \( 2 \sin^2 \theta = 1 - \cos 2\theta \) gives

\[ \int_0^L \sin^2(k_1 x) \, dx = \frac{L}{2} - \frac{1}{4k_1^2} \sin(2k_1 x) \biggr|_0^L \].

But \( k_1 L = n_1 \pi \), so the last term on the right is zero. The same result is obtained for the integrations over \( y \) and \( z \). Thus, normalization requires \( 1 = A^2 \left( \frac{L}{2} \right)^3 \) or \( A = \left( \frac{2}{L} \right)^{3/2} \) for any of the stationary states. Allowing the edge lengths to be different at \( L_1, L_2, \) and \( L_3 \) requires only that \( L_3^3 \) be replaced by the box volume \( L_1L_2L_3 \) in the final result: \( A = \left( \frac{2}{L_1} \right) \left( \frac{2}{L_2} \right) \left( \frac{2}{L_3} \right) \right]^{1/2} = \left( \frac{8}{L_1L_2L_3} \right)^{1/2} = \left( \frac{8}{V} \right)^{1/2} \)

where \( V = L_1L_2L_3 \) is the volume of the box. This follows because it is still true that the wave must vanish at the walls of the box, so that \( k_1 L_1 = n_1 \pi \), and so on.

Inside the box the electron is free, and so has momentum and energy given by the de Broglie relations \( |p| = h|k| \) and \( E = h\omega \) with \( E = \left( c^2 |p|^2 + m^2 c^4 \right)^{1/2} \) for this, the relativistic case. Here \( k = (k_1, k_2, k_3) \) is the wave vector whose components \( k_1, k_2, \) and \( k_3 \) are wavenumbers along each of three mutually perpendicular axes. In order for the wave to vanish at the walls, the box must contain an integral number of half-wavelengths in each direction. Since

\[ \lambda_1 = \frac{2\pi}{k_1} \]

and so on, this gives
Thus, \(|\mathbf{p}|^2 = \hbar|\mathbf{k}|^2 = h^2 \left( k_1^2 + k_2^2 + k_3^2 \right) = \left( \frac{\pi \hbar}{L} \right)^2 \left( n_1^2 + n_2^2 + n_3^2 \right) \) and the allowed energies are

\[
E = \left[ \left( \frac{\pi \hbar c}{L} \right)^2 \left( n_1^2 + n_2^2 + n_3^2 \right) + \left( m c^2 \right)^2 \right]^{1/2}.
\]

For the ground state \( n_1 = n_2 = n_3 = 1 \). For an electron confined to \( L = 10 \text{ fm} \), we use \( m = 0.511 \text{ MeV}/c^2 \) and \( \hbar c = 197.3 \text{ MeV} \text{ fm} \) to get

\[
E = \left[ 3 \left( \frac{(\pi)(197.3 \text{ MeV} \text{ fm})}{10 \text{ fm}} \right)^2 + (0.511 \text{ MeV})^2 \right]^{1/2} = 107 \text{ MeV}.
\]

8-10 \( n = 4 \), \( l = 3 \), and \( m_l = 3 \).

(a) \( L = [l(l+1)]^{1/2} \ h = [3(3+1)]^{1/2} \ h = 2\sqrt{3} \ h = 3.65 \times 10^{-34} \ \text{Js} \)

(b) \( L_z = m_l \ h = 3 \ h = 3.16 \times 10^{-34} \ \text{Js} \)
\[ \psi(r) = \left( \frac{1}{\pi} \right)^{\frac{1}{2}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-r/a_0} \]

(a) \[ \psi(r) \]

(b) The probability of finding the electron in a volume element \( dV \) is given by \( |\psi|^2 dV \). Since the wave function has spherical symmetry, the volume element \( dV \) is identified here with the volume of a spherical shell of radius \( r \), \( dV = 4\pi r^2 dr \). The probability of finding the electron between \( r \) and \( r + dr \) (that is, within the spherical shell) is \( P = |\psi|^2 dV = 4\pi r^2 |\psi|^2 dr \).

(c) \[ P \]

(d) \[ \int |\psi|^2 dV = 4\pi \int |\psi|^2 r^2 dr = 4\pi \left( \frac{1}{\pi} \right) \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \int_0^\infty e^{-2r/a_0} r^2 dr = \left( \frac{4}{a_0} \right)^{\frac{3}{2}} \int_0^\infty e^{-2r/a_0} r^2 dr \]

Integrating by parts, or using a table of integrals, gives

\[ \int |\psi|^2 dV = \left( \frac{4}{a_0} \right)^{\frac{3}{2}} \left[ 2 \left( \frac{a_0}{2} \right)^{\frac{3}{2}} \left( \frac{2}{a_0} \right)^{\frac{3}{2}} \right] = 1. \]

(e) \[ P = 4\pi \int_{r_1}^{r_2} |\psi|^2 r^2 dr \] where \( r_1 = \frac{a_0}{2} \) and \( r_2 = \frac{3a_0}{2} \).
\[ p = \left( \frac{4}{\pi a_0^3} \right) \int_{a_0}^{\infty} r^2 e^{-2r/a_0} dr \quad \text{let } z = \frac{2r}{a_0} \]

\[
\frac{1}{2} \int_1^3 z^2 e^{-z} dz \\
= -\frac{1}{2} \left[ (z^2 + 2z + 2)e^{-z} \right]_1^3 \\
= -\frac{17}{2} e^{-3} + \frac{5}{2} e^{-1} = 0.496
\]

8-13 \( Z = 2 \) for \( \text{He}^+ \)

(a) For \( n = 3 \), \( l \) can have the values of 0, 1, 2

\[
l = 0 \rightarrow m_l = 0 \\
l = 1 \rightarrow m_l = -1, 0, +1 \\
l = 2 \rightarrow m_l = -2, -1, 0, +1, +2
\]

(b) All states have energy \( E_3 = -\frac{Z^2}{3^2} (13.6 \text{ eV}) \)

\[ E_3 = -6.04 \text{ eV} . \]

8-14 \( Z = 3 \) for \( \text{Li}^{2+} \)

(a) \( n = 1 \rightarrow l = 0 \rightarrow m_l = 0 \)

\( n = 2 \rightarrow l = 0 \rightarrow m_l = 0 \)

and \( l = 1 \rightarrow m_l = -1, 0, +1 \)

(b) For \( n = 1 \), \( E_1 = -\frac{3^2}{1^2} (13.6) = -122.4 \text{ eV} \)

For \( n = 2 \), \( E_2 = -\frac{3^2}{2^2} (13.6) = -30.6 \text{ eV} \)
For a \( d \) state, \( l = 2 \). Thus, \( m_l \) can take on values \(-2, -1, 0, 1, 2\). Since \( L_z = m_l \hbar \), \( L_z \) can be \( \pm 2\hbar, \pm \hbar \), and zero.

(a) For a \( d \) state, \( l = 2 \)

\[
L = [l(l+1)]^{1/2} \hbar = (2)^{1/2} \left( 1.055 \times 10^{-34} \text{ Js} \right) = 2.58 \times 10^{-34} \text{ Js}
\]

(b) For an \( f \) state, \( l = 3 \)

\[
L = [l(l+1)]^{1/2} \hbar = (3)^{1/2} \left( 1.055 \times 10^{-34} \text{ Js} \right) = 3.65 \times 10^{-34} \text{ Js}
\]

The state is \( 6g \)

(a) \( n = 6 \)

(b) \( E_n = -13.6 \text{ eV} \), \( E_0 = \frac{-13.6}{6^2} \text{ eV} = -0.378 \text{ eV} \)

(c) For a \( g \)-state, \( l = 4 \)

\[
L = [l(l+1)]^{1/2} \hbar = (4)^{1/2} \left( 1.055 \times 10^{-34} \text{ Js} \right) = \sqrt{20}\hbar = 4.47\hbar
\]

(d) \( m_l \) can be \(-4, -3, -2, -1, 0, 1, 2, 3, 4\)

<table>
<thead>
<tr>
<th>( m_l )</th>
<th>(-4)</th>
<th>(-3)</th>
<th>(-2)</th>
<th>(-1)</th>
<th>(0)</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_z )</td>
<td>(-4\hbar)</td>
<td>(-3\hbar)</td>
<td>(-2\hbar)</td>
<td>(-1\hbar)</td>
<td>(0\hbar)</td>
<td>(1\hbar)</td>
<td>(2\hbar)</td>
<td>(3\hbar)</td>
<td>(4\hbar)</td>
</tr>
<tr>
<td>( \theta )</td>
<td>153.4°</td>
<td>132.1°</td>
<td>116.6°</td>
<td>102.9°</td>
<td>90°</td>
<td>77.1°</td>
<td>63.4°</td>
<td>47.9°</td>
<td>26.6°</td>
</tr>
</tbody>
</table>

When the principal quantum number is \( n \), the following values of \( l \) are possible:

\( l = 0, 1, 2, \ldots, n-2, n-1 \). For a given value of \( l \), there are \( 2l+1 \) possible values of \( m_l \). The maximum number of electrons that can be accommodated in the \( n^{th} \) level is therefore:

\[
(2(0)+1)+(2(1)+1)+\ldots+(2l+1)+\ldots+(2(n-1)+1) = 2 \sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} l = 2 \sum_{l=0}^{n-1} l + n.
\]

But \( \sum_{l=0}^{k} l = \frac{k(k+1)}{2} \) so the maximum number of electrons to be accommodated is

\[
\frac{2(n-1)n}{2} + n = n^2.
\]
8-21 (a) \[ \psi_{2s}(r) = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \]. At \( r = a_0 = 0.529 \times 10^{-10} \text{ m} \) we find

\[ \psi_{2s}(a_0) = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} (2 - 1) e^{-1/2} = (0.380) \left( \frac{1}{a_0} \right)^{3/2} \]

\[ = (0.380) \left[ \frac{1}{0.529 \times 10^{-10} \text{ m}} \right]^{3/2} = 9.88 \times 10^{14} \text{ m}^{-3/2} \]

(b) \[ |\psi_{2s}(a_0)|^2 = \left( 9.88 \times 10^{14} \text{ m}^{-3/2} \right)^2 = 9.75 \times 10^{29} \text{ m}^{-3} \]

(c) Using the result to part (b), we get \( P_{2s}(a_0) = 4\pi a_0^3 |\psi_{2s}(a_0)|^2 = 3.43 \times 10^{10} \text{ m}^{-1} \).

8-22 \( R_{2p}(r) = 4\pi A e^{-r/a_0} \) where \( A = \frac{1}{2(6)^{1/2} a_0^{3/2}} \)

\[ P(r) = r^2 R_{2p}^2(r) = A^2 r^4 e^{-r/a_0} \]

\[ \langle r \rangle = \int_0^\infty r P(r) \, dr = A^2 \int_0^\infty r^5 e^{-r/a_0} \, dr = A^2 a_0^5 5! = 5a_0 = 2.645 \text{ Å} \]
8-24 \( P_{1s}(r) = \frac{4}{a_0^2} r^2 e^{-2r/a_0} \) for hydrogen ground state, \( U(r) = -\frac{ke^2}{r} \) is potential energy (\( Z = 1 \))

\[
\langle U \rangle = \int_0^\infty U(r) P_{1s}(r) \, dr = -\frac{4ke^2}{a_0^2} \int_0^\infty r e^{-2r/a_0} \, dr
\]

\[
= -\frac{4ke^2}{a_0^2} \left( \frac{a_0}{2} \right)^2 \int_0^\infty ze^{-z} \, dz \quad \text{where} \quad z = \frac{2r}{a_0}
\]

\[
= -\frac{ke^2}{a_0} = -2(13.6 \text{ eV}) = -27.2 \text{ eV}.
\]

To find \( \langle K \rangle \), we note that \( \langle K \rangle + \langle U \rangle = \langle E \rangle = -\frac{ke^2}{2a_0} = -13.6 \text{ eV} \) so, \( \langle K \rangle = \frac{ke^2}{a_0} = +13.6 \text{ eV} \).
The averages \( \langle r \rangle \) and \( \langle r^2 \rangle \) are found by weighting the probability density for this state

\[
P_{1s}(r) = 4 \left( \frac{Z}{a_0^3} \right) r^2 e^{-2Zr/a_0}
\]

with \( r \) and \( r^2 \), respectively, in the integral from \( r = 0 \) to \( r = \infty \):

\[
\langle r \rangle = \int_0^\infty r P_{1s}(r) \, dr = 4 \left( \frac{Z}{a_0^3} \right) \int_0^\infty r e^{-2Zr/a_0} \, dr
\]

\[
\langle r^2 \rangle = \int_0^\infty r^2 P_{1s}(r) \, dr = 4 \left( \frac{Z}{a_0^3} \right) \int_0^\infty r^4 e^{-2Zr/a_0} \, dr
\]

Substituting \( z = \frac{2Zr}{a_0} \) gives
\[ \langle r \rangle = 4 \left( \frac{Z}{a_0} \right)^3 \left( \frac{a_0}{2Z} \right)^4 \int_0^{\infty} z^3 e^{-z} \, dz = \frac{3!}{4} \left( \frac{a_0}{Z} \right) = \frac{3}{2} \left( \frac{a_0}{Z} \right) \]

\[ \langle r^2 \rangle = 4 \left( \frac{Z}{a_0} \right)^3 \left( \frac{a_0}{2Z} \right)^5 \int_0^{\infty} z^4 e^{-z} \, dz = \frac{4!}{8} \left( \frac{a_0}{Z} \right)^2 = 3 \left( \frac{a_0}{Z} \right)^2 \]

and \( \Delta r = \left( \langle r^2 \rangle - \langle r \rangle^2 \right)^{1/2} = \frac{a_0}{Z} \left[ 3 - \frac{9}{4} \right]^{1/2} = 0.866 \left( \frac{a_0}{Z} \right). \) The momentum uncertainty is deduced from the average potential energy

\[ \langle U \rangle = -kZ^2 \int_0^\infty \frac{1}{r} P_1 (r) \, dr = -4kZ^2 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty e^{-2Zr/a_0} = -4kZ^2 \left( \frac{Z}{a_0} \right)^3 \left( \frac{a_0}{2Z} \right)^2 = -\frac{k(Ze)^2}{a_0}. \]

Then, since \( E = \frac{k(Ze)^2}{2a_0} \) for the 1s level, and \( a_0 = \frac{\hbar^2}{m_e k e^2} \), we obtain

\[ \langle p^2 \rangle = 2m_e \langle K \rangle = 2m_e (E - \langle U \rangle) = \frac{2m_e k(Ze)^2}{2a_0} = \left( \frac{Ze}{a_0} \right)^2. \]

With \( \langle p \rangle = 0 \) from symmetry, we get \( \Delta p = \left( \langle p^2 \rangle \right)^{1/2} = \frac{Ze}{a_0} \) and \( \Delta r \Delta p = 0.866 \hbar \) for any \( Z \), consistent with the uncertainty principle.