8

Quantum Mechanics in Three Dimensions

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

$L_x = L$, $L_y = L_z = 2L$. 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:

n_1	n_2	n_3	$\frac{E}{E_0}$		
1	1	1	6		ground state
1	2	1	9	*	first two excited states
1	1	2	9	*	
2	1	1	18		
1	2	2	12	*	next excited state
2	1	2	21		
2	2	1	21		
2	2	2	24		
1	1	3	14	*	next two excited states
1	3	1	14	*	

Therefore the first 6 states are ψ_{111}, ψ_{121}, ψ_{112}, ψ_{122}, ψ_{113}, and ψ_{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) $n_1=1$, $n_2=1$, $n_3=1$

$$E_0=\frac{3\hbar^2\pi^2}{2mL^2}=\frac{3h^2}{8mL^2}=\frac{3\left(6.626\times10^{-34}\text{ Js}\right)^2}{8\left(9.11\times10^{-31}\text{ kg}\right)\left(2\times10^{-10}\text{ m}\right)^2}=4.52\times10^{-18}\text{ J}=28.2\text{ eV}$$

(b) $n_1=2$, $n_2=1$, $n_3=1$ or

$n_1=1$, $n_2=2$, $n_3=1$ 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)

n_1	n_2	n_3	
1	1	3	
1	3	1	3-fold degenerate
3	1	1	

(c) $\psi_{113} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{3\pi z}{L}\right)$

$\psi_{131} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$

$\psi_{311} = A\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$

8-4 (a) $\psi(x, y) = \psi_1(x)\psi_2(y)$. In the two-dimensional case, $\psi = A(\sin k_1x)(\sin k_2y)$ where $k_1 = \frac{n_1\pi}{L}$ and $k_2 = \frac{n_2\pi}{L}$.

(b) $E = \frac{\hbar^2\pi^2\left(n_1^2 + n_2^2\right)}{2mL^2}$

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

n_1	n_2	$\frac{E}{E_0}$			
1	1	1	$\rightarrow$	ψ_{11}	
1	2	$\frac{5}{2}$	$\rightarrow$	ψ_{12}	doubly degenerate
2	1	$\frac{5}{2}$	$\rightarrow$	ψ_{21}	
2	2	4	$\rightarrow$	ψ_{22}	

8-7 The stationary states for a particle in a cubic box are, from Equation 8.10

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

where $k_1 = \frac{n_1\pi}{L}$, etc. Since Ψ 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:

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

Using $2\sin^2\theta = 1-\cos 2\theta$ gives $\int_0^L \sin^2(k_1 x)dx = \frac{L}{2}-\frac{1}{4k_1}\sin(2k_1 x)\Big|_0^L$. 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 be replaced by the box volume $L_1 L_2 L_3$ in the final result: $A = \left\{\left(\frac{2}{L_1}\right)\left(\frac{2}{L_2}\right)\left(\frac{2}{L_3}\right)\right\}^{1/2} = \left(\frac{8}{L_1 L_2 L_3}\right)^{1/2} = \left(\frac{8}{V}\right)^{1/2}$ where $V = L_1 L_2 L_3$ 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.

8-8 Inside the box the electron is free, and so has momentum and energy given by the de Broglie relations $|\mathbf{p}| = \hbar|\mathbf{k}|$ and $E = \hbar\omega$ with $E = \left(c^2|\mathbf{p}|^2 + m^2c^4\right)^{1/2}$ for this, the relativistic case. Here $\mathbf{k} = (k_1,\ k_2,\ k_3)$ 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

$$L = n_1\left(\frac{\lambda_1}{2}\right) \quad \text{or} \quad k_1 = \frac{n_1\pi}{L}$$
$$L = n_2\left(\frac{\lambda_2}{2}\right) \quad \text{or} \quad k_2 = \frac{n_2\pi}{L}$$
$$L = n_3\left(\frac{\lambda_3}{2}\right) \quad \text{or} \quad k_3 = \frac{n_3\pi}{L}$$

Thus, $|\mathbf{p}|^2 = \hbar|\mathbf{k}|^2 = \hbar^2\left\{k_1^2 + k_2^2 + k_3^2\right\} = \left(\frac{\pi\hbar}{L}\right)^2\left\{n_1^2 + n_2^2 + n_3^2\right\}$ and the allowed energies are $= \left[\left(\frac{\pi\hbar c}{L}\right)^2\left\{n_1^2 + n_2^2 + n_3^2\right\} + \left(mc^2\right)^2\right]^{1/2}$. 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 $\hbar c = 197.3\text{ MeV fm}$ to get

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

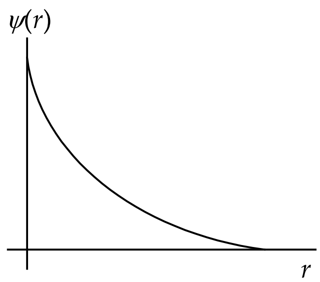
8-10 $n = 4$, $l = 3$, and $m_l = 3$.

(a) $L = [l(l+1)]^{1/2}\hbar = [3(3+1)]^{1/2}\hbar = 2\sqrt{3}\hbar = 3.65\times10^{-34}\text{ Js}$

(b) $L_z = m_l\hbar = 3\hbar = 3.16\times10^{-34}\text{ Js}$

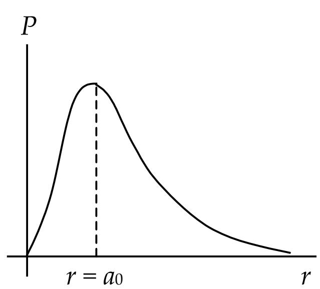
8-12 $\psi(r) = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(a)



(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)



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

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

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

(e) $P = 4\pi \int_{r_1}^{r_2} |\psi|^2\, r^2 dr$ where $r_1 = \frac{a_0}{2}$ and $r_2 = \frac{3a_0}{2}$

$$P = \left(\frac{4}{a_0^3}\right)\int_{r_1}^{r_2} r^2 e^{-2r/a_0}\,dr \qquad \text{let } z = \frac{2r}{a_0}$$
$$= \frac{1}{2}\int_1^3 z^2 e^{-z}\,dz$$
$$= -\frac{1}{2}\left(z^2 + 2z + 2\right)e^{-z}\Big|_1^3 \quad \text{(integrating by parts)}$$
$$= -\frac{17}{2}e^{-3} + \frac{5}{2}e^{-1} = 0.496$$

8-13 $Z = 2$ for 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 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 $n = 1$, $E_1 = -\left(\frac{3^2}{1^2}\right)(13.6) = -122.4\text{ eV}$

For $n = 2$, $E_2 = -\left(\frac{3^2}{2^2}\right)(13.6) = -30.6\text{ eV}$

8-16 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.

8-17 (a) For a *d* state, $l = 2$

$$L = [l(l+1)]^{1/2}\,\hbar = (6)^{1/2}\left(1.055\times10^{-34}\text{ Js}\right) = 2.58\times10^{-34}\text{ Js}$$

(b) For an *f* state, $l = 3$

$$L = [l(l+1)]^{1/2}\,\hbar = (12)^{1/2}\left(1.055\times10^{-34}\text{ Js}\right) = 3.65\times10^{-34}\text{ Js}$$

8-18 The state is 6*g*

(a) $n = 6$

(b) $E_n = -\dfrac{13.6\text{ eV}}{n^2}$ $\qquad E_6 = \dfrac{-13.6}{6^2}\text{ eV} = -0.378\text{ eV}$

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

$$L = [l(l+1)]^{1/2}\,\hbar = (4\times5)^{1/2}\,\hbar = \sqrt{20}\hbar = 4.47\hbar$$

(d) m_l can be –4, –3, –2, –1, 0, 1, 2, 3, or 4

$L_z = m_l\hbar$; $\cos\theta = \dfrac{L_z}{L} = \dfrac{m_l}{[l(l+1)]^{1/2}}\hbar = \dfrac{m_l}{\sqrt{20}}$

m_l	–4	–3	–2	–1	0	1	2	3	4
L_z	$-4\hbar$	$-3\hbar$	$-2\hbar$	$-\hbar$	0	$\hbar$	$2\hbar$	$3\hbar$	$4\hbar$
θ	153.4°	132.1°	116.6°	102.9°	90°	77.1°	63.4°	47.9°	26.6°

8-19 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 $\sum_{l=0}^{k} l = \dfrac{k(k+1)}{2}$ so the maximum number of electrons to be accommodated is $\dfrac{2(n-1)n}{2} + n = n^2$.

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 $r=a_0=0.529\times10^{-10}\text{ m}$ we find

$$\psi_{2s}(a_0)=\frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}(2-1)e^{-1/2}=(0.380)\left(\frac{1}{a_0}\right)^{3/2}$$
$$=(0.380)\left[\frac{1}{0.529\times10^{-10}\text{ m}}\right]^{3/2}=9.88\times10^{14}\text{ m}^{-3/2}$$

(b) $|\psi_{2s}(a_0)|^2=\left(9.88\times10^{14}\text{ m}^{-3/2}\right)^2=9.75\times10^{29}\text{ m}^{-3}$

(c) Using the result to part (b), we get $P_{2s}(a_0)=4\pi a_0^2|\psi_{2s}(a_0)|^2=3.43\times10^{10}\text{ m}^{-1}$.

8-22 $R_{2p}(r)=Are^{-r/2a_0}$ where $A=\frac{1}{2(6)^{1/2}a_0^{5/2}}$

$$P(r)=r^2R_{2p}^2(r)=A^2r^4e^{-r/a_0}$$
$$\langle r\rangle=\int_0^\infty rP(r)\,dr=A^2\int_0^\infty r^5e^{-r/a_0}\,dr=A^2a_0^6\,5!=5a_0=2.645\text{ Å}$$

8-24 $P_{1s}(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$ for hydrogen ground state, $U(r) = -\frac{ke^2}{r}$ is potential energy ($Z = 1$)

$$\langle U \rangle = \int_0^\infty U(r) P_{1s}(r)\, dr = -\frac{4ke^2}{a_0^3} \int_0^\infty r e^{-2r/a_0}\, dr$$

$$= -\frac{4ke^2}{a_0^3} \left(\frac{a_0}{2}\right)^2 \int_0^\infty z e^{-z}\, dz \quad \text{where } z = \frac{2r}{a_0}$$

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

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, $\langle K \rangle = \frac{ke^2}{a_0} = +13.6\text{ eV}$.

8-30 The averages $\langle r\rangle$ and $\langle r^2\rangle$ are found by weighting the probability density for this state $P_{1s}(r)=4\left(\frac{Z}{a_0^3}\right)r^2e^{-2Zr/a_0}$ with r and r^2, respectively, in the integral from $r=0$ to $r=\infty$:

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

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

Substituting $z=\frac{2Zr}{a_0}$ gives

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

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

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

$$\langle U \rangle = -kZe^2 \int_0^\infty \frac{1}{r} P_{1s}(r)\,dr = -4kZe^2\left(\frac{Z}{a_0}\right)^3 \int_0^\infty re^{-2Zr/a_0} = -4kZe^2\left(\frac{Z}{a_0}\right)^3\left(\frac{a_0}{2Z}\right)^2 = -\frac{k(Ze)^2}{a_0}.$$

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

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

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