Chapter 6 - Quantum Theory of the Hydrogen Atom

6-1: Whether in cartesian (x, y, z) or spherical coordinates, three quantities are needed to describe the variation of the wave function throughout space. The three quantum numbers needed to describe an atomic electron correspond to the variation in the radial direction, the variation in the azimuthal direction (the variation along the circumference of the classical orbit), and the variation with the polar direction (variation along the direction from the classical axis of rotation).

6-3: For the given function,

$$\frac{d}{dr}R_{10} = -\frac{2}{a_0^{5/2}}\,e^{-r/a_0}, \qquad \text{and}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\,\frac{dR_{10}}{dr}\right) = -\frac{2}{a_0^{5/2}}\,\frac{1}{r^2}\left(2\,r - \frac{r^2}{a_0}\right)\,e^{-r/a_0}$$

$$= \left(\frac{1}{a_0^2} - \frac{2}{r\,a_0}\right)\,R_{10}.$$

This is a solution to Equation (6.14) if $l = 0$ (as indicated by the index of R_{10}),

$$\frac{2}{a_0} = \frac{2\,m\,e^2}{\hbar^2\,4\pi\,\epsilon_0}, \qquad \text{or} \qquad a_0 = \frac{4\pi^2\,\epsilon_0\,\hbar^2}{m\,e^2},$$

which is the case, and

$$\frac{2\,m}{\hbar^2}\,E = -\frac{1}{a_0^2}, \qquad \text{or} \qquad E = -\frac{e^2}{8\pi\,\epsilon_0\,a_0} = E_1,$$

again as indicated by the index of R_{10}.

To show normalization,

$$\int_0^\infty |R_{10}|^2\,r^2\,dr = \frac{4}{a_0^3}\int_0^\infty r^2\,e^{-2\,r/a_0}\,dr = \frac{1}{2}\int_0^\infty u^2\,e^{-u}\,du,$$

where the substitution $u = 2\,r/a_0$ has been made. The improper definite integral in u is known to have the value 2 (see the discussion at the end of this chapter), and so the given function is normalized.

6-5: From Equation (6.15) the integral, apart from the normalization constants, is

$$\int_0^{2\pi} \Phi^*_{m_l}\,\Phi_{m_l'}\,d\phi = \int_0^{2\pi} e^{-i\,m_l\,\phi}\,e^{i\,m_l'\,\phi}\,d\phi.$$

It is possible to express the integral in terms of real and imaginary parts, but it turns out to be more convenient to do the integral directly in terms of complex exponentials;

$$\begin{aligned}\int_0^{2\pi} e^{-i\,m_l\,\phi}\,e^{i\,m_l'\,\phi}\,d\phi &= \int_0^{2\pi} e^{i\,(m_l' - m_l)\,\phi}\,d\phi \\ &= \frac{1}{i\,(m_l' - m_l)}\left[e^{i\,(m_l' - m_l)\,\phi}\right]_0^{2\pi} = 0.\end{aligned}$$

The above form for the integral is valid only for $m_l \neq m_l'$, which is given for this case. In evaluating the integral at the limits, the fact that $e^{i\,2\pi\,n} = 1$ for any integer n (in this case $(m_l' - m_l)$) has been used.

6-7: In the Bohr model, for the ground-state orbit of an electron in a hydrogen atom, $\lambda = \dfrac{h}{m\,v} = 2\pi\,r$, and so $L = p\,r = \hbar$. In the quantum theory, zero-angular-momentum states (ψ spherically symmetric) are allowed, and $L = 0$ for a ground-state hydrogen atom.

6-9: From Equation (6.22), L_z must be an integer multiple of $\hbar$; for L to be equal to L_z, the product $l(l+1)$, from Equation (6.21), must be the square of some integer less than or equal to l. But,

$$l^2 \leq l(l+1) < (l+1)^2$$

for any nonnegative l, with equality holding in the first relation only if $l = 0$. Therefore, $l(l+1)$ is the square of an integer only if $l = 0$, in which case $L_z = 0$ and $L = L_z = 0$.

6-11: From Equation (6.22), the possible values for the magnetic quantum number m_l are

$$m_l = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,$$

a total of nine possible values.

6-13: The fractional difference between L and the largest value of L_z is, for a given l,

$$\frac{L - L_{z,\,\max}}{L} = \frac{\sqrt{l(l+1)} - l}{\sqrt{l(l+1)}} = 1 - \frac{l}{\sqrt{l(l+1)}} = 1 - \sqrt{\frac{l}{l+1}}.$$

For a p state, $l = 1$ and $1 - \sqrt{\dfrac{1}{2}} = 0.29 = 29\%$.

For a d state, $l = 2$ and $1 - \sqrt{\dfrac{2}{3}} = 0.18 = 18\%$.

For an f state, $l = 3$ and $1 - \sqrt{\dfrac{3}{4}} = 0.13 = 13\%$.

6-15: Using $R_{10}(r)$ from Table 6.1 in Equation (6.25),

$$P(r) = \frac{4\,r^2}{a_0^3}\,e^{-2r/a_0}.$$

The most probable value of r is that for which $P(r)$ is a maximum. Differentiating the above expression for $P(r)$ with respect to r and setting the derivative equal to zero,

$$\frac{d}{dr}P(r) = \frac{4}{a_0^3}\left(2\,r - \frac{2\,r^2}{a_0}\right)e^{-2r/a_0} = 0, \qquad \text{or}$$

$$r = \frac{r^2}{a_0} \qquad \text{and} \qquad r = 0,\ a_0$$

for an extreme. At $r = 0$, $P(r) = 0$, and because $P(r)$ is never negative, this must be a minimum. $\dfrac{dP}{dr} \to 0$ as $r \to \infty$, and this also corresponds to a minimum. The only maximum of $P(r)$ is at $r = a_0$, which is the radius of the first Bohr orbit.

6-17: Using $R_{21}(r)$ from Table 6.1 in Equation (6.25), and ignoring the leading constants (which would not affect the position of extremes),

$$P(r) = r^6\,e^{-2r/3a_0}.$$

The most probable value of r is that for which $P(r)$ is a maximum. Differentiating the above expression for $P(r)$ with respect to r and setting the derivative equal to zero,

$$\frac{d}{dr}P(r) = \left(6\,r^5 - \frac{2\,r^6}{3\,a_0}\right)e^{-2r/3a_0} = 0, \qquad \text{or}$$

$$6\,r^5 = \frac{2\,r^6}{3\,a_0} \qquad \text{and} \qquad r = 0,\ 9\,a_0$$

for an extreme. At $r = 0$, $P(r) = 0$, and because $P(r)$ is never negative, this must be a minimum. $\dfrac{dP}{dr} \to 0$ as $r \to \infty$, and this also corresponds to a minimum. The only maximum of $P(r)$ is at $r = 9\,a_0$, which is the radius of the third Bohr orbit.

6-19: For the ground state, $n = 1$, the wave function is independent of angle, as seen from the functions $\Phi(\phi)$ and $\Theta(\theta)$ in Table 6.1, where for $n = 1$, $l = m_l = 0$ (see Problem 6-14). The ratio of the probabilities is then the ratio of the product $r^2\,(R_{10}(r))^2$ evaluated at the different distances. Specially,

$$\frac{P\,(a_0)\;dr}{P\,(a_0/2)\;dr} = \frac{(a_0)^2\;e^{-2a_0/a_0}}{(a_0/2)^2\;e^{-2\,(a_0/2)\,/a_0}} = \frac{e^{-2}}{(1/4)\,e^{-1}} = \frac{4}{e} = 1.47.$$

Similarly,

$$\frac{P\,(a_0)\;dr}{P\,(2\,a_0)\;dr} = \frac{(a_0)^2\;e^{-2a_0/a_0}}{(2\,a_0)^2\;e^{-2\,(2a_0)\,/a_0}} = \frac{e^{-2}}{4\,e^{-4}} = \frac{e^2}{4} = 1.85.$$

6-21: (a) Using $R_{10}(r)$ for the 1s radial function from Table 6.1,

$$\int_{a_0}^{\infty} |R(r)|^2\;r^2\,dr = \frac{4}{a_0^3}\int_{a_0}^{\infty} r^2\,e^{-2r/a_0}\,dr = \frac{1}{2}\int_{2}^{\infty} u^2\,e^{u}\,du,$$

where the substitution $u = 2r/a_0$ has been made.

There are numerous ways to find the definite integral, including consulting tabulated integrals or using symbolic-manipulation program; for example, the Maple command

```
>int((1/2)*u^2*exp(-u),u=2..infinity);
```

gives the result immediately. Using the method outlined at the end of this chapter to find the improper definite integral leads to

$$\frac{1}{2}\int_{2}^{\infty} u^2\,e^{u}\,du = \frac{1}{2}\left[-e^{-u}\;\left(u^2 + 2\,u + 2\right)\right]_2^{\infty} = \frac{1}{2}\left[e^{-2}\,10\right] = \frac{5}{e^2} = 0.68 = 68\%.$$

(b) Repeating the above calculation with $2\,a_0$ as the lower limit of the integral,

$$\frac{1}{2}\int_{4}^{\infty} u^2\,e^{u}\,du = \frac{1}{2}\left[-e^{-u}\;\left(u^2 + 2\,u + 2\right)\right]_4^{\infty} = \frac{1}{2}\left[e^{-4}\,26\right] = \frac{13}{e^4} = 0.24 = 24\%.$$

6-23: For $l = 0$, only $m_l = 0$ is allowed, $\Phi(\phi)$ and $\Theta(\theta)$ are both constants (from Table 6.1)), and the theorem is verified.

For $l = 1$, the sum is

$$\frac{1}{2\pi}\,\frac{3}{4}\,\sin^2\theta + \frac{1}{2\pi}\,\frac{3}{2}\,\cos^2\theta + \frac{1}{2\pi}\,\frac{3}{4}\,\sin^2\theta = \frac{3}{4\pi}.$$

In the above, $\Phi^*\Phi = \dfrac{1}{2\pi}$, which holds for any l and m_l, has been used. Note that one term appears twice, one for $m_l = -1$ and once for $m_l = 1$.

For $l = 2$, combining the identical terms for $m_l = \pm 2$ and $m_l = \pm 1$, and again using $\Phi^*\Phi = \dfrac{1}{2\pi}$, the sum is

$$2\,\frac{1}{2\pi}\,\frac{15}{16}\,\sin^4\theta + 2\,\frac{1}{2\pi}\,\frac{15}{4}\,\sin^2\theta\cos^2\theta + \frac{1}{2\pi}\,\frac{10}{16}\,\left(3\,\cos^2\theta - 1\right)^2.$$

The above may be simplified by extracting the commons constant factors, to

$$\frac{5}{16\pi}\left[(3\cos^2\theta - 1)^2 + 12\sin^2\theta\cos^2\theta + 3\,\sin^4\theta\right].$$

Of the many ways of showing the term in brackets is indeed a constant, the one presented here, using a bit of hindsight, seems to be one of the more direct methods. Using the identity $\sin^2\theta = 1 - \cos^2\theta$ to elminate $\sin\theta$,

$$\begin{aligned}
&(3\cos^2\theta - 1)^2 + 12\sin^2\theta\cos^2\theta + 3\,\sin^4\theta \\
&= \left(9\,\cos^4\theta - 6\,\cos^2\theta + 1\right) + 12\,\left(1 - \cos^2\theta\right)\,\cos^2\theta + 3\left(1 - 2\,\cos^2\theta + \cos^4\theta\right) \\
&= 1,
\end{aligned}$$

and the theorem is verified.

6-25: In the integral of Equation (6.35), the radial integral will never vanish, and only the angular functions $\Phi(\phi)$ and $\Theta(\theta)$ need to be considered. The $\Delta l = 0$ transition is seen to be forbidden, in that the product

$$\left(\Phi_0(\phi)\,\Theta_{00}(\theta)\right)^*\left(\Phi_0(\phi)\,\Theta_{00}(\theta)\right) = \frac{1}{4\pi}$$

is spherically symmetric, and any integral of the form of Equation (6.35) must vanish, as the argument $u = x$, y or z will assume positive and negative values with equal probability amplitudes.

If $l = 1$ in the initial state, the integral in Equation (6.35) will be seen to to vanish if u is chosen appropriately. If $m_l = 0$ initially, and $u = z = r\cos\theta$ is used, the integral (apart from constants) is

$$\int_0^\pi \cos^2\theta\,\sin\theta\,d\theta = \frac{2}{3} \neq 0.$$

If $m_l = \pm 1$ initially, and $u = x = r\,\sin\theta\,\cos\phi$ is used, the θ-integral is of the form

$$\int_0^\pi \sin^2\theta\,d\theta = \frac{\pi}{2} \neq 0$$

and the ϕ-integral is of the form

$$\int_0^{2\pi} e^{\pm i\phi}\,\cos\phi\,d\phi = \int_0^{2\pi} \cos^2\phi\,d\phi = \pi \neq 0,$$

and the transition is allowed.

6-27: The relevant integrals are of the form

$$\int_0^L x \sin\frac{n\,\pi\,x}{L}\,\sin\frac{m\,\pi\,x}{L}\,dx.$$

The integrals may be found in a number of ways, including consulting tables or using symbolic-manipulation programs (see, for instance, the solution to Problem 5-15 for sample Maple commands that are easily adpated to this problem).

One way to find a general form for the integral is to use the identity

$$\sin\alpha\,\sin\beta = \frac{1}{2}\left[\cos(\alpha-\beta)-\cos(\alpha+\beta)\right]$$

and the indefinite integral (found from integration by parts)

$$\int x\,\cos kx\,dx = \frac{x\,\sin kx}{k} - \frac{1}{k}\int \sin kx\,dx = \frac{x\,\sin kx}{k} + \frac{\cos kx}{k^2}$$

to find the above definite integral as

$$\frac{1}{2}\left[\begin{array}{l}\dfrac{L\,x}{(n-m)\,\pi}\,\sin\dfrac{(n-m)\,\pi\,x}{L} + \dfrac{L^2}{(n-m)^2\,\pi^2}\,\cos\dfrac{(n-m)\,\pi\,x}{L} \\ \qquad - \dfrac{L\,x}{(n+m)\,\pi}\,\sin\dfrac{(n+m)\,\pi\,x}{L} + \dfrac{L^2}{(n+m)^2\,\pi^2}\,\cos\dfrac{(n+m)\,\pi\,x}{L}\end{array}\right]_0^L,$$

where $n^2 \neq m^2$ is assumed. The terms involving sines vanish, with the result of

$$\frac{L^2}{2\pi^2}\left[\frac{\cos(n-m)\,\pi - 1}{(n-m)^2} - \frac{\cos(n+m)\,\pi - 1}{(n+m)^2}\right].$$

If n and m are both odd or both even, $n+m$ and $n-m$ are even, the arguments of the cosine terms in the above expression are even-integral multiples of π, and the integral vanishes. Thus, the $n = 3 \to n = 1$ transition is forbidden, while the $n = 3 \to n = 2$ and $n = 2 \to n = 1$ transitions are allowed.

To make use of symmetry arguments, consider that

$$\int_0^L \left(x - \frac{L}{2}\right)\sin\frac{n\,\pi\,x}{L}\,\sin\frac{m\,\pi\,x}{L}\,dx = \int_0^L x\,\sin\frac{n\,\pi\,x}{L}\,\sin\frac{m\,\pi\,x}{L}\,dx$$

for $n \neq m$, because the integral of L times the product of the wave functions is zero; the wave functions were shown to be orthogonal in Chapter 5 (again, see Problem 5-15). Letting $u = \dfrac{L}{2} - x$,

$$\sin\frac{n\,\pi\,x}{L} = \sin\frac{n\,\pi\,((L/2)-u)}{L} = \sin\left(\frac{n\,\pi}{2} - \frac{n\,\pi\,u}{L}\right).$$

This expression will be $\pm\cos\left(\dfrac{n\,\pi\,u}{L}\right)$ for n odd and $\pm\sin\left(\dfrac{n\,\pi\,u}{L}\right)$ for n even. The integrand is then an odd function of u when n and m are both even or both odd, and hence the integral is zero. If one of n or m is even and the other odd, the integrand is an even function of u and the integral is nonzero.

6-29: From Equation (6.39), the magnitude of the magnetic moment of an electron in a Bohr orbit is porportional to the magnitude of the angular momentum, and hence proportional to n. The orbital radius is proportional to n^2 (see Equation (4.13) or Problem 4-28), and so the magnetic moment is proportional to $\sqrt{r_n}$.

6-31: See Example 6.4; solving for B,

$$B = \frac{\Delta\lambda}{\lambda^2}\,\frac{4\pi\, m\, c}{e}$$
$$= \frac{\left(0.010 \times 10^{-9}\ \mathrm{m}\right)}{(400 \times 10^{-0}\ \mathrm{m})^2}\,\frac{4\pi\left(9.1095 \times 10^{-31}\ \mathrm{kg}\right)\left(2.998 \times 10^{8}\ \mathrm{m/s}\right)}{(1.602 \times 10^{-19}\ \mathrm{C})} = 1.34\ \mathrm{T}.$$

Evaluation of Integrals for Hydrogen Wave Functions

Many of the problems in this chapter involve integrals of the form

$$\int u^n\, e^{-u}\, du \qquad \text{or} \qquad \int_0^\infty u^n\, e^{-u}\, du$$

for n a nonnegative integer.

Such integrals are well-known and may be found from tables or by use of symbolic-manipulation programs. Standard methods of finding these integrals involve repeated integration by parts. Specifically, for $n = 0$, the idefinite integral is readily found,

$$\int e^{-u}\, du = -e^{-u}$$

and the improper definite integral is seen to be

$$\int_0^\infty e^{-u}\, du = 1.$$

Integrating the above indefinite integral by parts,

$$\int e^{-u}\,du = u\,e^{-u} - \int u\,d\left(-e^{-u}\right)$$
$$= u\,e^{-u} + \int u\,e^{-u}\,du,$$

so that
$$\int u\,e^{-u}\,du = -e^{-u}\,(u+1).$$

The improper definite integral is seen to be

$$\int_0^{\infty} u\,e^{-u}\,du = 1.$$

The process may be repeated, or the process of integration by parts may be generalized as

$$\int u^n\,e^{-u}\,du = u^{n+1}\,e^{-u}\,du + n\int u^{n+1}\,e^{-u}\,du.$$

The first few such integrals are:

$n=0$ $$\int e^{-u}\,du = -e^{-u}$$

$n=1$ $$\int u\,e^{-u}\,du = -e^{-u}\,(u+1)$$

$n=2$ $$\int u^2\,e^{-u}\,du = -e^{-u}\,\left(u^2+2\,u+2\right)$$

$n=3$ $$\int u^3 e^{-u}\,du = -e^{-u}\,\left(u^3+3\,u^2+6\,u+6\right)$$

$n=4$ $$\int u^4\,e^{-u}\,du = -e^{-u}\,\left(u^4+4\,u^3+12\,u^2+24\,u+24\right)$$

Further integrals may be found by, for instance, variations on the Maple command

```
>for m from 0 to 10 do int(u^m*exp(-u),u) od;
```

For the definite improper integrals, a pattern, easily verified by induction is found, the standard result

$$\int_0^{\infty} u^n\,e^{-u}\,du = n!.$$

The Maple command that would demonstrate this pattern is

```
>for n from 0 to 10 do int(u^n*exp(-u),u=0..infinity) od;
```