Chapter 39

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The probability that the electron is found in any interval is given by $P = \int^R |\psi|^2 \, dx$, where the integral is over the interval. If the interval width Δx is small, the probability can be approximated by $P = |\psi|^2 \, \Delta x$, where the wave function is evaluated for the center of the interval, say. For an electron trapped in an infinite well of width L, the ground state probability density is

$$|\psi|^2 = \frac{2}{L} \sin^2 \left(\frac{\pi x}{L} \right) ;$$

so

$$P = \left(\frac{2 \, \Delta x}{L} \right) \sin^2 \left(\frac{\pi x}{L} \right) :$$

(a) Take $L = 100\,\text{pm}$, $x = 25\,\text{pm}$, and $\Delta x = 5.0\,\text{pm}$. Then

$$P = \frac{2(5.0\,\text{pm})}{100\,\text{pm}} \sin^2 \left(\frac{\pi (25\,\text{pm})}{100\,\text{pm}} \right) = 0.050 :$$

(b) Take $L = 100\,\text{pm}$, $x = 50\,\text{pm}$, and $\Delta x = 5.0\,\text{pm}$. Then

$$P = \frac{2(5.0\,\text{pm})}{100\,\text{pm}} \sin^2 \left(\frac{\pi (50\,\text{pm})}{100\,\text{pm}} \right) = 0.10 :$$

(c) Take $L = 100\,\text{pm}$, $x = 90\,\text{pm}$, and $\Delta x = 5.0\,\text{pm}$. Then

$$P = \frac{2(5.0\,\text{pm})}{100\,\text{pm}} \sin^2 \left(\frac{\pi (90\,\text{pm})}{100\,\text{pm}} \right) = 0.0095 :$$

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The energy levels are given by

$$E_{n_x\, n_y} = \frac{h^2}{8m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] = \frac{h^2}{8mL^2} \left[n_x^2 + \frac{n_y^2}{4} \right] ;$$

where the substitutions $L_x = L$ and $L_y = 2L$ were made. In units of $h^2/8mL^2$, the energy levels are given by $n_x^2 + n_y^2/4$. The lowest five levels are $E_{1;1} = 1.25$, $E_{1;2} = 2.00$, $E_{1;3} = 3.25$, $E_{2;1} = 4.25$, and $E_{2;2} = E_{1;4} = 5.00$. A little thought should convince you that there are no other possible values for the energy less than 5.

The frequency of the light emitted or absorbed when the electron goes from an initial state i to a final state f is $f = (E_f - E_i)/h$ and in units of $h/8mL^2$ is simply the difference in the values of $n_x^2 + n_y^2/4$ for the two states. The possible frequencies are 0.75 ($1,2 \to 1,1$), 2.00 ($1,3 \to 1,1$), 3.00 ($2,1 \to 1,1$), 3.75 ($2,2 \to 1,1$), 1.25 ($1,3 \to 1,2$), 2.25 ($2,1 \to 1,2$), 3.00 ($2,2 \to 1,2$), 1.00 ($2,1 \to 1,3$), 1.75 ($2,2 \to 1,3$), 0.75 ($2,2 \to 2,1$), all in units of $h/8mL^2$.

There are 8 different frequencies in all. In units of $h=8mL^2$ the lowest is 0.75, the second lowest is 1.00, and the third lowest is 1.25. The highest is 3.75, the second highest is 3.00, and the third highest is 2.25.

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If kinetic energy is not conserved some of the neutron's initial kinetic energy is used to excite the hydrogen atom. The least energy that the hydrogen atom can accept is the difference between the first excited state ($n = 2$) and the ground state ($n = 1$). Since the energy of a state with principal quantum number n is $-(13.6\,\text{eV})/n^2$, the smallest excitation energy is $13.6\,\text{eV} - (13.6\,\text{eV})/(2)^2 = 10.2\,\text{eV}$. The neutron does not have sufficient kinetic energy to excite the hydrogen atom, so the hydrogen atom is left in its ground state and all the initial kinetic energy of the neutron ends up as the final kinetic energies of the neutron and atom. The collision must be elastic.

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The energy E of the photon emitted when a hydrogen atom jumps from a state with principal quantum number u to a state with principal quantum number ℓ is given by

$$E = A\left(\frac{1}{\ell^2} - \frac{1}{u^2}\right),$$

where $A = 13.6\,\text{eV}$. The frequency f of the electromagnetic wave is given by $f = E/h$ and the wavelength is given by $\lambda = c/f$. Thus

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{E}{hc} = \frac{A}{hc}\left(\frac{1}{\ell^2} - \frac{1}{u^2}\right).$$

The shortest wavelength occurs at the series limit, for which $u = \infty$. For the Balmer series, $\ell = 2$ and the shortest wavelength is $\lambda_B = 4hc/A$. For the Lyman series, $\ell = 1$ and the shortest wavelength is $\lambda_L = hc/A$. The ratio is $\lambda_B/\lambda_L = 4$.

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The proposed wave function is

$$\psi = \frac{1}{\sqrt{\pi}\,a^{3/2}}e^{-r/a},$$

where a is the Bohr radius. Substitute this into the right side of Schrödinger's equation and show that the result is zero. The derivative is

$$\frac{d\psi}{dr} = -\frac{1}{\sqrt{\pi}\,a^{5/2}}e^{-r/a};$$

so

$$r^2\frac{d\psi}{dr} = -\frac{r^2}{\sqrt{\pi}\,a^{5/2}}e^{-r/a}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{1}{\sqrt{\pi}\,a^{5/2}}\left(-\frac{2}{r} + \frac{1}{a}\right)e^{-r/a} = \frac{1}{a}\left(-\frac{2}{r} + \frac{1}{a}\right)\psi.$$

Now the energy of the ground state is given by $E = -me^4/8\varepsilon_0^2 h^2$ and the Bohr radius is given by $a = h^2\varepsilon_0/\pi me^2$, so $E = -e^2/8\pi\varepsilon_0 a$. The potential energy is given by $U = -e^2/4\pi\varepsilon_0 r$, so

$$\frac{8\pi^2 m}{h^2}[E - U]\psi = \frac{8\pi^2 m}{h^2}\left[-\frac{e^2}{8\pi\varepsilon_0 a} + \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi = \frac{8\pi^2 m}{h^2}\frac{e^2}{8\pi\varepsilon_0}\left[-\frac{1}{a} + \frac{2}{r}\right]\psi$$

$$= \frac{\pi m e^2}{h^2\varepsilon_0}\left[-\frac{1}{a} + \frac{2}{r}\right]\psi = \frac{1}{a}\left[-\frac{1}{a} + \frac{2}{r}\right]\psi:$$

The two terms in Schrödinger's equation obviously cancel and the proposed function ψ satisfies that equation.

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The radial probability function for the ground state of hydrogen is $P(r) = (4r^2/a^3)e^{-2r/a}$, where a is the Bohr radius. (See Eq. 39–44.) You want to evaluate the integral $\int_0^1 P(r)\,dr$. Eq. 15 in the integral table of Appendix E is an integral of this form. Set $n = 2$ and replace a in the given formula with $2/a$ and x with r. Then

$$\int_0^1 P(r)\,dr = \frac{4}{a^3}\int_0^1 r^2 e^{-2r/a}\,dr = \frac{4}{a^3}\frac{2}{(2/a)^3} = 1:$$

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(a) ψ_{210} is real. Simply square it to obtain the probability density:

$$|\psi_{210}|^2 = \frac{r^2}{32\pi a^5}e^{-r/a}\cos^2\theta:$$

(b) Each of the other functions is multiplied by its complex conjugate, obtained by replacing i with $-i$ in the function. Since $e^{iA}e^{-iA} = e^0 = 1$, the result is the square of the function without the exponential factor:

$$|\psi_{21+1}|^2 = \frac{r^2}{64\pi a^5}e^{-r/a}\sin^2\theta$$

$$|\psi_{21-1}|^2 = \frac{r^2}{64\pi a^5}e^{-r/a}\sin^2\theta:$$

The last two functions lead to the same probability density.

(c) For $m_\ell = 0$ the radial probability density decreases strongly with distance from the nucleus, is greatest along the z axis, and for a given distance from the nucleus decreases in proportion to $\cos^2\theta$ for points away from the z axis. This is consistent with the dot plot of Fig. 39–24 (a). For $m_\ell = \pm 1$ the radial probability density decreases strongly with distance from the nucleus, is greatest in the x, y plane, and for a given distance from the nucleus decreases in proportion to $\sin^2\theta$ for points away from that plane. Thus it is consistent with the dot plot of Fig. 39-24(b).

(d) The total probability density for the three states is the sum:

$$|\psi_{210}|^2 + |\psi_{21+1}|^2 + |\psi_{21-1}|^2 = \frac{r^2}{32\pi a^5}e^{-r/a}\left[\cos^2\theta + \frac{1}{2}\sin^2\theta + \frac{1}{2}\sin^2\theta\right]$$

$$= \frac{r^2}{32\pi a^5}e^{-r/a}:$$

The trigonometric identity $\cos^2 \mu + \sin^2 \mu = 1$ was used. The total probability density does not depend on μ or $\acute{A}$. It is spherically symmetric.

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The wave function is $\tilde{A} = Ce^{ikx}$. Substitute this function into Schrödinger's equation,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\tilde{A}}{dx^2} + U_0\tilde{A} = E\tilde{A}:$$

Since $d^2\tilde{A}/dx^2 = -Ck^2e^{ikx} = -k^2\tilde{A}$, the result is

$$\frac{h^2 k^2}{8\pi^2 m}\tilde{A} + U_0\tilde{A} = E\tilde{A}:$$

The solution for k is

$$k = \sqrt{\frac{8\pi^2 m}{h^2}(U_0 - E)}:$$

Thus the function given for $\tilde{A}$ is a solution to Schrödinger's equation provided k has the value calculated from the expression given above.