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PH 253 Exam 2: Solutions

1. Given the wave function

$$\psi(x) = \begin{cases} Ne^{\kappa x} & x < 0 \\ Ne^{-\kappa x} & x > 0 \end{cases} \tag{1}$$

(a) Find N needed to normalize ψ.
(b) Find $\langle x \rangle$, $\langle x^2 \rangle$, and Δx.

In order to normalize the wavefunction, we need to split up the usual integral into two integrals over $[-\infty, 0]$ and $[0, \infty]$ since the function is defined separately over those intervals. Since the wave function is piecewise continuous, this need not trouble us though.

$$1 = \int_{-\infty}^{\infty} |\psi|^2 \, dx = \int_{-\infty}^{0} |\psi|^2 \, dx + \int_{-0}^{\infty} |\psi|^2 \, dx = \int_{-\infty}^{0} N^2 e^{2\kappa x} \, dx + \int_{-0}^{\infty} N^2 e^{-2\kappa x} \, dx \tag{2}$$

$$= N^2 \left[\frac{1}{2\kappa} e^{2\kappa x} \bigg|_{-\infty}^{0} + \frac{1}{2\kappa} e^{-2\kappa x} \bigg|_{0}^{\infty} \right] = \frac{N^2}{\kappa} \tag{3}$$

$$\implies \qquad N = \sqrt{\kappa} \tag{4}$$

Next, we find $\langle x \rangle$ in the usual way, again taking care to split the integral into two bits:

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\psi|^2 \, dx = \int_{-\infty}^{0} xN^2 e^{2\kappa x} \, dx + \int_{-0}^{\infty} xN^2 e^{-2\kappa x} \, dx = 0 \tag{5}$$

By symmetry, the two integrals are equal in magnitude and opposite in sign, so the expected position is at the origin. Finding $\langle x^2 \rangle$ requires only a bit more math:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2|\psi|^2 \, dx = \int_{-\infty}^{0} x^2 N^2 e^{2\kappa x} \, dx + \int_{-0}^{\infty} x^2 N^2 e^{-2\kappa x} \, dx \tag{6}$$

$$= \frac{N^2}{4\kappa^3} \left(2\kappa^2 x^2 - 2\kappa x + 1 \right) e^{2\kappa x} \bigg|_{-\infty}^{0} + \frac{N^2}{4\kappa^3} \left(2\kappa^2 x^2 + 2\kappa x + 1 \right) \left(-e^{-2\kappa x} \right) \bigg|_{0}^{\infty} \tag{7}$$

$$= \frac{N^2}{2\kappa^3} = \frac{1}{2\kappa^2} \tag{8}$$

Given $\langle x \rangle$ and $\langle x^2 \rangle$,

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{1}{\sqrt{2}\kappa} \tag{9}$$

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2. An electron in a hydrogen atom is in a state described by the wave function

$$\psi = \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \tag{10}$$

where a_o is the Bohr radius.

(a) What is the *most probable* value of r?
(b) What is $\langle r \rangle$?

The most likely distance corresponds to the distance at which the probability of finding the electron is maximum. This is distinct from the expected value of the radius $\langle r \rangle$. The probability of finding an electron at a distance r in the interval $[r, r+dr]$, in spherical coordinates, is the squared magnitude of the wavefunction times the volume of a spherical shell of thickness dr and radius r:

$$P(r)\,dr = |\psi|^2 \cdot 4\pi r^2\,dr \qquad \text{or} \qquad P(r) = |\psi|^2 \cdot 4\pi r^2 \tag{11}$$

Given ψ above, we have

$$P(r) = \left| \frac{1}{\sqrt{3}\,(2a_o)^{3/2}} \frac{r}{a_o} e^{-r/2a_o} \right|^2 \cdot 4\pi r^2 = \frac{\pi r^4}{6a_o^5} e^{-r/a_o} \tag{12}$$

The most probable radius is when $P(r)$ takes a maximum value, which must occur when $dP/dr = 0$ and $d^2P/dr^2 < 0$. Thus:

$$\frac{dP}{dr} = 0 = \left(\frac{\pi}{6a_o^5}\right) \frac{d}{dr}\left(r^4 e^{-r/a_o}\right) = \left(\frac{\pi}{6a_o^5}\right)\left(4r^3 e^{-r/a_o} - \frac{r^4}{a_o} e^{-r/a_o}\right) \tag{13}$$

$$0 = \left(\frac{\pi r^3}{6a_o^5} e^{-r/a_o}\right)\left(4 - \frac{r}{a_o}\right) \tag{14}$$

$$\implies \quad r = \{0, 4a_o, \infty\} \tag{15}$$

One can either apply the second derivative test or make a quick plot of $P(r)$ to verify that $r = 4a_o$ is the sole maximum of the probability distribution, and hence the most probable radius, while $r = 0$ and $r = \infty$ are minima.

On to $\langle r \rangle$. We must first verify that the wave function is normalized to get a correct value for $\langle r \rangle$ – this did not matter for the most likely value of r, since we differentiated the wave function and any overall normalization constants are irrelevant. Let us now define an overall constant multiplier for the wave function A to fix normalization and find its value. That is, let $\psi \to A\psi$ and enforce normalization to find A.

$$1 = \int_0^\infty A^2 P(r)\,dr = A^2 \int_0^\infty \frac{\pi r^4}{6a_o^5} e^{-r/a_o}\,dr = \frac{A^2\pi}{6a_o} \int_0^\infty \frac{r^4}{a_o^4} e^{-r/a_o}\,dr \tag{16}$$

At this point, it most clever to change variables to $u = r/a_o$, so $du = dr/a_o$, which gives us a well-known integral:

$$1 = \frac{A^2\pi}{6a_o} \int_0^\infty \frac{r^4}{a_o^4} e^{-r/a_o}\,dr = \frac{A^2\pi}{6} \int_0^\infty u^4 e^{-u}\,du = \frac{A^2\pi}{6}\frac{4!}{1^5} = 4\pi A^2 \tag{17}$$

$$\implies \qquad A^2 = \frac{1}{4\pi} \tag{18}$$

Now we can find $\langle r \rangle$ correctly. Since the wave function is spherically symmetric, we can just integrate over radius using the volume element $dV = 4\pi r^2\,dr$:

$$\langle r \rangle = \int_0^\infty r A^2 |\psi|^2\, 4\pi r^2\,dr = \int_0^\infty \frac{r^5}{24 a_o^5} e^{-r/a_o}\,dr = \frac{1}{24} \int_0^\infty \left(\frac{r}{a_o}\right)^5 e^{-r/a_o}\,dr \tag{19}$$

Again, at this point, it most clever to change variables to $u = r/a_o$, so $du = dr/a_o$, which again gives us a well-known integral:

$$\langle r \rangle = \frac{a_o}{24} \int_0^\infty u^5 e^{-u}\,du = \frac{a_o}{24}\frac{5!}{1^6} = 5a_o \tag{20}$$

Of course, we did not check that this wave function is normalized.

3. *Quantum harmonic oscillator.* The harmonic oscillator potential is $V(x) = \frac{1}{2} m\omega_o^2 x^2$; a particle of mass m in this potential oscillates with frequency ω_o. The ground state wave function for a particle in the harmonic oscillator potential has the form

$$\psi(x) = Ae^{-ax^2} \tag{21}$$

(a) By substituting $V(x)$ and $\psi(x)$ into the one-dimensional time-independent Schrödinger equation, find expressions for the ground-state energy E and the constant a in terms of m, $\hbar$, and ω_o.
(b) Apply the normalization condition to determine the constant A in terms of m, $\hbar$, and ω_o.

Given the form of ψ, we note

$$\frac{\partial^2\psi}{\partial x^2} = \left(4a^2x^2 - 2a\right)\psi \tag{22}$$

And thus

$$E\psi = \frac{-\hbar^2}{2m}\left(4a^2x^2 - 2a\right)\psi + \frac{1}{2}m\omega_o^2x^2\psi \tag{23}$$

$$\text{or} \qquad E\psi = \left(\frac{1}{2}m\omega_o^2 - \frac{2a^2\hbar^2}{m}\right)x^2\psi + \frac{a\hbar^2}{m}\psi \tag{24}$$

If we are to have a unique solution for all x, the x^2 coefficients must vanish, i.e.,

$$\frac{1}{2}m\omega_o^2 - \frac{2a^2\hbar^2}{m} = 0 \qquad \Longrightarrow \qquad a = \frac{m\omega_o}{2\hbar} \tag{25}$$

Similarly, the terms of the form (constant)ψ must equate, giving:

$$E = \frac{a\hbar^2}{m} = \frac{1}{2}\hbar\omega_o \tag{26}$$

This is precisely what we have found before, the ground state energy of the harmonic oscillator is half the Planck energy quantum. Normalization requires that

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2\,dx \tag{27}$$

Noting that

$$\int_{-\infty}^{\infty} e^{-cx^2}\,dx = \sqrt{\frac{\pi}{c}} \tag{28}$$

we have

$$1 = \int_{-\infty}^{\infty} A^2e^{-2ax^2}\,dx = A^2\sqrt{\frac{\pi}{2a}} \tag{29}$$

$$\Longrightarrow \qquad A^2 = \sqrt{\frac{2a}{\pi}} \qquad \text{or} \qquad A = \sqrt[4]{\frac{2a}{\pi}} = \sqrt[4]{\frac{m\omega_o}{\pi\hbar}} \tag{30}$$

The ground state wave function is thus

$$\psi(x) = \sqrt[4]{\frac{m\omega_o}{\pi\hbar}}\,e^{-\left(\frac{m\omega_o}{2\hbar}\right)x^2} \tag{31}$$

4. By considering the visible spectrum of hydrogen and He^+, show how you could determine spectroscopically if a sample of hydrogen was contaminated with helium. (Hint: look for differences in the visible emission lines, $\lambda \approx 390 \sim 750$ nm. A difference of 10 nm is easily measured.)

We know the energies in a hydrogen atom are just $E_n = -13.6\,\text{eV}/n^2$ for a given level n. For the He^+ ion, the only real difference is the extra positive charge in the nucleus. If we have Z positive charges in the nucleus, the energies become $E_n = -13.6\,\text{eV}Z^2/n^2$. For $Z=2$, we just end up multiplying all the energies by a factor 4. The questions are: does this lead to any new radiative transitions, are they in the visible range, and are they well-separated enough? We can just list the energy levels for the two systems and see what we come up with.

We already know that the visible transitions in Hydrogen occur when excited states relax to the $n=2$ level, and that for large n the transitions will probably have an energy too high to be in the visible range. Thus, we can probably find a new transition for He^+ by just considering the first several levels alone.

n	H E_n (eV)	He^+ E_n (eV)
1	-13.6	$-13.6\cdot 4$
2	$-13.6\cdot\frac{1}{4}$	-13.6
3	$-13.6\cdot\frac{1}{9}$	$-13.6\cdot\frac{4}{9}$
4	$-13.6\cdot\frac{1}{16}$	$-13.6\cdot\frac{1}{4}$
5	$-13.6\cdot\frac{1}{25}$	$-13.6\cdot\frac{4}{25}$

We see a couple of things already. The $n=2$ state for He^+ happens to accidentally have the same energy as the $n=1$ state for H, likewise for the $n=4$ state for He^+ and the $n=2$ state for H. That means that we can't just pick transitions at random, some of them will accidentally have the same energy.

However, the $n=3$ state for He^+ has the curious fraction $4/9$ in it, which can't possibly occur for H. Transitions into the $n=3$ state should yield unique energies. Let's compute the visible transitions in hydrogen H, since there are only a few, and see if some He^+ transitions stick out in the in-between wavelengths:

H transition	λ_H (nm)	He^+ transition	λ_{He^+} (nm)
$3\to 2$	656	$4\to 3$	469
$4\to 2$	486	$3\to 2$	164
$5\to 2$	434		
$6\to 2$	410		

Already with just the $4\to 3$ transition in He^+, we have an expected emission (or absorption) at 469 nm, a full 17 nm from the nearest H line, and well in the visible range to boot (a nice pretty blue). Should be easy to pick out!

5. Find $\langle x\rangle$, $\langle x^2\rangle$, and $\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$ (in terms of a) for a particle in the ground state of the one-dimensional simple harmonic oscillator, where:

$$\psi_0 = \sqrt{\frac{1}{a\sqrt{\pi}}}e^{-x^2/2a^2} \tag{32}$$

The following integrals may be useful:

$$\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \qquad \int_{-\infty}^{\infty} x^3 e^{-ax^2}\,dx = \int_{-\infty}^{\infty} x e^{-ax^2}\,dx = 0 \qquad \int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\sqrt{\frac{\pi}{a^5}} \tag{33}$$

For the ground state, we have

$$\langle x\rangle = \int x|\psi_0|^2\,dx = \frac{1}{a\sqrt{\pi}}\int_{-\infty}^{\infty} x e^{-x^2/a^2}\,dx = 0 \tag{34}$$

The integral vanishes by symmetry, since the integrand is an odd function of x (and, it was given above).

Classically, a harmonic oscillator is something like a mass on a spring, which oscillates uniformly about its equilibrium point at $x=0$. This means that its average position, over a full cycle of motion, is just $x=0$. The quantum version is no different: if we made many repeated measurements of the particle's position, we would find the average position to be $x=0$. Evaluating $\langle x^2\rangle$ proceeds similarly, except that the integral will *not* vanish, since it is an *even* function of x

$$\langle x^2\rangle = \int x^2|\psi_o|^2\,dx = \frac{1}{a\sqrt{\pi}}\int_{-\infty}^{\infty} x^2 e^{-x^2/a^2}\,dx = \frac{1}{a\sqrt{\pi}}\cdot 2\cdot\frac{1}{4}\cdot\sqrt{\frac{\pi}{(1/a^2)^3}} = \frac{1}{2}a^2 \tag{35}$$

Here the factor of 2 comes from doubling the given integral, with limits of 0 and ∞, since the desired integral is symmetric about $x=0$ with limits of $-\infty$ and ∞. The expectation value of the potential energy can then be found if we like by noting $U=\frac{1}{2}kx^2$, and thus

$$\langle U\rangle_o = \frac{1}{2}k\langle x^2\rangle_o = \frac{1}{4}ka^2 = \frac{1}{4}m\omega_o^2\left(\frac{\hbar}{m\omega}\right) = \frac{1}{4}\hbar\omega = \frac{1}{2}E_o \tag{36}$$

As expected, the potential energy is one half the total ground state energy of $E_o=\frac{1}{2}\hbar\omega_o$. Finally, we can find the uncertainty in position for both the ground state:

$$\Delta x_o = \sqrt{\langle x^2\rangle_o - \langle x\rangle_o^2} = \sqrt{\langle x^2\rangle_o} = \frac{a}{\sqrt{2}} \tag{37}$$

6. A particle bound in a certain one-dimensional potential has a wave function described by the following equations:

$$\psi(x) = \begin{cases} 0 & x < -L \\ Ae^{-ikx}\cos\frac{\pi x}{L} & -L \leqslant x \leqslant L \\ 0 & x > L \end{cases} \tag{38}$$

(a) Find the value of the normalization constant A by enforcing the condition $\int_{\text{all } x}|\psi(x)|^2\,dx=1$.

(b) What is the probability that the particle will be found between $x=0$ and $x=L/4$?

We can find A by enforcing unit probability of finding the particle *somewhere*, i.e., by integrating $|\psi|^2$ over all x. Since ψ is zero outside of the region $0 \leqslant x \leqslant L$, we need only integrate over that range. Noting that $|e^{-ikx}| = (e^{-ikx})^* (e^{ikx}) = 1$,

$$1 = \int_0^L |\psi|^2 \, dx = \int_0^L A^2 \cos^2\left(\frac{\pi x}{L}\right) dx = A^2 \left[x + \frac{L}{\pi} \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right)\right]_0^L = A^2 L \tag{39}$$

$$\implies \qquad A = \sqrt{\frac{1}{L}} \tag{40}$$

The probability that the particle is found between 0 and $L/4$ is obtained by integrating the square of the wave function between those limits, rather than over all infinity:

$$P = \int_0^{L/4} |\psi(x)|^2 \, dx = \int_0^{L/4} \left|\sqrt{\frac{1}{L}} e^{ikx} \cos\left(\frac{\pi x}{L}\right)\right|^2 dx = \frac{1}{L} \int_0^{L/4} \cos^2 \frac{\pi x}{L} \, dx = \frac{1}{2L}\left[\frac{L}{4} + \frac{L}{\pi}\frac{1}{2}\right] = \frac{1}{8} + \frac{1}{4\pi} \approx 0.204$$

Constants:

$$N_A = 6.022\times10^{23}\ \text{things/mol}$$
$$k_e \equiv 1/4\pi\epsilon_o = 8.98755\times10^{9}\ \text{N}\cdot\text{m}^2\cdot\text{C}^{-2}$$
$$\epsilon_o = 8.85\times10^{-12}\ \text{C}^2/\text{N}\cdot\text{m}^2$$
$$\mu_o \equiv 4\pi\times10^{-7}\ \text{T}\cdot\text{m/A}$$
$$e = 1.60218\times10^{-19}\ \text{C}$$
$$h = 6.6261\times10^{-34}\ \text{J}\cdot\text{s} = 4.1357\times10^{-15}\ \text{eV}\cdot\text{s}$$
$$\hbar = \frac{h}{2\pi} \qquad hc = 1239.84\ \text{eV}\cdot\text{nm}$$
$$k_B = 1.38065\times10^{-23}\ \text{J}\cdot\text{K}^{-1} = 8.6173\times10^{-5}\ \text{eV}\cdot\text{K}^{-1}$$
$$c = \frac{1}{\sqrt{\mu_0\epsilon_0}} = 2.99792\times10^{8}\ \text{m/s}$$
$$m_e = 9.10938\times10^{-31}\ \text{kg} \qquad m_e c^2 = 510.998\ \text{keV}$$
$$m_p = 1.67262\times10^{-27}\ \text{kg} \qquad m_p c^2 = 938.272\ \text{MeV}$$
$$m_n = 1.67493\times10^{-27}\ \text{kg} \qquad m_n c^2 = 939.565\ \text{MeV}$$

Schrödinger

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi + V(x)\Psi \quad \text{1D time-dep}$$
$$E\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi \quad \text{1D time-indep}$$
$$\int_{-\infty}^{\infty}|\psi(x)|^2\,dx = 1 \qquad P(\text{in }[x, x+dx]) = |\psi(x)|^2 \qquad \text{1D}$$
$$\int_{0}^{\infty}|\psi(r)|^2\,4\pi r^2\,dr = 1 \qquad P(\text{in }[r, r+dr]) = 4\pi r^2|\psi(r)|^2 \qquad \text{3D}$$
$$\langle x^n\rangle = \int_{-\infty}^{\infty} x^n P(x)\,dx \qquad \text{1D} \qquad \langle r^n\rangle = \int_0^{\infty} r^n P(r)\,dr \qquad \text{3D}$$
$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

Basic Equations:

$$\vec{F}_{net} = m\vec{a} \ \text{ Newton's Second Law}$$
$$\vec{F}_{centr} = -\frac{mv^2}{r}\hat{r} \ \text{ Centripetal}$$
$$\vec{F}_{12} = k_e\frac{q_1q_2}{r_{12}^2}\hat{r}_{12} = q_2\vec{E}_1 \qquad \vec{r}_{12} = \vec{r}_1 - \vec{r}_2$$
$$\vec{E}_1 = \vec{F}_{12}/q_2 = k_e\frac{q_1}{r_{12}^2}\hat{r}_{12}$$
$$\vec{F}_B = q\vec{v}\times\vec{B}$$
$$0 = ax^2 + bx^2 + c \Longrightarrow x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

Oscillators

$$E = \left(n+\frac{1}{2}\right)hf$$
$$E = \frac{1}{2}kA^2 = \frac{1}{2}\omega^2 mA^2 = 2\pi^2 mf^2A^2$$
$$\omega = 2\pi f = \sqrt{k/m}$$

Approximations, $x \ll 1$

$$(1+x)^n \approx 1 + nx + \frac{1}{2}n(n+1)x^2 \qquad \tan x \approx x + \frac{1}{3}x^3$$
$$e^x \approx 1 + x + \frac{1}{2}x \qquad \sin x \approx x - \frac{1}{6}x^3 \qquad \cos x \approx 1 - \frac{1}{2}x^2$$

Misc Quantum

$$E = hf \qquad p = h/\lambda = E/c \qquad \lambda f = c \qquad \text{photons}$$
$$\lambda_f - \lambda_i = \frac{h}{m_e c}(1-\cos\theta)$$
$$\lambda = \frac{h}{|\vec{p}|} = \frac{h}{\gamma m v} \approx \frac{h}{mv}$$
$$\Delta x\Delta p \geqslant \frac{h}{4\pi} \qquad \Delta E\Delta t \geqslant \frac{h}{4\pi}$$
$$eV_{\text{stopping}} = KE_{\text{electron}} = hf - \varphi = hf - W$$

Bohr

$$E_n = -13.6\,\text{eV}/n^2 \quad \text{Hydrogen}$$
$$E_n = -13.6\,\text{eV}\left(Z^2/n^2\right) \quad Z\text{ protons, 1 }e^-$$
$$E_i - E_f = -13.6\,\text{eV}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = hf$$
$$L = mvr = n\hbar$$
$$v^2 = \frac{n^2\hbar^2}{m_e^2r^2} = \frac{k_e e^2}{m_e r}$$

Quantum Numbers

$$l = 0, 1, 2, \ldots, (n-1) \qquad L^2 = l(l+1)\hbar^2$$
$$m_l = -l, (-l+1), \ldots, l \qquad L_z = m_l\hbar$$
$$m_s = -\pm\frac{1}{2} \qquad S_z = m_s\hbar \qquad S^2 = s(s+1)\hbar^2$$
$$\text{dipole transitions: } \Delta l = \pm1, \Delta m_l = 0, \pm1, \Delta m_s = 0$$
$$\mu_{sz} = \pm\mu_B$$
$$\vec{\mu}_s = 2\vec{S}\mu_B$$
$$E_\mu = -\vec{\mu}\cdot\vec{B}$$
$$J^2 = j(j+1)\hbar^2 \qquad j = l\pm\frac{1}{2}$$
$$J_z = m_j\hbar \qquad m_j = -j, (-j+1), \ldots, j$$

Calculus of possible utility:

$$\int\frac{1}{x}\,dx = \ln x + c$$
$$\int u\,dv = uv - \int v\,du$$
$$\int\sin ax\,dx = -\frac{1}{a}\cos ax + C$$
$$\int\cos ax\,dx = \frac{1}{a}\sin ax + C$$
$$\frac{d}{dx}\tan x = \sec^2 x = \frac{1}{\cos^2 x}$$
$$\int e^{-ax}\,dx = -\frac{1}{a}e^{-ax} + C$$
$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$$
$$\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$
$$\int_{-\infty}^{\infty} x^3 e^{-ax^2}\,dx = \int_{-\infty}^{\infty} x e^{-ax^2}\,dx = 0$$
$$\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\sqrt{\frac{\pi}{a^5}}$$