

Homework 2

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1. (a) Evaluate the probability of locating a particle in the middle third of 1-D box. (b) Find the probability that a particle in a box L wide can be found between $x = 0$ and $x = L/n$ when it is in the n th state.

Solution: (a) $\frac{2}{L} \int_0^{L/3} \sin^2\left(\frac{\pi x}{L}\right) dx = 1/3$; (b) $\frac{2}{L} \int_0^{L/n} \sin^2\left(\frac{n\pi x}{L}\right) dx = 1/n$.

2. Consider two wave functions which describe any two different states of a particle in a box. Show that these satisfy the relation $\int_0^L \psi_i^* \psi_j dx = \delta_{ij}$, where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.

Solution: $\frac{2}{L} \int_0^L \sin\left(\frac{i\pi x}{L}\right) \sin\left(\frac{j\pi x}{L}\right) dx = 0$ if $i \neq j$ and 1 if $i = j$.

3. Verify the uncertainty principle for the particle in a box.

Solution: We need to verify that $\Delta x \Delta p_x \geq \hbar/2$, where $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ and similarly $\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$. Three expectation values are easily obtained: $\langle x \rangle = L/2$ (because of symmetry of the integral about $L/2$), $\langle p_x \rangle = 0$ (the particle has equal probability of going to the right or left), $\langle p_x^2 \rangle = 2mE_n = \frac{n^2 \pi^2 \hbar^2}{L^2}$ (because energy is solely kinetic). That leaves $\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2 \frac{\pi x}{L} dx = \left(\frac{L}{2\pi n}\right)^2 \left(\frac{4\pi^2 n^2}{3} - 2\right)$

4. Below are some general statements about wave functions for stationary states of unique energy for a particle bound in a one-dimensional potential well $V(x)$. Decide whether each statement is true or false. Name one or more counterexamples for false statements. Except where noted, these are meant to be general statements, true, for example, even if there is a classically forbidden region *inside* the well. The phrase "outside the well" for any given energy E means a continuous classically forbidden region ($E < V(x)$) extending to infinity.

- (a) There are no nodes in the wave function outside the well.
- (b) There are no nodes in classically forbidden regions.
- (c) If the potential has only one relative minimum, the ground state probability function $|\psi|^2$ has only one maximum.
- (d) The ground state probability function has no nodes.
- (e) The ground state probability function has only one maximum.
- (f) The probability function for any state is greater at positions of higher potential than at positions of lower potential.
- (g) For a given region outside the well, the probability function is smaller as one goes farther from the well.

Solution: True; True; False (only true if there was ONLY ONE minimum in the potential); True; False (only true if there was ONLY ONE minimum in the potential); False (harmonic oscillator ground state is a counter-example); True

5. Many proteins contain metal porphyrin molecules. These molecules are planar and contain 26 π electrons. If the length of the molecule is ~ 1000 pm, then what is the predicted lowest energy absorption of the porphyrin molecule?

Solution: Distribute the 26 π electrons (mass m) in the 13 lowest states of a square box of length, L , 1000 pm. The quantum numbers of the 13 lowest states are 11, (12,21), 22, (13,31), (23,32), (14,41), 33, (24,42). The highest occupied state has $\frac{20\hbar^2}{8mL^2}$. The energy of the next state that is unoccupied is $\frac{25\hbar^2}{8mL^2}$ corresponding to quantum number (34,43). The lowest energy absorption would correspond to an energy of $\frac{5\hbar^2}{8mL^2}$.

6. For a hydrogen atom in the ground state find the classically forbidden region and calculate the probability of finding the electron in this region.

Solution: The classically forbidden region are the values of r for which $V(r) > E$ - it is classically forbidden because classically the kinetic energy would be negative in this case. We know that for hydrogen atom $E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2n^2}$. The values of r for which $V(r) = -\frac{e^2}{4\pi\epsilon_0r}$ is greater than E_n , i.e., for $r > 2\frac{4\pi\epsilon_0\hbar^2n^2}{me^2}$. Calling this r_{cl} , the probability of finding the electron in the classically forbidden region is $\frac{4}{a_0^3} \int_{r_{cl}}^{\infty} e^{-\frac{2r}{a_0}} r^2 dr$

7. Compute the average value of r , the most probable value of r , and the root-mean-square value of r for the 1s and 2p levels of the hydrogen atom. Compare the three kinds of values and explain the origin of their differences.

Solution: If we write $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi)$, then because $\int_0^\pi \int_0^{2\pi} Y_{lm}^* Y_{lm} \sin\theta d\theta d\phi = 1$, we get

$$\langle r \rangle = \int_0^\infty R_{nl}(r)^* r R_{nl}(r) r^2 dr,$$

r_{mp} is the solution of r for which $\frac{d(r^2 R^2)}{dr} = 0$, and

$$r_{rms} = \sqrt{\langle r^2 \rangle} = \sqrt{\int_0^\infty R_{nl}(r)^* r^2 R_{nl}(r) r^2 dr}.$$

Only for a symmetric probability distribution are these three values equal. Remember that the Maxwell-Boltzmann distribution of molecular speeds also had different average, rms, and mps. For any skewed probability distribution, which the radial probability density $r^2 R^2$ is, this is true.

8. Show that the hydrogenlike atomic wave function ψ_{210} is normalized and that it is orthogonal to ψ_{200} .

Solution: This is a straightforward, but lengthy, integration problem provided that you know what normalization and orthogonality mean. For normalization, you would verify that $\int \psi_{nlm}^* \psi_{nlm} r^2 dr \sin\theta d\theta d\phi = 1$. For the hydrogen atom solutions, you can show that $\int \psi_{nlm}^* \psi_{n'l'm'} r^2 dr \sin\theta d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$, where $\delta_{ij} = 0$, if $i \neq j$ and $= 1$, if $i = j$, is called the Kronecker delta.

9. Calculate the probability that an electron described by a hydrogen 1s wave function will be found within one Bohr radius of the nucleus.

Solution: Another problem in integration.

$$\frac{4}{a_0^3} \int_0^{a_0} e^{-\frac{2r}{a_0}} r^2 dr$$

10. Prove that $V = 2E$ and, consequently, that $K = -E$, for a $2s$ electron.

Solution:

$$\langle V \rangle = \int_0^\infty R_{20}^* \left(-\frac{e^2}{4\pi\epsilon_0 r} \right) R_{20} r^2 dr$$

$$\langle K \rangle = \int_0^\infty R_{20}^* \left(-\frac{\hbar^2}{2m} \Delta^2 \right) R_{20} r^2 dr = \int_0^\infty R_{20}^* \left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right) R_{20} r^2 dr$$

11. Compute $\langle r \rangle$ in the $2s$, $2p$ states of the hydrogen atom. Compare your result with the general formula

$$r_{nl} = \frac{a_0}{2} [3n^2 - l(l+1)].$$

Solution:

$$\langle r \rangle = \int_0^\infty R_{nl}(r)^* r R_{nl}(r) r^2 dr,$$

12. Where do the maxima in $r^2 \psi_{2s}^2(r)$ occur?

Solution: The ψ_{2s} has 1 radial node, i.e., one zero crossing. It has two maxima, which are obtained by solving for r in the equation $\frac{dr^2 R_{2s}^2}{dr} = 0$

13. What combinations of the d ($l=2$) atomic orbitals will produce the Cartesian function $d_{xz} = xzR_{nl}(r)$ and $d_{xy} = xyR_{nl}(r)$.

Solution:

$$d_{xz} \propto R_{n2} \cos\theta \sin\theta (e^{i\phi} + e^{-i\phi}) = R_{n2} \cos\theta \sin\theta \cos\phi$$

$$d_{xy} \propto R_{n2} \sin^2\theta (e^{i2\phi} - e^{-i2\phi}) = R_{n2} \sin\theta \cos\phi \sin\theta \sin\phi$$