Chapter 10 Part 1

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Electron wavefunctions

- Since de Broglie indicated that matter should have wave properties, quantum mechanics uses wavefunctions to describe electrons.
- Wave functions are typically symbolized with a Ψ or ψ.
- Wavefunctions must be
  - Single-valued
  - Continuous
  - Differentiable
  - Bounded (may not equal $+\infty$ or $-\infty$)
- A wavefunction contains all possible information that can be known about a system.

Acceptable Wavefunctions

Which of the following expressions are acceptable wavefunctions, and which are not? For those that are not state why.

A. $f(x) = x^2 + 1$, where x can have any value

B. $f(x) = \pm\sqrt{x}, x \geq 0$

C. $\Psi = \frac{1}{\sqrt{2}} \sin\frac{x}{2}, -\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$

D. $\Psi = \frac{1}{4-x}, 0 \leq x \leq 10$

E. $\Psi = \frac{1}{4-x}, 0 \leq x \leq 3$

Acceptable Wavefunctions

A. $f(x) = x^2 + 1$, where x can have any value

Not acceptable, because as x approaches positive or negative infinity, the function also approaches infinity. It is not bounded.

B. $f(x) = \pm\sqrt{x}, x \geq 0$

Not acceptable, because the function is not single-valued

C. $\Psi = \frac{1}{\sqrt{2}} \sin\frac{x}{2}, -\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$

Acceptable, because it meets all criteria for acceptable wavefunctions

D. $\Psi = \frac{1}{4-x}, 0 \leq x \leq 10$

Not acceptable, because the function approaches infinity for $x = 4$, which is part of the range

E. $\Psi = \frac{1}{4-x}, 0 \leq x \leq 3$

Acceptable, because the function meets all criteria for acceptable wavefunctions within that stated range of the variable x

Observables

- Individual properties such as mass, volume, position, momentum, and energy are called observables because they are measured when studying the state of a system.
- To determine the value of an observable in quantum mechanics, one must perform a mathematical operation on the electron wavefunction.

Operators

- The mathematical functions used to determine the values of observables by operating on a wavefunction are called operators.
- Operators are indicated by a chapeau (^) appearing above them.
- Simple operators could include
  - Multiplication operator, $\widehat{M}$

$$\widehat{M}(2,3) = 6$$

  - First derivative operator, $\widehat{D}$

$$\widehat{D}(3x^3 + 4x^2 + 5) = 9x^2 + 8x$$

Operators

For each of the following combinations of operator and function, write the complete mathematical operation and evaluate the expression.

$$\hat{O} = \frac{d}{dx} \qquad \hat{B} = \frac{d^2}{dx^2} \qquad \hat{S} = \mathrm{e}^{\mathrm{x}}$$

$$\Psi_1 = 2x + 4 \qquad \Psi_2 = -3 \qquad \Psi_3 = \sin 4x$$

A. $\hat{S}\Psi_2$ (to three sig figs)
B. $\hat{O}\Psi_1$
C. $\hat{B}\Psi_3$

Operators

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A. $\hat{S}\Psi_2 = e^{-3} = 0.0498$

B. $\hat{O}\Psi_1 = \frac{d}{dx}(2x + 4) = 2$

C. $\hat{B}\Psi_3 = \frac{d^2}{dx^2}(\sin 4x) = \frac{d}{dx}(4\cos 4x) = -16\sin 4\mathrm{x}$

Eigenfunctions and eigenvalues

- Often, when an operator acts on a function, it yields another function.
- When an operator operates on a function to yield a constant times the original function, that function is called an eigenfunction, and the constant is called an eigenvalue
- This will have the general structure of $\hat{B}\Psi = K\Psi$
- For example,

$$\frac{d^2}{dx^2}(\sin 4x) = \frac{d}{dx}(4\cos 4x) = -16\sin 4x$$

  - In this example, the eigenvalue equation would be

$$\frac{d^2}{dx^2}(\sin 4x) = -16\,(\sin 4x)$$

  - Here, $\sin 4x$ is the eigenfunction, and -16 is the eigenvalue

Eigenvalues and Eigenfunctions

Which of the following operator/function combinations would yield eigenvalue equations? What are the eigenvalues of the eigenfunctions?

A. $\frac{d^2}{dx^2}\left(\cos\frac{\mathrm{x}}{4}\right)$

B. $\frac{d}{dx}\left(e^{-4x}\right)$

C. $\frac{d}{dx}\left(e^{-4x^2}\right)$

Eigenvalues and Eigenfunctions

A. $\frac{d^2}{dx^2}\left(\cos\frac{\mathrm{x}}{4}\right) = -\frac{1}{16}\cos\frac{x}{4}$

This is an eigenvalue equation with an eigenvalue of $-1/16$.

B. $\frac{d}{dx}(e^{-4x}) = -4(e^{-4x})$

This is an eigenvalue equation with an eigenvalue of -4.

C. $\frac{d}{dx}\left(e^{-4x^2}\right) = -8x\left(e^{-4x^2}\right)$

This is not an eigenvalue equation because although the original function is reproduced, it is not multiplied by a constant. Instead, it is multiplied by another function, $-8x$.

Physical Observables

- Another postulate of quantum mechanics states that for every physical observable of interest, there is a corresponding operator.
- The only values of the observable that will be obtained in a single measurement must be eigenvalues of the eigenvalue equation constructed from the operator and the wavefunction.
- The only possible values of the observables are those that are eigenvalues of the wavefunction when operated on by the corresponding operator. No other values can be observed.
- This implies that many observables on the atomic scale are quantized.

Some physical observables and their operators

- Position operator (in the x direction)

$$\hat{x} = x \cdot$$

- Momentum operator (in the x direction)

$$\widehat{p_x} = -i\hbar \frac{d}{dx}$$

  - i is the square root of -1
  - $\hbar$ is Planck's constant divided by 2π, $h/2\pi$

Hermitian Operators

- Despite some eigenfunctions and operators have imaginary roots, i, in them, all eigenvalues corresponding to observed quantities must be real.
- Hermitian operators are operators that only have real (nonimaginary) numbers as eigenvalues.
- All operators that yield quantum mechanical observables are Hermitian operators, since to be observed, a quantity must be real.

Observables

What is the value of the momentum observable if the wavefunction Ψ is e^{-i4x}?

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$$-i\hbar\frac{d}{dx}e^{-i4x} = (-i\hbar)(-i4)e^{-i4x} = -4\hbar e^{-i4x}$$

The value of the momentum from this wavefunction is $-4\hbar$.

Uncertainty Principle

- The uncertainty principle places a lower bound on how exact two observables can be measured simultaneously.
- The most popular instance of this is the uncertainty associated with simultaneously measuring position (x) and momentum (ρ_x) (both in the x direction).

$$\Delta x \times \Delta \rho_x \geq \frac{\hbar}{2}$$

$$\Delta x \times m \times \Delta v \geq \frac{\hbar}{2}$$

- Here, mass, m, is assumed to be a constant.
- For large masses, Δx and Δv can be so small that they're undetectable, but for very small masses Δx and Δv can be so large that they can't be ignored.

Uncertainty Principle

Determine the uncertainty in position, Δx, in the following cases:

A. A 1000.-kg race car traveling at 100 meters per second, and v is known to within 1.00 meter per second. (in m)

B. A 9.109×10^{-31} kg electron is traveling at 2.00×10^{6} meters per second (the approximate velocity of an electron in Bohr's first quantum level) with an uncertainty of 1% of the true value. (in Å)

Uncertainty Principle

A.

$$\Delta x \times m \times \Delta v \geq \frac{\hbar}{2}$$

$$\Delta x \times (1000\ \text{kg}) \times \left(1.00\,\frac{\text{m}}{\text{s}}\right) \geq \frac{6.626 \times 10^{-34}\ \text{Js}}{2 \times 2 \times \pi}$$

$$\Delta x \geq 5.27 \times 10^{-38}\ \text{m}$$

B.

$$\Delta x \times m \times \Delta v \geq \frac{\hbar}{2}$$

$$\Delta x \times (9.109 \times 10^{-31}\ \text{kg}) \times \left(2.00 \times 10^{4}\,\frac{\text{m}}{\text{s}}\right) \geq \frac{6.626 \times 10^{-34}\ \text{Js}}{2 \times 2 \times \pi}$$

$$\Delta x \geq 2.89 \times 10^{-9}\ \text{m}\left(\frac{10^{10}\,\text{Å}}{1\ m}\right) = 28.9\ \text{Å}$$

A quandary…

- If the behavior of an electron is described by a wavefunction, but the uncertainty principle limits the certainty with which one can measure various combinations of observables, how can one discuss the motion of electrons in detail?

Overcoming uncertainty with probability

- Max Born shifted the focus away from certainty to probability
- Born suggested that one not think of wavefunctions as indicating the specific path of an electron at a particular time but rather as indicating the electrons probability of being in a certain region over a long period of time.
- Born stated that the probability P of an electron being in a certain region between points a and b in space is

$$P = \int_b^a \Psi^* \times \Psi \, d\tau$$

  - Here, Ψ^* is the complex conjugate of Ψ (where every i in the wavefunction is replaced with –i).

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  - $d\tau$ is the infinitesimal of integration covering the dimensional space of interest
    - This is dx for one dimension, $dxdy$ for two dimensions, $dxdydz$ for three dimensions, and $r^2 \sin\theta \, dr d\theta d\phi$ for spherical polar coordinates.

Probability

Using the Born interpretation, for an electron having a one-dimensional wavefunction $\Psi = \sqrt{2}\sin \pi x$ in the range $x = 0$ to 1, what are the following probabilities?

A. The probability that the electron is in the first half of the range, from $x = 0$ to 0.5
B. The probability that the electron is in the middle half of the range from $x = 0.25$ to 0.75

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$$P = \int_b^a \left(\sqrt{2}\sin \pi x\right)^* \times \left(\sqrt{2}\sin \pi x\right) dx$$

$$P = 2\int_b^a \sin^2 \pi x \ dx = \frac{x}{2} - \frac{1}{4\pi}\sin 2\pi x \,|\, \frac{a}{b}$$

Probability (Part A)

$$2\left[\frac{x}{2}-\frac{1}{4\pi}\sin 2\pi x\,\Big|\,\frac{a}{b}\right]$$

A. Evaluating the region $x = 0$ to 0.5:

$$P = 2\left[\left(\frac{0.5}{2}-\frac{1}{4\pi}\sin 2\pi(0.5)\right)-\left(\frac{0}{2}-\frac{1}{4\pi}\sin 2\pi(0)\right)\right]$$

$$P = 2\left[\left(\frac{1}{4}-\frac{1}{4\pi}\sin \pi\right)-\left(-\frac{1}{4\pi}\sin 0\right)\right] = 2\left[\frac{1}{4}\right] = 0.5$$

Probability (Part B)

$$2\left[\frac{x}{2} - \frac{1}{4\pi}\sin 2\pi x \,\Big|\, \frac{a}{b}\right]$$

B. Evaluating the region $x = 0.25$ to 0.75:

$$P = 2\left[\left(\frac{0.75}{2} - \frac{1}{4\pi}\sin 2\pi(0.75)\right) - \left(\frac{0.25}{2} - \frac{1}{4\pi}\sin 2\pi(0.25)\right)\right]$$

$$P = 2\left[\left(\frac{3}{8} - \frac{1}{4\pi}\sin\frac{3\pi}{2}\right) - \left(\frac{1}{8} - \frac{1}{4\pi}\sin\frac{\pi}{2}\right)\right]$$

$$P = 2\left[\left(\frac{3}{8} + \frac{1}{4\pi}\right) - \left(\frac{1}{8} - \frac{1}{4\pi}\right)\right] = 2\left(\frac{1}{4} + \frac{1}{2\pi}\right) = 0.818$$

Stationary States

- Since the wavefunction in the last example doesn't depend on time, its probability distribution also doesn't depend on time.
- A stationary state is defined as a wavefunction that does not have time dependance, and thus who's probability distribution also has time independence.