

Physical Chemistry

Lecture 12

Wave Equations and States

Postulates of quantum mechanics

- Any state of a dynamical system of N particles is described as fully as is possible by a function, Ψ , such that the quantity $\Psi^*\Psi d^3r$ is proportional to the probability of finding r between r and $r + d^3r$.
- For every observable property of a system, there exists a corresponding linear hermitian operator
 - The physical properties of the observable can be inferred from the mathematical properties of its associated operator.
- The measurement of a physical observable gives only one of the eigenvalues corresponding to that observable.

Origins of quantum mechanics

- Hamilton's equation for the energy of a classical system

$$H = E$$

- Schrodinger's equation for the wave function of a system with a definite energy

$$\hat{H}\Psi = E\Psi$$

Where Ψ is the wave function corresponding to the energy

Expectation value of a property

- If a system is in a state with wave function, Ψ , the measured property is given by an integral
- Must know both the **state** and the **operator** to find the value
- Expectation values of measurables are real
 - Requirement on the wave function and operator
 - The operator must be a **hermitian** operator

$$\langle O \rangle = \int_{\text{all space}} \Psi^* \hat{O} \Psi dV$$

$$\int_{\text{all space}} \Psi^* (\hat{O}\Psi) dV = \int_{\text{all space}} (\hat{O}\Psi)^* \Psi dV$$

Choosing operators

- Operators for various observables are found by correspondence to classical equivalents
- For position, the operation is multiplication by the appropriate coordinate
- For momentum, the operation is related to differentiation with respect to the conjugate coordinate
- Other operators are found by correspondence through the momentum and position dependencies

$$x \Rightarrow x \bullet$$

$$p_x \Rightarrow -i\hbar \frac{\partial}{\partial x}$$

$$p^2 = p_x^2 + p_y^2 + p_z^2 \Rightarrow \hat{p}^2 = \left(-i\hbar \frac{\partial}{\partial x}\right)\left(-i\hbar \frac{\partial}{\partial x}\right) + \left(-i\hbar \frac{\partial}{\partial y}\right)\left(-i\hbar \frac{\partial}{\partial y}\right) + \left(-i\hbar \frac{\partial}{\partial z}\right)\left(-i\hbar \frac{\partial}{\partial z}\right) = -\hbar^2 \nabla^2$$

Orthogonality and completeness

- Eigenfunctions of a hermitian operator corresponding to different eigenvalues are **orthogonal**.
- The set of all eigenfunctions of a hermitian operator is **complete**. Any function of the coordinates on which it depends can be expressed as a linear combination of the members of the set.

$$\int_{\text{all space}} \Psi_a^* \Psi_b dV = 0 \text{ if } a \neq b$$

$$f(x, y, z) = \sum_k c_k \Psi_k(x, y, z)$$

Heisenberg's uncertainty principle

- ◆ Simultaneous measurement of two quantities, $\langle \alpha \rangle$ and $\langle \beta \rangle$

- ◆ Define uncertainty in one as

$$\Delta \alpha = \sqrt{\langle \alpha^2 \rangle - \langle \alpha \rangle^2}$$

- ◆ With some operator algebra, one can show that

$$\Delta \alpha \Delta \beta \geq \frac{1}{2} |\langle [\alpha, \beta] \rangle|$$

- ◆ Unless two operators commute, measurement of each with absolute precision is not possible when the system is in an arbitrary state.

Finding basis sets

- ◆ The complete set of eigenfunctions of an operator is special.

- Expresses all possible conditions of the system
- Can be used to express other arbitrary functions

- ◆ Operational plan

- Find the Hamiltonian operator for a system
- Set up Schroedinger's equation
- Solve for all solutions of Schroedinger's equation consistent with boundary conditions

- ◆ Usually study model systems, the mathematics of which are tractable

- Use model solutions to specify more complex systems approximately with various techniques.

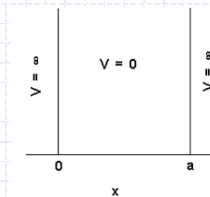
The particle in a 1D box

- ◆ A model for 1D translation of a gas molecule

- ◆ Two regions

- In the box, $V(x) = 0$
- Outside the box, $V(x) = \infty$

- ◆ In the box, the Hamiltonian is well known



$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

Eigenvalue equation for the particle in a 1D box

- ◆ Schroedinger's equation

- Inside the box

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} = E \Psi$$

- Outside the box

$$\infty \Psi = E \Psi$$

- ◆ The only solution outside the box is $\Psi(x) = 0$

- Provides a boundary condition on $\Psi(x)$ at the box edges

Particle-in-a-1D-box eigenvalue equation

- ◆ Differential equation

$$\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + E \Psi = 0$$

- ◆ Use methods of differential calculus to solve

$$\Psi_s(x) = A e^{sx}$$

- ◆ This gives an equation for s and Ψ :

$$s_E = \pm i \sqrt{\frac{2mE}{\hbar^2}}$$

$$\Psi_E(x) = A \exp\left(i \sqrt{\frac{2mE}{\hbar^2}} x\right) + B \exp\left(-i \sqrt{\frac{2mE}{\hbar^2}} x\right)$$

Particle-in-a-1D-box eigenvalue equation

- ◆ Solution may be written in terms of sines and cosines, which is more convenient

$$\Psi_E = C \sin\left(\sqrt{\frac{2mE}{\hbar^2}} x\right) + D \cos\left(\sqrt{\frac{2mE}{\hbar^2}} x\right)$$

- ◆ Boundary conditions give a quantum number n

- $\Psi(0) = 0 \Rightarrow D = 0$
- $\Psi(a) = 0 \Rightarrow \sqrt{\frac{2mE}{\hbar^2}} a = n\pi$

$$\Psi_n(x) = C \sin\left(\frac{n\pi x}{a}\right) \quad E_n = \frac{\hbar^2}{8ma^2} n^2$$

Normalized wave functions

- ◆ The coefficient, C, is so far undetermined
 - Use the requirement that the wave function be square integrable with an integral of 1

$$\int_{\text{all space}} \Psi^*(x)\Psi(x)dx = 1$$

- ◆ This gives the final specification of the wave function

$$\int_{-\infty}^{+\infty} \Psi^*(x)\Psi(x)dx = C^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx = 1$$

$$C = \sqrt{\frac{2}{a}}$$

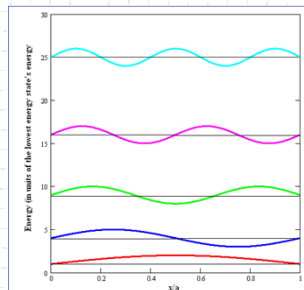
Grotrian diagram

- ◆ The particle in a 1D box
- ◆ Quantized energy levels
 - Quantum numbers are the positive integers
- ◆ Zero point energy
 - Lowest-energy state is not at E = 0
 - Particle is moving, even in the lowest-energy state
 - Consistent with Heisenberg's principle



Wave functions of the particle in a 1-D box

- The wave functions increase in number of nodes as the energy increases
- The probability of finding a particle is not uniform across the box
 - It would be uniform for a classical particle in a box



Summary

- ◆ Operator eigenvalue equations give the wave functions from which one obtains all system information
- ◆ Schrodinger's equation results in differential equations because of the presence of the momentum operators
- ◆ Solution requires finding Hamiltonian operator
- ◆ Boundary conditions determine quantum conditions
- ◆ Example: particle in a one-dimensional box