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 $\Psi^*\Psi d^3\mathbf{r}$ is proportional to the probability of finding **r** between **r** and **r** + d^3**r**.
- 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

$$H = E$$

- Schroedinger'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**

$$<O> = \int_{\substack{all\\space}} \Psi^* \hat{O} \Psi dV$$

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

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**

$$x \Rightarrow x\bullet$$

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

$$p^2 = p_x^2 + p_y^2 + p_z^2 \Rightarrow$$

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

$$= -\hbar^2\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} = -\hbar^2\nabla^2$$

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.**

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

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

Heisenberg's uncertainty principle

- Simultaneous measurement of two quantities, <α> and <β>
- Define uncertainty in one as

$$\Delta\alpha = \sqrt{<\alpha^2> - <\alpha>^2}$$

- With some operator algebra, one can show that

$$\Delta\alpha\Delta\beta \geq \frac{1}{2}|<[\alpha,\beta]>|$$

- 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 free particle in 1D

- A model for a totally isolated particle
- The particle senses no forces
  - V = 0 everywhere
  - The Hamiltonian operator contains only the kinetic-energy operator

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

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

The free particle in 1D

- Schroedinger's equation
- The wave function is found by simple solution of the differential equation

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

$$\Psi_{trial}(x) = Ae^{sx}$$

$$s = \pm\sqrt{-\frac{2mE}{\hbar^2}}$$

The free particle in 1D

- Wave function is a sum of particular solutions
- Wavevector, k, defines the state
  - May take on any value

$$\Psi_k(x) = Ae^{ikx} + Be^{-ikx}$$

$$s = \pm ik$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Another look at the free particle

- Determine the linear momentum of a particle in the state with wavevector k
- This function is an eigenfunction of the linear momentum operator

$$\hat{p}\Psi_k(x) = p\Psi(x)$$

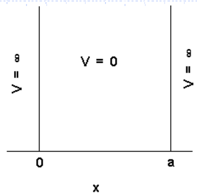
$$-i\hbar\frac{d\Psi}{dx} = p\Psi$$

$$-i\hbar\frac{d}{dx}\left(Ae^{ikx}\right) =$$

$$-i^2\hbar k\left(Ae^{ikx}\right) = k\hbar\left(Ae^{ikx}\right)$$

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) = ∞
- 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 Ψ(x) = 0
  - Provides a boundary condition on Ψ(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 a equation for s and Ψ:

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

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

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**
  - **Ψ(0) = 0 ⇒** $D = 0$
  - **Ψ(a) = 0 ⇒** $\sqrt{\frac{2mE}{\hbar^2}}a = n\pi$

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

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

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

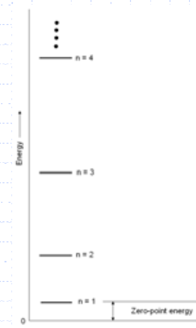
- This gives the final specification of the wave function

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

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

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



Summary

- Operator eigenvalue equations give the wave functions from which one obtains all system information
- Schroedinger'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