Physical Chemistry

Lecture 13

The Meaning of Wave Functions; Solving Complex Problems

Born's interpretation of the wave function

- It is not possible to measure all properties of a quantum system precisely
- Max Born suggested that the wave function was related to the probability that an observable has a specific value.
- Often called the Copenhagen interpretation
- A parameter of interest is position (x,y,z)

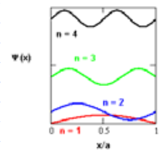
$$\Psi^*(x,y,z)\Psi(x,y,z)d^3\mathbf{r} \equiv P(x,y,z)d^3\mathbf{r}$$

Requirements on a wave function

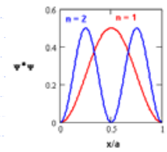
- To be consistent with the Born interpretation, a wave function has to have certain characteristics.
  - Square integrable over all space. (In this way it can be normalized and represent probability.)
  - Single-valued (so that the probability at any point is unique)
  - Continuous at all points in space.
  - First derivative must be continuous at all points where the potential is continuous.

Example: particle in a 1-D box

- Wave functions



- Square of wave functions



Expectation values for a particle in a 1-D box

- **Expectation value of the position**

$$\begin{aligned} \langle x \rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right) x \sin\left(\frac{n\pi x}{a}\right)dx \\ &= \frac{2a}{n^2\pi^2}\int_0^{n\pi} y\sin^2 y\,dy \\ &= \frac{a}{2} \end{aligned}$$

- **Expectation value of the square of the position**

$$\begin{aligned} \langle x^2 \rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right) x^2 \sin\left(\frac{n\pi x}{a}\right)dx \\ &= \frac{2a^2}{n^3\pi^3}\int_0^{n\pi} y^2\sin^2 y\,dy \\ &= a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) \end{aligned}$$

Expectation values for a particle in a 1-D box

- **Expectation value of the momentum**

$$\begin{aligned} \langle p_x \rangle &= -\frac{2i\hbar}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\frac{d}{dx}\sin\left(\frac{n\pi x}{a}\right)dx \\ &= -\frac{2i\hbar n\pi}{a^2}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right)dx \\ &= 0 \end{aligned}$$

- **Expectation value of the square of the momentum**
  - **An eigenvalue (!!!)**
  - **Must be an eigenstate of p_x^2**

$$\begin{aligned} \langle p_x^2 \rangle &= -\frac{2\hbar^2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{a}\right)dx \\ &= \frac{2\hbar^2 n\pi}{a^2}\int_0^{n\pi} \sin^2 y\,dy \\ &= \frac{n^2\pi^2\hbar^2}{a^2} \end{aligned}$$

Copenhagen interpretation for an arbitrary (mixed) state

- Particle in a 1D box in an arbitrary state
  - ψ written as a sum of the energy eigenstates
- The expectation value of the energy of the particle in this state is a sum of contributions
  - Importantly, if one determines the expectation value by repeated measurements, one ONLY finds among the measurements elements of $\{E_k\}$

$$\psi(x) = \sum_n c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$\begin{aligned} <E> &= \int_0^a \psi^*(x) H \psi(x) dx \\ &= \frac{2}{a} \sum_{j,k} c_j^* c_k \int_0^a \sin\left(\frac{j\pi x}{a}\right) H \sin\left(\frac{k\pi x}{a}\right) dx \\ &= \frac{2}{a} \sum_{j,k} c_j^* c_k E_k \int_0^a \sin\left(\frac{j\pi x}{a}\right) \sin\left(\frac{k\pi x}{a}\right) dx \\ &= \sum_{j,k} c_j^* c_k E_k \delta_{jk} \\ &= \sum_k c_k^* c_k E_k = \sum_k p_k E_k \end{aligned}$$

Particle in a 3-D box

- The actual space in which we live is three-dimensional.
- General problem of a particle in a 3-D box is appropriate to gas molecules
- Example of a complex problem decomposed into a simpler problem
- Hamiltonian

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Separation of variables

- There is only one way for the following kind of equation to be generally satisfied

$$\begin{aligned} f(x) &= g(y) \\ f(x) &= C \\ g(y) &= C \end{aligned}$$

- Each function must be equal to a constant, independent of either x or y

Application to the particle in a 3-D box

- Overall problem may be separated into three 1-D problems
- Hamiltonian must be a sum of Hamiltonians
  - Each depends on a single independent variable
- The wave function is a product of wave functions for each mode
- The energy is a sum of the energies of the modes

$$H(x,y,z)\Psi(x,y,z) = E\Psi(x,y,z)$$

$$\begin{aligned} H_x(x)\Psi_x(x) &= E_x\Psi_x(x) \\ H_y(y)\Psi_y(y) &= E_y\Psi_y(y) \\ H_z(z)\Psi_z(z) &= E_z\Psi_z(z) \end{aligned}$$

$$H(x,y,z) = H_x(x) + H_y(y) + H_z(z)$$

$$E = E_x + E_y + E_z$$

$$\Psi(x,y,z) = \Psi_x(x)\Psi_y(y)\Psi_z(z)$$

Solutions to the particle in a 3-D box

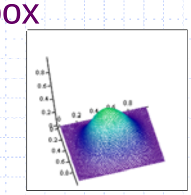
- Each mode is exactly like the particle in a 1-D box
- Solutions and energies of these modes are known
- Overall solution

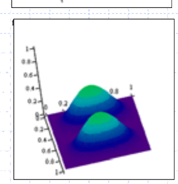
$$\Psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{2^3}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Probability plots for a particle in a 2-D box

- Upper graph
  - $n_x = 1$
  - $n_y = 1$
- Lower graph
  - $n_x = 1$
  - $n_y = 2$
- Note the symmetry of the graphs and how it changes depending on the relationship of the eigenvalues





Symmetry and degeneracy

- For the particle in a 3-D box, the energies depend on the size of the box in each direction
- When $a = b \neq c$, the states $(1,2,n_z)$ and $(2,1,n_z)$ necessarily have the same energy
- Symmetry increases the number of states at a particular energy
  - Degeneracy increases because of symmetry
  - Very important relation used to determine symmetry properties of systems

Quantum model problems

System	Model	Potential Energy	Differential Equation	Solutions
Gas molecule	Particle in a Box	Either 0 or ∞	Bounded wave equations	Sines and cosines
Bond vibration	Harmonic oscillator	$(k/2)(r-r_{eq})^2$	Hermite's equation	Hermite polynomials
Molecular rotation	Rigid rotor	Either 0 or ∞	Spherical harmonic (angular momentum)	Spherical harmonic functions
Hydrogen atom	Central-force problem	$-Ze^2/r$	Legendre's and Laguerre's equations	Legendre polynomials, Laguerre polynomials, spherical harmonic functions
Complex systems	Multi-mode systems	Complex	Complicated equations	Complex products of functions

Summary

- A system's wave function provides all possible information on it
- The wave function provides probabilities for values of properties
  - Born (Copenhagen) interpretation
  - When a system is in an eigenstate, the value is exact
    - Repeated measurements give the same result for the property's value
  - Example: particle in a 1-D box
    - Probability of position found from the square of the normalized wave function for that position
    - States are not eigenfunctions of position
    - Expectation value for the position by averaging over probability
    - Energy eigenstate is also an eigenstate of p_x^2
- Particle in a 3-D box
  - Example of decomposition of a complex problem into simpler problems
  - Symmetry and degeneracy of energy levels