de Broglie wavelength: \( \lambda = \frac{h}{p} \)

\( \lambda \nu = c \)

Energy: \( E = h \nu \)

Operator: \( \hat{A}f(x) = g(x) \)

To every physical property there corresponds a quantum mechanical hermitian operator

Convert a classical expression into a quantum mechanical operator by making these replacements:

momenta: \( \hat{p}_x = -i\hbar \frac{d}{dx} \)

coordinates: \( \hat{x} = x \)

Hamiltonian operator: \( \hat{H} = \hat{T} + \hat{V} \)

Hamiltonian operator for 1 particle in 1 dimension: \( \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \)

Hamiltonian operator for 1 particle in 3 dimensions: \( \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \)

Hamiltonian operator for n particles in 3 dimensions:

\[
\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, y_1, z_1, \ldots, x_n, y_n, z_n)
\]

Definition of linear operator \( \hat{A} \): \( \hat{A}[f + g] = \hat{A}f + \hat{A}g \) and \( \hat{A}[cf] = c\hat{A}f \)

\( \hat{A} \) and \( \hat{B} \) commute if \( [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \)

Bracket notation: \( \langle \phi_i | \hat{M} | \phi_i \rangle = \int \phi_i^* \hat{M} \phi_i \, d\tau \) where \( \tau \) includes all variables

Hermitian operator: \( \int \psi^* \hat{A} \phi \, d\tau = \int \phi \hat{A}^* \psi \, d\tau \) Examples: \( \hat{T}, \hat{V}, \hat{H} \)
Theorems about Hermitian operators:
1. real eigenvalues
2. orthonormal eigenfunctions
3. eigenfunctions form a complete set
4. $[\hat{A}, \hat{B}] = 0 \Rightarrow \hat{A}$ and $\hat{B}$ share a common complete set of eigenfunctions

Eigenfunction and eigenvalue: $\hat{B}f(x) = bf(x)$

Time-independent Schrödinger equation: $\hat{H}\psi_n(x) = E_n\psi_n(x)$

Time-dependent Schrödinger equation: $\frac{-\hbar}{i}\frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t)$

Stationary state: (assume $\hat{H}$ independent of time)
Solution to time-dependent Schrödinger equation with constant energy (also solution to time-independent Schrödinger equation)
$\Psi_n(x,t) = \exp\left(-iE_n t / \hbar\right)\psi_n(x)$

Probability density independent of time: $|\Psi'_n(x,t)|^2 = |\psi_n(x)|^2$

General solution to time-dependent Schrödinger equation:
$\Psi(x,t) = \sum_n c_n \Phi_n(x,t)$
$= \sum_n c_n \exp\left(-iE_n t / \hbar\right)\phi_n(x)$
$= \sum_n c_n(t)\phi_n(x)$

Here $c_n$ is time-independent and $c_n(t) = c_n \exp\left(-iE_n t / \hbar\right)$

**Note:** In general, $\Psi(x,t)$ is not an eigenfunction of $\hat{H}$
Expanding $\Psi(x,t)$ in terms of functions $\phi_n(x)$ that are eigenfunctions of $\hat{H}$
Expansion coefficients $c_n(t)$ given by
$c_n(t) = \langle \phi_n(x) | \Psi(x,t) \rangle = \int_{-\infty}^{\infty} \phi_n^*(x) \Psi(x,t) dx$
$|c_n(t)|^2 = |c_n|^2$

such that $\Psi(x,t) = \sum_n c_n(t)\phi_n(x)$
$\sum_n |c_n(t)|^2 = 1$
Measurement for non-stationary states

\[ \Psi(x,t) = \sum_n c_n(t) \phi_n(x) \]

\[ \langle \Psi | \Psi \rangle = 1 \]

\[ \hat{B} \phi_n = b_n \phi_n \]

Postulate: always get an eigenvalue \( b_n \) when we make measurement of property \( B \)

Theorem: when we measure property \( B \), the probability of measuring the value \( b_n \) is

\[ |c_n(t)|^2 = |\langle \phi_n | \Psi \rangle|^2 \]

Conditions on the wavefunction: continuous, derivatives piecewise continuous, single valued, quadratically integrable

Probability density: \( |\Psi(x,t)|^2 \)

Probability of \( x \) between \( x' \) and \( x'+dx' \) at time \( t \):

\[ |\Psi(x',t)|^2 \ dx' \]

Probability of \( x \) between \( a \) and \( b \):

\[ \int_a^b |\Psi(x,t)|^2 \ dx \]

3-dimensions, stationary state:

Probability of \( x \) between \( a \) and \( b \):

\[ \int_a^b \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\varphi(x,y,z)|^2 \ dx \ dy \ dz \]

Probability of \( x \) between \( a \) and \( b \) and \( y \) between \( c \) and \( d \):

\[ \int_a^b \int_c^d \int_{-\infty}^{\infty} |\varphi(x,y,z)|^2 \ dx \ dy \ dz \]

Normalized: \( \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \ dx = 1 \)

Stationary state: \( \int_{-\infty}^{\infty} |\varphi(x)|^2 \ dx = 1 \)

Multiple dimensions: \( \int |\varphi|^2 \ d\tau = 1 \)

Orthonormal wavefunctions: \( \int \varphi_i^* \varphi_j \ d\tau = \delta_{ij} \)

Kronecker delta function:

\[ \delta_{ij} = 0 \quad i \neq j \]

\[ \delta_{ij} = 1 \quad i = j \]
Average of property associated with operator: \[ \langle B \rangle = \int \psi^* \hat{B} \psi \, d\tau = \langle \psi | \hat{B} | \psi \rangle \]
Assumes that \( \Psi \) is normalized.

Stationary state: \[ \langle B \rangle = \int \psi^* \hat{B} \psi \, d\tau = \langle \psi | \hat{B} | \psi \rangle \]

Schmidt orthogonalization procedure

\( \phi \) and \( \psi \) are degenerate eigenfunctions of \( \hat{A} \) and are not orthogonal.
To make \( \phi \) orthogonal to \( \psi \), calculate overlap integral

\[ S = \int \phi^* \psi \, d\tau \]

Define new function \( \phi' = \phi - S\psi \)
Normalize \( \phi' \)

Correspondence principle: the predictions of quantum mechanics must pass smoothly into those of classical mechanics whenever we progress in a continuous way from the microscopic to the macroscopic realm.
Particle in a one-dimensional box: \( V(x) = 0 \) for \( 0 \leq x \leq l \), \( V(x) = \infty \) elsewhere

\[
\psi_n(x) = \frac{2}{l} \sin \left( \frac{n\pi x}{l} \right) \quad 0 \leq x \leq l
= 0 \quad x < 0, \ x > l
\]

\[
E_n = \frac{n^2 \hbar^2}{8ml^2}
\]

\( n = 1,2,3,\ldots \)

Energies: positive zero-point energy, quantized energy levels, non-degenerate levels, spacings increase as \( n \) increases, spacings increase as \( m \) and \( l \) decrease.

Wavefunctions: symmetric (\( n \) odd) or antisymmetric (\( n \) even) about middle of box, \( n \)-1 nodes, zero outside box

Applications to conjugated polymers

Particle in a three-dimensional box of dimensions \( a, b, c \)

Hamiltonian separable: multiply 1-D wavefunctions, add 1-D energies

\[
\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{2}{a}} \sin \left( \frac{n_x \pi x}{a} \right) \sqrt{\frac{2}{b}} \sin \left( \frac{n_y \pi y}{b} \right) \sqrt{\frac{2}{c}} \sin \left( \frac{n_z \pi z}{c} \right) \quad 0 \leq x \leq a, 0 \leq y \leq b, 0 \leq z \leq c
= 0 \quad \text{elsewhere}
\]

\[
E_{n_x,n_y,n_z} = \frac{n_x^2 \hbar^2}{8ma^2} + \frac{n_y^2 \hbar^2}{8mb^2} + \frac{n_z^2 \hbar^2}{8mc^2}
\]

\( n_x, n_y, n_z = 1,2,3,\ldots \)

Cube: degenerate energy levels

Can have accidental degeneracies

Particle in a ring of constant potential: \( V(\phi) = 0 \) for \( r = r_e \), \( V(\phi) = \infty \) for \( r \neq r_e \)

\[
\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i\phi}
= 0 \quad r \neq r_e
\]

\[
k = 2\pi \sqrt{2IE} / \hbar
I = m\ell^2
E_k = \frac{k^2 \hbar^2}{8\pi^2 I} \quad k = 0, \pm 1, \pm 2,\ldots
\]

Zero-point energy is zero, energies are quantized
One-dimensional harmonic oscillator: \( V(x) = \frac{1}{2} kx^2 \)

\[
\psi_n(y) = \left( \frac{\beta}{\sqrt{\pi}} \frac{1}{2^n n!} \right)^{1/2} H_n(y) \exp\left(\frac{-y^2}{2}\right), \quad n = 0, 1, 2, \ldots
\]

\[
\beta \equiv 2\pi\sqrt{mk / h} \\
y = \sqrt{\beta} x
\]

\[
H_n = (y) = (-1)^n \exp\left(y^2\right) \frac{d^n}{dy^n} \exp\left(-y^2\right)
\]

\[
E_n = (n + \frac{1}{2}) \hbar \nu
\]

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \text{use reduced mass } \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ in place of } m \text{ for diatomic molecules}
\]

Energies: positive zero-point energy, quantized energy levels, evenly spaced by \( \hbar \nu \), non degenerate

Wavefunctions: symmetric (\( \nu \) even) or antisymmetric (\( \nu \) odd) about \( x = 0 \), \( n \) nodes, finite probability for all \( x \), probability beyond classical turning points

Applications to diatomic molecules:

\[
E_{vib} = (n + \frac{1}{2}) \hbar \nu_e
\]

\[
\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

Anharmonic Morse potential: \( V(R) = D_e \left[ 1 - \exp\left(-a (R - R_e)\right) \right]^2 \)

\( R_e = \text{equilibrium position, } D_e = \text{dissociation energy} \)

\[
E_{vib} = (n + \frac{1}{2}) \hbar \nu_e - (n + \frac{1}{2})^2 \hbar \nu_e x_e
\]
Hydrogen-like atom: \( V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r} \)

Separate variables: \( \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \)

\[
R_{n,l}(\rho) = \left[ \frac{(2Z\rho)}{na_0} \right]^3 \frac{(n-l-1)!}{2n[(n+1)!]} \exp(-\rho/2)\rho^{2l+1} L_{n+l}^{2l+1}(\rho)
\]

\[
\Theta_{l,m}(\theta) = (-1)^m \frac{(2l+1)}{2} \frac{(l-\mid m \mid)!}{(l+\mid m \mid)!} \frac{n^2}{l^2} P_{l+|m|}^{m} (\cos \theta)
\]

\[
\Phi_{m}(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)
\]

\( n = 1, 2, 3, \ldots \)
\( l = 0, 1, 2, \ldots, n-1 \)
\( m = 0, \pm 1, \pm 2, \ldots, \pm l \)

\[
E_n = \frac{-Z^2}{n^2} \left( \frac{\mu e^4}{8\varepsilon_0^2 h^2} \right)
\]

Energies are negative, with the lowest energy \((n=1)\) being at \(-13.6058\) eV (1/2 a.u.). The energy spacing decreases with increasing \( n \). Energy levels are quantized and \( n^2 \)-fold degenerate.

Linear combinations of wavefunctions corresponding to different \( l \) and \( m \) values comprise the familiar orbitals that are expressed in terms of \( \sin \)’s and \( \cos \)’s of \( \theta \) and \( \phi \).

Some associated Laguerre and Legendre polynomials

\[
L_1(x) = 1; \ L_2(x) = 2x - 4; \ L_3(x) = -3x^2 + 18x - 18; \ L_4(x) = -6
\]

\[
P_0(x) = 1; \ P_1(x) = x; \ P_2(x) = \left( \frac{1}{2} \right) (3x^2 - 1); \ P_3(x) = \left( \frac{1}{2} \right) (5x^3 - 3x)
\]

\[
P_1^1(x) = (1-x^2)^{1/2}; \ P_2^1(x) = 3x(1-x^2)^{1/2}; \ P_2^2(x) = 3(1-x^2)
\]

\[
P_3^1(x) = \left( \frac{3}{2} \right) (1-x^2)^{1/2} (5x^3 - 1); \ P_3^2(x) = 15x(1-x^2); \ P_3^3(x) = 15(1-x^2)^{1/2}
\]

Atomic units: simplify electronic wavefunctions and energies

Spherical harmonics: angular part of solution to hydrogen-like atom

\[
Y_{l,m}(\theta, \phi) = \Theta(\theta)\Phi(\phi) = (-1)^m \left[ \frac{(2l+1)}{4\pi} \frac{(l-\mid m \mid)!}{(l+\mid m \mid)!} \right]^{1/2} P_{l+|m|}^{m}(\cos \theta) \exp(im\phi)
\]

Kinetic energy of rotation: \( \hat{T}_{r=\text{const}} = \frac{-\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \)
Related to angular momentum: \( \hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \)

Such that: \( \hat{T} |_{r=\text{const}} = \frac{1}{2I} \hat{L}^2 \), \( I = \mu r^2 \)

Spherical harmonics are eigenfunctions of \( \hat{T}, \hat{L}^2, \) and \( \hat{L}_z \)

where \( \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \)

Eigenvalues of \( \hat{L}^2 \) are \( l(l+1)\hbar^2 \)

and the eigenvalues of \( \hat{L}_z \) are \( m\hbar \)

The total angular momentum \( |\vec{L}| = \sqrt{l(l+1)} \hbar \)

And the z-component of the angular momentum vector is \( L_z = m\hbar \)

The magnetic moment of an electron in momentum state \( l \) lies parallel to the angular momentum vector \( \vec{L} \) and is given by \( \vec{\mu} = -\beta \vec{L} \), \( \beta_e = 9.274 \times 10^{-24} \text{ J T}^{-1} \)

The magnetic moment interacts with an external field, \( \vec{B} \), directed along the z-axis with energy \( E_{\text{int}} = -\mu_z \vec{B} = \beta_e L_z \vec{B} = \beta_e m \vec{B} \)

This interaction splits the degeneracy of the \( n \) levels of the hydrogen-like atom (which are \( n^2 \)-fold degenerate) according to the interaction energy.

The rotation of diatomic molecules can be described by the spherical harmonics

The energy levels are given by: \( E_j = \frac{J(J+1)\hbar^2}{2I} \)