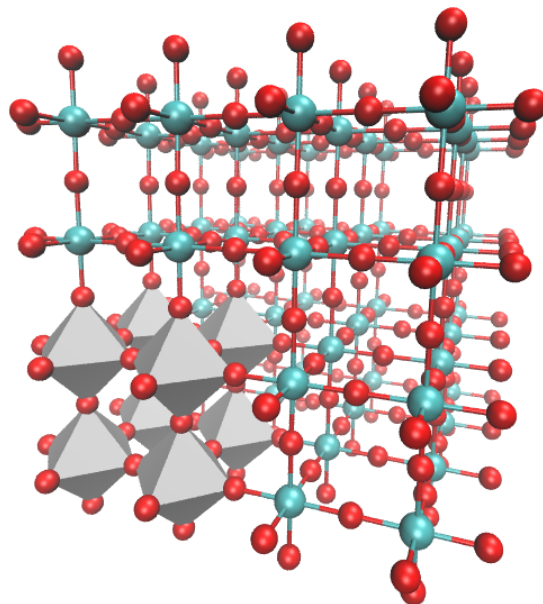


Operators, Wavefunctions and the Schrödinger Equation



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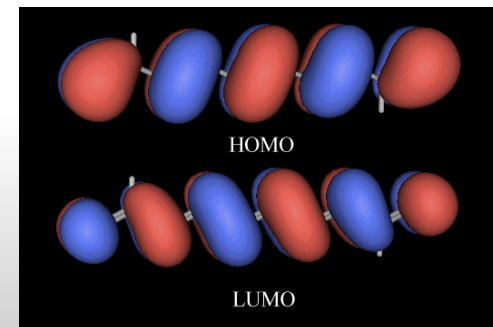
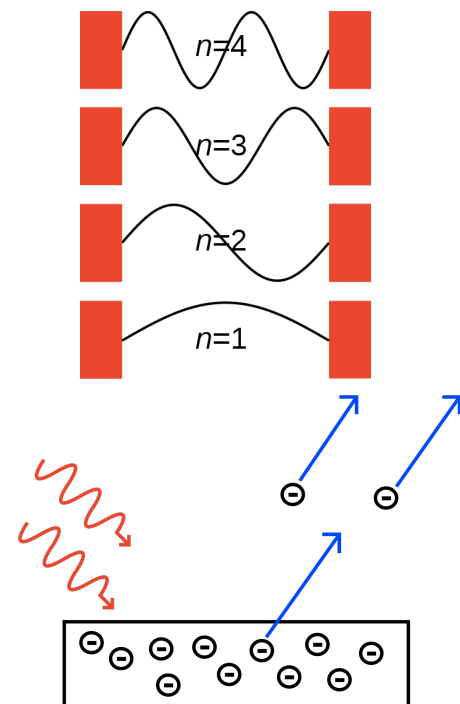
Wavefunction Origin

Quantum effects in Chemistry

- Stationary states and spectra
Atoms and molecules are in particular quantum state with specific energy - quantized as a result of boundary conditions
- Particle nature of light
Photoelectric effect demonstrates that photon energy is quantized according to the frequency

$$E = h\nu$$

- Wave nature of matter
Superposition of atomic orbitals gives molecular orbitals with wave-like nature, resulting in bonding and anti-bonding orbitals



Wavefunction Origin

De Broglie Relationship

$$\lambda = \frac{h}{p}$$

Description of wave-particle duality, and the length/velocity/time scales where it becomes significant $h = 6.626 \times 10^{-34} \text{ Js}$



Wavefunction

Wave nature of matter defined through *wavefunction* on which all physical properties depend

- defined at all points in space
- time dependent
- single-valued and finite everywhere
- square integrable

$$\int \Psi^* \Psi d\tau = 1$$

Wavefunction Meaning

Born interpretation

How to interpret wavefunction? Copenhagen school relates it to the probability density

$$p(x) = |\Psi(x)|^2$$

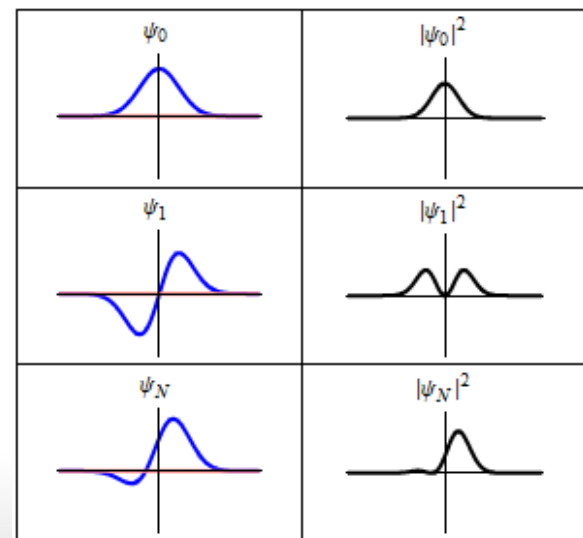
Time-independent quantum-mechanics

Wavefunction has time-dependent oscillation

$$\Psi(x, t) = \exp\left(\frac{-iEt}{\hbar}\right) \Psi(x, 0)$$

We can find “standing waves” where E is constant with time - stationary state

Stationary states can be described using a time-independent approach



Wavefunction Meaning

Expectation value

- For every observable quantity, there is a corresponding operator
- Where wavefunction is stationary state (eigenstate) of that operator, the associated energy (eigenvalue) is always returned
- Where wavefunction is a superposition, measurement gives an eigenvalue of the underlying stationary states, with probability depending on stationary state contribution to wavefunction
- Expectation value is the average measurement, determined from the probability weighted average of eigenvalues

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x) \hat{x} \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx}$$

Uncertainty principle

- Where wavefunction cannot be a stationary state of two operators simultaneously, we cannot measure both to infinite precision

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

Operators

- Value of every measurement determined by two objects:
 1. Operator
 2. Wavefunction

Constructing operators

- Different representations of QM (position, momentum)
- Generally the position representation used

$$x \rightarrow \hat{x}$$

$$p_x \rightarrow \frac{\hbar}{i} \hat{D}_x$$

Hamiltonian operator

- Returns the total conserved energy of the system

$$\hat{H} = \hat{T} + \hat{V}$$

Hamiltonian operator

kinetic energy operator

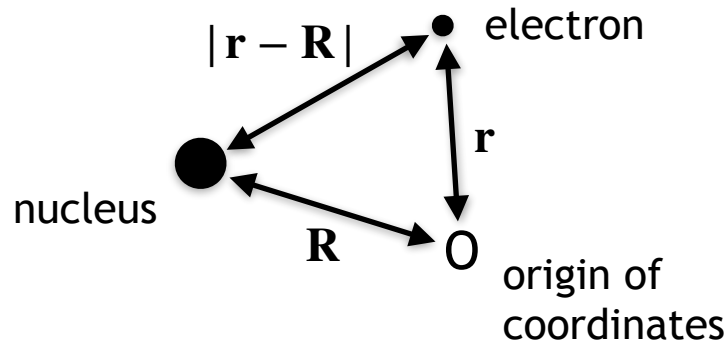
potential energy operator

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 \quad \nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad \hat{V} = V(\mathbf{r}) \quad \hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$$



Hamiltonian

Hamiltonian for hydrogen atom



$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

nuclear kinetic energy

electron kinetic energy

electron-nuclear attraction

Atomic Units

Simplify quantum mechanical equations

SI units:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

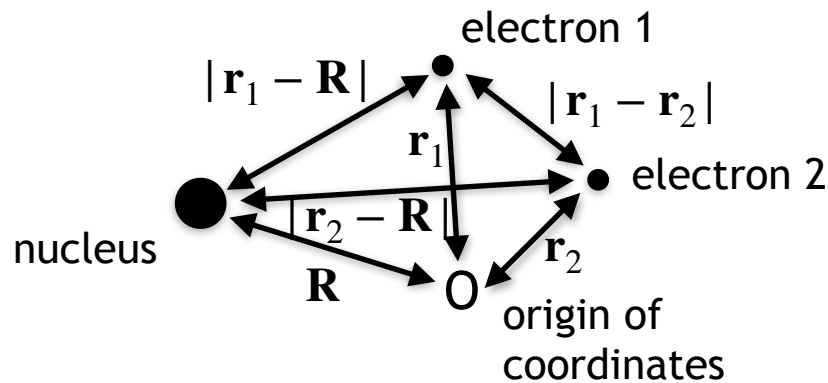
Atomic units:

$$\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{|\mathbf{r} - \mathbf{R}|}$$

Quantity	Atomic Unit	Value in SI
Energy	$\hbar^2/m_e a_0$	$4.36 \times 10^{-18} \text{ J}$
Charge	e	$1.60 \times 10^{-19} \text{ C}$
Length	a_0	$5.29 \times 10^{-11} \text{ m}$
Mass	m_e	$9.11 \times 10^{-31} \text{ kg}$

Hamiltonian

Hamiltonian for helium atom



$$\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

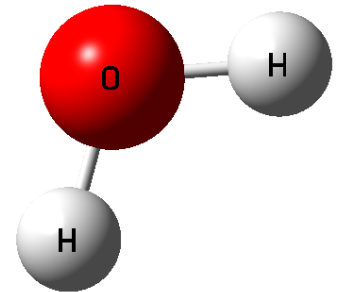
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nuclear kinetic energy electron 1 kinetic energy electron 2 kinetic energy electron 1 nuclear repulsion electron 2 nuclear repulsion electron-electron repulsion



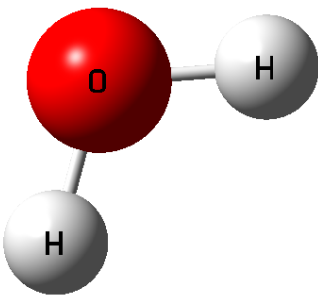
Hamiltonian

Hamiltonian for water



Hamiltonian

Hamiltonian for water

$$\begin{aligned}
 \hat{H} = & -\frac{1}{2M_O} \nabla_{\mathbf{R}_O}^2 - \frac{1}{2M_{H_1}} \nabla_{\mathbf{R}_{H_1}}^2 - \frac{1}{2M_{H_2}} \nabla_{\mathbf{R}_{H_2}}^2 - \sum_{i=1}^{10} \frac{1}{2} \nabla_{\mathbf{r}_i}^2 \\
 & - \sum_{i=1}^{10} \frac{8}{|\mathbf{r}_i - \mathbf{R}_O|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H_1}|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H_2}|} \\
 & + \sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{8}{|\mathbf{R}_O - \mathbf{R}_{H_1}|} + \frac{8}{|\mathbf{R}_O - \mathbf{R}_{H_2}|} + \frac{1}{|\mathbf{R}_{H_1} - \mathbf{R}_{H_2}|}
 \end{aligned}$$


$$\begin{aligned}
 \hat{H} = & - \sum_I^{N_{\text{atoms}}} \frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_{i=1}^{N_{\text{elec}}} \frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \sum_I^{N_{\text{atoms}}} \sum_{i=1}^{N_{\text{elec}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\
 & + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=i+1}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_I^{N_{\text{atoms}}} \sum_{J=I+1}^{N_{\text{atoms}}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}
 \end{aligned}$$



Schrödinger Equation

Wavefunction time evolution equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

Time and space separation

- Wavefunction can be separated into time-dependent and time-independent parts when the potential energy is time independent

$$\Psi(\mathbf{r}, t) = \Phi(\mathbf{r})\Theta(t)$$

$$i\hbar \Phi(\mathbf{r}) \frac{\partial \Theta(t)}{\partial t} = -\frac{\hbar^2}{2m} \Theta(t) \frac{d^2 \Phi(\mathbf{r})}{d\mathbf{r}^2} + V(\mathbf{r}) \Phi(\mathbf{r}) \Theta(t)$$

$$i\hbar \frac{1}{\Theta(t)} \frac{\partial \Theta(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\Phi(\mathbf{r})} \frac{d^2 \Phi(\mathbf{r})}{d\mathbf{r}^2} + V(\mathbf{r})$$

time



$$i\hbar \frac{\partial \Theta(t)}{\partial t} = E \Theta(t)$$

space



$$-\frac{\hbar^2}{2m} \frac{d^2 \Phi(\mathbf{r})}{d\mathbf{r}^2} + V(\mathbf{r}) \Phi(\mathbf{r}) = E \Phi(\mathbf{r})$$

Born-Oppenheimer Approx.

Time independent Schrödinger equation

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

Separation of mass scales

- Nuclei much heavier than electrons (1800×)
- Nuclei move much slower than electrons
- Approximate that electronic motions are instantaneous compared to nuclear motions
- Schrödinger equation can be re-written with parameterized nuclear coordinates

$$\begin{aligned} \hat{H} = & - \sum_I^{N_{\text{atoms}}} \frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_{i=1}^{N_{\text{elec}}} \frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \sum_I^{N_{\text{atoms}}} \sum_{i=1}^{N_{\text{elec}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ & + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=i+1}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_I^{N_{\text{atoms}}} \sum_{J=I+1}^{N_{\text{atoms}}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned}$$

Born-Oppenheimer Approx.

Electronic Schrödinger equation

$$\hat{H}_{\text{elec}} \Psi_{\text{elec}}(\mathbf{r}_i; \mathbf{R}_I) = E_{\text{elec}} \Psi_{\text{elec}}(\mathbf{r}_i; \mathbf{R}_I)$$

Electronic Hamiltonian

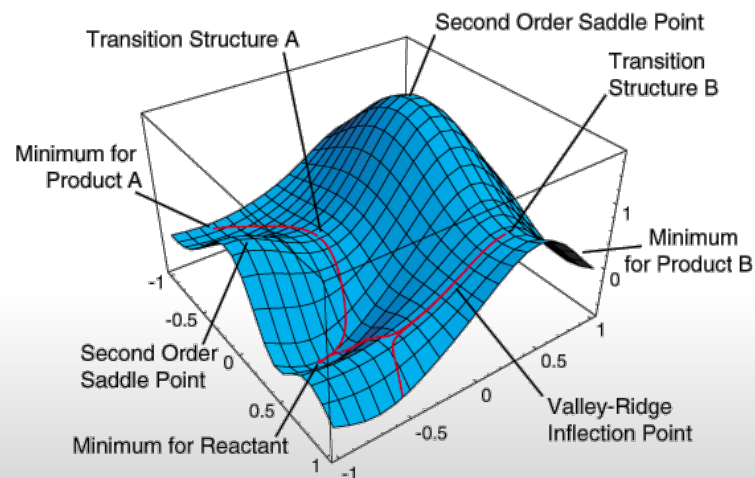
$$\hat{H}_{\text{elec}} = - \sum_{i=1}^{N_{\text{elec}}} \frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \sum_I^{N_{\text{atoms}}} \sum_{i=1}^{N_{\text{elec}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=i+1}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Potential Energy Surface

- Separation of nuclear and electronic coordinates enables construction of the PES - lowest electronic energy at a given nuclear coordinate

$$E_{\text{PES}}(\mathbf{R}_I) = E_{\text{elec}}(\mathbf{r}_i; \mathbf{R}_I) + V_N(\mathbf{R}_I)$$

$$V_N(\mathbf{R}_I) = \sum_I^{N_{\text{atoms}}} \sum_{J=I+1}^{N_{\text{atoms}}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$





Dirac Bra-ket notation

Integral shorthand

- Many complicated, similar-looking integrals in QM
- Can be made to look simpler using Dirac Bra-ket notation
- Widely adopted throughout theoretical chemistry literature

$$\int \Psi^*(\mathbf{x}) \hat{O} \Psi(\mathbf{x}) d\mathbf{x} \leftrightarrow \langle \Psi | \hat{O} | \Psi \rangle$$

- Bra denotes complex conjugate of function/vector

$$\Psi^*(\mathbf{x}) \leftrightarrow \langle \Psi |$$

- Ket denotes function or vector

$$\Psi(\mathbf{x}) \leftrightarrow | \Psi \rangle$$

- Bra-ket is the integral over both vectors/functions

$$\int \Psi^*(\mathbf{x}) \Psi(\mathbf{x}) d\mathbf{x} \leftrightarrow \langle \Psi | \Psi \rangle$$

- Bra is complex transpose (adjoint)/ complex conjugate of ket

$$| \Psi \rangle^* \leftrightarrow \langle \Psi |$$

$$\langle \Psi |^* \leftrightarrow | \Psi \rangle$$



Dirac Bra-ket notation

Dirac notation examples

$$\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \leftrightarrow \hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\int \Psi^*(\mathbf{x})\hat{H}\Psi(\mathbf{x})d\mathbf{x} = \int \Psi^*(\mathbf{x})E\Psi(\mathbf{x})d\mathbf{x} \leftrightarrow \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi|E|\Psi\rangle$$

$$\int \Psi^*(\mathbf{x})\hat{H}\Psi(\mathbf{x})d\mathbf{x} = E \int \Psi^*(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x} \leftrightarrow \langle\Psi|\hat{H}|\Psi\rangle = E\langle\Psi|\Psi\rangle$$

$$E = \frac{\int \Psi^*(\mathbf{x})\hat{H}\Psi(\mathbf{x})d\mathbf{x}}{\int \Psi^*(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x}} \leftrightarrow \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$



Dirac Bra-ket notation

Dirac notation practice

$$\int f(x)g^*(x)dx$$

$$\int f^*(x)[ag(x) + bh(x)]dx$$

$$\int f(x)g(x)dx$$

$$\int f^*(x)\hat{H}\hat{H}g(x)dx$$

$$\int f^*(x)g(x)dx$$

$$\int f^*(x)g^*(x)dx$$

$$\psi(x) \int \psi^*(x)f^*(x)dx$$



Operator Representation

Vector representation of wavefunctions

- Recall operators act on vectors/functions and can be represented by a matrix
- For a given operator, how do we construct the operator matrix?
- Wavefunctions can be viewed as vectors in infinite multidimensional Hilbert space. Dirac ket explicitly refers to these vectors

$$\Psi(\mathbf{x}) \leftrightarrow |\Psi\rangle$$

- Ket vector can be written referring to set of complete basis vectors

$$|\Psi\rangle = \sum_{i=1}^N c_i |i\rangle$$

$$|\Psi\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}$$

$$\langle\Psi| = [c_1^* \quad c_2^* \quad \dots \quad c_N^*]$$

$$\langle x|y\rangle = \mathbf{x} \cdot \mathbf{y}$$

$$\sum_i |i\rangle\langle i| = \mathbf{1}$$



Operator Representation

Matrix representation of operators

- Operators act on (transform) a ket (vector) to yield another ket

$$\hat{O}|i\rangle = \sum_j |j\rangle O_{ji}$$

- Acting on the left by a third ket reveals the matrix element

$$\langle k|\hat{O}|i\rangle = \sum_j \langle k|j\rangle O_{ji} = \sum_j \delta_{kj} O_{ji} = O_{ki}$$

$$\mathbf{O} = \begin{bmatrix} O_{11} & O_{12} & \cdots & O_{1n} \\ O_{21} & O_{22} & \cdots & O_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ O_{n1} & O_{n2} & \cdots & O_{nn} \end{bmatrix}$$



Hermitian Operators

Matrix representation of operators

- All experimental observables are real eigenvalues
- Only operators that give real eigenvalues permissible
- Hermitian operators have all real eigenvalues

$$\mathbf{A} = \mathbf{A}^\dagger$$

$$\langle i | \hat{A} | j \rangle = \langle j | \hat{A} | i \rangle^*$$

$$\langle i | \hat{A} | i \rangle = \langle i | \hat{A} | i \rangle^*$$

$$\langle i | a_i | i \rangle = \langle i | a_i^* | i \rangle$$

$$a_i \langle i | i \rangle = a_i^* \langle i | i \rangle$$

$$(a_i - a_i^*) \langle i | i \rangle = 0$$

$$a_i = a_i^*$$

- All QM operators that correspond to observables are Hermitian



Summary

- Wavefunction arises to describe wave nature of particles
- Expectation values give observable and require operator and wavefunction expression
- Construction of operators, with focus on derivation of Hamiltonian
- Operators can be represented as matrices and in order to give required real observables, operators are Hermitian
- Can use atomic units and Born-Oppenheimer approximation to simplify terms in Hamiltonian
- Schrödinger equation (SE) uses Hamiltonian to express wavefunction evolution in time
- Separation of SE into time dependent part and part that describes stationary states
- Wavefunctions can be expressed as vectors using Dirac notation