Chapter 5

Schrödinger Representation – Schrödinger Equation

Time dependent Schrödinger Equation

$$i\hbar \frac{\partial \Phi(x, y, z, t)}{\partial t} = \underline{H}(x, y, z, t)\Phi(x, y, z, t)$$

Developed through analogy to Maxwell's equations and knowledge of the Bohr model of the H atom.

$$H_{classical} = \frac{p^2}{2m} + V$$

Hamiltonian — kinetic energy — potential energy

Sum of kinetic energy and potential energy.

Q.M.

$$\underline{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

one dimension

recall $\underline{p} = -i\hbar \frac{\partial}{\partial x}$

$$\underline{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(x, y, z)$$

three dimensions

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The potential, *V*, makes one problem different form another H atom, harmonic oscillator.

Getting the Time Independent Schrödinger Equation

$\Phi(x,y,z,t)$ wavefunction

$$i\hbar \frac{\partial}{\partial t}\Phi(x,y,z,t) = \underline{H}(x,y,z,t)\Phi(x,y,z,t)$$

If the energy is independent of time $\longrightarrow$ $\underline{H}(x,y,z)$

Try solution

$$\Phi(x,y,z,t) = \phi(x,y,z)F(t)$$

product of spatial function and time function

Then

$$i\hbar \frac{\partial}{\partial t}\phi(x,y,z)F(t) = \underline{H}(x,y,z)\phi(x,y,z)F(t)$$

$$i\hbar\,\phi(x,y,z)\frac{\partial}{\partial t}F(t) = F(t)\,\underline{H}(x,y,z)\phi(x,y,z)$$

divide through by

$\Phi = \phi F$

independent of t

independent of x, y, z

$$\frac{i\hbar \frac{dF(t)}{dt}}{F(t)} = \frac{\underline{H}(x,y,z)\phi(x,y,z)}{\phi(x,y,z)}$$

depends only on *t*

depends only on *x, y, z*

Can only be true for any *x, y, z, t* if both sides equal a constant.

Changing *t* on the left doesn't change the value on the right.

Changing *x, y, z* on right doesn't change value on left.

$\Rightarrow$ **Equal constant**

$$\frac{i\hbar \frac{dF}{dt}}{F} = E = \frac{\underline{H}\phi}{\phi}$$

$$\frac{i\hbar \dfrac{dF}{dt}}{F} = E = \frac{\underline{H}\,\phi}{\phi}$$

Both sides equal a constant, *E*.

$$\underline{H}(x,y,z)\phi(x,y,z) = E\,\phi(x,y,z)$$

Energy eigenvalue problem – time independent Schrödinger Equation

$\underline{H}$ is energy operator.

Operate on ϕ get ϕ back times a number.

ϕ's are energy eigenkets; eigenfunctions; wavefunctions.

$E \longrightarrow$ **Energy Eigenvalues**
Observable values of energy

Time Dependent Equation (*H* time independent)

$$\frac{i\hbar \dfrac{dF(t)}{dt}}{F(t)} = E$$

$$i\hbar \frac{dF(t)}{dt} = E\,F(t)$$

$$\frac{dF(t)}{F(t)} = -\frac{i}{\hbar} E\,dt.$$

Integrate both sides

$$\ln F = -\frac{i\,E\,t}{\hbar} + C$$

Take initial condition at $t = 0$, $F = 1$, then $C = 0$.

$$F(t) = e^{-i\,E\,t/\hbar} = e^{-i\omega t}$$

Time dependent part of wavefunction for time independent Hamiltonian.

Time dependent phase factor used in wave packet problem.

Total wavefunction for time independent Hamiltonian.

$$\Phi_E(x,y,z,t)=\phi_E(x,y,z)e^{-iEt/\hbar}$$

E – energy (observable) that labels state.

Normalization

$$\langle\Phi_E|\Phi_E\rangle=\int\Phi_E^*\,\Phi_E\,d\tau=\int\phi_E^*\,e^{+iEt/\hbar}\,\phi_E\,e^{-iEt/\hbar}d\tau=\int\phi_E^*\,\phi_E\,d\tau$$

Total wavefunction is normalized if time independent part is normalized.

Expectation value of time independent operator $\underline{S}$.

$$\langle\underline{S}\rangle=\langle\Phi|\underline{S}|\Phi\rangle=\int\Phi_E^*\,\underline{S}\,\Phi_E\,d\tau=\int\phi_E^*\,e^{iEt/\hbar}\,\underline{S}\,\phi_E\,e^{-iEt/\hbar}d\tau$$

$\underline{S}$ **does not depend on** t, $e^{-iEt/\hbar}$ **can be brought to other side of** $\underline{S}$.

$$\langle\Phi|\underline{S}|\Phi\rangle=\int\phi_E^*\,\underline{S}\,\phi_E\,d\tau$$

Expectation value is time independent and depends only on the time independent part of the wavefunction.

Equation of motion of the Expectation Value in the Schrödinger Representation

Expectation value of operator representing observable for state $\left|S\right\rangle$

$$\langle \underline{A} \rangle = \langle S | \underline{A} | S \rangle$$

example - momentum $\langle \underline{P} \rangle = \langle S | \underline{P} | S \rangle$

In Schrödinger representation, operators don't change in time.

Time dependence contained in wavefunction.

Want Q.M. equivalent of

time derivative of a classical dynamical variable.

$P \longrightarrow \underline{P}$ **classical momentum goes over to momentum operator**

$\dot{P} = \dfrac{\partial P}{\partial t} \Rightarrow \ ?$ **want Q.M. operator equivalent of time derivative**

Definition: The time derivative of the operator $\underline{A}$, i. e., $\dot{\underline{A}}$
is defined to mean an operator whose expectation in
any state $\left|S\right\rangle$ is the time derivative of
the expectation of the operator $\underline{A}$.

Want to find

$$\frac{d\langle \underline{A}\rangle}{dt}=\frac{\partial}{\partial t}\langle S|\underline{A}|S\rangle$$

Use $\underline{H}|S\rangle = i\hbar\frac{\partial}{\partial t}|S\rangle$ **time dependent Schrödinger equation.**

$$\frac{\partial}{\partial t}\langle S|\underline{A}|S\rangle=\left(\frac{\partial}{\partial t}\langle S|\right)\underline{A}|S\rangle+\langle S|\underline{A}\frac{\partial}{\partial t}|S\rangle$$

product rule

time independent – derivative is zero

Use the complex conjugate of the Schrödinger equation $\langle S|\underline{H} = -i\hbar\frac{\partial}{\partial t}\langle S|$.

(operate to left)

Then $\left(\frac{\partial}{\partial t}\langle S|\right)=\frac{i}{\hbar}\langle S|\underline{H}$ **, and from the Schrödinger equation**

$$\frac{\partial}{\partial t}|S\rangle=\frac{-i}{\hbar}\underline{H}|S\rangle$$

$$\frac{\partial}{\partial t}\langle S|\underline{A}|S\rangle=\frac{i}{\hbar}\langle S|\underline{H}\,\underline{A}|S\rangle-\frac{i}{\hbar}\langle S|\underline{A}\underline{H}|S\rangle$$

$$\frac{\partial}{\partial t}\langle S|\underline{A}|S\rangle=\frac{i}{\hbar}\left[\langle S|\underline{H}\,\underline{A}|S\rangle-\langle S|\underline{A}\underline{H}|S\rangle\right]$$

Therefore

This is the commutator of $\underline{H}$ $\underline{A}$.

$$\frac{d\langle \underline{A} \rangle}{dt} = \frac{i}{\hbar}\langle S | \underline{H}\,\underline{A} - \underline{A}\,\underline{H} | S \rangle = \frac{i}{\hbar}[\underline{H}, \underline{A}]$$

$$\dot{\underline{A}} = \frac{i}{\hbar}[\underline{H}, \underline{A}]$$

The operator representing the time derivative of an observable is $i/\hbar$ times the commutator of $\underline{H}$ with the observable.

Solving the time independent Schrödinger equation

The free particle

momentum problem

$$\underline{P}\left|P\right\rangle = p\left|P\right\rangle$$

$$\psi_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \qquad p = \hbar k \qquad k = p/\hbar$$

Free particle Hamiltonian – no potential – *V* = 0.

$$\underline{H} = \frac{\underline{P}^2}{2m}$$

Commutator of $\underline{H}$ with $\underline{P}$

$$[\underline{P}, \underline{H}] = \frac{\underline{P}^3}{2m} - \frac{\underline{P}^3}{2m} = 0 \qquad \underline{P}^3\left|S\right\rangle = \underline{P}\,\underline{P}\,\underline{P}\left|S\right\rangle$$

$\underline{P}$ and $\underline{H}$ commute $\longrightarrow$ Simultaneous Eigenfunctions.

Free particle energy eigenvalue problem

$$\underline{H}\left|P\right\rangle = E\left|P\right\rangle$$

$$\underline{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Use momentum eigenkets.

$$\underline{H}\left|P\right\rangle = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\frac{1}{\sqrt{2\pi}}e^{ikx}\right)$$

$$= -\frac{\hbar^2}{\sqrt{2\pi}\,2m}(ik)^2 e^{ikx}$$

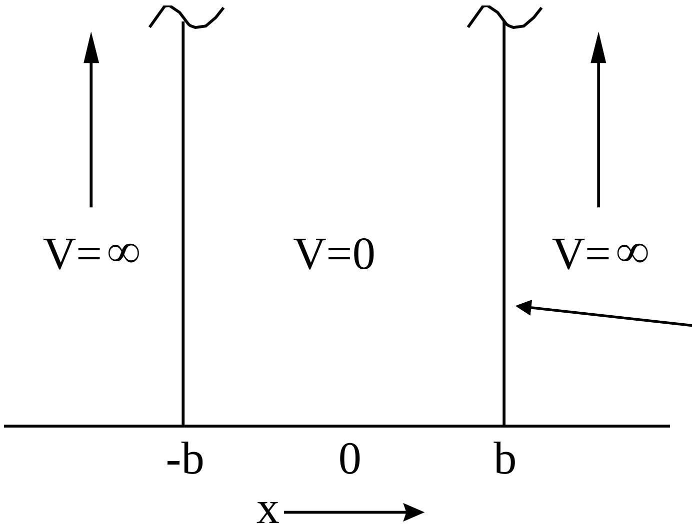
$$= \frac{\hbar^2 k^2}{2m}\left(\frac{1}{\sqrt{2\pi}}e^{ikx}\right)$$

$$= \frac{p^2}{2m}\left|P\right\rangle$$

energy eigenvalues

Therefore, $E = \dfrac{p^2}{2m}$ **Energy same as classical result.**

Particle in a One Dimensional Box



Infinitely high, thick, impenetrable walls

Particle inside box. Can't get out because of impenetrable walls.

Classically ⟶ E is continuous. E can be zero. One D racquet ball court.

Q.M. ⟶ $\Delta x \Delta p \geq \hbar/2$ E can't be zero.

$\underline{H}\left|\varphi\right\rangle = E\left|\varphi\right\rangle$ Energy eigenvalue problem

Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} + V(x)\varphi(x) = E\,\varphi(x)$$

$$V(x) = 0 \qquad |x| < b$$

$$V(x) = \infty \qquad |x| \geq b$$

For $|x| < b$

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} = E\,\varphi(x)$$

Want to solve differential Equation, but solution must by physically acceptable.

Born Condition on Wavefunction to make physically meaningful.

1. **The wave function must be finite everywhere.**
2. **The wave function must be single valued.**
3. **The wave function must be continuous.**
4. **First derivative of wave function must be continuous.**

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\varphi(x)$$

Second derivative of a function equals a negative constant times the same function.

Functions with this property $\longrightarrow$ sin and cos.

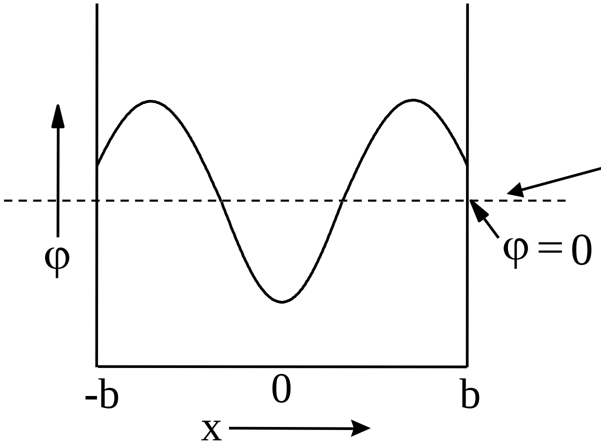
$$\frac{d^2 \sin(ax)}{dx^2} = -a^2 \sin(ax)$$

$$\frac{d^2 \cos(ax)}{dx} = -a^2 \cos(ax)$$

These are solutions provided

$$a^2 = \frac{2mE}{\hbar^2}$$

Solutions with any value of *a* don't obey Born conditions.



Well is infinitely deep.

Particle has zero probability of being found outside the box.

$$\varphi = 0 \text{ for } |x| \geq b$$

Function as drawn discontinuous at $x = \pm b$

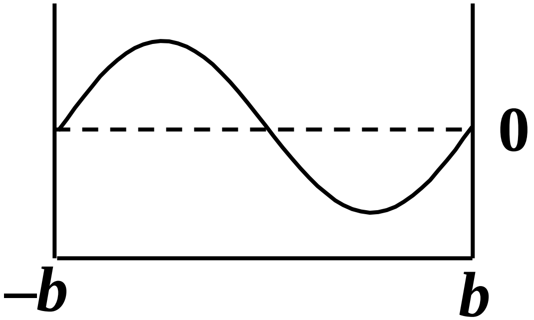
To be an acceptable wavefunction

$$\varphi \Rightarrow \text{sin and cos} \Rightarrow 0 \text{ at } |x| = b$$

φ **will vanish at** $|x| = b$ **if**

$$a = \frac{n\pi}{2b} \equiv a_n$$

n is an integer



$$\cos a_n x \qquad n = 1, 3, 5 \ldots$$

$$\sin a_n x \qquad n = 2, 4, 6 \ldots$$

Integral number of half wavelengths in box. Zero at walls.

Have two conditions for a^2.

$$a_n^2 = \frac{n^2\pi^2}{4b^2} = \frac{2mE}{\hbar^2}$$

Solve for *E*.

$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{8mL^2}$$

Energy eigenvalues – energy levels, not continuous.

$L = 2b$ – length of box.

Energy levels are quantized.
Lowest energy not zero.

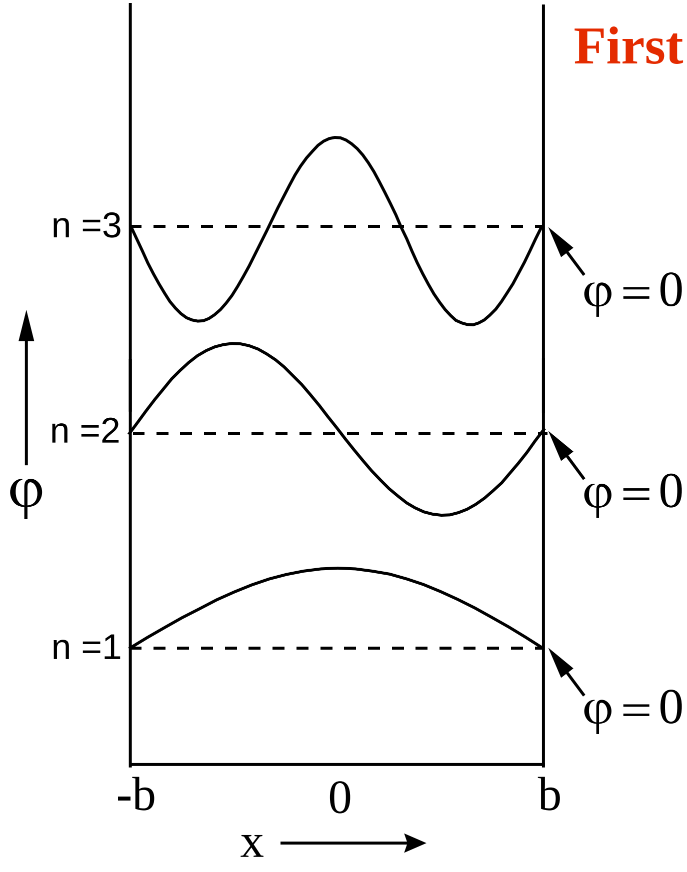
$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{8mL^2}$$

$L = 2b$ – length of box.

$$\varphi_n(x) = \left(\frac{1}{b}\right)^{\frac{1}{2}} \cos\frac{n\pi x}{2b} \qquad |x| \le b \qquad n = 1, 3, 5\cdots$$

$$\varphi_n(x) = \left(\frac{1}{b}\right)^{\frac{1}{2}} \sin\frac{n\pi x}{2b} \qquad |x| \le b \qquad n = 2, 4, 6\cdots$$

wavefunctions including normalization constants



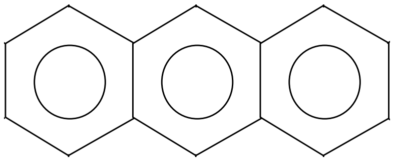
First few wavefunctions.

Quantization forced by Born conditions (boundary conditions)

Fourth Born condition not met –
first derivative not continuous.
Physically unrealistic problem because the potential is discontinuous.

Particle in a Box $\longrightarrow$ Simple model of molecular energy levels.

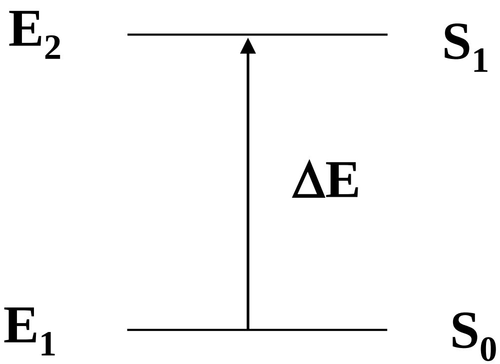
Anthracene



$\leftarrow L \rightarrow$ $\quad L \approx 6\ \text{Å}$

π electrons – consider "free" in box of length L.

Ignore all coulomb interactions.



Calculate wavelength of absorption of light.

Form particle in box energy level formula

$$\Delta E = E_2 - E_1 = \frac{3h^2}{8mL^2}$$

$$m = m_e = 9\times10^{-31}\ \text{kg}$$

$$L = 6\ \text{Å} = 6\times10^{-10}\ \text{m}$$

$$\text{h} = 6.6\times10^{-34}\ \text{Js}$$

$$\Delta\text{E} = 5.04\times10^{-19}\ \text{J}$$

$$\Delta\text{E} = \text{h}\nu$$

$$\nu = \Delta\text{E}/\text{h} = 7.64\times10^{14}\ \text{Hz}$$

$$\lambda = \text{c}/\nu = 393\ \text{nm} \quad \text{blue-violet}$$

Experiment $\Rightarrow$ 400 nm

Anthracene particularly good agreement.

Other molecules, naphthalene, benzene, agreement much worse.

Important point

Confine a particle with "size" of electron to box size of a molecule

Get energy level separation, light absorption, in visible and UV.

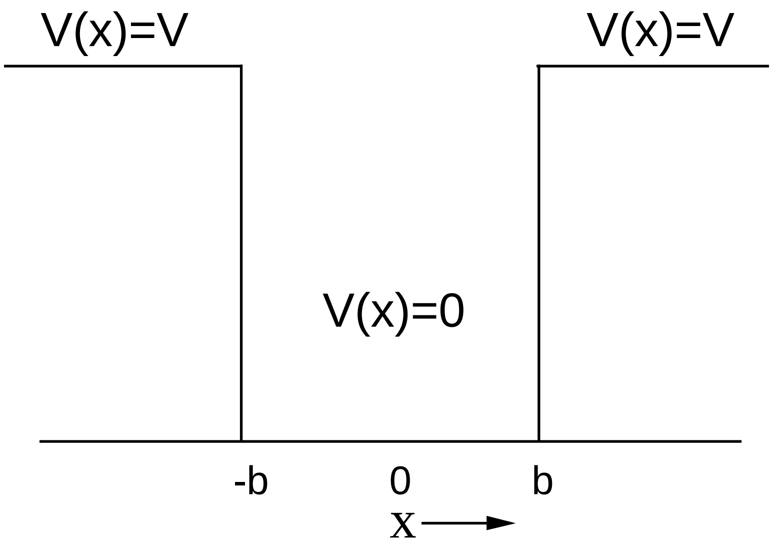
Molecular structure, realistic potential give accurate calculation, but it is the mass and size alone that set scale.

Big molecules $\longrightarrow$ **absorb in red.**

Small molecules $\longrightarrow$ **absorb in UV.**

Particle in a Finite Box – Tunneling and Ionization

Box with finite walls.



Time independent Schrödinger Eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2}+V(x)\varphi(x)=E\,\varphi(x)$$

$$V(x)=0 \qquad |x|<b$$

$$V(x)=V \qquad |x|\geq b$$

Inside Box $V = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2}=E\,\varphi(x)$$

$$\frac{d^2\varphi(x)}{dx^2}=-\frac{2mE}{\hbar^2}\varphi(x)$$

Second derivative of function equals negative constant times same function.

$\longrightarrow$ **Solutions – sin and cos.**

Solutions inside box

$$\varphi(x) = q_1 \sin\sqrt{\frac{2mE}{\hbar^2}}\,x$$

or

$$\varphi(x) = q_2 \cos\sqrt{\frac{2mE}{\hbar^2}}\,x$$

Outside Box

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{2m(E-V)}{\hbar^2}\varphi(x)$$

Two cases: Bound states, $E < V$

Unbound states, $E > V$

Bound States

$$\frac{d^2\varphi(x)}{dx^2} = \frac{2m(V-E)}{\hbar^2}\varphi(x)$$

Second derivative of function equals positive constant times same function.

$\longrightarrow$ Not oscillatory.

Try solutions

$$\exp(\pm ax) \longrightarrow \frac{d^2 e^{\pm ax}}{dx^2} = a^2 e^{\pm ax}$$

Second derivative of function equals positive constant times same function.

Then, solutions outside the box

$$\varphi(x) = e^{\pm\left[\frac{2m(V-E)}{\hbar^2}\right]^{1/2} x} \qquad |x| \geq b$$

Solutions must obey Born Conditions

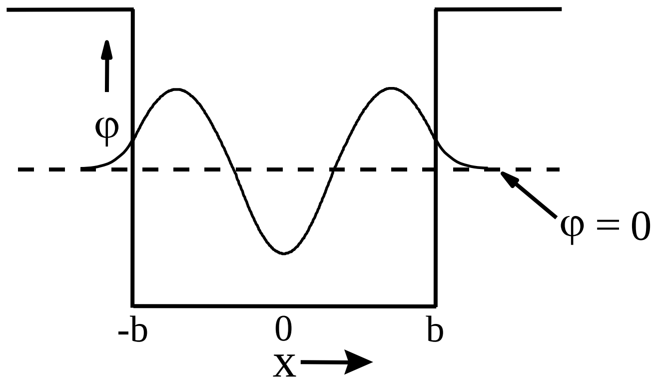
$\varphi(x)$ **can't blow up as** $|x| \to \infty$ **Therefore,**

$$\varphi(x) = r_1 e^{-\left[\frac{2m(V-E)}{\hbar^2}\right]^{1/2} x} \qquad x \geq b$$

$$\varphi(x) = r_2 e^{+\left[\frac{2m(V-E)}{\hbar^2}\right]^{1/2} x} \qquad x \leq -b$$

Outside box $\longrightarrow$ **exp. decays**

Inside box $\longrightarrow$ **oscillatory**

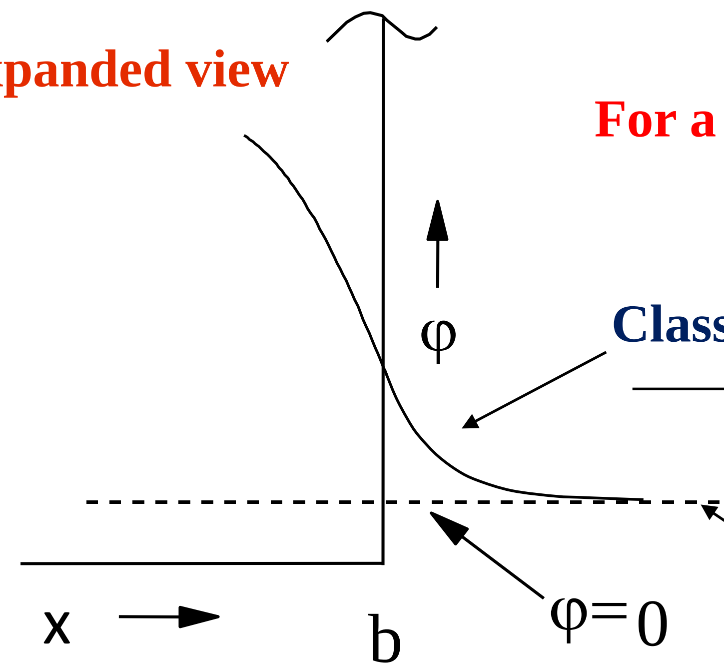


Outside box ⟶ exp. decays

Inside box ⟶ oscillatory

The wavefunction and its first derivative continuous at walls – Born Conditions.

Expanded view

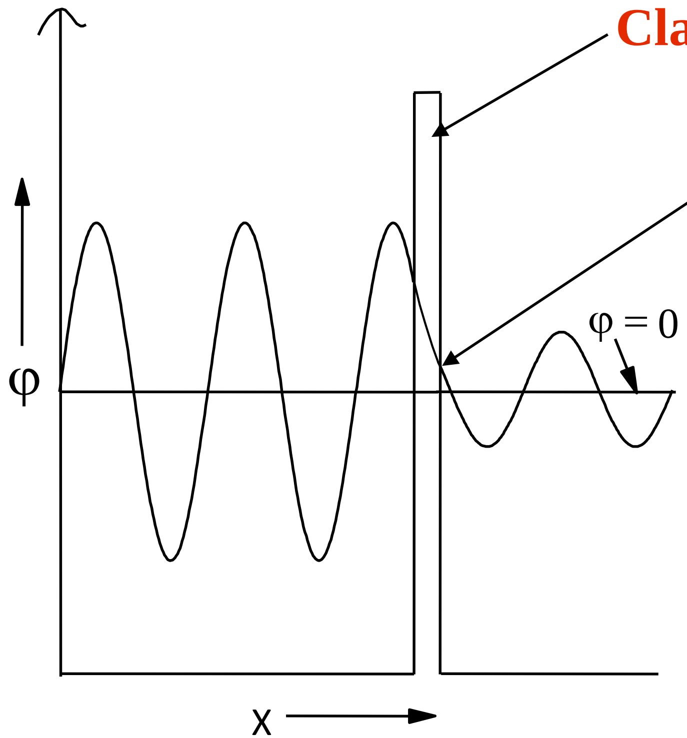


For a finite distance into the material finite probability of finding particle.

Classically forbidden region ⟶ $V > E$.

probability ⟶ 0

Tunneling - Qualitative Discussion



Classically forbidden region.

Wavefunction not zero at far side of wall.

Probability of finding particle finite outside box.

A particle placed inside of box with not enough energy to go over the wall

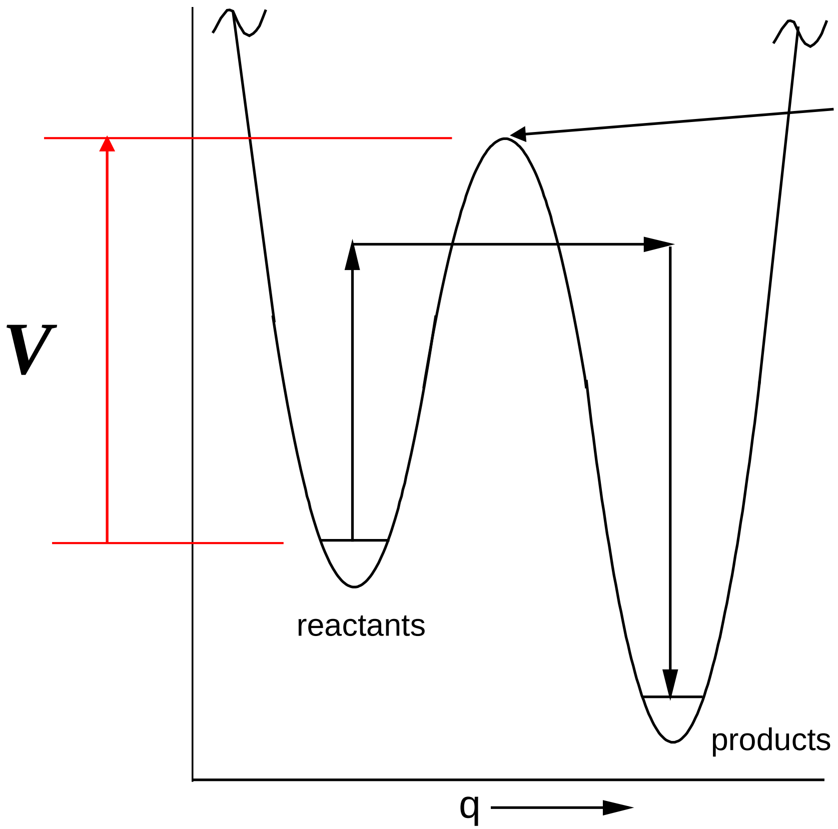
→ can Tunnel Through the Wall.

Formula derived in book $$e^{-2d[2m(V-E)/\hbar^2]^{1/2}}$$ **Ratio probs - outside vs. inside edges of wall.**

mass = m_e
E = 1000 cm^{-1}
V = 2000 cm^{-1}

Wall thickness (d)	1 Å	10 Å	100 Å
probability ratio	0.68	0.02	3×10^{-17}

Chemical Reaction



not enough energy to go over barrier

Temperature dependence of some chemical reactions shows to much product at low T. $V > kT$.

Decay of probability in classically forbidden region for parabolic potential.

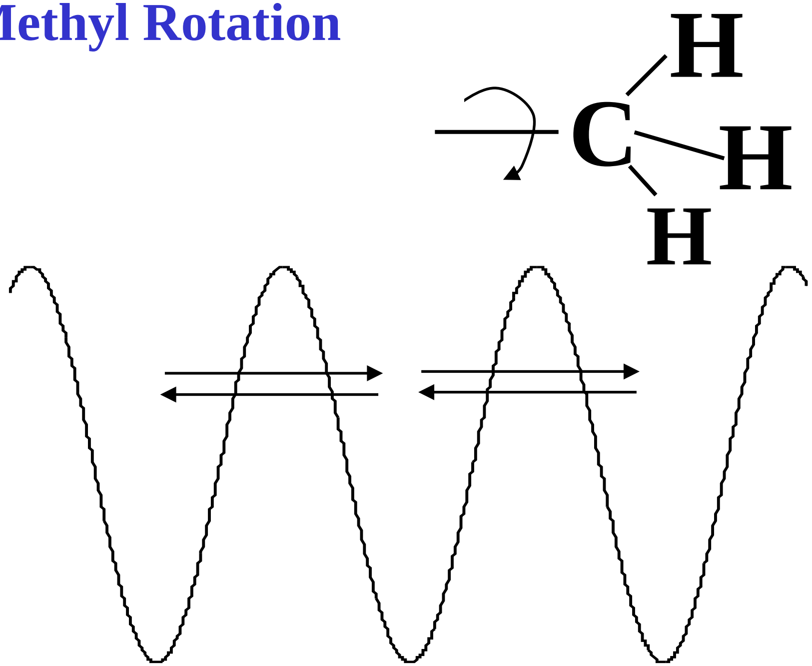
$$e^{-\lambda}$$

$$\lambda = d(2mV/\hbar^2)^{1/2}$$

light particles tunnel

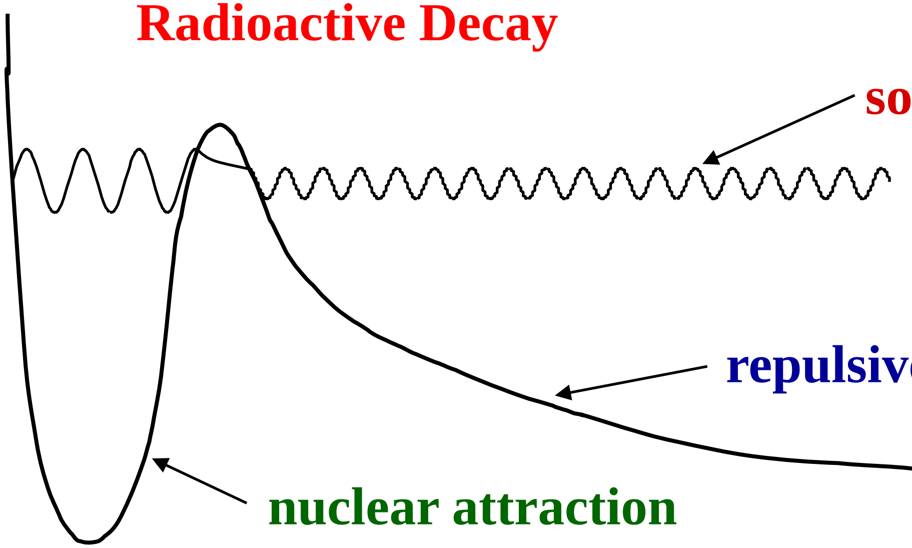
tunneling parameter — distance — mass — barrier height

Methyl Rotation



Methyl groups rotate even at very low T.

Radioactive Decay



some probability outside nucleus

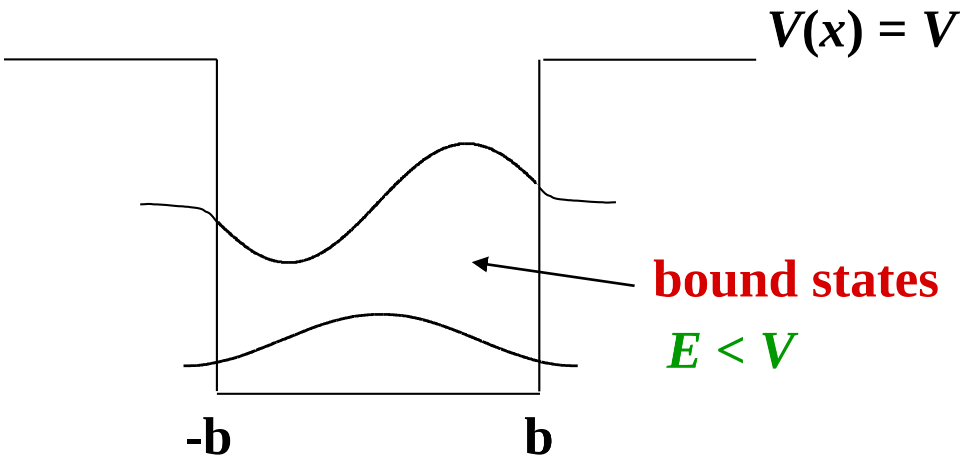
repulsive Coulomb interaction

nuclear attraction
strong interaction

Unbound States and Ionization

If $E > V$ - unbound states

E large enough - ionization



$$\frac{d^2\varphi(x)}{dx^2} = -\frac{2m(E-V)}{\hbar^2}\varphi(x)$$

Inside the box (between -b and b)

$V = 0$

$$\varphi(x) = q_1 \sin\sqrt{\frac{2mE}{\hbar^2}}x$$

$$\varphi(x) = q_2 \cos\sqrt{\frac{2mE}{\hbar^2}}x$$

Solutions oscillatory

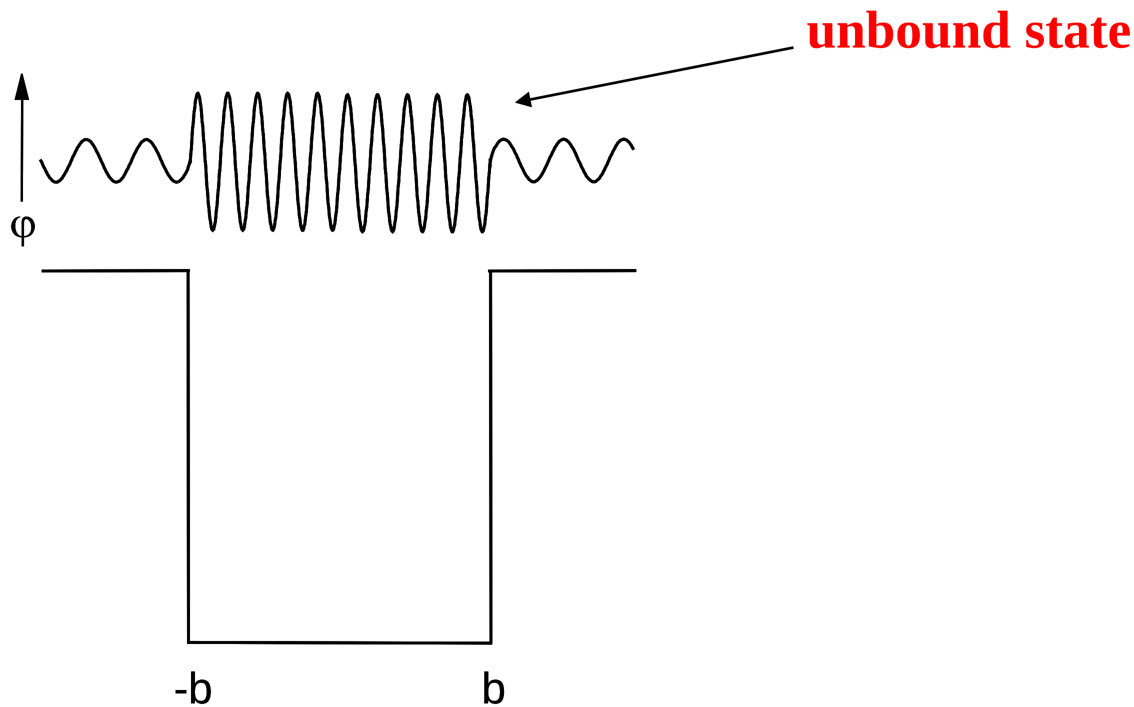
Outside the box (x > |b|)

$E > V$

$$\varphi(x) = s_1 \sin\sqrt{\frac{2m(E-V)}{\hbar^2}}x$$

$$\varphi(x) = s_2 \cos\sqrt{\frac{2m(E-V)}{\hbar^2}}x$$

Solutions oscillatory



To solve (numerically)
Wavefunction and first derivative equal at walls, for example at $x = b$

$$q_1 \sin\sqrt{\frac{2mE}{\hbar^2}}b = s_1 \sin\sqrt{\frac{2m(E-V)}{\hbar^2}}b$$

In limit

$$E \gg V$$

$$(E-V) \approx E$$

$$\therefore q_1 = s_1$$

Wavefunction has equal amplitude everywhere.

For $E >> V$

$$\varphi(x) = \sin\sqrt{\frac{2mE}{\hbar^2}}\,x \qquad \text{for all } x$$

As if there is no wall.

Continuous range of energies - free particle

Particle has been ionized.

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

$$\varphi(x) = \sin k\,x \qquad \text{Free particle wavefunction}$$

In real world potential barriers are finite.

Tunneling

Ionization