Chapter 2. Some simple cases

1. Translational motion (free particles)
2. Particle in a box
3. The harmonic oscillator

2.1 Free particles

Classically, a particle moving in one dimension without external forces has constant momentum. Quantum mechanically we expect to be able to find states of definite momentum. If the motion is along the x axis we need to look for solutions of the eigenvalue equation

$$\hat{p}_x \psi(x) = p\psi(x)$$

That is,

$$-i\hbar \frac{\mathrm{d}}{\mathrm{d}x}\psi = p\psi$$

The solution to this equation is

$$\psi_p = \exp(ipx/\hbar)$$

Remember that p is an eigenvalue — a *constant* with (in this case) dimensions of momentum.

The Hamiltonian for a free particle contains only the kinetic energy term:

$$H = \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

The wavefunction ψ_p is an eigenfunction of this operator too:

$$H\psi_p = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathrm{e}^{ipx/\hbar} = -\frac{\hbar^2}{2m}\left(\frac{ip}{\hbar}\right)^2\mathrm{e}^{ipx/\hbar} = \frac{p^2}{2m}\psi_p$$

Its energy is $p^2/2m$, just as we would expect for a particle with momentum p.

Notice that a particle with momentum $-p$ — i.e. with wavefunction $\psi_{-p} = \exp(-ipx/\hbar)$ — has the same energy $p^2/2m$.

The time-independent Schrödinger equation is

$$H\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

and the general solution of this is

$$\psi = a\mathrm{e}^{ikx} + b\mathrm{e}^{-ikx}$$

where $k = \sqrt{2mE}/\hbar$. If $E = p^2/2m$, then $k = p/\hbar$ and we arrive at the result

$$\psi = a\psi_p + b\psi_{-p}$$

This *superposition* or *linear combination* of two wavefunctions, both with energy $p^2/2m$, is also an eigenfunction of H with energy $p^2/2m$, for any values of the constants a and b. However it is not an eigenfunction of the operator p_x, unless $a = 0$ or $b = 0$, so it doesn't have a definite momentum. We can write the same wavefunction in the form

$$\psi = A\sin\left(px/\hbar\right) + B\cos\left(px/\hbar\right)$$

2.2 Particle in a box

Consider a ‘particle in a box’: suppose that the potential is zero for $0 < x < a$ and infinite outside this range. The Schrödinger equation is

$$H\psi = \left(\hat{T} + \hat{V}\right)\psi = \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V\right)\psi = E\psi$$

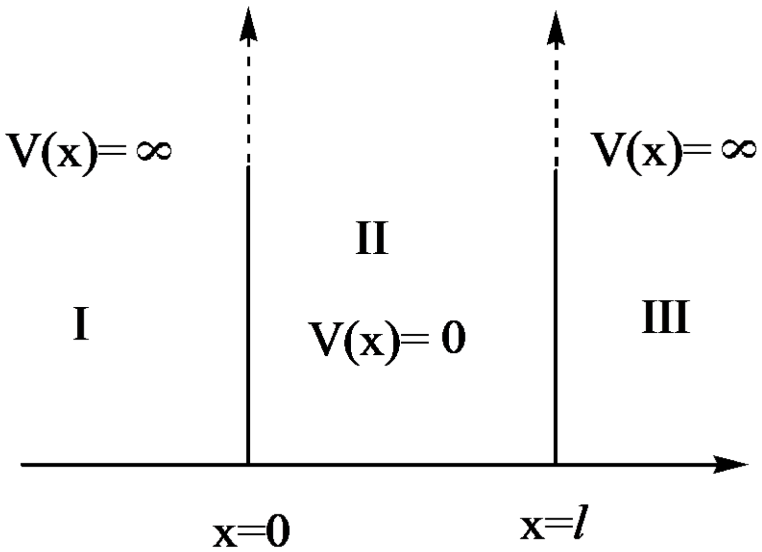
Outside the box, where V is infinite, the only solution is $\psi = 0$. Inside the box, possible solutions are $\exp(ipx/\hbar)$ and $\exp(-ipx/\hbar)$ both with energy $E = p^2/2m$.

However the wavefunction has to be continuous, so it must be zero at both ends of the box.

We can achieve this by using the wavefunction $A sin(px/\hbar) + B cos(px/\hbar)$.

If the wavefunction is to be zero when $x = 0$, then $B = 0$. If it is to be zero when $x = a$, then

$$\frac{pa}{\hbar} = n\pi \qquad \text{for integer } n$$



$$\hat{H} = -\frac{h^2}{8\pi^2 \mathrm{m}}\frac{d^2}{d\mathrm{x}^2} + \hat{V}$$

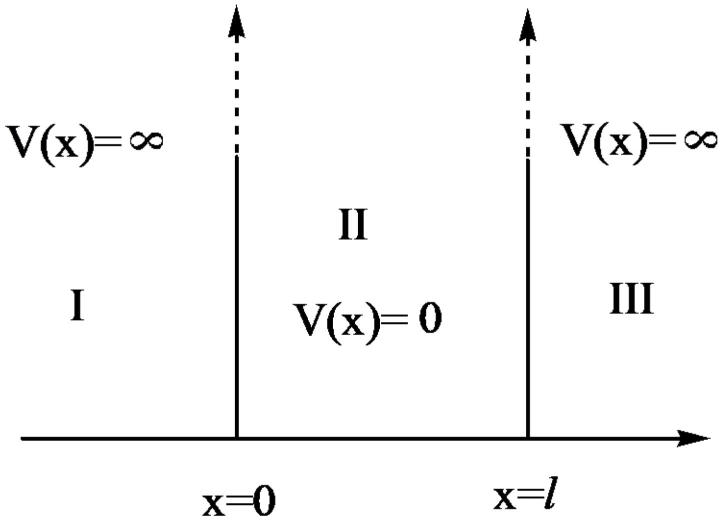
I, III:

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x} + V\psi = E\psi$$

$$\frac{\partial^2\psi}{\partial^2 x} - \frac{8\pi^2 m}{h^2}V\psi = 0 \qquad \because (V=\infty) \therefore V-E=V$$

$$\psi = \frac{\partial^2\psi}{\partial^2 x}\cdot\frac{h^2}{8\pi^2 mV} = 0$$

II: V=0



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

$$\hat{H} = -\frac{h^2}{8\pi^2 \mathrm{m}}\frac{d^2}{\mathrm{d}\mathrm{x}^2} + \hat{V} \quad \Rightarrow \quad \frac{d^2\psi}{d^2x} + \frac{8\pi^2 m}{h^2}E\psi = 0$$

$$\frac{d^2\psi}{d^2x} + \beta^2\psi = 0$$

$$\beta^2 = \frac{8\pi^2 mE}{h^2}$$

$$\boxed{\psi = A\cos\beta x + B\sin\beta x}$$

Boundary condition and continuous condition: $\psi(0)=0$, $\psi(a)=0$

Hence, $\psi(0) = A\cos 0 + B\sin 0$

$A=0$, $B\neq 0$ $\psi = B\sin\beta x$

$\psi(a) = B\sin\beta x = B\sin\beta a=0$, Thus, $\beta a = n\pi$, $\beta = n\pi/a$

$$\frac{8\pi^2 mE}{h^2} = \beta^2 = \frac{n^2\pi^2}{a^2}$$

$$E = \frac{n^2h^2}{8ma^2} \qquad (n=1,2,3\ldots)$$

$$\psi = B\sin\frac{n\pi}{a}x \xrightarrow{\text{Normalization}} \int_0^a B^2\sin^2\frac{n\pi}{a}x\,dx = 1 \Rightarrow B=\sqrt{\frac{2}{a}}$$

$$\psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x$$

2. The properties of the solutions

n=1 $$E_1 = \frac{h^2}{8ma^2} \quad \psi_1 = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

n=2 $$E_2 = \frac{4h^2}{8ma^2} \quad \psi_2 = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$$

n=3 $$E_3 = \frac{9h^2}{8ma^2} \quad \psi_3 = \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a} \cdots\cdots$$

1. The particle can exist in many states
2. quantization energy
3. The minimum energy ($h^2/8ma^2$)

Boundary conditions and quantization

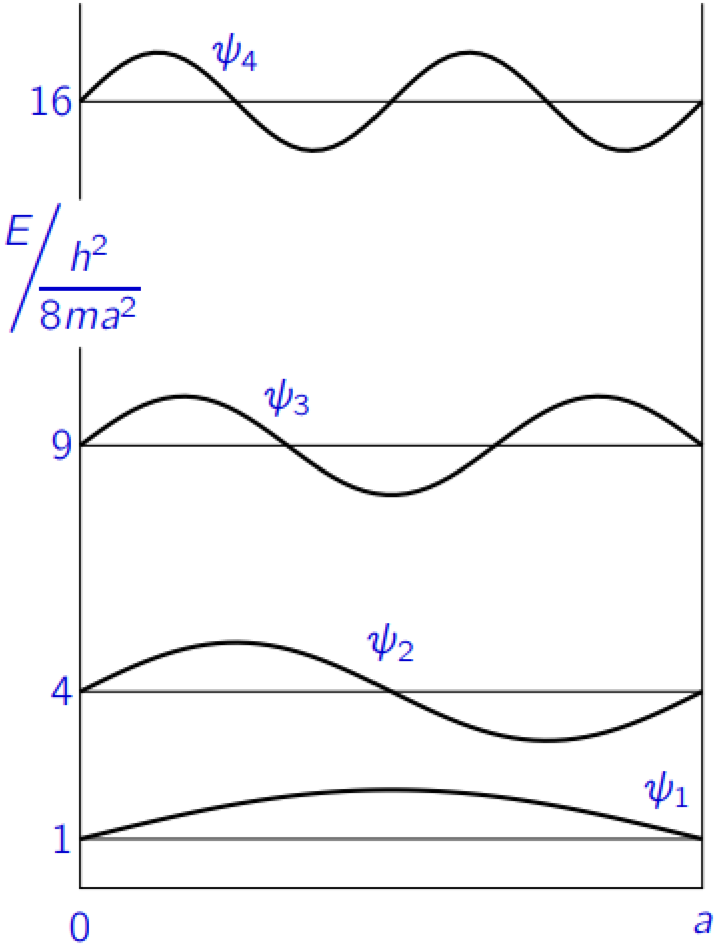
So the allowed wavefunctions for the particle in a box are

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x$$

for integer $n > 0$, and the corresponding energies are

$$E_n = \frac{p^2}{2m} = \frac{n^2 h^2}{8ma^2}$$

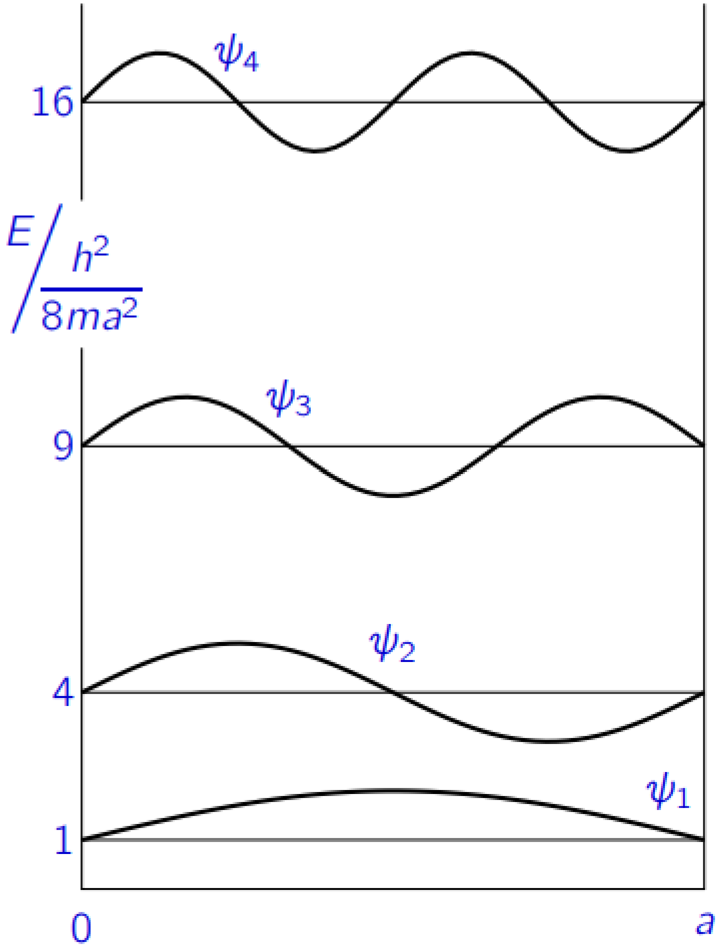
We see that the imposition of boundary conditions leads to *quantization*: only certain values of the energy are possible.



Wavefunctions for a particle in a box

Conventionally wavefunctions are displayed, as here, on a diagram showing the potential energy function, with the zero for each wavefunction at the level of its energy.

1. Note that the lowest-energy wavefunction has no nodes (points where the wavefunction is zero) except at the ends of the box where the zero is required by the boundary condition. The next wave function has 1 node, the next has 2, and so on, each wavefunction having one more node than the previous one.
2. even function (ground state)
   odd function (the first excited state)
   even (the second)
   odd (the third)
   …



Wavefunctions for a particle in a box

Sets of eigenfunctions

3. A general property (proved later) of the set of eigenfunctions of an operator like the Hamiltonian is that they are orthogonal; that is,

$$\int \psi_m{}^* \psi_n \mathrm{d}x = 0 \qquad \text{if } m \neq n.$$

In the present case, the orthogonality is easily demonstrated:

$$\int_0^a \sin\frac{m\pi x}{a}\sin\frac{n\pi x}{a}\mathrm{d}x = \frac{1}{2}\int_0^a\left(\cos\frac{(m-n)\pi x}{a} - \cos\frac{(m+n)\pi x}{a}\right)\mathrm{d}x$$

It is now easy to show that the result is zero unless $m = n$.

If the wavefunctions are normalised, so that $\int \psi_m{}^* \psi_m \mathrm{d}x = 1$ for all m, then

$$\int \psi_m{}^* \psi_n \mathrm{d}x = \delta_{mn} \qquad \text{(Kronecker delta)}$$

and the set is said to be *orthonormal*.

Expansion in eigenfunctions

4. Another important property is that **any function of the same variables with the same boundary conditions can be expressed as a linear combination of the** $\boldsymbol{\psi_n}$:

$$\psi = \sum_n c_n \psi_n$$

To find the coefficients we just multiply the above equation by $\psi_m{}^*$ and integrate:

$$\int_0^a \psi_m{}^* \psi \, \mathrm{d}x = \sum_n c_n \int_0^a \psi_m{}^* \psi_n \, \mathrm{d}x$$

$$= c_m \int_0^a \psi_m{}^* \psi_m \, \mathrm{d}x$$

since all other terms in the sum on the right vanish because of the orthogonality.

If the ψ_m are normalized this just reduces

$$c_m = \int_0^a \psi_m{}^* \psi \, \mathrm{d}x$$

Quantum-classical correspondence principle

Somewhere along the continuum from quantum to classical, the two descriptions must merge. Starting from the quantum end and noting that energies depend upon some quantum number, one would anticipate that for high enough quantum numbers, the quantum treatment should merge with the classical.

$$\Delta E = E_n - E_{n-1} = \frac{n^2 h^2}{8ma^2} - \frac{(n-1)^2 h^2}{8ma^2}$$

$$\frac{\Delta E}{E_n} = \frac{n^2 - (n-1)^2}{n^2} \xrightarrow{n\to\infty} 0$$

BTW, Planck’s constant h goes to zero…

More on measurement

The wavefunction ψ_n for the particle in a box can be expressed in terms of the eigenfunctions of $\hat{p}_x$:

$$\psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} = \frac{1}{i\sqrt{2a}}\exp\frac{ni\pi x}{a} - \frac{1}{i\sqrt{2a}}\exp\frac{-ni\pi x}{a} = \frac{1}{i\sqrt{2}}\psi_p - \frac{1}{i\sqrt{2}}\psi_{-p}$$

where $\psi_p = \sqrt{1/a}\exp(ipx/\hbar)$ is the normalised wavefunction with momentum $p = n\pi\hbar/a = nh/2a$.

Now a measurement of the energy will definitely give the value $E_n = n^2h^2/8ma^2 = p^2/2m$. A measurement of $\hat{p}_x$ must give a result consistent with this, i.e., $\pm p$. Moreover

$$\langle p_x \rangle = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}(-i\hbar)\frac{\mathrm{d}}{\mathrm{d}x}\sin\frac{n\pi x}{a}\,\mathrm{d}x = 0$$

so values of $+p$ and $-p$ must be equally probable; and since one or the other must occur, the probability of each is $1/2$.

Prediction of measurements

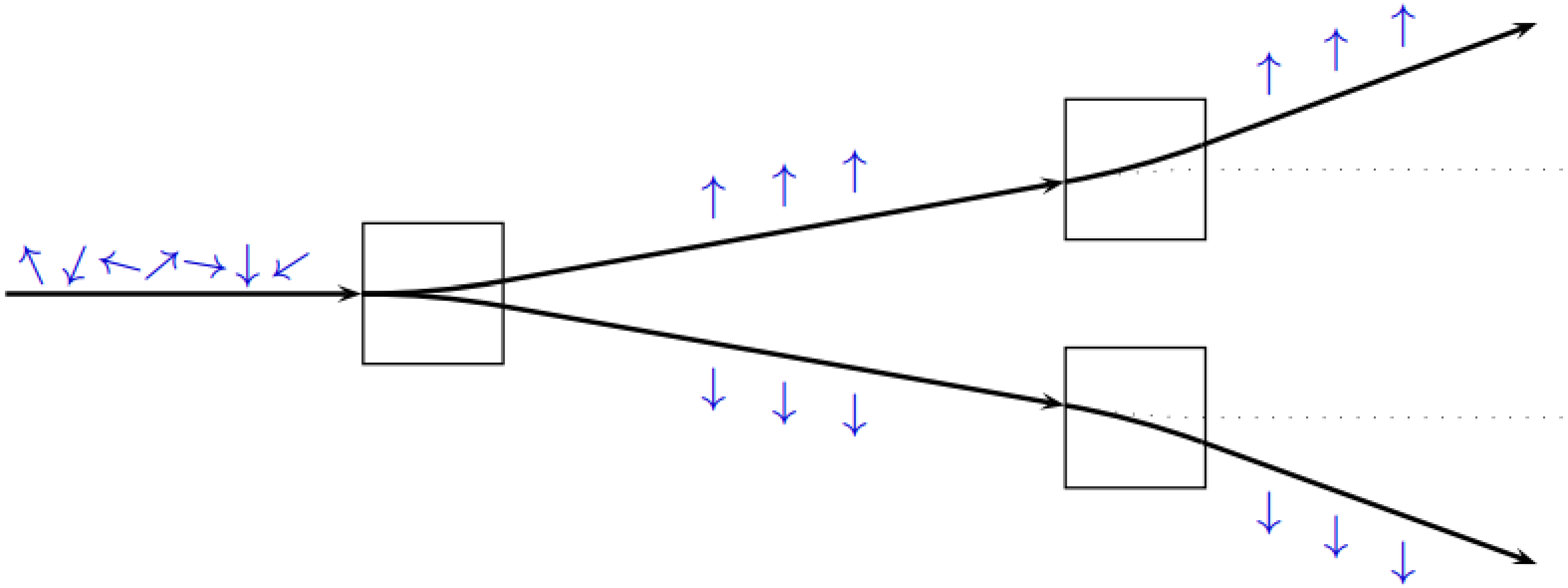
Any normalized wavefunction ψ of the same variables and satisfying the same boundary conditions can be expressed in terms of normalized eigenfunctions ψ_k of $\hat{Q}$, so that

$$\psi = \sum_k c_k \psi_k$$

Here $\hat{Q}\psi_k = q_k\psi_k$, and the c_k are numerical coefficients, possibly complex. Then for a state with this wavefunction,

- If a measurement of Q yields the result q, then immediately after the measurement the system is in a state for which Q definitely has the value q. Consequently a measurement of Q will definitely yield one of the eigenvalues q_k.
- We cannot predict in advance which value will occur, but the probability of observing q_k is $|c_k|^2$.

Example: Stern–Gerlach experiment



If a sodium atom travelling in a vacuum passes through a suitable inhomogeneous magnetic field, it is deflected in one direction (say up) if the unpaired electron has spin up, and in the other direction (down) if it has spin down. This setup is then a device for measuring the spin direction. In a beam of sodium atoms, the spins are oriented randomly, but the measurement forces them into one or other spin state. A measurement on either deflected beam shows that the spin-up beam is again deflected up, while the spin-down beam is again deflected down.

The general steps in the quantum mechanical treatment:

a. Obtain the potential energy functions followed by deriving the Hamiltonian operator and Schrödinger equation.
b. Solve the Schrödinger equation. (obtain ψ_n and E_n)
c. Study the characteristics of the distributions of ψ_n.
d. Deduce the values of the various physical quantities of each corresponding state.

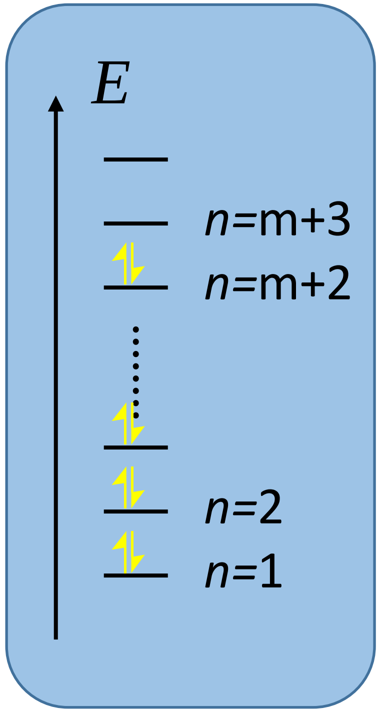
Example 1: The adsorption spectrum of cyanines

The general formula of the cyanine dye: $R_2\ddot{N}\text{-}(CH{=}CH\text{-})_mCH{=}\overset{+}{N}R_2$

Total π electrons: 2m+4

In the ground state, these electrons occupy m+2 molecular orbitals

The adsorption spectrum correspond to excitation of electrons from the highest occupied (m+2) orbital to the lowest unoccupied (m+3) orbital.



$$\Delta E = \frac{h^2}{8m_e a^2}[(m+3)^2-(m+2)^2] = \frac{h^2}{8m_e a^2}(2m+5)$$

$$\nu = \frac{\Delta E}{h} = \frac{h}{8m_e a^2}(2m+5)$$

$$\lambda = \frac{8m_e a^2 c}{h(2m+5)} = \frac{3.30a^2}{2m+5} \quad (pm)$$

Table 1. The absorption spectrum of the cyanine dye

m	λmax (calc) / nm	λmax (expt) /nm
1	311.6	309.0
2	412.8	409.0
3	514.6	511.0

Example 2: The delocalization effect of 1,3-butadiene

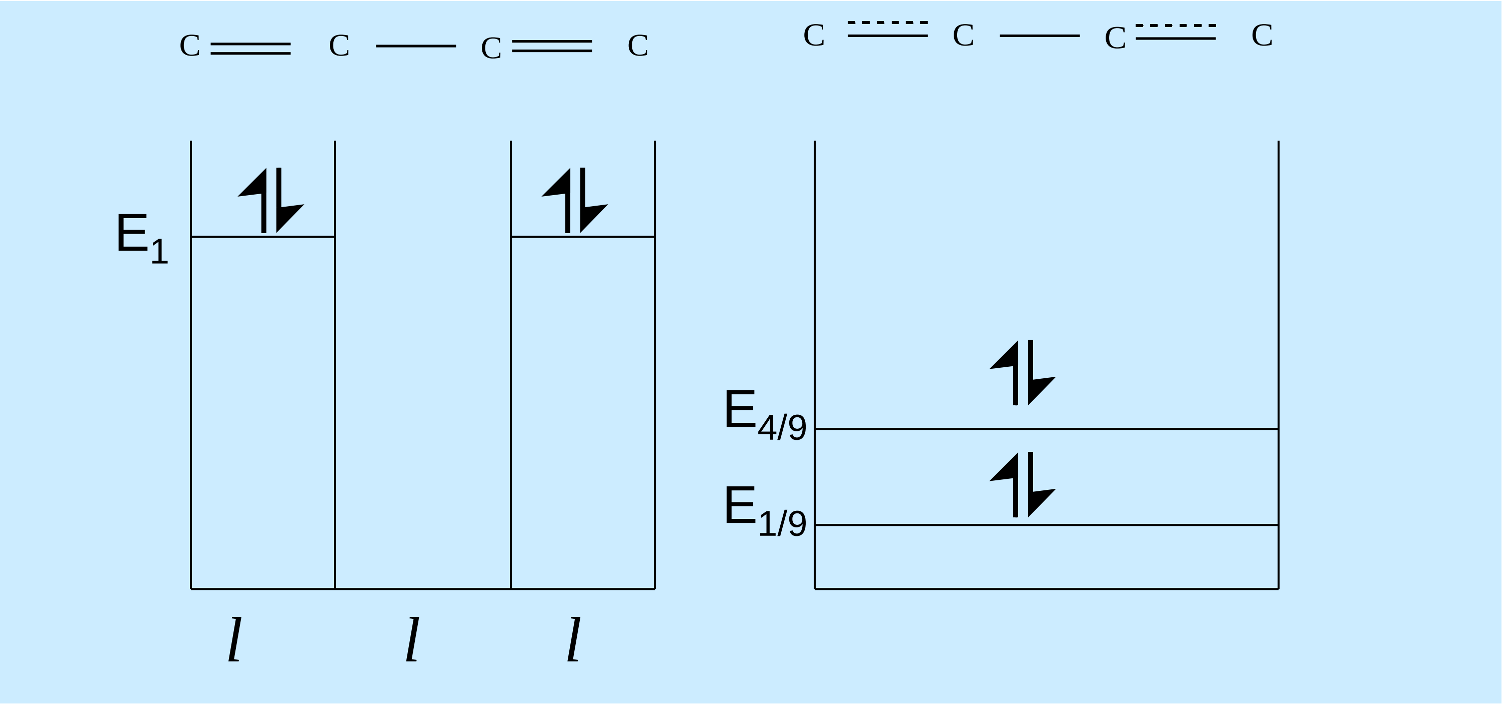
Four π electron form two π localized bonds

$$E=2\times 2\times h^2/8ml^2=4E_1$$

$$>$$

Four π electron form a π_4^4 delocalized bonds

$$E=2\times h^2/8m(3l)^2+2\times 2^2\times h^2/8m(3l)^2=(10/9)E_1$$

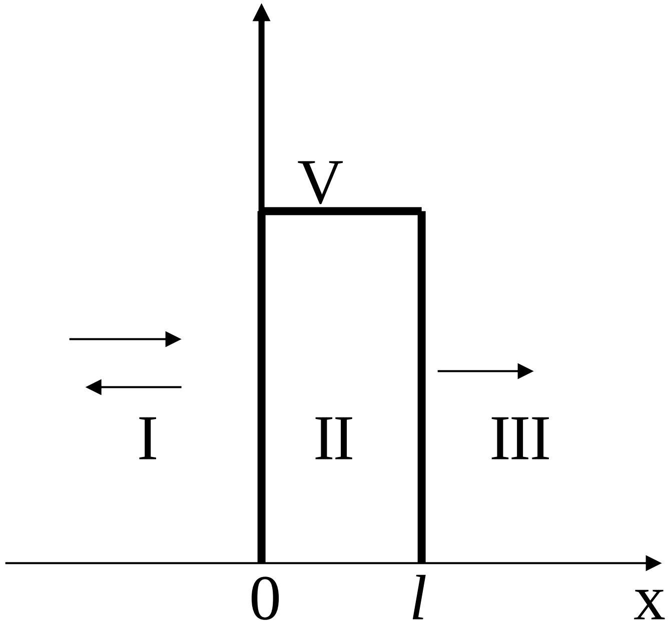


2.3 Quantum leaks --- tunneling

Quantum tunneling is an effect where a particle can pass through a barrier it would not normally have the energy to overcome.

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x}+V\psi=E\psi \qquad (0<x<l)$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial^2 x}=E\psi \qquad (x<0, x>l)$$

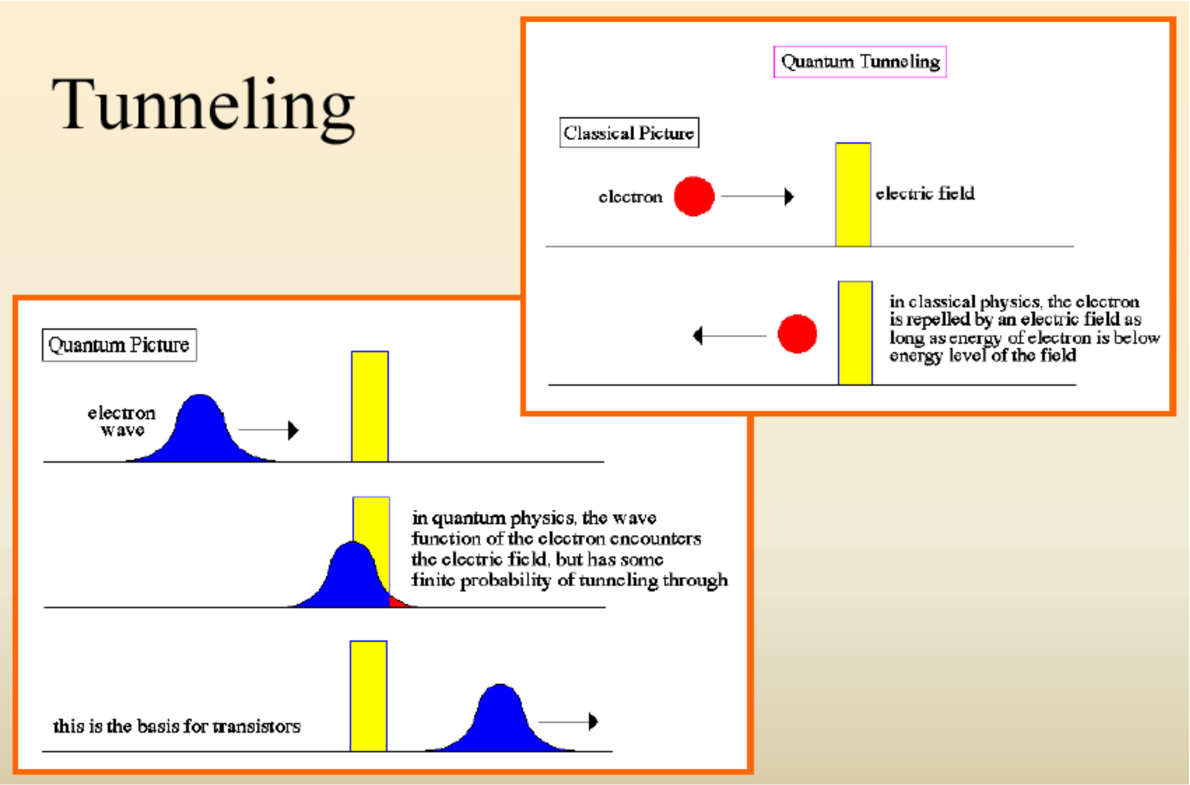


The probability of penertration is given by

$$P\approx 4(E/V)[1-(E/V)]e^{-\frac{2}{\hbar}\sqrt{2m(V-E)}l}$$

When E<V

CLASSICAL MECHANICS



Tunneling

Quantum Tunneling

Classical Picture

electron

electric field

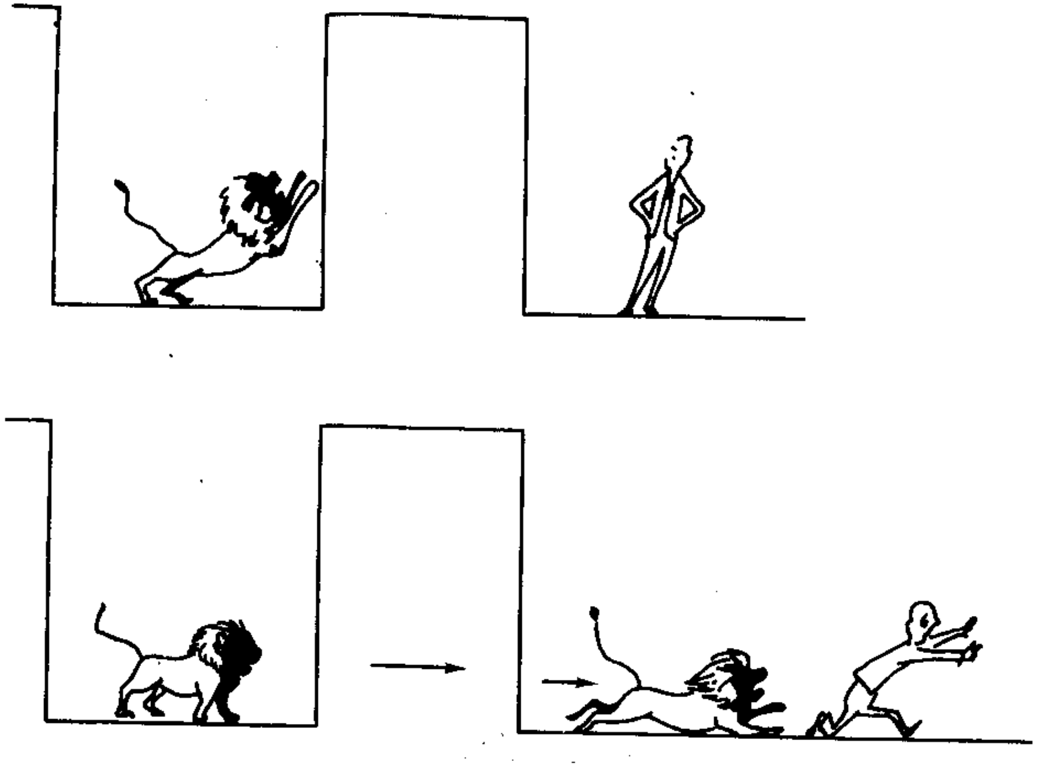
in classical physics, the electron is repelled by an electric field as long as energy of electron is below energy level of the field

Quantum Picture

electron wave

in quantum physics, the wave function of the electron encounters the electric field, but has some finite probability of tunneling through

this is the basis for transistors



QUANTUM MECHANICS

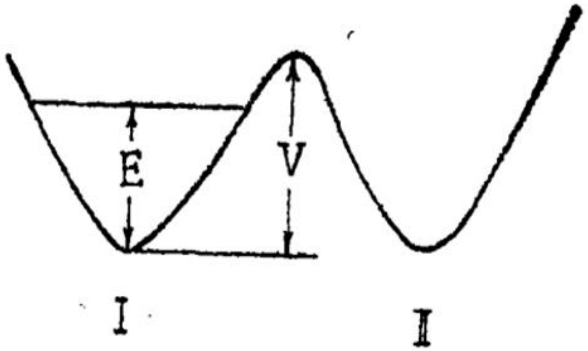
Tunneling in the “real world”

- Tunneling is used:

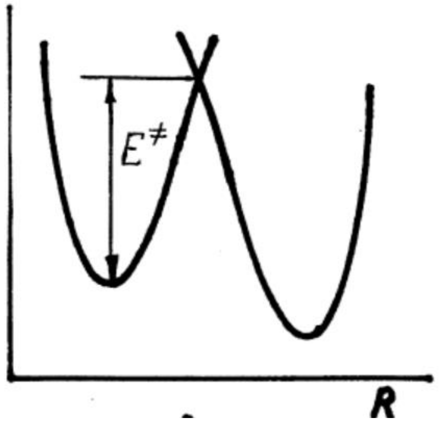
- for the operation of many microelectronic devices (tunneling diodes, flash memory, …)
- for advanced analytical techniques (scanning tunneling microscope, STM)

- Responsible for radioactivity (e.g. alpha particles)

a double-well potential



proton transfer



2.4 Particle in a 3-D box of dimensions a, b, c

Out of the box, V(x, y, z) = ∞; In the box, V(x, y, z) =0

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)\psi = E\psi$$

$$\boxed{\begin{array}{l} 0<x<a \\ 0<y<b \\ 0<z<z \end{array}}$$

Let ψ = ψ(x, y, z)= X (x) Y (y) Z (z) (separation of variables) Substituting into 3-D Schroedinger equation

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)\psi = E\psi$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)XYZ = EXYZ$$

$$-\frac{h^2}{8\pi^2 m}\left(\frac{YZ\partial^2 X}{\partial^2 x}+\frac{XZ\partial^2 Y}{\partial^2 y}+\frac{XY\partial^2 Z}{\partial^2 z}\right) = EXYZ$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 X}{X\partial^2 x} = E + \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2 Y}{Y\partial^2 y} + \frac{\partial^2 Z}{Z\partial^2 z}\right) = E_x$$

$E=E_x+E_y+E_z$ ⇓ Let $E_z = E - (E_x+E_y)$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 x}X = E_x X \qquad -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 y}Y = E_y Y \qquad -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial^2 z}Z = E_z Z$$

$$X(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x \pi x}{a} \qquad Y(y) = \sqrt{\frac{2}{b}}\sin\frac{n_y \pi y}{b} \qquad Z(z) = \sqrt{\frac{2}{c}}\sin\frac{n_z \pi z}{c}$$

$$\psi = XYZ = \sqrt{\frac{8}{abc}}\sin\frac{n_x \pi x}{a}\sin\frac{n_y \pi y}{b}\sin\frac{n_z \pi z}{c}$$

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

Multiply degenerate energy level when the box is cubic (a = b = c)

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

The ground state: $n_x = n_y = n_z = 1$

$$E = \frac{3h^2}{8ma^2}$$

The first excited state: $n_i = n_j = 1$, $n_k = 2$

$$E = \frac{6h^2}{8ma^2}$$

The wave-functions are called *degenerate* *(triply degenerate)*

$$\begin{cases} 1 & 1 & 2 \\ 1 & 2 & 1 \\ 2 & 1 & 1 \end{cases}$$

2.5 The Harmonic Oscillator

The Hamiltonian is

$$H = \frac{\hat{p}^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}kx^2$$

The ground state wavefunction

- should have no nodes, and
- should go to zero as $x \to \pm\infty$.

The wavefunction in ground state is

$$\psi_0 = N \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right) \qquad \text{and } N = \left[\frac{\sqrt{km}}{\pi\hbar}\right]^{1/4}$$

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega$$

Harmonic Oscillator can model many different systems around their equilibrium point

Nuclear Motion in Diatomic Molecules

$$\left[-\frac{\hbar^2}{2m_\alpha}\nabla_\alpha^2-\frac{\hbar^2}{2m_\beta}\nabla_\beta^2+U(R)\right]\psi_N=E\psi_N$$

The accurate solution of the electronic Schr ödinger equation is hard.
expand U(R) in a Taylor series about R_e

$$U(R)=U(R_e)+U^{'}(R_e)(R-R_e)+\frac{1}{2}U^{''}(R_e)(R-R_e)^2+\frac{1}{6}U^{'''}(R_e)(R-R_e)^3+\cdots$$

The second term is zero and the fourth term can be neglected. (Why?)

Defining the equilibrium force constant:

$$k_e\equiv U^{''}(R_e)$$

$$U(R)=U(R_e)+\frac{1}{2}k_e(R-R_e)^2$$

Phonon

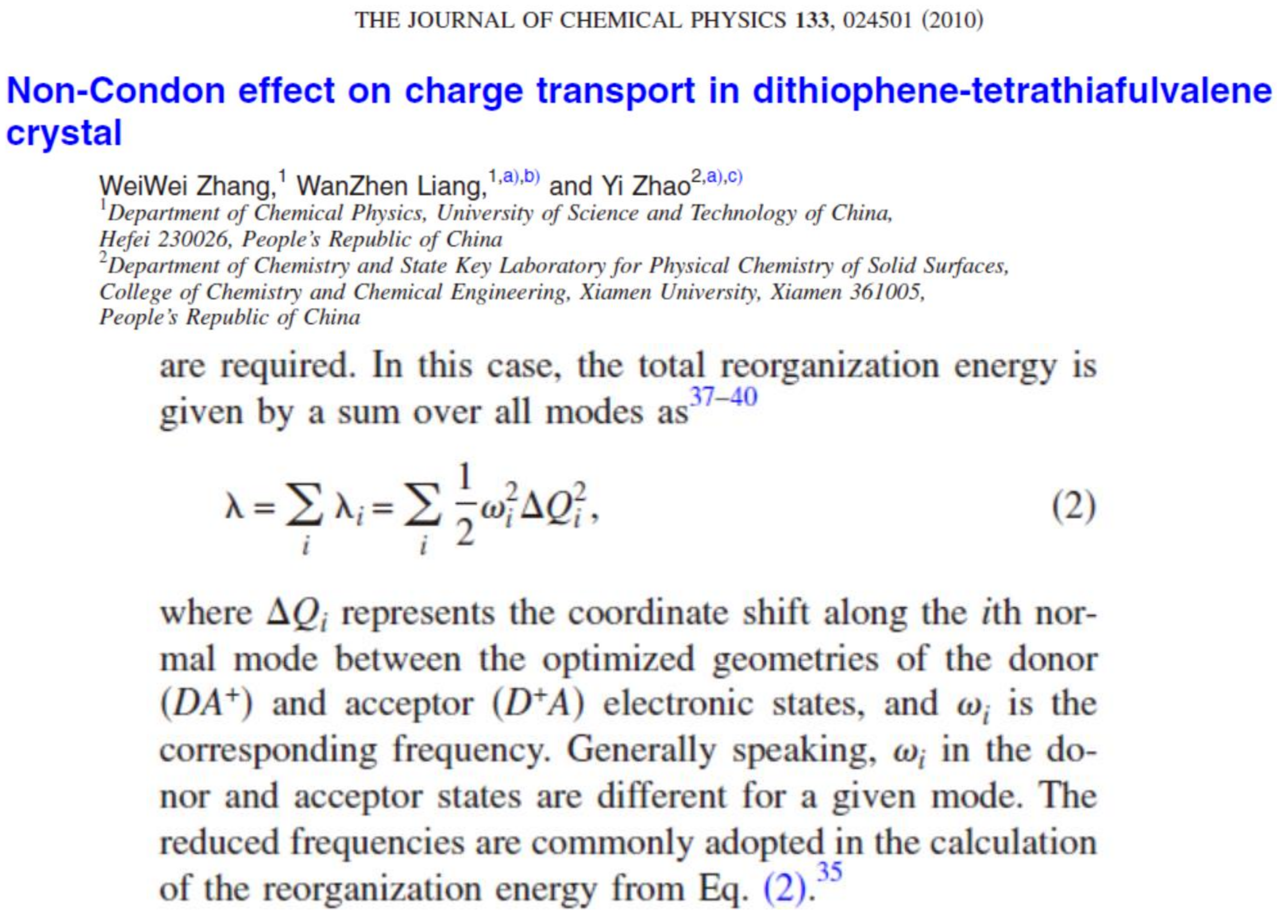
A unit of vibrational energy that arises from oscillating atoms within a crystal. Any solid crystal, consists of atoms bound into a specific repeating three-dimensional spatial pattern called a lattice.

$$U = \frac{1}{2} K \sum (x_n - x_{n+1})^2$$

$$\mathcal{H} = \sum_n \frac{p_n^2}{2M} + \frac{1}{2} K \sum_n (x_n - x_{n+1})^2$$

赵仪

https://chem.xmu.edu.cn/info/1188/1301.htm



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Non-Condon effect on charge transport in dithiophene-tetrathiafulvalene crystal

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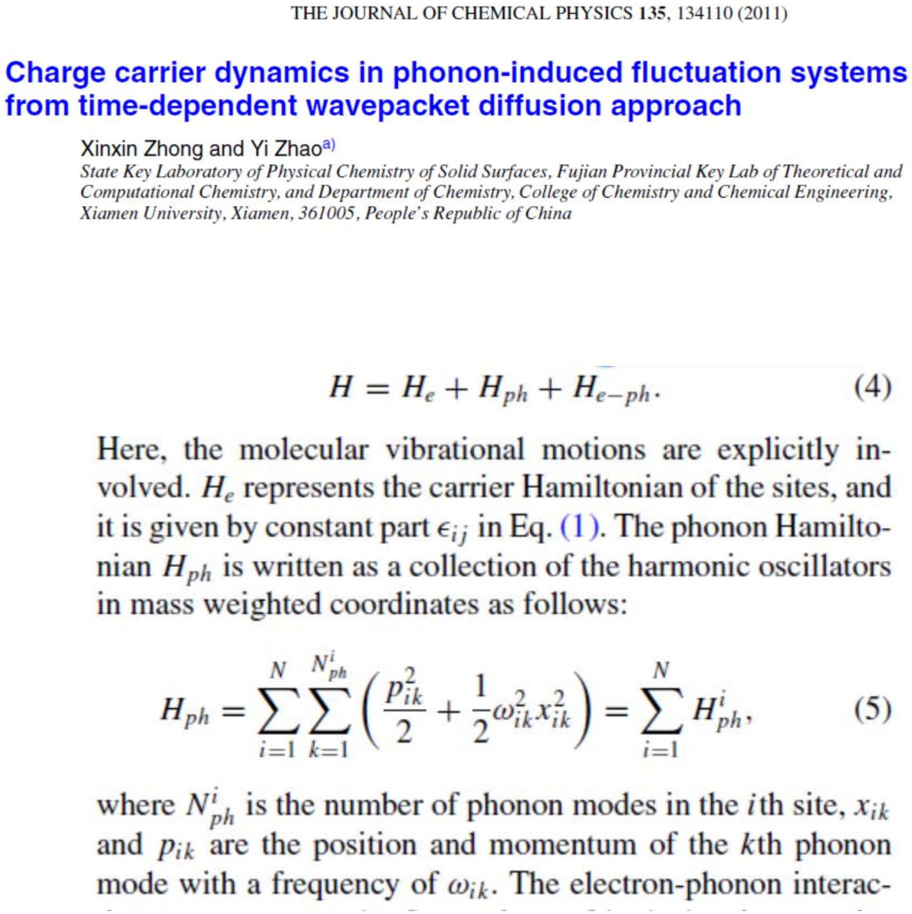
are required. In this case, the total reorganization energy is given by a sum over all modes as[37–40]

$$\lambda = \sum_i \lambda_i = \sum_i \frac{1}{2}\omega_i^2 \Delta Q_i^2, \tag{2}$$

where ΔQ_i represents the coordinate shift along the ith normal mode between the optimized geometries of the donor (DA^+) and acceptor (D^+A) electronic states, and ω_i is the corresponding frequency. Generally speaking, ω_i in the donor and acceptor states are different for a given mode. The reduced frequencies are commonly adopted in the calculation of the reorganization energy from Eq. (2).[35]



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Charge carrier dynamics in phonon-induced fluctuation systems from time-dependent wavepacket diffusion approach

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$$H = H_e + H_{ph} + H_{e-ph}. \tag{4}$$

Here, the molecular vibrational motions are explicitly involved. H_e represents the carrier Hamiltonian of the sites, and it is given by constant part ϵ_{ij} in Eq. (1). The phonon Hamiltonian H_{ph} is written as a collection of the harmonic oscillators in mass weighted coordinates as follows:

$$H_{ph} = \sum_{i=1}^{N} \sum_{k=1}^{N_{ph}^i} \left(\frac{p_{ik}^2}{2} + \frac{1}{2}\omega_{ik}^2 x_{ik}^2 \right) = \sum_{i=1}^{N} H_{ph}^i, \tag{5}$$

where N_{ph}^i is the number of phonon modes in the ith site, x_{ik} and p_{ik} are the position and momentum of the kth phonon mode with a frequency of ω_{ik}. The electron-phonon interac-

Zero-point energy and uncertainty

We have evaluated Δx for the harmonic oscillator ground state ψ_0 : it is $[\hbar^2/4km]^{1/4}$.

To evaluate Δp_x we proceed as follows. We know that $\langle x^2 \rangle = \frac{1}{2}\hbar/\sqrt{km}$, so the mean potential energy is $\langle V \rangle = \left\langle \frac{1}{2}kx^2 \right\rangle = \frac{1}{4}\hbar\sqrt{k/m} = \frac{1}{4}\hbar\omega$.

where ω is the angular frequency $\sqrt{k/m}$

Consequently $\langle T \rangle = E_0 - \langle V \rangle = \frac{1}{4}\hbar\sqrt{k/m}$ also.

But $T = {p_x}^2/2m$, so $\langle {p_x}^2 \rangle = 2m\langle T \rangle = \frac{1}{2}\hbar/\sqrt{km}$. Also $\langle p_x \rangle = 0$.

Therefore $\Delta p_x \ = (\hbar^2 km/4)^{1/4}$, and $\Delta x \Delta p_x = \frac{1}{2}\hbar$.

The ground state energy of the harmonic oscillator is as low as it can be without violating the uncertainty principle.

Other Harmonic Oscillator Wavefunctions

To find solutions, one procedure is to try $\psi = H(q)\exp(-q^2/2)$.

Substituting into $H\psi = E\psi$ yields a differential equation for $H(q)$; it is a standard differential equation called Hermite's equation. Imposing the boundary condition that the wavefunction goes to zero as $q \to \pm\infty$ leads to the conclusion that $H(q)$ must be one of the *Hermite polynomials* $H_v(q)$, and the corresponding eigenvalue is $(v+\frac{1}{2})\hbar\omega$.

$$\boxed{E_v = \left(v + \frac{1}{2}\right)\hbar\omega}$$

The first few Hermite polynomials are

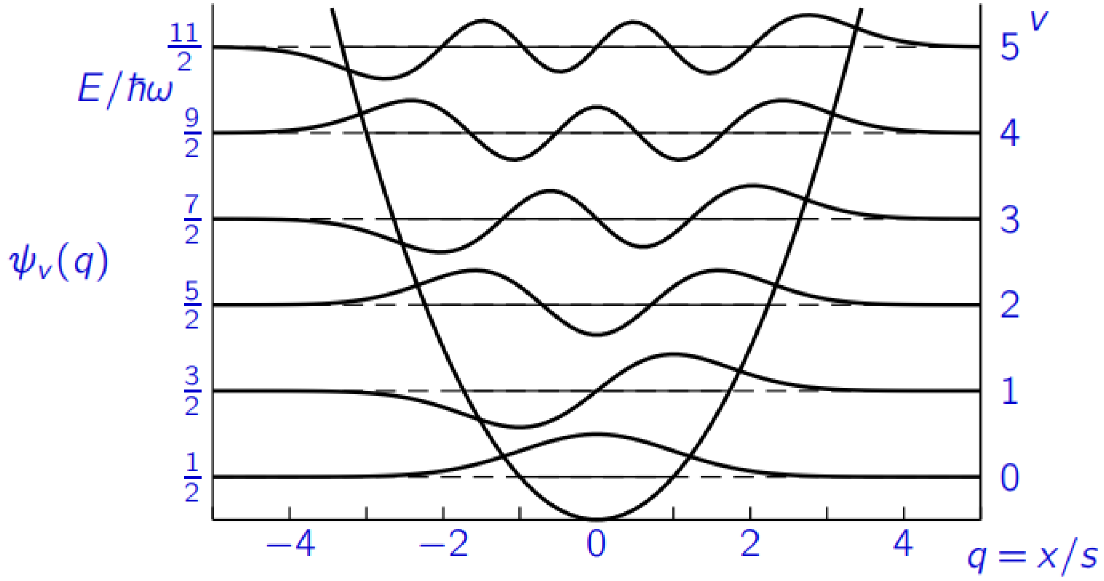
$$H_0(q) = 1$$

$$H_1(q) = 2q$$

$$H_2(q) = 4q^2 - 2$$

and generally

$$H_v(q) = (-1)^v \exp(q^2)\frac{\mathrm{d}^v}{\mathrm{d}q^v}\exp(-q^2)$$

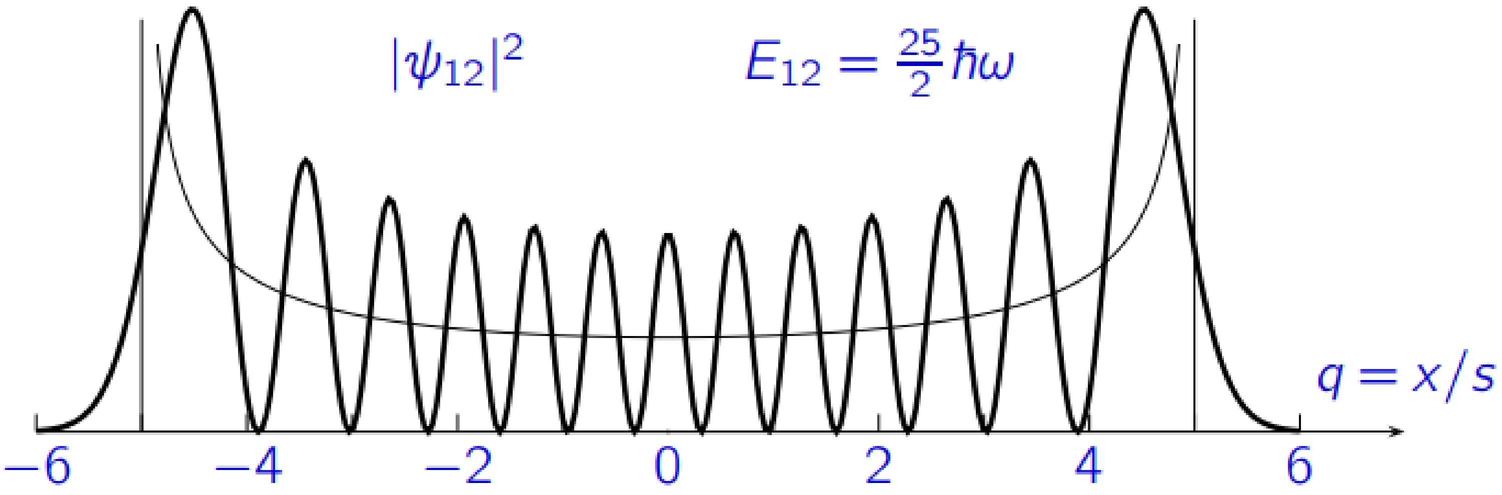


Compare the harmonic oscillator wavefunctions with those for the particle in a box. Note that

- The nodal structure is the same.
- The energies are now equally spaced.
- The wavefunction (and so the probability density) continues past the point where $V = E_v$, and thus enters the *classically forbidden region*, where $T<0$.

This is the mysterious phenomenon known as *quantum tunnelling*.

High vibrational levels



Features of high vibrational levels:

- The probability distribution $|\psi_0|^2$ approaches the classical distribution for large v, except for the quantum oscillations, and has a large peak near the classical turning-point.
- The probability of tunnelling outside the classical turning-point becomes smaller as v increases.

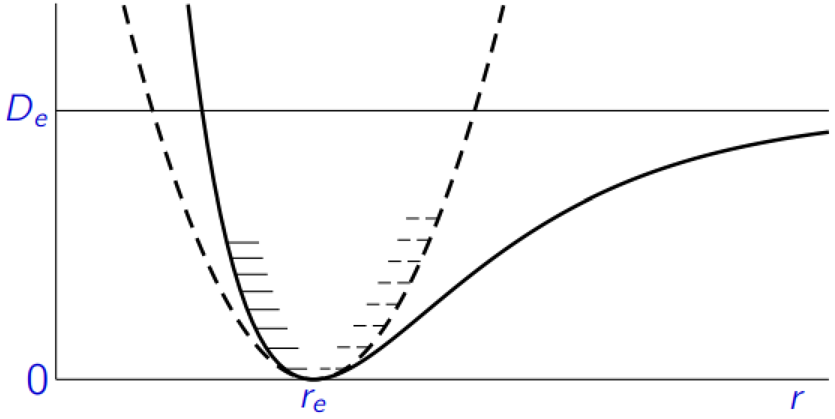
The Morse Oscillator

For a real diatomic molecule, the energy does not become infinite as the bond-length is increased indefinitely, but instead reaches an asymptotic value, the dissociation energy D_e. A better approximation to this behaviour is provided by the Morse potential:

$$V_M\left(r\right) = D_e[1 - \exp(-\beta(r - r_e))]^2$$

where r is the bond-length of the diatomic and r_e its value at the equilibrium geometry.

A Morse potential (solid curve) compared with the harmonic oscillator potential (dashed curve)



We can expand the Morse potential as a power series in $t = \beta(r - re)$:

$$V_M(r) = D_e[1 - \exp(-t)]^2 = D_e[1 - (1 - t + \frac{1}{2}t^2 - \cdots)]^2$$

$$= D_e[t - \frac{1}{2}t^2 + \cdots]^2 = D_e[t^2 - t^3 + \cdots]$$

$$= D_e[\beta^2(r - r_e)^2 - \beta^3(r - r_e)^3 + \cdots]$$

so the force constant is $k = 2\beta^2 D_e$.

The Schrödinger equation for the Morse potential can be solved exactly, but the wavefunctions are much more complicated than for the harmonic oscillator. The energy levels, however, take a relatively simple form:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2 \hbar\omega x_e$$

where $\omega = \sqrt{k/m}$ as usual and $x_e = \hbar\beta^2/2m\omega = \hbar\omega/4De$ is the *anharmonicity constant*.

Real molecules follow this formula quite closely for small v

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2 \hbar\omega x_e$$

$$E_3 = \tfrac{7}{2}\hbar\omega - \tfrac{49}{4}\hbar\omega x_e$$

$$E_2 = \tfrac{5}{2}\hbar\omega - \tfrac{25}{4}\hbar\omega x_e$$

$$E_1 = \tfrac{3}{2}\hbar\omega - \tfrac{9}{4}\hbar\omega x_e$$

$$E_0 = \tfrac{1}{2}\hbar\omega - \tfrac{1}{4}\hbar\omega x_e$$