Teoria quantistica Approccio con i Postulati

- **Eq. di Schroedinger (altra visione matematica)**

- **Operatori (senso fisico)**

Chimica Fisica 2
Laurea Tri. Chim. Industriale
2022-23

Prof. Antonio Toffoletti

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Principi Quanto-Meccanici

Dinamica delle particelle microscopiche – A (con massa dell'ordine di 1,66 10^{-27} Kg = 1 u.m.a. = 1 m_u ≈ massa$_{protone}$. massa$_{elettrone}$ = 9,1 10^{-31} Kg ≈ 1 u.m.a./1800)

Per sistemi **mono**-dimensionali

<div style="border: 2px solid teal;">

Eq. di Schrödinger

</div>

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

In cui $-\hbar^2/2m * d^2/dx^2$ è l'operatore $\hat{T}$ energia cinetica, V(x) è l'oper. energia potenziale della particella ed E è la sua energia totale.

Per sistemi **tri**-dimensionali

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

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Dinamica delle particelle microscopiche – B

Eq. di Schrödinger

Per sistemi **tri**-dimesionali

In coordinate cartesiane ortogonali

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

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

In coordinate polari sferiche

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\Lambda^2$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

in cui

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Dinamica delle particelle microscopiche – C

Eq. di Schrödinger

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

Equazione di Schrödinger **stazionaria** in forma compatta e del tutto generale
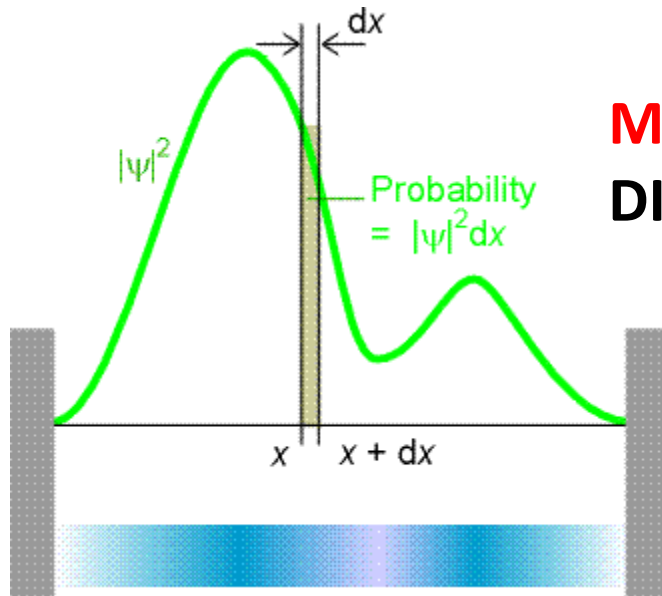
In cui

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

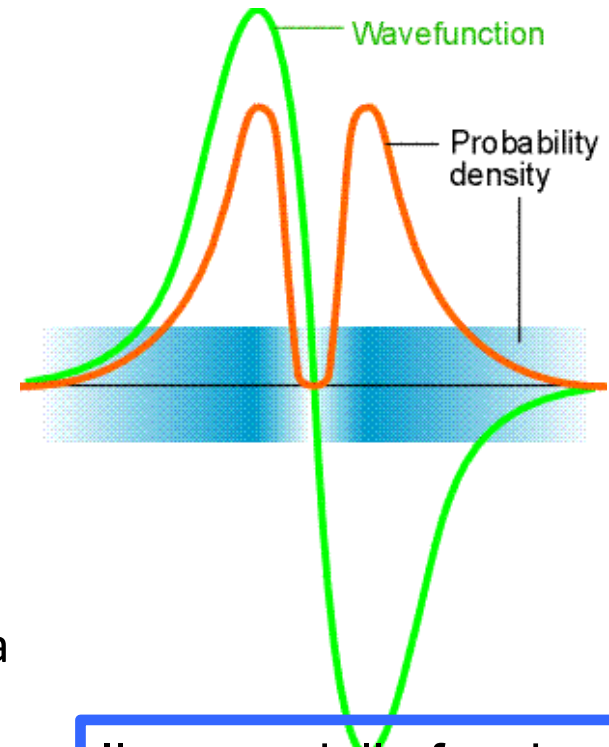Equazione di Schrödinger **dipendente dal tempo**

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

Interpretazione di Born della funzione d'onda - A

If the wavefunction of a particle has the value ψ at some point x, then the probability of finding the particle between x and $x + \mathrm{d}x$ is proportional to $|\psi|^2\mathrm{d}x$.

MONO-
DIMENSIONALE

La funzione d'onda ψ è una ampiezza di probabilità nel senso che il suo modulo quadro ($\psi*\psi$ oppure $|\psi|^2$) è una densità di probabilità (Prob./Vol. = probabilità per unità di volume).
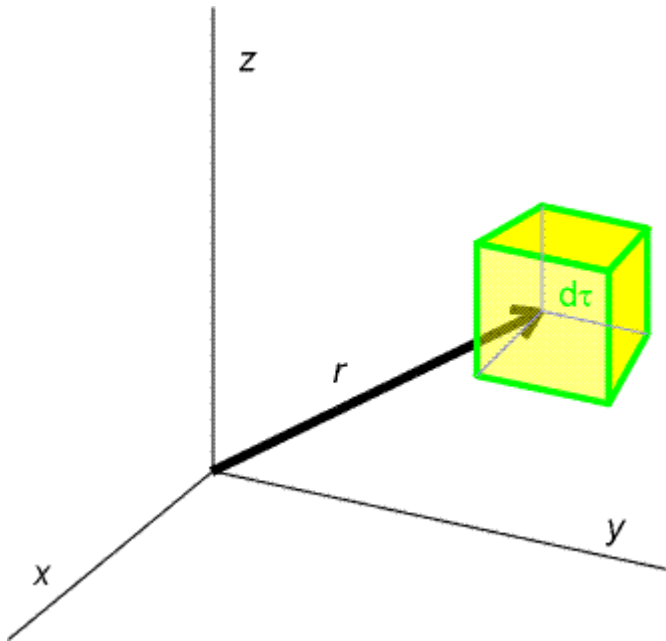Nella figura l'intensità del colore azzurro della fascia orizzontale rappresenta la densità di probabilità.

Il segno della funzione d'onda non ha un significato fisico diretto

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Interpretazione di Born della funzione d'onda - B

The Born interpretation. If the wavefunction of a particle has the value ψ at some point r, then the probability of finding the particle in an infinitesimal volume $d\tau = dxdydz$ at that point is proportional to $|\psi|^2 d\tau$.

TRI-DIMENSIONALE

Secondo l'interpretazione di Born della funzione d'onda tri-dimensionale, la probabilità di trovare la particella nell'elemento di volume $d\tau = dx\ dy\ dz$ nella posizione *r* è proporzionele al prodotto di $d\tau$ per il valore $|\psi|^2$ in quel punto.

Interpretazione di Born della funzione d'onda – C

Normalizzazione **mono**-dimensionale

se ψ è soluzione di $\hat{H}\psi = E\psi$ anche $N\psi$ è una soluzione
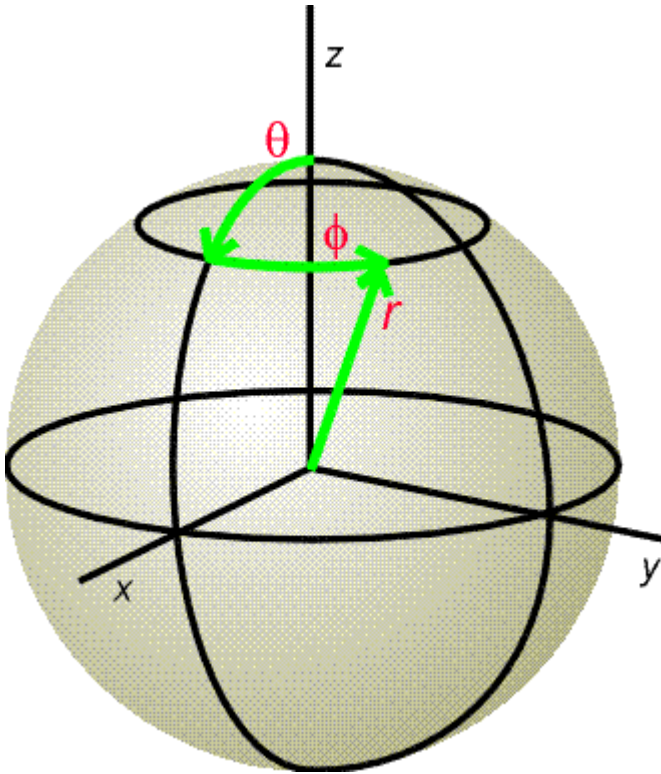
$$\int_{-\infty}^{+\infty} \psi_N^* \psi_N \, dx = 1$$ in cui $\psi_N = \psi_{Normalizzata} = N\psi$
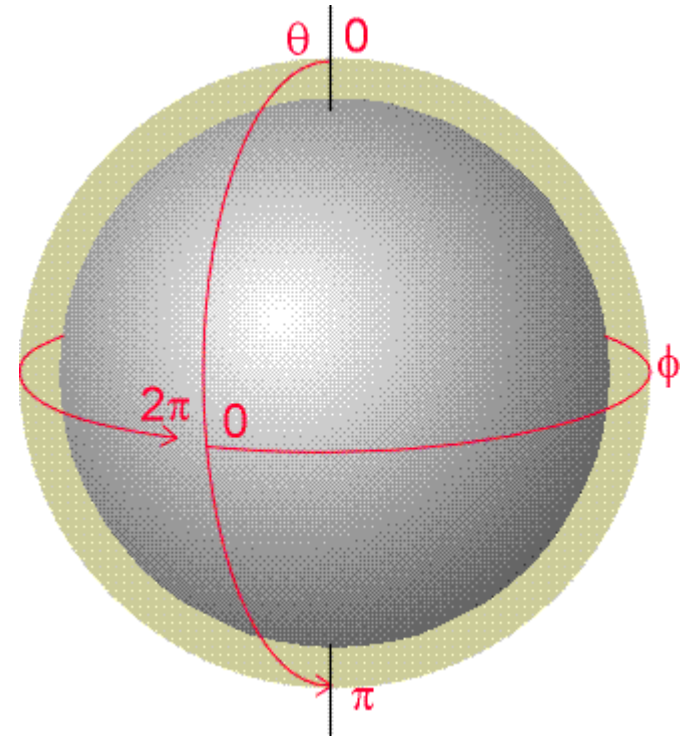
Condizione da imporre

$$N^2 \int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

$$N = \frac{1}{\left(\int_{-\infty}^{\infty} \psi^* \psi \, dx\right)^{1/2}}$$

Interpretazione di Born della funzione d'onda – D

Coordinate polari sferiche che si usano per descrivere sistemi con simmetria sferica.

La superficie sferica viene coperta completamente se si fa variare θ da 0 a π (producendo un semicerchio – cioè un meridiano terrestre) e poi facendo scorrere quel semicerchio di un giro completo, facendo variare ϕ da 0 a 2π.

Interpretazione di Born della funzione d'onda – E

Normalizzazione Tri-dimensionale

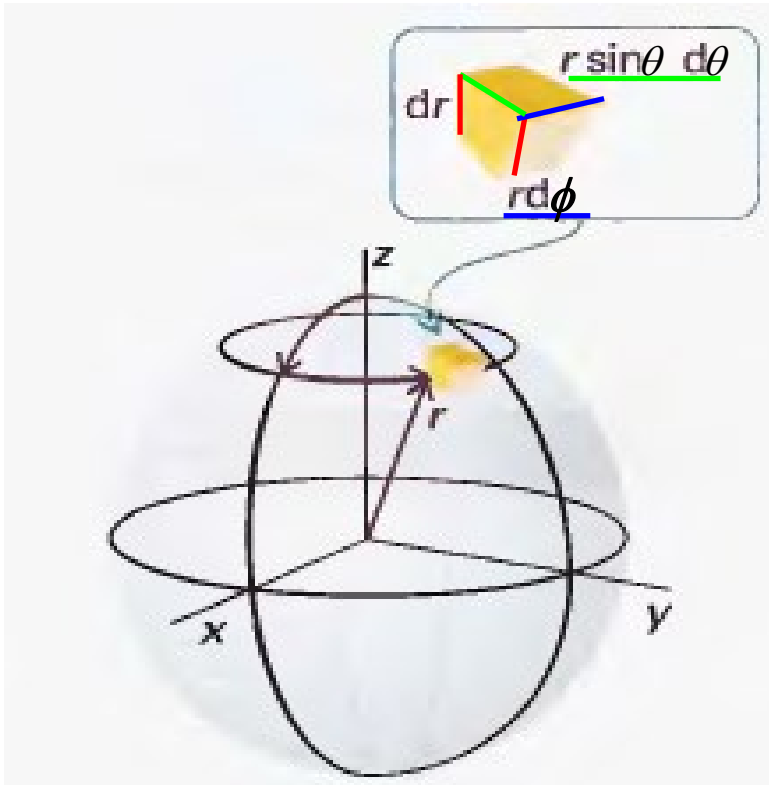$$\int_{-\infty}^{+\infty} \psi_N^* \, \psi_N \; d\tau = 1$$

Condizione da imporre

$$\psi_N = \psi_{Normalizzata} = N\psi$$

$$d\tau = r^2 \sin\theta \, dr d\theta d\phi.$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \psi \, dx dy dz = 1$$

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \psi^* \psi r^2 \sin\theta \, dr d\theta d\phi = 1$$

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Altre proprietà matematiche relative a: funzioni reali / complesse (come le funzioni d'o.) operatori lineari

- ortogonalità

- Non commutazione degli operatori

- Hermiticità degli operatori

Postulati della meccanica quantistica - A

1   *The wavefunction.* All dynamical information is contained in the wavefunction ψ for the system, which is a mathematical function found by solving the Schrödinger equation for the system. In one dimension:

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

2   *The Born interpretation.* If the wavefunction of a particle has the value ψ at some point r, then the probability of finding the particle in an infinitesimal volume $d\tau = dxdydz$ at that point is proportional to $|\psi|^2 d\tau$.

3   *Acceptable wavefunctions.* An acceptable wavefunction must be continuous, have a continuous first derivative, be single-valued, and be square-integrable.

Postulati della meccanica quantistica - B

4 *Observables.* Observables, Ω, are represented by operators, $\hat{\Omega}$, built from position and momentum operators of the form
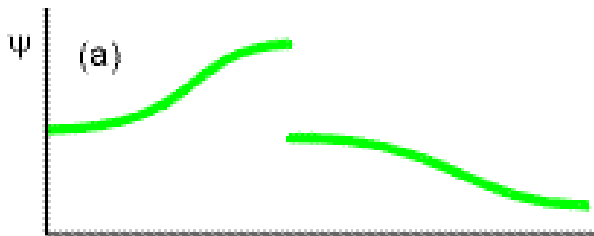
$$\hat{x} = x \times \qquad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

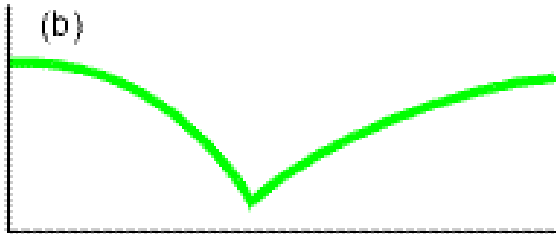or, more generally, from operators that satisfy the commutation relation $[\hat{x}, \hat{p}_x] = i\hbar$.

5 *The Heisenberg uncertainty principle.* It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle and, more generally, any pair of observable with operators that do not commute.

Dinamica dei sistemi microscopici
Accettabilità della funzione d'onda Ψ

La funzione d'onda deve soddisfare condizioni rigorose per essere accettabile.

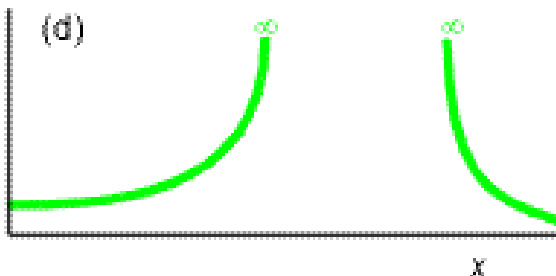Esempi di ψ INACCETATABILE

(a) perché non è continua; ;

(b) perché la sua pendenza non è continua;

(c) perché non è a un sol valore;

(d) perché è infinita su una regione finita.

$$\int_{-\infty}^{+\infty} \psi_N{}^* \psi_N \ dx = 1 \qquad \text{NON si potrebbe}$$

avere un integrale finito

Principi Quanto-Meccanici
Informazioni contenute nella funzione d'onda

La funzione d'onda contiene tutte le informazioni che è possibile ottenere sulle proprietà dinamiche della particella (ad esempio, la sua posizione e quantità di moto).

Da BORN $\rightarrow$ tutto ciò che possiamo sapere sulla posizione x.

Vogliamo trovare un metodo generale per ricavare informazioni dalla ψ, soluzione dell'eq. di Schroedinger

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

Ad esempio consideriamo un particella **libera** di massa m

Principi Quanto-Meccanici

Informazioni contenute nella funzione d'onda

Descrizione quantomeccanica del moto di una particella libera (V=0) e con energia cinetica = (mv)²/2m = p²/2m :

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}= E\psi$$

Eq. di Schroedinger

$$\hat{H}\psi = E\psi \qquad \hat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Forma compatta
e Hamiltoniano

$$\psi_k = Ae^{ikx} + Be^{-ikx} \qquad E_k = \frac{k^2\hbar^2}{2m}$$

Soluzioni dell' Eq. di Schroedinger (autofunzioni ψ_k e autovalori E_k)

Principi Quanto-Meccanici
Informazioni contenute nella funzione d'onda

verifica

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(Ae^{ikx} + Be^{-kx})$$

$$= -\frac{\hbar^2}{2m}\{A(ik)^2 e^{ikx} + B(-ik)^2 e^{-ikx}\}$$

$$= \frac{\hbar^2 k^2}{2m}(Ae^{ikx} + Be^{-ikx}) = E\psi$$

Principi Quanto-Meccanici
Informazioni contenute nella funzione d'onda

supponiamo $B = 0$

$$\psi = A e^{ikx}$$

$$|\psi|^2 = (A e^{ikx})^* (A e^{ikx}) = (A^* e^{-ikx})(A e^{ikx}) = |A|^2$$

QUANTO VALE IL MOMENTO LINEARE IN QUESTO STATO ?

dai postulati della meccanica quantistica (**4** $\hat{x} = x \times$ $\hat{p}_x = \dfrac{\hbar}{i} \dfrac{d}{dx}$)

$$\hat{p}_x \Psi = \frac{\hbar}{i} \frac{d}{dx} \Psi = \frac{\hbar}{i} A i k e^{ikx} = \hbar k \, A e^{ikx} = \hbar k \, \Psi$$

dunque il momento lineare $p_x = \hbar k$

Principi Quanto-Meccanici

Informazioni contenute nella funzione d'onda

se supponiamo $B = 0$

$$\psi = A e^{ikx}$$

$$|\psi|^2 = (A e^{ikx})^* (A e^{ikx}) = (A^* e^{-ikx})(A e^{ikx}) = |A|^2$$

se supponiamo $A = 0$

$$|\psi|^2 = |B|^2$$

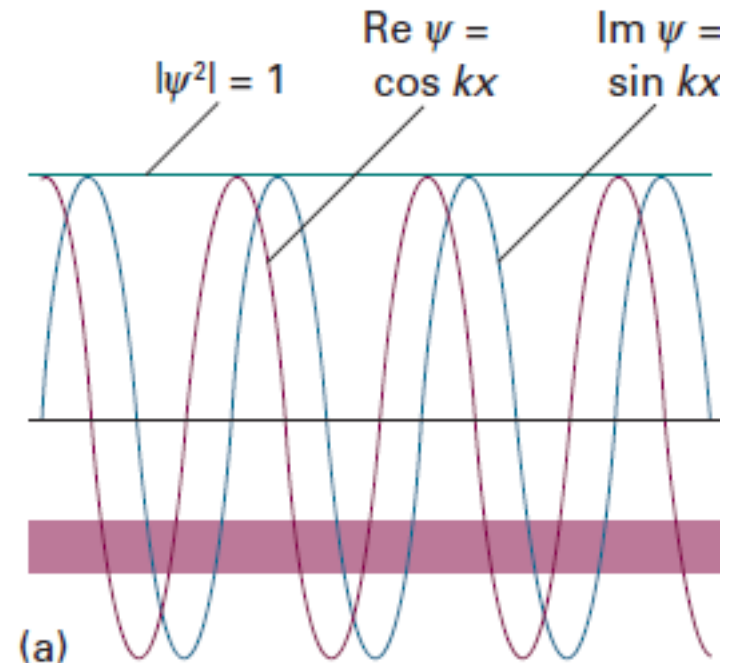Energia cinetica ($k^2\hbar^2/2m$) definita

$\Downarrow$

Momento lineare ($\pm k\hbar$) definito

$\Downarrow$

$|\psi|^2$ è una costante;

$\Downarrow$

Probabilità uniforme di trovare la particella ovunque

$|\psi^2| = 1$ Re $\psi =$ cos kx Im $\psi =$ sin kx

(a)

Principi Quanto-Meccanici

Informazioni contenute nella funzione d'onda

supponiamo $A = B$.

$$\psi = A(e^{ikx} + e^{-ikx}) = 2A \cos kx$$

$$|\psi|^2 = (2A \cos kx)^*(2A \cos kx) = 4|A|^2 \cos^2 kx$$
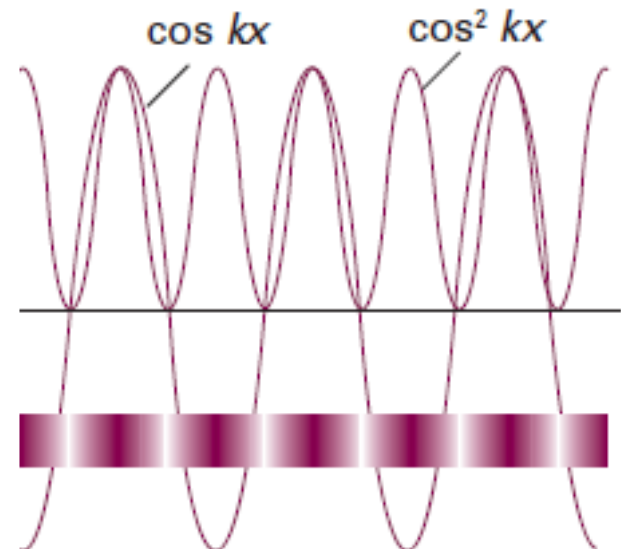
Energia cinetica ($k^2\hbar^2/2m$) definita
$\Downarrow$

Momento lineare ($\pm k\hbar$) definito
$\Downarrow$

$|\psi|^2$ **NON** è una costante;
$\Downarrow$

Probabilità **NON** uniforme di trovare la particella ovunque

$\cos kx$ $\cos^2 kx$

Principi Quanto-Meccanici

The construction of operators

Observables. Observables, Ω, are represented by operators, $\hat{\Omega}$, built from position and momentum operators of the form

$$\hat{x} = x \times \qquad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$$

Supponiamo di voler costruire l'operatore corrispondente all'energia potenziale $V(x) = \frac{1}{2}kx^2$, con k costante. Segue dal postulato 4 che

$$V(x) \rightarrow \boxed{\hat{V}(x) = \tfrac{1}{2}kx^2 \times} \text{ (moltiplica per } x^2 \text{ e poi per la}$$

costante ½k)

Analogamente per l'energia cinetica E_k in un moto monodimensionale lungo x ,

$$E_k = \tfrac{1}{2}mv_x^2 = p_x^2/2m , \quad \text{porta a :}$$

$$E_k \rightarrow \boxed{\hat{E}_k} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right) = \boxed{-\frac{\hbar^2}{2m}\left(\frac{d}{dx}\right)^2} \text{ (fai la derivata}$$

seconda e poi moltiplica per la costante $-\frac{\hbar^2}{2m}$)

Principi Quanto-Meccanici

Hermitian operators

Condizione di Hermiticità.

Se l'operatore $\hat{\Omega}$ è Hermitiano allora soddisfa la

$$\text{Hermiticity:} \int \psi_i^* \hat{\Omega} \psi_j \, \mathrm{d}x = \left\{ \int \psi_j^* \hat{\Omega} \psi_i \, \mathrm{d}x \right\}^*$$

E' facile facile confermare che l'operatore della posizione (x·) è hermitiano perché siamo liberi per cambiare l'ordine dei fattori nell'integranda

$$\int_{-\infty}^{\infty} \psi_i^* x \psi_j \, \mathrm{d}x = \int_{-\infty}^{\infty} \psi_j x \psi_i^* \mathrm{d}x = \left\{ \int_{-\infty}^{\infty} \psi_j^* x \psi_i \, \mathrm{d}x \right\}^*$$

Principi Quanto-Meccanici

Hermitian operators

Condizione di Hermiticità.
Se l'operatore $\hat{\Omega}$ è Hermitiano allora soddisfa la

$$\text{Hermiticity:} \int \psi_i^* \hat{\Omega} \psi_j \, dx = \left\{ \int \psi_j^* \hat{\Omega} \psi_i \, dx \right\}^*$$

Gli operatori hermitiani sono enormemente importanti in virtù di due proprietà:

1. i loro autovalori sono reali, e
2. le loro autofunzioni sono "ortogonali" tra loro.

Tutte le osservabili hanno valori reali (in senso matematico, come ad esempio x = 2m e E = 10 J), quindi tutte le osservabili sono rappresentate da operatori hermitiani.

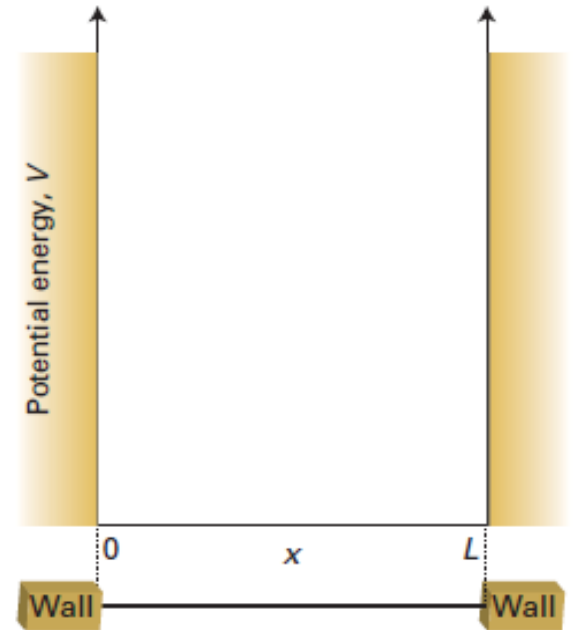$$\text{Orthogonality:} \int \psi_i^* \psi_j \, d\tau = 0$$

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Sistemi semplici Quanto-Meccanici
Particella nella scatola (di $E_{potenziale}$)

IMPORTANZA DI QUESTO SISTEMA

- Questa è una idealizzazione (è un modello) dell'energia potenziale di una molecola "gassosa" libera di muoversi in un contenitore mono-dimensionale.
  Oppure di una perlina confinata su un filo.

- Comunque è anche la base del trattamento della struttura elettronica dei metalli.

- È anche la base di una trattazione semplificata degli elettroni **p** delle molecole coniugate.

- La particella nella scatola viene anche usata in termodinamica statistica per stimare il contributo del moto traslazionale delle molecole alle loro proprietà termodinamiche.

A particle in a one-dimensional region with impenetrable walls. **Its potential energy is zero between x = 0 and x = L**, and rises abruptly to infinity as soon as it touches the walls.

Particella nella scatola (di E$_{potenziale}$)
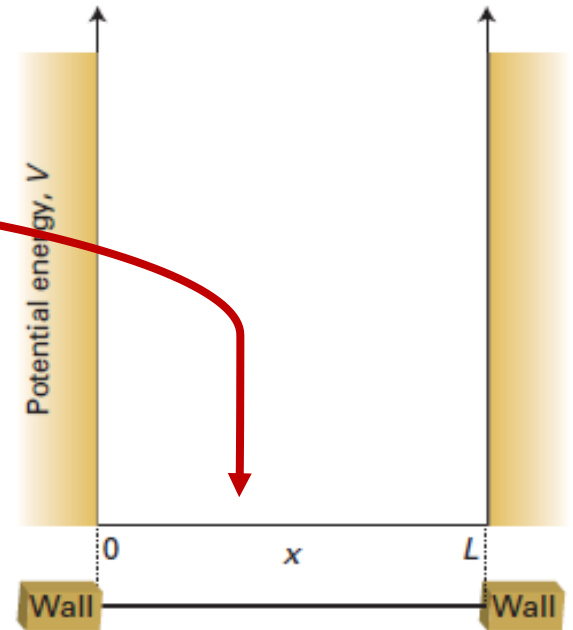
The acceptable solutions

Nella zona in cui V(x)=0

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

la equazione di Schroedinger e la soluzione generale sono uguali a quelle della particella libera:

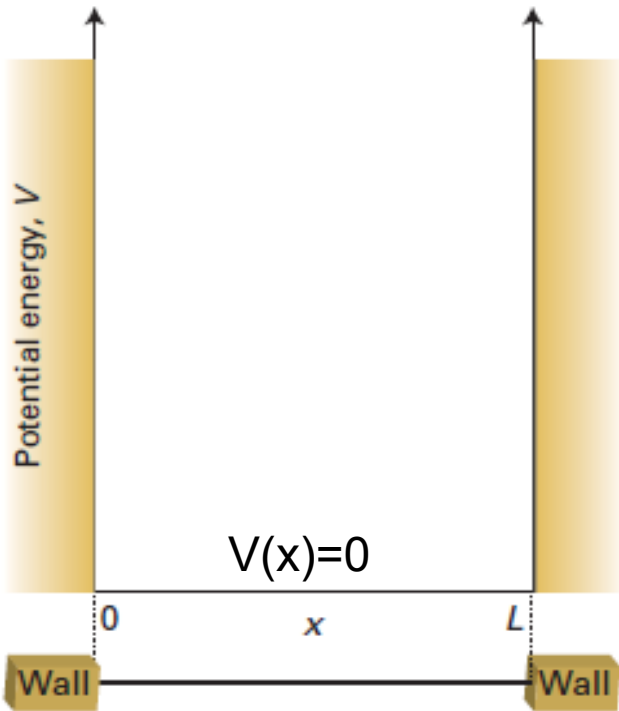$$\psi_k = Ae^{ikx} + Be^{-ikx} \qquad E_k = \frac{k^2\hbar^2}{2m}$$

Si può usare la relazione $e^{\pm ix} = \cos x \pm i \sin x$ per riscrivere la ψ_k in un'altra forma:

$$\psi_k = Ae^{ikx} + Be^{-ikx} = A(\cos kx + i \sin kx) + B(\cos kx - i \sin kx)$$
$$= (A + B)\cos kx + (A - B)i \sin kx$$

Particella nella scatola
Sistema monodimensionale

Potential energy, V

$V(x)=0$

0   x L

Wall   Wall

Una particella in una regione unidimensionale con pareti impenetrabili. La sua energia potenziale è zero tra x = 0 e x = L, e sale bruscamente all'infinito non appena tocca le pareti x = 0 and x = L,

$$\psi_k = Ae^{ikx} + Be^{-ikx} = A(\cos kx + i \sin kx) + B(\cos kx - i \sin kx)$$
$$= (A + B)\cos kx + (A - B)i \sin kx$$

$$\psi_k(x) = C \sin kx + D \cos kx \qquad E_k = \frac{k^2\hbar^2}{2m}$$

$$L = n \times \tfrac{1}{2}\lambda \qquad n = 1, 2, \ldots$$

$$\lambda = \frac{2L}{n} \qquad \text{with } n = 1, 2, \ldots$$

$$E = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2} \qquad \text{with } n = 1, 2, \ldots$$

$$kL = n\pi \qquad n = 1, 2, \ldots$$

$$\psi_n(x) = C \sin(n\pi x/L) \qquad n = 1, 2, \ldots$$

Teoria quantistica Sistemi semplici risolvibili esattamente

Oscillatore armonico

Chimica Fisica 2

Laurea Tri. Chim. Industriale
2022-23

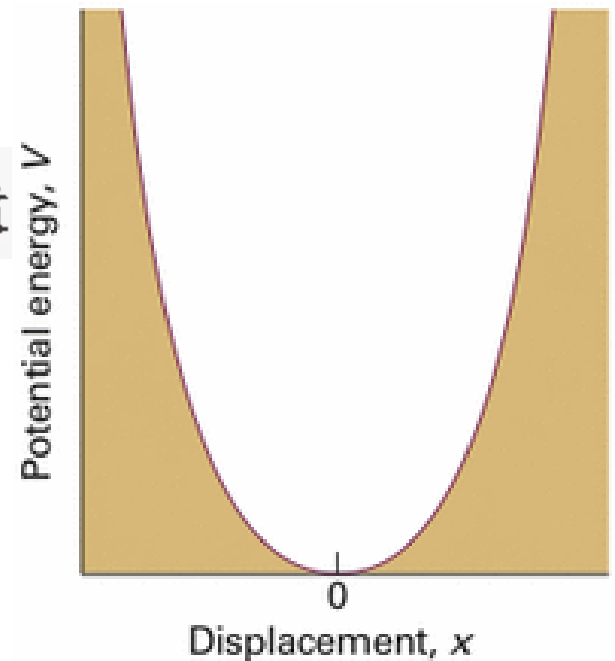*Prof. Antonio Toffoletti*

Vibrational motion
Harmonic motion

harmonic motion

$$F = -kx$$

k is the **force constant**

$$F = -dV/dx$$

Energia Potenziale $\qquad V = \frac{1}{2}kx^2$

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Vibrational motion

A particle undergoes **harmonic motion** if it experiences a 'Hooke's law' restoring force, in which the force is proportional to the displacement x, from the equilibrium position:
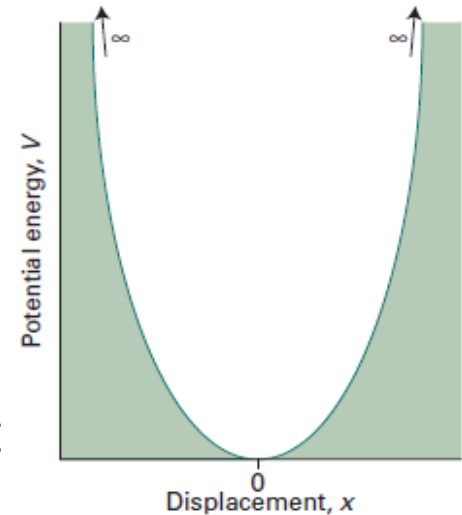
$$F = -k_f\, x \qquad (1)$$

Hooke's law

Here, k_f is the **force constant**: the stiffer the 'spring', the greater the value of k_f. Because force is related to potential energy by $F=-dV/dx$, the force in eq. (1) corresponds to a potential energy

$$V = \tfrac{1}{2}\, k_f\, x^2 \qquad (2)$$
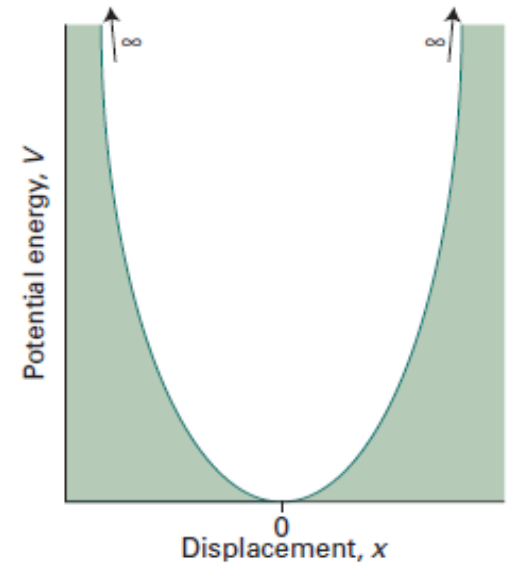
Parabolic potential energy

Vibrational motion

$$V = \tfrac{1}{2}\, k_f\, x^2 \qquad (2)$$

This expression, which is the equation of a parabola (see the Figure), is the origin of the term 'parabolic potential energy' for the potential energy characteristic of a harmonic oscillator. The Schrödinger equation for the particle is therefore

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}k_f x^2 \psi = E\psi \qquad (3)$$

The parabolic potential energy $V = \tfrac{1}{2}\, k_f\, x^2$ of a harmonic oscillator, where x is the displacement from equilibrium. The narrowness of the curve depends on the force constant k: the larger the value of k, the narrower the well.

The energy levels

Key point The energies of a quantum mechanical harmonic oscillator are quantized with energies that form an equally spaced ladder.
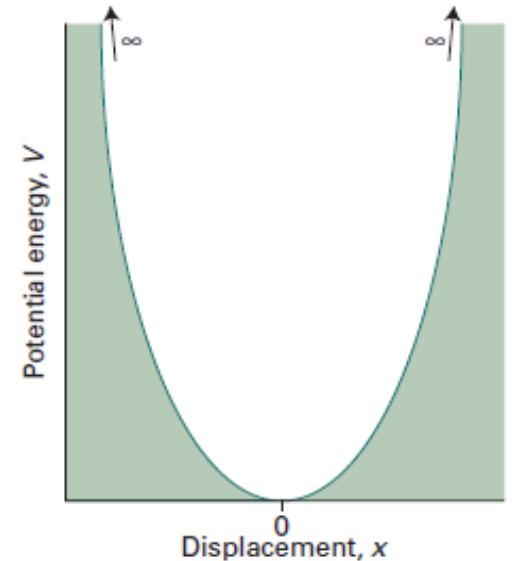
Vibrational motion

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}k_f x^2 \psi = E\psi \qquad (3)$$

The energy levels

Equation (3) is a standard equation in the theory of differential equations and its solutions are well known to mathematicians. Quantization of energy levels arises from the boundary conditions: the oscillator will not be found with infinitely large displacements from equilibrium, so the only allowed solutions are those for which $\psi = 0$ at $x = \pm\infty$. The permitted energy levels are

$$E_v = (v + 1/2)\hbar\omega \qquad \omega = (k_f/m)^{1/2} \quad v = 0, 1, 2, \ldots \quad (4)$$
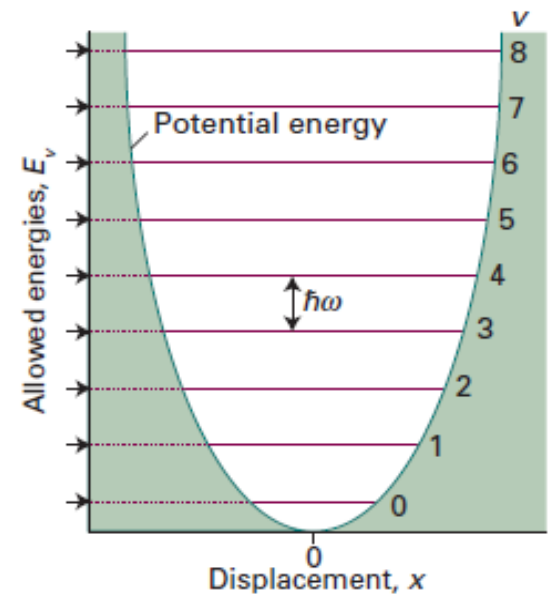
The parabolic potential energy $V = \frac{1}{2}k_f x^2$ of a harmonic oscillator, where x is the displacement from equilibrium.
The narrowness of the curve depends on the force constant k: the larger the value of k, the narrower the well.

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Vibrational motion

The energy levels

$E_v = (v + 1/2)\hbar\omega$

$\omega = (k_f / m)^{1/2}$ $v = 0, 1, 2, \ldots$ (4)

Note that ω (omega) increases with increasing force constant and decreasing mass. It follows from eqn (4) that the separation between adjacent levels is
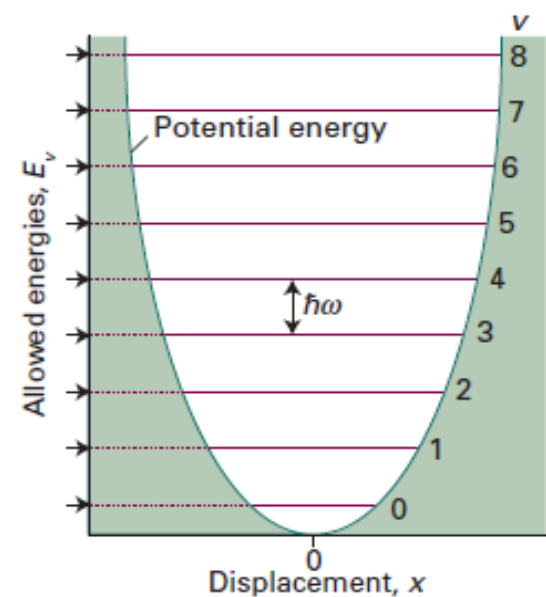
$$E_{v+1} - E_v = \hbar\omega \qquad (5)$$

which is the same for all v. Therefore, the energy levels form a uniform ladder of spacing $\hbar\omega$ (see Figure). The energy separation $\hbar\omega$ is negligibly small for macroscopic objects (with large mass), but is of great importance for objects with mass similar to that of atoms.

Vibrational motion

The energy levels

$E_v = (v + 1/2)\hbar\omega$
$\omega = (k_f / m)^{1/2}$ $v = 0, 1, 2, \ldots$ (4)

Because the smallest permitted value of v is 0, it follows from eqn (4) that a harmonic oscillator has a zero-point energy
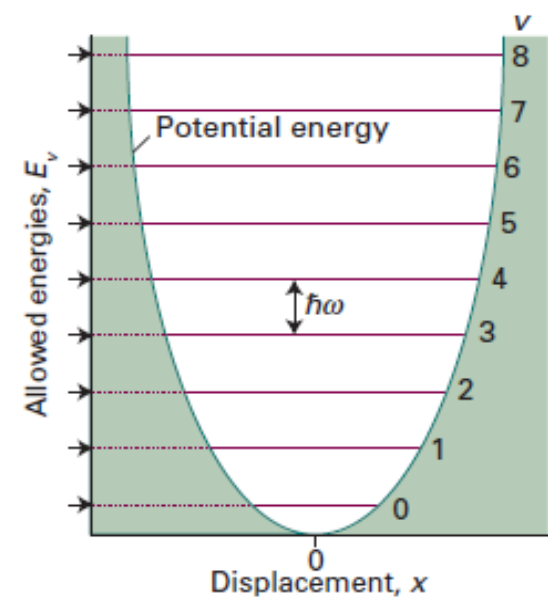
$$E_0 = \tfrac{1}{2}\hbar\omega \qquad (6)$$

The mathematical reason for the zero-point energy is that v cannot take negative values, for if it did the wavefunction would be ill-behaved. The physical reason is the same as for the particle in a square well: the particle is confined, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero.

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Vibrational motion

The energy levels

$E_v = (v + 1/2)\hbar\omega$

$\omega = (k_f/m)^{\frac{1}{2}}$ $v = 0, 1, 2, \ldots$ (4)

Because the smallest permitted value of v is 0, it follows from eqn (4) that a harmonic oscillator has a zero-point energy

$$E_0 = \tfrac{1}{2}\hbar\omega \qquad\qquad (6)$$

We can picture this zero-point state as one in which the particle fluctuates incessantly around its equilibrium position; classical mechanics would allow the particle to be perfectly still.
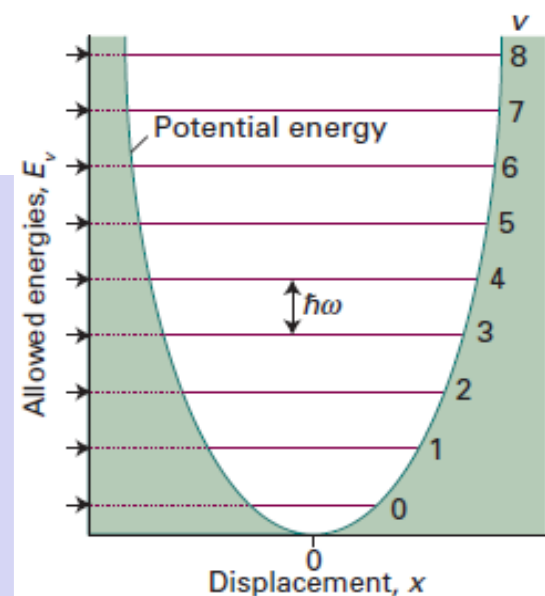
(Ferma)

Vibrational motion

The energy levels
(collegamento con l'energia in gioco nei moti interni di una molecola)

$E_v = (v + 1/2)\hbar\omega$

$\omega = (k_f / m)^{1/2}$ $v = 0, 1, 2, \ldots$ (4)

Potential energy

$\hbar\omega$

Allowed energies, E_v

0
Displacement, x

Atoms vibrate relative to one another in molecules with the bond acting like a spring. Consider an X–H bond, where a heavy X atom forms a stationary anchor for the very light H atom. That is, only the H atom moves, vibrating as a simple harmonic oscillator. Equation (4) describes the allowed vibrational energy levels of the bond. The force constant of a typical X–H chemical bond is around 500 N m^{-1}.

For example, k_f = 516.3 N m^{-1} for the ^{1}H^{35}Cl bond. Because the mass of a proton is about 1.7×10^{-27} kg, using k_f = 500 N m^{-1} in eqn (4) gives

$$\omega \approx 5.4 \times 10^{14} \text{ s}^{-1} \text{ } (5.4 \times 10^2 \text{ THz})$$
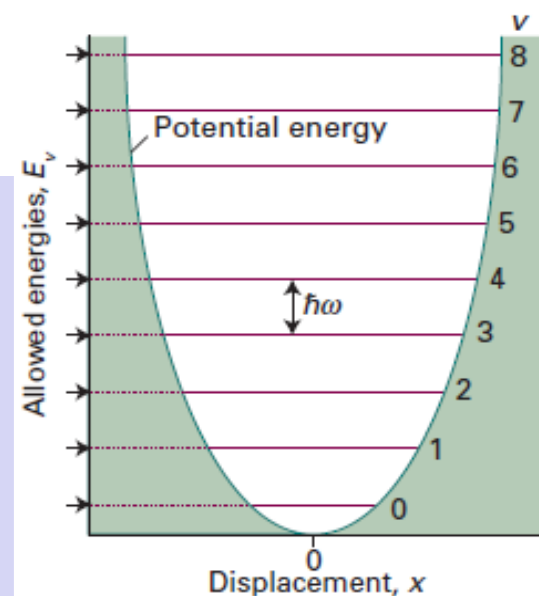
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Vibrational motion

The energy levels
(collegamento con l'energia in gioco nei moti interni di una molecola)

$E_v = (v + 1/2)\hbar\omega$

$\omega = (k_f / m)^{1/2}$ $v = 0, 1, 2, \ldots$ (4)

Consider an X–H bond, where a heavy X atom forms a stationary anchor for the very light H atom. That is, only the H atom moves, vibrating as a simple harmonic oscillator.

$$\omega \approx 5.4 \times 10^{14} \text{ s}^{-1} (5.4 \times 10^2 \text{ THz}).$$

From $E_{v+1} - E_v = \hbar\omega$, follows that the separation of adjacent levels is $\hbar\omega \approx 5.7 \times 10^{-20}$ J (57 zJ, about 0.36 eV). This energy separation corresponds to 34 kJ mol^{-1}, which is chemically significant.

The zero-point energy of this molecular oscillator is about 28 zJ, which corresponds to 0.18 eV, or 17 kJ mol^{-1}.

Vibrational motion

The wavefunctions

Key points

(a) The wavefunctions of a harmonic oscillator have the form $\psi(x) = N \times$ (Hermite polynomial in x) × (bell-shaped Gaussian function – vedi figura).
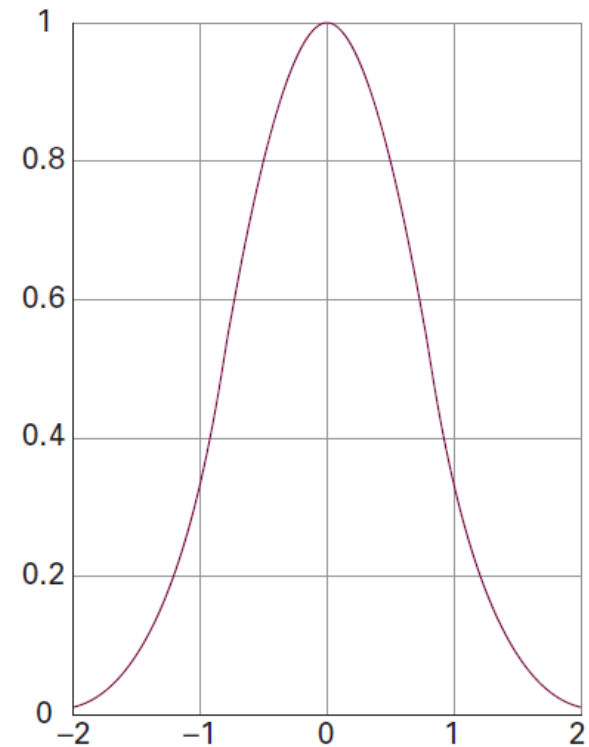
(b) The virial theorem states that, if the potential energy of a particle has the form

$$V = a\,x^b,$$

then its mean potential and kinetic energies are related by

$$2\langle E_k \rangle = b\,\langle V \rangle.$$

(c) A quantum mechanical oscillator may be found at extensions that are forbidden by classical physics.
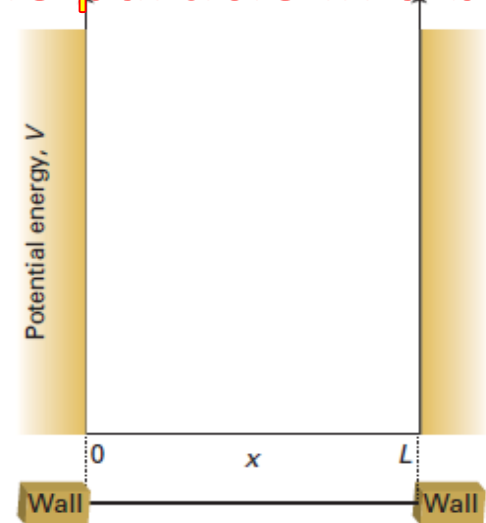
The graph of the Gaussian function, $f(x) = e^{-x^2}$. [37]
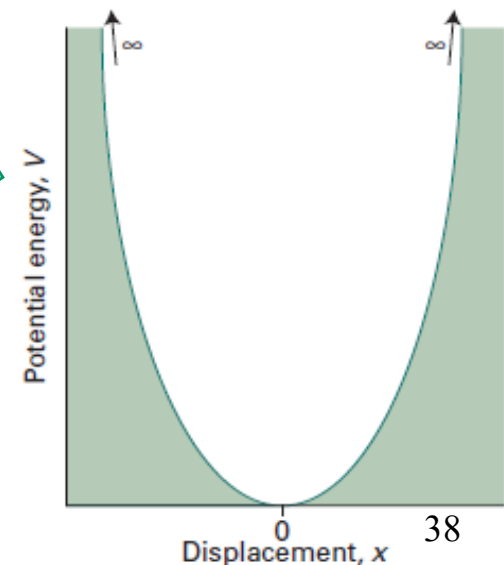
Vibrational motion

The wavefunctions

It is helpful at the outset to identify the similarities between the harmonic oscillator and the particle in a box, for then we shall be able to anticipate the form of the oscillator wavefunctions without detailed calculation.

Like the particle in a box, a particle undergoing harmonic motion is trapped in a symmetrical well in which the potential energy rises to large values (and ultimately to infinity) for sufficiently large displacements.

the Harmonic Oscillator

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Vibrational motion
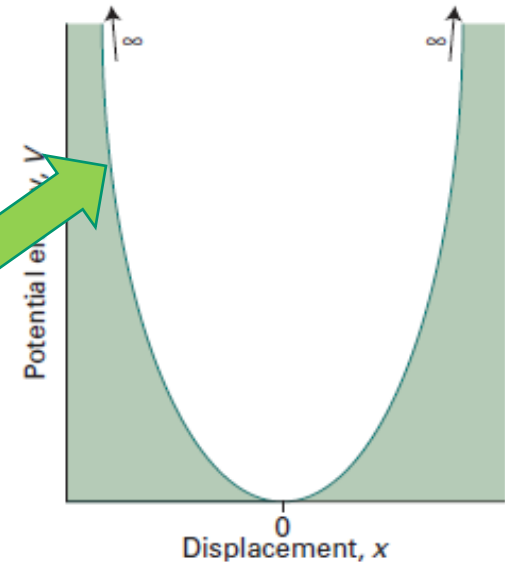
The wavefunctions

However, there are two important differences. First, because the potential energy climbs towards infinity only as x^2 and not abruptly, the wavefunction approaches zero more slowly at large displacements than for the particle in a box.

Second, as the kinetic energy of the oscillator depends on the displacement in a more complex way (on account of the variation of the potential energy), the curvature of the wavefunction also varies in a more complex way.

(a) The form of the wavefunctions

the particle in a box

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Vibrational motion

The wavefunctions

The form of the wavefunctions

The detailed solution of (3)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}k_f x^2 \psi = E\psi \qquad (3)$$
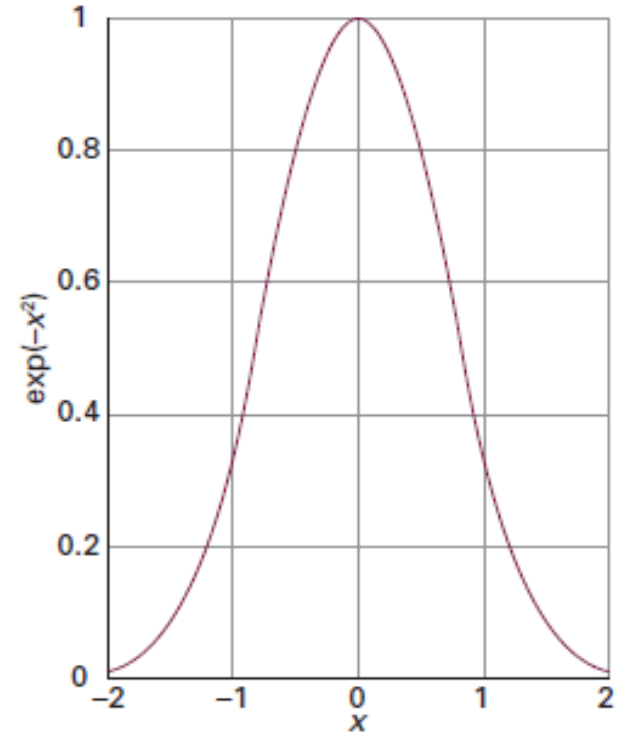
shows that the wavefunction for a harmonic oscillator has the form

$\psi(x) = N \times$ (polynomial in x) $\times$ (bell-shaped Gaussian function)

where N is a normalization constant.

A Gaussian function is a function of the form e^{-x^2} (see the Figure).

The precise form of the wavefunctions is

The graph of the Gaussian function, $f(x) = e^{-x^2}$.

Vibrational motion
Harmonic motion

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \qquad y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

The factor $H_v(y)$ is a **Hermite polynomial** (Table 8.1). Hermite polynomials are members of a class of functions called orthogonal polynomials. These polynomials have a wide range of important properties, which allow a number of quantum mechanical calculations to be done with relative ease.

Because $H_0(y) = 1$, the wavefunction for the ground state (the lowest energy state, with $v = 0$) of the harmonic oscillator is ….

Table 8.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

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Vibrational motion
Harmonic motion

$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2}$$
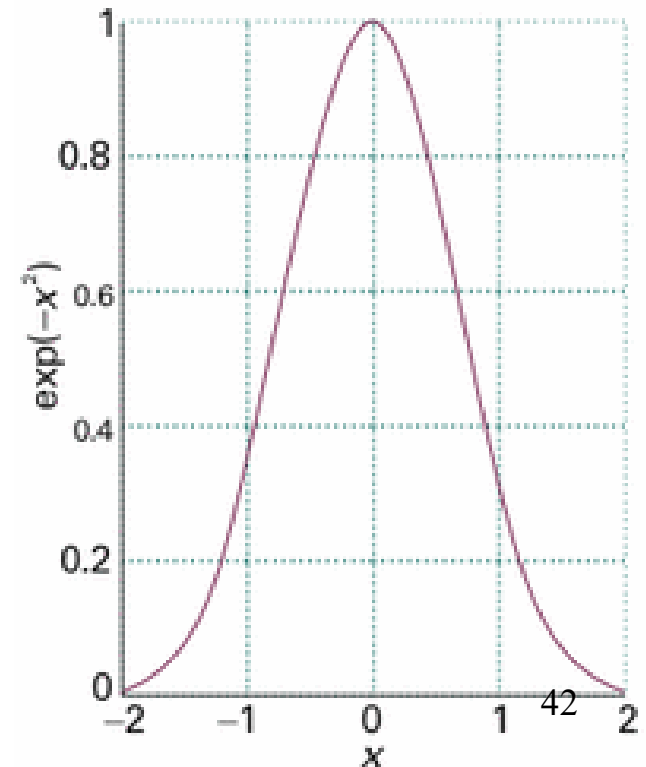
$$y = \frac{x}{\alpha}$$

$$\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

Because $H_0(y) = 1$, the wavefunction for the ground state (the lowest energy state, with $v = 0$) of the harmonic oscillator is

$$\psi_0(x) = N_0 e^{-y^2/2} = N_0 e^{-x^2/2\alpha^2}$$

It follows that the probability density is the bell-shaped Gaussian function

$$\psi_0^2(x) = N_0^2 e^{-x^2/\alpha^2}$$

Vibrational motion
Harmonic motion

The wavefunction and the probability distribution are shown in the Figure. Both curves have their largest values at zero displacement (at $x = 0$), so they capture the classical picture of the zero-point energy as arising from the ceaseless fluctuation of the particle about its equilibrium position.

Vibrational motion
Harmonic motion

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2}$$

$$y = \frac{x}{\alpha}$$

$$\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

The Hermite polynomials are solutions of the differential equation

$$H_v'' - 2yH_v' + 2vH_v = 0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2} dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2} 2^v v! & \text{if } v' = v \end{cases}$$

Table 9.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

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Vibrational motion
Harmonic motion

Table 9.1 The Hermite polynomials $H_v(y)$

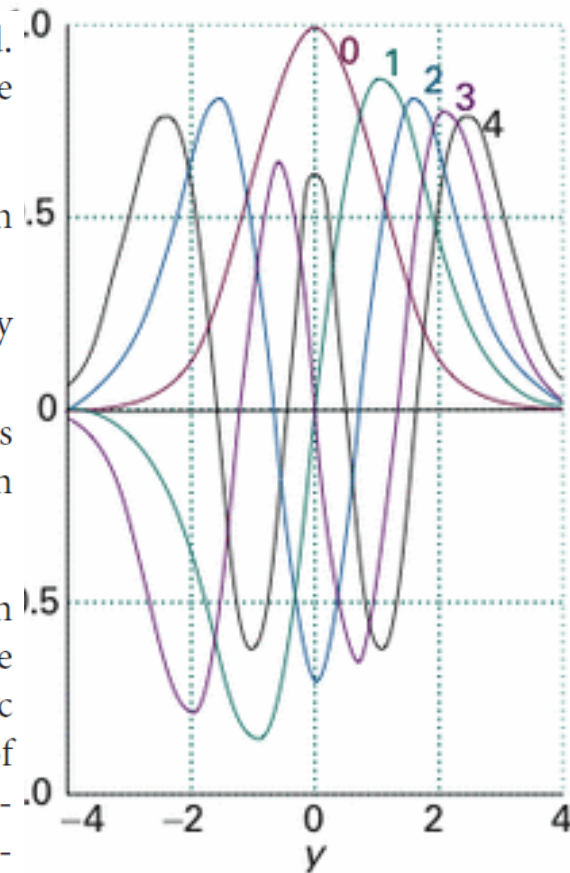| v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

Once again, we should interpret the mathematical expressions we have derived. In the case of the harmonic oscillator wavefunctions in eqn 8.27, we should note the following.

1. The Gaussian function goes quickly to zero as the displacement increases (in either direction), so all the wavefunctions approach zero at large displacements.

2. The exponent y^2 is proportional to $x^2 \times (mk_f)^{1/2}$, so the wavefunctions decay more rapidly for large masses and large force constants (stiff springs).

3. As v increases, the Hermite polynomials become larger at large displacements (as x^v), so the wavefunctions grow large before the Gaussian function damps them down to zero: as a result, the wavefunctions spread over a wider range as v increases.

The shapes of several of the wavefunctions are shown in Fig. 8.22. At high quantum numbers, harmonic oscillator wavefunctions have their largest amplitudes near the turning points of the classical motion (the locations at which $V = E$, so the kinetic energy is zero). We see classical properties emerging in the correspondence limit of high quantum numbers, for a classical particle is most likely to be found at the turning points (where it is briefly stationary) and is least likely to be found at zero displacement (where it travels most rapidly).

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Vibrational motion
Harmonic motion

3. As v increases, the Hermite polynomials become larger at large displacements (as x^v), so the wavefunctions grow large before the Gaussian function damps them down to zero: as a result, the wavefunctions spread over a wider range as v increases.
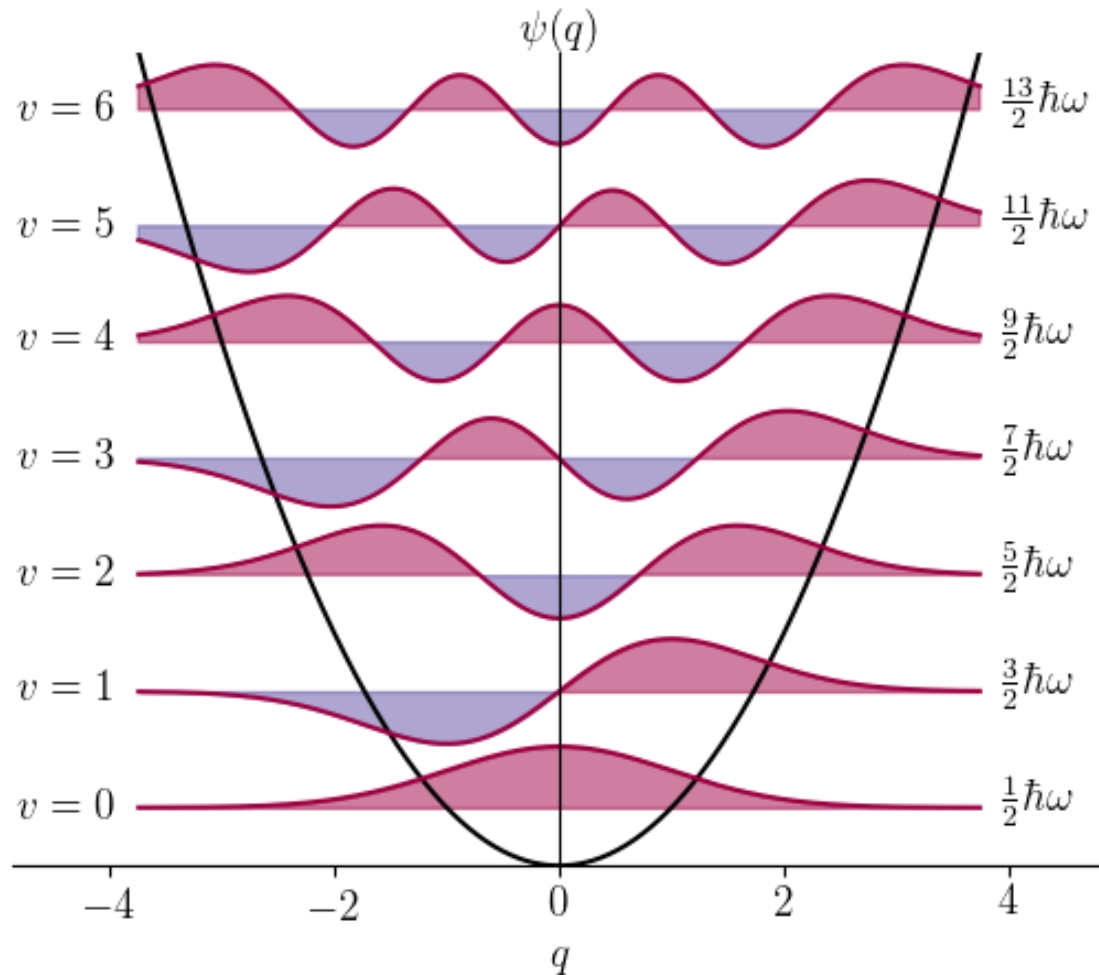
Vibrational motion
Harmonic motion
NORMALIZZAZIONE

Example 8.3 *Normalizing a harmonic oscillator wavefunction*

Find the normalization constant for the harmonic oscillator wavefunctions.

Method Normalization is always carried out by evaluating the integral of $|\psi|^2$ over all space and then finding the normalization factor from eqn 7.19. The normalized wavefunction is then equal to $N\psi$. In this one-dimensional problem, the volume element is dx and the integration is from $-\infty$ to $+\infty$. The wavefunctions are expressed in terms of the dimensionless variable $y = x/\alpha$, so begin by expressing the integral in terms of y by using $dx = \alpha dy$. The integrals required are given in Table 8.1.

Answer The unnormalized wavefunction is

$$\psi_v(x) = H_v(y)e^{-y^2/2}$$

It follows from the integrals given in Table 8.1 that

$$\int_{-\infty}^{\infty} \psi_v^* \psi_v dx = \alpha \int_{-\infty}^{\infty} \psi_v^* \psi_v dy = \alpha \int_{-\infty}^{\infty} H_v^2(y)e^{-y^2}dy = \alpha\pi^{1/2}2^v v!$$

where $v! = v(v-1)(v-2)\dots 1$. Therefore,

$$N_v = \left(\frac{1}{\alpha\pi^{1/2}2^v v!}\right)^{1/2}$$

Note that for a harmonic oscillator N_v is different for each value of v.

Vibrational motion
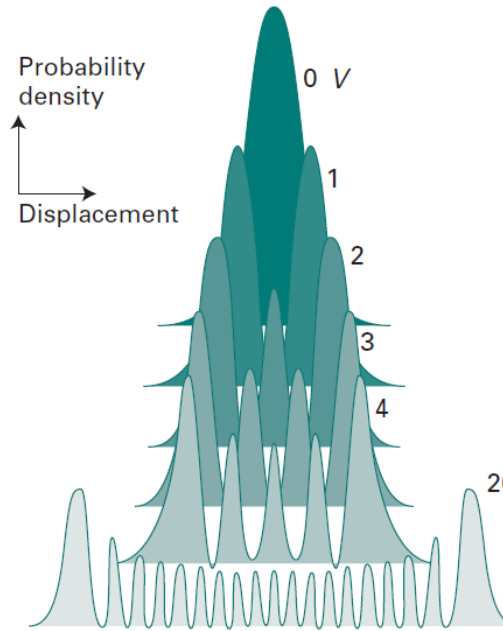## Harmonic motion

(b) The properties of oscillators

With the wavefunctions that are available, we can start calculating the properties of a harmonic oscillator. For instance, we can calculate the expectation values of an observable Ω by evaluating integrals of the type

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx \qquad (8.31)$$

(Here and henceforth, the wavefunctions are all taken as being normalized to 1.) When the explicit wavefunctions are substituted, the integrals look fearsome, but the Hermite polynomials have many simplifying features. For instance, we show in the following example that the mean displacement, $\langle x \rangle$, and the mean square displacement, $\langle x^2 \rangle$, of the oscillator when it is in the state with quantum number v are

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = (v + \tfrac{1}{2}) \frac{\hbar}{(mk_f)^{1/2}} \qquad (8.32)$$

The result for $\langle x \rangle$ shows that the oscillator is equally likely to be found on either side of $x = 0$ (like a classical oscillator). The result for $\langle x^2 \rangle$ shows that the mean square displacement increases with v. This increase is apparent from the probability densities in Fig. 8.23, and corresponds to the classical amplitude of swing increasing as the oscillator becomes more highly excited.

Probability density

Displacement

0 V

1

2

3

4

2(

Vibrational motion
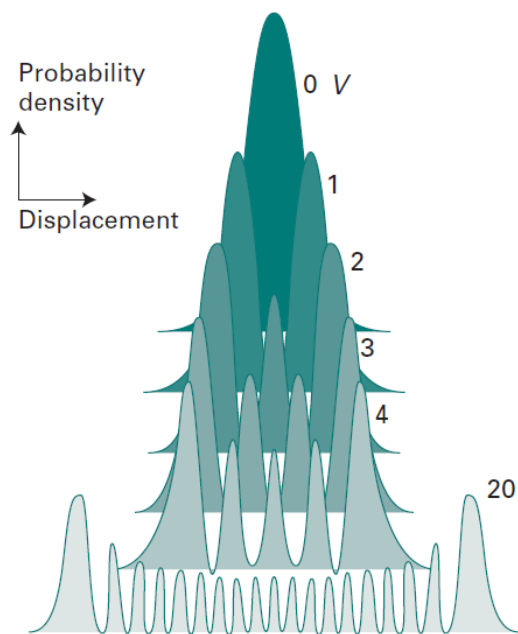## Harmonic motion
The properties of oscillators

Example 8.4 *Calculating properties of a harmonic oscillator*

We can imagine the bending motion of a CO_2 molecule as a harmonic oscillation relative to the linear conformation of the molecule. We may be interested in the extent to which the molecule bends. Calculate the mean displacement of the oscillator when it is in a quantum state v.

Method Normalized wavefunctions must be used to calculate the expectation value. The operator for position along x is multiplication by the value of x (Section 7.5c). The resulting integral can be evaluated either by inspection (the integrand is the product of an odd and an even function), or by explicit evaluation using the formulas in Table 8.1. To give practice in this type of calculation, we illustrate the latter procedure. We shall need the relation $x = \alpha y$, which implies that $dx = \alpha dy$.

Answer The integral we require is

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v^{\star} x \psi_v \, dx = N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) x (H_v e^{-y^2/2}) \, dx$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) y (H_v e^{-y^2/2}) \, dy$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy$$

Probability density

Displacement

0 V

1

2

3

4

20

50

Vibrational motion

Harmonic motion
The properties of oscillators

Answer The integral we require is

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v^{\star} x \psi_v \, dx = N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) x (H_v e^{-y^2/2}) \, dx$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) y (H_v e^{-y^2/2}) \, dy$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy$$

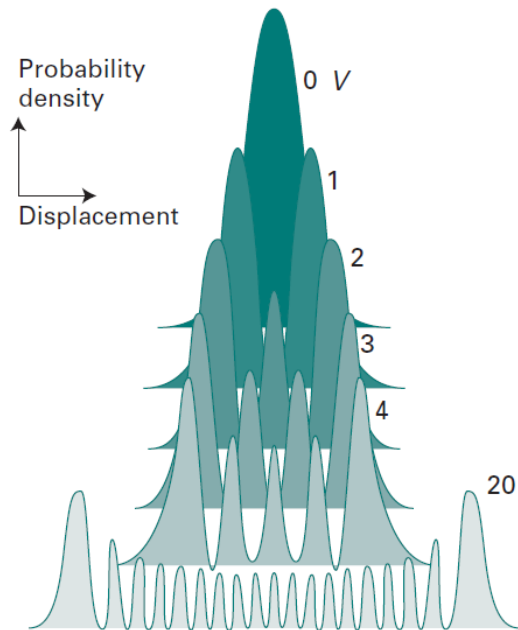Now use the recursion relation (see Table 8.1) to form

$$yH_v = vH_{v-1} + \tfrac{1}{2} H_{v+1}$$

which turns the integral into

$$\int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy = v \int_{-\infty}^{\infty} H_{v-1} H_v e^{-y^2} \, dy + \tfrac{1}{2} \int_{-\infty}^{\infty} H_{v+1} H_v e^{-y^2} \, dy$$

Both integrals are zero (see Table 8.1), so $\langle x \rangle = 0$. As remarked in the text, the mean displacement is zero because the displacement occurs equally on either side of the equilibrium position. The following *Self-test* extends this calculation by examining the mean square displacement, which we can expect to be non-zero and to increase with increasing v.

Probability density

Displacement

0 V
1
2
3
4
20

Self-test 8.7 Calculate the mean square displacement $\langle x^2 \rangle$ of the particle from its equilibrium position. (Use the recursion relation twice.)   [eqn 8.32]

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Vibrational motion

Harmonic motion
The properties of oscillators

The mean potential energy of an oscillator, the expectation value of $V = \frac{1}{2}kx^2$, can now be calculated very easily:

$$\langle V \rangle = \langle \tfrac{1}{2}k_f x^2 \rangle = \tfrac{1}{2}(v + \tfrac{1}{2})\hbar \left(\frac{k_f}{m}\right)^{1/2} = \tfrac{1}{2}(v + \tfrac{1}{2})\hbar\omega$$

Because the total energy E_v in the state with quantum number v is $(v + \frac{1}{2})\hbar\omega$, it follows that

$$\langle V \rangle = \tfrac{1}{2}E_v$$

The total energy is the sum of the potential and kinetic energies, so it follows at once that the mean kinetic energy of the oscillator is

$$\langle E_k \rangle = \tfrac{1}{2}E_v$$

The result that the mean potential and kinetic energies of a harmonic oscillator are equal (and therefore that both are equal to half the total energy) is a special case of the **virial theorem**:

If the potential energy of a particle has the form $V = ax^b$, then its mean potential and kinetic energies are related by

Virial theorem

$$2\langle E_k \rangle = b\langle V \rangle$$

For a harmonic oscillator $b = 2$, so $\langle E_k \rangle = \langle V \rangle$, as we have found. The virial theorem is a short cut to the establishment of a number of useful results, and we shall use it again.

Vibrational motion - Harmonic motion
The properties of oscillators

An oscillator may be found at extensions with $V > E$ that are forbidden by classical physics, because they correspond to negative kinetic energy. For example, it follows from the shape of the wavefunction (see Problem 8.15) that in its lowest energy state there is about an 8 per cent chance of finding an oscillator stretched beyond its classical limit and an 8 per cent chance of finding it with a classically forbidden compression.

These tunnelling probabilities are independent of the force constant and mass of the oscillator. The probability of being found in classically forbidden regions decreases quickly with increasing v, and vanishes entirely as v approaches infinity, as we would expect from the correspondence principle. Macroscopic oscillators (such as pendulums) are in states with very high quantum numbers, so the probability that they will be found in a classically forbidden region is wholly negligible. Molecules, however, are normally in their vibrational ground states, and for them the probability is very significant.

$V > E_v$

En. potenziale >

En. Totale

En. Cinetica < 0