Solving the Schrödinger equation in simple cases

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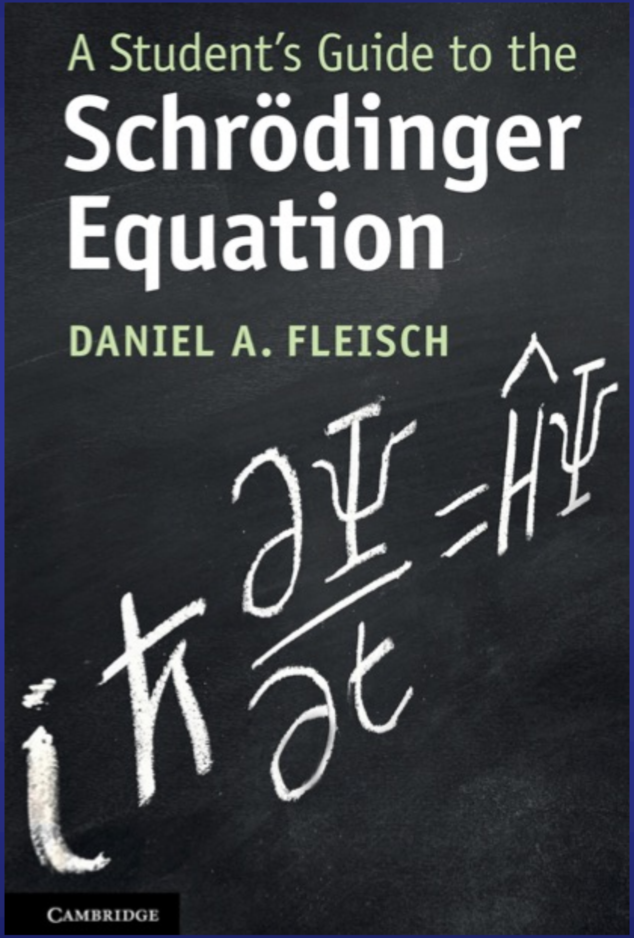
The most important reference followed in this lecture



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An EXTREMELY RECOMMENDED textbook for a new comer in the field

Outline:

The free electron gas (plane waves; metals)

The Hydrogen atom (atomic orbitals; pseudopotentials)

Quantum harmonic oscillator in 1D (thermal properties)

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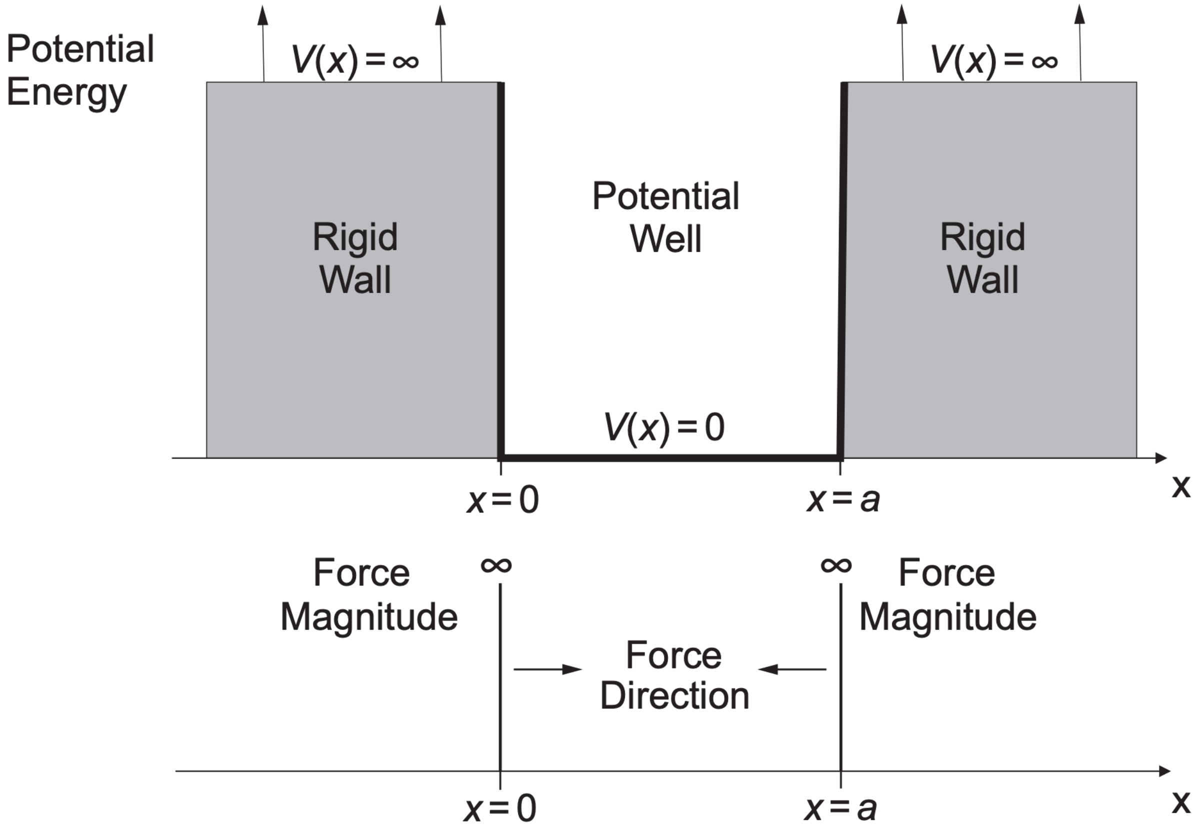
The Hydrogen atom (atomic orbitals; pseudopotentials)

Quantum harmonic oscillator in 1D (thermal properties)

The free electron gas confined in a box

Infinite rectangular potential well



A quantum particle is confined to a specified region of space (called the “potential well”) by infinitely strong forces at the edges of that region

Within the well, no force acts on the particle.

The free electron gas in an infinite square well potential (1D)

Goal:

Compute the ground state of a gas of:

- N free electrons (no interaction between themselves nor with the lattice)
- In 1-dimension
- Keeping only the Pauli exclusion principle

One electron of mass m is confined in an infinite square quantum well of length L.

The time independent Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

Kinetic energy

Energy levels of one electron in the wave function ψ_n

Boundary conditions

Due to the infinite barrier, the electrons cannot leave the crystal

$$\psi_n(x=0) = \psi_n(x=L) = 0$$

Normalization conditions

The electron is somewhere within the potential box

$$\int_{\text{box}} \psi_n^*(x)\psi_n(x)dx = 1$$

The free electron gas in an infinite square well potential (1D)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

Solution: similar to the stationary waves propagating in a string

$$\psi_n(x) = A\sin\left(\frac{2\pi}{\lambda_n}x\right)$$

$$\frac{1}{2}n\lambda_n = L$$

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right)$$

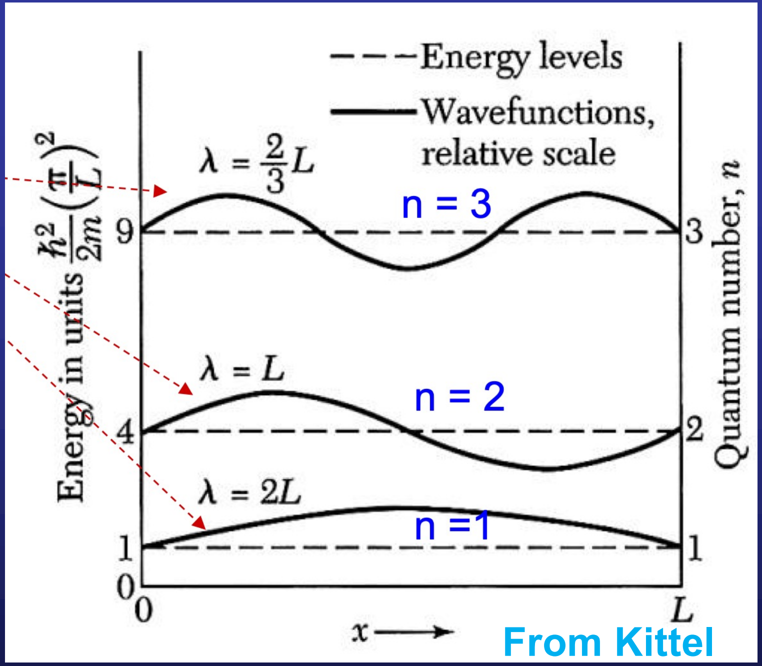
Normalization constant

$$A = \sqrt{\frac{2}{L}}$$

One electron energy levels

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

The energy is a quadratic function of the quantum number n



From Kittel

Eigenfunctions and eigenvalues of the TISE for the free electron gas in an infinite square well potential

Eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalues

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Possible outcomes of energy measurements

The wavenumbers associated with the energy eigenfunctions within the infinite rectangular well are *quantized*

They have a discrete set of possible values
the energy difference between adjacent wavefunctions increases with increasing n

The wavefunction must have zero amplitude at both edges of the well,
the only allowed wavefunctions are
those with an integer number of half-wavelengths within the well.

Fundamental differences with classical mechanics

Eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalues

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Possible outcomes of energy measurements

Classical mechanics

All positive values of the energy are allowed

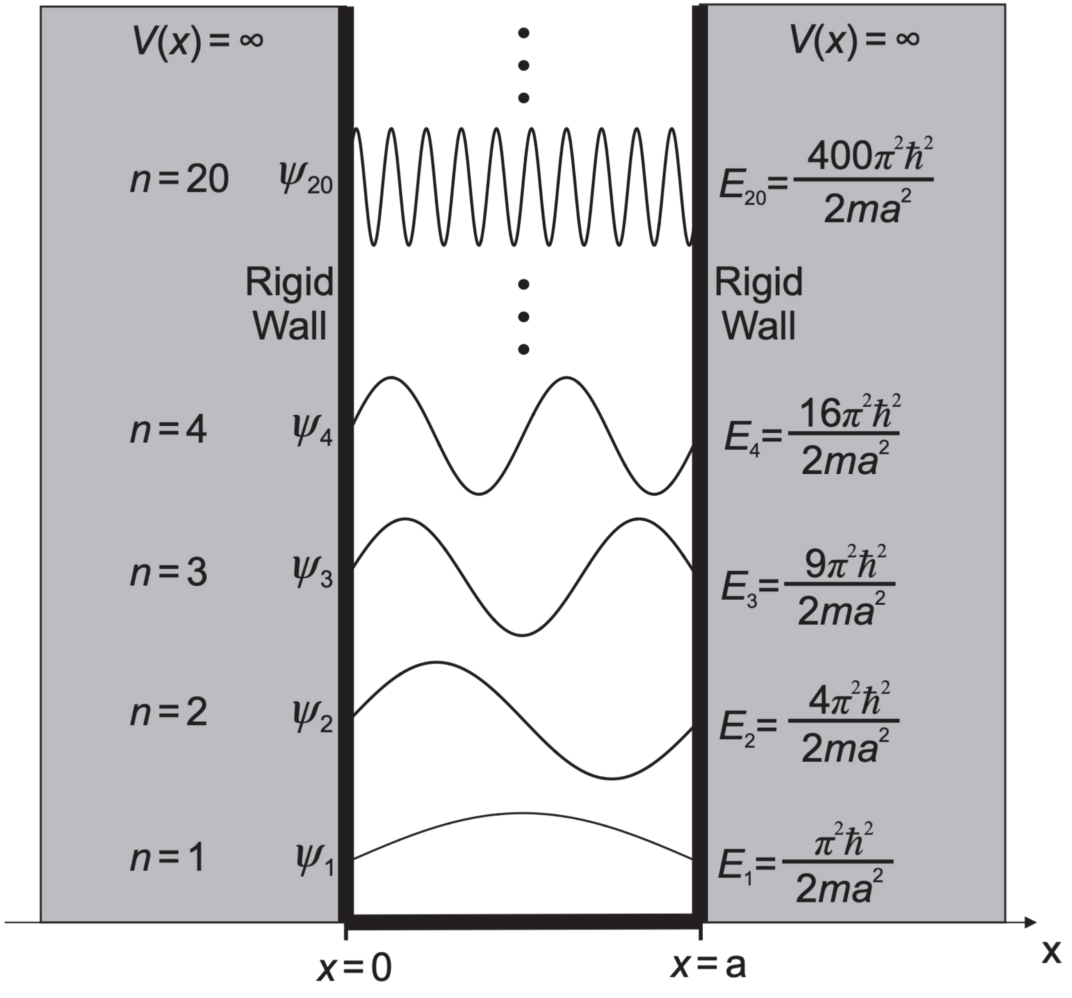
At zero temperature, the lowest energy state has zero energy

Quantum mechanics

The particle can take only certain values

At zero temperature, the lowest energy state has a non zero energy
“zero point energy”

Wave functions in an infinite quantum well



Excited states

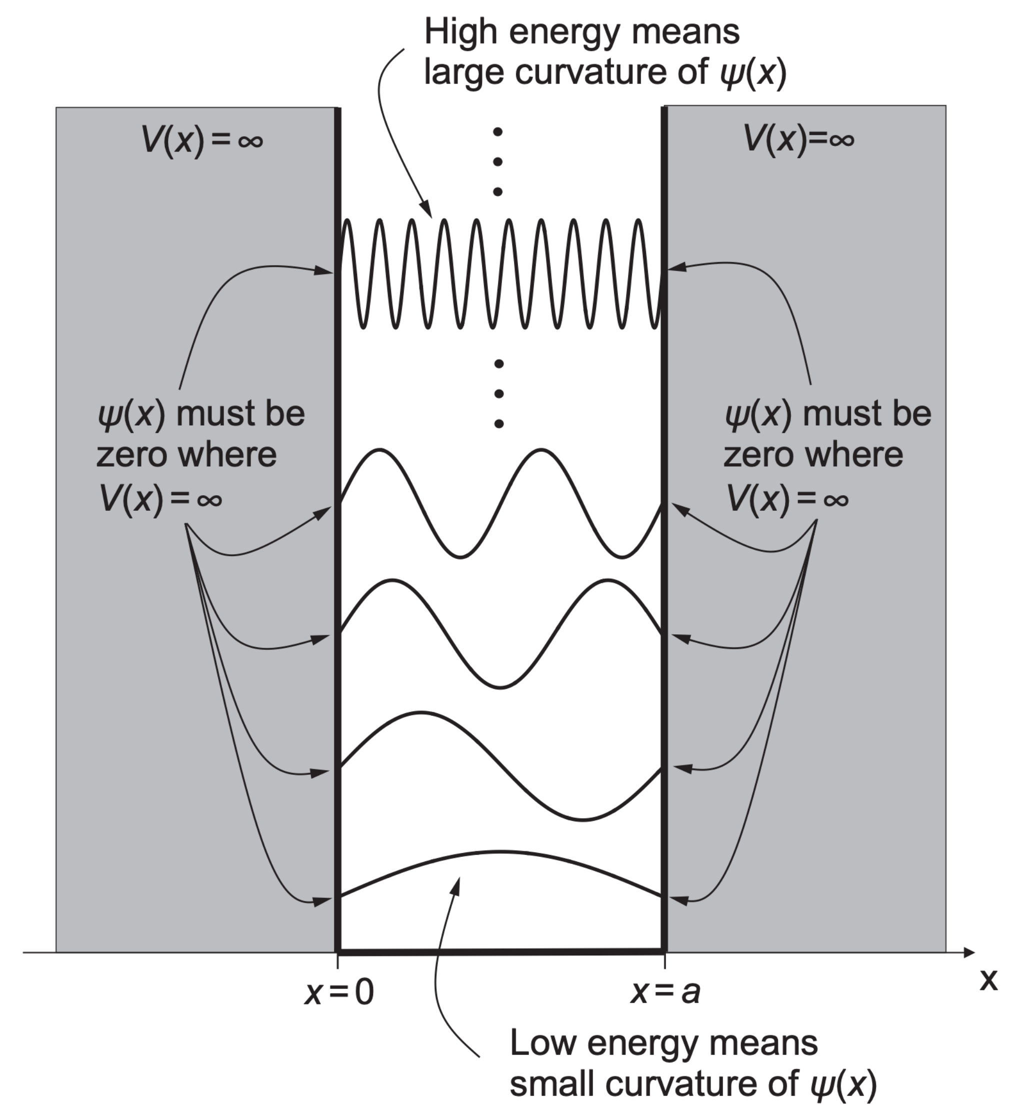
Each step up in energy level adds another half-cycle to the wavefunction across the well and another node within the well

The wavefunctions alternate between even and odd parity if the center of the well is taken as the origin

Ground state

Has a node (location of zero amplitude) at each boundary of the well, but no nodes within the well

Relation between shape of the wavefunction and energy



The free electron gas in an infinite square well: filling the one-electron levels with N electrons

Now, we have to accomodate N electrons according to the Pauli exclusion principle

There cannot be two electrons that have all their quantum numbers identical

Each orbital can be occupied by a maximum of one electron

Quantum numbers for our electrons in a 1D infinite square well

$$n$$

Positive integer

The state with $n=0$ cannot be normalized over the volumen and must be excluded

States with negative n give no new linearly independent solutions

$$m_s$$

Magnetic quantum number

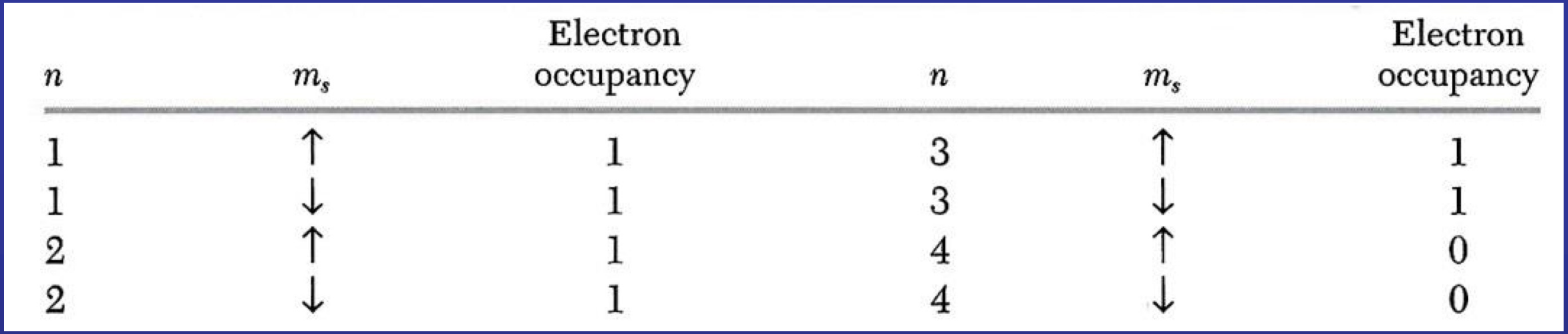
$$m_s = \pm\frac{1}{2}$$

According to spin orientation

The free electron gas in an infinite square well: filling the one-electron levels with N electrons

Example:

Filling of the one-energy levels if we have six electrons
Gound state would be



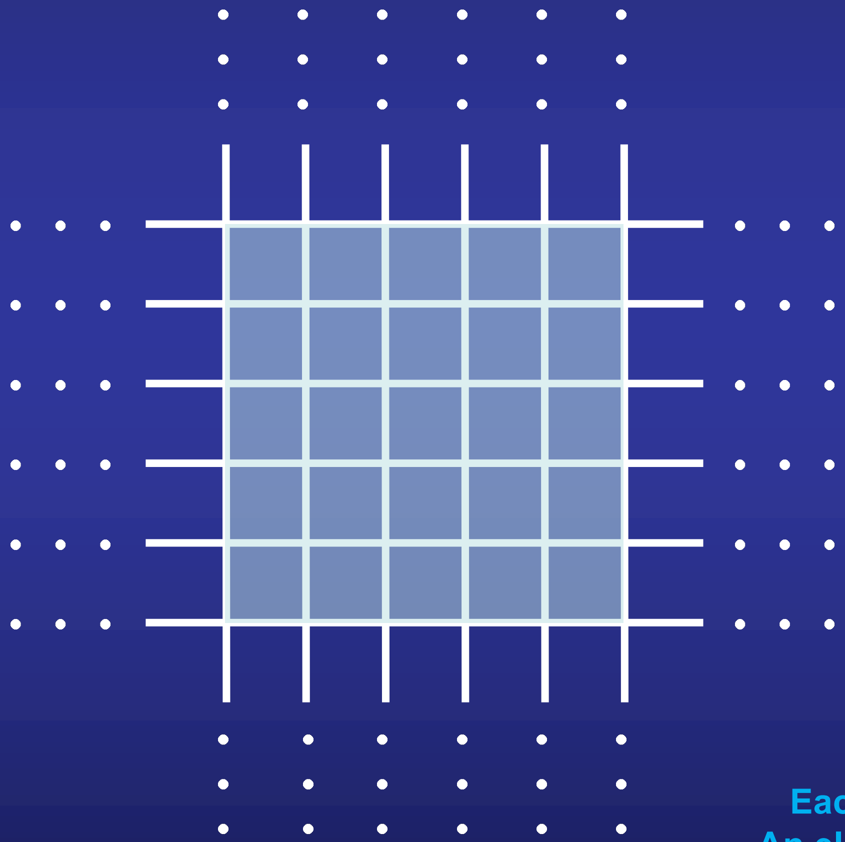
n	m_s	Electron occupancy	n	m_s	Electron occupancy
1	$\uparrow$	1	3	$\uparrow$	1
1	$\downarrow$	1	3	$\downarrow$	1
2	$\uparrow$	1	4	$\uparrow$	0
2	$\downarrow$	1	4	$\downarrow$	0

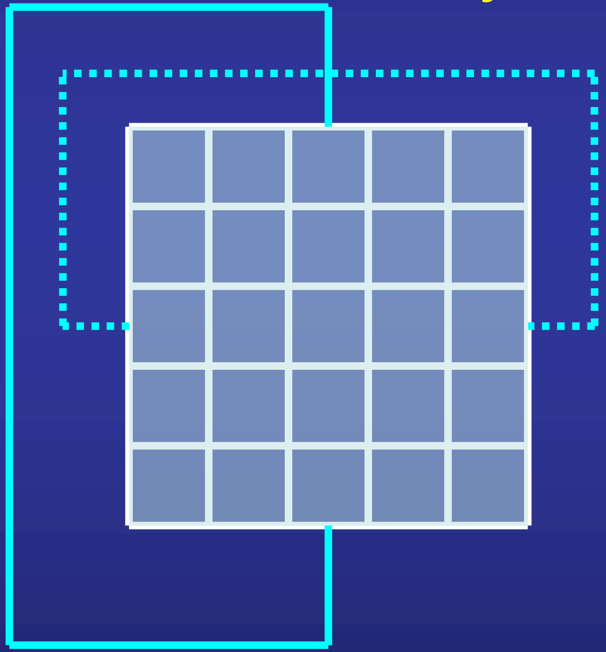
From Kittel

Periodic (Born-von Karman) boundary conditions

We should expect that the bulk properties to be unaffected by the presence of its surface.

A natural choice to emphasize the inconsequence of the surface by disposing of it altogether





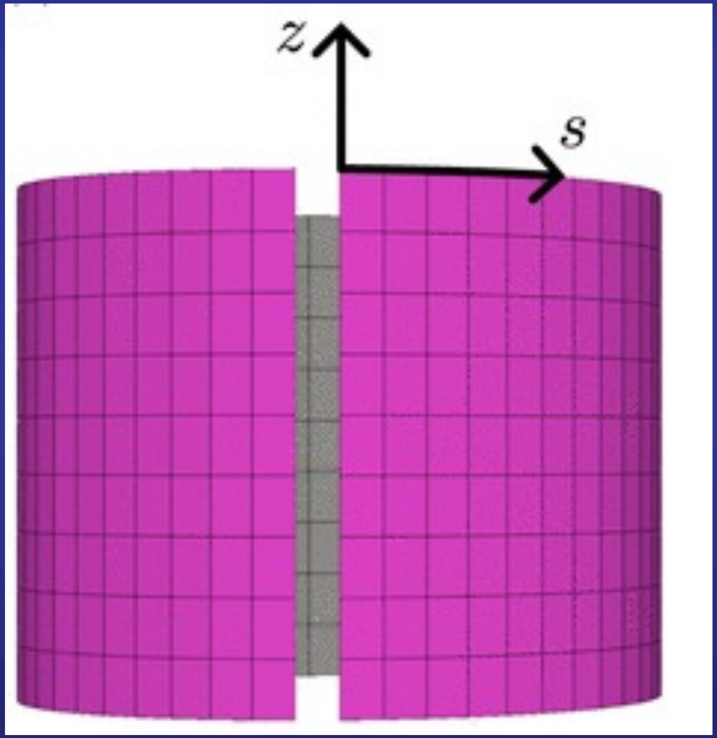
Supercell +

Born-von Karman boundary conditions

Each face of the cube is joined to the face opposite to it.
An electron coming to the “surface” is not reflected back in.
It leaves the metal, simultaneously reentering at the corresponding point on the opposite surface

Periodic (Born-von Karman) boundary conditions

Like playing "origami"



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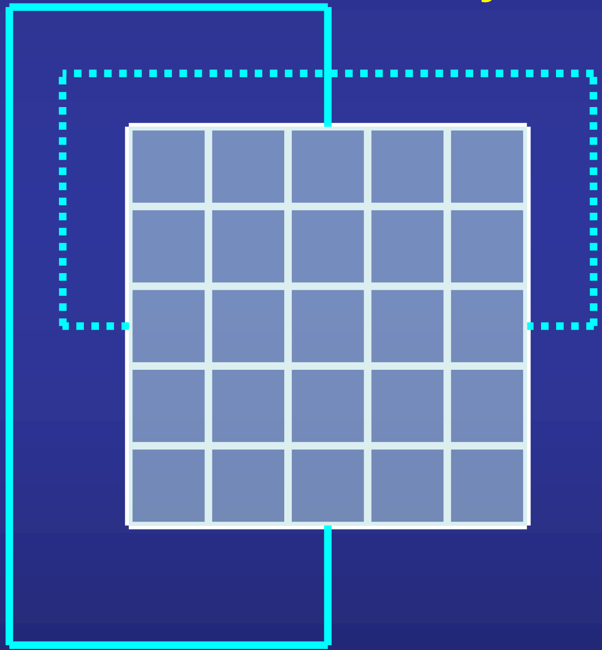
Born-von Karman boundary conditions



Each face of the cube is joined to the face opposite to it.
An electron coming to the "surface" is not reflected back in.
It leaves the metal, simultaneously reentering at the
corresponding point on the opposite surface

What happens with periodic boundary conditions?

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k})\psi_{\vec{k}}(\vec{r})$$

$$\psi_{\vec{k}}(x,y,z+L) = \psi_{\vec{k}}(x,y,z),$$
$$\psi_{\vec{k}}(x,y+L,z) = \psi_{\vec{k}}(x,y,z),$$
$$\psi_{\vec{k}}(x+L,y,z) = \psi_{\vec{k}}(x,y,z).$$

Solution: travelling plane waves

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{L^3}}e^{i\vec{k}\cdot\vec{r}}$$

These travelling waves,
in contrast with the stationary waves of the infinite well,
represent better the trasport of electronic charge

They look like plane waves with wave vector $\vec{k}$

Normalization condition $$1 = \int_V |\psi_{\vec{k}}(\vec{r})|^2 d\vec{r}$$

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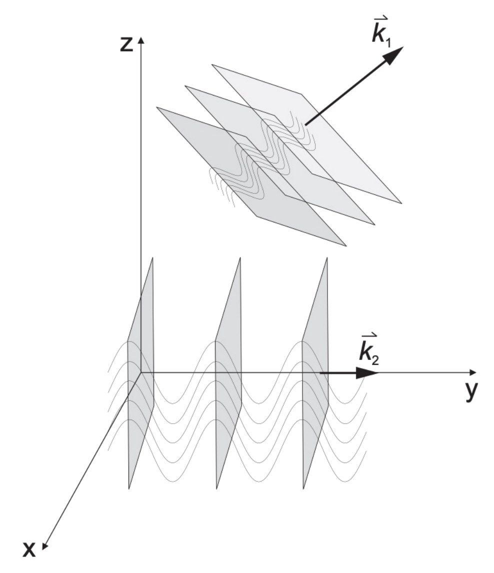
They look like plane waves with wave vector $\vec{k}$

The posible energy states are $\epsilon(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2\ k^2}{2m}$

Three dimensional plane waves

The plane wave $e^{i\vec{k}\cdot\vec{r}}$ will be constant in any plane perpendicular to and $\vec{k}$ periodic in the direction parallel to $\vec{k}$ with a wave length λ



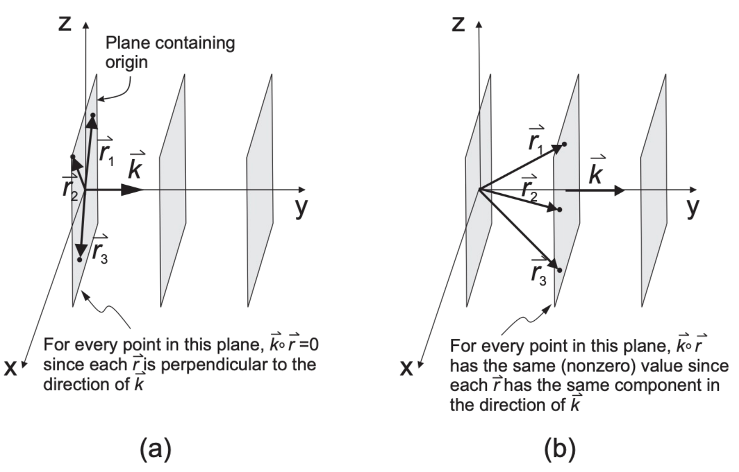


Figure 3.5 Plane-wave dot product for points in (a) plane containing origin and (b) plane displaced from origin.

The module of the wave vector is related with the wave length

$$k = \frac{2\pi}{\lambda}$$

de Broglie's wave length

A Student's Guide to the Schrödinger equation
Daniel A. Fleisch
Cambridge University Press, Cambridge, 2020
ISBN:978-1-108-81978-7

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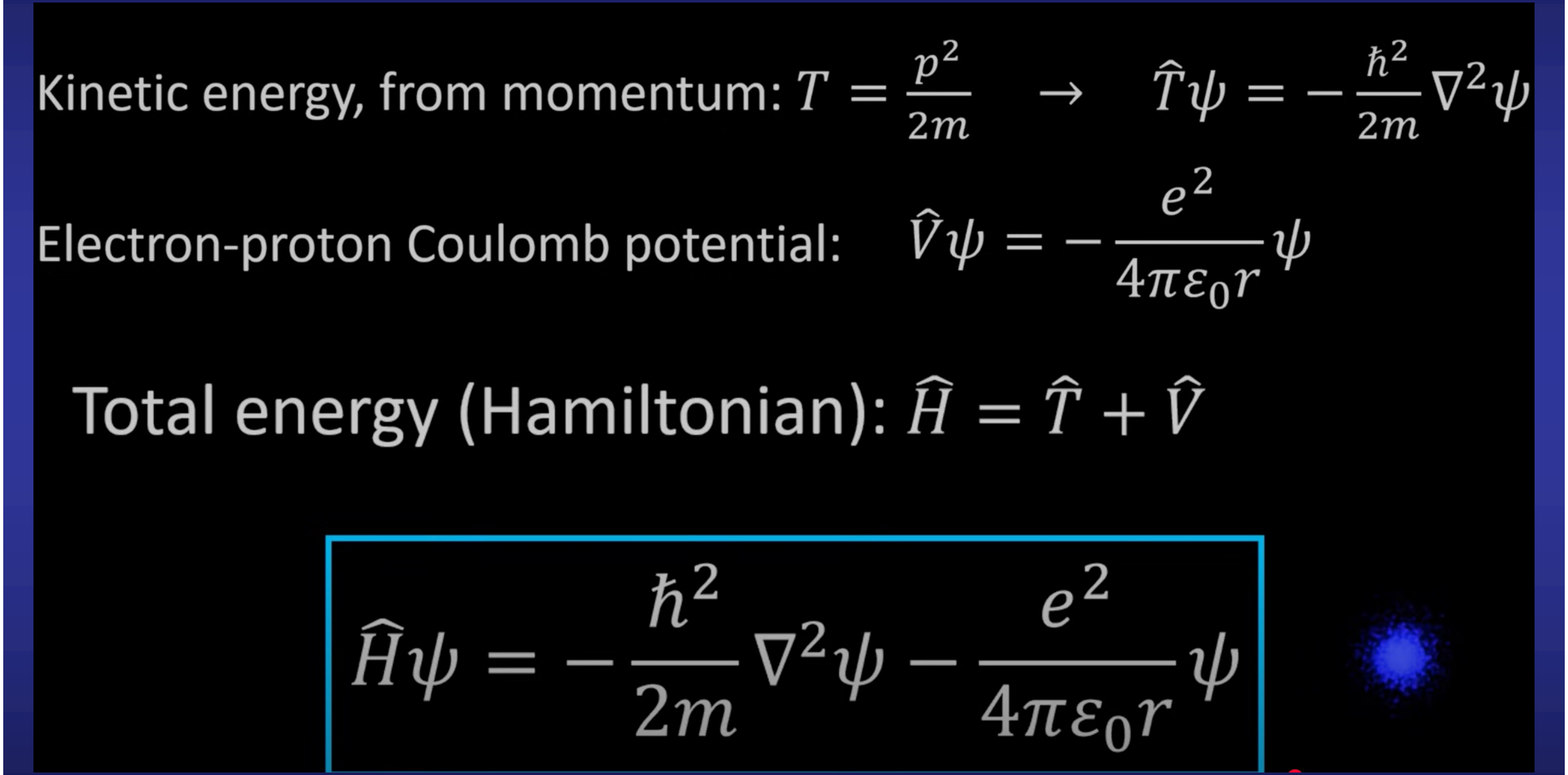
The Hydrogen atom (atomic orbitals; pseudopotentials)

Quantum harmonic oscillator in 1D (thermal properties)

Schrödinger equation for the Hydrogen atom



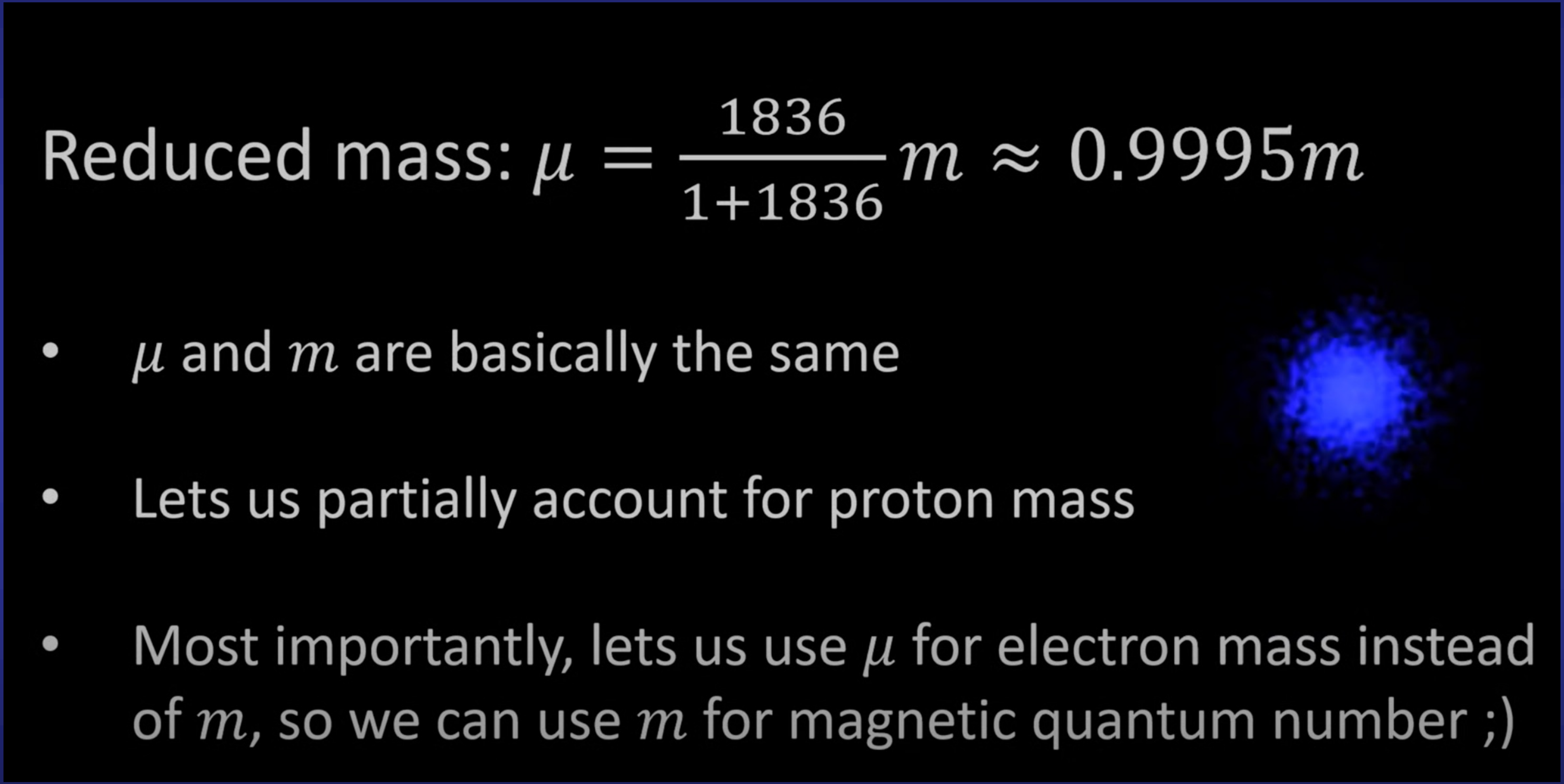
Kinetic energy, from momentum: $T = \frac{p^2}{2m} \quad \rightarrow \quad \hat{T}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi$

Electron-proton Coulomb potential: $\hat{V}\psi = -\frac{e^2}{4\pi\varepsilon_0 r}\psi$

Total energy (Hamiltonian): $\hat{H} = \hat{T} + \hat{V}$

$$\boxed{\hat{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi}$$

Schrödinger equation for the Hydrogen atom

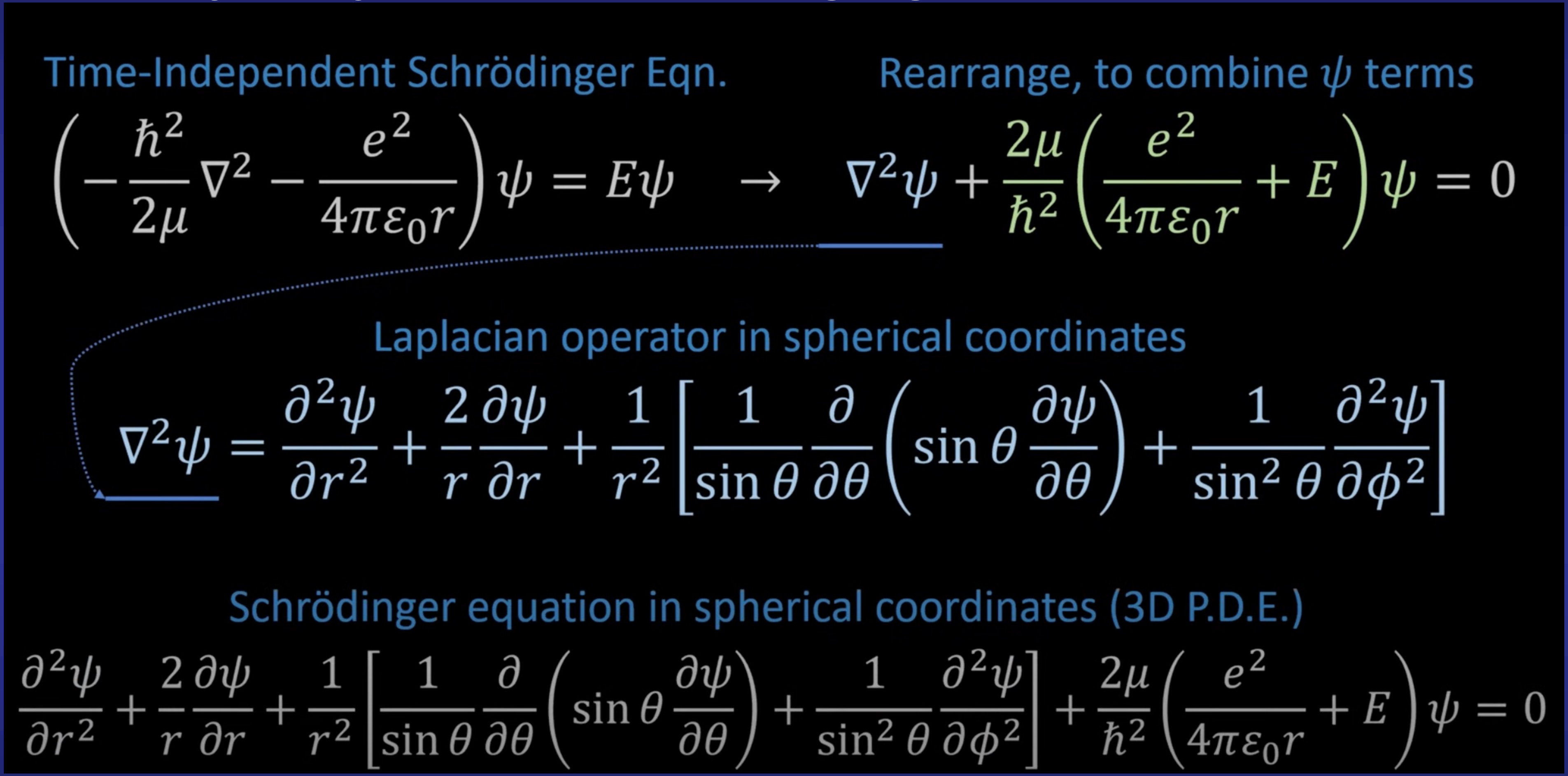


Reduced mass: $\mu = \frac{1836}{1+1836} m \approx 0.9995m$

- μ and m are basically the same
- Lets us partially account for proton mass
- Most importantly, lets us use μ for electron mass instead of m, so we can use m for magnetic quantum number ;)

Schrödinger equation for the Hydrogen atom

Due to the symmetry of the problem, we are going to use polar spherical coordinates



Time-Independent Schrödinger Eqn.

Rearrange, to combine ψ terms

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2-\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=E\psi \quad\rightarrow\quad \underline{\nabla^2\psi}+\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)\psi=0$$

Laplacian operator in spherical coordinates

$$\underline{\nabla^2\psi}=\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

Schrödinger equation in spherical coordinates (3D P.D.E.)

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)\psi=0$$

This equation can be solved by separation of variables

The wave functions are the product of a radial part times an function that only depends on the angular variables

Eigenfunctions and eigenvalues of the Schrödinger equation for the Hydrogen atom

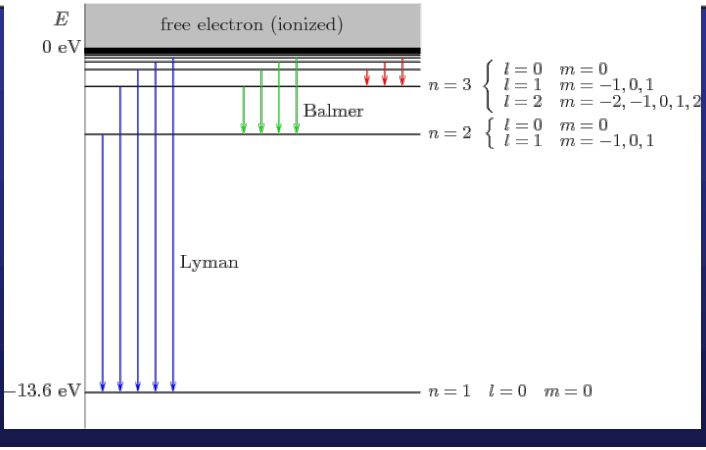
Eigenfunctions

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)e^{-iE_n t/\hbar}$$

Due to the symmetry of the problem, they are also eigenfunctions of the operators $\hat{\vec{L}}^2$ and L_z

Eigenvalues

$$\boxed{E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2} = \frac{E_1}{n^2} \qquad n = 1, 2, 3, \dots \qquad E_1 = -\frac{\hbar^2}{2m_e a_0^2} = -13.6057\ \text{eV}}$$



The atoms are not like this…
A fantastic video by “Quantum fracture”

[Los átomos no son así (The atoms are not like this)]

And also, the Hydrogen atom, by Richard Behiel

[The hydrogen atom]

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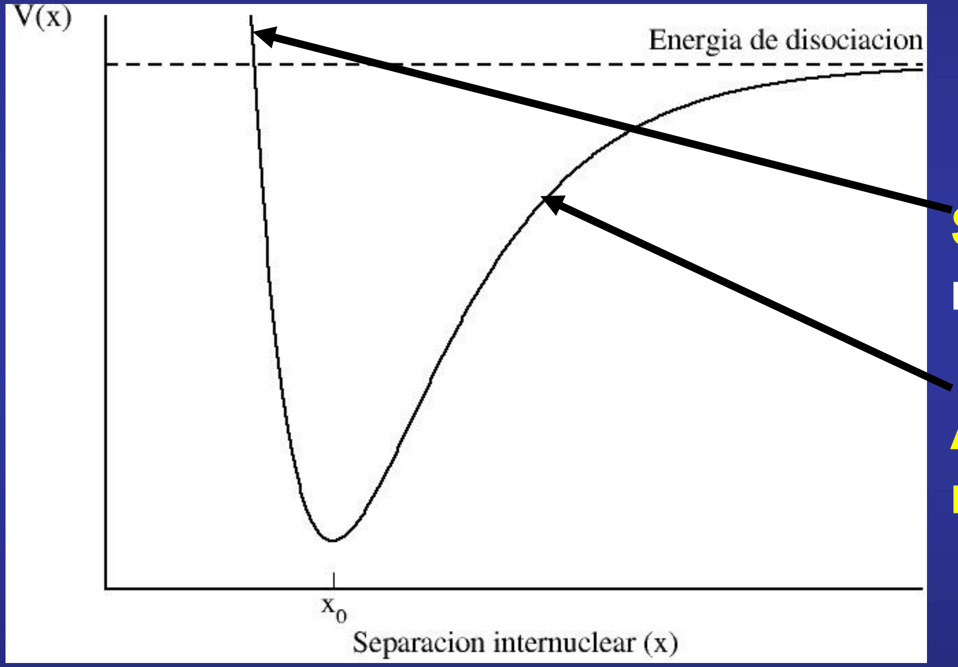
Harmonic approximation: displacements around a minimum of the potential

Consider a potential (whatever) with a minimum at x_0



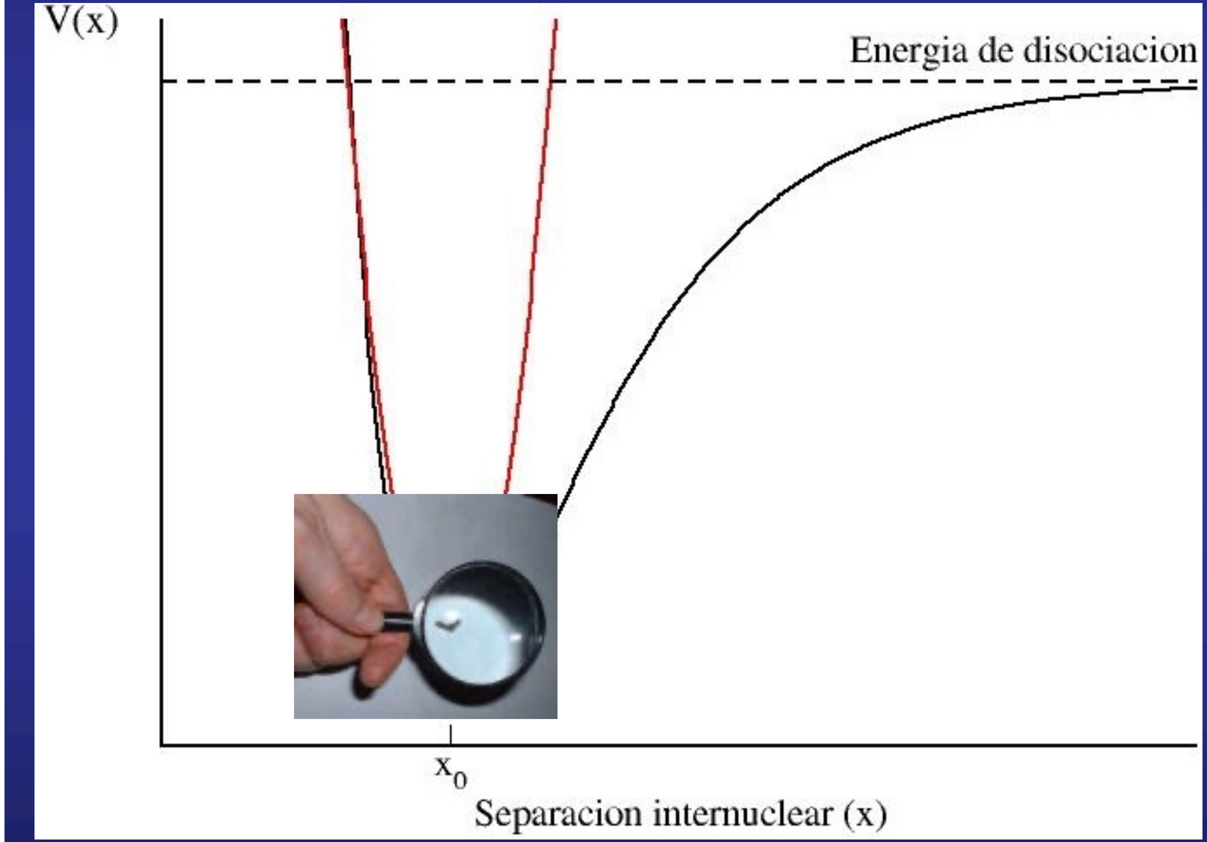
Example: interaction potential energy between two non polar molecules as a function of distance

Strong repulsion when the molecules are **very close together**

Atraction when the molecules are **more distant**

If we are interested only in what happens **only around the minimum…**

Harmonic approximation: displacements around a minimum of the potential

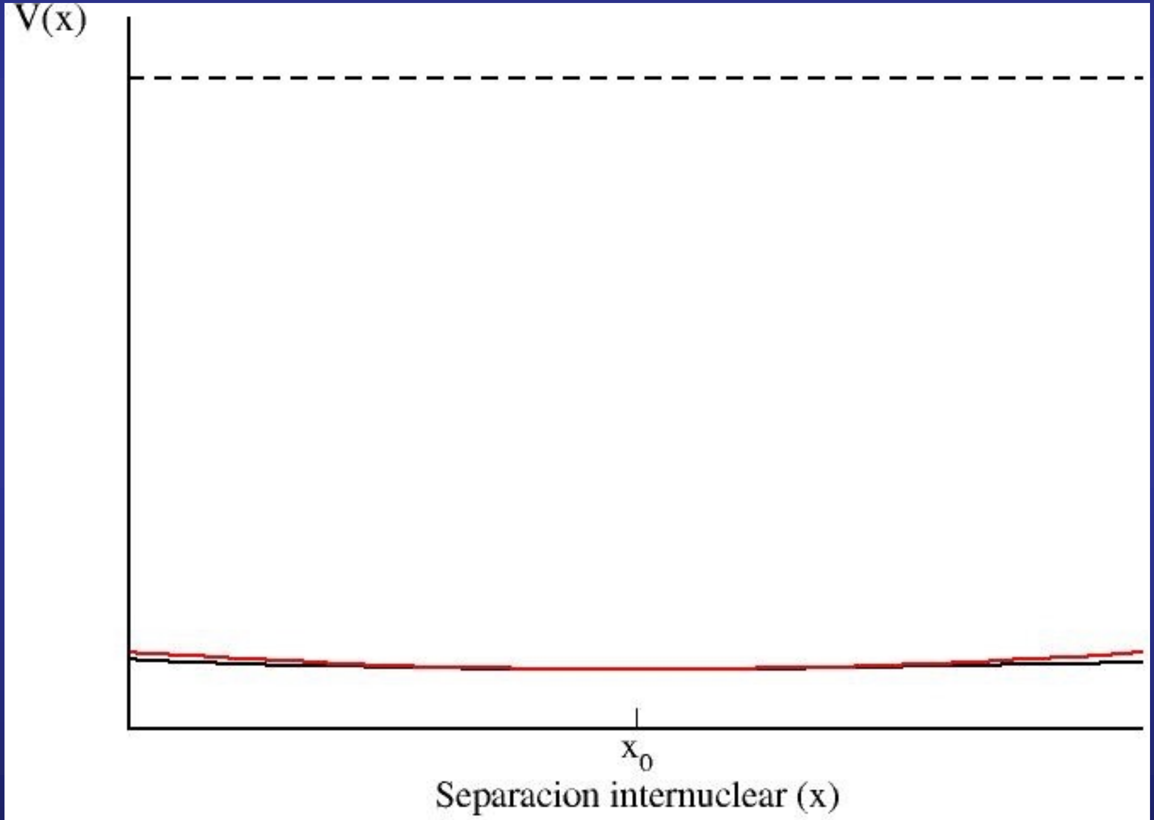


Around the minimum, we can aproximate the potential by a parabola

If the displacements are not very large, the force is proportional to the displacement

Equation of movement of the harmonic oscillator

Harmonic approximation: displacements around a minimum of the potential



Around the minimum, we can aproximate the potential by a parabola

If the displacements are not very large, the force is proportional to the displacement

Equation of movement of the harmonic oscillator

Harmonic approximation: mathematical approach

Taylor expansion of the potential around the minimum

$$V\left(x\right)=a+b\left(x-x_0\right)+c\left(x-x_0\right)^2+d\left(x-x_0\right)^3+\dots$$

$$a=V\left(x_0\right) \qquad b=\left.\frac{dV}{dx}\right|_{x=x_0} \qquad c=\left.\frac{1}{2}\frac{d^2V}{dx^2}\right|_{x=x_0} \qquad d=\left.\frac{1}{3!}\frac{d^3V}{dx^3}\right|_{x=x_0}$$

***If* x_0 is an stable equilibrium position:**

$$b=0 \qquad c>0$$

$$V\left(x\right)=a+\xcancel{b\left(x-x_0\right)}+c\left(x-x_0\right)^2+d\left(x-x_0\right)^3+\dots$$

If the displacements around x_0 are sufficiently small

$$\left(x-x_0\right) \quad \text{pequeño} \Rightarrow \left(x-x_0\right)^3<<\left(x-x_0\right)^2$$

$$V\left(x\right)\approx a+c\left(x-x_0\right)^2$$

Quantum harmonic oscillator in 1D

The potential energy is quadratic

$$V(x) = \frac{1}{2}kx^2$$

where x is the distance of the object from the equilibrium position

and k is the “spring constant”

(the force on the object per unit distance from the equilibrium position)

Quantum harmonic oscillator in 1D

The potential becomes infinite when

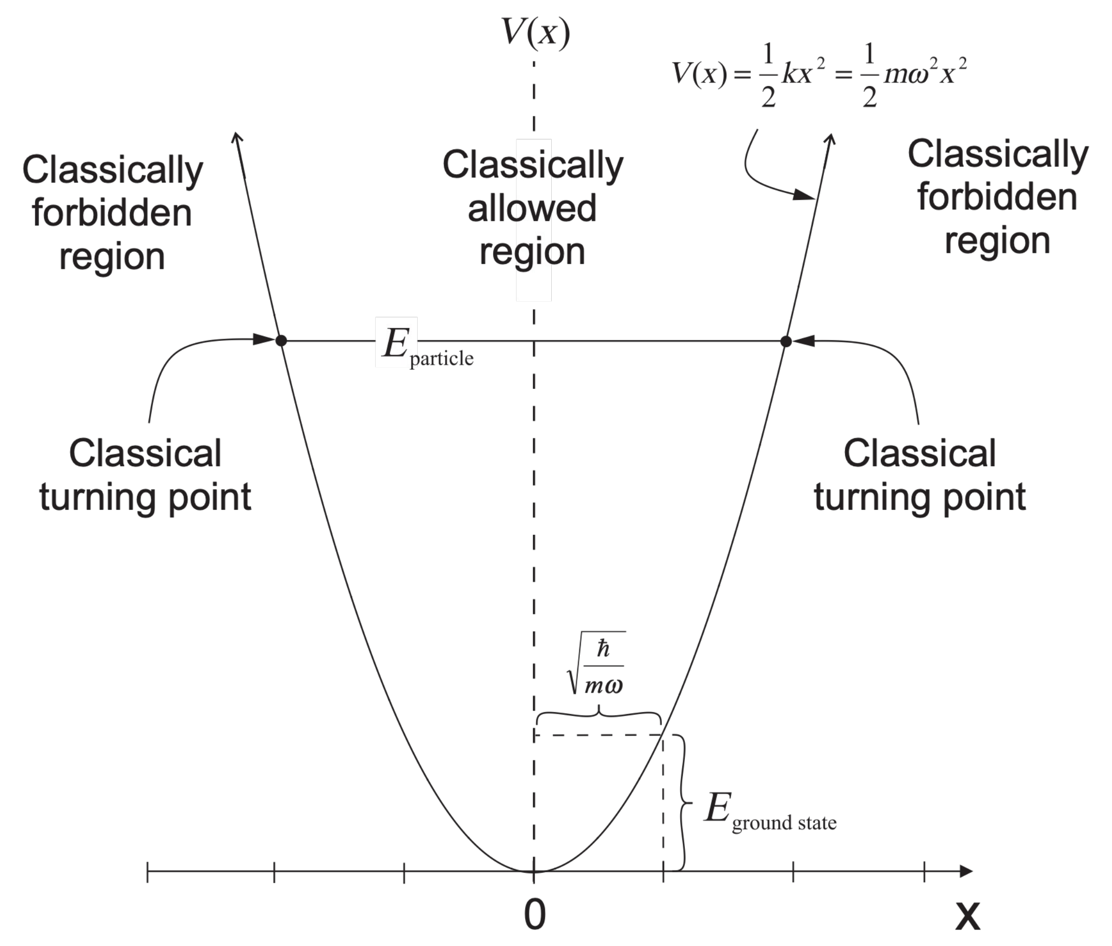
$$x \to \pm\infty$$

$$\Downarrow$$

$\psi(x)$ must be zero in regions in which the potential energy is infinite

$$\Downarrow$$

This provides the boundary conditions for the wave function of the quantum oscilator



The “depth of the well” varies continuosly with the position

The time-independent Schrödinger equation for the quantum harmonic oscillator in 1D

To find the energy levels and wave functions of the quantum harmonic oscillator, we need to solve

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

Writting the equation in terms of the angular frequency $\omega=\sqrt{k/m}$

$$\frac{d^2\psi(x)}{dx^2}-\frac{2m}{\hbar^2}\left[\frac{1}{2}m\omega^2x^2\psi(x)\right]=-\frac{2m}{\hbar^2}E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2}-\left[\frac{m^2\omega^2}{\hbar^2}x^2\psi(x)\right]+\frac{2m}{\hbar^2}E\psi(x)=0$$

$$\frac{d^2\psi(x)}{dx^2}+\left[\frac{2m}{\hbar^2}E-\frac{m^2\omega^2}{\hbar^2}x^2\right]\psi(x)=0.$$

The time-independent Schrödinger equation for the quantum harmonic oscillator in 1D

How to solve the TISE for the harmonic oscillator in 1D

$$\frac{d^2\psi(x)}{dx^2} + \left[\frac{2m}{\hbar^2}E - \frac{m^2\omega^2}{\hbar^2}x^2\right]\psi(x) = 0$$

"Analytical approach" **Use a power series**

"Algebraic approach" **Use factorization ans using a type of operator called "ladder operator"**

Eigenvalues and eigenfunctions of the TISE for the quantum harmonic oscillator in 1D

Allowed values for the energies

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

The ground-state energy

$$n = 0 \quad \Longrightarrow \quad E_0 = \frac{1}{2}\hbar\omega$$

The spacing between energy levels in the quantum harmonic oscillator is constant.

Each energy level E_n is precisely $\hbar\omega$ higher than the adjacent energy level E_{n-1}

Corresponding eigenfunctions

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(\frac{1}{\sqrt{2^n n!}}\right)H_n(\xi)e^{-\frac{\xi^2}{2}}$$

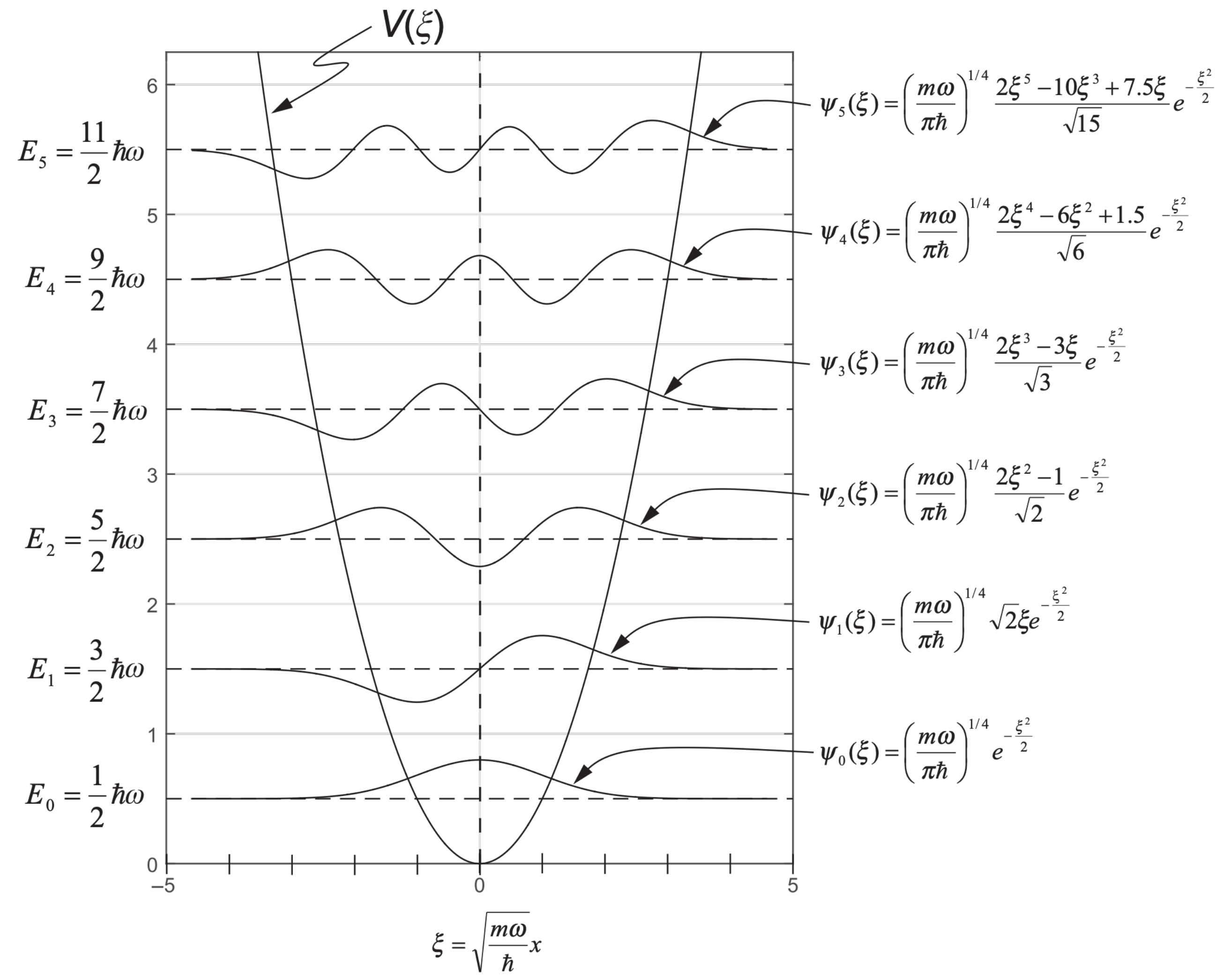
Rescaling the positions to make the solutions easer to find

Hermite polynomials

$$\xi = \frac{x}{x_{\text{ref}}} = \frac{x}{\sqrt{\frac{\hbar}{m\omega}}}$$

Complete derivation in the book by Daniel Fleisch

Eigenvalues and eigenfunctions of the TISE for the quantum harmonic oscillator in 1D



Odd
(5 nodes)

Even
(4 nodes)

Odd
(3 nodes)

Even
(2 nodes)

Odd
(1 node)

Even
(0 nodes)

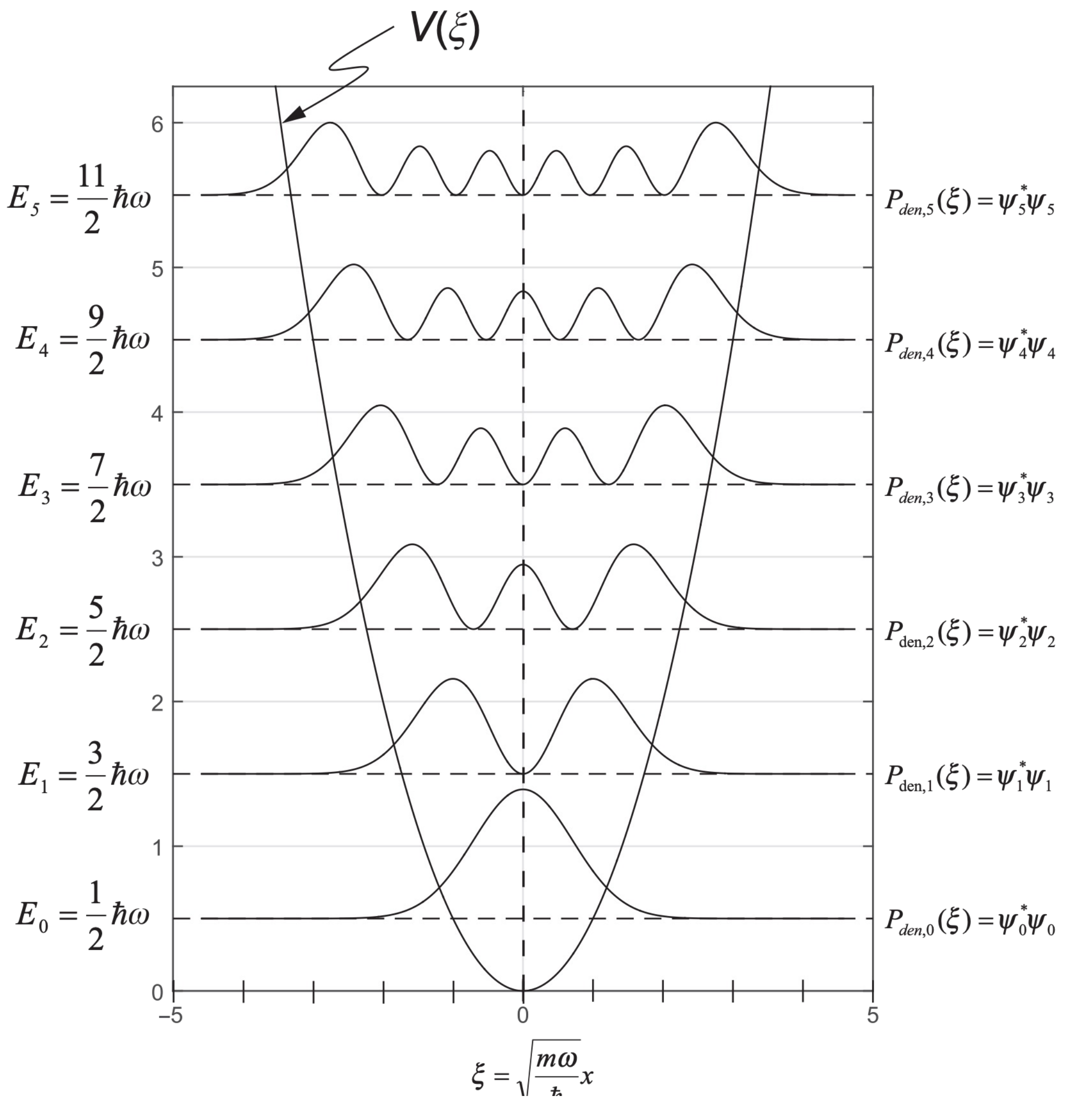
Oscillatory on the classical allowed region

In this region, the curvature of the wave functions increases with increasing energy

(more cycles between the classical turning points)

Exponentially decaying in the classically forbidden region

Probability density of the TISE for the quantum harmonic oscillator in 1D



At low energies, the behaviour of the harmonic oscillator differs significantly from the classical one

Classical mechanics:

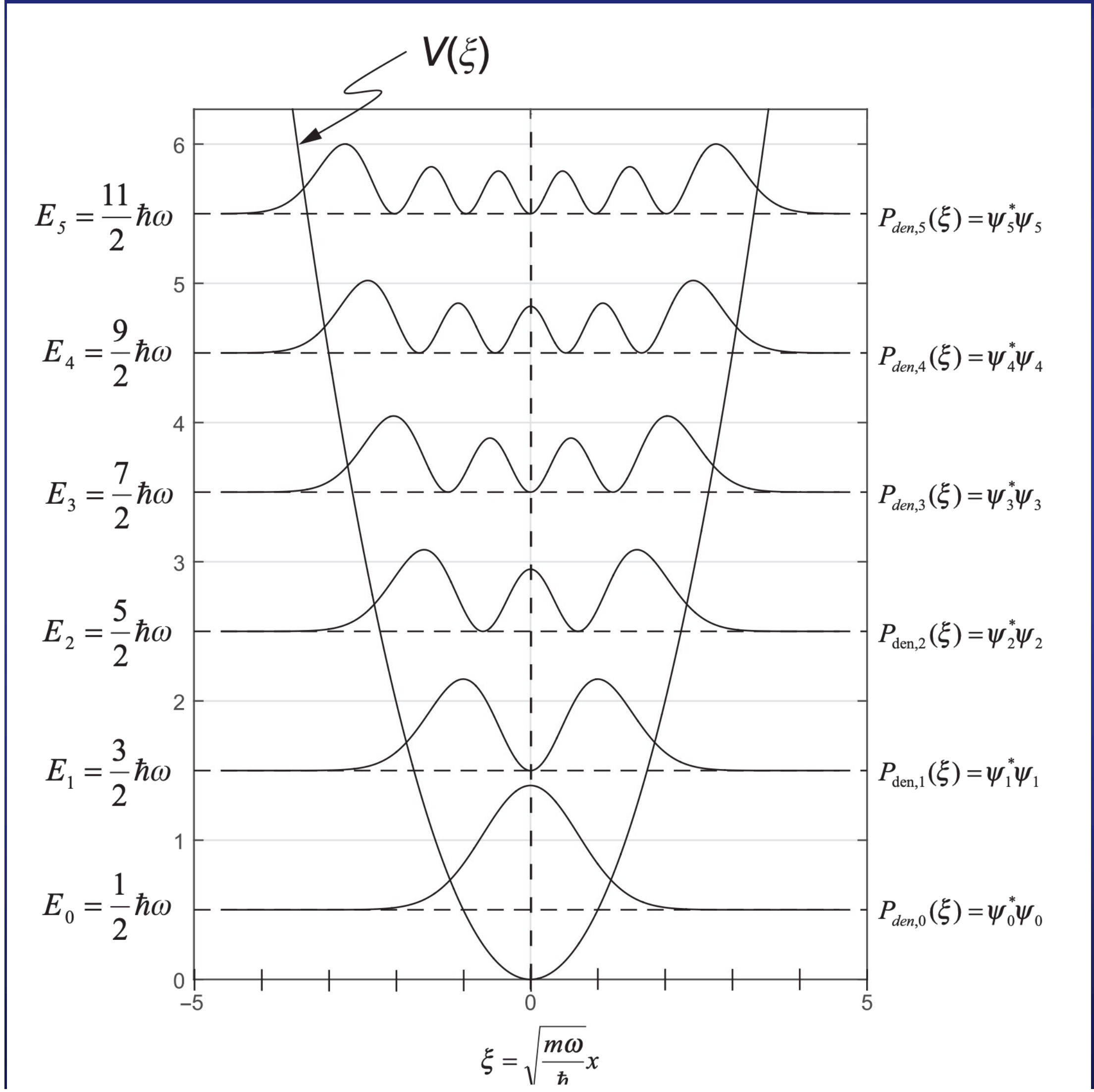
The object moves fastest at equilibrium and slowest at the turning points

Measurements of position taken at random times are more likely to yield results near the turning points, because the object spends more time there.

Quantum mechanics:

A measuremnt of the position of a particle in the ground state is more likely to yield a value near $x = 0$

Probability density of the TISE for the quantum harmonic oscillator in 1D



Higher energies:

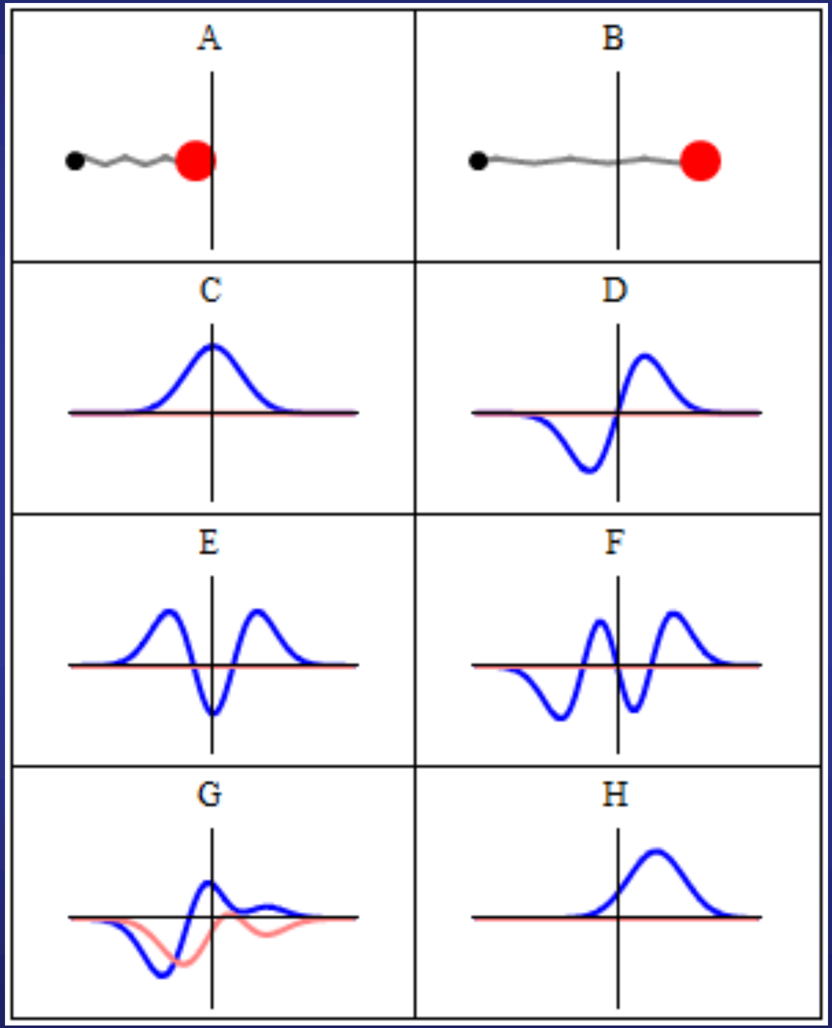
An excited state $\psi_n(\xi)$ has n locations with zero probability on the classially allowed region

As n increases, the probability of a position measurement producing a result near the classical turning points increases

The behavior of the quantum harmonic oscillator does begin to resemble that of the classical case at large values of n, as required by the Correspondence Principle

Stationary states of the TISE for the quantum harmonic oscillator in 1D

$$\Psi_n(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \left(\frac{1}{\sqrt{2^n n!}}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2} e^{-i\left(n+\frac{1}{2}\right)\omega t}$$



From Wikipedia

Classical solutions

Real part
Imaginary part
of the wavefunction of some energy eigenstates

Real part
Imaginary part
of the wavefunction of some states that are not eigenstates
(H is a coherent states)