

From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

Dr. Andreas Funk

Chapter II

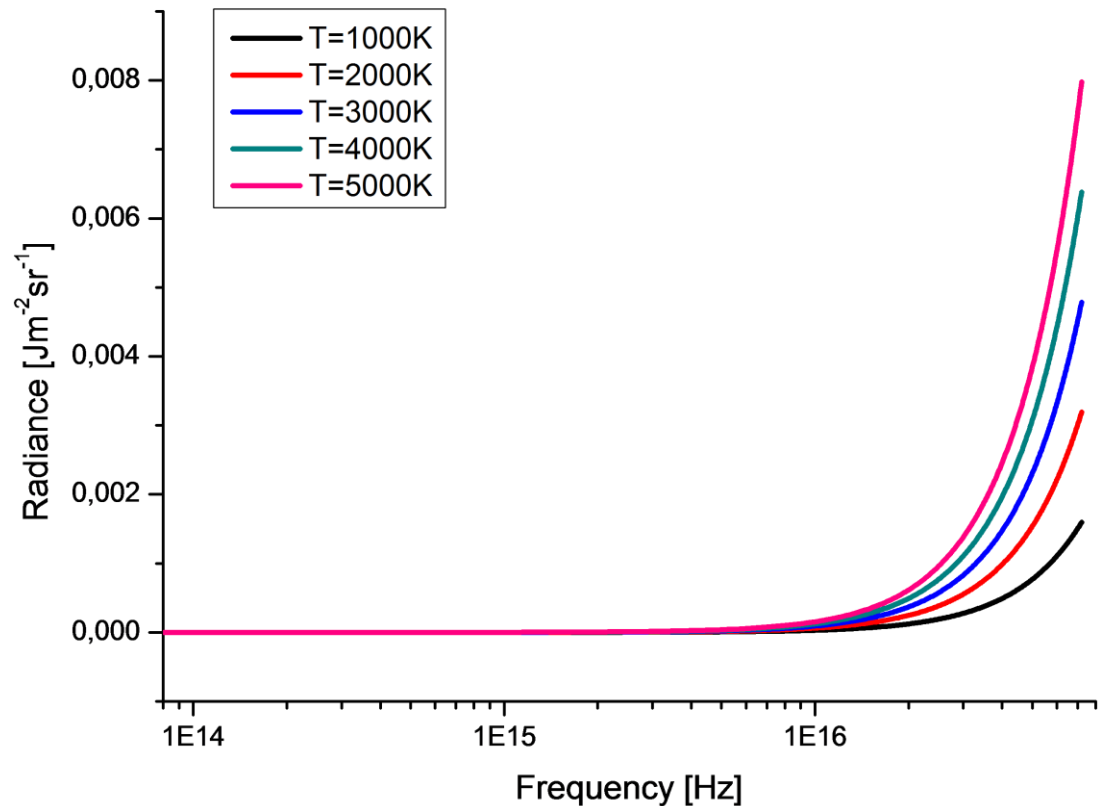
Single Particle Quantum Mechanics: Schrödinger's Equation

Where it all started: Black body radiation

Classically, the radiation of a black body is described by the Rayleigh-Jeans law

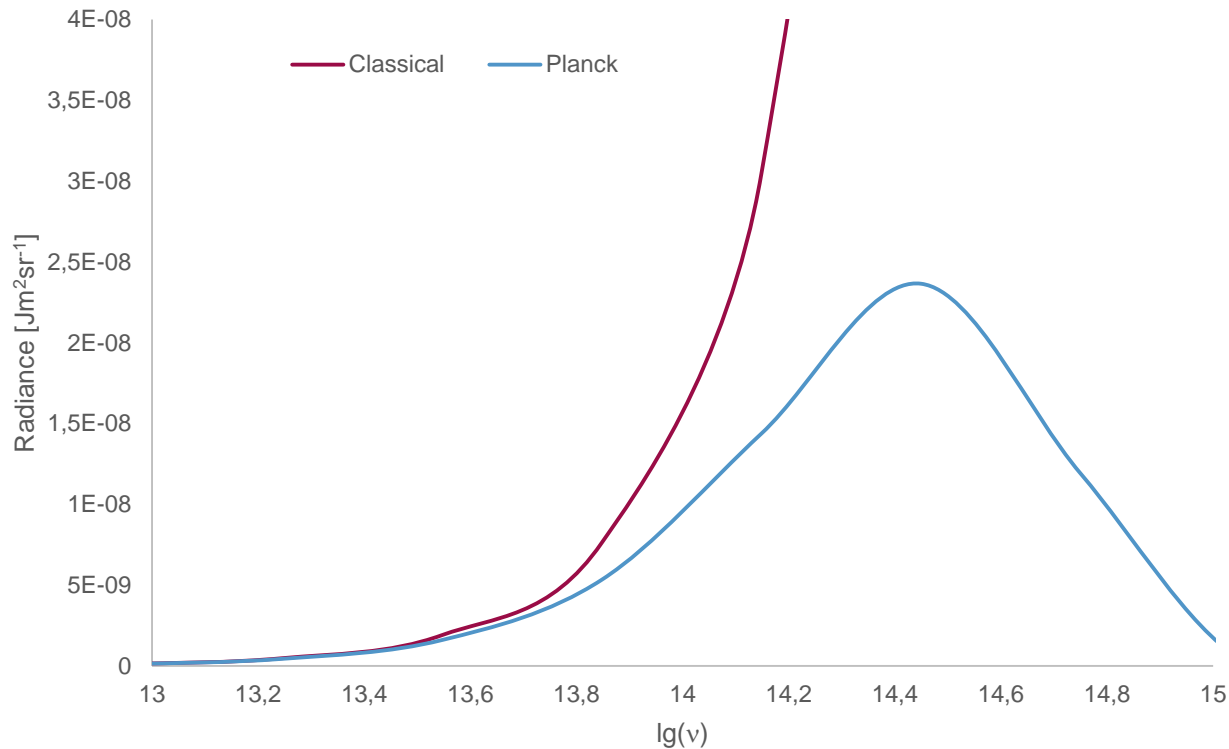
$$(1) \quad B_\nu(T) = \frac{2\nu^2 k_B T}{c^2}$$

Unfortunately, this law faces a problem at high frequencies.



The problem is solved with Planck's law.

$$(2) \quad B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$



How has this been derived?

Consider a free photon in a box of length L , then the wavelength of the photon can only be

$$(3) \quad \lambda = \frac{2L}{n}$$

In three dimensions, this yields a total energy of the system with r photons of

$$(4) \quad E_{n_x, n_y, n_z}(r) = \left(r + \frac{1}{2}\right) \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

Statistical mechanics yields a probability distribution

$$(5) \quad P(r) = \frac{\exp(-\beta E(r))}{Z(\beta)}$$

with

$$(6) \quad \beta = \frac{1}{k_B T}$$

With the partition function

$$(7) \quad Z(\beta) = \frac{\exp\left(-\beta \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}\right)}{1 - \exp\left(\beta \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}\right)}$$

we obtain the average energy of the system

$$(8) \quad \langle E \rangle = -\frac{d \log Z}{d\beta} = \frac{\varepsilon}{2} + \frac{\varepsilon}{\exp(\beta\varepsilon) - 1}$$

Here, we have defined

$$(9) \quad \varepsilon = \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

Expression 7 looks pretty much like Bose-Einstein statistics.

The density of states is then

$$(10) \quad U = \int_0^{\infty} \frac{\varepsilon}{\exp(\beta\varepsilon) - 1} g(\varepsilon) d\varepsilon = \int_0^{\infty} \frac{\varepsilon}{\exp(\beta\varepsilon) - 1} \frac{8\pi L^3}{h^3 c^3} \varepsilon^3 d\varepsilon$$

Now we are close to a solution. The spectral energy density as a function of the frequencies is

$$(11) \quad U_\nu(T) = \frac{U}{L^3} = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Now we take into consideration that radiation equally propagates in all directions and with speed of light we obtain

$$(12) \quad B_\nu(T) = U_\nu(T) \frac{c}{4\pi} = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Getting more systematic: Schrödinger's equation

Obviously it makes sense to have a Hamiltonian (energy-based) look on quantum problems. From classical mechanics we know that

$$(13) \quad H = T + V$$

Do not get confused by T , it means the kinetic energy in this case (which is closely related to temperature anyway). V is the total potential energy. All we need to do now is to get a systematic way to obtain both values.

The Planck-Einstein relation connecting frequency and energy is well-known as

$$(14) \quad E = h\nu$$

At the same time we know from special relativity that

$$(15) \quad E = mc^2$$

Combining both yields

$$(16) \quad mc^2 = h\nu$$

This is quite interesting: We can relate a mass to frequency!

Photons should have no mass as they are travelling with the speed of light. However, according to eq. 16, we can show that they are having a mass:

$$(17) \quad m = \frac{h\nu}{c^2}$$

If this works, why not relate a frequency to a mass as well?

We can conclude (as de Broglie did) that any particle (properties: mass and no wave behavior) can be described as a wave (properties: frequency and no point mass) and vice versa. As such, we can assign a wave function to any particle.

Interesting question: How do we obtain the correct wavefunction?

Let us consider that we already know the wavefunction ψ . In this case, the wavefunction should determine the energy. From linear algebra we know that in this case an operator \hat{O} must exist, which yields the correct energy when acting upon this wavefunction:

$$(18) \quad \hat{O}\psi = E\psi$$

It is obvious that this operator must represent the Hamiltonian, hence

$$(19) \quad \hat{H}\psi = \hat{T}\psi + \hat{V}\psi = \frac{\hat{p}^2}{2m}\psi + \hat{V}\psi$$

Now we have to transform our classical operators:

$$(20) \quad \mathbf{r} \rightarrow \hat{\mathbf{r}} = \mathbf{r}$$

For our potential energy we obtain:

$$(21) \quad V \rightarrow \hat{V} = V(\mathbf{r}, t)$$

Next we need the momentum operator:

$$(22) \quad \mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla$$

Here we defined

$$(23) \quad \hbar = \frac{h}{2\pi}$$

And finally, we define Energy in time-dependent representation

$$(24) \quad \hat{H} = i\hbar \frac{d}{dt}$$

Thus, our Schrödinger equation is

$$(25) \quad i\hbar \frac{d}{dt} \psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right) \psi(\mathbf{r}, t) = E\psi(\mathbf{r}, t)$$

If we combine many particles, their individual wavefunctions simply add. We are seeing a superposition of the wavefunctions. However, unless we measure a specific state, we the system is actually a superposition of all possible wavefunctions! Only measurement leads to a collapse into a specific quantum state (a localized wavepacket).

Unfortunately, the wavefunction itself does not tell us directly how the particle moves. Indeed, we can only tell where we can find it with a certain probability. The function

$$(26) \quad \rho(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2$$

is the probability distribution function of our system, and the probability to find our particle in a certain volume and time interval is

$$(27) \quad P = \int_{d\tau} \rho(\mathbf{r}, t) d\mathbf{r} dt$$

As we know that if the particle exists, it has to be found within our universe (all space and all time) we know that

$$(28) \quad \int \rho(\mathbf{r}, t) d\mathbf{r} dt = 1$$

Hence we know that our wavefunction must be normalized so that the integral of its square is one. If we are dealing with many particles, we obtain the number of particles instead of one.

At the same time we know that wavefunctions are additive, so that for two particles

$$(29) \quad \int (\psi_1 + \psi_2)^2 = \int \psi_1^2 + \psi_2^2 + \psi_1^* \psi_2 + \psi_1 \psi_2^* = 2$$

It is easy to see from eqs. 26-28 that

$$(30) \quad \int \psi_1^2 = \int \psi_2^2 = 1$$

This is only fulfilled when

$$(31) \quad \int \psi_1^* \psi_2 = - \int \psi_1 \psi_2^*$$

However, as we are dealing with a physical system, these integrals are part of a Hermitian matrix. They are of the same sign. The only solution for eq. 31 is then that both integrals are zero.

As such we can write for a wavefunctions which are eigenstates to the same Hamiltonian that

$$(32) \quad \int \psi_j \psi_k^* = \int \psi_j^* \psi_k = \delta_{jk}$$

An easy example: A particle in a one-dimensional box

Let us consider a one-dimensional box of length L . We obtain the potential

$$(B1) \quad V(x) = \begin{cases} 0 & \forall 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Hence, in the box the particle behaves as a free particle (it faces no potential), while it would need infinite energy to be outside the box.

Let us solve the time-independent part first. Inserting everything into the Schrödinger equation we get

$$(B2) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) = E \phi(x)$$

So all we need is a function which yields second derivatives being the same function multiplied with a constant. Well, this is easy:

$$(B3) \quad \phi(x) = A \sin(kt) + B \cos(kt)$$

The time-independent energy is then

$$(B4) \quad E = \frac{\hbar^2 k^2}{2m}$$

Now let us solve the time-dependent case. The Schrödinger equation is

$$(B5) \quad i\hbar \frac{d}{dt} \chi(t) = E \chi(t)$$

We need a function which yields itself times a factor after derivation, plus the result has to be real. This is also easy:

$$(B6) \quad \chi(t) = e^{-i\omega t}$$

This yields the energies

$$(B7) \quad E = \hbar\omega$$

As both wavefunctions do not share variables we obtain the total wavefunction by a product ansatz:

$$(B8) \quad \psi(x, t) = \phi(x)\chi(t) = [A \sin(kt) + B \cos(kt)]e^{-i\omega t}$$

And the energies are equivalent

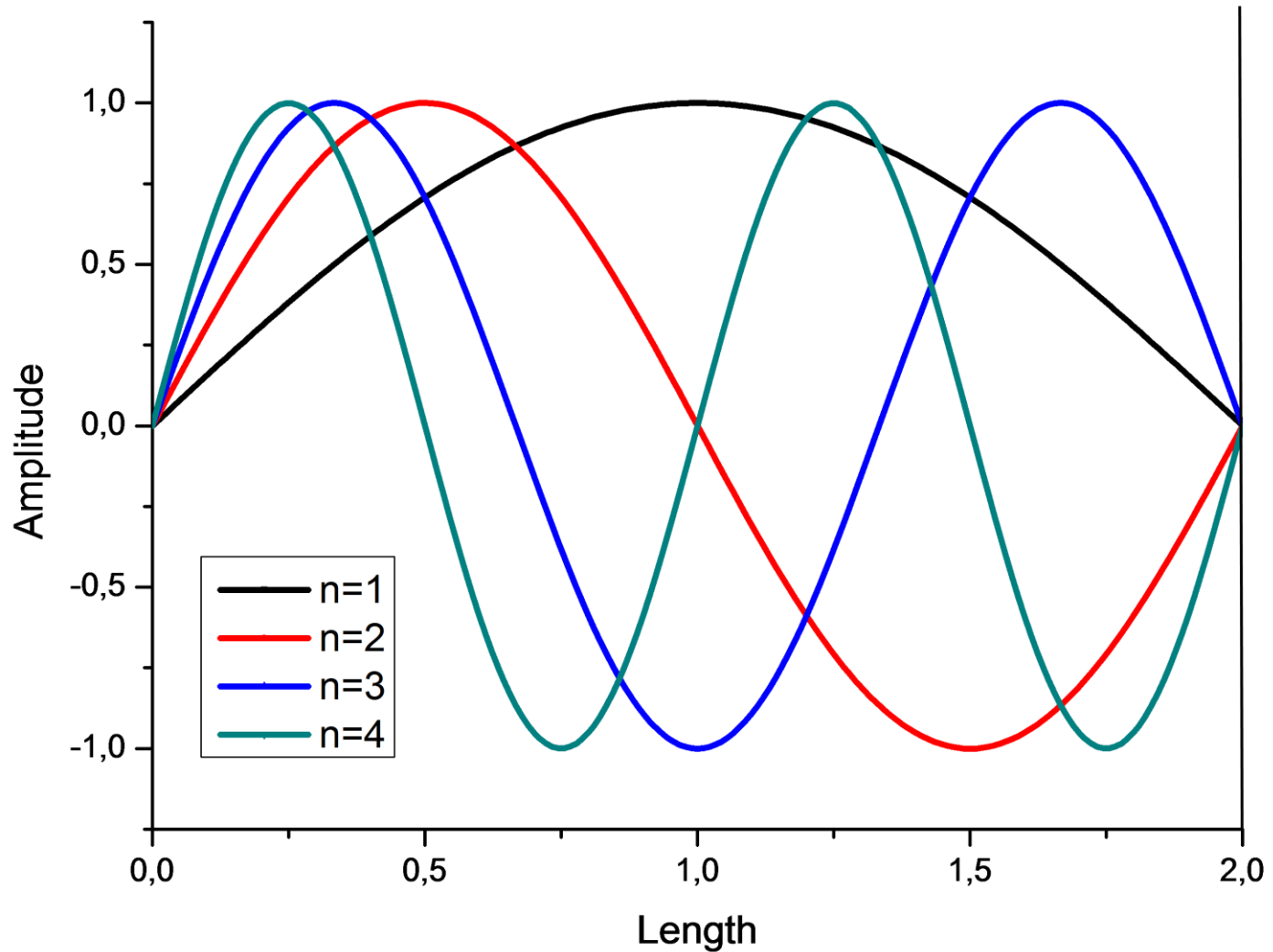
$$(B9) \quad E = \frac{\hbar^2 k^2}{2m} = \hbar\omega$$

Finally, we have to find an expression for k . Here we need to have a look at our boundary conditions. We know that the particle can only move within the box, and we know that the particle acts as a wave. Thus, we need to make sure that it becomes zero at the boundaries, which we achieve by:

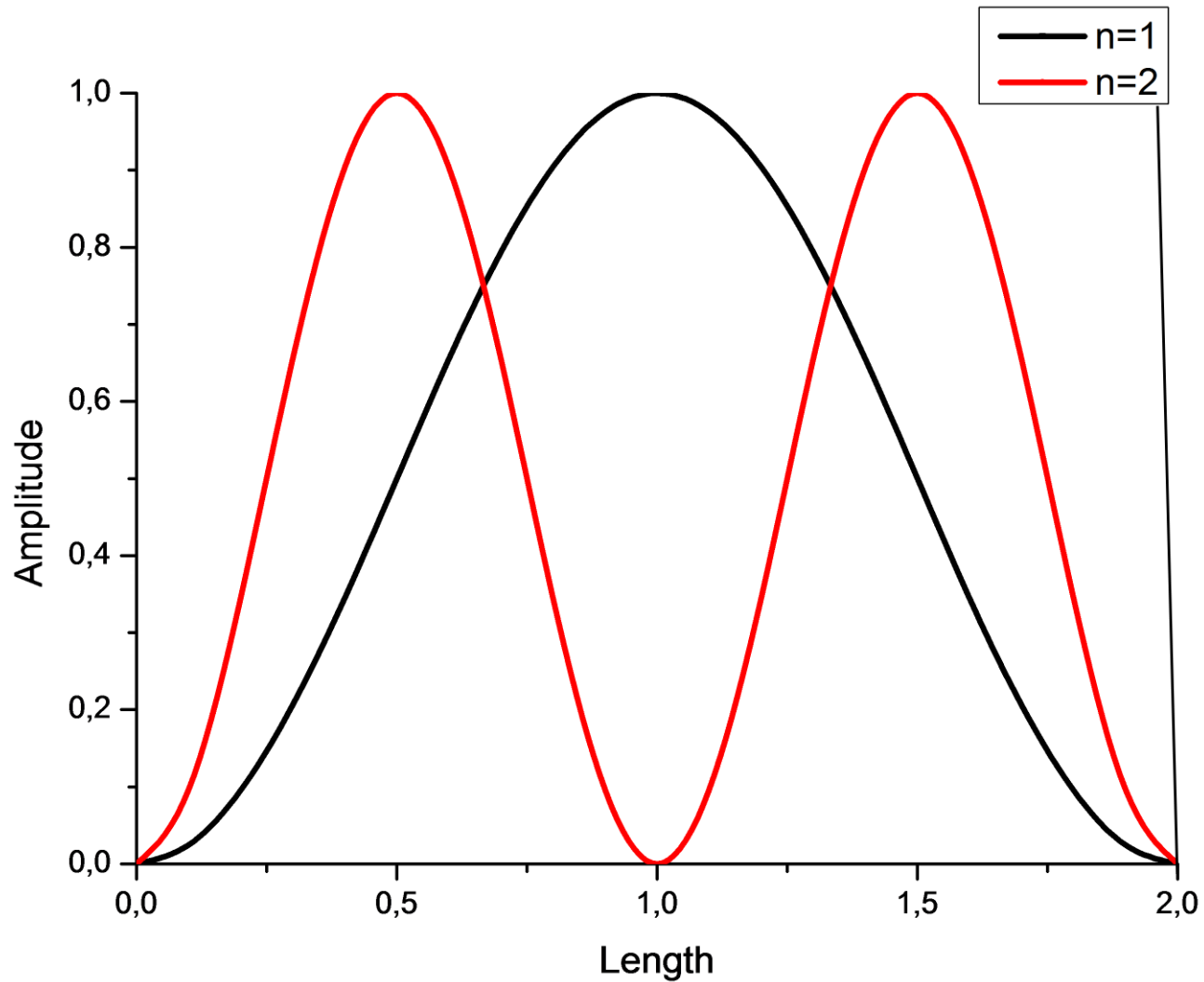
$$(B10) \quad k = \frac{n\pi}{L}$$

Finally, we normalize our wavefunction, which we can realize with a multiplying with a factor of $\sqrt{\frac{2}{L}}$.

Let us have a look at the first four wavefunctions:



Next, let us look at some squares of wavefunctions (not yet normalized):



A more challenging example: The harmonic oscillator

Here, our potential is

$$(H1) \quad V(x) = \frac{k}{2}x^2$$

This yields the time-independent Schrödinger equation

$$(H2) \quad \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{k}{2}x^2 \right) \psi(x) = E\psi(x)$$

This looks as if there may exist an already solved differential equation. Actually, it looks a little like

$$(H3) \quad \frac{d^2}{dx^2} f_n(x) - 2x \frac{d}{dx} f_n(x) + 2n f_n(x) = 0$$

This is Hermite's differential equation, and the solutions to this equation are Hermite polynomials. They are orthogonal if multiplied with a Gaussian function.

With $\omega = \sqrt{\frac{k}{m}}$ we obtain the general solutions

$$(H4) \quad \psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right)$$

with Hermite polynomials

$$(H5) \quad H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

Hermite functions are, despite their seemingly complicated nature, easy to handle by their recursion

$$(H6) \quad \frac{d}{dy} \psi_n(y) = \sqrt{\frac{n}{2}} \psi_{n-1}(y) - \sqrt{\frac{n+1}{2}} \psi_{n+1}(y)$$

With straightforward application of the Schrödinger equation we obtain

$$(H7) \quad E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

or, closer to Hermite's equation

$$(H7) \quad E_n = (2n + 1) \frac{\hbar}{2} \omega$$

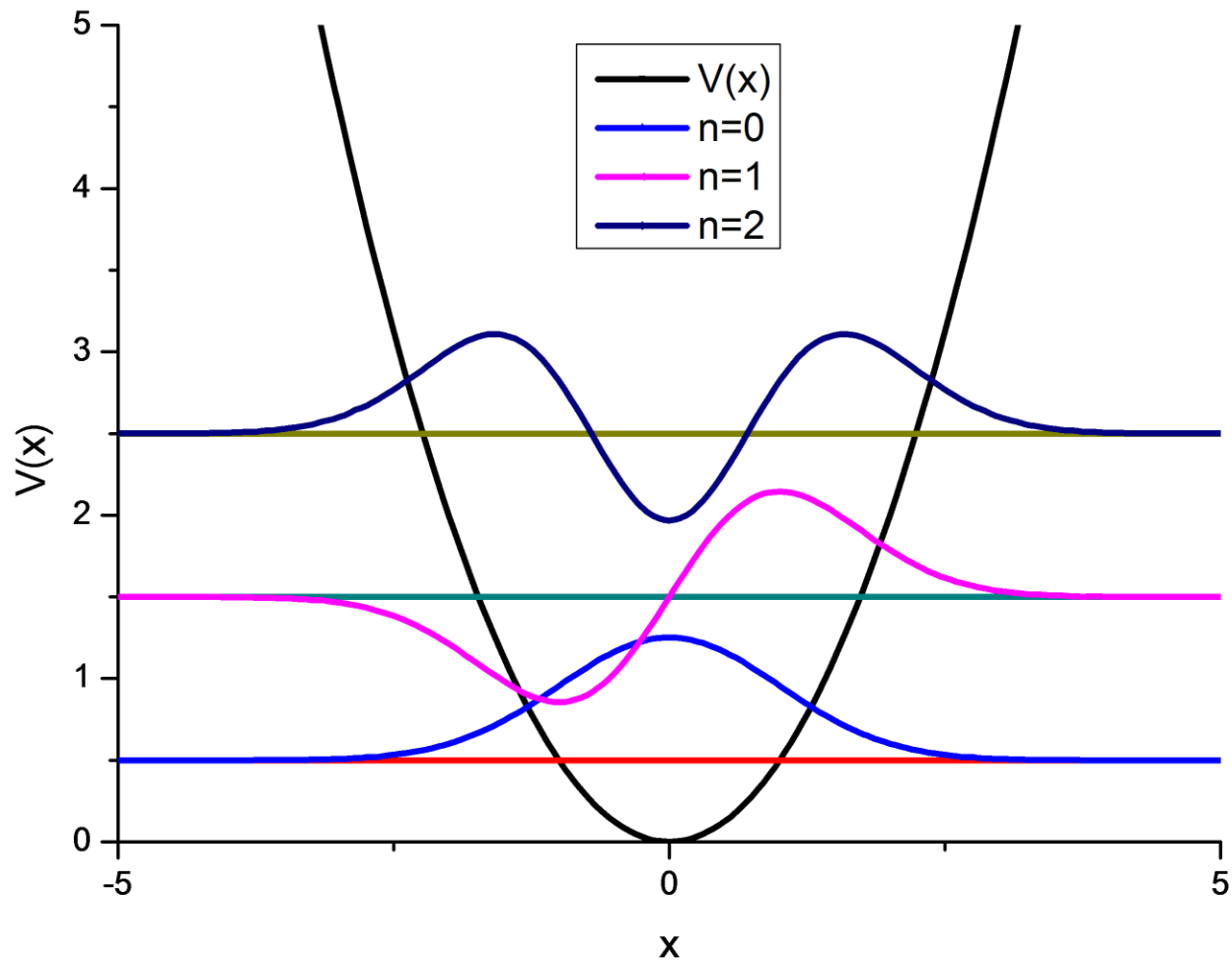
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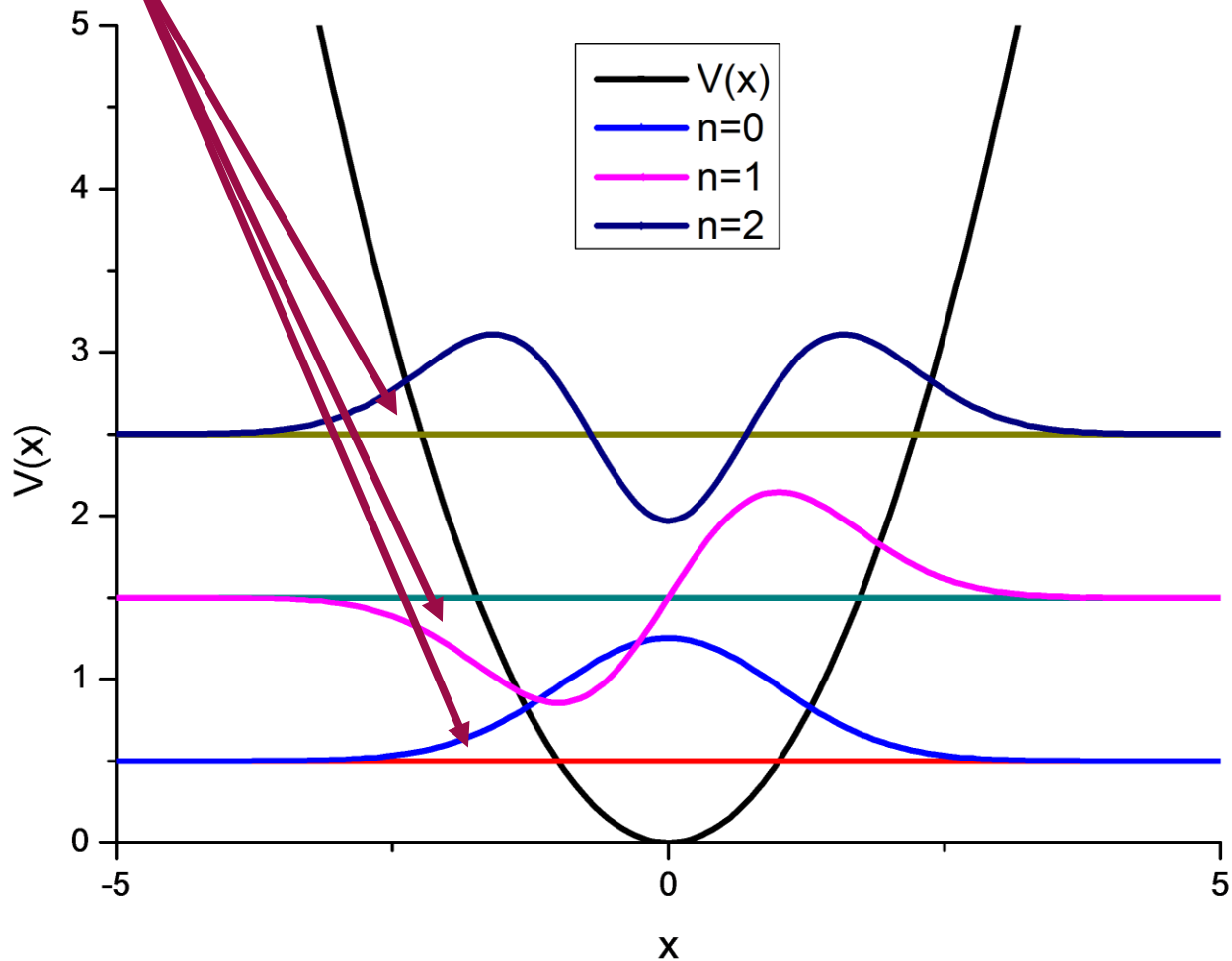
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Let us look some wavefunctions



Note that the amplitude of the wavefunctions is dimensionless and they are displayed at their respective energy eigenvalues wrt $V(x)$

What is going on here? Should the wavefunction not be zero?



Note that the amplitude of the wavefunctions is dimensionless and they are displayed at their respective energy eigenvalues wrt $V(x)$

This is what we call “tunneling”. The probability to find a particle outside its potential is, in general, not zero!