
General Assumptions

These are some general assumptions, the validity of which is required to generate a meaningful solution.

```
$Assumptions = {E > 0, ħ > 0, m > 0, L > 0, k > 0, T > 0, R > 0, s > 0};
```

Description of the problem

In quantum mechanics, we usually aim at solving Schrödinger's equation:

$$\hat{H}\Psi = E\Psi,$$

where \hat{H} is the Hamiltonian operator (assigned to energy), Ψ is the so-called wave function, and E is the value of energy.

One convenient way of writing out \hat{H} is to assume that

$$\hat{H} = \hat{T} + \hat{V},$$

that is, a sum of kinetic (\hat{T}) and potential energy (\hat{V}) operators.

While for most systems

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2},$$

definition of the potential energy depends on the interactions within the system. In case of a **particle in a box**, we usually assume that

$$\hat{V} = 0 \text{ if } 0 < x < L \text{ (where } L \text{ is the length of the box), otherwise } \hat{V} = \infty.$$

Solution of Schrödinger's Equation

Let us first solve the 2nd order ODE by specifying two boundary conditions:

```
solution[x_] = FullSimplify[Ψ[x] /. ReplaceAll[  
    First@DSolve[-(ħ^2/(2 m)) D[Ψ[x], {x, 2}] == E Ψ[x], Ψ[x], x], {C[1] → A, C[2] → B}]];  
Print["Ψ(x) = ", solution[x]]  
Ψ(x) = A Cos[ (√2 x √m E) / ħ ] + B Sin[ (√2 x √m E) / ħ ]
```

Note that this is a family of functions, where A and B could, in principle, take any values. We are only

concerned with cases in which $\Psi(0) = \Psi(L) = 0$. Thus let us solve the following set of equations:

```
Reduce[{
  solution[0] == 0,
  solution[L] == 0
}, {A, B}]
```

$$\left(\sin\left[\frac{\sqrt{2} L \sqrt{m E}}{\hbar}\right] == 0 \&\& A == 0 \right) \mid \mid \left(A == 0 \&\& \sin\left[\frac{\sqrt{2} L \sqrt{m E}}{\hbar}\right] \neq 0 \&\& B == 0 \right)$$

From the above two conditions, only the first one is physically meaningful. Thus, $A = 0$ and we have a constraint on the value of E :

```
A = 0;
```

```
E = E /. Solve[ $\frac{\sqrt{2} L \sqrt{m E}}{\hbar} == n \pi$ , E][[1]];
```

```
Print["E = ", E]
```

$$E = \frac{n^2 \pi^2 \hbar^2}{2 L^2 m}$$

The value of B can be calculated by normalizing the squared wave function to 1:

```
B = B /. FullSimplify[
  Solve[Integrate[solution[x]^2, {x, 0, L}] == 1, B], Assumptions -> {n ∈ Integers}][[2]];
Print["B = ", B]
```

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

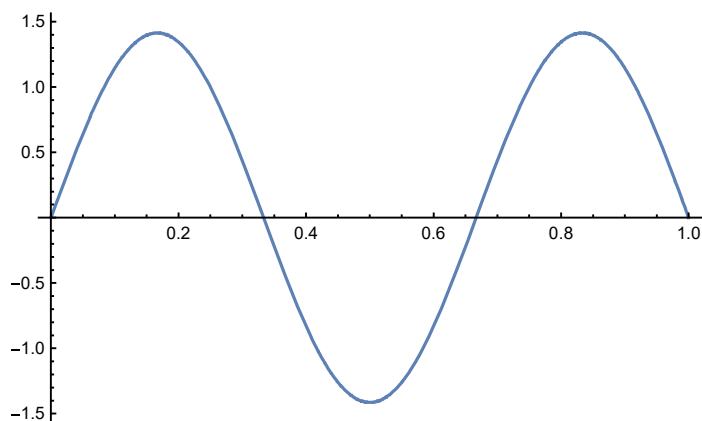
We can now do some test plotting:

```
L = 1;
```

```
 $\hbar$  = 1;
```

```
n = 3;
```

```
Plot[solution[x], {x, 0, L}]
```



```
Quit[];
```

Finding the fundamental equation

Let us start with the previously obtained energy expression:

$$\mathcal{E}n = n^2 \frac{\pi^2 \hbar^2}{2 L^2 m};$$

The probability of a given energy state to be filled is proportional to $\text{Exp}\left[-\frac{\mathcal{E}n}{kT}\right]$. Sum these up (that is, integrate) to get the sum of probabilities for one molecule:

$$\Omega_{\text{mol}} = \text{ReplaceAll}\left[\left(\text{Integrate}\left[\text{Exp}\left[-\frac{\mathcal{E}n}{kT}\right], \{n, 0, \infty\}\right]\right)^3, \{L^3 \rightarrow v\}\right]$$

$$\frac{(M R T)^{3/2} v}{2 \sqrt{2} N A^3 \pi^{3/2} \hbar^3}$$

The number of possible states for all molecules of 1 mole of the system is thus $\Omega = \frac{1}{N A!} \Omega_{\text{mol}}^{N A}$, from which:

$$\text{Smolar} = k (N A \text{Log}[\Omega_{\text{mol}}] - N A \text{Log}[N A] + k N A);$$

$$\text{Smolar} = R (\text{Log}[\Omega_{\text{mol}}] - \text{Log}[N A] + 1)$$

$$R \left(1 - \text{Log}[N A] + \text{Log}\left[\frac{(M R T)^{3/2} v}{2 \sqrt{2} N A^3 \pi^{3/2} \hbar^3}\right] \right)$$

Note that this is in fact the molar entropy. Rearrange this to express T as a function of the molar entropy s :

$$T /. \text{Solve}[\text{Smolar} == s, T][[1]]$$

$$\frac{2 e^{-\frac{2}{3} + \frac{2s}{3R}} N A^{8/3} \pi \hbar^2}{M R v^{2/3}}$$

Integrate to get the molar internal energy u :

$$u = \text{Integrate}[\%, s];$$

$$k = R / N A;$$

$$m = M / N A;$$

$$u = \text{FullSimplify}[u]$$

$$\frac{3 e^{\frac{2}{3} \left(-1 + \frac{s}{R}\right)} N A^{8/3} \pi \hbar^2}{M v^{2/3}}$$

Multiply by n to get the internal energy U , solve for s , switch to extensive variables:

$$s /. \text{FullSimplify}[\text{Solve}[U == n u, s], \text{Assumptions} \rightarrow \{C[1] == 0\}][[1]];$$

$$\text{FullSimplify}[n \text{ReplaceAll}[\%, \{v \rightarrow V / n\}], \text{Assumptions} \rightarrow \{n > 0\}]$$

$$n \left(R - \frac{3}{2} R \text{Log}\left[\frac{3 n^{5/3} N A^{8/3} \pi \hbar^2}{M U V^{2/3}}\right] \right)$$