# Introduction to QM and Atomic Structure:

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## These notes closely follow P. W. Atkins, Physical Chemistry

QM traces its origins to the failure of classical physics to explain a number of phenomena that could be measured accurately by the end of the 19th century. These included:

**Black Body Radiation:** At the end of the 19th century, classical physics was quite mature and Max Planck was told that for his PhD, he might wish to tackle one of the two great open problems: black body radiation.[1] When bodies are heated to high temperatures, they radiate energy with the following characteristics (determined experimentally):

The Wien displacement law:

$$T\lambda_{\max} = \frac{1}{5}c_2 \qquad c_2 = 1.44 \text{ cm K}$$

where $T$ is the temperature and of the black body and $\lambda_{\max}$ is the wavelength at which the energy distribution $\rho$ is maximum. $c_2$ is a constant (the second radiation constant).

The Stefan-Boltzmann law:

$$M = \sigma T^4$$

The excitance (power emitted per unit surface area) $M$ is proportional to the fourth power of the temperature. The constant of proportionality $\sigma$ (the Stefan-Boltzmann constant) has the value $\sigma = 5.67 \times 10^{-8}$ W m$^{-2}$ K$^{-4}$. This law forms the basis of optical pyrometry.

Lord Rayleigh (with help from James Jeans) attempted to find a formula for the energy density of an ideal black body by calculating the number of oscillators within a given volume. The Rayleigh-Jeans law states:

$$d\mathcal{E} = \rho d\lambda \qquad \rho = \frac{8\pi k_B T}{\lambda^4}$$

where $\mathcal{E}$ is the energy density (electromagnetic energy per unit volume) and $k_B$ is the Boltzmann constant $(1.381 \times 10^{-23}$ JK$^{-1})$. The law works OK for long wavelengths (low frequencies) but fails for high frequencies (short wavelengths).

Max Planck's contribution (in 1900) was to use the Rayleigh-Jeans law but under the proviso that the energy of the electromagnetic oscillators did not vary continuously but only took on discrete values. The permitted energies of the oscillators were suggested to be discrete multiples of some typical frequency:

$$E = nh\nu \qquad n = 0, 1, 2, \ldots$$

where $h$ is the Planck constant, $h = 6.62608 \times 10^{-34}$ Js. On the basis of this assumption, the energy density of black body radiation is modified to:

$$d\mathcal{E} = \rho d\lambda \qquad \rho = \frac{8\pi k_B T}{\lambda^5} \left( \frac{1}{e^{hc/\lambda k_B T} - 1} \right)$$

This corrected expression is found to fit experiment very well. Note the importance of Planck having said that in effect, energies in the world of the very small cannot take up arbitrary values — that they must take up certain fixed values. This is the notion of the *quantum*.

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[1] The other open problem, the onset of turbulence in fluids, continues to receive a great deal of attention

**The photoelectric effect:** It was known that when light fell on the surfaces of materials (particularly metallic elements such as Rb and Cs) electrons were ejected. Einstein (1905) proposed that the kinetic energy of the electron (called the photoelectron) was proportional to the frequency of the incident light minus a constant term, the work function $\phi$ which is characteristic of the material.

$$\frac{1}{2}m_{\mathrm{e}}v^2 = h\nu - \phi$$

Note that the photoelectron will be ejected only when the energy of the incident light $h\nu$ exceeds the work function $\phi$. Also note that the photoelectron energy is determined only by the incident frequency and not by the intensity.

**The deBroglie relation:** The constant dilemma that had dogged physics — whether light is better described as a wave or a particle, was somewhat clarified in 1924 by Louis deBroglie when he suggested that the matterlike property of momentum $p$ and the wavelike property of wavelength $\lambda$ of materials are related through the Planck constant:

$$\lambda = \frac{h}{p}$$

So why did it take so long. One reason is that most objects that we normally encounter (say a baseball thrown with a velocity of 70 mph) have immeasurably small wavelengths. It is only when objects are very light (such as electrons) that the wavelengths become significant.

**Atomic spectra:** Optical spectroscopy had reached quite a high level of sophistication by the late 19th century. It was known that the different elements had characteristic lines in their emission spectra (such as the orange-red D line of sodium). In fact, He had been discovered as a distinct element in solar spectra (*helios* = sun) before it was discovered on earth. The Swiss schoolteacher Johann Balmer rationalized the emission lines from H atoms by observing that the wavenumbers (inverse wavelengths) followed the rather simple law:

$$\tilde{\nu} = \frac{1}{2^2} - \frac{1}{n^2} \qquad n = 3, 4, \ldots$$

Further lines were then discovered and compiled into a single formula by Rydberg:

$$\tilde{\nu} = \mathcal{R}_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where the different series of lines correspond to $n_1 = 1$ (Lyman), $n_1 = 2$ (Balmer), $n_1 = 3$ (Paschen), $n_1 = 4$ (Brackett), $n_1 = 5$ (Pfund), $n_1 = 6$ (Humphreys) .... $\mathcal{R}_{\mathrm{H}}$ is the Rydberg constant, $\mathcal{R}_{\mathrm{H}} = 109677$ cm$^{-1}$. The fact that emission lines from atoms can only take on distinct energies (manifesting as sharp lines in the spectra) is another consequence of quantization. The Rydberg constant can be related to the Planck constant through:

$$\mathcal{R}_{\mathrm{H}} = \frac{m_{\mathrm{e}}e^4}{8\epsilon_0^2 h^3 c}$$

**The Schrödinger Equation:** The Austrian Physicist Erwin Schrödinger, in 1926, proposed an equation (this is the time-independent form) that for a quantum particle of mass $m$ moving in one dimension ($x$) subject to a potential $V(x)$, is described by:

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

Here $\hbar = h/(2\pi)$, $\psi$ is the wavefunction (*eigenfunction*) that describes everything that one would need to know about the particle, and $E$ is the energy (*eigenvalue*) associated with the $\psi$. A simpler way of writing the equation is to say that the Hamiltonian operator **H**:

$$\mathbf{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

operates on the eigenfunction $\psi$ to yield the energy eigenvalue $E$ multiplied by $\psi$, so we can write the Schrödinger equation in general as:

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

It is important to recognize that the LHS has an operator, operating on a function while the RHS just has a simple multiplier, the energy. Note that we have written in 1D, not 3D.

**The uncertainty principle:**   Werner Heisenberg (German, developed QM concurrently with Schrödinger) suggested that in QM, there are certain sets of quantities such as the momentum and position of a particle, that cannot be simultaneously specified to arbitrary precision. If $p_x$ is the momentum of the particle along $x$ and $x$ is the position, then the uncertainties (the variance) are respectively

$$\Delta p_x = \sqrt{<p_x^2> - <p_x>^2} \qquad \Delta x = \sqrt{<x^2> - <x>^2}$$

and the uncertainty principle states that:

$$\Delta p_x \Delta x \geq \frac{1}{2}\hbar$$

**Linear, purely kinetic motion (free particle):**   In the absence of any potential $[V(x) = 0]$, the SE in 1D is:

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - E\right)\psi = 0$$

A possible solution is:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad k = (2mE/\hbar^2)^{1/2}$$

$E = p^2/(2m) = k^2\hbar^2/(2m)$ so we know that $p = k\hbar = h/\lambda$.

When $B = 0$, $p = (\hbar/i)(\mathrm{d}/\mathrm{d}x)Ae^{ikx} = k\hbar\psi$, and similarly, when $A = 0$, $p = -k\hbar\psi$. The solution $\psi = Ae^{ikx} + Be^{-ikx}$ therefore describes the forward and backward motion of the particle.

An important point to note is that the solution for the energy $E = k^2\hbar^2/(2m)$ can take on *any* value, *ie.* the energy is not quantized for a free particle !

**1D box (infinite well):**   Consider a particle held within a 1D box through the following condition:



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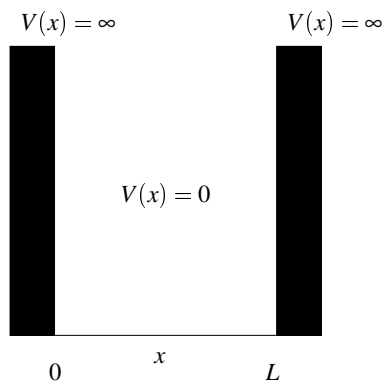
$$\mathbf{H} = -(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2) + V(x);$$
$$V(x) = 0 \text{ for } 0 \le x \le L$$
$$= \infty \text{ for } x < 0 \text{ and } x > L$$

We chose as a solution:

$$\psi(x) = A\cos kx + B\sin(kx) \qquad k = (2mE/\hbar^2)^{1/2}$$

and verify that it is valid by substituting it in the SE. The boundary conditions are dictated by the walls: at $x = 0$ and at $x = L$, the value of $\psi$ must be 0.

Note that at $x = 0, \psi = A$. Therefore $A = 0$, and we can write for the particle in the 1D box, $\psi = B\sin kx$. Now at $x = L$:

$$\psi(L) = B\sin kL = 0$$

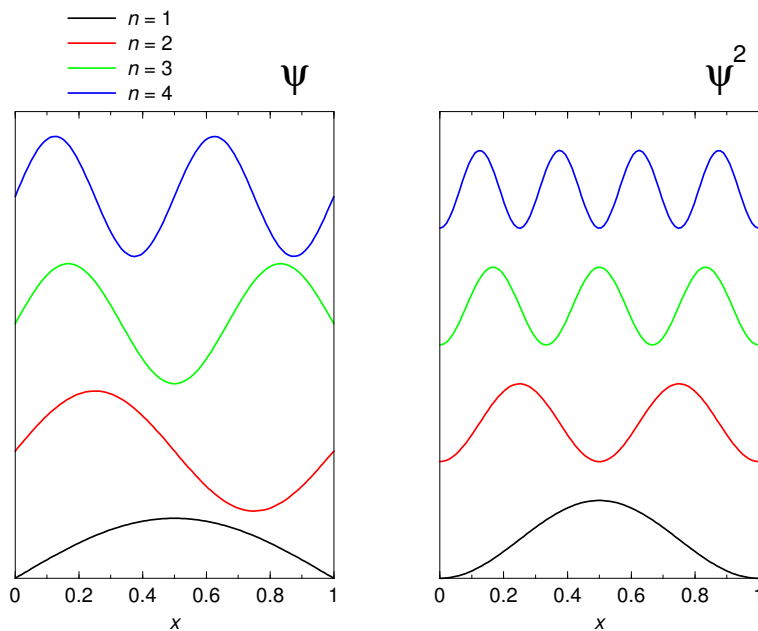This means $k = n\pi/L, \quad n = 1, 2, 3\ldots$. This means that the energy can only take on the values

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

and is quantized. The quantum number is $n = 1, 2, 3, \ldots$

When we *normalize* the solution, it looks like:

$$\psi_n = \sqrt{2/L}\sin(n\pi x/L) \qquad E = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots$$

The wavefunctions are plotted below:

Note that as $n$ increases, the energy increases and the number of nodes in the wavefunction increases. The *correspondence principle* states that for very large quantum numbers $n$, the system behaves classically. This is demonstrated by plotting $\psi$ and $\psi^2$ for $n = 100$:
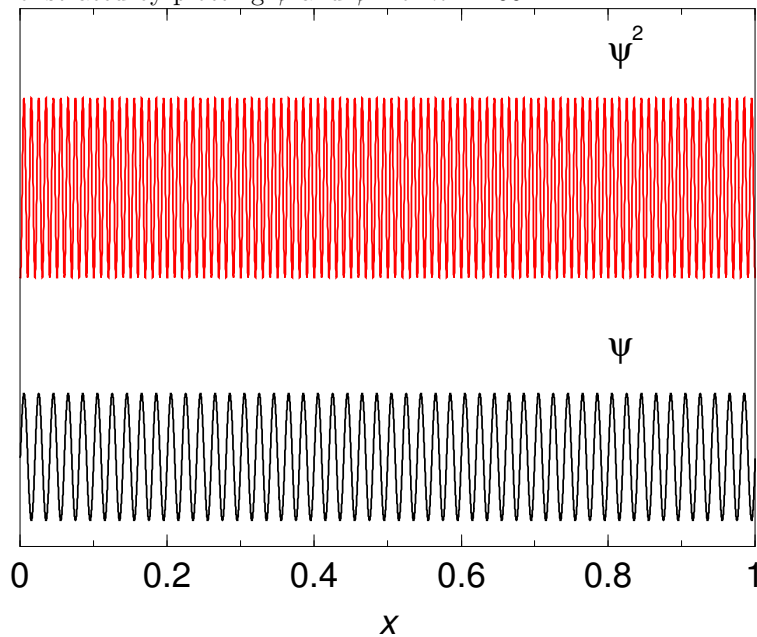


In recent years, through the use of STMs, the probabilities of electrons in 2D boxes (the squares of their wavefunctions in different quantum states) have been directly visualized by Don Eigler (IBM Almaden) and others. The Eigler group's work can be found at: http://www.almaden.ibm.com/vis/stm/gallery.html. Below, is an image from the IBM web pages of electrons confined within boxes of different shapes by arranging Fe atoms on a Cu surface.