

# QUANTUM MECHANICS

(cont'd)

## 2. In search of a mathematical formulation

### 2.1 Heisenberg's Matrix Mechanics

Werner Heisenberg formulated a mathematical theory in which classical “measureables” (like position, momentum, energy, time...) could be represented by *matrices*.

One “strange” thing about matrices is that they do not commute under multiplication:

$$q \cdot p \neq p \cdot q$$

In fact, Heisenberg showed that for certain pairs of variables (known as *complementary variables*, and whose units are energy x time) , the relation:

$$q \cdot p - p \cdot q = h/2\pi = \hbar$$

thus leading to the uncertainty relation.

Except for this result, Heisenberg's matrix mechanics was not particularly useful. However it formed the basis of other formulations based on non-commuting operators (notably by Paul A.M. Dirac). These later approaches are today considered "the best" formulations of quantum mechanics, but are mathematically quite involved.

## 2.2 Bohr's semiclassical approach

At the other extreme, Neils Bohr adopted a classical approach to which quantum "fixes" were made. This proved very useful in simple cases, but has severe limitations. The fact that it works at all can be attributed to the *complementarity principle*, namely that in the limit as things get larger the quantum equations must give the same results as classical physics.

We take as an example of the semiclassical approach Bohr's solution of the hydrogen atom.

Consider an electron orbiting a hydrogen nucleus. The electrostatic attraction between the two must provide the centripetal force:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad \dots(1)$$

The energy of the electron is given by:

$$\begin{aligned} E = KE + PE &= \frac{1}{2}mv^2 + \frac{e^2}{4\pi\epsilon_0 r} \\ &= \frac{-e^2}{2\pi\epsilon_0 r} \quad \dots(2) \end{aligned}$$

Bohr further *assumed* that the angular momentum is quantised in unit multiples of some constant:

$$mvr = n\hbar \quad \hbar = h/2\pi \quad n = 1,2,3\dots$$

This is a central assumption of quantum mechanics with far-reaching implications (not discussed here). This assumption can however be explained in terms of de Broglie's standing-wave interpretation:

$$\begin{aligned} p = mv &= \frac{n\hbar}{r} = \frac{nh}{2\pi r} \\ \lambda &= \frac{h}{p} = \frac{2\pi r}{n} \end{aligned}$$

where the circumference of the orbit is a whole multiple of the wavelength. Thus, Bohr's quantization of angular momentum means that the orbit of the electron should support a standing wave.

Returning to the main derivation, substituting the quantization condition into (1) gives:

$$r = \left( \frac{4\pi\epsilon_0\hbar^2}{e^2m} \right) n^2$$

Putting in some numbers, for  $n=1$  (the *ground state*),  $r=5.3 \times 10^{-11}\text{m}$ , which agrees with experiment.

Substituting this result into (2) gives:

$$E = \frac{-me^4}{2\hbar^2(4\pi\epsilon_0)^2} \left( \frac{1}{n^2} \right)$$

Again putting in some numbers, for  $n = 1$ ,  
 $E = -2.18 \times 10^{-18} \text{ J}$  or  $-13.6\text{eV}$  ( $1\text{eV} = 1.6 \times 10^{-19}\text{J}$ ).

This is *exactly* the energy required to remove the electron from the hydrogen atom (the *ionization energy*).

Bohr's model fitted experiment even more closely than that. The spectral lines emitted by hydrogen were shown to follow the relation:

$$\frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad n = 1, 2, \dots \quad m = n + 1, n + 2, \dots$$

Using Planck's formula  $E = hf = hc/\lambda$ ,

$$E = hcR\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

so the emission of a photon of energy  $E$  can be explained in terms of a transition of an electron from the energy level  $m$  to the energy level  $n$ , thus providing an explanation for the existence of line spectra.

### **2.3 Schrodinger's wave equation**

The most immediately “useful” mathematical approach to quantum mechanics was that taken by Erwin Schrodinger. It provided a relatively simple algebraic equation that could be solved in a number of different cases to give useful results.

Starting from de Broglie's hypothesis of “matter waves”, he reasoned that just as classical (ray) optics is an approximation to wave optics, so classical (particle) mechanics may be an approximation to wave mechanics.

This wave will have to follow the wave equation:

$$\frac{d^2 y}{dx^2} = -\frac{1}{v^2} \frac{d^2 y}{dt^2}$$

Suppose the wave has a standing-wave form:

$$y(x, t) = \Psi(x) \cos(\omega t)$$

Substituting,

$$\frac{d^2 \Psi(x)}{dx^2} \cos(\omega t) = \frac{\omega^2}{v^2} \Psi(x) \cos(\omega t)$$

Notice that the cos terms cancel, leaving a *time-independent* equation. This is because we chose a standing-wave solution.

Hence:

$$\begin{aligned} \frac{d^2 \Psi(x)}{dx^2} &= \frac{\omega^2}{v^2} \Psi(x) \\ &= \frac{(2\pi)^2}{\lambda^2} \Psi(x) \\ &= \left(\frac{2\pi}{h}\right)^2 (mv)^2 \Psi(x) \\ &= \frac{2m}{\hbar^2} \left(\frac{1}{2} mv^2\right) \Psi(x) \end{aligned}$$

Now, the kinetic energy  $\frac{1}{2}mv^2$  of a particle is not usually known: however, the total energy  $E$  is the sum of the potential energy  $U$  and the kinetic energy, so:

$$\frac{-\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = (E - U)\Psi(x)$$

which is Schrodinger's time-independent equation that can be used to solve for the stationary states of a particle or system of particles.

There is also a *time-dependent* Schrodinger equation, obtained without making the standing-wave assumption. The TISE can be used to evaluate the time-evolution of a system. The TDSE can be obtained as a special case of the TISE, which is therefore considered to be more fundamental than the TDSE.

The TDSE is usually written as:

$$\left( \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + U \right) \Psi = E\Psi$$

where the left-hand term is an *operator* indicating the total energy of the system, called the *Hamiltonian operator*:

$$H\Psi = E\Psi$$

If we take the analogy with classical mechanics further,

$$\left( \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + U \right) \text{ represents } E = \frac{1}{2}mv^2 + U$$

So:

$$\left( \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \right) \text{ represents } \frac{1}{2}mv^2 = \frac{(mv)^2}{2m}$$

and:

$$\left( -i\hbar \frac{d}{dx} \right) \text{ represents } mv_x$$

(the reason for the -ve sign is not discussed here)

This means that the wave-function can give us the momentum of a particle by solving the eigenvalue problem:

$$\left( -i\hbar \frac{d}{dx} \right) \Psi = p_x \Psi$$

Thus, in the formal QM, the momentum of a particle is represented by the operator  $i\hbar d/dx$



Similarly, the position of the particle is the solution of the trivial equation:

$$x\Psi = x\Psi$$

(mathematically, the  $x$  on the left is an operator while the  $x$  on the right is an eigenvalue). Clearly this equation only “makes sense” when  $\Psi$  is zero everywhere except at a single point, when it takes value 1 (a delta-function). For more “reasonable” functions, the position of the particle cannot be defined exactly.

The delta-function has no derivative, hence the momentum of a particle of with a precisely known position is undefined. Similarly, a momentum eigenstate is of the form  $Ae^{ikx}$  which is a wave that exists everywhere along the  $x$ -axis. Thus, the Schrodinger equation supports Heisenberg’s Uncertainty Principle.

Operators, particularly if they contain derivatives, are *non-commutating*, and this provides the link between Schrodinger’s wave mechanics and Heisenberg’s matrix scheme. A measurement of position followed by a measurement of momentum can be represented by:

$$\Psi \rightarrow \left( -i\hbar \frac{d}{dx} (x\Psi) \right)$$

while the reverse sequence of events can be represented by:

$$\Psi \rightarrow x \left( -i\hbar \frac{d\Psi}{dx} \right)$$

The two sequences of operations will give different results, as indicated by the commutator:

$$\begin{aligned} & \left( -i\hbar \frac{d}{dx} (x\Psi) \right) - x \left( -i\hbar \frac{d\Psi}{dx} \right) \\ &= x \left( -i\hbar \frac{d\Psi}{dx} \right) + \Psi \left( -i\hbar \frac{dx}{dx} \right) - x \left( -i\hbar \frac{d\Psi}{dx} \right) \\ &= -i\hbar\Psi \end{aligned}$$

which is numerically equivalent to Heisenberg's Uncertainty Principle.

The equation  $H\Psi = E\Psi$  is known to mathematicians as an *eigenvalue problem*, and in the general case has a solution only for particular values of  $E$ . These *eigenvalues* can be obtained without fully solving the equation, and correspond to the permitted energy states of the system.

It can thus be seen that the discrete energies of stationary states, which had to be put in as a special assumption in Bohr's theory, arises naturally from Schrodinger's equation.

The potential energy  $U$  describes the system in which the particle is moving. For example, in the hydrogen atom  $U$  is spherically symmetric and has the form:

$$U = \frac{e}{4\pi\epsilon_0 r}$$

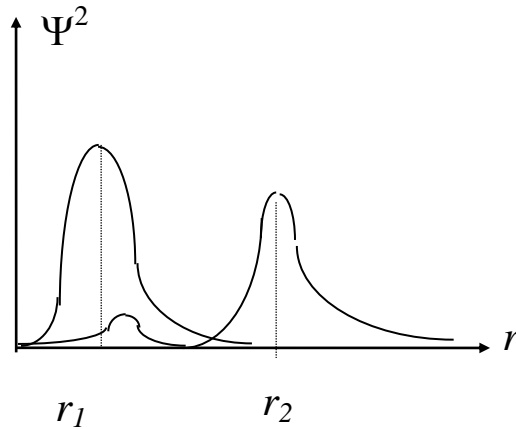
A solution of Schrodinger's equation with this potential, which is complicated mathematically only because it has to be done in 3-D using polar coordinates, gives:

$$E = \frac{-me^4}{2\hbar^2(4\pi\epsilon_0)^2} \left( \frac{1}{n^2} \right)$$

which is identical to Bohr's semiclassical result.

Although in many cases it is sufficient to find the eigenvalues of the TDSE, it can also be solved completely to find  $\Psi$ . In general, for each eigenvalue there will be a corresponding *eigenfunction* (also called an eigenvector).

This will be a wave-like function that describes the “matter wave” corresponding to the particle having that energy. As a solution to the wave equation, this “matter wave” behaves like a wave in all respects - it undergoes superposition, diffraction, interference and so on.



$r_1$  and  $r_2$  correspond to the Bohr radii for  $n=1$  and  $n=2$ .

So, Schrodinger’s model shows that the “matter wave” has maximum amplitude at the radii predicted by Bohr’s semiclassical theory, which agrees with experiment.

There is however a fundamental difference between Bohr’s model and Schrodinger’s.

In Bohr’s model the electron is definitely a particle: it is orbiting in a precise orbit with a well-defined velocity and radius. From Heisenberg’s uncertainty principle, we know that this cannot be so.

Schrodinger's result paints the "matter wave" as being spread out over space and so agrees with the uncertainty principle. On the other hand, what is meant by a "matter wave"? How can anything as particle-like as an electron be "smeared out" over a relatively large area?

Born's interpretation of Schrodinger's wavefunction was as the *probability* of finding the electron at that point: the electron is still a point-like particle but spends different amounts of time in different places, with a well-defined probability of being in a given place even though we cannot say which place it will be in at any time. This interpretation of quantum mechanics therefore replaces the definite trajectories of classical mechanics with probabilities. Since "real" objects contain very many atoms, these probability densities are sufficient to allow averages to be taken and macroscopic conclusions drawn.

The problems start when one starts thinking about just *one* particle...