

Wave Mechanics

ERWIN SCHRÖDINGER'S creation of his quantum wave function ψ followed LOUIS DE BROGLIE'S 1925 suggestion that a wave can be associated with a particle of matter - just as ALBERT EINSTEIN had associated a particle of energy with a light wave.

De Broglie predicted that the wavelength λ of a matter particle wave would be $\lambda = h/p$, since the wavelength of a photon is related to its frequency by $\lambda = c/\nu$. and Einstein had shown that the momentum of a light quantum should be $p = h\nu/c$.

In November, 1925, Schrödinger wrote to Einstein,

A few days ago I read with the greatest interest the ingenious thesis of Louis de Broglie, which I finally got hold of; with it section 8 of your second paper on degeneracy has also become clear to me for the first time.

A colleague pointed out to Schrödinger that to explain a wave, one needs a wave equation. With his extraordinary mathematical abilities, Schrödinger found his equation within just a few weeks.

Schrödinger started with the well-known equation for the amplitude ψ of a wave with wavelength λ in three dimensions,

$$\nabla^2 \psi - (4\pi^2/\lambda^2) \psi = 0.$$

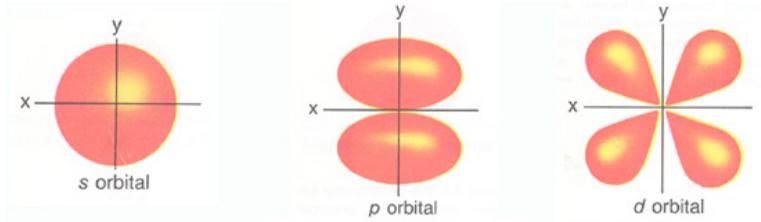
This equation gives us the density of classical electromagnetic waves ($8\pi\nu^2/c^3$) used by Planck and Einstein to derive the black-body radiation law.

In 1925, Bose and Einstein had eliminated classical theory completely, replacing the expression by the number of identical light quanta in a phase-space volume of h^3 . (See chapter 15.)

Schrödinger quickly converted from rectangular to spherical coordinates, R, Θ, Φ , because of the spherical symmetry of the nuclear electric charge potential $V = -e^2/r$. He could then replace the equation for $\psi(x, y, z)$ with one for $\psi(r, \theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi)$, which separates into three ordinary differential equations.

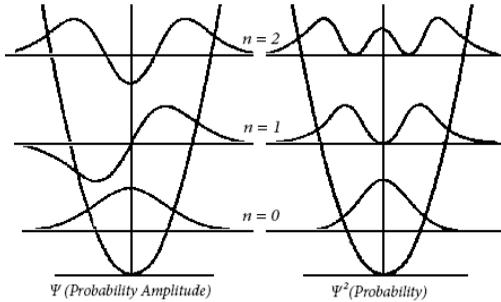
The angular functions lead to the spherical harmonics that correspond to different angular momentum states, visualized as the familiar electronic clouds in every chemistry textbook.



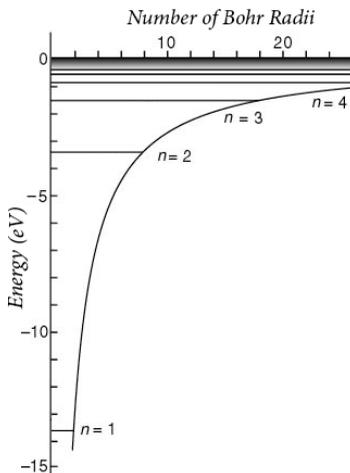
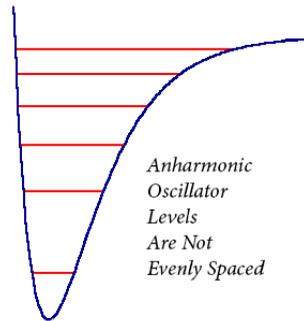


You can clearly imagine the nodes around electron orbits as they were seen by de Broglie, but now the waves are space filling.

The radial equation solves the time-independent Schrödinger equation with the electrostatic potential of the atomic nucleus as boundary conditions. It is important to note that the resulting wave is a *standing* wave, though it was inspired by de Broglie's concept of a *traveling* "pilot wave," with a particle riding on top.



Now WERNER HEISENBERG was familiar with standing waves. He looked first for solutions to the linear harmonic oscillator and the anharmonic oscillator, whose energy levels are not evenly spaced.



Compare the energy levels in the electrostatic potential $V = -e^2/r$ with the hydrogen atom term diagram in chapter 10.

Schrödinger's results for the bound energy levels in hydrogen matched Heisenberg's calculations exactly, but Schrödinger's math was much easier. All physicists, including Heisenberg himself,



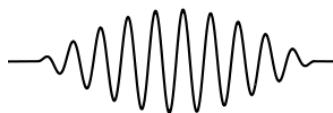
quickly replaced the awkward matrix mechanics with wave mechanics for all their calculations.

In December, 1925, Schrödinger wrote,

I think I can specify a vibrating system that has as eigen-frequencies the hydrogen *term* frequencies - and in a relatively natural way, not through *ad hoc* assumptions.

But Schrödinger went well beyond his standing wave eigenfunctions for bound states in hydrogen. He assumed that his wave mechanics could also describe *traveling* waves in free space.

Schrödinger wanted to do away with the idea of particles. He was convinced that a wave description could be a complete description of all quantum phenomena. He formulated the idea of a *wave packet*, in which a number of different frequencies would combine and interfere to produce a localized object. Where de Broglie, following Einstein, thought the wave was guiding the particle, Schrödinger wanted the wave *to be* the particle. But he soon learned that those different frequency components would cause the wave packet to rapidly disperse, not act at all like a localized particle.



Solving the Schrödinger equation for its eigenvalues works perfectly when it is a boundary value problem. Without boundary conditions, the idea of a wave as a particle has proved a failure.

All his life, Schrödinger denied the existence of particles and “quantum jumps” between energy levels, although the solution to his wave equation is a mathematical method of calculating those energy levels that is far simpler than the Heisenberg-Born-Jordan method of matrix mechanics, with its emphasis on particles.

The time-dependent Schrödinger equation is deterministic. Many physicists today think it restores determinism to physics. Although Einstein was initially enthusiastic that a wave theory might do so, he ultimately argued that the statistical character of quantum physics would be preserved in any future theory.¹

If determinism is restored, he said, it would be at a much deeper level than quantum theory, which “unites the corpuscular and undulatory character of matter in a logically satisfactory fashion.”

1 Schilpp, 1949, p.667

