

Quantum Mechanics

1 Big Picture

Quantum Theory has evolved/is evolving in three waves. These are sketched in Fig. 1.

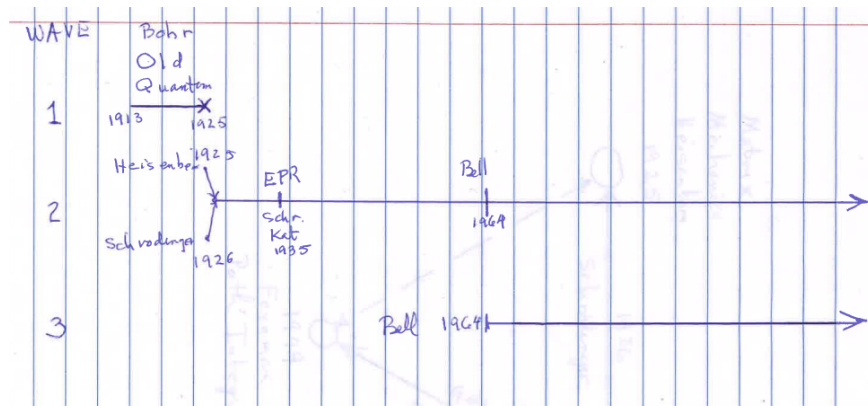


Figure 1: The Quantum Theory has evolved and/or is evolving in three waves. The time-lines for each are indicated.

Wave I: In 1913 Bohr introduced his planetary model of the hydrogen atom. He computed an electron trajectory in a Coulomb potential and kept only those trajectories that satisfied a certain externally imposed “quantization condition.” This model quantitatively explained the properties of this atom. Its success whetted the appetites of other physicists who had been frustrated by their inability to explain the enormous body of data that had built up over a century, since Spectroscopy evolved into a quantitative observational science. Unfortunately, this model failed to explain any/every-thing more complex.

Wave IIa - Matrix Mechanics: In 1925 Heisenberg (Bohr's protege) realized that tables of transition frequencies can be treated as matrices. He formulated a quantum theory in terms of matrices. In this theory these frequencies, or matrix elements, are the only observables. "If it isn't observed, it doesn't exist." Born, Heisenberg, and Jordan complete the "DreiMännerArbeit" ("Three men's work") in which they create a formal prescription (algorithm) that allows them to start from a Hamiltonian that describes a classical atomic puzzle (planetary model of an atom) and convert it to a Matrix Mechanics description of the same puzzle. This algorithm was very difficult to apply, especially given the fact that no physicists knew how to work with, or even knew about, matrices at that time. Only Pauli was able to use this prescription to solve the hydrogen atom problem. His solution involved not only the obvious symmetry (rotation symmetry, or $SO(3)$ symmetry), but the even larger symmetry [$SO(4)$, $SO(3,1)$] presented by the invariance of the Runge-Lenz vector. The "DreiMännerArbeit" served as the template for Herbert Goldstein's beautiful book *Classical Mechanics*, Addison-Wesley, 1950. This book was written with an eye to tailoring the foundations of Classical Mechanics for Quantum Mechanics courses.

Wave IIb - Wave Mechanics: In 1926 Schrödinger submitted his first Wave Mechanics paper (QAEP-1). It was sent to the journal simultaneously (and independently of) Pauli's solution of the hydrogen atom problem using Matrix Mechanics. In his paper Schrödinger formulated the hydrogen atom problem as a partial differential equation. At the time partial differential equations were *far* more familiar to physicists than matrices. In this paper he solved the hydrogen atom for both the discrete and the continuous spectrum using the (then) widely known and powerful techniques of complex variable theory.

Six months later Schrödinger showed the equivalence of his Wave Mechanics with the Matrix Mechanics of Born, Heisenberg, and Jordan. In the contest between partial differential equations and matrices, PDEs (Schrödinger) trumped matrices (Heisenberg) hands down. To get back into the ring, Heisenberg proposed the Uncertainty Principle in 1927.

In later years (after 1943) effective ways of solving PDEs by converting them to matrix equations are supplementing/ have supplemented Wave Mechanics. And later yet, in 1949 Feynman proposed a third very intuitive way of formulating Quantum Theory as a sum-over-all-paths theory.

The relations among these three ways of formulating Quantum Mechanics is summarized in Fig. 2.

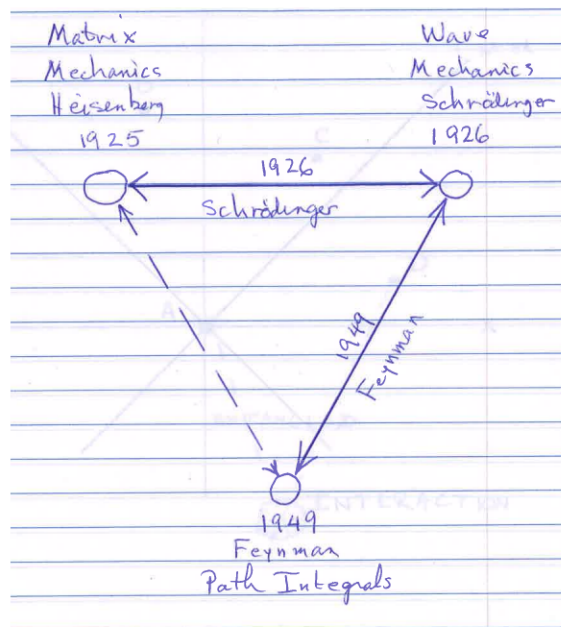


Figure 2: Matrix Mechanics was created in 1925 by Heisenberg and Wave Mechanics was created in 1926 by Schrödinger. Shortly afterwards, Schrödinger showed that the two formulations were equivalent, differing only by a choice of basis. Feynman created the Path Integral formulation of Quantum Mechanics in 1949 and also showed the equivalence with Wave Mechanics in his founding paper. Euclid filled in the dashed line.

III - Schrödinger and Einstein Strike Back: In 1935 both Schrödinger and Einstein vented their frustration with Quantum Theory. The EPR manifesto proposed a gedankenexperiment to highlight the incompleteness of quantum theory as then formulated. They introduced a concept that we now call “entanglement” (Schrödinger’s term for it is ‘intrication’). This paper encouraged Schrödinger to express his disenchantment with his own child. He did so by proposing the “Cat Paradox”. This is now usually addressed under the name “decoherence”, while the EPR challenge is discussed in terms of “Spooky Action at a Distance”.

The EPR challenge seemed to be a purely philosophical debate between Einstein and Bohr until

- a. In 1957 Bohm proposed a different way to formulate the experiment.
- b. In 1964 Bell showed how Einstein and Bohr predicted different outcomes for a class of experiments.

The result (so far): Before, only determinism could create correlations among measurements. Now, there is a brand new resource, *measurement*, that can create correlations. We (still) don’t fully understand how Nature works.

All these developments took place subject to the constraints of Thermodynamics and its Big Brother, Statistical Mechanics. The principles of these subjects, especially in the hands of Maxwell, Boltzmann, Wein, Planck, and Einstein, placed severe constraints on the evolution of the Quantum Theory of Radiation. They continue to do so, at least as of 1976 with the discovery of Black Hole Thermodynamics and Hawking Radiation.

2 Elaboration

Wave I: Bohr’s “Old Quantum Theory” is a beautiful theory for historical study. We won’t study it. It is not correct. In 1917 Einstein pointedly showed that it couldn’t be correct. In a paper that was largely ignored (uncited for 50 years) he showed that the Bohr-Sommerfeld quantization condition on trajectories could be written in the form

$$\oint_{C_i} \mathbf{p} \cdot d\mathbf{q} = n_i h \tag{1}$$

where the contour integral is taken around each of k independent loops of a k -degree of freedom system. This works when the classical system is integrable and trajectories live on a k -dimensional torus in a $2k$ -dimensional phase space. The loops C_i form a basis for the homotopy group of the torus T^k . If the system is not integrable this quantization condition falls apart. This fatal objection to the Old Quantum Theory did not kill it: It lasted until it could be replaced by (first) Matrix Mechanics and (very shortly afterward) by Wave Mechanics.

The Old Quantum Theory gave rise to several concepts that were radical and fascinating at the time, but have grown old and useless, if not outright wrong, at the present. Nevertheless, academic inertia is such that these (e.g. Correspondence Principle) have failed to be relegated to oblivion.

Wave II: Schrödinger did two things in the first two pages of his first paper on Wave Mechanics:

- a. He introduced a variational formulation for a field $\psi(x)$ (now called “wave function”):

$$\begin{aligned} J &= \int \left(K(\nabla\psi(x))^2 + V(x)(\psi(x))^2 \right) dV \\ \delta J &= 0 \quad K = \frac{\hbar^2}{2m} \end{aligned} \tag{2}$$

He also pointed out that the action J is a quadratic form in both ψ and $\nabla\psi$. The implications are profound (fast forward many years): This variation equation can “easily” be solved using matrix methods.

- b. He reduced the variational problem to a linear equation involving the potential $V(x)$ and the *second derivative* operator ∇^2 using a standard integration by parts procedure and separately addressing boundary conditions. Thus the Schrödinger equation is a *consequence* of the variational formulation of Wave Mechanics:

$$-\nabla(K\nabla\psi) + V\psi = E\psi \tag{3}$$

In this equation the energy, E , enters as a Lagrange multiplier and has a physical interpretation as energy.

The remainder of his first paper on Wave Mechanics is devoted to solving the hydrogen atom problem and wrestling with the interpretation of the new field, ψ , that he introduced.

3 Summary of Schrödinger's Annus Mirabilis of 1926

Schrödinger published six fundamental papers on Quantum Mechanics in 1926. They are collected in: *Collected Papers on Quantum Mechanics - Schrödinger*, AMS Chelsea Publishing Co., Providence, RI, 2001, 2003. This collection also contains three later papers and four of his lectures.

The six papers are summarized here.

Quantization as an Eigenvalue Problem I.

- a. Variational formulation, quadratic form in ψ and $\nabla\psi$
- b. Differential equation form
- c. Solution hydrogen atom
- d. ? What have I wrought ?

Quantization as an Eigenvalue Problem II.

- a. Wave optics — Wave mechanics analogy
- b. Harmonic oscillator
- c. Rigid rotors
- d. Rotating oscillator as model for molecules
- e. ? What have I wrought ?

The Continuous Transformation from Micro- to Macro-Mechanics

- a. Quantum system closest to classical harmonic oscillator
- b. Coherent states (now foundation of Quantum Optics)

On the Relation Between the Quantum Mechanics of Born, Heisenberg, and Jordan and that of Schrödinger

- a. Two two are equivalent
- b. They differ by a change of basis

Quantization as an Eigenvalue Problem III.

- a. Time independent perturbation theory introduced
- b. Applied to describe the Stark effect

Quantization as an Eigenvalue Problem IV.

- a. Time dependent Schrödinger Equation introduced
- b. Time dependent perturbation theory introduced
- c. Excited atoms, discrete and continuous spectra
- d. Resonances
- e. Magnetic and relativistic generalizations
- f. ? What have I wrought ?

4 Bell and the Third Wave

Bohr and Einstein carried out an argument about Quantum Mechanics that was unresolved at their deaths. In essence, Einstein argued that the ultimately measured properties of a physical system were written into the wave at the time of its creation. Bohr argued that they were created only at the time of the measurement of the wavefunction. The rest of the Physics community regarded their argument as akin to the medieval argument about how many angels could dance on the head of a pin.

With the greatest of apologies to Bohr and Einstein, their argument on the foundations of Quantum Mechanics is summarized in Fig. 3. In this figure a measurement is carried out at spacetime point A . The question is: Are measurements at spacetime points B , C , D correlated with those at A ? Everybody agrees that measurements at A and B can be correlated, since B can be connected to A by a time-like signal. Same for A and C . Everybody also agrees that measurements at B and C can also be correlated, even if these two points are space-like separated, if both are in the lightcone of A , as both can be influenced by events at A .

Einstein argues that events at A cannot influence measurements at D when A and D are spacelike separated. Bohr argues that measurements at A and D can be correlated provided that the two have interacted sometime in the past and they are in an “entangled” state.

Experiments have been done. At present, they show that Bohr is correct and Einstein is not. This raises philosophical issues. These results show us that we do not “understand” the working of Nature. These results also open a brand new resource for Physicists. This resource allows correlations among events in nature to be created in a *third* way: Not only by direct causality (B and A in Fig. 3) and indirect causality (B and C in Fig. 3), but also through “entanglement”. This resource is currently being exploited in securing communications.

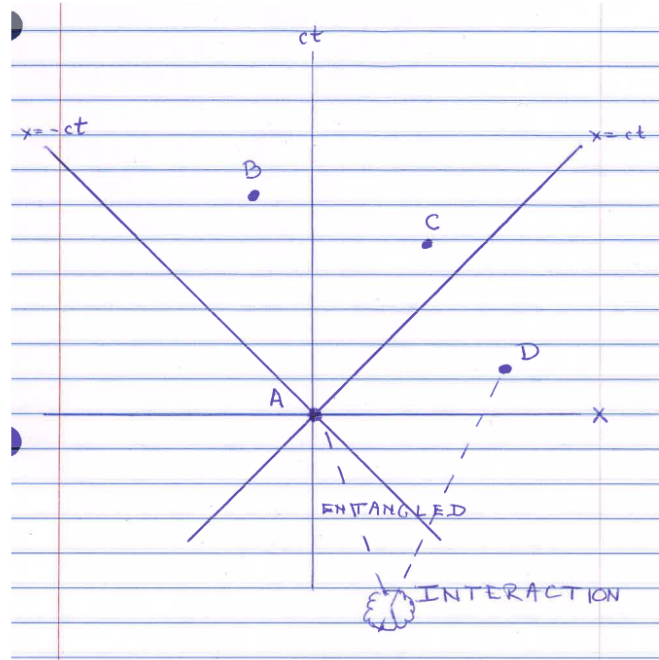


Figure 3: Everybody agrees: Measurements at B can be correlated with those at A because B is in the light cone of A . That is, events at B can be “caused” (are causally related) by events at A . Same for C and A . In addition, events at B and C can be correlated, even if they are space-like separated. This is because both can be influenced by events at A , since both are in the light-cone of A . Here agreement ends. Einstein contends that there can be no correlations between events at A and D , who are space-like separated (unless both are in the light cone of some previous causal influence). Bohr contends that measurements at A can “force” correlations with measurements at D . Experiments have been done. They show that Quantum Mechanics provides a *new* resource that has hardly begun to be understood.

5 Schrödinger's First Paper

Schrödinger's initial formulation of Wave Mechanics was through the following variational principle:

$$J = \int (K(\nabla\psi)^2 + V(x)\psi^2) dV \quad (4)$$

$$\delta J = 0 \quad \text{and} \quad \int \psi^2 d^3x = 1$$

The normalization condition $\int \psi^2 dV = 1$ is enforced to avoid the uninteresting trivial solution $\psi(x) = 0$. For dimensional reasons $[KL^{-2}] = [V] = ML^2T^{-2} \Rightarrow [K] = (ML^2T^{-1})^2/M$. This means that K is \hbar^2/m , up to a proportionality factor. He determined this proportionality factor by solving this equation for the hydrogen atom and comparing the predicted spectrum with the observed spectra. He found $K = \hbar^2/2m$. At this time he did not seem to be aware that the wave function could be complex.

His next step was to convert this equation from an expression quadratic in gradients to linear in second derivative operators. The standard way for doing this was used. The function ψ was modified: $\psi(x) \rightarrow \tilde{\psi}(x) = \psi(x) + \epsilon\phi(x)$ and this modified expression was used in the variational expression. This produced a function, $J(\epsilon)$, quadratic in the perturbation parameter ϵ . It was also quadratic in ϕ and $\nabla\phi$. The standard procedure involves computing $dJ(\epsilon)/d\epsilon$ and setting this derivative equal to zero in an attempt to find stationary solutions for J :

$$\left. \frac{dJ(\epsilon)}{d\epsilon} \right|_{\epsilon=0} = 2 \int K \nabla\phi \cdot \nabla\psi + \phi(V(x) - E)\psi d^3x \quad (5)$$

The normalization condition of Eq. (4) is enforced by introducing a Lagrange multiplier, called E here in view of its subsequent interpretation as an energy.

In order to convert the dependence on $\nabla\phi$ in the first term to a dependence on ϕ the first term is integrated by parts:

$$\int K \nabla\phi \cdot \nabla\psi d^3x = \int \nabla(K\phi\nabla\psi) d^3x - \int \phi(\nabla(K\nabla\psi)) d^3x \quad (6)$$

The first term on the right leads to a surface integral and the second can be combined with the remaining terms linear in ϕ in Eq. (5), which becomes

$$\left. \frac{dJ(\epsilon)}{d\epsilon} \right|_{\epsilon=0} = 2K \oint \phi \nabla\psi \cdot d\mathbf{S} + 2 \int \phi(-\nabla K \nabla\psi + (V(x) - E)\psi) d^3x = 0 \quad (7)$$

This expression is required to vanish for an arbitrary test function $\phi(x)$. To this end the surface integral (on the left) and the volume integral (on the right) must separately vanish. We assume the integral extends over all space. We force the surface integral to vanish by requiring $\phi\nabla\psi$ goes to zero faster than $1/r^2$ as $r \rightarrow \infty$. As for the volume integral, if we set ϕ equal to the rest of the expression in that integral (*i.e.*, $\phi = -\nabla K\nabla\psi + (V(x) - E)\psi$), we find that the volume integral of a perfect square over all space must vanish. That is

$$\left(-K\nabla^2 + V(x)\right)\psi = E\psi \quad (8)$$

This is the Schrödinger equation with $K = \hbar^2/2m$:

$$\left(-\frac{(\hbar\nabla)^2}{2m} + V(x)\right)\psi = E\psi \quad (9)$$

This expression looks suspiciously like the classical Hamiltonian for a particle of mass m :

$$\mathcal{H} = \frac{p^2}{2m} + V(x) \quad (10)$$

As a consequence, through this correspondence it is possible to create a beautiful algorithm for the transition from classical to quantum mechanics:

1. Write down the Hamiltonian for the classical system, expressed in terms of the coordinates q_i and canonically conjugate momenta p_j .
2. Replace $p_j \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial q_j}$.
3. Let this operator act on functions $\psi(q)$ that are defined on the configuration part (q) of the total phase space (q, p).
4. Solve the eigenvalue equation.

The formal statement representing the step from Classical Mechanics to Quantum Mechanics involves defining the commutator in Quantum Mechanics in terms of the Poisson Bracket of Classical Mechanics:

$$[A, B] = i\hbar \{A, B\} \quad (11)$$

The classical Poisson bracket is defined by $\{A, B\} = \sum_{j=1}^n \frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} - \frac{\partial A}{\partial p_j} \frac{\partial B}{\partial q_j}$.

We will solve the hydrogen atom problem in two ways. First by the variational principle, Eq. (4), and then by the Schrödinger equation Eq. (9).

For a spherically symmetric potential, *e.g.*, $V(x) = -e^2/|\mathbf{x}|$, where e is the charge on the central proton and $-e$ is the charge on the electron, we can assume that the wavefunction separates in the usual way

$$\psi(\mathbf{x}) \rightarrow \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (12)$$

The pieces of this product obey the following normalization conditions

$$\int \int (\Theta(\theta)\Phi(\phi))^* (\Theta(\theta)\Phi(\phi)) \sin \theta d\theta d\phi = 1 \quad \int_0^\infty R^2(r)r^2 dr = 1 \quad (13)$$

The gradient is

$$\nabla\psi \rightarrow \hat{\mathbf{r}} \frac{dR}{dr} \Theta(\theta)\Phi(\phi) + \frac{\hat{\theta}}{r} R(r) \frac{d\Theta}{d\theta} \Phi(\phi) + \frac{\hat{\phi}}{r \sin \theta} R(r)\Theta(\theta) \frac{d\Phi}{d\phi} \quad (14)$$

and the inner product of the gradient with itself reduces to

$$\nabla\psi \cdot \nabla\psi \rightarrow \left(\frac{dR}{dr}\right)^2 \Theta^2 \Phi^2 + R^2 \left(\frac{1}{r} \frac{d\Theta}{d\theta}\right)^2 \Phi^2 + R^2 \Theta^2 \left(\frac{1}{r \sin \theta} \frac{d\Phi}{d\phi}\right)^2 \quad (15)$$

Some simplifications are possible. First, the function $\Phi(\phi)$ must be single valued: $\Phi(\phi + 2\pi) = \Phi(\phi)$. The only possible solutions have the form $\cos m\phi$, $\sin m\phi$ or $e^{\pm im\phi}$. Using the real functions the last term in Eq. (15) becomes proportional to $(mR\Theta\Phi)^2$. A similar but more difficult argument, which is postponed until later, shows that the function $\Theta(\theta)$ must also be single valued, and that the two terms together consolidate themselves to $R^2 \frac{l(l+1)}{r^2} \Theta^2 \Phi^2$. When the θ, ϕ dependence is integrated out, what is left is

$$J_{\text{rad}} = \int_0^\infty K \left(\left(\frac{dR}{dr}\right)^2 + \frac{l(l+1)}{r^2} R^2 \right) + V(r)R^2 - ER^2 r^2 dr \quad (16)$$

In general, there are only a few radial potentials $V(r)$ that can be solved analytically. We (Schrödinger) is lucky that the Coulomb potential $V(r) = -e^2/r$ is one of them. In more general cases another approach must be taken

to construct radial solutions and spectra. We will hint at these methods after this equation is solved.

The variational problem is a quadratic form in both the unknown function $R(r)$ and its first derivative dR/dr . We assume that $R(r)$ is a known solution and look at how a perturbation affects it: $R(r) \rightarrow R(r) + \epsilon g(r)$. This ansatz is substituted into Eq. (16), the derivative with respect to ϵ is taken, and the result is set to zero. This is done since we assume that $R(r)$ (set $\epsilon = 0$) is an actual solution:

$$\frac{dJ(\epsilon)}{d\epsilon}\Big|_{\epsilon=0} = 2 \int K \left(\left(\frac{dR}{dr} \frac{dg(r)}{dr} \right) + \frac{l(l+1)}{r^2} R(r)g(r) \right) + \quad (17)$$

$$V(r)R(r)g(r) - \lambda R(r)g(r) r^2 dr = 0$$

It is essential that this holds for any value of the function $g(r)$. In order to replace dg/dr by $g(r)$ an integration by parts is carried out:

$$\int \frac{dR}{dr} \frac{dg(r)}{dr} r^2 dr = \int \frac{d}{dr} \left(g(r) \frac{dR}{dr} r^2 \right) - g(r) \frac{d}{dr} \left(\frac{dR}{dr} r^2 \right) dr = \quad (18)$$

$$\left(g(r) \frac{dR}{dr} r^2 \right)_0^\infty - \int_0^\infty \frac{1}{r^2} \frac{d}{dr} \left(\frac{dR}{dr} r^2 \right) r^2 dr$$

The surface term must vanish at $r = 0$ and as $r \rightarrow \infty$. The remaining integral is combined with the terms containing the potential energy and the energy to give

$$\int_0^\infty g(r) \left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(\frac{dR}{dr} r^2 \right) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + (V(r) - E)R(r) \right) = 0 \quad (19)$$

Since $g(r)$ is arbitrary, the expression within the brackets must vanish. This gives the radial equation

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(\frac{dR}{dr} r^2 \right) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + (V(r) - E)R(r) = 0 \quad (20)$$

To proceed we multiply through by $-2m/\hbar^2$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} + \frac{2me^2}{\hbar^2} \frac{1}{r} R(r) + \frac{2mE}{\hbar^2} R(r) = 0 \quad (21)$$

It is convenient to use the identity

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = \left(\frac{1}{r} \frac{d}{dr} r \right)^2 R(r) = \frac{1}{r} \left(\frac{d}{dr} \right)^2 r R(r) \quad (22)$$

This identity cries out for the simplification $R(r) = \frac{1}{r} f(r)$. The radial equation correspondingly simplifies to

$$\frac{d^2 f(r)}{dr^2} + \left(-\frac{l(l+1)}{r^2} + \frac{2me^2}{\hbar^2} \frac{1}{r} + \frac{2mE}{\hbar^2} \right) f(r) = 0 \quad (23)$$

At this point we could be tempted to look up the solution. We expect solutions to all reasonable second order ODEs to be tabulated for many years. There is a slight problem. This equation carries dimensions (r is a distance) and it is reasonable to tabulate only dimensionless equations. Accordingly, we introduce a dimensionless parameter z and a scale factor γ whose dimensions are L and substitute $r = \gamma z$ into the equation above. After a slight amount of housecleaning we find

$$\frac{d^2 f(z)}{dz^2} + \left(-\frac{l(l+1)}{z^2} + \frac{\gamma}{\hbar^2} \frac{2me^2}{z} + \frac{\gamma^2}{\hbar^2} \frac{2mE}{z} \right) f(z) = 0 \quad (24)$$

We then search through a convenient tabulation of second order differential equations, as occurs in Abramowitz and Stegun, *Handbook of Mathematical Functions*, and we find in Table 22.6.17 on p. 781 (*Google*: Abramowitz and Stegun, click on ‘Electronic page index’, go to 781 22.6 Differential Equations, and viola!)

$$\frac{d^2 y(x)}{dx^2} + \left(\frac{1 - \alpha^2}{4x^2} + \frac{2n + \alpha + 1}{2x} - \frac{1}{4} \right) y(x) = 0 \quad (25)$$

The solution of this equation is $y(x) = e^{-x/2} x^{\alpha+1/2} L_n^\alpha(x)$ where the strange functions $L_n^\alpha(x)$ are associated Laguerre polynomials.

It is now time to compare the physical parameters with the mathematical:

Physics	Mathematics	\Rightarrow	
$-l(l+1)$	$\frac{1}{4} - \left(\frac{\alpha}{2}\right)^2$	$\alpha = 2l + 1$	(26)
$\frac{\gamma \cdot 2me^2}{\hbar^2}$	$n + \frac{\alpha + 1}{2}$	$\gamma = \frac{\hbar^2}{2me^2}(n + l + 1)$	
$\frac{\gamma^2 \cdot 2mE}{\hbar^2}$	$-\frac{1}{4}$	$-\frac{me^4}{2\hbar^2} \frac{1}{(n + l + 1)^2}$	

The wave function is constructed from these pieces as

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = \frac{1}{r}f(r)Y_m^l(\theta, \phi) = \frac{1}{x}e^{-x/2}x^{l+1}L_n^{(2l+1)}(x)Y_m^l(\theta, \phi) \quad (27)$$

where $x = r/\gamma$ and $\gamma = \frac{1}{2}Na_B$, where the principle quantum number N is related to the orbital angular momentum quantum number l and the radial quantum number n by $N = n + l + 1$ and a_B is the expression for the radius of the hydrogen atom in its ground state: $a_B = \hbar^2/me^2$ (Bohr radius or Bohr orbit).

The spectrum of the hydrogen atom is shown in Fig. 4. The ground state has energy -13.59 eV . The negative sign indicates that the state is bound. All other discrete states shown in this figure are also bound. The states are organized in terms of their energy or principal quantum number N , plotted vertically, and their orbital angular momentum quantum number l , plotted horizontally. There are $2l + 1$ states with orbital angular momentum quantum number l . The total number of states with principal quantum number N is N^2 . The radial quantum number is $n = N - l - 1$, which decreases from $n = N - 1$ to $n = 0$ along a row of states with the same N . The energy decreases like E_1/N^2 with increasing N . $N = 1, 2, \dots, \infty$, $l = 0, 1, 2, \dots, N - 1$, $n = 0, 1, 2, \dots, N - 1$ and $N = n + l + 1$.

The radial wavefunctions are presented in Figs. 5 where they are presented as a function of r (units of $[r] = L$), and in Fig. 6, where they are presented in atomic units (AU).

The radial wavefunctions are plotted in Fig. 7 as a function of r/a_B : these are Atomic Units. These are probability amplitudes. The corresponding probabilities, which are the squares of these wavefunctions, are shown in Fig. 8.

Some of the more useful integrals of the radial wavefunctions are collected in Fig. 9.

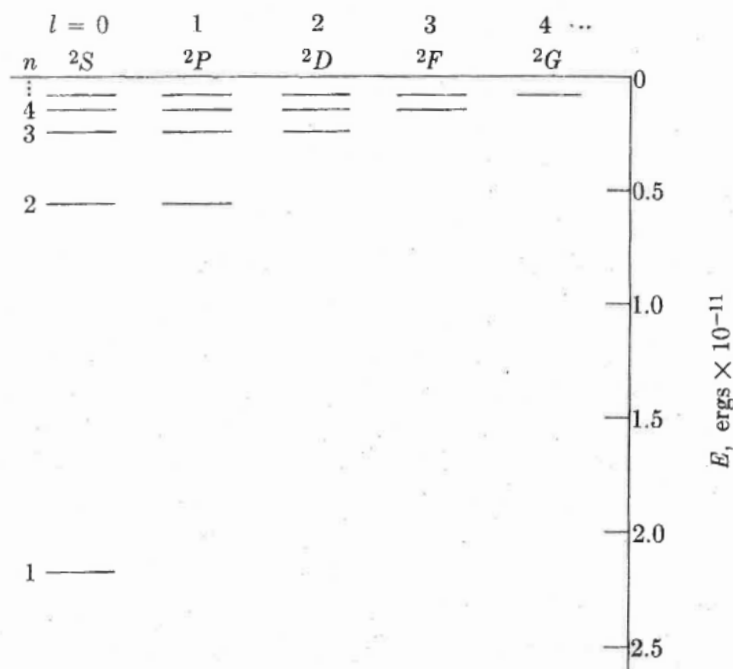


FIG. 10-7. An energy-level diagram for the hydrogen atom. The principal quantum numbers n are indicated at the left of the figure, and the spectroscopic notation for the various terms is given at the top. Compare these energy levels with Fig. 10-4.

Figure 4: Spectrum of the hydrogen atom. This is obtained by solving the Schrödinger nonrelativistic wave equation. The degeneracy of the level with angular quantum number l is $2l + 1$. All N^2 energy levels with the same principal quantum number N have the same energy. The radial quantum number n decreases from $n = N - 1$ for the $l = 0$ states (left of each row) to $n = 0$ at the right end of the row. This quantum number identifies the number of zero crossings of the radial wavefunction. From Dicke and Wittke, Fig. 10-7.

SEVERAL RADIAL WAVE FUNCTIONS
FOR HYDROGENIC ATOMS

$$R_{nl}(r) \equiv \frac{1}{r} u_{nl}$$

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} \cdot 2 \exp\left(-\frac{Zr}{a_0}\right)$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \cdot 2 \left(1 - \frac{1}{2} \frac{Zr}{a_0}\right) \exp\left(-\frac{1}{2} \frac{Zr}{a_0}\right)$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \cdot \frac{1}{\sqrt{3}} \frac{Zr}{a_0} \exp\left(-\frac{1}{2} \frac{Zr}{a_0}\right)$$

$$R_{30}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot 2 \left[1 - \frac{2}{3} \frac{Zr}{a_0} + \frac{2}{27} \left(\frac{Zr}{a_0}\right)^2\right] \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$$

$$R_{31}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{4\sqrt{2}}{3} \frac{Zr}{a_0} \left(1 - \frac{1}{6} \frac{Zr}{a_0}\right) \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$$

$$R_{32}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$$

Figure 5: Radial wavefunctions for the hydrogen atom. These are obtained by solving the Schrödinger equation. They are normalized to one. From Dicke and Wittke, Tab 10-1.

TABLE 1⁵. *Normalized radial eigenfunctions for Z=1.**

$$\begin{array}{ll}
 R(1s) = -2re^{-r} & R(3p) = -\frac{8}{27\sqrt{6}}r^2e^{-\frac{1}{3}r}(1-\frac{1}{3}r) \\
 R(2s) = -\frac{1}{\sqrt{2}}re^{-\frac{1}{2}r}(1-\frac{1}{2}r) & R(4p) = -\frac{1}{16}\sqrt{\frac{5}{3}}r^2e^{-\frac{1}{4}r}(1-\frac{1}{4}r+\frac{1}{80}r^2) \\
 R(3s) = -\frac{2}{3\sqrt{3}}re^{-\frac{1}{3}r}(1-\frac{2}{3}r+\frac{2}{27}r^2) & R(3d) = -\frac{4}{81\sqrt{30}}r^3e^{-\frac{1}{3}r} \\
 R(4s) = -\frac{1}{4}re^{-\frac{1}{4}r}(1-\frac{3}{4}r+\frac{1}{8}r^2-\frac{1}{192}r^3) & R(4d) = -\frac{1}{64\sqrt{5}}r^3e^{-\frac{1}{4}r}(1-\frac{1}{2}r) \\
 R(2p) = -\frac{1}{2\sqrt{6}}r^2e^{-\frac{1}{2}r} & R(4f) = -\frac{1}{768\sqrt{35}}r^4e^{-\frac{1}{4}r}
 \end{array}$$

Figure 6: Radial wavefunctions of the hydrogen atom, expressed in terms of atomic units. From Condon and Shortley, Table 1⁵.

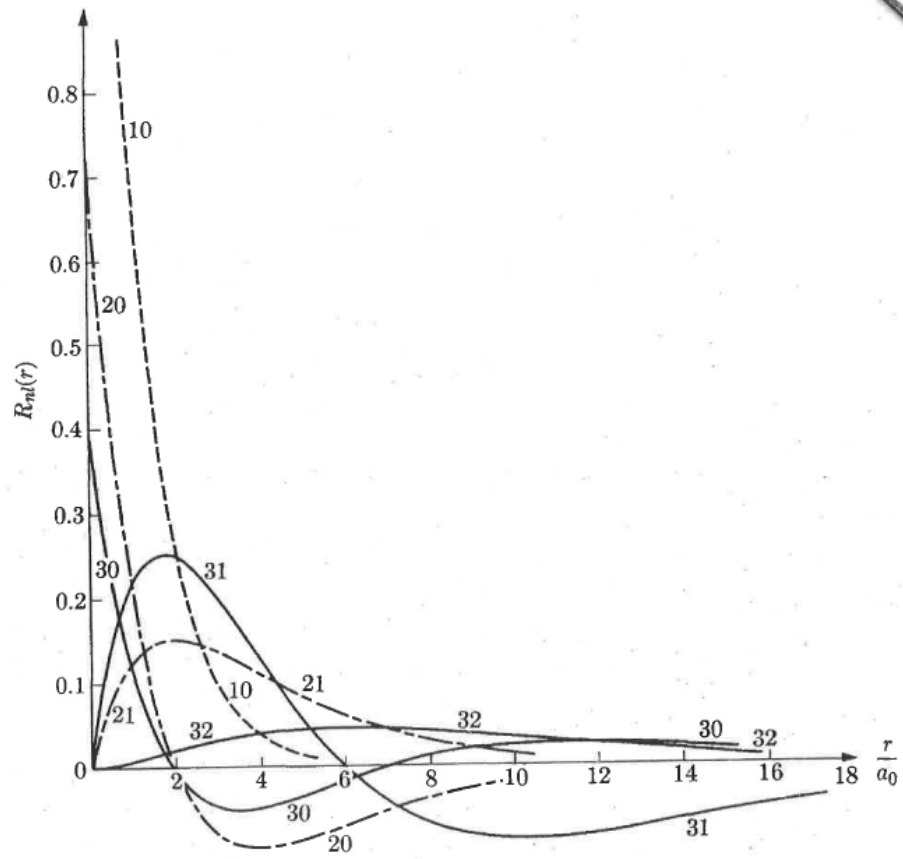


FIG. 10-6. The radial wave functions $R_{nl}(r)$ for hydrogenic atoms for $n = 1, 2, 3$. Each curve is labeled with two integers, representing the corresponding n and l values. Note the effect of the centrifugal force in "pushing out" the wave function from the center of the atom. Note also that the functions have $n - l - 1$ nodes.

Figure 7: Radial wavefunctions for the hydrogen atom, plotted as a function of r/a_B , where a_B is the Bohr radius. These are obtained by solving the Schrödinger equation. They are normalized to one. From Dicke and Wittke, Fig. 10-6.

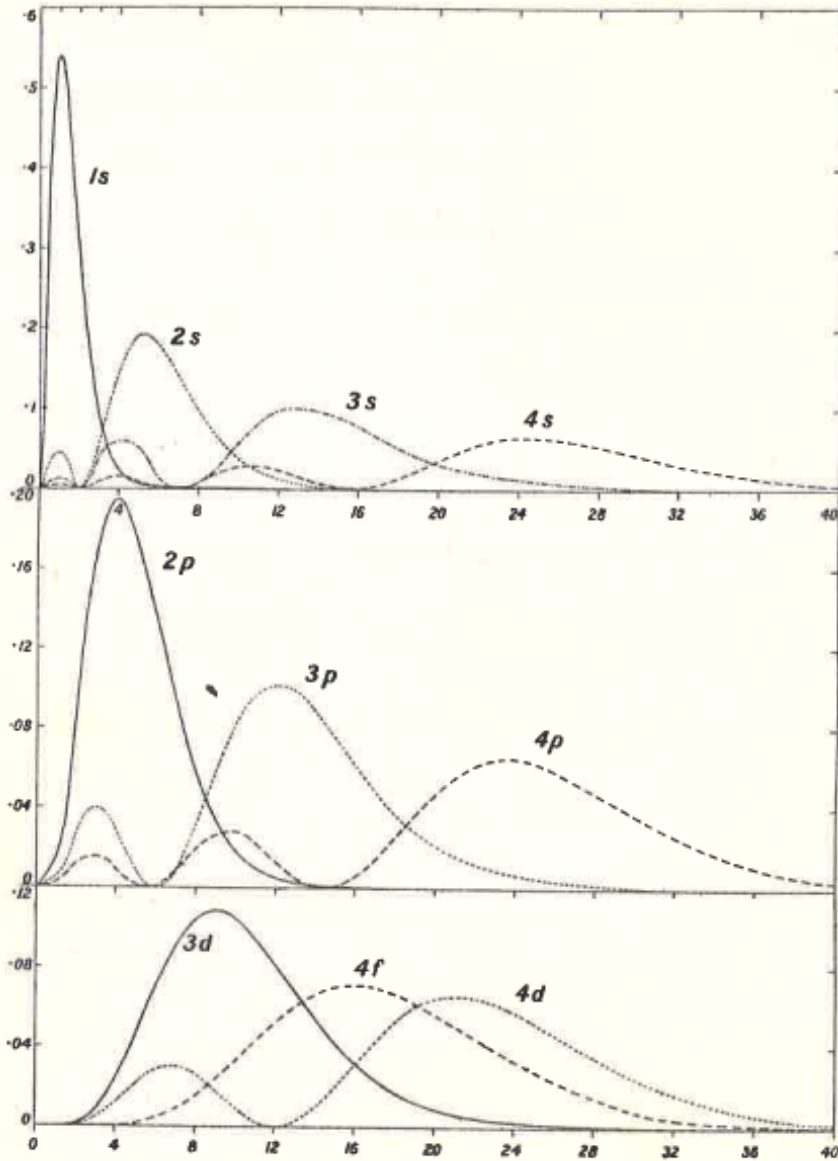


Fig. 15. Radial probability distribution $R^2(nl)$ for several of the lowest levels in hydrogen. (Abscissa is the radius in atomic units.)

In order to normalize the radial functions we need the result

$$\int_0^{\infty} \rho^{2l+2} e^{-\rho} [L_{n+l}^{2l+1}(\rho)]^2 d\rho = \frac{2n[(n+l)!]^3}{(n-l-1)!}, \quad (17)$$

Figure 8: Squares of the radial wavefunctions for the hydrogen atom. These present the probability distributions, rather than the amplitudes, of the radial wavefunctions. From Condon and Shortley, fig. 1⁵.

TABLE 27.

k	$a^{-k} \int_0^{\infty} r^k R^2(nl) dr$
1	$\frac{1}{2Z}[3n^2 - l(l+1)]$
2	$\frac{n^2}{2Z^2}[5n^2 + 1 - 3l(l+1)]$
3	$\frac{n^2}{8Z^3}[35n^2(n^2 - 1) - 30n^2(l+2)(l-1) + 3(l+2)(l+1)l(l-1)]$
4	$\frac{n^4}{8Z^4}[63n^4 - 35n^2(2l^2 + 2l - 3) + 5l(l+1)(3l^2 + 3l - 10) + 12]$
-1	$\frac{Z}{n^2}$
-2	$\frac{Z^2}{n^3(l + \frac{1}{2})}$
-3	$\frac{Z^3}{n^3(l+1)(l + \frac{1}{2})l}$
-4	$\frac{Z^4 \frac{1}{2}[3n^2 - l(l+1)]}{n^5(l + \frac{3}{2})(l+1)(l + \frac{1}{2})l(l - \frac{1}{2})}$

* In this table r is measured in atomic units. The general eigenfunctions for any Z and arbitrary length unit are obtained by multiplying the functions of this table by $\sqrt{Z/a}$ and replacing r by Zr/a .

† The average values of r^{-5} and r^{-6} may be found in VAN VLECK, Proc. Roy. Soc. A143, 679 (1934).

Figure 9: Some useful diagonal matrix elements of the radial wavefunctions. From Condon and Shortley, Table 2⁵.

Copenhagen Interpretation of Quantum Mechanics

Formulated after Bohm (1952)

1. Every Quantum system Q is described by a state vector $|\psi\rangle$ in some Hilbert space.
2. This state contains all the information that can ever be known about Q .
3. The state vector evolves dynamically according to Schrödinger's equation.
4. In order to extract information about Q , an interaction must take place between Q and a measuring apparatus A .
5. The measuring apparatus is a classical object and gives classical results.
6. It is outside the scope of analysis.
7. The entire system $A + Q$ interacts to produce a measurement of Q .
8. Replacing A by a different apparatus A' changes the entire system $A + Q$ to a different system $A' + Q$, and the results of the measurements need not be similar.
9. Only quantities that have been measured can be considered real.
10. The only values of an observable that can be observed in a measurement are eigenvalues a_n of the observable, which is a hermitian operator on the Hilbert space.
11. The probability of observing eigenvalue a_n when the experiment is carried out is $|\langle\phi_n|\psi\rangle|^2$, where $|\phi_n\rangle$ is an eigenvector of A with eigenvalue a_n .
12. Immediately after the measurement the state of Q is $|\phi_n\rangle$ if the measurement is a_n .

Remarks:

2. This philosophical point is not universally shared.
4. “Measuring apparatus” remains undefined.
5. It is claimed that von Neumann formulated things so the measuring apparatus could also be quantum mechanical. In view of his failures (Bohm’s hidden variables theory is a counterexample to his “proof” that hidden variables theories are impossible; the laser is a counterexample to his and Bohr’s adamant claims that masers/lasers violate the uncertainty relations and are therefore impossible), I cannot give credence to this claim.
6. This is a cop out.
8. **Complementarity!**
9. Einstein, Schrödinger have difficulty with this.
11. Born’s probabilistic interpretation.
12. **Collapse of the wavefunction.** There is no theory for this.

Some Questions:

1. What is the origin and meaning of the uncertainty relations? Or more generally of the noncommutativity of observables?
2. Where is the boundary in $A + Q$?
3. How does the apparatus force the “collapse of the wavefunction” $|\psi\rangle \rightarrow |\phi_n\rangle$ during a measurement?

“Newtonian Formulation” of Copenhagen Interpretation

Definition of Coordinate System: The playing field on which Quantum Mechanics takes place is a Hilbert space. A quantum system Q is represented by a state vector $|\psi\rangle$ in this Hilbert space, or more generally by a density operator ρ on this space. Observables are represented by hermitian operators acting on this space.

Dynamics: The state $|\psi\rangle$ or ρ representing a quantum system evolves under the Schrödinger equation.

Action and Reaction — Measurement: The quantum system Q and the apparatus A measuring the value of an observable interact with each other during a measurement. Q acts on A to produce an eigenvalue a_n with probability $|\langle\phi_n|\psi\rangle|^2$, where $|\phi_n\rangle$ is a normalized eigenvector of the hermitian operator A with eigenvalue a_n . A back-reaction of A on Q guarantees that Q is in the eigenstate $|\phi_n\rangle$ immediately after the measurement.