

# Quantum theory

Hans A. Bethe

Floyd R. Newman Laboratory of Nuclear Studies, Cornell University,  
Ithaca, New York 14853

[S0034-6861(99)04202-6]

## I. EARLY HISTORY

Twentieth-century physics began with Planck's postulate, in 1900, that electromagnetic radiation is not continuously absorbed or emitted, but comes in quanta of energy  $h\nu$ , where  $\nu$  is the frequency and  $h$  Planck's constant. Planck got to this postulate in a complicated way, starting from statistical mechanics. He derived from it his famous law of the spectral distribution of blackbody radiation,

$$n(\nu) = [e^{h\nu/kT} - 1]^{-1}, \quad (1)$$

which has been confirmed by many experiments. It is also accurately fulfilled by the cosmic background radiation, which is a relic of the big bang and has a temperature  $T = 2.7$  K.

Einstein, in 1905, got to the quantum concept more directly, from the photoelectric effect: electrons can be extracted from a metal only by light of frequency above a certain minimum, where

$$h\nu_{\min} = w, \quad (2)$$

with  $w$  the "work function" of the metal, i.e., the binding energy of the (most loosely bound) electron. This law was later confirmed for x rays releasing electrons from inner shells.

Niels Bohr, in 1913, applied quantum theory to the motion of the electron in the hydrogen atom. He found that the electron could be bound in energy levels of energy

$$E_n = -\frac{Ry}{n^2}, \quad (3)$$

where  $n$  can be any integer. The Rydberg constant is

$$Ry = \frac{me^4}{2\hbar^2}. \quad (4)$$

Light can be emitted or absorbed only at frequencies given by

$$h\nu = E_m - E_n, \quad (5)$$

where  $m$  and  $n$  are integers. This daring hypothesis explained the observed spectrum of the hydrogen atom. The existence of energy levels was later confirmed by the experiment of J. Franck and G. Hertz. Ernest Rutherford, who had earlier proposed the nuclear atom, declared that now, after Bohr's theory, he could finally believe that his proposal was right.

In 1917, Einstein combined his photon theory with statistical mechanics and found that, in addition to absorption and spontaneous emission of photons, there

had to be stimulated emission. This result, which at the time seemed purely theoretical, gave rise in the 1960s to the invention of the laser, an eminently practical and useful device.

A. H. Compton, in 1923, got direct evidence for light quanta: when x rays are scattered by electrons, their frequency is diminished, as if the quantum of energy  $h\nu$  and momentum  $h\nu/c$  had a collision with the electron in which momentum and energy were conserved. This Compton effect finally convinced most physicists of the reality of light quanta.

Physicists were still confronted with the wave/particle duality of light quanta on the one hand and the phenomena of interference, which indicated a continuum theory, on the other. This paradox was not resolved until Dirac quantized the electromagnetic field in 1927.

Niels Bohr, ever after 1916, was deeply concerned with the puzzles and paradoxes of quantum theory, and these formed the subject of discussion among the many excellent physicists who gathered at his Institute, such as Kramers, Slater, W. Pauli, and W. Heisenberg. The correspondence principle was formulated, namely, that in the limit of high quantum numbers classical mechanics must be valid. The concept of oscillator strength  $f_{mn}$  for the transition from level  $m$  to  $n$  in an atom was developed, and dispersion theory was formulated in terms of oscillator strength.

Pauli formulated the exclusion principle, stating that only one electron can occupy a given quantum state, thereby giving a theoretical foundation to the periodic system of the elements, which Bohr had explained phenomenologically in terms of the occupation by electrons of various quantum orbits.

A great breakthrough was made in 1925 by Heisenberg, whose book, *Physics and Beyond* (Heisenberg, 1971), describes how the idea came to him while he was on vacation in Heligoland. When he returned home to Göttingen and explained his ideas to Max Born the latter told him, "Heisenberg, what you have found here are matrices." Heisenberg had never heard of matrices.

Born had already worked in a similar direction with P. Jordan, and the three of them, Born, Heisenberg, and Jordan, then jointly wrote a definitive paper on "matrix mechanics." They found that the matrices representing the coordinate of a particle  $q$  and its momentum  $p$  do not commute, but satisfy the relation

$$qp - pq = i\hbar 1, \quad (6)$$

where 1 is a diagonal matrix with the number 1 in each diagonal element. This is a valid formulation of quantum mechanics, but it was very difficult to find the matrix

elements for any but the simplest problems, such as the harmonic oscillator. The problem of the hydrogen atom was soon solved by the wizardry of W. Pauli in 1926. The problem of angular momentum is still best treated by matrix mechanics, in which the three components of the angular momentum are represented by noncommuting matrices.

Erwin Schrödinger in 1926 found a different formulation of quantum mechanics, which turned out to be most useful for solving concrete problems: A system of  $n$  particles is represented by a wave function in  $3n$  dimensions, which satisfies a partial differential equation, the “Schrödinger equation.” Schrödinger was stimulated by the work of L. V. de Broglie, who had conceived of particles as being represented by waves. This concept was beautifully confirmed in 1926 by the experiment of Davisson and Germer on electron diffraction by a crystal of nickel.

Schrödinger showed that his wave mechanics was equivalent to Heisenberg’s matrix mechanics. The elements of Heisenberg’s matrix could be calculated from Schrödinger’s wave function. The eigenvalues of Schrödinger’s wave equation gave the energy levels of the system.

It was relatively easy to solve the Schrödinger equation for specific physical systems: Schrödinger solved it for the hydrogen atom, as well as for the Zeeman and the Stark effects. For the latter problem, he developed perturbation theory, useful for an enormous number of problems.

A third formulation of quantum mechanics was found by P. A. M. Dirac (1926), while he was still a graduate student at Cambridge. It is more general than either of the former ones and has been used widely in the further development of the field.

In 1926 Born presented his interpretation of Schrödinger’s wave function:  $|\psi(x_1, x_2, \dots, x_n)|^2$  gives the probability of finding one particle at  $x_1$ , one at  $x_2$ , etc.

When a single particle is represented by a wave function, this can be constructed so as to give maximum probability of finding the particle at a given position  $x$  and a given momentum  $p$ , but neither of them can be exactly specified. This point was emphasized by Heisenberg in his uncertainty principle: classical concepts of motion can be applied to a particle only to a limited extent. You cannot describe the orbit of an electron in the ground state of an atom. The uncertainty principle has been exploited widely, especially by Niels Bohr.

Pauli, in 1927, amplified the Schrödinger equation by including the electron spin, which had been discovered by G. Uhlenbeck and S. Goudsmit in 1925. Pauli’s wave function has two components, spin up and spin down, and the spin is represented by a  $2 \times 2$  matrix. The matrices representing the components of the spin,  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$ , do not commute. In addition to their practical usefulness, they are the simplest operators for demonstrating the essential difference between classical and quantum theory.

Dirac, in 1928, showed that spin follows naturally if the wave equation is extended to satisfy the require-

ments of special relativity, and if at the same time one requires that the differential equation be first order in time. Dirac’s wave function for an electron has four components, more accurately  $2 \times 2$ . One factor 2 refers to spin, the other to the sign of the energy, which in relativity is given by

$$E = \pm c(p^2 + m^2 c^2)^{1/2}. \quad (7)$$

States of negative energy make no physical sense, so Dirac postulated that nearly all such states are normally occupied. The few that are empty appear as particles of positive electric charge.

Dirac first believed that these particles represented protons. But H. Weyl and J. R. Oppenheimer, independently, showed that the positive particles must have the same mass as electrons. Pauli, in a famous article in the *Handbuch der Physik* (Pauli, 1933), considered this prediction of positively charged electrons a fundamental flaw of the theory. But within a year, in 1933, Carl Anderson and S. Neddermeyer discovered positrons in cosmic radiation.

Dirac’s theory not only provided a natural explanation of spin, but also predicted that the interaction of the spin magnetic moment with the electric field in an atom is twice the strength that might be naively expected, in agreement with the observed fine structure of atomic spectra.

Empirically, particles of zero (or integral) spin obey Bose-Einstein statistics, and particles of spin  $\frac{1}{2}$  (or half-integral), including electron, proton, and neutron, obey Fermi-Dirac statistics, i.e., they obey the Pauli exclusion principle. Pauli showed that spin and statistics should indeed be related in this way.

## II. APPLICATIONS

1926, the year when I started graduate work, was a wonderful time for theoretical physicists. Whatever problem you tackled with the new tools of quantum mechanics could be successfully solved, and hundreds of problems, from the experimental work of many decades, were around, asking to be tackled.

### A. Atomic physics

The fine structure of the hydrogen spectrum was derived by Dirac. Energy levels depend on the principal quantum number  $n$  and the total angular momentum  $j$ , orbital momentum plus spin. Two states of orbital momentum  $\ell = j + \frac{1}{2}$  and  $j - \frac{1}{2}$  are degenerate.

The He atom had been an insoluble problem for the old (1913–1924) quantum theory. Using the Schrödinger equation, Heisenberg solved it in 1927. He found that the wave function, depending on the position of the two electrons  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ , could be symmetric or antisymmetric in  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . He postulated that the complete wave function should be antisymmetric, so a  $\Psi$  symmetric in  $\mathbf{r}_1$  and  $\mathbf{r}_2$  should be multiplied by a spin wave function antisymmetric in  $\sigma_1$  and  $\sigma_2$ , hence belonging to a singlet state (parahelium). An antisymmetric spatial wave func-

tion describes a state with total spin  $S=1$ , hence a triplet state (orthohelium). Heisenberg thus obtained a correct qualitative description of the He spectrum. The ground state is singlet, but for the excited states, the triplet has lower energy than the singlet. There is no degeneracy in orbital angular momentum  $L$ .

Heisenberg used a well-designed perturbation theory and thus got only qualitative results for the energy levels. To get accurate numbers, Hylleraas (in 1928 and later) used a variational method. The ground-state wave function is a function of  $r_1$ ,  $r_2$ , and  $r_{12}$ , the distance of the two electrons from each other. He assumed a “trial function” depending on these variables and on some parameters, and then minimized the total energy as a function of these parameters. The resulting energy was very accurate. Others improved the accuracy further.

I also was intrigued by Hylleraas’s success and applied his method to the negative hydrogen ion  $H^-$ . I showed that this ion was stable. It is important for the outer layers of the sun and in the crystal LiH, which is ionic:  $Li^+$  and  $H^-$ .

For more complicated atoms, the first task was to obtain the structure of the spectrum. J. von Neumann and E. Wigner applied group theory to this problem, and could reproduce many features of the spectrum, e.g., the feature that, for a given electron configuration, the state of highest total spin  $S$  and highest total orbital momentum  $L$  has the lowest energy.

In the late 1920’s J. Slater showed that these (and other) results could be obtained without group theory, by writing the wave function of the atom as a determinant of the wave functions of the individual electrons. The determinant form ensured antisymmetry.

To obtain the electron orbitals, D. R. Hartree in 1928 considered each electron as moving in the potential produced by the nucleus and the charge distribution of all the other electrons. Fock extended this method to include the effect of the antisymmetry of the atomic wave function. Hartree calculated numerically the orbitals in several atoms, first using his and later Fock’s formulation.

Group theory is important in the structure of crystals, as had been shown long before quantum mechanics. I applied group theory in 1929 to the quantum states of an atom inside a crystal. This theory has also been much used in the physical chemistry of atoms in solution.

With modern computers, the solution of the Hartree-Fock system of differential equations has become straightforward. Once the electron orbitals are known, the energy levels of the atom can be calculated. Relativity can be included. The electron density near the nucleus can be calculated, and hence the hyperfine structure, isotope effect, and similar effects of the nucleus.

## B. Molecules

A good approximation to molecular structure is to consider the nuclei fixed and calculate the electron wave function in the field of these fixed nuclei (Born and Oppenheimer, 1927). The eigenvalue of the electron en-

ergy, as a function of the position of nuclei, can then be considered as a potential in which the nuclei move.

Heitler and F. London, in 1927, considered the simplest molecule,  $H_2$ . They started from the wave function of two H atoms in the ground state and calculated the energy perturbation when the nuclei are at a distance  $R$ . If the wave function of the electrons is symmetric with respect to the position of the nuclei, the energy is lower than that of two separate H atoms, and they could calculate the binding energy of  $H_2$  and the equilibrium distance  $R_0$  of the two nuclei. Both agreed reasonably well with observation. At distances  $R < R_0$ , there is repulsion.

If the wave function is antisymmetric in the positions of the two electrons, there is repulsion at all distances. For a symmetric wave function, more accurate results can be obtained by the variational method.

Linus Pauling was able to explain molecular binding generally, in terms of quantum mechanics, and thereby helped create theoretical chemistry—see Herschbach (1999).

An alternative to the Heitler-London theory is the picture of molecular orbitals: Given the distance  $R$  between two nuclei, one may describe each electron by a wave function in the field of the nuclei. Since this field has only cylindrical symmetry, electronic states are described by two quantum numbers, the total angular momentum and its projection along the molecular axis; for example,  $p\sigma$  means a state of total angular momentum 1 and component 0 in the direction of the axis.

## C. Solid state

In a metal, the electrons are (reasonably) free to move between atoms. In 1927 Arnold Sommerfeld showed that the concept of free electron obeying the Pauli principle could explain many properties of metals, such as the relation between electric and thermal conductivity.

One phenomenon in solid-state physics, superconductivity, defied theorists for a long time. Many wrong theories were published. Finally, the problem was solved by John Bardeen, Leon Cooper, and Robert Schrieffer. Pairs of electrons are traveling together, at a considerable distance from each other, and are interacting strongly with lattice vibrations [see Schrieffer and Tinkham (1999)].

## D. Collisions

The old (pre-1925) quantum theory could not treat collisions. In quantum mechanics the problem was solved by Born. If a particle of momentum  $\mathbf{p}_1$  collides with a system  $\Psi_1$ , excites that system to a state  $\Psi_2$ , and thereby gets scattered to a momentum  $\mathbf{p}_2$ , then in first approximation the probability of this process is proportional to the absolute square of the matrix element,

$$\mathcal{M} = \int \exp[i(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{r}/\hbar] \Psi_1 \Psi_2^* V d\tau, \quad (8)$$

where  $V$  is the interaction potential between particle and system, and the integration goes over the coordinates of the particle and all the components of the system. More accurate prescriptions were also given by Born.

There is an extensive literature on the subject. Nearly all physics beyond spectroscopy depends on the analysis of collisions see Datz *et al.* (1999).

### E. Radiation and electrodynamics

The paradox of radiation's being both quanta and waves is elucidated by second quantization. Expanding the electromagnetic field in a Fourier series,

$$F(\mathbf{r},t) = \sum a_k \exp i(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad (9)$$

one can consider the amplitudes  $a_k$  as dynamic variables, with a conjugate variable  $a_k^\dagger$ . They are quantized, using the commutation relation

$$a_k a_k^\dagger - a_k^\dagger a_k = 1. \quad (10)$$

The energy of each normal mode is  $\hbar \omega (n + \frac{1}{2})$ .

Emission and absorption of light is straightforward. The width of the spectral line corresponding to the transition of an atomic system from state  $m$  to state  $n$  was shown by E. Wigner and V. Weisskopf to be

$$\Delta \omega = \frac{1}{2} (\gamma_m + \gamma_n), \quad (11)$$

where  $\gamma_m$  is the rate of decay of state  $m$  (reciprocal of its lifetime) due to spontaneous emission of radiation.

Heisenberg and Pauli (1929, 1930) set out to construct a theory of quantum electrodynamics, quantizing the electric field at a given position  $\mathbf{r}_m$ . Their theory is self-consistent, but it had the unfortunate feature that the electron's self-energy, i.e., its interaction with its own electromagnetic field, turned out to be infinite.

E. Fermi (1932) greatly simplified the theory by considering the Fourier components of the field, rather than the field at a given point. But the self-energy remained infinite. This problem was only solved after World War II. The key was the recognition, primarily due to Kramers, that the self-energy is necessarily included in the mass of the electron and cannot be separately measured. The only observable quantity is then a possible *change* of that self-energy when the electron is subject to external forces, as in an atom.

J. Schwinger (1948) and R. Feynman (1948), in different ways, then constructed relativistically covariant, and finite, theories of quantum electrodynamics. Schwinger deepened the existing theory while Feynman invented a completely novel technique which at the same time simplified the technique of doing actual calculations. S. Tomonaga had earlier (1943) found a formulation similar to Schwinger's. F. J. Dyson (1949) showed the equivalence of Schwinger and Feynman's approaches and then showed that the results of the theory are finite in any order of  $\alpha = e^2/\hbar c$ . Nevertheless the perturbation series diverges, and infinities will appear in order exp

$(-\hbar c/e^2)$ . An excellent account of the development of quantum electrodynamics has been given by Schweber (1994).

It was very fortunate that, just before Schwinger and Feynman, experiments were performed that showed the intricate effects of the self-interaction of the electron. One was the discovery, by P. Kusch and H. M. Foley (1948) that the magnetic moment of the electron is slightly (by about 1 part in 1000) greater than predicted by Dirac's theory. The other was the observation by W. Lamb and R. Retherford (1947) that the  $2s$  and the  $2p_{1/2}$  states of the H atom do not coincide,  $2s$  having an energy higher by the very small amount of about 1000 megaHertz (the total binding energy being of the order of  $10^9$  megaHertz).

All these matters were discussed at the famous Shelter Island Conference in 1947 (Schweber, 1994). Lamb, Kusch, and I. I. Rabi presented experimental results, Kramers his interpretation of the self-energy, and Feynman and Schwinger were greatly stimulated by the conference. So was I, and I was able within a week to calculate an approximate value of the Lamb shift.

After extensive calculations, the Lamb shift could be reproduced within the accuracy of theory and experiment. The Lamb shift was also observed in  $\text{He}^+$ , and calculated for the  $1s$  electron in Pb. In the latter atom, its contribution is several Rydberg units.

The "anomalous" magnetic moment of the electron was measured in ingenious experiments by H. Dehmelt and collaborators. They achieved fabulous accuracy, viz., for the ratio of the anomalous to the Dirac moments

$$a = 1\ 159\ 652\ 188\ (4) \times 10^{-12}, \quad (12)$$

where the 4 in parenthesis gives the probable error of the last quoted figure. T. Kinoshita and his students have evaluated the quantum electrodynamic (QED) theory with equal accuracy, and deduced from Eq. (12) the fine-structure constant

$$\alpha^{-1} = \hbar c/e^2 = 137.036\ 000. \quad (13)$$

At least three other, independent methods confirm this value of the fine-structure constant, albeit with less precision. See also Hughes and Kinoshita (1999).

### III. INTERPRETATION

Schrödinger believed at first that his wave function gives directly the continuous distribution of the electron charge at a given time. Bohr opposed this idea vigorously.

Guided by his thinking about quantum-mechanical collision theory (see Sec. II.D.) Born proposed that the absolute square of the wave function gives the probability of finding the electron, or other particle or particles, at a given position. This interpretation has been generally accepted.

For a free particle, a wave function (wave packet) may be constructed that puts the main probability near a

position  $x_0$  and near a momentum  $p_0$ . But there is the uncertainty principle: position and momentum cannot be simultaneously determined accurately, their uncertainties are related by

$$\Delta x \Delta p \geq \frac{1}{2} \hbar. \quad (14)$$

The uncertainty principle says only this: that the concepts of classical mechanics cannot be directly applied in the atomic realm. This should not be surprising because the classical concepts were derived by studying the motion of objects weighing grams or kilograms, moving over distances of meters. There is no reason why they should still be valid for objects weighing  $10^{-24}$  g or less, moving over distances of  $10^{-8}$  cm or less.

The uncertainty principle has profoundly misled the lay public: they believe that everything in quantum theory is fuzzy and uncertain. Exactly the reverse is true. Only quantum theory can explain why atoms exist at all. In a classical description, the electrons hopelessly fall into the nucleus, emitting radiation in the process. With quantum theory, and only with quantum theory, we can understand and explain why chemistry exists—and, due to chemistry, biology.

(A small detail: in the old quantum theory, we had to speak of the electron “jumping” from one quantum state to another when the atom emits light. In quantum mechanics, the orbit is sufficiently fuzzy that no jump is needed: the electron can move continuously in space; at worst it may change its velocity.)

Perhaps more radical than the uncertainty principle is the fact that you cannot predict the result of a collision but merely the probability of various possible results. From a practical point of view, this is not very different from statistical mechanics, where we also only consider probabilities. But of course, in quantum mechanics the result is unpredictable *in principle*.

Several prominent physicists found it difficult to accept the uncertainty principle and related probability predictions, among them de Broglie, Einstein, and Schrödinger. De Broglie tried to argue that there should be a deterministic theory behind quantum mechanics. Einstein forever thought up new examples that might contradict the uncertainty principle and confronted Bohr with them; Bohr often had to think for hours before he could prove Einstein wrong.

Consider a composite object that disintegrates into  $A + B$ . The total momentum  $P_A + P_B$  and its coordinate separation  $x_A - x_B$  can be measured and specified simultaneously. For simplicity let us assume that  $P_A + P_B$  is zero, and that  $x_A - x_B$  is a large distance. If in this state

the momentum of  $A$  is measured and found to be  $P_A$ , we know that the momentum of  $B$  is definitely  $-P_A$ . We may then measure  $x_B$  and it seems that we know both  $P_B$  and  $x_B$ , in apparent conflict with the uncertainty principle. The resolution is this: the measurement of  $x_B$  imparts a momentum to  $B$  (as in a  $\gamma$ -ray microscope) and thus destroys the previous knowledge of  $P_B$ , so the two measurements have no predictive value.

Nowadays these peculiar quantum correlations are often discussed in terms of an “entangled” spin-zero state of a composite object  $AB$ , composed of two spin-one-half particles, or two oppositely polarized photons (Bohm and Aharonov). Bell showed that the quantum-mechanical correlations between two such separable systems,  $A$  and  $B$ , cannot be explained by any mechanism involving hidden variables. Quantum correlations between separated parts  $A$  and  $B$  of a composite system have been demonstrated by some beautiful experiments (e.g., Aspect *et al.*). The current status of these issues is further discussed by Mandel (1999) and Zeilinger (1999), in this volume.

## REFERENCES

- Born, M., and J. R. Oppenheimer, 1927, *Ann. Phys. (Leipzig)* **84**, 457.
- Datz, S., G. W. F. Drake, T. F. Gallagher, H. Kleinpoppen, and G. zu Putlitz, 1999, *Rev. Mod. Phys.* **71**, (this issue).
- Dirac, P. A. M., 1926, Ph.D. Thesis (Cambridge University).
- Dyson, F. J., 1949, *Phys. Rev.* **75**, 486.
- Fermi, E., 1932, *Rev. Mod. Phys.* **4**, 87.
- Feynman, R. P., 1948, *Rev. Mod. Phys.* **76**, 769.
- Heisenberg, W., 1971, *Physics and Beyond* (New York, Harper and Row).
- Heisenberg, W., and W. Pauli, 1929, *Z. Phys.* **56**, 1.
- Heisenberg, W., and W. Pauli, 1930, *Z. Phys.* **59**, 168.
- Herschbach, D., 1999, *Rev. Mod. Phys.* **71** (this issue).
- Hughes, V., and T. Kinoshita, 1999, *Rev. Mod. Phys.* **71** (this issue).
- Kusch, P., and H. M. Foley, 1948, *Phys. Rev.* **73**, 412; **74**, 250.
- Lamb, W. E., and R. C. Retherford, 1947, *Phys. Rev.* **72**, 241.
- Mandel, L., 1999, *Rev. Mod. Phys.* **71** (this issue).
- Pauli, W., 1933, *Handbuch der Physik*, 2nd Ed. (Berlin, Springer).
- Schrieffer, J. R., and M. Tinkham, 1999, *Rev. Mod. Phys.* **71** (this issue).
- Schweber, S. S., 1994, *QED and the Men who Made It* (Princeton University Press, Princeton, NJ), pp. 157–193.
- Schwinger, J., 1948, *Phys. Rev.* **73**, 416.
- Tomonaga, S., 1943, *Bull. IPCR (Rikenko)* **22**, 545 [Eng. Translation 1946].
- Zeilinger, A., 1999, *Rev. Mod. Phys.* **71** (this issue).