PHYSICS TODAY VOL 19 NO 8

Paths to Quantum Theory Historically Viewed

If Bohr had been a lawyer, if, for some reason, one or more of the great discoveries had not been made, physicists would still have arrived at a complete and consistent quantum theory, stepping on the stones provided by other men's work. A few roads not taken might have made things happen faster than they did.

by Friedrich Hund

THE ACTUAL COURSE of history is a complicated network. In the development of science it is less complicated than in political history because in science there is more internal consistency and more compulsion from the object of study. But in science history, too, we have chance and accident along with consistency and consequence. Let us now consider how far the growth of quantum theory, the different ways it has actually gone, has been by consistency and how far by chance.

Figure 1 shows, in a very simplified way, some lines of development and the principal events: Max Planck's energy quanta (1900), Albert Einstein's light particles (1905), his understanding of specific heat (1907), the unity of spectra, the atomic model and quanta by Niels Bohr (1913), Louis de Broglie's waves (1923), matrix mechanics (1925), Erwin Schrödinger's equation (1926) and, at the far right, consistent quantum mechanics.

The author, who is best known for Hund's rules for electronic configurations, got his PhD in 1922 under Max Born and since then has been professor of theoretical physics at Rostock, Leipzig, Jena, Frankfurt/Main and the Institute of Theoretical Physics in Göttingen, where he now is. His work has been concerned with quantum theory of atoms, molecules and solids and general questions of quantum theory. At the moment he is working on the history of physics.

We will consider each line separately. We are allowed to ask: How might it have been if some accident had not occurred? Imagine, for example, that Bohr had become, let us say, a lawyer and not a physicist.

Spectra

A frequency is a difference of two "terms," and the order of the terms is much simpler than the order of the frequencies. Johannes Rydberg knew this about 1890 (figure 1) for simple spectra. His notation was equivalent to

$$\nu = \frac{R}{(n_1 - \alpha_1)^2} - \frac{R}{(n_2 - \alpha_2)^2} \qquad (1)$$

For the terms he had the well known scheme

1s	2s	3s	4s	. . .
	2p	3p	4p	. . .
		3d	4d	. . .

and at least as early as 1893 he wrote the frequencies in a rectangular array, which afterwards could be called a "matrix." But between Rydberg's step and the interpretation of the terms as atomic states is a gap of 20 years. Why?

Certainly equation 1 was too special; α was not exactly a constant in one series of terms, and R was not exactly the same for all elements. For this reason there were eminent spectroscopists who did not like equation 1. And only very late (1908) did Walter Ritz write the general form

$$\nu = f(n_1 \ldots) - f(n_2 \ldots) \tag{2}$$

Fritz Paschen immediately used it and found a lot of new spectral lines. But equation 2 also was not much recognized by physicists; we shall see this lack of recognition in a wrong path that Friedrich Hasenöhrl took, and we have learned from Léon Rosenfeld that Bohr got notice of equation 2 only a few weeks before he finished his famous 1913 paper.

Now imagine that the quantum of action had not been detected by Planck and light quanta not conceived by Einstein. Then certainly the question would be: Has equation 2 something to do with the frequency $\nu(E, \ldots)$ of the motion of a particle depending on energy (and perhaps other constants of motion)? Is equation 2 a key to atom dynamics different from macroscopic dynamics? Then the correspondence between the classical frequencies (harmonic overtones) $\tau\nu_1(E)$ and the actual frequencies of equation 4 might not be too distant. The classical relation $\nu_1 = dE/d\phi$ with

$$\phi = \oint p \; dx \tag{3}$$

(for one degree of freedom) was familiar at least to Ludwig Boltzmann's school (for example to Hasenöhrl) and the following system could be established

$$\begin{array}{ll} \nu = \tau \, \nu_1(E) & \nu = f(n) - f(n - \tau). \\ \nu_1 = dE/d\phi & \nu_1 = \Delta f / \Delta n \end{array} \tag{4}$$

$$E = hf \qquad \phi = hn \tag{5}$$

This would have been a correspondence principle and preliminary quantum theory similar to Bohr's —quantum theory without Planck and Einstein. Also it would not have been too difficult to recognize from the spectral series of the hydrogen atom

$$\nu = \frac{R}{n_1^2} - \frac{R}{n_2^2}$$

the energies $E \propto -1/n^2$ and for large n the frequencies

$$\nu \propto \frac{dE}{dn} \propto \frac{1}{n^3}$$

leading to the relation

$$\nu^2 \propto |E|^3$$

This is a well known relation for classical motion in a Coulomb field of force. The system would have been quantum theory of the hydrogen atom without Rutherford. History did not happen that way; other things grew faster.

Because there is a logical path from the preliminary quantum theory of the correspondence principle to the matrix form of quantum mechanics (a path that is well known), we can say: Spectral laws as the only empirical basis could have led to a full quantum theory.

The atom

Quantum theory in its perfection made it possible to think of the atom without contradiction. Classical physics only offers us different aspects of the atom which contradict one another. But in the

PLANCK

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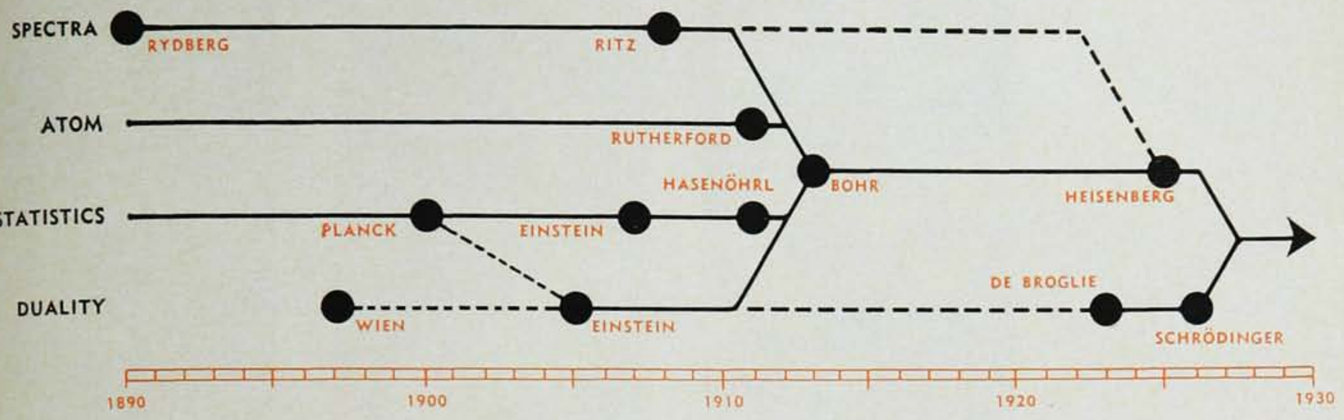

DIFFERENT ROADS, principally those of spectral analysis, atomic structure, statistical mechanics and thermodynamics, and the wave-particle duality of both light and matter, have led to our present understanding of quantum mechanics. —FIG. 1

early days of quantum theory, except for spectra, the atom was not a key.

Chemical properties of the atom must have looked very strange to physicists at the beginning of the 20th century. The periodic table was nearly closed. The importance of something like atomic number was largely conceived. But the numbers 2, 8, 8, 18, 18 that represent the lengths of the periods could not be used as a key. Now, after we have come to the end of the story, we know that $N = 2n^2$ has to do with spin and Wolfgang Pauli's exclusion principle and has little to do with the fundamentals of common quantum mechanics.

At the beginning of the century physicists did not know much more of the structure of the atom than that there were electrons in it. But soon afterwards they had at least some feeling that atoms had ionization energies well defined for each element. Still this fact and the problem of stability and uniqueness of the atom did not become biting questions before Ernest Rutherford's model (1911); they were central questions for Bohr.

Statistics

There were some phenomena, perhaps related to the atom, but not dependent on its special structure. They had to do with temperature.

In 1900, William Thomson, Lord Kelvin, called the rules for specific heat one of the two "clouds over the dynamical theory of heat and light." According to the equipartition law, each particle must contribute $3k/2$ to the kinetic part of the specific heat; but actual values of specific heat are generally lower. The decrease of specific heat at low temperature was not well known then. But we can imagine that some years later physicists—without Planck and Einstein—could have conceived of degrees of freedom going to sleep at low temperature and contributing to the energy only at higher temperatures. Thus oscillators only contribute if T/ν is high enough, and such a condition could not be well expressed in any other manner than

$$kT/h\nu > 1 \qquad (6)$$

Rotators contribute only if TI is high enough (I is the moment of inertia). Such a condition is equivalent to

$$kTI/h^2 > 1 \qquad (7)$$

In both of these examples measurements give h in the order of magnitude 10^{-27} erg-sec.

But around 1900 black-body radiation gave more information than specific heat. So actually the question "Why doesn't a cold piece of iron glow?" (a formulation of H. A. Lorentz in 1911) stood at the beginning of quantum theory. Planck's hypothesis concerning the harmonic oscillator was better understood when he wrote

$$\phi = \oint p\,dx = h\,n \qquad (8)$$

as the rule for extension in the phase plane. He offered it as a secondary comment in 1906 and emphasized it more at the Solvay Congress in 1911. Hasenöhrl comprehended it and extended it to any system with one degree of freedom. Acquainted with the relation

$$dE = \nu(E)d\phi \qquad (9)$$

for systems with one degree of freedom in classi-

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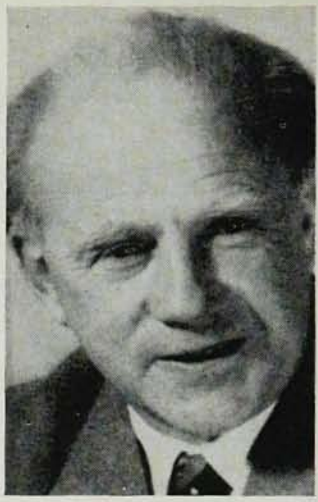


HEISENBERG

SCHROEDINGER

cal mechanics, he wrote a quantum condition

$$\int_{E(n-1)}^{E(n)} d\phi = \int_{E(n-1)}^{E(n)} dE/\nu(E) = h \qquad (10)$$

for calculation of the energy states $E(n)$ of a system with any classical dependence $\nu(E)$. Up to this point we are concerned only with statistical physics—with quantum statistics, not quantum dynamics. As in classical statistics statistical weight or number of cases is determined by phase extension, and equation 8 or 10 can be called a correspondence principle for statistics.

Not much is missing, and Hasenöhrl would have arrived at a correspondence principle for frequencies. He had the key in equation 9, but he went astray. From Balmer's formula for the hydrogen atom

$$\nu = R\,\frac{n^2-4}{4n^2} \qquad (11)$$

he calculated the energies $E(n)$ of the hydrogen atom by integration of $dE = h\nu dn$ getting

$$E(n) = Rh\,\frac{n^2+4}{4n}$$

which (as we now know) has nothing to do with reality.

He did not read the right-hand side of equation 11 as a difference although in 1911 Paschen's series

$$\nu = R\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

was also known. Otherwise Hasenöhrl would not have taken $\nu = dE/d\phi$ literally but as an analogy corresponding to

$$\nu = \frac{1}{h}[E\ (n) - E\ (n-1)]$$

We see how difficult it was to make two steps in the right direction. Since 1913 Peter Debye had also been using the quantum conditions of equation 8, and in his lectures at Göttingen he put that equation into the center. He did not apply it to spectra, however, until he could refer to Bohr; that is, he restricted his quantum theory to statistics.

We see that temperature dependence could lead to a large part of quantum physics, but to connect $\nu(E)$ in equation 10 with a dynamical property, an experience with actual frequencies was necessary—the combination principle or the hydrogen series in difference form. Unfortunately Hasenöhrl did not appreciate this requirement.

Duality of light

To illustrate his formula for cavity radiation

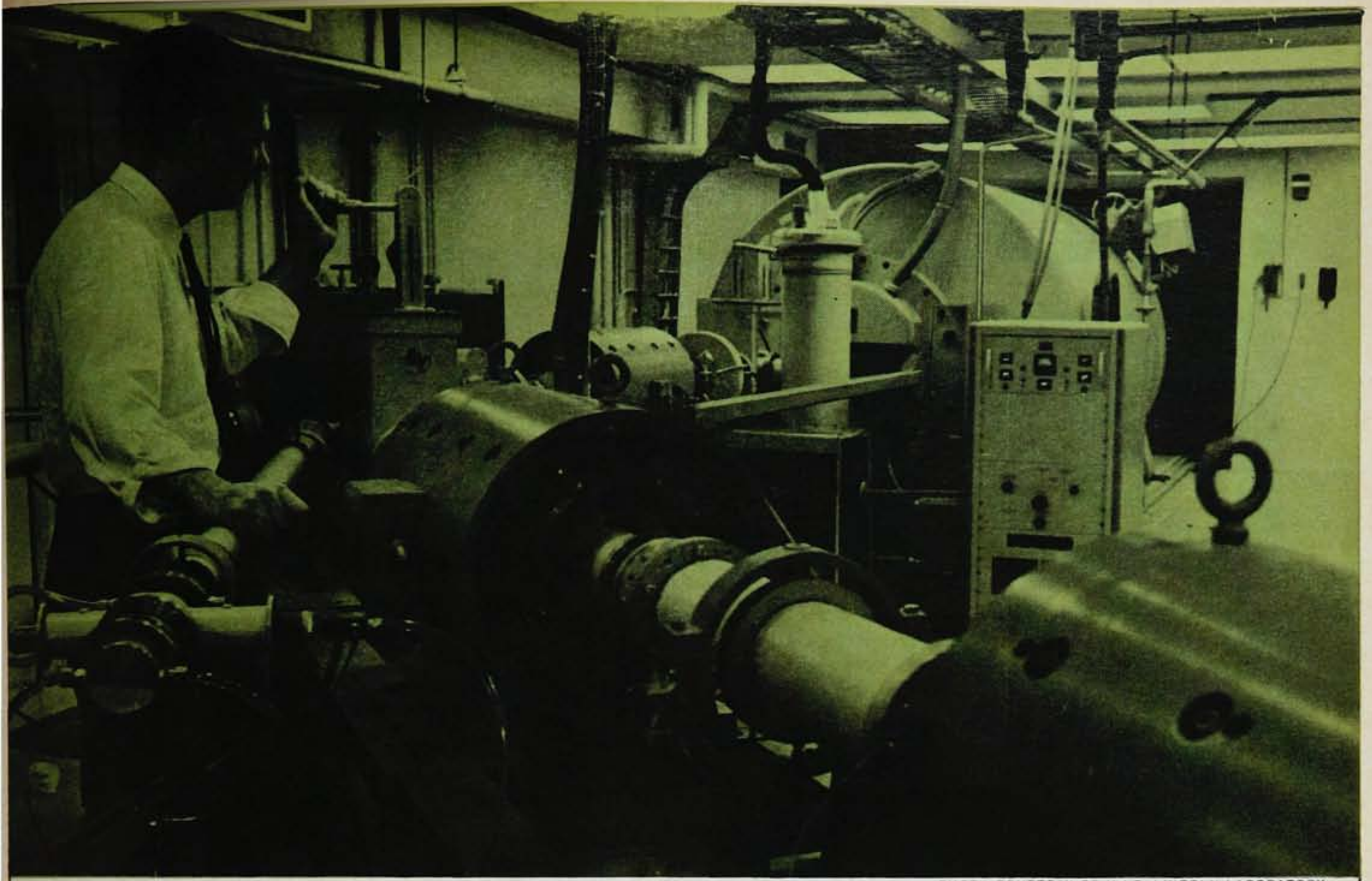
$$W \propto \nu^3\, e^{-h\nu/kT} \qquad (12)$$

Wilhelm Wien in 1897 discussed a model: a gas of molecules with velocities v depending on a frequency ν. Statistics and Wien's displacement law then led to equation 12 and to an energy $E \propto \nu$ of the molecules. He did not write it

$$E \propto h\nu \qquad (13)$$

In 1905 Einstein explained Wien's formula (equation 12) in a more definite manner with light quanta having the energy of equation 13.

Experiments with x rays had shown that greater frequency produced a greater effect; the photoelectric effect had pointed in the same direction. So the second question that stimulated quantum theory was, "Why do we not get brown by sitting a long time beside a hot stove?" Johannes Stark had wild fantasy, great ambition, and he wrote very much. But he also had a good feeling for



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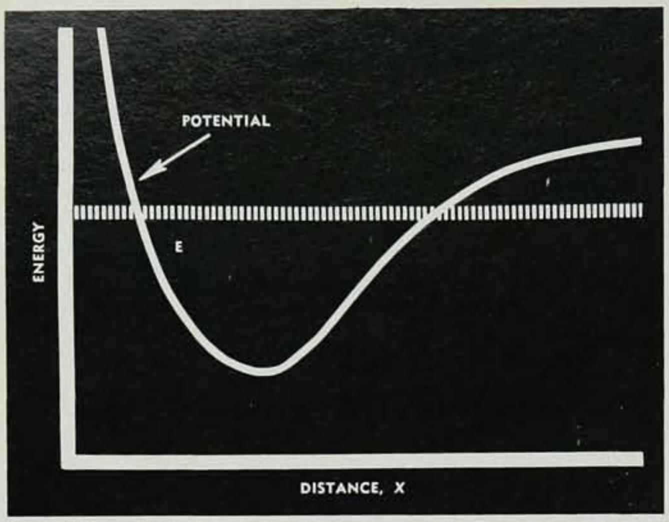
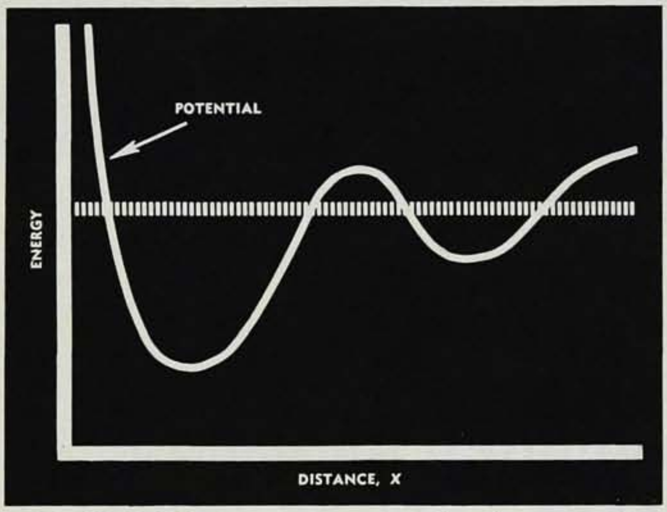


PHASE-INTEGRAL calculations consider only region in which potential is less than or equal to the energy of the system and neglects potential outside well. —FIG. 2



MORE REFINED treatment requires that the one making calculations consider the potential outside the well and also lower and higher states of the system. —FIG. 3

the qualitative features of atomic processes. Perhaps from his earlier thoughts that faster electrons cross atoms in a shorter time and therefore produce radiation of higher frequencies, he used the equation

$$h\,\nu = \Delta E \tag{14}$$

in both directions: transformation of radiation energy into energy of an atomic system and transformation of electron energy into radiation (1907). It is difficult to say how far he was independent of Einstein.

Of course the step from equation 14 to full quantum theory affords an instruction for calculating the energies $E(n)$ of an atomic system, an instruction like the correspondence principle.

From phase integral to matrix

$$\phi = \oint p\,dx = hn \tag{15}$$

was an instruction for calculating energy values $E(n)$ [consider a system with a unique relation for $\nu(E)$] fitting the correspondence principle. In fact the actual frequencies

$$\nu = \frac{1}{h}[E\,(n) - E\,(n - \tau)]$$

become more and more nearly equal to the classical frequencies

$$\nu = \tau\, dE/d\phi$$

the smoother the function $E(n)$ is.

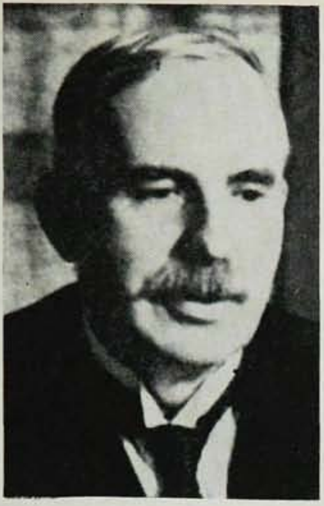
About 12 years intervened between the conception of the correspondence principle by Bohr and Werner Heisenberg's form of quantum mechanics although the path from one to the other was rather consistent. The long time can be explained by the many special problems related to spectra, the anomalous Zeeman effect and multiplets that were related to a mixture of spin, the Pauli principle and some fundamental quantum theory. This wickerwork was hard to untangle, and more special features distracted from the direct approach.

The phase-integral method not only failed during calculations with many-particle systems. The method of equation 15 and its generalization to more degrees of freedom had internal inconsistencies. In the calculation, classical frequencies of a part of the system or of an approximation to the system were used—frequencies that actually did not exist. On the way to quantum mechanics these frequencies were replaced by quantum frequencies.

Another internal inconsistency can be demonstrated in simple systems with one degree of freedom, for example an anharmonic oscillator. Calculation of the energies with equation 15 uses only the potential $V(x)$ in the region $V(x) \leqq E$ (figure 2), but the actual properties of a special quantum state E, for example its frequencies, have to do with lower and higher states, that is, with the potential in the region $V(x) \geqq E$ also. Large deviations from equation 15 are therefore expected in systems like those of figure 3. It appears that such systems had not been considered for refinement of the correspondence principle.

For the step from matrix mechanics to more general formulations of matter-wave quantum mechanics, the path of de Broglie and Schrödinger would not have been necessary. Paul Dirac, for example, treated quantum mechanics in a more algebraic manner. Max Born and Norbert Wiener

HASENOEHRL



RUTHERFORD

WIEN

used operators instead of matrices, and a young listener to a lecture Born gave in America in 1926, Carl Eckart, fulfilled the commutation relation

$$i\,(pq - qp) = \hbar$$

by substituting $\hbar\partial/i\partial q$ for p. But in a "note added in proof" he had to state that in a paper just published, Schrödinger had done the same thing.

Duality of matter

There are several accesses to wave theory or field theory of matter: experiments showing interference in matter beams, chemical forces, discrete states of the atom, analogy with light. But to get clear interferences with matter was technically more difficult than with light or x rays. To develop a field equation of matter in atoms from the short range of chemical forces was certainly too difficult.

De Broglie's conception of phase waves corresponding to particle motion apparently has two roots: In 1918–22 Marcel Brillouin had the idea that the curious properties of the atom have to do with a special state of the ether near the nucleus; de Broglie knew about these ideas. The other root was analogy with light. Schrödinger was influenced by de Broglie.

A more logical way than Schrödinger went would have been to derive from relativistic invariance a nonrelativistic "classical" field theory of matter containing a field equation like

$$-\frac{1}{2\lambda}\,\Delta\,\Psi + \zeta\,U\,\Psi - i\,\frac{d\Psi}{dt} = 0$$

(U = electric potential; ζ, λ constants of matter). Of course this would not have been a correct theory because it contains no elementary particles. But used as a one-particle equation with the particle constants $m = \hbar\lambda$, $e = \hbar\zeta$, it s the Schrödinger equation. To go from a field theory of matter to a many-body Schrödinger equation, one must have field quantization, which actually was invented after particle quantization and would not have been invented without it.

Why did not field theory of matter come earlier? The answer could be: Duality of light, detected by Einstein, was not taken seriously by other physicists before detection of the Compton effect (1922), and Einstein himself was too much occupied by general relativity.

Without de Broglie matter waves also would have come. Duality of light affords duality of matter. A 1923 paper of William Duane shows some of the possibilities.

What it means

We study the history of science for better understanding of science itself. Concerning quantum theory, for example, the question arises: How should one teach it? Of course the answer depends on audience maturity and the teacher's taste. I am now too old for teaching. But in the years before, I preferred a way of some symmetry between the particle aspect and the field aspect of matter and light. Of course I know that a matter field is in some respect paler than the electromagnetic field. But I see no good access to relativistic quantum theory of matter without the matter field.

Logically ordinary (nonrelativistic) quantum mechanics can be built from particle aspects alone, and it also can be built from field aspects alone. In handling quantum mechanics, perhaps building from the particle aspects is to be preferred (canonical variables of particles, commutation relation, Schrödinger equation). But there is a difference between handling and understanding. And understanding is no longer pure physics. □