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Quantum theory

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Quantum theory was born in 1900 with an important paper by Max Planck on the black-body radiation. In this paper, he introduced quanta of vibrational energy E which are proportional to their frequency ν, and his famous constant currently known to take the value (Mohr & Taylor, 2000)

$$\frac{E}{\nu} = h = 6.62606876(52)\ 10^{-34}\ \text{Joule second}\ .$$

Ten years after its formulation, Planck's hypothesis had been extraordinarily successful, explaining the light spectrum of black-body radiation, the photoelectric effect, and the low-temperature reduction of heat capacity in solids.

Using Rutherford's planetary model of atoms, Niels Bohr showed in 1913 that Planck's hypothesis helps to understand the spectral lines of hydrogen by deriving their frequencies in terms of h and the electron mass and charge. The success of Bohr's atomic model led to the formulation of Bohr–Sommerfeld quantization rule for classically integrable systems possessing as many invariants of motion as degrees of freedom:

$$\oint p_j\ dq_j = h\left(n_j + \frac{\mu_j}{4}\right)\ , \qquad j = 1, 2, ..., f\ ,$$

where (q_j, p_j) are the canonically conjugate position-momentum variables in terms of which the system is integrable (also said separable), n_j are integers, μ_j are the so-called Maslov indices which characterize the topology of the motion (e.g. $\mu_j = 0$ for rotation, $\mu_j = 2$ for libration), and f is the number of degrees of freedom.

In 1917, Albert Einstein pointed out that the Bohr–Sommerfeld quantization rule cannot be applied to classically non-integrable systems (such as helium atom), and it slowly became apparent that radically new ideas were required. In 1923, Louis de Broglie suggested that massive particles should behave as waves and he completed Planck's hypothesis by his famous relation, $p\lambda = h$, between the particle momentum p and its wavelength λ.

Finally in 1925 and 1926, Werner Heisenberg and Erwin Schrödinger established quantum mechanics in two equivalent formulations. The first represents the observable quantities as matrices and the second is based on the famous Schrödinger equation

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial\vec{r}^2} + V(\vec{r},t)\ \psi\ , \qquad (1)$$

for the wave function $\psi(\vec{r},t)$ of a particle of mass m moving in the energy potential $V(\vec{r},t)$, with $\hbar = h/2\pi$ and $\mathrm{i} = \sqrt{-1}$. In 1927, Max Born proposed to interpret the square of the modulus of the wavefunction, $|\psi(\vec{r},t)|^2$, as the probability density to observe the particle at position $\vec{r}$ and time t if the wavefunction is normalized to unity over the whole configuration space according to

$$\int |\psi(\vec{r},t)|^2 d\vec{r} = 1\ . \qquad (2)$$

In this formulation, physical observables are represented by linear Hermitian operators $\hat{A}$ acting on the wave function. The expectation value of an observable is given by

$$\langle A\rangle = \int \psi^*(\vec{r},t)\ \hat{A}\psi(\vec{r},t)\ d\vec{r}\ ,$$

if the particle is in the state described by the normalized wave function ψ. The wave property prevents a quantum particle to have simultaneously well-defined position and momentum as in the classical world. This impossibility (which follows from Fourier transform theory) is expressed by Heisenberg's uncertainty relation between the uncertainties on position Δx and momentum Δp

$$\Delta x \; \Delta p \geq \hbar/2 \; ,$$

which finds its origin in the noncommutativity of position and momentum operators.

The normalization condition (2) has the pivotal role of selecting the physically acceptable wave functions among all the possible solutions of the Schrödinger equation (1). In particular, it is the normalization condition which leads to the quantization of energy into well-defined eigenvalues associated with the stationary states. Without the normalization condition, the wave function would present spatial instabilities which are not physically meaningful.

Because of their spatial extension, wave functions are allowed to penetrate into classically forbidden regions where the classical kinetic energy of the particle would be negative. In these regions, the normalization condition (2) forces the wave function to decrease exponentially and precludes its instability. A consequence is the phenomenon of quantum tunneling, which manifests itself in cold electronic emission or α radioactivity and finds technological applications in Leo Esaki's semiconductor tunneling diode, Ivar Giaever's superconducting tunneling diode, and the electron tunneling microscope.

Together with the normalization condition, the Schrödinger equation shares with nonlinear systems the general scheme:

$$\text{instability} \;\rightarrow\; \text{saturation} \;\rightarrow\; \text{structure} \, .$$

In quantum mechanics, the instability mechanism is spatial and the saturation is provided by the normalization condition which selects spatially stable wave functions such as the electronic orbitals of atoms, molecules, and solids. The selection of normalizable wavefunctions generates the molecular structures of stereochemistry.

However, Schrödinger's equation is linear and thus obeys the principle of linear superposition (Dirac, 1930). Accordingly, the linear combination

$$\psi = \sum_n c_n \psi_n \; ,$$

(with complex numbers c_n) is a physically acceptable solution of Equation (1). Following studies by Steven Weinberg and others (Weinberg, 1989), extremely stringent limits have been put on hypothetical nonlinear corrections to quantum mechanics. These limits have been obtained by searching for nonlinearly induced detuning of resonant transitions between two atomic levels, putting the following upper bounds on a hypothetical nonlinear term $\Delta E(\psi, \psi^*)\psi$ supposed to correct the right-hand side of Schrödinger Equation (1):

$$\begin{aligned} |\Delta E| \; &< 2.4 \; 10^{-20} \, \text{eV in } {}^{9}\text{Be}^{+} \text{ ion (Bollinger } et\ al., 1989) \, , \\ |\Delta E| \; &< 1.6 \; 10^{-20} \, \text{eV in } {}^{201}\text{Hg atom (Majumder } et\ al., 1990) \, . \end{aligned}$$

The principle of linear superposition of quantum mechanics has thus been confirmed by these investigations.

Nevertheless, in low-temperature many-body quantum systems, effective nonlinearities may arise if some wave function describing a subset of degrees of freedom has a feedback effect onto itself. Examples of effectively nonlinear quantum equations include the Hartree–Fock equation for fermionic systems, the Ginzburg–Landau equation for superconductors, the Gross–Pitaevskii equation for Bose–Einstein condensates, or the Ginzburg–Landau equation coupled to a Chern–Simon gauge field for the fractional quantum Hall effect.

Another problem where nonlinearities are associated with Schrödinger's equation is the theory of the optimal control of quantum systems by external electromagnetic field. The optimal external field can be obtained as a solution of coupled nonlinear Schrödinger equations, where nonlinearity arises by a feedback mechanism of the quantum system onto itself through the external field and the desired control. Such feedback mechanisms have been experimentally implemented for laser control of chemical reactions (Rice & Zhao, 2000).

Nonlinear effects also emerge out of wave mechanics in the semiclassical limit, where the motion can be described in terms of classical orbits (solutions of nonlinear Hamiltonian equations). In the 1970s starting from Schrödinger's equation, Gutzwiller derived a semiclassical trace formula that expresses the density of energy eigenvalues in terms of periodic orbits (Gutzwiller, 1990). The periodic orbits are unstable and proliferate exponentially in chaotic systems, where semiclassical quantization can be performed thanks to the Gutzwiller trace formula as an alternative to the Bohr–Sommerfeld quantization rule.

In summary, nonlinear effects manifest themselves in quantum systems as phenomena emerging out of the linear wave mechanics in particular limits such as the semiclassical limit or the many-body limit at low temperature.

See also Bose-Einstein condensation; Hartree approximation; Nonlinear Schrödinger equations; Quantum chaos; Superconductivity; Superfluidity.

Further Reading

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