

SCHRÖDINGER EQUATION AND QUANTUM CHEMISTRY

Renato Colle

Dipartimento di Chimica Applicata, Università di Bologna, Italy,

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Contents

1. Introduction
 2. The Schrödinger equation
 - 2.1 Foundation of wave mechanics
 - 2.2 Properties of the Schrödinger equation
 - 2.3 Generalization of the Schrödinger equation for many-body systems
 - 2.4 General remarks on the Schrödinger equation
 3. Quantum Chemistry
 - 3.1 Hartree-Fock theory and molecular orbitals
 - 3.2 Correlated wavefunctions
 - 3.3 Density Functional Theory
 - 3.4 Time-dependent problems
- Acknowledgement
Glossary
Bibliography
Biographical Sketch

Summary

Aims, topics and methods of quantum chemistry are discussed, together with the relationship between quantum mechanics and quantum chemistry.

Foundation of wave mechanics and derivation of the one-particle Schrödinger equation are summarized. The main properties of this equation are analyzed, together with its generalization for many-body systems.

Quantum mechanical methods developed for studying static and dynamic properties of molecules are described.

1. Introduction

Quantum chemistry is the science that studies molecules and processes involving molecules using methods of quantum mechanics. If we consider that under the word “molecules” one can include the largest part of chemical substances, like e.g. organic and inorganic complexes, clusters and macromolecules, and if we consider that quantum mechanics is a formal theory well-established in its general principles and almost

universally accepted to interpret and quantitatively predict phenomena on the atomic scale, we should conclude that quantum chemistry is not simply a branch of chemistry, but aims to give a conceptual framework able to interpret in depth properties of chemical substances and processes involving these substances.

To summarize briefly the novelty of quantum mechanics and its deep revision of concepts of Newtonian macroscopic science, we can follow U.Fano's analysis "... common to all modern science is a primary reliance on *reproducible* experimental observations. Consider, however, that when Galileo rolled marbles down an incline, measuring their speed and acceleration, his observation process clearly had negligible influence on the results, thus keeping in effect the observer fully *separate* from the objects under study. Atomistic experiments sample instead the behavior of matter or radiation from equivalent sources in *alternative* ways, drawing conclusions from *combined statistical* results.... These procedures contrast with those employed to determine the mechanical state of macroscopic objects, by measuring the position and velocity of *each* individual object through actions viewed as fully *compatible* with one another. Measurements performed sequentially, even though on equivalent objects, are instead viewed as independent. This contrast of basic *measurement procedures* provides common to light polarization and atomic phenomena; it is the earmark of quantum mechanics's novelty... Atomic experiments have actually taught us that science should deal *only* with inferences from observations done by humans, *caution* being of the essence when extrapolating such evidence on dubious grounds... This essay casts quantum physics in terms of three *distinct* conceptual elements: A) Experiments on transfers of dynamical parameters (moments, energy, angular moments) between atomic systems and their environment show that : 1) each transfer's magnitude is discrete and set by rules perceived *only* at atomic scales; 2) these rules hinge on *geometrical* and *time*-dependent elements previously foreign to dynamics. B) The outcome of experiments conducted with beams (or equivalent ensembles) of particles of radiations is *reproducible* on a statistical basis, yet *wholly random* when observing single events, viewing randomness as *primitive*, rather than as resulting from manifold unobserved circumstances, introduces a *novel* concept to physics. C) Quantum mechanics describes relationships among observed parameters through sets of mathematical *symbols* called "probability amplitudes"... Among these abstract, complex-valued constructs, that serve to correlate *observable* parameters, the wave functions are a particular – if major – class of probability amplitudes...". This last remark sends us back to the Schrödinger equation and formal theory on which quantum chemistry is based. This is the subject of selection 2. Here we discuss, first, the relationship between quantum mechanics and quantum chemistry and, second, the main topics of quantum chemistry.

The first clear statement on the relationship between quantum mechanics and chemistry is contained in the Dirac famous sentence: "...The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation...". This sentence contains the two main lines of development of quantum chemistry: on the one hand, that based on the idea that a

correct application of first principles, i.e., of quantum mechanics, if supported by an appropriate computation effort, allows one to produce numbers directly comparable, or even better than those obtained from experiments. In this connection, the well-known sentence reported in the introduction of the textbook by Eyring, Walter, Kimball on quantum chemistry: “..In so far as quantum mechanics is correct, chemical questions are problems in applied mathematics...” springs to mind. On the other hand, the line suggested by the second part of Dirac’s sentence and clearly defined by Coulson “...Chemistry is an experimental subject, whose results can be built into a pattern around quite elementary concepts. The role of quantum chemistry is to understand these concepts and to say that the electronic computer shows that dissociation energy of HF is much bigger than dissociation of F_2 is not an explanation at all, but merely a confirmation of experiment. Any acceptable “explanation” must be in terms of repulsions between non-bonding electrons, dispersion forces between atomic “cores”, and the like...”

Quantum chemistry is now a mature science, whose evolution has followed the two main lines sketched above: development of new quantum mechanical methods and computational algorithm for calculating chemical properties, and definition of new concepts, the so-called “patterns of understanding”, for the interpretation of chemical problems. Since what is seen as the beginning of quantum chemistry, the Heitler-London paper on the hydrogen molecule in 1927, for about forty years, quantum chemistry has been essentially a “theory of valence”, i.e. a theory that was intended to answer the following fundamental questions: Why do molecules form? Why do the same atoms form different compounds in definite but different proportions? What is the origin of the stereochemistry of molecules? During these years a solid theory developed, endowed with predicting capabilities and able to answer in depth the above questions. Since, in a profound sense, the description of bonds in a molecule is simply the description of the distribution of its electrons around the nuclei, the theory of valence is based essentially on methods for obtaining approximate solutions of the time-independent Schrödinger equation for the ground state of molecules and on the analysis and interpretation of the wavefunctions that are obtained from these solutions. Methods proposed for solving these problems and general concepts introduced for interpreting obtained results are discussed in section 3.

At the end of the fifties electronic computers became available for chemical applications. Their rapid growth in speed and power has produced a real change in quantum chemistry: on the one hand, the possibility of implementing quantum mechanical methods already known, but too difficult or too sophisticated to be used without computers on real problems; on the other hand, the possibility of applying these methods to interpret, from first principles, the results of new spectroscopic techniques, like those based on the use of laser sources, synchrotron radiation, strong magnetic fields, collimated molecular beams, with the consequent development of new quantum mechanical methods.

Quantum chemistry has also become an analytical tool suitable for applications in different branches of chemistry and is used to obtain information bypassing direct measurements: in *physical chemistry*, to predict thermodynamic properties of gases, to calculate transition states and rate constants of chemical reactions, to obtain information

on structural and electronic properties of molecules from the interpretation of spectroscopic data; in *organic and inorganic chemistry*, to compare the stability of different compounds, to study reaction intermediates and reaction mechanisms; in *biochemistry*, despite difficulties due to the large size of the biologically important molecules, to study conformations and salvation of these molecules, enzyme- substrate interactions and related problems.

The quality of the results that can be obtained applying quantum chemistry to chemical problems depends mainly on two elements: the modeling of the actual systems and the methods used to study this model. As for the first point, one has to define the portion of matter and the physical interactions that are important for the problem and construct a model that takes into account the specific features of the quantities to be calculated and the degree of accuracy achievable in the experiment that has to be interpreted. Thus, for example, an isolated molecule described as an ensemble of point charges of different masses that interact via coulomb forces is a sufficiently accurate model for calculating structural and spectroscopic properties of real molecules made up of atoms with nuclear charges less than 20 and belonging to a low-density gas. For molecules with heavier atoms, instead, accurate calculations of several properties require the inclusion of interaction due to the spin of the particles. Similarly, for molecules in condensed phases or in solution, the environmental effects play an important role that has to be taken into account either via some mean-field approach or including explicitly in the calculation, the molecular structure of a portion of the environment.

The second step is the choice of the quantum mechanical method appropriate for studying the problem. This means, essentially, the choice of the approximations necessary to approach the exact solutions of the Schrödinger equation and the capability of estimating the degree of accuracy of the calculation. Currently available quantum mechanical methods guarantee the accepted standard of chemical accuracy for small and medium-size molecules. Moreover, for electronic, rotovibrational and collisional spectra of molecules with up to about 10 electrons, quantum chemistry reaches a degree of accuracy that is comparable or, in some cases, even better than the experimental one.

The advantage of performing accurate *ab initio* calculations of chemical properties, instead of measuring them directly, is relevant. First of all, in several cases the interpretation of experimental data is dubious, since the experimental evidence can rarely be directly referred to the property of interest. Quantum mechanical calculations, instead, can be specifically organized in view of the properties of interest. Moreover, there are performed on a model of the chemical system whose parameters can be changed or adjusted in order to test their influence on the final results and the degree of accuracy of the calculations can be increased to test the stability of the results.

Finally, one can observe that the continuous progress in experimental techniques has made possible the direct measurement of quantities that previously were available only from computation. Examples are electronic density that can be measured via diffraction techniques, and time-evolution of simple chemical reactions, that can be followed using time-resolved laser spectroscopy. The continuous feedback between theory and experiment is a strong indication of the importance and vitality of quantum chemistry.

2. The Schrödinger equation

In this section we first summarize a way in which the Schrödinger equation can be derived. This step represents the foundation of Wave Mechanics (Schrödinger, 1925-26) as a specific version of quantum mechanics. The other equivalent formulation of quantum mechanics, proposed and developed by Heisenberg, Born in Jordan (1925), is known as *Matrix Mechanics* and is based on the association of a matrix with each physical observable quantity. In section 3, we analyze properties of the Schrödinger equation and the generalization of this equation for many-body systems.

2.1 Foundation of wave mechanics

In his paper on “quantization as an eigenvalue problem”, Schrödinger gave the exact mathematical formulation of the analogy, suggested by de Broglie, between the conditions for having stationary waves and the Bohr-Sommerfeld by de Broglie, between the conditions for having stationary waves and the Bohr-Sommerfeld conditions for the allowed motions in a system with f degrees of freedom. The latter can be written as,

$$\oint p_i dq_i = n_i h \quad (i=1,2,\dots,f) \quad (1)$$

Where q_i is a position coordinate and p_i the corresponding conjugate momentum n_i a non-negative integer number, h the Planck constant and the integral is taken over a whole period of the coordinate. For a circular orbit of the electron in the hydrogen atom, Eq. (1) gives the Bohr condition on the angular momentum L of the electron

$$\oint \vec{p} \cdot d\vec{q} = \oint p dq = 2\pi L = n h \quad (2)$$

and, as a consequence, the terms of the Balmer formula for the discrete energy spectrum of the hydrogen atom

$$E_n = -\frac{2\pi^2 e^4 m}{h^2 n^2} \quad (n=1,2,\dots) \quad (3)$$

where $-e$ and m are respectively the electron charge and mass. If one interprets the quantity $\lambda = h/p$ as the length of a wave associated with an electron of momentum p (as suggested by de Broglie to interpret result of various experiments), the Bohr condition (2) becomes

$$\oint \frac{dq}{\lambda} = n \quad (4)$$

that is exactly the condition for stationary waves in a vibrating string. This problem requires the solution of the D'Alembert equation

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2}{\partial t^2}\right) \psi(x,t) = 0 \quad (5)$$

where v is a constant representing the phase velocity of the wave propagation. A stationary solution of Eq. (5) is

$$\psi(x,t) = u(x) e^{-i\omega t} \quad (6)$$

Where $u(x)$ fulfils a time-independent equation containing the angular frequency $\omega = 2\pi v$ as a parameter

$$\frac{d^2}{dx^2} u(x) + k^2 u(x) = 0; \quad k = \frac{\omega}{v} = \frac{2\pi}{\lambda} \quad (7)$$

and the boundary conditions for a string of length l , fixed at the ends, give the eigenvalues of the problem

$$k = k_n = \frac{\pi}{l} n = \frac{2\pi}{\lambda_n} \quad (8)$$

Following the de Broglie hypothesis that the particles too possess the dual character of light: as an electromagnetic wave is associated with each photon, so a material particle of energy E and momentum \vec{p} is associated with a wave of angular frequency $\omega = 2\pi v$ and wave vector \vec{k} , the following pair correspondence $(E, \vec{p}) \leftrightarrow (\omega, \vec{k})$, that is a relativistic invariant, can be postulated both for photons and for particles

$$E = \hbar\omega; \quad \vec{p} = \hbar\vec{k} \quad (9)$$

with $\hbar = h/2\pi$. In particular, for photons one has

$$k = \frac{\omega}{c}; \quad p = \frac{E}{c} \quad (10)$$

where c is the velocity of light, while for particles the relativistic invariance requires

$$\vec{p} = \frac{m\vec{v}}{\sqrt{1-v^2/c^2}}; \quad (11)$$

$$E = \frac{mc^2}{\sqrt{1-v^2/c^2}} = c\sqrt{p^2 + m^2c^2}$$

and, therefore, gives

$$\frac{\omega}{c} = \sqrt{k^2 + \frac{m^2c^2}{\hbar^2}} \quad (12)$$

Starting from these results, Schrödinger developed his wave mechanics as a generalization of classical mechanics considered as an approximate theory that becomes inadequate at the atomic level; exactly as geometrical optics is an approximation of wave optics, useful only whenever the wavelength of light may be considered negligibly small. By analogy with optics, for describing the motion of a particle, Schrödinger introduced a complex wavefunction $\psi(\vec{r};t)$, that he called “scalar field” but now is usually called “probability amplitude” since its square modulus (the analogous of wave intensity) gives the “probability amplitude” since its square modulus (the analogous of wave intensity) gives the probability density of finding the particle around \vec{r} at time t . The better the localization of the particle, the more restricted is the domain of definition of the wavefunction. Validity of classical mechanics requires that the extension of the wavefunction remains so small, in the course of time, that the function can be approximated by a point following a trajectory. This can be realized by identifying the particle with a wave packet, superposition of plane waves

$$\psi(\vec{r},t) = \int |f(\vec{k})| e^{i[\vec{k}\cdot\vec{r}-\omega(\vec{k})t+\alpha(\vec{k})]} d\vec{k} \quad (13)$$

localized in a volume ΔV around a centre \vec{r}_0 , that moves with a well-defined velocity \vec{v}_g , called *group velocity*. These quantities can be defined as follows

$$\Delta V \sim \frac{1}{\Delta K}; \quad \vec{r}_0 = \int_{\Delta K} \vec{r} |f(\vec{k})| d\vec{k} \quad (14)$$

$$t \vec{v}_g = \vec{\nabla}_{\vec{k}} \alpha \Big|_{\vec{k}=\vec{k}_0}; \quad \vec{v}_g = \vec{\nabla}_{\vec{k}} \omega \Big|_{\vec{k}=\vec{k}_0}$$

Where ΔK is a volume inside which $|f(\vec{k})|$ is appreciably different from zero and takes its maximum at \vec{k}_0 . To compare the motion of the wave packet with that of a classical particle, as suggested by the analogy between geometrical optics and classical mechanics, it is necessary to establish the identity between rays of frequency ω and classical trajectories of energy $E = \hbar\omega$ between group velocities along each ray an velocity of the classical particle. Since both trajectories and rays can be obtained from a variational principle, the exact correspondence between the two quantities requires that between the two variational principles. In particular, trajectories of a classical particle of momentum \vec{p} can be obtained from the *principle of least action*

$$\delta I = \delta \int_{M_1}^{M_2} \vec{p} \cdot d\vec{r} = 0 \quad (15)$$

The actual trajectory is that which makes stationary the integral I , calculated between the two fixed points M_1 and M_2 . On the other hand, rays of geometrical optics can be obtained from the *Fermat principle* that, for a given frequency ω and wave vector \vec{k} requires

$$\delta J = \delta \int_{M_1}^{M_2} \vec{k} \cdot d\vec{r} = 0 \quad (16)$$

The actual ray is the optical path that joins M_1 and M_2 and makes stationary the integral J . Because of the formal analogy between the two variational principles, the exact correspondence between rays and trajectories is obtained if $\vec{p} = \beta \vec{k}$. The constant of proportionality β is determined by requiring the identity between the velocity or the classical particle: $\vec{v} = \vec{\nabla}_{\vec{p}} E$ and group velocity \vec{v}_g of the wave packet. The identity requires $\beta = \hbar$ and brings us back to Eq. (9) in a completely general way.

If we assume, now, that the wavefunction $\psi(\vec{r}, t)$ completely defines the dynamical state of the particle, in the sense that all its properties, at any given time t , can be deduced from the knowledge of $\psi(\vec{r}, t)$, we are led to the central problem of the theory, that is the determination of the wavefunction at any instant t from the knowledge of ψ at a given initial time t_0 . The solution of this problem requires the knowledge of the equation of propagation of ψ , i.e. of the wave equation.

As one can see from Eq. (11, 12, 13) the wave packet fulfils the scalar, relativistic equation

$$\left(\Delta - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \psi(\vec{r}, t) = \frac{m^2 c^2}{\hbar^2} \psi(\vec{r}, t); \quad (17)$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

a fact that suggests a fundamental relationship between differential operators and classical quantities

$$i\hbar \frac{\partial}{\partial t} \leftrightarrow E; \quad -i\hbar \frac{\partial}{\partial x_\alpha} \leftrightarrow p_\alpha \quad (18)$$

Schrödinger initially proposed Eq. (17) as the appropriate wave equation. This equation, however, which is known as the Klein-Gordon equation and plays an important role in relativistic quantum mechanics, presents a few relevant difficulties in this context. It can be observed, for example, that Eq.(17) is second order in time and, therefore, to define the latter evolution of the wavefunction one has to specify not only $\psi(\vec{r}, t_0)$, but also its time derivative at t_0 . This fact contradicts the basic assumption that $\psi(\vec{r}, t)$ can be derived only from the knowledge of $\psi(\vec{r}, t_0)$. Because of these and other difficulties, Eq. (17) cannot be adopted as the appropriate wave equation without reinterpreting the physical meaning of ψ inside a more general theory.

As a matter of fact, indeed, the assumption that the dynamical state of a single particle is represented by a single wavefunction is fully justified only in the non-relativistic limit, where the law of conservation of the number of particles is satisfied. Assuming the

validity of the non-relativistic approximation, that formally corresponds to the limit: $c \rightarrow \infty$ (i.e. $v \ll c, p \ll mc$), one gets from Eqs. (11,12)

$$E = mc^2 + \frac{p^2}{2m} + \dots = mc^2 + E_k + \dots$$

$$\omega = \frac{E}{\hbar} = \frac{mc^2}{\hbar} + \frac{\hbar k^2}{2m} + \dots = \frac{mc^2}{\hbar} + \omega' + \dots \quad (19)$$

where $E_k = p^2/2m$ is the kinetic energy of the particle and $\omega' = \hbar k^2/2m$, a shifted frequency. Defining

$$\psi(\vec{r}, t) = e^{-i\frac{mc^2}{\hbar}t} \psi'(\vec{r}, t) =$$

$$e^{-i\frac{mc^2}{\hbar}t} \int |f(\vec{k})| e^{i[\vec{k}\cdot\vec{r} - \omega'(\vec{k})t + \alpha(\vec{k})]} d\vec{k} \quad (20)$$

And using this expression in Eq.(17), one finds that $\psi'(\vec{r}, t)$ fulfils the following equation

$$(\Delta + i \frac{2m}{\hbar} \frac{\partial}{\partial t}) \psi'(\vec{r}, t) = 0 \quad (21)$$

We see that, in the non-relativistic limit, the energy is shifted by a constant and the wavefunction multiplied by a phase factor. Neither of these facts, however, really changes the physical meaning of the solution. Furthermore, Eq. (21) is first order in time and does not present the drawbacks of the Klein-Gordon equation. Therefore, it can be chosen as the appropriate wave equation. This equation, indeed, is the *time-dependent Schrödinger equation* for a free particle of mass m .

The Generalization of Eq. (21) for a particle moving with non-relativistic velocities in a scalar potential $V(\vec{r})$ can be realized by imposing the correspondence between motion of the centre of the wave packet and classical motion of the particle, whose energy, momentum, and position (E, \vec{p}, \vec{r}) are connected by the relationship

$$E = \frac{p^2}{2m} + V(\vec{r}) = H(\vec{p}, \vec{r}) \quad (22)$$

where $H(\vec{p}, \vec{r})$ is the classical Hamiltonian. If the wave packet is a superposition of plane waves having angular frequencies and wave vector respectively close to E/\hbar and \vec{p}/\hbar and if the potential does not change appreciably in the region where the wave packet is appreciably different from zero, one has

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) &\approx E \psi(\vec{r}, t) ; \\
 -\hbar^2 \Delta \psi(\vec{r}, t) &\approx p^2 \psi(\vec{r}, t)
 \end{aligned}
 \tag{23}$$

that, together with Eq...(22), gives the wave equation

$$\left(i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \Delta - V \right) \psi(\vec{r}, t) \approx 0
 \tag{24}$$

This equation is approximately satisfied by a wave packet of the type (13) under the conditions of validity of geometrical optics, but we are led, in a very natural way, to postulate that the wavefunction $\psi(\vec{r}, t)$ fulfils in general the equation

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) &= \\
 \left[-\frac{\hbar^2}{2m} \Delta - V(\vec{r}) \right] \psi(\vec{r}, t) &= \hat{H} \psi(\vec{r}, t)
 \end{aligned}
 \tag{25}$$

That is the *time-dependent Schrödinger equation* for a particle of mass m moving in the scalar potential $V(\vec{r})$. We can also postulate that this equation applies generally to all motions, independently of the energy of the system. The main feature of this equation is the presence of an operator \hat{H} , that has the same formal structure as the classical Hamiltonian, but the components of \vec{p} replaced by differential operators

$$p_\alpha \rightarrow -i\hbar \frac{\partial}{\partial x_\alpha}
 \tag{26}$$

as in Eq.(18). One immediately sees that, if the Hamiltonian does not depend explicitly on time, i.e. the system is conservative Eq. (25) admits solutions of the type

$$\psi(\vec{r}, t) = u(\vec{r}) e^{-iEt/\hbar}
 \tag{27}$$

that represents periodic time-dependent states of definite E (*stationary states*), with the spatial motion described by a wavefunction solution of the equation

$$H u(\vec{r}) = E u(\vec{r}); \quad \hat{H} = -\frac{\hbar^2}{2m} \Delta + V(\vec{r})
 \tag{28}$$

This is the *time-independent Schrödinger equation* for a particle of mass m moving in the scalar potential $V(\vec{r})$. Eq. (25,28) are the two fundamentals equations of the non-relativistic wave mechanics for a single particle.

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Biographical Sketch

Renato Colle was born in Belluno, Italy, on 9 October 1949, studied at Scuola Normale Superiore (SNS) of Pisa during 1973-75 for Ph.D., and worked there as Assistant Professor of Chemistry during 1975-81. In 1978 and 1980 respectively he visited Technisch-Chemisches Labor der ETH of Zurich and the Department of Physics, University of Chicago, as a Research Associate. During 1981-90 he was Associate Professor of Chemical Physics at the SNS. In 1985 he was a Visiting Professor at the Department of Physics, University of Chicago. Since 1991 he is a Full Professor of "Chimica Fisica dei Materiali Solidi" at the University of Bologna and was Scientific Director of a Joint Research Project of the European Community during 1994-98.