

TO THE PROBLEM OF FORMULATION OF BASIC PRINCIPLES IN THE THEORY OF MOLECULAR STRUCTURE AND DYNAMICS

L. A. Gribov

Institute of Geochemistry and Analytical Chemistry
Russian Academy of Science, Moscow, Russian Federation

Y. B. Magarshak

MathTech Inc.

New York, USA

e-mail: ym4@nyu.edu

(Received 22 August 2007; accepted 8 December 2007)

Abstract

In this contribution some basic problems of practical applications of quantum mechanics to the functioning of microsystems have been discussed. In particular, it has been shown that starting from fundamental principles one cannot calculate 3D-configurations of atoms in molecules. In order to get meaningful results in these calculations, the empirical information about the configuration of molecule is necessary. The problem of variables separation in quantum chemistry was discussed. It has been shown that the separation of electronic and

nuclear parts in nuclear-electronic problem of quantum chemistry can be performed in the adiabatic approximation only. The Schroedinger equation with the stationary operator H , common for all isomers of any molecule, cannot be written as well.

1 Introduction

In this contribution, some basic problems of practical applications of quantum mechanics to the functioning of micro-systems have been discussed. Apparently the attention, adequate to the importance of these problems for quantum mechanical analysis of molecular systems, has not been paid so far.

At the very beginning of the development of quantum mechanics, soon after the theory of hydrogen atom and H_2 molecule were developed, it has been shown that, in a reasonable approximation, one can consider molecules as stable sets of electrons and atomic nucleus in the Coulomb field. It has also been noticed that the huge mass difference between electron and proton allows separation of motion of nuclei and electron, using either Born-Oppenheimer or adiabatic approximation[1]. At present, the opinion that Schroedinger equation in a general form can solve any problem of structure and properties of a micro-world dominates and only a finite speed of computers has been considered as a real obstacle and restriction.

We analyze some fundamental aspects of the formulation of quantum problems in applications to complex systems like chemical compounds and molecular transformations.

2 The role of empirical parameters in the fundamental approach

As a rule, the solution of any theoretical problem related to the structure and properties of microsystems starts with the Schroedinger equation. In a reasonable approximation, the description of the molecular object can be restricted with the binary Coulomb interactions of the shell electrons with atom nuclei (V_{ee}, V_{en}, V_{nn}). The corresponding Hamiltonian has the following form:

$$H_{en} = T_e + T_n + V_{ee} + V_{en} + V_{nn}.$$

Apparently, the only problem remaining is the Schroedinger equation with this operator. Such solution depends only on the mathematical methods, the computer speed, *etc.* This is the mainstream of the activity in this area.

As shown below, such point of view is fundamentally incorrect. Certain considerations in this respect have been expressed already by the first author [2],[3],[4],[5]. In the present contribution, these considerations will be developed further. It is known, that any molecular object with given "gross-formula" (e.g., chemical formula, which does not take into account the three-dimensional conformation of the molecules) can exist in a large number of structural isomers. For example, the system C_6H_6 exists not only in the form of benzene, but as dozens other isomers as well. For the molecular system consisting of 30 – 40 atomic objects the number of possible stable structures might be as large as hundreds of thousands. In the Hamiltonian written above, this fact is not taken into account. So, it is clear that the differential equation $\mathbf{H}_{en}\psi_{en} = E_{en}\psi_{en}$ cannot yield a solution to the isomerization problem because the existence of multiple isomers is not well defined in it. Strictly speaking, this is not a well-defined problem. In order to get solution, which is reasonably close to the actual structure, Schroedinger approach needs additional restrictions on the system to be imposed. So far, these restrictions were not derived from the basic quantum mechanical principles. One of the most natural restrictions is a requirement for the system not deviate from the given state too far. In practice, the states, which will be determined from the Schroedinger equation, are taken from experiments and never, or almost never, are derived from any theory existing today. In quantum chemistry, these empirical supplement to quantum chemistry is crucially important, because only a very small part of all possible isomeric structures is present in real molecular systems.

In chemistry, the purely fundamental approach (i.e., the solution of a problem, which is based on the basic principles and fundamental equations only) is simply inadequate to the experiments. This very important aspect of the problem is not mentioned in the vast majority of publications on quantum mechanics and quantum chemistry at all.

3 To the problem of separation of the electronic and nuclear parts in the nuclear-electronic problems of quantum chemistry

The natural additional restriction, which permits to determine the desirable stable structure, is the condition that nuclei motion takes place in the potential "well", which minimum is close to one known from the experiments but not from theory. For example, for the set of atoms C_6H_6 this desired configuration might be a configuration of benzene. When configuration of the molecule is postulated, one has two ways to go further:

- One can consider the electronic states in the field created by the set of nuclei of atoms, which constitute a molecule[6]. This problem, which below will be called an *electronic* one, according to the standard model, is determined by the fundamental electromagnetic field, in practice considered as the Coulomb force. The coordinate system, which is commonly used in this formalism is the Cartesian one.
- According to the second approach (which will be called a nuclear one), the potentials, as well as other fundamental fields, explicitly are absent at all. Instead, one uses parameters of different kind, such as elasticity, which are derived from the Hooke's law in harmonic approximation, and other semi-empirical data.

If relative disposition of nuclei is changed, the eigenvalues E_{ek} and wave functions ψ_{ek} for the electronic problem will parametrically depend on the coordinates of the nuclei. In this case, the additive component, i.e., the energy of the Coulomb repulsion of nuclei at their relative disposition, is added to the eigenvalues of energy levels of the electronic solution. It is obvious that such a problem might be mathematically formulated and solved without imposing additional restrictions. The problem of the nuclei motion, or their stationary states, can also be formulated and solved independently, if one introduces some potential function dependent on the coordinates of the nuclei. We do not discuss now the questions how both problems can be mathematically solved in general case. We only note that, in principle, such solution is always possible.

However, if our final goal is comparison with experimental data, the question what to do with solutions obtained this way remains unsolved. If from the very beginning one has in view the molecule, which electrons and nuclei are inseparable, the determination of general equation for the common states of both electrons and nuclei must be made. In this case, independent solution of two problems for the generalized system is possible only when the operator (Hamiltonian \mathbf{H}_{en}) leads to the sum of the operators, each of which depends on its coordinates only. The coordinates are separated in this and only in this case. Such a procedure for the operator \mathbf{H}_{en} in general case cannot be accomplished.

If the variables have been separated, the eigenvalues of the general problem (i.e., the energy levels) can be expressed through the sums of the energy of each particular problem, whereas eigenfunctions can be written in the form of products of eigenfunctions, corresponding to them. In this case, the question arises, whether the same method is applicable to the general nuclei-electronic problem. The total Hamiltonian in this case is of the form:

$$\mathbf{H}_{en} = \mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{en} + \mathbf{V}_{nn} + \mathbf{T}_n.$$

If one writes

$$\mathbf{H}_{en} = \mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{en} + \mathbf{V}_{nn} - \mathbf{W} + \mathbf{T}_n + \mathbf{W} = \mathbf{H}_e - \mathbf{W} + \mathbf{H}_n,$$

where

$$\mathbf{H}_e = \mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{en} + \mathbf{V}_{nn},$$

$$\mathbf{H}_n = \mathbf{T}_n + \mathbf{W}$$

nothing is changed. Here the symbols \mathbf{T}_e and \mathbf{T}_n designate kinetic operators, \mathbf{V}_{ee} and similar symbols are related to other potential functions of electron-electronic and other interactions, symbol \mathbf{W} is the potential function, chosen during the formulation of the problem of nuclei motions ($\mathbf{H}_e \psi_n = E_e \psi_n$). If the problem of the electronic states in the field of immovable nuclei would be solved at different dispositions of these nuclei in the 3D space, then

$$\mathbf{H}_e(Q) \psi_e(Q) = (\mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{en}(Q) + \mathbf{V}_{nn}(Q)) \psi_e(Q) =$$

$$= E_e(Q) \psi_e(Q).$$

Let us consider only the case of small deviations from the potential minimum. Now

$$E_e(Q) = E_e(0) + \Delta E_e(Q)$$

and

$$\psi_e(Q) = \psi_e(0) + \left(\frac{\partial \psi_e}{\partial Q} \right)_0 Q.$$

Here the symbol Q designates the coordinates, originated at the minimum of the potential function. It corresponds to the disposition of the atom nuclei of the molecule relative to each other. Let's consider the action of the operator \mathbf{H}_{en} on the product of the functions $\psi_e(Q) \psi_n(Q)$ assuming that the function $\psi_n(Q)$ corresponds to the operator $\mathbf{H}_n = \mathbf{T}_n + \mathbf{W}$. Let's also take into consideration that in the operator \mathbf{T}_e the differentiation must be performed with respect to the coordinates of the electron only. Now we have:

$$\begin{aligned} \mathbf{H}_{en} [\psi_e(Q) \psi_n(Q)] &= (\mathbf{H}_e - \mathbf{W} + \mathbf{H}_n) [\psi_e(Q) \psi_n(Q)] = \\ &= [E_e(0) + \Delta E_e(Q)] [\psi_e(Q) \psi_n(Q)] - \\ &- \mathbf{W} [\psi_e(Q) \psi_n(Q)] + \mathbf{H}_n [\psi_e(Q) \psi_n(Q)] = \\ &= [E_e(0) + \Delta E(Q) + E_n] [\psi_e(Q) \psi_n(Q)] - W [\psi_e(Q) \psi_n(Q)] + \\ &+ \psi_e(Q) \mathbf{T}_e \psi_n(Q) + 2\psi_e'(Q) \psi_e'(Q) = \\ &= [E_e(0) + \Delta E(Q) + E_n] [\psi_e(Q) \psi_n(Q)] - W [\psi_e(Q) \psi_n(Q)] + \\ &+ 2\psi_e'(Q) \psi_e'(Q). \end{aligned}$$

Here, it has been taken into account that

$$\mathbf{T}_n \psi_e(Q) = \mathbf{T}_n \left[\psi_e(0) + \left(\frac{\partial \psi_e}{\partial Q} \right)_0 Q \right] = 0,$$

because the action of the operator \mathbf{T}_n on the function provides double differentiation with respect to the coordinates Q relative to the nuclei arrangement. This expression can be simplified if one takes into consideration that $W = \Delta E_e(Q)$ leads to different W for different electronic states and presumes that the "well" center W coincides with the point of the energy minimum $E_e(0)$:

$$\mathbf{H}_{en}[\psi_e(Q)\psi_n(Q)] = [E_e(0) + E_n][\psi_e(Q)\psi_n(Q)] + 2\psi'_e(Q)\psi'_n(Q), \quad (1)$$

where E_n is the energy in the nuclei motion problem with the Hamiltonian $\mathbf{H}_n = \mathbf{T}_n + \Delta E_e(Q)$. One can see that the function $\psi_e(Q)\psi_n(Q)$ satisfies Schroedinger [7] equation with the Hamiltonian \mathbf{H}_{en} only up to the term, which contains the first derivatives of the function $\psi_e(Q)$ and $\psi_n(Q)$ with respect to the coordinates Q . However, this term does not change the average energy value:

$$\begin{aligned} \bar{H} &= \int \psi_e\psi_n\mathbf{H}_{en}\psi_e\psi_n dv_e dv_n = [E_e(0) + E_n] + \\ &+ 2 \int \left(\int \psi_e\psi'_e dv_e \right) \psi_n\psi'_n(Q) dv_n = E_e(0) + E_n. \end{aligned} \quad (2)$$

Here it is taken into account that functions ψ_e, ψ_n are real (as usually takes place in quantum chemistry). One should also note that the normalization $\int \psi_e^2(Q) dv_e = 1$ is valid for any coordinates Q corresponding to wavefunctions $\psi_e(Q)$. Hence, the derivative of this integral with respect to Q equals to zero

$$\int \psi_e(Q)\psi'_e(Q) dv_e = 0. \quad (3)$$

This result leads to an important conclusion. Although the sum $E_{en} = E_e(0) + E_n$ and the function $\psi_e(Q)\psi_n(Q)$ do not correspond to the Schroedinger equation with the Hamiltonian \mathbf{H}_{en} , in this particular case the average energy value is considered to be equal $E_{en} = E_e(0) + E_n$. This means that the solutions of the nuclear problem and the solution of the electronic problem are separated. All quantum chemical calculations are based on these results. These considerations also justify the adiabatic approximation in quantum

chemistry, which is widely used without proper analysis of its validity in application to each particular problem.

The linear dependence $\psi_e(Q)$ on Q , presumed in equations (2) and (3) means that the function $\Delta E(Q)$ is a quadratic form, i.e., corresponds to the harmonic potential. All these considerations lead to the conclusion that the solution of the nuclear-electronic problem in the adiabatic approximation is a model approach, which is rather close to the solution needed in a number of applications. However, it works under assumptions, which validity is not self-assumed and must be thoroughly verified in each particular case. However, such verification usually is not performed. Moreover, the calculation of E_{en} and ψ_{en} according to the algorithm outlined above, is often used when the adiabatic separation of problems is incorrect. For example, adiabatic approximation is commonly used for the analysis of the anharmonic oscillations of multi atomic molecules. It is clear that in this case one gets even less precise expression for \bar{H} . The verification whether the adiabatic approach is applicable to anharmonic oscillations in molecules is necessary prior to application of the adiabatic formalism to any specific molecular system in which the anharmonicity is substantial.

A priori it is clear that the adiabatic approach in quantum chemistry often is not valid at all. The question about validity of the adiabatic simplification, which allows separation of the nuclear-electronic problem into two independent problems, must be answered in each particular case. Nevertheless, the fact that the adiabatic solution is only an approximate one usually is not mentioned, and the applicability of the adiabatic approach is not verified.

In short, the adiabatic conditions can be formulated as follows:
Assume that

- I. The electronic energy of the molecule in the interval ΔQ of the nuclear coordinates has the minimum $E_e(Q_0)$

and

- II. the dependence of the electronic function on nuclei coordinates is linear

$$\psi_e(Q) = \psi_e(0) + \left(\frac{\partial \psi}{\partial Q} \right)_0 Q.$$

III. Under these conditions one can select the potential energy for the problem of the nuclei motion in the form

$$W = E_e(Q) - E_e(Q_0) = \frac{1}{2}k(Q - Q_0)^2.$$

If conditions I, II and III are fulfilled, the nuclear-electronic problem can be separated into two problems, namely, the electronic and the nuclear one. The general solution of the problem in the adiabatic approximation can be represented as follows:

$$E_{en} = E_e(Q) + E_n,$$

$$\psi_{en} = \psi_e(\mathbf{r}, Q) \psi_n(Q). \quad (4)$$

In all other cases the conditions for adiabatic approximation are not fulfilled.

4 To the problem of writing the Schroedinger equation common for all nuclei-electronic configurations of a molecule

The solution of purely electronic problem based on the fundamental interactions, in principle, is possible at any disposition of nuclei (under condition that spatial limitations are given *a priori* and that their determination is not a part of the problem). However, each 3D-arrangement of nuclei (for example, in the benzene molecule) corresponds to different Schroedinger equation. Verifying the coordinates of the atoms nuclei in the system (using, for instance, the splines method) one can compute the electronic configurations and their properties. However, **writing a single Schroedinger equation common for all configurations of a molecule, with the stationary operator H_{en} , which gives to solution the same and even approximately correct result, is impossible.**

The Schroedinger equation for multi-nuclei dynamics problem is formed for each nuclear-electronic state with "its own" potential. The single equation for all isomers and all configurations does not exist. The attempts

(A) to solve the problem of the molecular world on the bases of the equations, which remain the same for all nuclei-electronic states

and

(B) to take into account the fundamental fields and fundamental equations

only leads to the incorrectness of the formulation of the nuclei-electronic problem in the sense, which has been described above. This approach also makes impossible the comparison of the results of the calculations with experimental data.

As has been demonstrated above, even for different electronic states of the same molecule one cannot use the general form of the electronic-nucleus Hamiltonian. If one tries to formulate the problem in the adiabatic approximation, one has to select in each a different potential functions $W = \Delta E(Q)$. The situation becomes even more complicated if one considers the problem like isomer-isomer transformations. In this case, one must indicate from the very beginning that the motion of nuclei is possible only in areas where the selected isomer shape (for example, the configuration of benzol) permits. The restricting potential takes the form of the potential well with two minima. The dependence of the electronic wave function on the relative nuclei coordinates becomes very complicated. Even if the problem of the nucleus motion is solved, one cannot consider the product $(\psi_e \psi_n)$ to be an eigenfunction of the Schroedinger equations of the general form. The sum $E = E_e + E_n$ is not the eigenvalue of this Schroedinger equations as well. However, one still can construct an approximate energy matrix using the Ritz method with adiabatic functions as basis functions. In the case of two isomers problem, it is reasonable to choose distinct basis functions for each well. Both theoretically and practically, we come to general conclusion that the "matrix" formulation of quantum mechanics is more general than the operator approach.

5 Conclusions

Starting from basic principles, in a number of cases one can formulate algorithms, which give a reasonable agreement with the experiment. In particular, semi-fundamental-semi-empirical approach

works when adiabatic conditions are valid. However, even in this case one must introduce "by force" the configurations of molecules, which cannot be derived from fundamental equations of physics. The Schroedinger equation with the stationary operator \mathbf{H}_{en} , common to all configurations of a molecule, cannot be written either. The question concerning the reason of the theoretical and conceptual gap between fundamental world structure, which follows from the laws of modern physics, and non-fundamental world, which is obvious at any attempt to solve the practical problems of chemistry, is intriguing.

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Comment on
**TO THE PROBLEM OF FORMULATION OF
BASIC PRINCIPLES IN THE THEORY OF
MOLECULAR STRUCTURE AND DYNAMICS**

F. A. Bogomolov

Courant Institute of Mathematical Studies

New York University

It is an interesting article which touches a serious difficulty in the systematic application of quantum theory to chemistry. It must be said that Schroedinger equation looks deceptively simple, but there are many caveats in its applications to concrete systems. One of the general difficult problems is that we are forced to deal with time dependent potential H which variation depends on the configuration of the system. Since the parameters of the system are now described by function the operator H itself has also be considered in a similar manner and we have to apply to H a Schroedinger type operator equation for a ψ function of H . Thus we have to deal with a "distribution of operators" I dont think it is possible to perform this procedure effectively in any concrete system, unless we assume that the variation of H is guided by parameters subjected to nonquantum laws. It is therefore almost impossible to consider potentials substantially depending on the positions of individual particles involved.

There is an approach based on the treatment of isomers as differ-

Comment

ent states of the same "molecule". In this approach the ground states of the "molecule" are actually not the individual isomers, but their weighted combinations. This approach provides an explanation for some interesting phenomena. However the parameters of the individual isomers and the corresponding space configurations are treated within the classical framework and quantum effects are calculated via perturbation theory only.