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Trends in the Development and Tasks of Modern Quantum Chemistry†

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The main advances are surveyed and the principal trends in the development of modern quantum chemistry are noted. The intensification of the linkage between theoretical and experimental research is emphasised. The tasks in various branches of quantum chemistry of greatest current interest are analysed. The electron clouds and the electronic processes in molecules and solids, intermolecular interaction, intramolecular dynamics, elementary processes in gas and condensed phases, and phenomena determined by the non-adiabatic electronic-nuclear interaction are examined. The tasks associated with the development of a theory of the application of physical research methods in chemistry and also those concerned with the applied quantum chemistry, namely theoretical materials science and quantum molecular biology, are discussed. The role of computer modelling is emphasised and the trends in the development of quantum-chemical methods are briefly analysed.
The bibliography includes 269 references.

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I. INTRODUCTION

Quantum chemistry was born as the science of the electronic structure and reactions of molecules in the gas phase based on quantum mechanics. At the same time, these quantum-mechanical methods have come to be used to explain spectroscopic and other physical properties of molecules. However, experiment required the theory to explain the structure, properties, and reactions not only of molecules as such but also of substances in the liquid and solid states. Together with quantum mechanics, it became necessary to start using the methods of statistical and mathematical physics and computer mathematics for the solution of these problems. Thus modern quantum chemistry is a broad science located between chemistry and physics whose subject is theoretical study of the structure, properties, and transformations of substances at the atomic-molecular level with the aid of methods of quantum mechanics, statistical physics, computational mathematics, and mathematical physics.

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1. Strengthening of the Linkage between Theory and Experiment

Still comparatively recently, in assessing the contribution of quantum chemistry to chemical sciences it was pointed out that it explained many chemical phenomena and regular features, created the system of concepts and the language of modern chemistry, and imparted a physical significance to the existing chemical ideas. These were indeed major advances. However, the success and the role of present-day quantum chemistry are much greater. It is able not only to explain but also to predict the possibility of the existence of new chemical compounds and materials and their structure and properties, as well as new effects, and to calculate the characteristic parameters of molecules which are inaccessible to experiment or can be determined experimentally with difficulty. Quantum chemistry proved able to solve also more complex problems: to recommend, for example, the optimum synthesis of a new compound with specified properties, to indicate how one can measure, in principle, any characteristic parameter or property, and to assist in planning a new experiment. Problems which are ultimately very relevant to practical applications, to the creation of the new engineering, are being solved with increasing frequency. All this characterises the new stage in the development of quantum chemistry. Its role in modern chemistry has changed significantly.

Thus one of the main trends in the development of modern quantum chemistry is strengthening of the linkage with experiment. Whereas 20–30 years ago, the bulk of the literature on quantum chemistry was devoted to methodological developments and trial calculations, nowadays most of the theoretical studies are associated with a specific experiment, with its interpretation, or with predictions. This is due to several causes. On the one hand, quantum-chemical methods have been greatly improved, having reached a level of development where they can really satisfy many of the requirements of experimenters. There has been enormous growth in the power of modern computer techniques. The application of methods of mathematical physics, which make it possible to find solutions to quantum-chemical problems in a closed form or to bring them to the stage where it is rational to resort to computers, has become more effective. The application of methods of statistical physics has been expanded, which gave rise to the possibility of obtaining results in a form which can be compared directly with experiment.

On the other hand, the above tendency is associated with colossal progress in physical experimental methods and their application in chemistry. However, the application of new physical research methods in chemistry is based on special theoretical developments. Quantum chemistry has been concerned to an increasing extent with the solution of this problem.

The increasing role of physical research methods in chemistry led to an enhancement of interest by quantum chemists in the physical properties of molecules. The existence of this trend is already evident from the following example: at the Vth International Congress on Quantum Chemistry in 1985 (Canada), among the new reports delivered by invitation, whose selection is usually made on the basis of a sober assessment of what is new, about 60% were devoted to physical problems important for chemistry and the remaining 40% were concerned with chemical tasks and problems significant for both chemistry and physics (methodological studies).

The main cause of the strengthening of the linkage between quantum chemistry and experiment is ultimately determined by practical requirements: new experiments and new experimental methods are essential for the solution of problems of practical importance. A theory applied to chemistry, namely quantum chemistry, must provide a basis for such experiments and methods and an interpretation of the results.

A vital task for theoreticians is to carry out investigations in close contact with experimenters. In practice this has by no means always been achieved, but it is known that the joint investigations by theoreticians and experimenters always greatly assist in the successful outcome of research.

The Figure presents a schematic illustration of the structure of modern quantum chemistry. Quantum mechanics has made the main contribution to the development of its methods. Statistical physics, computer mathematics, and mathematical physics also play a significant role. Quantum-chemical investigations based on the adiabatic approximation are divided into two fields: the study of electron clouds and the study of the motion of atomic nuclei. The first includes the electronic structure and electronic processes in molecules and solids and intermolecular interaction. The second field embraces the intramolecular dynamics of nuclei, the elementary processes in the gas phase, and the dynamics of the processes in condensed phases and at interfaces. It is known that there exist many systems and phenomena to the description of which the adiabatic approximation is inapplicable and account must be taken of non-adiabatic electronic-nuclear interaction. A separate bunch of quantum chemistry is devoted to such systems.

The development of theories of the application of physical research methods to chemistry, which is related to the fields mentioned above, is a very important component of quantum chemistry. The solution of applied problems is a comparatively new branch of quantum chemistry, which, however, is of very great current importance. In particular it embraces the large field of materials science. Many applied problems are being solved successfully with the aid of computer modelling. One of the most important problems of this kind involves the development of quantum molecular biology.

Some of the most important problems of modern quantum chemistry, in each of the fields mentioned above, are characterised briefly below. The examples quoted are illustrative. In conclusion, the general trends in the development of quantum chemical methods are briefly analysed.

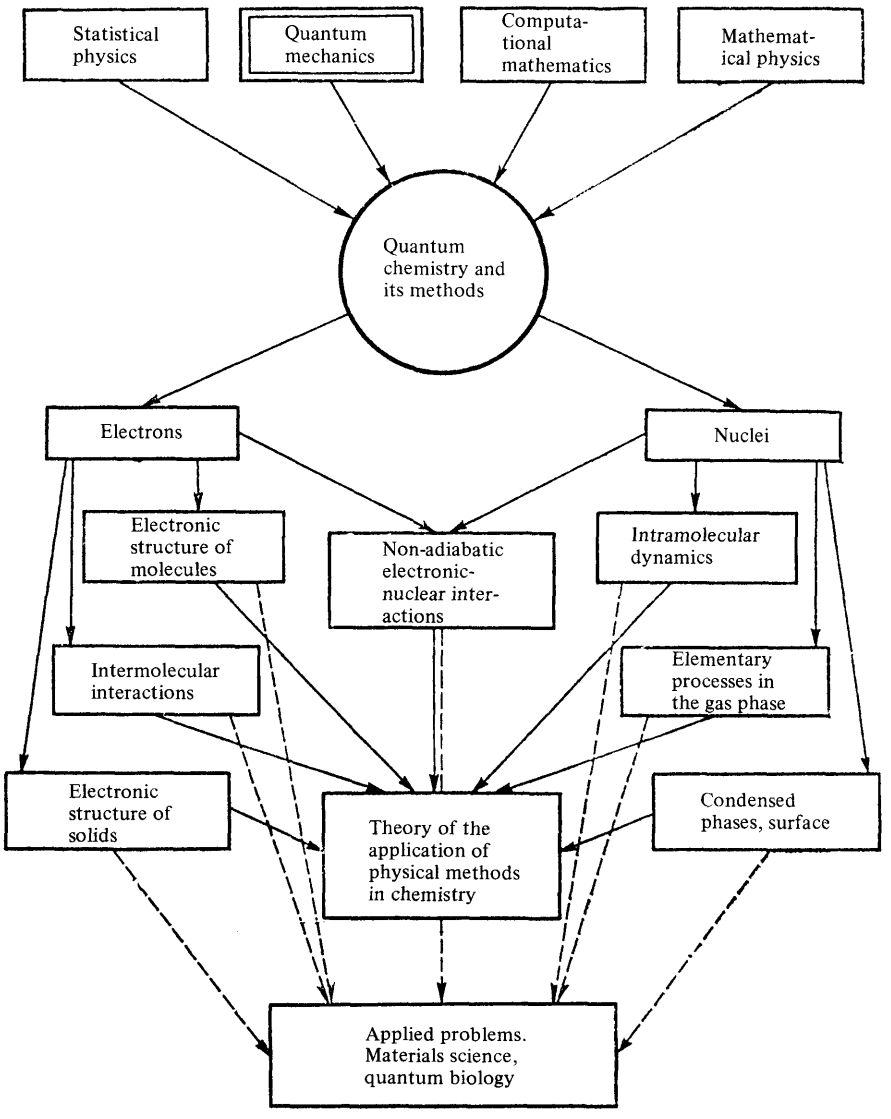
II. ELECTRON CLOUDS

1. Electron Clouds of Molecules

One of the quantum-chemical problems of greatest current importance involves the establishment of a relation between the properties of molecules and their electronic structure. The most important chemical property of molecules is their reactivity. An enormous amount of experimental data, characterising the relation between the reactivity and the electronic structure of molecules has accumulated in this field. There have been major advances also in the theoretical treatment, such as, for example, the principle of the conservation of orbital symmetry of Hoffmann and Woodward,[1] the concept of frontier orbitals,[2–4] and the principle of isolobal analogy.[5,6] The principal trend in the development of the modern theory of reactivity involves an increase in the number and improvement in the quality of calculations of the potential energy surfaces (PES) of reacting systems. Quantum-chemical calculations of the transition states (the saddle point on the PES) and calculations of the directions of motion of atomic nuclei in the given molecular configuration make it possible to predict the reaction path and the nature of the

final products. Hundreds of PES have been calculated[7-14] and the mechanisms of many reactions have been determined with a high degree of probability, which has made it possible to estimate the kinetic parameters necessary for the calculation of their rates. This branch of the theory of reactivity has been very fruitful and in the immediate future will probably influence significantly synthetic chemistry (mainly organic chemistry).

On the other hand, many problems of chemical reactivity have been solved at an empirical level without theoretical justification or have not been solved at all. Thus various empirical rules of different kinds, many of which lack theoretical justification and the limits of the applicability of which are not known, are widely used in organic chemistry. As regards the reactivity of molecules, quantum chemists are therefore faced by a broad field of activity which is of great interest to experimenters. We shall indicate several questions which await an answer. For example, how can one justify the Brønsted–Polanyi–Semenov rule and to what factors are the observed deviations from this rule related:[15] when does the nucleophilic substitution reaction proceed via the S_N2 mechanism and when does it involve the formation of a radical-ion; why do some reactions proceed in general via a concerted mechanism, while others involve intermediate stages; in what cases are metastable intermediate complexes formed; what is the influence of low-lying electronically



The structure of modern quantum chemistry.

excited states on the rates of reaction; how can one increase the selectivity of chemical reactions, i.e. how can one avoid their occurrence via a multiplicity of channels leading to the formation of side products and greatly complicating the manufacturing process and increasing its cost. (We may note that, for certain types of major chemical manufacturing processes, an increase in the yield of product by 2–3% would result in an annual saving equivalent to the cost of construction of a new large factory!)

Various approaches can be usefully resorted to for the solution of numerous problems of the theory of the reactivity of chemical compounds. Together with the calculations of the PES mentioned above, semiquantitative approaches are of interest for specific reactions:[7–14] the construction of semiempirical PES[10] or the estimation of diabatic terms modelling certain cross-sections through the PES for the reacting system.[15] Calculations of the electronic structure and properties of the intermediate formations, which are not susceptible or are little susceptible to experimental study, are also important.

It is noteworthy that, as a result of the improvement of experimental techniques, many chemical reactions known previously only in solutions have now been investigated also in the gas phase;[16,17] this makes possible the comparison of the results of the calculation of reactivity with the "pure" experiment.

There are many problems in the theory of electronic structure which are not related directly to reactivity but are important for chemistry. They include, for example, the development and application of the model of "additional spherical electron density",[18] which justifies the Lewis–Sidgwick rule. According to this rule, electronic configurations resembling those in inert gas atoms are especially stable in coordination compounds. Calculations of the electronic structure of compounds with heavy atoms taking into account relativistic effects are very important. It is now clear that, without taking the latter into account, it is impossible to explain satisfactorily either the chemical or physical properties of compounds of the actinides, lanthanides, and other elements with a high anionic number.[19,20] Many characteristic features of compounds with heavy atoms are influenced, in a manner which is not yet fully understood, by the presence in these atoms of a large number of closely spaced energy levels.[20–23] In general, the theory of chemical bonding involving the atoms of heavy elements still has to be constructed. The nature of the metal–metal bonds,[24,25] the structure of compounds involving variable-valence metal atoms,[26] and many others have to be investigated.

Among the physical methods for the study of matter, the most important information about the electronic structure of molecules is provided by spectroscopic methods: spectroscopy in the visible, ultraviolet, and X-ray regions, X-ray and photoelectron spectroscopy, Auger spectroscopy, EPR, and NQR. The task of quantum chemistry is primarily a correct interpretation of the wide variety of information obtained by these methods: data on the energies of electronic transitions, the form, intensity, and polarisation of electronic, vibronic, and rovibronic spectra, their fine structure, their behaviour in external fields, and many others. Calculations of the energies of excited electronic states as a function of nuclear coordinates (PES) are of special interest. The modern quantum-chemical methods so far permit the calculation with an adequate accuracy of the structure and spectra only of small molecules.[14,21] However, their characteristics are important for the solution of many practical problems.

The development of laser techniques during the last decade has allowed the investigation of many fast chemical, physical, and biophysical processes on the nanosecond and picosecond time scales. The development of the appropriate theories is essential for the interpretation of these experiments. Theoretical study of the rates of the transfer and capture of the electronic excitation energy of molecules, calculations of the lifetimes of excited states in relation to radiative and non-radiative decompositions, and the study of the pathways and rates of relaxation processes are of special interest: the calculations of the ionisation, autoionisation, and dissociation cross-sections of molecules and the cross-sections of their excitation and superexcitation by single-photon and multiphoton irradiation and other types of ionising radiation, the cross-sections of the resonance and non-resonance light scattering, etc. are also important. The solution of these problems, which characterise the leading front of present day science of the interaction of radiation with electron clouds, is necessary for the construction of a theory of elementary reactions, the development of theories of vibronic interactions, the usual and laser photochemistry, radiation chemistry, and plasma chemistry, for the calculation of the conditions governing the operation of molecular, excimer, and chemical lasers, etc.[27–34]

The modern spectroscopic methods are characterised by a high resolving power and a high sensitivity. This imposes enhanced requirements on quantum-chemical calculations. It is important to be able to calculate fine effects for the understanding of which it is necessary to resort to the entire range of procedures of modern theoretical physics. The high sensitivity of modern spectroscopic instruments has made it possible to observe a series of previously unknown or little investigated metastable species, the nature, structure, and properties of which have to be studied jointly by experimenters and quantum chemists. Such species have been detected in gas-phase chemical reactions, electrical discharges, and by the action of strong electromagnetic fields and ionising radiation in plasma, space, etc.

2. Intermolecular Interactions

The theory of intermolecular interactions has always attracted the attention of scientists because of the role which such interactions play in various physicochemical phenomena in both gaseous and (especially) condensed media.[35] During the last 10–15 years, the theoretical research in this field has advanced appreciably in connection with the creation and development of a series of new effective experimental methods for the investigation of the interaction of molecules in the gas phase.[36] These studies yielded extensive new information about the intermolecular interaction, which, on the one hand, required theoretical interpretation and, on the other, served as a basis for checking calculations.

The main task of the theory of intermolecular interaction involves the study of potential energy surfaces in both ground and electronically excited states. The relevant information can be obtained experimentally only in the simplest one-dimensional cases, mainly for the ground electronic states. For problems associated with the study of the physical properties of molecular complexes, liquids, solutions, and clusters, it is in many cases sufficient to know the PES in the vicinity of the equilibrium position for the ground electronic state. For the theory of elementary processes, especially chemical and photochemical ones, the theory of chemical laser systems, and the solution of many other problems, it is essential to know the changes in potential energy over a wide range of variation of nuclear coordinates for both ground and electronically excited and ionised states taking into account the possibility of the existence of several reaction channels.[7–14]

The study of the effect of the molecules of the medium (the solvent) on the rate of the chemical reaction constitutes an independent problem. Disregarding the questions concerning the dynamic action of the medium (see subsection 3 of Section III), the solution of this problem reduces to the calculation of a multidimensional PES taking into account the molecules of the medium. Model calculations have made it possible in a number of instances to take this phenomenon into account qualitatively.[7,37] Here the natural question arises what number of solvent molecules must be taken into account. At first sight it may turn out that this number should be very great, especially when the reacting system is charged, since Coulombic forces decrease slowly with distance. However, recent experiments involving the study of the multistage solvation of ions in the gas phase have shown that the nearest ligands play the main role in this process and that the influence of more remote ones may be neglected.[16,17] The qualitative difference between gaseous and solvated systems is determined in many instances by the action of only a single ligand. Hence it apparently follows that, in theoretical estimates of solvation effects in both thermodynamic and kinetic problems, the treatment can be restricted in most cases to clusters comprising a small number (6–8) of ligands. A model calculation of the potential energy curve for proton transfer in the $FH...NH_3$ system shows that for the gas phase this curve has only one minimum while for the solution, when account is taken of the hydration shell of this complex consisting of six water molecules, a second fairly deep minimum appears.[38] The question of the influence of solvation on elementary processes requires thorough investigation.

In certain cases interesting conclusions concerning the influence of intermolecular interaction on the rate of reaction can be reached without any calculation. For example, the reaction $Cl_2 + Br_2 \rightarrow 2ClBr$ is known to be symmetry-prohibited (it requires a high activation energy[1]). However, the same reaction involving the van der Waals complex $(Cl_2)_2$ takes place readily, since the symmetry prohibition has been removed.[39] Application of the orbital symmetry conservation rules to reactions involving van der Waals complexes may prove useful also in other cases.

It has been frequently suggested that the form of the activated complex for a bimolecular reaction resembles that of the corresponding stable molecular complex. Such similarity would be important because the form of the latter complex can be determined experimentally. However, it has been found that in general no such similarity exists.[39] The problem of the theoretical analysis of the conditions under which it can nevertheless occur therefore arises.

An important task of the theory is also the study of the changes in various characteristic parameters and properties of molecules under the influence of their interaction: on formation of molecular complexes, especially hydrogen-bonded complexes, in solvation, adsorption, etc.[36,40]

An increasing amount of experimental data, indicating the important role of cooperative (multispecies) interactions of molecules in condensed phases, has accumulated in recent years.[36,41,42] Such interactions are manifested by the nonadditivity of the interaction energy and the sharp changes in vibrational spectra, equilibrium geometry, and other characteristics of the molecules on passing from a dimer to an aggregate. The theory of the cooperative interactions of molecules is as yet far from being complete.

3. The Electronic Structure of Solids

During the last two decades, the theory of the solid state has developed vigorously. We shall not be concerned with the general problems of the solid state physics and shall characterise briefly only some of the problems of the theory of the electronic structure of solids relevant to chemistry. These include in the first place problems associated with the properties of the surface.

The creation in the 1970's of a series of new extremely effective methods for the experimental investigations of the surface led to an unprecedented advance in theoretical research into the electronic structure and properties of the surfaces of solids and interfaces. Among the new methods designed to investigate the composition, geometry, and electronic structure of surfaces, mention should be made of slow electron diffraction, photoemission,[43] the spectroscopy of energy losses by electrons,[44] photoelectron and X-ray electronic spectroscopy,[45–47] etc. In connection with the development of these methods, many specific theoretical problems, whose formulation would have been premature in the absence of these methods, have arisen.

One such problem involved the determination of the difference between the electronic structures and the arrangements of atoms in the surface layer and in the bulk of a crystal and also the elucidation of the way in which these characteristics change under the influence of adsorption and local defects. It is also important to know how adsorbed molecules and defects influence the position of the local energy levels, the density of states, the form of the photoemission spectrum, etc.[43]

In connection with one of the most important problems in chemistry, that of heterogeneous catalysis, numerous tasks involving the theoretical study of the adsorption of molecules, molecular fragments, and various intermediate complexes on the active centres of catalysts have arisen.[48–50] Analogous calculations are also necessary for the theory of metal complex catalysis.[51–53] The accumulation of calculated data on the steric orientation of the adsorbed molecules and the nature of their bond with the active centre, the relative adsorption energies of different species on different centres with different types of orientation, the rearrangement of the surface in adsorption, and the interaction of adsorbed molecules is very important. In particular, such calculations can assist in the search for the optimum catalytic reaction pathway. Calculations of the characteristic parameters of adsorbed molecules and other species, namely the frequencies of the electronic and vibrational transitions, dipole moments, and distribution of electron density, as well as various NMR and EPR parameters, are also important for the interpretation of data obtained by physical research methods.[54]

The study of the electronic structure not only of the surface but also of the bulk of the solid, i.e. the local states and defects in the bulk phase, their excitations, ionisation, tunnel recombination, autoionisation, luminescence, etc., is likewise of interest for chemistry.[52,55,56]

The development of the theory of electronic structure and electronic processes in organic crystals with a quasi-one-dimensional structure constitutes a separate problem.[57,58] In a number of instances such structures, which include, in particular, oriented polymers with conjugated bonds,[59] have completely unusual dielectric, conducting, and magnetic properties.

Methodologically, one of the main trends in the development of the theory of the electronic structure of solids is the endeavour to transfer to this theory the methods and approaches developed in the theory of the electronic structure of molecules. This applies in the first place to the treatment of the properties which are determined to a significant extent by the short-range order and local characteristics of the structure—point defects in the bulk phase and on the surface, the presence of adsorbed atoms and molecules, optical and X-ray excitations, etc. The joint application of the methods of the theories of molecular and

solid state structures will undoubtedly prove useful in the treatment of the properties of non-crystalline solids and alloys, the stability of materials with respect to the action of radiation, corrosion, etc. The cluster model, within the framework of which the methods of the theory of the electronic structure of molecules are also applied, has been used successfully in the study of these properties.[60,61]

It is noteworthy that in the theory of the electronic structure of solids, as in the theory of molecules, clear models play an important role. For example, the representation of molecular orbitals by a linear combination of atomic orbitals makes it possible to describe many features of the structure and a number of properties of not only molecules but also of solids.[62,63] Further development of clear representations of the electronic structures of solids is therefore useful, especially for experimenters.

III. DYNAMICS OF THE MOTION OF NUCLEI

1. Intramolecular Dynamics of Nuclei

Under the influence of the development and wide-scale application of new physical research methods, the theoretical study of the dynamic properties of substances has greatly intensified. The intramolecular dynamics of nuclei occupies an outstanding place in such research.

Until recently, in the study of intramolecular non-radiative processes most attention was devoted to electronic relaxation. In recent years, the research into the vibrational and rotational relaxation of molecules has grown appreciably, which is directly related to advances in the development of the laser technique. By virtue of these advances, the dynamics of various intramolecular processes,[64-72] including isomerisation, decomposition, tunnelling, relaxation time, etc., have become susceptible to detailed investigation.

The study of the exchange of vibrational energy is of primary interest.[64,70,71] A definite amount of energy, calculated to produce a local excitation of a specific vibrational mode, is imparted with the aid of a laser to a molecule having a very low rotational and vibrational temperature. The creation of such a non-equilibrium distribution under the conditions of a high vacuum can lead to the dissociation of the molecule if the rate of this reaction is higher than the rate of redistribution of the additional energy among other vibrational degrees of freedom, i.e. than the rate of intramolecular vibrational randomisation (stochastisation). The task of the theory is to facilitate with the aid of calculations the search for the selective vibrational excitation of the molecule in which this condition would be fulfilled. Calculations can help to elucidate the causes of the observed deviation from the experimental data of the rates of photoinitiated dissociation calculated on the basis of a statistical model.[73] The deviations can be caused by the incomplete randomisation of the energy, kinematic effects, insufficiently accurate calculations of the PES, etc. Calculations not only of the PES but also of the vibrational energy levels for the ground and electronically excited states, the constants for the anharmonic and kinematic interactions of modes, the probabilities of energy transfer between the modes, etc. are therefore necessary. Questions of this kind are part of the broader problem of the relation between the ergodic and random motions in the molecule, a problem which should be solved by means of the joint efforts of experimenters and theoreticians (see, for example, Noid et al.[74] and Krivoshei et al.[75]).

The problem of the influence of the non-equilibrium distribution of energy on the rate of unimolecular decomposition of molecules does not arise solely in connection with laser excitation. A non-equilibrium distribution can arise for different reasons; in particular, it is created in the course of the reaction itself. It can be neglected only in terms of the rapid mixing (randomisation) approximation. The development of these problems is of very urgent interest for chemical kinetics.[76,77]

A series of theoretical problems in intramolecular nuclear dynamics and as regards the structure of electron clouds are related to the increase in the sensitivity and resolving power of spectroscopic instruments. Thus the improvement of the resolution of the rotational and vibrational-rotational spectra to 10^{-3} cm^{-1} for a line width up to approximately 5×10^{-4} cm^{-1} imposes new requirements on the accuracy of the calculations and interpretation of the spectra.[67,78-80] To characterise the complexity of this problem, we may mention the high-resolution laser IR spectrum of the comparatively simple ion H_3O^+: approximately 100 transitions have been detected for this ion in the region of 3500 cm^{-1} in plasma cooled with liquid nitrogen, whereas in plasma cooled with liquid air an additional ~240 transitions were observed, but these have not as yet been interpreted.[67] The interpretation of such complex spectra requires the development of new computational methods, such as, for example, the method of computer modelling. New approaches have also arisen in the calculations of the force constants of molecules.[81]

The problem of the calculation of the vibrational spectra of non-rigid molecules, in particular molecules with pseudo-rotation,[82,83] molecules with conformational transitions, etc. is also of urgent interest. In the treatment of such spectra, it is necessary to solve the problem of the motion of atomic nuclei in a field with a complex potential.[84,85]

Many new fairly puzzling data concerning the dynamics of strong hydrogen bonds have appeared in recent years. These findings have not as yet been explained satisfactorily within the framework of a single approach. Such phenomena include, for example, various "anomalous" isotope effects for geometrical parameters,[86] the frequencies and intensities of stretching and deformation vibrations,[87,88] etc.

A number of interesting theoretical problems in intramolecular dynamics have arisen in connection with NMR.[89,90] Here information about the character of the motion of nuclei (for example, about their hindered rotation) is extracted with the aid of the theory of the NMR line form.[91]

2. Dynamics of Elementary Processes in the Gas Phase

The main task of the theory of elementary processes in a gas is the elucidation of the mechanisms of these processes and the calculation of the corresponding rate constants. Knowledge of the latter permits the calculation of the rates of complex multistage chemical reactions, the determination of the pathway followed in the degradation of energy and of the rate of such degradation in photochemical processes, calculations for laser gas-phase systems, processes in plasma, ultrasonic flow, etc. The experimental determination of the elementary constants, especially at high temperatures, is frequently difficult. The role of the theory is especially great in this instance. The study of the dynamics of gas-phase reactions is not important solely for practical purposes; investigation of such reactions makes it possible to learn about the mechanisms of the chemical reaction in a "pure" form uncomplicated by the influence of the medium.

As in the theory of molecular structure, theoretical investigations of elementary processes in the gas phase have received a new stimulus during the last decade by experiments using the new technology, in the first place lasers. Here it must

be emphasised that successful experimental studies of chemical reactions became possible by virtue of their combination with theoretical calculations.

The elementary processes, the calculation of the cross-sections of which is urgently necessary, are extremely varied. They include processes involving the transfer of electronic, vibrational, and rotational energy, charge transfer, ionisation, and decomposition, photodissociation, substitution, etc. reactions,[34,92,93] Many processes take place non-adiabatically.[94,95] The tunnel effect sometimes plays an important role.[96] Whereas two decades ago measurements were made mainly of the cross-sections of processes averaged with respect to rates and the quantum numbers of the initial and final species, in recent years the new technology has made it possible to measure cross-sections with a high resolution with respect to energy in molecular beams, the dependence of the cross-sections on the quantum numbers, the distribution of the products with respect to quantum states, etc. New requirements as regards the quality of the theory have therefore arisen. Thus it has become clear that, when the vibrational relaxation of molecules is considered, account must be taken of the change in their rotational state; it is important to take into account the anharmonic and Coriolis interaction of the modes, the occurrence of the van der Waals interaction of molecules which have collided, and the possibility of their chemical reaction.[97-99] Interesting problems arise in the interpretation of the results of the study of the transfer of rotational energy in beams taking into account the changes in the projection of the angular momentum.[100]

One of the new tasks of the theory of elementary processes consists in finding the transverse cross-sections of chemical reactions between species one of which (a molecule) was subjected beforehand to selective vibrational or rotational excitation.[101,102] For example, it is known that the reaction $N_2O + Cu \rightarrow N_2 + CuO$ on the surface of copper under the conditions of the excitation by a laser of the antisymmetric longitudinal vibrational of the N_2O molecule is 5×10^3 times faster than the thermal reaction on the same surface at 363 K.[101] It has been observed that the rates of the $N_2^+ + Ar$ and $H_2^+ + Ar$ reactions are a maximum on excitation of a specific vibrational level in the initial molecule; this maximum is apparently associated with the resonance (still incompletely understood) between the vibrations of the initial and final molecules.[103] Such resonance-induced increase in the rate of reaction has been observed in certain cases also for a specific translational energy of the species which have collided.

It is of interest to interpret theoretically the experimentally observed appearance of two maxima on the curve describing the dependence of the population of the rotational levels of the product molecules on the rotational quantum number of the initial molecule, which apparently indicates the existence of two decisive configurations of the activated complex (for example, in the reaction $MgH_2 \rightarrow MgH + H$).[103] It is also urgently necessary to obtain an answer to the question in what cases does the distribution of energy in the intermediate state become statistical and in what cases is there sufficient time for the reaction to occur before the randomisation of the energy.

A weak point in the theory of elementary processes is the calculation of the PES, which is usually performed with an inadequate accuracy. As regards the dynamics of the process itself, extremely effective methods have been developed for its treatment, which in the presence of a sufficiently accurate PES make it possible to achieve satisfactory estimates of the collision cross-sections. The calculations of cross-sections based on the solution of the Schrödinger equation have been most widely used (see the relevant reviews[92,104-106]). The success of the calculations of the rates of reaction depends to an appreciable extent on the successful choice of the curvilinear coordinates in terms of which the problem is solved.[106,107]

A number of other quantum-chemical methods of the collision theory are in the stage of intense development (see the reviews[108,109]). Together with these methods, trajectory calculations have become fairly common[110-113] in which classical trajectories of the motions of the representative point of the reaction are calculated with the aid of Newton's equation on a specified PES under different initial (quantum) conditions. In order to obtain the rate constant, the flux of particles is averaged over the thermal distribution. Allowance for quantum effects (tunnelling, interference, resonances) requires a more sophisticated calculation. The corresponding method is called semiclassical.[114]

However, it is necessary to recognise that the application of the above methods to systems with more than three atoms involves considerable computational difficulties. The statistical method for the calculation of reaction rates—the transition state method—has therefore come to be widely used. This method requires much less detailed information about the PES than the other methods.

The principal disadvantage of the initial transition state theory[115] was that no account was taken in it of the trajectory of the reverse motion on the PES of the representative points of the reaction towards the initial state, as a result of which the calculated rate constant was overestimated.[116] Furthermore, an insufficiently complete account was taken of tunnelling. A weak point of the theory was also the hypothesis of the separation of coordinates corresponding to different degrees of freedom and the neglect of the anharmonicity of the vibrations in the calculation of the vibrational partition functions. The subsequent development of the theory was directed mainly towards the elimination of these disadvantages.[117-123] As a result, a general transition state theory was developed, the central place in which is occupied by allowance for the trajectories of the reverse motion with the aid of a variational procedure (see the review of Truhlar et al.[124]).

We may note that the transition state theory is not always applicable to reactions in solution, because it does not take into account the stochastic character of the molecular motion (see the following subsection).

3. Dynamics of Elementary Processes in Condensed Phases and at Interfaces

For a long time the influence of the medium on elementary chemical processes in the liquid phase was taken into account in the majority of theoretical studies mainly in terms of the static approximation where only the change in the profile of the reaction path under the influence of the interaction with solvent molecules is taken into consideration.[125,126] The dynamic character of the influence was taken into account inadequately. For example, in the investigation of the kinetics of electron transfer by Marcus no account was taken of the Brownian character of the motion of the system in the formation of the activated state; only the reorganisation of the solvent and its influence on the activation energy were taken into consideration.[125] In a number of other studies, the charge transfer process was treated as non-adiabatic within the framework of a fairly special model.[127,128]

Later two approaches came to be used for the treatment of elementary processes in the liquid phase: the model based on the Brownian character of the motion of the reacting system along the reaction pathway (Kramers[129]) and the generalised Langevin equation.[130] According to the latter, the motion of the representative point in the liquid phase takes place under the influence of a random force in the presence of time-dependent friction. A common feature of these approaches is allowance for the deactivating influence of the collisions of the reacting molecules with the molecules of the medium, which diminishes the rate constant compared with the value calculated from the transition state theory. It has been shown recently that the two approaches are in essence equivalent.[131] An adiabatic theory of charge transfer has been developed within the framework of the Kramers model.[132–137] The generalised Langevin equation combined with the formalism of the time correlation function has found extensive application in the treatment of various reactions (see the relevant reviews[138–142]). Proton transfer processes[143–144] isomerisation reactions,[144–147] atom transfer reactions,[148] etc.[147,149–152] have been investigated. This branch of the theory of liquid phase reactions undoubtedly merits constant attention and development.

One of the fundamental problems in liquid-phase kinetics involved the solution of the problem of the character of the breakdown of the equilibrium distribution of the populations of the energy levels under the influence of the reaction. An experimental solution of this problem has become possible by virtue of the development of the laser technique.[32] It is important to understand how such breakdowns affect the rate and mechanism of the process.

New possibilities for the development of research into elementary processes in the condensed phase have arisen as a result of the application of picosecond and subpicosecond laser spectroscopy[153] and especially the method of laser-induced fluorescence.[154] Comparatively recently it has become possible to measure with the aid of ultrashort light pulses the rate of ultrafast elementary processes with durations in the range 10^{-11}–10^{-15} s.[155–157] Measurements of the characteristic times of the collisions of molecules in the liquid phase, of the redistribution of energy between different degrees of freedom in the excited molecule, of the times required for the dissipation of the excitation energy, of the intermolecular and intramolecular transitions of the electron and protons, of photodissociation, of the redistribution of atoms in the molecular system, etc. have been initiated. The application of this technique has led to a revolution in the study of ultrafast processes and made it possible to achieve a series of exceptionally interesting investigations.[153–156] For example, it has been shown that the rate of the intramolecular transition of an electron is controlled by the molecular motion.[157] This conclusion is based on the observation of proportionality between the relaxation time of the electronic transition and the corrected dielectric relaxation time of the medium. On the basis of results of similar measurements, it is possible to model confidently the corresponding processes.

Definite progress in the theory of liquid-phase reactions may be expected in connection with the application of the methods of molecular dynamics and in general of computer modelling, naturally subject to a sufficiently realistic approximation of the PES.[158–160] These methods have been used successfully in the study of not only elementary processes but also of molecular spectra.[158–160] We may note, however, that the dynamic effect of the liquid medium on the form and width of the bands in the rotational and vibrational spectra of molecules[161–163] and also in the EPR and NMR spectra[164,165] has already been successfully investigated for a long time on the basis of model approaches with the aid of methods of theoretical physics.

The computer modelling methods have found applications also in the study of the structure and dynamic properties of solids.[166]

One of the most important problems in quantum chemistry involves the study of the dynamics of elementary processes on the surfaces of solids.[167–170] It has already been demonstrated comparatively recently that the atoms distributed on the surface cannot as a rule be regarded as immobile when gas-phase molecules collide with them. However, the number of degrees of freedom which must then be taken into account is much greater than in calculations on the collisions of molecules with one another. Therefore theoretical study of the collisions of molecules with the surface has become appreciably more complicated. The first problem which arises here involves, as for a liquid medium, the determination of the minimum number of molecules which must be explicitly taken into account in the calculations on elementary processes on the surface. It is then necessary to find the PES. The main difficulty in the treatment of processes involving the collision of molecules with the surface is the inapplicability of the standard Born distorted wave method because the interactions are strong and the velocities of the molecules are low. Furthermore, a number of problems are associated with the need to take account of a large number of interacting reaction channels; it is difficult to take into account the quantum effects, especially for light atoms (interference, tunnelling), and also the energy exchange between molecules and phonons both in the bulk phase and on the surface. Nevertheless, many dynamic problems of the interaction of gas species with the surface of a solid have been solved successfully.[167–171] For example, the dynamics of the adsorption of diatomic ions on the surface of a metal, the reactions of oxygen atoms with the surface of carbon-containing platinum,[172] the dynamics of the recombination of hydrogen atoms on tungsten,[173] the adsorption of atoms taking into account relaxation processes,[174–178] the dynamics of adsorption in the presence of interaction with phonons,[179,180] the migration of atoms along the surface,[181] and other processes have been investigated.

A number of interesting problems in the dynamics of surface processes arise in connection with the development of new research methods. Among the latter, mention may be made of the molecular beam method,[167] desorption with angular resolution stimulated by electrons and phonons,[182] the spectroscopy of the energy losses by the electrons scattered by the surface,[44,183] Raman spectroscopy,[184] and other methods.

The promising nature of the method of the laser-induced fluorescence,[154] which provides unique detailed information about the distribution of energy in different stages of the reaction, in particular, for a reaction on the surface and in desorption, about the concentration and nature of radicals appearing in heterogeneous catalysis, and about other processes, which is extremely important under experimental conditions when other spectroscopic methods are inapplicable, must be specially emphasised. Such information should play a primary role both in the formulation of the theoretical problem of the dynamics of surface phenomena and in comparing the theory with experiment. We may note that the generalised Langevin equation has been used with some success for the description of the dynamics of the surface–gas system.[167,172,185]

The study of the dynamics of elementary processes plays an important role in the theory of catalysis (see, for example, Kiselev and Krylov,[186] Chapter 5). Here the initial problem is to discover the elementary stages comprising the catalytic process. It is known that even seemingly simple reactions, for example the catalytic synthesis of methanol,[187] involve a large number of intermediate stages. Theoreticians can assist in the analysis of reactions of this type by studying not only the PES but also the dynamics of individual stages. However, calculations for

only the simplest processes are in fact possible at the present time. Some of these were mentioned above.

In addition, it is useful to involve quantum chemists in the solution of fundamental interrelated problems of catalysis: concerning the mechanism of the decrease in the activation energy and of the change in the reaction pathway under the influence of catalysts and also in seeking an answer to the most important question how to avoid multichannel occurrence in catalytic reactions and how to reduce the amount of side products. Enzyme catalysis is known to be an example of high selectivity (see, for example, Refs.188–190). A high selectivity of the reaction implies that it is faster along one channel than along another. This optimum reaction pathway is probably associated with the self-organisation of the system, which presumably reduces to the choice of the most "favourable" sequence of stages and the optimum mutual orientation of the components of the reacting system in combination with the optimum character of their activation at each stage of the process. The natural question arises why these conditions are fulfilled in enzyme catalysis with such unvarying rigour. For this reason, modelling, especially computer modelling, of the possible mechanisms of the catalytic action of enzymes (and also of ordinary catalysts) constitutes an important task in quantum chemistry.

When the temperature is sharply reduced, the rates of many chemical reactions in the solid state are known to decrease initially in accordance with the Arrhenius law after which they cease to depend on temperature and the reaction proceeds at a low rate, which, however, is higher than the rate corresponding to the Arrhenius equation at the given temperature.[191,192] The existence of this low-temperature limit has been explained by Gol'danskii[192] by a tunnel reaction mechanism. However, the problem cannot be regarded as entirely elucidated. Its solution requires calculations for specific models. For example, Bazilevskii and co-workers[193,194] proposed a model for the ionic polymerisation reaction in crystalline formaldehyde in which the polymer chain propagation stage, which determines the rate of the entire process, takes place with a "favourable" mutual orientation of the molecules and involves very slight atomic displacements. If the height of the corresponding potential barrier is then fairly small, the atomic displacements can in general occur via both the tunnel mechanism and over the barrier. At a low temperature, the rate of reaction can then be determined both by the low tunnelling probability and by the low probability of the realisation of the "favourable" orientation of the molecules. In the absence of a barrier, only the second cause will naturally operate. At the usual temperatures, the reaction proceeds via another (activated) pathway, since the latter is faster. Fairly correct calculations have been performed for hydrogen transfer reactions[195] and the quantum nature of the low-temperature limit of the reaction rate has been demonstrated (see also Refs.72, 123, and 196).

IV. NON-ADIABATIC ELECTRONIC-NUCLEAR INTERACTIONS

It is known that the behaviour and properties of atomic-molecular systems can be largely treated in terms of the adiabatic approximation. However, under certain conditions the adiabatic separation of the electronic and nuclear motions is illegitimate. Studies in recent years have shown that in any molecular system there is a possibility of a situation where it is essential to take into account the non-adiabatic electronic-nuclear interaction, i.e. the situation where the electrons and nuclei must be regarded as a single dynamic system.

The interaction of nuclei and electrons is manifested in different ways for bound and unbound states. In the former case, the interaction is referred to as vibronic. It can be disregarded if the characteristic vibration frequency ν_{vibr} is much lower than the frequency ν_{el} corresponding to the electronic transition between the ground and first excited states. The limiting situation, which infringes this condition, occurs when the electronic energy states are degenerate ($\nu_{el} = 0$) in a certain region or at one point in space. If the degeneracy is associated with the symmetry of the system, then, according to the Jahn–Teller theorem, the symmetrical configuration of the nuclei proves to be unstable because of the mixing of the electronic states by nuclear displacements. Depending on the nature of the degeneracy, two or more distorted configurations will be stable. Such manifestation of the vibronic interaction is referred to as the Jahn–Teller effect.[197,198]

Thus, in the situation indicated, the Jahn–Teller effect actually determines the real structure of the molecular system and also its dynamics and certain physical and chemical properties which depend on the structure. During the last 20 years, manifestations of the Jahn–Teller effect have been observed in many compounds with the aid of various experimental methods: EPR, IR, Raman, and UV spectroscopy, photoelectron spectroscopy, and studies of the polarisability and magnetic susceptibility of substances. The Jahn–Teller effect is significant in crystal chemistry and influences structural phase transitions (the cooperative Jahn–Teller effect), especially the transitions associated with the spontaneous polarisation of crystals (ferroelectric phase transition). The theory explains satisfactorily the observed effects and has been used successfully in many instances for prediction.[197–202] A model of the fusion of solids has been recently proposed[203] on the basis of the Jahn–Teller effect.

The vibronic interaction is manifested also in those cases where ν_{el} is non-zero but is of the same order of magnitude as ν_{vibr}.[197,198] The corresponding effect is frequently referred to as the pseudo-Jahn–Teller effect. This situation is frequently encountered, for example, in molecules which are in highly excited electronic Rydberg states[199] and in compounds with transition metals.[21–23,26] Thus, in the energy range from 0 to 0.54 eV, the iron molecule $Fe_2(^7\Delta_u)$ has 112 electronic states.

With the aid of the pseudo-Jahn–Teller effect, it is possible to explain in many instances the shape of the molecule—for example, the stability of the planar form of the ammonia or methane molecule.[204] It is also noteworthy that the mathematical formulation of a theory of this effect helped to justify and extend the Woodward–Hoffmann orbital symmetry conservation rules.[205] Furthermore, it is also possible to obtain other useful results of a qualitative character; for example, one can explain the characteristics of the mutual influence of ligands, the relative stabilities of the isomers of coordination compounds, the geometrical features of metalloporphyrin molecules, etc.[204] In certain cases, recommendations concerning the formulation of the experiment in order to observe a new phenomenon follow from the theory.

The main task in the future application of the vibronic inter action theory lies apparently in the field of chemical reactions. It may be hoped that the existing theory will permit a deeper understanding of the mechanisms of elementary chemical reactions. The applications of the theory to the solution of certain problems in materials science (see below), in the theory of structural phase transitions, and in other applied problems, may prove very useful. At the same time, it is important to improve the theory itself: to learn to perform calculations correctly in the presence of a large number of

closely spaced states, in the presence of the spin–orbit interaction, etc.[22,23,206]

The manifestation of non-adiabatic conditions for unbound states, for example, in collisions between molecules, consist in the fact that, under its influence, any regular system can under certain conditions undergo a non-radiative transition with a finite probability from one electronic energy state to another having the same symmetry. For this, it is essential that the nuclei (the "slow" subsystem) should fall within the region of the configuration space where these energy states are at fairly short distances from one another and the rate at which the nuclei move is not too low. This effect plays a primary role in non-radiative transitions, in electronic relaxation, in the theory of non-elastic and reactive collisions, etc.[29,34,94,95,207] Situations are encountered in which non-adiabatic transitions occur between vibronic energy states, and not simply between electronic states, under the influence of a strong vibronic interaction.[99]

It has been demonstrated in recent years that, by analogy with the theory of the non-adiabatic transitions in atom–molecule collisions, it is possible to devise a theory of the interactions of radiation with molecules.[208,209] This analogy is based on the concept of quasi-energy.[210] In the theory, which has so far been constructed for diatomic molecules, a wide variety of situations are observed, not all of which are encountered in atom–molecule collisions. This applies, for example, to the resonance Raman scattering, hot luminescence, and related phenomena, which can be treated from a single standpoint.[211]

The problems associated with non-adiabatic transitions are extremely varied. If one considers molecular collisions, then it is important to learn to calculate the probabilities of non-adiabatic transitions for multidimensional PES. Hitherto, theoretical studies have been restricted to cases where the PES depends only on one or at most two coordinates.[29] In certain cases more stringent requirements are imposed on the accuracy of the calculations of the PES, for example when the region of the quasi-intersection of the energy states is calculated. A fairly high accuracy is then essential for a reliable calculation of the probabilities of non-adiabatic transitions taking into account tunnelling.[29]

With the aid of the model of non-adiabatic transitions between quasi-energy surfaces, it is possible to formulate the important problem of the dynamics of electronically excited polyatomic molecules. For this purpose, it is necessary to extend the dynamic theory of non-resonance Raman scattering developed for diatomic molecules.[209,211] Further development of the theory of the interaction of a strong alternating field with molecules,[212] the dynamic theory of multiphoton processes in atoms and molecules,[213] etc. is also important. In particular, such a theory can indicate a way of determining the parameters of the non-adiabatic linkages in molecules from experimental scattering intensities and phase relations.

V. DEVELOPMENT OF THEORIES OF THE APPLICATION OF PHYSICAL RESEARCH METHODS TO CHEMISTRY

Theory has always played a significant role in the development of ways of applying physical methods to chemistry. It is sufficient to recall the Debye method for the determination of the electrical dipole moments or the theory of optical spectra without which molecular spectroscopy would simply not exist and which has in fact become the basis of the theory of molecular structure. Hundreds of such examples could be quoted. The corresponding theories have become an inseparable component of quantum chemistry. Among recent studies along these lines, mention should be made of the theoretical justification of the multipulse NMR method, which made it possible to resolve the fine structure of NMR spectra of solids and which has proved exceptionally important to chemistry,[214,215] the development of a theory for the investigation of the character of molecular motion in a condensed medium with the aid of a paramagnetic label,[216] and proof of the possibility of using the angular anisotropy of the Auger spectra for the investigation of the geometry of surface layers and adsorbed molecules.[217]

The appearance of a new physical method useful for chemistry frequently begins with the discovery of some kind of physical phenomenon which serves as the basis for a new research method after the appropriate theoretical interpretation. Theoreticians sometimes suggest how an existing method should be modified or amplified in order to apply it to chemical objects and to obtain a new type of information. Several theoretical problems whose solution may culminate with the creation of new experimental research methods in chemistry are quoted below as examples.

(1) Physicists have learned how to obtain beams of polarised electrons. The diffraction of such beams by the surface of a solid can undoubtedly yield unique information about the magnetic and spin states of the surface. However, it has so far been possible to obtain polarised beams only at very low temperatures and in an ultrahigh vacuum and the intensity of the beams has been low.[218] This very greatly restricts the scope of their application. The task for quantum chemists is, on the one hand, to find systems which polarise electrons under less severe conditions and ensure a sufficiently high intensity of the beams and, on the other hand, to develop a theory of the diffraction of polarised electrons in relation to chemical problems.

(2) It has been recently discovered that, when fast molecular ions pass through films, their electron clouds are "stripped off" and the molecule decomposes into charged fragments which fly apart under the influence of Coulombic forces ("Coulombic explosion").[219] The angular and energy distributions of these fragments can, generally speaking, reflect both the structure of the initial molecular ions and the properties of the film. It is extremely likely that the development of the appropriate theory will permit the creation of a new research method.

(3) The method for the indirect detection of electron magnetic resonance (IDMR), for example, detection with the aid of luminescence, made it possible, by virtue of its high sensitivity, to obtain much unique information about the intermediate species in chemical reactions, about the mechanism of the transfer of valence, etc.[220,221] It is promising and feasible to apply the IDMR method to the study of a process involving charge transfer between ions in the liquid phase. It is also of interest to examine the question of the specific features of the application of the IDMR method to the study of processes on the surface of a solid. It is natural to begin the solution of these problems with the development of appropriate theories.

(4) It is known that, under the conditions of a shock wave in the solid phase, many interesting effects are observed, for example, intense polarisation of the specimen, a change in the direction and rate of reactions, etc.[222,223] Apart from high pressure, a high temperature is characteristic of a shock wave. It would be very attractive to create a theoretical model of such processes and to show experimenters what experiments should be formulated in order to test the model and then to explain the observed effects at the molecular level and possibly to create a new method for the investigation of shock waves.

(5) Laser chemistry has so far taken only the first steps. It is known that the chemical action of the laser beam can involve not only the selective excitation of vibrations but also the excitation of the electron cloud.[224] For example, appropriate action by a laser entails the ready occurrence of the reaction[225]

$$Na + HgCl_2 \rightarrow NaCl + HgCl$$

The laser method for the separation of isotopes is based on the selective excitation of electrons. The task for quantum chemistry is to develop a detailed mechanism of the reactions of the laser-excited species and to recommend how experiments should be set up in order to achieve the catalytic action of the laser beam on chemical reactions.

VI. APPLIED PROBLEMS

1. Materials Science; Computer Search for New Compounds and Materials

As mentioned above, quantum chemistry has always served as the foundation which ensured the development of new ways of investigating matter and even the creation of whole branches of natural science, which ultimately has had enormous practical importance. It is sufficient to recall molecular spectroscopy mentioned above, which would be unable to solve many applied problems without the appropriate quantum-chemical theory. However, apart from such indirect influence on practice, quantum-chemical methods are resorted to with increasing frequency for the direct solution of specific applied problems, for example, the problems arising in materials science. One may quote a series of examples where quantum-chemical calculations proved useful in determining the relation between the macroscopic properties of materials and their atomic-molecular structure and ultimately in the solution of technological problems.

We may mention the calculations of diffusion coefficients in solid materials as one such example. These calculations are of special interest if the study of diffusion is hindered as a consequence of say, high radioactivity. Theoretical investigation of diffusion at the atomic-molecular level is also important in order to be able to understand the mechanics of the process and to create a basis for the treatment of more complex transport processes.[226] A model calculation of the activation energy for the diffusion of helium in nickel made it possible to understand the nature of the potential barrier and to elucidate the role of electronic relaxation and of the degree of involvement in the process of various electron layers of the nickel atom.[226,227]

Calculations of the physical characteristics of impurities and of their influence on the properties of materials are also important. For example, the geometrical and energy characteristics of the impurity centre, its influence on the intrinsic defects in the solid, etc. have been calculated by quantum-chemical methods. Such calculations for impurity carbon in iron helped to explain many effects important for engineering.[226]

Quantum-chemical methods have helped in the solution of certain problems of interest for the theory of solar cells, for example, the probabilities of the non-radiative decomposition of excitons in solid hydrogen fluoride have been calculated.[226]

An interesting quantum-chemical calculation has been performed to elucidate the mechanism of the oxidation (and inactivation) of a graphite moderator in a nuclear reactor. Calculations showed that the oxidation takes place at defects on the graphite surface and that the diffusion to these defects of molecules such as those of H_2O and CH_4 is much faster than the diffusion of oxygen. The addition of a small amount of, for example, methane to the coolant (CO_2) slows down the oxidation of graphite, because methane rapidly occupies its active centres.[226]

Quantum-chemical calculations have made an important contribution to the solution of the problem involving the search for the optimum accumulator (carrier) of hydrogen as a source of chemical (fuel) and nuclear energy.[228] Transition metal alloys are usually employed for this purpose. Calculations permitted the determination of the maximum possible store of hydrogen in the given alloy and showed, in particular, that amorphous bodies are capable of carrying more hydrogen than crystals of similar composition.

The development of the theory of the Jahn–Teller effect led to the prediction of a practically important phenomenon—giant magnetostriction.[201,229] The theory has been confirmed experimentally.[230]

One may point to a striking example where quantum chemistry played an important role in the solution of one of the fundamental problems in the physics of elementary particles—in the determination of the true mass of the neutrino at rest. Kaplan and co-workers[231,232] investigated the rearrangement of the electron clouds of a number of molecules of tritiated hydrocarbons and certain other compounds occurring on β-decomposition. The results of the calculations were used to interpret experiments designed to find the rest mass of the neutrino.[233] Analogous but more accurate calculations were subsequently performed by other workers.[234,235]

An increasing tendency to calculate by quantum-chemical methods the stability and properties of compounds which have not yet been synthesised, to make recommendations for the optimisation of the conditions and pathways leading to the synthesis of new medicinal preparations, etc. has been observed in recent years. For example, the stability of the C_{60} molecule, which, in view of its spherical shape has been called footballene, has been demonstrated theoretically.[236,237] Its stability was predicted as early as 1973 by the Hückel method.[238] Footballene has not yet been synthesised, but there are experimental data confirming its existence and high stability.[239,240] We may also note that quantum-chemical calculations have helped in the synthesis of a new effective antibiotic—quantamycin.[241] According to the recommendation arising from the quantum-chemical calculations, it has the composition and structure such that the negative qualities of its analogue (lincomycin) are eliminated.

The computer assisted search for new chemical compounds and materials with properties specified beforehand and the development of the optimum methods of their synthesis will undoubtedly be expanded still further in the immediate future. Computer modelling will also be directed to the search for means of protecting materials against radiation,[242] the study of their behaviour under extreme conditions, and the solution of many other problems important for practical purposes.[243]

2. Quantum Molecular Biology

One of the most important fields in which quantum chemistry has been applied is molecular biology. During the last decade, considerable progress has been seen in this direction and has been represented increasingly at international congresses and conferences on quantum chemistry; conferences devoted specifically to this topic have also been organised. Analysis of the relevant questions is outside the

scope of our task. However, in order to demonstrate the specific features of this extensive field, we shall quote one example.

The striking selectivity of photochemical biosynthesis is known: under natural conditions, billions of tonnes of green matter are generated each spring in several weeks virtually without waste, while under laboratory conditions in analogous processes the yield of the required product reaches no more than 50%. The question arises what is the mechanism of this surprising single-channel nature of the process (purity of the biosynthesis), which is comparable to the selectivity of the action of enzymes. Quantum chemistry should help in the solution of this problem.

The specific features of molecular biology and the exceptional advances in gene engineering give grounds for the expectation that the use of biomaterials and biotechnology is more promising for the creation of the new generation of electronic computers[244] than that of the usual chemical compounds and methods.[245] Theoretical analysis of the possible versions of the structure of the constituent elements of a biocomputer is a task of current importance, to the solution of which modern quantum chemistry can make a definite contribution.

It must be emphasised that many major problems in molecular biology and pharmacology can be solved and are already being solved with the aid of computer modelling. These problems include, for example, the prediction of the biological activity of chemical compounds.[246,247] The simplest version of such predictions is as follows. The structures of a series of compounds, already known as active in the desired sense, are calculated quantum-chemically, the structural and electronic feature characteristic of the given activity are established, and new compounds having these features are then synthesised.

VII. DEVELOPMENT OF QUANTUM-CHEMICAL METHODS

As mentioned above, effective research methods have now been developed in various fields of quantum chemistry. Powerful procedures have been created in the theory of elementary processes in the gas phase, in the theory of magnetic, electronic, and vibrational relaxation of condensed phases, theoretical methods for reactions in solutions, theories of the interaction of matter with radiation, and many others have been greatly developed. Considerable efforts by theoreticians and mathematicians have been directed to the solution of the many-electron problem. Here studies have been prosecuted in two directions: (a) the improvement of semiempirical computational methods; (b) the development of effective non-empirical computational methods (calculations from first principles—*ab initio*). *Ab initio* methods have been developed mainly by expanding the initial basis set of one-electron functions in order to achieve the maximum possible approach to the Hartree–Fock limit and to develop effective methods for taking into account the correlation of electrons.[248]

At one time it appeared that non-empirical calculations should displace the semiempirical methods, because the former are more rigorous and in the limit yield accurate results. However the improvement of *ab initio* methods was very slow: on average (according to the data over a period of 20 years) the size of the systems in which it was possible to take into account correlation effects increased only by one and a half electrons per year.[249] The chemistry of large molecules therefore developed independently of these calculations. Furthermore, it was found that, as the non-methods are improved and the number of electrons in the system is increased, there is a catastrophic growth in the necessary computer time, which leads to a dramatic increase in the cost of calculations. When ultrafast computers (supercomputers) are used, the machine time is shortened, but the cost of the calculations does not fall but actually increases (approximately by a factor of 100) as a consequence of the increase in the cost of the work of the computer per unit time.[250]

Thus the view that *ab initio* calculations on molecules with a high degree of accuracy are not promising for the majority of chemical fields, since such calculations have to be confined in practice to comparatively small molecules, merits consideration. The problem of the development of sufficiently effective semiempirical methods, which would be comparatively cheap and "fast" and which would reproduce correctly the principal characteristics of molecular systems therefore comes to the fore. Certain promising approaches to the improvement of semiempirical computational methods have been published recently. For example, on the basis of the idea put forward by Burshtein and Isaev,[251] Dewar[250] proposed a new version of a semiempirical method, which is almost free of the most significant disadvantages of the previous versions.

It is possible to find in the literature a number of convincing examples where the semiempirical calculations, using the already existing methods, proved to be extremely useful and were found to have a predictive power (see, for example, Refs. 252–262), although, as is well known, not all the properties of molecules can be reproduced with equal adequacy by such calculations.

Together with this, there remains naturally the task of finding new methods for the solution of the many-electron problem. Such methods are essential in the first place for calculations on very large molecules, for which entirely satisfactory methods have not yet been created.[263] It may be that here one should abandon the standard procedure involving a simple extension of the models existing for small molecules and that an attempt should be made to find new modelling methods. The method of the density functional[264–267] merits attention. One cannot rule out the possibility that progress in computational quantum chemistry will be achieved using approaches in which wave functions do not appear at all.[263] Mention should also be made of a promising but more specific possibility of studies where new (sometimes quite unexpected) relations are established between different properties of molecules or physical quantities, without solving the Schrödinger equation, on the basis of general theorems such as the Hellmann–Feynman theorem or the hypervirial theorems.[268]

The following comment should also be made concerning non-empirical calculations and the prospect of obtaining with their aid highly accurate results. As the calculation becomes more accurate, there is a gradual abandonment of simple models. In the limit of the "accurate" calculation, the clarity of the results is completely lost; as in the case of an experiment, the latter must be re-interrupted anew, since otherwise the result of the calculation will be merely a "dead" numerical value. In other words, even after very extensive computerisation of quantum chemistry the physical model will not lose its heuristic role. The development of science during the last 10–20 years confirms this view. It is sufficient to recall, for instance, the role which orbital symmetry conservation rules[1] or the concept of frontier orbitals[2–4] have played and are playing in the development of chemistry. Such generalisations are perhaps more important for progress in science than hundreds of other laborious calculations.

The same may be said also about other ways of applying computers in quantum chemistry. The method of molecular

dynamics and the method of statistical sampling (the Monte Carlo method) can only supplement but not replace studies based on physical models. Clearly, there exist very complex processes which cannot be investigated by procedures other than those involving computer modelling.

It is known that the computer itself does not generate directly new physical or chemical ideas. It is a means for the completion of the development of a new idea or a new method and in this sense computers play a very important but subsidiary role in the development of science. At the same time, one should also bear in mind two factors. In systematic studies using a computer, the investigator acquires a new ("computer") form of thinking: a computer experiment suggests to him an effective way of solving the problem which is in essence associated with the computer. Thus, a kind of feedback is generated. The Luzanov method—the method for the operator reduction of the density matrix—may serve as an example of such a situation.[269] It is based on the idea of developing a mathematical apparatus for taking into account the correlation effects which could be readily translated into machine language. The specific features of computers suggested that an algebraic apparatus can serve for this purpose. With its aid, the author was able to develop a method which takes into account effectively configuration interaction without an explicit use of wave functions.

The second factor is associated with the fact that the computer is in essence an effective instrument for carrying out a kind of computer experiment. If one expects from such an experiment not a simple individual numerical value of some kind of parameter but a broader kind of information about the test system, then as in any experiment, the results have to be interpreted after the completion of the calculations. Such interpretation can lead to the appearance of new representations and new ideas important for the solution of the problem as a whole and in this way the computer can prove to be an indirect source of new ideas.

Fundamental ideas in quantum chemistry are known to have appeared before the invention of computers. Among them one may include the Heitler–London method (1927), the idea of molecular orbitals [Hückel, Mulliken (1930–1932)], the crystal field–ligand field theory [Boethe, Van Vleck (1929–1935)], the self-consistent field method [Fock (1930)], the Jahn–Teller theorem (1937), the transition state method [Eyring, Polanyi (1935)], the Kramers method in the theory of reactions (1940), and others. Unfortunately one should note that by no means all the major ideas were properly understood and adopted sufficiently rapidly. This happened with ligand field theory, whose principles are being introduced into chemistry only after 25 years had elapsed since the first publications; the Jahn–Teller theory appeared in the scientific literature for more than a quarter of a century as an elegant artifice without experimental confirmation and application; the Kramers method remained unknown to chemists for more than 30 years. As a result of the last factor, virtually no account was taken for a long time of dynamic effects, as mentioned above, in the theory of reactions in solutions. The task for theoreticians apparently consists, in particular, in helping the penetration of new ideas into practical experimental research.

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It follows from the foregoing that quantum chemistry has been playing an increasingly important role in the development of chemistry as a whole and has been making increasing contributions to practical research and to new technology. This mission of quantum chemistry is being achieved in conjunction with experiment. The task is to strengthen comprehensively such linkages with experiment, to strengthen the influence of theory on experimental research, and to seek new ways of applying physical research methods in chemistry. At the same time it is necessary to improve quantum-chemical methods and to develop effective and cheap methods for calculations on molecular systems. It is to be expected that the general trends in the development of quantum chemistry in the coming years will involve the theory of chemical reactions, theoretical materials science, and molecular biology. The advances in the development of these theories during the coming decades may prove comparable to the advances in the theory of molecular structure during the last 20–30 years.

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