

References and Notes

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Must a Molecule Have a Shape?

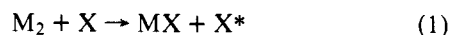
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Abstract: The idea of molecular structure is discussed from the point of view of the quantum theory: we show that the modern picture of a molecule as a bound collection of electrons and nuclei is not invariably equivalent to the classical molecular model of atoms joined by bonds, and hence molecular structure is not an intrinsic property. High-resolution gas-phase experiments on "small" molecules in dilute gases and molecular beams are characterized as being concerned with a *novel state of matter distinct from the classical gas* since they probe the *molecular stationary states* which cannot be understood in terms of molecular structures: these experiments thus need to be distinguished from investigations of dense gases and condensed matter (or "large" molecules generally) for which the notion of structure is the key concept that essentially "solves" the macroscopic many-body problem. These ideas can be applied to a wide area of physical chemistry; for example, the kinetic theory of gases, optical activity, "polar" and "nonpolar" gases, high-resolution spectroscopy, and much else.

Introduction

In recent years there has been a growing awareness of the limitations of the conventional Born-Oppenheimer approximation in the analysis of chemical experiments: the inclusion of vibronic interactions is essential for a proper understanding of molecular properties deriving from the excited states of "large" molecules, as may be seen in the modern theory of radiationless transitions.¹ At the same time similar difficulties have been identified in discussions of the reactions and spectroscopy of "small" molecules: according to Faist and Levine,² "If a system existed which contained a multitude of curve-crossings, the flow of electronic energy could be essentially unrestricted; in such a situation, one may expect a nearly statistical electronic state product distribution". They cite the alkali dimer-halogen atom reactions



as a class of reactions of this type. Another example is to be found in the analysis of the visible spectrum of NO₂ under high resolution.³ Several writers have given theoretical discussions of the adiabatic hypothesis and the general features of potential energy surfaces, and have concluded that there must necessarily be regions of nuclear configuration space where the adiabatic hypothesis fails completely.⁴⁻⁶ The existence of branch-cut singularities in the potential energy surfaces of systems containing more than two atoms, and the related discontinuities in the electronic wave function, known since the

work of Teller,⁷ have recently been discussed again by Davidson.⁶

The adiabatic separation of electronic and nuclear motion has always been regarded as a sine qua non of (quantum) chemistry, it being understood that due consideration of vibronic perturbations may be needed in order to obtain the correct physical or chemical interpretation of experiments. Textbooks of molecular quantum theory usually suggest that without the Born-Oppenheimer separation of electronic and nuclear motion it would not be possible to perform calculations of the quantum states of molecules, or understand their properties; actually, however, it seems much more likely that the real motivation for the conventional methods of quantum chemistry arises from a powerful "felt need" to make contact with the classical idea of *molecular structure*. This feeling appears to be the main barrier hindering the development of "nonadiabatic" calculational procedures since it seems likely that nonadiabatic computations on small molecules, for example, the hydrides of the first-row elements, in which electrons and nuclei are treated on the *same* footing, are perfectly feasible.⁸ Although the accuracy obtainable now is not of spectroscopic quality, we can expect improvements as experience is gained with such calculations.

The quantum theory of molecular structure and the role of the Born-Oppenheimer approximation has been discussed in some detail in the recent literature:⁹⁻¹⁵ this paper is a continuation of this discussion in a chemical context, and argues that it will be essential in the future to try to understand an im-

portant class of experiments in physical chemistry *without* reference to the notion of molecular structure (for examples of what this means in specific cases see ref 10 and 11). This radical idea is a consequence of an analysis of the idea of molecular structure from "first principles", which shows that if one starts from a description of a molecule as an *isolated*, dynamical system consisting of the number of electrons and nuclei implied by the stoichiometric formula that interact via electromagnetic forces,¹⁰ one cannot even calculate the most important parameters in chemistry, namely, those that describe the molecular structure.¹⁶ This fact does not mean that "the quantum theory is wrong", nor does it deprive the idea of molecular structure of its general usefulness, for the key word in the above *ab initio* description is "isolated": it does mean that it is wrong to regard molecular structure as an intrinsic property of a molecule. The idea that molecular "shape" is not an invariable property of molecules is much more than a mere philosophical curiosity: it has the practical consequence of directing our attention to the need for a new motivation and interpretation for high-resolution experiments in terms consistent with quantum mechanics. As far as I can see this argument could only be invalidated by a demonstration that *molecules, unlike atoms*, can never be isolated sufficiently in experiments to warrant a discussion of their properties in terms of the true stationary states of an isolated molecular system. I suggest that isolation of a molecule *is* a real possibility in a dilute gas or molecular beam of a species of low molecular weight, and our description should be modified accordingly to take account of this feature of what is in effect, a novel state of matter distinct from the classical gas. There is a *prima facie* case that the current quantum chemical interpretations of some experiments in chemical physics are incomplete and at variance with the requirements of quantum mechanics.^{10,11}

Molecular Structure

Those sciences that are concerned with the molecular aspects of the properties of matter, principally chemistry, but also molecular physics and biochemistry, are founded on the belief that all experiments involving molecules can be understood in terms of the relative dispositions of the constituent atoms in the molecules. This idea of molecular structure (or "molecular shape") has been fundamental to the development of our understanding of the physicochemical properties of matter, and is now so familiar and deeply ingrained in our thinking that it is usually taken for granted—it is the *central dogma of molecular science*.

In classical chemistry a molecule is pictured as a collection of atoms held together by chemical bonds: the atoms in the molecule only have significance so to speak "within" the molecule, in relation to the other atoms. The "laws" that govern the spatial relationships between the atoms are the classical valency rules, for example, the requirement for a tetrahedral arrangement of atoms about four-coordinate carbon. It is, however, common today to regard a molecule as a collection of electrons and nuclei, and thus we are lead directly to consider what sort of understanding of the concept of molecular structure can be achieved from the point of view of the quantum theory, since electrons and nuclei are governed by the laws of quantum mechanics, among which there is no reference to the notion of chemical structures.

The quantum mechanical analysis of the idea of molecular structure that I sketch here is partly an attempt to make clear the fact that quantum theories of the physical and chemical properties of bulk matter could not have been developed to their present-day form without *borrowing* the notion of molecular structure from classical chemistry. One cannot therefore claim that the hitherto mysterious structural concept underlying chemical explanation is derivable from physical theory and therefore "explained" by quantum mechanics. We have to

recognize a qualitative distinction between the methods used in the quantum mechanics of "small" and "large" aggregates of elementary particles, inasmuch that the theories of small systems do not pass smoothly into those appropriate to large ones; in short, we see, if we take the trouble to look, a real discontinuity expressed in the mathematics and in the physical concepts used to rationalize the experimental information obtained from these two types of system.

The commonly accepted hierarchical classification of the microscopic description of matter puts atoms and nuclei in with the elementary particles *per se*, but recognizes that even the smallest molecule, (H_2^+), is conventionally treated by methods which are based on the Born-Oppenheimer approximation and the structural concept, and which can be extended through to solid-state physics and the electronic theory of matter in bulk. I shall argue that the natural criteria on which this division is based are (1) the accuracy with which measurements of *energy* can be made, and (2) the experimental circumstances that obtain, for example, dilute or dense matter, and that the conventional dividing line between atoms and molecules can no longer be drawn so sharply since there are now experiments on "small" molecules in the gas phase (laser spectroscopy, molecular beam studies, electron scattering, etc.) which are most naturally discussed in a framework analogous to that customarily employed in atomic physics *without* reference to the classical notion of molecular structure. On the other hand, for our understanding of classical chemistry and the rationalization of the properties of liquids and solids, the notion of *structure* is the essential synthesizing concept that states the answer without knowing how to solve the (many-body) problem.

We ought to expect at the outset of a study of the quantum theory of molecular structure that some aspects of these two manifestly separate strands of thought will prove to be incompatible, since *prima facie* there is no reason to suppose that the same basic ideas can provide a valid basis for the discussion of *all* molecular experiments. This is understandable if one recognizes that every physical and chemical concept is only defined with respect to a certain class of experiments, so that it is perfectly reasonable for different sets of concepts, although mutually incompatible, to be applicable to different experimental situations.¹⁷

Quantum Description

One can summarize the essential difference between classical and quantum mechanical descriptions as follows. It is characteristic of classical theory, and of our ordinary thinking habits, that the results of experiments permit inferences about an "observed object", for example, a molecule, which exists separately and independently in the sense that it can consistently be said to "have" certain properties, whether or not it interacts with anything else such as an "observing apparatus", and this leads to a belief in intrinsic properties such as molecular weight and molecular structure. In quantum theory, however, one is faced with a description of experiments in terms of the properties of only those quantum *states* that are probed by the experiment under consideration; a different type of experiment may lead to information about other states of the "system" under study, but if one is not concerned with commuting operators in these experiments one cannot "add" to the original information in the way one does classically. The essential meaning¹⁸ of the uncertainty principle is that the potential or actual separability of "observed object" and "observing apparatus" cannot properly be carried out in any physical situation *where quantum properties are important*.¹⁹

The sweet bye and bye character of this remark should not cause too many difficulties in actual applications but perhaps it would be helpful to consider an example from elementary

physical chemistry. The fact that the classical and quantum theories of some physical system give the same answers does not imply that the system is to be understood in terms of a classical model; for example, the quantum theory of the ideal gas faithfully yields the usual results of the kinetic theory of gases,²⁰ but one now has a description of the gas based on a wave function (state vector) and the uncertainty principle can be important. Many years ago Einstein studied the black-body radiation of a gas in thermal equilibrium with the radiation field in a cavity, and showed that the absorption and emission of radiation by the gas, which is a mechanism for thermal equilibration, must involve quantized transfers of energy *and* linear momentum if the emission spectrum of the gas is to conform to the Planck black-body law *and* the gas is to have a Maxwellian velocity distribution as implied by the theory of heat.²¹ This is a manifestation of quantum properties of both gas and radiation: the knowledge that the gas has a Maxwellian velocity distribution means that we have made a measurement of a thermal distribution of *momentum eigenstates*, so that the uncertainty in the position of the molecules emitting the radiation is very large. Einstein showed that provided the interaction between gas and radiation involves photons of definite linear momentum, i.e., what we would now call momentum eigenstates of the radiation (plane waves), a Maxwellian velocity distribution persists; however, the solutions obtained from classical electrodynamics for an emitting system are *spherical waves*, corresponding to the emission of photons of definite *angular momentum*. In quantum theory this paradox is resolved by noting that spherical wave emission can only occur when the uncertainty in the *position* of the emitting system is much less than one wavelength of the emitted photon; on the other hand, when the uncertainty in the position of the emitting system is much greater than the photon wavelength, as, for example, in the momentum eigenstates of our gas, we can speak of recoil and plane wave emission occurs.²² These distinct and mutually exclusive possibilities are required by the uncertainty principle since the linear momentum operators of the gas (or of the radiation) do not commute with the position and angular momentum operators. In numerical terms the quantized momentum effect (recoil) is much smaller than the exchange of energy, but is essential if one is to formulate the correct interpretation of these particular experiments. Notice that what we say about the quantum states of one part of the experiment (e.g., the gas) is necessarily correlated with what we can say about the states of the other (the radiation); this is the meaning of “nonseparability”.¹⁹ Very similar remarks apply to the famous discussion of the role of the uncertainty principle in the measurements of the position and momentum of an electron with the aid of Heisenberg’s γ -ray microscope;²² essentially two different, and mutually exclusive, sets of apparatus are required here since which of these measurements is actually made depends on whether the detector for the radiation scattered through the optical system of the microscope is placed in the image plane or in the focal plane of the microscope.²³ The accuracy with which these measurements are made then determines the uncertainty in the values of the conjugate variables according to the indeterminacy relations $\Delta p_i \Delta q_i \gtrsim \hbar$.

In chemical discussions special relativity can be neglected and conservation of mass in a closed system is therefore guaranteed for all possible quantum states by a superselection rule that forbids absolutely quantum transitions between states of different total mass²⁴ (Lavoisier’s law of conservation of mass is a *quantum* law!); hence there are no difficulties about the idea of molecular weight as an invariable property. This is an exceptional circumstance and a discussion of the meaning of molecular structure in quantum mechanical terms must address itself to some such question as: can a molecular structure be associated consistently with the totality of ob-

servable quantum states of a molecule, as implied by the central dogma, or only with a particular subset of the experimentally accessible states?

The dynamical aspects of the quantum-mechanical description of molecular phenomena are ultimately based on the time-dependent Schrödinger equation for the quantum state vectors. The “character” of these quantum states is partially determined by the boundary conditions that must be specified in order to complete the correspondence between Schrödinger’s equation and the actual experimental setup; physical considerations also determine whether we must bear in mind the macroscopic nature of the sample of matter, or simply focus on an “isolated” molecule. Perhaps it would be as well to discuss this a little further since the division between “the quantum mechanical system” under investigation and “the boundary conditions” is not clear cut. Our initial guide in deciding what should be included in the specification of the dynamical system, i.e., the Hamiltonian operator, is the recognition in physical phenomena of the existence of distinctive and widely varying time scales (with characteristic time constants τ), since this allows an approximate separation of a “system” from much of its environment in the sense that significant energy exchange between the system and its environment can be assumed to take place over times much greater than τ : the description of the environment is what we mean by the specification of the boundary conditions. Consider first the situation with respect to the investigation of the chemical and physical properties of compounds in the liquid and solid phases and its quantum mechanical description: this covers most of the experimental situations of classical bulk chemistry from which the concept of molecular structure originally emerged. We could regard the macroscopic sample of matter as an isolated quantum system with a fixed total energy but we would then have to solve the Schrödinger equation for a Hamiltonian operator describing the interactions among (of the order of) Avogadro’s number of charged particles; on the other hand, the boundary conditions appropriate to a single molecule, regarded as a mobile collection of interacting electrons and nuclei, moving in a liquid or solid are far too complicated to specify in detail even at a phenomenological level. Both apparently insuperable problems are “solved” by the assumption of the molecular structure hypothesis which suggests that we can describe the situation in terms of *a model time-independent Schrödinger equation for an individual molecule with a definite “structure”*. The form of quantum theory we are led to is a many-body theory in which the electrons are treated in a fully quantum-mechanical fashion, whereas the nuclei are treated quasi-classically. We hold the nuclei at rest and calculate the electron distribution for the specified, fixed nuclear configuration; only after this calculation is performed would we consider the modifications required because of nuclear motion.¹⁶ This is the content of the Born–Oppenheimer argument.²⁵ The process of holding the nuclei at rest can be thought of as formally arising from making the masses of the nuclei infinite, or equivalently, from the imposition of forces of constraint of infinite magnitude; these infinities are the origin of the discontinuities I referred to above as providing a qualitative distinction between “small” and “large” systems. In technical terms the Born–Oppenheimer separation of electronic and nuclear motion can be characterized as an asymptotic expansion about the essential singularity in the complete internal state wave function associated with the infinite nuclear mass limit;^{12–15} in many respects it is analogous to the well-known quasi-classical (WKB) approximation in quantum mechanics which is associated with the singular limit of $\hbar \rightarrow 0$.

The molecular structure hypothesis “solves” the macroscopic many-body problem by identifying individual atoms or molecules as the ‘quasi-particles’ of the many-body system, i.e.,

as those entities that interact with one another only relatively weakly.²⁶ The crucial point, however, is that these atoms and molecules must *not* be thought of as being essentially the same as *isolated* individual atoms and molecules, for we are concerned with quantum states that reflect the influence of the many-body environment; among the new properties "created" by the many-body system are the *size and shape* of an individual atom or molecule. A central argument of this paper is that such terms have no meaning for the quantum stationary states of an isolated atom or molecule. This is entirely analogous to the situation in the electronic theory of condensed matter where we identify "electrons" as the quasi-particles that move almost independently of one another in an external field created by the fixed nuclei and all the electrons in the system; the electron here is much the same entity as the chemist's electron but has quite different properties from the isolated, "free" electron studied in high-energy physics experiments, for example, an apparent (effective) mass $\neq m_e$ and a finite lifetime. We are thus led to a description of condensed matter in terms of individual atoms that are located at definite positions and interact with one another mainly through their "electron clouds", and we can conclude that a molecular structure description in terms of atomic positions can be given a quantum-theoretical form at a quasi-classical (asymptotic) level of approximation.

Essen has given arguments based on the virial theorem to show how the classical idea of molecular structure can be associated with the low-lying states of a many-body system with Coulombic interactions; these arguments also rest on asymptotic analysis and are not valid for the eigenstates of molecules in the sense that the "molecular structure representation" is not unitarily related to the representation of eigenstates in inertial reference frames.⁹⁻¹² The emergence of an approximate classical picture in a quantum theory requires a change in the interpretation of configuration space. The classical bond model of a molecule describes the relative dispositions of atoms in our ordinary three-dimensional physical space, which is fully equivalent to the configuration space used in classical mechanics; the analogue of configuration space in quantum theory is obtained from the coordinate representation of some abstract Hilbert space which is *not* trivially equivalent to ordinary space. Indeed a theory of space needs to be based on the evolution in time of the interaction between microsystems, i.e., on the idea that the physical world is constituted by changing things. In quantum theory an atom or molecule in a stationary state has no extension in space or time, so that it makes no sense to talk about the size or shape of an atom or molecule in such a state.²² Molecular structure has thus to be associated with those intrinsically time-dependent quantum states for which the identification between classical and quantum configuration spaces can be made, since only then is it valid to relate notions of molecular structure to maxima in the molecular wave function in position representation; *how* this identification is to be made remains an unsolved problem which is usually glossed over.

It is clear that a molecular structure description in the quantum theory of molecules is intimately connected with the Born-Oppenheimer separation of electronic and nuclear motion, for only then can we talk about a potential energy surface and chemical bonds.²⁷ A corollary of this statement is that molecular structure makes *no* appearance in a quantum treatment of molecules starting from first principles.¹⁵ We are thus dealing with a *qualitative* change in the theory which is expressed in the mathematics by a discontinuous approximation, and one is bound to question whether invoking the structure hypothesis is always "the right thing to do", since this would imply that only intrinsically time-dependent quantum states of molecules are accessible in experiments. Consideration of very precise experiments on small molecules in dilute gases

and molecular beams leads me to answer this question, and hence also the question posed in the title of this article, in the negative. It will try to explain why I should advocate a view completely at variance with the conventional chemical wisdom that such experiments can lead to ever more accurate determinations of molecular structures.²⁸

Until recently it was difficult to avoid the loss in energy resolution caused by molecular collisions and the Doppler effect in gas-phase experiments such as elastic and inelastic scattering of light by small molecules, i.e., birefringence and optical spectroscopy in its various forms, in analogous scattering experiments involving light charged particles such as electrons and positrons, and in mixed scattering processes such as photoemission. The effects of these line broadening processes can, however, be largely avoided by using the molecular beam technique, and by taking advantage of the high power and directional properties of laser radiation.²⁹ Moreover, supersonic nozzle sources can produce beams of molecules in local thermal equilibrium at effective temperatures of a few degrees Kelvin or less.³ Thus in these experiments the resolution in energy of the molecular quantum states that can now be achieved is so fine as to suggest that high-resolution experiments on "small" molecules should be interpreted in terms of the stationary states of *isolated* molecules, i.e., the *molecular eigenstates*, just as we deal with atomic eigenstates in the analogous experiments involving atoms. Physically this is reasonable because the experimental arrangement is such as to minimize intermolecular interactions, so that we can base our theory on the complete Hamiltonian for a single molecule (electrons + nuclei) with time-independent (constant energy) boundary conditions; naturally we now need no assumptions about fixed nuclei or structures. Experiments on molecules in electric fields such as electric deflection of molecular beams and field-induced optical anisotropy of gases can also be conveniently considered in this group of experiments since they are concerned with dilute gases, and we wish to interpret the experiments ultimately in terms of the molecular quantum states in the absence of the field, i.e., the field is regarded as a perturbation. I have presented elsewhere^{10,11} an interpretation of these experiments using the molecular eigenstates; it may be noted here that the practical distinctions between "polar" and "nonpolar" gases can be derived from the molecular polarizability tensor *without* reference to a fictitious "dipole moment".

It seems inevitable that experimental technique will continue to improve under the impact of new technologies, and hence a critical evaluation of the theoretical framework used for the discussion of these experiments seen desirable, even imperative, since quantum properties are so important as to invalidate the classical mode of description. We note in passing that many of the underlying ideas still used in chemical spectroscopy, for example, were developed in the years immediately following the First World War before the discovery of quantum mechanics;¹⁰ if we look at the Born-Oppenheimer argument in this historical context we see that it can be understood as a plausible rationalization for already well-established classical procedures.^{25,30}

The quantum theory of atoms, which can serve as a prototype for the theory of molecular stationary states,¹⁰ is well documented³¹ and need not be described in any detail here; three points deserve to be mentioned, however. The wave functions for the molecular stationary states must have the appropriate permutation symmetry (boson or fermion statistics) for all the electrons *and* for any groups of identical nuclei. Next, no finite isolated system of particles interacting via electromagnetic forces can distinguish between left- and right-handed perturbations, i.e., one must be able to choose a representation for the stationary states of atoms and molecules that is diagonal with respect to the space inversion (parity) operator. Finally, mechanical models disappeared

from atomic theory when the Bohr theory of the atom gave way to the quantum theory, and atomic physics is now a quantitative science based on the abstract framework of group theory in quantum mechanics.^{31,32}

It is characteristic of the molecular structure description that identical nuclei can be dynamically inequivalent; the definition of a molecular shape involves the selection of one or more reference configurations of the nuclei, for example, an "equilibrium configuration" for the nuclei can often be chosen unambiguously from chemical information or by specification of a potential energy surface, and this *rigid* arrangement of the nuclei defines the stereochemistry of the molecule. These assumptions can only be embodied in the mathematics as asymptotic approximations since they can be shown to be inconsistent with the general properties of quantum eigenstates.⁹⁻¹⁴ The parity conservation requirement shows dramatically that molecular structure is a consequence of environmental perturbations rather than an intrinsic molecular property, for it implies that an isolated molecule in a stationary state *cannot* exhibit optical activity.³³ One can imagine the following gedanken experiment: we start with a resolved isomer of a small optically active molecule in the gas phase and look at its optical activity; we then do everything possible to eliminate intermolecular interactions and increase the resolution in energy. Eventually this process of isolation may cause the optical activity to disappear abruptly when absorption is still measurable, signaling the observation of transitions between stationary states; this is *not* the familiar classical process of racemization. Alternatively we may find a negative result in this experiment: the inability to observe a stationary state of the smallest optically active molecule would imply that even at the greatest dilution attainable there is still correlation between the individual molecules, and this would indicate something about the scale involved in the distinction between "small" and "large" molecules. A worthwhile experiment on these lines is probably possible now, for one can certainly prepare optically active isomers of small organic molecules (say <10 atoms) involving the isotopes of hydrogen, which cannot be resolved by classical techniques, using enzymatic synthetic procedures,³⁴ and with great effort one could prepare optically active isomers containing only five atoms. Experimental work of this kind seems to be entirely lacking, and it can hardly be surprising that no detailed understanding of this broken symmetry¹⁰ phenomenon exists (but see ref 33).

The emphasis on all of these general symmetries (permutation symmetry, rotational symmetry, parity) is only relevant when the stationary states are individually resolved. In liquids and solids one is always dealing with intrinsically time-dependent quantum states of (atoms) molecules that can be represented as superpositions of the (atomic) molecular eigenstates with time-dependent coefficients; such a superposition in general will exhibit a much lower symmetry than the individual eigenstates. Furthermore we know empirically that the energy separations of adjacent stationary states in molecules containing more than, say, ~ 10 atoms are so small that existing experimental methods cannot fully resolve the individual eigenstates;³⁵ in this situation, which is equivalent to looking at a "small" molecule under *low* resolution, one is again concerned with a time-dependent quantum state for which a molecular structure description may be valid.

These remarks refer to "nonrelativistic" (i.e., Galilean relativistic) eigenstates: the "relativistic" and radiative corrections which cause additional shifts and term splittings may not be resolved in smaller molecules, and some aspects of "molecular structure" might be attributed to superpositions of these sublevels. We know very little about the factors that govern the characteristic spectral patterns of molecules. Let me give an example: it is perfectly conceivable that *nonadiabatic, nonrelativistic* calculations on, say, NH_3 (or any other small

"inversion" system) would predict a pattern of degenerate states in place of the "inversion splitting" that dominates the electronic spectrum, and one would have to look to the Lamb shift and vacuum polarization effects for potential mechanisms to lift the degeneracies. The real origin of the observed splittings is an important question which could and should soon be settled by nonadiabatic computations. The reader may object that degeneracies are connected with symmetry operators, and that the symmetries of the Hamiltonian of any molecule are only those connected with the improper Galilean group and the appropriate permutation groups.¹⁰ This is true as far as *known, identifiable* constants of the motion are concerned; however, similar remarks apply in classical mechanics, and we now know that general nonseparable dynamical systems generate some trajectories that are confined to f -dimensional manifolds of the $2f$ -dimensional phase space (assuming that the system has f degrees of freedom), i.e., there are orbits that behave as though f constants of the motion existed. Such periodic orbits provide the usual basis for quantization in semiclassical mechanics, and arguably similar behavior can occur in quantum dynamics.

The idea that a structural interpretation of a molecular eigenstate is *meaningless* has been generally ignored. It is absolutely characteristic of quantum phenomena that the refinement of a molecular structure can only be taken so far by improving the resolution in energy, since the appearance of the individual molecular eigenstates causes, so to speak, the abrupt disappearance of the "structure" into thin air. Chemical spectroscopists still analyze their experiments using ideas derived from the historic old quantum theory; in my view the traditional theory of molecular models, which can be formally characterized as a quasi-classical (asymptotic) approximation, does not adequately reflect the quantum nature of some of the experimental measurements that are now possible. The molecular models contain disposable parameters that describe the molecular structure to which the observations are to be fitted, and they continue to survive because one can always add extra terms to account for anomalies; thus there can apparently be good agreement between "theory" and "experiment". Moreover, the quest for even more accurate determinations of potential energy surfaces and molecular structures for small molecules is a prime motivation for chemical spectroscopy and molecular beam experiments.³⁶ These familiar asymptotic procedures based on potential energy surfaces may give accurate *numerical* results, but need not provide a valid basis for the interpretation of the physics (chemistry) of a high-resolution experiment because quasi-classical conditions may not obtain; it also appears to be true that in favorable cases transition frequencies can now be measured to a greater accuracy than the *theoretical* accuracy of a Born-Oppenheimer type treatment.¹⁴ The quantum interpretation of molecular stationary states suggests that the parameters of this conventional theory (bond lengths, spectroscopic constants, etc.) have no place in a general quantum mechanical description of those experiments that can reasonably be associated with the eigenstates of isolated molecules, since the physics (chemistry) must be derived from the properties of the eigenstates and *not* their asymptotic approximations. The belief in molecular structure as a universal attribute in molecular science is therefore a prejudice that is not securely founded in quantum theory.

Concluding Remarks

It has to be emphasized that as yet, in contrast to the recent dramatic improvement of the experimental situation,²⁹ we have very little detailed theoretical information about the properties of molecular stationary states as compared with atomic theory, although some general statements can be derived from group theory. The theoretical study (analytical and computational)

of the stationary states of the molecular Hamiltonian is as challenging a problem as anything to be found in the currently active areas of research in quantum-mechanical theory; there can be little doubt that the quantum interpretation appropriate to these experiments on "small" molecules will be much more abstract than has been the case hitherto in chemistry. Although the abstract and counterintuitive nature of quantum description as compared with the models of classical theory was recognized soon after the discovery of quantum mechanics,^{19,22} even the most physical aspects of the molecular sciences have remained relatively immune from the potentially far-reaching modifications required by the quantum theory of stationary states. One reason for this has been stated succinctly by Dyson:³⁷ "The reason why new concepts in any branch of science are hard to grasp is always the same; contemporary scientists try to picture the new concept in terms of ideas which existed before." In the case at hand the previously existing dominant concept was molecular structure which had already been incorporated in the old quantum theory with spectacular success.³⁸ Naturally I recognize that since much of the quantum theory appropriate here has yet to be worked out, experimentalists will regard this critique of molecular theory as being of little direct help to them; equally one hopes that these experiments are still performed to investigate primarily the properties of matter, which need not be the same as "the determination of very precise molecular structures", and without some agreement about the theoretical principles that will be useful in the last quarter of the 20th century, this area of physical chemistry may well find itself up a blind alley as its traditional molecular models become less and less relevant to contemporary experiments.

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References and Notes

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