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Quantum Theory and Chemistry: Two Propositions

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QUANTUM THEORY AND CHEMISTRY: TWO PROPOSITIONS

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A necessary condition for the applicability of quantum mechanics to chemistry is that an assemblage of nuclei and electrons can never be partitioned to yield specific molecules; interactions among the components generally also lead to a subtle form of irreversibility.

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1. Introduction

The conventional wisdom is that in order to get something out of the Schrödinger equation (such as molecules) something must be put in. The price for molecules is the adiabatic approximation in some form; it is a price cheerfully paid by quantum chemists in order to move on to problems of interest. Woolley [1, 2], among others, has questioned both the invocation and justification of the adiabatic approximation, since it is an asymptotic theory. Moreover, there are concerns as to losses incurred when thinking in terms of specific molecular shape and structure. Very recently, these problems have been subjected to intense scrutiny [3]. It is the purpose of this communication to establish two important points. The first is the proposition that the nonrelativistic Schrödinger equation, where the Hamiltonian operator is associated with an assemblage of nuclei and electrons, can _never_ be arranged to yield specific molecules in the chemists' sense. That is, no amount of manipulation or partitioning will yield the "benzene" molecule, for example, from a Hamiltonian operator associated with an assemblage of 6 carbon nuclei, 6 hydrogen nuclei and 42 electrons. Moreover, it will be argued that this result is a necessary condition if the Schrödinger equation has relevancy to chemistry, as is commonly assumed.

The second proposition is a consequence of both the first proposition and the fact that the Schrödinger equation behaves in a peculiar fashion with respect to interactions. The proposition is that once a system is in a particular state with regard to interactions among its components (the assemblage of nuclei and electrons), it cannot

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spontaneously eliminate any of those interactions. This, in turn, leads to a subtle form of irreversibility.

2. Proposition 1

The proposition that the Schrödinger equation must be ambiguous with respect to any specific molecular species (for it to be applicable to chemistry) results from a superselection rule. Suppose that the Hilbert space associated with a nonrelativistic Hamiltonian (which in turn describes an assemblage of interacting nuclei and electrons) could be decomposed into orthogonal subspaces, where each subspace could be associated with a specific molecular species. We claim that it would then be impossible to change one molecular species into another molecular species even though they share the same Hamiltonian. This follows from the fact that there can be no matrix elements (thus no spontaneous transitions) connecting two orthogonal subspaces, each of which is assumed to be associated with a physical entity [4]. Cubane (empirical formula C_8H_8) could never rearrange by a shift in electron density to yield cyclooctatetraene (empirical formula C_8H_8), for example. Similarly, tautomeric species could exist as distinct entities with infinite lifetimes as another consequence. Therefore, we conclude that the Hilbert space associated with a particular Hamiltonian cannot be decomposed into a direct sum of orthogonal subspaces that can be associated with specific molecular entities $1, \ldots, n$. That is, the Hilbert space

$$H \neq H_1 \oplus H_2 \oplus \ldots \oplus H_n .$$

This result, as noted above, is indeed fortunate, because if such direct associations between molecular entities and subspaces were possible, then

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quantum theory could not address conversions (i.e., reactions) since they would be forbidden by a superselection rule. This reasoning is in accord with previous arguments [5]. Quantum theory, however, is applicable but the price is that, at the most fundamental level, isomers cannot exist as totally unique and distinct entities.

3. Proposition 2

Consider two noninteracting isolated systems, I and II, each an assemblage of nuclei and electrons. Their respective Hamiltonians are H_I and H_{II}. Since the systems do not interact, the combined Hamiltonian is given by

$$H_{total,0} = H_I + H_{II} .$$

On the other hand, the Hamiltonian for an assemblage comprised of the same number of electrons as contained in I and II, as well as equal numbers and types of nuclei as those associated with I and II, will be given by

$$H_{total,1} = H_I + H_{II} + H_{I,II} .$$

$H_{I,II}$ are the appropriate additional interactions between electrons among themselves, nuclei among themselves, and electrons with nuclei. The labels I and II are completely artificial with respect to $H_{total,1}$, since electrons not only are identical and belong to the full assemblage but also cannot be constrained to subassemblages. Thus, though $H_{total,0}$ and $H_{total,1}$ superficially can be made to resemble each other, they are, in fact, describing entirely different and distinct physical systems. Furthermore, there is no overlap between the two since the physical system

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described by $H_{total,1}$ can only achieve a physical state described by $H_{total,0}$ through a unique limit process. There are no transition elements coupling the two systems.

If it is assumed that there exists a Hilbert space, H_G, which is associated with both $H_{total,0}$ and $H_{total,1}$, then the association must be that $H_{total,0}$ and $H_{total,1}$ are associated with _orthogonal_ subspaces of H_G, i.e.,

$$H_G = H_{total,0} \oplus H_{total,1} \oplus \cdots$$

As an example, consider the possible physical systems which can be realized for the set of an electron and a proton. They may not "see" each other at all, or they may interact. These two possibilities exhaust the physical systems that may be realized with a proton and an electron. Thus,

$$H_G = H_{total,0} \oplus H_{total,1}$$

exactly. Here also,

$$H_{total,0} = H_e \oplus H_p ,$$

since the Hilbert space associated with systems whose components are completely noninteracting can be represented as the direct product of the Hilbert spaces associated with the respective Hamiltonians for the components. $H_{total,1}$ is the Hilbert space associated with the Hamiltonian that describes the system, wherein the proton and electron interact. The superselection rule is operative; there is no vector of H_G able to span both subspaces, $H_{total,0}$ and $H_{total,1}$, and be associated with a physical state. As one consequence, the momentum eigenfunctions of the free electron and proton (noninteracting) cannot be used to describe the

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hydrogen atom, because the set of vectors belonging to $H_{total,0}$ cannot be in one-to-one correspondence with those which belong to $H_{total,1}$. This corroborates the observation made by Weyl [6] some time ago that the H atom represented a phenomenon that could not be described with the "language" of a free electron and proton. By extension, no combination of the product of eigenvectors associated with two noninteracting assemblages of (proton + electron) can yield an eigenvector associated with an assemblage of (two protons + two electrons). This analysis can be readily extended to any arbitrary assemblage of nuclei and electrons. It is not surprising, from the above considerations, that the specific properties and behavior of sodium chloride, for example, cannot be predicted a priori from those of sodium and chlorine.

Another point is that the very stipulation of an assemblage of nuclei and electrons precludes differentiation between phases (e.g., solid, gaseous), because the phases would have to be assigned different orthogonal subspaces, and no equilibrium among the various phases would be possible for a totally isolated system. Thus, quantum mechanics allows for the experimental fact that a solid is in equilibrium with its gas phase at any temperature. This is only offered as a crude correspondence, for no phase separation appears possible with a finite assemblage of nuclei and electrons.

Independent of the size of the isolated system, it follows as a consequence of the arguments in this section that the subspace associated with a neutral system of interacting nuclei and electrons does not include any totally ionized forms, e.g., an electron totally removed and non-interactive with the rest of the system. Thus, if we picture an assemblage

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contained in a well with moveable but infinitely high walls, the system cannot be ionized, using this level of quantum mechanics, irrespective of how the volume is changed. That is, pressure alone cannot cause ionization, because this would represent a transition to a new orthogonal subspace. It requires an external perturbation to move the system from one orthogonal subspace associated with a physical state to another subspace. This has an interesting consequence. Cessation of the external perturbation traps the system in the new orthogonal subspace, since there are no spontaneous transitions possible between these orthogonal subspaces. Thus a form of irreversibility becomes manifest. All information on the history of a system resides with the perturbations it has been subjected to; therefore, the history of a system cannot be disclosed by examination of its present state. As an example, suppose we took a crystal of anhydrous aluminum chloride and some water, enclosed them in a vessel of arbitrary size, and mixed them. The Hamiltonian for this system (ignoring the vessel except for its imposition of boundary conditions) is comprised of aluminum, chlorine, hydrogen and oxygen nuclei with the appropriate numbers of electrons. This Hamiltonian is perfectly reversible with respect to time but no longer reflects nor contains information about the original state of the two components completely isolated from each other. Furthermore, we would conclude, from the considerations in this paragraph, that there is no way (without the introduction of a very specific and unique external perturbation) that this system could return to original conditions. One consequence is that all chemical reactions exhibit a type of irreversibility that, to our knowledge, has not been explicitly recognized previously.

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4. Conclusion

It was appreciated some time ago that, in quantum theory, the whole can be greater than the combination of its parts [6]. This feature, in fact, permits quantum mechanics to be relevant to chemistry. Molecular entities, which we view as unique and distinct, for example, are but very good constructs belonging to a greater whole. Quantum theory deals with reality at a level subtler than the instantaneously rigid nuclear structures permitted by the adiabatic approximation [7, 8]. Moreover, it has been shown that true uniqueness is impossible for chemical entities that share the same Hamiltonian [5]. Uniqueness is introduced upon making certain approximations as to suitable self-consistent (or variational) wavefunctions. Thus, treating isomers as truly distinct and unique degrades information about the system.

Furthermore, a pure state cannot be assigned to a particular structure. The designation of a pure state must be reserved for the whole system. Benzene, for example, is an isomeric structure in a system composed of 6 carbon and 6 hydrogen nuclei along with 42 electrons. The eigenfunctions of the Hamiltonian associated with this assemblage of nuclei and electrons are the pure states; in this context, benzene cannot have "pure" states. Moreover, the introduction of specific interactions introduces a subtle form of irreversibility whereby a system's past history is eradicated by the new interactions; these interactions also destroy any spontaneous pathway to that past that might have existed. This result implies that the kinematical aspects of a system cannot be rigorously separated from its dynamical behavior. This result has been well known in relativistic treatments [9, 10], but, now, on a

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nonrelativistic level, it emphasizes that some complex skeins of inter-acting components can never be fully disentangled or reassembled, unless unique (and conceivably impossible) external perturbations are applied. It appears that the blurring feature inherent in quantum theory, which ultimately affects all structures, makes the theory relevant to physical reality while introducing a facet of irreversibility in a fundamental fashion.

Acknowledgment

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