Role of the Born-Oppenheimer approximation in the vibrational excitation of molecules by electrons

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The role of the Born-Oppenheimer approximation in the resonant vibrational excitation of diatomic molecules by electrons is reexamined in the light of a recent paper on the hybrid theory and calculation of $e + N_2$ scattering by Chandra and Temkin. It is pointed out that it is not necessary to resort to a nonadiabatic vibrational close-coupling expansion to reproduce the substructure seen in the resonant vibrational excitation cross section of N_2 by electrons. Finally, comment is made on the reasons for the slow convergence of the vibrational close-coupling treatment from a compound-state point of view of the scattering process.

The purpose of this paper is to clarify the role of the Born-Oppenheimer (BO) approximation in the resonant vibrational excitation of electrons to diatomic molecules. The essential features of these scattering processes have been discussed many times in the literature.[1-7] The reason for this comment stems from a recent paper on the hybrid theory and calculation of $e + N_2$ scattering by Chandra and Temkin[8] and some discussions between Temkin, Herzenberg, and the author.

The "hybrid" theory developed by Chandra and Temkin seems to imply that a proper description of resonant vibrational excitation lies outside the framework of an adiabatic picture and that non-adiabatic coupling of electronic and nuclear motion is essential to describe the substructure seen in the vibrational cross section. The term "non-adiabatic" here means the use of a nonseparable wave function in the electronic-vibrational coordinates of the scattering electron. The basis of their argument is that when an electron spends a significant amount of time in the vicinity of a molecule (resonant process) one must abandon the adiabatic nuclei theory of electron-molecule scattering and resort to vibrational close coupling to reproduce the detailed structure seen in the cross section. However, if one carries this argument one step further one is faced with the difficulty of explaining why the BO approximation works for bound states where an electron spends an infinite amount of time near the nuclei.

The resolution of this problem lies in the very definition of the adiabatic nuclei theory. The standard procedure is to perform an electronic scattering calculation for each internuclear distance and then to project the fixed-nuclei electronic amplitude onto the initial and final vibrational states of the target. Implicit in this procedure is the assumption that the nuclei do not have time to move during the course of the collision. This is a much more restrictive condition than the BO approximation which allows the nuclei to adjust, albeit adiabatically in the field of the electrons. The usual adiabatic-nuclei theory will fail in a resonant scattering process because the nuclei want to move in the field of $(N+1)$, not N electrons. The failure of the adiabatic-nuclei theory does not necessarily imply that one cannot separate electronic and vibrational degrees of freedom as is done in the BO approximation. Clearly, the nuclei must adjust to the change in force due to the presence of the incoming electron. However, this adjustment *can be adiabatic* if the electrons energy is larger than the vibrational energy of the nuclei in the new potential well. One can identify two extreme limits, one when the electron passes quickly and one when the electron passes slowly compared to a vibrational period. In the former case the nuclei see the potential due to N electrons and the usual adiabatic-nuclei theory should yield correct results. In the latter case the appropriate description is in terms of the electronic state of the compound $(N+1)$ electron system. This state can by its very definition absorb a significant fraction of the change in force on the nuclei due to the presence of the incident electron. In each instance one must associate a vibrational wave function with the electronic state. The proper vibrational wave function in the case of resonant scattering is that of the compound electronic state. This vibrational wave function reflects the new environment of the two nuclei and the finite lifetime of the compound state. The potential in this new Schrödinger equation is complex, nonlocal and energy dependent. Thus the vibrational levels acquire a lifetime, and a full treatment requires consideration of the magnitude and dependence on internuclear distance of this quantity. However, the gross features of the scattering can be explained using the BO electronic state and associated vibrational levels of the compound system.

The qualitative discussion just given can be put on a much-more-rigorous mathematical basis using the Bloch L-operator formalism[9] and the R-matrix method.[10] The essential difference between the compound state theories and the "hybrid" theory of Chandra and Temkin lies in the choice of zeroth-order wave functions used to expand the wave function in the Schrödinger equation for the scattering process. The "hybrid" theory uses an expansion in terms of the electronic-vibrational states of the target while the compound state model focuses on the "resonant" electronic state of the $(N+1)$ electron system. Both basis sets are capable of yielding the exact solution if carried to completeness. However, for practical calculations the expansion must be truncated and the more rapidly convergent theory is to be preferred. In the case of a resonant process where the electron spends a great deal of time near the nuclei, the compound state approach seems the more physical as well as the one which would be more rapidly convergent. If one applies the R-matrix method to solve the electronic scattering problem and makes the simplifying assumption that only one electronic R-matrix state is important one gets equations identical to those in Ref. 2. Moreover, these equations can now be solved using the *ab initio* techniques developed by the author and already applied to $e+H_2$ and $e+F_2$ scattering.[10] If more than one electronic R-matrix state is important in the scattering process it is still possible to solve the electronic problem first as a function of the internuclear distance and to treat the residual interaction as a perturbation. Since we are dealing with the wave functions of the $(N+1)$ electron system in the internal region only we can examine the potential curves for avoided crossings to ascertain the validity of the BO separation on the compound state. Although it would be difficult to treat the coupling of all of these curves exactly approximate treatments are not beyond the capability of present day computational methods.

In contrast to the compound state theories which account for the electron-molecule interaction using bound-state-like methods the "hybrid" theory expands the wave function in the electronic-vibrational states of the target and treats the electron-molecule interaction through the solution of a set of coupled integro-differential equations. It is intrinsically a nonadiabatic theory in that it explicitly couples electronic and vibrational motion. The set of coupled integro-differential equations must be large enough to account for all open channels as well as those closed channels needed to describe the change in electronic configuration due to the incident electrons. For a resonant

process this can be quite large. In practice the effect of the closed channels has been treated using a polarization potential with adjustable parameters used to "tune" the resonance. In an *ab initio* theory an optical potential could be used to achieve the same effect. In spite of this the number of integro-differential equations which need to be solved to obtain convergence is often quite large. This is due mainly to the large number of angular momentum states needed to expand the electron-molecule interaction, although the presence of even a moderate number of vibrational levels can render the problem intractable. From the point of view of *ab initio* calculations of electron-molecule collision cross sections there is little doubt in this authors mind that the compound state method will be capable of producing quantitative results for resonant scattering processes with a minimum of computational effort.

The physical picture which emerges from the compound state model depends crucially on two factors; the Franck-Condon overlaps between the vibrational levels of the compound and target electronic states and the "energies" of the vibrational levels of the compound state. If the resonant electronic state is displaced from the target state or is of a different shape, one can expect significant vibrational excitation only when the Franck-Condon factors between the vibrational levels of the two wells are substantial. Under these conditions one would expect to see structure in the vibrational cross-section characteristic of the vibrational levels of the compound electronic state. The separation of the peaks should reflect the vibrational spacings in the resonant state. When the resonant state is not shifted and of the same shape as the target electronic state vibrational excitation is usually small and little structure appears in the cross section. However, it should be pointed out, that under certain circumstances the compound-state vibrational wave function can have a significant overlap with one of the final vibrational levels of the target molecule. If the overlap between the initial vibrational level is not too small, electronic factors may cause significant vibrational excitation which is sharply peaked at threshold and then dies off rapidly.

In the vibrational excitation of N_2, the compound state is flatter and shifted to the right of the N_2 curve.[11] This is not surprising since N_2 is a closed-shell molecule and the added electron goes into a Π_g antibonding orbital. Birtwistle and Herzenberg[12] have pointed out that the systematic variation of the energies and spacings of the vibrational excitation cross section in N_2 with final vibrational state cannot be accounted for using the simple Franck-Condon picture described

above. In particular the variation of the lifetime of the compound state with internuclear distance must be properly treated. This can still be accomplished with the confines of the BO approximation and quite satisfactory agreement with experiment is then obtained. Thus it is not necessary to resort to a full nonadiabatic vibrational close-coupling treatment to reproduce the observed cross sections in N_2.

The most disturbing features of the hybrid theory are the lack of rapid convergence in vibrational and angular-momentum quantum numbers. The latter is particularly disturbing since Birtwistle and Herzenberg[12] were able to treat the electron as a pure d wave. The reason for the slow convergence can be traced directly to the use of the vibrational levels of N_2 as a basis for the vibrational close coupling and a single center expansion of the electron-molecule interaction potential. Since the N_2^- state is shifted to the right and flatter than the N_2 potential curve, a fair number of vibrational levels of N_2 are needed to expand the N_2^- vibrational wave function. The *converged* eigenphases for the adiabatic-nuclei calculation reveal that the $l = 2$ eigenphase is

about two orders of magnitude larger than any of the other elements. Since the vibrational excitation cross section only depends on the *asymptotic* form of the scattered wave in the electronic coordinate, it is not surprising that only the $l = 2$ component need to be considered. Although these statements refer to the fixed nuclei eigenphases, we are convinced that Chandra and Temkin would find similar results in their hybrid-theory calculation.

In conclusion then it is not necessary to resort to vibrational close coupling to reproduce the structure seen in resonant vibrational excitation. Calculations performed wholly within the confines of the BO approximation provide for a clear understanding of the physical features seen in the experimental cross section for $e + N_2$ vibrational excitation.

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