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Validity of the adiabatic nuclei theory for vibrational excitation of molecules by electron impact: The e-H_2 system

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The widely used adiabatic nuclei approximation of electron-molecule scattering is shown to introduce serious errors into near-threshold e-H_2 vibrational-excitation cross sections. An alternative method, in which only the rotational motion of the nuclei is treated adiabatically, provides a computationally tractable procedure that yields highly accurate differential and integral cross sections.

Theoretical methods for calculating cross sections for electron-impact excitation of rotational and vibrational states of molecules at near-threshold energies have recently come under increasing scrutiny.[1-3] Impetus for this activity is provided partly by observations of near-threshold "spikes" in vibrational excitation cross sections for a variety of systems.[4] Further stimulus for the theoretical study of these excitations comes from applied and experimental needs. For example, published inelastic cross sections measured in different types of experiments exhibit serious discrepancies,[5] which accurate theoretical studies might resolve. Indirect schemes for determining momentum-transfer cross sections require as input accurate cross sections for selected rovibrational scattering processes,[6] which theory could provide.

For many years the method of choice for computing near-threshold electron-molecule cross sections has been the adiabatic nuclei (AN) theory.[1,7-11] Based on the assumption that the quantal motion of the scattering electron is adiabatic with respect to the nuclear motion,[12] this formulation is conceptually and computationally much simpler than one in which the dynamical interaction is incorporated exactly.[13,14] Indeed, the computational demands of an exact theory are so great that, to date, it has been applied only to e-H_2 collisions.[1]

The validity of adiabatic approximations is an important concern in fields far removed from electron-molecule collision theory. Such approximations underlie the theoretical analysis of a wide variety of physical problems, such as molecular structure (the Born-Oppenheimer approximation) and energy bands in solids.

The AN approximation of electron-molecule scattering is expected to break down as the scattering energy is decreased towards the threshold for a particular excitation.[12,15] Physical reasons for this failure[16] and rough qualitative criteria for its occurrence[9] have been discussed. The primary goal of our reseach is to investigate *quantitatively* the severity and extent of this breakdown. We recently reported our findings for rotational excitation;[3] the present paper concerns vibrational excitation.

At issue is how to incorporate into the theory the influence of the nuclear dynamics on the scattering electron. In a rigorous quantum-mechanical formulation, this effect is inherent in the Schrödinger equation.[1,16] *Rigorously, this equation is not separable*, and the nuclear motion is inextricably coupled to that of the projectile. The computational procedure resulting from exact inclusion of this dynamical interaction is the laboratory-frame close-coupling (LFCC) method.[13,14]

For systems more complicated than e-H_2, the set of coupled LFCC scattering equations that must be solved numerically is intractably large. This difficulty arises from two facts:[16] (1) the lack of spherical symmetry that characterizes the electron-molecule interaction causes substantial partial-wave coupling; and (2) an enormous number of nuclear target states are coupled by the nuclear Hamiltonian.

The introduction of the AN formulation[7-10] enabled progress to be made in the computational study of nuclear excitations. The essential approximation of this theory is the replacement of the system wave function by the product of a nuclear target function and an *adiabatic* electron scattering function that depends *parametrically* on the slowly varying nuclear coordinates. The scattering equations for the adiabatic function are much simpler than the LFCC equations, although they may still manifest considerable partial-wave coupling. Once the scattering matrix is extracted numerically from the asymptotic scattering function, approximate inelastic cross sections are easily calculated as matrix elements (in the space of the nuclear coordinates) of this matrix.

To probe the validity of this theory, we compare AN cross sections to corresponding LFCC values. To ensure that observed differences reflect the validity of the adiabatic approximation—rather than, say, numerical inconsistencies—both calculations are based on the same *ab initio* model interaction potential and are carried out to identical criteria of numerical accuracy.[3] (Cross sections are converged in the parameters of the computations[17] to better than 1%.)

The interaction potential[16] consists of static, exchange, and polarization contributions. Each term is evaluated at internuclear separations from 0.5 to 3.0 a_0. The static term is calculated from newly determined near-Hartree-Fock $X\,^1\Sigma_g^+$ H_2 wave functions.[3] Exchange effects are approximated by a local model exchange potential based on free-electron-gas theory.[18] Rigid-rotator studies have demonstrated the ability of this model to accurately mimic the exact, nonlocal exchange interaction for a wide variety of systems. Finally, polarization effects are incorporated via an *ab initio* model potential in which a nonpenetrating approximation is used to approximate short-range bound-free correlation effects.[19] Rigid-rotator cross sections calculated with this polarization potential agree very well with those from accurate, optical potential studies.[20]

This interaction potential was used in our earlier study of rotational excitation of H_2 in the rigid-rotator approximation.[3] We found the breakdown of the AN approximation for rotation to be more severe than anticipated at energies equal to a few times threshold ($E_{th} = 44$ meV for the transition from initial state $j_0 = 0$ to final state $j = 2$).

Because of the magnitude of the vibrational Hamiltonian (compared to the rotational Hamiltonian), the breakdown of the AN approximation for vibration[10] is expected to be more serious than that of its counterpart for rotation.[1-3] To illustrate this breakdown, we shall consider the representative excitations $(v_0 = 0, j_0 = 0) \rightarrow (v = 1, j = 0, 2)$. The threshold energies are $E_{th} = 0.52$ and 0.56 eV for the $(0,0) \rightarrow (1,0)$ and $(0,0) \rightarrow (1,2)$ excitations, respectively.

Using the LFCC integrated cross sections as a standard, we have determined the percentage error in their AN counterparts. These percentage differences, which are presented in Fig. 1, show that the AN approximation introduces unexpectedly large errors into cross sections for near-threshold vibrational excitation. Even at energies equal to several times E_{th}, the AN and LFCC cross sections differ significantly.

In Fig. 2, we show AN and LFCC differential cross sections for the $(0,0) \rightarrow (1,0)$ excitation at 0.7 eV. This result illustrates the inability of the AN approximation to yield *qualitatively* correct dependence on scattering angle, let alone quantitative validity. With increasing energy, the AN results improve, as they should.

We carried out extensive internal consistency and convergence checks to ensure the validity of these massive differences. For example, two independent packages of computer programs are used for the AN and LFCC calculations. By artificially equating the channel energies in the LFCC code, we could make it "mimic" an AN calculation. The resulting "degenerate LFCC" cross sections agreed with those from the AN computations to better than 1% over the energy range from threshold to 15.0 eV.

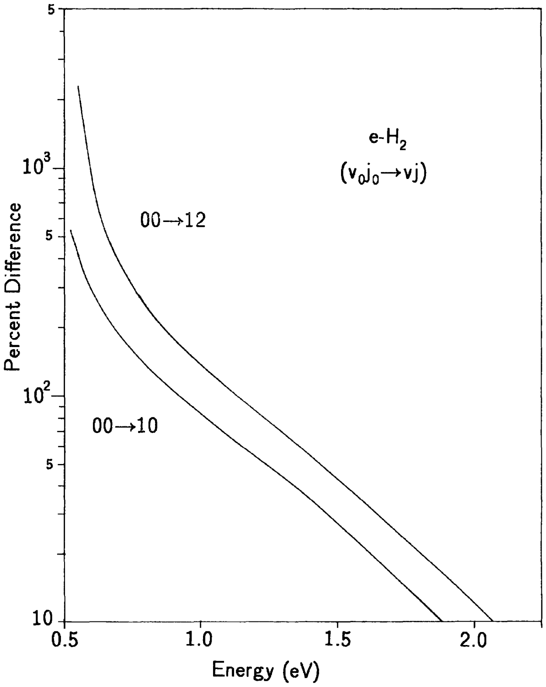

FIG. 1. Percentage deviation of AN e-H_2 integrated cross sections for the $(0,0) \rightarrow (1,0)$ and $(0,0) \rightarrow (1,2)$ excitations from LFCC values.

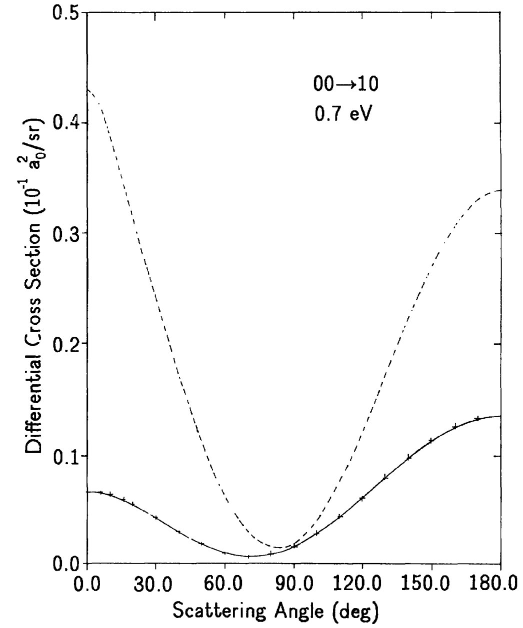

FIG. 2. Differential cross sections for the $(0,0) \rightarrow (1,0)$ excitation of H_2 at 0.7 eV as determined from LFCC (solid curve), AN (dashed curve), and BFVCC (pluses) calculations.

The AN approximation is manifestly unsatisfactory for low-energy vibrational excitation—at least for H_2 targets. Chandra and Temkin[21]—in a study of e-N_2 scattering—proposed a "hybrid theory" that incorporates the effect of the vibrational Hamiltonian more accurately than does the AN method. In this theory, only the *rotational* motion is treated adiabatically; the vibrational motion is fully coupled to that of the scattering electron, and the target vibrational states are properly nondegenerate. By analogy with LFCC theory, we shall here refer to this method as body-frame vibrational close coupling (BFVCC).

The BFVCC theory requires solving far fewer coupled equations than does the LFCC method and gives results in excellent agreement with LFCC cross sections. For example, differential and integrated BFVCC cross sections for the $(0,0) \rightarrow (1,0)$ excitation are shown in Fig. 2 and Table I, respectively. Nonetheless, this formulation makes considerable computational demands and will probably be inapplicable to targets with a highly complex vibrational state structure (e.g., SF_6).

TABLE I. Integrated e-H_2 rovibrational cross sections (a_0^2).

	$(0,0) \rightarrow (1,0)$		
E (eV)	AN[a]	LFCC	BFVCC[b]
0.700	0.1540	0.0536	0.0539
1.500	0.5852	0.4572	0.4612
3.000	0.7531	0.7812	0.7806
4.500	0.5824	0.6186	0.6177

[a] AN results include the wave number ratio $k_{vj}/k_{v_0j_0}$. See Ref. 9.

[b] BFVCC results were calculated using the SANR theory. See Ref. 3.

The present study of e-H_2 collisions has quantified the inaccuracy of the AN approximation for near-threshold vibrational excitation. The BFVCC theory represents an improvement over this approximation, but further research into alternate collision theories for low-energy vibrational excitation is imperative. In addition, we are currently studying electron scattering from N_2 and CO to determine if the breakdown of the AN approximation for vibration is as serious for other targets as it is for H_2.

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