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Calculating vibrational-excitation cross sections off the energy shell: A first-order adiabatic theory

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We report the implementation of a first-order nondegenerate adiabatic theory for vibrational excitation of H_2 by electrons with energies from threshold to 10 eV. Solution of the scattering equations in this method is far simpler than in a full close-coupling calculation because the method is based on an adiabatic factorization of the electron-molecule scattering ket. The method, however, yields low-energy cross sections that are far more accurate than those of traditional adiabatic-nuclei approximations because its transition matrix is calculated off the energy-momentum shell.

Vibrational excitation of molecules by low-energy electrons plays a seminal role in such applications as laser design, discharge switches, and the electrical properties of gases. Recent advances in experimental techniques —increased precision of very-low-energy crossed-beam[1] and time-of-flight measurements,[2] and increased sophistication in the Boltzmann analysis of transport data[3] for electron swarms—have focused attention on the critical near-threshold region. At these energies serious discrepancies exist between the results of crossed-beam and swarm experiments and between recent theoretical cross sections and those unfolded from transport analysis.[4] Interest in near-threshold scattering was stimulated by the discovery[5] of anomalous structures—near-threshold spikes—in vibrational-excitation cross sections for electron scattering from several polar and nonpolar molecules.[6] But theoretical methods for calculation of near-threshold inelastic cross sections are bedeviled by difficulties in both the determination of the interaction potential and the numerical solution of the Schrödinger equation.[6,7]

Particularly troublesome is the strong coupling that characterizes the electron-molecule problem: coupling of a large number of angular-momentum eigenstates of the projectile by the nonspherical electron-molecule interaction potential, and of a large number of target states by the Hamiltonian of nuclear motion, $\mathcal{H}^{(n)}$. One can eliminate the latter coupling by imposing approximate separability (in the Born-Oppenheimer sense[8]) on the electron-molecule continuum state vector, writing it as the tensor product of a nuclear-motion ket and an adiabatic projectile ket. The resulting scattering matrix is first order in $\mathcal{H}^{(n)}$. One can further simplify the scattering problem by assuming that the target states in the entrance and exit channels are degenerate. This additional assumption yields the second-order scattering matrix of the adiabatic-nuclei (AN) approximation.

This strategy for developing a second-order approximation to an inelastic-scattering matrix was first suggested (in the context of nucleon-nucleon scattering) by Chase.[9] Its subsequent application to rovibrational electron-molecule scattering by Hara[10] and Temkin and coworkers[10,11] made possible the study of rotational and vibrational excitation of such diverse molecules as H_2, HF, CH_4, and CO_2.[6,7,12]

For several years, we have been exploring the accuracy of AN approximations and the viability of alternative scattering theories for low-energy rovibrational excitation. A prior study on low-energy e-H_2 scattering[13] showed that the AN approximation for rotation (ANR) introduces errors in rotational-excitation cross sections as large as 30% near threshold. This breakdown of the ANR approximation has recently been confirmed in a cross-beam experiment.[14] A subsequent study[15] showed that far larger errors befall the AN approximation for vibration (ANV), which when applied to excitation of the first vibrational manifold of H_2 introduces errors of hundreds of percent at near-threshold energies.

These studies indicated that a major factor in the breakdown of AN approximations is the (second-order) assumption of target-state degeneracy. In particular, accurate calculation of low-energy vibrational-excitation cross sections apparently requires treating the target states in the entrance and exit channels as nondegenerate. One way to correctly incorporate the target-state energies in the asymptotic states—while still preserving the simplifications that ensue from adiabatic factorization of the state vector—is to calculate the inelastic transition matrix off the energy-momentum shell. This is the essential idea of the first-order nondegenerate adiabatic (FONDA) method of this Rapid Communication.

Shugard and Hazi[8] first proposed using an off-shell theory in electron-molecule scattering, and this idea has been applied (in a formalism based on the integral equation for the transition matrix) to rotational excitation in the rigid-rotator approximation by Ficocelli Varraccio and Lamanna.[16] The FONDA implementation was designed to maximize computational efficiency and extensibility to complex electron-molecule systems. To this end, the formalism is based on the radial scattering functions of conventional body-frame fixed-nuclei (BF-FN) theory—functions whose physical and numerical properties have been exhaustively explored during the past two decades.[6,7] The FONDA prescription thus permits use of standard computer programs for calculation of these radial functions, evaluation of the required coupling coefficients, and determination of differential and integrated cross sections from the scattering matrix.

In a recent paper,[17] the FONDA transition matrix for rotational excitation (in the rigid-rotator approximation) was derived and evaluated for pure rotational excitation of H_2. The resulting cross sections were accurate to better than 5% even within 3 meV of threshold and to better than 1% at energies above about twice threshold. The marked improvement of the FONDA cross sections over those of ANR theory illustrated the importance of correctly treating the entrance- and exit-channel energies for rotational excitation. But the breakdown of the AN approximation for vibration is far more severe than that of its rotational counterpart,[15] so implementation and evaluation of the FONDA prescription for vibrational excitation is critical. We report here the results of this extension.

The essential result of the FONDA theory is a first-order approximation to the laboratory-frame rovibrational transition matrix in the coupled angular momentum representation.[18] In this formulation, asymptotic channels are labeled by quantum numbers for the vibrational (v) and rotational (j) states of the target, the orbital angular momentum of the projectile (l), the total angular momentum (J), and its projection on the space-fixed z axis (M). The total energy in each channel is the sum of the kinetic energy of the projectile, $k_{vj}^2/2$, and that of the target

$$\epsilon_{vj} = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + B_v j(j+1) - D_e j^2(j+1)^2 , \tag{1}$$

where ω_e, x_e, B_v, and D_e are molecular constants.[19] The FONDA reactance matrix $\mathcal{K}^J_{vjl,v_0j_0l_0}$ for the excitation $v_0j_0 \rightarrow vj$ is written in terms of integrals involving the BF-FN radial functions for the entrance channel $w^{\Lambda}_{l'l_0}(r;k_0,R)$. These functions, which are labeled by the projection Λ of the electron's orbital angular momentum on the internuclear axis, are evaluated at internuclear separation R and body energy $E_b = k_0^2/2$. The FONDA integrals also include the Legendre projections $v_\lambda(r,R)$ of the electron-molecule interaction potential and a Ricatti-Bessel function (free wave) for the exit channel, $\hat{j}_l(k_{vj}r)$. With these integrals,

$$I^{\Lambda}_{l',\lambda}(l,l_0;k_{vj},R) = \int_0^\infty \hat{j}_l(k_{vj}r)v_\lambda(r,R)w^{\Lambda}_{l',l_0}(r;k_0,R)dr , \tag{2}$$

and the target vibrational wave functions $\phi_v(R)$, the FONDA reactance matrix is

$$\mathcal{K}^J_{vjl,v_0j_0l_0} = -\frac{2}{(k_{vj}k_0)^{1/2}} \sum_\Lambda A^{Jl}_{j\Lambda} \left[\sum_{l',\lambda} g_\lambda(l,l';\Lambda) \langle \phi_v(R) \,|\, I^{\Lambda}_{l',\lambda}(l,l_0;k_{vj},R) \,|\, \phi_{v_0}(R) \rangle \right] A^{Jl_0}_{j_0\Lambda} . \tag{3}$$

The explicit matrix element in Eq. (3) implies integration over R. The constants $A^{Jl}_{j\Lambda}$ and $g_\lambda(l,l';\Lambda)$ are the matrix elements of the rotational frame transformation[20] and the coupling constants of BF-FN theory,[7] respectively. [The structural similarity of Eq. (3) to the equations of ANV theory[10] explains why the calculation of FONDA cross sections requires little more time than an ANV calculation.] Equation (3) reduces to the frame-transformed ANV reactance matrix[6,7] if one imposes on the FONDA K matrix the further assumption of target-state degeneracy.

The e-H_2 system is sufficiently simple that one can per-

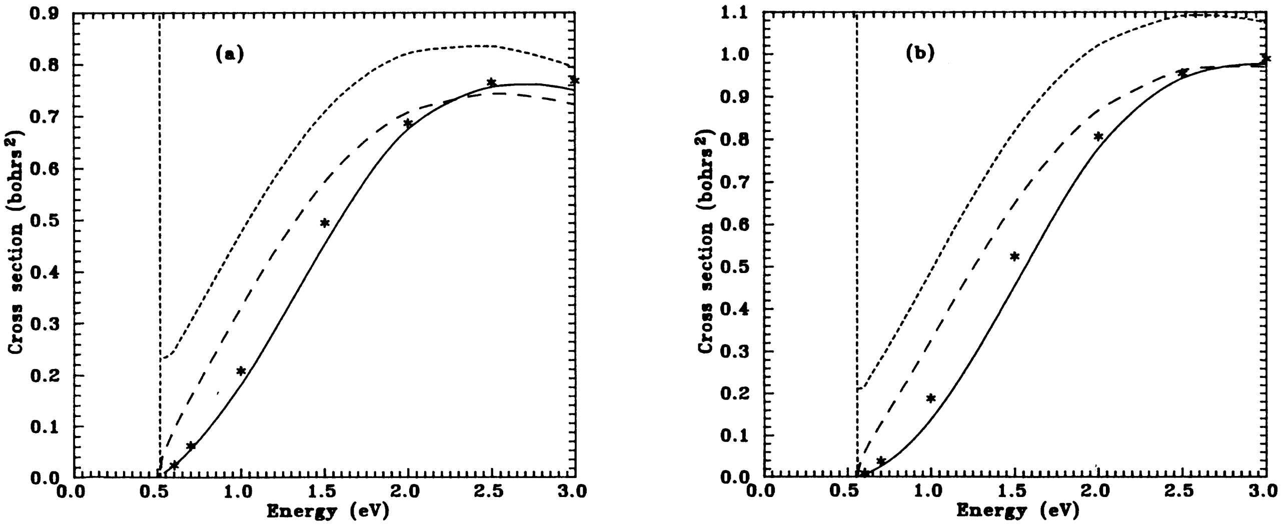

FIG. 1. Integrated cross sections for (a) the pure vibrational excitation 00 → 10, and (b) the rovibrational excitation 00 → 12 of H_2 as calculated using the LFCC (solid curve), ANV (short-dashed curve), and FONDA (stars) methods. The long-dashed curves were obtained by multiplying the ANV cross sections by k_{vj}/k_0. The dotted vertical lines are the thresholds 515.23 meV for excitation to $vj = 10$ and 556.84 meV for $vj = 12$.

TABLE I. Integrated e-H_2 rovibrational cross sections $\sigma(00 \rightarrow vj)$ (a_0^2).

E_0 (eV)	vj	FONDA	LFCC	ANV	ANV (scaled)[a]
0.60	10	0.024	0.024	0.248	0.093
	12	0.008	0.006	0.215	0.058
0.70	10	0.062	0.055	0.304	0.156
	12	0.037	0.026	0.280	0.127
1.00	10	0.208	0.181	0.476	0.331
	12	0.187	0.137	0.488	0.325
3.00	10	0.767	0.748	0.792	0.720
	12	0.989	0.978	1.073	0.968
5.00	10	0.531	0.527	0.524	0.496
	12	0.750	0.745	0.748	0.705
7.00	10	0.350	0.348	0.345	0.332
	12	0.488	0.489	0.484	0.464
10.00	10	0.209	0.210	0.209	0.203
	12	0.277	0.276	0.272	0.264

[a] ANV cross sections times k_{vj}/k_0.

form fully-converged scattering calculations without having to make either the approximation of separability of the scattering ket or that of target-state degeneracy.[15] The resulting laboratory-frame close-coupling (LFCC) cross sections are the "benchmarks" for assessing the AN and FONDA approximations.

In this initial implementation, we have simplified the scattering calculations by approximating the nonlocal exchange potential in the Schrödinger equation for the scattering function by a local, energy-dependent model potential calculated from the probability density of the target.[21] The accuracy of this potential and its optimization for vibrational excitation have been discussed in recent publications.[4,22,23] The other terms in the electron-molecule potential arise from electrostatic and polarization interactions. We calculate the former from near-Hartree-Fock $X\,^1\Sigma_g^+ H_2$ electronic wave functions at 11 internuclear separations using a basis that has been described elsewhere.[14,23] We incorporate polarization effects using a parameter-free variationally-determined potential that includes an approximate treatment of short-range correlation.[22–24] Using the resulting potential, we calculated FONDA, LFCC, and ANV cross sections that are converged to better than 1% in all parameters of the scattering calculation.

In Figs. 1(a) and 1(b), FONDA integrated cross sections for pure vibrational (00→ 10) and rovibrational (00→ 12) excitations of H_2 are compared to LFCC and ANV results. The values in Table I of these cross sections at selected energies show the improvement in accuracy that derives from proper treatment of the target-state energies.

We show two ANV curves in Fig. 1, because the "raw" inelastic cross sections one calculates from an AN transition matrix (e.g., the short-dashed curves) do not go to zero at threshold,[6] $k_{vj} \rightarrow 0$. The standard way out of this predicament is the *ad hoc* procedure[11] of multiplying all AN cross sections by the dimensionless ratio k_{vj}/k_0; this gambit yields the long-dashed curves in Fig. 1. [But if this procedure is used at energies well above threshold, where the "raw" ANV results agree well with their LFCC counterparts, the resulting "scaled" ANV cross sections are in error by several percent (see Table I). Unfortunately, unless one already has LFCC benchmarks, one cannot determine *a priori* the energy at which multiplication by the wave number ratio begins to do more harm than good.] No such procedure is necessary in the FONDA prescription, for the FONDA scattering matrix determined from (3) goes to zero at threshold and does so according to the correct threshold laws.[6]

A more sensitive test of the FONDA approximation is afforded by differential cross sections. In Fig. 2, we compare differential cross sections at 0.7 eV for excitations to

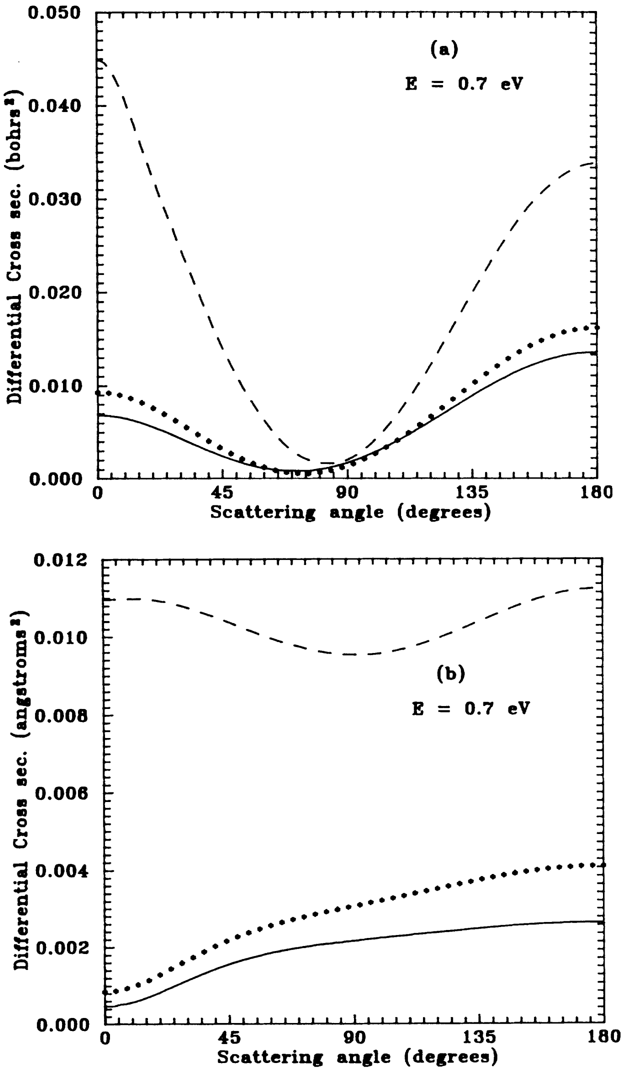

FIG. 2. Differential cross sections at 0.7 eV for (a) the pure vibrational excitation 00→ 10 and (b) the rovibrational excitation 00→ 12 of H_2 from LFCC (solid curve), ANV (dashed curve), and FONDA (dots) scattering matrices. The ANV results were multiplied by k_{vj}/k_0.

$v=1$ from our FONDA, (scaled) ANV, and LFCC calculations. With increasing energy, the FONDA cross sections come into even better agreement with the LFCC results; indeed, above 1.0 eV, the two cross sections are indistinguishable to within the 1% accuracy of these calculations.

This implementation of the FONDA approximation shows that by venturing off the energy shell while retaining adiabatic factorization of the scattering ket, one can calculate cross sections of far greater accuracy than ANV results, with little concomitant increase in computer time. The next step in the development of this method — inclusion of nonlocal exchange effects exactly — is now underway.

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