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Scaled adiabatic-nuclear-rotation theory for near-threshold rotational excitation in electron-molecule scattering

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The adiabatic-nuclei theory, which is widely used in electron-molecule scattering calculations of cross sections for nuclear excitation, is known to be invalid near threshold. A new "scaling procedure" for correcting the adiabatic-nuclei theory *for rotational excitation* is introduced and applied to e-H_2 collisions in the rigid-rotor approximation. At near-threshold energies, the resulting cross sections are shown to be in very good agreement with accurate laboratory-frame close-coupling results.

The adiabatic-nuclei (AN) formulation of electron-molecule scattering theory has played an important role ever since its introduction by Drozdov[1] and Chase.[2] The importance of this theory[3-15] derives primarily from the conceptual and computational simplifications that result from separation of the nuclear dynamics and the distortion of the scattering function.[13] This formulation treats the motion of the scattering electron as adiabatic with respect to the nuclear motions of the molecule, and thus is valid only at high enough scattering energies so that the system can be treated in this fashion. (Thus the AN approximation is expected to be invalid for near-threshold collisions.[16-19]) Even when, as is often the case, the rigid-rotor approximation[20] is used, the adiabatic-nuclear-rotation (ANR) theory is very useful, since an exact treatment of the effect of the rotational dynamics on the scattering electron is computationally intractable for almost all systems.

In previous papers[19] we have shown that the ANR theory for the calculation of differential and integrated cross sections (as applied to rotational excitation of H_2 by electron impact) breaks down at energies surprisingly far from threshold. Laboratory-frame close-coupling[21] (LFCC) calculations,[22] which accurately account for the effects of the nuclear motion, were used to obtain benchmark cross sections for comparison. These studies showed that the accuracy of the ANR integrated cross sections deteriorates as threshold is approached, from more than 10% error at scattering energies of 3 times the rotational threshold energy. More seriously, at scattering energies of over 100 times the threshold energy, significant qualitative errors were found in the ANR differential cross sections. In an effort to correct these deficiencies, a procedure based on Nesbet's energy-modified adiabatic (EMA) theory[18,19(b)] was implemented. Even at energies where this produces accurate integrated cross sections, it is unable to consistently reproduce the qualitative dependence of the LFCC differential cross sections on scattering angle.

The principal reason for this serious breakdown of the ANR theory near threshold is found in the energy dependence of the ANR scattering matrix. As discussed in Sec. II C of paper I[19(b)] as the scattering energy approaches threshold, the ANR K matrix (transformed into the laboratory representation via the rotational-frame transformation of Chang and Fano[23]) does not have the correct energy dependence, nor does it approach the correct zero-energy limit. Specifically, the elements of the LFCC K matrix go to zero as the final state wave number $k_j \rightarrow 0$ according to the threshold law

$$K^J_{jl,j_0l_0} \underset{k_j \rightarrow 0}{\sim} k_j^{l+1/2}. \tag{1}$$

In contrast, the ANR K-matrix elements, evaluated at the *body energy*[19(b)] k_b^2 and transformed to the laboratory representation, behave according to the threshold law

$$\mathcal{K}^J_{jl,j_0l_0} \underset{k_b \rightarrow 0}{\sim} k_b\ , \tag{2}$$

independent of the final-state wave number (for the quadrupole interaction). This behavior is illustrated in Fig. 1, which shows LFCC and ANR $d \rightarrow s$ and $p \rightarrow p$ K-matrix elements for initial and final rotor states $j_0 = 0$, $j = 2$ as a function of the initial-state wave number k_0.[24]

Physically, the incorrect near-threshold behavior of $\mathcal{K}^J_{jl,j_0l_0}$ arises from the neglect of the rotational Hamiltonian $\hat{\mathcal{H}}_{\text{rot}}$ in the calculation of the body-frame fixed-nuclei scattering function. Perturbations due to this Hamiltonian are important at very low scattering energies, since significant distortion of the scattering function occurs in the long-range region where $\hat{\mathcal{H}}_{\text{rot}}$ is a dominant term in the system Hamiltonian.

The *scaled adiabatic-nuclear-rotation* (SANR) theory derives from the fact that near threshold most of the LFCC and ANR K-matrix elements reduce to their counterparts in the first Born approximation[25] (FBA), which, of course,

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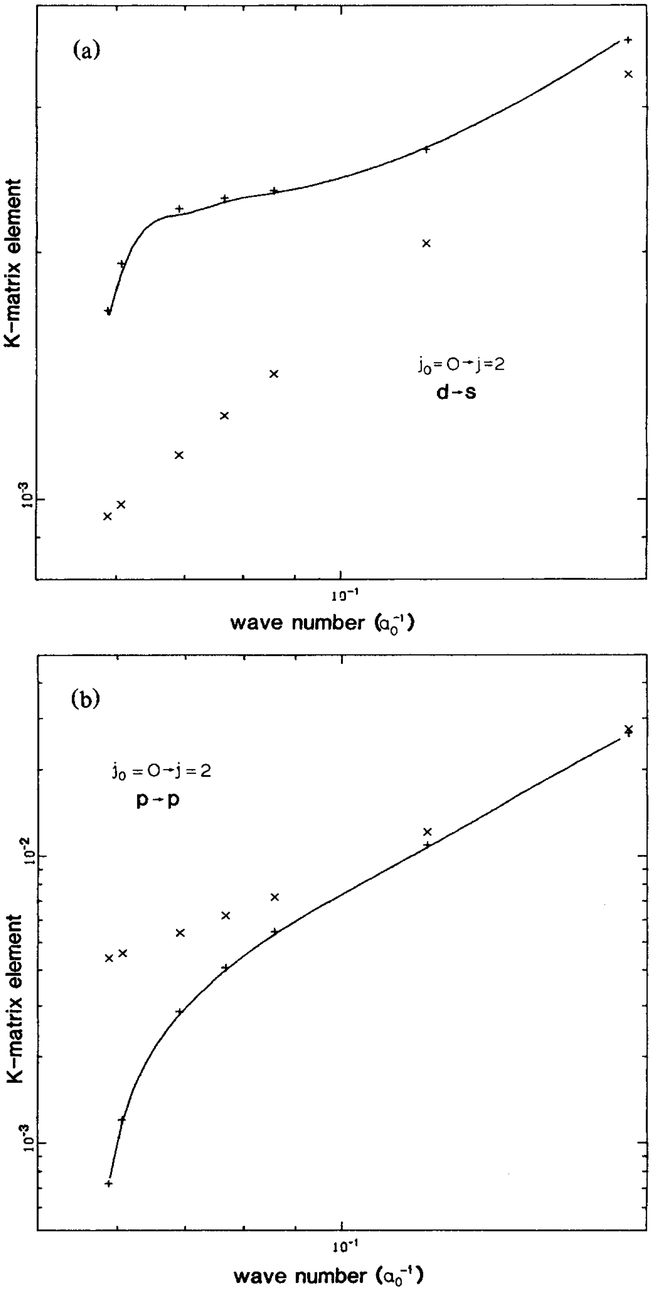

FIG. 1. Near-threshold energy dependence of the most important K-matrix elements for the $j_0=0\rightarrow j=2$ excitation of H_2 in the rigid-rotor approximation (with $R=1.4a_0$). Matrix elements shown were determined using the LFCC (solid curve), SANR (plusses), and ANR (crosses) theories. In the latter two calculations, body-frame K-matrix elements were transformed into the laboratory representation [Ref. (23)]. (a) $d\rightarrow s$ element ($K^2_{20,02}$); (b) $p\rightarrow p$ element ($K^1_{21,01}$).

obey the threshold laws (1) and (2). The FBA itself is a poor approximation for rotational excitation except *very* near threshold.[19(b)] However, we can correct the energy dependence of the ANR scattering matrix by "scaling" each element by the ratio of the corresponding laboratory-frame FBA and body-frame FBA matrix elements. Since the K matrix is an analytic function of energy[26] (at the energies of interest), it is reasonable to expect the resulting SANR K matrix to yield accurate rotational-excitation cross sections at energies where the FBA and ANR theories fail to do so. Clearly, the fact that the laboratory-frame and body-frame Born approximations are different (cf. Sec. II C of paper I) is crucial to the SANR procedure.

The formulas for the FBA K matrices are derived in the appendix of paper I. In the present paper we consider *electronically elastic scattering from linear molecules in the rigid-rotor approximation.* The LAB-FBA and (frame-transformed) ANR-FBA K-matrix elements that are required in the SANR procedure [as obtained from Eqs. (A1), (A3), and (A14) of paper I] are

$$K^J_{jl,j_0l_0}=-2(k_jk_0)^{1/2}\sum_\lambda f\lambda(j,l;j_0,l_0;J)R^L_\lambda(j,l;j_0,l_0;k_j,k_0)\ , \quad (3)$$

$$K^J_{jl,j_0,l_0}=-2k_b\sum_\lambda f\lambda(j,l;j_0,l_0;J)R^B_\lambda(l,l_0;k_b)\ , \quad (4)$$

where J is the total angular momentum, l is the orbital angular momentum, k_0 and k_j are initial- and final-state channel wave numbers, respectively, k_b is the body wave number, f_λ is an angular-coupling coefficient,[21] and R^L_λ and R^B_λ are radial integrals over the potential [given in Eqs. (A6) and (A16) of paper I].

In "conventional" ANR theory, where $k_b=k_0$, the cross section for rotational excitation must be multiplied by the wave-number ratio k_j/k_0 to ensure that they go to zero at threshold.[6] At near-threshold energies, where the FBA is valid and the cross section is therefore proportional to the square of the appropriate K-matrix element, this correction is equivalent to premultiplying Eq. (4) by $(k_j/k_0)^{1/2}$. This modification effectively makes Eqs. (3) and (4) identical *except for the fact* that the radial integrals R^L_λ and R^B_λ are different.

The SANR procedure which follows is intended to correct the energy dependence of the ANR K matrices taking this difference into account: (1) Calculate the K matrix in the body-frame fixed-nuclei representation;[20,22] (2) transform this K matrix into the laboratory representation using the rotational frame transformation of Chang and Fano;[23] (3) scale the resultant K matrix by multiplying each element by the corresponding ratio of LAB-FBA to ANR-FBA K-matrix elements given by Eqs. (3) and (4); (4) from this scaled K matrix, obtain the T matrix [cf. paper I, Eq. (21)] and from it desired cross sections.[20,21,27]

To check the utility of this procedure we shall compare SANR cross sections with those obtained from benchmark LFCC calculations.[19(b)] These comparisons are shown in Table I and Figs. 1–4 for e-H_2 scattering. [The interaction potential used in calculating these results includes static,[28] exchange (tuned-free-electron gas model[29]), and *ab initio* nonadiabatic polarization[30] contributions. The potential, scattering theory, and computational procedures are described in Secs. III and IV of paper I.] Although results only for $j_0=0\rightarrow j=2$ are shown in Figs. 2–4, similar results were obtained for other excitations (cf., Table I).

Figure 1 illustrates the excellent agreement between SANR and LFCC K-matrix elements at near-threshold energies, agreement that is not obtained when the ANR theory is used. In Fig. 2, the percent differences from benchmark LFCC integrated cross sections are compared for the ANR, EMA, and SANR theories. At scattering energies below 0.1 eV, the SANR cross sections are the most ac-

TABLE I. Integrated e-H_2 rotational-excitation cross sections for fixed $R = 1.4a_0$. Comparison of SANR and benchmark LFCC results (cross sections in a_0^2).

	$0 \rightarrow 2^a$		$1 \rightarrow 3^b$	
E (meV)	SANR	LFCC	SANR	LFCC
44.19	0.0131	0.0124		
45.0	0.0346	0.0328		
47.0	0.0607	0.0578		
50.0	0.0857	0.0821		
65.0	0.1553	0.1505		
80.0	0.1979	0.1923	0.0426	0.0403
100	0.2405	0.2336	0.0873	0.0834
200	0.3908	0.3784	0.1998	0.1906
500	0.8077	0.7140	0.4603	0.4393

[a] Threshold = 44.05 meV. [b] Threshold = 73.00 meV.

curate of these three approximate results. At higher scattering energies, the EMA yields slightly more accurate integrated cross sections, although examination of the differential cross sections for this excitation reveals that one must still use the SANR theory to obtain the correct dependence on scattering angle (see especially Fig. 4). Of course, as the scattering energy increases from threshold, the LFCC K-matrix elements deviate from the simple threshold law (1), and one would not expect the SANR procedure to give the correct energy dependence. Indeed, for scattering above about 1.0 eV, conventional ANR theory leads to more accurate integrated cross sections than does the SANR method. This observation emphasizes that *the SANR procedure is suitable for near-threshold rotational excitation*, where the AN approximation is invalid. Examination of Figs. 3 and 4 shows that the SANR differential cross sections at near-threshold energies are in quantitative agreement with the LFCC results. Note that even the low-angle "dip" in the 0.1-eV LFCC differential cross section is reproduced by the SANR method, in contrast to the ANR and EMA procedures.

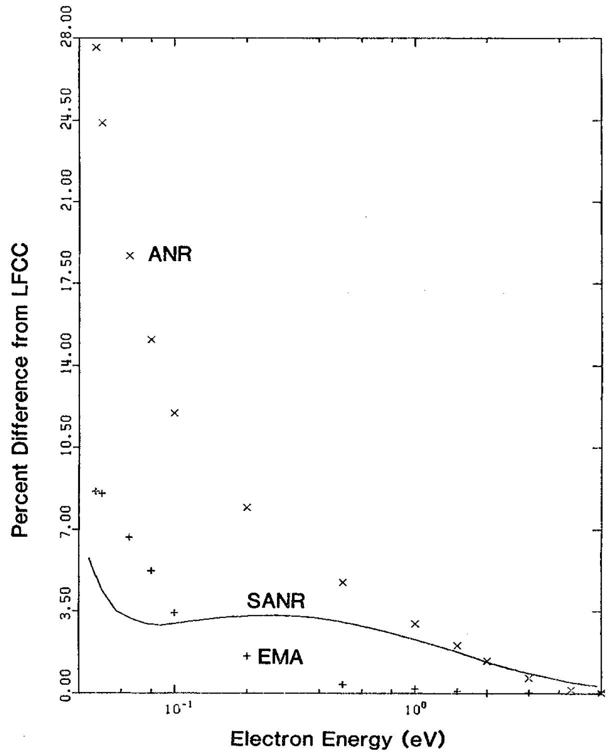

FIG. 2. Test of the validity of three approximate scattering theories for the $j_0 = 0 \rightarrow j = 2$ excitation of the H_2 in the rigid-rotor approximation (with $R = 1.4a_0$). For the ANR (crosses), EMA (plusses), and SANR (solid curve) theories, the percent difference of the approximate cross section from the LFCC cross section is shown.

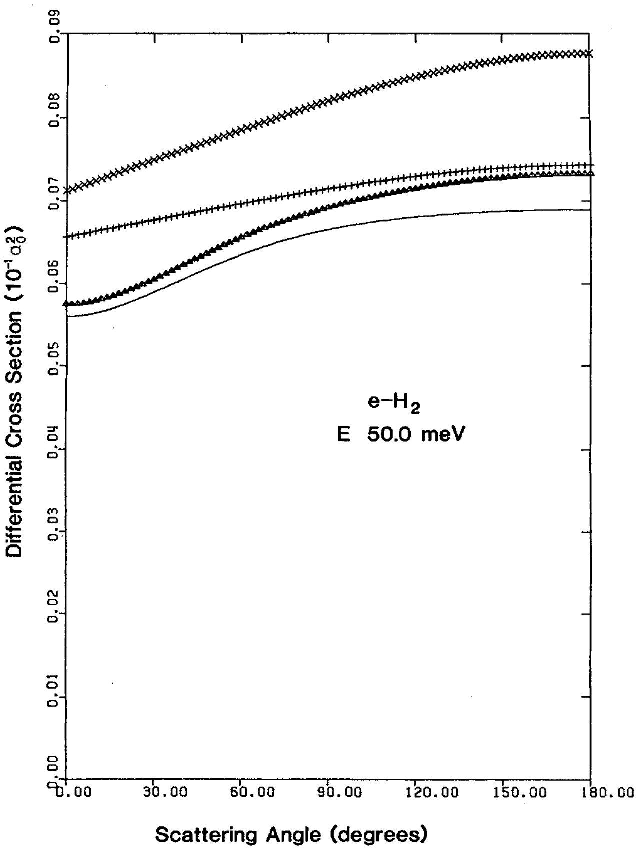

FIG. 3. Differential cross section for the $j_0 = 0 \rightarrow j = 2$ rotational excitation of H_2 in the rigid-rotor approximation (with $R = 1.4a_0$) at a scattering energy of 50.0 meV. Results from calculations using the LFCC (solid curve), ANR (crosses), EMA (plusses), and SANR (triangles) theories are shown. See Ref. 19(b) for more extensive graphs of differential cross sections in the first two theories.

Perhaps surprisingly, the SANR percent differences in Fig. 2 do not approach zero at threshold. This result is a consequence of a small "mismatch" in the exit-channel wave numbers for the FBA K-matrix elements used in the SANR procedure. At very low energies (below about 65.0 meV), the $d \rightarrow s$ K-matrix elements make the dominant contribution to the $j_0 = 0 \rightarrow j = 2$ cross section.[31] The LAB-FBA and ANR-FBA approximations to these matrix elements are not equally accurate at these energies, since the LFCC exit-channel wave number k_j is approaching zero

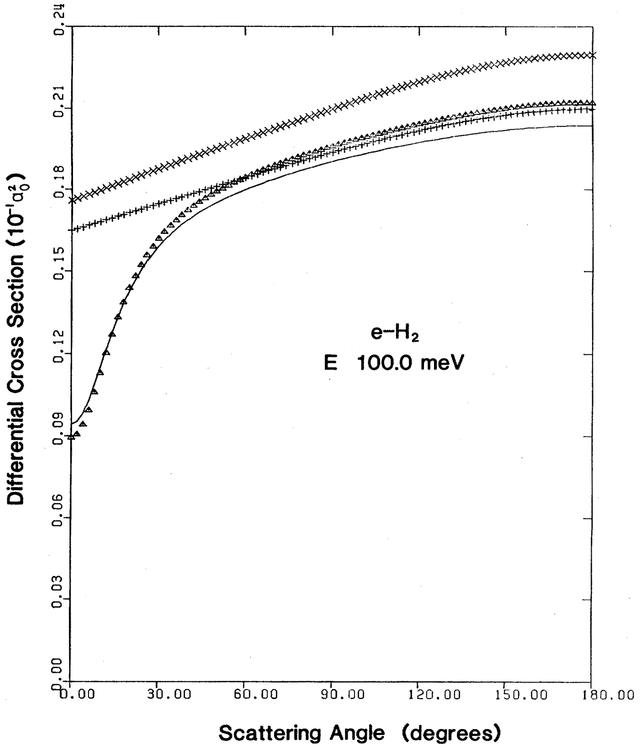

FIG. 4. Same as Fig. 3 for a scattering energy of 100.0 meV. An explanation of the small-angle "dip" in this cross section can be found in Ref. 19(b).

while the body wave number k_b is approaching $k_{\text{thresh}}=[2(\epsilon_j-\epsilon_{j_0})]^{1/2}$, where ϵ_j is the target energy in the jth rotational state. For the $j_0=0\rightarrow j=2$ excitation in H_2, $k_{\text{thresh}}=0.057a_0^{-1}$, a large enough value that the resulting mismatch affects the SANR procedure very near threshold. (This problem is peculiar to the e-H_2 system, which has an anomalously large rotational constant.) At energies above 65.0 meV, this inconsistency in the exit-channel wave number has no effect.

In summary, we have introduced a procedure for correcting the ANR K matrix for near-threshold rotational excitation; for e-H_2 collisions, this procedure gives excellent agreement with LFCC results. This SANR method is easy to implement and requires very little additional computing time. This paper has not dealt with vibrational excitation, for which the AN theory is much less accurate than for rotational excitation.[32] Because the FBA is not very accurate for near-threshold vibrational excitation,[20] the SANR method is not likely to be extendable to vibration.

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