

## Breakdown of the adiabatic-nuclear-rotation approximation for near-threshold e–H<sub>2</sub> collisions

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**Abstract.** The validity of the adiabatic-nuclear-rotation theory of electron–molecule scattering is assessed for near-threshold rotational excitation of H<sub>2</sub>. Integrated and differential cross sections calculated using this theory are compared with those determined using the more accurate laboratory frame close-coupling theory. A recently proposed energy-modified adiabatic theory is tested and shown to lead to marked improvement in the approximate integrated (but not differential) cross sections.

Accurate cross sections for the excitation of the nuclear degrees of freedom of small molecules by low-energy electron impact are required for a wide range of applications, from e-beam initiated gas discharge lasers to models of planetary atmospheres. Theoretical calculations of cross sections for ro-vibrational excitation rely heavily on the adiabatic nuclei (AN) theory (Lane 1980). Indeed, use of this theory, instead of the more accurate laboratory frame close-coupling (LFCC) method, is necessary for all but the simplest systems by the huge number of target states that are energetically accessible and by the substantial partial-wave coupling that obtains at low energies. A variety of procedures are available for solving the fixed-nuclei scattering equations, including  $L^2$  variational methods (e.g.,  $R$  matrix, Schneider 1975;  $T$  matrix, Levin *et al* 1980; and Schwinger variational methods, Watson *et al* 1980) and body frame close coupling. These theories can lead directly to *total* cross sections (i.e., summed over final nuclear states), but to obtain information regarding specific excitations ( $ju \rightarrow j'v'$ ) recourse must be made to the AN approximation (cf Levin *et al* 1980).

A rough criterion for the validity of this approximation can be obtained by comparing the 'collision time',  $t_c$ , with the period of the relevant molecular motion. Thus, if  $t_c \leq 10^{-12}$  s, then the rotational motion of the nuclei can be treated adiabatically. If  $t_c \leq 10^{-14}$  s, the vibrational motion can be considered to be adiabatic. This crude picture would lead one to expect the AN approximation to be invalid for scattering events in which the electron moves very slowly.

This situation obtains near the threshold for a ro-vibrational excitation, and poses a substantial theoretical problem, since it prohibits calculation of inelastic cross sections by the AN theory in this important energy region. Unfortunately, experimental determination of near-threshold cross sections (Golden *et al* 1971, Crompton 1969) is quite difficult, and many existing experimental results are plagued by discrepancies.

The feasibility of using the AN theory to determine cross sections for rotational and vibrational excitation of small molecules has been clearly demonstrated (cf Chang and

Temkin 1970, Temkin and Faisal 1971). Moreover, some theoretical attention has been given to the anticipated breakdown of this approximation near threshold (Shugard and Hazi 1975, Chang and Temkin 1969, 1970, Domcke *et al* 1979). But to date, no *quantitative* studies of the nature and extent of this problem have been reported. Requisites for such studies include benchmark cross sections obtained using a 'non-adiabatic' theory such as LFCC, a high degree of numerical accuracy in the scattering calculations, and a realistic representation of the electron-molecule interaction potential,  $V_{\text{int}}$ . The latter requirement is especially important, since theoretically the validity of the AN theory hinges on the commutator of  $V_{\text{int}}$  and the Hamiltonian of the nuclear motion  $H^{(n)}$  being small, i.e.,

$$[V_{\text{int}}, H^{(n)}] \ll 1$$

(Chang and Fano 1972).

The present paper reports the results of the first phase in an extensive study of near-threshold electron-molecule scattering; these results pertain to rotational excitation. Specifically, we have explored the validity of the *adiabatic-nuclear-rotation* (ANR) approximation for inelastic ( $j \rightarrow j'$ ) e-H<sub>2</sub> collisions. Hydrogen is sufficiently simple that highly accurate scattering calculations can be performed using *both* the LFCC and ANR theories. Moreover, one can construct a realistic interaction potential for this system. Thus, differences between the LFCC and ANR cross sections reflect deficiencies in the AN approximation, rather than, say, vagaries of the numerical calculations.

In addition, we have examined a recently proposed method (Nesbet 1979) for partially correcting for the deficiencies of the AN theory near threshold: the energy-modified adiabatic (EMA) theory. The usefulness of this procedure, which is very easy to implement, is assessed by comparison with our LFCC and ANR results.

To model accurately the electron-molecule interaction potential,  $V_{\text{int}}$ , for low-energy collisions, it is necessary to include static, exchange and induced-polarisation contributions (Lane 1980), namely

$$V_{\text{int}} = V_{\text{st}} + V_{\text{ex}} + V_{\text{pol}}. \quad (1)$$

In the present study, an *ab initio* static potential was calculated (Morrison 1980, Collins *et al* 1980a, b) from newly determined near-Hartree-Fock wavefunctions of the  $X^1\Sigma_g^+$  (ground) electronic state of H<sub>2</sub>. Since we are not concerned at present with vibrational excitation, the internuclear separation of H<sub>2</sub> was fixed as its equilibrium value, 1.4  $a_0$ †. Our calculated ground-state energy for this case is  $-1.132\,906E_h$ . The corresponding permanent quadrupole moment is  $0.4158ea_0^2$ .

This H<sub>2</sub> wavefunction was also used in the calculation of the exchange potential,  $V_{\text{ex}}$  in (1). We incorporated exchange effects using a model exchange potential, the 'tuned free-electron gas' exchange potential, that has been shown (Gibson and Morrison 1981, Morrison and Collins 1978) to produce total cross sections in excellent agreement with those of exact iterative static-exchange calculations (Collins *et al* 1980a, b). The theoretical background for this model has been discussed in detail elsewhere (Gibson and Morrison 1981), and details concerning its implementation will accompany a forthcoming computer program (Weitzel *et al* 1982).

We note here that to ensure maximum consistency with the static contributions to  $V_{\text{int}}$ , we retuned the model exchange potential of Morrison and Collins (1978) to agree

† Atomic units have been used throughout so that  $\hbar = m_e = a_0 = e = 1$ . The unit of energy is  $\hbar^2/(m_e a_0^2) = 1$ ,  $E_h = 2 \text{ Ryd} = 27.212 \text{ eV}$ . The unit of distance is the first Bohr radius,  $a_0 = 1 \text{ Bohr} = 0.52918 \times 10^{-10} \text{ m}$ .

with newly calculated *exact static-exchange* cross sections based on the aforementioned near-Hartree-Fock  $H_2$  wavefunction. A value of  $I = 0.0834E_h$  for the 'ionisation potential parameter' in the form of  $V_{ex}$  (see equation (3.12) of Morrison and Collins (1978)) produced a body frame/fixed-nuclei eigenphase sum in the  $\Sigma_g$  electron-molecule symmetry at 0.04 Ryd that agreed with the exact result,  $-0.4260$  rad, to four decimal places.

The final contribution to  $V_{int}$ , the polarisation potential, represents a second-order effect arising from the interaction of the scattering electron with the distorted molecular charge cloud. Our representation of this potential is based on the *ab initio* variation-perturbation calculations of Lane and Henry (1968) and, as such, partly accounts for non-adiabatic effects. Expanded in Legendre polynomials of  $\cos \theta$ , where  $\theta$  is the scattering angle in the body-fixed reference frame, the polarisation potential we used is

$$V_{pol}(r) = v_0^{pol}(r) + v_2^{pol}(r)P_2(\cos \theta) \quad (2)$$

where

$$v_0(r) = -\frac{\alpha_0}{2(r^2 + r_1^2)^2} [1 - \exp[-(r/r_a)^3]] \quad (3a)$$

and

$$v_2(r) = -\frac{\alpha_2}{2(r^2 + r_2^2)^2} [1 - \exp[-(r/r_b)^4]]. \quad (3b)$$

In equations (3),  $\alpha_0 = 5.5 a_0^3$  and  $\alpha_2 = 1.38 a_0^3$  are the spherical and non-spherical polarisabilities of  $H_2$ , respectively, and the constants have the values  $r_1 = 1.22 a_0$ ,  $r_2 = 1.1 a_0$ ,  $r_a = 1.7 a_0$ ,  $r_b = 1.6 a_0$ .

Turning now to the scattering calculations, we note first that two full sets of calculations were carried out, one using LFCC theory, the other implementing the ANR approximation. The same numerical procedure, based on an integral-equations algorithm (Sams and Kouri 1969, Morrison 1979), was used in both studies. Furthermore, the same interaction potential (equation (1), described above) was used and (identical) stringent convergence criteria enforced. Five channels were used in each of six symmetries in the ANR calculations while four rotor states and a maximum total angular momentum of six were used in the LFCC calculations. Further details of these calculations will be reported in a future paper.

The LFCC formulation (Arthurs and Dalgarno 1960, Lane and Geltman 1967, Lane and Henry 1968) is based on the expansion of the electron-molecule system wavefunction in a basis set of coupled angular momentum eigenfunctions. These basis functions depend on the angular coordinates of the scattering electron and of the internuclear axis (in a space-fixed reference frame) and therefore allow for full interplay of the nuclear dynamics and the quantum 'motion' of the scattering electron. Asymptotic scattering channels are defined by the quantum numbers  $J$ ,  $j$  and  $l$  for the total angular momentum, rotational angular momentum, and orbital angular momentum of the scattering electron, respectively. Solution of the coupled scattering equations yields laboratory  $T$ -matrix elements,  $T_{j'v',jv}^J$ , that are used to calculate integrated, momentum transfer and differential cross sections for excitations  $j \rightarrow j'$  of interest.

In contrast to the LFCC theory, the ANR formulation of the collision problem assumes a Born-Oppenheimer separation of the nuclear motion from that of the electrons, including the scattering electron (Shugard and Hazi 1975, Lane 1980). To implement this formulation we first solve the scattering equations with fixed-nuclear

orientation (Temkin and Vasavada 1967, Hara 1969) in a body-fixed reference frame. These calculations produce a body frame fixed-nuclei  $T$  matrix,  $T_{l'm}^m$ , the elements of which are labelled by the quantum numbers  $l$  and  $m$  of the orbital angular momentum of the scattering electron. This  $T$  matrix is then transformed into the laboratory frame via a simple unitary transformation based on the rotation matrices (Lane 1980). Finally, the resulting laboratory frame  $T$  matrix is used to determine the ANR approximation to the desired  $T$  matrix ( $T_{j'l',jl}^J$ ). This approximate  $T$  matrix is used to calculate cross sections.

In the present paper we report integrated and differential cross sections for the excitation  $j = 0 \rightarrow j' = 2$ . These results show the salient features of the breakdown of the ANR theory. These features were also exhibited by cross sections for other inelastic excitations.

Integrated cross sections  $\sigma(0 \rightarrow 2)$  obtained from LFCC and ANR calculations are shown as functions of the scattering energy in figure 1. The anticipated deterioration of the ANR results with decreasing energy is evident in this figure. We note that the differences between the ANR cross sections and the 'exact' LFCC results are significant at somewhat higher energies than would be anticipated by the semi-quantitative arguments that have been discussed in previous work (cf, Chang and Temkin 1970). Also shown in figure 1 are  $0 \rightarrow 2$  cross sections as calculated in the first Born approximation (Dalgarno and Moffett 1963), taking into account the long-range quadrupole and induced-polarisation interactions. We note that even at the lowest energy considered, the Born approximation does not precisely reproduce the LFCC cross sections.

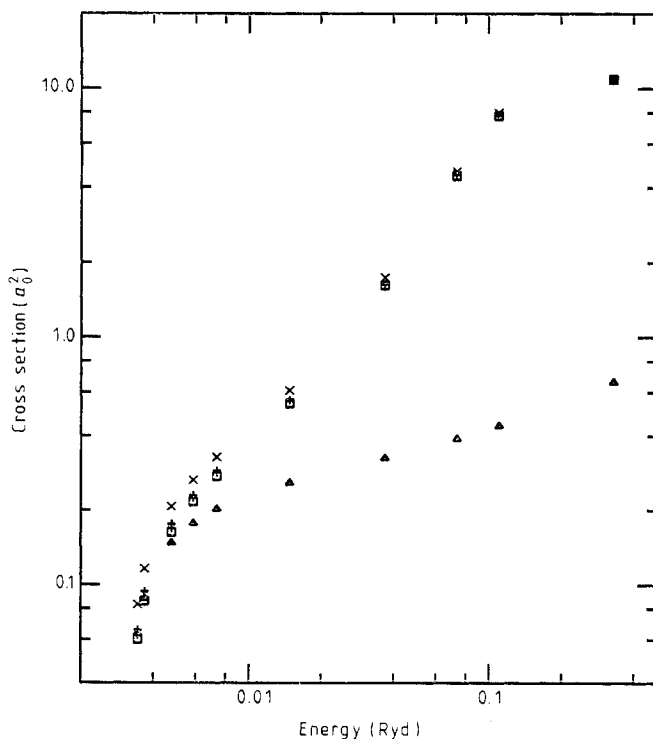
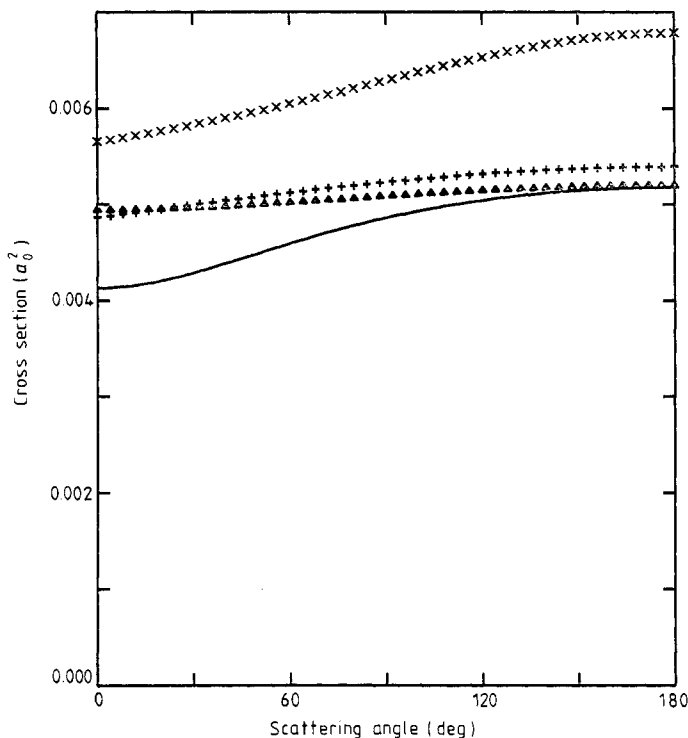


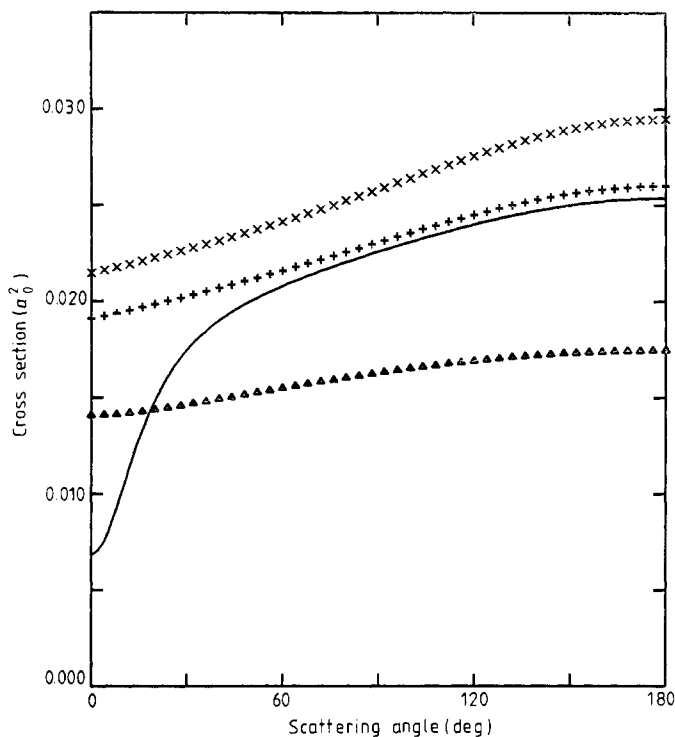
Figure 1. Integrated cross sections for the  $j = 0 \rightarrow j' = 2$  excitation of  $H_2$  by low-energy electrons as calculated in various theories: LFCC,  $\square$ ; ANR,  $\times$ ; EMA,  $+$  and Born,  $\blacktriangle$ .



**Figure 2.** Differential cross sections for the  $j=0 \rightarrow j'=2$  excitation of  $\text{H}_2$  by electrons with energy  $k^2 = 0.00346$  Ryd, as calculated in various theories: LFCC, full curve; ANR,  $\times$ ; EMA,  $+$  and Born,  $\blacktriangle$ . The integrated cross sections  $\sigma(0 \rightarrow 2)$  at this energy are: LFCC,  $0.0603 a_0^2$ ; ANR,  $0.0833 a_0^2$ ; EMA,  $0.0655 a_0^2$  and Born,  $0.0639 a_0^2$ .

More insight into the nature of the breakdown of the ANR approximation near threshold can be gained by examining the differential cross sections for the  $0 \rightarrow 2$  excitation. Selected cross sections from the energy range considered in the present study ( $k^2 = 0.00346$  Ryd to  $k^2 = 0.331$  Ryd) are shown in figures 2, 3 and 4. At  $k^2 = 0.00346$  Ryd (figure 2) the difference between the LFCC and Born *integrated* cross sections seen in figure 1 is due to a slight dip in the forward direction in the LFCC results. This dip is not present in the Born or ANR approximation results; in point of fact, it is almost entirely due to the deviation from the Born approximation of the LFCC  $l = 1$ ,  $l' = 1$  ( $p \rightarrow p$ )  $T$ -matrix elements. This dip becomes more pronounced as the energy increases, as shown by the  $k^2 = 0.00735$  Ryd result in figure 3, and then disappears again by  $k^2 = 0.0735$  Ryd (figure 4). The ANR cross sections fail to produce this small-angle behaviour, although the near agreement between the ANR and LFCC differential cross sections seen in figure 4 continues to improve with increasing energy until, by  $k^2 = 0.331$  Ryd, the two results are virtually indistinguishable.

An appealingly straightforward way to partially correct the deficiencies of the AN approximation near threshold is afforded by the EMA theory recently proposed by Nesbet (1979). In this theory, the effects of the kinetic energy operator for the nuclear motion,  $H^{(n)}$ , which are completely neglected in the usual AN approximation, are partially taken into account. The EMA approximation to the  $T$ -matrix element connecting channels  $(jl; J)$  and  $(j'l'; J)$  is easily obtained from the fixed-nuclei body

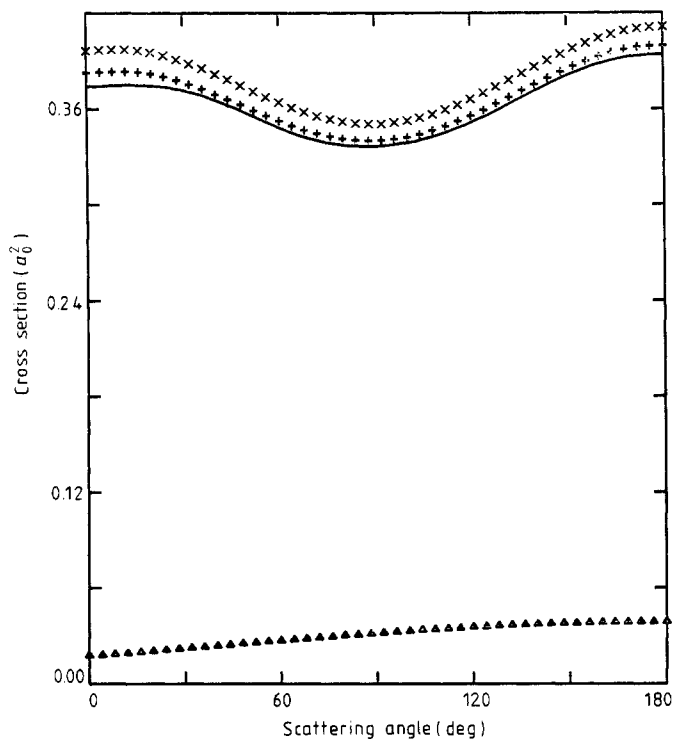


**Figure 3.** Differential cross sections for  $j = 0 \rightarrow j' = 2$  e-H<sub>2</sub> scattering at  $k^2 = 0.00735$  Ryd; curves labelled as in figure 2. At this energy, the integrated cross sections,  $\sigma(0 \rightarrow 2)$  are: LFCC,  $0.276 a_0^2$ ; ANR,  $0.330 a_0^2$ ; EMA,  $0.289 a_0^2$  and Born,  $0.203 a_0^2$ .

frame  $T$  matrix evaluated at the geometric mean of the initial- and final-state scattering energies. As illustrated in figure 1, near-threshold integrated cross sections  $\sigma(0 \rightarrow 2)$  calculated using the EMA modification to conventional ANR theory are in much better agreement with the LFCC results than are the ANR results. However, the EMA results in figures 2 and 3 indicate that this modification is unable to correct deficiencies of the ANR in contributions to the cross sections from higher partial waves, which are primarily responsible for the defects in the EMA and ANR differential cross sections.

The results of this study provide a quantitative assessment of the nature and extent of the breakdown of the ANR approximation near the threshold for the  $j = 0 \rightarrow j' = 2$  excitation of H<sub>2</sub> and of the ability of the EMA theory to correct for this breakdown. The onset of the failure of the ANR theory to reproduce the corresponding LFCC integrated cross sections occurs at a somewhat higher energy than previously anticipated. This situation is markedly improved by the EMA approximation, but even this theory cannot significantly improve the adiabatic differential cross sections.

We are currently extending this examination of the validity of the AN theory to vibrational excitation of H<sub>2</sub>, where serious discrepancies exist between the results of beam and swarm experiments (Crompton *et al* 1970, Golden *et al* 1971). Implementation of a more accurate polarisation potential, which is now under development, will enable us to generate cross sections for ro-vibrational excitation of a quality that warrants comparison with experimental data and that may help to resolve these discrepancies.



**Figure 4.** Differential cross sections for  $j = 0 \rightarrow j' = 2$   $e\text{-H}_2$  scattering at  $k^2 = 0.0735$  Ryd; curves labelled as in figure 2. At this energy, the integrated cross sections,  $\sigma(0 \rightarrow 2)$  are: LFCC,  $4.45 a_0^2$ ; ANR,  $4.65 a_0^2$ ; EMA,  $4.50 a_0^2$  and Born,  $0.392 a_0^2$ .

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