Threshold behaviour of rotational cross sections in e⁻–H₂ scattering

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Abstract. Rotational excitation cross sections, in the e⁻–H₂ system, are evaluated within a recently suggested off-shell formalism. Numerical results of the theory are generally found in good agreement with close-coupling values of the literature. It is found, in particular, that total cross sections correctly tend to zero at threshold and that angular distributions present, at low energies, deep minima in the forward direction. Such characteristic features of the theory are physically interpreted.

1. Introduction

Difficulties associated with the evaluation of e⁻–molecule vibro-rotational cross sections stem from two different sources.

(i) On one side there is the need for an accurate determination of the system interaction potential and, chief among all the terms contributing to this, the all-important polarisation effect. The investigation of such 'kinematical' aspects of the full collision process is far from being solved, so that this still represents a very active area of research (Klonover and Kaldor 1978, Truhlar *et al* 1979, Gibson and Morrison 1982, Padial and Norcross 1983, Onda and Temkin 1983);

(ii) On the other side there are all the numerical difficulties associated with the actual dynamical computations, that might generally be referred to as the many-channel problem of molecular low-energy scattering theory. In particular, the lowest-order solution to the numerical difficulties mentioned in point (ii), above, corresponds to solving for the dynamics in the so-called 'adiabatic nuclei' (AN) approximation (Chase 1956). This amounts to considering the molecule fixed in space during the energy exchange process, thereby obtaining an (on-shell) T matrix, parametrically dependent on the target position in space, to be sandwiched, later on, between the vibrorotational states of interest. The AN model has been shown, anyway (Lane 1980) to break down at the threshold of the rotational (and/or vibrational) excitation process considered, or in the presence of a resonant mechanism of energy transfer. In both such situations the projectile spends a 'long' time close to the target, so that the presuppositions of the AN approximation are violated. For such situations one has then to introduce back into the dynamics some of the information relevant to the full many-channel situation, short of treating the process exactly, e.g. in a close-coupling (CC) formulation. In this regard there have been quite a few suggestions during the last few years, all of these

tending to extend the range of validity of the AN collisional model (see Lane 1980 and references therein). In particular, the breakdown at threshold, for rotational processes, has been studied, in detail, by Morrison and co-workers (Feldt and Morrison 1982, 1984, Morrison *et al* 1984), who have compared, for the e^-–H_2 system, the results of different approximations with benchmark CC calculations.

The breakdown of the AN approximation has also been recently investigated in this laboratory (Ficocelli Varracchio 1981a, b) and a new expansion for the resolvent operator of e^-–molecule scattering processes has been suggested. This reduces, in lowest order, to an 'off-shell' generalisation of the AN model that, together with the higher-order terms (in the form of space and energy differentiations of the T amplitude) should completely correct for the many-channel aspects of threshold and resonant energy exchanges, respectively. A preliminary numerical application of this formalism (Ficocelli Varracchio and Lamanna 1983) has shown the general usefulness of the theory proposed, at least in so far as total cross sections, for rotational processes, are concerned. In this paper we now wish to present some details of the numerical procedure followed for the determination of the off-shell T matrix of interest, along with a more extensive comparison of rotational cross section data, in the e^-–H_2 system, for both two- and multi-quanta transitions. We have also investigated the behaviour of differential cross sections that undoubtedly represent a more stringent test of the formalism proposed. As it will be explicitly shown, the corresponding results present a dip in the forward direction, similarly to what was found by Morrison and co-workers, in their accurate CC calculations. The theory thus seems most convenient for applications to e^-–molecule rotational processes, also near threshold, and future developments of the formalism will be discussed.

2. Theory

2.1. The scattering equations

The present formulation of the collision process is based on a formal rearrangement of the scattering resolvent operator that we briefly summarise below for completeness. It has been shown (Ficocelli Varracchio 1981b) that the T matrix of a vibrorotational energy exchange process, for an e^-–diatomic molecule collision, can be written as

$$T_{\alpha_f \alpha_i}(\mathbf{k}'_f, \mathbf{k}'_i) = \langle \alpha_f | \exp(\hat{C}) T(\mathbf{k}'_f, \mathbf{k}'_{ij}; \mathbf{R}) | \alpha_i \rangle. \tag{1}$$

In (1) $\alpha_n = (j_n, m_n, v_n)$ stands for the collection of quantum numbers labelling the $|\alpha_n\rangle$ target state, $\mathbf{R}$ is the internuclear separation vector, while the T amplitudes, on the two sides of the equality, are meant to represent laboratory-frame T matrices (this is explicitly denoted by using primed initial, $\mathbf{k}'_i$, and final, $\mathbf{k}'_f$, electron momenta respectively). Equation (1) has the same general structure of the conventional AN approximation to e^-–molecule collision processes, from which it differs for the following two important aspects: (i) the T amplitudes in (1) are 'off-shell' quantities; (ii) the 'exp($\hat{C}$)' operator, on the RHS of (1), explicitly introduces into the dynamics the influence of the nuclear motion. As for point (i), above, the 'off-shell' nature of the formalism reflects the physical information that the electron is characterised by different values of the momenta in the entrance $(\mathbf{k}'_i)$ and exit $(\mathbf{k}'_f)$ channels, respectively. It should be pointed out, in this regard, that the relevance of off-shell amplitudes for fixed-nuclei pictures of e^-–molecule scattering had already been suggested in the literature a few

years ago (Shugard and Hazi 1975). From a numerical point of view, this aspect of the theory suggests that, in solving for the scattering process of interest, one should deal with equations for the T matrices directly, rather than solving for the scattering wavefunction first. This aspect will be analysed in greater detail in the next section. Continuing with consideration of point (ii), above, we explicitly report the full expression for the $\hat{C}$ operator, which is given by (Ficocelli Varracchio 1981b)

$$\hat{C} = -(\hat{P}_N^2/2\mu + \varepsilon_i^{(N)} - \omega_{\alpha_i}^{(N)}) \frac{\mathrm{d}}{\mathrm{d}E_i}. \tag{2}$$

In (2) $\hat{P}_N$ represents the momentum operator of the nuclei, $\varepsilon_i^{(N)}$ and $\omega_{\alpha_i}^{(N)}$ refer to the electronic only and Born–Oppenheimer energies of the molecule, respectively, while the differentiation is with respect to the E_i energy of the impinging projectile. We refer to the original papers for more details on the rearrangement of the resolvent operator, leading to (1) and (2). Here we simply wish to point out that, by expanding the exponential operator, the T matrix of interest can conveniently be expressed as the following grouping of terms

$$T_{\alpha_f \alpha_i}(\mathbf{k}'_f, \mathbf{k}'_i) = \langle \alpha_f | T(\mathbf{k}'_f, \mathbf{k}'_i; \mathbf{R}) | \alpha_i \rangle + \left\langle \alpha_f \left| \left(\hat{C} + \frac{\hat{C}^2}{2!} + \ldots \right) T(\mathbf{k}'_f, \mathbf{k}'_i; \mathbf{R}) \right| \alpha_i \right\rangle. \tag{3}$$

In particular, the first of these (first term on the RHS of (3)) has the same structure of the conventional AN approximation, from which it simply differs for the off-shell nature of the T amplitude. The remaining quantity (second term on the RHS of (3)) contains, instead, the full influence of the $\hat{C}$ operator and, as already pointed out (Ficocelli Varracchio 1981b), this should essentially be responsible for reproducing the resonant behaviour of vibrational energy exchange processes. For the present process of rotational excitation, in the e^-–H_2 system, we have then simply kept the first term on the RHS of (3), completely neglecting, then, the effect of the nuclear motion operator, $\hat{C}$. The approximation used by us in the present computations amounts, then, to enforcing

$$T_{j_f m_f : j_i m_i}(\mathbf{k}'_f, \mathbf{k}'_i) \simeq \langle j_f m_f | T(\mathbf{k}'_f, \mathbf{k}'_i; \hat{\mathbf{R}}) | j_i m_i \rangle \tag{4}$$

where we have specialised our notation to the rotational problem of interest. As pointed out earlier, the only difference between (4) and the corresponding AN approximation of rotational processes is in the off-shell nature of the T matrices involved. We shall explicitly verify, in the numerical section, that this characteristic of (4) is able to introduce, among other aspects, the correct energy behaviour of the cross sections, at threshold.

The essential quantity of the present theory is, then, a *body*-frame T matrix, to be denoted, in the following, as $T^B(\mathbf{k}_f, \mathbf{k}_i)$ (from now on the absence of primes, on the momenta, will indicate that the corresponding quantities are evaluated in the body frame of the molecule). Once T^B has been obtained, it can be rotated, by conventional techniques (Lane 1980), to the laboratory frame and the required matrix element (4) evaluated. This T^B amplitude has the conventional partial-wave expansion

$$T^B(\mathbf{k}_f, \mathbf{k}_i) = \frac{2}{\pi} \sum_{l_i l_f m} \mathrm{i}^{l_i - l_f} Y^*_{l_f m}(\hat{\mathbf{k}}_f) T^{B(m)}_{l_f l_i}(k_f, k_i) Y_{l_i m}(\hat{\mathbf{k}}_i) \tag{5}$$

with 'm' representing, as usual, the component of the angular momentum along the internuclear axis, which is conserved for the $^1\Sigma_g^+$ electronic state of the H_2 target. The amplitudes on the RHS of (5) can most conveniently be evaluated by considering, at

the outset, the standard coupled T-matrix equations (atomic units are used throughout)

$$T_{l'l}^{B(m)}(k_f, k_i) = V_{l'l}^{(m)}(k_f, k_i) + \frac{4}{\pi} \sum_{l''} \int_0^\infty dk \frac{V_{l'l''}^{(m)}(k_f, k) T_{l''l}^{B(m)}(k, k_i)}{k_i^2 - k^2 + i\eta}. \tag{6}$$

The numerical procedure followed for a solution of (6) will be considered in detail in the next section. Here we wish to concentrate on the $V^{(m)}$ quantities, that represent the matrix elements of the e^-–molecule interaction potential and are explicitly defined according to

$$V_{l'l}^{(m)}(k_f, k_i) = \frac{2}{\sqrt{k_f k_i}} \int dr\, dr'\, j_{l'}(k_f r')\, Y_{l'm}^*(\hat{r}')\, V(r', r)\, Y_{lm}(\hat{r}) j_l(k_i r) \tag{7}$$

with $V(r', r)$ the coordinate-space interaction potential. This last quantity has been accurately modelled, in the present computations, as the conventional static-exchange interaction, augmented by a recently suggested approximation to the polarisation interaction (Gibson and Morrison 1982), according to

$$V = -\sum_i \frac{1}{|R_i - r|} + \sum_j (\hat{J}_j - \hat{K}_j) + V_{\text{pol}} \tag{8}$$

in a conventional notation (Lane 1980). In particular, $\hat{J}$ and $\hat{K}$, in (8), represent the Coulomb and exchange operators, and these have been explicitly realised, in the present computations, using the near Hartree–Fock wavefunction of Fraga and Ransil (1961), as

$$\hat{J}(r)f(r) = \sum_i^{N_B} n_i \int dr' \frac{|\Phi_i(r')|^2}{|r - r'|} f(r)$$

$$\hat{K}(r)f(r) = \sum_i^{N_B} \frac{n_i}{2} \int dr' \frac{\Phi_i^*(r')f(r')}{|r - r'|} \Phi_i(r). \tag{8a}$$

In (8a) N_B represents the number of shells in the configuration, while n_i gives the number of electrons in each shell and Φ_i is the normalised molecular orbital corresponding to the ith shell. Putting (8) into (7) leads to oscillatory integrals, due to the presence of the j_l spherical Bessel's functions. Such integrals have been evaluated numerically, by a trapezoidal rule, generally using six mesh points for the half wavelength of the most rapidly oscillating function. Numerical integration has generally been carried out up to 20 atomic units, while the tails of the integrals have been evaluated by using the asymptotic forms of the Bessel's functions. The Fraga and Ransil wavefunction leads to an equilibrium separation in the H_2 molecule corresponding to $R = 1.402\, a_0$ while the total energy and quadrupole moment result in -1.1335 Hartree and $0.480\, ea_0^2$, respectively. As for the polarisation potential, this is given by the following two-term expansion

$$V_{\text{pol}}(r) = v_0(r) + v_2(r) P_2(\cos \hat{r} \cdot \hat{R}) \tag{9}$$

with the v_0 and v_2 components assuming different analytical forms, at increasing distance from the molecular centre of mass, as described in detail in the original paper of Gibson and Morrison (1982).

To conclude this section, we would like to point out that our treatment of the interaction potential is certainly very realistic and, in this respect, a comparison of our numerical results with experimental data would certainly be meaningful. As a matter

of fact, such a partial comparison with experimental data has already been favourably considered in our preliminary analysis of the theory (Ficocelli Varracchio and Lamanna 1983). In the present paper, instead, our emphasis will be more on a comparison of theory with theory. We shall then concentrate, first of all, on a comparison of our proposed off-shell approximation with the more conventional AN formulation, in order to obtain a better feeling for the range of validity of this last one. Secondly, we shall attempt a more stringent test of our off-shell results with the exact CC values of Morrison *et al* (1984) and, to some extent, with the energy-modified approximation (EMA) formulation of Nesbet (1979), that also tries to overcome the basic limitations of the conventional fixed-nuclei picture of scattering. Before proceeding to such a detailed analysis, anyway, we wish to consider, in the next section, for completeness, the numerical technique used for a solution of the coupled integral equations represented by (6).

2.2. Numerical scheme of solution for the T matrix

In this section we wish to give some details on the numerical technique used for a solution of the body-frame T matrix, (6), that we rewrite, below, as

$$T_{ll''}^{B(m)}(k_f, k_i) = V_{ll''}^{(m)}(k_f, k_i) + \frac{4}{\pi} \sum_{l''} P \int_0^\infty dk \frac{V_{ll''}^{(m)}(k_f, k) T_{l''l'}^{B(m)}(k, k_i)}{k_i^2 - k^2}$$

$$-i\frac{2}{k_i} \sum_{l''} V_{ll''}^{(m)}(k_f, k_i) T_{l''l'}^{B(m)}(k_i, k_i) \qquad (10)$$

in a convenient separation of principal value ($P \int_0^\infty dk$) and on-shell contributions to the dk integration, respectively. The $V_{ll''}^{(m)}$ matrix elements, in (10), explicitly defined according to (7), have been evaluated numerically, by using the representation (8) for the e^-–molecule interaction. For such a purpose, the Fraga–Ransil $^1\Sigma_g^+$ wavefunction has been expanded about the molecular centre of mass, by using the computer program developed by Faisal and Tench (1971). The only remaining task, for a numerical solution of (10), corresponds, then, to transforming the set of coupled integral equations into linear algebraic relations, by choosing a suitable mesh of integration, for the principal value integral. We have found it very convenient, for this purpose, to use a numerical technique suggested by Mongan (1969), that we shall now briefly outline. The technique will be illustrated with reference to a generic principal value integral, I, that we shall explicitly write as

$$I = \lim_{\Delta \to 0} \left(\int_0^{k_i - \Delta} dk \frac{f(k)}{k_i^2 - k^2} + \int_{k_i + \Delta}^\infty dk \frac{f(k)}{k_i^2 - k^2} \right). \qquad (11)$$

As we shall see, the two terms contributing to I, in (11), can most conveniently be evaluated by means of Gaussian integration meshes, after preliminary transformation of the limits of integrations to the $(-1, 1)$ interval. This can be achieved by changing variable, in the first integral, according to

$$k(\alpha) = \tfrac{1}{2}(k_i - \Delta)(1 + \alpha)$$

$$dk(\alpha) = \tfrac{1}{2}(k_i - \Delta) d\alpha \qquad (12)$$

so that $k(-1) = 0$ and $k(1) = k_i - \Delta$. The second integral, in (11), can be similarly

transformed by means of

$$k(\beta) = \frac{2(k_i + \Delta)}{1 - \beta}$$

$$dk(\beta) = \frac{2(k_i + \Delta)}{(1 - \beta)^2} d\beta$$

(13)

corresponding to $k(-1) = k_i + \Delta$ and $k(1) = \infty$. By putting (12) and (13) into (11), the principal value integrals then become

$$I = \lim_{\Delta \to 0} \left(\frac{k_i - \Delta}{2} \int_{-1}^{1} d\alpha \frac{f(k(\alpha))}{k_i^2 - k^2(\alpha)} + 2(k_i + \Delta) \int_{-1}^{1} d\beta \frac{f(k(\beta))}{(1 - \beta)^2 (k_i^2 - k^2(\beta))} \right).$$

(14)

The two integrals, in (14), may now be approximated by N-point Gaussian quadrature rules, with abscissas $\{\alpha_j\}$ and $\{\beta_j\}$, respectively, and common weights $\{\omega_j\}$. The interesting aspect of this quadrature rule is that, since Gaussian meshes never assume the values -1 or $+1$, the integrands, in (14), will never have to be evaluated at $k(\alpha = 1) = k_i - \Delta$ or $k(\beta = -1) = k_i + \Delta$. The limit for $\Delta \to 0$ can then be taken analytically, in (14), and the Gaussian quadrature rule enforced, to yield

$$I \simeq \sum_{j=1}^{N} \omega_j \frac{k_i}{2} \frac{f(k(\alpha_j))}{k_i^2 - k^2(\alpha_j)} + \sum_{j=1}^{N} \omega_j \frac{2k_i}{(1 - \beta_j)^2} \frac{f(k(\beta_j))}{k_i^2 - k^2(\beta_j)}.$$

(15)

By specialising the $f(k)$ function, in (15), to the case of interest (see (10)), the coupled set of equations for the T matrix takes the 'discretised' form

$$T_{ll'}^{B(m)}(k_f, k_i) = V_{ll'}^{(m)}(k_f, k_i) - i \frac{2}{k_i} \sum_{l''} V_{ll''}^{(m)}(k_f, k_i) T_{l''l'}^{B(m)}(k_i, k_i)$$

$$+ \frac{4}{\pi} \sum_{j=1}^{N} \sum_{l''} \omega_j \frac{k_i}{2} \frac{V_{ll''}^{(m)}(k_f, k(\alpha_j))}{k_i^2 - k^2(\alpha_j)} T_{l''l'}^{B(m)}(k(\alpha_j), k_i)$$

$$+ \frac{4}{\pi} \sum_{j=1}^{N} \sum_{l''} \omega_j \frac{2k_i}{(1 - \beta_j)^2} \frac{V_{ll''}^{(m)}(k_f, k(\beta_j))}{k_i^2 - k^2(\beta_j)} T_{l''l'}^{B(m)}(k(\beta_j), k_i).$$

(16)

It is now convenient to define a set, $\{q_j\}$, of $2N + 1$ points, corresponding to increasing values of the momenta, according to

$$\{q_j\} = \{k(\alpha_j), k_i, k(\beta_j)\}$$

(17)

in terms of which one can introduce the $K_{ll'}^{(m)}$ matrix, as

$$K_{ll'}^{(m)}(p_m, q_j) = -i \frac{2}{k_i} V_{ll'}^{(m)}(p_m, q_j) \delta_{j, N+1} + \vartheta(k_i - q_j) \frac{2}{\pi} \omega_j k_i \frac{V_{ll'}^{(m)}(p_m, q_j)}{k_i^2 - q_j^2}$$

$$+ \vartheta(q_j - k_i) \frac{8}{\pi} \omega_{j-(N+1)} \frac{k_i}{(1 - \beta_{j-(N+1)})^2} \frac{V_{ll'}^{(m)}(p_m, q_j)}{k_i^2 - q_j^2}$$

(18)

where $\{p_j\} = \{q_j\}$ and $\vartheta(x)$ represents the step function. In terms of the $K_{ll'}^{(m)}$ matrix, (18), the linear set (16) can conveniently be rewritten as

$$T_{ll'}^{B(m)}(p_m, k_i) = V_{ll'}^{(m)}(p_m, k_i) + \sum_{j=1}^{2N+1} \sum_{l''} K_{ll''}^{(m)}(p_m, q_j) T_{l''l'}^{B(m)}(q_j, k_i).$$

(19)

We now introduce an $A^{(m)}$ matrix, whose rows and columns are labelled according to

both the l angular momentum and k values of the momenta, respectively, according to

$$A^{(m)}_{lm;l'j} = \delta_{ll'}\delta_{mj} - K^{(m)}_{ll''}(p_m, q_j).$$ (20)

By defining, similarly, $B^{(m)}$ and $T^{B(m)}$ vectors, as

$$B^{(m)}_{lm} = V^{(m)}_{ll''}(q_m, k_i)$$

$$T^{(m)}_{lm} = T^{B(m)}_{ll'}(q_m, k_i)$$ (21)

the set of equations (16) takes the final convenient form

$$A^{(m)}T^{(m)} = B^{(m)}$$ (22)

that can be readily solved, by conventional matrix inversion techniques (it should be pointed out that the $A^{(m)}$ matrix, in (22), is in general complex, as follows from (20) and (18)). To conclude, we point out that the $T^{B(m)}(k_f, k_i)$ matrix element of interest will generally not be included, directly, into the solution of (22), unless the k_f final momentum value explicitly appears in the $\{q_j\}$ set. Anyway, once the $T^{B(m)}(q_j, k_i)$ elements have been obtained from (22), equation (19) can be used a second time, with $p_m = k_f$, to yield the off-shell T matrix of interest and this procedure has been followed in the present computations. It has been found, in our numerical applications, that each of the two terms in (15) could be accurately represented by a 10 point Gaussian integration mesh. This leads to $A^{(m)}$ matrices, in (22), of order $(\Delta l \times 21) \times (\Delta l \times 21)$, with Δl representing the total number of coupled partial waves, in (19). In the present calculations we have coupled, at most, two partial waves of the same parity, corresponding to $\Delta l = 2$. This has led to satisfactory agreement with standard phaseshift values of the literature (Ficocelli Varracchio and Lamanna 1983) but, if necessary, the numerical technique can certainly treat problems with much higher dimensionalities. It should be pointed out that the $T^{B(m)}$ vector, solution of (22), includes also the $T^{B(m)}(k_i, k_i)$ on-shell amplitude, which is the key quantity of the conventional fixed nuclei approximation. This readily follows from the fact that the k_i value of the momentum is present in the $\{q_j\}$ set, (17), at the $(N+1)$th position. Such a quantity has then been used to check both the numerical stability of the approach and the convergence properties, for all the expansions implicitly involved in the definitions of the various quantities, in (19), such as those for the total system wavefunction (Fraga and Ransil 1961) and interaction potential, respectively. More details on such aspects of the computations can be found elsewhere (Ficocelli Varracchio and Lamanna 1983).

Having considered the technique of solution used in our computations, we start analysing, in the next section, the numerical results obtained.

3. Numerical results

3.1. Total cross sections

In this section we wish to analyse the results obtained by enforcing the off-shell approximation, (4), to the problem of e^-–H_2 rotational excitation, and to compare these with different treatments of the scattering problem. In this regard, we shall consider, in particular, some recent computations of Morrison and co-workers (Feldt and Morrison 1984, Morrison *et al* 1984), who have analysed in detail the threshold behaviour of cross sections, for e^-–H_2, in both the AN and EMA approximations, and

by solving exactly the scattering equations, in the CC formulation. Our first comparison will be for total cross sections that can be readily evaluated from the T-matrix elements (5) by rotating to the laboratory frame and summing over intermediate angular momenta (Lane 1980). In figure 1 we plot total cross sections for the $0 \rightarrow 2$ process, evaluated in both the conventional AN approximation and off-shell formulations of the present theory. Also shown, for a comparison, are the exact CC results of Morrison *et al.* Our first comment is on the very different behaviours of the AN and off-shell approximations, at threshold for the rotational excitation process. The AN results have been evaluated by using the $T^B(k_i, k_i)$ matrix elements, that are also automatically obtained from our numerical scheme of solution, as outlined in § 2.2. It should be pointed out that all the on-shell results of this paper have not been multiplied by the arbitrary factor k_f/k_i, in agreement with the complete degeneracy of the rotational states, in the AN approximation. The curves in figure 1 show that while the off-shell results correctly tend to zero, at threshold, the AN curve presents its biggest deviation just in this energy range. On the other hand, it can be seen from the figure that it is only at energies above 1 eV (i.e. more than twenty times above threshold) that the two curves become indistinguishable and the results of the off-shell theory agree with those of the conventional AN approximation.

The correct threshold behaviour of the off-shell approximation can be understood, at the same time, in terms of the following simple argument. It is well known (Morrison *et al* 1984) that rotational excitation, near threshold, is caused mostly by the long range components of the interaction, so that one should expect the first Born approximation (FBA) to be almost quantitative under such conditions. From (6) and (7) it then
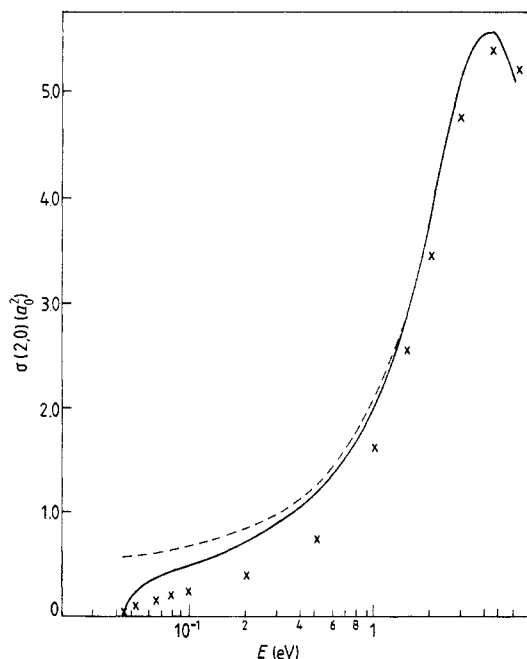

Figure 1. Total cross sections for the $0 \rightarrow 2$ rotational excitation process: ———, off-shell results of the present theory; ————, on-shell results (AN approximation); ×, crosses are the close-coupling results of Morrison *et al* (1984).

follows that, near threshold, the off-shell T^B matrix should reduce to

$$T_{l'l}^{B(m)}(k_f, k_i) \simeq \frac{2}{\sqrt{k_f k_i}} \int d\mathbf{r} \, d\mathbf{r}' \, j_{l'}(k_f r') \, Y_{l'm}^*(\hat{r}') \, V(\mathbf{r}', \mathbf{r}) \, Y_{lm}(\hat{r}) j_l(k_i r) \qquad (23)$$

so that its energy dependence appears as an overall multiplicative factor $(k_f k_i)^{-1/2}$, in front of the integral, and as the k_f and k_i momenta being present in the arguments of the final motion and entrance channel Bessel's functions, respectively. However, as pointed out by Morrison, this is exactly the energy dependence of the CC theory, in the FBA, so that, as long as one can assume the FBA to be a valid model, the only deviation of the off-shell and CC results must be due to differences in the interaction potential, rather than to deficiencies in our scattering model.

We wish to comment, next, on a quantitative comparison with the CC values, that have been obtained by Morrison and co-workers by using an interaction potential that differs from the one employed by us for both the static and exchange contributions. This is due both to a choice of a different $^1\Sigma_g^+$ ground-state wavefunction and to an approximate treatment of exchange, in Morrison's computations, according to a variant of the free-electron-gas model. On account of such differences, the CC values deviate from our results also at higher energies, e.g. when the AN theory is known to be a very good approximation to the dynamics. In spite of this, a quantitative comparison with the CC results can still be attempted, as we shall indicate below. One can consider, in fact, that the present on-shell total cross sections and the corresponding AN values of Morrison (multiplied by a k_i/k_f energy factor) differ by an overall 'scale factor', that essentially contains full information on differences in static and exchange terms, in the two treatments of the dynamics. At each energy, this factor can be extracted by dividing the AN results of Morrison into our own, as explicitly shown in table 1, from which it clearly appears that the 'f' scale factor is strongly energy dependent. While we do not wish to speculate on which of the potential terms (static or exchange) influences mostly such 'f' numbers, here we simply wish to point out that the off-shell $0 \rightarrow 2$ cross sections can now be multiplied, at each energy, by the corresponding value

Table 1. Total cross sections for the $0 \rightarrow 2$ process in the AN approximation, evaluated with different interaction potentials: MFA, Morrison *et al* (1984); on-shell, present results. The f scale factors, given by the ratio MFA/on-shell, account for differences in the interaction potentials.

E (eV)	MFA	On-shell	f
0.047	0.297	0.568	0.523
0.050	0.296	0.575	0.515
0.065	0.314	0.608	0.516
0.080	0.330	0.638	0.517
0.1	0.350	0.688	0.509
0.2	0.462	0.858	0.539
0.5	0.860	1.278	0.673
1.0	1.705	2.044	0.834
1.5	2.648	2.951	0.897
2.0	3.537	3.909	0.905
3.0	4.809	5.293	0.909
4.5	5.426	5.647	0.961
6.0	5.218	5.156	1.012

of *f.* This should, in principle, account for differences in the total cross sections, imputable to the different interaction potentials used by us and Morrison, respectively. All remaining numerical deviations should, then, essentially be due to differences in the treatments of the dynamics. Scaled off-shell $0 \rightarrow 2$ cross sections are reported in table 2, where they are compared with the results of both the CC and EMA computations, both performed by Morrison. It can be seen, from this table, that the off-shell and EMA schemes perform almost equivalently, with EMA theory being perhaps slightly favoured very close to threshold. Anyway, when considering, in the next section, angular distributions, it will be seen that while both the off-shell and CC theories present minima in the forward direction, such a detailed feature is absent from the EMA scheme.

Table 2. Total cross sections for the $0 \rightarrow 2$ process in different approximations: the close coupling (CC) and energy modified approximation (EMA) results are those of Morrison *et al* (1984). Off-shell are the present results, scaled by the *f* factors of table 1 to account for the different interaction potentials of the two computations.

E (eV)	CC	Off-shell	EMA
0.047	0.058	0.088	0.063
0.050	0.082	0.117	0.089
0.065	0.151	0.184	0.160
0.080	0.192	0.217	0.202
0.1	0.234	0.248	0.242
0.2	0.378	0.355	0.384
0.5	0.714	0.793	0.787
1.0	1.619	1.629	1.622
1.5	2.557	2.564	2.559
2.0	3.450	3.448	3.450
3.0	4.742	4.727	4.740
4.5	5.391	5.365	5.387
6.0	5.201	5.174	5.197

Having discussed in detail $0 \rightarrow 2$ total cross sections, we can now briefly consider $1 \rightarrow 3$ rotational transitions, that we plot in figure 2. The same general comments, as for the $0 \rightarrow 2$ case, apply also to the present situation. We simply wish to point out that a slight disagreement between on-shell and off-shell values persists, in the present situation, even at energies higher than for the $0 \rightarrow 2$ case. This is essentially due to the threshold energy of the $1 \rightarrow 3$ process being higher than that of the $0 \rightarrow 2$ transition. Also in the present situation a more quantitative comparison with the CC results of Morrison can be attempted, by scaling the off-shell total cross sections by a factor evaluated on the basis of the present and Morrison's AN approximations, as discussed for the $0 \rightarrow 2$ transition. The corresponding values of the *f* scale factors are almost identical to those previously obtained and are listed, for completeness, in table 3. Scaled $1 \rightarrow 3$ total cross sections are finally given in table 4, where these are compared with both CC and EMA results. The off-shell theory is again seen to perform in good agreement with the exact CC values and to be, in general, equivalent to the EMA approximation.

To conclude, we finally list, in table 5, values obtained for $0 \rightarrow 4$ rotational transitions, in both the on-shell and off-shell approximations. It can be seen that the conventional
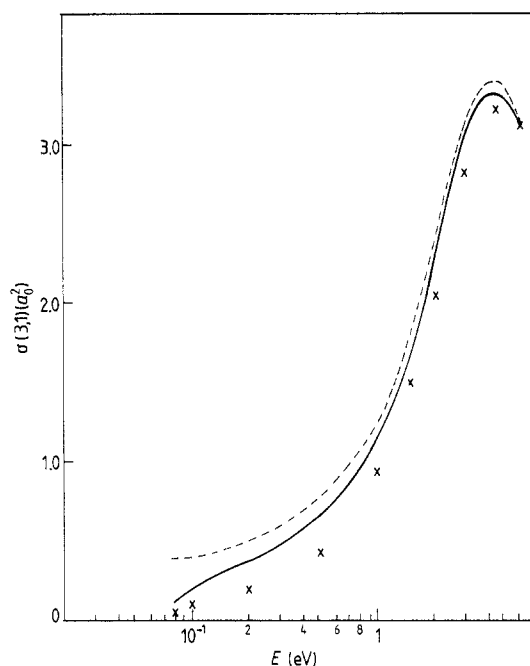
Figure 2. Total cross sections, for the $1 \rightarrow 3$ rotational excitation process. The notation is as in figure 1.

Table 3. Total cross sections for the $1 \rightarrow 3$ process in the AN approximation, evaluated with different interaction potentials: MFA, Morrison *et al* (1984); on-shell, present results. The f scale factors, given by the ratio MFA/on-shell, account for differences in the interaction potentials.

E (eV)	MFA	On-shell	f
0.08	0.200	0.385	0.520
0.1	0.210	0.408	0.515
0.2	0.277	0.511	0.542
0.5	0.516	0.771	0.669
1.0	1.023	1.231	0.831
1.5	1.589	1.777	0.894
2.0	2.122	2.351	0.903
3.0	2.886	3.183	0.907
4.5	3.256	3.397	0.959
6.0	3.131	3.132	1.0

AN theory generally overestimates the cross section results and differences persist up to the highest energies explored.

3.2. Differential cross sections

An analysis of differential cross sections is certainly a more stringent test of any theory of scattering, because more detailed features of the dynamical behaviour of the system

Table 4. Total cross sections for the $1 \to 3$ process in different approximations: the close coupling (cc) and energy-modified approximation (EMA) results are those of Morrison *et al* (1984). Off-shell are the present results scaled according to the f factors of table 3, in order to account for the differences in the interaction potentials of the two computations.

E (eV)	cc	Off-shell	EMA
0.08	0.040	0.061	0.048
0.1	0.083	0.106	0.092
0.2	0.191	0.205	0.198
0.5	0.439	0.448	0.443
1.0	0.937	0.948	0.940
1.5	1.498	1.504	1.500
2.0	2.034	2.033	2.035
3.0	2.817	2.803	2.817
4.5	3.219	3.195	3.217
6.0	3.113	3.088	3.111

Table 5. Total cross sections, for the $0 \to 4$ rotational transition, in the AN approximation (on-shell) and in the scheme of the present theory (off-shell).

E (eV)	On-shell	Off-shell
0.2	8.72 (−3)	3.05 (−3)
0.5	1.04 (−2)	7.56 (−3)
1.0	1.20 (−2)	1.04 (−2)
1.5	1.29 (−2)	1.18 (−2)
2.0	1.37 (−2)	1.28 (−2)
3.0	1.53 (−2)	1.46 (−2)
4.5	1.79 (−2)	1.74 (−2)
6.0	2.11 (−2)	2.11 (−2)

become apparent, from the angular distributions. In particular, the differential cc calculations of Morrison have put in evidence that, close to threshold, both the $0 \to 2$ and $1 \to 3$ transitions present pronounced minima in the forward direction. Such features, completely absent in the AN scheme, are not even present in the EMA approximation (Morrison *et al* 1984), that therefore reveals some partial limitations in this angular distribution test. On the other hand, the origin of such deep minima has been discussed by Morrison, who has pointed out that it depends on the subtle numerical interplay of $p \to p$ and $d \to s$ partial-wave T-matrix elements (or, better, K-matrix elements in Morrison's computations) close to threshold for the transition considered. The $p \to p$ transition represents the leading contribution over most of the energy range, whereas the $d \to s$ coupling becomes predominant, over a very narrow energy interval, close to threshold for the process. Such a behaviour, put in evidence by exact cc calculations, is not reproduced by the AN or EMA dynamical schemes, as considered in detail in the original papers. On the other hand it has already been pointed out by us, in our preliminary application of the off-shell theory (Ficocelli Varracchio and Lamanna 1983), that the present scheme is able to predict correctly such more detailed numerical aspects of the dynamics. One should then expect to

observe pronounced minima in the forward direction, coming out of the off-shell angular distributions, as for the CC calculations. This is clearly shown in figure 3, where differential cross sections are plotted, for the $1 \rightarrow 3$ process, at an energy $E = 0.2$ eV, for both our present theory and CC calculations. It should be stressed, at this point, that a comparison of the curves, in figure 3, can hardly be carried out beyond
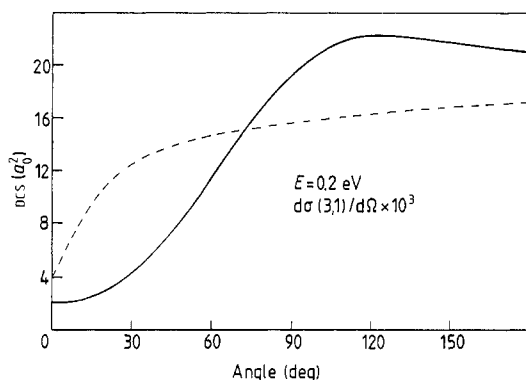

Figure 3. Angular distribution for the $1 \rightarrow 3$ transition at an incident energy $E = 0.2$ eV: ——, off-shell results of the present theory; ————, close-coupling results of Morrison *et al* (1984).

a simple qualitative level. The two curves in this figure have, in fact, been calculated using different static and exchange potentials and such differences cannot be compensated by a simple scale factor (as we have done for total cross sections) over the whole angular range. In particular, Morrison and co-workers have approximated the non-local exchange potential by a local electron-gas approximation, whereas in the present calculations exchange has been treated exactly. One should then expect that such different treatments of this effect should deeply influence the angular distributions, in the corresponding numerical results. With all the above limitations in mind, it is then comforting to see, from figure 3, that the qualitative features of the two curves are rather similar, which is essentially a clear indication of the fact that both refer to closely related physical contents. Similar conclusions can be drawn from an analysis of $0 \rightarrow 2$ differential cross sections, plotted in figure 4, for energies of 0.047 and 0.1 eV, respectively. In particular, at the higher of these two energies, the off-shell results, at first lower than CC, cross the corresponding curve around 70 deg, and dominate over the remaining portion of the angular range. This leads to compensating effects in the evaluation of the total cross section, which is therefore very close to the CC value, as shown in table 2. At the lower energy, instead, the off-shell curve tends to dominate over the CC values, for the whole angular range, thus leading to a total cross section, at $E = 0.047$ eV, higher than in the CC computations.

We wish to conclude this section by pointing out that, if necessary, one could next introduce into the computations, with limited extra numerical efforts, the first few corrective terms involving the nuclear motion $\hat{C}$ operator, present on the RHS of (3). We believe, anyway, on the basis of the previous results, that such quantities will not be required and that the present off-shell formlism may constitute a satisfactory approach to the dynamics of rotational processes.
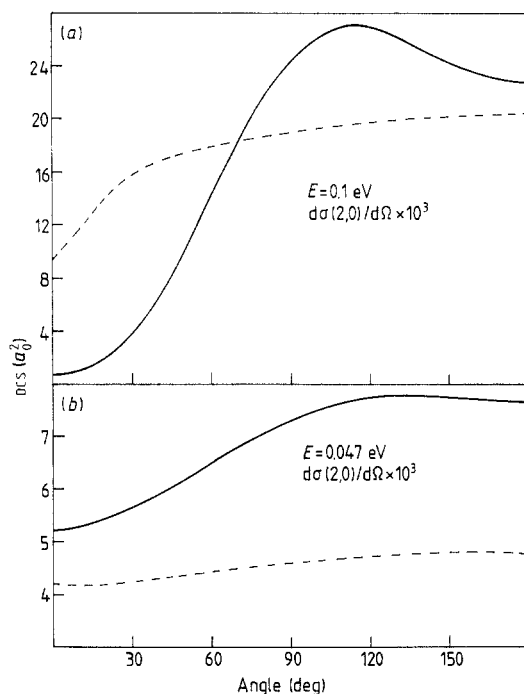
Figure 3. Angular distributions for the $0 \to 2$ transition at incident energies (a) $E = 0.047$ eV, and (b) $E = 0.1$ eV, respectively: ———, off-shell results of the present theory; ————, close-coupling results of Morrison *et al* (1984).

4. Summary

In this paper we have analysed, in some detail, the threshold behaviour of rotational excitation cross sections, for the $e^- - H_2$ system. We have applied, for this purpose, the lowest-order form of a recently suggested theory (Ficocelli Varracchio 1981a, b), that represents a generalisation of the conventional AN approximation. The main numerical step of this formalism involves the determination of an off-shell fixed-nuclei T matrix, explicitly involving the initial and final energies of the electron, for the rotational transition considered. Such a quantity can most conveniently be obtained by solving directly for the (body-frame) integral equation obeyed by the T matrix of interest, rather than for the total system wavefunction. We have used, for this purpose, a scheme of solution (Mongan 1969) that essentially amounts to considering a suitable discretisation of the momentum space integral equation for the body-frame T matrix. This leads to a non-iterative solution for the quantities of interest, according to a matrix formulation, whose dimensionalities are directly related to the total number of coupled angular momenta, and are not influenced by the presence of exchange terms. We believe that the present numerical approach could be easily extended, with some minor modifications, to the evaluation of off-shell T matrices also for molecular targets involving a higher number of electrons.

Our numerical analysis of total cross sections has pointed out that, contrary to the conventional AN approximation, the present theory correctly goes to zero at threshold, as in exact CC calculations. This aspect has been related to the energy dependence of

the off-shell T matrix, in the FBA (supposedly valid at threshold), that has been shown to be identical to the exact CC formulation. Besides, the AN approximation and the present theory have been shown to differ up to energies quite a few times that of threshold, as already pointed out by Morrison in an exact CC treatment of this problem. We have next attempted a semiquantitative comparison of our data with results available in the literature, by suitably 'scaling' our cross sections, in order to account for the different interaction potentials adopted in the computations considered. This has shown, in particular, that the off-shell theory favourably compares with exact CC calculations. Total cross sections are, besides, generally similar to those obtained in the EMA scheme, but an analysis of the angular distributions has pointed out that the present theory is more likely to be in better agreement with an exact CC theory.

In summary, we believe that the off-shell theory analysed in this paper may represent a very convenient generalisation of fixed nuclei models of e^-–molecule collisions. As for the higher-order terms of the present formalism, it is unlikely, in our opinion, that these will be needed for a numerical treatment of the rotational excitation problem. Anyway, these terms could be easily included, if necessary, and would certainly be required for a consideration of resonant mechanisms, in vibrational energy transfers, a problem that is presently under investigation.

Acknowledgments

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