COMPUTATIONAL TESTS OF THE FACTORIZATION OF CROSS SECTIONS IN THE SUDDEN APPROXIMATION

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The factorization expressions for cross sections reported by Goldflam, Green and Kouri and independently by Khare are tested using accurate close coupling input for $e^- + H_2$, $H + H_2$, $He + (HF, DF, HCl, DCl)$ and $Ar + N_2$. The results at the degeneracy averaged cross section level are used to illustrate accuracy criteria given for the factorization. Effects studied include variation of the projectile reduced mass, influence of initial and final rotor state, collision energy and potential anisotropy.

1. Introduction

Recently, it has been shown by Goldflam, Green and Kouri [1,2] that within the infinite order sudden (IOS) approximation, see, e.g., ref. [3] +, all cross sections are expressible as sums of products of system independent coefficients containing detailed state-to-state information and system dependent coefficients containing all dependence on detailed dynamics. For general degeneracy averaged cross sections (both integral and differential), these dynamical coefficients are simply cross sections for scattering out of the $j = 0$ rotor state. Independently, Khare [6] has considered the l_z-conserving energy sudden (ES) approximation and has obtained essentially the same type of factorization of cross sections. This result indicates that the factorization does not depend on the centrifugal sudden (CS) part [7,8] of the IOS and therefore suggests an even wider range of validity for the factorization [1–3]. Similar factorizations of ordinary cross sections have been obtained in various

ways by several authors [9]. The results are potentially useful for a variety of applications, including synthesis of the complete matrix of cross sections when only a single column of cross sections is given. This single column of cross sections could in principle be gotten from experiment, quantal calculations, classical or semiclassical methods, etc.

In this paper, we suggest simple quantitative tests for predicting whether the factorization is expected to be accurate. Three effects are considered. These are (a) energy effects such as the role of total energy and rotational spacings (b) effects of the potential anisotropy and (c) the effect of the reduced mass of the projectile. The last of these does not appear to have been included in earlier test criteria and we find it to be of considerable importance. In order to illustrate these effects, we have analysed results of some exact close coupling (CC) studies of the systems $e^- + H_2$ [10], $H + H_2$ [11], $He + (HF, DF, HCl, DCl)$ [12] and $Ar + N_2$ [13]. We have used the CC results for the $0 \rightarrow j$ transitions as the basic dynamical input and compared the factorization predictions with the CC results for general $j \rightarrow j'; j, j' \neq 0$ transitions. The results are encouraging and indicate the factorization can be quite useful in predicting the full matrix of cross sections from limited dynamical calculations, provided the accuracy test criteria are satisfied.

2. Brief summary of the factorization equations

In this paper, we shall restrict our attention to degeneracy averaged state-to-state integral cross sections. Then it has been shown that the degeneracy averaged cross section $\sigma(j_i \rightarrow j_f)$ from state j_i to state j_f is [1,2,6]

$$\sigma(j_i \rightarrow j_f) = (k_0/k_{j_i})^2 (2j_f + 1)$$

$$\times \sum_j \begin{pmatrix} j_i & j & j_f \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma(0 \rightarrow j), \tag{1}$$

where k_0, k_{j_i} are the wavenumbers for the states $j' = 0$ and $j' = j_i$ resepctively. $\sigma(0 \rightarrow j)$ is the degeneracy averaged integral cross section to state j from state $j = 0$, the sum over j is between the limits

$$|j_f - j_i| \leqslant j \leqslant j_{max}, \tag{2}$$

j_{max} is either the highest open rotor state or $j_f + j_i$ (whichever is lower), and $(:::)$ is the usual 3-j symbol (see, e.g. ref. [14]).

The ratio $(k_0/k_{j_i})^2$ arises when one requires that detailed balance be satisfied. The wavenumbers are given by the usual relation

$$E = \hbar^2 k_0^2/2M, \tag{3}$$

$$= (\hbar^2 k_{j_i}^2/2M) + B j_i(j_i + 1), \tag{4}$$

where E is the total energy, B is the rotational energy constant for the target and M is the reduced mass of the projectile relative to the diatom center of mass.

The energy sudden approximation basically assumes that the collision time is short compared to the target rotation time. Given a suitable rotation velocity of the target V_{rot}, and projectile velocity V_{proj}, the sudden condition requires that

$$V_{rot}/V_{proj} \ll 1. \tag{5}$$

We shall take for V_{rot} and V_{proj} the expressions

$$V_{rot} = \tfrac{1}{2} |[2B j_f(j_f + 1)/\mu]^{1/2} - [2B j_i(j_i + 1)/\mu]^{1/2}|, \tag{6}$$

$$V_{proj} = \{ [2E - B\{j_f(j_f + 1) + j_i(j_i + 1)\}]/M \}^{1/2}. \tag{7}$$

Here, μ is the reduced mass of the diatom. Thus, if both j_f and j_i are small, V_{rot} will be small and as E gets larger, eq. (5) is well satisfied. As $|j_f - j_i| = \Delta j$ increas-

es, eq. (5) eventually is violated. Explicitly, for A + BC, the reduced masses M and μ are given by

$$M = m_A(m_B + m_C)/(m_A + m_B + m_C), \tag{8}$$

and

$$\mu = m_B m_C/(m_B + m_C). \tag{9}$$

Then eq. (5) can be expressed as

$$\lambda_M \lambda_E \ll 1, \tag{10}$$

where the mass dependent parameter λ_M is given by

$$\lambda_M = [m_A/m_B m_C(m_A + m_B + m_C)]^{1/2}(m_B + m_C), \tag{11}$$

and the energy dependent parameter λ_E is

$$\lambda_E = \frac{|[j_f(j_f + 1)]^{1/2} - [j_i(j_i + 1)]^{1/2}|}{\{E/B - \tfrac{1}{2}[j_f(j_f + 1) + j_i(j_i + 1)]\}^{1/2}}. \tag{12}$$

We note that low j_f and j_i tend to make λ_E small, as does also large E and small B. Thus, λ_E is consistent with the usual qualitative statements regarding the validity of the ES approximation. Furthermore, the new parameter λ_M will be small when m_A is small compared with $m_B + m_C$. Further, for a given BC molecule, it is clear that eq. (10) is better satisfied as the projectile mass m_A decreases.

In addition to the energy and mass effects, there will also be a dependence of the accuracy of the ES on the strength of the anisotropy of the potential. For example, when the potential is spherically symmetric, only elastic transitions are allowed and one finds that $\sigma(j \rightarrow j)$ at energy E' is essentially equal to $\sigma(0 \rightarrow 0)$ at the energy $E = E' + Bj(j + 1)$. This is because, with a spherical potential, the sole effect of a nonzero j is to change the relative kinetic energy. However, as shown by Secrest [3], by Goldflam, Green and Kouri [1,2], and by Khare [6], the IOS and ES use a closure over all rotor states such that the energetically closed states are not treated properly. For potentials that cause significant virtual excitations, the ES will break down. Such virtual excitations will be most important for the highest open rotor states and become increasingly important as the potential is made more anisotropic. In addition, if the potential has an extremely long ranged tail which contributes significantly to the excitation process, then the ES approximation suffers. This is because the collision duration increases with the range of the potential and it permits

the rotor to move significantly (and therefore change its orientation) before the collision is over. This leads to a loss of suddenness.

In order to define a quantitative test parameter for this effect, it is convenient to analyse the potential in the usual Legendre expansion

$$V(R, \theta) = \sum_{l=0}^{L} V_l(R) P_l(\cos \theta), \qquad (13)$$

where

$$V_l(R) = \tfrac{1}{2}(2l+1) \int_0^\pi d\theta \sin \theta \, P_l(\cos \theta) V(R, \theta). \quad (14)$$

Then $V_0(R)$ is the spherically symmetric part of the potential and the $V_l(R)$, $l = 1, 2, ...$ measure the importance of various anisotropic contributions. If we could associate an "importance number" A_l to each $V_l(R)$, then we could say that the factorization will be better the larger A_0 is in comparison with the other A_l values. Then we could define λ_S by

$$\lambda_S = \left(\sum_{l=1}^{L} A_l / A_0 \right), \qquad (15)$$

along with the validity condition

$$\lambda_S \ll 1. \qquad (16)$$

For short range potentials (which will be our primary concern here), the $V_l(R)$ are often approximated by exponentials of R:

$$V_l(R) = a_l \exp(-R/\alpha_l). \qquad (17)$$

In this case, we can take our A_l to equal the a_l in eq. (17). Then it is straightforward to calculate λ_S prior to any scattering calculations.

In the next section, we describe the use of eq. (1) to analyse a number of CC results. The systems studied are chosen to illustrate the test parameters λ_M, λ_E, and λ_S.

3. Numerical tests

We now turn to discuss the numerical results obtained for a variety of systems chosen to illustrate the validity criteria. The basic input required in eq. (1) is the $\sigma(0 \rightarrow j)$ for a sufficient number of j values. We shall use accurate close coupling (CC) results for these cross sections. Then as shown by Khare [6], the validity of the factorization will depend not on whether the CS approximation is valid but rather only on the ES approximation. The systems to be studied are $e^- + H_2$, $H + H_2$, $He + (HF, DF, HCl, DCl)$ and $Ar + N_2$. In table 1 we give the values of the accuracy parameters λ_M and λ_S, along with the rotational energy constant B_e, the diatom reduced mass and the projectile reduced mass. The asymmetry parameters λ_S were calculated only for the family of systems $He + (HF, DF, HCl, DCl)$ using the model potential surfaces of Collins and Lane [12]. In reporting our results, we designate with an asterisk results which were obtained using an incomplete set of CC input cross sections $\sigma(0 \rightarrow j)$.

3.1. Mass effects

To illustrate the effect of the projectile reduced mass, we chose to compare factorization results for two systems having the same λ_E values (i.e., at the

Table 1
Rotation constants and energy independent validity parameters for the considered systems [a]

System	Diatomic rotation constant (eV)	M	μ	λ_M	λ_S
$e^- - H_2$	7.3471×10^{-3}	5.446×10^{-4}	0.50	0.0330	–
$H - H_2$	7.3471×10^{-3}	0.666	0.50	1.155	–
$He - HF$	2.5960×10^{-3}	3.333	0.95	1.873	0.4227
$He - DF$	1.3633×10^{-3}	3.360	1.810	1.363	0.6129
$He - HCl$	1.3116×10^{-3}	3.605	0.9726	1.925	5.318
$He - DCl$	6.7485×10^{-4}	3.614	1.893	1.382	6.213
$Ar - N_2$	2.4921×10^{-4}	16.470	7.0035	1.534	–

[a] All mass units are in gram/mole.

Table 2
Total cross sections for H + H$_2$ in A^2

$j_i \rightarrow j_f$	$E = 0.5$ eV		$E = 1.0$ eV		$E = 1.5$ eV	
	a)	b)	a)	b)	a)	b)
$2 \rightarrow 2$	41.3	46.48	38.6	42.11	36.7	39.6
$2 \rightarrow 4$	0.63	2.30	1.75	2.81	1.70	2.45
$2 \rightarrow 6$	0.0004	0.052	0.046	0.210*	0.068	0.163*
$4 \rightarrow 4$	43.3	59.85	40.4	46.97*	38.3	42.47*
$4 \rightarrow 6$	0.014	2.62	0.48	2.77*	0.83	2.32*

a) Chu and Dalgarno [10].   b) Factorization

same total energy and the same target molecule) but with quite different values of λ_M. The systems chosen were [10,11] e$^-$ + H$_2$ and H + H$_2$. In table 1, we see that λ_M for e$^-$ + H$_2$ is orders of magnitude smaller than for H + H$_2$. In tables 2 and 3 are given the factorization results. Even though a number of the results were obtained with incomplete input ($\sigma(0 \rightarrow 8)$ and $\sigma(0 \rightarrow 10)$ missing for e$^-$ + H$_2$ and $\sigma(0 \rightarrow 6)$ and $\sigma(0 \rightarrow 8)$ for H + H$_2$) we do not believe they will significantly alter the results. These cross sections are quite small at the energy of interest. We also note that the input values $\sigma(0 \rightarrow j)$ for e$^-$ + H$_2$ were computed at a constant value of kinetic energy. In eq. (1), this was taken into account by replacing the factor $k_0^2/k_{j_i}^2$ by one. In table 2, it is seen that the factorization results for H + H$_2$ are in only fair agreement with exact CC results for the elastic $j \rightarrow j$ transitions. The agreement is worse in H + H$_2$ for the inelastic transitions. By contrast, in table 3 we see that both elastic and inelastic transitions are quite well described by the fac-

torization for e$^-$ + H$_2$. It is important to realize that the e$^-$ + H$_2$ system is very poorly described by the IOS since the CS approximation breaks down badly in this system [15]. Thus, the present results also very nicely illustrate the dependence of the factorization only on the ES approximation. In summary, the results in tables 2 and 3 are a strong indication of the usefulness of the λ_M parameter for the accuracy of the factorization and also illustrate the dependence of factorization only on the ES.

3.2. Initial and final state dependence

To illustrate the variation of accuracy of factorization with initial and final state, we have chosen to study the Ar + N$_2$ system using the CC results of Pack [13]. In table 4 we compare the CC and factorization results for some inelastic transitions. The elastic transitions were not calculated since they are dominated by $\sigma(0 \rightarrow 0)$ and the CC results for this transition are not

Table 3
Total cross sections for e$^-$ + H$_2$ in A^2

$j_i \rightarrow j_f$	$(\hbar^2/2M)k^2 = 0.408$ eV		$(\hbar^2/2M)k^2 = 1.225$ eV		$(\hbar^2/2M)k^2 = 2.041$ eV	
	a)	b)	a)	b)	a)	b)
$1 \rightarrow 1$	49.36	49.34	51.87	51.85	52.25	52.23
$1 \rightarrow 3$	0.314	0.339	0.864	0.887	1.491	1.516
$1 \rightarrow 5$	1.4×10^{-6}	$2.0 \times 10^{-6}*$	1.90×10^{-5}	$2.03 \times 10^{-5}*$	6.38×10^{-5}	$6.67 \times 10^{-5}*$
$2 \rightarrow 2$	49.29	49.27	51.70	51.68	51.96	51.94
$2 \rightarrow 4$	0.253	0.291*	0.719	0.761*	1.260	1.299*
$3 \rightarrow 3$	49.27	49.26*	51.66	51.65*	51.90	51.89*
$3 \rightarrow 5$	0.210	0.269*	0.648	0.704*	1.149	1.203*

a) Lane and Geltman [9].   b) Factorization.

Table 4

Total cross-sections for the Ar–N$_2$ system at 0.06618 eV; dependence on initial and final rotational states

Transition	Cross section		λ_E	Error (%)
	a)	b)		
$2 \rightarrow 4$	14.4	14.77	0.13	2.6
$2 \rightarrow 6$	10.5	10.04	0.26	4.4
$2 \rightarrow 8$	6.6	6.63	0.40	0.5
$2 \rightarrow 10$	1.86	2.75	0.56	47.8
$4 \rightarrow 6$	12.8	13.10	0.13	2.3
$4 \rightarrow 8$	7.9	7.95	0.27	0.6
$4 \rightarrow 10$	3.5	5.37*	0.42	53.4
$6 \rightarrow 8$	11.0	13.05*	0.14	18.6
$6 \rightarrow 10$	5.9	7.81*	0.29	32.4
$8 \rightarrow 10$	10.8	14.45*	0.15	33.8

a) Pack [11].   b) Factorization.

given in Pack's paper [13]. Also $\sigma(0 \rightarrow 14)$ is not given so some inelastic cross sections are obtained with an incomplete set of $\sigma(0 \rightarrow j)$ (however, we expect the contribution of $\sigma(0 \rightarrow 14)$ to be very small). In addition to the cross sections, we give the value of λ_E in table 4 and the percent error defined by

$$\text{error} = \frac{|\sigma_{cc} - \sigma_{factored}|}{\sigma_{cc}} \times 100, \qquad (18)$$

We note that for a fixed j_i, the results become worse as $|j_i - j_f|$ becomes larger. In addition, for a fixed value of Δ_j, the results become worse as j_i, j_f are larger. (We note that the results are not totally consistent since, e.g., the result for $\sigma(2 \rightarrow 8)$ is unexpectedly accurate. This is probably fortuitous.) The results do appear to correlate reasonably well with λ_E values. Physically, the higher j-values correspond to shorter rotation times and therefore to less sudden collisions.

3.3. Effect of potential asymmetry

To study the influence of the potential asymmetry, we have used the CC results of Collins and Lane [12] for the He + (HF, DF, HCl, DCl) collision systems. The factorization results are compared to CC in table 5. The transitions included are $\sigma(1 \rightarrow 2)$, $\sigma(1 \rightarrow 3)$ and $\sigma(2 \rightarrow 3)$ at several energies. In addition, we indicate the value of the combined validity parameter $\lambda_M \lambda_E$. The first feature which is evident is the fact that at higher energies, the product $\lambda_M \lambda_E$ is smaller and gen-

Table 5

Total cross sections for the systems He + (HF, DF, HCl, DCl); energy dependence parameters

System energy (eV)	$\sigma(1 \rightarrow 2)$			$\sigma(1 \rightarrow 3)$			$\sigma(2 \rightarrow 3)$		
	a)	b)	$\lambda_M \lambda_E$	a)	b)	$\lambda_M \lambda_E$	a)	b)	$\lambda_M \lambda_E$
He–HF									
0.017	0.7	3.65	1.22	–	–	–	–	–	–
0.025	2.6	4.21	0.82	–	–	–	–	–	–
0.050	5.9	5.85	0.51	0.8	1.74	1.11	3.3	6.78	0.60
0.100	7.8	7.00	0.34	2.8	2.85*	0.69	7.0	6.82*	0.36
He–DF									
0.025	1.8	0.71	0.37	0.5	0.67	0.83	0.8	0.72	0.45
0.050	3.1	2.27	0.25	1.6	1.52*	0.51	2.2	1.99*	0.26
0.100	4.4	3.80	0.17	3.1	2.53*	0.34	3.8	3.17*	0.17
He–HCl									
0.015	8.8	7.43	0.73	–	–	–	–	–	–
0.025	10.1	8.73	0.51	2.1	2.21	1.14	7.5	9.93	0.62
0.050	10.6	9.14	0.34	6.2	5.26*	0.71	10.1	8.77*	0.36
He–DCl									
0.015	6.6	5.08	0.34	1.0	0.66*	0.73	4.0	4.75	0.39
0.025	7.4	6.12	0.25	2.1	1.46*	0.52	5.5	5.09*	0.26
0.050	7.6	6.77	0.17	4.3	3.02*	0.35	6.4	5.25*	0.17

a) Collins and Lane [11].   b) Factorization.

erally better agreement is obtained. However, this is only a general trend and isolated counter examples can be seen in table 5. (For instance, in the case of $\sigma(1 \to 2)$ for He + HF, the result at 0.05 eV is surprisingly good. This is likely fortuitous.)

Using the potentials as given by Collins and Lane [12], we have calculated the λ_S using the short range parameters. It is seen that the λ_S indicate that the two fluoride molecules are more isotropic than the chloride molecules. We see in table 5 that the factorization appears to work better for HF and DF than for HCl and DCl. However, again things are not completely clear cut and in about 1/3 of the transitions studied, the factorization results were actually better for the HCl and DCl systems. This is somewhat surprising in view of what appears to be a large difference in anisotropy between the two systems. A possible explanation of the results may be that as the collision energy increases, the role of potential anisotropy decreases. Furthermore, due to the smaller B_e constant for HCl (DCl) compared to that for HF(DF), the $\lambda_M \lambda_F$ product for the chloride molecules is smaller than for the fluorides. Thus, one may be seeing results of a competition between the mass—energy and potential anisotropy effects.

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