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Quantum-mechanical impulse approximation for vibro-rotational excitation in atom-diatom collisions

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The quantum-mechanical impulse approximation (IA) has been successfully applied to vibrational and rotational excitation in atom–diatomic-molecule collisions. An additional closure approximation used previously to calculate total vibrational transition probabilities is discussed. A comparison with exact IA calculations shows that the closure approximation overestimates large vibrational transitions. This discrepancy is due to the fact that the vibrational transitions are accompanied by large rotational excitations.

Applications of the quantum-mechanical impulse approximation[1] (IA) to inelastic molecular collisions were formerly restricted to the case of collinear vibrational excitation.[2] Recently, the IA has been applied to three-dimensional atom–diatomic-molecule collisions by Bogan[3] and by Eckelt, Korsch, and Philipp.[4–6] Eckelt *et al.* calculated differential cross sections for vibrational and rotational excitation for homonuclear molecules[4] ($N_2 + Li^+$ and $H_2 + H^+$) and for heteronuclear molecules[5] ($CO + Li^+$). Bogan used the IA to evaluate total vibrational transition probabilities for $CO + O$ collisions.[3] It is the aim of the present paper to discuss the approximations made by Bogan in addition to the IA.

In the IA the differential cross section for transition from vibrational-rotational state (n, l) to state (n', l') is given as a superposition of two scattering amplitudes, which describe the scattering of the impinging atom A by only one of the molecular atoms B and C, while the other atom acts as a spectator[3,4]:

$$\frac{d\sigma}{d\Omega}(n'l' \leftarrow nl;\theta) = \frac{k'}{k}\frac{1}{2l+1}\sum_{m,m_0} |f_B(\vec{k}', \vec{k}) + f_C(\vec{k}', \vec{k})|^2 . \tag{1}$$

(We use the center-of-mass system throughout this paper.) $\vec{k}$ ($\vec{k}'$) is the initial (final) relative momentum of atom A. Because of summation and averaging over the magnetic quantum numbers m' and m, the differential cross section depends only on the scattering angle θ, and not on the azimuthal angle φ. The scattering amplitudes f_B and f_C decompose into an off-shell scattering amplitude for free scattering by one of the atoms, and a target form factor (TFF) (or bound-state form factor):

$$f_B(\vec{k}', \vec{k}) = (\mu_r/\mu_{AB})\tilde{f}((\mu_{AB}/\mu_r)\vec{k} + \vec{q}, (\mu_{AB}/\mu_r)\vec{k}) \times F_{n'l'm',nlm}(m_C\vec{q}/(m_B + m_C)) , \tag{2}$$

and a similar equation for f_C. m_A, m_B, m_C are the masses of the atoms A, B, C, and the reduced masses are given by

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \quad \text{and} \quad \mu_r = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} ;$$

$\vec{q} = \vec{k}' - \vec{k}$ is the momentum transferred in the collision.

Equation (2) is derived by Bogan.[3] Eckelt *et al.*[4,5] give the same formula, apart from a slightly different choice of the arguments of the off-shell amplitude $\tilde{f}$, which treats the initial and final channels more symmetrically (see the discussion in Ref. 4). In this note we will concentrate on the TFF. The further treatments of the TFF in Refs. 3 and 4 are quite parallel; summation and averaging over the magnetic quantum numbers m' and m are performed analytically:

$$\begin{aligned} F^2_{n'l',nl}(\kappa) &= \frac{1}{(2l+1)}\sum_{m',m} |F_{n'l'm',nlm}(\vec{\kappa})|^2 \\ &= (2l'+1)\sum_{\lambda}(2\lambda+1)\left|\begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0\end{pmatrix} f^{(\lambda)}_{n'l',nl}(\kappa)\right|^2 , \end{aligned} \tag{3}$$

with $\kappa = |\vec{\kappa}|$. The radial form factors $f^{(\lambda)}_{n'l',nl}$ are given by

$$f^{(\lambda)}_{n'l',nl}(\kappa) = \int_0^\infty \chi^*_{n'l'}(y) j_\lambda \frac{\kappa y}{\hbar} \chi_{nl}(y) y^2\, dy , \tag{4}$$

where χ_{nl} is the radial wave function of the molecule. The radial wave functions are approximated by harmonic-oscillator wave functions. The vibrorotational energy eigenvalues are in this approximation

$$\epsilon_{nl} = (n + \tfrac{1}{2})\hbar\omega + l(l+1)B , \tag{5}$$

where B is the rotational constant.

Eckelt *et al.*[4] calculate the differential cross section for vibro-rotational excitation at fixed scattering angle as a function of the transferred energy (so-called "energy-loss spectra"), while Bogan[3] makes no use of the possibility to calculate detailed transition cross sections and introduces the following approximation in addition to the IA: Bogan argues, that the dependence of ϵ_{nl} upon l is weak, and approximates the energies in Eq. (5) by the vibrational term only. In this approximation

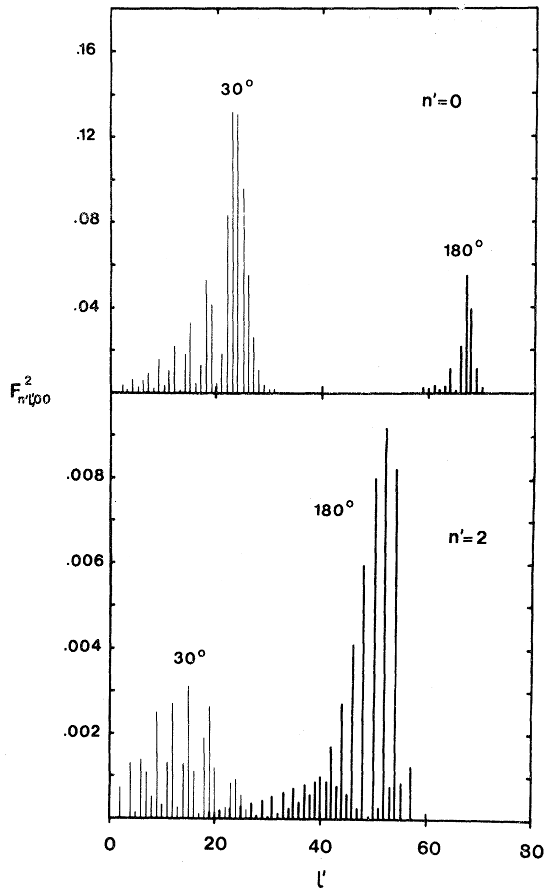

FIG. 1. Target form factor (TFF) for vibrational-rotational excitation from the ground state $(0,0) \rightarrow (n',l')$ for oxygen-carbon collisions in the CO + O collision system. The l' dependence shows the dominance of large rotational transitions in the vibrationally elastic ($n'=0$) and inelastic ($n'=2$) cases. Two typical scattering angles are chosen ($\theta = 30°$ and 180°), and the center-of-mass collision energy is 1.32 eV.

the transferred momentum $\vec{q}$ is independent of the rotational quantum numbers. This closure approximation makes it possible to perform the l' summation of the TFF in Eq. (3) analytically:

$$\sum_{l'} F^2_{n'l',nl}(\kappa) \approx \frac{\gamma(n'+\frac{1}{2},\kappa^2)}{2n'!\kappa}, \qquad (6)$$

where γ is the incomplete gamma function. By integrating over the scattering angle, Bogan evaluates the total vibrational transition probabilities.

The neglect of the rotational term in Eq. (5) is a good approximation, if only small rotational transitions occur with considerable intensity. This assumption has not yet been proved, either theoretically or experimentally, at least in the case of relatively heavy molecules like CO or N_2. If the collision is dominated by rotational energy transfers as large as $\hbar\omega$, the approximation based on the neglect of the rotational term in Eq. (5) can introduce significant errors. Here we want to point out that in the IA the rotational transitions are by no means negligible. The vibrationally elastic and inelastic processes are coupled with very large rotational transitions. This behavior is pronounced in the backward direction, which is especially important for vibrational transitions. For backward scattering we found that rotational energy transfers as large as several vibrational quanta $\hbar\omega$ are dominant.[4]

In order to demonstrate the l' dependence of the TFF we calculated the m-averaged and m'-summed TFF given in Eq. (3). We used the CO + O data of Ref. 3 and a typical collision energy $E = 1.32$ eV in the center-of-mass system (this gives a collision velocity of $V = 5$ km/sec in the laboratory system used by Bogan[3]). The molecule is in the ground state initially ($n = l = 0$). Figure 1 shows the TFF for carbon-oxygen collision as a function of the final rotational quantum number l' for different final vibrational quantum numbers ($n'=0, n'=2$) and two typical scattering angles $\theta = 30°$ and $\theta = 180°$. The dominance of large rotational transitions is clearly seen. As a justification of his

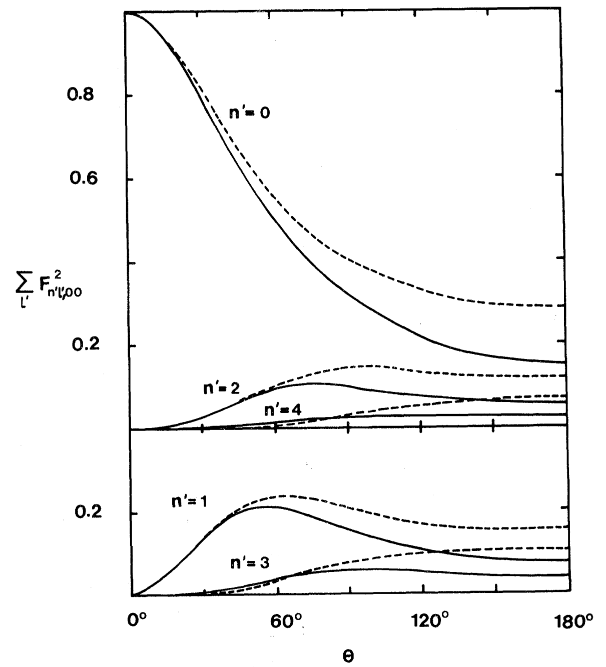

FIG. 2. Target form factors summed over the final rotational quantum number l'. The exact IA results (full lines) and Bogan's prediction given in Eq. (6) (dashed lines) for all accessible vibrational states n' are compared. The collision system and the collision energy are the same as in Fig. 1.

TABLE I. Total vibrational excitation probabilities for oxygen-oxygen ($P^{(\mathrm{O})}_{0\to n'}$) and oxygen-carbon ($P^{(\mathrm{C})}_{0\to n'}$) collisions. Comparison of the closure approximation given by Bogan (Ref. 3) (CA) with exact IA results. Collision energy: 1.32 eV.

	$P^{(\mathrm{O})}_{0\to n'}$		$P^{(\mathrm{C})}_{0\to n'}$	
n'	CA	IA	CA	IA
0	8.119−1	8.424−1	7.497−1	7.898−1
1	1.196−1	1.041−1	1.354−1	1.218−1
2	4.888−2	3.925−2	6.954−2	5.710−2
3	1.647−2	1.215−2	3.393−2	2.451−2
4	3.093−3	2.146−3	1.139−2	6.806−3

approximation, Bogan argues that the TFF vanishes for large l' (in the case $l=0$).[3] This is correct in principle, but the breakdown of the TFF appears at values of l' large enough to reach the region of vibrational excitation. At $\theta=180^\circ$ ($n'=0$), for example, the maximum of the l' distribution appears at $l'=68$. This corresponds to an energy transfer of 1.12 eV (for comparison, the threshold energy for vibrational transition to the first excited state is 0.27 eV, corresponding to $l'=33$). The above considerations have shown the dominance of large rotational transitions, so that the neglect of the rotational energy transfer is not justified. Especially the rotational dependence of the scattering amplitude $\bar{f}$ must be taken into account, so that the l' summation of the TFF in Eq. (6) cannot be performed separately.

Apart from the question of the l' dependence of f we finally want to make some comments concerning the l' sum of the TFF alone. Figure 2 shows a comparison of the exact TFF summed over l' and Bogan's prediction given in Eq. (6). At small scattering angles, where the rotational energy transfers are small, excellent agreement is found, as expected. But vibrational transitions are predominantly produced in the case of large-angle scattering, and in this case Bogan's approximation is worse: with increasing scattering angles we found increasing discrepances, which are due to the large rotational energy transfers dominating at these scattering angles. The discrepancies are especially pronounced for large vibrational transitions: for $n'=4$ and $\theta=180^\circ$ the exact value of the sum is 0.02, while Bogan's approximation gives 0.07, which is too large by a factor of 3. As can be seen from Fig. 2, Bogan's approximation overestimates large vibrational transitions. In order to get a quantitative estimate of the error introduced by this approximation in the evaluation of the total vibrational excitation probabilities, we computed exact IA excitation probabilities, using exactly the same approximation to the off-shell scattering amplitude $\bar{f}$ as Bogan. In Table I, the results for oxygen-oxygen and oxygen-carbon collisions are compared with the approximate values given by Bogan.[3] With increasing final vibrational quantum number n' we find increasing discrepancies and a clear overestimation of large vibrational transitions, as expected.

To summarize, the main purpose of this comment is to demonstrate the dominant large rotational transitions (occurring at least in the framework of the IA). This restricts the value of approximations based on the assumption of only small rotational transitions. It was discussed that in order to calculate total vibrational transition probabilities the product of the two-body scattering amplitude $\bar{f}$ and the TFF should be summed over l'. Apart from this, it was shown that Bogan's approximation overestimates large vibrational transitions.

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[1] See, for instance, G. F. Chew, Phys. Rev. 80, 196 (1950); and J. P. Coleman, in *Case Studies in Atomic Collision Physics*, edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1969), Vol. 1, p. 99–167.

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