Rotationally Inelastic, Classical Rigid Shell Scattering

The Influence of Initial Rotation

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Rotationally inelastic atom-diatom collisions at wide angles and energies large compared to the attractive potential well depth are approximately described by classical scattering of structureless particles and rigid rotor molecules interacting by a rigid potential shell of \( C_{\infty v} \) symmetry. The double differential cross section for deflection and rotational energy transfer is analytically related to the geometry of the shell. In continuation of previous work the influence of molecular rotation before collision is considered. It is found: The conspicuous structure of bulge scattering or orientational rainbows in this cross section persists, but is modified by initial rotation. The modifications are angle dependent. The (classical) information of bulge scattering on the anisotropy of the potential is increasingly averaged out by higher initial rotation. In experiments exploiting this new probe to the anisotropy of the repulsive molecular interaction initial rotation should be kept as low as possible.

I. Introduction

The observation of the bulge effect or orientational rainbows in collisions of \( K+N_2, C^{16}O, C^{18}O \) \([1, 2]\), \( Na_2+He, Ne, Ar \) \([3-6]\), \( K+O_2 \) \([7]\), and probably also of \( D_2+CO \) \([8]\) has indicated that this strong, classical feature of rotationally inelastic scattering is a general, direct and sensitive probe to the anisotropy of the repulsive intermolecular potential. Its essence is in short: Let atoms and unoriented diatomic (or linear) molecules collide with momentum of relative motion \( p \) and magnitude of molecular angular momentum \( j \) sufficiently well defined. Then the distributions of excited rotation states \( j' \) or equivalently of final momenta \( p' \) at some fixed scattering angle \( \theta \) may exhibit rather sharpe bounds and a characteristic maxima structure therein \([9]\). Sufficient conditions for this to occur have been discussed \([1]\): Collisions should be (i) overwhelmingly repulsive, (ii) rotationally sudden (initially and finally) and (iii) of high (exciting) action. Experimentally these requirements may be met with by observations at \( \theta \geq 1 \) rad, low initial \( j \), collision energies above thermal up to \( E \sim 1 \) eV, and a preference for non-hydrogenic, molecular partners with small rotational quanta. Conventional translation energy loss experiments \([1, 8]\) work with molecular rotation temperatures \( T_{rot} \sim 35^\circ K \) or below before collision, i.e. \( j \leq 2.5 \) for \( N_2 \) or \( CO \), and a correspondingly narrow initial \( j \) distribution. They scan \( p' \). A resolving power of about 5 % has been sufficient to resolve the structure of bulge scattering well, but, for non-hydrogenic molecules, is not enough to distinguish individual rotational transitions. Enormously more selective pump-and-probe laser techniques have also been used \([4, 6]\). They are capable of labelling single \( j \) levels and, probing for \( j' \), resolve level-to-level transitions. While the former is highly desired to achieve well defined initial preparation, the latter is of minor importance in the study of bulge scattering. The message of this phenomenon on the repulsive anisotropy is tied to (iii), i.e. to (semi-) classical excitation with the desired information residing in collections of many ("fine-grained") quantized channels.

The description of bulge scattering has had a number of relevant preludes from which it was difficult to assess its importance \([10]\). Model calculations of two
varieties made it more evident. One [11] simply uses classical mechanics and an anisotropic, rigid shell interaction of \(C_v\) symmetry; for the special case of vanishing initial rotation, \(j=0\), it relates the geometry of the shell analytically to the double differential cross section for scattering at angle \(\beta\) and reduced recoil velocity \(u^*=p'/p\), \(J(u^*, \beta)|\beta/p=0\), i.e., to the quantity, which (ideally) is measured in translation energy loss experiments. This model is the most naive account of the non-trivial effect. Although it explains all dominant features hitherto observed, its main benefit is heuristic power deriving from analytic tractability [12]. The second kind of calculations employs semiclassical versions of the IOS approximation and more realistic potentials to obtain essentially the same type of cross section in a numerical way. The first results [13, 14] referred to an interference pattern in the \(\beta\) dependence which is related to the bulge effect, but will be more difficult to observe. It was, however, rapidly made apparent [15-17] that the method also describes the available observations, i.e., the characteristic, classical structure in the \(u^*\) or \(j'/\beta\) dependence of \(J\) and the angular halo associated with it. It has been tested for quantitative accuracy by comparison with the coupled states approximation [16]. But more stringent tests are certainly needed. Satisfying the superposition principle the method also yields a "supernumerary" interference in \(J(j', \beta = \text{const})\), some kind of which is reasonably expected as a companion of a rainbow-type phenomenon, but is beyond the reach of the former, purely classical description. The other vista of these oscillations, i.e., in \(J(j' = \text{const}, \beta)\), is the interference which had first been noticed in [13, 14]. It is found to be rapidly washed out by initial molecular rotation [17]. This and lack of experimental resolving power are the reasons why this kind of interference has not yet been observed with certainty [18].

Improvements of the latter approach have the promise of accuracy with them which will eventually be needed to use bulge scattering as a sensitive source of quantitative information on the anisotropy of repulsive intermolecular potentials. Presently, the far greater ease and the analytic nature of the classical and rigid shell approximations may still be helpful to make the relation of scattering and potential more transparent and thereby serve as a guide to new experiments or calculations. In this paper the extension of previous results [11] to the case of non-vanishing molecular rotation before collision, \(j \neq 0\), is given. Initial rotation has been finite and widely different in the available experiments. Except for the above quoted mere statement of its quenching effect on oscillations, its influence on the classical features of bulge scattering is not known. In the following Sect. II the cross section \(J(u^*, \beta)|\beta/p\) is obtained in the form of an integral containing the geometry of the rigid shell interaction, explicitly. This result is compared to that for vanishing initial rotation and further discussed in Sect. III.

II. Rigid Shell Cross Section for Finite Initial Rotation

In the following the notation and some results of Ref. 11 are used. Figure 1 depicts the simple collision dynamics of the rigid shell interaction. The incoming momentum of relative motion \(\mathbf{p} = \mu \mathbf{v} (\mu: \text{Reduced atom-rigid rotor mass}, \mathbf{v}: \text{Relative partner velocity})\) defines the positive \(x_3\)-direction of the space-fixed coordinate system \(S(x_1, x_2, x_3)\). It encounters the shell at "contact position" \(R\) with respect to the molecular center of mass. It is reflected to be \(\mathbf{p}' = \mathbf{p} + \Delta \mathbf{p}\) after collision, thereby transferring angular momentum and energy into molecular rotation. Let \(\hat{n}(R)\) be the outward normal unit vector to the shell at \(R\). Then, from the definition of a rigid shell that the transferred momentum have the direction of \(\hat{n}\), \(\Delta \mathbf{p} = \hat{n} \Delta \mathbf{p}\), from conservation of energy and angular momentum the outcome of the collision is completely determined as a function of the initial scattering asymptote \(\{b, (\chi - \alpha), \beta, \beta, \Gamma\}\). Here \(b = \{b, \chi\}\) is the 2-dimensional impact parameter, \(j = \{j, \beta, \alpha\}\) is the molecular angular momentum, these quantities being specified in plane and spherical polar coordinates, respectively, as indicated in Fig. 1. \(e = (j^2/I)/(p^2/\mu)\) is the ratio of initial rotation to translation (collision) energy, \(I\) being the moment of inertia of the molecule, and \(F\) is the phase angle of rotation at some instant on the initial asymptote. The representation of the initial asymptote by \((\chi - \alpha)\), instead of these azimuthal angles separately, reflects isotropic space, the appearance of \(e\) (or \(j/p\)) instead of \(j\) and \(p\) is a feature of the rigid shell interaction (which presupposes that also on the final asymptote reduced quantities like \(u^* = p'/p\) are used).

Classical scattering analysis requires knowledge of the deflection functions of the process, i.e., the final as a function of the initial variables, and the prescription to calculate the cross section of concern. The relations presently needed are taken from [11] to be

\[
\begin{align}
& u^* = p'/p \\
& = \left[1 - 4(\hat{n} \cdot \hat{\mathbf{p}})^2 \frac{1 - q}{1 + \mu I (R \times \hat{n})^2} \left(1 - \frac{1 - q}{1 + \mu I (R \times \hat{n})^2}\right)^\frac{1}{2}\right]^{\frac{1}{2}} 
\end{align}
(1)
\]