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Comment on "Inelastic scattering in atom-diatom molecule collisions I. Rotational transitions in the sudden approximation"*

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The purpose of this comment is to point out that the recent paper with this title by Stallcop¹ contains conflicting approximations, so that the resulting theory is not valid. In the order in which they appear, the pertinent approximations and assumptions are: (1) The semiclassical sudden approximation is used; (2) the resulting (unitary) S matrix is then approximated by a second order distorted wave expansion; (3) the rotational quantum number j of the molecule is large; (4) the impact parameter b is large enough that straight-line trajectories can be used; and (5) the long range attractive part of the intermolecular potential is neglected.

In a series of papers,^{2,3} most of which were referred to by Stallcop, we have formulated a quantum-mechanical sudden approximation and shown⁴ how to reduce it to Approximation (1), the usual semiclassical sudden approximation. By comparison of numerical results with accurate quantum mechanical close coupling calculations² and also by detailed examination of the neglected terms,³ we showed that the "centrifugal sudden"³ or " J_z -conserving"⁵ part of the sudden approximation is best at *small* impact parameters b (i. e., at small partial waves l or small total angular momentum J) and fails at large b . This centrifugal sudden approximation can be introduced explicitly using either space-fixed² or body-fixed^{3,5} axes or implicitly by averaging the potential as in Rabitz' effective Hamiltonian method⁶ or by using the b -conserving trajectories common to semiclassical methods such as those of Stallcop,¹ but it is inherent in *every* classical, semiclassical, or quantum mechanical approximate molecular collision theory which does not include coupling between different b or different l . Notwithstanding Stallcop's claims to the contrary in the following Reply,⁷ this approximation is inherent in his approximation; his attempt to prove otherwise is invalid because the equations of Lawley and Ross that he uses also contain part of the same approximation [compare with the exact Eq. (36) of Ref. 3]. Thus, Approximation (1) is valid only at *small* b . But Approximations (2) and (4) are admittedly¹ valid only at *large* b ; hence, (2) and (4) are not consistent with (1). To be more precise, the terms neglected in the centrifugal sudden approximation are of the order of the differences between the centrifugal potentials of the coupled channels, namely,

$$\frac{\hbar^2 [l'(l'+1) - l(l+1)]}{2\mu r^2} \geq \frac{\hbar^2 (l+1)}{\mu r^2} \geq \frac{\hbar b v}{r^2},$$

and the approximation neglecting these terms fails for

all b or l large enough that at the classical turning point these terms are as large or larger than the off-diagonal parts of the intermolecular potential. From this one finds that for Stallcop's model Ar-O₂ problem, (1) is only valid for $b < 3.4 \text{ \AA}$, and since Stallcop shows (see his Fig. 2) that (2) and (4) are valid only for $b > 3.4$, the approximations are not consistent for any b .

Also, the centrifugal sudden or J_z -conserving approximation has been shown³ to be best when j is *small* and to fail when j is large; hence, (3) is not consistent with (1). Finally, Approximations (4) and (5) are rarely consistent: Stallcop¹ notes that for his Ar-O₂ example system, molecular beam experiments⁸ have shown that the potential well has its minimum at an Ar-O₂ distance of about 3.9 \AA . Using the empirical⁸ 12-6 potential, one finds that the potential crosses zero at about 3.5 \AA , so that for $b > 3.5 \text{ \AA}$, collisions are dominated by the long range attractive potential and (5) is invalid. Indeed, (5) is not valid even at $b = 3.413 \text{ \AA}$, the smallest impact parameter at which Stallcop considered use of his theory justified in his Fig. 2.

Because the sudden approximation (1) (which is valid for Stallcop's Ar-O₂ problem⁹) is often qualitatively correct even when quantitatively wrong, it should be noted that when it is valid for small b , it can also be used for large b when the energy is high enough that the contribution of the large b (attractive potential) region to the cross section is small compared to the contribution of the small b (repulsive potential) region. However, in such cases it is still important to include the attractive part of the potential to cut off the repulsive potential and prevent it from giving the spurious large b contribution shown in Fig. 2 of Stallcop's paper.

Finally, it should be noted that Approximations (2)-(5) are not needed. Many authors¹⁰ have carried through calculations that use Approximation (1) only; the calculations are not expensive. Indeed, as we have pointed out, the calculation of complete quantum mechanical infinite-order sudden cross sections requires a trivial amount of computer time.^{3,9} In this connection we also note that since Stallcop's paper was submitted, Secret¹¹ and Hunter¹² have independently shown how to generalize the quantum mechanical infinite order sudden approximation^{2,3} to an infinite basis of rotational states and an arbitrary intermolecular potential, rather than the model potentials for which our derivation was valid. Their approximation is numerically even simpler than ours; it is entirely analogous to the classical sudden approximation, and the S matrix is obtained by simply computing WKB phase shifts as a

function of the intermolecular angle and doing a Gaussian quadrature over that angle.

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¹J. R. Stallcop, J. Chem. Phys. 61, 5085 (1974).

²See T. P. Tsien, G. A. Parker, and R. T. Pack, J. Chem. Phys. 59, 5373 (1973) and references therein.

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⁴R. T. Pack, Chem. Phys. Lett. 14, 393 (1972).

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⁶H. Rabitz, J. Chem. Phys. 57, 1718 (1972).

⁷J. R. Stallcop, J. Chem. Phys. 64, 1258 (1976), following comment.

⁸F. P. Tully and Y. T. Lee, J. Chem. Phys. 57, 866 (1972).

⁹For calculations testing this and other semiclassical methods against accurate quantum close coupling results for the similar system, Ar-N₂, see R. T. Pack, J. Chem. Phys. 62, 3143 (1975).

¹⁰See, for examples, Refs. 19-30 in the bibliography of Ref. 1.

¹¹D. Secrest, J. Chem. Phys. 62, 710 (1975).

¹²L. W. Hunter, J. Chem. Phys. 62, 2855 (1975).

Reply to "Comment on inelastic scattering in atom-diatom molecule collisions. I. Rotational transition in the sudden approximation"

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Pack¹ bases his criticism of the use of the semiclassical sudden approximation in paper I² upon their "centrifugal sudden" approximation. He claims that their approximation fails when the differences in the centrifugal potentials becomes as large or larger than the off diagonal parts of the potential. However, one expects, obviously, that the angular momentum channels become uncoupled (in the approach of paper I) at the limit of vanishing potentials. Lawley and Ross³ have formulated and examined rotational scattering with a body fixed coordinate system for both the time independent and time dependent case. From their results for the latter case, one finds that the equations, analogous to the semiclassical sudden approximation of paper I, can be written in the form

$$\frac{d}{dt} A_{j'\mu'} = \frac{1}{i\hbar} \sum_{j\mu} \left(\langle j'\mu' | V | j\mu \rangle - i\hbar\delta_{j'j} W_{\mu\mu'} \frac{L}{2\mu_0 R^2} \right) A_{j\mu} \quad (1)$$

$$W_{\mu\mu'} = [(j - \mu + 1)(j + \mu)]^{1/2} \delta_{\mu', \mu-1} - [(j + \mu + 1)(j - \mu)]^{1/2} \delta_{\mu', \mu+1}, \quad (2)$$

where $L = \mu_0 v b$ is the angular momentum of the relative motion. If one neglects the coupling of the molecular angular momentum with L (i. e., neglect intermultiplet transitions³ by setting the second term within the parenthesis equal to zero), then the quantum number μ is conserved because the Hamiltonian is invariant under rotation about the z axis in the body fixed coordinate system. This approximation of neglecting the Coriolis interaction in the time independent case is called " j_x conserving" by McGuire and Kouri⁴; it yields the physically displeasing situation of transitions occurring even in the limit of $V \rightarrow 0$ ⁵. Secrest⁵ has shown that the angular momentum decoupling approximations of Pack and coworkers are equivalent to this " j_x conserving"

approximation. This approximation has *not* been used in paper I. (For example, one can show that if the Eqs. (1) are solved to first order in V , but exactly with respect to the intermultiplet transitions, then the transition probability (17a) of paper I is obtained upon summing over the projection quantum numbers). Therefore, Pack's argument about the failure of the " j_x conserving" approximation at large b applies to their unusual semiclassical sudden approximation and is not relevant to the approach of paper I.

The effect of changes in the angular momentum or reorientation of the molecular symmetry axis on the classical trajectory have not been included in paper I. Physically, one expects that this is valid as long as $\Delta j\hbar/J$ and $\Delta m\hbar/J$, where $J(\sim \mu_0 v b \gg j\hbar)$ is the total angular momentum, are both small. Clearly, the fulfillment of these criterion at large b , even for a large j , is consistent with the semiclassical approximation (which is valid for large $\mu_0 v$).

From the results of Sec. III of paper I, one finds that the major contribution to the scattering comes from a very short separation interval, $b - b + \Delta R$, where $\Delta R \sim 1/4\alpha$ ($\approx 0.1 \text{ \AA}$ for Ar-O₂ collisions!); hence, it is usually not necessary to cut off the repulsive potential because of the long range attractive forces. Nevertheless one should note that the results of paper I may be directly applied to an attractive potential, as well as a repulsive one, since the transition probability does not depend upon the sign of the potential (see Sec. III).

At low velocities the rotational scattering is dominated by the long range multipole forces; but at high velocities, as pointed out in paper I, a number of potential surfaces are required to calculate inelastic scattering in atom-diatom molecule collisions. These