Projection-reduced close coupling calculations of cross sections for vibrational relaxation in collisions of diatomic molecules with atoms

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This work investigates the possibility of performing converged close coupling calculations of cross sections for vibrational relaxation in atom–diatom collisions with basis sets reduced by neglecting states with high values of angular momentum projection. The calculations for the Ar+HF system show that if the molecule is initially in the state with vibrational and rotational quantum numbers \( v = 1, j_i \), it may be possible to neglect states with projections of angular momentum greater than \( j_i \) for all rotational levels in the basis set. © 2001 American Institute of Physics. [DOI: 10.1063/1.1427025]

Despite the recent progress in computational capabilities, rigorous quantum-mechanical calculations of cross sections and rate constants for vibrationally inelastic collisions of diatomic molecules with atoms are still impossible except for a few systems involving light molecules. The time-independent close coupling (CC) approach to the problem of atom–molecule collisions is based on expansion of the total scattering wave function in terms of products of molecular translational, vibrational, and rotational functions. Substitution of this expansion in the Schrödinger equation leads to a system of second order differential equations whose dimension is equal to the number of basis functions. For typical problems of vibrational relaxation in atom–diatom collisions the basis set should include several vibrational states of the diatomic molecule each represented by a manifold of rotational levels. Every rotational level corresponding to the rotational angular momentum \( j \) is \((2j + 1)\)-degenerate and the system of differential equations to be solved becomes prohibitively large as the number of rotational states in the basis set increases. Because all states up to a certain energy limit larger than the collision energy must be included in the basis set, the CC calculation of vibrational relaxation in diatomic molecules is a formidable task even when the collision energy is small and the molecule is initially at low levels of rotational excitation of the \( v = 1 \) vibrational state. The \((2j + 1)\)-degeneracy of high rotational states of \( v = 0 \) limits computational efficiency in this case.

Various approximate decoupling schemes have been proposed as an alternative to the rigorous CC method for calculations of vibrational energy transfer in atom (A)–diatomic molecule (BC) collisions (see, e.g., Ref. 1). The most accurate of these approximations is the coupled-states (CSA) approach\(^2,3\) based on the assumption that all transitions between states with different body-fixed projections of total angular momentum can be neglected. As a result, the coupled \( 2j + 1 \) problem for each initial \( j \)-state is reduced to \( j + 1 \) independent problems. The CS approximation has been investigated and used by many researchers\(^4\) due to its simplicity and closeness to the CC method. As has been pointed out by Hahne,\(^5\) however, most of the studies mentioned employed a generally incorrect (but asymptotically valid) law of transformation between \( R \)- and \( P \)-helicity amplitudes. Thus, Eq. (24) instead of Eq. (25) of Ref. 5 must be used to transform between the two helicities and the final S-matrix contains "insufficient information to infer the detailed structure of this operator in the basis in which \( R \)-helicity is diagonal."\(^5\) The predictions as to the accuracy of the CS approximation based on examination of the initial coupling matrix can, therefore, not be generally made and the performance of the CS approach should be verified against more rigorous calculations in every particular case. Other decoupling schemes involve even more approximations and can hardly be used without prior verification of their validity.

In the present work we propose a methodology of computing cross sections for vibrational relaxation using projection-reduced CC (PR-CC) calculations that are intended to be as accurate as the full CC results but require significantly less computational effort. The method is tested on the Ar+HF collision system.

Vibrational relaxation in HF+Ar collisions has attracted considerable interest of researchers over the last two decades due to participation of HF molecules in laser systems,\(^6\) and a peculiar mechanism of vibrational energy transfer in this system\(^7,8\) leading to an inverse rotational population of HF in the ground vibrational state.\(^9,10\) Extensive coupled-states calculations of rate constants for vibrational relaxation in HF+Ar collisions have recently been compared with experimental data in a wide range of temperatures.\(^11,12\) The calculations are performed on two most recent and accurate potentials and in order to make this comparison more meaningful it is necessary to delineate the validity of the CS approximation for vibrationally inelastic HF+Ar collisions. In our previous work\(^13\) we have computed rate constants for one-quantum rotational transitions in Ar+HF collisions using the CS approach and the CC method. The observed deviation of the CS results from the CC rate constants reached 40% and it is interesting to see if the performance of the
projection of both $V$ cated at rovibrational levels corresponding to some energy $n$ based on the expansion of the total scattering wavefunction

$$J \text{tum for the collision is denoted by } U \text{ and the symbols in brackets are the 3-j numbers is used throughout the paper: } J \text{ denotes the total angular momentum for the collision, } j \text{ is the rotational angular momentum of the diatomic molecule, } \Omega \text{ is the BF projection of both } j \text{ and } \Omega \text{, and } v \text{ is the vibrational quantum number of the diatomic molecule. The orbital angular momentum for the collision is denoted by } l. \text{ The hat over the symbol denotes the corresponding operator.}$

The CC approach to dynamics of A+BC collisions is based on the expansion of the total scattering wavefunction in products of translational ($F_{vj\Omega}$), vibrational ($\chi_f^j$) and rotational ($Y_{j\Omega}$) wave functions of the isolated diatomic molecule as follows: 14

$$\Psi^j = \frac{1}{R} \sum_v \sum_j \sum_{\Omega=-n}^n F^j_{vj\Omega}(R) \chi_f^j(r) Y_{j\Omega}(\Theta,0),$$  \hspace{1cm} (1)

where $n$ is limited by min($J,j$) and the summation is truncated at rovibrational levels corresponding to some energy higher than the collision energy $E$. This expansion leads to a system of CC equations:

$$\left[ \frac{d^2}{dR^2} + k^2_{v,j} \right] F^j_{vj\Omega}(R) = 2\mu \sum_{v',j',\Omega'} [V_{vj\Omega,v'j'\Omega'} + U^j_{vj\Omega,v'j'\Omega'}] F^j_{v'j'\Omega'}(R).$$  \hspace{1cm} (2)

In this expression $k^2_{v,j} = 2\mu(E - \epsilon_{v,j})$, $\epsilon_{v,j}$ is the energy of the BC molecule in the state $|v,j\rangle$, $V_{vj\Omega,v'j'\Omega'}$ is the matrix of the interaction potential and $U^j_{vj\Omega,v'j'\Omega'}$ is the matrix of the $l^2/R^2$ operator. The elements of the $V$ matrix can be given by the following expressions: 15

$$V_{vj\Omega,v'j'\Omega'} = \delta_{\Omega,\Omega'} \sum_{j=0}^{\lambda_{\text{max}}} (-1)^\Omega [(2j+1)(2j'+1)]^{1/2} \times \left| \begin{array}{ccc} j' & j & \lambda \\ 0 & -\Omega & j \end{array} \right| \times \langle v|V_h(r,R)|v'\rangle,$$  \hspace{1cm} (3)

where $\lambda$ are the Legendre components of the interaction potential, the symbols in brackets are the $3\cdot j$ symbols and the one-dimensional integrals $\langle v|V_h(r,R)|v'\rangle$ are evaluated numerically. The elements of the $U^j$ matrix can be readily written as follows: 15

$$U^j_{vj\Omega,v'j'\Omega'} = \delta_{j,j'} \delta_{\Omega,\Omega'} \frac{1}{R} \left[ J(j+1)+j(j+1) - 2\Omega^2 \right],$$  \hspace{1cm} (4)

The system of Eq. (2) is propagated to the asymptotic $R = \infty$ region where the solution is used to construct the scattering $S$-matrix. The cross sections and rate constants for rovibrational transitions are then obtained from the $S$-matrix elements as usual.

In order to test the method proposed we perform test calculations for Ar+HF collisions on a highly anisotropic PES. 13 The vibrational wave functions entering matrix elements in Eq. (3) and the rovibrational energy levels of the diatomic molecules $\epsilon_{v,j}$ are determined by numerical solution of the Schrödinger equation for a diatomic molecule using the interaction potential from the work of Stark and Werner. 18 Selected rovibrational levels of HF thus obtained are listed in Table 1.

Table II presents cross sections for VR in Ar+HF collisions computed using different number of projections allowed for each rotational state of HF in the basis set. The
TABLE II. Cross sections (Å²) for total (summed over all final j'-levels) vibrational relaxation of the |v=1, j⟩ levels of HF by Ar. The total collision energy is indicated. The notation $\Omega_{\text{max}}$ is used for the maximum value of projection allowed for all basis states with $j'>\Omega_{\text{max}}$ and $N$ denotes the total number of basis states.

<table>
<thead>
<tr>
<th>$\Omega_{\text{max}}$</th>
<th>$N$</th>
<th>$j_i=0$</th>
<th>$j_i=1$</th>
<th>$j_i=2$</th>
<th>$j_i=3$</th>
<th>$j_i=4$</th>
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<tr>
<td>0</td>
<td>21</td>
<td>3.973×10^{-4}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>59</td>
<td>4.648×10^{-4}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>93</td>
<td>4.645×10^{-4}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>231</td>
<td>4.645×10^{-4}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Full CC</td>
<td>261</td>
<td>4.645×10^{-4}</td>
<td>E=6007.1 cm^{-1}</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>2.022×10^{-5}</td>
<td>5.445×10^{-5}</td>
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<td>–</td>
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<td>8.717×10^{-5}</td>
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<td>–</td>
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<td>–</td>
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<tr>
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<td>2.402×10^{-4}</td>
<td>8.869×10^{-5}</td>
<td>–</td>
<td>–</td>
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</table>

Calculations are performed at three energies and $\Omega_{\text{max}}$ corresponds to $n$ in Eq. (1). A total number of 120 partial waves are taken in the summation over total angular momentum that gives converged cross sections at the collision energies considered. All open (energetically accessible) rovibrational states and a number of closed channels are included in the basis set for the calculations. The cross section for VR of HF(v=1, j=0) is well converged with $\Omega_{\text{max}}=1$ at all collision energies. This is so despite the fact that the cross section for total vibrational relaxation of HF(v=1, j=0) in collisions with Ar is predominantly determined by the cross sections for the |v=1, j=0⟩→|v=0, j=1⟩ and |v=1, j=0⟩→|v=0, j=14⟩ transitions. The cross sections for VR of HF(v=1, j=2) are well converged with $\Omega_{\text{max}}=2$, the cross sections for VR of HF(v=1, j=3) are converged to within 1% when $\Omega_{\text{max}}=3$ and the calculations with $\Omega_{\text{max}}=4$ give essentially the same results for VR of HF(v=1, j=4) as the full CC calculations. The difficulty of numerically solving Eq. (2) usually scales with the number of basis states as $N^3$ and it follows from Table II that the PR-CC calculations giving essentially the same results as the full CC calculations are significantly (at least one or two orders of magnitude) more efficient.

The proposed methodology of PR-CC calculations makes it possible to check the performance of the CS approximation for vibrationally inelastic Ar+HF collisions at high temperatures. Figure 1 presents cross sections for VR of HF(v=1, j) computed using the PR-CC method with $\Omega_{\text{max}}=5$. The number of basis states considered in the calculations is 292 and a total number of 200 partial waves are taken in the summation over total angular momentum in order to obtain converged results. The corresponding full CC calculations would require 530 states in the basis set which would make the calculations impossible. The CS results shown in Fig. 1 are computed as described in our previous work and correspond to the Boltzmann averaged rate constants presented in a preceding article. The cross sections computed in the CS approximation agree well with the more accurate results, the agreement being better at high collision energies. The largest deviation of the CS results from the PR-CC values is observed for VR of HF in the ground rotational state of v=1 at low collision energies. Despite these differences the CS approach reproduces the structure in the
energy dependence of cross sections quite well. We have estimated that the error due to the CS approximation may affect the Boltzmann averaged rate constants for VR in HF+Ar collisions by a maximum of 20% at low temperatures (T ≤ 100 K) and a maximum of 10% at higher temperatures.

In summary, the methodology of PR-CC calculations neglecting states with high values of angular momentum projection is proposed and tested on a highly anisotropic Ar+HF collision systems. It is shown that convergence of degeneracy-averaged cross sections for vibrational relaxation in atom–diatom collisions can be sought by gradually increasing the maximum value of the projection Ω allowed for each rotational state in the basis set and if the vibrational relaxation starts from the \(|v=1, j_1\rangle\) level of the diatomic molecule it may be enough to consider only projections \(\Omega \leq j_1\). Since the initial \(j_1\)-numbers of vibrationally excited levels are generally significantly smaller than the \(j\)-numbers of the corresponding rotational levels of the ground vibrational state in the basis set, the PR-CC calculations greatly reduce the effort of computing accurate cross sections for vibrational relaxation.

The PR-CC method can be used together with the vibrationally reduced close coupling methodology suggested in our previous work\(^1\) that will allow efficient and accurate calculations of cross sections for vibrational relaxation of diatomic molecules initially in high levels of vibrational excitation.

The validity of the coupled-states approximation is tested in calculations of cross sections for Ar+HF vibrationally inelastic collisions in a wide range of internal and collision energies. The largest deviation of the CS results from the PR-CC values is less than 25% of the absolute magnitude and the agreement between the different methods becomes better at higher collision energies.

Note added in proof. We have found, after this article was accepted for publication, that a similar procedure of projection reduced calculations has been used in several reactive scattering calculations (for some particular examples see Ref. 19). Although the physical interpretation of the success or failure of this approximation in the reactive scattering calculations is less transparent, the results of the works in Ref. 19 should support the methodology proposed here for ro-vibrationally inelastic collisions.

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10. Many excellent reviews have been published about CC calculations of vibrationally inelastic atom–diatom scattering. For a particular example, see W. A. Lester, in *Dynamics of Molecular Collisions*, edited by W. H. Miller (Plenum, New York, 1976).