Magnetic field modification of ultracold molecule–molecule collisions

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Abstract. We present an accurate quantum mechanical study of molecule–molecule collisions in the presence of a magnetic field. The work focuses on the analysis of elastic scattering and spin relaxation in collisions of \( \text{O}_2(\Sigma_g^-) \) molecules at cold \((\sim 0.1 \text{ K})\) and ultracold \((\sim 10^{-6} \text{ K})\) temperatures. Our calculations show that magnetic spin relaxation in molecule–molecule collisions is extremely efficient except at magnetic fields below 1 mT. The rate constant for spin relaxation at \( T = 0.1 \text{ K} \) and a magnetic field of 0.1 T is found to be as large as \( 6.1 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \). The magnetic field dependence of elastic and inelastic scattering cross sections at ultracold temperatures is dominated by a manifold of Feshbach resonances with the density of \( \sim 100 \text{ resonances per Tesla} \) for collisions of molecules in the absolute ground state. This suggests that the scattering length of ultracold molecules in the absolute ground state can be effectively tuned in a very wide range of magnetic fields. Our calculations demonstrate that the number and properties of the magnetic Feshbach resonances are dramatically different for molecules in the absolute ground and excited spin states. The density of Feshbach resonances for molecule–molecule scattering in the low-field-seeking Zeeman state is reduced by a factor of 10.

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1. Introduction

The experimental work with cold and ultracold molecules is predicted to lead to many fundamental applications in quantum computation [1], condensed-matter physics [2], precision spectroscopy [3] and physical chemistry [4]. Recent theoretical work has shown that ultracold ensembles of molecules trapped in optical lattices can be used to develop novel schemes for quantum information processing [6], design experiments for quantum simulations of condensed-matter physics [2, 7], engineer novel phases with topological order [8] and explore many-body dynamics of strongly interacting systems [9]. Polar molecules in external field traps may form chains, which can be used to study rheological phenomena with non-classical behavior [2]. The creation of a Bose–Einstein condensate of molecules may enable the study of Bose-enhanced chemistry [10] and the effects of symmetry breaking on chemical interactions at ultracold temperatures [11]. The realization of these proposals as well as the creation of dense ensembles of ultracold molecules depend critically on the possibility of controlling binary molecule–molecule interactions in molecular gases by external electromagnetic fields. The discovery of magnetic Feshbach resonances in atomic collisions [12, 13] opened the door to many groundbreaking experiments with ultracold gases such as the realization of the BEC–BCS crossover [14], the observation of quantum phase transitions [7] and the creation of ultracold molecules using time-varying magnetic fields [15]. Extension of this work to molecular collisions may similarly lead to the development of new research directions such as cold controlled chemistry [4], quantum coherent control of bimolecular reactions [16] and quantum condensed-matter physics with molecular condensates [5].

Fueled by the promise of new discoveries, the experimental research into cold and ultracold molecular collisions is expanding rapidly. Some recent landmark experiments include the observation of threshold collision laws in Xe–OH scattering using slow molecular beams [17], measurements of cross sections for D₂–OH collisions in a magnetic trap [18] and the detection of magnetic Feshbach resonances in collisions of Cs₂ molecules [19]. Further progress in the experimental study of complex molecule–molecule collisions and
chemical reactions at cold and ultracold temperatures requires rigorous theoretical calculations elucidating the mechanisms of energy transfer in ultracold molecular collisions. Theoretical studies of molecule–molecule collisions at low temperatures are also necessary to understand the prospects for evaporative cooling of molecules in a magnetic trap. The evaporative cooling relies on elastic molecule–molecule collisions as the trap depth is gradually reduced \([13]\). In order to sustain efficient evaporative cooling down to quantum degeneracy, the ratio of the probabilities for elastic scattering and spin relaxation \((\gamma)\) in molecule–molecule collisions must exceed \(10^4\) \([13]\). The magnitudes of the rate constants for elastic and inelastic collisions and the dependence of the scattering observables in molecule–molecule encounters on the magnetic field are, however, completely unknown.

Previous theoretical work by Krems and Dalgarno \([20]\) and Volpi and Bohn \([24]\) identified the main mechanisms of spin relaxation in atom–molecule collisions. It was found that spin relaxation in collisions of \(3\Sigma\) molecules with He atoms occurs through coupling to rotationally excited states mediated by the spin–spin interaction \([20]\). While the mechanisms of spin relaxation in molecule–molecule collisions should be similar, an accurate computational study of molecule–molecule scattering in a magnetic field is urgently needed to elucidate the rates of energy relaxation in dense ensembles of trapped molecules and understand the prospects for evaporative cooling of molecules. The quantum dynamics of ultracold molecule–molecule collisions in the absence of external fields has been studied by several authors (see, e.g. \([21]–[23]\)). Avdeenkov and Bohn calculated the rates of spin relaxation in collisions of \(O_2(\Sigma_g^+)\) molecules at zero magnetic field and observed Feshbach resonances due to molecular rotation \([25\), 26\]). Krems and Dalgarno \([20]\) presented a formalism for quantum scattering calculations of cross sections for molecule–molecule collisions in a magnetic field. However, they did not consider the symmetrization procedure required to properly describe collisions between identical molecules. Here, we extend the approach of Krems and Dalgarno to study collisions of identical \(3\Sigma\) molecules. The use of exchange symmetry reduces the number of scattering channels by a factor of two, which allowed us to obtain converged cross sections for elastic scattering and spin relaxation of \(O_2(\Sigma_g^+)\) molecules in an external magnetic field.

We consider ultracold collisions of \(O_2\) molecules in their ground electronic state of \(3\Sigma_g^−\) symmetry. \(O_2\)–\(O_2\) collisions play an important role in atmospheric chemistry \([29\), 30\]). The \(O_2\)–\(O_2\) dimer is an interesting molecular complex \([27]–[36]\) (for a recent review, see \([34]\)). The binding in the complex is affected by the Heisenberg exchange interaction and the formation of incipient chemical bond \([31\), 32\]). Molecular beam scattering experiments \([31\), 32\] and high-level \textit{ab initio} calculations \([33]\) have previously been used to elucidate the nature of the chemical bond in the \(O_2\)–\(O_2\) dimer. Here, we calculate the magnetic field dependence of the probabilities for spin relaxation in \(O_2\)–\(O_2\) collisions at both ultracold (down to \(10^{-6}\) K) and cold (0.5 K) temperatures relevant for magnetic trapping experiments. Our calculations elucidate the possibility of evaporative cooling of paramagnetic \(3\Sigma\) molecules in a magnetic trap and indicate that spin depolarization in molecular collisions can be controlled by an external magnetic field. The results of our work will be useful for the interpretation of collision experiments involving slow beams of \(O_2\) molecules produced by Zeeman deceleration \([37]\) and cryogenic cooling \([38]\).
2. Theory

2.1. Hamiltonian and symmetrized basis functions

The Hamiltonian for two $^3\Sigma$ molecules in an external magnetic field can be written as [20, 25]

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\ell^2}{2\mu R^2} + V_\text{el}(\mathbf{R}, \mathbf{r}_A, \mathbf{r}_B) + \hat{H}_\text{as},$$

where the vectors $\mathbf{r}_A$ and $\mathbf{r}_B$ describe the orientation of the molecules A and B in the space-fixed (SF) frame, $\mathbf{R}$ is the vector joining the molecules, $\ell$ is the orbital angular momentum of the collision complex, $\mu$ is the reduced mass and $V_\text{el}$ is the electrostatic interaction potential (see section 2.2). The asymptotic Hamiltonian $\hat{H}_\text{as}$ describes the individual molecules A and B in the presence of a magnetic field [20]:

$$\hat{H}_\text{as} = \hat{H}_A + \hat{H}_B.$$  \hfill (2)

The Hamiltonian of an individual $^3\Sigma^-$ molecule can be written as [39]

$$\hat{H}_\nu = B_\nu \hat{N}_\nu^2 + 2\mu_\text{B} \mathbf{B} \cdot \hat{\mathbf{S}}_\nu + \gamma_{\text{SR}} \hat{N}_\nu \cdot \hat{\mathbf{S}}_\nu + \frac{2\lambda_{\text{SS}}}{3} \left( \frac{24\pi}{5} \right)^{1/2} \sum_q Y_{2q}^* (\hat{r}_\nu) \left[ \hat{\mathbf{S}}_\nu \otimes \hat{\mathbf{S}}_\nu \right]^{(2)}_q,$$

where the index $\nu = A, B$ labels the molecule, $\hat{N}_\nu^2$ is the rotational angular momentum, $B_\nu$ is the rotational constant, $\mu_\text{B}$ is the Bohr magneton, $\mathbf{B}$ is the magnetic field vector and $\hat{\mathbf{S}}_\nu$ is the electron spin. The spin–rotation and spin–spin interactions in equation (3) are parametrized by the phenomenological constants $\gamma_{\text{SR}}$ and $\lambda_{\text{SS}}$, which do not depend on $\nu$ since we consider collisions of identical molecules. The spin–spin interaction given by the last term in equation (3) can be represented as a sum of tensor products of two identical spin operators and spherical harmonics, which depend on the orientation $\hat{r}_\nu$ of the diatomic molecule in the SF coordinate frame [39]. We use the rigid rotor approximation ($\mathbf{r}_\nu = \hat{r}_\nu$) and neglect the weak magnetic dipole–dipole interaction and the hyperfine interaction of $^{17}\text{O}$ [25].

We solve the scattering problem for two identical bosonic molecules by expanding the total wavefunction in a SF uncoupled basis introduced in [20]. The uncoupled basis functions are products of the eigenfunctions of the operators $\hat{N}_\nu^2$ and $\hat{\mathbf{S}}_\nu^2$, their projections along the SF z-axis $\hat{N}_\nu$ and $\hat{\mathbf{S}}_\nu$, and the spherical harmonics $|\ell m_\ell\rangle$.

$$|\tau_A \tau_B \ell m_\ell\rangle = |\tau_A\rangle |\tau_B\rangle |\ell m_\ell\rangle,$$

where $|\tau_\nu\rangle = |N_\nu M_{N_\nu}\rangle |S_\nu M_{S_\nu}\rangle$. The matrix elements of the Hamiltonians (1) and (2) in the basis (4) were derived by Krems and Dalgarno [20] for the case of distinguishable molecules. The basis functions for identical molecules must be the eigenfunctions of the permutation operator $\hat{P} : \mathbf{r}_A \rightarrow \mathbf{r}_B; \mathbf{r}_B \rightarrow \mathbf{r}_A; \mathbf{R} \rightarrow - \mathbf{R}$, which commutes with the total Hamiltonian (1). The symmetrized basis functions can be constructed by applying the operator $1 + \hat{P}$ to equation (4) and normalizing the result [20, 22, 40, 41]

$$\phi_{\tau_A \tau_B \ell m_\ell}^{\eta} = \frac{1}{\left[2(1 + \delta_{\tau_A \tau_B})\right]^{1/2}} \left[ |\tau_A\rangle \tau_B\rangle + \eta \epsilon |\tau_B\rangle \tau_A\rangle \right] |\ell m_\ell\rangle,$$

where $\epsilon = (-)^\ell$ and the symmetry of the basis functions with respect to the interchange of identical molecules is given by index $\eta$, which is equal to 1 for composite bosons and $-1$ for composite fermions [42]. In what follows, we assume that the first basis function in each product
on the right-hand side of equation (5) depends on the coordinates of molecule A, and the second basis function depends on the coordinates of molecule B. Equation (5) defines the well-ordered (combined) molecular states with $\tau_A \geq \tau_B$. The normalization factor $[2(1 + \delta_{\tau_A\tau_B})]^{1/2}$ takes into account the fact that the basis function (5) with $\tau_A = \tau_B$ need not be symmetrized when $\eta \epsilon = +1$ (i.e. when the colliding molecules are in the same state). The symmetrized function (5) with $\tau_A = \tau_B$ vanishes identically when $\eta \epsilon = -1$.

The basis functions given by equations (4) and (5) are also the eigenfunctions of the inversion operator, with eigenvalues given by $(-)^{N_A+\ell}$ \cite{41}. Since for homonuclear molecules both $N_A$ and $N_B$ are either even or odd, the quantity $\epsilon = (-)^{\ell}$ is conserved as well. Thus, it is convenient to rewrite equation (5) in a factorized form

$$\phi^{\eta\epsilon}_{\tau_A,\tau_B,\ell m} = \mathcal{T}^{\eta\epsilon}_{\tau_A,\tau_B}(\hat{r}_A, \hat{r}_B)|\ell m\rangle, \quad (6)$$

where

$$\mathcal{T}^{\eta\epsilon}_{\tau_A,\tau_B}(\hat{r}_A, \hat{r}_B) = \frac{1}{[2(1 + \delta_{\tau_A\tau_B})]^{1/2}} |\tau_A \tau_B + \eta \epsilon \tau_A\rangle. \quad (7)$$

We note that no such symmetry exists for heteronuclear molecules, where the basis functions with $\Delta \ell = \pm 1$ are coupled by the interaction potential, and $\epsilon$ is not conserved.

The uncoupled symmetrized basis functions given by equation (5) are not the eigenfunctions of the asymptotic Hamiltonian (2) because the spin–rotation and spin–spin interactions couple the states with different $N$, $M_N$ and $M_S$. Since the scattering $S$-matrix must be defined in terms of the eigenfunctions of $\hat{H}_{as}$, it is necessary to transform the wavefunction to a new basis [20]

$$\mathcal{T}^{\eta\epsilon}_{\gamma_A\gamma_B}(\hat{r}_A, \hat{r}_B) = \sum_{\tau_A \geq \tau_B} C^{\eta\epsilon}_{\tau_A,\tau_B,\gamma_A\gamma_B} \mathcal{T}^{\eta\epsilon}_{\tau_A,\tau_B}(\hat{r}_A, \hat{r}_B), \quad (8)$$

where the coefficients $C^{\eta\epsilon}_{\tau_A,\tau_B,\gamma_A\gamma_B}$ form the matrix which diagonalizes the asymptotic Hamiltonian in the symmetrized basis (5). More explicitly, $C^{\eta\epsilon}_1 = E$, where $E$ is the diagonal matrix of asymptotic energies and $\epsilon_{\gamma_A\gamma_B} = \epsilon_{\gamma_A} + \epsilon_{\gamma_B}$. The energies of individual molecules $\epsilon_\nu$ can be obtained by diagonalization of individual molecule Hamiltonians $\hat{H}_\nu$ (2) in the subspace of functions $|\tau_\nu\rangle$. Exploiting the properties of the interchange operator $\hat{P}^\dagger = \hat{P}$ and $\hat{P}^2 = 1$ and using equation (5), we obtain the following expression for the matrix elements of $\hat{H}_A$:

$$\{\phi^{\eta\epsilon}_{\tau_A,\tau_B,\ell m} | \hat{H}_A | \phi^{\eta\epsilon}_{\tau'_A,\tau'_B,\ell' m'}\} = \frac{\delta_{\ell\ell'} \delta_{m m'}}{[(1 + \delta_{\tau_A\tau_B})(1 + \delta_{\tau'_A\tau'_B})]^{1/2}} \left[ \delta_{\tau_B - \tau'_B} \langle \tau_A | \hat{H}_A | \tau_A \rangle + \eta \epsilon \delta_{\tau_A - \tau'_A} \langle \tau_A | \hat{H}_A | \tau'_B \rangle \right]. \quad (9)$$

This expression provides a convenient method of constructing the matrix elements of the asymptotic Hamiltonian (2) in the symmetrized basis. Alternatively, one can obtain the transformation coefficients (8) directly from the eigenvectors of $\hat{H}_A$ defined as

$$|\gamma_A\rangle = \sum_{\tau_A} C^{\eta\epsilon}_{\gamma_A,\tau_A} |\tau_A\rangle. \quad (10)$$

The transformation can be derived by multiplying equation (10) by a similar expression for $|\gamma_B\rangle$ and rearranging the terms. The result is

$$C^{\eta\epsilon}_{\gamma_A,\gamma_B} = \frac{1}{[(1 + \delta_{\tau_A\tau_B})(1 + \delta_{\gamma_A\gamma_B})]^{1/2}} \left[ C^{\eta\epsilon}_{\gamma_A,\gamma_B} + \eta \epsilon C^{\eta\epsilon}_{\gamma_A,\gamma_B} C^{\eta\epsilon}_{\gamma_B,\gamma_A} \right]. \quad (11)$$

7 The index $S_z$ is omitted because the electron spin of the molecule is conserved in a collision.

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We have verified by numerical tests that equations (8) and (11) give identical results up to an unimportant overall phase. In practice, however, it is more convenient to use equation (11) because it requires the evaluation and the diagonalization of smaller matrices.

2.2. Interaction potential

The spin-dependent interaction potential between two $^3\Sigma$ molecules can be represented in the form

$$V_{\text{el}}(\vec{R}, \hat{r}_A, \hat{r}_B) = \sum_{S=-1}^{1} \sum_{M_S=-S}^{S} V_S(\vec{R}, \hat{r}_A, \hat{r}_B)|SM_S\rangle\langle SM_S|,$$

(12)

where $\hat{S} = \hat{S}_A + \hat{S}_B$ is the total spin and $M_S = M_{S_A} + M_{S_B}$. The representation (12) is often used to describe the interactions of ultracold alkali metal atoms [12]. Here, we choose an alternative approach proposed by van der Avoird and Brocks [27] and Bussery and Wormer [28], in which the full interaction potential is separated into the spin-independent and spin-dependent parts

$$V_{\text{el}}(\vec{R}, \hat{r}_A, \hat{r}_B) = V_{\text{si}}(\vec{R}, \hat{r}_A, \hat{r}_B) + V_{\text{sd}}(\vec{R}, \hat{r}_A, \hat{r}_B).$$

(13)

The spin-dependent part, also known as the Heisenberg exchange interaction [27, 28], can be parametrized for two $^3\Sigma$ molecules as

$$V_{\text{sd}}(\vec{R}, \hat{r}_A, \hat{r}_B) = -2J(\vec{R}, \hat{r}_A, \hat{r}_B)\hat{S}_A \cdot \hat{S}_B,$$

(14)

where $J(\vec{R}, \hat{r}_A, \hat{r}_B)$ is a scalar function similar to the interaction potential but decreasing exponentially with $R$ [28]. We expand the interaction potential in the angular basis [20, 27]

$$V_{\text{si}}(\vec{R}, \hat{r}_A, \hat{r}_B) = (4\pi)^{3/2} \sum_{\lambda_A, \lambda_B, \lambda} V_{\lambda_A\lambda_B\lambda}(R)A_{\lambda_A\lambda_B\lambda}(\hat{R}, \hat{r}_A, \hat{r}_B),$$

(15)

with the SF angular basis functions defined as

$$A_{\lambda_A\lambda_B\lambda}(\hat{R}, \hat{r}_A, \hat{r}_B) = \sum_{m_{\lambda_A}, m_{\lambda_B}, m_{\lambda}} Y_{\lambda_A m_{\lambda_A}}(\hat{r}_A)Y_{\lambda_B m_{\lambda_B}}(\hat{r}_B)Y_{\lambda m_{\lambda}}(\hat{R}),$$

(16)

where $\langle \lambda : \lambda \rangle$ denotes a 3-$j$ symbol. An efficient procedure for the evaluation of the radial expansion coefficients in equation (15) is described in appendix A.

The matrix elements of the spin-independent interaction potential between the symmetrized basis functions (5) have the form

$$\langle \phi_{\tau_A \tau_B \ell \epsilon_l} | V_{\text{si}} | \phi_{\tau_A' \tau_B' \ell' \epsilon'_l} \rangle = \frac{1}{[(1 + \delta_{\tau_A \tau_B})(1 + \delta_{\tau_A' \tau_B'})]^1/2} \times \left[ (\tau_A \tau_B \ell \epsilon_l \langle \tau_A' \tau_B' \ell' \epsilon'_l \rangle(V_{\text{si}}|_{\tau_A' \tau_B' \ell' \epsilon'_l}) + \eta \epsilon (\tau_A \tau_B \ell \epsilon_l | V_{\text{si}} | \tau_A' \tau_B' \ell' \epsilon'_l) \right].$$

(17)

The first (direct) term on the right-hand side is a matrix element in the unsymmetrized basis. Krems and Dalgarno [20] evaluated this matrix element using the expansion of $V_{\text{si}}$ in terms

8 The expansion of $J(\vec{R}, \hat{r}_A, \hat{r}_B)$ is identical to that of the interaction potential. We therefore do not repeat it here.
of the angular basis functions (15). Using the conservation of the total angular momentum projection \( M = M_{N_A} + M_{S_A} + M_{N_B} + M_{S_B} + m_\ell \) for collisions in a magnetic field, we obtain

\[
\langle \tau_A \tau_B \ell m_\ell | V_{si} | \tau_A' \tau_B' \ell' m'_\ell \rangle = \delta_{M_{N_A} - M_{N_B} + m_\ell} \delta_{M_{S_A}, M_{S_A}'} \sum_{\lambda_A, \lambda_B, \lambda} V_{\lambda_A \lambda_B \lambda}(R) [(2N_A + 1)(2N_A' + 1)] \\
\times (2N_B + 1)(2N_B' + 1)(2\ell + 1)(2\ell' + 1)(2\lambda_A + 1)(2\lambda_B + 1) \\
\times (2\lambda + 1)^{1/2} (-)^{M_{N_A} + M_{N_B} + m_\ell} \left( \begin{array}{ccc}
\lambda_A & \lambda_B & \lambda \\
M_{N_A} & M_{N_A}' & M_{N_B}' \\
m_\ell & -m_\ell & m'_\ell
\end{array} \right) \\
\times \left( \begin{array}{ccc}
N_A & \lambda_A & N_A' \\
-M_{N_A} & M_{N_A} - M_{N_B}' & 0 \\
0 & 0 & 0
\end{array} \right) \\
\times \left( \begin{array}{ccc}
N_B & \lambda_B & N_B' \\
-M_{N_B} & M_{N_B} - M_{N_B}' & 0 \\
0 & 0 & 0
\end{array} \right) \\
\times \left( \begin{array}{ccc}
\ell & \lambda & \ell' \\
-m_\ell & m_\ell - m'_\ell & m'_\ell \\
0 & 0 & 0
\end{array} \right). \tag{18}
\]

The second (exchange) matrix element appears as a result of the symmetrization procedure (5). It can be obtained from equation (18) by interchanging the indexes \( N_A' \leftrightarrow N_B', M_{N_A}' \leftrightarrow M_{N_B}', \) and \( M_{S_A}' \leftrightarrow M_{S_B}'. \)

The matrix elements of the Heisenberg exchange interaction are obtained using the same procedure:

\[
\langle \phi_{\tau_A \tau_B \ell m_\ell} \rangle_{V_{sd}} = \frac{1}{[1 + \delta_{\tau_A, \tau_B}][1 + \delta_{\ell, \ell'}]} \times \left[ \langle S_A M_{S_A} | (S_B M_{S_B} | S_A M_{S_A}') | S_B M_{S_B}' \rangle \langle \tau_A \tau_B \ell m_\ell | -2J | \tau_A' \tau_B' \ell' m'_\ell \rangle + \eta \epsilon \langle S_A M_{S_A} | (S_B M_{S_B} | S_A M_{S_A}') | S_A M_{S_A}' \rangle \langle \tau_A \tau_B \ell m_\ell | -2J | \tau_A' \tau_B' \ell' m'_\ell \rangle \right]. \tag{19}
\]

The matrix elements of the prefactor \(-2J(R, \theta_A, \theta_B, \varphi)\) are given by equation (18) with \( V_{\lambda_A, \lambda_B, \lambda}(R) \) replaced by \(-2J_{\lambda_A, \lambda_B, \lambda}(R)\). Equation (19) shows that unlike the spin-independent matrix elements (17), both the direct and exchange contributions to the Heisenberg exchange matrix element are not diagonal in spin quantum numbers \( M_{S_A} \) and \( M_{S_B} \). For completeness, we give here the expressions for the matrix elements of the operator \( \hat{S}_A \cdot \hat{S}_B \). The direct matrix element has the form [20]

\[
\langle S_A M_{S_A} | (S_B M_{S_B} | \hat{S}_A \cdot \hat{S}_B | S_A M_{S_A}' ) | S_B M_{S_B}' \rangle = \delta_{M_{S_A}, M_{S_A}'} \delta_{M_{S_B}, M_{S_B}'} \frac{1}{2} \delta_{M_{S_A} + M_{S_A}', M_{S_B} + M_{S_B}'} \times \delta_{M_{S_B} + M_{S_B}'} \left[ (S_A(S_A + 1) - M_{S_A}(M_{S_A} + 1))^{1/2} \left[ (S_B(S_B + 1) - M_{S_B}(M_{S_B} + 1))^{1/2} \right], \right. \tag{20}
\]

and the exchange matrix element can be obtained from equation (20) by interchanging the indexes \( M_{S_A}' \) and \( M_{S_B}' \).
2.3. Close-coupling equations, scattering amplitudes and cross sections

The symmetrized wavefunction of the collision complex can be expanded as

\[ \psi^\eta = \frac{1}{R} \sum_{\gamma_A \gamma_B} \sum_{\ell, m} F^\eta_{\gamma_A \gamma_B \ell m} (R) Y_{\ell m} (\hat{R}) T^\eta_{\gamma_A \gamma_B} (\vec{r}_A, \vec{r}_B). \]  

Substituting this expansion into the Schrödinger equation, \( H \psi^\eta = E \psi^\eta \), where \( E \) is the total energy, we obtain the close-coupling equations for the radial expansion coefficients

\[ \left[ \frac{d^2}{dR^2} - \frac{\ell (\ell + 1)}{R^2} + 2\mu E \right] F^\eta_{\gamma_A \gamma_B \ell m} (R) = \sum_{\gamma_A \gamma_B} \sum_{\ell', m'} \left[ C^T V C \right]_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} F^\eta_{\gamma_A' \gamma_B' \ell' m'} (R). \]  

The asymptotic form of the solutions \( F^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} (R) \) at \( R \to \infty \) defines the symmetrized scattering matrix

\[ F^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} (R \to \infty) \to \delta_{\gamma_A' \gamma_A} \delta_{\gamma_B' \gamma_B} \delta_{\ell \ell'} \delta_{m m'} \exp[-i(k_{\gamma_A \gamma_B} R - \pi \ell / 2)] - \frac{k_{\gamma_A \gamma_B}}{k_{\gamma_A' \gamma_B'}}^{1/2} S^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} \exp[i(k_{\gamma_A' \gamma_B'} R - \pi \ell' / 2)]. \]  

The scattering amplitude for indistinguishable molecules can be written as \([23, 50]\)

\[ q^\eta_{\gamma_A \gamma_B \to \gamma_A' \gamma_B'} (\hat{R}, \hat{R}) = q_{\gamma_A \gamma_B \to \gamma_A' \gamma_B} (\hat{R}, \hat{R}) + \eta q_{\gamma_A \gamma_B \to \gamma_A' \gamma_B'} (\hat{R}, -\hat{R}), \]  

where the scattering amplitudes on the right-hand side can be written in terms of unsymmetrized \( T \)-matrix elements

\[ q_{\gamma_A \gamma_B \to \gamma_A' \gamma_B'} (\hat{R}, \hat{R}) = 2\pi \sum_{\ell, m, \ell', m'} i^{\ell - \ell'} Y^*_{\ell m} (\hat{R}) T_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} (\hat{R}) T^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'}. \]  

Substituting this expression into equation (24) and rearranging the terms, we find

\[ q^\eta_{\gamma_A \gamma_B \to \gamma_A' \gamma_B'} (\hat{R}, \hat{R}) = 2\pi [(1 + \delta_{\gamma_A \gamma_B'})(1 + \delta_{\gamma_A' \gamma_B})]^{1/2} \sum_{\ell, m, \ell', m'} i^{\ell - \ell'} Y^*_{\ell m} (\hat{R}) \times Y_{\ell' m'} (\hat{R}) T^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'}. \]  

where

\[ T^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} = \frac{1}{[(1 + \delta_{\gamma_A \gamma_B'})(1 + \delta_{\gamma_A' \gamma_B})]^{1/2}} \left[ T_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} + \eta \epsilon T_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} \right]. \]  

These \( T \)-matrix elements are exactly the same as those obtained from the solution of the close-coupling equations in the symmetrized basis set (as described above). They are related to the \( S \)-matrix elements via \([46]\)

\[ T^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} = \delta_{\gamma_A' \gamma_A} \delta_{\gamma_B' \gamma_B} \delta_{\ell \ell'} \delta_{m m'} S^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'}. \]  

The integral cross section for indistinguishable molecules in fully polarized nuclear spin states can be obtained from the scattering amplitude as described in appendix B. The final result is

\[ \sigma_{\gamma_A \gamma_B \to \gamma_A' \gamma_B'} = \frac{\pi}{k^2} \sum_{\ell, m, \ell', m'} \left| T^\eta_{\gamma_A \gamma_B \ell m; \gamma_A' \gamma_B' \ell' m'} \right|^2. \]
where \( k_{\gamma A \gamma B}^2 = 2 \mu (E - \epsilon_{\gamma A} - \epsilon_{\gamma B}) \) is the wavevector for the initial collision channel. This equation shows that the elastic cross section of indistinguishable bosons (or fermions) is twice as large as that of distinguishable particles. Our equation (29) agrees with the results presented by Avdeenkov and Bohn [25] and Burke [45].

2.4. Computational details

To parametrize the asymptotic Hamiltonian (2), we used the accurate spectroscopic constants of \(^{17}\text{O}_2\) (in units of cm\(^{-1}\)): \(B_2 = 1.353\), \(\gamma_{SR} = -0.00396\), \(\lambda_{SS} = 1.985\) [51]. In order to obtain converged cross sections at collision energies below 0.5 K, we used a basis set comprising three rotational states \((N_A, N_B = 0 - 4)\) and four partial waves \((\ell = 0 - 6)\). These parameters resulted in 2526 coupled differential equations for \(M = 0\). At the lowest collision energy of \(10^{-6}\) K, four partial waves were sufficient to achieve convergence. The coupled equations (22) were solved on a grid of \(R\) from 2\(a_0\) to 200\(a_0\) with a step size of 0.04 \(a_0\) yielding the cross sections converged to within 10%. The spin-independent and spin-dependent parts of the interaction potential for the oxygen dimer were constructed to reproduce the integral cross sections measured in molecular beam scattering experiments [31, 32]. The lowest-order isotropic part \(V_{000}(R)\) was determined with high accuracy from an analysis of the glory pattern in high-velocity collisions of rotationally ‘hot’ \(^{17}\text{O}_2\) molecules. The anisotropic coefficients \(V_{202}(R), V_{220}(R)\) and \(V_{222}(R)\) were inferred from the scattering experiments with rotationally cold, supersonic beams of aligned \(^{17}\text{O}_2\) [31, 32]. Recent \textit{ab initio} studies [35, 36] have shown that the \(^{17}\text{O}_2–^{17}\text{O}_2\) interaction may be more anisotropic than suggested in [31]. The inelastic transition probabilities in molecule–molecule collisions increase with the anisotropy of the interaction potential [20], so the cross sections for spin relaxation presented in this work should be viewed as lower bounds to the actual magnitudes.

3. Results and discussion

We consider collisions of two identical oxygen molecules in the ground electronic state \(3\Sigma_g^-\). We choose the \(^{17}\text{O}\) isotope because the \(^{17}\text{O}_2\) molecule is characterized by the \(J_A = 1\) ground state required for magnetic trapping (where \(J_A = \hat{N}_A + \hat{S}_A\) is the total angular momentum of \(O_2\) exclusive of nuclear spin). The Zeeman levels of \(^{17}\text{O}_2\) obtained by diagonalizing the asymptotic Hamiltonian are shown in figure 1(a). Magnetic fields split the \(J_A = 1\) ground state of \(^{17}\text{O}_2\) into three Zeeman states corresponding to \(M_{S_A} = 0, -1\) and +1. We first consider collisions of two oxygen molecules in the spin-aligned state \(|M_{S_A} = 1, M_{S_B} = 1\rangle\), relevant for magnetic trapping and cryogenic cooling experiments. Molecules prepared in this state can scatter elastically or undergo spin-changing inelastic transitions. The lower panel of figure 2 shows that spin-changing collisions are suppressed at low magnetic fields (<1 mT) leading to a large value of the elastic to inelastic ratio \(\gamma \sim 10^4\) which is favorable for evaporative cooling. Since \(M\) is conserved, the spin relaxation transitions must be accompanied by the transition \(\ell = 0 \rightarrow \ell' = 2\), which leads to a centrifugal barrier in the outgoing reaction channel suppressing the s-wave inelastic scattering. Because the \(\ell = 2\) barrier has a fixed height of 13 mK [25], this suppression occurs only at low magnetic fields where the energy difference between the initial and final Zeeman states does not exceed the barrier height [24, 25]. At larger magnetic fields, the spin-changing transitions are much more efficient, as shown in figure 2(b). This suggests that evaporative cooling of \(3\Sigma\) molecules in a deep magnetic trap will be challenging. However,
Figure 1. (a) Energy levels of the $^{17}\text{O}_2(3\Sigma^-_g)$ molecule as functions of the magnetic field. (b) A schematic illustration of spin relaxation in collisions of $3\Sigma$ molecules.

our results indicate that evaporative cooling may be possible in shallow magnetic traps ($<1$ mT deep). The maximum temperature of the molecules that can be held in such a trap is determined by the parameter

$$\eta = \frac{[\mu B]}{k_B T},$$

(30)

where $T$ is the temperature, $k_B$ is Boltzmann’s constant and $\mu = 2\mu_0$ for $3\Sigma$ molecules. Efficient trapping requires $\eta > 5$ [57], which corresponds to a temperature of 0.25 mK for $3\Sigma$ molecules at $B = 1$ mT. Such temperatures can be reached using optical Stark deceleration [56] or Zeeman slowing [37].

Spin relaxation in collisions of $\Sigma$-state molecules in fully spin-stretched states can only occur through coupling to the rotationally excited states assisted by the spin–spin interaction [20]. This is a two-step mechanism illustrated schematically in figure 1(b). The spin–spin interaction (denoted by $V_{SS}$ in figure 1) mixes the ground rotational state $|N = 0, M_N = 0, M_S = 1\rangle$ with the excited rotational states $|N = 2, M_N, M_S = -1\rangle$. Spin relaxation is then induced by the anisotropy of the interaction potential leading to the $|N = 2, M_N, M_S = -1\rangle \rightarrow |N' = 0, M'_N, M'_S = -1\rangle$ transition. The anisotropy of molecule–molecule interaction potentials is usually very strong; our results yield the rate constant for spin relaxation $6.1 \times 10^{-11}$ cm$^3$ s$^{-1}$ at $T = 0.1$ K and $B = 0.1$ T.

Figure 3 shows the magnetic field dependence of $\text{O}_2$–$\text{O}_2$ scattering at a collision energy of $10^{-6}$ K. The spin relaxation cross section increases from zero to a large value over a narrow region of magnetic fields $B = 0$–1 mT. For magnetic fields larger than 10 mT, the spin relaxation cross section summed over all final Zeeman states is a factor of 10 larger than the elastic scattering cross section. The cross section displays several broad resonances. Figure 1(b)
Figure 2. The cross sections for elastic scattering (a) and spin relaxation (b) in $\text{O}_2({}^3\Sigma^-) – \text{O}_2({}^3\Sigma_g^-)$ collisions as functions of the collision energy at different magnetic fields: $10^{-4}$ T (circles), $10^{-3}$ T (squares) and 0.1 T (diamonds). The ratio of the cross sections for elastic scattering and spin relaxation is shown in panel (c).

illustrates that at certain magnetic fields, the energy in the incoming collision channel becomes degenerate with that of a quasi-bound state supported by the uppermost curve. This results in the formation of a long-lived complex in which one of the molecules is in the $N = 2$ rotationally excited state [25]. The lifetime of the complex is determined by the strength of the couplings induced by the spin–rotation interaction and the intermolecular potential as well as the presence of inelastic loss processes. In particular, the peaks shown in figure 3 are relatively broad because inelastic spin relaxation leads to suppression of the $S$-matrix poles [52].

The magnetic field dependence of the scattering cross sections for collisions of molecules in the absolute ground high-field-seeking state $|M_{S_A} = -1, M_{S_B} = -1\rangle$ is dramatically different (see figure 4). The s-wave elastic scattering cross section displays a manifold of resonance peaks, which we attribute to the combined action of the interaction potential and the spin–spin interaction (1). As a result of an interplay between these interactions, avoided crossings occur between the incoming scattering state $|M_{S_A} = -1, M_{S_B} = -1\rangle$ and the quasi-bound states of the
Figure 3. The cross sections for elastic scattering (full line) and spin relaxation (dashed line) in collisions of \( \text{O}_2(3\Sigma_g^-) \) molecules in the low-field-seeking state \( |M_{S_A} = 1, M_{S_B} = 1\rangle \) as functions of the magnetic field. The spin relaxation cross section is summed over all final spin states and divided by 10 to fit the scale of the figure. The collision energy is \( 10^{-6} \) K.

Figure 4. The s-wave elastic scattering cross section for collisions of \( \text{O}_2(3\Sigma_g^-) \) molecules in the lowest high-field-seeking state \( |M_{S_A} = -1, M_{S_B} = -1\rangle \) as a function of the magnetic field. The collision energy is \( 10^{-6} \) K.

\( \text{O}_2-\text{O}_2 \) complex shown in figure 1(b) leading to the resonant variation of the elastic cross section. This suggests that the resonances depicted in figure 4 are similar to the magnetic Feshbach resonances in collisions of the alkali metal atoms \([12]\) and that the s-wave scattering length in an ultracold gas of \( 3\Sigma \) molecules can be efficiently manipulated with magnetic fields.
Figure 5. The ratio of the cross sections for elastic scattering and spin relaxation in collisions of O\(_2\)\(^{(3} \Sigma_g^-)\) molecules in the low-field-seeking state \(|M_{S_A} = 1, M_{S_B} = 1\rangle\) as a function of the rotational constant at different collision energies. The magnetic field is 1 T.

In order to elucidate the possibility for evaporative cooling of \(^3 \Sigma\) molecules, it is useful to analyze the dependence of the spin relaxation rates on the rotational constant [20, 53]. In figure 5, we plot the ratio of the cross sections for elastic scattering and spin relaxation as a function of the splitting between the rotational levels. All other parameters of the Hamiltonian were unchanged in this calculation. The probability for spin relaxation in atom–molecule and molecule–molecule collisions decreases with increasing \(B_e\) because the matrix element between the different spin states due to the spin–spin interaction scales as \(\lambda_{SS}/B_e\) [20, 53]. Figure 5 shows that the elastic to inelastic ratio at a collision energy of 0.1 K improves dramatically with increasing the rotational constant. The dependence on \(B_e\) is, however, not monotonic because of the manifold of Feshbach resonances (see figures 3 and 4), which are most pronounced at low collision energies. The results shown in figure 5 indicate that evaporative cooling of molecules with larger rotational constants should generally be more efficient.

Previous theoretical and experimental work has established that the cross sections for spin-changing transitions in \(^3 \Sigma\) molecules are sensitive to the splitting between the \(N = 0\) and the

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Figure 6. Energy levels of $^{17}$O$_2$(3$\Sigma_g^-$) in superimposed magnetic and off-resonant laser fields. The levels are shown as functions of the laser field intensity at a fixed magnetic field of 1 T. The dashed line shows the highest low-field-seeking state $|M_{S_A}| = 1$. The laser field intensity is defined as $I_0 = \epsilon_0^2$ (see text for details).

$N = 2$ rotational levels. The approximate $1/B_e^2$ scaling law [53] suggests that spin relaxation occurs at a slower rate in collisions of atoms and molecules with larger rotational constants. This result is important because the splitting between different rotational levels can be altered with electric, microwave, or off-resonant laser fields, thereby enabling control over the spin degrees of freedom of cold molecules. We illustrate the idea using the example of a nonpolar $3\Sigma$ molecule such as O$_2$ in the presence of a far off-resonant, continuous-wave laser field. The energy levels are determined by the Hamiltonian (3) with an additional term [55]

$$\hat{V}_L = -\frac{\epsilon_0^2}{4} \left[ \Delta\alpha \cos^2 \chi + \alpha_\perp \right],$$

where $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the polarizability anisotropy, $\chi$ is the angle between the molecular axis and the laser polarization vector (which we assume to be parallel to $B$), and $\epsilon_0$ is the amplitude of the laser field. Figure 6 shows the energy levels of $^{17}$O$_2$ as functions of the laser field strength (we transform away the $\chi$-independent terms by properly choosing the zero of energy). The effective rotational constant defined as the splitting between the closest field-dressed Zeeman levels in the $N = 0$ and $N = 2$ manifolds, increases by a factor of 1.6 as the laser field intensity is varied from 0 to $5 \times 10^{11}$ W cm$^{-2}$. For polar molecules, similar effects can be induced by dc and microwave laser fields [54].

As shown in figure 6, any substantial modification of molecular energy levels requires laser field intensities of the order of $10^{11}$ W cm$^{-2}$. The maximum cw laser field intensity currently available in the laboratory is about $2.5 \times 10^5$ W cm$^{-2}$ for a 0.5 mm size sample. However, if the trapped cloud is compressed to one-tenth of its original size, the maximum attainable laser intensity increases by a factor of 100, so the required field strengths of $10^{11}$ W cm$^{-2}$ are well within reach with microscopic clouds ($10^{-3}$ mm). Samples of such size can be produced and stored in magnetic microtraps recently demonstrated for cold polar molecules [58]. An
alternative solution is to use pulsed lasers, whose intensity is typically much stronger than that of cw lasers. However, the time-independent description used in this work can only be applied if the duration of the laser pulse is long compared to the collision time. This condition is necessary to ensure the validity of the quasi-static approximation for the molecule–field interaction [55].

Figures 7 and 8 show the cross sections for spin relaxation and elastic scattering in O$_2$–O$_2$ collisions as functions of the rotational constant at different collision energies. At the highest energy of 0.1 K, the cross section for spin relaxation decreases monotonically and that for elastic scattering increases with increasing $B_e$. For a molecule with $B_e/B_{O_2} > 10$, the spin relaxation would be suppressed by two orders of magnitude. As the collision energy decreases, the variation of the cross sections with $B_e$ becomes more complicated. At the lowest collision energy of $10^{-6}$ K, both the elastic and spin-changing cross sections decrease with increasing $B_e$, and the suppression of spin relaxation is very efficient for large rotational constants. In contrast, for the intermediate kinetic energy of 1 mK, the probability for spin relaxation remains large even for $B_e/B_{O_2} > 10$, and the cross sections show oscillations due to Feshbach resonances (see figure 4). The results shown in figures 7 and 8 indicate that off-resonant laser fields may be used to suppress spin-changing transitions and induce Feshbach resonances in ultracold collisions.
Elastic cross section (in units of Å$^2$)

Rotational constant (in units of $\text{Be}$)

$E = 0.1 \text{ K}$

$E = 10^{-3} \text{ K}$

$E = 10^{-6} \text{ K}$

Figure 8. The cross sections for elastic scattering in collisions of $\text{O}_2(^3\Sigma^-)$ molecules in the low-field-seeking state $|M_{S_A} = 1, M_{S_B} = 1\rangle$ as functions of the rotational constant at different collision energies. The magnetic field is 1 T.

of $^3\Sigma$ molecules. We note that in order to establish that the laser-induced magnetic Feshbach resonances do occur at practicable laser field intensities, it will be necessary to perform accurate quantum scattering calculations in superimposed magnetic and off-resonant laser fields. Such calculations can be carried out using the formalism presented in this work.

4. Summary

We have presented a quantum mechanical theory and converged quantum mechanical calculations for collisions of identical $^3\Sigma$ molecules in a magnetic field. The cross sections for spin relaxation at magnetic fields above 1 mT are comparable to the elastic cross sections, and they are not very sensitive to the applied field. At low magnetic fields, the spin–flipping transitions are suppressed by d-wave centrifugal barriers in the outgoing collision channel, suggesting that $^3\Sigma$ molecules can be evaporatively cooled in shallow magnetic traps. Our calculations shown in figure 4 suggest that the cross sections for collisions of molecules in the absolute ground state display a dense spectrum of Feshbach resonances, which may be used to tune molecule–molecule scattering lengths in a very wide range of magnetic fields.
These resonances can be used to create tetra-atomic molecules via magnetoassociation [19], manipulate molecule–molecule interactions in optical lattices [7], control chemical reactions of polyatomic molecules [4], or facilitate evaporative cooling of molecules in an optical dipole trap [59]. Our results show that the number of Feshbach resonances for molecule–molecule scattering in the absolute ground state (∼100 T⁻¹) is larger by a factor of 10 than the density of the resonances for the low-field-seeking states.

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Appendix A. Matrix elements of the interaction potential

In principle, the radial coefficients $V_{\lambda\lambda_1b_1}(R)$ can be obtained by inverting equation (15) using the orthonormality properties of the spherical harmonics. This procedure requires the evaluation of six-dimensional integrals over the angles ($\hat{R}, \hat{r}_A, \hat{r}_B$), which poses a difficult practical problem. A more convenient method of evaluating the expansion coefficients in equation (15) involves a transformation to the body-fixed (BF) frame. The $z$-axis of the BF frame coincides with the vector $R$ [40, 41]. The tensor product in equation (16) is invariant under rotations of the coordinate system [43, 44], so we can substitute $\hat{R} = \hat{\Theta}$ into equation (15) and use equation (16) to obtain

$$V_{si}(\hat{R}, \hat{r}_A, \hat{r}_B) = (4\pi)^{3/2} \sum_{\lambda_\lambda_\lambda_\lambda\lambda\lambda} \left( \frac{2\lambda + 1}{4\pi} \right)^{1/2} V_{\lambda\lambda_\lambda_\lambda\lambda\lambda}(R)$$

$$\times \sum_{m} \left( \frac{\lambda_\lambda_\lambda_\lambda\lambda\lambda}{m} \right)^{\lambda_\lambda_\lambda_\lambda\lambda\lambda} \times \left( \frac{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}{-m} \right)^{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda} Y_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}(r_A') Y_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}(r_B'), \quad (A.1)$$

where the primes indicate the BF angles. In deriving equation (A.1), we have used the fact that $Y_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}(\hat{\Theta}) = [(2\lambda + 1)/4\pi]^{1/2}$. We define the BF angular basis functions [31, 40, 41]

$$A_{\lambda\lambda_\lambda_\lambda_\lambda_\lambda}(r_A', r_B') = (2\lambda + 1)^{1/2} \sum_{m} \left( \frac{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}{m} \right)^{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda} \times \left( \frac{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}{-m} \right)^{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda} Y_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}(r_A') Y_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda}(r_B'), \quad (A.2)$$

to expand the interaction potential as follows:

$$V_{si}(\hat{R}, \hat{r}_A, \hat{r}_B) = 4\pi \sum_{\lambda_\lambda_\lambda_\lambda_\lambda_\lambda} A_{\lambda\lambda_\lambda_\lambda_\lambda_\lambda}(r_A', r_B') V_{\lambda\lambda_\lambda_\lambda_\lambda_\lambda}(R). \quad (A.3)$$

We note that the radial coefficients $V_{\lambda\lambda_\lambda_\lambda_\lambda_\lambda}(R)$ in equations (A.3) and (15) are exactly the same. This is not the case for the basis functions expressed in different coordinate systems.

The BF basis functions span a coordinate subspace defined by four angles, $\hat{r}_A' = (\theta_A, \varphi_A)$ and $\hat{r}_B' = (\theta_B, \varphi_B)$. However, the interaction potential depends on the dihedral angle $\varphi = \varphi_A - \varphi_B$ and not on the azimuthal angles separately. By separating the sum in equation (A.2) into three contributions from $m > 0$, $m = 0$ and $m < 0$, respectively, and changing the sign of the
expressed in terms of the symmetrized scattering amplitude \( \tilde{A}_{\lambda,\lambda B} \), Appendix B. Differential scattering cross sections for identical molecules

A.4

\[ A_{\lambda,\lambda B} (\rho_A, \rho_B') = \frac{(2\lambda + 1)^{1/2}}{2\pi} \sum_{m=0}^{\max} \binom{\lambda_A}{m} \binom{\lambda_B}{-m} \Theta_{\lambda,\lambda m}(\theta_A) \Theta_{\lambda_B m}(\theta_B) \] \times [2 - \delta_{m,0}] (-)^m \cos(m\varphi), \tag{A.4}

where \( \Theta_{\lambda m}(\theta_B) \) are the normalized associated Legendre polynomials. Here, we have used the relation \((-)^{\lambda+\lambda_B} = +1\) that holds for two identical homonuclear molecules.

In practice, it is more convenient to use the basis functions that depend on the angles \( \theta_A, \theta_B \) and \( \varphi \). Even though the right-hand side of equation (A.4) depends on the three angles, the functions on the left-hand side are defined in a four-angle space. Therefore, we need to renormalize equation (A.4) to exclude the integration over one extra angle. We define a reduced orthonormal basis set of functions, which span the three-dimensional subspace of angles \( (\theta_A, \theta_B, \varphi) \)

\[ \tilde{A}_{\lambda,\lambda B} (\theta_A, \theta_B, \varphi) = \sqrt{2\pi} A_{\lambda,\lambda B} (\rho_A, \rho_B') \]

\[ = \frac{(2\lambda + 1)^{1/2}}{2\pi} \sum_{m=0}^{\max} \binom{\lambda_A}{m} \binom{\lambda_B}{-m} \Theta_{\lambda,\lambda m}(\theta_A) \Theta_{\lambda_B m}(\theta_B) [2 - \delta_{m,0}] (-)^m \cos(m\varphi). \tag{A.5} \]

We emphasize that unlike equation (A.4), this expression defines an orthonormal basis in the subspace of three independent angular variables. This suggests the following expansion:

\[ V_{s_i}(R, \theta_A, \theta_B, \varphi) = \sum_{\lambda,\lambda B,\lambda} \tilde{V}_{\lambda,\lambda B,\lambda}(R) \tilde{A}_{\lambda,\lambda B,\lambda}(\theta_A, \theta_B, \varphi). \tag{A.6} \]

We note that the coefficients \( \tilde{V}_{\lambda,\lambda B,\lambda}(R) \) are not the same as in equation (15). Multiplying equation (A.6) by \( \tilde{A}_{\lambda,\lambda B,\lambda}(\theta_A, \theta_B, \varphi) \) and integrating over all angles, we find

\[ \tilde{V}_{\lambda,\lambda B,\lambda}(R) = \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\theta_A \sin \theta_A \int_{0}^{\pi} d\theta_B \sin \theta_B \tilde{A}_{\lambda,\lambda B,\lambda}(\theta_A, \theta_B, \varphi) V(R, \theta_A, \theta_B, \varphi). \tag{A.7} \]

Comparing the expansion (A.6) with equation (A.3) and using equation (A.5), we obtain the relation between the original coefficients defined by equations (15), (A.1), (A.3) and those given by equation (A.7)

\[ V_{\lambda,\lambda B,\lambda}(R) = \frac{1}{\sqrt{8\pi}} \tilde{V}_{\lambda,\lambda B,\lambda}(R). \tag{A.8} \]

To summarize, the expansion coefficients \( V_{\lambda,\lambda B,\lambda}(R) \) can be obtained by (i) evaluating the reduced basis functions (A.5); (ii) integrating the interaction potential with these functions following equation (A.7), and (iii) using equation (A.8) to obtain the original expansion coefficients (15).

Appendix B. Differential scattering cross sections for identical molecules

The differential cross section (DCS) for collisions of indistinguishable molecules can be expressed in terms of the symmetrized scattering amplitude \( \tilde{q}^{\lambda}_{\gamma A\gamma B} \rightarrow \tilde{q}^{\lambda}_{\gamma A\gamma B} \) \( (\tilde{R}_i, \tilde{R}) \) given by equation (24)

\[ \frac{d\sigma_{\gamma A\gamma B}^{\rightarrow \gamma A\gamma B}}{d\tilde{R}_i d\tilde{R}} (\tilde{R}_i, \tilde{R}) = \frac{1}{k_f^{2\gamma A\gamma B}} \left| \tilde{q}^{\lambda}_{\gamma A\gamma B} \rightarrow \tilde{q}^{\lambda}_{\gamma A\gamma B} (\tilde{R}_i, \tilde{R}) \right|^2. \]
The integral cross section can be obtained by integrating the DCS over the coordinates of the final flux and averaging over all possible directions of the initial flux.

\[
\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'} = \frac{1}{4\pi} \int \int d\hat{R} \frac{d\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'}}{d\hat{R}}(\hat{R}, \hat{R}).
\] (B.1)

Since the scattered molecules in the same internal state are not distinguishable after the collision, the integration over \( \hat{R} \) in equation (B.1) has to be restricted over half-space [25, 47] for the final states satisfying \( \gamma_A' = \gamma_B' \). Thus, equation (B.1) can be written as

\[
\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'} = \frac{1}{4\pi} \int_0^{\pi} d\phi \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi \int_0^{\theta_{\text{max}}} \sin \theta d\theta \frac{d\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'}}{d\hat{R}}(\theta, \phi, \theta, \phi),
\] (B.2)

where \( \hat{R} = (\theta, \phi) \), \( \hat{R} = (\theta, \phi) \) and we have defined \( \theta_{\text{max}} = \pi / 2 \) if \( \gamma_A' = \gamma_B' \) and \( \pi \) otherwise. The integration in equation (B.2) can be performed trivially for \( \theta_{\text{max}} = \pi \) to yield [40, 41]

\[
\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'} = \frac{\pi(1 + \delta_{\gamma_A \gamma_B})}{k_{\gamma_A \gamma_B}} \frac{1}{2} \left[ \sum_{\ell, m_1} \sum_{\ell', m_1'} \sum_{\ell_2, m'_2} \int_0 \int_0^{\pi} Y_{\gamma_A \gamma_B \ell_1 m_1}^* Y_{\gamma_A \gamma_B \ell_1' m_1'} \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi Y_{\ell_2 m'_2}^* (\theta, \phi) \right] \left[ \sum_{\ell_1, m_1} \sum_{\ell_2, m'_2} \int_0 \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi Y_{\ell_1 m_1}^* (\theta, \phi) \right].
\] (B.3)

All that remains is to consider the special case \( \gamma_A' = \gamma_B' \). Expanding the square modulus in equation (B.2) yields

\[
\sigma_{\gamma_A \gamma_B \rightarrow \gamma_A' \gamma_B'} = \frac{\pi(1 + \delta_{\gamma_A \gamma_B})}{k_{\gamma_A \gamma_B}} \left[ \sum_{\ell_1, m_1} \sum_{\ell_2, m_1} \int_0 \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi Y_{\ell_1 m_1}^* (\theta, \phi) Y_{\ell_2 m_1}^* (\theta, \phi) \right] \left[ \sum_{\ell_1, m_1} \sum_{\ell_2, m_1} \int_0 \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi Y_{\ell_1 m_1}^* (\theta, \phi) Y_{\ell_2 m_1}^* (\theta, \phi) \right].
\] (B.4)

The first integral is the usual normalization integral of two spherical harmonics. The second integral can be separated into two parts [43]

\[
\int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi Y_{\ell_1 m_1}^* (\theta, \phi) Y_{\ell_2 m_1}^* (\theta, \phi) = \int_0^{\pi} \int_0^{\pi} \sin \theta d\theta \int_0^{\pi} d\phi \Phi_{\ell_1 m_1}^* (\theta, \phi) \Phi_{\ell_2 m_1}^* (\theta, \phi).
\] (B.5)

The one-dimensional integral over \( \phi \) is equal to \( \delta_{m_1, m_2} \), so that the integral (B.5) becomes

\[
\delta_{m_1, m_2} \int_0^{\pi} \sin \theta d\theta \Theta_{\ell_1 m_1}^* (\theta) \Theta_{\ell_2 m_2}^* (\theta).
\] (B.6)

Since for identical molecules \( \ell_1 \) and \( \ell_2 \) are of the same parity (either even or odd)\(^9\), and the index \( m_1 \) is fixed, the associated Legendre polynomials in equation (B.6) are both even or odd functions of \( \cos \theta \) [43, 44]. Therefore, their product is always an even function of \( \cos \theta \).

\(^9\) This applies to homonuclear as well as heteronuclear molecules. In both cases, the states with \( \gamma_A = \gamma_B \) are present only when \( \eta(-)^{\ell} = +1 \).
in this case the substitution $\theta \to \pi - \theta$ leaves the integrand in equation (B.6) unchanged, we can halve the $\theta$ integration range and obtain
\[
\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta \, d\theta \, Y_{\ell_1 m_1}^* (\theta, \phi) Y_{\ell_2 m_2}^* (\theta, \phi) = \frac{1}{2} \delta_{\ell_1 \ell_2} \delta_{m_1 m_2}.
\] (B.7)

Substituting this result into equation (B.4) and performing the integration leads to the cancellation of the prefactor $(1 + \delta_{\gamma_1 \gamma_2} A_{\gamma_1} B_{\gamma_2})$ by the $\frac{1}{2}$ from equation (B.7). This completes the derivation of equation (29).

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