

Theory of slow-atom collisions

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A general theory of slow-atom collisions is presented with special emphasis on the effects of nuclear statistics and atomic fine and/or hyperfine structures. Symmetry properties of the collision complex and correlations between the molecular states and the separated-atom states are carefully examined. The frame transformations between various angular momentum coupling schemes are derived, which, in combination with the multichannel quantum defect theory, provides a solid foundation for the computation and the physical interpretation of slow-atom collision processes. The theory reduces to those of Stoof *et al.* [Phys. Rev. B **38**, 4688 (1988)] and Zygelman *et al.* [Phys. Rev. A **49**, 2587 (1994); **50**, 3920 (1994)] in their respective ranges of validity. [S1050-2947(96)02108-7]

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I. INTRODUCTION

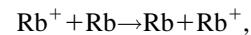
The importance and the novelty of cold-atom collisions are well documented. A review of the theoretical aspects of this problem can be found in [1]. The experimental aspects are reviewed in [2]. The recent discovery of Bose-Einstein condensation in a weakly interacting atomic vapor [3] is a further motivation for a careful examination of this subject.

Compared to atomic collisions at room temperatures or above, cold-atom collisions have a number of distinctive features. First, long-range interactions are important [4]. Second, hyperfine structures, if there are any, play a significant role in determining the collision dynamics [2,5]. This is easily understood. For a typical ground hyperfine splitting of 1 GHz, the atomic kinetic energy becomes comparable to the hyperfine structure at around 0.1 K, which is where the hyperfine effects become important. Third, if the collision happens in a near-resonant laser field, the effects of spontaneous decay and optical pumping also become important [6,1,2]. Lastly, cold-atom collisions are sensitive to the potential, i.e., a small error in the potential can lead to a large uncertainty in the cross section [4,7,8]. This is, for the most part, a general feature of slow-atom collisions, due mainly to the fact that atoms are much heavier than electrons (see Sec. III A).

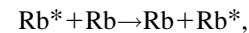
There are many theories of slow-atom collisions [9–19]. But the effects of the atomic hyperfine structure and the nuclear statistics have not been treated in a fully systematic manner. It should be pointed out that the notion of nuclear statistics is more fundamental than the notion of atomic statistics. For example, is a ^{85}Rb atom in the ground $F=3$ state distinguishable from a ^{85}Rb atom in the ground $F=2$ state? What about a $^{85}\text{Rb}^+$ ion and a ^{85}Rb atom? These are important questions related to the quantum statistics of an atomic vapor. We will get back to them in Sec. IV. The point to be made here is that at a more fundamental level, the task is to ensure that the total wave function has proper symmetry under the exchange of nuclei.

The theory of Stoof and Verhaar and their collaborators [20,21] has captured almost all the essential physics of cold collisions between alkali-metal atoms in their ground states. However, owing to the effective-atom nature of their theory, one basically has to develop a different theory for atoms with

different angular momenta or for the same atoms in different electronic states. The theory presented in this paper is more general. For example, it is capable of treating resonant charge exchange processes such as



which have not been studied at cold temperatures achievable in atom traps. It is also capable of treating resonance exchange processes such as



provided that the collision proceeds sufficiently fast so that spontaneous emission (and laser pumping if the collision happens inside a laser field) can be ignored during the collision. Furthermore, as the success of previous works of Mies and Julienne [17,22] and Gribakin and Flambaum [4,8,23] indicates, the effects of long-range interactions can be treated most naturally and effectively using the multichannel quantum defect theory (MQDT) [24–28]. The work of Stoof and Verhaar and their collaborators [20,21] has not taken full advantage of it. By incorporating MQDT and the frame transformation technique [29–33], we provide a method for quickly obtaining complete information about hyperfine collisions from existing single channel calculations [34,8,23]. The method can be refined systematically, and it leaves the door open for an R -matrix [35–40] type of treatment of short-range interactions, which may be needed if highly accurate results are desired.

Our theory of a slow-atom collision between atoms A and B is presented in Sec. II and is divided into subsections according to the classification of a collision into three different categories. Section II A deals with the case of $Z_A \neq Z_B$, which represents a collision between two different atoms, such as $\text{Rb} + \text{Ar}$. It is of interest in the understanding of optical properties of gas cells and atomic spectroscopy. Section II B deals with the case of a collision between two similar atoms whose nuclei have the same charge ($Z_A = Z_B$), but are otherwise distinguishable (due to either different spin or different mass). An example of this type of collision is $^{85}\text{Rb} + ^{87}\text{Rb}$. Section II C deals with the collision between two atoms with identical nuclei, such as $^{85}\text{Rb} + ^{85}\text{Rb}$ and

$^{85}\text{Rb}^+ + ^{85}\text{Rb}$. It is our hope that by putting these different cases together in a concise fashion, their similarities and differences will become more transparent. Various angular momentum coupling schemes are discussed in Sec. II D and Appendix A. Frame transformations and the MQDT are discussed in Sec. II E.

II. THEORY

We consider a collision between two atoms A and B in a pair of LS coupled manifolds $(\alpha_1 L_1 S_1)$ and $(\alpha_2 L_2 S_2)$. The atoms are identified by their respective nuclei. If the two nuclei are identical, this identification is facilitated by labeling one of them A and the other one B .

The Hamiltonian describing the two colliding atoms can be written as

$$H = -\frac{\hbar^2}{2\mu} \nabla_R^2 + H_{BO} + H_f + H_{hf}, \quad (1)$$

where μ is the reduced mass of the two atoms. H_f represents the spin-orbital interactions, and H_{hf} represents the hyperfine interactions. Equation (1) serves to *define* the adiabatic Born-Oppenheimer Hamiltonian H_{BO} to be used in this paper [41].

For a collision between two atoms having fine and/or hyperfine structures, a fragmentation channel [42] having a total angular momentum T and a projection on a space-fixed axis M_T is specified by a set of quantum numbers such as

$$(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F I T M_T,$$

where F results from the coupling of F_1 and F_2 ; l is the relative orbital angular momentum of the centers of mass of the two atoms. This set of quantum numbers specifies an angular momentum coupling scheme which diagonalizes both the spin-orbital and the hyperfine interactions at large interatomic separations. We will identify this coupling scheme as $J_1 F_1 J_2 F_2 F$, or FF coupling for short.

There are other possible representations of channels corresponding to different angular momentum coupling schemes. One of them is specified by quantum numbers such as

$$(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L I \mathcal{L} S K I T M_T,$$

where $\mathcal{L} = \mathbf{L} + \mathbf{I}$, and $\mathbf{K} = \mathcal{L} + \mathbf{S}$. Thus \mathcal{L} represents the total orbital angular momentum, and K represents the total angular momentum excluding nuclear spin. This coupling scheme will be identified by $L \mathcal{L} S K I$, or LS coupling for short. Another channel representation is specified by a set of quantum numbers such as

$$(\alpha_1 L_1 S_1 J_1 I_1)_A (\alpha_2 L_2 S_2 J_2 I_2)_B J I K I T M_T,$$

where $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$, $\mathbf{K} = \mathbf{J} + \mathbf{I}$, and $\mathbf{T} = \mathbf{K} + \mathbf{I}$. This coupling scheme will be identified by $J_1 J_2 J K I$, or JJ coupling for short.

The total wave function for the collision complex having definite T and M_T can be expanded in terms of adiabatic channel functions as

$$\psi^{TM_T P_T} = \sum_b \Phi_b^{TM_T P_T}(\mathbf{R}) G_b^{TM_T P_T}(R)/R, \quad (2)$$

where the summation is over one set of channels. (I will use indices a and b to refer to any set of channels, i and j to refer to the fragmentation channels. Indices α and β will be reserved for condensation channels [43].) The channel functions $\Phi_a^{TM_T P_T}(\mathbf{R})$ contain both the electronic wave function and the angular part of the relative motion of the centers of mass. They have different symmetry properties for three classes of collisions mentioned earlier, and will be discussed in detail in Secs. II A–II C.

Substituting Eq. (2) into the Schrödinger equation,

$$H \psi^{TM_T P_T} = E \psi^{TM_T P_T},$$

and making use of the orthogonality properties of the channel functions, we obtain, upon ignoring both the radial and the angular nonadiabatic coupling terms [41], a set of close-coupling equations:

$$\begin{aligned} & \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{l_a(l_a+1)\hbar^2}{2\mu R^2} - E \right) G_a^{TM_T P_T}(R) \\ & + \sum_b [V_{ab}^{BO}(R) + V_{ab}^f(R) + V_{ab}^{hf}(R)] G_b^{TM_T P_T}(R) = 0, \end{aligned} \quad (3a)$$

in which

$$V_{ab}^{BO}(R) \equiv \langle \Phi_a^{TM_T P_T} | H_{BO} | \Phi_b^{TM_T P_T} \rangle, \quad (3b)$$

$$V_{ab}^f(R) \equiv \langle \Phi_a^{TM_T P_T} | H_f | \Phi_b^{TM_T P_T} \rangle, \quad (3c)$$

$$V_{ab}^{hf}(R) \equiv \langle \Phi_a^{TM_T P_T} | H_{hf} | \Phi_b^{TM_T P_T} \rangle. \quad (3d)$$

We look for solutions which satisfy the physical boundary conditions

$$\psi_i^{TM_T P_T} \xrightarrow{R \rightarrow \infty} \sum_{j \in o} \Phi_j^{TM_T P_T} [f_j \delta_{ji} - g_j K_{ji}^{(T)}(E)]/R, \quad (4)$$

where the sum over j is over the open *fragmentation* channels only. Functions f_j and g_j are determined by the asymptotic behavior of $V_{ij}^{BO}(R)$. For a collision between two neutral atoms, they are given explicitly by

$$f_{k_j l_j}(R) = \frac{1}{\hbar} \left(\frac{2\mu}{\pi k_j} \right)^{1/2} k_j R j_{l_j}(k_j R), \quad (5a)$$

$$g_{k_j l_j}(R) = \frac{1}{\hbar} \left(\frac{2\mu}{\pi k_j} \right)^{1/2} k_j R y_{l_j}(k_j R), \quad (5b)$$

where j_l and y_l are the spherical Bessel functions [44], and we have chosen the normalization constants such that the wave function defined by Eq. (4) is normalized per unit energy. The collision cross sections and other physical observables can be extracted from $K_{ji}^{(T)}(E)$ in a pretty standard

fashion (see Appendix B). We note that unless $V^{hf} \equiv 0$, the physical K matrix has to be defined in the fragmentation (FF coupled) channels.

A. The case of $Z_A \neq Z_B$

The adiabatic Born-Oppenheimer states and potentials are defined as the eigenfunctions and eigenvalues of H_{BO} at a fixed interatomic separation R :

$$\begin{aligned} H_{BO}|M_L(\hat{\mathbf{R}})SM_S(\hat{\mathbf{R}})\Gamma;R\rangle \\ = \mathcal{E}_{M_L S \Gamma}(R)|M_L(\hat{\mathbf{R}})SM_S(\hat{\mathbf{R}})\Gamma;R\rangle, \end{aligned} \quad (6)$$

where the magnetic quantum numbers M_L and M_S are both quantized along the molecular axis $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$. These adiabatic states correspond one to one (the Wigner-Witmer rule [45,46]) to the properly antisymmetrized two-atom states defined by [16]

$$\begin{aligned} & |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L S M_S\rangle \\ &= \frac{(N_1 + N_2)!}{N_1! N_2!} \mathcal{A} \sum_{M_{L1} M_{L2} M_{S1} M_{S2}} \langle L_1 M_{L1}, L_2 M_{L2} | L M_L \rangle \\ & \times \langle S_1 M_{S1} S_2 M_{S2} | S M_S \rangle | \alpha_1 L_1 M_{L1} S_1 M_{S1} \rangle_A \\ & \times | \alpha_2 L_2 M_{L2} S_2 M_{S2} \rangle_B, \end{aligned} \quad (7)$$

where N_1 and N_2 are numbers of electrons corresponding to states $| \alpha_1 L_1 M_{L1} S_1 M_{S1} \rangle$ and $| \alpha_2 L_2 M_{L2} S_2 M_{S2} \rangle$, respectively. \mathcal{A} is an antisymmetrization operator that operates on all electrons. For the sake of simplified notation, the normalization constant and the operator \mathcal{A} will be dropped in further references to the two-atom states [47].

This one-to-one correspondence implies that there exist quasimolecular states

$$|(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle,$$

which are linear combinations of Born-Oppenheimer states, that satisfy

$$\begin{aligned} & |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\ & \xrightarrow{R \rightarrow \infty} |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle. \end{aligned} \quad (8)$$

Here the state

$$|(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle$$

is a two-atom state as defined by Eq. (7) except that it is quantized along the molecular axis. They are related to each other through the relationship

$$\begin{aligned} & |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle \\ &= \sum_{M'_L M'_S} D_{M'_L M_L}^L(\phi, \theta, 0) D_{M'_S M_S}^S(\phi, \theta, 0) \\ & \times |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M'_L S M'_S\rangle, \end{aligned} \quad (9)$$

where the angles θ and ϕ specify the direction of the molecular axis $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ in a space-fixed frame, which by definition always points from the nucleus B to the nucleus A .

The symmetry properties of the quasimolecular states defined by Eq. (8) can be derived from their corresponding two-atom states. It can be shown that the two-atom states have the following symmetry properties [48]:

$$\begin{aligned} & \hat{\sigma}_e |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle \\ &= P_1 P_2 (-1)^{L-M_L} |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L \\ & \quad - M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle, \end{aligned} \quad (10)$$

$$\begin{aligned} & \hat{P}_T |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}})\rangle \\ &= P_1 P_2 (-1)^{L+S+M_L+M_S} e^{-i(M_L+M_S)\pi} \\ & \times |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L - M_L(\hat{\mathbf{R}}) S - M_S(\hat{\mathbf{R}})\rangle, \end{aligned} \quad (11)$$

where $\hat{\sigma}_e$ refers to the reflection of electronic coordinates in a plane containing the molecule axis, and \hat{P}_T refers to the total parity operation which inverts both the electronic and the nuclear coordinates. P_1 and P_2 are the parities of LS manifolds $(\alpha_1 L_1 S_1)$ and $(\alpha_2 L_2 S_2)$, respectively [49]. In arriving at Eq. (11), we have used

$$D_{MM'}^J(\pi + \phi, \pi - \theta, 0) = e^{-iM'\pi} (-1)^{J+M'} D_{M-M'}^J(\phi, \theta, 0). \quad (12)$$

Since molecular interactions cannot break these symmetries [50], the quasimolecular states defined by Eq. (8), and the corresponding Born-Oppenheimer states from which they are constructed, must also have the same symmetry, i.e.,

$$\begin{aligned} & \hat{\sigma}_e |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\ &= P_1 P_2 (-1)^{L-M_L} |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L \\ & \quad - M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle, \end{aligned} \quad (13)$$

$$\begin{aligned} & \hat{P}_T |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\ &= P_1 P_2 (-1)^{L+S+M_L+M_S} e^{-i(M_L+M_S)\pi} \\ & \times |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L \\ & \quad - M_L(\hat{\mathbf{R}}) S - M_S(\hat{\mathbf{R}}); R\rangle. \end{aligned} \quad (14)$$

Specifically, Eq. (13) implies that a quasimolecular state with $M_L = 0$ is an eigenstate of $\hat{\sigma}_e$ with an eigenvalue

$$\sigma_e = P_1 P_2 (-1)^L. \quad (15)$$

Other symmetry properties of the quasimolecular states to be discussed later are all derived this way (i.e., from their corresponding two-atom states).

The quasimolecular state defined by Eq. (8) is generally a linear combination of Born-Oppenheimer states having the same M_L , S , and M_S , and the symmetry properties as specified by Eqs. (13) and (14). If there is only one such Born-

Oppenheimer (BO) state, then the two have to be equal (up to a global phase factor). If there is more than one BO state satisfying the same criteria, further disentanglement can be achieved by comparing additional symmetry properties, if there are any (see, e.g., Sec. II B), or by comparing the

asymptotic forms of $\mathcal{E}_{M_L S \Gamma}(R)$ with the asymptotic potentials calculated using the two-atom states [18].

We are now in the position to derive the fragmentation (FF coupled) channel functions defined by the desired asymptotic behavior:

$$\begin{aligned} \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l}^{T M_T P_T} &\xrightarrow{R \rightarrow \infty} \sum_{M_1 M_2 M_F m_l} \langle F_1 M_1, F_2 M_2 | F M_F \rangle \\ &\times \langle F M_F, l m_l | T M_T \rangle | \alpha_1 L_1 S_1 J_1 I_1 F_1 M_1 \rangle_A | \alpha_2 L_2 S_2 J_2 I_2 F_2 M_2 \rangle_B Y_{l m_l}(\theta, \phi), \end{aligned} \quad (16)$$

which diagonalizes both the asymptotic spin-orbital and the asymptotic hyperfine interactions, and in which all magnetic quantum numbers are quantized along a space-fixed axis. The task is to find a proper superposition of the quasimolecular states, which are linear combinations of the adiabatic Born-Oppenheimer states, such that the desired asymptotic behavior is satisfied for all orientations. From Eqs. (7)–(9), one can show that this proper superposition is given by

$$\begin{aligned} \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l}^{T M_T P_T} &= [J_1, J_2, F_1, F_2]^{1/2} \sum_{L S J I} \sum_{\text{all } m} [L, S, J, I]^{1/2} \\ &\times \langle L M'_L, S M'_S | J M'_J \rangle \langle J M_J, I M_I | F_i M_F \rangle \langle F M_F, l m_l | T M_T \rangle \\ &\times \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_1 & J_2 & J \end{Bmatrix} \begin{Bmatrix} J_1 & J_2 & J \\ I_1 & I_2 & I \\ F_1 & F_2 & F \end{Bmatrix} D_{M_J M'_J}^{J^*}(\phi, \theta, 0) Y_{l m_l}(\theta, \phi) \\ &\times |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M'_L(\hat{\mathbf{R}}) S M'_S(\hat{\mathbf{R}}); R\rangle | (I_1)_A (I_2)_B I M_I \rangle. \end{aligned} \quad (17)$$

Not only does this channel function have the desired asymptotic behavior characterized by Eq. (16), but one can also show from Eqs. (12) and (14) that it is an eigenstate of the total parity operator with an eigenvalue

$$P_T = P_1 P_2 (-1)^l. \quad (18)$$

With channel functions given in terms of the quasimolecular states, we can now express the potential $V_{ij}^{BO}(R)$ that enters the close-coupling equation (3) in terms of the adiabatic Born-Oppenheimer potentials. Some calculations lead to

$$\begin{aligned} &\langle \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l_i}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l_j}^{T_j M_{T_j} P_{T_j}} \rangle \\ &= \delta_{T_i T_j} \delta_{M_{T_i} M_{T_j}} \delta_{P_{T_i} P_{T_j}} (-1)^{F_i - F_j} [J_{1i}, J_{2i}, F_{1i}, F_{2i}, F_i, l_i, J_{1j}, J_{2j}, F_{1j}, F_{2j}, F_j, l_j]^{1/2} \\ &\times \sum_{M_L M_S} \sum_{L S K I J_i J_j} (-1)^{J_j - J_i} [L, S, K, I, J_i, J_j] \begin{Bmatrix} l_i & K & J_i \\ I & F_i & T_i \end{Bmatrix} \begin{Bmatrix} l_j & K & J_j \\ I & F_j & T_j \end{Bmatrix} \\ &\times \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1i} & J_{2i} & J_i \end{Bmatrix} \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1j} & J_{2j} & J_j \end{Bmatrix} \begin{Bmatrix} J_{1i} & J_{2i} & J_i \\ I_1 & I_2 & I \\ F_{1i} & F_{2i} & F_i \end{Bmatrix} \begin{Bmatrix} J_{1j} & J_{2j} & J_j \\ I_1 & I_2 & I \\ F_{1j} & F_{2j} & F_j \end{Bmatrix} \\ &\times \begin{pmatrix} L & S & J_i \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_j \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_i & l_i & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\ &\times \begin{pmatrix} J_j & l_j & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \mathcal{E}_{M_L S \Gamma}(R), \end{aligned} \quad (19)$$

where $\delta_{P_{T_i}P_{T_j}}$ implies $l_i - l_j = \text{even}$ [cf. Eq. (18)].

If both atoms have zero nuclear spin, i.e., $I_1 = I_2 = 0$, Eq. (19) reduces to

$$\begin{aligned}
V_{ij}^{BO} = & \delta_{T_i T_j} \delta_{M_{T_i} M_{T_j}} \delta_{P_{T_i} P_{T_j}} (-1)^{J_i - J_j} [J_{1i}, J_{2i}, J_i, l_i, J_{1j}, J_{2j}, J_j, l_j]^{1/2} \sum_{M_L M_S L S} [L, S] \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1i} & J_{2i} & J_i \end{Bmatrix} \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1j} & J_{2j} & J_j \end{Bmatrix} \\
& \times \begin{pmatrix} L & S & J_i \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_j \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_i & l_i & T \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\
& \times \begin{pmatrix} J_j & l_j & T \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \mathcal{E}_{M_L S \Gamma}(R), \tag{20}
\end{aligned}$$

which agrees with the result of Zygelman *et al.* [18,19,51].

To determine the potentials associated with H_f and H_{hf} , one should, in principle, calculate the matrix elements of these interactions with the fragmentation channel functions given by Eq. (17). At large R , they both become diagonalized and are given by

$$V_{ij}^f + V_{ij}^{hf} \xrightarrow{R \rightarrow \infty} (\Delta E_i^f + \Delta E_i^{hf}) \delta_{ij}, \tag{21}$$

where ΔE_i^f is the sum of fine-structure splitting for the two colliding atoms, and ΔE_i^{hf} is the total hyperfine splitting. For simplicity, we will use this asymptotic potential for all R .

The close-coupling equation (3) can now be solved subject to the physical boundary condition of Eq. (4). The S matrix, the scattering amplitude, and the differential cross sections are derived in the standard fashion (see Appendix B) and are given by

$$S^{(T)}(E) = [I + iK^{(T)}(E)][I - iK^{(T)}(E)]^{-1}, \tag{22}$$

where I represents a unit matrix, and

$$\begin{aligned}
& f((\alpha_1 L_1 S_1 J_{1i} F_{1i} M_{1i})_A (\alpha_2 L_2 S_2 J_{2i} F_{2i} M_{2i})_B \mathbf{k}_i \rightarrow (\alpha_1 L_1 S_1 J_{1j} F_{1j} M_{1j})_A (\alpha_2 L_2 S_2 J_{2j} F_{2j} M_{2j})_B \mathbf{k}_j) \\
& = \sum_{l_i m_{l_i} l_j m_{l_j}} \frac{2\pi i}{(k_i k_j)^{1/2}} i^{l_i - l_j} Y_{l_i m_{l_i}}^*(\hat{\mathbf{k}}_i) Y_{l_j m_{l_j}}(\hat{\mathbf{k}}_j) \sum_{F_i M_{F_i} F_j M_{F_j} T M_T} \langle F_{1j} M_{1j}, F_{2j} M_{2j} | F_j M_{F_j} \rangle \langle F_j M_{F_j}, l_j m_{l_j} | T M_T \rangle [S^{(T)}(E) - I]_{ji} \\
& \times \langle F_{1i} M_{1i}, F_{2i} M_{2i} | F_i M_{F_i} \rangle \langle F_i M_{F_i}, l_i m_{l_i} | T M_T \rangle, \tag{23}
\end{aligned}$$

$$\frac{d\sigma}{d\Omega}((\alpha_1 L_1 S_1 J_{1i} F_{1i} M_{1i})_A (\alpha_2 L_2 S_2 J_{2i} F_{2i} M_{2i})_B \mathbf{k}_i \rightarrow (\alpha_1 L_1 S_1 J_{1j} F_{1j} M_{1j})_A (\alpha_2 L_2 S_2 J_{2j} F_{2j} M_{2j})_B \mathbf{k}_j) = \frac{k_j}{k_i} |f(i \rightarrow j)|^2, \tag{24}$$

where $f(i \rightarrow j)$ is a short-hand notation for the amplitude given by Eq. (23).

B. The case of similar ($Z_A = Z_B$) atoms with distinguishable nuclei

An example of this case would be the collision between a ^{85}Rb atom and a ^{87}Rb atom.

As long as $Z_A = Z_B$, the Born-Oppenheimer states defined by Eq. (6) have inversion symmetry with respect to the center of the molecule, provided that nonadiabatic couplings are ignored [52]. On the other hand, the quasimolecular state defined by Eq. (8) may or may not have this symmetry. From its corresponding two-atom state, one can show that the quasimolecular state behaves under inversion as [47,48]

$$\begin{aligned}
& \hat{I}_e |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\
& = P_1 P_2 (-1)^{N_1 N_2 + L_1 + L_2 - L + S_1 + S_2 - S} |(\alpha_2 L_2 S_2)_A \\
& \times (\alpha_1 L_1 S_1)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle, \tag{25}
\end{aligned}$$

where \hat{I}_e refers to the inversion of electronic coordinates with respect to the center of the molecule. Two distinctive cases need to be addressed separately here.

1. $\alpha_2 L_2 S_2 = \alpha_1 L_1 S_1$

The situation in this case does not differ very much from the case of $Z_A \neq Z_B$ discussed in the previous section, since the quasimolecular states of Eq. (8) already have the proper inversion symmetry. From Eq. (25), we have

$$\begin{aligned}
& \hat{I}_e |(\alpha_1 L_1 S_1)_A (\alpha_1 L_1 S_1)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\
& = W_{LS} |(\alpha_1 L_1 S_1)_A (\alpha_1 L_1 S_1)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \tag{26}
\end{aligned}$$

with

$$W_{LS} = (-1)^{L+S}. \tag{27}$$

Thus the potential is again given by Eq. (19) except that we can add one more quantum number to the notation by replacing $\mathcal{E}_{M_L S \Gamma}$ by $\mathcal{E}_{M_L S W_L S \Gamma}$. Everything else remains unchanged.

2. $\alpha_2 L_2 S_2 \neq \alpha_1 L_1 S_1$

The situation becomes much different here since the quasimolecular state,

$$|(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle$$

no longer has the proper inversion symmetry. However, its relationship with BO states of the proper symmetry is rather simple. From Eq. (25), one can choose a phase convention such that

$$|(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle = \frac{1}{\sqrt{2}} [|M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}) g \Gamma; R\rangle + |M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}) u \Gamma; R\rangle], \quad (28a)$$

$$\begin{aligned} & |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\ &= P_1 P_2 (-1)^{N_1 N_2 + L_1 + L_2 - L + S_1 + S_2 - S} \frac{1}{\sqrt{2}} [|M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}) g \Gamma; R\rangle - |M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}) u \Gamma; R\rangle], \end{aligned} \quad (28b)$$

where the symbols g and u refer to gerade and ungerade states, respectively. A more important difference introduced by the similarity of the atoms is that there are now additional channels described by channel functions:

$$\begin{aligned} & \Phi_{(\alpha_2 L_2 S_2 J_2 I_1 F_2)_A (\alpha_1 L_1 S_1 J_1 I_2 F_1)_B}^{T M_T P_T} \\ &= [J_1, J_2, F_1, F_2]^{1/2} \sum_{L S J I} \sum_{\text{all } m} [L, S, J, I]^{1/2} \langle L M'_L, S M'_S | J M'_J \rangle \langle J M_J, I M_I | F_i M_F \rangle \langle F M_F, l m_l | T M_T \rangle \\ & \times \begin{pmatrix} L_2 & L_1 & L \\ S_2 & S_1 & S \\ J_2 & J_1 & J \end{pmatrix} \begin{pmatrix} J_2 & J_1 & J \\ I_1 & I_2 & I \\ F_2 & F_1 & F \end{pmatrix} D_{M_J M'_J}^{J*}(\phi, \theta, 0) Y_{l m_l}(\theta, \phi) \\ & \times |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B L M'_L(\hat{\mathbf{R}}) S M'_S(\hat{\mathbf{R}}); R\rangle | (I_1)_A (I_2)_B I M_I \rangle, \end{aligned} \quad (29)$$

which corresponds to interchanging the electronic states of the two atoms in Eq. (17). These two sets of channels are coupled, and it is this coupling that gives rise to the resonance exchange.

The complete potential V_{ij}^{BO} is now given in terms of the BO potentials by the following set of equations:

$$\begin{aligned} & \langle \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B}^{T_j M_{T_j} P_{T_j}} \rangle \\ &= \delta_{T_i T_j} \delta_{M_{T_i} M_{T_j}} (-1)^{F_i - F_j} [J_{1i}, J_{2i}, F_{1i}, F_{2i}, F_i, l_i, J_{1j}, J_{2j}, F_{1j}, F_{2j}, F_j, l_j]^{1/2} \sum_{M_L M_S L S I K J_i J_j} (-1)^{J_i - J_j} [L, S, I, K, J_i, J_j] \\ & \times \begin{pmatrix} l_i & K & J_i \\ I & F_i & T_i \end{pmatrix} \begin{pmatrix} l_j & K & J_j \\ I & F_j & T_j \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1i} & J_{2i} & J_i \end{pmatrix} \begin{pmatrix} J_{1i} & J_{2i} & J_i \\ I_1 & I_2 & I \\ F_{1i} & F_{2i} & F_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1j} & J_{2j} & J_j \end{pmatrix} \begin{pmatrix} J_{1j} & J_{2j} & J_j \\ I_1 & I_2 & I \\ F_{1j} & F_{2j} & F_j \end{pmatrix} \\ & \times \begin{pmatrix} L & S & J_i \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_j \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_i & l_i & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\ & \times \begin{pmatrix} J_j & l_j & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \frac{1}{2} (\mathcal{E}_{M_L S M_S g \Gamma} + \mathcal{E}_{M_L S M_S u \Gamma}), \end{aligned} \quad (30a)$$

$$\begin{aligned} & \langle \Phi_{(\alpha_2 L_2 S_2 J_2 I_1 F_2)_A (\alpha_1 L_1 S_1 J_1 I_2 F_1)_B}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_2 I_1 F_2)_A (\alpha_1 L_1 S_1 J_1 I_2 F_1)_B}^{T_j M_{T_j} P_{T_j}} \rangle \\ &= \delta_{T_i T_j} \delta_{M_{T_i} M_{T_j}} (-1)^{F_i - F_j} [J_{1i}, J_{2i}, F_{1i}, F_{2i}, F_i, l_i, J_{1j}, J_{2j}, F_{1j}, F_{2j}, F_j, l_j]^{1/2} \sum_{M_L M_S L S I K J_i J_j} (-1)^{J_i - J_j} [L, S, I, K, J_i, J_j] \end{aligned}$$

$$\begin{aligned}
& \times \begin{Bmatrix} l_i & K & J_i \\ I & F_i & T_i \end{Bmatrix} \begin{Bmatrix} l_j & K & J_j \\ I & F_j & T_j \end{Bmatrix} \begin{Bmatrix} L_2 & L_1 & L \\ S_2 & S_1 & S \end{Bmatrix} \begin{Bmatrix} J_{2i} & J_{1i} & J_i \\ F_{2i} & F_{1i} & F_i \end{Bmatrix} \begin{Bmatrix} L_2 & L_1 & L \\ S_2 & S_1 & S \end{Bmatrix} \begin{Bmatrix} J_{2j} & J_{1j} & J_j \\ F_{2j} & F_{1j} & F_j \end{Bmatrix} \\
& \times \begin{pmatrix} L & S & J_i \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_j \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_i & l_i & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\
& \times \begin{pmatrix} J_j & l_j & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \frac{1}{2} (\mathcal{E}_{M_L S M_S \Gamma} + \mathcal{E}_{M_L S M_S \Gamma}), \tag{30b}
\end{aligned}$$

$$\begin{aligned}
& \langle \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_2 I_2 F_2)_A (\alpha_1 L_1 S_1 J_1 I_1 F_1)_B}^{T_j M_{T_j} P_{T_j}} \rangle \\
& = \langle \Phi_{(\alpha_2 L_2 S_2 J_2 I_2 F_2)_A (\alpha_1 L_1 S_1 J_1 I_1 F_1)_B}^{T_j M_{T_j} P_{T_j}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B}^{T_i M_{T_i} P_{T_i}} \rangle \\
& = \delta_{T_i T_j} \delta_{M_{T_i} M_{T_j}} P_1 P_2 (-1)^{F_i - F_j + N_1 N_2} [J_{1i}, J_{2i}, F_{1i}, F_{2i}, F_i, l_i, J_{1j}, J_{2j}, F_{1j}, F_{2j}, F_j, l_j]^{1/2} \\
& \times \sum_{M_L M_S L S I K J_i J_j} (-1)^{J_{1j} + J_{2j} - J_i} [L, S, I, K, J_i, J_j] \begin{Bmatrix} l_i & K & J_i \\ I & F_i & T_i \end{Bmatrix} \begin{Bmatrix} l_j & K & J_j \\ I & F_j & T_j \end{Bmatrix} \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \end{Bmatrix} \begin{Bmatrix} J_{1i} & J_{2i} & J_i \\ F_{1i} & F_{2i} & F_i \end{Bmatrix} \\
& \times \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \end{Bmatrix} \begin{Bmatrix} J_{2j} & J_{1j} & J_j \\ I_1 & I_2 & I \end{Bmatrix} \begin{pmatrix} L & S & J_i \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_j \\ M_L & M_S & -M_L - M_S \end{pmatrix} \\
& \times \begin{pmatrix} J_i & l_i & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_j & l_j & K \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \frac{1}{2} (\mathcal{E}_{M_L S M_S \Gamma} - \mathcal{E}_{M_L S M_S \Gamma}). \tag{30c}
\end{aligned}$$

Note that the coupling which gives rise to the resonance exchange [Eq. (30c)] is determined by the energy differences between the gerade and the ungerade states.

The notations for the scattering amplitude and the cross section need to be changed from those in Eqs. (23) and (24) to

$$f(((\alpha L S)_{1i} J_{1i} F_{1i} M_{1i})_A ((\alpha L S)_{2i} J_{2i} F_{2i} M_{2i})_B \mathbf{k}_i \rightarrow ((\alpha L S)_{1j} J_{1j} F_{1j} M_{1j})_A ((\alpha L S)_{2j} J_{2j} F_{2j} M_{2j})_B \mathbf{k}_j),$$

$$\frac{d\sigma}{d\Omega} (((\alpha L S)_{1i} J_{1i} F_{1i} M_{1i})_A ((\alpha L S)_{2i} J_{2i} F_{2i} M_{2i})_B \mathbf{k}_i \rightarrow ((\alpha L S)_{1j} J_{1j} F_{1j} M_{1j})_A ((\alpha L S)_{2j} J_{2j} F_{2j} M_{2j})_B \mathbf{k}_j),$$

to account for the possibility of resonance exchange. Here $(\alpha L S)$ can either be $\alpha_1 L_1 S_1$ or $\alpha_2 L_2 S_2$.

C. The case of identical nuclei

The new element in this case is that the total wave function must have proper symmetry under the exchange of nuclei. From the corresponding two-atom state and Eq. (12), one can show that the quasimolecular state defined by Eq. (8) behaves as [47,48]

$$\begin{aligned}
& \hat{X}_n |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M_L(\hat{\mathbf{R}}) S M_S(\hat{\mathbf{R}}); R\rangle \\
& = (-1)^{N_1 N_2 + L_1 + L_2 - L + S_1 + S_2 - S} \\
& \quad \times |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B L M_L(-\hat{\mathbf{R}}) S M_S(-\hat{\mathbf{R}}); R\rangle \\
& = (-1)^{N_1 N_2 + L_1 + L_2 + S_1 + S_2 + M_L + M_S} e^{-i(M_L + M_S)\pi} \\
& \quad \times |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B L - M_L(\hat{\mathbf{R}}) S - M_S(\hat{\mathbf{R}}); R\rangle \tag{31}
\end{aligned}$$

under the exchange of nuclei, an operation denoted by \hat{X}_n .

From this equation and Eq. (12), it is straightforward to show that the channel function defined by Eq. (17) behaves as

$$\begin{aligned}
& \hat{X}_n \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B}^{T M_{T P T}}(\mathbf{R}) \\
& = (-1)^{N_1 N_2 + F_1 + F_2 - F + l} \\
& \quad \times \Phi_{(\alpha_2 L_2 S_2 J_2 I_2 F_2)_A (\alpha_1 L_1 S_1 J_1 I_1 F_1)_B}^{T M_{T P T}}(\mathbf{R}) \tag{32}
\end{aligned}$$

(keeping in mind that identical nuclei implies, of course, $I_2 = I_1$). Thus a channel function with the desired symmetry property,

$$\begin{aligned}
& \hat{X}_n \Phi_{\{\alpha_1 L_1 S_1 J_1 I_1 F_1, \alpha_2 L_2 S_2 J_2 I_2 F_2\}}^{T M_{T P T}}(\mathbf{R}) \\
& = (-1)^{2I_1} \Phi_{\{\alpha_1 L_1 S_1 J_1 I_1 F_1, \alpha_2 L_2 S_2 J_2 I_2 F_2\}}^{T M_{T P T}}(\mathbf{R}), \tag{33}
\end{aligned}$$

can be written in terms of channel functions given by Eq. (17) as

$$\begin{aligned} & \Phi_{\{\alpha_1 L_1 S_1 J_1 I_1 F_1, \alpha_2 L_2 S_2 J_2 I_2 F_2\} F l}^{T M_T P_T}(\mathbf{R}) \\ &= C^{FF} [\Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l}^{T M_T P_T}(\mathbf{R}) \\ &+ (-1)^{N_1 N_2 + 2I_1 + F_1 + F_2 - F + l} \\ &\times \Phi_{(\alpha_2 L_2 S_2 J_2 I_2 F_2)_A (\alpha_1 L_1 S_1 J_1 I_1 F_1)_B F l}^{T M_T P_T}(\mathbf{R})], \quad (34) \end{aligned}$$

in which C^{FF} is a normalization constant given by

$$C^{FF} = \{2[1 + \delta(\alpha_2 L_2 S_2 J_2 I_2 F_2, \alpha_1 L_1 S_1 J_1 I_1 F_1)]\}^{-1/2}.$$

Equation (34) implies that if

$$(\alpha_2 L_2 S_2 J_2 I_2 F_2) = (\alpha_1 L_1 S_1 J_1 I_1 F_1)$$

(implying, of course, $N_1 = N_2$), only states satisfying

$$F + l = \text{even} \quad (35)$$

are possible [53], regardless of whether the nuclei are bosons or fermions.

The potential V_{ij}^{BO} is given in this case by

$$\begin{aligned} & \langle \Phi_{\{\alpha_1 L_1 S_1 J_1 I_1 F_1 i, \alpha_2 L_2 S_2 J_2 I_2 F_2 i\} F l_i}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{\{\alpha_1 L_1 S_1 J_1 I_1 F_1 j, \alpha_2 L_2 S_2 J_2 I_2 F_2 j\} F l_j}^{T_j M_{T_j} P_{T_j}} \rangle \\ &= 2 C_i^{FF} C_j^{FF} [\langle \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l_i}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l_j}^{T_j M_{T_j} P_{T_j}} \rangle \\ &+ (-1)^{N_1 N_2 + 2I_1 + l_j + F_{1j} + F_{2j} - F_j} \langle \Phi_{(\alpha_1 L_1 S_1 J_1 I_1 F_1)_A (\alpha_2 L_2 S_2 J_2 I_2 F_2)_B F l_i}^{T_i M_{T_i} P_{T_i}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_2 I_2 F_2)_A (\alpha_1 L_1 S_1 J_1 I_1 F_1)_B F l_j}^{T_j M_{T_j} P_{T_j}} \rangle], \quad (36) \end{aligned}$$

where the matrix elements on the right-hand side are given by Eq. (30) for $(\alpha_1 L_1 S_1) \neq (\alpha_2 L_2 S_2)$, and by Eq. (19) for $(\alpha_1 L_1 S_1) = (\alpha_2 L_2 S_2)$.

The differential cross section in the center-of-mass frame is given by (see Appendix B)

$$\begin{aligned} & \frac{d\sigma}{d\Omega} [\{(\alpha LS)_{1j} J_{1j} F_{1j} M_{1j}, (\alpha LS)_{2i} J_{2i} F_{2i} M_{2i}\} \mathbf{k}_i \rightarrow \{(\alpha LS)_{1j} J_{1j} F_{1j} M_{1j}, (\alpha LS)_{2j} J_{2j} F_{2j} M_{2j}\} \mathbf{k}_j] \\ &= \frac{k_j}{k_i} \frac{|C_j^{FF}|^2}{|C_i^{FF}|^2} |f(i \rightarrow j, \mathbf{k}_j) + (-1)^{N_1 N_2 + 2I_1} f(i \rightarrow j, -\mathbf{k}_j)|^2, \quad (37) \end{aligned}$$

where $f(i \rightarrow j, \mathbf{k}_j)$ is a short-hand notation for the full expression

$$\begin{aligned} & f(\{(\alpha LS)_{1j} J_{1j} F_{1j} M_{1j}, (\alpha LS)_{2i} J_{2i} F_{2i} M_{2i}\} \mathbf{k}_i \\ & \rightarrow \{(\alpha LS)_{1j} J_{1j} F_{1j} M_{1j}, (\alpha LS)_{2j} J_{2j} F_{2j} M_{2j}\} \mathbf{k}_j), \end{aligned}$$

which is related to the S matrix by Eq. (23). Equation (37) implies that

$$\frac{d\sigma}{d\Omega}(-\mathbf{k}_j) = \frac{d\sigma}{d\Omega}(\mathbf{k}_j)$$

(in the center-of-mass frame) is generally applicable to collisions between atoms with identical nuclei, which may be in different states or carry different charge.

D. LS coupling

In previous sections, we have established the proper identification of fragmentation channels and the close-coupling equations to be solved for different types of collisions. The rest of this paper deals basically with the question of how to solve these equations effectively.

The potentials given by Eqs. (19), (30), and (36) are complicated because the fragmentation channel functions do not reflect the symmetry of H_{BO} . A much simpler representation of V^{BO} can be obtained in the LS coupled condensation channels [43], which are defined, in the case of distinguishable nuclei, by the asymptotic behavior

$$\begin{aligned} & \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L I S K I}^{T M_T P_T} \xrightarrow{R \rightarrow \infty} \sum_{\text{all } m} \langle L_1 M_{L_1}, L_2 M_{L_2} | L M_L \rangle \langle L M_L, l m_l | L M_L \rangle \langle S_1 M_{S_1}, S_2 M_{S_2} | S M_S \rangle \langle L M_L, S M_S | K M_K \rangle \\ & \times \langle K M_K, I M_I | T M_T \rangle | \alpha_1 L_1 M_{L_1} S_1 M_{S_1} \rangle_A | \alpha_2 L_2 M_{L_2} S_2 M_{S_2} \rangle_B Y_{l m_l}(\theta, \phi) | (I_1)_A (I_2)_B I M_I \rangle, \quad (38) \end{aligned}$$

where all the magnetic quantum numbers are quantized along a space-fixed axis. A channel function with such an asymptotic behavior can be written in terms of the quasimolecular states defined by Eq. (8) as

$$\begin{aligned} \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L L S K I}^{T_\alpha M T P T} &= \sum_{\text{all } m} \langle L M_L, l m_l | \mathcal{L} M_{\mathcal{L}} \rangle \langle \mathcal{L} M_{\mathcal{L}}, S M_S | K M_K \rangle \\ &\quad \times \langle K M_K, I M_I | T M_T \rangle D_{M_L M'_L}^{L*}(\phi, \theta, 0) D_{M_S M'_S}^{S*}(\phi, \theta, 0) Y_{l m_l}(\theta, \phi) |(\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B \\ &\quad \times L M'_L(\hat{R}) S M'_S(\hat{R}); R \rangle | (I_1)_A (I_2)_B I M_I \rangle. \end{aligned} \quad (39)$$

The potential V^{BO} becomes much simplified in this coupling scheme and is given by

$$\begin{aligned} &\langle \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L_\alpha l_\alpha S_\alpha K_\alpha I_\alpha}^{T_\alpha M T_\alpha P T_\alpha} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L_\beta l_\beta S_\beta K_\beta I_\beta}^{T_\beta M T_\beta P T_\beta} \rangle \\ &= \delta_{T_\beta T_\alpha} \delta_{M_\beta M_\alpha} \delta_{P_\beta P_\alpha} \delta_{L_\beta L_\alpha} \delta_{l_\beta l_\alpha} \delta_{S_\beta S_\alpha} \delta_{K_\beta K_\alpha} \delta_{I_\beta I_\alpha} [l_\alpha, l_\beta]^{1/2} \sum_{M_L} \begin{pmatrix} L_\alpha & l_\alpha & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \begin{pmatrix} L_\alpha & l_\beta & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \mathcal{E}_{M_L S_\alpha L_\alpha}(R), \end{aligned} \quad (40)$$

which is block diagonal in all quantum numbers except l . This potential is consistent with Eq. (22) of Ref. [19].

In the case of similar atom ($Z_A = Z_B$) with distinguishable nuclei and $(\alpha_1 L_1 S_1) \neq (\alpha_2 L_2 S_2)$, there are additional channels characterized by

$$\begin{aligned} \Phi_{(\alpha_2 L_2 S_2 I_2)_A (\alpha_1 L_1 S_1 I_1)_B L L S K I}^{T_\alpha M T P T} &= \sum_{\text{all } m} \langle L M_L, l m_l | \mathcal{L} M_{\mathcal{L}} \rangle \langle \mathcal{L} M_{\mathcal{L}}, S M_S | K M_K \rangle \langle K M_K, I M_I | T M_T \rangle D_{M_L M'_L}^{L*}(\phi, \theta, 0) D_{M_S M'_S}^{S*}(\phi, \theta, 0) \\ &\quad \times Y_{l_\alpha m_l}(\theta, \phi) |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B L M'_L(\hat{R}) S M'_S(\hat{R}); R \rangle | (I_1)_A (I_2)_B I M_I \rangle, \end{aligned} \quad (41)$$

which is a result of interchanging the electronic states in Eq. (39). With the help of Eq. (28), we obtain the potential $V_{\alpha\beta}^{BO}$:

$$\begin{aligned} &\langle \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L_\alpha l_\alpha S_\alpha K_\alpha I_\alpha}^{T_\alpha M T_\alpha P T_\alpha} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L_\beta l_\beta S_\beta K_\beta I_\beta}^{T_\beta M T_\beta P T_\beta} \rangle \\ &= \langle \Phi_{(\alpha_2 L_2 S_2 I_2)_A (\alpha_1 L_1 S_1 I_1)_B L_\alpha l_\alpha S_\alpha K_\alpha I_\alpha}^{T_\alpha M T_\alpha P T_\alpha} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 I_2)_A (\alpha_1 L_1 S_1 I_1)_B L_\beta l_\beta S_\beta K_\beta I_\beta}^{T_\beta M T_\beta P T_\beta} \rangle \\ &= \delta_{T_\beta T_\alpha} \delta_{M_\beta M_\alpha} \delta_{P_\beta P_\alpha} \delta_{L_\beta L_\alpha} \delta_{l_\beta l_\alpha} \delta_{S_\beta S_\alpha} \delta_{K_\beta K_\alpha} \delta_{I_\beta I_\alpha} [l_\alpha, l_\beta]^{1/2} \sum_{M_L} \begin{pmatrix} L_\alpha & l_\alpha & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \\ &\quad \times \begin{pmatrix} L_\alpha & l_\beta & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \frac{1}{2} [\mathcal{E}_{M_L S_\alpha g L_\alpha}(R) + \mathcal{E}_{M_L S_\alpha u L_\alpha}(R)], \end{aligned} \quad (42a)$$

$$\begin{aligned} &\langle \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_2)_B L_\alpha l_\alpha S_\alpha K_\alpha I_\alpha}^{T_\alpha M T_\alpha P T_\alpha} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 I_2)_A (\alpha_1 L_1 S_1 I_1)_B L_\beta l_\beta S_\beta K_\beta I_\beta}^{T_\beta M T_\beta P T_\beta} \rangle \\ &= \delta_{T_\beta T_\alpha} \delta_{M_\beta M_\alpha} \delta_{P_\beta P_\alpha} \delta_{L_\beta L_\alpha} \delta_{l_\beta l_\alpha} \delta_{S_\beta S_\alpha} \delta_{K_\beta K_\alpha} \delta_{I_\beta I_\alpha} P_1 P_2 \\ &\quad \times (-1)^{N_1 N_2 + L_1 + L_2 - L_\beta + S_1 + S_2 - S_\beta} [l_\alpha, l_\beta]^{1/2} \sum_{M_L} \begin{pmatrix} L_\alpha & l_\alpha & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \begin{pmatrix} L_\alpha & l_\beta & \mathcal{L}_\alpha \\ M_L & 0 & -M_L \end{pmatrix} \\ &\quad \times \frac{1}{2} [\mathcal{E}_{M_L S_\alpha g L_\alpha}(R) - \mathcal{E}_{M_L S_\alpha u L_\alpha}(R)]. \end{aligned} \quad (42b)$$

In the case of identical nuclei, the channel functions must have a proper symmetry under the exchange of nuclei. From Eqs. (12) and (31), we have

$$\begin{aligned} &\hat{X}_n \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_1)_B L L S K I}^{T M T P T}(\mathbf{R}) \\ &= (-1)^{N_1 N_2 + L_1 + L_2 - L + S_1 + S_2 - S + 2I_1 - I + I} \\ &\quad \times \Phi_{(\alpha_2 L_2 S_2 I_1)_A (\alpha_1 L_1 S_1 I_1)_B L L S K I}^{T M T P T}(\mathbf{R}). \end{aligned} \quad (43)$$

Thus a channel function with proper symmetry under the exchange of nuclei is given by

$$\begin{aligned} &\Phi_{\{\alpha_1 L_1 S_1 I_1, \alpha_2 L_2 S_2 I_1\} L L S K I}^{T M T P T}(\mathbf{R}) \\ &= C^{LS} [\Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_1)_B L L S K I}^{T M T P T}(\mathbf{R}) \\ &\quad + (-1)^{N_1 N_2 + L_1 + L_2 - L + S_1 + S_2 - S - I + I} \\ &\quad \times \Phi_{(\alpha_2 L_2 S_2 I_1)_A (\alpha_1 L_1 S_1 I_1)_B L L S K I}^{T M T P T}(\mathbf{R})], \end{aligned} \quad (44)$$

which satisfies

$$\begin{aligned} \hat{X}_n^{TM_T P_T} \Phi_{\{\alpha_1 L_1 S_1 I_1, \alpha_2 L_2 S_2 I_1\} L L S K I}(\mathbf{R}) \\ = (-1)^{2I_1} \Phi_{\{\alpha_1 L_1 S_1 I_1, \alpha_2 L_2 S_2 I_1\} L L S K I}(\mathbf{R}). \end{aligned} \quad (45)$$

The constant C^{LS} is a normalization constant:

$$C^{LS} = \{2[1 + \delta(\alpha_2 L_2 S_2, \alpha_1 L_1 S_1)]\}^{-1/2}.$$

Equation (44) implies that if

$$(\alpha_2 L_2 S_2) = (\alpha_1 L_1 S_1)$$

(implying, of course, $N_1 = N_2$), only states satisfying

$$L + S + I + l = \text{even} \quad (46)$$

are possible [53]. The same condition holds whether the nuclei are fermions or bosons. The potential $V_{\alpha\beta}^{BO}$ is now

$$\begin{aligned} & \langle \Phi_{\{\alpha_1 L_1 S_1 I_1, \alpha_2 L_2 S_2 I_1\} L \alpha' l \alpha' \mathcal{L} \alpha' S \alpha' K \alpha' I \alpha'}^{T \alpha M T \alpha P T \alpha} | H_{BO} | \Phi_{\{\alpha_1 L_1 S_1 I_1, \alpha_2 L_2 S_2 I_1\} L \beta' l \beta' \mathcal{L} \beta' S \beta' K \beta' I \beta'}^{T \beta M T \beta P T \beta} \rangle \\ & = 2 C_{\alpha}^{LS} C_{\beta}^{LS} [\langle \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_1)_B}^{T \alpha M T \alpha P T \alpha} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_1)_B}^{T \beta M T \beta P T \beta} \rangle \\ & \quad + (-1)^{N_1 N_2 + L_1 + L_2 - L_{\beta} + S_1 + S_2 - S_{\beta} - I_{\beta} + l_{\beta}} \langle \Phi_{(\alpha_1 L_1 S_1 I_1)_A (\alpha_2 L_2 S_2 I_1)_B}^{T \alpha M T \alpha P T \alpha} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 I_1)_A (\alpha_1 L_1 S_1 I_1)_B}^{T \beta M T \beta P T \beta} \rangle], \end{aligned} \quad (47)$$

with the matrix elements on the right-hand side given by Eq. (42) if $(\alpha_2 L_2 S_2) \neq (\alpha_1 L_1 S_1)$ and by Eq. (40) if $(\alpha_2 L_2 S_2) = (\alpha_1 L_1 S_1)$.

It is clear that the representation of V^{BO} is much simpler in the LS coupling than in the FF coupling. The catch is, of course, that H_f and H_{hf} are no longer diagonal. The more serious problem is that since the channel couplings due to H_f and H_{hf} do not vanish at large R , the physical K matrix cannot be defined in the LS coupling unless H_f and H_{hf} are strictly zero. This is where frame transformation and MQDT come into play.

E. Frame transformations and MQDT

It can be shown (see Appendix A) that the FF coupled channel functions [Eq. (17)] are related to the LS coupled channel functions [Eq. (39)] by a frame transformation

$$\Phi_j^{TM_T P_T} = \sum_{\beta} U_{j\beta}^{(T)} \Phi_{\beta}^{TM_T P_T}(\mathbf{R}), \quad (48)$$

where

$$\begin{aligned} U_{i\beta}^{(T)} & = \delta_{l_i l_{\beta}} (-1)^{F_i + \mathcal{L}_{\beta} + S_{\beta} + K_{\beta} + I_{\beta}} \\ & \quad \times [J_{1i}, F_{1i}, J_{2i}, F_{2i}, F_i, L_{\beta}, \mathcal{L}_{\beta}, S_{\beta}, K_{\beta}, I_{\beta}]^{1/2} \\ & \quad \times \sum_{J_x} (-1)^{J_x} [J_x] \begin{Bmatrix} l_i & K_{\beta} & J_x \\ S_{\beta} & L_{\beta} & \mathcal{L}_{\beta} \end{Bmatrix} \begin{Bmatrix} l_i & K_{\beta} & J_x \\ I_{\beta} & F_i & T \end{Bmatrix} \\ & \quad \times \begin{Bmatrix} L_1 & L_2 & L_{\beta} \\ S_1 & S_2 & S_{\beta} \\ J_{1i} & J_{2i} & J_x \end{Bmatrix} \begin{Bmatrix} J_{1i} & J_{2i} & J_x \\ I_1 & I_2 & I_{\beta} \\ F_{1i} & F_{2i} & F_i \end{Bmatrix}. \end{aligned} \quad (49a)$$

From Eqs. (34) and (44), it is clear that in the case of identical nuclei, the properly symmetrized channel functions are related by the frame transformation

$$\begin{aligned} U_{\{i\}\{\beta\}}^{(T)} & = (C_i^{FF}/C_{\beta}^{LS}) U_{i\beta}^{(T)} \\ & = \{1 + \delta(\alpha_2 L_2 S_2, \alpha_1 L_1 S_1) \\ & \quad \times [1 - \delta(J_{2i} F_{2i}, J_{1i} F_{1i})]\}^{1/2} U_{i\beta}^{(T)}. \end{aligned} \quad (49b)$$

For the sake of simplified notation, $U_{\{i\}\{\beta\}}^{(T)}$ will also be denoted by $U_{i\beta}^{(T)}$, with the understanding that the proper transformation is to be used for different cases. We emphasize that the normalization factor in Eq. (49b) is important. The transformation would not be unitary without it.

The goal of this section is to present a simple method which gives complete information about a hyperfine collision from either the existing LS coupled calculations [34,8,23] or a JJ coupled calculation discussed in Appendix A. It is an approximate method that combines the use of frame transformation and MQDT. The concept of this method is well known, and has been very successful in interpreting the spin-orbital effects on photoionization [29–33]. It leads in our case to a multichannel effective range theory which is the same as the one developed previously for electron-atom scattering [54]. I will first present the method. The underlying assumptions and future refinements will then be discussed.

Briefly summarizing the method, we first solve the close-coupling equations in the LS coupled (condensation) channels ignoring both the spin-orbital and the hyperfine interactions, or in the JJ coupled channels ignoring only the hyperfine interactions. An energy-insensitive short-range K matrix ($K_{\alpha\beta}^{0(T)}$ in LS coupling; $K_{xy}^{0(T)}$ in JJ coupling) is extracted from this set of solutions, from which the energy-insensitive short-range K matrix in the fragmentation channels, $K_{ij}^{0(T)}$, is obtained through a frame transformation. MQDT is then applied to give the physical K matrix $K_{ij}^{(T)}$ in terms of $K_{ij}^{0(T)}$.

Specifically, $K_{\alpha\beta}^{0(T)}$ is defined by the large R expansion of the wave function in LS coupled condensation channels as follows:

$$\psi_{\beta}^{TM_T P_T} = \sum_{\alpha} \Phi_{\alpha}^{TM_T P_T}(\mathbf{R})(f_{\alpha}^0 \delta_{\alpha\beta} - g_{\alpha}^0 K_{\alpha\beta}^{0(T)})/R. \quad (50)$$

Here f_{α}^0 and g_{α}^0 are a pair of linearly independent solutions corresponding to the asymptotic potential in a condensation channel α . They differ from the usual f_{α}, g_{α} pair in that they are required to have energy-independent normalization at the origin. If the interaction in a condensation channel can be treated as a short-range interaction, f_{α}^0 and g_{α}^0 are specifically a pair of analytic functions of energy (see Appendix C):

$$f_{\alpha}^0(\epsilon_{\alpha}) = \frac{1}{k_{\alpha}^{l_{\alpha}}} R j_{l_{\alpha}}(k_{\alpha} R), \quad (51a)$$

$$g_{\alpha}^0(\epsilon_{\alpha}) = k_{\alpha}^{l_{\alpha}+1} R y_{l_{\alpha}}(k_{\alpha} R), \quad (51b)$$

where

$$\epsilon_{\alpha} = E - E_{\alpha},$$

$$k_{\alpha} = (2\mu\epsilon_{\alpha})^{1/2}/\hbar.$$

Note that the expansion Eq. (50) with an R -independent K^{0T} at large R is possible only when the spin-orbital and the hyperfine interactions are ignored (this is why the physical K matrix cannot be defined in LS coupling unless there are no such interactions).

The energy-insensitive $K_{ij}^{0(T)}$ is defined in a similar fashion by a large R expansion of the wave function in fragmentation channels:

$$\psi_j^{TM_T P_T} = \sum_i \Phi_i^{TM_T P_T}(\mathbf{R})(f_i^0 \delta_{ij} - g_i^0 K_{ij}^{0T})/R. \quad (52)$$

After solving for $K_{\alpha\beta}^{0(T)}$ in the condensation channels, $K_{ij}^{0(T)}$ is obtained by using the frame transformation Eq. (49):

$$K_{ij}^{0T} = \sum_{\alpha\beta} U_{i\alpha}^{(T)} K_{\alpha\beta}^{0T} U_{j\beta}^{(T)}. \quad (53)$$

The wave functions satisfying the proper physical boundary conditions are then constructed as linear superpositions of solutions specified by Eq. (52). This is a standard procedure in MQDT [26,28], and lead in our case to the multichannel-effective-range equation [54], which relates the physical K matrix to K_{ij}^{0T} :

$$\begin{aligned} K^{(T)}(E) &= k^{l+1/2} \{ K_{oo}^{0(T)} - K_{oc}^{0(T)} \kappa^{l+1/2} \\ &\quad \times [(-1)^l + \kappa^{l+1/2} K_{cc}^{0(T)} \kappa^{l+1/2}]^{-1} \\ &\quad \times \kappa^{l+1/2} K_{co}^{0(T)} \} k^{l+1/2}. \end{aligned} \quad (54)$$

Here $k^{l+1/2}$ is an $N_o \times N_o$ diagonal matrix with elements $k_i^{l_i+1/2}$, with N_o being the number of open channels at energy E . $\kappa^{l+1/2}$ is an $N_c \times N_c$ diagonal matrix with elements $\kappa_i^{l_i+1/2}$, with N_c being the number of closed channels at energy E , and

$$\kappa_i = [2\mu(E_i - E)]^{1/2}/\hbar.$$

$(-1)^l$ is an $N_c \times N_c$ diagonal matrix with elements $(-1)^{l_i}$. $K_{oo}^{0(T)}$, $K_{oc}^{0(T)}$, $K_{co}^{0(T)}$, and $K_{cc}^{0(T)}$, are submatrices of $K^{0(T)}$ corresponding to open-open, open-close, close-open, and close-close channels, respectively. It should be remembered that the $K^{0(T)}$ matrix referred to here is the one in fragmentation channels. It is related to the one in condensation channels by Eq. (53).

If all channels are closed, the physical boundary conditions can only be satisfied at discrete energy levels determined by

$$\det[(-1)^l + \kappa^{l+1/2} K^{0(T)} \kappa^{l+1/2}] = 0, \quad (55)$$

which gives the relationship between bound state energy levels and the scattering matrix.

Specializing to the case of collision between alkali-metal atoms in their ground states, Eqs. (49), (53), and (54) enable one to generate complete information about the collision from single channel calculations such as those of [34,8,23]. Numerical results of this sort will be presented later.

If the spin-orbit interaction is significant, the $K_{\alpha\beta}^{0T}$ matrix in Eq. (53) should be replaced by K_{xy}^{0T} calculated by solving the close-coupling equations in the JJ coupling scheme (see Appendix A), and the frame transformation $U_{i\beta}^{(T)}$ is replaced by $U_{ix}^{(T)}$ given by Eqs. (A6) and (A15).

The theory presented in this section is, of course, only an approximation with a certain range of validity. It relies on Eq. (53), which is strictly valid only when there are no spin-orbit and hyperfine interactions. The corresponding transformation from JJ coupling requires the hyperfine interactions to be zero. However, they are useful approximations even in the presence of such interactions. First, it is obviously a good method to account for the hyperfine effects at energies much greater than the hyperfine splitting. This covers a wide energy range that is of great importance in many applications [2]. Second, the degree to which these approximations fail is a direct measure of the effects of long-range interactions. This is because Eq. (53) is always going to be valid inside an R_0 where the LS coupled (JJ coupled) potential is much greater than the spin-orbital (hyperfine) interactions. Thus the frame transformation method presented in this section basically assumes that after R_0 the electrostatic and the exchange interactions are sufficiently weak or that they drop off so quickly that their effects can be ignored. Third, it can be systematically improved upon. Specifically, the effect of long-range interactions in the outside region where the hyperfine interaction is dominant can be incorporated by a proper choice of the f^0 and g^0 pair. For a $1/r^6$ potential, the proper pair can be obtained either by the usual perturbation theory or by a method of Cavagnero [55]. Any error after such a correction reflects the evolution of the wave function through the intermediate region where the electrostatic and the exchange interaction is comparable to the hyperfine interactions. This region can be treated by solving the close-coupling equation in the FF coupled channels, if needed. It will be interesting to identify the significance of this contribution, especially its energy dependence.

III. DISCUSSIONS

A. Sensitivity to the potential

It is well recognized and understood that cold-atom collisions are very sensitive to the potential [4,7,8]. We give here a brief discussion of some issues of interest in our present work.

The total phase shift of a collision comprises contributions from both short-range and long-range interactions. We will assume that the asymptotic potentials are known precisely and look at the dependence of the short-range phase on the potential.

For atom-atom collisions, the short-range phase can be estimated by the integral of

$$k(R) = [(2\mu)^{1/2}/\hbar][E - V(R)]^{1/2},$$

the uncertainty of which is related to the uncertainty in V by

$$|\Delta k| = (\mu/2\hbar^2)^{1/2}[E - V(R)]^{-1/2}|\Delta V|.$$

If the distance over which the potential may be in error is denoted by d , the condition that the phase is determined within π is roughly $|\Delta k|d < \pi$. For slow-atom collisions, the corresponding requirement on the uncertainty in potential can be estimated by

$$|\Delta V| < \frac{\pi}{d} \left(\frac{2\hbar^2}{\mu} \right)^{1/2} |V_{\min}|^{1/2}, \quad (56)$$

where V_{\min} is the depth or some typical value of the potential. Thus we see that the sensitive dependence of slow-atom collisions is due mainly to the large mass of an atom. Since atoms are thousands times heavier than electrons and the distance over which the potential may be incorrect is about a few times bigger, it follows that the potential has to be about 10^4 times more accurate if the atom-atom phase shift is to be determined to the same degree of accuracy as the electron-atom scattering. This is why quantities such as the angular distribution are so much more difficult to determine for atom-atom collision as opposed to electron-atom collisions.

What is unique about cold-atom collisions is that if the last bound state happens to be very close to the threshold, the error in the short-range phase gets further amplified in the determination of cross sections [4].

Note that a sensitive dependence on potential also implies a sensitive dependence on energy, since

$$|\Delta k| = (\mu/2\hbar^2)^{1/2}[E - V(R)]^{-1/2}|\Delta E|.$$

Fortunately, it is easily verified that ignoring hyperfine interaction over a range of 10 a.u. does not change the phase significantly, which is actually an assumption that makes the approximation in the preceding section useful.

B. MQDT and frame transformation as a numerical tool

We point out here that the method of MQDT and frame transformation is useful even when the goal is to solve the FF coupled close-coupling equations numerically. MQDT provides an elegant and systematic way of imposing the physical boundary conditions, and the frame transformations lead us to basis sets in which the potential is approximately

block diagonalized in certain regions of the configuration space. For example, the LS coupling block-diagonalizes the Born-Oppenheimer part of the potential. The spin-orbit and hyperfine interactions are not diagonalized. Specifically, if we take this part of the interaction to be that of two separate atoms, their matrix elements are given by

$$V_{\alpha\beta}^f = \sum_x U_{x\alpha}^{(T)} \Delta E_x^f U_{x\beta}^{(T)}, \quad (57)$$

$$V_{\alpha\beta}^{hf} = \sum_i U_{i\alpha}^{(T)} \Delta E_i^{hf} U_{i\beta}^{(T)}, \quad (58)$$

where ΔE_x^f is the total fine-structure splitting for the two atoms in a JJ coupled channel x (see Appendix A). $U_{x\alpha}^{(T)}$ is the LS to JJ frame transformation given by Eqs. (A4) and (A14). ΔE_i^{hf} is the total hyperfine splitting for the two atoms in a fragmentation channel i , and $U_{i\alpha}^{(T)}$ is the LS to FF frame transformation given by Eq. (49). It is obvious that in the region where the electrostatic and exchange interactions dominate, the LS coupled channel functions provide a better basis set for numerical integration [21]. Thus, depending on the strength of the spin-orbital interaction, one can separate the space into three or four regions. The outermost region is handled by MQDT; the innermost region is integrated in LS coupling. The middle region is handled in FF coupling or a combination of JJ and FF coupling. Matching at various boundaries is facilitated by the frame transformations. Such a scheme fits especially well with Gordon's method of solving the close-coupling equations [56].

IV. CONCLUSIONS

A general theory of slow-atom collisions has been presented with special emphasis on the effects of nuclear spin statistics and atomic fine and/or hyperfine structures. It reduces to the theory of Stoof *et al.* [20] for collisions between alkali-metal atoms in their ground state, and to the theory of Zygelman *et al.* [18] if there are no hyperfine interactions and if the nuclei are either distinguishable, or indistinguishable (in which case the atoms must be in the same electronic states). By employing the frame transformation and MQDT techniques, we arrived at an approximate method which gives complete information about hyperfine collisions from much simpler LS coupled or JJ coupled calculations. The method can be systematically improved upon, and it tells one where each contribution comes from.

The next natural step is to compare the results obtained by solving the close-coupling equations in the FF coupled channels and the results obtained by various approximations discussed in Sec. II E. Reference pair functions f^0 and g^0 for $1/r^n$ potentials, especially for $n=6$ and $n=3$, also deserve a closer look.

Getting back to the question of whether a ^{85}Rb atom in the ground $F=3$ state is distinguishable from a ^{85}Rb atom in the ground $F=2$ state, the answer is that it is an ill-posed question that can be deceiving. If the atoms are given one at a time (implying that their wave functions do not overlap), one can of course tell which one is in $F=2$ and which one is in $F=3$. But that is missing the point of indistinguishability.

The point is that when the wave functions overlap, we cannot tell which one is in $F=2$. We only know that one of the atoms is in it and the other one is in $F=3$. Thus the system of two ^{85}Rb atoms, one in $F=2$ and one in $F=3$, should be treated as two identical atoms in different component states, just as the two different spin orientations of an electron. The same conclusion is, of course, applicable to any two atoms with the same constituents and in any states. However, for a system made up of an ion and an atom of the same species (or ions of the same species but of different charge), one needs to think in terms of nuclear statistics.

Finally, it seems clear that the ultimate theory of cold-atom collisions should be an R -matrix type of approach [35–40] in which short-range interactions are treated by a complete basis set expansion including both the electronic and the nuclear degrees of freedom. Close-coupling equations, such as the ones presented here, are used only beyond a

certain R_0 . Such sophistication may not be necessary at high temperatures, but may be needed for cold collisions due to their sensitive dependence on the potential.

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APPENDIX A: FRAME TRANSFORMATIONS AND JJ COUPLING

The frame transformation Eq. (49) is derived by going through JJ coupled channel functions, which are defined, for distinguishable nuclei, by the asymptotic behavior

$$\begin{aligned} \Phi_{(\alpha_1 L_1 S_1 J_1 I_1)_A (\alpha_2 L_2 S_2 J_2 I_2)_B J I K I}^{T M_T P_T} &\xrightarrow{R \rightarrow \infty} \sum_{\text{all } m} \langle J_1 M_1, J_2 M_2 | J M_J \rangle \langle J M_J, l m_l | K M_K \rangle \\ &\times \langle K M_K, I M_I | T M_T \rangle | \alpha_1 L_1 S_1 J_1 M_1 \rangle_A | \alpha_2 L_2 S_2 J_2 M_2 \rangle_B Y_{l m_l}(\theta, \phi) | (I_1)_A (I_2)_B I M_I \rangle, \end{aligned} \quad (\text{A1})$$

where all magnetic quantum numbers are quantized along a space-fixed axis. From Eq. (8), it can be shown that the JJ coupled channels functions can be written in terms of the quasimolecular states as

$$\begin{aligned} \Phi_{(\alpha_1 L_1 S_1 J_1 I_1)_A (\alpha_2 L_2 S_2 J_2 I_2)_B J I K I}^{T M_T P_T} &= [J_1, J_2]^{1/2} \sum_{L S} \sum_{\text{all } m} [L, S]^{1/2} \langle L M'_L, S M'_S | J M'_J \rangle \langle J M_J, l m_l | K M_K \rangle \langle K M_K, I M_I | T M_T \rangle \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_1 & J_2 & J \end{Bmatrix} \\ &\times D_{M_J M'_J}^{J*}(\phi, \theta, 0) Y_{l m_l}(\theta, \phi) | (\alpha_1 L_1 S_1)_A (\alpha_2 L_2 S_2)_B L M'_L(\hat{R}) S M'_S(\hat{R}); R \rangle | (I_1)_A (I_2)_B I M_I \rangle. \end{aligned} \quad (\text{A2})$$

This channel function, to be identified by an index x , is related to the LS coupled channel functions [cf. Eq. (39)], identified by the indices β , by the frame transformation [9,18,19]

$$\Phi_x^{T M_T P_T}(\mathbf{R}) = \sum_{\beta} U_{x\beta}^{(T)} \Phi_{\beta}^{T M_T P_T}(\mathbf{R}), \quad (\text{A3})$$

where

$$\begin{aligned} U_{x\beta}^{(T)} &= \delta_{l_x l_{\beta}} \delta_{K_x K_{\beta}} \delta_{I_x I_{\beta}} (-1)^{l_x + J_x + \mathcal{L}_{\beta} + S_{\beta}} \\ &\times [J_{1x}, J_{2x}, J_x, L_{\beta}, \mathcal{L}_{\beta}, S_{\beta}]^{1/2} \\ &\times \begin{Bmatrix} l_x & K_{\beta} & J_x \\ S_{\beta} & L_{\beta} & \mathcal{L}_{\beta} \end{Bmatrix} \begin{Bmatrix} L_1 & L_2 & L_{\beta} \\ S_1 & S_2 & S_{\beta} \\ J_{1x} & J_{2x} & J_x \end{Bmatrix}. \end{aligned} \quad (\text{A4})$$

An FF coupled channel function [cf. Eq. (17)], identified by the index i , is related to the JJ coupled channel functions by a similar frame transformation,

$$\Phi_i^{T M_T P_T}(\mathbf{R}) = \sum_{\beta} U_{i\beta}^{(T)} \Phi_{\beta}^{T M_T P_T}(\mathbf{R}), \quad (\text{A5})$$

where

$$\begin{aligned} U_{i\beta}^{(T)} &= \delta_{l_i l_{\beta}} \delta_{J_{1i} J_{1\beta}} \delta_{J_{2i} J_{2\beta}} (-1)^{l_i + F_i + K_x + I_x} \\ &\times [F_{1i}, F_{2i}, F_i, J_x, K_x, I_x]^{1/2} \\ &\times \begin{Bmatrix} l_i & K_x & J_x \\ I_x & F_i & T \end{Bmatrix} \begin{Bmatrix} J_{1i} & J_{2i} & J_x \\ I_1 & I_2 & I_x \\ F_{1i} & F_{2i} & F_i \end{Bmatrix}. \end{aligned} \quad (\text{A6})$$

The LS to FF frame transformation is then obtained through

$$U_{i\beta}^{(T)} = \sum_x U_{ix}^{(T)} U_{x\beta}^{(T)}, \quad (\text{A7})$$

which gives Eq. (49).

In cases where spin-orbit interaction is significant, the starting point for the frame transformation and MQDT method described in Sec. II E is the solution of close-coupling equations in the JJ coupling. For a collision be-

tween two different atoms or a collision between similar atoms with distinguishable nuclei and $(\alpha_2 L_2 S_2) = (\alpha_1 L_1 S_1)$, the potential V_{xy}^{BO} that enters into the close-coupling equation in JJ coupling is determined by

$$\begin{aligned}
& \langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_1)_A (\alpha_2 L_2 S_2 J_{2x} I_2)_B J_x I_x K_x I_x}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_{1y} I_1)_A (\alpha_2 L_2 S_2 J_{2y} I_2)_B J_y I_y K_y I_y}^{T_y M_{T_y} P_{T_y}} \rangle \\
&= \delta_{T_x T_y} \delta_{M_{T_x} M_{T_y}} \delta_{P_{T_x} P_{T_y}} \delta_{K_x K_y} \delta_{I_x I_y} (-1)^{J_x - J_y} [J_{1x}, J_{2x}, J_x, l_x, J_{1y}, J_{2y}, J_y, l_y]^{1/2} \sum_{M_L M_S L S} [L, S] \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1x} & J_{2x} & J_x \end{Bmatrix} \\
&\times \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1y} & J_{2y} & J_y \end{Bmatrix} \begin{pmatrix} L & S & J_x \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_y \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_x & l_x & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\
&\times \begin{pmatrix} J_y & l_y & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \mathcal{E}_{M_L S \Gamma}(R). \tag{A8}
\end{aligned}$$

In the case of a collision between two similar atoms with distinguishable nuclei and $(\alpha_2 L_2 S_2) \neq (\alpha_1 L_1 S_1)$, there are additional channels characterized by

$$\begin{aligned}
& \Phi_{(\alpha_2 L_2 S_2 J_{2y} I_2)_B (\alpha_1 L_1 S_1 J_{1y} I_1)_A}^{T M T P T} = [J_1, J_2]^{1/2} \sum_{L S J I} \sum_{\text{all } m} [L, S]^{1/2} \langle L M'_L, S M'_S | J M'_J \rangle \langle J M_J, l m_l | K M_K \rangle \langle K M_K, I M_I | T M_T \rangle \\
&\times \begin{Bmatrix} L_2 & L_1 & L \\ S_2 & S_1 & S \\ J_2 & J_1 & J \end{Bmatrix} D_{M_J M'_J}^{J*}(\phi, \theta, 0) Y_{l, m_l}(\theta, \phi) |(\alpha_2 L_2 S_2)_A (\alpha_1 L_1 S_1)_B \\
&\times L M'_L(\hat{R}) S M'_S(\hat{R}); R \rangle | (I_1)_A (I_2)_B I M_I \rangle. \tag{A9}
\end{aligned}$$

The complete potential V_{xy}^{BO} is specified in this case by

$$\begin{aligned}
& \langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_1)_A (\alpha_2 L_2 S_2 J_{2x} I_2)_B J_x I_x K_x I_x}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_{1y} I_1)_A (\alpha_2 L_2 S_2 J_{2y} I_2)_B J_y I_y K_y I_y}^{T_y M_{T_y} P_{T_y}} \rangle \\
&= \delta_{T_x T_y} \delta_{M_{T_x} M_{T_y}} \delta_{P_{T_x} P_{T_y}} \delta_{K_x K_y} \delta_{I_x I_y} (-1)^{J_x - J_y} [J_{1x}, J_{2x}, J_x, l_x, J_{1y}, J_{2y}, J_y, l_y]^{1/2} \sum_{M_L M_S L S} [L, S] \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1x} & J_{2x} & J_x \end{Bmatrix} \\
&\times \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1y} & J_{2y} & J_y \end{Bmatrix} \begin{pmatrix} L & S & J_x \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_y \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_x & l_x & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \\
&\times \begin{pmatrix} J_y & l_y & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \frac{1}{2} [\mathcal{E}_{M_L S \alpha g L \alpha}(R) + \mathcal{E}_{M_L S \alpha u L \alpha}(R)], \tag{A10a}
\end{aligned}$$

$$\begin{aligned}
& \langle \Phi_{(\alpha_2 L_2 S_2 J_{2x} I_2)_A (\alpha_1 L_1 S_1 J_{1x} I_1)_B J_x I_x K_x I_x}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_{2y} I_2)_A (\alpha_1 L_1 S_1 J_{1y} I_1)_B J_y I_y K_y I_y}^{T_y M_{T_y} P_{T_y}} \rangle \\
&= (-1)^{J_{1x} + J_{2x} + J_x + J_{1y} + J_{2y} + J_y} \langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_1)_A (\alpha_2 L_2 S_2 J_{2x} I_2)_B J_x I_x K_x I_x}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_{1y} I_1)_A (\alpha_2 L_2 S_2 J_{2y} I_2)_B J_y I_y K_y I_y}^{T_y M_{T_y} P_{T_y}} \rangle, \tag{A10b}
\end{aligned}$$

$$\begin{aligned}
& \langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_{1x})_A (\alpha_2 L_2 S_2 J_{2x} I_{2x})_B}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_{2y} I_{2y})_A (\alpha_1 L_1 S_1 J_{1y} I_{1y})_B}^{T_y M_{T_y} P_{T_y}} \rangle \\
& = \delta_{T_x T_y} \delta_{M_{T_x} M_{T_y}} \delta_{P_{T_x} P_{T_y}} \delta_{K_x K_y} \delta_{I_x I_y} P_1 P_2 (-1)^{N_1 N_2 + J_{1y} + J_{2y} - J_x} [J_{1x}, J_{2x}, J_x, I_x, J_{1y}, J_{2y}, J_y, I_y]^{1/2} \\
& \times \sum_{M_L M_S L S} [L, S] \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1x} & J_{2x} & J_x \end{Bmatrix} \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_{1y} & J_{2y} & J_y \end{Bmatrix} \begin{pmatrix} L & S & J_x \\ M_L & M_S & -M_L - M_S \end{pmatrix} \begin{pmatrix} L & S & J_y \\ M_L & M_S & -M_L - M_S \end{pmatrix} \\
& \times \begin{pmatrix} J_x & I_x & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \begin{pmatrix} J_y & I_y & K_y \\ M_L + M_S & 0 & -M_L - M_S \end{pmatrix} \frac{1}{2} [\mathcal{E}_{M_L S_{\alpha} g L_{\alpha}}(R) - \mathcal{E}_{M_L S_{\alpha} u L_{\alpha}}(R)]. \quad (A10c)
\end{aligned}$$

For a collision between two atoms with identical nuclei, a JJ coupled channel function with proper symmetry under the exchange of nuclei is

$$\begin{aligned}
& \Phi_{\{\alpha_1 L_1 S_1 J_{1x} I_{1x}, \alpha_2 L_2 S_2 J_{2x} I_{2x}\} JKl}^{TM_T P_T}(\mathbf{R}) \\
& = C^{JJ} [\Phi_{(\alpha_1 L_1 S_1 J_{1x} I_{1x})_A (\alpha_2 L_2 S_2 J_{2x} I_{2x})_B}^{TM_T P_T}(\mathbf{R}) \\
& + (-1)^{N_1 N_2 + J_1 + J_2 - J - I + l} \\
& \times \Phi_{(\alpha_2 L_2 S_2 J_{2x} I_{2x})_A (\alpha_1 L_1 S_1 J_{1x} I_{1x})_B}^{TM_T P_T}(\mathbf{R})], \quad (A11)
\end{aligned}$$

where

$$C^{JJ} = \{2[1 + \delta(\alpha_2 L_2 S_2 J_2, \alpha_1 L_1 S_1 J_1)]\}^{-1/2}$$

is a normalization constant.

From Eq. (A11), it is clear that if

$$(\alpha_2 L_2 S_2 J_2) = (\alpha_1 L_1 S_1 J_1),$$

only states satisfying

$$J + I + l = \text{even} \quad (A12)$$

are possible. This is true regardless of whether the nuclei are fermions or bosons.

The potential V_{xy}^{BO} for the case of identical nuclei is therefore

$$\begin{aligned}
& \langle \Phi_{\{\alpha_1 L_1 S_1 J_{1x} I_{1x}, \alpha_2 L_2 S_2 J_{2x} I_{2x}\} J_x I_x K_x I_x}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{\{\alpha_1 L_1 S_1 J_{1y} I_{1y}, \alpha_2 L_2 S_2 J_{2y} I_{2y}\} J_y I_y K_y I_y}^{T_y M_{T_y} P_{T_y}} \rangle \\
& = 2 C_x^{JJ} C_y^{JJ} [\langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_{1x})_A (\alpha_2 L_2 S_2 J_{2x} I_{2x})_B}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_1 L_1 S_1 J_{1y} I_{1y})_A (\alpha_2 L_2 S_2 J_{2y} I_{2y})_B}^{T_y M_{T_y} P_{T_y}} \rangle \\
& + (-1)^{N_1 N_2 + J_{1y} + J_{2y} - J_y - I_y + l_y} \langle \Phi_{(\alpha_1 L_1 S_1 J_{1x} I_{1x})_A (\alpha_2 L_2 S_2 J_{2x} I_{2x})_B}^{T_x M_{T_x} P_{T_x}} | H_{BO} | \Phi_{(\alpha_2 L_2 S_2 J_{2y} I_{2y})_A (\alpha_1 L_1 S_1 J_{1y} I_{1y})_B}^{T_y M_{T_y} P_{T_y}} \rangle], \quad (A13)
\end{aligned}$$

where the matrix elements on the right-hand side are given by Eq. (A10) for $(\alpha_1 L_1 S_1) \neq (\alpha_2 L_2 S_2)$, and by Eq. (A18) for $(\alpha_1 L_1 S_1) = (\alpha_2 L_2 S_2)$.

The LS to JJ frame transformation for identical nuclei is

$$\begin{aligned}
U_{\{\alpha\}\{\beta\}}^{(T)} & = (C_x^{JJ} / C_{\beta}^{LS}) U_{x\beta}^{(T)} = \{1 + \delta(\alpha_2 L_2 S_2, \alpha_1 L_1 S_1) \\
& \times [1 - \delta(J_{2x}, J_{1x})]\}^{1/2} U_{x\beta}^{(T)}. \quad (A14)
\end{aligned}$$

The JJ to FF frame transformation for identical nuclei is

$$\begin{aligned}
U_{\{i\}\{x\}}^{(T)} & = (C_i^{FF} / C_x^{JJ}) U_{ix}^{(T)} = \{1 + \delta(\alpha_2 L_2 S_2 J_{2i}, \alpha_1 L_1 S_1 J_{1i}) \\
& \times [1 - \delta(F_{2i}, F_{1i})]\}^{1/2} U_{ix}^{(T)}. \quad (A15)
\end{aligned}$$

The JJ coupled channel functions diagonalize the asymptotic spin-orbit interactions, i.e.,

$$V_{xy}^f \xrightarrow{R \rightarrow \infty} \Delta E_x^f \delta_{xy}, \quad (A16)$$

where ΔE_x^f is the total fine-structure splitting for the two atoms. The asymptotic hyperfine interactions are, however, not diagonalized in JJ coupling. Specifically,

$$V_{xy}^{hf} \xrightarrow{R \rightarrow \infty} \sum_i U_{ix}^{(T)} \Delta E_i^{hf} U_{iy}^{(T)}, \quad (A17)$$

where ΔE_i^{hf} is the total hyperfine splitting for the two atoms in a fragmentation channel i , in which the asymptotic hyperfine interactions are diagonalized. $U_{ix}^{(T)}$ is the JJ to FF frame transformation given by Eqs. (A6) and (A15).

A question that naturally arises here is why the spin-orbit interaction is not included in our definition of the adiabatic Hamiltonian, which seems to be the reasonable thing to do, especially if the spin-orbit interaction is strong. Such a theory can indeed be established. It is not presented here because of some subtleties associated with nonadiabatic coupling effects.

By starting from an LS coupled molecular basis, one can ignore the nonadiabatic coupling if the LS coupled molecular potentials have no avoided crossing or if the crossings occur only at small internuclear distances where the atoms are unlikely to be. This is the case at least for collisions between alkali-metal atoms in their ground state. The nonadiabatic couplings due to spin-orbit and hyperfine interactions are left to be treated by solving the close-coupling equations in the proper fragmentation channels. But a similar condition is not satisfied if one starts from a JJ coupled molecular basis set. To treat the nonadiabatic coupling rigorously in this case, one needs to carefully take into account the subtle difference between one- and two-center rotations, as pointed out in the important work of Zygelman *et al.* [18]. Even though their work may be equivalent to previous theories when nonadiabatic coupling is ignored, it is expected to lead to different nonadiabatic coupling terms. This issue deserves further examination in the future.

APPENDIX B: SCATTERING BOUNDARY CONDITIONS AND CROSS SECTIONS

Owing to the new features introduced by identical nuclei, we give here a brief discussion of scattering boundary con-

ditions and the related cross section formulas.

The wave function having proper scattering boundary conditions is constructed in a standard fashion out of solutions which define the physical K matrix. First, a proper linear superposition of these functions gives a set of solutions that defines the T matrix:

$$\begin{aligned} \psi_i^{TM_T P_T} \xrightarrow{R \rightarrow \infty} \sum_{j \in o} \Phi_j^{TM_T P_T} \left\{ \frac{1}{k_j R} \sin(k_j R - l_j \pi/2) \delta_{ji} \right. \\ \left. + \frac{e^{ik_j R}}{R} \left[-(-i)^{l_j} \pi k_j^{-1/2} T_{ji}^{(T)}(E) k_i^{-1/2} \right] \right\}, \end{aligned} \quad (\text{B1})$$

where

$$T^{(T)}(E) = (-2\pi i)^{-1} [S^{(T)}(E) - I], \quad (\text{B2})$$

in which $S^{(T)}(E)$ is given by Eq. (22) and I is a unit matrix. In terms of this set of solutions, the wave function with a proper scattering boundary condition is given by

$$\begin{aligned} \psi = \sum_{F_i, l_i; TM_F m_i} i^{l_i} Y_{l_i m_i}^*(\hat{k}_i) \langle F_{1i} M_{1i}, F_{2i} M_{2i} | F_i M_F \rangle \\ \times \langle F_i M_F, l_i m_i | TM_T \rangle \psi_i^{TM_T P_T}. \end{aligned} \quad (\text{B3})$$

In the case of nonidentical nuclei, the asymptotic form of ψ is rather standard and leads to Eqs. (23) and (24).

For identical nuclei, we obtain from Eqs. (34) and (16)

$$\begin{aligned} \psi \xrightarrow{R \rightarrow \infty} C_i^{FF} [| \alpha_1 L_1 S_1 J_1 I_1 F_{1i} M_{1i} \rangle_A | \alpha_2 L_2 S_2 J_2 I_2 F_{2i} M_{2i} \rangle_B e^{i\mathbf{k}_i \cdot (\mathbf{R}_A - \mathbf{R}_B)} \\ + (-1)^{N_1 N_2 + 2I_1} | \alpha_2 L_2 S_2 J_2 I_2 F_{2i} M_{2i} \rangle_A | \alpha_1 L_1 S_1 J_1 I_1 F_{1i} M_{1i} \rangle_B e^{i\mathbf{k}_i \cdot (\mathbf{R}_B - \mathbf{R}_A)}] \\ + \sum_j \frac{e^{ik_j R}}{R} C_j^{FF} [f(i \rightarrow j, \mathbf{k}_j) | \alpha_1 L_1 S_1 J_1 I_1 F_{1j} M_{1j} \rangle_A | \alpha_2 L_2 S_2 J_2 I_2 F_{2j} M_{2j} \rangle_B \\ + (-1)^{N_1 N_2 + 2I_1} f(i \rightarrow j, -\mathbf{k}_j) | \alpha_2 L_2 S_2 J_2 I_2 F_{2j} M_{2j} \rangle_A | \alpha_1 L_1 S_1 J_1 I_1 F_{1j} M_{1j} \rangle_B], \end{aligned} \quad (\text{B4})$$

which gives Eq. (37). Note that both terms in the incoming part of this wave function describe the *same* physical state in which an atom in state $| \alpha_1 L_1 S_1 J_1 I_1 F_{1i} M_{1i} \rangle$ is moving in the center-of-mass frame with momentum $\hbar \mathbf{k}_i$, and an atom in state $| \alpha_2 L_2 S_2 J_2 I_2 F_{2i} M_{2i} \rangle$ is moving in the center-of-mass frame with momentum $-\hbar \mathbf{k}_i$. The only difference is that we have labeled the two atoms differently, i.e., they have been exchanged. The amplitudes $f(i \rightarrow j, \mathbf{k}_j)$ and $f(i \rightarrow j, -\mathbf{k}_j)$ interfere with each other because they are the amplitudes for scattering into the *same* state in which an atom in state $| \alpha_1 L_1 S_1 J_1 I_1 F_{1j} M_{1j} \rangle$ is moving in the center-of-mass frame with momentum $\hbar \mathbf{k}_j$, and an atom in state $| \alpha_2 L_2 S_2 J_2 I_2 F_{2j} M_{2j} \rangle$ is moving in the center-of-mass frame with momentum $-\hbar \mathbf{k}_j$.

APPENDIX C: PROPERTIES OF f^0 AND g^0

For the sake of completeness, we summarize here properties of f^0 and g^0 as defined by Eq. (51) for short-range potentials. They are used in the derivation of the effective range Eq. (54). Refer to [24,25,28] for more details and for reference pair functions defined for other potentials.

$f_i^0(\epsilon_i)$ and $g_i^0(\epsilon_i)$ are both analytic functions of energy ϵ_i . This is easily verified through series expansions of j_l and y_l [44], from which it is to be observed that f^0 and g^0 depend on k only through powers of k^2 , which is proportional to energy.

The behavior of f^0 and g^0 at small R is characterized by

$$f_i^0(\epsilon_i) \xrightarrow{R \rightarrow 0} \frac{1}{(2l_i+1)!!} R^{l_i+1}, \quad (\text{C1})$$

$$g_i^0(\epsilon_i) \xrightarrow{R \rightarrow 0} -\frac{1}{2l_i+1} (2l_i+1)!! R^{-l_i}. \quad (\text{C2})$$

Their behavior at large R is characterized by

$$f_i^0(\epsilon_i) \xrightarrow{R \rightarrow \infty} k_i^{-l_i-1} \sin(k_i R - l_i \pi/2), \epsilon_i > 0, \quad (\text{C3})$$

$$f_i^0(\epsilon_i) \xrightarrow{R \rightarrow \infty} \kappa_i^{-l_i-1} [e^{\kappa_i R} - (-1)^{l_i} e^{-\kappa_i R}], \epsilon_i < 0, \quad (\text{C4})$$

$$g_i^0(\epsilon_i) \xrightarrow{R \rightarrow \infty} -k_i^{l_i} \cos(k_i R - l_i \pi/2), \epsilon_i > 0, \quad (\text{C5})$$

$$g_i^0(\epsilon_i) \xrightarrow{R \rightarrow \infty} -\kappa_i^{l_i} [(-1)^{l_i} e^{\kappa_i R} + e^{-\kappa_i R}], \epsilon_i < 0. \quad (\text{C6})$$

Finally,

$$W(f_i^0, g_i^0) \equiv f_i^0 g_i^{0'} - f_i^{0'} g_i^0 = 1. \quad (\text{C7})$$

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- [41] See the discussion at the end of Appendix A.
- [42] Fragmentation channels refer to channels in which long-range interactions are diagonalized.
- [43] Condensation channels refer to channels in which short-range interactions are (approximately) block diagonalized. See Sec. II D.
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- [47] It is important to remember that Eq. (7) also serves to define a phase convention in which the electrons associated with the nucleus A are labeled 1 through N_1 (or N_2 if atom A is in state $|\alpha_2 L_2 M_{L2} S_2 M_{S2}\rangle$), and the electrons associated with the nucleus B are labeled N_1+1 (or N_2+1 if atom A is in state $|\alpha_1 L_1 M_{L1} S_1 M_{S1}\rangle$) through N_1+N_2 . This convention, or any other convention one might like to choose, has to be maintained consistently.

- [48] A good discussion of the symmetry properties of the two-atom and their corresponding molecular states can be found in [16].
- [49] The phase factor in Eq. (11) comes about due to the reversal of the quantization axis.
- [50] Both $\hat{\sigma}_e$ and \hat{P}_T commute with H_{BO} .
- [51] There is actually a phase difference of $(-1)^{J_i - J_j}$ between our result and Eq. (3) of Ref. [19]. However, this difference is inconsequential as long as the same phase convention is maintained consistently when defining the scattering amplitude.
- [52] If the nuclei have different mass, the inversion symmetry is actually broken by the nonadiabatic coupling. It is this effect that gives rise to the small but nonzero dipole moment of the HD molecule. See, e.g., A. L. Ford and J. C. Browne, Phys. Rev. A **16**, 1992 (1977), and references therein.
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