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Ab initio calculation of Feshbach resonances in cold atomic collisions: s- and p-wave Feshbach resonances in $^6Li_2$

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We present a model applicable to cold diatomic collisions and solve the close-coupled equations for the particular $^6Li_2$ system. Feshbach resonances are determined *ab initio* for both s and p waves. The s-wave scattering lengths are reported for all possible hyperfine states as a function of magnetic field strengths between 0 and 1500 G. In addition, p-wave scattering lengths are calculated for selected hyperfine states. Matrix elements for the hyperfine, Zeeman, and rotational Hamiltonian were worked out by the use of the molecular Hund's case (a) basis set. All relevant matrix elements are reported. The short-range hyperfine interaction has been included in the calculations, and its effect on the scattering length are investigated. Hyperfine parameters were obtained from separate *ab initio* calculations.

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I. INTRODUCTION

Feshbach resonances [1] named after Herman Feshbach have become very important in ultracold atomic and molecular physics for the last ten years. Feshbach resonances are important ingredients in the ongoing exploration of these systems and in the tremendous progress made after the first successful creation of a Fermi gas [2]. In ultracold atomic and molecular physics, the important and relevant Feshbach resonances occur when the energy of a bound molecular state coincides with that of two colliding atoms. The coupling between the bound molecular state and the continuum of states is caused by the hyperfine interaction in homonuclear molecules and by the hyperfine interaction together with electronic spin-dependent interactions in heteronuclear molecules. Thus, the hyperfine interaction plays an important role. The experimental and theoretical focus this far has been on alkali atoms.

The attractive properties of these systems stem from the possibility of tuning the interatomic interaction by varying the magnetic field around a Feshbach resonance. The scattering length is the important parameter which characterizes the atom-atom interaction in ultracold gases [3] (together with the Pauli principle). The scattering length behaves in a peculiar way as one passes through a Feshbach resonance—it diverges and changes sign (see, e.g., Fig. 6). This makes it possible for the experimentalists to attain full control of the interactions by varying the magnetic field strength. Many systems have Feshbach resonances that are accessible through relatively low magnetic field strengths.

The Feshbach resonances also offer the opportunity to produce weakly bound ultracold molecules [4]. Using a sequence of magnetic pulses, the ultracold atoms can be converted into molecules with lifetimes of several seconds [5–9]. Initially, one thought that such highly excited molecules would decay very fast. This is true for bosonic atoms, where inelastic collisions with other atoms or molecules give a rapid decay. However, for fermionic atoms, the molecules have a much longer lifetime due to quenching of the inelastic collision rates as a result of the Pauli principle. In part, this is why the fermionic isotope ^6Li are preferred over the bosonic isotope ^7Li, which is far less studied. The first molecular Bose-Einstein condensates (BECs) observed in November 2003 utilized molecules created from Feshbach resonances. Jochim *et al.* [10] used ^{40}K atoms, while Greiner *et al.* [11] and Bartenstein *et al.* [12] worked with ^6Li atoms. The nK temperature range and BEC were eventually reached by evaporative cooling.

Finally, the ability to tune the scattering length made the so-called BEC-BCS transition experimentally accessible [13,14]. In short, this is a transition from a molecular BEC to atomic Cooper pairs via a regime where the scattering length diverges and becomes infinite. In the crossover regime, the interaction is independent of the scattering length as well as the range and details of the interatomic potential [15].

This paper focuses on cold diatomic collisions in general, and, in particular, the $^6Li_2$ system and on the Feshbach resonances in this system. Most attention is given to the wave Feshbach resonances, but we also calculate Feshbach resonances occurring in p waves. Rather than to set up a model with one or more tunable parameters, our philosophy has been to perform *ab initio* calculations of the various resonances using a fully coupled-channel approach. No empirical data have been included in the calculations. The calculations are performed with the diatomic Hund's case (a) basis set, describing the system as a molecule rather than two free atoms. This allows for a realistic and more accurate description of the short-range hyperfine interaction through the calculation of only a few molecular hyperfine parameters. Most, if not all, studies of diatomic collisions make no distinction between the short-range and the long-range hyperfine interaction, i.e., the hyperfine interaction is assumed to be independent of the internuclear separation. Our approach to the hyperfine interaction enables us to test this approximation. However, in the present case we find that the long-range atomic hyperfine interaction makes a reasonable approximation to the short-range case. This fact is due to the very shallow character of the relevant molecular state. In the next sections, we give a thorough explanation of the particular

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model that we use and relate the Hund's case (a) basis set to the more standard atomic FF-coupled basis sets.

The model and the expressions we present in this paper are not fully general. Some simplifications have been possible due to the particular alkali system studied. However, we do make it clear whenever special assumptions have been made. Throughout this paper, atomic units $\hbar = m_e = e = a_0 = 1$ are used, and we work within the Born-Oppenheimer approximation.

II. THEORY

The diatomic Hamiltonian can be written as

$$H = -\frac{1}{2\mu}\nabla^2 + H_{\mathrm{ev}}(\mathbf{r},\mathbf{x}) + H_{\mathrm{hf}}(\mathbf{r},\mathbf{x}) + H_Z(\mathbf{r},\mathbf{x}), \tag{1}$$

where $\mathbf{r}$ is the internuclear vector pointing from nuclei A to nuclei B and $\mathbf{x} = [\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n]^T$ contains the electronic coordinates. H_{ev} is the electronic and vibrational Hamiltonian, H_{hf} is the hyperfine Hamiltonian, and finally H_Z denotes the Zeeman interaction. H_{ev} can also include all types of relativistic contributions such as spin-orbit and spin-spin interactions if needed. μ is the reduced mass. The first task is to expand the total wave function in a chosen basis, e.g., the eigenstates of H_{ev} or some other operator. At short range, the eigenstates of H_{ev} are well suited; whereas at long range the eigenstates of $H_{\mathrm{hf}} + H_Z$ diagonalizes the interaction. To solve the time-independent Schrödinger equation for the whole molecule

$$H\Psi(\mathbf{r},\mathbf{x}) = E\Psi(\mathbf{r},\mathbf{x}), \tag{2}$$

we write

$$\Psi(\mathbf{r},\mathbf{x}) = \sum_b \frac{1}{r}\psi_b(r)\phi_b(\mathbf{r},\mathbf{x}), \tag{3}$$

where $\psi_b(r)$ is the radial-wave functions for the relative motion of the two nuclei for a molecule in electronic state b. The angular part of the relative motion is included in $\phi_b(\mathbf{r},\mathbf{x})$. Thus, we may write the time-independent Schrödinger equation (2) as

$$\begin{aligned} -\frac{1}{2\mu}\nabla^2 \sum_b \frac{1}{r}\psi_b(r)\phi_b(\mathbf{r},\mathbf{x}) &+ (H_{\mathrm{ev}} + H_{\mathrm{hf}} + H_Z) \\ &\times \sum_b \frac{\psi_b(r)}{r}\phi_b(\mathbf{r},\mathbf{x}) \\ &= E\sum_b \frac{\psi_b(r)}{r}\phi_b(\mathbf{r},\mathbf{x}). \end{aligned} \tag{4}$$

Multiplying with $\phi_a^*(\mathbf{r},\mathbf{x})$ and integrating over the electronic coordinates yields

$$\begin{aligned} -\frac{1}{2\mu}\frac{d^2\psi_a(r)}{dr^2} + \frac{l_a(l_a+1)}{2\mu r^2}\psi_a(r) + \sum_b [V_{ab}^{\mathrm{ev}} + V_{ab}^{\mathrm{hf}} + V_{ab}^{Z}]\psi_b(r) \\ = E\psi_a(r), \end{aligned} \tag{5}$$

where

$$V_{ab}^{\mathrm{ev}}(r) = \langle \phi_a(\mathbf{r},\mathbf{x}) | H_{\mathrm{ev}} | \phi_b(\mathbf{r},\mathbf{x}) \rangle, \tag{6}$$

$$V_{ab}^{\mathrm{hf}}(r) = \langle \phi_a(\mathbf{r},\mathbf{x}) | H_{\mathrm{hf}} | \phi_b(\mathbf{r},\mathbf{x}) \rangle, \tag{7}$$

$$V_{ab}^{Z} = \langle \phi_a(\mathbf{r},\mathbf{x}) | H_Z | \phi_b(\mathbf{r},\mathbf{x}) \rangle, \tag{8}$$

and l_a is the quantum number associated with the angular momentum of the relative motion of the two atoms. Deriving Eq. (5) from Eq. (4), it has been assumed that the nonadiabatic coupling terms can be ignored, and we make the approximation [16]

$$\sum_b \int \phi_a(\mathbf{r},\mathbf{x})^* \nabla^2 \phi_b(\mathbf{r},\mathbf{x}) \frac{\psi_b(r)}{r} d\mathbf{x} = \frac{d^2\psi_a}{dr^2} + \frac{l_a(l_a+1)}{r^2}\psi_a(r). \tag{9}$$

Finally, we have the boundary conditions $\psi_a(0) = 0$ and

$$\psi_a(r) \underset{r\to\infty}{\to} \sum_b \phi_b(\mathbf{r},\mathbf{x}) \frac{1}{\sqrt{k_b}} [j_b(k_b r)\delta_{ab} + g_b(k_b r) K_{ba}], \tag{10}$$

where K is the so-called reaction matrix determined from Eq. (10). $j_l(x)$ and $g_l(x)$ are the Riccati-Bessel functions [17] for real $k_b = \sqrt{2\mu(E - E_b)}$ (i.e., open channels $E > E_b$) but must be replaced with the modified spherical Bessel functions [17] of first and third kinds multiplied with $k_b\sqrt{r}$ for all closed channels. The important S matrix can be determined once K is known [18],

$$S = \frac{I + iK_{00}}{I - iK_{00}}, \tag{11}$$

where K_{00} is a submatrix of K containing all the elements connecting open channels (I is the identity matrix). The S-matrix elements readily yield the important phase shift δ_l from the simple expression

$$S_{aa} = e^{2i\delta_l}, \tag{12}$$

where l is the partial-wave quantum number.

A. Choice of basis set

To simplify the equations presented in this section, the two colliding atoms have been assumed to be in S states. For atoms in other states, e.g., P states, a nonzero angular momentum must be included. See the Appendix for more details.

1. Long-range basis: FF-coupled states

The long-range electronic potential energy $V(r)$ for two atoms, where $L_i = 0$ is proportional to r^{-6} [19]. Asymptotically, as $r \to \infty$, we are then left with the hyperfine Hamiltonian together with the Zeeman interaction set up by an external magnetic field. To fulfill the boundary condition imposed as $r \to \infty$, we choose a basis in which these interactions are diagonal. Consider the situation where atom 1 has total angular momentum $\mathbf{F}_1$ and atom 2 has total angular momentum $\mathbf{F}_2$. The atomic hyperfine interaction is diagonal in this basis if $\mathbf{J}_1 \equiv \mathbf{L}_1 + \mathbf{S}_1$, $\mathbf{J}_2 \equiv \mathbf{L}_2 + \mathbf{S}_2$, $\mathbf{I}_1$ and $\mathbf{I}_2$ are good quantum numbers together with M_{F_1} and M_{F_2}. The total two-atom angular-momentum states are constructed by adding the single atom angular momentum $\mathbf{F}_i$ from both atoms together with the mechanical rotation of the relative motion $\mathbf{L}$ (not to be confused with $\mathbf{L}_1$ or $\mathbf{L}_2$) to give the *total* angular momentum $\mathbf{F}$. First, we define the total atomic angular momentum $\mathbf{F}_a=\mathbf{F}_1+\mathbf{F}_2$,

$$|F_1F_2F_aM_{F_a}\rangle = \sum_{M_{F_1},M_{F_2}} \langle F_1M_{F_1}F_2M_{F_2}|F_aM_{F_a}\rangle|F_1M_{F_1}\rangle \times|F_2M_{F_2}\rangle. \tag{13}$$

Finally, we include also the angular momentum $\mathbf{L}$ from the relative motion of the two collision partners and construct the total angular momentum $\mathbf{F}=\mathbf{F}_a+\mathbf{L}$. The quantum numbers l and m_l are introduced as eigenvalues of the operators $\mathbf{L}^2$ and L_z, respectively, with the spherical harmonics $\langle\mathbf{r}|lm_l\rangle=Y_{lm_l}(\theta,\phi)$ as their eigenfunctions,

$$|F_alFM_F\rangle = \sum_{M_{F_a},m_l} \langle F_aM_{F_a}lm_l|FM_F\rangle|F_aM_{F_a}\rangle|lm_l\rangle. \tag{14}$$

We will refer to this basis as the *FF*-coupled basis.

Whenever an external magnetic field B is introduced, the Zeeman interaction couples the magnetic field to the electronic spins and $|F_alFM_F\rangle$ are no longer eigenstates of the long-range interaction. The long-range interaction is the sum $H_{\mathrm{hf}}+H_{\mathrm{Z}}$ which are diagonalized numerically. The remaining good quantum numbers in an external magnetic field are the total projection $M_F=M_{F_1}+M_{F_2}$ on a space-fixed axis and the mechanical rotation quantum number l.

2. Short-range basis: Molecular Hund's case (a) states

Here we define the molecular Hund's case (a) states. The matrix elements of the different interactions will be represented in this basis. For small distances r, the intuitive choice is a basis which describes the system as a molecule rather than two atoms. One possible choice is then to quantize $\mathbf{S}^2=(\mathbf{S}_1+\mathbf{S}_2)^2$ together with S_z and L_z with quantum numbers S,Σ, and Λ. The quantum numbers Σ and Λ are projections on the interatomic axis in a molecule-fixed system. We also need the nuclear-spin states $|I_1\Omega_{I_1}\rangle$ and $|I_2\Omega_{I_2}\rangle$. Similarly, Ω_{I_1} and Ω_{I_2} are projections of the nuclear spin on the internuclear axis in the molecule-fixed system. Combined to give the total angular momentum $\mathbf{F}$ (see the Appendix), we obtain the basis states

$$|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}F\Omega_FM_F\rangle = |q\Lambda S\Sigma\rangle|\Omega_{I_1}\Omega_{I_2}\rangle|F\Omega_FM_F\rangle, \tag{15}$$

where $\Omega_F=\Sigma+\Lambda+\Omega_{I_1}+\Omega_{I_2}$ is the projection of the total spin on the internuclear axis. These are the Hund's case (a) basis states. The letter q in the state symbol represents the other quantum numbers necessary to specify the electronic state. The quantum numbers I_1 and I_2 are constants and have been suppressed in the notation.

3. Unitary transformation between the short-range basis and the long-range basis

Although we will be mostly concerned with the molecular Hund's case (a) states, we obtain the useful unitary transformation between the *FF*-coupled states, where the K matrix is defined [see Eq. (10)], and the Hund's case (a) states. The unitary transformation has been worked out in detail in the Appendix; here we merely give the final expression in terms of 3j-symbols,

$$\begin{aligned}
&\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F|qF_1F_2F_alFM_F\rangle \\
&\quad = (-1)^f \sum_{\substack{M_{F_a},m_l\\ M_{F_1},M_{F_2}}} \sum_{\substack{M_{S_1},M_{S_2},\\ M_{I_1},M_{I_2}}} \sum_{\substack{J,I,\\ M_S}} (2J+1)(2I+1)(2F+1)[F_a][F_1][F_2][S][l] \begin{pmatrix} l & F_a & F \\ m_l & M_{F_a} & -M_F \end{pmatrix} \begin{pmatrix} F_1 & F_2 & F_a \\ M_{F_1} & M_{F_2} & -M_{F_a} \end{pmatrix} \\
&\qquad \times \begin{pmatrix} S_1 & I_1 & F_1 \\ M_{S_1} & M_{I_1} & -M_{F_1} \end{pmatrix} \begin{pmatrix} S_2 & I_2 & F_2 \\ M_{S_2} & M_{I_2} & -M_{F_2} \end{pmatrix} \begin{pmatrix} S_1 & S_2 & S \\ M_{S_1} & M_{S_2} & -M_S \end{pmatrix} \begin{pmatrix} S & l & J \\ M_S & m_l & -M_J \end{pmatrix} \begin{pmatrix} S & l & J \\ \Sigma & 0 & -\Omega \end{pmatrix} \\
&\qquad \times \begin{pmatrix} I_1 & I_2 & I \\ M_{I_1} & M_{I_2} & -M_I \end{pmatrix} \begin{pmatrix} I_1 & I_2 & I \\ \Omega_{I_1} & \Omega_{I_2} & -\Omega_I \end{pmatrix} \begin{pmatrix} J & I & F \\ M_J & M_I & -M_F \end{pmatrix} \begin{pmatrix} J & I & F \\ \Omega & \Omega_I & -\Omega_F \end{pmatrix},
\end{aligned} \tag{16}$$

with $f=F_a-l+F_1-F_2+M_{F_a}+2S_1-I_1+M_{F_1}-I_2+M_{F_2}+M_S+\Omega+\Omega_I+\Omega_F-M_J-M_I$, $[F_a]=\sqrt{2F_a+1}$, and similar for other quantities in square brackets. When $L_i\neq 0$, the unitary transformation (16) is no longer valid.

The unitary transformation from the case (a) basis to the *FF*-coupled basis is often called a frame transformation in the present context (see [20,21]). For further discussion of other convenient basis states and a more in-depth treatment, we refer to [16,22] and references therein.

B. Pauli exclusion principle

Due to the Pauli principle, the wave function describing our system must have certain symmetries upon the interchange of identical particles. Working with two identical atoms, the proper wave function must fulfill two requirements. (1) Interchanging an even (odd) number of electrons should yield a phase factor +1(−1), whereas (2) interchanging the nuclei should give +1 or −1 depending on whether $I_1=I_2$ is integer or half integer (boson or fermion, respectively). The long-range and short-range states introduced in Sec. II A must respect these symmetries. The following discussion is, in particular, relevant for two alkali atoms with identical nuclei $L_1=L_2=0$ and $S_1=S_2\neq 0$. However, for $L_1=L_2\neq 0$, the modifications to the expressions given are rather straightforward.

In addition to the previously mentioned Hund's case (a) basis, we introduce the Hund's case (b) basis as the symmetries are easier to deduce in this basis. This is due to the fact that both the electronic and the nuclear spin is quantized in a space-fixed system ($\Sigma\rightarrow M_S$, $\Omega_{I_1}\rightarrow M_{I_1}$, and $\Omega_{I_2}\rightarrow M_{I_2}$) in a case (b) basis. See [23] for a further discussion of the different Hund's cases.

Both basis set $|q\Lambda S\Sigma\rangle$ [case (a)] and $|q\Lambda SM_S\rangle$ [case (b)] can be constructed as eigenstates for the total inversion operator I_t (spatial inversion in a space-fixed system) for all diatomic molecules. We denote the eigenvalues of I_t with ±. Assuming $M_{L_1}=M_{L_2}=0$, it can be shown that the only possible eigenvalue for I_t is +1 [24]. For homonuclear diatomic molecules, there are two additional symmetry operations. These are inversion of the spatial nuclear coordinates I_n and inversion of the spatial electronic coordinates I_e with eigenvalue $(-1)^{i_e}$. For all operators, inversion is performed in a space-fixed coordinate system. Electronic states with $i_e=1$ are denoted u (ungerade), whereas states with $i_e=0$ are g states (gerade). These three symmetry operations are also related through the relation $I_t=I_nI_e$. We will assume that we are working with states $|q\Lambda S\Sigma\rangle$ and $|q\Lambda SM_S\rangle$ that are eigenstates for the symmetry operators I_t, I_e and I_n.

The electronic case (b) states $|q\Lambda SM_S\rangle$ are linear combinations of spin orbitals $q_\Lambda(\mathbf{x},r)|SM_S\rangle$. To determine their behavior under symmetry operations, it suffices to consider $q_\Lambda(\mathbf{x},r)$ and $|SM_S\rangle$ separately [25,26]. However, it is important to realize that the separation $|q\Lambda SM_S\rangle=|q\Lambda\rangle|SM_S\rangle$ is only generally valid for one- and two-electron molecules.

Next we introduce the electronic permutation operator P_e that permutes all the electrons. Both the spatial and the spin part of $|q\Lambda SM_S\rangle$ are eigenstates of P_e. The eigenvalues corresponding to the spatial functions $q_\Lambda(\mathbf{x},r)$ are $(-1)^{p_e}$ where $p_e=0$ (symmetric) and $p_e=1$ (antisymmetric). There exists an intimate but not obvious connection between the eigenvalues of the operators I_e and P_e when acting on $q_\Lambda(\mathbf{x},r)$. It can be shown [26] that the eigenvalues are related through the relation $(-1)^{i_e}=\pm(-1)^{p_e}$, where ± are the eigenvalues of the I_t operator, restricted to +1 for the present system. It then follows that $(-1)^{i_e}=(-1)^{p_e}$, hence P_e and I_e have identical eigenvalues acting on $q_\Lambda(\mathbf{x},r)$.

The result of the operation $P_e|SM_S\rangle$ is easily worked out due to the symmetry of the Clebsch-Gordan coefficients, and one obtains $P_e|SM_S\rangle=(-1)^{2S_1-S}|SM_S\rangle$. To summarize, we may then write

$$P_e|q\Lambda SM_S\rangle=(-1)^{i_e+2S_1-S}|q\Lambda SM_S\rangle. \tag{17}$$

However, the Pauli principle requires

$$P_e|q\Lambda SM_S\rangle=(-1)^{N_1}|q\Lambda SM_S\rangle, \tag{18}$$

where N_1 is the number of electron permutations. Combined with Eq. (17), this implies $(-1)^{i_e+2S_1-S}=(-1)^{N_1}$. Since $(-1)^{2S_1}=(-1)^{N_1}$, it follows that only electronic states where $(-1)^{i_e-S}=+1$ are allowed. These are the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states found in diatomic alkali molecules.

In general, the allowed combinations of g/u and electronic spin S can be worked out from the Wigner-Witmer rules [27]. See also [26] and references therein for a more accessible derivation of the Wigner-Witmer rules.

We have found that $I_t|q\Lambda SM_S\rangle=+1|q\Lambda SM_S\rangle$ and that $I_e|q\Lambda SM_S\rangle=(-1)^{i_e}|q\Lambda SM_S\rangle$ (I_t, I_e and I_n only act on the spatial coordinates, leaving the spin states $|SM_S\rangle$ unaffected). From the relation $I_n=I_tI_e$, it then follows that $I_n|q\Lambda SM_S\rangle=(-1)^{i_e}|q\Lambda SM_S\rangle$. However, inversion and permutation of two nuclei (in a diatomic molecule) in space-fixed axis with origin at the center-of-mass position are the same two operations. Thus we conclude

$$I_n|q\Lambda SM_S\rangle=P_n|q\Lambda SM_S\rangle=(-1)^{i_e}|q\Lambda SM_S\rangle. \tag{19}$$

However, it is not obvious how the electronic case (a) states defined in molecule-fixed axes are affected by P_n. To determine this, we use the relation between case (a) and case (b) states

$$|q\Lambda SM_S\rangle=\sum_{\Sigma}\mathcal{D}^S_{M_S,\Sigma}(\phi,\theta,0)^*|q\Lambda S\Sigma\rangle, \tag{20}$$

where $\mathcal{D}$ is the rotation matrix [28] that rotates the space-fixed component of M_S into the molecule-fixed Σ component. The effect of P_n is the same as a rotation of the axis of the molecule by an angle π, which is equivalent to the transformation $[(\theta,\phi)\rightarrow(\pi-\theta,\phi+\pi)]$. The property

$$\begin{aligned}P_n\mathcal{D}^S_{M_S,\Sigma}(\phi,\theta,0)^*&=\mathcal{D}^S_{M_S,\Sigma}(\phi+\pi,\pi-\theta,0)^*\\&=(-1)^S\mathcal{D}^S_{M_S,-\Sigma}(\phi,\theta,0)^*,\end{aligned} \tag{21}$$

which follows from the definition of the $\mathcal{D}$ matrix elements is then very useful. Knowing how P_n acts on both $|q\Lambda SM_S\rangle$ and $\mathcal{D}^S_{M_S\Sigma}(\phi,\theta,0)^*$, it is seen from Eq. (20) that

$$P_n|q\Lambda S\Sigma\rangle=(-1)^{-S+i_e}|q\Lambda S-\Sigma\rangle, \tag{22}$$

in agreement with [29]. For a more detailed treatment, see Zare *et al.* [25] and references therein.

We also need to consider the nuclear-spin states $|I_1M_{I_1}\rangle|I_2M_{I_2}\rangle=|I_1M_{I_1}I_2M_{I_2}\rangle$ under permutation of the nuclei P_n. Working with the case (b) basis in space-fixed axis, it follows immediately that $P_n|I_1M_{I_1}I_2M_{I_2}\rangle=|I_2M_{I_2}I_1M_{I_1}\rangle$. However, to obtain $P_n|I_1\Omega_{I_1}I_2\Omega_{I_2}\rangle$ we write

$$|I_1M_{I_1}I_2M_{I_2}\rangle=\sum_{\Omega_{I_1}}\mathcal{D}^{I_1}_{M_{I_1},\Omega_{I_1}}(\phi,\theta,0)^*|I_1\Omega_{I_1}I_2M_{I_2}\rangle, \tag{23}$$

or alternatively

$$\begin{aligned}|I_2M_{I_2}I_1M_{I_1}\rangle &= \sum_{\Omega_{I_1}} \mathcal{D}^{I_1}_{M_{I_1},\Omega_{I_1}}(\phi,\theta,0)^*|I_2M_{I_2}I_1\Omega_{I_1}\rangle \\ &= P_n\Bigg[\sum_{\Omega_{I_1}} \mathcal{D}^{I_1}_{M_{I_1},\Omega_{I_1}}(\phi,\theta,0)^*|I_1\Omega_{I_1}I_2M_{I_2}\rangle\Bigg] \\ &= (-1)^{I_1}\sum_{\Omega_{I_1}} \mathcal{D}^{I_1}_{M_{I_1},-\Omega_{I_1}}(\phi,\theta,0)^*P_n|I_1\Omega_{I_1}I_2M_{I_2}\rangle, \quad (24)\end{aligned}$$

hence $P_n|I_1\Omega_{I_1}I_2M_{I_2}\rangle=(-1)^{-I_1}|I_2M_{I_2}I_1-\Omega_{I_1}\rangle$. Similarly, rotating M_{I_2} into Ω_{I_2} yields

$$P_n|I_1\Omega_{I_1}I_2\Omega_{I_2}\rangle = (-1)^{-2I_1}|I_2-\Omega_{I_2}I_1-\Omega_{I_1}\rangle. \quad (25)$$

Finally, we determine the effect of P_n on the total angular-momentum states $|FM_F\Omega_F\rangle$. $\langle\mathbf{r}|FM_F\Omega_F\rangle$ are given in terms of the $\mathcal{D}^F_{M_F\Omega_F}(\phi,\theta,0)^*$ rotation matrix elements [30],

$$\Psi_{FM_F\Omega_F}(\phi,\theta) = \langle\mathbf{r}|FM_F\Omega_F\rangle = \sqrt{\frac{2F+1}{4\pi}}\mathcal{D}^F_{M_F\Omega_F}(\phi,\theta,0)^*, \quad (26)$$

and the phase factor is easily determined from Eq. (21) with F in place of S, and with similar replacements for M_F and Ω_F. The result is

$$P_n|FM_F\Omega_F\rangle = (-1)^F|FM_F-\Omega_F\rangle. \quad (27)$$

Combining Eqs. (22), (25), and (27), we obtain

$$\begin{aligned}&P_n|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F\rangle \\ &\quad = (-1)^{-S+i_e-2I_1+F}|q\Lambda S-\Sigma-\Omega_{I_1}-\Omega_{I_2}FM_F-\Omega_F\rangle, \quad (28)\end{aligned}$$

and case (a) states that are eigenstates for the P_n operator *and*, fulfill, the Pauli principle can be constructed,

$$\begin{aligned}|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F) = \frac{1}{\sqrt{2}}(&|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F\rangle \\ &+(-1)^{-S+i_e+F}|q-\Lambda S-\Sigma-\Omega_{I_2} \\ &-\Omega_{I_2}FM_F-\Omega_F). \quad (29)\end{aligned}$$

The Pauli principle requires the states $|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F\rangle$ to have the following symmetry:

$$P_n|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F\rangle = (-1)^{2I_1}|q\Lambda S\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F\rangle, \quad (30)$$

which has been used to obtain Eq. (29).

Similarly, the long-range basis must also fulfill the Pauli principle. The long-range basis is defined in Eq. (14) and is a linear combination of basis states $|F_1F_2F_AM_{F_a}\rangle$ and $|lm_l\rangle$. The two atoms may or may not be in the same hyperfine state. Permuting the nuclei in the states $|F_aM_{F_a}\rangle$ gives

$$\begin{aligned}P_n|F_1F_2F_aM_{F_a}\rangle = &\sum_{M_{F_1},M_{F_2}}\sum_{M_{S_1},M_{I_1}}\sum_{M_{S_2},M_{I_2}}\langle F_1M_{F_1}F_2M_{F_2}|F_aM_{F_a}\rangle \\ &\times\langle S_1M_{S_1}I_1M_{I_1}|F_1M_{F_1}\rangle \\ &\times\langle S_1M_{S_2}I_1M_{I_2}|F_2M_{F_2}\rangle P_n[|qS_1M_{S_1}S_2M_{S_2}\rangle \\ &\times|I_1M_{I_1}I_2M_{I_2}\rangle]. \quad (31)\end{aligned}$$

To continue, we decouple the electronic spin S in the sates $|q\Lambda SM_S\rangle$,

$$|qS_1M_{S_1}S_2M_{S_2}\rangle = \sum_{S,M_S}\langle S_1M_{S_1}S_1M_{S_2}|SM_S\rangle|q\Lambda SM_S\rangle, \quad (32)$$

and obtain $P_n|qS_1M_{S_1}S_1M_{S_2}\rangle$,

$$P_n|qS_1M_{S_1}S_1M_{S_2}\rangle = \sum_{S,M_S}\langle S_1M_{S_1}S_1M_{S_2}|SM_S\rangle(-1)^{i_e}|q\Lambda SM_S\rangle, \quad (33)$$

where we have used Eq. (19) and $(-1)^{i_e}=(-1)^{S-2S_1+N_1}$, which follows from Eq. (17) and requirement (18). Finally, we exploit the symmetry of the Clebsch-Gordan coefficients and write $\langle S_1M_{S_1}S_2M_{S_2}|SM_S\rangle=(-1)^{S_1+S_2-S}\langle S_2M_{S_2}S_1M_{S_1}|SM_S\rangle$ to obtain

$$\begin{aligned}P_n|qS_1M_{S_1}S_2M_{S_2}\rangle &= \sum_{S,M_S}\langle S_2M_{S_2}S_1M_{S_1}|SM_S\rangle(-1)^{N_1}|q\Lambda SM_S\rangle \\ &= (-1)^{N_1}|qS_2M_{S_2}S_1M_{S_1}\rangle. \quad (34)\end{aligned}$$

The nuclear-spin states $|I_1M_{I_1}I_1M_{I_2}\rangle$ can be permuted without introducing any phase factor and we can conclude

$$\begin{aligned}P_n|F_1F_2F_aM_{F_a}\rangle = &\sum_{M_{F_1},M_{F_2}}\sum_{M_{S_1},M_{I_1}}\sum_{M_{S_2},M_{I_2}}\langle F_1M_{F_1}F_2M_{F_2}|F_aM_{F_a}\rangle \\ &\times\langle S_1M_{S_1}I_1M_{I_1}|F_1M_{F_1}\rangle\langle S_1M_{S_2}I_1M_{I_2}|F_2M_{F_2}\rangle \\ &\times(-1)^{N_1}|qS_2M_{S_2}S_1M_{S_1}\rangle|I_2M_{I_2}I_1M_{I_1}\rangle \\ = &(-1)^{N_1+F_1+F_2-F_a}|F_2F_1F_aM_{F_a}\rangle. \quad (35)\end{aligned}$$

The phase factor $(-1)^{F_1+F_2-F_a}$ stems from a rearrangement of the Clebsch-Gordan coefficient. Finally, we determine the sign of the states $|lm_l\rangle$ under nuclear permutation

$$P_n|lm_l\rangle = (-1)^l|lm_l\rangle, \quad (36)$$

which follows from the properties of the spherical harmonics. All together, the FF-coupled basis states fulfill the equation

$$P_n|F_1F_2F_alFM_F\rangle = (-1)^{N_1+F_1+F_2-F_a+l}|F_2F_1F_alFM_F\rangle, \quad (37)$$

hence we can construct eigenstates for the P_n operator,

$$|F_1F_2F_alFM_F\rangle = \frac{1}{\sqrt{2}}[|F_1F_2F_alFM_F\rangle + (-1)^{N_1+F_2+F_2-F_a+l+2I_1}|F_2F_1F_alFM_F\rangle]. \tag{38}$$

The phase factor is in agreement with the expression obtained by Bo Gao [16] working with similar basis states.

III. INTERACTIONS

Consider again the diatomic Hamiltonian, now written in the abbreviated form

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + H_{\mathrm{ev}} + H_{\mathrm{hf}} + H_{\mathrm{ss}} + H_{\mathrm{Z}} + H_{\mathrm{rot}}, \tag{39}$$

where H_{ev} denotes the electronic and vibrational contribution. H_{hf} represents the hyperfine operator, H_{Z} is the Zeeman interaction operator, and H_{rot} is the rotational energy operator. H_{ss} is the spin-spin interaction operator included explicitly. Other relativistic effects are included in H_{ev}. In this section, we obtain the matrix elements for these operators in the molecular Hund's case (a) basis. Working with the case (a) basis enables rather compact expressions for the relevant matrix elements. The CPU time is also reduced by avoiding the all too familiar Clebsch-Gordan coefficients often present in large numbers in both hyperfine and Zeeman interaction terms. Furthermore, it is very easy to write down the different matrices in this basis, yielding an easy and transparent algorithm less susceptible to errors.

A. Diatomic magnetic hyperfine interaction in Hund's case (a) basis

The general diatomic hyperfine Hamiltonian is given in [31]. Only interactions that depend on the electronic spin are of current interest. We will start with a microscopic hyperfine Hamiltonian that takes the form

$$H_{\mathrm{hf}} = \sum_{j=1}^{2}\sum_{\mu=-1}^{1}(-1)^{\mu}I_{j-\mu}\sum_{i=1}^{N}s_{i\mu}a(\mathbf{r}_{ij}), \tag{40}$$

where N is the total number of electrons. $I_{j-\mu}$ and $s_{i\mu}$, respectively, denote spherical components of the nuclear spin $\mathbf{I}_j$ and the electronic spin $\mathbf{s}_i$. The quantity $a(\mathbf{r}_{ij})$ depends on the position of electron i relative to nucleus j. The Hamiltonian in Eq. (40), in particular, applies to the dominant Fermi-contact interaction, with $a(\mathbf{r}_{ij})$ defined by

$$a(\mathbf{r}_{ij}) = \frac{16\pi}{3}g_{I_j}\mu_0\mu_N\delta(\mathbf{r}_{ij}), \tag{41}$$

where g_{I_j} denotes the g factor of nucleus j.

We are considering the states $|qS\Sigma\Omega_{I_1}\Omega_{I_2}\rangle$ and have omitted $|FM_F\Omega\rangle$ as the hyperfine interaction is diagonal in the corresponding quantum numbers. Λ is also ignored as it is zero in alkali-metal diatomic molecules (or it may be included in the collective quantum number q). The relevant matrix element can then be written as

$$\begin{aligned}\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|H_{\mathrm{hf}}|q'S'\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle &= \sum_{\mu=-1}^{1}(-1)^{\mu}\langle\Omega_{I_1}|I_{1-\mu}|\Omega'_{I_1}\rangle\langle qS\Sigma|\sum_{i=1}^{N}s_{i\mu}a(\mathbf{r}_{i1})\\ &\quad\times|q'S'\Sigma'\rangle\delta_{\Omega_{I_2},\Omega'_{I_2}} + \sum_{\mu=-1}^{1}(-1)^{\mu}\langle\Omega_{I_2}|I_{2-\mu}|\Omega'_{I_2}\rangle\\ &\quad\times\langle qS\Sigma|\sum_{i=1}^{N}s_{i\mu}a(\mathbf{r}_{i2})|q'S'\Sigma'\rangle\delta_{\Omega_{I_1},\Omega'_{I_1}}.\end{aligned} \tag{42}$$

For the elements diagonal in spin ($S=S'$), it follows from Eq. (42) and the Wigner-Eckart theorem

$$\begin{aligned}\langle qS\Sigma|\sum_{i=1}^{N}s_{i\mu}a(\mathbf{r}_{i1})|qS\Sigma'\rangle &= \sum_{i=1}^{N}\langle S\Sigma|s_{i\mu}|S\Sigma'\rangle\langle qS\Sigma'|a(\mathbf{r}_{i1})|qS\Sigma'\rangle\\ &= \langle S\Sigma|S_{\mu}|S\Sigma'\rangle\sum_{i=1}^{N}\langle S||s_i||S\rangle\langle qS\Sigma'|a(\mathbf{r}_{i1})|qS\Sigma'\rangle\\ &= \langle S\Sigma|S_{\mu}|S\Sigma'\rangle b_1,\end{aligned} \tag{43}$$

where b_1 has been defined as

$$b_1 \equiv \sum_{i=1}^{N}\langle S||s_i||S\rangle\langle qS\Sigma'|a(\mathbf{r}_{i1})|qS\Sigma'\rangle, \tag{44}$$

and a similar definition holds for b_2 related to the other nucleus. S_{μ} is the spherical component μ of the *total* electronic spin. For two identical nuclei $b_1=b_2=b$. Combining Eqs. (42)–(44), the hyperfine interaction diagonal in S can be written as

$$\begin{aligned}\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|H_{\mathrm{hf}}|qS\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle &= b(\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|\mathbf{I}_1\cdot\mathbf{S}|qS\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle\delta_{\Omega_{I_2},\Omega'_{I_2}}\\ &\quad+\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|\mathbf{I}_2\cdot\mathbf{S}|qS\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle\delta_{\Omega_{I_1},\Omega'_{I_1}}),\end{aligned} \tag{45}$$

where the matrix elements in Eq. (45) are defined by

$$\begin{aligned}\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|\mathbf{I}_j\cdot\mathbf{S}|qS\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle &= \Sigma\Omega_{I_j}\delta_{\Sigma,\Sigma'}\delta_{\Omega_{I_j},\Omega'_{I_j}} + \frac{1}{2}[S(S+1)-\Sigma(\Sigma-1)]^{1/2}\\ &\quad\times[I_j(I_j+1)-\Omega_{I_j}(\Omega_{I_j}+1)]^{1/2}\delta_{\Sigma',\Sigma-1}\delta_{\Omega'_{I_j},\Omega_{I_j}+1}\\ &\quad+\frac{1}{2}[S(S+1)-\Sigma(\Sigma+1)]^{1/2}\\ &\quad\times[I_j(I_j+1)-\Omega_{I_j}(\Omega_{I_j}-1)]^{1/2}\delta_{\Sigma',\Sigma+1}\delta_{\Omega'_{I_j},\Omega_{I_j}-1},\end{aligned} \tag{46}$$

with $j=1,2$. Equation (46) has been worked out by standard ladder operator techniques.

We now return to Eq. (42) and to the part of the hyperfine interaction off diagonal in S. Again, using the Wigner-Eckart theorem,

$$\langle qS\Sigma|\sum_{i=1}^{N} s_{i\mu}a(\mathbf{r}_{i1})|q'S'\Sigma'\rangle = \sum_{i=1}^{N}\langle qS\Sigma|s_{i\mu}|q'S'\Sigma'\rangle\langle qS\Sigma|a(\mathbf{r}_{i1}) \times|q'S'\Sigma'\rangle, \tag{47}$$

$$=\langle 1\mu S'\Sigma'|S\Sigma\rangle\sum_{i=1}^{N}\langle S\|s_i\|S'\rangle\langle q|a(\mathbf{r}_{i1})|q'\rangle = g_1\langle 1\mu S'\Sigma'|S\Sigma\rangle, \tag{48}$$

where g_1 has been defined

$$g_1 \equiv \frac{1}{\langle 1\mu S'\Sigma'|S\Sigma\rangle}\langle qS\Sigma|\sum_{i=1}^{N} s_{i\mu}a(\mathbf{r}_{i1})|q'S'\Sigma'\rangle = \sum_{i=1}^{N}\langle S\|s_i\|S'\rangle\langle q|a(\mathbf{r}_{i1})|q'\rangle. \tag{49}$$

A similar expression applies to g_2 for the other nucleus. We will return to the explicit connection between g_1 and g_2 later on. We note, however, that g_1 and g_2 are independent of μ. $\langle 1\mu S'\Sigma'|S\Sigma\rangle$ denotes the Clebsch-Gordan coefficient from the Wigner-Eckart theorem that couples a spherical tensor of rank 1 to the electronic spin S' to yield S. The off-diagonal matrix elements in terms of g_1 and g_2 are written as [combining Eqs. (42) and (48)]

$$\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|H_{\mathrm{hf}}|qS'\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle = g_1\sum_{\mu=-1}^{1}(-1)^{\mu}\langle 1\mu S'\Sigma'|S\Sigma\rangle\langle\Omega_{I_1}|I_{1-\mu}|\Omega'_{I_1}\rangle\delta_{\Omega_{I_2},\Omega'_{I_2}} + g_2\sum_{\mu=-1}^{1}(-1)^{\mu}\langle 1\mu S'\Sigma'|S\Sigma\rangle\langle\Omega_{I_2}|I_{2-\mu}|\Omega'_{I_2}\rangle\delta_{\Omega_{I_1},\Omega'_{I_1}}. \tag{50}$$

The matrix elements in Eq. (50) are readily calculated, and the results are

$$\langle\Omega_{I_i}|I_{i\pm 1}|\Omega'_{I_i}\rangle = \mp\frac{1}{\sqrt{2}}[I_i(I_i+1)-\Omega_{I_i}(\Omega_{I_i}\mp 1)]^{1/2}\delta_{\Omega'_{I_i},\Omega_{I_i}\mp 1}, \tag{51}$$

$$\langle\Omega_{I_i}|I_{i0}|\Omega'_{I_i}\rangle = \Omega_{I_i}\delta_{\Omega'_{I_i},\Omega_{I_i}}. \tag{52}$$

Finally, we specialize to the alkali atoms where $S_1=S_2=\frac{1}{2}$ and $S\in\{0,1\}$. It is readily seen from Eq. (49) that g_1 and g_2 are independent of μ. To simplify the calculation of g_1 and g_2, we set $\mu=1$ which yields $\langle 1100|11\rangle=1(S'=0,\Sigma'=0)$. The relation between g_1 and g_2 is obtained by decoupling the total electronic spin S,

$$|q,S=1,\Sigma=1\rangle = |q,S_1,\Sigma_1=1/2,S_2,\Sigma_2=1/2\rangle, \tag{53}$$

$$|q,S=0,\Sigma=0\rangle = \frac{1}{\sqrt{2}}(|q',S_1,\Sigma_1=1/2,S_2,\Sigma_2=-1/2\rangle - |q'S_1\Sigma_1=-1/2,S_2,\Sigma_2=1/2\rangle), \tag{54}$$

and we obtain

$$g_1 = -\frac{1}{\sqrt{2}}\langle qS_1,\Sigma_1=1/2|\sum_{i=1}^{N} s_{i1}a(\mathbf{r}_{i1})|q'S_1,\Sigma'_1=-1/2\rangle. \tag{55}$$

In a similar way, we obtain for g_2

$$g_2 = \frac{1}{\sqrt{2}}\langle qS_2\Sigma_2=1/2|\sum_{i=1}^{N} s_{i1}a(\mathbf{r}_{i2})|q'S_2,\Sigma'_2=-1/2\rangle, \tag{56}$$

which means that we have $g_1=-g_2$. Thus, we see that just two hyperfine parameters are needed. For the $^3\Sigma$ state the only parameter is b, and for the $^3\Sigma-{}^1\Sigma$ hyperfine interaction there is a single parameter $g_1=-g_2$.

B. *Ab initio* calculation of the molecular hyperfine parameters

First, we consider the Fermi-contact hyperfine interaction. The parameter b_1 of Eq. (44) is then denoted b_{1F}, and in the case of two identical nuclei $b_{1F}=b_{2F}=b_F$. The Fermi-contact parameter b_F, which is independent of μ, is from Eqs. (43) and (41) given by

$$b_F = \frac{16\pi}{3}g_I\mu_0\mu_N\frac{1}{\Sigma}\langle qS\Sigma|\sum_{i=1}^{N} s_{iz}\delta(\mathbf{r}_{i1})|qS\Sigma\rangle. \tag{57}$$

The expressions for b_F above applies to the interaction that is diagonal in the spin ($S=S'$), i.e., to the triplet state for the alkali molecules.

For the Fermi-contact interaction that is off diagonal in S, i.e., triplet-singlet interaction in the alkali case, the corresponding parameters $b'_{1F}=g_1$ and $b'_{2F}=g_2$ are obtained from Eq. (49). Specializing to the diatomic alkali molecules, we see from Eqs. (55) and (56) that $b'_{1F}=-b'_{2F}$, and

$$b'_F = b'_{1F} = -\frac{16\pi}{3}g_I\mu_0\mu_N\frac{1}{\sqrt{2}}\left\langle q,S_1=\frac{1}{2},\Sigma=\frac{1}{2}\right|\sum_{i=1}^{N} s_{i1}\delta(\mathbf{r}_{i1}) \times\left|q'S_1=\frac{1}{2},\Sigma'_1=-\frac{1}{2}\right\rangle. \tag{58}$$

For a diatomic molecule, there is furthermore an anisotropic spin-dependent hyperfine interaction that is generally included through the parameter c (cf. [31]). In this case, the quantity $a(\mathbf{r}_{ij})$ in the Hamiltonian of Eq. (40) will also depend on the component μ. The Fermi-contact hyperfine parameters b_F and b'_F were computed *ab initio* for ^{6}Li$_2$ for several internuclear separations. Extensive configuration interaction (CI) calculations were performed to obtain *ab initio* values of the parameters b_F and b'_F in ^{6}Li$_2$. The results are shown in Fig. 10, with a corresponding discussion in Sec. VI C 1.

The anisotropic part of the diatomic hyperfine Hamiltonian yields two additional hyperfine parameters. For interactions diagonal in the spin S, there is an extra parameter c, and terms off diagonal in S (singlet-triplet interaction) introduces a parameter c' (cf. [31]). Basically, the anisotropic part adds corrections to the Fermi-contact parameters b_F and b'_F in the matrix elements of the hyperfine Hamiltonian as follows:

$$b_F \rightarrow b_F + \frac{2}{3}c, \quad \mu = 0,$$

$$b_F \rightarrow b_F - \frac{1}{3}c, \quad \mu = \pm 1,$$

$$b'_F \rightarrow b'_F + \frac{2}{3}c', \quad \mu = 0,$$

$$b'_F \rightarrow b'_F - \frac{1}{3}c', \quad \mu = \pm 1. \tag{59}$$

Ab initio values for the parameters c and c' were obtained from calculations similar to those performed to obtain values for b_F and b'_F. The results are shown in Fig. 10 for the $^6\mathrm{Li}_2$ molecule. We notice that the contribution from the anisotropic hyperfine interaction is rather insignificant compared with the dominant Fermi-contact interaction.

C. Diatomic molecular Zeeman interaction in Hund's case (a) basis

Calculations similar to those presented in this section can be found in [32], although this reference only considers diatomic molecules with one nuclear spin I. We extend the theory to include atoms with two nuclear spins I_1 and I_2, but we ignore some of the smaller second-order effects treated in [32]. We write the Zeeman Hamiltonian as

$$H_Z = \mu_0 g_S \mathbf{S} \cdot \mathbf{B} = \mu_0 g_S \sum_{\mu=-1}^{1} (-1)^{\mu} S_{\mu} B_{-\mu}, \tag{60}$$

and neglect the terms $\mu_0(g_I\mathbf{I}+g_N\mathbf{N})\cdot\mathbf{B}$ (μ_0 is the Bohr magneton), which are all expected to be much smaller than the electronic spin contribution. In Eq. (60), it has been assumed that $\mathbf{L}=0$. S_μ and $B_{-\mu}$ refer to space-fixed spherical components. The space-fixed components S_μ are related to the molecule-fixed components $S'_{\mu'}$ by the usual $\mathcal{D}$ matrix elements

$$S_\mu = \sum_{\mu'} \mathcal{D}^1_{\mu\mu'}(\phi,\theta,0)^* S'_{\mu'}. \tag{61}$$

Inserted in Eq. (60), this gives the Hamiltonian

$$H_Z = \mu_0 g_S \sum_{\mu,\mu'=-1}^{1} (-1)^{\mu} \mathcal{D}^1_{\mu\mu'}(\phi,\theta,0)^* S'_{\mu'} B_{-\mu}. \tag{62}$$

Labeling all quantum numbers except the total angular momentum F by $w(|w\rangle = |qS\Sigma\Omega_{I_1}\Omega_{I_2}\rangle)$, the matrix elements are worked out as

$$\begin{aligned}\langle wFM\Omega_F|H_Z|w'F'M'\Omega'_F\rangle &= \mu_0 g_S \sum_{\mu,\mu'=-1}^{1} (-1)^{\mu}\langle w|S'_{\mu'}B_{-\mu}|w'\rangle \\ &\times \langle FM_F\Omega_F|\mathcal{D}^1_{\mu,\mu'}(\phi,\theta,0)^*|F'M'_F\Omega'_F\rangle.\end{aligned} \tag{63}$$

The integral $\langle w|\mathcal{D}^1(\phi,\theta,0)^*|w'\rangle$ is easily evaluated as an integral over the product of three $\mathcal{D}$ matrices [cf. Eq. (26)]. By convention we assume that the magnetic field is along the space-fixed z axis with magnetic field strength B. Thus, there is only a contribution from $\mu=0$ in Eq. (63) and we obtain

$$\begin{aligned}\langle wFM_F\Omega_F|H_Z|w'F'M'_F\Omega'_F\rangle &= B\mu_0 g_S\sqrt{(2F+1)(2F'+1)} \sum_{\mu'=-1}^{1} \begin{pmatrix} F & 1 & F' \\ M_F & 0 & -M_F \end{pmatrix} \\ &\times \begin{pmatrix} F & 1 & F' \\ \Omega_F & -\mu' & -\Omega'_F \end{pmatrix} (-1)^{M_F-\Omega'_F-\mu'} \langle w|S'_{\mu'}|w'\rangle \delta_{M_F,M'_F}.\end{aligned} \tag{64}$$

As expected, it is clear from Eq. (64) that different M_F quantum numbers are not mixed. After a short piece of algebra, we obtain the matrix elements with $F'=F$,

$$\langle wFM_F\Omega_F|H_Z|wFM_F\Omega_F\rangle_{\mu'=0} = B\mu_0 g_s \frac{M_F\Omega_F}{F(F+1)}\Sigma, \tag{65}$$

$$\begin{aligned}\langle wFM_F\Omega_F|H_Z|w'FM_F\Omega'_F\rangle_{\mu'=\pm 1} &= -B\mu_0 g_s \frac{M_F\sqrt{(F\pm\Omega_F)(F\mp\Omega_F+1)}}{2F(F+1)}\langle w|S'_{\pm 1}|w'\rangle \\ &\times \delta_{\Omega'_F,\Omega_F\mp 1},\end{aligned} \tag{66}$$

and for $F'=F+1$,

$$\langle wFM_F\Omega_F|H_Z|w(F+1)M_F\Omega_F\rangle_{\mu'=0} = -B\mu_0 g_s \sqrt{\frac{(F-\Omega_F+1)(F+\Omega_F+1)(F-M_F+1)(F+M_F+1)}{(F+1)^2(2F+1)(2F+3)}}\Sigma, \tag{67}$$

$$\langle wFM_F\Omega_F|H_Z|w'(F+1)M_F\Omega'_F\rangle_{\mu'=\pm 1} = \pm B\mu_0 g_s \sqrt{\frac{(F-M_F+1)(F+M_F+1)(F\mp\Omega_F+1)(F\mp\Omega_F+2)}{(2F+2)^2(2F+1)(2F+3)}}\langle w|S'_{\pm 1}|w'\rangle \delta_{\Omega'_F,\Omega_F\mp 1}, \tag{68}$$

finally for $F=F-1$,

$$\langle wFM_F\Omega_F|H_Z|w(F-1)M_F\Omega_F\rangle_{\mu'=0} = -B\mu_0 g_s\frac{\sqrt{F^2-M_F^2}}{F}\sqrt{\frac{F^2-\Omega_F^2}{(2F-1)(2F+1)}}\Sigma, \tag{69}$$

$$\begin{aligned}\langle wFM_F\Omega_F|H_Z|w'(F-1)M_F\Omega'_F\rangle_{\mu'=\pm1} &= \mp B\mu_0 g_s\frac{\sqrt{F^2-M_F^2}}{2F}\\ &\quad\times\sqrt{\frac{(F\pm\Omega_F-1)(F\pm\Omega_F)}{(2F-1)(2F+1)}}\langle w|S'_{\pm1}|w'\rangle\delta_{\Omega'_F,\Omega_F\mp1}.\end{aligned} \tag{70}$$

Deriving these matrix elements from Eq. (64), it is important to be aware that the total angular momentum **F** has components that obey anomalous commutation relations [33]. For completeness, we also give

$$\begin{aligned}\langle w|S'_{\pm1}|w'\rangle &= \langle qS\Sigma\Omega_{I_1}\Omega_{I_2}|S'_{\pm1}|q'S'\Sigma'\Omega'_{I_1}\Omega'_{I_2}\rangle\\ &= \sqrt{S(S+1)-\Sigma(\Sigma\mp1)}\\ &\quad\times\delta_{q,q'}\delta_{S,S'}\delta_{\Omega_{I_1},\Omega'_{I_1}}\delta_{\Omega_{I_2},\Omega'_{I_2}}\delta_{\Sigma',\Sigma\mp1}.\end{aligned} \tag{71}$$

D. Diatomic molecular rotational interaction in Hund's case (a) basis

The rotational energy operator is simply written $B(r)\mathbf{R}^2$ with $B(r)=\frac{\hbar^2}{2\mu r^2}$, where **R** is the orbital angular momentum of the relative motion of the nuclei A and B. However, the case (a) states are not eigenstates for this operator and the Hamiltonian is rewritten as

$$\begin{aligned}H_{\text{rot}} &= B(r)[\mathbf{F}-(\mathbf{L}+\mathbf{S}+\mathbf{I})]^2\\ &= B(r)(\mathbf{F}-\mathbf{F}_a)^2 = B(r)(\mathbf{F}^2-2\mathbf{F}\cdot\mathbf{F}_a+\mathbf{F}_a^2).\end{aligned} \tag{72}$$

H_{rot} is in general diagonal in the quantum numbers q,S,I_1,I_2,F,M_F but off diagonal in $\Omega(\Omega=\Sigma+\Lambda)$, Ω_{I_1}, and Ω_{I_2}.

To work out the diagonal contribution, it is convenient to define $\mathbf{J}_a\equiv\mathbf{L}+\mathbf{S}$. Consider

$$\begin{aligned}\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{F}_a^2|\Omega\Omega_{I_1}\Omega_{I_2}\rangle &= \langle\Omega\Omega_{I_1}\Omega_{I_2}|(\mathbf{J}_a+\mathbf{I}_1+\mathbf{I}_2)^2|\Omega\Omega_{I_1}\Omega_{I_2}\rangle\\ &= \langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{J}_a^2|\Omega\Omega_{I_1}\Omega_{I_2}\rangle + I_1(I_1+1)\\ &\quad + I_2(I_2+1) + 2\Omega_{I_1}\Omega_{I_2} + 2\Omega(\Omega_{I_1}\\ &\quad + \Omega_{I_2}).\end{aligned} \tag{73}$$

The remaining element in Eq. (73) can be worked out: $\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{J}_a^2|\Omega\Omega_{I_1}\Omega_{I_2}\rangle=\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{L}^2+2\mathbf{L}\cdot\mathbf{S}|\Omega\Omega_{I_1}\Omega_{I_2}\rangle+S(S+1)$. Effectively, this gives $S(S+1)$ when $L=0$. However, if $L\neq0$ the terms $\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{L}^2+2\mathbf{L}\cdot\mathbf{S}|\Omega\Omega_{I_1}\Omega_{I_2}\rangle$ can be included in H_{ev}. Hence, we obtain for the diagonal matrix element

$$\begin{aligned}\langle\Omega\Omega_{I_1}\Omega_{I_2}|H_{\text{rot}}|\Omega\Omega_{I_1}\Omega_{I_2}\rangle &= B(r)[F(F+1)-2(\Omega+\Omega_{I_1}+\Omega_{I_2})^2\\ &\quad + S(S+1)+I_1(I_1+1)+I_2(I_2+1)\\ &\quad + 2\Omega_{I_1}\Omega_{I_2}+2\Omega(\Omega_{I_1}+\Omega_{I_2})].\end{aligned} \tag{74}$$

Next we turn to the off-diagonal elements. Consider first the elements off diagonal in both Ω_{I_1} and Ω_{I_2}. The only relevant operator in this case is $2B(r)\mathbf{I}_1\cdot\mathbf{I}_2$ and the corresponding matrix element is

$$\begin{aligned}&2B(r)\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{I}_1\cdot\mathbf{I}_2|\Omega\Omega'_{I_1}\Omega'_{I_2}\rangle\\ &\quad = B(r)\sqrt{(I_1+\Omega_{I_1})(I_1-\Omega_{I_1}+1)(I_2+\Omega_{I_2}+1)(I_2-\Omega_{I_2})}\\ &\qquad\times\delta_{\Omega'_{I_1},\Omega_{I_1}-1}\delta_{\Omega'_{I_2},\Omega_{I_2}+1}+B(r)\\ &\qquad\times\sqrt{(I_1-\Omega_{I_1})(I_1+\Omega_{I_1}+1)(I_2+\Omega_{I_2})(I_2-\Omega_{I_2}+1)}\\ &\qquad\times\delta'_{\Omega_{I'_1},\Omega_{I_1}}\delta_{\Omega'_{I_2},\Omega_{I_2}-1}.\end{aligned} \tag{75}$$

The operator $-2B(r)\mathbf{F}_a\cdot\mathbf{F}$ will yield matrix elements off diagonal in $\Omega_{I_1}(\Omega_{I_2})$ but diagonal in both $\Omega_{I_2}(\Omega_{I_1})$ and Ω. Keeping in mind that **F** obeys anomalous commutation relations, we obtain

$$-2B(r)\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{F}_a\cdot\mathbf{F}|\Omega\Omega'_{I_1}\Omega_{I_2}\rangle = -B(r)\sqrt{(I_1\pm\Omega_{I_1}+1)(I_1\mp\Omega_{I_1})(F\pm\Omega_F+1)(F\mp\Omega_F)}\,\delta_{\Omega'_{I_1},\Omega_{I_1}\pm1}, \tag{76}$$

with a similar expression for the elements off diagonal in Ω_{I_2}.

In Eq. (72) we also have additional operators of the type $2B\mathbf{J}_a\cdot\mathbf{I}_j$ with $j=1,2$. The corresponding matrix elements are off diagonal in both Ω and Ω_{I_i},

$$\begin{aligned}&2B(r)\langle\Omega\Omega_{I_i}\Omega_{I_j}|\mathbf{J}_a\cdot\mathbf{I}_i|\Omega'\Omega'_{I_i}\Omega_{I_j}\rangle\\ &\quad = B(r)\langle\Omega|L_\pm+S_\pm|\Omega'\rangle\sqrt{(I_i\pm\Omega_{I_i}+1)(I_i\mp\Omega_{I_i})}\,\delta_{\Omega'_{I_i},\Omega_{I_i}\pm1},\end{aligned} \tag{77}$$

with $j=1,2$ and $j\neq i$. The matrix element in Eq. (77) is easily evaluated: $\langle\Omega|L_\pm+S_\pm|\Omega'\rangle=\sqrt{S(S+1)-\Sigma(\Sigma\mp1)}\,\delta_{\Sigma',\Sigma\mp1}$, when $L=0$ is assumed.

Finally, we give the matrix elements off diagonal in Ω but diagonal in both Ω_{I_1} and Ω_{I_2} coupled by the operator $\mathbf{J}_a\cdot\mathbf{F}$,

$$\begin{aligned}&-2B\langle\Omega\Omega_{I_1}\Omega_{I_2}|\mathbf{J}_a\cdot\mathbf{F}|\Omega'\Omega_{I_1}\Omega_{I_2}\rangle\\ &\quad = -B\sqrt{S(S+1)-\Sigma(\Sigma\mp1)}\\ &\qquad\times\sqrt{(F\mp\Omega_F+1)(F\pm\Omega_F)}\,\delta_{\Sigma',\Sigma\mp1}.\end{aligned} \tag{78}$$

All other matrix elements for the rotational Hamiltonian are zero.

E. Diatomic $^3\Sigma$ spin-spin interaction in Hund's case (a) basis

The electronic spin-spin Hamiltonian takes the form [34]

$$H_{\mathrm{ss}} = D\left(S_z^2 - \frac{1}{3}\mathbf{S}^2\right) + E(S_x^2 - S_y^2). \tag{79}$$

For $^3\Sigma$ states, $E=0$ and D is equal to twice the standard spin-splitting parameter $\lambda(r)$. *Ab initio* calculations of the spin-spin parameter $\lambda(r)$ seem to be nonstandard, an implementation of such a calculation is found in [35]. The spin-spin interaction is diagonal in the basis $|q\Lambda S\Sigma\rangle$, and the matrix element can be written as

$$\langle qS\Sigma|H_{\mathrm{ss}}|qS\Sigma\rangle = 2\lambda(r)\left[\Sigma^2 - \frac{1}{3}S(S+1)\right]. \tag{80}$$

If we omit the constant diagonal contribution equal to $-\frac{D}{3}S(S+1)$, the spin-spin matrix elements take the simple form,

$$\langle qS\Sigma|H_{\mathrm{ss}}|qS\Sigma\rangle = 2\lambda(r)\Sigma^2, \tag{81}$$

i.e., $\Sigma = \pm 1$ are degenerate and shifted up or down in energy relative to states with $\Sigma=0$, depending on the sign of $\lambda(r)$.

IV. COMPUTATIONAL DETAILS

To solve the coupled Eq. (5), we have implemented the log-derivative method of Johnson [18]. Our routine determines which basis states to include based on the input from the user. The basis should be chosen in such a way that the important interactions are well represented. The restrictions imposed by the Pauli principle are also important as nonexisting states would interact with the allowed states otherwise. Computationally, the Pauli principle is also convenient in the sense that it restricts the number of states included in the calculation and thereby the dimension of the matrices. The interactions are set up in the Hund's case (a) basis using the matrix elements worked out in the previous section. Interatomic potentials are necessary input along with values for the hyperfine parameters, which were handled in Sec. III B.

The various matrix elements in Eq. (5) must be evaluated at different values of r. However, the Zeeman interaction is independent of r and the Zeeman matrix elements are set up only once. Similarly, the matrix elements of the rotational operator (72) depend on r only through $B(r)$. This is in contrast with the hyperfine interaction which depends on r in a more complex manner; hence the matrix elements repeatedly need to be updated. The spin-spin interaction is diagonal and depends on r through $\lambda(r)$.

The integration of Eq. (5) extends from 2.75 to 300 a.u. Interpolation in the interatomic potentials, hyperfine interaction parameters, and the spin-spin parameter $\lambda(r)$ were performed with cubic splines. The reduced mass used for ^{6}Li is 5482.264721 a.u. calculated with the isotope mass obtained from [36].

The unitary transformation given in Sec. II A 3 is used to transform from Hund's case (a) basis to the FF-coupled basis. Finally, we perform another unitary transformation to a basis that diagonalizes both the hyperfine interaction and the Zeeman interaction terms. This final transformation defines the K matrix. From the output, we can extract the S matrix and the scattering lengths, in principle, for any partial wave l.

TABLE I. Comparison of the van der Waals coefficients C_6, C_8, C_{10}. All numbers in atomic units.

	Yan *et al.*[a]	Zemke and Stwalley[b]	Marinescu *et al.*[c]
C_6	1393.39(16)	1381 ± 8	1388
C_8	83425.8(4.2)	82616 ± 2288	83240
C_{10}	$73721(1) \times 10^2$	$(64250 \pm 5140) \times 10^2$	73650×10^2

[a] Reference [44].
[b] Reference [41].
[c] Reference [45].

V. SINGLET AND TRIPLET INTERACTION POTENTIAL CURVES

Reliable interaction potentials are very important in ultracold physics. Fortunately, the Li$_2$ interatomic potentials have been extensively studied experimentally and theoretically, both for the ground state $X\,^1\Sigma_g^+$ and for the lowest electronic triplet state $A\,^3\Sigma_u^+$.

For the $X\,^1\Sigma_g^+$ Li$_2$ interatomic potential, we use the *ab initio* potential calculated by Zavitsas [37] for distances between $3.4a_0$ and $12.0a_0$. We extend the data of Zavitsas [37] with three values from Barakat *et al.* [38] at $12.6a_0$, $13.4a_0$, and $14.5a_0$. In addition, we use two values from Konowalow and Olsen [39] at $2.75a_0$ and $3.00a_0$, and a value of Schmidt Mink *et al.* [40] at $3.25a_0$. The interatomic potential curve was smoothly joined with cubic splines to the long-range potential in Eq. (82).

For the $^3\Sigma_u^+$ state, we use the interatomic potential discussed by Zemke and Stwalley [41] for distances between $6.39a_0$ and $15.5a_0$. We have supplemented this potential with seven values (at $3.00a_0$, $3.50a_0$, $4.00a_0$, $4.50a_0$, $5.00a_0$, $5.50a_0$, and $6.00a_0$) from Konowalow *et al.* [42]. Cubic splines were used to join the short- and long-range potentials.

At large separations, both the singlet and triplet interaction potentials can be written as a sum of dispersion terms [43]

$$V(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^6} - \frac{C_{10}}{r^{10}}. \tag{82}$$

The dispersion coefficients (also called van der Waals coefficients) C_6, C_8, and C_{10} for Li$_2$ have been calculated by several authors. In Table I, we compare some of the most recent calculations which show rather good agreement. We have adopted the values obtained by Yan *et al.* for C_6, C_8, and C_{10}.

The adopted singlet and triplet interatomic potentials are shown in Fig. 1. The long-range potential was used for distances greater than $\simeq 16.5a_0$.

With the combined short- and long-range interatomic potentials described in this section, we obtained the elastic s-wave scattering lengths $a_s^T = -2090.94a_0$ and a_s^S

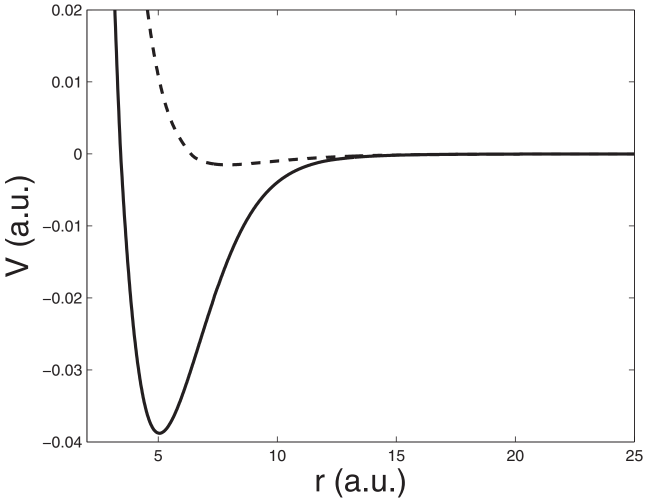

FIG. 1. Interatomic potential curves for the electronic states ${}^1\Sigma_g^+$ (solid line) and ${}^3\Sigma_u^+$ in Li$_2$.

$=45.558\,2a_0$ for the triplet (T) and singlet (S) potentials, respectively. The singlet elastic-scattering length is experimentally determined with rather high accuracy to be $a_s^S=45.151\,9(16)a_0$ [46], whereas the triplet scattering length is not that well known. Abraham *et al.* [47] reported the value $a_s^T=-2160\pm 250a_0$.

The different short- and long-range interatomic potentials available in the literature yield deviating results for the scattering lengths. Thus it seems hard to obtain *ab initio* scattering lengths with an accuracy comparable with the experimental values, without of course somehow fitting the combined (short and long range) potential to reproduce the experimental results. *Ab initio* scattering lengths are therefore very demanding to calculate. Without the experimental values available to guide the search for reliable interatomic potentials, a_s^S and, in particular, a_s^T would be reported with large uncertainties. One should also be aware that a completely inadequate interatomic potential can give excellent values for the scattering lengths; thus there are no one-to-one correspondence.

It has been reported previously that most s-wave Feshbach resonances observed in ^{6}Li are very sensitive to the singlet potential and rather insensitive to the triplet potential curve. An exception is the broad well-known Feshbach resonance at $B\simeq 837$ G (see next section), which is highly sensitive to both. Thus, the rather small difference between the *ab initio* calculated a_s^S compared to the experimental value may indicate that the calculated resonance positions are systematically shifted relative to the observed positions. We explore this further in the next section and we will see that this shift is roughly plus a few Gauss for all resonances.

VI. RESULTS

A. Calculation of s-wave scattering lengths and Feshbach resonances

In this section, we report s-wave scattering lengths and Feshbach resonances for two colliding ^{6}Li atoms. The s-wave scattering length is defined as

$$a_s=-\lim_{k\to 0}\frac{\tan\,\delta_0(k)}{k}, \tag{83}$$

where the phase shift δ_0 has been defined in Eq. (12). In alkali-metal diatomic molecules where $L_1=L_2=0$, the molecular mechanical rotation quantum number N corresponds to the partial-wave quantum number l. In the following, $N=l$ and we write N rather than l.

The ^{6}Li isotope has a nuclear spin $I_1=1$ and an electronic spin $S_1=1/2$ with a total angular momentum $\mathbf{F}_1=\mathbf{S}_1+\mathbf{I}_1\in\{\frac{1}{2},\frac{3}{2}\}$, i.e., two hyperfine levels for zero external magnetic field. The subscript 1 is used as a label to distinguish atom 1 from atom 2. Collisions can occur between atoms in the hyperfine levels $F_1=F_2=\frac{1}{2}$, $F_1=F_2=\frac{3}{2}$ and $F_i=\frac{1}{2}$, $F_j=\frac{3}{2}$, $\{i,j\}=1,2$ and $i\neq j$. Experimentally, most studied are collisions between atoms in the lowest-allowed energetic states $|F_1M_{F1}\rangle=|\frac{1}{2},\frac{1}{2}\rangle$ and $|F_2M_{F2}\rangle=|\frac{1}{2},-\frac{1}{2}\rangle$. Collisions between atoms in excited states may be inelastic and give spin relaxation. We have calculated s-wave scattering lengths for all possible collisions, including atoms in different hyperfine levels. The results are presented in Fig. 3 for magnetic field strengths up to 1500 G ($1\ \text{G}=10^{-4}$ T).

The states are identified by the quantum numbers N and M_F and in addition a label n to distinguish states with equal quantum numbers N and M_F. The new notation is motivated by the fact that the quantum numbers F_1,F_2,F_a and F are generally mixed in external magnetic fields. Table II lists all relevant states $|nNM_F\rangle$ and their correspondence with the low- or zero-field states $|F_1F_2FM_F\rangle$. Since $N=0$, the quantum number $F_a=F$ and is suppressed in the notation. The possible molecular levels corresponding to $N=0$ (no mechanical rotation, lowest rotational level) are shown schematically in Fig. 2.

From the discussion in Sec. II A, it is clear that the states $|F_1F_2FM_F\rangle$ can be written as linear combinations of states

TABLE II. Correspondence between the states $|n,N,M_F\rangle$ and the zero-field states $|F_1,F_2,F,M_F\rangle$. F_1,F_2 and F are good quantum numbers only at zero magnetic field.

$\lvert nNM_F\rangle$	$\lvert F_1F_2FM_F\rangle$	$\lvert nNM_F\rangle$	$\lvert F_1F_2FM_F\rangle$	$\lvert nNM_F\rangle$	$\lvert F_1F_2FM_F\rangle$
$\lvert 1,0,0\rangle$	$\lvert\frac{1}{2},\frac{1}{2},0,0\rangle$	$\lvert 1,0,-2\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,-2\rangle$	$\lvert 2,0,1\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,1\rangle$
$\lvert 2,0,0\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,0\rangle$	$\lvert 2,0,-2\rangle$	$\lvert\frac{3}{2},\frac{3}{2},2,-2\rangle$	$\lvert 3,0,1\rangle$	$\lvert\frac{3}{2},\frac{1}{2},1,1\rangle$
$\lvert 3,0,0\rangle$	$\lvert\frac{3}{2},\frac{1}{2},1,0\rangle$	$\lvert 1,0,2\rangle$	$\lvert\frac{3}{2},\frac{3}{2},2,2\rangle$	$\lvert 1,0,-1\rangle$	$\lvert\frac{3}{2},\frac{1}{2},1,-1\rangle$
$\lvert 4,0,0\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,0\rangle$	$\lvert 2,0,2\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,2\rangle$	$\lvert 2,0,-1\rangle$	$\lvert\frac{3}{2},\frac{1}{2},2,-1\rangle$
$\lvert 5,0,0\rangle$	$\lvert\frac{3}{2},\frac{3}{2},0,0\rangle$	$\lvert 1,0,1\rangle$	$\lvert\frac{3}{2},\frac{3}{2},2,1\rangle$	$\lvert 3,0,-1\rangle$	$\lvert\frac{3}{2},\frac{3}{2},2,-1\rangle$

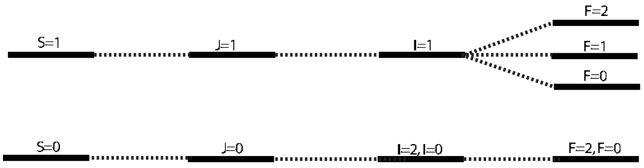

FIG. 2. Schematic diagram of the hyperfine energy levels in ^{6}Li$_2$ consistent with $N=0$. Quantum numbers at short range in accordance with Hund's case (b) are indicated. Missing levels are excluded by the Pauli exclusion principle (e.g., all $N=I=0$ levels).

$|\phi_n\rangle$ which are eigenstates for the total electronic spin operator $\mathbf{S}^2=(\mathbf{S}_1+\mathbf{S}_2)^2$ [e.g., Hund's case (a) or Hund's case (b) states]

$$|F_1F_2FM_F\rangle=\sum_n c_{mn}|\phi_n\rangle. \tag{84}$$

At zero field, none of the states $|nNM_F\rangle$ can be written as linear combinations of only singlet states $|\phi_n(S=0)\rangle$ as such states would have zero hyperfine energy as $r\rightarrow\infty$. However, pure triplet states $|nNM_F\rangle$ do exist. In fact, at zero magnetic field the states $|3,0,0\rangle$, $|3,0,1\rangle$, and $|2,0,-1\rangle$ have total electronic spin $S=1$, and corresponding s-wave scattering lengths equal to a_s^T. As the magnetic field is increased from zero, singlet states are introduced in the linear combinations (84), and the sensitive s-wave scattering length changes very rapidly. This particular behavior is not resolved in Fig. 3.

The states $|4,0,0\rangle$, $|1,0,2\rangle$, and $|1,0,1\rangle$ have s-wave scattering lengths that show a steep decrease when the magnetic field is increased. At zero magnetic field, the scattering lengths are moderate, but at higher magnetic field strengths they attain the triplet scattering length a_s^T. In fact, at $B\gtrsim 1000$ G these states are almost pure triplet states. To confirm, this we have plotted the sum of coefficients $\Sigma_n|c_{mn}(S=1)|^2$ vs magnetic field for the states $|4,0,0\rangle$, $|2,0,-1\rangle$, and $|2,0,2\rangle$ in Fig. 4. The states $|2,0,-1\rangle$ and $|2,0,2\rangle$ are also included for comparison and are seen to have rather different behaviors.

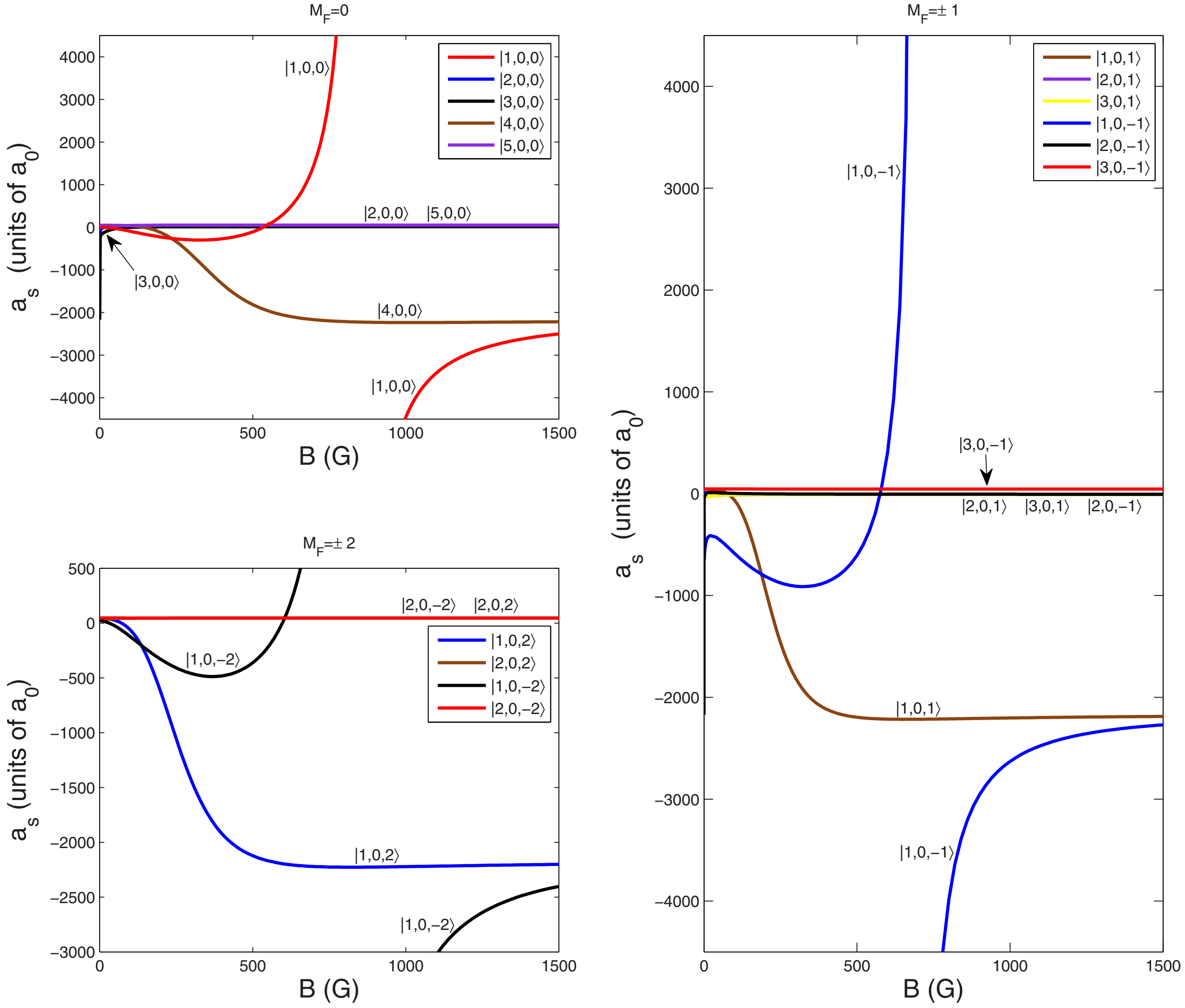

FIG. 3. (Color online) Scattering lengths (s wave) vs magnetic field B for all states with $N=0$. Upper left panel includes all states with $M_F=0$, lower left panel includes all states with $M_F\pm 2$, whereas the right panel includes all states with $M_F\pm 1$. Each of the three panels shows one well-resolved Feshbach resonance.

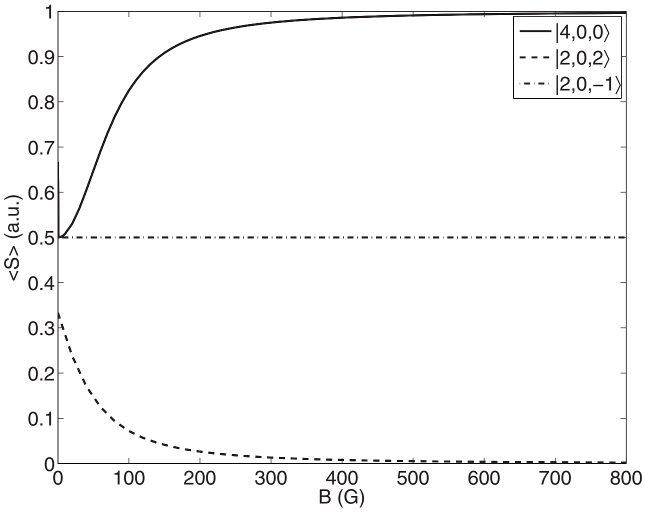

FIG. 4. $\langle S\rangle$ as a function of magnetic field for $|4,0,0\rangle$ and $|2,0,2\rangle$ (dotted line).

In general, the scattering length varies only weakly with the magnetic field, a property that is seen to hold for a majority of the states in Fig. 3. In fact, most states appear largely unaffected by the magnetic field, e.g., the states $|2,0,0\rangle$, $|2,0,2\rangle$, $|5,0,0\rangle$, $|3,0,-1\rangle$, $|2,0,1\rangle$, and $|2,0,-2\rangle$ all have moderate scattering lengths at all investigated magnetic field strengths. There are several reasons for this, some of which will be discussed later on.

The states $|3,0,1\rangle$ and $|2,0,-1\rangle$ share a particular property. Their energy eigenvalues are not affected by the increasing magnetic field strength. Both states are part of (different) three level systems of interacting states in which one of the eigenvalues retains a nearly constant value due to particular relations among the matrix elements for the hyperfine and Zeeman interactions. At large magnetic fields, both $|3,0,1\rangle$ and $|2,0,-1\rangle$ have scattering lengths of roughly $-6a_0$ and are found to be in a 50/50 superposition of singlet and triplet basis states (see also Fig. 4).

Further, the states $|2,0,-2\rangle$, $|2,0,2\rangle$, and $|2,0,0\rangle$ have energy eigenvalues that approach zero when the magnetic field strength increases. Hence, in larger magnetic fields these states are almost pure singlet states with a moderate scattering length a_s^S. Finally, $|3,0,-1\rangle$ shares much of the same behavior, although the energy is decreasing toward zero more slowly.

The most prominent features in Fig. 3 are the three clearly visible Feshbach resonances, among them the broad well-known $^6\mathrm{Li}_2$, $F_1=F_2=\frac{1}{2}$ resonance in $|1,0,0\rangle$. All Feshbach resonances reported in the present paper originate when the hyperfine energy levels of the colliding atoms are Zeeman shifted into resonance with the highest vibrational level ($v=38$) of the $X\,^1\Sigma_g^+$ electronic state (the molecular ground state). The precise resonance positions are shifted by the hyperfine interaction and depend upon the state in question and its interacting partners. We remark that states where $F_1=F_2=\frac{3}{2}$ (low-field quantum numbers) will not have Feshbach resonances as the corresponding energy eigenvalues are larger than zero even at the highest magnetic field strengths investigated. In the upper left panel of Fig. 3, we recognize the broad Feshbach resonance. In our calculation it is located at $B=837.13$ G, experimentally it is found at $B_0\in[822-834]$ G [46]. Part of this discrepancy might be caused by the *ab initio* singlet and triplet potential curves which do not reproduce the *precise* experimental scattering lengths. Similar discrepancies can be seen in the positions of all calculated Feshbach resonances. The $B\simeq 837$ G resonance is accessible through collisions of atoms in the states $|F_1M_{F_1}\rangle=|\frac{1}{2},\frac{1}{2}\rangle$ and $|F_2M_{F_2}\rangle=|\frac{1}{2},-\frac{1}{2}\rangle$. This is a very broad resonance which makes it well suited for experiments as it is easy to control the scattering length with high precision.

Two additional broad Feshbach resonances are visible in Fig. 3 (lower left and right panels). In the lower left panel, we report a Feshbach resonance experimentally less accessible as it occurs in $|1,0,-1\rangle$ which is a linear combination [see Eq. (13)] of the FF-coupled states $|\frac{3}{2},-\frac{3}{2},\frac{1}{2},\frac{1}{2}\rangle$ and $|\frac{3}{2},-\frac{1}{2},\frac{1}{2},-\frac{1}{2}\rangle$. The precise location of this Feshbach resonance is $B=692.89$ G in our calculation. Furthermore, we also find a Feshbach resonance in $|1,0,-2\rangle$ accessible through collisions of atomic pairs in the atomic states $(|F_i,M_{F_i}\rangle)|\frac{3}{2},-\frac{3}{2},\rangle$ and $|\frac{1}{2},-\frac{1}{2}\rangle$ (low-field quantum numbers), with a combined total angular-momentum projection $M_F=-2$. The resonance is clearly visible in Fig. 3 (lower left plot). A detailed calculation locates this resonance at $B=813.98$ G.

In addition to the three s-wave resonances at $B\simeq 690-840$ G discussed above, a narrow Feshbach resonance in the state $|1,0,0\rangle$ can be seen in Fig. 6 at the precise magnetic field strength $B=544.90$ G. Experimentally, the resonance is observed at 543.28 ± 0.08 G [46]. It has been reported that this particular resonance has a total nuclear spin $I=2$, whereas the broad $B\simeq 837$ G resonance has $I=0$ [46]. In contrast to $|1,0,0\rangle$, the states $|1,0,-1\rangle$ and $|1,0,-2\rangle$ do not have two Feshbach resonances as they do not interact with any $I=0$ states. However, at much larger field strengths the $v=37$ singlet vibrational level will become energetically accessible and make additional Feshbach resonances possible [48].

Figure 5 sums up the discussion of the s-wave scattering lengths as a function of magnetic field. States with corresponding energy eigenvalues that are easily tunable by magnetic fields will become pure triplet states in high magnetic fields with large and negative scattering lengths $\simeq a_s^T$. States with energy eigenvalues that are Zeeman shifted to lower energies may be tuned into resonance with the singlet $v=38$ vibrational level and give rise to Feshbach resonances. However, most states are only weakly influenced by the applied field, with moderate scattering lengths that show small dependencies on the magnetic field strength.

B. Calculation of the *p*-wave scattering volume

It is well known that s-wave collisions between two fermions in identical spin states are forbidden by the Pauli principle. However, p-wave collisions are possible although suppressed at ultracold temperatures as $\delta_p\propto E^{3/2}$, whereas $\delta_s\propto E^{1/2}$. Whenever s-wave scattering is not allowed, the p-wave scattering volume V_p replaces the usual s-wave scattering length as one of the important parameters. The p-wave scattering volume is defined as

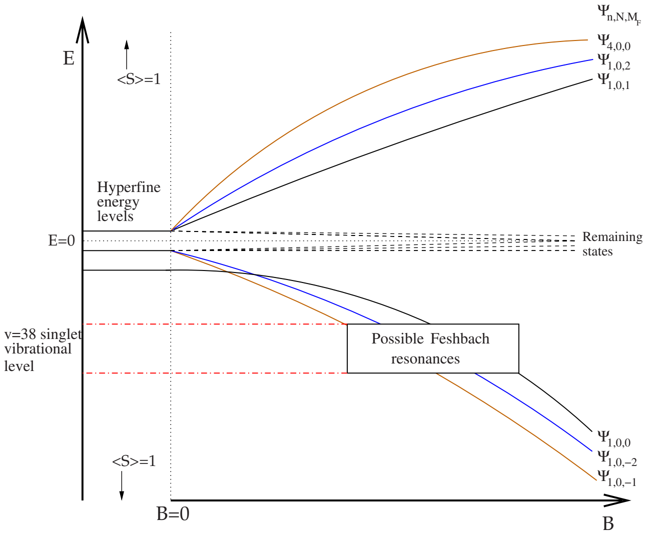

FIG. 5. (Color online) Schematic presentation of the Zeeman shift for different states as a function of the magnetic field strength. At zero field, there are only three hyperfine levels. At nonzero magnetic field, three states with different M_F quantum numbers are shifted sufficiently low in energy to enable Feshbach resonances. The energy differences are not correctly displayed in this figure.

$$V_p \equiv -\lim_{k\to 0}\frac{\tan\,\delta_p(k)}{k^3}, \tag{85}$$

and $a_p=\sqrt[3]{V_p}$ is sometimes referred to as the p-wave scattering length. δ_p is the p-wave phase shift and as usual k is the wave number. To avoid the cube root, we report V_p instead of a_p.

Knowledge of the p-wave scattering volume is in general of importance for experiments involving fermions. The p-wave scattering volume has also been discussed in relation with p-wave Cooper pairs [49] and p-wave scattering is an important mechanism in a three-body recombination of identical spin-polarized fermions [50].

We present calculations of the p-wave scattering volume as a function of magnetic field for selected spin states. We have focused on states where s-wave scattering is forbidden and restricted the calculations to states corresponding to the lowest atomic hyperfine level, that is, $F_1=F_2=\frac{1}{2}$. A sketch of molecular hyperfine levels corresponding to $N=1$ is presented in Fig. 7.

We have used the same singlet and triplet potentials as described in Sec. V. The corresponding singlet and triplet p-wave scattering volumes are $V_p^S=62\,298a_0^3$ and $V_p^T=-48\,252a_0^3$, respectively. This yields p-wave scattering lengths $a_p^S=39.6a_0$ and $a_p^T=-36.4a_0$. The a_p^T value should be compared to $-45a_0$ obtained in [51].

V_p as a function of B is shown in Fig. 8. Because of the Pauli principle, the total atomic spin $F_a=F_1+F_2=1$ for all zero-field states. The definition and correspondence between the states $|nNM_F\rangle$ and the zero-field states $|F_1F_2F_aFM_F\rangle$ are given in Table III.

Three different Feshbach resonances are visible in Fig. 8, at the magnetic fields $B_1=162.99$ G, $B_2=189.02$ G, and $B_3=218.72$ G. All states corresponding to the lowest hyperfine level $F_1=F_2=\frac{1}{2}$ at zero field show one of these resonances, which one depends on the detailed interaction, i.e., the response to the magnetic field.

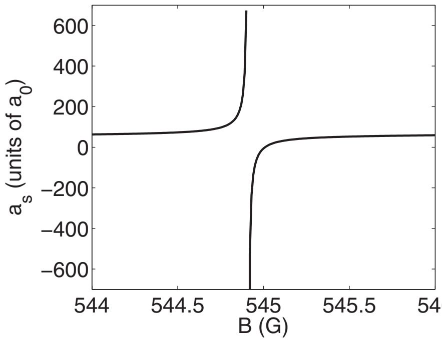

FIG. 6. Scattering length a_s vs magnetic field showing a narrow Feshbach resonance in the $|1,0,0\rangle$ state at $B=544.90$ G.

There are three different FF-coupled states $|F_1M_{F_1}F_2M_{F_2}\rangle$ corresponding to $F_1=F_2=\frac{1}{2}$. These are $|\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2}\rangle$, $|\frac{1}{2},\frac{1}{2}\frac{1}{2},-\frac{1}{2}\rangle$, and $|\frac{1}{2},-\frac{1}{2},\frac{1}{2},-\frac{1}{2}\rangle$. The magnetic field only interacts with the atomic spin; thus the corresponding energies should only depend on the quantum numbers F_1,M_{F_1},F_2,M_{F_2}. The energy eigenvalues corresponding to the states $|FM_F\rangle$ will therefore be degenerate with only three distinct values at all magnetic field strengths. Figure 9 show the energy of all states as a function of magnetic fields $B\in[0,100]$ G.

Collisions between atoms with $M_{F_1}=M_{F_2}=\frac{1}{2}$ enable a p-wave Feshbach resonances at B_1, whereas collisions between atoms in $M_{F_1}=M_{F_2}=-\frac{1}{2}$ enables a p-wave Feshbach resonance at B_3. Finally, there exists a p-wave Feshbach resonance at B_2 from collisions between atoms in $M_{F_1}=\frac{1}{2}$, $M_{F_2}=-\frac{1}{2}$. The different magnetic field strengths where the resonances occur reflect the different Zeeman shifts experienced in the various states, i.e., states that resonate at B_1 have eigenvalues that are most easily perturbed to lower values by an external magnetic field. The resonances reported here have all been experimentally observed in [46] at the magnetic field strengths $B_{1e}=159.14$ G, $B_{2e}=185.09$ G, and $B_{3e}=214.94$ G. As previously emphasized, the calculated values are a result of an *ab inito* calculation and the small

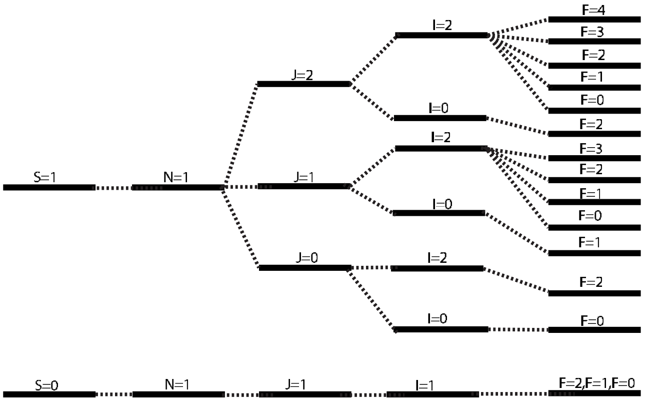

FIG. 7. Schematic diagram of the hyperfine structure in the $N=1$ rotational level of $^6Li_2$. The Pauli exclusion principle has been taken into account.

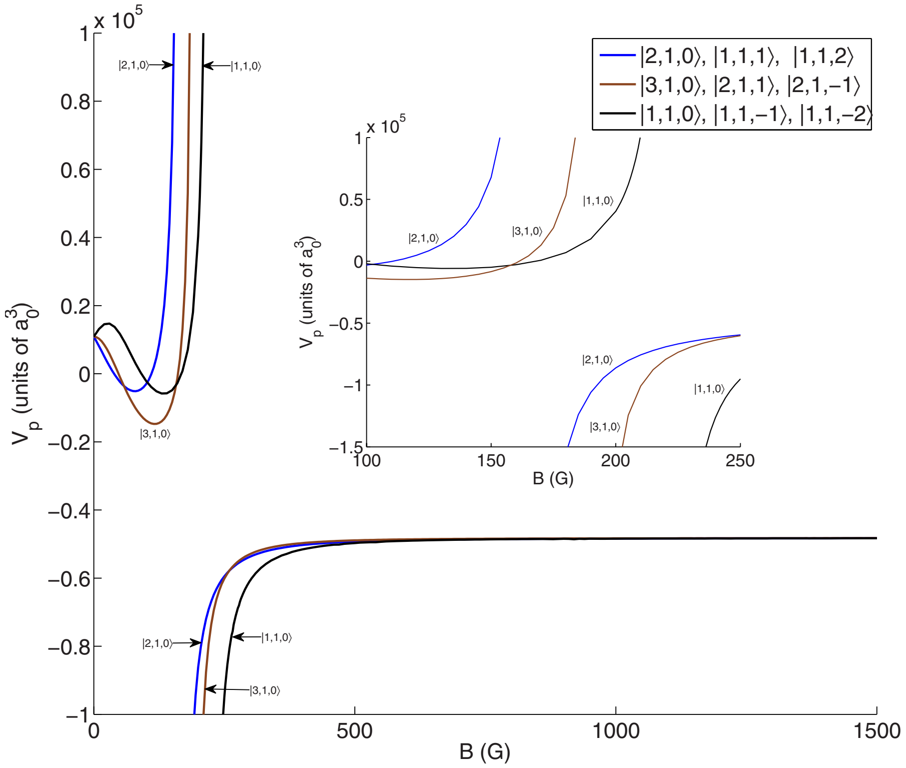

FIG. 8. (Color online) p-wave scattering volume as a function of magnetic field strength for all channels with $F_1=F_2=1/2$.

deviation in the resonance positions can be contributed to small errors in the singlet potential. All the p-wave resonances are found to be insensitive to the triplet potential.

Note that the relative positions of the calculated and experimentally observed resonances are in almost perfect agreement: $B_2-B_1=26.03$ G in the present *ab initio* calculation whereas the experimental value is 25.95 G. Correspondingly, $B_3-B_2=29.70$ G *ab initio* and $B_3-B_2=29.85$ G experimentally.

Whereas the s-wave resonances had a total nuclear spin of $I=0$ or $I=2$, the relevant nuclear spin for p-wave resonances is $I=1$. In analogy with the s-wave scattering lengths, the value of the p-wave scattering volume approaches the triplet value V_p^T at high magnetic field strengths. The total electronic spin together with the total nuclear spin are both approximately good quantum numbers at high magnetic field strengths with the values 1 and 2, respectively.

The p-wave scattering volume as a function of magnetic field strength for states with $F_1=F_2=3/2$ (zero field) has a behavior which resembles that of the s-wave scattering length. Many states have p-wave scattering volumes that are approximately constant, whereas a few attains the triplet p-wave scattering volume in stronger fields.

TABLE III. Correspondence between the states $|nNM_F\rangle$ and the zero-field states $|F_1F_2F_a lFM_F\rangle$. F_1,F_2,F_a and F are good quantum numbers only at zero magnetic field. At zero field $F_1=F_2=\frac{1}{2}$, $F_a=1$, and $N=1$ for all states.

$\lvert nNM_F\rangle$	$\lvert FM_F\rangle$	$\lvert nNM_F\rangle$	$\lvert FM_F\rangle$	$\lvert nNM_F\rangle$	$\lvert FM_F\rangle$
$\lvert 1,1,0\rangle$	$\lvert 0,0\rangle$	$\lvert 1,1,1\rangle$	$\lvert 1,1\rangle$	$\lvert 2,1,-1\rangle$	$\lvert 2,-1\rangle$
$\lvert 2,1,0\rangle$	$\lvert 1,0\rangle$	$\lvert 2,1,1\rangle$	$\lvert 2,1\rangle$	$\lvert 1,1,2\rangle$	$\lvert 2,2\rangle$
$\lvert 3,1,0\rangle$	$\lvert 2,0\rangle$	$\lvert 1,1,-1\rangle$	$\lvert 1,-1\rangle$	$\lvert 1,1,-2\rangle$	$\lvert 2,-2\rangle$

C. Short-range hyperfine- and spin-spin interaction

1. Hyperfine interaction

The convenient representation of the hyperfine interaction in the Hund's case (a) basis easily allows for experimentation with the short-range ($r<20$ a.u.) interaction. At $r>20$ a.u. the hyperfine interaction is well described by the simpler atomic hyperfine Hamiltonian

$$H_{\text{hf}}=b_f(\mathbf{S}_1\cdot\mathbf{I}_1+\mathbf{S}_2\cdot\mathbf{I}_2), \tag{86}$$

but this is not the case for $r<20$ a.u. as the electronic spin of atom 2 will start to couple to the nuclear spin of atom 1 and vice versa. In Sec. III A, it has been described how the hyperfine interaction is determined for all r by the four molecular parameters $b_f(r)$, $b_f'(r)$, $c(r)$, and $c'(r)$. These hyperfine parameters were calculated as described in Sec. III B and are plotted in Fig. 10. For reference, the atomic values are indicated with dotted lines. We see from Fig. 10 that the calculated hyperfine parameters are rather similar to the atomic hyperfine parameters. As expected the difference is completely negligible for $r>20$ a.u., whereas there are only minor differences for 20 a.u.$>r>9$ a.u.; in fact the only difference is the b_f' parameter that slowly decreases, coupling the singlet and triplet states. For $r<9$ a.u., the molecular hyperfine parameters are rather different from the atomic values, hence the molecular hyperfine interactions deviates from the atomic interaction.

In scattering calculations, it is often assumed that the molecular hyperfine interaction at short range is equal to the atomic hyperfine interaction. It can be argued from Fig. 10 that one can safely use the atomic hyperfine interaction also at small distances for the present and similar systems without introducing significant errors, as the hyperfine parameters are

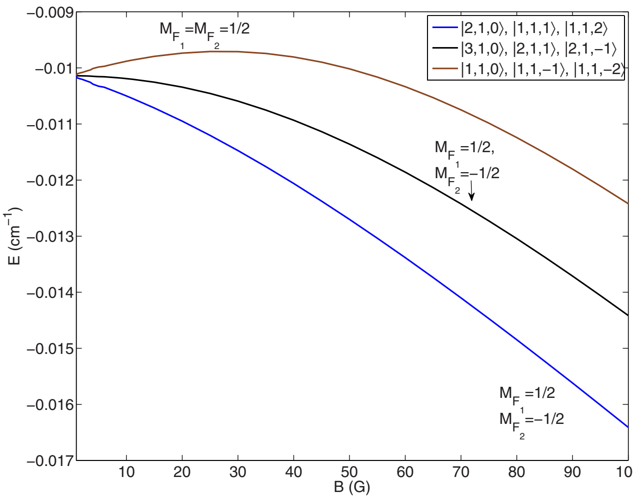

FIG. 9. (Color online) Energy vs magnetic field for states corresponding to the lowest hyperfine level.

only slowly varying. On the other hand, the molecular hyperfine parameters show significant deviations from the atomic values for small r.

We have tested the effect of the short-range molecular interaction by repeating some of the s-wave scattering calculations. The results obtained using the atomic hyperfine interaction have been compared with the results from a calculation including the complete r-dependent molecular hyperfine interaction. To investigate this effect, we have looked at the broad Feshbach resonance located at $B \simeq 837$ G and calculated how much the resonance position is shifted upon changes in the short-range hyperfine interaction. As expected the resonance position is rather insensitive to the detailed short-range molecular hyperfine interaction. The shift is only +0.02 G when we replace the molecular interaction with the asymptotic atomic interaction. The much more narrow resonance at $B \simeq 545$ G is even less affected. Thus, we are led to conclude that the scattering length is quite insensitive to small changes in the hyperfine energy in the region of small r.

The strength of the short-range hyperfine interaction has been varied and the effect calculated. The hyperfine parameters were varied by multiplying the functions $b_f(r)$, $c(r)$, $b_f'(r)$, and $c'(r)$ with a factor m to yield a stronger or weaker short-range hyperfine interaction. The atomic hyperfine interaction valid at $r > 20$ was left unchanged. Again we used the Feshbach resonance at $B \simeq 837$ G to test the reaction. The results are presented in Fig. 11, which shows that the short-range hyperfine interaction needs a substantial increase to shift the resonance positions in a significant way. Finally, we also investigated the position of a p-wave Feshbach resonance and found the same insensitivity to changes in the short-range molecular hyperfine interaction.

It seems reasonable to expect that systems with similar electronic structures (i.e., other alkali molecules) have hyperfine interactions that are well described by the atomic interaction. This conclusion is valid with respect to cold collisions where the results are rather insensitive to small changes in the short-range potential. Diatomic molecules with several open-shell electrons that couple to the nuclear spin may have a much stronger short-range hyperfine interaction. Figure 11 shows that in such cases, the above conclusion does not hold and the short-range molecular hyperfine interaction becomes important also in cold collisions.

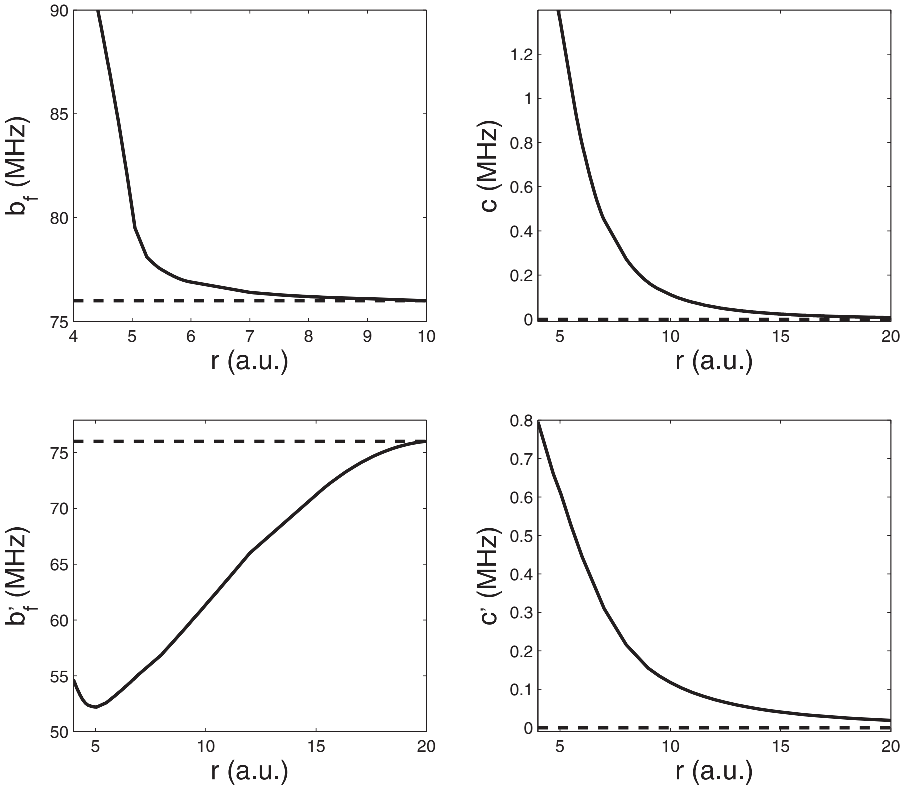

FIG. 10. Hyperfine parameters b_f, c, c' and b_f' as a function of r. See Sec. III B for a definition of the hyperfine parameters. Dotted lines show atomic hyperfine values included for comparison.

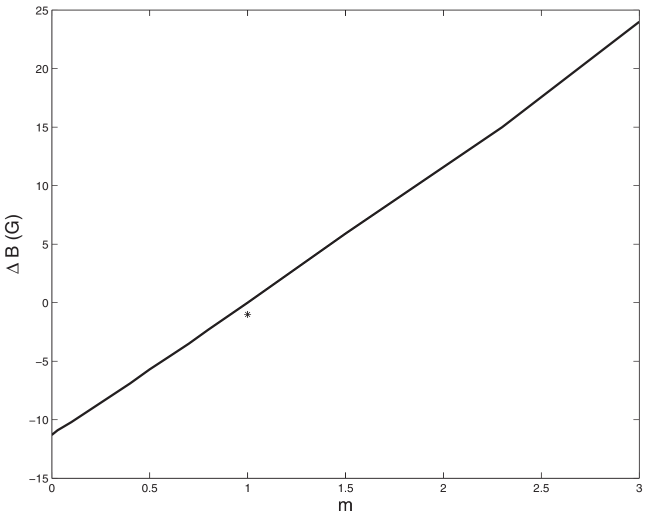

FIG. 11. Shift in resonance position vs strength of short-range hyperfine interaction. The hyperfine parameters are multiplied with a dimensionless factor m to yield a stronger or weaker interaction keeping their original functional form. A stronger short-range hyperfine interaction changes the resonance position by tens of Gauss, whereas the integration in ^{6}Li$_2$ is too weak relative to the atomic values. The star (*) indicates resonance shift position using only the atomic hyperfine interaction for all r.

2. Spin-spin interaction

The spin-spin interaction was treated in Sec. III E. The spin-spin parameter $\lambda(r)$ has been calculated *ab initio* in [52] for selected values of r between 3.77 and 18.9 a.u. In Li$_2$ the spin-spin parameter $\lambda(r)$ is very small, on the order of $-0.01\ \text{cm}^{-1}$. We have, however, included the spin-spin interaction in the present calculations and investigated its effect on the various Feshbach resonances.

As might be expected, Feshbach resonances that are sensitive to the triplet interatomic potential are also very sensitive to the spin-spin interaction. For ^{6}Li$_2$, this means that the Feshbach resonances at $B \simeq 837$, 814, and 693 G are sensitive to the spin-spin interaction, whereas the other ones are not.

To enable a more quantitative conclusion regarding the effect of the spin-spin interaction, the calculations were repeated for a series of different choices of $\lambda(r)$. In these repeated calculations, the function $\lambda(r)$ from [52] was multiplied by a factor m, with m ranging from −5 to 5. The results are presented in Fig. 12, which shows the results for three representative Feshbach resonances.

The three different Feshbach resonances investigated in Fig. 12 are representable for all the Feshbach resonances calculated. The three broad s-wave resonances behave similar to the 850 G resonance, whereas the p-wave resonances behave similarly to the p-wave resonance in 12. We have let the spin-spin parameter $\lambda(r)$ go to zero at $r \simeq 21$ a.u. as a natural continuation of the function $D(r) = 2\lambda(r)$ plotted in Fig. 3 in [52].

We conclude that Feshbach resonances in states sensitive to the triplet potential are affected by the spin-spin interaction. For these states, the spin-spin interaction is important (see also Fig. 12). Feshbach resonances in states insensitive to the triplet potential are also insensitive to the spin-spin interaction as $S \simeq 0$ with $\Sigma = 0$ in such states.

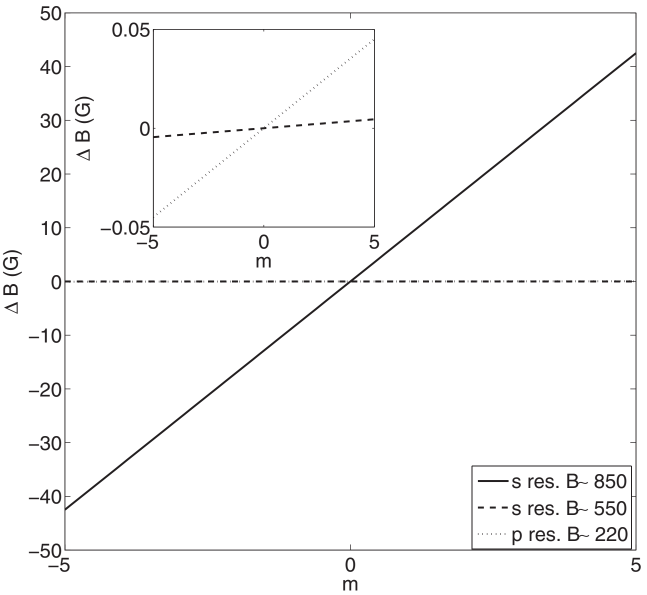

FIG. 12. Shift in resonance positions as a function of the spin-spin interaction strength for three different Feshbach resonances. The dimensionless factor m is multiplied with the spin-spin parameter $\lambda(r)$ to control the spin-spin interaction strength.

VII. SUMMARY

We have used rather accurate *ab initio* potentials available for ^{6}Li$_2$ and solved the coupled equations to obtain s- and p-waves scattering lengths for magnetic field strengths up to 1500 G. Hund's case (a) basis states were used to work out the molecular matrix elements required for the hyperfine, Zeeman, and rotational operators. Basis states which are in accordance with the Pauli principle upon the interchange of identical nuclei were constructed and used. Emphasis was put on including and working with the molecular hyperfine interaction in the short-range regime. However, it was found that the results of the scattering calculations were rather insensitive to the short-range hyperfine structure.

Several Feshbach resonances of both s and p types were found. The Feshbach resonance positions determined *ab initio* deviated with plus 2–4 G from the experimentally measured positions available for comparison. By inspection, the deviations are found to be well represented by a constant shift. Using the p-wave resonance at $B = 218.72$ G as a reference, one obtains $B_{\text{shift}} = B_{ab\ initio} - B_{\text{exp}} = 3.78$ G. Subtracting B_{shift} from the calculated Feshbach resonance positions yields corrected positions $B_{\text{corrected}}$ which are in very good agreement with the experimental values. Table IV summarizes the discussion above. The constant shift is determined from a reference state which is sensitive to the singlet potential curve but insensitive to the triplet potential curve. Hence, B_{shift} can be seen as a correction to the singlet potential. The broad s-wave resonances at $B = 837$, 814, and 693 G are in addition sensitive to the triplet potential, but there is no ob-

TABLE IV. Summary of calculated Feshbach resonances compared with experimentally observed ones. $\Delta B = B_{ab\ initio} - B_{\mathrm{exp}}$. See the text for a definition of $B_{\mathrm{corrected}}$ and a further discussion of this quantity. The star (*) indicates that there is no one-to-one correspondence between the state $|nNM_F\rangle$ and a unique free-atom state $|F_1 M_{F_1} F_2 M_{F_2}\rangle$.

State $\lvert nNM_F\rangle$	$\lvert F_1 M_{F_1}\rangle\lvert F_2 M_{F_2}\rangle$	$B_{ab\ initio}$ (G)	B_{exp} (G)	ΔB (G)	$B_{\mathrm{corrected}}$ (G)
$\lvert 1,0,0\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle\lvert\frac{1}{2},-\frac{1}{2}\rangle$	837.13	822–834	3.70–15.1	833.35
$\lvert 1,0,0\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle\lvert\frac{1}{2},-\frac{1}{2}\rangle$	544.90	543.28 ± 0.08	1.62 ± 0.08	541.12
$\lvert 1,0,-1\rangle$	$*$	692.89			689.11
$\lvert 1,0,-2\rangle$	$\lvert\frac{3}{2},-\frac{3}{2}\rangle\lvert\frac{1}{2},-\frac{1}{2}\rangle$	813.98			810.20
$\lvert 1,1,0\rangle,\lvert 1,1,-1\rangle,\lvert 1,1,-2\rangle$	$\lvert\frac{1}{2},-\frac{1}{2}\rangle\lvert\frac{1}{2},-\frac{1}{2}\rangle$	218.72	214.94 ± 0.08	3.78 ± 0.08	214.94
$\lvert 2,1,0\rangle,\lvert 1,1,1\rangle,\lvert 1,1,2\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle\lvert\frac{1}{2},\frac{1}{2}\rangle$	162.99	159.14 ± 0.14	3.85 ± 0.14	159.21
$\lvert 3,1,0\rangle,\lvert 2,1,1\rangle,\lvert 2,1,-1\rangle$	$\lvert\frac{1}{2},\frac{1}{2}\rangle\lvert\frac{1}{2},-\frac{1}{2}\rangle$	189.02	185.09 ± 0.08	3.93 ± 0.08	185.24

vious way to obtain an additional correction for the triplet state that would affect only those particular resonances.

APPENDIX: TRANSFORMATION BETWEEN *FF*-COUPLED STATES AND MOLECULAR HUND'S CASE (A) STATES

We start with the *FF*-coupled states $|qS_1 M_{S_1} S_2 M_{S_2}\rangle$ and specialize to alkali atoms where $L_1 = L_2 = 0$. For this reason, L_1 and L_2 are suppressed in the notation. The *FF*-coupled states $|qS_1 M_{S_1} S_2 M_{S_2}\rangle$ have both a spatial part with collective quantum number q and an electronic spin part. To obtain the connection with the Hund's case (a) states, we form the total electronic spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$,

$$|qSM_S\rangle = \sum_{M_{S_1},M_{S_2}} \langle S_1 M_{S_1} S_2 M_{S_2} | SM_S\rangle |qS_1 M_{S_1} S_2 M_{S_2}\rangle. \tag{A1}$$

The states $|qSM_S\rangle$ are assumed to be eigenstates of the operators I_t, I_e and I_n (see Sec. II B). It follows from Eq. (A1) that the states $|qS_1 M_{S_1} S_2 M_{S_2}\rangle$ can be written as

$$|qS_1 M_{S_1} S_2 M_{S_2}\rangle = \sum_{SM_S} \langle S_1 M_{S_1} S_2 M_{S_2} | SM_S\rangle |qSM_S\rangle, \tag{A2}$$

thus they are in general not eigenstates for the symmetry operators I_e and I_n. At this point, it is appropriate to make a comment regarding the situation when $L_i \neq 0$. In such cases, the expression (A1) would still be valid although the replacement $|qSM_S\rangle \rightarrow |qL_1 L_2 M_{L_1} M_{L_2} S\Sigma\rangle$ is needed. To form the states $|q\Lambda SM_S\rangle$, we would then write

$$|q\Lambda SM_S\rangle = \sum_{M_{L_1}+M_{L_2}=\Lambda} C_{M_{L_1},M_{L_2}} |L_1 L_2 M_{L_1} M_{L_2} SM_S\rangle, \tag{A3}$$

where the coefficients $C_{M_{L_1},M_{L_2}}$ are determined by the interaction between the atoms. In Eqs. (A1) and (A3) the quantum number M_S refers to the space-fixed axis. The relation between space-fixed and molecule-fixed states is

$$|qSM_S\rangle = \sum_{\Sigma} \mathcal{D}^{S}_{M_S,\Sigma}(\phi,\theta,0)^* |qS\Sigma\rangle, \tag{A4}$$

where $\mathcal{D}$ is the rotation matrix [28]. We also need the diatomic rotational wave function [53],

$$\Psi_{NM_N\Lambda}(\phi,\theta) = \left(\frac{2N+1}{4\pi}\right)^{1/2} \mathcal{D}^{N}_{M_N,\Lambda}(\phi,\theta,0)^*. \tag{A5}$$

N is the total molecular angular momentum excluding electronic and nuclear spin. When $L_i = 0$, N represents only the mechanical rotation. In addition, whenever $\Lambda = 0$, the rotational wave function simplifies to the spherical harmonics $\Psi_{NM_N 0}(\phi,\theta) = Y_{N,M_N}(\theta,\phi)$.

Multiplying the states $|qSM_S\rangle$ and $|NM_N\Lambda\rangle$, using Eq. (A5) for the rotational wave function and contracting the two $\mathcal{D}$ matrices gives

$$\begin{aligned}
\Psi_{qSM_SNM_N\Lambda} &= \left(\frac{2N+1}{4\pi}\right)^{1/2} \sum_{\Sigma} \mathcal{D}^{S}_{M_S,\Sigma}(\phi,\theta,0)^* \mathcal{D}^{N}_{M_N,\Lambda}(\phi,\theta,0)^* \psi_{qS\Sigma}, \\
&= \left(\frac{2N+1}{4\pi}\right)^{1/2} \sum_{\Sigma,J} (2J+1) \begin{pmatrix} S & N & J \\ M_S & M_N & -M_J \end{pmatrix} \begin{pmatrix} S & N & J \\ \Sigma & \Lambda & -\Omega \end{pmatrix} \mathcal{D}^{J}_{-M_J,-\Omega}(\phi,\theta,0) \psi_{qS\Sigma}, \\
&= \left(\frac{2N+1}{4\pi}\right)^{1/2} (-1)^{\Omega-M_J} \sum_{\Sigma,J} (2J+1) \begin{pmatrix} S & N & J \\ M_S & M_N & -M_J \end{pmatrix} \begin{pmatrix} S & N & J \\ \Sigma & \Lambda & -\Omega \end{pmatrix} \mathcal{D}^{J}_{M_J,\Omega}(\phi,\theta,0)^* \psi_{qS\Sigma}.
\end{aligned} \tag{A6}$$

At this point, we introduce the nuclear-spin states $|I_1M_{I_1}\rangle\,|I_2M_{I_2}\rangle$ and rotate them into the molecule-fixed coordinate system. The projections M_{I_1} and M_{I_2} are defined on the space-fixed axis. We have the relations

$$|I_iM_{I_i}\rangle=\sum_{\Omega_{I_i}}\mathcal{D}^{I_i}_{M_{I_i},\Omega_{I_i}}(\phi,\theta,0)^*|I_i\Omega_{I_i}\rangle, \tag{A7}$$

for $i=1,2$. Contracting the matrices $\mathcal{D}^{I_1}_{M_{I_1},\Omega_{I_1}}(\phi,\theta,0)^*\mathcal{D}^{I_2}_{M_{I_2},\Omega_{I_2}}(\phi,\theta,0)^*$ ($\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2$), and using $\mathcal{D}^{I}_{-M_I,\Omega_I}(\phi,\theta,0)=(-1)^{\Omega_I-M_I}\mathcal{D}^{I}_{M_I,\Omega_I}(\phi,\theta,0)^*$, we may write

$$\Psi_{qNM_N\Lambda S\Sigma I_1M_{I_1}I_2M_{I_2}}=\left(\frac{2N+1}{4\pi}\right)^{1/2}\sum_{\substack{\Sigma,J,I,\\ \Omega_{I_1},\Omega_{I_2}}}(-1)^{\Omega-M_J+\Omega_I-M_I}(2J+1)(2I+1)\begin{pmatrix} S & N & J\\ M_S & M_N & -M_J\end{pmatrix}\begin{pmatrix} S & N & J\\ \Sigma & \Lambda & -\Omega\end{pmatrix}\begin{pmatrix} I_1 & I_2 & I\\ M_{I_1} & M_{I_2} & -M_I\end{pmatrix}$$
$$\times\begin{pmatrix} I_1 & I_2 & I\\ \Omega_{I_1} & \Omega_{I_2} & -\Omega_I\end{pmatrix}\mathcal{D}^{I}_{M_I,\Omega_I}(\phi,\theta,0)^*\mathcal{D}^{J}_{M_J,\Omega}(\phi,\theta,0)^*\psi_{qS\Sigma I_1\Omega_{I_1}I_2\Omega_{I_2}}, \tag{A8}$$

or if we define $\mathbf{F}=\mathbf{J}+\mathbf{I}$ together with the total angular-momentum function [53]

$$\Psi_{FM_F\Omega_F}(\phi,\theta)=\left(\frac{2F+1}{4\pi}\right)^{1/2}\mathcal{D}^{F}_{M_F,\Omega_F}(\phi,\theta,0)^*, \tag{A9}$$

this can be written as

$$|qSM_S\rangle|NM_N\Lambda\rangle|I_1M_{I_1}\rangle|I_2M_{I_2}\rangle=\sqrt{(2N+1)}\sum_{\substack{\Sigma,J,I,F\\ \Omega_{I_1},\Omega_{I_2}}}(-1)^{\Omega+\Omega_I+\Omega_F-M_J-M_I-M_F}(2J+1)(2I+1)\sqrt{2F+1}\begin{pmatrix} S & N & J\\ M_S & M_N & -M_J\end{pmatrix}$$
$$\times\begin{pmatrix} S & N & J\\ \Sigma & \Lambda & -\Omega\end{pmatrix}\begin{pmatrix} I_1 & I_2 & I\\ M_{I_1} & M_{I_2} & -M_I\end{pmatrix}\begin{pmatrix} I_1 & I_2 & I\\ \Omega_{I_1} & \Omega_{I_2} & -\Omega_I\end{pmatrix}\begin{pmatrix} J & I & F\\ M_J & M_I & -M_F\end{pmatrix}\begin{pmatrix} J & I & F\\ \Omega & \Omega_I & -\Omega_F\end{pmatrix}$$
$$\times|qS\Sigma\rangle|I_1\Omega_{I_1}\rangle|I_2\Omega_{I_2}\rangle|FM_F\Omega_F\rangle. \tag{A10}$$

To establish Eq. (A10), we have contracted $\mathcal{D}^{J}_{M_J,\Omega_J}(\phi,\theta,0)^*$ and $\mathcal{D}^{I}_{M_I,\Omega_I}(\phi,\theta,0)^*$.

The *FF*-coupled basis states $|qF_1F_2F_alFM_F\rangle$ are easily written in terms of the states $|qS_1M_{S_1}S_2M_{S_2}\rangle$ together with the nuclear-spin states $|I_1M_{I_1}\rangle\,|I_2M_{I_2}\rangle$, and after a piece of algebra one obtains the transformation to the $|qSM_S\rangle|NM_N\rangle|I_1M_{I_1}\rangle|I_2M_{I_2}\rangle$ basis,

$$|qF_1F_2F_alFM_F\rangle=\sum_{\substack{M_{F_a},m_l,\\ M_{F_1},M_{F_2}}}\sum_{\substack{M_{S_1},M_{S_2}\\ M_{I_1},M_{I_2}}}\sum_{S,M_S}(-1)^{F_a-l+M_F+F_1-F_2+M_{F_a}+S_1-I_1+M_{F_1}+S_2-I_2+M_{F_2}+S_1-S_2+M_S}$$
$$\times\sqrt{(2F+1)(2F_a+1)(2F_1+1)(2F_2+1)(2S+1)}\begin{pmatrix} l & F_a & F\\ m_l & M_{F_a} & -M_F\end{pmatrix}\begin{pmatrix} F_1 & F_2 & F_a\\ M_{F_1} & M_{F_2} & -M_{F_a}\end{pmatrix}$$
$$\times\begin{pmatrix} S_1 & I_1 & F_1\\ M_{S_1} & M_{I_1} & -M_{F_1}\end{pmatrix}\begin{pmatrix} S_2 & I_2 & F_2\\ M_{S_2} & M_{I_2} & -M_{F_2}\end{pmatrix}\begin{pmatrix} S_1 & S_2 & S\\ M_{S_1} & M_{S_2} & -M_S\end{pmatrix}|qSM_S\rangle|NM_N\Lambda\rangle|I_1M_{I_1}\rangle|I_2M_{I_2}\rangle, \tag{A11}$$

an expression which is lengthy, but rather easy to derive. Combining Eqs. (A10) and (A11) yields the relevant transformation matrix elements $\langle qS\Sigma\Omega_{I_1}\Omega_{I_2}FM_F\Omega_F|qF_1F_2F_alFM_F\rangle$ reported in Eq. (16).

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