Long-Range Interactions of Hydrogen Atoms in Excited States. II. Hyperfine-Resolved 2S-2S Systems

Ulrich D. Jentschura  
*Missouri University of Science and Technology, ulj@mst.edu*

Vincent Debierre

Chandra Mani Adhikari

Arthur N. Matveev

*et. al. For a complete list of authors, see [https://scholarsmine.mst.edu/phys_facwork/849](https://scholarsmine.mst.edu/phys_facwork/849)*

Follow this and additional works at: [https://scholarsmine.mst.edu/phys_facwork](https://scholarsmine.mst.edu/phys_facwork)

Part of the Physics Commons

**Recommended Citation**

U. D. Jentschura et al., "Long-Range Interactions of Hydrogen Atoms in Excited States. II. Hyperfine-Resolved 2S-2S Systems," *Physical Review A - Atomic, Molecular, and Optical Physics*, vol. 95, no. 2, pp. 022704-1-022704-16, American Physical Society (APS), Feb 2017.

The definitive version is available at [https://doi.org/10.1103/PhysRevA.95.022704](https://doi.org/10.1103/PhysRevA.95.022704)

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.
Long-range interactions of hydrogen atoms in excited states. II. Hyperfine-resolved 2S-2S systems

U. D. Jentschura,1 V. Debierre,1 C. M. Adhikari,1 A. Matveev,2,3 and N. Kolachevsky2,3,4

1Department of Physics, Missouri University of Science and Technology, Rolla, Missouri 65409-0640, USA
2P. N. Lebedev Physics Institute, Leninsky Prospekt 53, Moscow 119991, Russia
3Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching, Germany
4Russian Quantum Center, Business-center “Ural,” 100A Novaya Street, Skolkovo, Moscow 143025, Russia

The interaction of two excited hydrogen atoms in metastable states constitutes a theoretically interesting problem because of the quasidegenerate \(2P_{3/2}\) levels that are removed from the 2S states by the Lamb shift. The total Hamiltonian of the system is composed of the van der Waals Hamiltonian, the Lamb shift, and the hyperfine effects. The van der Waals shift becomes commensurate with the 2S-2P\(_{3/2}\) fine-structure splitting only for close approach (\(R < 100\alpha_0\), where \(\alpha_0\) is the Bohr radius) and one may thus restrict the discussion to the levels with \(n = 2\) and \(J = 1/2\) to a good approximation. Because each \(S\) or \(P\) state splits into an \(F = 1\) triplet and an \(F = 0\) hyperfine singlet (eight states for each atom), the Hamiltonian matrix \(a priori\) is of dimension 64.

A careful analysis of the symmetries of the problem allows one to reduce the dimensionality of the most involved irreducible submatrix to 12. We determine the Hamiltonian matrices and the leading-order van der Waals shifts for states that are degenerate under the action of the unperturbed Hamiltonian (Lamb shift plus hyperfine structure). The leading first- and second-order van der Waals shifts lead to interaction energies proportional to \(1/R^3\) and \(1/R^6\) and are evaluated within the hyperfine manifolds. When both atoms are metastable 2S states, we find an interaction energy of order \(E_\alpha \chi (\alpha_0/R)^6\), where \(E_\alpha\) and \(\chi\) are the Hartree and Lamb shift energies, respectively, and \(\chi = E_\alpha/L \approx 6.22 \times 10^8\) is their ratio.

DOI: 10.1103/PhysRevA.95.022704

I. INTRODUCTION

Inspired by recent optical measurements of the 2S hyperfine splitting using an atomic beam [1], we here aim to carry out an analysis of the hyperfine-resolved 2S-2S system composed of two hydrogen atoms. In the preceding paper [2] we analyzed the long-range interaction between two hydrogen atoms, one of which was in the 1S ground state and the other one in the metastable 2S state. Here we turn to the case where both atoms are in an excited state. For that we use the simplest case at hand, namely, that where both atoms are in the 2S state. The 2S-2S van der Waals interaction has been analyzed before in Refs. [3,4], but without any reference to the resolution of the hyperfine splitting [5].

The entire problem needs to be treated using degenerate perturbation theory, because the van der Waals Hamiltonian couples the problem to observable consequences. In a more general context, one may regard our investigations as example cases for a more general setting, in which two excited atoms interact, while in metastable states (with quasidegenerate levels nearby).

The present work combines the challenges described in Ref. [3], where the 2S-2S interaction is studied (but without taking account of the fine and hyperfine structures), with the intricacies of the hyperfine correction to the long-range interaction of two atoms, which have been studied in Refs. [6–9].

Indeed, it had been anticipated in Ref. [3] that a more detailed study of the combined hyperfine and van der Waals effects will be required for the 2S-2S system when a more detailed understanding is sought. The main limitation of the method followed here is that we will only consider dipole-dipole terms in the interatomic interaction, in contrast to Refs. [3,4]. Hence, our analysis only yields reliable results for sufficiently large interatomic separation. Inspection of the higher-order multipole terms obtained in Refs. [3,4] clarifies that the dipole-dipole approximation is already largely valid for interatomic separations of the order of \(R = 20\alpha_0\). This is true for the 2S-2S system, upon which we focus here. Judging from Fig. 2 in Ref. [4], for higher principal quantum number (\(n = 4\), the range of relevance of higher-order multipole terms extends further out, but these cases are beyond the scope of the current investigation.)

Throughout this article, we work in SI mksA units and keep all factors of \(\hbar\) and \(c\) in the formulas. In the choice of the unit system for this paper, we attempt to optimize the accessibility of the presentation to two different communities. The QED community in general uses the natural unit system with \(\hbar = c = \epsilon_0 = 1\) and the electron mass is denoted by \(m\). The relation \(\epsilon^2 = 4\pi \epsilon_0\) then allows us to identify the expansion in the number of quantum electrodynamic corrections with powers of the fine-structure constant \(\alpha\). This unit system is used, e.g., in the investigation reported in Ref. [10] on relativistic corrections to the Casimir-Polder interaction (with a strong overlap with QED). In the atomic unit system, we have \(|e| = \hbar = m = 1\) and \(4\pi \epsilon_0 = 1\). The speed of light, in the atomic unit system, is \(c = 1/\alpha \approx 137.036\). This system of units is especially useful for the analysis of purely atomic properties without radiative effects. As the subject of the current study lies in between the two mentioned fields of interest, we choose the SI mksA unit system as the most appropriate reference frame for our calculations. The formulas
do not become unnecessarily complex and can be evaluated with ease for any experimental application.

We organize this paper as follows. The combination of the orbital and spin electron angular momenta and the nuclear spin adds up to give the total angular momentum of the hydrogen atom; the conserved quantities are discussed in Sec. II, together with the relevant two-atom product wave functions. In Sec. III we proceed to investigate the Hamiltonian matrices in the subspaces of the spectrum of the total Hamiltonian into which it naturally decouples. Namely, the magnetic projection of the subspaces of the spectrum of the total Hamiltonian into which we proceed to investigate the Hamiltonian matrices in the states, namely, either 2S or 2P) are analyzed in Sec. IV. A summary is given and conclusions are drawn in Sec. V.

II. FORMALISM

A. Total Hamiltonian of the system

In order to evaluate the 2S-2S long-range interaction, including hyperfine effects, one needs to diagonalize the Hamiltonian

\[ H = H_{LS,A} + H_{LS,B} + H_{hfs,A} + H_{hfs,B} + H_{vdW}. \]  

(1)

Here \( H_{LS} \) is the Lamb shift Hamiltonian, while \( H_{hfs} \) describes hyperfine effects; these Hamiltonians have to be added for atoms \( A \) and \( B \). They are given as

\[
H_{hfs} = \frac{\mu_0}{4\pi} \mu_B \mu_N g_s g_p \sum_{i=A,B} \left[ \frac{8\pi}{3} \mathbf{S}_i \cdot \hat{r}_i \delta^3(\mathbf{r}_i) + \frac{3(\mathbf{S}_i \cdot \mathbf{r}_i)(\mathbf{I}_i \cdot \mathbf{r}_i) - \mathbf{S}_i \cdot \mathbf{I}_i \mathbf{r}_i}{|\mathbf{r}_i|^2} + \frac{\mathbf{I}_i \cdot \mathbf{I}_i}{|\mathbf{r}_i|^4} \right],
\]

(2a)

\[
H_{LS} = \frac{4}{3} \alpha^2 mc^2 \left( \frac{\hbar}{mc} \right)^3 \ln(\alpha^2) \sum_{i=A,B} \delta^3(\mathbf{r}_i),
\]

(2b)

\[
H_{vdW} = \alpha \hbar c \left( x_{A,B} + y_{A,B} - 2z_{A,B} \right). \]

(2c)

Here \( \alpha \) is the fine-structure constant; \( m \) is the electron mass; \( \mathbf{r}_i \), \( \hat{r}_i \), and \( L_i \) are the position (relative to the respective nucleus), linear momentum, and orbital angular momentum operators for electron \( i \); and \( \mathbf{S}_i \) is the spin operator for electron \( i \) and \( \mathbf{I}_i \) is the spin operator for proton \( i \) (both are dimensionless). The electronic and protonic \( g \) factors are \( g_s \simeq 2.002319 \) and \( g_p \simeq 5.158695 \), while \( \mu_B \simeq 9.274010 \times 10^{-24} \) A m\(^2\) is the Bohr magneton and \( \mu_N \simeq 5.050784 \times 10^{-27} \) A m\(^2\) is the nuclear magneton. The subscripts \( A \) and \( B \) refer to the relative coordinates within the two atoms, while \( R \) is the interatomic distance. The expression for \( H_{LS} \) shifts \( S \) states relative to \( P \) states by the Lamb shift, which is given in the Welton approximation [11], which is convenient within the formalism used for the evaluation of matrix elements. (The important property of \( H_{LS} \) is that it shifts \( S \) states upward in relation to \( P \) states; the prefactor multiplying the Dirac \( \delta \) can be adjusted to the observed Lamb shift splitting.) Indeed, for the final calculation of energy shifts, we will replace

\[
\left\langle 2S_{1/2} | H_{LS} | 2S_{1/2} \right\rangle - \left\langle 2P_{1/2} | H_{LS} | 2P_{1/2} \right\rangle = \frac{4\alpha^2 \alpha^4}{3\pi} mc^2 \ln(\alpha^2) \rightarrow \mathcal{L},
\]

(3)

where \( \mathcal{L} = h/1057.845(9) \) MHz is the classic 2S-2P\(_{1/2}\) Lamb shift [12]. The Hamiltonian \( H \) given in Eq. (1) defines the zero of the energy to be the hyperfine centroid frequency of the 2P\(_{1/2}\) states. The result for \( H_{vdW} \) in the given form is taken from Ref. [13]. The Hamiltonians \( H_{hfs,A} \) and \( H_{hfs,B} \) are obtained from \( H_{hfs} \) by specializing the coordinate \( \mathbf{r} \) to be the relative coordinate (electron-proton) in atoms \( A \) and \( B \), respectively, and correspondingly for \( H_{LS,A} \) and \( H_{LS,B} \).

We will focus on the interatomic separation regime where the van der Waals energy is commensurate with the hyperfine splitting and Lamb shift energies, but much smaller than the fine structure (the 2P\(_{1/2}\)-2P\(_{3/2}\) splitting and likewise the 2S-2P\(_{3/2}\) splitting). Hence,

\[
E_{vdW} \sim E_{hfs} \sim \mathcal{L} \ll E_{FS}.
\]

(4)

This is fulfilled for \( R > 100a_0 \), as can be seen from Eq. (2c) and will be confirmed later. Hence, we only consider 2S and 2P\(_{1/2}\) states. We will neglect the influence of the 2P\(_{3/2}\) states, assuming that they are sufficiently displaced. Because the van der Waals interaction (2c) has nonvanishing diagonal elements between 2S and 2P states, the interaction energy between the two 2S atoms can be of order 1/R\(^2\).

The \( z \) component of the total angular momentum operator of both atoms is

\[
F_z = F_{z,A} + F_{z,B} = J_{z,A} + J_{z,B} + I_{z,A} + I_{z,B},
\]

\[
L_{z,A} + L_{z,B} + S_{z,A} + S_{z,B} + I_{z,A} + I_{z,B},
\]

\[
L_{z,A} + L_{z,B} + \frac{1}{2} \sigma_{e,z,A} + \frac{1}{2} \sigma_{e,z,B} + \frac{1}{2} \sigma_{p,z,A} + \frac{1}{2} \sigma_{p,z,B},
\]

(5)

where \( \mathbf{J} = \mathbf{L} + \mathbf{S} \) is the total angular momentum of the electron. Let us investigate if \( F_z \) commutes with the total Hamiltonian \( H \). In Eq. (5) the subscript \( e \) denotes the electron, while \( p \) denotes the proton. The following commutators vanish separately: \([S_{z,a} + S_{z,b}, H_{LS}] = [S_{z,a} + S_{z,b}, H_{vdW}] = [I_{z,a} + I_{z,b}, H_{LS}] = [I_{z,a} + I_{z,b}, H_{vdW}] = 0\). We then turn to the nontrivial commutators. For that, it is very useful to notice that the orbital angular momentum \( \mathbf{L} \) of electron \( i \) commutes with all spherically symmetric functions of the radial position operator \( |\mathbf{r}_i| \) of the same electron. This immediately yields

\[
[L_{z,a} + L_{z,b}, H_{LS}] = 0.
\]

We can also show that

\[
[S_{z,a} + S_{z,b}, H_{hfs}] = [I_{z,a} + I_{z,b}, H_{hfs}] = [L_{z,a} + L_{z,b}, H_{hfs}] = 0,
\]

\[
[L_{z,a} + L_{z,b}, H_{vdW}] = \alpha \hbar c \left( y_{A,B}x_{A,B} - y_{A,B}x_{A,B} - x_{A,B}y_{A,B} \right),
\]

(6)

The component \( F_z \) of the total angular momentum of the two-atom system [see Eq. (5)] thus commutes with the total Hamiltonian \( H \). We can classify states according to the eigenvalues of the operator \( F_z = F_{z,a} + F_{z,b} \).
B. Addition of momenta and total hyperfine quantum number

In order to calculate the matrix elements of the total Hamiltonian (1), we first need to identify the relevant states of the two atoms. For each atom, we easily identify the following quantum numbers within the hyperfine manifolds:

\[ 2S_1/2 (F = 0): \ell = 0, J = 1/2, F = 0 \Rightarrow g_F = 1, \]  
\[ 2S_1/2 (F = 1): \ell = 0, J = 1/2, F = 1 \Rightarrow g_F = 3, \]  
\[ 2P_1/2 (F = 0): \ell = 1, J = 1/2, F = 0 \Rightarrow g_F = 1, \]  
\[ 2P_1/2 (F = 1): \ell = 1, J = 1/2, F = 1 \Rightarrow g_F = 3. \]

Thus, we have to generate the matrix, diagonalize it, and choose the eigenvalues that correspond to the unperturbed (with respect to dipole-dipole interaction) states.

Let us add angular momenta to obtain the single-atom states of definite hyperfine quantum number. First, we add the electron spin with its orbital angular momentum to obtain the \( J = 1/2 \) states within the \( n = 2 \) manifold of hydrogen. These are given as

\[ |\ell = 0, F = 0, F_z = 0\rangle = \frac{1}{\sqrt{2}} |\ell = 0, m = 0\rangle_e, \]  
\[ |\ell = 1, F = 0, F_z = 0\rangle = \frac{1}{\sqrt{2}} |\ell = 1, m = 0\rangle_e, \]  
\[ |\ell = 1, F = 1, F_z = 1\rangle = \frac{1}{\sqrt{2}} |\ell = 1, m = 1\rangle_e. \]

Here \(|\pm\rangle_e\) is the electron spin state and \(|\ell, m\rangle_e\) denotes the Schrödinger eigenstate (without spin). The principal quantum number \(\ell = 2\) throughout. We also remember that the \( J = 3/2 \) states are displaced by the fine-structure shift and therefore far away in the energy landscape given the scale of energies considered here. With the help of Clebsch-Gordan coefficients, we add the nuclear (proton) spin \(|\pm\rangle_p\) to obtain the eight states in the single-atom hyperfine basis. First, we have for the four \( S \) states

\[ |\ell = 0, F = 0, F_z = 0\rangle = \frac{1}{\sqrt{2}} |\ell = 0, m = 0\rangle_e, \]  
\[ |\ell = 1, F = 0, F_z = 0\rangle = \frac{1}{\sqrt{2}} |\ell = 1, m = 0\rangle_e, \]  
\[ |\ell = 1, F = 1, F_z = 1\rangle = \frac{1}{\sqrt{2}} |\ell = 1, m = 1\rangle_0_e. \]

The \( P \) states are more complicated,

\[ |\ell = 1, F = 0, F_z = 0\rangle = \frac{1}{\sqrt{3}} |\ell = 1, m = 0\rangle_0_e |1, 0\rangle_e + \frac{1}{\sqrt{6}} |\ell = 1, m = 1\rangle_0_e |1, 0\rangle_e + \frac{1}{\sqrt{6}} |\ell = 1, m = 1\rangle_0_e |1, 0\rangle_e, \]  
\[ |\ell = 1, F = 1, F_z = 0\rangle = \frac{1}{\sqrt{3}} |\ell = 1, m = 0\rangle_0_e |1, 0\rangle_e + \frac{1}{\sqrt{6}} |\ell = 1, m = 1\rangle_0_e |1, 0\rangle_e + \frac{1}{\sqrt{6}} |\ell = 1, m = 1\rangle_0_e |1, 0\rangle_e, \]  
\[ |\ell = 1, F = 1, F_z = 1\rangle = \frac{1}{\sqrt{3}} |\ell = 1, m = 0\rangle_0_e |1, 0\rangle_e - \frac{1}{\sqrt{6}} |\ell = 1, m = 1\rangle_0_e |1, + 1\rangle_e. \]

In the following, we will use the notation \(|\ell, F, F_z\rangle\) for the eigenstates of the unperturbed Hamiltonian

\[ H_0 = H_{\text{hfs},A} + H_{\text{hfs},B} + H_{\text{LS},A} + H_{\text{LS},B}, \]  

C. Matrix elements of the total Hamiltonian

We now turn to the computation of the matrix elements of the total Hamiltonian (1) in the space spanned by the two-atom states that are product states built from any two states of the types (10) and (11). We choose a basis in which the Lamb shift and hyperfine Hamiltonians are diagonal, so the only nontrivial

within the \(2S-2P_{1/2}\) manifold. The notation \(|\ell, F, F_z\rangle\) is rather intuitive; the first entry clarifies if we have an \( S \) (with \( \ell = 0 \)) or a \( P \) state (with \( \ell = 1 \)), the second entry specifies if we have a hyperfine triplet \((F = 1)\) or a hyperfine singlet \((F = 0)\) state, and the last entry is the magnetic projection of the total angular momentum.
the interatomic separation

\[
\langle \ell_F, M_F | H_{1S} | \ell_F, M_F \rangle = \mathcal{L}\delta(0),
\]

The hyperfine splitting energy between \(2P_{1/2}(F = 1)\) and \(2P_{1/2}(F = 0)\) states thus amounts to \(\mathcal{H}\), while the \(S\)-state splitting is \(3\mathcal{H}\). Additionally, the energies of the \(S\) states are lifted upward by \(\mathcal{L}\), irrespective of the hyperfine effects. For the product state of atoms \(A\) and \(B\), we will use the notation

\[
|\ell_A, F_A, F_z_A, \lambda_A(\ell_B, F_B, F_z_B)\rangle,
\]

which summarizes the quantum numbers of both atoms. We anticipate that some of the eigenstates of the combined and total Hamiltonian (Lamb shift plus hyperfine effects plus van der Waals interaction) do not decouple into simple unperturbed eigenstates of the form \(|\ell_F, M_F, \lambda_F(\ell_B, F_B, F_z_B)\rangle\) but may require the use of superpositions of these states, as we had already experienced for the \((1S; 2S)\) interaction in Ref. [2].

## III. Hamiltonian Matrices in the Hyperfine Subspaces

### A. Manifold \(F_z = +2\)

We have already pointed out that the \(n = 2, J = 1/2\) Hilbert space naturally separates into subspaces with fixed total hyperfine quantum number \(F_z = F_{z,a} + F_{z,b}\), according to Eq. (8). We can identify two irreducible subspaces within the \(F_z = +2\) manifold. The subspace I is composed of the states

\[
|\phi_{1}^{(I)}\rangle = |(0, 1, 1)_{A}(0, 1, 1)_{B}\rangle, \quad (18a)
\]

\[
|\phi_{2}^{(I)}\rangle = |(1, 1, 1)_{A}(1, 1, 1)_{B}\rangle, \quad (18b)
\]

where the Hamiltonian matrix reads

\[
H_{F_z = +2}^{(I)} = \begin{pmatrix}
2\mathcal{L} + \frac{3}{2}\mathcal{H} & -2\mathcal{V} \\
-2\mathcal{V} & \frac{1}{2}\mathcal{H}
\end{pmatrix}.
\]

Subspace II is composed of the states

\[
|\phi_{1}^{(II)}\rangle = |(0, 1, 1)_{A}(1, 1, 1)_{B}\rangle, \quad (20a)
\]

\[
|\phi_{2}^{(II)}\rangle = |(1, 1, 1)_{A}(0, 1, 1)_{B}\rangle, \quad (20b)
\]

where the Hamiltonian matrix reads

\[
H_{F_z = +2}^{(II)} = \begin{pmatrix}
\mathcal{L} + \mathcal{H} & -2\mathcal{V} \\
-2\mathcal{V} & \mathcal{L} + \mathcal{H}
\end{pmatrix}.
\]

These subspaces are completely uncoupled. Namely, no state in subspace I is coupled to a state in subspace II.

The eigenvalues of \(H_{F_z = +2}^{(I,II)}\) are given by

\[
E_{+}^{(I)} = \mathcal{H} + \mathcal{L} + \sqrt{4\mathcal{V}^2 + \left(\frac{1}{2}\mathcal{H} + \mathcal{L}\right)^2},
\]

\[
= \frac{1}{2}\mathcal{H} + 2\mathcal{L} + 4\mathcal{V}^2 + \mathcal{O}(\mathcal{V}^3),
\]

\[
E_{-}^{(I)} = \mathcal{H} + \mathcal{L} - \sqrt{4\mathcal{V}^2 + \left(\frac{1}{2}\mathcal{H} + \mathcal{L}\right)^2},
\]

\[
= \frac{1}{2}\mathcal{H} - 4\mathcal{V}^2 + \mathcal{O}(\mathcal{V}^4),
\]

with the corresponding eigenvectors

\[
|u_{+}^{(I)}\rangle = \frac{1}{\sqrt{a^2 + b^2}}(a|\phi_{1}^{(I)}\rangle + b|\phi_{2}^{(I)}\rangle), \quad (23a)
\]

\[
|u_{-}^{(I)}\rangle = \frac{1}{\sqrt{a^2 + b^2}}(b|\phi_{1}^{(I)}\rangle - a|\phi_{2}^{(I)}\rangle). \quad (23b)
\]
Here the coefficients $a$ and $b$ are given by

$$a = -\frac{2L + \mathcal{H} + \sqrt{(2L + \mathcal{H})^2 + (4V)^2}}{4V},$$  \hspace{1cm} (24a)$$

$$b = 1.$$ \hspace{1cm} (24b)

The eigenenergies of $H^{(II)}_{F_z=+2}$ are given by

$$E^{(II)}_{\pm} = \mathcal{H} \pm L \pm 2V,$$  \hspace{1cm} (25)

with the corresponding eigenvectors

$$|\phi^{(II)}_{\pm}\rangle = \frac{1}{\sqrt{2}}( |\phi_1^{(II)}\rangle \pm |\phi_2^{(II)}\rangle).$$ \hspace{1cm} (26)

For $V \to 0$, which corresponds to the large separation limit $R \to +\infty$, these eigenvalues tend toward the (degenerate) diagonal entries of the matrix $H^{(II)}_{F_z=+2}$.

The eigenstates within the degenerate subspace II experience a shift of first order in the van der Waals interaction energy $\mathcal{V}$, because of the degeneracy of the diagonal entries $L + \mathcal{H}$ in Eq. (21); this pattern will be observed for other subspaces in the following. In Fig. 1 we plot the evolution of the eigenvalues (22) and (25) with respect to interatomic separation. The two levels within the subspace II noticeably experience a far larger interatomic interaction shift from their asymptotic value $L + \mathcal{H}$, commensurate with the parametric estimate of the corresponding energy shifts.

### B. Manifold $F_z = +1$

We can identify two irreducible subspaces within the $F_z = +1$ manifold. Subspace I is composed of the following states, with either both atoms being in $S$ or both in $P$ states,

$$|\psi_1^{(I)}\rangle = |0,0,0\rangle_s |0,0,0\rangle_p, \quad |\psi_2^{(I)}\rangle = |0,1,0\rangle_s |0,0,0\rangle_p, \quad |\psi_3^{(I)}\rangle = |0,1,0\rangle_s |0,0,0\rangle_p, \quad |\psi_4^{(I)}\rangle = |0,0,0\rangle_s |0,0,0\rangle_p,$$

$$|\psi_5^{(I)}\rangle = |0,1,0\rangle_s |0,1,0\rangle_p, \quad |\psi_6^{(I)}\rangle = |0,1,0\rangle_s |0,1,0\rangle_p, \quad |\psi_7^{(I)}\rangle = |0,1,0\rangle_s |0,1,0\rangle_p, \quad |\psi_8^{(I)}\rangle = |0,1,0\rangle_s |0,1,0\rangle_p,$$

and the Hamiltonian matrix reads

$$H^{(I)}_{F_z=+1} = \begin{pmatrix}
2L - \frac{2}{3} \mathcal{H} & 0 & 0 & 0 & 0 & 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} \\
0 & 2L + \frac{2}{3} \mathcal{H} & 0 & 0 & -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} \\
0 & 0 & 2L - \frac{2}{3} \mathcal{H} & 0 & \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} \\
0 & 0 & 0 & 2L + \frac{2}{3} \mathcal{H} & -\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 \\
-2\mathcal{V} & \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} & 0 & 0 & 0 \\
\mathcal{V} & -\mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} & 0 & 0 & 0 \\
-\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 & 0 & 0 & \frac{1}{2} \mathcal{H} & 0 \\
\mathcal{V} & -\mathcal{V} & -2\mathcal{V} & 0 & 0 & 0 & \frac{1}{2} \mathcal{H} & 0
\end{pmatrix}. \hspace{1cm} (28)$$

Subspace II is composed of the following states, where one atom is in an $S$ state and the other in a $P$ state,

$$|\psi_1^{(II)}\rangle = |0,0,0\rangle_s |1,1,1\rangle_p, \quad |\psi_2^{(II)}\rangle = |0,0,0\rangle_s |1,1,1\rangle_p, \quad |\psi_3^{(II)}\rangle = |0,0,0\rangle_s |1,1,1\rangle_p,$$

$$|\psi_4^{(II)}\rangle = |0,1,0\rangle_s |1,1,1\rangle_p, \quad |\psi_5^{(II)}\rangle = |0,0,0\rangle_s |1,1,1\rangle_p, \quad |\psi_6^{(II)}\rangle = |0,1,0\rangle_s |1,1,1\rangle_p,$$

$$|\psi_7^{(II)}\rangle = |0,1,0\rangle_s |0,0,0\rangle_p, \quad |\psi_8^{(II)}\rangle = |0,1,0\rangle_s |0,0,0\rangle_p,$$ \hspace{1cm} (29)
and the Hamiltonian matrix reads

\[
H_{F_i=+1}^{(II)} = \begin{pmatrix}
\mathcal{L} - 2\mathcal{H} & 0 & 0 & 0 & 0 & 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} \\
0 & \mathcal{L} + \mathcal{H} & 0 & 0 & -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} & 0 \\
0 & 0 & \mathcal{L} & 0 & 0 & \mathcal{L} & 0 & -\mathcal{V} & \mathcal{V} \\
0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} & \mathcal{L} & 0 & 0 & 0 & 0 \\
-2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 & 0 \\
\mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} & 0 & 0 & \mathcal{L} - 2\mathcal{H} & 0 & 0 \\
-\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 \\
\end{pmatrix}.
\]  

These two submanifolds are again completely uncoupled, as a consequence of the selection rules between \(S\) and \(P\) states. One observes that within the subspace \(I\), no two degenerate levels are coupled to each other, resulting in second-order van der Waals energy shifts. On the other hand, the following subspaces, within the subspace \(II\), can be identified as being degenerate with respect to the unperturbed Hamiltonian and having states coupled by nonvanishing off-diagonal elements. We first have a subspace spanned by

\[
|\psi_1^{(A)}\rangle = |\psi_1^{(II)}\rangle, \quad |\psi_2^{(A)}\rangle = |\psi_7^{(II)}\rangle.
\]

The eigenvalues are

\[
E^{(A)}_{\pm} = \mathcal{L} - 2\mathcal{H} \pm \sqrt{\mathcal{V}},
\]

with the corresponding eigenvectors

\[
|\mu^{(A)}_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\psi_1^{(A)}\rangle \pm |\psi_7^{(A)}\rangle).
\]

Note that the designation of a degenerate subspace, for the \(F_i = +1\) subspace, does not imply that there are no couplings to any other states within the manifold; however, the couplings relating the degenerate states will become dominant for close approach.

A second degenerate subspace is given as

\[
|\psi_1^{(B)}\rangle = |\psi_3^{(II)}\rangle, \quad |\psi_2^{(B)}\rangle = |\psi_5^{(II)}\rangle.
\]

These states are composed of a singlet \(S\) and a triplet \(P\) state and hence the diagonal entries in the Hamiltonian matrix are \((-\frac{3}{4}\mathcal{H} + \mathcal{L}) + (\frac{3}{4}\mathcal{H}) = -2\mathcal{H} + \mathcal{L}\). The Hamiltonian matrix is

\[
H_{F_i=+1}^{(B)} = \begin{pmatrix}
\mathcal{L} - 2\mathcal{H} & \mathcal{V} \\
\mathcal{V} & \mathcal{L}
\end{pmatrix}.
\]

The eigenvalues are

\[
E^{(B)}_{\pm} = \mathcal{L} \pm \sqrt{\mathcal{V}},
\]

with the corresponding eigenvectors

\[
|\mu^{(B)}_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\psi_1^{(B)}\rangle \pm |\psi_2^{(B)}\rangle).
\]

The most complicated degenerate subspace is given by the vectors

\[
|\psi_1^{(C)}\rangle = |\psi_2^{(II)}\rangle, \quad |\psi_2^{(C)}\rangle = |\psi_4^{(II)}\rangle, \quad |\psi_3^{(C)}\rangle = |\psi_6^{(II)}\rangle, \quad |\psi_4^{(C)}\rangle = |\psi_8^{(II)}\rangle.
\]

The Hamiltonian matrix is

\[
H_{F_i=+1}^{(C)} = \begin{pmatrix}
\mathcal{L} + \mathcal{H} & 0 & 0 & \mathcal{V} \\
0 & \mathcal{L} + \mathcal{H} & \mathcal{V} & 0 \\
\mathcal{V} & 0 & \mathcal{L} + \mathcal{H} & 0 \\
0 & 0 & 0 & \mathcal{L} + \mathcal{H}
\end{pmatrix}.
\]

which again decouples into two \(2 \times 2\) matrices, just like we saw in the case of \(H_{F_i=+2}\). The eigenvalues are

\[
E^{(C)}_{\pm} = \mathcal{L} + \mathcal{H} \pm \sqrt{\mathcal{V}},
\]
where the eigenvectors for $|u_{i}^{(C)}\rangle$ (with $i = 1, 2$ because of the degeneracy of the eigenvalues) are given by

$$|u_{1}^{(C)}\rangle = \frac{1}{\sqrt{2}}(|\psi_{1}^{(C)}\rangle \pm |\psi_{4}^{(C)}\rangle),$$

$$|u_{2}^{(C)}\rangle = \frac{1}{\sqrt{2}}(|\psi_{2}^{(C)}\rangle \pm |\psi_{3}^{(C)}\rangle).$$

In Figs. 2 and 3 we plot the evolution of the eigenvalues of the matrices (28) and (30) with respect to interatomic separation. The larger energy shifts within the subspace II are noticeable. A feature exhibited by the $F_{z} = +1$ manifold that was not present in the $F_{z} = +2$ manifold is that of level crossings: For sufficiently small interatomic separation ($R < 500a_{0}$), the eigenenergies of some of the states from the submanifolds I and II in fact cross (these crossings would be visible if one were to superimpose Figs. 2 and 3), while there are no level crossings between states belonging to the same submanifold.

### C. Manifold $F_{z} = 0$

We can identify two irreducible subspaces within the $F_{z} = 0$ manifold. The subspace I is composed of states with both atoms in S or both atoms in P levels

\begin{equation}
H_{F_{z}=0}^{(I)} = \begin{pmatrix}
2\mathcal{L} - \frac{9}{2}\mathcal{H} & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -\mathcal{V} \\
0 & 2\mathcal{L} - \frac{3}{2}\mathcal{H} & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} \\
0 & 0 & 2\mathcal{L} + \frac{1}{2}\mathcal{H} & 0 & 0 & 0 & -\mathcal{V} & -\mathcal{V} & 2\mathcal{V} & -\mathcal{V} & 0 & -\mathcal{V} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -2\mathcal{V} & -\mathcal{V} & 2\mathcal{V} & -\mathcal{V} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} & 0 & -\frac{1}{2}\mathcal{H} \\
0 & 0 & 0 & 0 & -\mathcal{V} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\mathcal{H} \\
-\mathcal{V} & -\mathcal{V} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \mathcal{H} & 0 & 0 \\
-2\mathcal{V} & -\mathcal{V} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \mathcal{H} & 0 & 0 \\
-\mathcal{V} & -\mathcal{V} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \mathcal{H} & 0 & 0
\end{pmatrix}
\end{equation}

Subspace II is composed of the S-P and P-S combinations

\begin{equation}
|\Psi_{1}^{(II)}\rangle = |(0, 0, 0)_{A}(1, 0, 0)_{B}\rangle, \quad |\Psi_{2}^{(II)}\rangle = |(0, 0, 0)_{A}(1, 1, 0)_{B}\rangle, \quad |\Psi_{3}^{(II)}\rangle = |(0, 1, -1)_{A}(1, 1, 1)_{B}\rangle,
\end{equation}

\begin{equation}
|\Psi_{4}^{(II)}\rangle = |(0, 1)_{A}(1, 0, 0)_{B}\rangle, \quad |\Psi_{5}^{(II)}\rangle = |(0, 1)_{A}(1, 1, 0)_{B}\rangle, \quad |\Psi_{6}^{(II)}\rangle = |(0, 1)_{A}(1, 1, -1)_{B}\rangle,
\end{equation}

\begin{equation}
|\Psi_{7}^{(II)}\rangle = |(1, 0, 0)_{A}(0, 0, 0)_{B}\rangle, \quad |\Psi_{8}^{(II)}\rangle = |(1, 0, 0)_{A}(0, 1, 0)_{B}\rangle, \quad |\Psi_{9}^{(II)}\rangle = |(1, 1, -1)_{A}(0, 1, 1)_{B}\rangle,
\end{equation}

\begin{equation}
|\Psi_{10}^{(II)}\rangle = |(1, 1, 0)_{A}(0, 0, 0)_{B}\rangle, \quad |\Psi_{11}^{(II)}\rangle = |(1, 1, 0)_{A}(0, 1, 0)_{B}\rangle, \quad |\Psi_{12}^{(II)}\rangle = |(1, 1)_{A}(0, 1, -1)_{B}\rangle
\end{equation}
and the Hamiltonian matrix reads

\[
H_{F,z=0}^{(II)} = \begin{pmatrix}
\mathcal{L} - 3\mathcal{H} & 0 & 0 & 0 & 0 & 0 & -\nu & 0 & -2\nu & -\nu \\
0 & \mathcal{L} - 2\mathcal{H} & 0 & 0 & 0 & 0 & 0 & -\nu & 2\nu & 0 \\
0 & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 & 0 & -\nu & -2\nu & -\nu & 0 \\
0 & 0 & 0 & \mathcal{L} & 0 & 0 & -2\nu & -\nu & 0 & 0 \\
0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & -\nu & -\nu & 0 & 0 \\
0 & 0 & 0 & -\nu & 0 & 0 & \mathcal{L} & 0 & 0 & 0 \\
-\nu & -\nu & 2\nu & -\nu & 0 & 0 & 0 & \mathcal{L} & 0 & 0 \\
-2\nu & -\nu & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{L} - 2\mathcal{H} & 0 \\
-\nu & -\nu & 0 & 0 & \nu & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 \\
-2\nu & -\nu & 0 & 0 & \nu & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 \\
-\nu & -\nu & 0 & 0 & \nu & 2\nu & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} \\
\end{pmatrix}
\]  

(47)

Again, we notice that within subspace I, no two degenerate levels are coupled to each other. On the other hand, the following subspaces, within subspace II, can be identified as being degenerate with respect to the unperturbed Hamiltonian and having states coupled by nonvanishing off-diagonal elements.

The first degenerate subspace is given as

\[|\Psi_1^{(A)}\rangle = |\Psi_2^{(A)}\rangle, \quad |\Psi_2^{(A)}\rangle = |\Psi_{10}^{(II)}\rangle.\]  

(48)

The Hamiltonian matrix reads

\[
H_{F,z=0}^{(A)} = \begin{pmatrix}
\mathcal{L} - 2\mathcal{H} & -2\nu \\
-2\nu & \mathcal{L} - 2\mathcal{H} \\
\end{pmatrix}
\]  

(49)

The eigensystem is given by

\[E_{\pm} = \mathcal{L} - 2\mathcal{H} \pm 2\nu, \quad |u_{\pm}^{(A)}\rangle = \frac{1}{\sqrt{2}}(|\Psi_1^{(A)}\rangle \mp |\Psi_2^{(A)}\rangle).\]  

(50)

The six-dimensional submatrix is

\[
H_{F,z=0}^{(C)} = \begin{pmatrix}
\mathcal{L} + \mathcal{H} & 0 & 0 & 2\nu & -\nu & 0 \\
0 & \mathcal{L} + \mathcal{H} & 0 & \nu & 0 & 0 \\
0 & 0 & \mathcal{L} + \mathcal{H} & 0 & \nu & 0 \\
2\nu & -\nu & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 \\
\nu & 0 & \nu & 0 & \mathcal{L} + \mathcal{H} & 0 \\
0 & \nu & 2\nu & 0 & 0 & \mathcal{L} + \mathcal{H} \\
\end{pmatrix}
\]  

(55)

The eigenvalues are

\[E_{\pm,1} = \mathcal{H} \pm \mathcal{L} \pm 2\nu,\]  

\[E_{\pm,2} = \mathcal{H} + \mathcal{L} + (\sqrt{3} - 1)\nu,\]  

\[E_{\pm,3} = \mathcal{H} + \mathcal{L} + (\sqrt{3} - 1)\nu,\]  

(56)

and the eigenvectors are

\[u_{\pm,1}^{(C)} = \frac{1}{2}(|\Psi_1^{(C)}\rangle - |\Psi_3^{(C)}\rangle + |\Psi_4^{(C)}\rangle - |\Psi_6^{(C)}\rangle),\]  

(57a)

\[u_{\pm,2}^{(C)} = \frac{1}{2\sqrt{3} - \sqrt{3}}(|\Psi_1^{(C)}\rangle + (\sqrt{3} - 1)|\Psi_2^{(C)}\rangle + |\Psi_3^{(C)}\rangle + |\Psi_4^{(C)}\rangle + |\Psi_5^{(C)}\rangle + |\Psi_6^{(C)}\rangle),\]  

(57c)
The coefficients $\alpha$ and $\beta$ are determined by second-order perturbation theory and are given by Eq. (83).
FIG. 6. Evolution of the energy levels of the $2^2P$-2$^2P$ states within the $F_z = 0$ hyperfine manifold (subspace I) as a function of interatomic separation (close-up of the lower levels in Fig. 4). Asymptotic eigenstates used in the legend mix for finite separation. No offsets are used here. Notice that we witness one level crossing. The coefficients $\alpha_\pm$ and $\beta_\pm$ are determined by second-order perturbation theory and are given by Eq. (83).

Let us first examine the submanifold with $F_z = +1$. The following states have the atom $A$ in the singlet hyperfine $2S$ level:

$$\left| \psi^{(I)}_1 \right> = \left| (0,0,0)_A (0,1,1)_B \right>, \quad (60a)$$

$$\left| \psi^{(I)}_2 \right> = \left| (0,0,0)_A (1,1,1)_B \right>, \quad (60b)$$

while

$$\left| \psi^{(II)}_1 \right> = \left| (0,1,0)_A (0,1,1)_B \right>, \quad (61a)$$

$$\left| \psi^{(II)}_2 \right> = \left| (0,1,0)_A (1,1,1)_B \right>, \quad (61b)$$

have the atom $A$ in the hyperfine triplet $S$ state. The state of the spectator atom is preserved in the transitions $|\psi^{(I)}_1\rangle \rightarrow |\psi^{(I)}_2\rangle$ and $|\psi^{(II)}_1\rangle \rightarrow |\psi^{(II)}_2\rangle$.

For the states $|\psi^{(I)}_1\rangle$ and $|\psi^{(II)}_1\rangle$, the spectator atom is in a $P$ state. For both of these states, we can find energetically degenerate levels that are coupled to the reference state by the van der Waals interaction. Specifically, $|\psi^{(III)}_1\rangle$ is energetically degenerate with respect to $|\psi^{(III)}_7\rangle = |(1,1,1)_A (0,0,0)_B\rangle$, with the off-diagonal element

$$\langle \psi^{(III)}_1 | H_{vdW} | \psi^{(III)}_7 \rangle = V, \quad (62)$$

as can be seen in Eqs. (31) and (32). Furthermore, $|\psi^{(III)}_2\rangle$ is energetically degenerate with respect to $|\psi^{(III)}_8\rangle = |(1,1,1)_A (0,1,0)_B\rangle$, with the off-diagonal element

$$\langle \psi^{(III)}_2 | H_{vdW} | \psi^{(III)}_8 \rangle = V, \quad (63)$$

as can be seen in Eqs. (39) and (41). This implies that a hyperfine transition or energy difference, with the spectator atom being in a $P$ state, undergoes a first-order van der Waals energy shift proportional to $V$ [see Eq. (15c)].
A close inspection of the matrix (28) reveals that the levels $|\psi_1^{(I)}\rangle$ and $|\psi_2^{(I)}\rangle$ are not coupled to any energetically degenerate levels by the van der Waals interaction; hence, their leading-order shift is of second order in $\nu$. From the previous analysis [2] of the (1S; $nS$) van der Waals interaction, however, we know that this observation does not imply that $|\psi_1^{(I)}\rangle$ and $|\psi_2^{(I)}\rangle$ decouple from any other levels in terms of the eigenstates of the total Hamiltonian $H$ given in Eq. (1); there may still be admixtures due to second-order effects in $H_{vdw}$ that involve energetically degenerate levels, even if these are not coupled directly to the reference state. In the case of the (1S; $nS$) van der Waals interaction, we had constructed an effective Hamiltonian $H_{vdw}(1/(E_0 - H))H_{vdw}$ and evaluated its matrix elements in the basis of degenerate states. The same approach is taken here, but with the Hamiltonian matrix restricted to the relevant $F_S$ submanifold of states.

Let us illustrate the procedure. We have the degenerate state

$$|\psi_3^{(I)}\rangle = |(0,1,1)_A(0,0,0)_B\rangle,$$

which is obtained from $|\psi_3^{(I)}\rangle$ by permuting the atoms $A$ and $B$, and construct the Hamiltonian matrix

$$h_{1,3}^{(I)} = \lim_{\epsilon \to 0} \left[ \langle \psi_1^{(I)} | H_{\text{eff}}^{(e)} | \psi_3^{(I)} \rangle \langle \psi_3^{(I)} | H_{\text{eff}}^{(e)} | \psi_3^{(I)} \rangle - \langle \psi_1^{(I)} | H_{\text{eff}}^{(e)} | \psi_3^{(I)} \rangle \langle \psi_3^{(I)} | H_{\text{eff}}^{(e)} | \psi_1^{(I)} \rangle \right].$$

One defines the effective Hamiltonian $H_{\text{eff}}^{(e)}$ as follows. Let $H_1$ be the off-diagonal part of $H_{F_{1,3}^{(I)}}$, equivalently given by the expression of $H_{F_{1,3}^{(I)}}$ given in Eq. (28) with $\mathcal{H} \to 0$ and $\mathcal{L} \to 0$. Also, let $H_0$ be the diagonal part of $H_{F_{1,3}^{(I)}}$, equivalently given by the expression of $H_{F_{1,3}^{(I)}}$ with $\mathcal{V} \to 0$. Then

$$H_{\text{eff}}^{(e)} = H_1 \cdot \frac{1}{E_{0,\psi_1^{(I)}} - H_0 + \epsilon} \cdot H_1,$$

where the centered dot denotes the matrix multiplication and the Green’s function matrix $\{1/\mathcal{E}_{0,\psi_1^{(I)}} - H_0 + \epsilon\}$ is obtained as the inverse of the diagonal matrix $\mathcal{E}_{0,\psi_1^{(I)}} - H_0 = 1/E_{0,\psi_1^{(I)}} - H_0$. Since $\langle \psi_1^{(I)} | H_1 | \psi_3^{(I)} \rangle = 0$, it is not necessary to use the reduced Green’s function (which excludes degenerate states); the limit $\epsilon \to 0$ is finite for all elements in $h_{1,3}^{(I)}$. The matrix $h_{1,3}^{(I)}$ takes the form

$$h_{1,3}^{(I)} = \begin{pmatrix} \frac{5}{2} \mathcal{L} - \mathcal{H} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & -\frac{2\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \\ -\frac{2\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{5}{2} \mathcal{L} - \mathcal{H} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \\ \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{5}{2} \mathcal{L} - \mathcal{H} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \end{pmatrix},$$

with eigenvalues

$$\epsilon_{1,3}^{(I)\pm} = \frac{5}{2} \mathcal{L} - \mathcal{H} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \pm \frac{2\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}},$$

akin to the formula $C_0 = D_0 \pm M_0$ encountered in Ref. [2], with eigenvectors

$$|\psi_{1,3}^{(I)\pm}\rangle = \frac{1}{\sqrt{2}} (|\psi_1^{(I)}\rangle \pm |\psi_3^{(I)}\rangle).$$

Note that the eigenvalues $\epsilon_{1,3}^{(I)}$ only refer to the interaction energy; in order to obtain the eigenvalue of the total Hamiltonian $H$ given in Eq. (1), one has to add the unperturbed entry $2L - \frac{1}{2}\ell h$.

For the reference state $|\psi_2^{(II)}\rangle$, we have the degenerate state $|\psi_4^{(I)}\rangle = |(0,1,1)_A(0,1,0)_B\rangle$ [see Eq. (27)]. The matrix $h_{1,3}^{(I)}$ has the same structure as (but different elements from) $h_{1,3}^{(I)}$ given in Eq. (67) and we find [see Eq. (28)]

$$\epsilon_{2,4}^{(I)\pm} = \frac{5}{2} \mathcal{L} - \mathcal{H} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \pm \frac{2\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}}.$$

The expression for $\epsilon_{2,4}^{(I)\pm}$ is obtained from $\epsilon_{1,3}^{(I)\pm}$ by a sign change in $\mathcal{H}$. The eigenvectors are

$$|\psi_{2,4}^{(I)\pm}\rangle = \frac{1}{\sqrt{2}} (|\psi_2^{(II)}\rangle \pm |\psi_4^{(I)}\rangle).$$

The unperturbed energy for the states $|\psi_2^{(I)}\rangle$ and $|\psi_4^{(I)}\rangle$ is $2L - \frac{1}{2}\ell h$. Hence, in the transition $|\psi_2^{(I)}\rangle \rightarrow |\psi_2^{(II)}\rangle$, where both atoms are in $S$ states, one has only second-order van der Waals shifts. We recall that the transition is $|(0,0,0)_A(0,1,1)_B\rangle \rightarrow |(0,0,0)_A(0,1,1)_B\rangle$.

We also need to analyze the space with $F_S = 0$. The following states have the atom $A$ in the singlet hyperfine $2S$ level,

$$|\Psi_1^{(I)}\rangle = |(0,0,0)_A(0,0,0)_B\rangle,$$

$$|\Psi_2^{(I)}\rangle = |(0,0,0)_A(0,1,0)_B\rangle,$$

$$|\Psi_3^{(I)}\rangle = |(0,0,0)_A(1,0,0)_B\rangle,$$

$$|\Psi_4^{(I)}\rangle = |(0,0,0)_A(1,1,0)_B\rangle,$$

while the 2S hyperfine triplet state of atom $A$ is present in the states

$$|\Psi_3^{(II)}\rangle = |(0,0,0)_A(0,0,0)_B\rangle,$$

$$|\Psi_4^{(II)}\rangle = |(0,1,0)_A(0,0,0)_B\rangle,$$

$$|\Psi_5^{(II)}\rangle = |(0,0,0)_A(1,0,0)_B\rangle,$$

$$|\Psi_6^{(II)}\rangle = |(0,0,0)_A(1,1,0)_B\rangle.$$

The transitions in question are $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(II)}\rangle$, $|\Psi_2^{(I)}\rangle \rightarrow |\Psi_3^{(III)}\rangle$, $|\Psi_1^{(II)}\rangle \rightarrow |\Psi_4^{(II)}\rangle$, and $|\Psi_2^{(II)}\rangle \rightarrow |\Psi_5^{(III)}\rangle$. In view of the results

$$\langle \psi_4^{(II)} | H_{vdw} | \psi_3^{(III)}\rangle = \langle \psi_2^{(II)} | H_{vdw} | \psi_1^{(I)}\rangle = -2\mathcal{V},$$

and

$$\langle \psi_5^{(III)} | H_{vdw} | \psi_3^{(III)}\rangle = \langle \psi_5^{(II)} | H_{vdw} | \psi_2^{(II)}\rangle = -2\mathcal{V},$$

which we obtain from Eq. (47), both transitions $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(II)}\rangle$ and $|\Psi_2^{(II)}\rangle \rightarrow |\Psi_5^{(III)}\rangle$ undergo first-order van der Waals shifts. The spectator atom in these cases is in a $P$ state.

By contrast, for the transitions within the submanifold I, namely, $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(I)}\rangle$ and $|\Psi_2^{(I)}\rangle \rightarrow |\Psi_3^{(I)}\rangle$, the van der Waals shift only enters in second order. We first analyze the transition $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(I)}\rangle = |(0,0,0)_A(0,0,0)_B\rangle \rightarrow$
\(|(0,1,0)_A(0,0,0)_B\). There is no energetically degenerate state available for \(|\Psi^{(i)}_1\rangle\) and hence one obtains

\[
\Delta E_{\Psi_i}^{(n)} = \frac{6\gamma^2}{2\mathcal{L} - 5\mathcal{H}} + \frac{\gamma^2}{2\mathcal{L} - \mathcal{H}},
\]

(76)

from Eq. (45). The levels \(|\Psi^{(i)}_2\rangle\) and \(|\Psi^{(i)}_4\rangle\) are energetically degenerate with respect to their unperturbed energy \(2\mathcal{L} - \frac{3}{2}\mathcal{H}\), but there is no direct van der Waals coupling between them. The matrix \(\mathcal{H}_{2,4}^{(i)}\) is easily calculated in analogy to \(\mathcal{H}_{1,3}^{(i)}\) given in Eq. (67), the difference being that the effective interaction Hamiltonian (66) needs to be calculated with respect to \(H_{F_i=0}\), not \(H_{F_i=\pm 1}\). We find the eigenvalues

\[
E_{2,4}^{(i)\pm} = \frac{\gamma^2}{\mathcal{L} - \mathcal{H}} + \frac{4\gamma^2}{2\mathcal{L} - \mathcal{H}} \pm \frac{\gamma^2}{-\mathcal{L} + \mathcal{H}},
\]

(77)

with eigenvectors

\[
|\Psi_{2,4}^{(i)\pm}\rangle = \frac{1}{\sqrt{2}} (|\Psi_{2}^{(i)}\rangle \pm |\Psi_{4}^{(i)}\rangle),
\]

(78)

The last state whose van der Waals interaction energy needs to be analyzed is \(|\Psi^{(i)}_5\rangle\). This state forms a degenerate set together with the states \(|\Psi^{(i)}_3\rangle\) and \(|\Psi^{(i)}_6\rangle\),

\[
|\Psi^{(i)}_5\rangle = |(0,1,-1)_A(0,1,1)_B\rangle, \quad (79a)
\]

\[
|\Psi^{(i)}_3\rangle = |(0,1,0)_A(0,1,0)_B\rangle, \quad (79b)
\]

\[
|\Psi^{(i)}_6\rangle = |(0,1,1)_A(0,1,-1)_B\rangle, \quad (79c)
\]

which are both composed of two hyperfine triplet states. Under the additional approximation \(\mathcal{H} \ll \mathcal{L}\), one finds through Eq. (45) the Hamiltonian matrix

\[
\mathcal{H}_{3,5,6}^{(i)} \approx \begin{pmatrix}
4\gamma^2 & 2\gamma^2 & 0 \\
2\gamma^2 & 3\gamma^2 & 2\gamma^2 \\
0 & 2\gamma^2 & 4\gamma^2
\end{pmatrix}.
\]

(80)

The energy eigenvalues are

\[
E_{3,5,6}^{(i)(1)} \approx \frac{7 + \sqrt{33}}{2} \frac{\gamma^2}{\mathcal{L}},
\]

(81a)

\[
E_{3,5,6}^{(i)(2)} \approx \frac{4\gamma^2}{\mathcal{L}},
\]

(81b)

\[
E_{3,5,6}^{(i)(3)} \approx \frac{7 - \sqrt{33}}{2} \frac{\gamma^2}{\mathcal{L}},
\]

(81c)

with eigenvectors

\[
|\Psi_{3,5,6}^{(i)(1)}\rangle \approx \alpha_- |\Psi_3^{(i)}\rangle + \beta_- |\Psi_5^{(i)}\rangle + \alpha_+ |\Psi_6^{(i)}\rangle,
\]

(82a)

\[
|\Psi_{3,5,6}^{(i)(2)}\rangle \approx -\frac{1}{\sqrt{2}} |\Psi_3^{(i)}\rangle + \frac{1}{\sqrt{2}} |\Psi_6^{(i)}\rangle,
\]

(82b)

\[
|\Psi_{3,5,6}^{(i)(3)}\rangle \approx \alpha_+ |\Psi_3^{(i)}\rangle + \beta_+ |\Psi_5^{(i)}\rangle + \alpha_+ |\Psi_6^{(i)}\rangle,
\]

(82c)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, \quad |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, \quad |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, \quad |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, \quad |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, \quad |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, \quad |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, \quad |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, \quad |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, \quad |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, \quad |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, \quad |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, \quad |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, \quad |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)

\[|\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_1\rangle, |\Psi^{(i)}_2\rangle \rightarrow |\Psi^{(i)}_4\rangle, |\Psi^{(i)}_3\rangle \rightarrow |\Psi^{(i)}_2\rangle, |\Psi^{(i)}_4\rangle \rightarrow |\Psi^{(i)}_3\rangle, |\Psi^{(i)}_5\rangle \rightarrow |\Psi^{(i)}_6\rangle, |\Psi^{(i)}_7\rangle \rightarrow |\Psi^{(i)}_8\rangle.
\]

(84)
TABLE III. Energy shifts with the spectator atom in an $S$ state with $F = 0$: numerical values of the van der Waals shift to the energy difference $\Delta E^{(i)}$ between the symmetric superposition $(1/\sqrt{2})[|0,0,0\rangle_a (0,0,0)_B + |0,0,0\rangle_a (0,1,0)_B]$ and $|0,0,0\rangle_a (0,0,0)_B$ and of the energy difference $\Delta E^{(i)}$ between the antisymmetric superposition $(1/\sqrt{2})[(0,1,0)_a (0,0,0)_B] - [0,0,0\rangle_a (0,0,0)_B]$ and $|0,0,0\rangle_a (0,0,0)_B$ as a function of the interatomic separation $R$. The energies are given in units of the hyperfine splitting constant $\mathcal{H}$ defined by (15a).

| $R$  | $\Delta E^{(i)}_+$ | $\Delta E^{(i)}_-$ |
|------|-----------------|-----------------|
| $\infty$ | 0               | 0               |
| 750a₀ | $-4.7272 \times 10^{-2}$ | $1.9331 \times 10^{-2}$ |
| 500a₀ | $-2.9284$       | $-1.8165$       |
| 250a₀ | $2.4319 \times 10^{-1}$ | $-2.9082$       |

In Tables I–IV we provide some numerical values for the modification of the $2S$ hyperfine splitting, as a function of interatomic distance. The spectator atom is in an $S$ state for Tables I and III and in a $F_z$ manifold, while Tables III and IV treat (some of) the relevant transitions within the $F_z = 0$ manifold. The relevant transitions within the $F_z = -1$ manifold have the same transition energies as those within the $F_z = +1$ for all separations and the corresponding results can thusly be read from Tables I and II, with the substitutions

\[ |0,0,0\rangle_a (0,1,1)_B \rightarrow |0,0,0\rangle_a (0,1, -1)_B, \quad (85a) \]
\[ |0,1,0\rangle_a (0,1,1)_B \rightarrow |0,1,0\rangle_a (0,1, -1)_B, \quad (85b) \]
\[ |0,0,0\rangle_a (1,1,1)_B \rightarrow |0,0,0\rangle_a (1,1, -1)_B, \quad (85c) \]
\[ |0,1,0\rangle_a (1,1,1)_B \rightarrow |0,1,0\rangle_a (1,1, -1)_B. \quad (85d) \]

V. CONCLUSION

We analyzed the $(2S; 2S)$ interaction at the dipole-dipole level with respect to degenerate subspaces of the hyperfine-resolved unperturbed Hamiltonian. Full account was taken of the manifolds with $n = 2$ and $J = 1/2$ ($2S$ and $2P_{1/2}$ states), while the fine-structure splitting was supposed to be large against the van der Waals energy shifts (the $2P_{3/2}$ state was not included in the treatment).

We found that the total Hamiltonian given in Eq. (1) commutes with the magnetic projection $F_z$ of the total angular momentum of the two atoms. Hence, we could separate the manifolds with $n = 2$ and $J = 1/2$ into submanifolds with $F_z = +2,1,0, -1, -2$. In each of these manifolds, we could identify two irreducible submanifolds, uncoupled to one another because of the usual selection rules of atomic physics. In each of these submanifolds the Hamiltonian matrix could readily be evaluated [see Eqs. (19), (21), (28), (30), (45), (47), (A2), (A4), (A8), and (A11)]. Several degenerate subspaces with first-order van der Waals shifts [in the parameter $\gamma$ defined by (15c) and hence of order $1/R^3$] could be identified. The corresponding shifts are of course the relevant ones for large interatomic separations.

However, it should be noted that those hyperfine transitions where both atoms are in $S$ states actually undergo only second-order van der Waals shifts, where the energy shifts are given by expressions proportional to $\gamma^2/\alpha$, with $\gamma$ being defined in Eq. (15c). The relevant states and energy shifts are given in Eqs. (60a), (61a), (68), and (70) (for the $F_z = 1$ manifold). For the $F_z = 0$ manifold, we have the states given in Eqs. (72a), (73a), as well as (72b) and (73b), and the energy eigenvalues are provided in Eqs. (76), (77), and (81). The transitions are labeled $|\Psi^{(1)}_0\rangle \rightarrow |\Psi^{(0)}_1\rangle$ and $|\Psi^{(0)}_1\rangle \rightarrow |\Psi^{(0)}_0\rangle$ in Sec. IV. Experimentally, the states with both atoms in an $S$ level are most interesting, because they are the only ones that survive for an appreciable time in an atomic beam; $P$ states (and thus states with $P$ admixtures) decay with typical lifetimes on the order of $10^{-8}$s (see Ref. [15]).

The dipole-dipole interaction results in level crossings (see Figs. 4–10), which is a feature of the hyperfine-resolved treatment of the problem. We were able to confirm that,
Of particular phenomenological interest are the $2S$ hyperfine singlet to hyperfine triplet transitions with $|0(0,0)_{S1}\rangle \rightarrow |0(1,0)_{S1}\rangle$ with the spectator atom $B$ in a specific state. We found that all transitions with the spectator atom in a $P$ state undergo first-order van der Waals shifts (of order $1/R^5$), while the shift is of order $1/R^6$ if the spectator atom is in an $S$ state, that is, of second order in $V$. This is due to the fact that $2S-2S$ states are not coupled to energetically degenerate states (they are only coupled to $2P-2P$ states), while $2S-2P$ states are coupled to $2P-2S$ states with which they are energetically degenerate. In other words, these different behaviors are ultimately due to the selection rules. The spectator atom in a $P$ state, however, decays very fast to the ground state by one-photon emission, with a lifetime of approximately $1.60 \times 10^{-9}$ s [15], so, depending on the exact experimental setup, the large van der Waals interaction energy shifts of the $2S(F=0) \rightarrow 2S(F=1)$ hyperfine transition (with the spectator atom being in a $2P$ state) do not play a role in the analysis of atomic beam experiments. Otherwise, we observe that a spectator atom in a $P$ state induces larger frequency shifts, comparing, e.g., the shifts in Tables I and II for $R =$ 750$a_0$ and 500$a_0$.

As shown in Sec. IV, the precise numerical coefficients of the van der Waals shifts of the hyperfine singlet to hyperfine triplet transitions $|0(0,0)_{S1}\rangle \rightarrow |0(1,0)_{S1}\rangle$ depend on the symmetry of the wave function superposition of atoms $A$ and $B$ and cannot be uniquely expressed in terms of a specific state of the spectator atom $B$ alone; a symmetrization term is required [see the term prefixed with $\pm$ in Eqs. (68), (70), and (77); the same is true in the $F_z = -1$ subspace]. For spectroscopy, one essential piece of information to be derived from the results given in Eqs. (68), (70), (77), and (81) is that the van der Waals interaction energy shift for $2S(F=0) \rightarrow 2S(F=1)$ hyperfine transitions (with the spectator atom in a metastable $2S$ state) is of order $V^2/L$, where the parameters are defined in Eq. (15) [see also the remark in the text following Eq. (83)]. It is straightforward to see from Eq. (15c) that, for interatomic separation $R \sim 5 \times 10^7a_0 \approx 2.6 \times 10^{-5}$ m, the van der Waals shift reaches the experimental accuracy of the $2S$ hyperfine frequency measurements [1].

Expressed more conveniently, still in SI mksA units, the shift is of order

$$E_{2S2S}(R) \sim \frac{V^2}{L} \sim E_h\left(\frac{a_0}{R}\right)^6 \frac{E_h}{L},$$

where $E_h$ is the Hartree energy, $a_0$ is the Bohr radius, and $L \sim a^3E_h$ is the Lamb shift energy [see Eq. (3)].

A quick word is in order about how the present results can be transposed to hydrogenlike systems such as positronium and muonium. For positronium, the hierarchy between the fine structure, Lamb shift, and hyperfine structure is not the same as that for hydrogen, so the treatment used here, based on that hierarchy, does not apply. For muonium, on the other hand, our analysis remains relevant. Given that the reduced mass for the muonium system is very close to that of the hydrogen atom, the fine-structure and Lamb-shift-type splittings are almost identical to those of hydrogen. The hyperfine splitting is $(g_s/g_S)(m_p/m_\mu) \sim 3.2$ times larger than that of atomic hydrogen. Finally, given the close proximity of the reduced masses, muonium has a Bohr radius very close
to that of hydrogen, so the intensity of the dipole-dipole interactions will be essentially identical, for equal separations, between two hydrogen atoms and between two muonium atoms.

In this work as well as in the preceding paper [2], we have treated dipole-dipole interactions between atoms sitting in S states (though, in the present case, we had to treat the 2P1/2 state on the same footing as 2S, given their quasi-degeneracy). Finally, we should comment on the distance range for which our calculations remain applicable. We have used the nonretardation approximation in Eq. (2c). For the 2S-2S interaction via adjacent 2P1/2 states, retardation sets in when the phase of the atomic oscillation during a virtual (Lamb shift) transition changes appreciably on the time scale it takes light to travel the interatomic separation distance R, i.e., when

$$\frac{R}{c} \sim \frac{\hbar}{c} \tag{87}$$

We have $R \sim \hbar c/L$ when $R$ is on the order of the Lamb shift wavelength of about 30 cm. The nonretardation approximation thus is valid over all distance ranges of physical interest, for the (2S; 2S) system.

**ACKNOWLEDGMENTS**

The authors acknowledge insightful conversations with R. N. Lee. The high-precision experiments carried out at MPQ Garching under the guidance of Professor T. W. Hänisch have been a major motivation and inspiration for the current theoretical work. This project was supported by the National Science Foundation (Grant PHY-1403973).

**APPENDIX: FURTHER MANIFOLDS**

1. **Manifold $F_z = -1$**

We can identify two irreducible subspaces within the $F_z = -1$ manifold: subspace I composed of the states

$$|\psi_1^{(I)}\rangle = |(0,0,0)_A(0,1, -1)_B\rangle, \quad |\psi_2^{(I)}\rangle = |(0,1, -1)_A(0,0,0)_B\rangle, \quad |\psi_3^{(I)}\rangle = |(0,1, -1)_A(0,1,0)_B\rangle,$$

$$|\psi_4^{(I)}\rangle = |(0,1,0)_A(0,1, -1)_B\rangle, \quad |\psi_5^{(I)}\rangle = |(1,0,0)_A(1,1, -1)_B\rangle, \quad |\psi_6^{(I)}\rangle = |(1,1, -1)_A(0,1,0)_B\rangle,$$

$$|\psi_7^{(I)}\rangle = |(1,1, -1)_A(1,1,0)_B\rangle, \quad |\psi_8^{(I)}\rangle = |(1,1,0)_A(1,1, -1)_B\rangle. \tag{A1}$$

where the Hamiltonian matrix reads

$$H^{(I)}_{F_z=-1} = \begin{pmatrix}
2L - \frac{3}{2}H & 0 & 0 & 0 & 0 & V & V & 2V \\
0 & 2L - \frac{3}{2}H & 0 & 0 & V & 0 & 2V & V \\
0 & 0 & 2L + \frac{3}{2}H & 0 & 2V & 0 & V & 0 \\
0 & 0 & 2L + \frac{3}{2}H & 2V & V & 0 & 0 & 0 \\
V & 0 & 2V & V & 0 & 0 & 0 & \frac{1}{2}H \\
V & 2V & 0 & V & 0 & 0 & 0 & \frac{1}{2}H \\
2V & V & V & 0 & 0 & 0 & 0 & \frac{1}{2}H \\
\end{pmatrix}, \tag{A2}$$

and subspace II composed of the states

$$|\psi_1^{(II)}\rangle = |(0,0,0)_A(1,1, -1)_B\rangle, \quad |\psi_2^{(II)}\rangle = |(0,1, -1)_A(1,0,0)_B\rangle, \quad |\psi_3^{(II)}\rangle = |(0,1, -1)_A(1,1,0)_B\rangle,$$

$$|\psi_4^{(II)}\rangle = |(0,1,0)_A(1,1, -1)_B\rangle, \quad |\psi_5^{(II)}\rangle = |(1,0,0)_A(0,1, -1)_B\rangle, \quad |\psi_6^{(II)}\rangle = |(1,1, -1)_A(0,0,0)_B\rangle,$$

$$|\psi_7^{(II)}\rangle = |(1,1, -1)_A(0,1,0)_B\rangle, \quad |\psi_8^{(II)}\rangle = |(1,1,0)_A(0,1, -1)_B\rangle. \tag{A3}$$

where the Hamiltonian matrix reads

$$H^{(II)}_{F_z=-1} = \begin{pmatrix}
L - 2H & 0 & 0 & 0 & 0 & V & V & 2V \\
0 & L & 0 & 0 & V & 0 & 2V & V \\
0 & 0 & L + H & 0 & V & 2V & 0 & V \\
0 & 0 & L + H & 2V & V & 0 & 0 & 0 \\
V & 0 & 2V & V & 0 & L - 2H & 0 & 0 \\
V & 2V & 0 & V & 0 & L & 0 & 0 \\
2V & V & V & 0 & 0 & 0 & L + H & 0 \\
\end{pmatrix}, \tag{A4}$$

Surprisingly, the Hamiltonian matrix is a little different from the case with $F_z = +1$, even if one reorders the basis vectors accordingly. The energy eigenvalues of course are the same.
Again within subspace I there are no degenerate subspaces with nonzero coupling, while, in subspace II we can identify degenerate states coupled to each other. The analysis carried out in Sec. III B applies here if we make the following substitutions:

\[
|\psi_1^{(II)}\rangle \rightarrow |\psi_1^{(III)}\rangle, \quad |\psi_2^{(II)}\rangle \rightarrow |\psi_3^{(III)}\rangle, \quad |\psi_3^{(II)}\rangle \rightarrow |\psi_1^{(III)}\rangle, \quad |\psi_4^{(II)}\rangle \rightarrow |\psi_4^{(III)}\rangle, \quad |\psi_5^{(II)}\rangle \rightarrow |\psi_5^{(III)}\rangle, \quad |\psi_6^{(II)}\rangle \rightarrow |\psi_6^{(III)}\rangle, \quad |\psi_7^{(II)}\rangle \rightarrow |\psi_8^{(III)}\rangle, \quad |\psi_8^{(II)}\rangle \rightarrow |\psi_6^{(III)}\rangle. \tag{A5}
\]

so we need not go over the analysis of degenerate subspaces again. (Even when making this reordering, many off-diagonal terms have different signs in \(H_{F_z,+1}^{(II)}\) and \(H_{F_z,-1}^{(II)}\). However, only the couplings between nondegenerate states have different signs, while coupling between degenerate states remain identical. This latter point means that the analysis of Sec. III B also applies to \(H_{F_z,-1}^{(II)}\).) However, for the sake of completeness and clarity, in Figs. 9 and 10 we plot the evolution of the eigenvalues with respect to interatomic separation. Notice that the evolution of the energy eigenstates is identical to the eigenstates in the \(F_z = +1\) manifold.

2. Manifold \(F_z = -2\)

We can identify two irreducible subspaces within the \(F_z = +2\) manifold: subspace I composed of the states

\[
|\phi_1^{(II)}\rangle = |(0,1,-1)_A(0,1,-1)_B\rangle, \quad |\phi_2^{(II)}\rangle = |(1,1,-1)_A(1,1,-1)_B\rangle. \tag{A6}
\]

\[
|\phi_1^{(III)}\rangle = |(1,0,-1)_A(1,0,-1)_B\rangle, \quad |\phi_2^{(III)}\rangle = |(0,1,-1)_A(0,1,-1)_B\rangle. \tag{A7}
\]

where the Hamiltonian matrix reads

\[
H_{F_z=-2}^{(II)} = \begin{pmatrix} 2\mathcal{L} + \frac{3}{2}\mathcal{H} & -2\sqrt{2}\gamma & -\frac{1}{2}\gamma \\ -2\sqrt{2}\gamma & -\frac{1}{2}\gamma & 2\mathcal{L} + \frac{3}{2}\mathcal{H} \\ -\frac{1}{2}\gamma & 2\mathcal{L} + \frac{3}{2}\mathcal{H} & -2\sqrt{2}\gamma \end{pmatrix}. \tag{A8}
\]

and subspace II composed of the states

\[
|\phi_1^{(IV)}\rangle = |(0,1,-1)_A(1,1,-1)_B\rangle, \quad |\phi_2^{(IV)}\rangle = |(1,1,-1)_A(0,1,-1)_B\rangle. \tag{A9}
\]

where the Hamiltonian matrix reads

\[
H_{F_z=-2}^{(III)} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & -2\sqrt{2}\gamma \\ -2\sqrt{2}\gamma & -2\sqrt{2}\gamma \end{pmatrix}. \tag{A11}
\]

We do not repeat the analysis of the eigensystem and refer the reader to Sec. III A. The results given there are immediately transposed to the present case, by the simple substitution \(|\phi_1\rangle \rightarrow |\phi_1^{(II)}\rangle\). However, for the sake of completeness and clarity, in Fig. 11 we still plot the evolution of the eigenvalues with respect to interatomic separation. Notice that the evolution of the energy eigenstates is identical to the eigenstates in the \(F_z = +2\) manifold.

[1] N. Kolachevsky, A. Matveev, J. Alnis, C. G. Parthey, S. G. Karshenboim, and T. W. Hänsch, Measurement of the 2S Hyperfine Interval in Atomic Hydrogen, Phys. Rev. Lett. 102, 213002 (2009).

[2] C. M. Adhikari, V. Debiere, A. Matveev, N. Kolachevsky, and U. D. Jentschura, Long-range interactions of hydrogen atoms in excited states. I. 2S-1S interactions and Dirac-δ perturbations, preceding paper, Phys. Rev. A 95, 022703 (2017).

[3] S. Jonsell, A. Saenz, P. Froelich, R. Côté, and A. Dalgarno, Long-range interactions between two 2s excited hydrogen atoms, Phys. Rev. A 65, 042501 (2002).

[4] S. I. Simonsen, L. Kochbach, and J. P. Hansen, Long-range interactions and state characteristics of interacting Rydberg atoms, J. Phys. B 44, 165001 (2011).

[5] More accurately, the conclusions of Ref. [3] announce a future work where “the effects of spin-orbit coupling and the Lamb shift” would be taken into account. As far as we could find, no such work has been published yet.

[6] S. Ray, J. D. Lyons, and T. P. Das, Hyperfine pressure shift and van der Waals interactions. I. Hydrogen-helium system, Phys. Rev. 174, 104 (1968); 181, 465(E) (1969).

[7] S. Ray, J. D. Lyons, and T. P. Das, Hyperfine pressure shift and van der Waals interactions. II. Nitrogen-helium system, Phys. Rev. 174, 112 (1968); 181, 465(E) (1969).

[8] B. K. Rao and T. P. Das, Hyperfine pressure shift and van der Waals interactions. III. Temperature dependence, Phys. Rev. 185, 95 (1969).

[9] B. K. Rao and T. P. Das, Hyperfine pressure shift and van der Waals interactions. IV. Hydrogen–rare-gas systems, Phys. Rev. A 2, 1411 (1970).

[10] K. Pachucki, Relativistic corrections to the long-range interaction between closed-shell atoms, Phys. Rev. A 72, 062706 (2005).

[11] J. Itzykson and J. B. Zuber, Quantum Field Theory (McGraw-Hill, New York, 1980).

[12] S. R. Lundeen and F. M. Pipkin, Measurement of the Lamb Shift in Hydrogen, n = 2, Phys. Rev. Lett. 46, 232 (1981).

[13] U. D. Jentschura and V. A. Yerokhin, Quantum electrodynamic corrections to the hyperfine structure of excited 5 states, Phys. Rev. A 73, 062503 (2006).

[14] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, Singapore, 1988).

[15] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Springer, Berlin, 1957).