Long–Range Interactions for Hydrogen: $6P–1S$ and $6P–2S$ Systems

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The collisional shift of a transition constitutes an important systematic effect in high-precision spectroscopy. Accurate values for van der Waals interaction coefficients are required in order to evaluate the distance-dependent frequency shift. We here consider the interaction of excited hydrogen $6P$ atoms with metastable atoms (in the $2S$ state), in order to explore the influence of quasi-degenerate $2P$, and $6S$ states on the dipole-dipole interaction. The motivation for the calculation is given by planned high-precision measurements of the transition. Due to the presence of quasi-degenerate levels, one can use the non-retarded approximation for the interaction terms over wide distance ranges.

**Keywords:** Long-range interactions, quasi-degenerate states, hyperfine levels, matrix element, interatomic interactions

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I. INTRODUCTION

The long-range interaction of identical atoms, one of which is in an excited state, constitutes an interesting physical problem [1, 2]. This is mainly due to energetic degeneracies connected with the “exchange” of the states among the two atoms. For $nS–1S$ interactions (atomic hydrogen), this problem has recently been investigated in Ref. [3]. It was found that the interesting oscillatory $1/R^2$ long-range tails [4–10] are numerically suppressed and become dominant only for excessively large interatomic distances, in a region where the absolute magnitude of the interaction terms is numerically insignificant. Indeed, the Casimir–Polder regime of a $1/R^2$ interaction is never reached for systems with at least one atom in an excited state [9, 10].

A completely different situation is encountered when both atoms are in excited states, or, when the excited state is accessible from the ground state via an allowed electric-dipole transition [11]. In this case, one encounters nonvanishing first-order van der Waals interaction matrix elements instead of second-order effects. We recall that the van der Waals Hamiltonian for the interaction of atoms $A$ and $B$ reads as [in SI MKSA (meter-kilogram-second-Ampere) units],

$$H_{vdW} = \frac{1}{4\pi \epsilon_0} \beta_{ij} \frac{d_A d_B}{R^3}, \quad \beta_{ik} = \delta_{ik} - 3\frac{R_i R_k}{R^2},$$  

(1)

where $\vec{R} = \vec{R}_A - \vec{R}_B$, $R = |\vec{R}|$, $\vec{R} = \vec{R}/R$. Furthermore, $\vec{d}_A = e \vec{r}_A$ is the electric dipole moment operator for atom $A$ and $\vec{d}_B$ is the same for atom $B$ ($\vec{r}_i$ with $i = A, B$ is the electron coordinate relative to the atomic nucleus). States of the form, e.g., $|6P_A 1S_B\rangle$ are energetically degenerate with respect to states of the form $|1S_A 6P_B\rangle$, and are coupled by the van der Waals Hamiltonian. For the $2S–2P$ system, this problem has been analyzed in Ref. [12], on the basis of nonrelativistic Schrödinger theory. However, in order to evaluate the distance-dependent frequency shift of hyperfine-resolved transitions, one has to invoke a more sophisticated analysis, which has recently been performed in Ref. [11]. A complete rediagonalization of the total Hamiltonian, comprising Lamb shift, fine-structure, and hyperfine effects, becomes necessary.

In order to analyze the problem, one has to define a quantization axis, which we choose as the line of separation of the two atoms. This brings the van der Waals Hamiltonian into the form

$$H_{vdW} = \frac{e^2}{4\pi \epsilon_0} \frac{x_A x_B + y_A y_B - 2 z_A z_B}{R^3}.$$  

(2)

We should add that the interaction remains non-retarded over very wide distance ranges, commensurate with the fine-structure and Lamb shift transition wavelengths in the quasi-degenerate system.

Here, we engage in the endeavor of evaluating long-range interactions for the hydrogen $6P–1S$ and $6P–2S$ systems. In the latter case, we find it necessary to include, in our basis of states, all $2S$, $2P$, $6S$ as well as $6P_{3/2}$ and $6P_{5/2}$ hyperfine-resolved atomic levels. The calculations are motivated, in part, by the prospect of a future high-precision measurement of the $2S–6P$ transition in atomic hydrogen [13], to supplement ongoing efforts for a resolution of the proton charge radius puzzle [14–16] (see the recent work [17] for a discussion of systematic effects in $4P–2S$ hydrogen systems, which are closely related to the systems under investigation here).
II. GENERAL FORMALISM

The total Hamiltonian is

\[ H = H_{\text{LS}, A} + H_{\text{LS}, B} + H_{\text{HFS}, A} + H_{\text{HFS}, B} + H_{\text{FS}, A} + H_{\text{FS}, B} + H_{\text{vdW}}, \]  

(3)

where \( H_{\text{LS}} \) stands for the Lamb shift, \( H_{\text{HFS}} \) describes hyperfine effects, and \( H_{\text{FS}} \) describes fine-structure splittings. These Hamiltonians have to be added for atoms \( A \) and \( B \),

\[
H_{\text{HFS},i} = \frac{\mu_0}{4\pi} \mu_B \mu_N g_p g_d \left[ \frac{8\pi}{3} \vec{S}_i \cdot \vec{I}_i \delta^{(3)}(\vec{r}_i) + \frac{3(\vec{S}_i \cdot \vec{r}_i)(\vec{I}_i \cdot \vec{r}_i) - \vec{S}_i \cdot \vec{I}_i}{|\vec{r}_i|^5} |\vec{r}_i|^2 + \frac{\vec{L}_i \cdot \vec{I}_i}{|\vec{r}_i|^3} \right],
\]

(4a)

\[
H_{\text{LS},i} = \frac{4 \hbar^3 \alpha^2}{3 m_e^2 c^2} \left( \frac{\hbar}{m_e c} \right)^3 \ln (\alpha^{-2}) \delta^{(3)}(\vec{r}_i),
\]

(4b)

\[
H_{\text{FS},i} = -\frac{\vec{p}_i^4}{8m_e^2 c^2} + \frac{\pi \hbar^3 \alpha}{2m_e^2 c} \delta^{(3)}(\vec{r}_i) + \frac{\hbar^3 \alpha}{4m_e^2 c^3} \vec{g} \cdot \vec{L}.
\]

(4c)

Here, \( i = A, B \) denotes either atom, while \( \alpha \) is the fine-structure constant and \( m_e \) is the electron mass. The momentum operators for the atomic electrons are denoted as \( \vec{p}_i \), while \( \vec{L}_i \) is the orbital angular momentum operator. The (dimensionless) spin operator for electron \( i \) is \( \vec{S}_i \), while \( \vec{I}_i \) is the spin operator for proton \( i \). The CODATA (Committee on Data for Science and Technology) values (see Ref. \([18]\)) for the electronic and protonic \( g \) factors are \( g_e \approx 2.002319 \) and \( g_p \approx 5.585695 \). The Bohr magneton is \( \mu_B \approx 9.274010 \times 10^{-24} \text{Am}^2 \), while \( \mu_N \approx 5.050784 \times 10^{-27} \text{Am}^2 \) is the nuclear magneton. The expression for \( H_{\text{LS}} \) in Eq. (4b) follows the Welton approximation \([19]\), which is sufficient for our purposes of calculating long-range interaction coefficients.

For the \( 6P-1S \) and \( 6P-2S \) systems, we define the zero of the energy as the sum of the Dirac energies of the \( 1S \) and \( 6P_{1/2} \) states, and to the sum of the \( 2S \) and \( 6P_{1/2} \) states, respectively. The zero point of the energy excludes both Lamb shift as well as hyperfine effects; in the following, we add the Lamb shift energy to the \( 2S \) states but leave the \( P \) states untouched by Lamb shift effects. So, our definition of the zero point of the energy corresponds to the hyperfine centroid of the \( |(6P_{1/2},A)(1S)_B) \rangle \) states, and to the hyperfine centroid of the \( |(6P_{1/2},A)(2P_{1/2})_B) \rangle \) system, respectively. The fine-structure energy is added for the \( 6P_{3/2} \) states.

The matrix elements of the van der Waals Hamiltonian have to be calculated in a hyperfine-resolved basis. Let us take the \( 6P_{1/2}-1S \) interaction as an example, and exclude the \( 6P_{3/2} \) states for the time being. The unperturbed states carry the quantum numbers

\[
\begin{align*}
1S_{1/2}(F = 0) : n = 1, \ell = 0, J = \frac{1}{2}, F = 0, \\
1S_{1/2}(F = 1) : n = 1, \ell = 0, J = \frac{1}{2}, F = 1, \\
6P_{1/2}(F = 0) : n = 6, \ell = 1, J = \frac{1}{2}, F = 0, \\
6P_{1/2}(F = 1) : n = 6, \ell = 1, J = \frac{1}{2}, F = 1.
\end{align*}
\]

(5a), (5b), (5c), (5d)

Here, the quantum numbers have their usual meaning, i.e., \( n \) is the principal quantum number, while \( \ell, J, \) and \( F \), respectively, are the electronic orbital angular momentum, the total (orbital+spin) electronic angular momentum, and the total (electronic+protonic) atomic angular momentum. The multiplicity of the hyperfine-resolved state is \( g_F = 2F + 1 \).

After adding the electron orbital and spin angular momenta, and the nuclear (proton) spin \(|\pm\rangle_p\), the four \( 1S \) states within the hyperfine manifold are given by

\[
\begin{align*}
|n = 1, \ell = 0, J = \frac{1}{2}, F = 0, F_z = 0 \rangle &= \frac{|+\rangle_p |(-)_e - |(-)_e \rangle_p |+\rangle_e}{\sqrt{2}} |1, 0, 0\rangle_e, \\
|n = 1, \ell = 0, J = \frac{1}{2}, F = 1, F_z = 0 \rangle &= \frac{|+\rangle_p |(-)_e + |(-)_e \rangle_p |+\rangle_e}{\sqrt{2}} |1, 0, 0\rangle_e, \\
|n = 1, \ell = 0, J = \frac{1}{2}, F = 1, F_z = \pm 1 \rangle &= |\pm\rangle_p |\pm\rangle_e |1, 0, 0\rangle_e,
\end{align*}
\]

(6a), (6b), (6c)
TABLE I. Multiplicities in the $6P_{1/2}$–$6P_{3/2}$–$1S$ system. One might wonder why $F_z = \pm 3$ is possible for $F = 2$. The answer is that $F = 2$ here refers to the total angular momentum (electron orbital plus electron spin plus nuclear spin) of one of the atoms, while $F_z = \pm 3$ refers to the angular momentum projection of the sum of the total angular momenta of both electrons.

| $F_z = 0$ | $F_z = 1$ | $F_z = \pm 2$ | $F_z = \pm 3$ |
|------------|------------|---------------|---------------|
| $(J = \frac{1}{2}, F = 2)$ | 8 | 8 | 6 | 2 |
| $(J = \frac{1}{2}, F = 1)$ | 8 | 6 | 2 | 0 |
| $(J = \frac{3}{2})$ | 16 | 14 | 8 | 2 |
| $(J = \frac{3}{2}, F = 1)$ | 8 | 6 | 2 | 0 |
| $(J = \frac{3}{2}, F = 0)$ | 4 | 2 | 0 | 0 |
| $(J = 1/2)$ | 12 | 8 | 2 | 0 |
| $(J = \frac{1}{2}) + (J = \frac{3}{2})$ | 28 | 22 | 10 | 2 |

while the hyperfine singlet $6P_{1/2}$ ($F = 0$) state is given by

$$
\left| n = 6, \ell = 1, J = \frac{1}{2}, F = 0, F_z = 0 \right> = \frac{1}{\sqrt{3}} \left[ + \right]_p \left[ + \right]_e |6, 1, -1\rangle_e - \frac{1}{\sqrt{6}} \left[ + \right]_p \left[ - \right]_e |6, 1, 0\rangle_e + \frac{1}{\sqrt{3}} \left[ - \right]_p \left[ - \right]_e |6, 1, 1\rangle_e - \frac{1}{\sqrt{6}} \left[ - \right]_p \left[ + \right]_e |6, 1, 0\rangle_e .
$$

The hyperfine triplet states in the $6P$ manifold read as follows,

$$
\left| n = 6, \ell = 1, J = \frac{1}{2}, F = 1, F_z = 0 \right> = - \frac{1}{\sqrt{3}} \left[ + \right]_p \left[ + \right]_e |6, 1, -1\rangle_e + \frac{1}{\sqrt{6}} \left[ + \right]_p \left[ - \right]_e |6, 1, 0\rangle_e + \frac{1}{\sqrt{3}} \left[ - \right]_p \left[ - \right]_e |6, 1, 1\rangle_e - \frac{1}{\sqrt{6}} \left[ - \right]_p \left[ + \right]_e |6, 1, 0\rangle_e ,
$$

and

$$
\left| n = 6, \ell = 1, J = \frac{1}{2}, F = 1, F_z = \pm 1 \right> = \mp \frac{1}{\sqrt{3}} \left[ \pm \right]_p \left[ \pm \right]_e |6, 1, 0\rangle_e - \sqrt{2} \left[ \mp \right]_e |6, 1, \pm 1\rangle_e .
$$

Here and in the following, we use the notation $|n, \ell, J, F, F_z\rangle$ for the unperturbed states with the specified quantum numbers.

III. $6P$–$1S$ INTERACTION

A. Orientation

We need to diagonalize the Hamiltonian given in Eq. (3), in a quasi-degenerate basis, composed of two atoms, the first being in a $6P$ state, the second being in a substate of the $1S$ hyperfine manifold. Retardation does not need to be considered. For the manifolds composed of the $(6P)_A(1S)_B$ and $(1S)_A(6P)_B$ states, with all hyperfine levels resolved, we obtain the following total multiplicities when all $6P_{1/2}$ and $6P_{3/2}$ states are added into the basis (see also Table 1): $g(F_z = \pm 3) = 2$, $g(F_z = \pm 2) = 10$, $g(F_z = \pm 1) = 22$, $g(F_z = 0) = 28$. The multiplicities are the sums of the multiplicities in the $6P_{3/2}$–$1S$ and the $6P_{1/2}$–$1S$ system.

We now turn to the computation of the matrix elements of the total Hamiltonian (3) in the space spanned by the two-atom states which are product states built from any two states of the types given in Eqs. (6) (for the $1S$ states) and (9) (for the $6P_{1/2}$ states), as well as the $6P_{3/2}$ states. Matrix elements of the van der Waals interaction
Hamiltonian are determined with the help of a computer symbolic program [20]. We define the parameters

\[
\mathcal{H} \equiv \frac{\alpha^4}{18} g_p \frac{m_e}{m_p} m_e c^2 = h 59.21498 \text{ MHz}, \quad \mathcal{L}_2 \equiv h 1057.845(9) \text{ MHz},
\]

\[
\mathcal{L}_6 \equiv h \times \frac{1}{27} \times 1057.845(9) \text{ MHz}, \quad \mathcal{F} \equiv \frac{\alpha^4 m_e c^2}{864} = h 405.529 \text{ MHz},
\]

\[
\mathcal{V} \equiv \frac{3 c^2}{4 \pi \varepsilon_0 R^3} = \frac{3 E_h}{\rho^3}, \quad \mathcal{W} = \frac{215 \times 3^5 \times 5^7 c^2}{4 \pi \varepsilon_0 R^3} = \frac{215 \times 3^5 \times 5^7 E_h}{717 \rho^3},
\]

where \( R = a_0 \rho \), and \( a_0 \) is the Bohr radius. \( E_h = \alpha^2 m_e c^2 \) is the Hartree energy. Our scale \( \mathcal{H} \) is equal to one-third of the hyperfine splitting of the 2S state [21], while \( \mathcal{L}_2 \) is the 2S-2P_{1/2} Lamb shift [22], and \( \mathcal{L}_6 \) approximates the 6S-6P_{1/2} Lamb shift. The natural scale for the constants \( \mathcal{H} \) and \( \mathcal{L} \) is an energy of order \( \alpha^3 E_h \). Hence, we write

\[
\mathcal{H} = \alpha^3 E_h C_\mathcal{H}, \quad \mathcal{L}_n = \alpha^3 E_h C_{\mathcal{L}, n}, \quad \mathcal{F} = \alpha^3 E_h C_F,
\]

where we set \( C_\mathcal{H} = 0.0231596, C_F = 0.158606 \) and \( C_{\mathcal{L}, 2} = 27 C_{\mathcal{L}, 6} = 0.413734 \). Typical second-order energy shifts encountered in our calculations may be expressed as

\[
\frac{\mathcal{V}^2}{T_1 \mathcal{H} + T_2 \mathcal{L}_n + T_3 \mathcal{F}} = \frac{9}{T_1 C_\mathcal{H} + T_2 C_{\mathcal{L}, n} + T_3 C_F} \frac{E_h}{\alpha^3 \rho^6},
\]

where \( T_1, T_2 \) and \( T_3 \) are numerical coefficients of order unity.

Particular attention should be devoted to mixing terms of the Hamiltonian, in the space of the 6P_{1/2} and 6P_{3/2} states, within the \( F = 1 \) manifolds, with the mixing matrix element being given by \( \langle 6P_{F=1}^F | H_{\text{HFS}} | 6P_{F=1}^{F'} \rangle = X \) (see Ref. [23] for an outline of the calculation).

In order to illustrate the mixing term, we temporarily restrict the discussion here to one atom only, say, atom \( A \), omitting the subscript on \( H_{\text{HFS}} \equiv H_{\text{HFS}, A} \). For the two states, with the same magnetic projection \( F_z = \mu \), we consider the basis of states

\[
|a\rangle = |6P_{F=1,1}^Z (F_z = \mu)\rangle = |6, 1, \frac{1}{2}, 1, \mu\rangle, \quad |b\rangle = |6P_{3/2}^Z (F_z = \mu)\rangle = |6, 1, \frac{3}{2}, 1, \mu\rangle, \quad \mu = -1, 0, 1.
\]

The matrix of the Hamiltonian \( H_{\text{HFS}} + H_{\text{FS}} \) in the basis \(|a\rangle, |b\rangle\) is evaluated as

\[
H_{\text{HFS+FS}} = \begin{pmatrix} D & X \\ X & -D + \mathcal{F} \end{pmatrix}, \quad D = g_p \frac{\alpha^4 m_e^2 c^2}{1944 m_p}, \quad X = -g_p \frac{\alpha^4 m_e^2 c^2}{3888 \sqrt{2} m_p}.
\]

Here, \( g_p \) is the proton \( g \) factor, while \( D \) is a diagonal matrix element, and \( X \) is the off-diagonal element given above. The eigenvalues of \( H_{\text{HFS+FS}}^Z \) are given by

\[
\mathcal{E}_+ = -D + \mathcal{F} + \frac{X^2}{\mathcal{F} - 2D} + \mathcal{O}(X^4), \quad \mathcal{E}_- = D - \frac{X^2}{\mathcal{F} - 2D} + \mathcal{O}(X^4).
\]

The second-order shift in the eigenvalues, \( \Delta = X^2 / (\mathcal{F} - 2D) \), is numerically equal to \( 1.412129 \times 10^{-13} E_h \), where \( E_h = \alpha^2 m_e c^2 \) is the Hartree energy. For simplicity, we thus define the parameter

\[
\Delta = 1.412129 \times 10^{-14}, \quad \frac{\Delta E_h}{h} = 92.9137 \text{ Hz}.
\]

The hyperfine splitting energy between 6P_{1/2}(F = 1) and 6P_{1/2}(F = 0) states thus amounts to \( \mathcal{H}/27 \), while between 6P_{3/2}(F = 2) and 6P_{3/2}(F = 1) states, it is \( 2\mathcal{H}/135 \). The 1S-state hyperfine splitting is \( 24 \mathcal{H} \). For the product state of atoms \( A \) and \( B \), we shall use the notation \(|\langle n_A, \ell_A, J_A, F_A, F_z, A \rangle, n_B, \ell_B, J_B, F_B, F_z, B \rangle\rangle \), which summarizes the quantum numbers of both atoms.

### B. States with \( F_z = 3 \)

The atomic states can be classified according to the quantum number \( F_z \); the \( z \) component of the total angular momentum commutes [11] with the total Hamiltonian given in Eq. (3). Within the 6P_{1/2}–6P_{3/2}–1S_{1/2} system, the states in the manifold \( F_z = 3 \) are given as follows,

\[
|\phi_1\rangle = |(1, 0, \frac{1}{2}, 1, 1), A(6, 1, \frac{3}{2}, 2, 2), B\rangle, \quad |\phi_2\rangle = |(6, 1, \frac{3}{2}, 2, 2), A(1, 0, \frac{1}{2}, 1, 1), B\rangle.
\]
Here, we have ordered the basis vectors in ascending order of the quantum numbers, starting from the last member in the list. The Hamiltonian matrix evaluates to

\[ H_{F_s=3} = \left( \begin{array}{cc} \frac{1081}{180} \mathcal{H} + \mathcal{F} & \frac{2^{15} \times 3^5 \times 5^7}{7^{17}} \mathcal{V} \\ \frac{2^{15} \times 3^5 \times 5^7}{7^{17}} \mathcal{V} & \frac{1081}{180} \mathcal{H} + \mathcal{F} \end{array} \right). \]  

(18)

We have subtracted the sum of the Dirac energies of the 1S and 6P_{1/2} hyperfine centroids, and the 1S Lamb shift is absorbed in the definition of the 1S hyperfine centroid energy, as outlined in Sec. II. The energy eigenvalues and eigenvectors corresponding to \( H_{F_s=3} \) are given as follows,

\[ E_{\pm} = \frac{1081}{180} \mathcal{H} + \mathcal{F} \mp \frac{2^{15} \times 3^5 \times 5^7}{7^{17}} \mathcal{V}, \quad |u_{\pm}\rangle = \frac{1}{\sqrt{2}} (|\phi_1\rangle \pm |\phi_2\rangle). \]  

(19)

The average of the first-order shifts (linear in \( \mathcal{V} \)) vanishes; there are no second-order shifts (quadratic in \( \mathcal{V} \)).

C. Manifold \( F_s = 2 \)

We order the 10 states in this manifold in order of ascending quantum numbers,

\[ |\psi_1\rangle = |(1, 0, \frac{1}{2}, 0, 0)_{A} (6, 1, \frac{3}{2}, 2, 2)_{B}\rangle, \quad |\psi_2\rangle = |(1, 0, \frac{1}{2}, 1, 0)_{A} (6, 1, \frac{3}{2}, 2, 2)_{B}\rangle, \]  

(20a)

\[ |\psi_3\rangle = |(1, 0, \frac{1}{2}, 1, 1)_{A} (6, 1, \frac{1}{2}, 1, 1)_{B}\rangle, \quad |\psi_4\rangle = |(1, 0, \frac{1}{2}, 1, 1)_{A} (6, 1, \frac{1}{2}, 1, 1)_{B}\rangle, \]  

(20b)

\[ |\psi_5\rangle = |(1, 0, \frac{1}{2}, 1, 1)_{A} (6, 1, \frac{3}{2}, 2, 1)_{B}\rangle, \quad |\psi_6\rangle = |(6, 1, \frac{1}{2}, 1, 1)_{A} (1, 0, \frac{1}{2}, 1, 1)_{B}\rangle, \]  

(20c)

\[ |\psi_7\rangle = |(6, 1, \frac{3}{2}, 1, 1)_{A} (1, 0, \frac{1}{2}, 1, 1)_{B}\rangle, \quad |\psi_8\rangle = |(6, 1, \frac{3}{2}, 2, 1)_{A} (1, 0, \frac{1}{2}, 1, 1)_{B}\rangle, \]  

(20d)

\[ |\psi_9\rangle = |(6, 1, \frac{3}{2}, 2, 2)_{A} (1, 0, \frac{1}{2}, 0, 0)_{B}\rangle, \quad |\psi_{10}\rangle = |(6, 1, \frac{3}{2}, 2, 2)_{A} (1, 0, \frac{1}{2}, 1, 0)_{B}\rangle. \]  

(20e)

States \( |\psi_3\rangle \) and \( |\psi_6\rangle \) are 6P_{1/2} states, the rest are 6P_{3/2} states (see also the multiplicities indicated in Table I). Among the 6P_{3/2} states, \( |\psi_4\rangle \) and \( |\psi_7\rangle \) have \( F = 1 \), the rest have \( F = 2 \). The Hamiltonian matrix \( \mathcal{H} = H_{F_s=2} \) is 10-dimensional,

\[ \mathcal{H} = \begin{pmatrix} \mathcal{F} - \frac{3259 \mathcal{H}}{180} & 0 & 0 & 0 & 0 & -\sqrt{3}W & \sqrt{5}W & 0 & 0 & 0 \\ 1081\mathcal{H} & 0 & 0 & 0 & 0 & \frac{2}{\sqrt{216}^2} & \frac{2}{\sqrt{216}^2} & 0 & 0 & 0 \\ 0 & 0 & \frac{649\mathcal{H}}{180} & \frac{647\mathcal{H}}{180} & \mathcal{F} & 0 & -\sqrt{2}W & -\sqrt{2}W & -\sqrt{3}W & -\sqrt{5}W \\ 0 & 0 & 0 & \frac{2}{\sqrt{216}^2} & \frac{2}{\sqrt{216}^2} & \frac{2}{\sqrt{216}^2} & \frac{2}{\sqrt{216}^2} & 0 & 0 & 0 \\ -\sqrt{3}W & \sqrt{5}W & -\sqrt{2}W & -\sqrt{2}W & -\sqrt{2}W & -\sqrt{3}W & \sqrt{3}W & 0 & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} \\ \sqrt{5}W & \sqrt{5}W & \sqrt{5}W & \sqrt{5}W & \sqrt{3}W & \sqrt{3}W & 0 & 0 & 0 & 0 \\ -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & -\frac{2}{\sqrt{216}^2} & 0 & 0 & 0 \\ \sqrt{3}W & \sqrt{3}W & \sqrt{3}W & \sqrt{3}W & \sqrt{3}W & \sqrt{3}W & \sqrt{3}W & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{F} - \frac{3259 \mathcal{H}}{180} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{F} - \frac{3259 \mathcal{H}}{180} \end{pmatrix}. \]  

(21)

An adjacency graph [11, 24] shows that the matrix is irreducible, which in particular implies that there are no hidden symmetries in the Hamiltonian matrix \( H_{F_s=2} \) which would otherwise lead to a further decomposition into irreducible submatrices.

Of particular interest are second-order van der Waals shifts, within the \( (F_s = 2) \) manifold. We have the quantum number \( J, F, \) and \( F_s \) at our disposal. A weighted average over the possible values of \( F \), namely, \( F = 1 \) and \( F = 2 \),
TABLE II. Second-order van der Waals shifts for $6P_J$ hydrogen atoms interacting with ground-state hydrogen atoms. Entries marked with a long hyphen (--) indicate unphysical combinations of $F$ and $F_z$ values. We denote the scaled interatomic distance by $\rho = R/a_0$ and give all energy shifts in atomic units, i.e., in units of the Hartree energy $E_h = \alpha^2 m_e c^2$. Recall that $F_z = F_{z,A} + F_{z,B}$. The results still involve an averaging over the quantum numbers of the spectator atom; e.g., the result for $J = 3/2$, $F = 2$, and $F_z = 2$ involves and averaging over the second-order shifts of the states $|\Psi_0\rangle$ and $|\Psi_{10}\rangle$ given in Eq. (20e). We define $\Delta$ in Eq. (16).

| $F_z$ | $F_z = 0$ | $F_z = \pm 1$ | $F_z = \pm 2$ | $F_z = \pm 3$ |
|-------|-----------|----------------|----------------|----------------|
| $(J = 3/2, F = 2)$ | $1.07795 \times 10^5$ | $8.75949 \times 10^4$ | $8.06860 \times 10^4$ | $0$ |
| $(J = 3/2, F = 1)$ | $\Delta - 1.06590 \times 10^5$ | $\Delta - 1.15780 \times 10^5$ | $\Delta - 2.40919 \times 10^5$ | $-\Delta - 1.13849 \times 10^3$ |
| $(J = 1/2, F = 1)$ | $-\Delta + 9.99477 \times 10^3$ | $-\Delta + 3.52047 \times 10^4$ | $-\Delta - 1.13849 \times 10^3$ | $-\Delta - 1.13849 \times 10^3$ |
| $(J = 1/2, F = 0)$ | $-2.23999 \times 10^4$ | $1.08654 \times 10^5$ | $-\Delta - 1.13849 \times 10^3$ | $-\Delta - 1.13849 \times 10^3$ |

keeping $J = 1/2, 3/2$ and $F_z = \pm 2$ fixed, leads to the result

$$\langle E(6P_{1/2}, F_z = 2) \rangle_F = \left( -\Delta - \frac{1.13849 \times 10^3}{\rho^6} \right) E_h , \quad (22a)$$

$$\langle E(6P_{3/2}, F_z = 2) \rangle_F = \left( \frac{1}{4} \Delta + \frac{2.84623 \times 10^2}{\rho^6} \right) E_h . \quad (22b)$$

The weighted average vanishes,

$$2 \langle E(6P_{1/2}, F_z = 2) \rangle_F + 8 \langle E(6P_{3/2}, F_z = 2) \rangle_F = 0 . \quad (23)$$

Observe that the $\Delta$ term, which is the HFS–FS (hyperfine-structurefinestructure) mixing term, only occurs for the $F = 1$ states, and vanishes for the $F = 2$ states (see also the entries in Table II). Furthermore, observe that there are no $6P_{1/2}$ states with $F = 0$ in the manifold $F_z = 2$, because of angular momentum selection rules (we have $F_z = 2$ and hence $F \geq 1$ for all states in the manifold).

D. States with $F_z = 1, 0, -1, -2, -3$

We would like to list some of the 22 states in the $F_z = 1$ manifold in order of ascending quantum numbers, $|\Psi_1\rangle = |(1, 0, 1/2, 0, 0), A(6, 1, 1/2, 1, 1/2)\rangle$, $|\Psi_2\rangle \equiv |(1, 0, 1/2, 0, 0), A(6, 1, 1/2, 1, 1/2)\rangle$, $|\Psi_3\rangle = |(1, 0, 1/2, 0, 0), A(6, 1, 1/2, 1, 1/2)\rangle$, $|\Psi_4\rangle = |(1, 0, 1/2, 1, -1), A(6, 1, 1/2, 1, 1/2)\rangle$, and so on, up to $|\Psi_{23}\rangle = |(6, 1, 1/2, 2, 1), A(1, 0, 1/2, 1), 0\rangle$ and $|\Psi_{24}\rangle = |(6, 1, 1/2, 2, 1), A(1, 0, 1/2, 1), 0\rangle$. We refer to Table II for the averaged second-order van der Waals shifts in the $F_z = 0, F_z = +1, F_z = +2, F_z = +3$ manifolds. The Hamiltonian matrix for $F_z = -3$ manifold is identical to that of $F_z = +3$. The $F_z = -2$ manifold has identical diagonal entries to that of $F_z = +2$ while some off-diagonal entries are different. The same is true of the $F_z = \pm 1$ manifolds. Yet, we have checked that the distance-dependent Born–Oppenheimer energy curves for $F_z = \pm 2$ and $F_z = \pm 1$ are alike.
E. Second–Order Energy Shifts

As a function of $J$ and $F$, within the $6P$–$1S$ system, a global averaging over all the states with different individual magnetic quantum numbers leads to the results

$$\langle E(6P_{1/2}, F = 0) \rangle_{F_z} = -\frac{6.552.65 \times 10^4}{\rho^6} E_h ,$$  
(24a)

$$\langle E(6P_{1/2}, F = 1) \rangle_{F_z} = \left(-\Delta + \frac{2.074.42 \times 10^4}{\rho^6}\right) E_h ,$$  
(24b)

$$\langle E(6P_{3/2}, F = 1) \rangle_{F_z} = \left(\Delta - \frac{1.335.73 \times 10^5}{\rho^6}\right) E_h ,$$  
(24c)

$$\langle E(6P_{3/2}, F = 2) \rangle_{F_z} = \frac{8.080.28 \times 10^4}{\rho^6} E_h .$$  
(24d)

Comparing to Table II, this average would correspond to an average over the entries in the different rows, for given $F$ (for the multiplicities, see Table I).

One can also average over the possible orientations of $F$, namely, $F = J \pm \frac{1}{2}$, for given $J$ and $F_z$. This amounts to an averaging over the first two entries in the columns, and the third and fourth entry in every column, of Table II. The results are

$$\langle E(6P_{1/2}, F_z = 0) \rangle_F = \left(-\frac{2}{3} \Delta - \frac{8.034.54 \times 10^2}{\rho^6}\right) E_h ,$$  
(25a)

$$\langle E(6P_{1/2}, F_z = \pm 1) \rangle_F = \left(\frac{3}{4} \Delta - \frac{7.597.33 \times 10^2}{\rho^6}\right) E_h ,$$  
(25b)

$$\langle E(6P_{1/2}, F_z = \pm 2) \rangle_F = \left(-\Delta - \frac{1.138.49 \times 10^3}{\rho^6}\right) E_h ,$$  
(25c)

and

$$\langle E(6P_{3/2}, F_z = 0) \rangle_F = \left(\frac{1}{2} \Delta + \frac{6.025.91 \times 10^2}{\rho^6}\right) E_h ,$$  
(26a)

$$\langle E(6P_{3/2}, F_z = \pm 1) \rangle_F = \left(\frac{3}{4} \Delta + \frac{4.341.33 \times 10^2}{\rho^6}\right) E_h ,$$  
(26b)

$$\langle E(6P_{3/2}, F_z = \pm 2) \rangle_F = \left(\frac{1}{4} \Delta + \frac{2.846.23 \times 10^2}{\rho^6}\right) E_h ,$$  
(26c)

$$\langle E(6P_{3/2}, F_z = \pm 3) \rangle_F = 0 .$$  
(26d)

As a function of $J$, averaging over $F$ and $F_z$ leads to the results

$$\langle E(6P_{1/2}/F, F_z) \rangle_{F_z} = \left(-\frac{3}{4} \Delta - \frac{8.234.74 \times 10^2}{\rho^6}\right) E_h ,$$  
(27a)

$$\langle E(6P_{3/2}/F, F_z) \rangle_{F_z} = \left(\frac{3}{8} \Delta + \frac{4.117.37 \times 10^2}{\rho^6}\right) E_h .$$  
(27b)

Without hyperfine resolution, there are four $J = \frac{3}{2}$ states and two $J = \frac{1}{2}$ states. Hence, the fine-structure average of the latter two results vanishes.

IV. $6P$–$2S$ INTERACTION

A. Selection of the States

We are now turning our attention to the interaction of excited $6P$ states with metastable $2S$ atoms. If we could restrict the basis of states to the $6P_{1/2}$, $6P_{3/2}$, and $2S$ states, just replacing the $1S$ state from the previous calculation with the metastable $2S$ states, then the calculation would be relatively easy. However, as it turns out, there is
an additional complication: namely, the $|(6P_{1/2})_A (2S)_B \rangle$ states are energetically quasi-degenerate with respect to $|(6S)_A (2P_{1/2})_B \rangle$ states, and removed from each other only by the classic $2S-2P_{1/2}$ Lamb shift (the $n = 6$ Lamb shift is much smaller). It is thus necessary to augment the basis of states with the $6S-2P_{1/2}$ states. This turns the interaction into a $6P_{1/2}-6P_{3/2}-(6S;2P_{1/2})-2S$ system, where the notation indicates that the $6S-2P_{1/2}$ states are merely added as virtual states, for the calculation of second-order energy shifts. Among the basis states, the reference states of interest are the $6P_{1/2}$ and $6P_{3/2}$ states.

A priori, we have $4 + 4 + 4 + 4 = 24$ one-atom states in the $6P_{1/2}-6P_{3/2}-(6S;2P_{1/2})-2S$ system, which amounts to $24^2 = 576$ states for the two atoms, and the Hamiltonian matrix would have $576^2 = 331776$ entries. In order to remain within the quasi-degenerate basis, we should select only those two-atom states composed of an $S$ and a $P$ state, and only those where the principal quantum numbers add up to $2 + 6 = 8$. These selection rules drastically reduce the number of states in the basis, according to Table III. Furthermore, the total Hamiltonian (3) commutes with the total angular momentum $\vec{F}$. From the $6P_{1/2}-6P_{3/2}-2S$ system, we obtain multiplicities of 28, 22, 10 and 2, for the manifolds with $F_z = 0$, $F_z = \pm 1$, $F_z = \pm 2$, and $F_z = \pm 3$. By the addition of the $(6S,2P_{1/2})$ states, we end up with multiplicities of 40, 30, 12 and 2, for the manifolds with $F_z = 0$, $F_z = \pm 1$, $F_z = \pm 2$, and $F_z = \pm 3$.

Roughly, one proceeds as in the $6P_{1/2}-6P_{3/2}-2S$ system, sets up the matrices of the total Hamiltonian (3) for every $F_z$ manifold, and then, convinces oneself that the averages of the first-order energy shifts vanish, both for the entirety of states within every $F_z$ manifold as well as for every fine-structure submanifold individually. Then, one takes as reference states the $6P-2S$ system and evaluates the second-order shifts for every state in a given $(J,F,F_z)$ manifold. The individual multiplicities are given in Table III. Observe that even for given $(J,F,F_z)$, the $6P_J-2S$ reference levels need not all be energetically degenerate in view of a freedom of choice for the hyperfine-resolved complementary $2S$ state in the two-atom basis.

### B. Second–Order Energy Shifts

For the states within the individual $(J,F,F_z)$ manifolds, the averaged second-order energy shifts of the $6P_J-2S$ reference levels are given in Table IV. As a function of $J$ and $F$, an averaging over the magnetic quantum numbers

| $F_z = 0$ | $F_z = \pm 1$ | $F_z = \pm 2$ | $F_z = \pm 3$ |
|-----------|----------------|----------------|----------------|
| $J = \frac{1}{2}, F = 2$ | 8 | 8 | 6 | 2 |
| $J = \frac{3}{2}, F = 1$ | 8 | 6 | 2 | 0 |
| $J = \frac{3}{2}$ | 16 | 14 | 8 | 2 |
| $J = \frac{3}{2}, F = 1$ | 8 | 6 | 2 | 0 |
| $J = \frac{3}{2}, F = 0$ | 4 | 2 | 0 | 0 |
| $J = 1/2$ | 12 | 8 | 2 | 0 |
| $(J = \frac{3}{2}) + (J = \frac{1}{2})$ | 28 | 22 | 10 | 2 |
| $(6S,2P_{1/2})$ States | 12 | 8 | 2 | 0 |
| Total # of States | 40 | 30 | 12 | 2 |
TABLE IV. Average second-order van der Waals shifts for 6P_J hydrogen atoms interacting with 2S metastable atoms. Entries marked with a long hyphen (---) indicate unphysical combinations of F and F_z values. We denote the scaled interatomic distance by ρ = R/a_0 and give all energy shifts in atomic units, i.e., in units of the Hartree energy E_h = α^2 m_e c^2. The notation Δ is defined in Eq. (16).

| F_z = 0     | F_z = ±1     | F_z = ±2     | F_z = ±3     |
|-------------|-------------|-------------|-------------|
| (J = 3/2, F = 2) | 3.942 40 \times 10^{10}  | 3.283 90 \times 10^{10}  | 1.773 16 \times 10^{10}  | 0 |
| (J = 3/2, F = 1) | Δ + 3.492 60 \times 10^{10}  | Δ + 2.635 84 \times 10^{10}  | Δ + 8.531 51 \times 10^{9}  | --- |
| (J = 1/2, F = 1) | -Δ + 4.262 61 \times 10^{10}  | -Δ + 3.744 79 \times 10^{10}  | -Δ + 2.375 05 \times 10^{10}  | --- |
| (J = 1/2, F = 0) | 3.871 53 \times 10^{10}  | 3.536 58 \times 10^{10}  | ---  | --- |

F_z leads to the results

\[
\langle E(6P_{1/2}, F = 0) \rangle_{F_z} = \frac{3.704 05 \times 10^{10}}{\rho^6} E_h , \quad (28a)
\]

\[
\langle E(6P_{1/2}, F = 1) \rangle_{F_z} = \left( -\Delta + \frac{3.689 14 \times 10^{10}}{\rho^6} \right) E_h , \quad (28b)
\]

\[
\langle E(6P_{3/2}, F = 1) \rangle_{F_z} = \left( \Delta + \frac{2.624 34 \times 10^{10}}{\rho^6} \right) E_h , \quad (28c)
\]

\[
\langle E(6P_{3/2}, F = 2) \rangle_{F_z} = \frac{2.633 99 \times 10^{10}}{\rho^6} E_h . \quad (28d)
\]

These results are obtained from the entries in Table IV, using the weighting factors from Table III for an averaging over the rows.

One can also average over the possible orientations of F, namely, F = J ± 1/2, for given J and F_z. This amounts to an averaging over the first two entries in the columns (for J = 1/2), and the third and fourth entry (for J = 3/2) in every column of Table IV. The results of the latter procedure are

\[
\langle E(6P_{1/2}, F_z = 0) \rangle_F = \left( -\frac{2}{3} \Delta + \frac{4.132 32 \times 10^{10}}{\rho^6} \right) E_h , \quad (29a)
\]

\[
\langle E(6P_{1/2}, F_z = ±1) \rangle_F = \left( -\frac{3}{4} \Delta + \frac{3.692 74 \times 10^{10}}{\rho^6} \right) E_h , \quad (29b)
\]

\[
\langle E(6P_{1/2}, F_z = ±2) \rangle_F = \left( -\Delta + \frac{2.375 05 \times 10^{10}}{\rho^6} \right) E_h , \quad (29c)
\]

and

\[
\langle E(6P_{3/2}, F_z = 0) \rangle_F = \left( \frac{1}{2} \Delta + \frac{3.717 54 \times 10^{10}}{\rho^6} \right) E_h , \quad (30a)
\]

\[
\langle E(6P_{3/2}, F_z = ±1) \rangle_F = \left( \frac{3}{4} \Delta + \frac{3.006 16 \times 10^{10}}{\rho^6} \right) E_h , \quad (30b)
\]

\[
\langle E(6P_{3/2}, F_z = ±2) \rangle_F = \left( \frac{1}{4} \Delta + \frac{1.543 15 \times 10^{10}}{\rho^6} \right) E_h , \quad (30c)
\]

\[
\langle E(6P_{3/2}, F_z = ±3) \rangle_F = 0 . \quad (30d)
\]
As a function of $J$, averaging over both $F$ and $F_z$ leads to the results

\[
\langle E(6P_{1/2}) \rangle_{F,F_z} = \left( -\frac{3}{4} \Delta + \frac{3.69287 \times 10^{10}}{\rho^6} \right) E_h , \tag{31a} \]

\[
\langle E(6P_{3/2}) \rangle_{F,F_z} = \left( \frac{3}{8} \Delta + \frac{2.632037 \times 10^{10}}{\rho^6} \right) E_h . \tag{31b} \]

Without hyperfine resolution, there are four $J = 3/2$ states and two $J = 1/2$ states. Hence, an additional average over the fine-structure levels leads to a cancellation of the term proportional to $\Delta$, but the $1/\rho^6$ energy shift remains as an overall repulsive interaction among $6P-2S$ atoms.

We had seen in Eqs. (27a) and Eqs. (27b) that the fine-structure average of the van der Waals interaction vanishes for the $6P-1S$ interaction, in the quasi-degenerate basis which we are using. For the $6P_{1/2}-2S$ and $6P_{3/2}-2S$ systems, the van der Waals interactions are found to be repulsive and the van der Waals coefficients are of order $10^{10}$ in atomic units [see Eqs. (31a) and (31b)]. The latter, comparatively large van der Waals coefficients mainly are due to the virtual $(6S; 2P_{1/2})$ states which have to be added to the quasi-degenerate basis if the spectator atom is in the metastable $2S$ state.

V. TIME DEPENDENCE AND OSCILLATORY TERMS

A few remarks on the role of the time dependence of the interaction and the no-retardation approximation are in order, in view of recent works [5, 7–10, 25], part of which discuss time-dependent effects in van der Waals interactions. First of all, let us emphasize that the Hamiltonian (3) is manifestly time-independent. As such, it cannot generate oscillatory terms in energy shifts, for reasons of principle. In order to see this, let us consider the time evolution of a matrix element $M = \langle \phi |H|\phi' \rangle$ under the action of $H$, where $|\phi\rangle$ and $|\phi'\rangle$ are arbitrary basis states. The matrix element transforms into $M(t) = \langle \phi \exp(iHt/\hbar)H \exp(-iHt/\hbar)|\phi' \rangle = M(0) = M$ and therefore is time-independent. The time-independent Hamiltonian matrix therefore has stationary eigenvalues, which describe the time-independent energy eigenvalues of the system. This approach is canonically taken in the analysis of the van der Waals interaction within manifolds of quasi-degenerate states (see also Ref. [12]).

The time-independence of our Hamiltonian (2) corresponds to the non-retardation approximation for the van der Waals approximation. Just like in our recent paper [11], the validity of the non-retardation approximation, is tied to the energetic (quasi-)degeneracy of the levels in our hyperfine-resolved basis. In general, retardation sets in when the phase of the virtual oscillation of an atom changes appreciably over the time that it takes light to travel from one atom to the other, and back [see the discussion surrounding Eqs. (8) and (9) of Ref. [26]]. For our case, the transition wavelengths correspond to fine-structure, Lamb shift and hyperfine-structure transitions. The largest of these is the fine-structure interval $E_{FS} \sim a^4 m_e c^2$. The validity of the non-retardation approximation is thus equivalent to the condition

\[
\frac{R}{c} \ll \frac{\hbar}{E_{FS}} , \quad R \ll \frac{\hbar}{a_0^4 m_e c^2} = \frac{a_0}{\alpha^3} \approx 0.136 \text{ mm}. \tag{32} \]

Thus, in the distance range where retardation becomes relevant, the overall magnitude of the van der Waals interaction is completely negligible. The interaction, within the manifold of quasi-degenerate states, is thus “instantaneous” from the point of view of virtual transitions, and the no-retardation approximation is justified.

In recent works [9, 10], a somewhat related but different situation is considered: An atomic interaction is treated where it is assumed that there are optical transitions available, to energetically lower states as compared to the excited reference state, which act as “virtual resonant transitions” and lead to long-range oscillatory tails in the van der Waals interaction, where the oscillations are functions of the interatomic distance (not of time). This is the case, e.g., for an excited $3S-1S$ system, with the virtual $2P$ states in the $3S$ atom acting as virtual resonant states [see also Ref. [3]].

Additionally, in Refs. [5, 7, 8, 25], time-dependent effects have been studied in the context of retarded van der Waals interactions for non-identical atoms. A comparison to formulas given in Refs. [7] and [8], and [5, 25], is in order. First, one should observe that the second-order shifts investigated in Ref. [7] diverge in the limit of identical atoms, i.e., for the case of the “interatomic detuning” $\Delta_{AB} \to 0$. Also, the energy shifts given in Eqs. (6) and (7) of Ref. [8] diverge, because (in the notation of Ref. [8]) one has $\mathcal{U}_{ijpq} \propto \mu_i \mu_j \mu_p \mu_q / \Delta_{AB}$ where $\mathcal{U}_{ijpq}$ is a tensor that enters the calculation of the energy shift, and the $\mu_i$ are the dipole moment operators of non-identical atoms $A$ and $B$. For the case of perfect degeneracy, we thus have to calculate one-photon rather than two-photon exchange (in the non-retardation approximation). This has been done here and in our recent work [11]. We find, in full analogy to the discussion in Ref. [11], that the average first-order shifts of the hyperfine-resolved levels, in first order of the van der Waals Hamiltonian, vanish.
The interaction with the quantized modes of the radiation field (which mediate the van der Waals interaction) is “switched on” at distance \( R \) and time \( t = 0 \) in Refs. [7, 8]. We here refrain from a discussion on the relevance of this approximation. Otherwise, the interatomic interaction energy otherwise increases as the atoms approach each other from infinity to a finite distance \( R \). We only explore the consequences of the results reported in Refs. [7, 8]. Let \( |\Psi\rangle = |6P\rangle_A|1S\rangle_B \) denote a specific state within the \( 6P-1S \) hyperfine manifold, and let \( |\Psi\rangle = |1S\rangle_A|6P\rangle_B \) denote a different state, displaced by an energy shift of order

\[
\Delta_{\text{HFS}} \sim \Delta_{AB} \sim \mathcal{H}.
\]  

We concentrate on the second-order shifts due to quasi-degenerate levels \( |\Psi\rangle = |1S\rangle_A|6P\rangle_B \), in which case the formalism of [8] and [5] becomes applicable. In Eqs. (20) and (6) of Ref. [8], it is claimed that the “usual” result for the van der Waals energy shift holds only in the limit

\[
\Gamma \ll \hbar \Omega \ll \Delta_{AB},
\]

where \( \Gamma \) is the natural line width of the state (expressed in units of energy), \( \Omega \) is the Rabi frequency of the excitation, and \( \Delta_{AB} \) is the detuning \( E_{\Psi'} - E_\Psi \). This condition cannot be met in our setting for any Rabi frequency \( \Omega \), because we evidently have \( \Gamma \gg \Delta_{\text{HFS}} \gg \Delta_{AB} \) (the natural line width of the \( 6P \) states is greater than the hyperfine splitting). Otherwise, time-dependent oscillatory terms are obtained in Ref. [8].

Likewise, it is claimed in Ref. [7] that upon a sudden excitation of atom \( A \) at \( t = 0 \), at a later time \( T \), there are oscillatory terms in the energy which for our case would be proportional to

\[
\cos \left( \frac{2(E_{6P} - E_{1S})R}{\hbar c} + \frac{\Delta_{AB} T}{\hbar} \right),
\]

and thus oscillatory in both space and time. These terms are claimed to influence the energy shift dynamically, after an observation time \( T \). Note that the first term on the right-hand side of Eq. (4) of Ref. [7] reproduces the usual second-order van der Waals contribution (proportional to \( R^{-6} \)) to an energy shift in the limit of a vanishing wave vector for the transition of atom \( A \), namely, \( k_A \to 0 \) (in the notation of Ref. [7]), which is relevant for our quasi-degenerate manifolds. This term is non-oscillatory in \( T \) and gives the leading contribution to the interaction energy for quasi-degenerate systems in the non-retardation limit, as also remarked in Ref. [9].

In any case, the additional oscillatory terms obtained in Eqs. (20) and (6) of Ref. [8] and in Eq. (4) of Ref. [8] average out to zero over the observation time \( T \). If we are to evaluate position-dependent energy shifts (pressure shifts) within an atomic beam, then we do not know the time \( T \) at which an atomic collision occurs, within the beam, after excitation. The oscillatory terms in the energy shifts thus average out to zero, in the calculation of the pressure shifts due to atomic collisions within the beam.

In order to avoid “switching on” the interaction with the quantized modes of the radiation field, suddenly at time \( t = 0 \), one generally assumes the excited state to be an asymptotic state (in the context of the \( S \)-matrix formalism, see Refs. [19, 27]). For a didactic presentation of the application of this formalism to the ac (“alternating-current”, oscillatory-field) Stark energy shift due to an oscillatory external laser field, see Ref. [28]. Specifically, for manifestly oscillatory terms in the interaction Hamiltonian such as a laser field, or the quantized electromagnetic field, one damps the interaction infinitesimally at infinity and uses an infinitesimally damped time-evolution operator [see Eq. (21) of Ref. [28]] in order to formulate the energy shift within the Gell–Mann–Low theorem. Or, one matches the \( S \)-matrix amplitude with the energy shift generated by the interatomic interaction [9, 10, 27]. Finally, the calculation of the pressure shift within an atomic beam, using the time-independent van der Waals potentials as input, is discussed in Chaps. 36 and 37 of Ref. [29] (within the impact approximation).

VI. CONCLUSIONS

In this paper, we have studied the van der Waals interaction of excited \( 6P \) hydrogen atoms with ground-state \( 1S \) and metastable \( 2S \) atoms. Within our hyperfine-resolved basis, in order to obtain reliable estimates of the van der Waals interaction coefficients, one needs to consider all off-diagonal matrix elements of the van der Waals interaction Hamiltonian. Specifically, for hydrogen, the nuclear spin \( I = \frac{1}{2} \) needs to be added to the total electron angular momentum \( J \), resulting in states with the total angular momentum \( F = J \pm \frac{1}{2} \) of electron+nucleus. The explicit construction of the hyperfine-resolved states is discussed in Sec. II. For the \( 6P-1S \) system, one needs to include both the \( 6P_{1/2} \) as well as the \( 6P_{3/2} \) states in the quasi-degenerate basis, because the \( 6P \) fine-structure frequency is commensurate with the \( 1S \) hyperfine transition splitting (see Sec. III). The matrix elements of the total Hamiltonian involve the so-called hyperfine–fine–structure mixing term (see Sec. III), which couples the \( 6P_{1/2}(F = 1) \) to the \( 6P_{3/2}(F = 1) \) levels [see Eq. (14)].
The explicit matrices of the total Hamiltonian (3) in the manifolds with \( F_z = 3, 2 \) are described in Secs. III B and III C. Due to mixing terms of first order in the van der Waals interaction between degenerate states in the two-atom system, the leading term in the van der Waals energy, upon rediagonalization of the Hamiltonian matrix, is of order \( 1/R^2 \) for the 6\( P \)-1S interaction, but it averages out to zero over the magnetic projections. The phenomenologically important second-order shifts of the energy levels are given in Sec. III E, with various averaging procedures illustrating the dependence of the shifts on the quantum numbers, and the dependence of the repulsive or attractive character of the interaction on the hyperfine-resolved levels.

The same procedure is applied to the 6\( P \)-2S interaction in Sec. IV, with the additional complication that virtual quasi-degenerate (6\( S \); 2\( P_{1/2} \)) also need to be included in the basis. The treatment of the 6\( P \)-1S and 6\( P \)-2S long-range interactions reveals the presence of numerically large coefficients multiplying the \( 1/\rho^6 \) interaction terms, due to the presence of quasi-degenerate levels. The interaction remains nonretarded over all phenomenologically relevant distance scales. The repulsive character of the 6\( P \)-2S interaction due to the quasi-degenerate virtual (6\( S \); 2\( P_{1/2} \)) levels is obtained as a surprise conclusion from the current investigation.

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