Long-range interactions of hydrogen atoms in excited states. III.
\[ nS-1S \] interactions for \( n \geq 3 \)

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The long-range interaction of excited neutral atoms has a number of interesting and surprising properties, such as the prevalence of long-range, oscillatory tails, and the emergence of numerically large van der Waals \( C_6 \) coefficients. Furthermore, the energetically quasi-degenerate \( nP \) states require special attention and lead to mathematical subtleties. Here, we analyze the interaction of excited hydrogen atoms in \( nS \) states \((3 \leq n \leq 12)\) with ground-state hydrogen atoms, and find that the \( C_6 \) coefficients roughly grow with the fourth power of the principal quantum number, and can reach values in excess of 240,000 (in atomic units) for states with \( n = 12 \). The nonretarded van der Waals result is relevant to the distance range \( R \ll a_0/\alpha \), where \( a_0 \) is the Bohr radius and \( \alpha \) is the fine-structure constant. The Casimir–Polder range encompasses the interatomic distance range \( a_0/\alpha \ll R \ll \hbar c/L \), where \( L \) is the Lamb shift energy. In this range, the contribution of quasi-degenerate excited \( nP \) states remains nonretarded and competes with the \( 1/R^2 \) and \( 1/R^4 \) tails of the pole terms which are generated by lower-lying \( mP \) states with \( 2 \leq m \leq n - 1 \), due to virtual resonant emission. The dominant pole terms are also analyzed in the Lamb shift range \( R \gg \hbar c/L \). The familiar \( 1/R^2 \) asymptotics from the usual Casimir–Polder theory is found to be completely irrelevant for the analysis of excited-state interactions. The calculations are carried out to high precision using computer algebra in order to handle a large number of terms in intermediate steps of the calculation, for highly excited states.

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I. INTRODUCTION

In general, the analysis of long-range interactions among neutral atoms in excited states is less trivial than one would expect at first glance. This is true for hydrogen atoms (in excited \( S \) states), which form the basis of the current investigation, as much as any other atom. The reasons are threefold. First, we note the presence of quasi-degenerate excited \( nP \) states, which are only displaced from the \( nS \) states by the Lamb shift or the fine structure \([1]\). Due to the long wavelength of the involved virtual transitions, the contribution of the quasi-degenerate states remains non-retarded over wide distance ranges. Second, the presence of lower-lying virtual \( mP \) states with \( m \leq n \) leads to both oscillatory energy shifts and distance-dependent corrections to the decay width of the excited state \([2-4]\). Third, for \( nS-1S \) interactions, there is a gerade–ungerade mixing term that depends on the symmetry of the excited-state contributions to the two-atom wave function. The mixing term is numerically large for \( 2S-1S \) interactions \([1, 5]\). The eigenstates of the total Hamiltonian are composed of coherent superpositions of \( nS-1S \) and \( 1S-nS \) states in the two-atom system.

Let us try to provide some background on these issues. We have recently analyzed \([1]\) the interaction of metastable \( 2S \) hydrogen atoms with ground-state atoms. A long-standing discrepancy regarding the numerical value of the van der Waals \( C_6 \) coefficient could be resolved, and the mixing term was treated for \( 2S-1S \) interactions \([1, 5-7]\). In \([8]\), we have analyzed \( 2S-2S \) interactions, and we have determined the hyperfine-resolved eigenstates of the van der Waals interaction, both among the \( S-S, P-P \) as well as the \( S-P \) submanifolds of the \( n = 2 \) hydrogen states. The physically interesting oscillatory tails of van der Waals interactions involving excited states were recently discussed in Refs. \([2, 3, 9]\). The special role of quasi-degenerate excited states was analyzed in \([1]\). All of these concepts are relevant to the current investigation.

Finally, we should mention that the numerical evaluation of the van der Waals \( C_6 \) coefficient for excited states demands the rather sophisticated use of recurrence relations in order to express the polarizability matrix elements in terms of hypergeometric functions. This phenomenon is familiar from Lamb shift calculations \([10, 11]\). The numerical calculations lead to van der Waals \( C_6 \) coefficients that grow rapidly with the principal quantum number.

Throughout this article, we work in SI mksA units and keep all factors of \( \hbar \) and \( c \) in the formulas. With this choice, we attempt to extend the accessibility of the presentation to two different communities, namely, the quantum electrodynamics community which in general uses the natural unit system, and the atomic physics community where the atomic unit system is canonically employed. In the former, one sets \( \hbar = c = \epsilon_0 = 1 \), the electron mass is denoted by \( m_e \), and one has the relation \( e^2 = 4\pi\alpha \). The Casimir–Polder interaction. In the atomic unit system, one has \( |e| = \hbar = m_e = 1 \), 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 atomic properties without radiative corrections. 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 problem is somewhat involved; after an orientation (in Sec. II), we focus on the 3S–1S interaction in Sec. III. In Sec. IIIA, we study the van der Waals range. The very-large-distance limit is discussed in Sec. IIIB. States with 4 ≤ n ≤ 12 are analyzed in Sec. IV. Numerical examples are discussed in Sec. V. We summarize in Sec. VI.

II. ORIENTATION

As we are not interested in the hyperfine structure of the excited nS state (n ≥ 3), we may write the total Hamiltonian of the two-atom system as

\[ H_{\text{total}} = H_S + H_{FS} + H_{LS} + H_{vdW}. \]  

Here, \( H_S \) is the Schrödinger Hamiltonian, while \( H_{FS} \) is the fine structure Hamiltonian, which can be approximated as (see Chap. 34 of Ref. [13])

\[ H_{FS} = \sum_{i=A,B} \left[ \frac{-\vec{p}_i^4}{8m_e^2c^2} + \frac{1}{2} \frac{\hbar^2 g_s}{2m_e^2c} \frac{\vec{E}_i \cdot \vec{S}_i}{|\vec{r}_i|^3} \right] + \frac{\hbar^3}{8m_e^2c^2} 4\pi \alpha \delta^{(3)}(\vec{r}_i), \]  

where \( m_e \) is the electron mass. The momenta of the two atomic electrons are denoted by \( \vec{p}_i \) (here, \( i \) runs over the atoms A and B), and the distance vectors \( \vec{r}_i = \vec{x}_i - \vec{R}_i \) are the coordinates relative to the nuclei (the electron and nucleus coordinates are \( \vec{x}_i \) and \( \vec{R}_i \), respectively). The fine-structure constant is denoted by \( \alpha \approx 1/137.036 \), and the electronic g factor is \( g_s \approx 2.002319 \). As van der Waals interactions are relevant only for neutral systems, we restrict the discussion to neutral hydrogen atoms (nuclear charge number \( Z = 1 \)). In leading logarithmic approximations, the Lamb shift Hamiltonian is approximated by [14]

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

From Eq. (6) of Ref. [1], we recall the van der Waals Hamiltonian

\[ H_{vdW} = \frac{e^2}{4\pi \epsilon_0} \frac{\vec{r}_A \cdot \vec{r}_B - 3(\vec{r}_A \cdot \vec{R})(\vec{r}_B \cdot \vec{R})}{R^3}, \]  

where \( \vec{R} = \vec{R}_A - \vec{R}_B, R = |\vec{R}| \) and \( \hat{R} = \vec{R}/R \). We shall assume that the hierarchy

\[ \langle H_{vdW} \rangle \ll \langle H_{LS} \rangle \ll \langle H_{FS} \rangle \]  

is fulfilled for the entire distance range relevant to the current investigation (\( R \gtrsim 30 a_0 \)).

We carefully distinguish different asymptotic regimes for the interatomic interaction. In the so-called van der Waals range of interatomic distances,

\[ a_0 = \frac{\hbar}{\alpha m_e c} \ll R \ll \frac{\hbar}{\alpha^2 m_e c} = \frac{a_0}{\alpha}, \]  

the interatomic distance \( R \) is much larger than the Bohr radius \( a_0 = \hbar/(\alpha m_e c) \), but much smaller than the wavelength \( \approx a_0/\alpha \) of a typical optical transition, and the interaction is of the usual \( R^{-6} \) functional form. This remains valid if one atom is in an excited \( nS \) state. In the so-called Casimir–Polder range,

\[ R \gg \frac{\hbar}{\alpha^2 m_e c} = \frac{a_0}{\alpha}, \]  

the interatomic distance is much larger than the wavelength of an optical transition, and the interaction of ground-state atoms has a \( R^{-7} \) functional form. For the long-range interaction involving excited metastable atoms, however, we have to distinguish a third range of very large interatomic distances,

\[ R \gg \frac{\hbar c}{\mathcal{L}}, \]  

which we would like to refer to as the Lamb shift range (where \( \mathcal{L} \) is a typical Lamb shift energy). Care is needed in the intermediate range

\[ \frac{\hbar}{\alpha^2 m_e c} = \frac{a_0}{\alpha} \ll R \ll \frac{\hbar c}{\mathcal{L}}. \]  

A further complication arises. The state with atom A in the excited state and atom B in the ground state, \( |nS\rangle_A |1S\rangle_B \), is degenerate with respect to the state \( |1S\rangle_A |nS\rangle_B \) with the quantum numbers reversed. While there is no direct first-order coupling between the states due to the van der Waals interaction, an off-diagonal term is obtained in second order. It is of the same order-of-magnitude as the diagonal term, i.e., the term with the same in and out states. The Hamiltonian matrix in the basis of the degenerate states \( |nS\rangle_A |1S\rangle_B \) and \( |1S\rangle_A |nS\rangle_B \) then has off-diagonal (“exchange” or “mixing”) terms of second order in the van der Waals interaction [1, 5].

A. Formalism for the Direct Terms

For nS–1S interactions, the long-range interaction energy is the sum of three terms, namely, (i) a Wick-rotated interaction integral involving the nondegenerate states of the excited atom, (ii) a Wick-rotated interaction with the quasi-degenerate states of the excited atom, and (iii) the sum of pole terms, due to lower-lying \( mP \) states with \( m \leq n - 1 \). For details of the derivations, see Refs. [1, 4, 9].
First, we here restrict the discussion to the “direct” term and indicate the specific contributions; a summary of all contributing terms will be given in Sec. II C. The first contribution to the Wick-rotated term, involving nondegenerate states, is given as follows,

\[
\tilde{\mathcal{W}}^{(\text{dir})}(R) = -\frac{\hbar}{\pi e^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \tilde{\alpha}_{nS}(i\omega) \alpha_{1S}(i\omega) \\
\times e^{-2\omega_R/c \omega^4/R^2} \left[ 1 + 2 \left( \frac{c}{\omega_R} \right) + 5 \left( \frac{c}{\omega_R} \right)^2 \\
+ 6 \left( \frac{c}{\omega_R} \right)^3 + 3 \left( \frac{c}{\omega_R} \right)^4 \right]. \tag{10}
\]

The nondegenerate contribution to the nS-state polarizability (denoted by a tilde) is given as

\[
\tilde{\alpha}_{nS}(\omega) = \tilde{P}_{nS}(\omega) + \tilde{P}_{nS}(-\omega), \tag{11a}
\]

\[
\tilde{P}_{nS}(\omega) = \frac{1}{3} \sum_{m \neq n} \langle nS|\tilde{d}|mP \rangle \cdot \langle mP|\tilde{d}|nS \rangle.
\tag{11b}
\]

Here, \(\tilde{d} = e \vec{r}\) is the dipole operator. The sum over \(m\) includes the continuum states, and the sum over the magnetic quantum numbers of the virtual \(P\) states is implied. However, note the restriction to nondegenerate states in the sum over virtual states \((m \neq n)\). The ground-state polarizability is

\[
\alpha_{1S}(\omega) = P_{1S}(\omega) + P_{1S}(-\omega), \tag{12a}
\]

\[
P_{1S}(\omega) = \frac{1}{3} \sum_m \langle nS|d|mP \rangle \cdot \langle mP|d|nS \rangle.
\tag{12b}
\]

The second Wick-rotated term, involving the degenerate states, is given as follows,

\[
\mathcal{W}^{(\text{dir})}(R) = -\frac{\hbar}{\pi e^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \sigma_{nS}(i\omega) \alpha_{1S}(i\omega) \\
\times e^{-2\omega_R/c \omega^4/R^2} \left[ 1 + 2 \left( \frac{c}{\omega_R} \right) + 5 \left( \frac{c}{\omega_R} \right)^2 \\
+ 6 \left( \frac{c}{\omega_R} \right)^3 + 3 \left( \frac{c}{\omega_R} \right)^4 \right]. \tag{13}
\]

Here, the degenerate part of the polarizability involves the \(nP\) states, with the same principal quantum number as the reference state,

\[
\sigma_{nS}(\omega) = \sigma_{nS}(\omega) + \sigma_{nS}(-\omega), \tag{14a}
\]

\[
\sigma_{nS}(\omega) = \frac{1}{9} \langle nS|d|nP \rangle \cdot \langle nP|d|nS \rangle - \frac{2}{9} \langle nS|d|nP \rangle \cdot \langle nP|d|nS \rangle.
\tag{14b}
\]

where \(\mathcal{L}_n\) and \(\mathcal{F}_n\) are the Lamb shift and fine structure splittings between quasi-degenerate levels with principal quantum number \(n\). (We have previously denoted by \(L\) an energy commensurate with the Lamb shift energies \(\mathcal{L}_n\) in the range \(2 \leq n \leq 12\).) Explicitly,

\[
\mathcal{L}_n = E(nS_{1/2}) - E(nP_{1/2}), \tag{15a}
\]

\[
\mathcal{F}_n = E(nP_{3/2}) - E(nS_{1/2}). \tag{15b}
\]

Both the Lamb shift, \(\mathcal{L}_n\), and the fine structure splitting, \(\mathcal{F}_n\), decrease approximately as \(1/n^3\) as the principal quantum number \(n\) increases [15, 16]. The pole term [4, 9] due to energetically lower \(|mP\rangle\) states \((m < n)\) becomes

\[
Q^{(\text{dir})}(R) = -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \\
\times \sum_{m < n} \langle nS|\tilde{d}|mP \rangle \cdot \langle mP|\tilde{d}|nS \rangle \alpha_{1S} \left( \frac{E_{mn}}{hc} \right)^3 + \left( \frac{E_{mn}}{hc} \right)^4 \right]. \tag{16}
\]

The Schrödinger energy difference is

\[
E_{mn} = -\frac{\hbar^2}{2} \left( \frac{1}{m^2} - \frac{1}{n^2} \right),
\tag{17}
\]

where \(E_h = \alpha^2 m_e c^2\) is the Hartree energy. The real part of the pole term energy shift is

\[
\mathcal{P}^{(\text{dir})}(R) = -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \\
\times \sum_{m < n} \langle nS|\tilde{d}|mP \rangle \cdot \langle mP|\tilde{d}|nS \rangle \alpha_{1S} \left( \frac{E_{mn}}{hc} \right)^3 + \left( \frac{E_{mn}}{hc} \right)^4 \right]. \tag{18}
\]

The corresponding width term \(\Gamma^{(\text{dir})}(R)\) is obtained from the relation

\[
Q^{(\text{dir})}(R) = \mathcal{P}^{(\text{dir})}(R) - \frac{1}{2} \Gamma^{(\text{dir})}(R) \tag{19}
\]

and reads

\[
\Gamma^{(\text{dir})}(R) = -\frac{4}{3(4\pi\epsilon_0)^2 R^6} \\
\times \sum_{m < n} \langle nS|\tilde{d}|mP \rangle \cdot \langle mP|\tilde{d}|nS \rangle \alpha_{1S} \left( \frac{E_{mn}}{hc} \right)^3 + \left( \frac{E_{mn}}{hc} \right)^4 \right]
\tag{20}
\]
B. Formalism for the Mixing Terms

Just as for the direct term, we need to identify a non-degenerate contribution \( \hat{W}^{(\text{mix})}(R) \) to the Wick-rotated term, a degenerate contribution \( \hat{W}^{(\text{mix})}_R(R) \), and pole term \( \mathcal{P}^{(\text{mix})}(R) \). The first Wick-rotated term, involving nondegenerate states, is given as follows,

\[
\hat{W}^{(\text{mix})}(R) = -\frac{\hbar}{\pi c^3 (4 \pi \epsilon_0)^2} \int_0^\infty d\omega \overline{\alpha_{nS1S}(i\omega)} \alpha_{nS1S}(i\omega) \\
\times e^{-2\omega R/c} \frac{\omega^4}{R^2} \left[ 1 + 2 \left( \frac{c}{\omega R} \right) + 5 \left( \frac{c}{\omega R} \right)^2 \right] \\
+ 6 \left( \frac{c}{\omega R} \right)^3 + 3 \left( \frac{c}{\omega R} \right)^4 . \tag{21}\]

The mixed polarizabilities are given as

\[
\overline{\alpha_{nS1S}(\omega)} = \frac{1}{3} \sum_{m \neq n} \frac{\langle nS|d|nP \rangle \cdot \langle nP|d|1S \rangle}{E_m - E_{nS} \pm \hbar \omega - i \epsilon} , \tag{22a}\]

\[
\alpha_{nS1S}(\omega) = \frac{1}{3} \sum_n \frac{\langle nS|d|nP \rangle \cdot \langle nP|d|1S \rangle}{E_m - E_{1S} \pm \hbar \omega - i \epsilon} . \tag{22b}\]

Note the restriction to nondegenerate states \((m \neq n)\) in the sum over virtual states, in the expression for \(\overline{\alpha_{nS1S}(\omega)}\). The second Wick-rotated term, involving the degenerate states, is given as follows,

\[
\hat{W}^{(\text{mix})}_R(R) = -\frac{\hbar}{\pi c^3 (4 \pi \epsilon_0)^2} \int_0^\infty d\omega \overline{\alpha_{nS1S}(i\omega)} \alpha_{nS1S}(i\omega) \\
\times e^{-2\omega R/c} \frac{\omega^4}{R^2} \left[ 1 + 2 \left( \frac{c}{\omega R} \right) + 5 \left( \frac{c}{\omega R} \right)^2 \right] \\
+ 6 \left( \frac{c}{\omega R} \right)^3 + 3 \left( \frac{c}{\omega R} \right)^4 . \tag{23}\]

Here, the degenerate part of the polarizability involves the \(nP\) states, with the same principal quantum number as the reference state,

\[
\overline{\alpha_{nS1S}(\omega)} = \frac{1}{9} \frac{\langle nS|d|nP \rangle \cdot \langle nP|d|1S \rangle}{-\mathcal{E}_n + \hbar \omega - i \epsilon} \\
+ \frac{2}{9} \frac{\langle nS|d|nP \rangle \cdot \langle nP|d|1S \rangle}{\mathcal{F}_n + \hbar \omega - i \epsilon} . \tag{24}\]

The mixed pole term due to energetically lower \(|mP\) states becomes

\[
Q^{(\text{mix})}(R) = -\frac{2}{3(4 \pi \epsilon_0)^2 R^6} \\
\times \sum_{m<n} \langle nS|d|mP \rangle \cdot \langle mP|d|1S \rangle \alpha_{nS1S} \left( \frac{E_{mn}}{\hbar} \right) \\
\times \exp \left\{ -2i \frac{E_{mn} R}{\hbar c} \left[ 3 + 6i \frac{E_{mn} R}{\hbar c} - 5 \left( \frac{E_{mn} R}{\hbar c} \right)^2 \right] \\
- 2i \left( \frac{E_{mn} R}{\hbar c} \right)^3 \right\} . \tag{25}\]

The real part is

\[
\mathcal{P}^{(\text{mix})}(R) = -\frac{2}{3(4 \pi \epsilon_0)^2 R^6} \\
\times \sum_{m<n} \langle nS|d|mP \rangle \cdot \langle mP|d|1S \rangle \alpha_{nS1S} \left( \frac{E_{mn}}{\hbar} \right) \\
\times \left\{ \cos \left( \frac{2E_{mn} R}{\hbar c} \right) \left[ 3 - 5 \left( \frac{E_{mn} R}{\hbar c} \right)^2 + \left( \frac{E_{mn} R}{\hbar c} \right)^4 \right] \right\} . \tag{26}\]

The corresponding width term \(\Gamma^{(\text{mix})}(R)\) is obtained from the relation

\[
Q^{(\text{mix})}(R) = \mathcal{P}^{(\text{mix})}(R) - \frac{i}{2} \Gamma^{(\text{mix})}(R) \tag{27}\]

and reads

\[
\Gamma^{(\text{mix})}(R) = -\frac{4}{3(4 \pi \epsilon_0)^2 R^6} \\
\times \sum_{m<n} \langle nS|d|mP \rangle \cdot \langle mP|d|1S \rangle \alpha_{nS1S} \left( \frac{E_{mn}}{\hbar} \right) \\
\times \left\{ \sin \left( \frac{2E_{mn} R}{\hbar c} \right) \left[ 3 - 5 \left( \frac{E_{mn} R}{\hbar c} \right)^2 + \left( \frac{E_{mn} R}{\hbar c} \right)^4 \right] \right\} . \tag{28}\]

C. Adding direct and mixed terms

Depending on the symmetry of the two-atom wave function, we have for the eigenenergies of the two-atom system \([1, 5]\)

\[
E(R) = E^{(\text{dir})}(R) \pm E^{(\text{mix})}(R) , \tag{29a}\]

\[
E^{(\text{dir})}(R) = \hat{W}^{(\text{dir})}(R) + \hat{W}^{(\text{mix})}(R) + Q^{(\text{dir})}(R) , \tag{29b}\]

\[
E^{(\text{mix})}(R) = \hat{W}^{(\text{mix})}(R) + \hat{W}^{(\text{mix})}_R(R) + Q^{(\text{mix})}(R) . \tag{29c}\]
For the real part of the interaction energy,
\[ \text{Re } E(R) = \text{Re } E^{(\text{dir})}(R) \pm \text{Re } E^{(\text{mix})}(R), \] (30)
one has
\[ \text{Re } E^{(\text{dir})}(R) = W^{(\text{dir})}(R) + P^{(\text{dir})}(R) \]
\[ = \frac{\nu W^{(\text{dir})}(R) + \nu W^{(\text{dir})}(R) + P^{(\text{dir})}(R)}{1} \] (31a)
\[ \text{Re } E^{(\text{mix})}(R) = W^{(\text{mix})}(R) + P^{(\text{mix})}(R) \]
\[ = \frac{\nu W^{(\text{mix})}(R) + \nu W^{(\text{mix})}(R) + P^{(\text{mix})}(R)}{1} \] (31b)

The sign of the mixing term depends on the symmetry of
the wave function of the two-atom system [5]. In the following, we will concentrate on the real part of the energy
shift and use the symbols \( E(R) \) and \( \text{Re } E(R) \) synonymously, for both the direct as well as the mixing terms.

III. 3S–1S INTERACTION

A. Van der Waals range

In the van der Waals distance range (6),
\[ a_0 \ll R \ll a_0 \alpha, \] (32)
the interaction is nonretarded, and the interaction energy
is well approximated by the form
\[ E(R) \approx -\frac{C_6}{R^6} = -\frac{D_6 \pm M_6}{R^6}. \] (33)
The van der Waals coefficient \( C_6 = D_6 \pm M_6 \) contains
a direct term \( D_6 \) and a mixing coefficient \( M_6 \).

First, we focus on the direct term. According to Sec. II A, \( D_6 \) is the sum of a nondegenerate Wick-rotated
term \( \overline{D}_6 \), a degenerate Wick-rotated term \( \overline{\overline{D}}_6 \), and a pole contribution \( \overline{P}_6 \). One writes
\[ D_6(3S; 1S) = \overline{D}_6(3S; 1S) + \overline{\overline{D}}_6(3S; 1S) + \overline{P}_6(3S; 1S). \] (34)

Let us start with the nondegenerate contribution
\[ \overline{D}_6(3S; 1S) = \frac{3 }{\pi (4\pi \epsilon_0^2)} \int_0^\infty d\omega \overline{\alpha}_{3S}(i\omega) \alpha_{1S}(i\omega), \] (35)
where \( \overline{\alpha}_{3S}(\omega) \) has been defined in Eq. (11a). For
the 1S polarizability, the result was recently given in
Eqs. (15), (27a) and (27b) of Ref. [1]. For the 3S state,
one obtains the nondegenerate matrix element
\[ \overline{P}_{3S}(\omega) = \frac{e^2 a_0^2 \epsilon}{E_h} \begin{bmatrix} 54 \tau^2 \\ -13283 \tau^{10} + 2090 \tau^9 + 2871 \tau^8 + 40 \tau^7 - 62 \tau^6 \\ -492 \tau^5 + 128 \tau^4 + 236 \tau^3 - 95 \tau^2 - 46 \tau + 23 \]
\[ + \frac{6912 \tau^9}{(1 - \tau)^8 (1 + \tau)^6} (-1 + 9 \tau^2) (3 - 7 \tau^2)^2 \]
\[ \times \frac{\Gamma(1 - 3 \tau, 1 - 3 \tau)}{\Gamma(1 - \tau^2, 1 - \tau^2)} \frac{972 \tau^2}{1 - \tau^2} \end{bmatrix}, \]
\[ \tau = \left(1 + \frac{18 \hbar \omega}{\alpha^2 m c^2} \right)^{-1/2}. \] (36)
The virtual \( 3P \) state is excluded from the sum over states in Eq. (36) by the explicit subtraction of the term
\( 972 \tau^2 (1 - \tau^2) = 54 E_h / (\hbar \omega) \). One can verify that the expression (36) is finite in the limit \( \tau \to 1 \), which is
equivalent to vanishing photon energy \( \omega \to 0 \).

The polarizability \( \tilde{\alpha}_{3S}(\omega) \) is recovered according to
Eq. (11a), namely,
\[ \tilde{\alpha}_{3S}(\omega) = \tilde{P}_{3S}(\omega) + \tilde{P}_{3S}(-\omega). \] (37)
A numerical evaluation of Eq. (35) leads to the result
\[ \overline{D}_6(3S; 1S) = 180.320073947 E_h a_0^6. \] (38)
The degenerate contribution to \( D_6 \) can be handled
analytically. It reads
\[ \overline{\overline{D}}_6(3S; 1S) = \frac{3 }{\pi (4\pi \epsilon_0^2)} \int_0^\infty d\omega \overline{\alpha}_{3S}(i\omega) \alpha_{1S}(0), \] (39)
Using Eqs. (23) and (24) of Ref. [1], one easily obtains
the result for \( \overline{D}_6(3S; 1S) \),
\[ \overline{D}_6(3S; 1S) = 729 E_h a_0^6, \] (40)
In the calculation, one uses the well-known result
\[ \alpha_{1S}(0) = \frac{9 e^2 a_0^2}{2 E_h} \]  
for the static polarizability of hydrogen.

In the van der Waals range, the pole term given in Eq. (18) can be approximated as
\[ P^{(\text{dir})}(R) \approx -\frac{2}{(4\pi\epsilon_0)^2 R^6} \times \sum_{m<n} \langle nS|\vec{d}|mP \rangle \cdot \langle mP|\vec{d}|nS \rangle \alpha_{1S} \left( \frac{E_{mn}}{\hbar} \right), \]  
(42)
in view of the fact that \( E_{mn}/(\hbar c) \sim \alpha R/a_0 \to 0 \). For the 3S–1S interaction, this implies that the pole term yields another nontrivial contribution to \( D_6 \), which can be expressed as follows,
\[ D_6^P(3S;1S) = \frac{2}{(4\pi\epsilon_0)^2} \langle 3S|\vec{d}|2P \rangle \cdot \langle 2P|\vec{d}|3S \rangle \times \alpha_{1S} \left( \omega = \frac{E_{2PS}}{\hbar} \right), \]  
(43)
where the sum over magnetic projections of the virtual 2P state is implied,
\[ \langle 3S|\vec{d}|2P \rangle^2 = \frac{2^{15} \times 3^8}{512} e^2 a_0^2. \]  
(44)
The polarizability \( \alpha_{1S}(\omega = E_{2PS}/\hbar) \) slightly differs from the static value given in Eq. (41),
\[ \alpha_{1S} \left( \omega = \frac{E_{2PS}}{\hbar} \right) = 4.632 \times 10^8 \frac{e^2 a_0^2}{E_h}. \]  
(45)
Thus, the direct pole term, \( D_6^P(3S;1S) \), is given by
\[ D_6^P(3S;1S) = 8.158 \times 10^7 \, E_h a_0^6. \]  
(46)

Adding the results from Eq. (38), (40) and (46), one finally obtains the complete result for the \( D_6 \) coefficient of the 3S–1S interaction,
\[ D_6(3S;1S) = \tilde{D}_6(3S;1S) + D_6^P(3S;1S) = 9.478 \times 10^7 \, E_h a_0^6. \]  
(47)

We have verified the result (47) by two alternative numerical methods. A discrete lattice representation of the radial Schrödinger equation and its spectrum (Ref. [17]) can be used in order to approximate the radial component of the Schrödinger–Coulomb propagator. This leads to an alternative evaluation of the \( D_6 \) coefficient in terms of an explicit sum over virtual states comprising the pseudo-spectrum (see Ref. [6]). The result confirms that \( D_6(3S;1S) = 9.478(1) \). Another possibility to verify the result (47) consists in an approach based on “intermediate quantum numbers”, as outlined in the text surrounding Eq. (33) of Ref. [1]. The basic idea is that one can shift the reference-state quantum numbers artificially in the integrals describing the van der Waals energy, provided the bound-state energies of both involved states combined add up to the same total reference-state energy in the two-atom system. This second approach also confirms the result (47).

Similarly, the mixing term \( M_6 \) is obtained as the sum of a Wick-rotated nondegenerate term \( \tilde{M}_6(3S;1S) \), a Wick-rotated degenerate contribution \( \tilde{M}_6(3S;1S) \), and a pole term \( M_6^P(3S;1S) \),
\[ M_6(3S;1S) = \tilde{M}_6(3S;1S) + \tilde{M}_6(3S;1S) + M_6^P(3S;1S). \]  
(48)
The nondegenerate Wick-rotated contribution
\[ \tilde{M}_6(3S;1S) = \frac{3}{(4\pi\epsilon_0)^2} \int_0^\infty d\omega \bar{\alpha}_{3S1S}(\omega) \alpha_{3S1S}(\omega) = -5.588 \times 10^8 \, E_h a_0^6. \]  
(49)
The degenerate coefficient \( \tilde{M}_6(3S;1S) \) is given by
\[ \tilde{M}_6(3S;1S) = \frac{3}{(4\pi\epsilon_0)^2} \int_0^\infty d\omega \bar{\alpha}_{3S1S}(\omega) \alpha_{3S1S}(0) = -5.588 \times 10^8 \, E_h a_0^6. \]  
(50)

where we refer to Eq. (24) for the definition of \( \bar{\alpha}_{3S1S}(\omega) \). We first carry out the integration and then take the limit \( L_3 \to 0, F_3 \to 0 \) at the end of the calculation. The product of the matrix element of the dipole moment operators (with the sum over the magnetic projections implied) is
\[ \langle 1S|\vec{d}|3P \rangle \cdot \langle 3P|\vec{d}|3S \rangle = -\frac{243\sqrt{3} e^2 a_0^2}{64}. \]  
(52)
The mixed static polarizability $\alpha_{3S1S}(0)$ is given by

$$\alpha_{3S1S}(0) = -\frac{621 \sqrt{3} e^2 a_0^2}{512 E_h}. \quad (53)$$

An analytic calculation of the integral in Eq. (51) thus gives the result

$$\overline{M}_6(3S; 1S) = \frac{3^9 \times 23}{215} E_h a_0^6 = 13.815 \, 582 \, 275 \, E_h a_0^6. \quad (54)$$

Similar to the direct pole term, the mixing pole term $M^P_6(3S; 1S)$ is given by

$$M^P_6(3S; 1S) = \frac{2}{(4\pi \epsilon_0)^2} (1S|\vec{d}|2P) \cdot (2P|\vec{d}|3S) \times \alpha_{3S1S} \omega = \frac{E_{2P3S}}{h} \left( \omega = \frac{E_{2P3S}}{h} \right)$$

$$= \frac{2}{(4\pi \epsilon_0)^2} \left( -2.159 \, 394 \, 993 e^2 a_0^2 \right) \frac{E_{2P3S}}{h} 5^6 \times \sqrt{3}$$

$$= -5.229 \, 153 \, 219 \, E_h a_0^6. \quad (55)$$

Thus, the total mixing contribution $M_6(3S; 1S)$ is

$$M_6(3S; 1S) = \overline{M}_6(3S; 1S) + M^P_6(3S; 1S) = 2.998 \, 269 \, 538 \, E_h a_0^6. \quad (56)$$

While the direct and mixing coefficients are of the same order-of-magnitude for 2S–1S interactions ($\approx 176.75$ versus $\approx 27.98$), they differ by two orders-of-magnitude in the case of the 3S–1S system.

### B. Intermediate distance

In the intermediate range of interatomic distances,

$$\frac{a_0}{\alpha} \ll R \ll \frac{\hbar c}{\mathcal{L}}, \quad (57)$$

the treatment becomes a little sophisticated. As far as $\overline{W}$ is concerned, we are in the Casimir–Polder regime where the result is given by an $R^{-7}$ interaction. However, we incur a contribution proportional to $R^{-6}$ from the quasi-degenerate 3P states, i.e., from $\overline{W}$. This contribution competes with the oscillatory long-range tails from the pole terms, which eventually drop off only as $1/R^2$.

From the quasi-degenerate states, using the approach outlined in Eqs. (23) and (24) of Ref. [1], one obtains

$$\overline{W}^{(\text{dir})}_{3S; 1S}(R) = -\frac{D_6(3S; 1S)}{R^6} = -729 \, E_h \left( \frac{a_0}{R} \right)^6. \quad (58)$$

The Wick-rotated contribution to the interaction is thus still of the $R^{-6}$ form, as it is in the van der Waals range, but the coefficient is reduced in magnitude as compared to Eq. (47). In the intermediate range, the nondegenerate contribution $\overline{W}^{(\text{dir})}_{3S; 1S}(R)$ is much smaller than $\overline{W}^{(\text{dir})}_{3S; 1S}(R)$; it follows a $1/R^7$ law.

Let us now look into the pole term contribution, $P^{(\text{dir})}_{3S; 1S}(R)$, in the Casimir-Polder range. The Wick rotation from the positive real axis onto the imaginary axis picks up two poles at $\omega = -E_{3P_{1/2},3S}/\hbar + i\epsilon = -L_3 + i\epsilon$ and $\omega = -E_{3P_{3/2},3S}/\hbar + i\epsilon$, which, respectively, are due to the presence of the quasi degenerate $3P_{1/2}$ level and the low lying $2P$ level. The contribution of the quasi degenerate $3P_{1/2}$ level to the $1/R^6$-part of the pole term is already contained in Eq. (58); we observe that the $1/R^6$ term in Eq. (18) does not have additional factors.
of $E_{mn}\sim \mathcal{L}_3$ and is therefore not suppressed by the Lamb shift numerators. By contrast, the terms of order $1/R^4$ and $1/R^2$ in Eq. (18) from the pole term due to the $3P_{3/2}$ levels are suppressed by the very small energy factor in the numerators of Eq. (18) (proportional to $\mathcal{L}_3^2$ and $\mathcal{L}_3^3$, respectively). For simplicity, we treat the contribution of the $3P_{1/2}$ and $3P_{3/2}$ levels uniformly by assigning their contribution to the Wick-rotated term. This procedure follows the one adopted in Eqs. (45a), (45b) and (46) of Ref. [1].

Finally, the direct pole term for the $3S$–$1S$ system (contribution of the lower-lying $2P$ states) reads

$$\mathcal{P}_{3S:1S}^{(\text{dir})}(R) = -\frac{2^{15}}{5^{12}} \times 3^8 \frac{E_h a_0^6}{R^6} \alpha_{1S}^{\text{dir}} \left( \frac{5 E_h}{72 h} \right) \times \left\{ \cos \left( \frac{5 \alpha R}{36 a_0} \right) \left[ 3 - 5 \left( \frac{5 \alpha R}{72 a_0} \right)^2 + \left( \frac{5 \alpha R}{72 a_0} \right)^4 \right] + \frac{5 \alpha R}{36 a_0} \sin \left( \frac{5 \alpha R}{36 a_0} \right) \left[ 3 - \left( \frac{5 \alpha R}{72 a_0} \right)^2 \right] \right\}.$$  

Here, $\alpha_{1S}^{\text{dir}}(\omega)$ is the dimensionless polarizability, which we define as follows,

$$\alpha_{1S}^{\text{dir}}(\omega) = \frac{E_h}{e^2 a_0^2} \alpha_{1S}(\omega).$$

For clarity, we add that our dimensionless polarizability could otherwise be characterized as the numerical value of the atomic polarizability in atomic units.

The Wick-rotated part of the mixing term is the sum

$$\mathcal{W}_{3S:1S}^{(\text{mix})}(R) = \mathcal{W}_{3S:1S}^{(\text{dir})}(R) + \mathcal{W}_{3S:1S}^{(\text{mix})}(R).$$

The nondegenerate part $\mathcal{W}_{3S:1S}^{(\text{mix})}(R)$ follows an $R^{-7}$ power law, whereas the degenerate part $\mathcal{W}_{3S:1S}^{(\text{mix})}(R)$ is still proportional to $R^{-6}$. Thus, to a good approximation, we have

$$\mathcal{W}_{3S:1S}^{(\text{mix})}(R) \approx \mathcal{W}_{3S:1S}^{(\text{mix})}(R) = -\frac{3^9 \times 23}{2^{15}} E_h \left( \frac{a_0}{R} \right)^6$$

in the intermediate distance range. The mixed pole term is obtained as

$$\mathcal{P}_{3S:1S}^{(\text{mix})}(R) = \frac{2^{15} \times \sqrt{3}}{3^2 \times 5^6} \frac{E_h a_0^6}{R^6} \alpha_{3S:1S}^{\text{dir}} \left( \frac{5 E_h}{72 h} \right) \times \left\{ \cos \left( \frac{5 \alpha R}{36 a_0} \right) \left[ 3 - 5 \left( \frac{5 \alpha R}{72 a_0} \right)^2 + \left( \frac{5 \alpha R}{72 a_0} \right)^4 \right] + \frac{5 \alpha R}{36 a_0} \sin \left( \frac{5 \alpha R}{36 a_0} \right) \left[ 3 - \left( \frac{5 \alpha R}{72 a_0} \right)^2 \right] \right\},$$

where $\alpha_{3S:1S}^{\text{dir}}$ represents the dimensionless mixed $\alpha_{3S:1S}$ polarizability, defined according to Eq. (22b).

### C. Very large interatomic distance

We are entering the regime

$$R \gg \frac{\hbar c}{\mathcal{E}}.$$  

This range is irrelevant for interactions in the laboratory but not for interactions relevant to astrophysical processes [18, 19]. Expressed in units of the Hartree energy $E_h$, the physical values of the Lamb shift and fine structure energies are [15, 16, 20]

$$\mathcal{L}_3 = 4.78 \times 10^{-8} E_h,$$

$$\mathcal{F}_3 = 4.46 \times 10^{-7} E_h \approx 10 \mathcal{L}_3.$$  

| System     | $\mathcal{M}_6$ | $M_6$  | $M_6^P$ | $M_6 = \mathcal{M}_6 + M_6 + M_6^P$ |
|------------|----------------|--------|---------|----------------------------------|
| 3S–1S     | 13.815582275   | -5.588 159 518 | -5.229 153 219 | 2.998 269 538 |
| 4S–1S     | 8.015439766    | -3.063 629 332 | -4.033 187 464 | 0.918 622 970 |
| 5S–1S     | 5.716898855    | -2.006 704 605 | -3.302 240 659 | 0.407 953 591 |
| 6S–1S     | 4.480588908    | -1.435 991 892 | -2.825 817 540 | 0.218 779 478 |
| 7S–1S     | 3.702266657    | -1.085 159 560 | -2.485 383 226 | 0.131 723 872 |
| 8S–1S     | 3.163734811    | -0.851 710 237 | -2.224 628 639 | 0.087 395 934 |
| 9S–1S     | 2.767122768    | -0.687 554 678 | -2.020 512 545 | 0.059 055 545 |
| 10S–1S    | 2.461858057    | -0.567 328 345 | -1.851 944 579 | 0.042 585 133 |
| 11S–1S    | 2.219074417    | -0.476 448 189 | -1.711 091 985 | 0.031 534 242 |
| 12S–1S    | 2.021036738    | -0.405 984 611 | -1.590 955 009 | 0.024 097 118 |
TABLE III. Dimensionless dipole matrix elements $F_{mn}$. For given $m$, dipole matrix elements decrease with $n$. For given $n$, they grow with $m$. Most of the matrix elements are expressed in terms of their prime factors. Some of them are given as the approximate real numbers in order to save space in the table.

| $m$ | 2       | 3       | 4       | 5       | 6       |
|-----|---------|---------|---------|---------|---------|
| 3   | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 4   | 215 $\cdot$ 64 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 64 |
| 5   | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 6   | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 7   | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 8   | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 9   | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |
| 10  | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 | 215 $\cdot$ 38 | 215 $\cdot$ 64 |

TABLE IV. Numerical values of the dimensionless polarizabilities $G_{mn}$. The polarizability follows the following trends: It increases with the principal quantum number $n$ of the reference state; for given $n$, the polarizability decreases with $m$ and approaches the ground state static value 9/2 in the limit $m \to \infty$.

| $m$ | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      | 11      |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 3   | 4.63234 |       |         |         |         |         |         |         |         |         |
| 4   | 4.74778 | 4.51576 |         |         |         |         |         |         |         |         |
| 5   | 4.81570 | 4.53388 | 4.50337 |         |         |         |         |         |         |         |
| 6   | 4.85682 | 4.54668 | 4.50803 | 4.50099 |         |         |         |         |         |         |
| 7   | 4.88315 | 4.55541 | 4.51181 | 4.50255 | 4.50036 |         |         |         |         |         |
| 8   | 4.90086 | 4.56150 | 4.51465 | 4.50395 | 4.50098 | 4.50015 |         |         |         |         |
| 9   | 4.91331 | 4.56587 | 4.51679 | 4.50509 | 4.50158 | 4.50043 | 4.50007 |         |         |         |
| 10  | 4.92236 | 4.56909 | 4.51840 | 4.50599 | 4.50210 | 4.50072 | 4.50021 | 4.50004 |         |         |
| 11  | 4.92913 | 4.57152 | 4.51964 | 4.50670 | 4.50253 | 4.50036 | 4.50011 | 4.50002 |         |         |
| 12  | 4.93434 | 4.57340 | 4.52061 | 4.50727 | 4.50289 | 4.50121 | 4.50050 | 4.50019 | 4.50006 | 4.50001 |

The approximation (64) is valid in the region

$$R \gg \frac{\hbar}{\alpha E_k} = \frac{a_0 E_k}{\alpha E_k} = 2.864 \times 10^9 a_0 = 0.1516 \text{ m}.$$  \hspace{1cm} (66)

For very large interatomic separation $R \to \infty$, the integrands in Eqs. (10) and (13) are significantly damped by exponential damping in $\omega$. For large $R$, we may thus carry out the following approximations in the integrands of the van der Waals energy [Eqs. (10) and (13)]

$$\alpha_{3S}(\omega) \approx \alpha_{3S}(0) \approx \overline{\alpha}_{3S}(0), \quad \alpha_{1S}(\omega) \approx \alpha_{1S}(0).$$  \hspace{1cm} (67)
of the excited $3S$ state comes from the virtual $3P_{1/2}$ and $3P_{3/2}$ levels,

$$\varpi_{3S}(0) = 2\varpi_{3S}(0) = 36 e^2 a_0^2 \left( \frac{2}{F_3} - \frac{1}{L_3} \right).$$  \hspace{1cm} (69)$$

From Eqs. (41), (68) and (69), we find that the long-distance limit of the *Wick-rotated contribution* to the $3S$–$1S$ interaction energy is positive (repulsive),

$$W^{(\text{dir})}_{3S:1S}(R) \sim -\infty \left( \frac{E_h}{R} \right)^7 \left( \frac{E_h}{L_3} - \frac{E_h}{F_3} \right).$$  \hspace{1cm} (70)$$

This interaction is valid only for very large interatomic distances given in Eq. (66).

The remaining integral is evaluated as follows,

$$\text{Re} \left\{ \frac{\hbar}{\pi e^2} \int_0^\infty d\omega \, e^{-2\omega R_c/c} \omega^4 \frac{R^2}{R^2} \left[ 1 + \frac{2}{\omega R} + 5 \left( \frac{c}{\omega R} \right)^2 \right] + 6 \left( \frac{c}{\omega R} \right)^3 + 3 \left( \frac{c}{\omega R} \right)^4 \right\} = \frac{23 \hbar c}{4 \pi R^2}. $$  \hspace{1cm} (68)

The interaction is known as the retarded Casimir–Polder interaction and is proportional to $R^{-7}$.

The dominant contribution to the static polarizability of the excited $3S$ state comes from the virtual $3P_{1/2}$ and $3P_{3/2}$ levels,

$$\varpi_{3S}(0) = 2\varpi_{3S}(0) = 36 e^2 a_0^2 \left( \frac{2}{F_3} - \frac{1}{L_3} \right).$$  \hspace{1cm} (69)$$

From Eqs. (41), (68) and (69), we find that the long-distance limit of the *Wick-rotated contribution* to the $3S$–$1S$ interaction energy is positive (repulsive),

$$W^{(\text{dir})}_{3S:1S}(R) \sim -\infty \left( \frac{E_h}{R} \right)^7 \left( \frac{E_h}{L_3} - \frac{E_h}{F_3} \right).$$  \hspace{1cm} (70)$$

This interaction is valid only for very large interatomic distances given in Eq. (66).

The dominant term in the range (64) comes from the pole contribution in Eq. (59) and reads

$$p_{3S:1S}^{(\text{dir})}(R) = -\frac{2^3}{5^8} \frac{\alpha_0^4}{\rho^2} \frac{\alpha_1^{\text{dir}}}{\alpha_1^{\text{S}}} \left( \frac{5 E_h}{72 \hbar} \right) \cos \left( \frac{5 \alpha_0}{36} \right),$$  \hspace{1cm} (71)$$

where $\rho = R/a_0$. The pole term falls off as $R^{-2}$ and dominates the interaction energy (see Fig. 1). We note the numerical identities

$$\frac{2^3}{5^8} = 2.048 \times 10^{-5}, \quad \frac{\alpha_1^{\text{dir}}}{\alpha_1^{\text{S}}} \left( \frac{5 E_h}{72 \hbar} \right) = 4.63234. $$  \hspace{1cm} (72)$$

The coefficient multiplying the leading oscillatory $1/R^2$ term given in Eq. (71) thus is of order $10^{-4}$; this is in contrast to the $D_6$ and $\tilde D_6$ coefficients, which are of order $10^3$ (in atomic units). The numerical coefficients are thus in part responsible for a certain suppression of the long-range tail, as evident (in the intermediate region) from Fig. 2. The same trend is observed for $nD$–$1S$ interactions [4].

We should supplement the result for the mixing term in the very-long-range (66). As far as the mixing type contribution to the Casimir–Polder term is concerned, the degenerate part dominates the nondegenerate one.
One has

$$W_{3S;1S}^{(\text{mix})}(R) \approx \frac{3^2 \times 23^2 \frac{E_h}{R}}{216} a_0 \left( \frac{a_0}{R} \right)^7 \left( \frac{E_h}{E_0} - 2 \frac{E_h}{E_0} \right). \quad (73)$$

By contrast, the leading $1/R^2$ contribution to the mixing pole term reads as [see Eq. (63)]

$$p_{3S;1S}^{(\text{mix})}(R) = - \frac{3^2 \times 3! \times 2^3}{3!} \frac{\alpha^4 E_h}{R} \left( \frac{a_0}{R} \right)^2 \times \alpha_{3S;1S} \left( \frac{5 E_h}{72 \hbar} \right) \cos \left( \frac{5 \alpha R}{36 a_0} \right), \quad (74)$$

and it dominates in the very-long-range limit [Eq. (66)].

**IV. STATES WITH $4 \leq n \leq 12$**

**A. Van der Waals range**

First, we discuss the $nS$–$1S$ interaction, with $4 \leq n \leq 12$, in the van der Waals regime (32),

$$a_0 \ll R \ll \frac{a_0}{\alpha}. \quad (75)$$

In this range, the interaction is described to good approximation by the functional form (33). One should mention that the calculation of polarization-type matrix elements that generalize Eq. (36) to states with $n \geq 4$ requires the sophisticated use of contiguous relations for hypergeometric functions [21, 22]. Eventually, one can bring the matrix elements into a form that involves a rational function of the variable

$$\tau_n = \left( 1 + \frac{n^2 \hbar c}{\alpha^2 m c^2} \right)^{1/2}, \quad (76)$$

where $n$ is the principal quantum number, and a further term where a rational function of $\tau_n$ multiplies the hypergeometric function

$$2F_1 \left( 1, -n \tau_n, 1 - n \tau_n, \frac{(1 - \tau_n)^2}{(1 + \tau_n)^2} \right). \quad (77)$$

Here we describe calculations of the polarization-type matrix elements (11b) for $nS$ states with principal quantum numbers as high as $n = 12$; several thousand terms are encountered in intermediate steps of the calculations; these are handled with the help of computer algebra systems [23]. For the mixed polarizabilities given in Eqs. (22a) and (22b), the calculations are even a little more involved because the radial wave functions of the bra and ket states are different; one may still express them in terms of a rational function of the $\tau_n$ variable, and a hypergeometric function. Note that lattice methods that lead to a pseudospectrum of virtual states (see Ref. [17]) cannot be used with good effect for highly excited states, because of numerical problems associated with the modeling of wave functions with many nodes. These numerical difficulties may be one reason why early numerical calculations for $C_6(2S;1S)$ coefficients [5, 6] were never generalized to higher excited $S$ states. Eventually, for $4 \leq n \leq 12$, the $D_6$ and $M_6$ coefficients are given in Tables I and II as the generalizations of Eqs. (47) and (56), respectively.

**B. Intermediate distance**

We discuss the intermediate distance range

$$\frac{a_0}{\alpha} \ll R \ll \frac{\hbar c}{E}. \quad (78)$$

In Table II, we generalize the result (58) and (62) to higher excited $nS$ states. The nonretarded $1/R^6$ tail of the direct term has the functional form

$$W_{nS;1S}^{(\text{dir})}(R) = -\frac{D_6(nS;1S)}{R^6}, \quad (79)$$

mainly due to the contribution from the degenerate $nP$ states. The degenerate $D_6$ coefficient can be brought into the general form

$$D_6(nS;1S) = \frac{81}{8} n^2 (n^2 - 1) E \frac{a_0^6}{\hbar c}, \quad (80)$$

for $n \geq 2$. The leading contribution to the mixing term is

$$W_{nS;1S}^{(\text{mix})}(R) = -\frac{W_{nS;1S}}{R^6}, \quad (81)$$

again due to the contribution from the degenerate $nP$ states. In the intermediate range, the Wick-rotated term of order $1/R^6$ competes with the pole term given in Eq. (18), due to lower-lying $mP$ states. We express the latter as follows,

$$p^{(\text{dir})}(R) = -\frac{2E_h}{3\hbar c} \sum_{m=2}^{n-1} \frac{\langle nS|mP \rangle \cdot \langle mP|d\rangle}{e^2 a_0^2}$$

$$\times \alpha_{3S;1S}^{\text{mix}} \left( \frac{d_m \alpha E_h}{2 \hbar} \right) \times \left\{ \cos (d_m \alpha \rho) \left( 3 - 5 \left( \frac{d_m \alpha \rho}{2} \right)^2 + \left( \frac{d_m \alpha \rho}{2} \right)^4 \right) \right. \right.$$  

$$+ d_{mn} \alpha \rho \sin (d_m \alpha \rho) \left( 3 - \left( \frac{d_{mn} \alpha \rho}{2} \right)^2 \right) \right\}, \quad (82)$$

where $\rho = R/a_0$. We have used the identities

$$\frac{E_{mn}}{\hbar} = -\frac{d_{mn} \alpha E_h}{2 \hbar}, \quad \frac{2E_{mn} R}{\hbar c} = -d_{mn} \alpha \rho, \quad (83)$$
TABLE VI. Numerical values of the dimensionless polarizabilities \( I_{mn} \). In contrast to the dimensionless polarizabilities \( G_{mn} \), the trend in the numerical data implies lower values of \( I_{mn} \) for higher excited reference states. Also, \( I_{mn} \) for given \( n \) decreases as the value of \( m \) increases.

| \( n \) | \( m \) | \( 2 \) | \( 3 \) | \( 4 \) | \( 5 \) | \( 6 \) | \( 7 \) | \( 8 \) | \( 9 \) | \( 10 \) | \( 11 \) |
|------|------|------|------|------|------|------|------|------|------|------|------|
| 3    | -2.15939 | - | - | - | - | - | - | - | - | - | - |
| 4    | -1.18140 -1.13568 | - | - | - | - | - | - | - | - | - | - |
| 5    | -0.78285 -0.74972 -0.74594 | - | - | - | - | - | - | - | - | - | - |
| 6    | -0.57151 -0.54645 -0.54313 -0.54252 | - | - | - | - | - | - | - | - | - | - |
| 7    | -0.44247 -0.42273 -0.41992 -0.41932 -0.41917 | - | - | - | - | - | - | - | - | - | - |
| 8    | -0.35643 -0.34036 -0.33798 -0.33743 -0.33728 -0.33723 | - | - | - | - | - | - | - | - | - | - |
| 9    | -0.29546 -0.28206 -0.27953 -0.27938 -0.27933 -0.27932 | - | - | - | - | - | - | - | - | - | - |
| 10   | -0.25031 -0.23891 -0.23671 -0.23657 -0.23652 -0.23650 -0.23650 | - | - | - | - | - | - | - | - | - | - |
| 11   | -0.21554 -0.20587 -0.20332 -0.20393 -0.20380 -0.20376 -0.20374 -0.20373 -0.20373 | - | - | - | - | - | - | - | - | - | - |
| 12   | -0.18850 -0.17987 -0.17850 -0.17815 -0.17804 -0.17799 -0.17798 -0.17797 -0.17796 -0.17796 | - | - | - | - | - | - | - | - | - | - |

TABLE VII. Numerical values of the degenerate contributions to the direct \( D_T \) and mixed \( M_T \) Casimir-Polder coefficients for two-atom systems. The coefficients are given in units of \( \frac{1}{\pi^2} E_0^2 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) a_0^2 \) (which is a negative quantity), explaining why the overall interaction term is repulsive.

| System | \( D_T \) | \( M_T \) |
|--------|---------|---------|
| 3S-1S  | 1.864 \(\times 10^3\) | 17.653 244.019 |
| 4S-1S  | 3.105 | 10.241 950.813 |
| 5S-1S  | 5.255 \(\times 10^3\) | 7.304 926.315 |
| 6S-1S  | 6.205 \(\times 10^3\) | 5.725 169.938 |
| 7S-1S  | 30.429 | 4.730 674.062 |
| 8S-1S  | 52.164 | 4.042 550.036 |
| 9S-1S  | 83.835 | 3.553 767.981 |
| 10S-1S | 152.327 \(\times 2\) | 3.145 707.517 |
| 11S-1S | 375.705 \(\times 2\) | 2.835 483.977 |
| 12S-1S | 266.409 | 2.582 435.832 |

where

\[
d_{mn} = \frac{1}{m^2} - \frac{1}{n^2}.
\]

Values for the (dimensionless) dipole matrix elements

\[
F_{mn} = \frac{\langle nS|d|^mP\rangle \cdot \langle mP|d^\dagger|nS\rangle}{e^2 a_0^2} \quad m < n, \quad n \leq 12,
\]

are given in Table III. While it is possible to give a semi-analytic expression for the matrix elements (see the Appendix and Ref. [24]), these are quite complicated. It is instructive to have an explicit reference to the absolute magnitude of the coefficients; hence, we include Table III. The (dimensionless) polarizabilities

\[
G_{mn} = \alpha^d_{1S} \left( \frac{d_{mn} \alpha E_h}{2\hbar} \right) \quad m < n, \quad n \leq 12,
\]

are given in Table IV, for all states relevant to the current investigation. The real part of the mixing pole term has
TABLE IX. Numerical values of the Wick-rotated type $W_{4S,1S}(R)$ and the pole type $P_{4S,1S}(R)$ long-range interaction frequency shift in the $(4S;1S)$ system. The $\pm$ sign corresponds to the $\pm$ sign in the $|1S\rangle$/$|4S\rangle$ or $|4S\rangle/|1S\rangle$ superposition.

| $R$ (Å) | $W_{4S,1S}(R)$ [Hz] | $P_{4S,1S}(R)$ [Hz] |
|---------|---------------------|---------------------|
| 20      | $-(6.425 \pm 0.011) \times 10^6$ | $-(1.249 \pm 0.091) \times 10^8$ |
| 40      | $-(1.004 \pm 0.002) \times 10^6$ | $-(1.951 \pm 0.146) \times 10^6$ |
| 80      | $-(1.568 \pm 0.003) \times 10^6$ | $-(3.048 \pm 0.229) \times 10^4$ |
| 200     | $-(6.416 \pm 0.011) \times 10^5$ | $-(1.246 \pm 0.094) \times 10^2$ |
| 400     | $-(1.000 \pm 0.002) \times 10^2$ | $-(1.936 \pm 0.151) \times 10^0$ |
| 800     | $-(1.554 \pm 0.003) \times 10^0$ | $-(2.962 \pm 0.256) \times 10^{-2}$ |
| 2000    | $-(8.851 \pm 0.003) \times 10^{-3}$ | $-(5.984 \pm 0.462) \times 10^{-3}$ |
| 20 000  | $-(5.822 \pm 0.016) \times 10^{-9}$ | $-(1.152 \pm 0.994) \times 10^{-6}$ |
| 200 000 | $-(5.519 \pm 0.018) \times 10^{-15}$ | $-(1.658 \pm 1.321) \times 10^{-8}$ |

been given in Eq. (26),

$$p^{(\text{mix})}(R) = \frac{2E_h}{3\rho^6} \sum_{m<n} \langle nS|\tilde{d}|nP\rangle \cdot \langle mP|\tilde{d}|1S\rangle e^{2\alpha R}$$

$$\times \cos(d_{mn}\alpha \rho) \left( 1 - 5 \frac{d_{mn}\alpha \rho}{2} + \left( \frac{d_{mn}\alpha \rho}{2} \right)^2 \right)$$

$$+ d_{mn}\alpha \rho \sin(d_{mn}\alpha \rho) \left( 1 - \left( \frac{d_{mn}\alpha \rho}{2} \right)^2 \right).$$  

Numerical values for the (dimensionless) dipole matrix elements

$$H_{mn} = \frac{\langle nS|\tilde{d}|mP\rangle \cdot \langle mP|\tilde{d}|1S\rangle}{e^2\alpha R}, \quad m<n, \quad n \leq 12,$$  

and the (dimensionless) polarizabilities

$$I_{mn} = a_{nS1S}^d \left( \frac{d_{mn}\alpha E_h}{2h} \right) \quad m<n, \quad n \leq 12,$$  

are given in Tables V and VI, respectively. For a discussion of the evaluation of the $H_{mn}$, see the Appendix. As the principal quantum number $n$ of the excited state of the hydrogen atom interacting with the ground state increases, it takes longer and longer for the pole term to finally assume dominance over the Wick-rotated term (see Figs. 3, 4 and 5).

A few words on the precise formulation of the intermediate distance range are perhaps in order. Namely, in principle, one might argue that the intermediate range should be bounded from above by $h\epsilon/F_n$ instead of $h\epsilon/L_n$, as the former quantity is smaller than the latter.

In the rather narrow window where $h\epsilon/F_n < R < h\epsilon/L_n$, transitions between $nS$ and $nP_{3/2}$ states are suppressed by retardation while those between $nS$ and $nP_{1/2}$ states are not. We do not enter the details of this regime due to its narrow character, which would make it difficult to reliably clarify the asymptotic behavior of the interaction energy. Mathematically speaking, the inequality $R \ll h\epsilon/L_n$ implies $R \ll h\epsilon/F_n$ because $F_n$ and $L_n$ are apart by only a single order-of-magnitude [see Eq. (65)]. If desired, then the regime $h\epsilon/F_n < R < h\epsilon/L_n$ could only be accessed reliably by a numerical calculation.
C. Very large distances

The regime

\[ R \gg \frac{\hbar c}{L} \]  

(90)

is characterized by two competing terms, a \(1/R^7\) term from the Wick-rotated contribution and an oscillatory contribution from the pole term. In Table VII, we give a generalization of (70) and (73) to higher excited \(S\) states,

\[ \mathcal{W}^{(\text{dir})}_{nS;1S}(R) = \frac{D_7(nS;1S)}{R^7}. \]  

(91)

The \(D_7\) coefficients obey the relationship

\[ D_7(nS;1S) = \frac{207}{16} n^2 (n^2 - 1) \frac{a_S^2 E_h}{\alpha \pi} \left( \frac{E_h}{L_n} + \frac{2}{F_n} \right). \]  

(92)

The Wick-rotated contribution to the mixing term has the functional form

\[ \mathcal{W}^{(\text{mix})}_{nS;1S}(R) = \frac{M_7(nS;1S)}{R^7}, \]  

(93)

where we refer to Table VII for the numerical values. However, the \(1/R^7\) tails are suppressed, in the very-long-range limit, in comparison to the pole terms, which go as \(1/R^2\).

In fact, due to the trend in the numerical coefficients recorded in Tables III—VI, the dominant contributions from the pole terms (direct and mixing term) comes from virtual \(2P\) states and can be expressed as

\[ P^{(\text{dir})}(R) \approx -\frac{d_{2n} E_h \alpha^4}{24 \rho^2} F_{2n} G_{2n} \cos(d_{2n} \alpha \rho), \]  

(94)

and

\[ P^{(\text{mix})}(R) \approx -\frac{d_{2n} E_h \alpha^4}{24 \rho^2} H_{2n} I_{2n} \cos(d_{2n} \alpha \rho), \]  

(95)

respectively. Contributions from \(nP\) states with \(3 \leq m \leq n - 1\) are numerically, but not parametrically, suppressed. The quantity \(d_{mn}\) was defined in Eq. (84), and \(\rho\) was defined in the text following Eq. (71).

V. NUMERICAL EXAMPLES

It can be helpful to have numerical reference data available for the pole term, as well as the Wick-rotated contribution to the interaction energy, for sample values of the interatomic distance. These are given in Tables VIII and IX. We concentrate on the \(3S–1S\) and \(4S–1S\) systems. One can clearly discern the dominance of the pole term in the long-range limit, and its suppression in the van der Waals range (6). Note that both the direct as well as the mixing terms are indicated in Tables VIII and IX. In entries with \(\mp\), the positive sign refers to the gerade configuration of the wave functions, and the negative sign is relevant to the ungerade configuration. The opposite happens for the numerical entries involving the \(\mp\) sign.

VI. CONCLUSIONS

We have studied \(nS–1S\) van der Waals interactions among hydrogen atoms in detail, for \(n \geq 3\). In a brief orientation in Sec. II, we discuss the nondegenerate Wick-rotated contribution \(\tilde{\mathcal{W}}(R)\), the degenerate term \(\mathcal{W}(R)\), and the pole term \(\mathcal{Q}(R)\), which splits into a real energy shift \(\mathcal{P}(R)\), and a width term \(\mathcal{P}(R)\). We treat the \(3S–1S\) interaction in great detail in Sec. III, before generalizing the approach to the \(nS–1S\) case in Sec. IV \((4 \leq n \leq 12)\). Numerical reference data are given in Sec. V. These numerical data are crucial in a reliable determination of pressure shifts in high-precision spectroscopy experiments involving highly excited \(S\) states [25, 26].

We differentiate three distance ranges given in Eqs. (6), (7), and (8), which we recall for convenience:

van der Waals: \(\frac{\hbar}{\alpha m_e c} \ll R \ll \frac{\hbar}{\alpha^2 m_e c}\)  

(96a)

Casimir–Polder: \(\frac{\hbar}{\alpha^2 m_e c} \ll R \ll \frac{\hbar c}{L_n}\)  

(96b)

Lamb shift: \(R \gg \frac{\hbar c}{L_n}\)  

(96c)

In the van der Waals range, the interatomic interaction is described to good accuracy by a functional form \(-C_6(A;B)/R^6\), where \(C_6(A;B) = D_6(A;B) + M_6(A;B)\) is the van der Waals coefficient. The direct coefficient \(D_6\) is the sum of a nondegenerate contribution \(\tilde{D}_6\), a degenerate contribution \(\bar{D}_6\), and a pole term \(D_6^P\). Analogously, one has \(M_6 = \bar{M}_6 + \tilde{M}_6 + M_6^P\), where \(\bar{M}_6\) is the nondegenerate contribution to the mixing van der Waals interaction in great detail in Sec. III, before generalizing the approach to the \(nS–1S\) case in Sec. IV \((4 \leq n \leq 12)\). Numerical reference data are given in Sec. V. These numerical data are crucial in a reliable determination of pressure shifts in high-precision spectroscopy experiments involving highly excited \(S\) states [25, 26].
coefficients for the “direct” and “mixing” terms have been obtained, for $nS$–$1S$ interactions, in Tables I and II, on the basis of rather involved analytic calculations of polarizability-type matrix elements [see Eq. (11b)], with several thousand terms in intermediate steps of the calculations; these were handled using computer algebra [23]. The data show a surprising trend: Namely, the dominant contributions to polarizability-type matrix elements [see Eq. (11b)] are due to the smallness of the overall numerical factors multiplying the energy shifts, as evident from Figs. 1, 3, 4, and 5.

(iii) The analysis presented here also raises interesting further questions. E.g., for $nS$–$1S$ interactions, the oscillatory cosine terms, proportional to $1/R^6$, eventually dominate in the long-range limit [see Eqs. (94) and (95)], and the Casimir-Polder tail of order $R^{-7}$ is found to be phenomenologically irrelevant for interactions involving higher excited states. Based on a parametric analysis, one might think that the $R^{-2}$ oscillatory tails should also dominate over the $R^{-6}$ van der Waals interactions, in the intermediate range of interatomic distances. However, as evident from Figs. 1, 3, 4, and 5, the dominance sets in only after the absolute magnitude of the energy shift has decreased to well below 1 Hz in frequency units. As already stated, one can attempt to justify this trend based on the dependence of the energy differences $d_{mn}$ on the principal quantum numbers. For example, one has $d_{(n-1)n} \approx n^{-3}$ and the fact that $d_{mn}$ enters the leading $R^{-2}$ contribution to the pole term in the fourth power [see Eq. (82)]. This compensates the growth of the $F_{mn}$ given in Table III with $m$ for given $n$, and suppresses the contribution from energetically close, lower-lying virtual states to the pole terms, for given $n$ of the reference state. We also observe the decreasing trend in the dipole matrix elements given in Table III with $n$, for given $m$. However, it would be interesting to investigate if there is further, deeper reason for the apparent, non-parametric (there is no factor of the fine-structure constant involved) suppression of the pole terms, and mixing terms, in long-range interactions involving higher excited states of simple atomic systems. This analysis is left for further study.

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Appendix A: Dipole matrix elements $F_{mn}$ and $H_{mn}$

We are concerned with the evaluation of dipole matrix elements of bound-state Schrödinger hydrogen wave functions,

$$G_{n_1n_2}^{\ell_1\ell_2} = \langle n_1\ell_1m_1|\hat{d}|n\ell m\rangle \cdot \langle n\ell m|\hat{d}|n_2\ell_2m_2\rangle, \quad (A1)$$

\[215 \times 3^8 \overset{51}{\approx} 0.88060, \quad (97)\]

\[2^{21} \times 3^8 \times 5^{18} \overset{730}{\approx} 0.00233, \quad (98)\]
where \( \vec{d} = e \vec{r} \) is the dipole operator and the dimensionless dipole matrix elements \( F_{mn} \) and \( H_{mn} \) are given by

\[
F_{mn} = \frac{G_{010}^{mn}}{a^2 a'_0}, \quad H_{mn} = \frac{G_{010}^{mn}}{a^2 a'_0}. \tag{A2}
\]

The well-known expression for the radial function \( R_{n\ell}(r) \),

\[
R_{n\ell}(r) = \left[ \frac{(n - \ell - 1)!}{(n + \ell)!} \right] \frac{2}{n^2 a_0^{n/2}} \left( \frac{2r}{a_0 n} \right)^\ell \exp \left( -\frac{r}{a_0 n} \right) L_{2\ell+1}^{2\ell+1} \left( \frac{2r}{a_0 n} \right); \tag{A3}
\]

allows us to bring the dipole transition matrix element into the form

\[
\int_0^\infty dr^3 r^{n+\ell} R_{n\ell}^*(r) R_{n\ell}(r) = \frac{(n' - \ell' - 1)!}{(n' + \ell')!} \frac{a_0}{4n'^{\ell+2} a_0^{n'^{\ell+2}} \int_0^\infty dx x^{3+\ell'}} \times \exp \left[ -\frac{x}{2} \left( 1 - \frac{1}{n'} \right) \right] \times \frac{1}{n', \ell'} \left( \frac{x'}{n'} \right) L_{2\ell' + 1}^{2\ell' + 1} \left( \frac{x'}{n'} \right), \tag{A4}
\]

where \( x = 2r/a_0 \). A result obtained for the radial matrix element in Ref. [24] is reproduced in Eq. (63.2) of Ref. [27]; the latter appears to benefit from some corrections for typographical errors that occurred in the original work [24]. Direct application of Eq. (63.2) of Ref. [27] leads to the formula

\[
G_{n_1 n_2}^{010} = (-1)^{n_1 + n_2} \frac{16 n^5 n_1^{5/2} n_2^{5/2} (n^2 - 1) e^2 a_0^2}{(n - n_1)^4 (n - n_2)^4} \times \left( \frac{n - n_1}{n + n_1} \right)^{n+n_1} \left( \frac{n - n_2}{n + n_2} \right)^{n+n_2} \times T_1 \times T_2, \tag{A5a}
\]

where

\[
T_1 = 2F_1 \left( 2, n - 1 - n_1, 2, u_1 \right) - \frac{(n - n_1)^2}{(n + n_1)^2} \left( 2, n - 1 - n_1, 2, u_1 \right),
\]

\[
T_2 = 2F_1 \left( 2, n - 1 - n_2, 2, u_2 \right) - \frac{(n - n_2)^2}{(n + n_2)^2} \left( 2, n - 1 - n_2, 2, u_2 \right), \tag{A5b}
\]

and the arguments of the hypergeometric functions are

\[
u_1 = -\frac{4n n_1}{(n - n_1)^2}, \quad u_2 = -\frac{4n n_2}{(n - n_2)^2}. \tag{A5c}
\]

As it stands, formula (A5) is not applicable to the case \( n = n' \) and has to be supplemented by the result

\[
G_{n n}^{010} = \frac{9}{4} n^2 (n^2 - 1) e^2 a_0^2. \tag{A6}
\]

An alternative representation of the transition matrix elements, to encompass both formulas (A5) and (A6), would thus be desirable. However, a literature search including Sec. 2.1.9.4 of [28] does not reveal any immediately applicable integral formulas for integrals of the type (A4). However, an entry in a recently published online database [29] allows us to express the integral (A4) as a finite nested double sum over terms involving the Pochhammer symbol \((a)_n = \Gamma(a+n)/\Gamma(a)\),

\[
\int_0^\infty dt t^{a-1} \exp \left( -pt \right) L^n_m (a t) L_\ell^\beta (bt) = \frac{\Gamma(a) (\lambda + 1)_m (\beta + 1)_n p^{-\alpha}}{m! n!} \times \sum_{j=0}^m \frac{(-m)_j (\alpha)_j}{j! (\lambda + 1)_j} \frac{a}{p} \sum_{k=0}^n \frac{(-n)_k (j + \alpha)_k}{k! (\beta + 1)_k} \frac{b}{p}^k. \tag{A7}
\]

The inner sum can be expressed in terms of a terminating hypergeometric function. The coefficient \( G_{n_1 n_2}^{010} \) is finally written in a rather compact form, as follows,

\[
G_{n_1 n_2}^{010} = e^2 a_0^2 a'_0^{10} \frac{(n_1 n_2)^{7/2} n^5 (n^2 - 1)}{(n + n_1)^5 (n + n_2)^5} \times \sum_{\zeta=0}^{n_1 - 1} \frac{1}{\zeta! (2\zeta)} \frac{2n}{(n + n_1)^\zeta} \times 2F_1 \left( 2, 5 + \zeta, 4, \frac{2n_1}{n + n_1} \right) \times \sum_{\beta=0}^{n_2 - 1} \frac{1}{\beta! (2\beta)} \frac{2n}{(n + n_2)^\beta} \times 2F_1 \left( 2, 5 + \beta, 4, \frac{2n_2}{n + n_2} \right). \tag{A8}
\]

The case \( n_1 = n_2 = n \), which is excluded from the treatment described in Ref. [24], is important in the derivation of Eq. (80).

[1] C. M. Adhikari, V. Debierre, 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,” Phys. Rev. A 95, 022703 (2017).

[2] H. Safari and M. R. Karimpour, “Body-Assisted van der Waals Interaction between Excited Atoms,” Phys. Rev. Lett. 114, 013201 (2015).
[3] M. Donaire, R. Guérout, and A. Lambrecht, “Quasiresonant van der Waals Interaction between Nonidentical Atoms,” Phys. Rev. Lett. 115, 033201 (2015).
[4] U. D. Jentschura, C. M. Adhikari, and V. Debierre, “Virtual Resonant Emission and Long-Range Tails in van der Waals Interactions of Excited States: QED Treatment and Applications,” Phys. Rev. Lett. 118, 033201 (2017).
[5] M. I. Chibisov, “Dispersion Interaction of Neutral Atoms,” Opt. Spectrosc. 32, 1–3 (1972).
[6] W. J. Deal and R. H. Young, “Long-Range Dispersion Interactions Involving Excited Atoms; the H(1s)−H(2s) Interaction,” Int. J. Quantum Chem. 7, 877–892 (1973).
[7] A. Z. Tang and F. T. Chan, “Dynamic multipole polarizability of atomic hydrogen,” Phys. Rev. A 33, 3671–3678 (1986).
[8] U. D. Jentschura, V. Debierre, C. M. Adhikari, A. Matveev, and N. Kolachevsky, “Long-range interactions of excited hydrogen atoms. II. Hyperfine-resolved 2S−2S system,” Phys. Rev. A 95, 022704 (2017).
[9] U. D. Jentschura and V. Debierre, “Long-range tails in van der Waals interactions of excited-state and ground-state atoms,” Phys. Rev. A 95, 042506 (2017).
[10] U. Jentschura and K. Pachucki, “Higher-order binding corrections to the Lamb shift of 2P states,” Phys. Rev. A 54, 1853–1861 (1996).
[11] A. Czarnecki, U. D. Jentschura, and K. Pachucki, “Calculation of the One- and Two-Loop Lamb Shift for Arbitrary Excited Hydrogenic States,” Phys. Rev. Lett. 95, 180404 (2005).
[12] K. Pachucki, “Relativistic corrections to the long-range interaction between closed-shell atoms,” Phys. Rev. A 72, 062706 (2005).
[13] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, Quantum Electrodynamics, Volume 4 of the Course on Theoretical Physics, 2nd ed. (Pergamon Press, Oxford, UK, 1982).
[14] U. D. Jentschura, “Corrections to Bethe Logarithms induced by Local Potentials,” J. Phys. A 36, L229 (2003).
[15] U. D. Jentschura, S. Kotochigova, E.-O. Le Bigot, P. J. Mohr, and B. N. Taylor, “Precise calculation of hydrogenic energy levels using the method of least squares,” Phys. Rev. Lett. 95, 163003 (2005).
[16] For an interactive database of hydrogen and deuterium transition frequencies, see the URL http://physics.nist.gov/hdel.
[17] S. Salomonson and P. Öster, “Solution of the pair equation using a finite discrete spectrum,” Phys. Rev. A 40, 5559–5567 (1989).
[18] E. R. Switzer and C. M. Hirata, Phys. Rev. D 77, 083006 (2008).
[19] J. Chluba and R. A. Sunyaev, “Two-photon transitions in hydrogen and cosmological recombination,” Astron. Astrophys. 480, 629–645 (2008).
[20] C. W. Fabjan and F. M. Pipkin, “Resonance narrowed Lamb shift measurement in hydrogen,” Phys. Lett. A 36, 69–70 (1971).
[21] H. Bateman, Higher Transcendental Functions, Vol. 1 (McGraw-Hill, New York, 1953).
[22] H. Bateman, Higher Transcendental Functions, Vol. 2 (McGraw-Hill, New York, 1953).
[23] S. Wolfram, The Mathematica Book, 4th ed. (Cambridge University Press, Cambridge, UK, 1999).
[24] W. Gordon, “Zur Berechnung der Matrizen beim Wassermolekül,” Ann. Phys. (Leipzig) 394, 1031–1056 (1929).
[25] J. C. deVries, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, MA (2002), available at https://dspace.mit.edu/handle/1721.1/4108.
[26] T. Udem, private communication (2017).
[27] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Springer, Berlin, 1957).
[28] A. P. Prudnikov, Y. A. Brychkov, and O. I. Marichev, Integrals and Series, Volume II: Special Functions (Taylor and Francis, London, 1998).
[29] See http://functions.wolfram.com/05.08.21.0009.01.