Long-range interactions of hydrogen atoms in excited states.
I. $2S$-$1S$ interactions and Dirac-δ perturbations

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

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

The theory of the long-range interaction of metastable excited atomic states with ground-state atoms is analyzed. We show that the long-range interaction is essentially modified when quasidegenerate states are available for virtual transitions. A discrepancy in the literature regarding the van der Waals coefficient $C_6(2S;1S)$ describing the interaction of metastable atomic hydrogen ($2S$ state) with a ground-state hydrogen atom is resolved. In the the van der Waals range $a_0 \ll R \ll a_0/\alpha$, where $a_0 = \hbar/\alpha m c$ is the Bohr radius and α is the fine-structure constant, one finds the symmetry-dependent result $E_{2S;1S}(R) \approx (-176.75 \pm 27.98)E_h(a_0/R)^6$ (E_h denotes the Hartree energy). In the Casimir-Polder range $a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$, where $\mathcal{L} \equiv E(2S_{1/2}) - E(2P_{1/2})$ is the Lamb shift energy, one finds $E_{2S;1S}(R) \approx (-121.50 \pm 46.61)E_h(a_0/R)^6$. In the the Lamb shift range $R \gg \hbar c/\mathcal{L}$, we find an oscillatory tail with a negligible interaction energy below 10^{-36} Hz. Dirac-δ perturbations to the interaction are also evaluated and results are given for all asymptotic distance ranges; these effects describe the hyperfine modification of the interaction or, expressed differently, the shift of the hydrogen $2S$ hyperfine frequency due to interactions with neighboring $1S$ atoms. The $2S$ hyperfine frequency has recently been measured very accurately in atomic beam experiments.

I. INTRODUCTION

The purpose of this paper is twofold. First, we aim to revisit the calculation of the long-range (van der Waals and Casimir-Polder) interactions for ground-state hydrogen interacting with an excited-state atom in a $2S$ state. Second, we aim to study the perturbation of the van der Waals interactions by a Dirac-δ potential perturbing the metastable excited state that participates in the interaction. Such a Dirac-δ potential can be due to the electron-nucleus (hyperfine) interaction in one of the atoms [1] or due to a self-energy radiative correction [2]. Special emphasis is laid on the role of quasidegenerate levels and on the exchange term, which is due to the possibility of $1S$-$2S$ atoms becoming a $2S$-$1S$ pair after the exchange of two virtual photons [3].

It is interesting to notice that two results given in the literature for the so-called van der Waals coefficient of the $1/R^6$ nonretarded interaction between $1S$ and $2S$ states are in significant mutual disagreement (numerically, the authors of Ref. [4] obtain a value of roughly 177 a.u., while a result of about 57 a.u. has been derived in Refs. [3,5]). We attempt a thorough analysis of the discrepancy. Two different methods of calculation were employed in Ref. [4] (direct sum over virtual atomic states, including the continuum) and Refs. [3,5] (integration over analytic expressions representing the polarizability).

The role of the virtual, quasidegenerate $2P$ states deserves special attention. For $2S$ reference states, the $2P_{1/2}$ and $2P_{3/2}$ levels are displaced only by the Lamb shift and fine structure, respectively. Significant modifications of the long-range interactions result from the presence of the quasidegenerate states.

Recently, precision measurements of the $2S$ hyperfine splitting have been carried out using an atomic beam consisting of a mixture of ground-state $1S$ hydrogen atoms and metastable $2S$ atoms [6,7]. To leading order, the van der Waals interaction shifts all hyperfine-structure components equally. However, there is a correction to the van der Waals interaction due to the hyperfine structure (hfs), which depends on the total (electron plus nucleus) angular momentum quantum number F. This correction shifts hfs components closer to each other. This latter effect is analyzed in the current paper; it is of phenomenological significance because of van der Waals interactions inside the atomic beam. Again, special attention is required in the treatment of the quasidegenerate atomic levels.

Let us recall here that the general subject of long-range interactions of simple atoms is very well known to the physics community and a few investigations on simple atomic systems can be found in Refs. [4,5,8–17]. Various aspects of the problem have been studied in depth: For example, the importance of multipole mixing effects and of perturbations by hyperfine effects has been stressed in Refs. [10–13]. Higher-order effects such as dipole-octupole mixing terms were discussed in detail for hydrogen in Ref. [5] and for helium in Ref. [16]. The dipole-dipole interaction potential of helium, including retardation, has been discussed in great detail in Refs. [18,19], including a number of numerical examples. More complex alkali-metal dimers have been considered in Refs. [20,21].

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 enhance the accessibility of the presentation to two different communities, namely, the quantum electrodynamics (QED) 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 $\hbar = c = \epsilon_0 = 1$ and the electron mass is denoted as m. The relation $e^2 = 4\pi\alpha$ then allows us to identify the expansion

in the number of quantum electrodynamic corrections with powers of the fine-structure constant $\alpha \approx 1/137.036$. This unit system is used, e.g., in the investigation reported in Ref. [22] on relativistic corrections to the Casimir-Polder interaction (with a strong overlap with QED). In the atomic unit system, we have $|e| = \hbar = m = 1$ and $4\pi\epsilon_0 = 1$. The speed of light, in the atomic unit system, is $c = 1/\alpha \approx 137.036$. This system of units is especially useful for the analysis of purely atomic properties without radiative effects. As the subject of the current study lies in between the two mentioned fields of interest, we choose the SI 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; as such, we attempt to orient ourselves in Sec. II. The direct term in the 2S-1S interaction is analyzed in Sec. III. In Sec. III B we study that interaction in the van der Waals range. The very-large-distance limit is discussed in Sec. III C (atomic distance larger than the wavelength of the Lamb shift transition) and the intermediate Casimir-Polder range in Sec. III D. The mixing term in the 2S-1S interaction is analyzed in Sec. IV. We then analyze a Dirac-δ-induced (hfs-induced) modification both for the 2S-1S interaction and for the 1S-1S interaction in Sec. V. In Sec. VI we numerically evaluate the shift of the 2S hyperfine frequency due to the long-range interaction with a ground-state hydrogen atom. A summary is given and conclusions are drawn in Sec. VII.

II. ORIENTATION

In order to evaluate the van der Waals correction to the 2S-1S hyperfine frequency, one needs to diagonalize the total Hamiltonian

$$H_{\text{total}} = H_S + H_{\text{FS}} + H_{\text{LS}} + H_{\text{hfs}} + H_{\text{vdW}}. \tag{1}$$

Here H_S is the Schrödinger Hamiltonian and H_{FS} is the fine-structure Hamiltonian, which can be approximated as (see Chap. 34 of Ref. [23])

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

where m is the electron mass, the $\vec{p}_i$ denote the momenta of the two atomic electrons relative to their nuclei (i runs over the atoms A and B), and the $\vec{r}_i = \vec{x}_i - \vec{R}_i$ denote the coordinates relative to the nuclei (the electron and nucleus coordinates are $\vec{x}_i$ and $\vec{R}_i$, respectively). We restrict the discussion to neutral hydrogen atoms and thus assume a nuclear charge number of $Z = 1$. We will use the following approximation to the Lamb shift Hamiltonian, which constitutes an effective Hamiltonian useful in the evaluation of the leading radiative correction to dynamic processes [24,25]:

$$H_{\text{LS}} = \sum_{i=A,B} \frac{4}{3}\alpha^2 mc^2 \left(\frac{\hbar}{mc}\right)^3 \ln(\alpha^{-2})\delta^{(3)}(\vec{r}_i). \tag{3}$$

We will use this Hamiltonian later in the analysis of the radiative correction to the long-range interatomic interaction. The Hamiltonian for the hyperfine interaction [1,26] reads

$$H_{\text{hfs}} = \frac{\mu_0}{4\pi}\mu_B\mu_N g_s g_p \sum_{i=A,B} \left[\frac{8\pi}{3}\vec{S}_i \cdot \vec{I}_i\delta^{(3)}(\vec{r}_i) \right.$$
$$\left. + \frac{3(\vec{S}_i \cdot \hat{r}_i)(\vec{I}_i \cdot \hat{r}_i) - (\vec{S}_i \cdot \vec{I}_i)}{|\vec{r}_i|^3} + \frac{\vec{L}_i \cdot \vec{\mu}_i}{\hbar|\vec{r}_i|^3} \right]. \tag{4}$$

Here the unit vectors are $\hat{r}_i = \vec{r}_i/|\vec{r}_i|$. The spin operator for the electron i is $\vec{S}_i = \vec{\sigma}_i/2$, while $\vec{I}_i$ is the spin operator for proton i (both spin operators are dimensionless). The electronic and protonic g factors are $g_s \simeq 2.002\,319$ and $g_p \simeq 5.585\,695$, while $\mu_B \simeq 9.274\,010 \times 10^{-24}$ A m^2 is the Bohr magneton and $\mu_N \simeq 5.050\,784 \times 10^{-27}$ A m^2 is the nuclear magneton [27]. It is well known that, for S states, the second term in the fine-structure Hamiltonian (2) and the second and third terms in the hyperfine-structure Hamiltonian (4) have vanishing contributions. For S states, the relevant term in the hyperfine Hamiltonian therefore is of the Dirac-δ type. Hence, we put special emphasis on the modifications occasioned by such Dirac-δ potentials.

The van der Waals energy is normally derived as follows. One first writes the attractive and repulsive terms that describe the electron-electron, electron-proton, and proton-proton interactions in the two atoms (excluding the intra-atomic terms). This leads to the total Coulomb interaction

$$V_C = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{|\vec{R}_A - \vec{R}_B|} + \frac{1}{|\vec{x}_A - \vec{x}_B|} \right.$$
$$\left. - \frac{1}{|\vec{x}_A - \vec{R}_B|} - \frac{1}{|\vec{x}_B - \vec{R}_A|}\right). \tag{5}$$

One then uses the fact that the separation $|\vec{R}_A - \vec{R}_B|$ between the two nuclei (protons) is much larger than that between a given proton and its respective electron, that is, much larger than both $|\vec{r}_A| = |\vec{x}_A - \vec{R}_A|$ and $|\vec{r}_B| = |\vec{x}_B - \vec{R}_B|$. One then writes $\vec{x}_A - \vec{R}_B = \vec{r}_A + (\vec{R}_A - \vec{R}_B)$ and $\vec{x}_B - \vec{R}_A = \vec{r}_B + (\vec{R}_B - \vec{R}_A)$. Expanding in $\vec{r}_A$ and $\vec{r}_B$, one obtains

$$H_{\text{vdW}} = \frac{e^2}{4\pi\epsilon_0}\frac{\vec{r}_A \cdot \vec{r}_B - 3(\vec{r}_A \cdot \hat{R})(\vec{r}_B \cdot \hat{R})}{R^3}$$
$$= \frac{e^2}{4\pi\epsilon_0 R^3}(\delta_{k\ell} - 3\hat{R}_k\hat{R}_\ell)r_{Ak}r_{B\ell}, \tag{6}$$

where $\vec{R} = \vec{R}_A - \vec{R}_B$, $R = |\vec{R}|$, and $\hat{R} = \vec{R}/R$. The indices k and ℓ corresponding to the Cartesian coordinates are summed over (Einstein summation convention). The van der Waals interaction term, for a 2S-1S system, has vanishing elements in first-order perturbation theory. Both atoms A and B have to undergo a virtual dipole transition to a P state for a nonvanishing effect and the leading-order van der Waals interaction is obtained in second-order perturbation theory, leading to a $1/R^6$ interaction energy. The propagator denominator in the standard Rayleigh-Schrödinger expression for the second-order energy shift due to H_{vdW} is equal to the sum of the virtual excitation energies of both atoms [4].

The close-range asymptotics of the interatomic interaction energy thus goes as $1/R^6$ [4]. For an interatomic distance of $R \sim 30a_0, \ldots, 100a_0$ (100 a.u.), the energy shift is on the order of $10^{-8}, \ldots, 10^{-12}$ a.u. (Hartree). The hierarchy

$$\langle H_{\mathrm{vdW}} \rangle \ll \langle H_{\mathrm{hfs}} \rangle \ll \langle H_{\mathrm{LS}} \rangle \ll \langle H_{\mathrm{FS}} \rangle \tag{7}$$

is thus fulfilled for $R \gtrsim 30a_0$. For sufficiently large interatomic distance, the Dirac δ potential of the hfs acts as a perturbation and can be treated as such; we will focus on this regime in the current paper.

For clarity, we should point out that the Hamiltonian (6) remains valid in the nonretardation approximation. One can understand retardation as follows: When the phase of the atomic oscillation during a virtual transition changes appreciably on the time scale it takes light to travel the interatomic separation distance R, then the retarded form of the van der Waals interaction has to be used. The criterion for the validity of the nonretardation approximation thus is

$$\frac{R}{c} \ll \frac{\hbar}{E_h} = \frac{a_0}{\alpha c} \tag{8}$$

or, more precisely,

$$a_0 = \frac{\hbar}{\alpha m c} \ll R \ll \frac{\hbar}{\alpha^2 m c} = \frac{a_0}{\alpha}, \tag{9}$$

if we take into account that substantial overlap of the electronic wave functions is to be avoided.

The retarded interatomic interaction cannot be obtained on the basis of Eq. (6) alone; one has to use the atom-field interaction term [see Eq. (85.4) of Ref. [23]]

$$V(t) = -\vec{E}(\vec{R}_A, t) \cdot \vec{d}_A(t) - \vec{E}(\vec{R}_B, t) \cdot \vec{d}_B(t), \tag{10}$$

where $\vec{d}_i = e\vec{r}_i$ is the dipole operator for atom i (for atoms with more than one electron, one has to sum over all the electrons in the atoms $i = A, B$). The $\vec{R}_A$ and $\vec{R}_B$ are the positions of the atomic nuclei and $\vec{E}$ denotes the operator of the quantized electric field. An elegant way of deriving the retarded Casimir-Polder interaction, described in Eq. (85.4) of Ref. [23], then consists in the matching of the scattering amplitude obtained from quantum electrodynamics, against the effective interatomic interaction Hamiltonian. Alternative derivations use time-ordered perturbation theory [28].

The functional form of the interaction depends on the distance range. In the van der Waals range (9) of interatomic distances, the interaction of ground-state atoms is of the usual R^{-6} functional form. This remains valid if one atom is in a metastable excited state. In the so-called Casimir-Polder range

$$R \gg \frac{\hbar}{\alpha^2 m c}, \tag{11}$$

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

$$R \gg \frac{\hbar c}{\mathcal{L}}, \tag{12}$$

which we would like to refer to as the Lamb shift range. Here $\mathcal{L}$ is the Lamb shift energy. For metastable atoms, the

Casimir-Polder range is bounded from above by the Lamb shift range and the condition (11) should be modified to read

$$\frac{\hbar c}{\mathcal{L}} \gg R \gg \frac{\hbar}{\alpha^2 m c} \tag{13}$$

(the Casimir-Polder I range). For the 1S-1S interaction, the interaction energy reaches the Casimir-Polder asymptotic form, proportional to $1/R^7$, in both regimes described by Eqs. (12) and (13). For the 2S-1S interaction, it is only in the very-long-range regime (12) that we have an R^{-7} interaction, with competing oscillatory terms [29–31] proportional to $(\mathcal{L}^4/R^2) \cos(\mathcal{L}R/\hbar c)$.

A further complication arises. The state with atom A in an excited state and atom B in the ground state, $|2S\rangle_A |1S\rangle_B$, is degenerate with the state $|1S\rangle_A |2S\rangle_B$ with the quantum numbers reversed among the atoms. There is no direct first-order coupling between $|2S\rangle_A |1S\rangle_B$ and $|1S\rangle_A |2S\rangle_B$ due to the van der Waals interaction (6), but in second order, an off-diagonal term is obtained that 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 $|2S\rangle_A |1S\rangle_B$ and $|1S\rangle_A |2S\rangle_B$ has off-diagonal (exchange) terms of second order in the van der Waals interaction [3]. The energy eigenvalues and eigenstates are easily found in the degenerate basis and are studied in Sec. IV.

III. THE 2S-1S DIRECT INTERACTION

A. Formalism

According to Eq. (85.17) in Chap. 85 of Ref. [23], the interaction energy between two atoms A and B in states $|A\rangle$ and $|B\rangle$ is given by

$$E_{A;B}^{(\mathrm{dir})}(R) = \mathrm{Re} \frac{i\hbar}{\pi c^4 (4\pi \epsilon_0)^2} \int_0^\infty d\omega \, \alpha_A(\omega) \alpha_B(\omega) e^{2i\omega R/c} \frac{\omega^4}{R^2}$$

$$\times \left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 \right.$$

$$\left. + 3\left(\frac{c}{\omega R}\right)^4 \right]. \tag{14}$$

Here the superscript (dir) stands for direct, as we anticipate that this interaction energy is to be supplemented by the so-called exchange interaction, to be discussed in Sec. IV. The integral (14) constitutes the generalization of the second-order van der Waals shift given by the application of Eq. (6) to the long-range limit, where retardation sets in. Equation (14) contains the atom-field interaction at the lowest relevant order in the elastic scattering case, where the initial and final states are identical (e.g., all photons emitted are reabsorbed and vice versa). We here restrict the discussion to the leading effect in the multipole expansion, given by the dipole polarizability α_i ($i = A, B$). The designation of the real part of the energy shift is necessary because the integrand constitutes a complex rather than real quantity and the poles of the integrand are displaced from the real axis according to the Feynman prescription. For the dipole polarizability $\alpha_A(\omega)$ (of atom A), we

have

$$\alpha_A(\omega) = P_A(\omega) + P_A(-\omega),$$

$$P_A(\omega) = \frac{e^2}{3} \langle \psi_A | \vec{r} \, \frac{1}{H - E_A + \hbar\omega - i\epsilon} \vec{r} | \psi_A \rangle \quad (15)$$

$$= \frac{e^2}{3} \sum_n \sum_{i=1}^{3} \frac{|\langle \psi_A | \vec{r} \, | \psi_n \rangle|^2}{E_n - E_A + \hbar\omega - i\epsilon},$$

where H in the propagator denominator denotes the Schrödinger Hamiltonian of the relevant atom. The ϵ parameter in Eq. (15) ensures that the integration (14) is carried along the Feynman contour; the limit $\epsilon \to 0^+$ is taken after the integration is carried out. Under appropriate conditions, which are discussed in detail below, we may perform a Wick rotation $d\omega \to id\omega$ in the integral (14). The resulting Wick (W) rotated expression is the familiar one that is usually taken as the starting point of the investigations (see, e.g., Ref. [22]),

$$E_{A;B}^{(\text{dir})\text{W}}(R) = -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \, \alpha_A(i\omega)\alpha_B(i\omega)$$

$$\times \, e^{-2\omega R/c} \frac{\omega^4}{R^2} \left[1 + 2\left(\frac{c}{\omega R}\right) + 5\left(\frac{c}{\omega R}\right)^2 \right.$$

$$\left. + 6\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4 \right]. \quad (16)$$

We do not explicitly indicate the real part on the right-hand side of this equation, because the polarizability $\alpha_A(i\omega)$ is manifestly real if we set $\epsilon = 0$ in Eq. (15), and there are no poles near the integration contour in Eq. (16) to be considered. If both atoms are in their $|1S\rangle$ ground state, then the expressions (14) and (16) are equal $[E_{1S;1S}^{(\text{dir})}(R) = E_{1S;1S}^{(\text{dir})\text{W}}(R)]$ and the Wick rotation is permissible.

Let us now study the case $|A\rangle = |2S\rangle$ and $|B\rangle = |1S\rangle$ for atomic hydrogen as a paradigmatic example of a long-range interaction involving a metastable excited state. In this case, the Wick rotated integral (16) is not equal to (14) and extra care is needed (see also Appendix A). The dipole polarizability α_{2S} can naturally be split into two contributions, the first of which is due to the quasidegenerate $|2P_{1/2}\rangle$ and $|2P_{3/2}\rangle$ states that are displaced from $|2S\rangle$ only by the Lamb shift and by the fine structure, respectively. The second contribution is due to nP states with principal quantum number $n \geqslant 3$. After doing the angular algebra for the $|2P_{1/2}\rangle$ and $|2P_{3/2}\rangle$ states whose oscillator strengths [32] with respect to $2S$ are distributed in a ratio $\frac{1}{3}:\frac{2}{3}$, we obtain

$$\alpha_{2S}(\omega) = \bar{\alpha}_{2S}(\omega) + \tilde{\alpha}_{2S}(\omega), \quad (17a)$$

$$\bar{\alpha}_{2S}(\omega) = \bar{P}_{2S}(\omega) + \bar{P}_{2S}(-\omega), \quad (17b)$$

$$\tilde{\alpha}_{2S}(\omega) = \tilde{P}_{2S}(\omega) + \tilde{P}_{2S}(-\omega), \quad (17c)$$

$$\bar{P}_{2S}(\omega) = \frac{e^2}{9} \sum_\mu \frac{|\langle 2S | \vec{r} \, | 2P(m = \mu)\rangle|^2}{-\mathcal{L} + \hbar\omega - i\epsilon}$$

$$+ \frac{2e^2}{9} \sum_\mu \frac{|\langle 2S | \vec{r} \, | 2P(m = \mu)\rangle|^2}{\mathcal{F} + \hbar\omega - i\epsilon}$$

$$= 3e^2 a_0^2 \left(\frac{1}{-\mathcal{L} + \hbar\omega - i\epsilon} + \frac{2}{\mathcal{F} + \hbar\omega - i\epsilon} \right), \quad (17d)$$

$$\tilde{P}_{2S}(\omega) = \frac{e^2}{3} \sum_{n \geqslant 3} \sum_\mu \frac{|\langle 2S | \vec{r} \, | n P(m = \mu)\rangle|^2}{E_n - E_{2S} + \hbar\omega - i\epsilon}. \quad (17e)$$

The nondegenerate contribution to the 2S polarizability is denoted by $\tilde{\alpha}_{2S}$ (the quasidegenerate $2P$ levels are excluded). The quasidegenerate $2P$ levels are contained in $\bar{\alpha}_{2S}$. All sums are over the nonrelativistic P states with magnetic projection quantum numbers $\mu = -1, 0, 1$. The Lamb shift energy $\mathcal{L}$ and the fine-structure energy $\mathcal{F}$ are defined as

$$E(2S_{1/2}) - E(2P_{1/2}) \equiv \mathcal{L},$$

$$E(2P_{3/2}) - E(2S_{1/2}) \equiv \mathcal{F}. \quad (18)$$

The leading-order expressions for $\mathcal{L}$ and $\mathcal{F}$ read $\mathcal{L} = \frac{\alpha}{6\pi} \alpha^4 mc^2 \ln[\alpha^{-2}]$ and $\mathcal{F} = \alpha^4 mc^2/32$, respectively [26] [see also Eq. (3)].

B. van der Waals range $a_0 \ll R \ll a_0/\alpha$

We investigate the 2S-1S interaction in the van der Waals regime (9). There is no exponential or oscillatory suppression of any atomic transition in this regime, but we can approximate

$$E_{A;B}^{(\text{dir})}(R) = \text{Re} \, \frac{i\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \, \alpha_A(\omega)\alpha_B(\omega) e^{2i\omega R/c}$$

$$\times \, \frac{\omega^4}{R^2} \left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 \right.$$

$$\left. - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4 \right]$$

$$\approx \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2 R^6} \text{Re} \, i \int_0^\infty d\omega \, \alpha_A(\omega)\alpha_B(\omega). \quad (19)$$

The functional form therefore is of the van der Waals type

$$E_{A;B}^{(\text{dir})}(R) \approx -\frac{D_6(A;B)}{R^6}, \quad (20)$$

with the van der Waals coefficient

$$D_6(A;B) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \text{Re}\left(-i \int_0^\infty d\omega \, \alpha_A(\omega)\alpha_B(\omega)\right). \quad (21)$$

For the 2S-1S interaction, this implies that

$$D_6(2S; 1S) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \text{Re}\left(-i \int_0^\infty d\omega \right.$$

$$\left. \times [\bar{\alpha}_{2S}(\omega) + \tilde{\alpha}_{2S}(\omega)]\alpha_{1S}(\omega)\right) \quad (22a)$$

$$= \bar{D}_6(2S; 1S) + \tilde{D}_6(2S; 1S). \quad (22b)$$

For $|A\rangle = |2S\rangle$ and $|B\rangle = |1S\rangle$, D_6 therefore is the sum of two contributions $\bar{D}_6$ and $\tilde{D}_6$, which correspond to the degenerate $\bar{\alpha}_{2S}$ and nondegenerate $\tilde{\alpha}_{2S}$ contributions to the 2S polarizability, respectively. The degenerate contribution to D_6 can be handled analytically. We use the integral identity

$$-\frac{i}{\pi} \int_{-\infty}^\infty dx \, \frac{ab}{[(a - i\epsilon)^2 - x^2][(b - i\epsilon)^2 - x^2]} \xrightarrow{\epsilon \to 0^+} \frac{1}{a + b}, \quad (23)$$

which is valid for a and b real (regardless of their sign). A change in integration limits to the interval $(0, \infty)$ can be absorbed in a prefactor 2. The result for $\bar{D}_6(2S; 1S)$ reads

$$
\bar{D}_6(2S; 1S) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \frac{2e^2}{3} \sum_k |\langle 1S|\vec{r}|k\rangle|^2
$$
$$
\times \frac{2e^2}{9} \sum_\mu |\langle 2S|\vec{r}|2P(m=\mu)\rangle|^2
$$
$$
\times \frac{\pi}{2\hbar} \left(\frac{1}{E_k - E_{1S} - \mathcal{L}} + \frac{2}{E_k - E_{1S} + \mathcal{F}} \right)
$$
$$
\approx \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \left\{ \frac{2e^2}{3} \sum_k \frac{|\langle 1S|\vec{r}|k\rangle|^2}{E_k - E_{1S}} \right\}
$$
$$
\times \left(\frac{2e^2}{9} (27 a_0^2) \right) \times 3 \frac{\pi}{2\hbar}
$$
$$
\approx \frac{3}{\pi} \frac{\hbar e^2 a_0^2}{(4\pi\epsilon_0)^2} \{\alpha_{1S}(0)\} \times (6) \times 3 \frac{\pi}{2\hbar}
$$
$$
= \frac{243}{2} E_h a_0^6, \tag{24}
$$

where we took the limit $\mathcal{L} \to 0$, $\mathcal{F} \to 0$ at the end of the calculation. We have used the known result

$$
\alpha_{1S}(0) = \frac{9}{2} \frac{e^2 a_0^2}{E_h}, \tag{25}
$$

where $E_h = \alpha^2 m c^2$ is the Hartree energy. We can now give a more thorough analysis of the discrepancy of the results for the $(2S; 1S)$ van der Waals coefficient reported in Refs. [3–5]. Namely, the denominator $a + b$ in Eq. (23) just corresponds to the sum of the excitation energies of the two atoms in the calculation of the van der Waals coefficient; the contribution of a virtual P state in one of the atoms is seen to be nonvanishing even if it is displaced from the reference state only by an infinitesimal shift $a = \mathcal{L}$, $\mathcal{F} \to 0$. By contrast, if one takes the limit $\mathcal{L}$, $\mathcal{F} \to 0$ too early, i.e., before evaluating the integral (23), then in Eq. (17b), one obtains $\bar{\alpha}_{2S}(\omega) = 0$, because the two terms $\tilde{P}_{2S}(\pm\omega)$ just cancel each other. Alternatively, expressed more concisely, because of the exact energetic degeneracy of the $2S$ and $2P$ states in the nonrelativistic theory, the virtual $2P$ states are excluded from the sum over virtual states in the nonrelativistic expression of the polarizability, which leads to the erroneous result reported in Refs. [3,5]. Only if the formulation of the nonrelativistic expression of the polarizability is enhanced by the fine-structure and Lamb shift denominators, as in Eq. (17), can we obtain the missing contribution $\bar{D}_6(2S; 1S)$ given in Eq. (24). The contribution of the quasidegenerate levels is more obvious in the sum-over-states approach chosen in Ref. [4], where according to Eq. (23), the sum of the excitation energies of both atoms enters the propagator denominator [see also Eqs. (12a) and (12b) of Ref. [4]].

For the nondegenerate contribution, we can perform the Wick rotation and obtain the following integral representation

$$
\tilde{D}_6(2S; 1S) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \mathrm{Re} \left(-i \int_0^\infty d\omega\, \tilde{\alpha}_{2S}(\omega) \alpha_{1S}(\omega) \right)
$$
$$
= \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \int_0^\infty d\omega\, \tilde{\alpha}_{2S}(i\omega) \alpha_{1S}(i\omega), \tag{26}
$$

which is convenient for a numerical evaluation. Namely, according to Eq. (15), one can write the corresponding polarizabilities as the sum over two matrix elements $P(\omega)$ and $P(-\omega)$ of a resolvent operator, where the P matrix elements can be written in terms of hypergeometric functions. The calculation of a convenient representation of the polarizability of low-lying S states [33–35] becomes easier if one uses a coordinate-space integration based on the Sturmian decomposition of the radial hydrogen Green's function in terms of Laguerre polynomials [36]. After the radial integrals, one evaluates the sum over the Sturmian integrals in terms of hypergeometric functions with the help of formulas contained in Ref. [37]. The result of this calculation for the ground state is

$$
P_{1S}(\omega) = -\frac{e^2 a_0^2}{E_h} \left[\frac{2t^2}{3(1-t)^5(1+t)^4} (38t^7 + 26t^6 \right.
$$
$$
+ 19t^5 - 19t^4 - 12t^3 + 12t^2 + 3t - 3)
$$
$$
\left. + \frac{256 t^9}{3(t-1)^5(t+1)^5} {}_2F_1\left(1, -t, 1-t, \left(\frac{1-t}{1+t}\right)^2\right) \right],
$$
$$
t = \left(1 + \frac{2\hbar\omega}{\alpha^2 m c^2} \right)^{-1/2}, \tag{27a}
$$

where

$$
P_{1S}(\omega) = \frac{e^2}{3} \sum_{n \geqslant 2} \sum_\mu \frac{|\langle 1S|\vec{r}|nP(m=\mu)\rangle|^2}{E_n - E_{1S} + \hbar\omega - i\epsilon}, \tag{27b}
$$

and the sum includes the continuum. We here take the opportunity to correct a typographical error in Eq. (3a) of Ref. [38], which led to an inconsistent sign of the term involving the hypergeometric function. For the $2S$ state, one obtains the nondegenerate matrix element

$$
\tilde{P}_{2S}(\omega) = \frac{e^2 a_0^2}{E_h} \left[\frac{16\tau^2}{3(\tau-1)^6(1+\tau)^4} (1181\tau^8 - 314\tau^7 \right.
$$
$$
- 16\tau^6 - 166\tau^5 + 14\tau^4 + 138\tau^3 - 48\tau^2
$$
$$
- 42\tau + 21) - \frac{16\,384\tau^9(4\tau^2 - 1)}{3(\tau-1)^6(\tau+1)^6}
$$
$$
\times {}_2F_1\left(1, -2\tau, 1-2\tau, \left(\frac{1-\tau}{1+\tau}\right)^2\right) - \frac{72\tau^2}{(1-\tau^2)} \right],
$$
$$
\tau = \left(1 + \frac{8\hbar\omega}{\alpha^2 m c^2} \right)^{-1/2}. \tag{27c}
$$

Indeed, the $2P$ state is excluded from the sum over states in Eq. (27c) by the subtraction of the term $72\tau^2/(1 - \tau^2)$: One can verify that the expression (27c) is finite in the limit $\tau \to 1$, which is equivalent to vanishing photon energy $\omega \to 0$.

A numerical integration of Eq. (26) then yields the following value for $\tilde{D}_6(2S; 1S)$:

$$
\tilde{D}_6(2S; 1S) = 55.252\,266\,285 E_h a_0^6. \tag{28}
$$

We have verified this result using discrete numerical methods [39], where the radial Schrödinger equation is evaluated on a lattice and a discrete pseudospectrum (due to the finite size of the lattice) represents the continuum spectrum. The result for $D_6(2S; 1S)$ according to Table VI of Ref. [5] reads $56.7999 E_h a_0^6$, while according to Table 2 of Ref. [3], it is $(56.5 \pm 0.5) E_h a_0^6$. Both results are not in perfect agreement

with our result, though numerically close. This observation is consistent with the derivations outlined in Refs. [3,5], which suggest that the results reported in the cited investigation may correspond to the nondegenerate contribution. The total van der Waals coefficients D_6 is obtained as the sum of the contributions given in Eqs. (24) and (28),

$$D_6(2S;1S) = \tilde{D}_6(2S;1S) + \bar{D}_6(2S;1S)$$

$$= 176.752\,266\,285\,E_h a_0^6, \tag{29}$$

where we confirm all significant digits of the previously reported result [4] of 176.752. For the $1S$-$1S$ interaction, we confirm the known result [4,40] of $D_6(1S;1S) = 6.499\,026\,705\,E_h a_0^6$ and add a few digits of numerical significance. In particular, this result shows that the result for $D_6(1S;1S)$ is numerically close to $\frac{13}{2}$, but not exactly equal to a rational number. We should add that the numerical accuracy of the strictly nonrelativistic results given in Eqs. (28) and (29) extends to all digits indicated. However, reduced-mass, relativistic, and radiative corrections contribute on the level of $10^{-4}, \ldots, 10^{-3}$. For definiteness, we should also clarify that the electron mass m is used as the mass of the hydrogen atom, not the reduced mass of the electron-proton system (see also the discussion in Sec. VI).

An alternative treatment is possible in the present van der Waals range. There exists an integral identity similar to (23), namely,

$$\frac{1}{\pi} a'b' \int_{-\infty}^{\infty} \frac{dx}{(a'^2 + x^2)(b'^2 + x^2)} = \frac{\text{sgn}(a')\text{sgn}(b')}{|a'| + |b'|}. \tag{30}$$

The two integrals (23) and (30) are thus equal for $a + b = a' + b'$ if and only if a' and b' are both positive.

Notice from (15) and (22a) that $D_6(2S;1S)$ is given by an integral of the type (23), namely, by

$$D_6(2S;1S) \equiv \text{Re} - i \frac{4\hbar}{3\pi} \frac{e^4}{(4\pi\epsilon_0)^2} \sum_{mn} \int_0^{\infty} d\omega$$

$$\times \frac{(E_m - E_{1S})\langle 1S|\vec{r}|m\rangle \cdot \langle m|\vec{r}|1S\rangle}{[(E_m - E_{1S} - i\epsilon)^2 - (\hbar\omega)^2]}$$

$$\times \frac{(E_n - E_{2S})\langle 2S|\vec{r}|n\rangle \cdot \langle n|\vec{r}|2S\rangle}{[(E_n - E_{2S} - i\epsilon)^2 - (\hbar\omega)^2]}. \tag{31}$$

At this point we may not perform the Wick rotation that takes us from an integral of the type (23) to an integral of the type (30). Indeed, for $n = 2P_{1/2}$, we have $b = E_n - E_{2S} = -\mathcal{L} < 0$ and the conditions for the equality of (23) and (30) is not fulfilled. However, as was noticed by Deal and Young in Ref. [4], any integral of the type (30) is equivalent to an integral of the type (23) provided we are able to replace the (possibly negative) quantities a and b by two *positive* quantities a' and b' so that $a + b = a' + b'$. Hence, we can rewrite (31) as

$$D_6(2S;1S) = \text{Re} - i \frac{4\hbar}{3\pi} \frac{e^4}{(4\pi\epsilon_0)^2} \sum_{mn} \int_0^{\infty} d\omega$$

$$\times \frac{\left[E_m - \frac{1}{2}(E_{1S} + E_{2S})\right]\langle 1S|\vec{r}|m\rangle \cdot \langle m|\vec{r}|1S\rangle}{\left[E_m - \frac{1}{2}(E_{1S} + E_{2S}) - i\epsilon\right]^2 - (\hbar\omega)^2}$$

$$\times \frac{\left[E_n - \frac{1}{2}(E_{1S} + E_{2S})\right]\langle 2S|\vec{r}|n\rangle \cdot \langle n|\vec{r}|2S\rangle}{\left[E_n - \frac{1}{2}(E_{1S} + E_{2S}) - i\epsilon\right]^2 - (\hbar\omega)^2}. \tag{32}$$

In what follows we will make use of the space-saving notation

$$E_{\overline{1S2S}} \equiv \frac{1}{2}(E_{1S} + E_{2S}). \tag{33}$$

Notice that for all single-atom hydrogen eigenstates (except for $1S$, which never enters as a virtual state in the expression of $2S$ polarizabilities), we have $E_m, E_n > E_{\overline{1S2S}}$. In other words, identifying (32) with the model integral (23), we have a and b positive. Hence the condition for the equality of (23) and (30) is fulfilled. We then perform the Wick rotation and rewrite (32) as

$$D_6(2S;1S) = \frac{4\hbar}{3\pi} \frac{e^4}{(4\pi\epsilon_0)^2} \sum_{mn} \int_0^{\infty} d\omega$$

$$\times \frac{\left[E_m - \frac{1}{2}(E_{1S} + E_{2S})\right]\langle 1S|\vec{r}|m\rangle \cdot \langle m|\vec{r}|1S\rangle}{\left[E_m - \frac{1}{2}(E_{1S} + E_{2S})\right]^2 + (\hbar\omega)^2}$$

$$\times \frac{\left[E_n - \frac{1}{2}(E_{1S} + E_{2S})\right]\langle 2S|\vec{r}|n\rangle \cdot \langle n|\vec{r}|2S\rangle}{\left[E_n - \frac{1}{2}(E_{1S} + E_{2S})\right]^2 + (\hbar\omega)^2}. \tag{34}$$

We introduce the following polarizabilities, which have the mean energy $E_{\overline{1S2S}}$ in the propagator denominators:

$$\alpha_{1S(2S)}(\omega) = \frac{e^2}{3} \sum_{\pm} \langle 1S|\vec{r} \frac{1}{H - E_{\overline{1S2S}} \pm \hbar\omega} \vec{r}|1S\rangle$$

$$= P_{1S(2S)}(\omega) + P_{1S(2S)}(-\omega), \tag{35a}$$

$$\alpha_{2S(1S)}(\omega) = \frac{e^2}{3} \sum_{\pm} \langle 2S|\vec{r} \frac{1}{H - E_{\overline{1S2S}} \pm \hbar\omega} \vec{r}|2S\rangle$$

$$= P_{2S(1S)}(\omega) + P_{2S(1S)}(-\omega). \tag{35b}$$

We finally obtain

$$D_6(2S;1S) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \int_0^{\infty} d\omega\, \alpha_{1S(2S)}(i\omega)\alpha_{2S(1S)}(i\omega)$$

$$= 176.752\,266\,285\,E_h a_0^6. \tag{36}$$

This matches the value (29) found by the previously followed method. With such a choice of the reference energies in the denominators, we have shown that the Wick rotation is made automatically valid by the inequality $E_m > E_{\overline{1S2S}}$ for the virtual P states with energies E_m. This procedure also results in the automatic inclusion of the quasidegenerate states.

C. Very large interatomic distance $R \gg \hbar c/\mathcal{L}$

For very large interatomic separations, the classic result is that of Casimir and Polder [41] and it is given, when both atoms are in the ground state, by

$$E_{1S;1S}^{(\text{dir})}(R) \approx -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2} \frac{1}{R^7} \alpha_{1S}(0)\alpha_{1S}(0), \tag{37}$$

which can be obtained by the Wick-rotated version (16) of the integral. When one of the atoms sits in an excited state, however (here, the $2S$ state), there is an extra term coming from the contribution of the pole that is picked up when carrying out the Wick rotation. The pole corresponds to the $2P_{1/2}$ level. We thus have two competing contributions in the very-long-range limit, the first being the generalization of Eq. (37) to the $2S$-$1S$

interaction

$$E_{2S;1S}^{(\mathrm{dir})\,\mathrm{I}}(R) \approx -\frac{23}{4\pi}\frac{\hbar c}{(4\pi\epsilon_0)^2}\frac{1}{R^7}\alpha_{1S}(0)\alpha_{2S}(0), \qquad (38)$$

the other being an oscillatory term [29–31] of the functional form

$$E_{2S;1S}^{(\mathrm{dir})\,\mathrm{II}}(R) \sim \frac{e^2}{(4\pi\epsilon_0)^2 R^2}\left(\frac{\mathcal{L}}{\hbar c}\right)^4 \cos\left(\frac{2\mathcal{L}R}{\hbar c}\right)$$
$$\times \sum_\mu |\langle 2S|\vec{r}\,|2P(m=\mu)\rangle|^2\alpha_{1S}(0). \quad (39)$$

The term $E_{2S;1S}^{(\mathrm{dir})\,\mathrm{I}}$ is the Wick-rotated term (16) in the long-range limit. The term $E_{2S;1S}^{(\mathrm{dir})\,\mathrm{II}}$ is the pole contribution from the $2P_{1/2}$ level, which lies lower than the $2S$ level. In the van der Waals range (9), both the Wick-rotated and pole contributions decay as $1/R^6$. However, in the present large separation regime (12), we see that the pole term exhibits a long-range tail proportional to R^{-2}. For the $2S$-$1S$ interaction, it is the ratio $\mathcal{L}R/\hbar c$ that determines which one of these powers yields the dominant contribution. Hence, we have a regime change around $R = \hbar c/\mathcal{L}$, with long-range tails extending beyond such separations. Parametrically, using $\mathcal{L} \sim \alpha^5 mc^2$ and $\hbar c/\mathcal{L} \sim a_0/\alpha^4$, one obtains the estimates

$$E_{2S;1S}^{(\mathrm{dir})\,\mathrm{I}}(R) \sim \frac{E_h}{\alpha^4(R/a_0)^7}, \qquad (40a)$$

$$E_{2S;1S}^{(\mathrm{dir})\,\mathrm{II}}(R) \sim \frac{\alpha^{16}\cos(2\alpha^4 R/a_0)E_h}{(R/a_0)^2}. \qquad (40b)$$

Both of these estimates are relevant for $R \gtrsim \hbar c/\mathcal{L}$. The transition region where $E_{2S;1S}^{\mathrm{I}}(R)$ becomes commensurate with $E_{2S;1S}^{\mathrm{II}}(R)$ is thus reached for

$$R \sim \frac{\hbar c}{\mathcal{L}} \sim \frac{a_0}{\alpha^4}, \quad E_{2S;1S}^{\mathrm{I}}(R) \sim E_{2S;1S}^{\mathrm{II}}(R) \sim \alpha^{24}E_h. \quad (41)$$

The frequency shift in this region is of the order of 10^{-36} Hz and thus far too small to be of any relevance for experiments. In view of the prefactor $\mathcal{L}^4$ in Eq. (39), the same conclusion is reached as recently found in Ref. [42] for atom-surface interactions: Namely, for long-range interactions involving the metastable $2S$ state, a potentially interesting oscillating long range is found, but its numerical coefficient is too small to be of significance.

Our very-long-range regime is given by (12). Expressed in units of the Hartree energy E_h, the physical values of the Lamb shift and fine-structure energies are

$$\mathcal{L} = 1.61 \times 10^{-7}E_h, \qquad (42a)$$

$$\mathcal{F} = 1.67 \times 10^{-6}E_h \approx 10\mathcal{L}. \qquad (42b)$$

The long-range approximation is thus valid in the region

$$R \gg \frac{\hbar c}{\mathcal{L}} = \frac{a_0}{\alpha}\frac{E_h}{\mathcal{L}} = 8.206 \times 10^8 a_0 = 0.0434 \text{ m}. \quad (43)$$

According to Eq. (41), the oscillatory tail and the $1/R^7$ Casimir-Polder term have comparable magnitude as we enter the very-long-range regime (12), but the oscillatory tail given in Eq. (40b) could be assumed to dominate for distances

exceeding the Lamb shift transition wavelength. This consideration, though, should be viewed with skepticism. Namely, in the long-range limit, one has to take into consideration the fact that the width of the $2P_{1/2}$ state is of the same order of magnitude ($\alpha^5 mc^2$) as the Lamb shift itself [32]. For $R \gg \hbar c/\mathcal{L}$, the oscillatory tails are thus exponentially suppressed according to the factor $\exp[2i(\mathcal{L}+i\Gamma/2)R)/\hbar c] \sim \exp(-2\Gamma R/\hbar c)$, where Γ is the natural energy width of the $2P_{1/2}$ state. Still, it is of academic interest to note that the oscillatory long-range tail exists.

D. Intermediate distance $a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$

It is very interesting indeed to also investigate the intermediate range of interatomic distances, given by (13). The treatment becomes a little sophisticated. Namely, as far as virtual transitions with a change in the principal quantum number are concerned, we are in the Casimir-Polder regime where the result is given by an R^{-7} interaction (only the virtual $2P_{1/2}$ state gives rise to an oscillatory tail and this occurs, without any change in the principal quantum number, only for the $2S$-$1S$ interaction). The $2S$-$1S$ interaction would therefore be proportional to R^{-7} if the $2S$ polarizability were restricted to the term $\tilde{\alpha}_{2S}$. However, the frequency range corresponding to the intermediate-distance range (13) is so low that the frequency-dependent quasidegenerate polarizability $\bar{\alpha}_{2S}$ in the integral (14) is not exponentially suppressed. We thus have

$$E_{2S;1S}^{(\mathrm{dir})}(R) \approx \bar{E}_{2S;1S}^{(\mathrm{dir})}(R)$$
$$= 3\frac{\hbar}{(4\pi\epsilon_0)^2}\mathrm{Re}\left(i\int_0^\infty d\omega\,\alpha_{1S}(0)\bar{\alpha}_{2S}(\omega)\right). \quad (44)$$

The static ground-state polarizability $\alpha_{1S}(0)$ is given in Eq. (25). Furthermore, on the scale of distances in the intermediate range, we may approximate the Lamb shift and the fine-structure energy by zero after computing the integrals. This yields

$$\lim_{\mathcal{L}\to 0}\mathrm{Re}\left(i\int_0^\infty d\omega\frac{2\mathcal{L}}{(-\mathcal{L}-i\epsilon)^2-(\hbar\omega)^2}\right) = \frac{\pi}{\hbar}. \quad (45a)$$

Due to the different pole structure under the sign change from the Lamb shift as compared to the fine-structure transition ($-\mathcal{L} < 0$, but $\mathcal{F} > 0$), it is nontrivial to check that

$$\lim_{\mathcal{F}\to 0}\mathrm{Re}\left(-i\int_0^\infty d\omega\frac{2\mathcal{F}}{(\mathcal{F}-i\epsilon)^2-(\hbar\omega)^2}\right) = \frac{\pi}{\hbar}. \quad (45b)$$

The result for the asymptotics in the intermediate range thus reads

$$\bar{E}_{2S;1S}^{(\mathrm{dir})}(R) = -\frac{\bar{D}_6(2S;1S)}{R^6} = -\frac{243}{2}E_h\left(\frac{a_0}{R}\right)^6. \quad (46)$$

The interaction is thus still of the R^{-6} form, as it is in the range, but the coefficient is reduced in magnitude as compared to Eq. (29).

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 $\hbar c/\mathcal{F}$, instead of $\hbar c/\mathcal{L}$, as the former quantity is smaller than the latter. In the rather narrow window where $\hbar c/\mathcal{F} < R < \hbar c/\mathcal{L}$, transitions between $2S$ and $2P_{3/2}$ states

are suppressed while those between $2S$ and $2P_{1/2}$ states are not. We do not dwell further on the details of this regime, because an order-of-magnitude estimate of the frequency shifts, analogous to the one carried out in Sec. III C, reveals that they do not exceed 10^{-21} Hz in the discussed distance range. Mathematically speaking, the inequality $R \ll \hbar c/\mathcal{L}$ implies $R \ll \hbar c/\mathcal{F}$ because $\mathcal{F}$ and $\mathcal{L}$ are apart by only a single order of magnitude [see Eq. (42)]. The regime $\hbar c/\mathcal{F} < R < \hbar c/\mathcal{L}$ can only be accessed reliably by a numerical calculation (see Sec. VI).

IV. THE $2S$-$1S$ EXCHANGE INTERACTION

A. Formalism

We now consider the $2S$-$1S$ exchange interaction. The states $|1S\rangle_A|2S\rangle_B$ and $|2S\rangle_A|1S\rangle_B$ are energetically degenerate, which induces the need for special care in the treatment of the van der Waals interaction. The general eigenvalue problem reads

$$(H_S + H_{\text{vdW}})|\Psi\rangle = E|\Psi\rangle, \qquad (47)$$

where H_S is the Schrödinger Hamiltonian (sum over both atoms). In what follows we will attempt to give a somewhat streamlined derivation of the van der Waals mixing term resulting from the energetic degeneracy, which confirms the results obtained in Ref. [3]. The basis states are

$$|\Psi_1\rangle = |1S\rangle_A|2S\rangle_B, \qquad (48a)$$

$$|\Psi_2\rangle = |2S\rangle_A|1S\rangle_B. \qquad (48b)$$

The first-order perturbations to these wave functions are

$$|\delta\Psi_{j=1,2}\rangle = \left(\frac{1}{E_0 - H_S}\right)' H_{\text{vdW}}|\Psi_{j=1,2}\rangle, \qquad (49)$$

where $E_0 = E_{1S} + E_{2S}$ is the unperturbed energy of the metastable, noninteracting two-atom system. The prime on the Green's function indicates that the degenerate states have been excluded from the sum over virtual states. One calculates the Hamiltonian matrix with elements

$$H_{ij} = ((\langle\Psi_i| + \langle\delta\Psi_i|)(H_S + H_{\text{vdW}})(|\Psi_j\rangle + |\delta\Psi_j\rangle)), \qquad (50)$$

with $i,j = 1,2$. The result has the structure

$$H = \begin{pmatrix} E_0 + X & Y \\ Y & E_0 + X \end{pmatrix}, \qquad (51)$$

where

$$X = \sum_{mn}' \frac{|\langle 1S2S|H_{\text{vdW}}|mn\rangle|^2}{E_{1S} + E_{2S} - (E_m + E_n)}, \qquad (52a)$$

$$Y = \sum_{mn}' \frac{\langle 2S1S|H_{\text{vdW}}|mn\rangle\langle mn|H_{\text{vdW}}|1S2S\rangle}{E_{1S} + E_{2S} - (E_m + E_n)}. \qquad (52b)$$

Again, the prime on the sum denotes the exclusion of the reference state. This matrix thus assumes the form

$$H = \begin{pmatrix} E_0 - \frac{D_6(2S;1S)}{R^6} & -\frac{M_6(2S;1S)}{R^6} \\ -\frac{M_6(2S;1S)}{R^6} & E_0 - \frac{D_6(2S;1S)}{R^6} \end{pmatrix}, \qquad (53)$$

where we define the two coefficients

$$D_6(2S;1S) = \frac{2}{3}\frac{e^4}{(4\pi\epsilon_0)^2}\sum_{mn}'\frac{|\langle 1S|\vec{r}|m\rangle|^2|\langle 2S|\vec{r}|n\rangle|^2}{E_m + E_n - (E_{1S} + E_{2S})}, \qquad (54a)$$

$$M_6(2S;1S) = \frac{2}{3}\frac{e^4}{(4\pi\epsilon_0)^2}\sum_{mn}'\frac{1}{E_m + E_n - (E_{1S} + E_{2S})}$$
$$\times \langle 1S|\vec{r}|n\rangle\cdot\langle n|\vec{r}|2S\rangle\langle 2S|\vec{r}|m\rangle\cdot\langle m|\vec{r}|1S\rangle. \qquad (54b)$$

It can be shown that $D_6(2S;1S)$, as defined by (54a), agrees with the earlier expression (21). The eigenenergies and corresponding eigenvectors of matrix (53) are

$$E_{\pm} = E_0 - \frac{D_6 \pm M_6}{R^6}, \qquad (55a)$$

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\Psi_1\rangle \pm |\Psi_2\rangle), \qquad (55b)$$

so we obtain a symmetry-dependent van der Waals coefficient

$$C_6 = D_6 \pm M_6, \qquad (56)$$

which is obtained from a direct term and a mixing term, depending on the sign in the coherent superposition (55b). Using the integral representation (23), one can bring M_6 into the form (31)

$$M_6(2S;1S) \equiv \text{Re} - i\frac{4\hbar}{3\pi}\frac{e^4}{(4\pi\epsilon_0)^2}\sum_{mn}\int_0^\infty d\omega$$
$$\times \frac{(E_m - E_{1S})\langle 1S|\vec{r}|m\rangle\cdot\langle m|\vec{r}|2S\rangle}{[(E_m - E_{1S} - i\epsilon)^2 - (\hbar\omega)^2]}$$
$$\times \frac{(E_n - E_{2S})\langle 2S|\vec{r}|n\rangle\cdot\langle n|\vec{r}|1S\rangle}{[(E_n - E_{2S} - i\epsilon)^2 - (\hbar\omega)^2]}. \qquad (57)$$

Expressed in terms of polarizabilities, one obtains

$$D_6(2S;1S) = \text{Re}\frac{-3i\hbar}{\pi(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\alpha_{1S}(\omega)\alpha_{2S}(\omega), \qquad (58a)$$

$$M_6(2S;1S) = \text{Re}\frac{-3i\hbar}{\pi(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\alpha_{\underline{1S2S}}(\omega)\alpha_{1S\underline{2S}}^*(\omega), \qquad (58b)$$

where we define the mixed polarizabilities via

$$\alpha_{\underline{A}B}(\omega) = \frac{e^2}{3}\sum_{\pm}\langle A|\vec{r}\frac{1}{H - E_A - i\epsilon \pm \hbar\omega}\vec{r}|B\rangle \qquad (59a)$$

$$= P_{\underline{A}B}(\omega) + P_{\underline{A}B}(-\omega), \qquad (59b)$$

$$\alpha_{A\underline{B}}(\omega) = \frac{e^2}{3}\sum_{\pm}\langle A|\vec{r}\frac{1}{H - E_B - i\epsilon \pm \hbar\omega}\vec{r}|B\rangle \qquad (59c)$$

$$= P_{A\underline{B}}(\omega) + P_{A\underline{B}}(-\omega). \qquad (59d)$$

For the $(2S; 1S)$ system, one obtains

$$P_{1S2S}(\omega) = \frac{e^2 a_0^2}{E_h} \frac{512\sqrt{2}\nu^2}{729(-1+\nu^2)^2(-4+\nu^2)^3}$$
$$\times \Bigg[128 - 272\nu^2 + 120\nu^4 + 253\nu^6$$
$$+ 972\nu^7 + 419\nu^8 - 1944\nu^7 {}_2F_1 \qquad (60)$$
$$\times \left(1, -\nu; 1-\nu; \frac{1-\nu}{1+\nu}\frac{2-\nu}{2+\nu} \right) \Bigg],$$
$$\nu = n_{\text{eff}} \left(1 + \frac{2n_{\text{eff}}^2 \hbar\omega}{\alpha^2 mc^2} \right)^{-1/2}.$$

Here we will typically choose the effective quantum number n_{eff} to be either 1 (which yields P_{1S2S}) or 2 (which yields $P_{1S\underline{2S}}$), as required for input into Eq. (58). Another possibility, less physically transparent but quite handy for numerical calculations, is to choose n_{eff} such that the reference energy $E_{n_{\text{eff}}} = -\alpha^2 mc^2/2n_{\text{eff}}^2$ in the propagator corresponds to the average (33) of the energies of the $n = 1$ and $n = 2$ levels (see Secs. III B and IV B). The latter choice corresponds to $n_{\text{eff}} = 2\sqrt{2/5}$.

Taking retardation into account, the generalization of Eq. (55) (minus the unperturbed energy E_0) to the Casimir-Polder energy is

$$E_\pm = \text{Re}\,\frac{i}{\pi} \frac{\hbar}{c^4(4\pi\epsilon_0)^2} \int_0^\infty d\omega\, e^{2i\omega R/c} \frac{\omega^4}{R^2}$$
$$\times [\alpha_{1S}(\omega)\alpha_{2S}(\omega) \pm \alpha_{\underline{1S2S}}(\omega)\alpha_{1S\underline{2S}}^*(\omega)]$$
$$\times \left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4 \right]$$
$$= E_{2S;1S}^{(\text{dir})}(R) \pm E_{2S;1S}^{(\text{mxd})}(R). \qquad (61)$$

This result generalizes Eq. (55a) to the Casimir-Polder regime. It involves the mixed polarizabilities defined in Eq. (59). We refer to the second summand $E_{2S;1S}^{(\text{mxd})}$ as the exchange term. Diagrammatically, it is obtained from a process in which an initial $|1S\rangle_A|2S\rangle_B$ atom makes a transition to a $|2S\rangle_A|1S\rangle_B$ state via the exchange of two photons. As was the case for the direct $2S$-$1S$ interaction term, we can single out three different distance regimes for the exchange term, which we now investigate.

B. van der Waals range $a_0 \ll R \ll a_0/\alpha$

In the van der Waals range (9), we proceed in a similar way to Sec. III B and have

$$E_{2S;1S}^{(\text{mxd})}(R) \approx \text{Re}\,\frac{3i}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \frac{1}{R^6} \int_0^\infty d\omega\, \alpha_{\underline{1S2S}}(\omega)\alpha_{1S\underline{2S}}(\omega)$$
$$= \text{Re}\,\frac{3i}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \frac{1}{R^6} \int_0^\infty d\omega\, \alpha_{\underline{1S2S}}(\omega)$$
$$\times [\tilde{\alpha}_{1S\underline{2S}}(\omega) + \bar{\alpha}_{1S\underline{2S}}(\omega)]. \qquad (62a)$$

This can be rewritten as

$$E_{2S;1S}^{(\text{mxd})}(R) = -\frac{M_6(2S; 1S)}{R^6}, \qquad (62b)$$

where $M_6(2S; 1S) = \tilde{M}_6(2S; 1S) + \bar{M}_6(2S; 1S)$ is the sum of the nondegenerate $\tilde{M}_6(2S; 1S)$ and degenerate $\bar{M}_6(2S; 1S)$ contributions to the mixed van der Waals coefficient, with notation obvious from (62a). As was done before, we can, for the nondegenerate contribution, perform the Wick rotation. For the degenerate contribution, we follow the same procedure as in Sec. III B, centered on the integral identity (23). This yields

$$E_{2S;1S}^{(\text{mxd})}(R) = -\left(-18.630\,786\,871 + \frac{917\,504}{19\,683} \right) E_h \left(\frac{a_0}{R}\right)^6$$
$$= -27.983\,245\,543\, E_h \left(\frac{a_0}{R}\right)^6, \qquad (63)$$

where we make use of (60), whence

$$M_6 = 27.983\,245\,543\, E_h a_0^6, \qquad (64)$$

to be compared to D_6 as given by Eq. (36). The two terms in Eq. (63) correspond to the nondegenerate $(-18.630\,786\ldots)$ and degenerate $(\frac{917\,504}{19\,683})$ contributions, respectively. Their sum matches the results found in Refs. [3,4].

As was the case for the direct interaction (see Sec. III B), an alternative treatment exists whereby we make use of the integral identities (23) and (30). This yields the following expression for the van der Waals coefficient M_6:

$$M_6(2S; 1S) = \frac{3}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \int_0^\infty d\omega\, |\alpha_{\overline{1S2S}}(\omega)|^2, \qquad (65)$$

where the mixed polarizability $\alpha_{\overline{1S2S}}$ with average reference energy (33) is defined by

$$\alpha_{\overline{1S2S}}(\omega) = \frac{e^2}{3} \sum_\pm \langle 1S|\vec{r}\, \frac{1}{H - E_{\overline{1S2S}} \pm \hbar\omega} \vec{r}|2S\rangle$$
$$= P_{\overline{1S2S}}(\omega) + P_{\overline{1S2S}}(-\omega). \qquad (66)$$

A numerical calculation based on Eq. (65) confirms the result given in Eq. (63).

C. Very large interatomic distance $R \gg \hbar c/\mathcal{L}$

For very large interatomic separations, the paradigm of Sec. III C applies. In particular, the order-of-magnitude estimates given in Eq. (40) apply to the mixing term as well. We do not consider here the tiny frequency shifts of order 10^{-36} Hz or less in this range any further.

D. Intermediate distance $a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$

In the intermediate range of interatomic distances, the treatment follows that of Sec. III D. Namely, only quasidegenerate intermediate states contribute non-negligibly to the interaction and we find

$$E_{2S;1S}^{(\text{mxd})}(R) \approx -\frac{\bar{M}_6(2S; 1S)}{R^6} = -\frac{917\,504}{19\,683} E_h \left(\frac{a_0}{R}\right)^6. \quad (67)$$

The interaction is thus still of the R^{-6} form, as it is in the van der Waals range, but the coefficient $(-46.614\,032\,414)$ is different from the one relevant to the van der Waals range, given in Eq. (63).

V. DIRAC-δ-INDUCED MODIFICATION OF THE LONG-RANGE INTERACTION

A. Formalism and notation

In order to analyze the perturbation of the Casimir-Polder energy by an external potential proportional to a Dirac δ acting one of the two atoms (say, atom A), we now have to consider the perturbation of the polarizability of atom A in Eq. (61). For the perturbation of the Casimir-Polder interaction due to a Dirac-δ potential, we use this potential in the standard

normalization [43], which results in a unit prefactor in the energy shift,

$$\delta V = \alpha m c^2 \left(\frac{\hbar}{mc}\right)^3 \pi \delta^{(3)}(\vec{r}_A),$$

$$\langle nS|\delta V|nS\rangle = \frac{\alpha^4 m c^2}{n^3}. \tag{68}$$

We will consider atom A (not B) to be perturbed. The perturbation of the interaction energy (61) is

$$\delta_A E_{A;B}(R) = \text{Re} \frac{i\hbar}{\pi c^4} \int_0^\infty d\omega \frac{e^{2i\omega R/c}}{(4\pi\epsilon_0)^2} ([\delta_A\alpha_A(\omega)]\alpha_B(\omega) \pm \{[\delta_A\alpha_{\underline{AB}}(\omega)]\alpha_{A\underline{B}}(\omega) + \alpha_{\underline{AB}}(\omega)[\delta_A\alpha_{A\underline{B}}(\omega)]\})$$

$$\times \frac{\omega^4}{R^2}\left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right]. \tag{69}$$

Here $\delta_A\alpha_A(\omega)$ is the Dirac-δ perturbation of the polarizability of atom A due to the potential δV and $\delta_A\alpha_{\underline{AB}}$ and $\delta_A\alpha_{A\underline{B}}$ are the corrections to the mixed polarizabilities of the type (59). All of these corrections entail both an energy and a wave function correction. We do not consider atom B to be perturbed in our treatment. We will focus in what follows on the δ corrections to the Casimir-Polder interaction of the system $|A\rangle = |2S\rangle$ and $|B\rangle = |1S\rangle$. As evident from Eq. (69) and expected from Secs. III and IV, we need to investigate the correction to the direct and exchange terms.

More concretely, in the case of the $2S$-$1S$ system, we have

$$\delta_{2S} E_{2S;1S}(R) = \text{Re} \frac{i\hbar}{\pi c^4(4\pi\epsilon_0)^2} \int_0^\infty d\omega\, e^{2i\omega R/c} \frac{\omega^4}{R^2}([\delta_{2S}\alpha_{2S}(\omega)]\alpha_{1S}(\omega) \pm \{[\delta_{2S}\alpha_{\underline{1S2S}}(\omega)]\alpha_{1S\underline{2S}}(\omega) + \alpha_{\underline{1S2S}}(\omega)[\delta_{2S}\alpha_{1S\underline{2S}}(\omega)]\})$$

$$\times \left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right], \tag{70}$$

with the corrections to the various polarizabilities given by

$$\delta_{2S}\alpha_{2S}(\omega) = \delta_{2S}P_{2S}(\omega) + \delta_{2S}P_{2S}(-\omega),$$

$$\delta_{2S}P_{2S}(\omega) = \frac{e^2}{3}\langle 2S|\vec{r}\frac{1}{(H-E_{2S}-i\epsilon+\hbar\omega)^2}\vec{r}|2S\rangle\langle 2S|\delta V|2S\rangle + \frac{2}{3}e^2\langle 2S|\vec{r}\frac{1}{H-E_{2S}-i\epsilon+\hbar\omega}\vec{r}|\delta 2S\rangle, \tag{71a}$$

$$\delta_{2S}\alpha_{\underline{1S2S}}(\omega) = \delta_{2S}P_{\underline{1S2S}}(\omega) + \delta_{2S}P_{\underline{1S2S}}(-\omega),$$

$$\delta_{2S}P_{\underline{1S2S}}(\omega) = \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{(H-E_{1S}-i\epsilon+\hbar\omega)^2}\vec{r}|\delta 2S\rangle, \tag{71b}$$

$$\delta_{2S}\alpha_{1S\underline{2S}}(\omega) = \delta_{2S}P_{1S\underline{2S}}(\omega) + \delta_{2S}P_{1S\underline{2S}}(-\omega),$$

$$\delta_{2S}P_{1S\underline{2S}}(\omega) = \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{(H-E_{2S}-i\epsilon+\hbar\omega)^2}\vec{r}|2S\rangle\langle 2S|\delta V|2S\rangle + \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{H-E_{2S}-i\epsilon+\hbar\omega}\vec{r}|\delta 2S\rangle. \tag{71c}$$

The first term in Eq. (71a) and that in Eq. (71c) are identified as energy-type corrections, because they describe modifications to the respective polarizabilities due to the change in the $2S$ reference energy. We refer to the corresponding corrections to the respective polarizabilities as $\delta_{2S}\alpha_{2S}^{(E)}$ and $\delta_{2S}\alpha_{1S2S}^{(E)}$.

Notice that (71b) does not feature such a term, as the reference energy in the denominator of α_{1S2S} is that of the $1S$ state. The second term in Eq. (71a) and that in Eq. (71c), as well as the lone term in Eq. (71b), are called wave function-type corrections, because the corresponding terms are modifications to the respective polarizabilities due to the change in the $2S$ state (and hence wave function). We refer to the corresponding corrections to the respective polarizabilities as $\delta_{2S}\alpha_{2S}^{(\psi)}$, $\delta_{2S}\alpha_{\underline{1S2S}}^{(\psi)}$, and $\delta_{2S}\alpha_{1S\underline{2S}}^{(\psi)}$. The correction $|\delta 2S\rangle$ to the

$|2S\rangle$ state is given by the usual expression

$$|\delta 2S\rangle = \frac{1}{(E_{2S}-H)'}\delta V|2S\rangle. \tag{72}$$

The corresponding wave function is

$$\delta\psi_{2S}(\vec{r}) = \frac{\alpha^2}{\sqrt{2}}\frac{1}{\sqrt{4\pi}}\left(\frac{1}{a_0}\right)^{5/2}\exp\left(-\frac{r}{2a_0}\right)$$

$$\times \left[-\frac{a_0^2}{2r} - \frac{a_0[3 - 4\gamma_E - 4\ln\left(\frac{r}{a_0}\right)]}{4}\right.$$

$$\left. - \frac{r[-13 + 4\gamma_E + 4\ln\left(\frac{r}{a_0}\right)]}{8} - \frac{r^2}{8a_0}\right], \tag{73}$$

where $\gamma_E \simeq 0.577\,216$ is the Euler-Mascheroni constant. Finally, the first-order correction to the Hamiltonian due to δV in the propagator vanishes because the only contributing states are P states whose probability density vanishes at the origin. Namely,

$$\langle nS|\vec{r}\frac{1}{(H - E + \hbar\omega)'}\delta V \frac{1}{(H - E + \hbar\omega)'}\vec{r}|mS\rangle = 0 \quad (74)$$

regardless of the choice of E and that of the principal quantum numbers n and m. With (70) and (71) we are equipped for the investigation of the various distance regimes.

B. Dirac-δ perturbation in the van der Waals range $a_0 \ll R \ll a_0/\alpha$

For small separations, the energy shift (69) is approximated by an R^{-6} interaction, as was done in Secs. III B and IV B. We will use intermediate reference energies of the type (33) in the propagators and thus start from the expressions (36) and (65) for the direct (D_6) and mixed (M_6) coefficients, duly perturbed by the Dirac-δ potential. This allows us to treat both nondegenerate and quasidegenerate contributions to these coefficients at once. Both energy and wave function corrections contribute to $\delta C_6 = \delta D_6 \pm \delta M_6$. This adds complexity on top of the degenerate-nondegenerate dichotomy and the use of the intermediate reference energies in the propagator denominators ensures that we can avoid dealing with the degenerate and nondegenerate states separately.

We obtain the correction to the D_6 and M_6 coefficients either by taking the short-range limit of (69) and using the mean excitation energy $E_{1\bar{S}2S}$ or by perturbing the explicit expressions (36) and (65) by the Dirac δ. In both approaches, the result is

$$\delta D_6(2S;1S) = \frac{3}{\pi}\frac{\hbar}{c^4(4\pi\epsilon_0)^2}\int_0^\infty d\omega[\delta_{2S}\alpha_{1S(2S)}(i\omega)\alpha_{2S(1S)}(i\omega)$$
$$+ \alpha_{1S(2S)}(i\omega)\delta_{2S}\alpha_{2S(1S)}(i\omega)] \quad (75)$$

and

$$\delta M_6(2S;1S) = \frac{6}{\pi}\frac{\hbar}{c^4(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\alpha_{\overline{1S2S}}(i\omega)\delta_{2S}\alpha_{\overline{1S2S}}(i\omega). \quad (76)$$

The Dirac-δ corrections to the polarizabilities (35) and (66) involve the mean excitation energy (33) in the propagator,

$$\delta_{2S}\alpha_{1S(2S)}(\omega) = \delta_{2S}P_{1S(2S)}(\omega) + \delta_{2S}P_{1S(2S)}(-\omega),$$
$$\delta_{2S}P_{1S(2S)}(\omega) = \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{(H - E_{\overline{1S2S}} + \hbar\omega)^2}\vec{r}|1S\rangle$$
$$\times \frac{1}{2}\langle 2S|\delta V|2S\rangle, \quad (77a)$$
$$\delta_{2S}\alpha_{2S(1S)}(\omega) = \delta_{2S}P_{2S(1S)}(\omega) + \delta_{2S}P_{2S(1S)}(-\omega),$$
$$\delta_{2S}P_{2S(1S)}(\omega) = \frac{e^2}{3}\langle 2S|\vec{r}\frac{1}{(H - E_{\overline{1S2S}} + \hbar\omega)^2}\vec{r}|2S\rangle$$
$$\times \frac{1}{2}\langle 2S|\delta V|2S\rangle$$
$$+ \frac{2}{3}e^2\langle 2S|\vec{r}\frac{1}{H - E_{\overline{1S2S}} + \hbar\omega}\vec{r}|\delta 2S\rangle, \quad (77b)$$

$$\delta_{2S}\alpha_{\overline{1S2S}}(\omega) = \delta_{2S}P_{\overline{1S2S}}(\omega) + \delta_{2S}P_{\overline{1S2S}}(-\omega),$$
$$\delta_{2S}P_{\overline{1S2S}}(\omega) = \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{(H - E_{\overline{1S2S}} + \hbar\omega)^2}\vec{r}|2S\rangle$$
$$\times \frac{1}{2}\langle 2S|\delta V|2S\rangle$$
$$+ \frac{e^2}{3}\langle 1S|\vec{r}\frac{1}{H - E_{\overline{1S2S}} + \hbar\omega}\vec{r}|\delta 2S\rangle. \quad (77c)$$

We recall that the use of the mean energy $E_{\overline{1S2S}}$ amounts to making the choice of the intermediate effective quantum number $n_{\rm eff} = 2\sqrt{2/5}$ [see discussion below Eq. (60)]. Again, we distinguish the energy-type corrections, which correspond to the first summand in Eq. (77b) and that in Eq. (77c), as well as the lone term in Eq. (77a). We write them as $\delta_{2S}\alpha^{(E)}_{2S(1S)}$, $\delta_{2S}\alpha^{(E)}_{\overline{1S2S}}$, and $\delta_{2S}\alpha^{(E)}_{1S(2S)}$, respectively. The wave-function-type corrections correspond to the second summand in Eq. (77b) and that in Eq. (77c) and we write them as $\delta_{2S}\alpha^{(\psi)}_{2S(1S)}$ and $\delta_{2S}\alpha^{(\psi)}_{\overline{1S2S}}$, respectively.

By a generalization of numerical techniques described previously [34,35], we find that the numerical value of (75) is

$$\delta D_6(2S;1S) = 367.914\,605\,710\alpha^2 a_0^6 E_h. \quad (78)$$

By a similar procedure we find the numerical value of (76),

$$\delta M_6(2S;1S) = -58.095\,351\,093\alpha^2 a_0^6 E_h. \quad (79)$$

Details on the calculation of (78) and (79) are given in Appendix B.

C. Dirac-δ perturbation for intermediate distance $a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$

As was the case for the unperturbed interaction, it is very interesting to focus on the intermediate-distance range. Here again, as far as virtual transitions with a change in the principal quantum number are concerned, we are deeply in the Casimir-Polder regime, where the result is given by an R^{-7} interaction. However, for virtual transitions to the quasidegenerate states, the frequency range is so low that the contribution to the Casimir-Polder integral (69) is not exponentially suppressed. We therefore obtain

$$\delta_A E_{A;B}(R) \approx {\rm Re}\,\frac{i\hbar}{\pi c^4(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,e^{2i\omega R/c}\frac{\omega^4}{R^2}$$
$$\times([\delta_A\bar{\alpha}_A(\omega)]\alpha_B(0) \pm \{[\delta_A\alpha_{\underline{AB}}(0)]\bar{\alpha}_{\underline{AB}}(\omega)$$
$$+ \alpha_{\underline{AB}}(0)[\delta_A\bar{\alpha}_{\underline{AB}}(\omega)]\})$$
$$\times\left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2\right.$$
$$\left. - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right]. \quad (80)$$

The rationale here is that the quasiresonant terms (overlined α's) have to be kept in dynamic form (the dependence on ω is retained), while the complementary terms can be taken in the static limit.

We will treat the energy-type and wave-function-type corrections separately. In the present Casimir-Polder range (13), the energy-type correction to the direct $2S$-$1S$ interaction is

$$\delta_{2S}E_{2S;1S}^{(\text{dir})(E)}(R) = \text{Re}\,\frac{i\hbar\alpha_{1S}(0)}{\pi c^4}\int_0^\infty d\omega\,\frac{e^{2i\omega R/c}}{(4\pi\epsilon_0)^2}\delta_{2S}\bar{\alpha}_{2S}^{(E)}(\omega)\frac{\omega^4}{R^2}\left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right]$$

$$= -\text{Re}\,\frac{i\hbar\alpha_{1S}(0)}{\pi c^4(4\pi\epsilon_0)^2}\langle 2S|\delta V|2S\rangle\int_0^\infty d\omega\,e^{2i\omega R/c}\frac{\omega^4}{R^2}\left[\frac{\partial}{\partial\mathcal{L}}\frac{-\mathcal{L}}{(-\mathcal{L}-i\epsilon)^2-(\hbar\omega)^2} + 2\frac{\partial}{\partial\mathcal{F}}\frac{\mathcal{F}}{(\mathcal{F}-i\epsilon)^2-(\hbar\omega)^2}\right]$$

$$\times\left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right]\frac{e^2}{3}\sum_\mu\langle 2S|\vec{r}\,|2P(m=\mu)\rangle\cdot\langle 2P(m=\mu)|\vec{r}\,|2S\rangle.$$

$$(81)$$

Because of the pole structure of the integrand, it is not possible to simply set the retardation function

$$R(\omega) = e^{2i\omega R/c}\frac{\omega^4}{R^2}\left[1 + 2i\frac{c}{\omega R} - 5\left(\frac{c}{\omega R}\right)^2 - 6i\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4\right] \tag{82}$$

equal to unity (as was done in Secs. III D and IV D); the residue at the poles of the integrand in Eq. (81) otherwise cannot be calculated correctly. In the $\mathcal{L}\to 0, \mathcal{F}\to 0$ limit, this gives

$$\delta_{2S}E_{2S;1S}^{(\text{dir})(E)}(R) = -\frac{11}{6\pi}\frac{\alpha_{1S}(0)}{(4\pi\epsilon_0)^2\hbar c R^5}\langle 2S|\delta V|2S\rangle\frac{e^2}{3}\sum_\mu\langle 2S|\vec{r}\,|2P(m=\mu)\rangle\cdot\langle 2P(m=\mu)|\vec{r}\,|2S\rangle. \tag{83}$$

Note that the individual terms of the retardation function $R(\omega)$, when used in Eq. (81), give rise to logarithmic terms proportional to $\ln(2\mathcal{F}R)/R^5$ and $\ln(2\mathcal{L}R)/R^5$; these cancel in the final result. From a similar procedure we obtain the correction to the exchange $2S$-$1S$ interaction as

$$\delta_{2S}E_{2S;1S}^{(\text{mxd})(E)}(R) = -\frac{11}{6\pi}\frac{\alpha_{\underline{1S2S}}(0)}{(4\pi\epsilon_0)^2\hbar c R^5}\langle 2S|\delta V|2S\rangle\frac{e^2}{3}\sum_\mu\langle 1S|\vec{r}\,|2P(m=\mu)\rangle\cdot\langle 2P(m=\mu)|\vec{r}\,|2S\rangle. \tag{84}$$

The energy-type correction induces an R^{-5} interaction (see Appendix A). The wave-function-type corrections, on the other hand, are treated in exactly the same way as the degenerate $\bar{D}_6$ and $\bar{M}_6$ coefficients of Secs. III D and IV D, respectively. We can make use of (45a) and (45b) and obtain

$$\delta\bar{D}_6^{(\psi)}(2S;1S) = \frac{2}{(4\pi\epsilon_0)^2}\alpha_{1S}(0)\sum_\mu\langle 2S|\vec{r}\,|2P(m=\mu)\rangle\cdot\langle 2P(m=\mu)|\vec{r}\,|\delta 2S\rangle \tag{85}$$

and

$$\delta\bar{M}_6^{(\psi)}(2S;1S) = \frac{1}{(4\pi\epsilon_0)^2}\sum_\mu\langle 1S|\vec{r}\,|2P(m=\mu)\rangle\left[\delta\alpha_{\underline{1S2S}}^{(\psi)}(0)\langle 2P(m=\mu)|\vec{r}\,|2S\rangle + \alpha_{\underline{1S2S}}(0)\langle 2P(m=\mu)|\vec{r}\,|\delta 2S\rangle\right]. \tag{86}$$

From Eq. (83) we find that for intermediate distances the energy-type correction to the interaction is given by

$$\delta_{2S}E_{2S;1S}^{(\text{dir})(E)}(R) = -\frac{891}{32}\frac{\alpha^3}{\pi}\left(\frac{a_0}{R}\right)^5 E_h, \tag{87}$$

while the wave-function correction is

$$\delta_{2S}E_{2S;1S}^{(\text{dir})(\psi)}(R) = -\frac{81}{4}\alpha^2\left(\frac{a_0}{R}\right)^6 E_h. \tag{88}$$

It is thus seen that, in the present intermediate range (13), the dominant contribution comes from the energy-type correction (87).

From (84) we find that for intermediate distances the energy-type correction to the exchange interaction is given by

$$\delta_{2S}E_{2S;1S}^{(\text{mxd})(E)}(R) = \frac{630\,784}{59\,049}\frac{\alpha^3}{\pi}\left(\frac{a_0}{R}\right)^5 E_h, \tag{89}$$

while the wave-function correction is

$$\delta_{2S}E_{2S;1S}^{(\text{mxd})(\psi)}(R) = -\frac{8192}{19\,683}\left[95 + 112\ln\left(\frac{3}{2}\right)\right]\alpha^2\left(\frac{a_0}{R}\right)^6 E_h. \tag{90}$$

As was the case for the direct interaction above, the dominant contribution comes from the energy-type correction (89).

D. Very-long-range Dirac-δ perturbation $R \gg \hbar c / \mathcal{L}$

For very large interatomic separation, the considerations from Secs. III C and IV C carry over. Perturbing the Lamb shift $\mathcal{L}$ in Eq. (40) by the Dirac-δ potential (68), one realizes that the Dirac-δ-induced modification of the long-range interaction does not exceed $(\langle 2S|\delta V|2S\rangle/\mathcal{L}) \times 10^{-36}$ Hz. This shift is too small to be of conceivable experimental relevance and thus is not considered any further.

VI. NUMERICAL EXAMPLES: MODIFICATION TO THE HYPERFINE STRUCTURE AND TRANSITION FREQUENCIES

In order to estimate the relevance of the current study, let us recall that, e.g., the hyperfine frequency of a hydrogen atom in an S state is determined by a Dirac-δ potential [see Eq. (4) and discussion below]. Hyperfine frequencies belong to the most accurately measured frequencies today [44–46]. Consequently, it becomes necessary to investigate small perturbations to these frequencies caused, e.g., by interactions with buffer gas atoms or by interactions with other atoms in the atomic beam (the latter would be an atom of the same kind as that whose hyperfine frequency is being studied). The perturbations of hyperfine frequencies due to van der Waals interactions have been considered in Refs. [10–13,15]. Hyperfine-perturbation coefficients in the van der Waals range have been given in Table II of Ref. [15] for H-He and H-Ne. (The hyperfine modification of the long-range interaction for two hydrogen atoms, however, is not indicated in Ref. [15]. Also, in Ref. [15], only ground-state interactions were considered.)

In Eqs. (78), (79), (87), and (89), we had indicated results for the Dirac-δ-induced perturbation to the van der Waals interaction, in the close-range limit and in the intermediate range. These results, which are reproduced for convenience in Eqs. (95) and (96) below, can be used directly in order to calculate the modification of the hyperfine frequency under the influence of the long-range interaction. As explained in Sec. II, a possible interference term due to the non-Dirac-δ terms in the hyperfine Hamiltonian [see Eq. (4)], which might be assumed to influence the virtual P states that are responsible for the van der Waals interaction, vanishes after doing the angular Racah algebra [47]. In order to interpolate between the three asymptotic regimes, a numerical integration of Eq. (69) is required. The leading asymptotic terms indicated in Eqs. (95) and (96) contain the essence of the changes in the interaction in a very concise form and can be used in order to estimate the effect of the long-range 2S-1S interaction on, e.g., the 2S hyperfine frequency.

Let us now calculate the van der Waals shift of the hyperfine frequency of an atom A in a 1S or metastable 2S state due to its long-range interaction with a ground-state atom B. The first summand in H_{hfs} in Eq. (4) is used as the perturbative potential instead of the standard potential (68). Only the term acting on

TABLE I. Numerical values of the modification $\delta\nu_{\text{hfs}(1S)}$ to the frequency splitting between the 1S hyperfine components in hydrogen, due to the long-range interaction with a 1S atom, as a function of the interatomic separation.

Distance (Å)	$\delta\nu_{\text{hfs}}(1S)$ (Hz)
20	-3.387×10^{1}
40	-5.291×10^{-1}
80	-8.806×10^{-3}
200	-3.019×10^{-5}
400	-3.919×10^{-7}
800	-4.296×10^{-9}
2000	-1.059×10^{-12}
20 000	-1.059×10^{-19}

atom A is required. One can check that

$$\delta H_{\text{hfs}} = \frac{2}{3} g_s g_p \frac{m}{M} \delta V(\vec{r}_A) \vec{S}_A \cdot \vec{I}_A, \tag{91}$$

where M is the proton mass. The splitting between the two hyperfine components of the $1S_{1/2}$ level is given by $1\,420\,405\,751.773(1)$ Hz [44–46]. This experimental value is very accurate (up to 10^{-3} Hz), which indicates that modifications to it due to long-range interatomic interactions could be relevant for future experiments and, in particular, measurable. We can work out how this splitting is affected by the interaction of the 1S atom with another 1S hydrogen atom. The corresponding values are given in Table I. Note that the interaction *reduces* the energy splitting between the two hyperfine components of the $1S_{1/2}$ level. Likewise, the splitting between the two hyperfine components of the $2S_{1/2}$ level has been measured [7] as $177\,556\,834.3(6.7)$ Hz. From Eqs. (95) and (96) (as well as numerical computations for the separations that do not clearly find themselves in either the van der Waals or Casimir-Polder ranges) we can work out how this splitting is affected by the interaction of the 2S atom with a 1S hydrogen atom. The corresponding values are given in Table II. Again, the interaction reduces the energy splitting between the two hyperfine components of the $2S_{1/2}$ level.

From the results of Secs. III and IV we can also deduce the modifications to the 2S-1S transition frequency due to

TABLE II. Numerical values of the modification $\delta\nu_{\text{hfs}(2S)}$ to the frequency splitting between the 2S hyperfine components in hydrogen, due to the long-range interaction with a 1S atom, as a function of the interatomic separation. The $\mp$ sign corresponds to the $\pm$ sign in the $|1S\rangle|2S\rangle \pm |2S\rangle|1S\rangle$ superposition.

Distance (Å)	$\delta\nu_{\text{hfs}}(2S)$ (Hz)
20	$-(3.592 \mp 0.567) \times 10^{2}$
40	$-(5.612 \mp 0.886) \times 10^{0}$
80	$-(8.769 \mp 1.441) \times 10^{-2}$
200	$-(3.592 \mp 0.549) \times 10^{-4}$
400	$-(5.635 \mp 0.781) \times 10^{-6}$
800	$-(9.023 \mp 0.861) \times 10^{-8}$
2000	$-(2.584 \mp 1.486) \times 10^{-10}$
20 000	$-(2.406 \mp 0.973) \times 10^{-15}$

TABLE III. Numerical values of the modification $\delta\nu_{1S\text{-}2S}$ to the hydrogen $2S$-$1S$ transition frequency, due to the long-range interaction with a $1S$ atom, as a function of the interatomic separation. The $\pm$ sign corresponds to the $\pm$ sign in the $|1S\rangle|2S\rangle \pm |2S\rangle|1S\rangle$ superposition.

Distance (Å)	$\delta\nu_{1S\text{-}2S}$ (Hz)
20	$-(3.843 \pm 0.631) \times 10^8$
40	$-(6.005 \pm 0.987) \times 10^6$
80	$-(9.365 \pm 1.552) \times 10^4$
200	$-(3.806 \pm 0.651) \times 10^2$
400	$-(5.838 \pm 1.069) \times 10^0$
800	$-(8.776 \pm 1.821) \times 10^{-2}$
2000	$-(3.521 \pm 1.310) \times 10^{-4}$
20 000	$-(2.820 \pm 1.078) \times 10^{-10}$

long-range interaction with a ground-state hydrogen atom. We indicate numerical values for various interatomic separations in the van der Waals and Casimir-Polder (intermediate) ranges in Table III. The $2S$-$1S$ transition has been measured [48] to be $2\,466\,061\,413\,187\,035(10)$ Hz (for the hyperfine centroid). The experimental accuracy is thus more than sufficient for the modifications predicted here to be relevant (see Table III). For the values $R = 2000$ and $20\,000$ Å of the distance that we choose for the Casimir-Polder (intermediate) range ($\hbar c/\mathcal{L} \gg R \gg a_0/\alpha$), the R^{-7} contribution due to the P levels that are nondegenerate with $2S$ is not quite negligible, in contrast to larger R. We therefore include the nondegenerate contributions in the calculation of the numerical value of the frequency shifts. For definiteness, the value of the mass m used in the numerical calculations is always chosen as the electron mass, not the reduced mass of the electron-proton system. If we were to choose the reduced mass instead, then we would have to differentiate in the Dirac-δ term given in Eq. (68) the factor $1/m^2$, which still goes with the electron mass, and the reduced mass cubed, which enters the numerator as it is proportional to the probability density at the origin $|\psi(0)|^2$. For definiteness, and in order to facilitate a numerical comparison of the results to other (conceivably, future) investigations, we neglect further relativistic and reduced-mass corrections, as well as quantum electrodynamic radiative corrections. When applied to hydrogen, these approximations limit the accuracy of the results given in Tables I–III to a relative accuracy of about $10^{-4}, \ldots, 10^{-3}$.

It is also interesting to look at how these results are modified if we consider the positronium instead of the hydrogen atom as the system of interest. It can be shown that the plain (unperturbed) van der Waals interaction energies will be scaled by a factor of approximately $2^6 = 64$, as a result of the fact that the reduced mass of positronium is roughly half the reduced mass of hydrogen [hence the expectation values of $\vec{r}$ operators will scale with a factor of 2, as will the resolvent operators $1/(H - E)$]. The latter scaling factor is due to the fact that the transition frequencies are only half of those of the hydrogen atom (e.g., the $2S$-$1S$ transition in positronium has been measured at a value of $\approx 1.233 \times 10^{15}$ Hz; see Ref. [49].) The van der Waals modifications to the $2S$-$1S$ transition frequency in positronium as compared to hydrogen will exhibit the same scaling. The relative modification of a positronium transition frequency will thus be 128 times larger than for hydrogen. Similar scaling arguments show that the modification to the hyperfine splittings will be scaled by a factor of $2^7 g_s/g_p \simeq 45.845\,112$.

Likewise, the leading effective QED radiative Lamb shift Hamiltonian for atom A can be obtained as a specialization of the expression given in Eq. (3) to atom A,

$$\delta H_{\text{rad}} = \frac{4\alpha}{3\pi} \ln(\alpha^{-2}) \delta V, \tag{92}$$

where again we express the relevant Hamiltonian in terms of the standard potential δV defined in Eq. (68). The ratio of the prefactors as compared to the hyperfine Hamiltonian (91) is

$$\frac{2}{\pi}\alpha \ln(\alpha^{-2}) \frac{1}{g_s g_p} \frac{m_p}{m} \frac{1}{\langle \vec{S}_A \cdot \vec{I}_A \rangle} \simeq 7.505\,166.$$

The operator $\vec{S}_A \cdot \vec{I}_A$ assumes the numerical value $+1/4$ for an $F = 1$ state and the numerical value $-3/4$ for an $F = 0$ state. Hence, for the hyperfine splitting, it can be replaced by unity. We thus note that the leading logarithmic QED radiative corrections to the $1S$-$1S$ and $2S$-$1S$ van der Waals interactions are larger than the van der Waals modification of the hyperfine splitting, by a factor of roughly 7.5. The results given in Tables I and II should be multiplied by this factor to obtain the leading radiative term. The QED radiative correction to the van der Waals interaction shifts both hyperfine components by the same frequency and in the same direction and thus does not additionally modify the hyperfine splitting. We also note that the QED radiative correction to the van der Waals interaction could be interpreted alternatively as a van der Waals correction to the Lamb shift. However, it is not the dominant modification of atomic transition frequencies mediated by long-range atomic interactions. Namely, the main effect on an atomic transition frequency with a change in the principal quantum number is caused by the direct van der Waals effect on the atomic levels, which is given (for the $2S$-$1S$) in Table III.

VII. CONCLUSION

We have studied $2S$-$1S$ van der Waals interactions among hydrogen atoms in detail and carefully differentiate three distance ranges given in Eqs. (9), (11), and (12). 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 $C_6(A;B) = D_6(A;B) \pm M_6(A;B)$ is the van der Waals coefficient, which depends on the atomic states $|A\rangle$ and $|B\rangle$ of the two atoms. As mentioned above, a paradigmatic example for an interaction involving metastable atoms is the $2S$ state of atomic hydrogen. Indeed, for the interaction of a $2S$ hydrogen atom with a ground-state atom, the result of $D_6(2S;1S) = 176.752 E_h a_0^6$ has been obtained in Ref. [4].

As discussed, there is an interesting discrepancy with the results $D_6(2S;1S) = 56.8 E_h a_0^6$ [5] and $D_6(2S;1S) = (56.5 \pm 0.5) E_h a_0^6$ [3]. We find that the result given in Ref. [4] is the correct one and trace the likely explanation for the discrepancy to the rather subtle treatment of the quasidegenerate $2P$ levels of the excited atom (see Sec. III B).

In an atomic beam, one typically has a few excited metastable $2S$ atoms interacting with a "background" of $1S$

atoms. The $2S$ atoms are typically of interest, which is why we have chosen the sequence $2S$-$1S$ in order to designate their interaction in our mathematical formulas (the *first* atom mentioned is the one of primary spectroscopic interest). A typical application would consist in the measurement of the $2S$ hyperfine interval by optical spectroscopy [6,7].

For the plain interaction of a $2S$ atom with a ground-state hydrogen atom, we find for the van der Waals regime ($a_0 \ll R \ll \frac{a_0}{\alpha}$) [see Eqs. (29) and (63)]

$$E_{2S;1S}(R) \approx -(176.752\,266 \pm 27.983\,245)E_h\left(\frac{a_0}{R}\right)^6. \quad (93)$$

The term with the $\pm$ sign depends on the symmetry of the wave function of the two-atom state, as explained in Sec. IV. In Eq. (93) we thus confirm the result presented in Ref. [4] but add a few more significant decimal digits of nominal numerical accuracy [see Eq. (29)]. In the Casimir-Polder range ($\frac{a_0}{\alpha} \ll R \ll \frac{\hbar c}{\mathcal{L}}$), we also have an interaction of the R^{-6} type, with a coefficient determined by the quasidegenerate states [see Eqs. (46) and (67)]

$$E_{2S;1S}(R) \approx -\left(\frac{243}{2} \pm \frac{917\,504}{19\,683}\right)E_h\left(\frac{a_0}{R}\right)^6. \quad (94)$$

In the Lamb shift range $R \gg \hbar c/\mathcal{L}$, the plain interaction changes to a superposition of a Casimir-Polder term of the form $1/R^7$ and a long-range oscillating term of the type $\cos(2\mathcal{L}R/\hbar c)/R^2$, while the magnitude of the interaction is too small to be of conceivable relevance for experiments. For details, see Secs. III and IV.

For the correction $\delta E_{2S;1S}(R)$ caused by a Dirac-δ potential, due to the long-range interaction, the evolution of the asymptotic behavior is interesting. For the van der Waals range ($a_0 \ll R \ll \frac{a_0}{\alpha}$), our leading-order result is [see Eqs. (78) and (79)]

$$\delta_{2S}E_{2S;1S}(R) \approx -(367.914\,605 \mp 58.095\,351)\alpha^2 E_h\left(\frac{a_0}{R}\right)^6. \quad (95)$$

In the Casimir-Polder range ($\frac{a_0}{\alpha} \ll R \ll \frac{\hbar c}{\mathcal{L}}$), the result is [see Eqs. (87) and (89)]

$$\delta_{2S}E_{2S;1S}(R) \approx -\left(\frac{891}{32} \mp \frac{630\,784}{59\,049}\right)\frac{\alpha^3}{\pi}E_h\left(\frac{a_0}{R}\right)^5, \quad (96)$$

where the coefficient is exclusively given by the quasidegenerate states. In the Lamb shift range $R \gg \hbar c/\mathcal{L}$, the perturbed interaction also changes to a superposition of a Casimir-Polder term and a long-range oscillating term, while the overall perturbation of the interaction is negligibly small. All these results are derived in Secs. III and IV.

Recently, long-range oscillatory tails of van der Waals interactions have received renewed interest in the literature [29,30]. These oscillatory tails are caused by states with a lower energy than the excited reference state, in an interaction of excited-state and ground-state atoms, which can be reached from the

excited state by an allowed dipole transition. As discussed in this paper, for the $2S$-$1S$ interaction, the $2S \to 2P_{1/2}$ Lamb shift transition provides for such a transition. However, the energy shifts typically are proportional to the fourth power of the transition energy (or wave number of the transition). For the Lamb shift transition, this transition energy is very low and in consequence the oscillatory tails are suppressed in the van der Waals interaction of the $2S$-$1S$ system [see Eq. (40)].

APPENDIX A: MODEL INTEGRALS

In order to illustrate the analytic considerations in Secs. III–V, we numerically study the model integrals

$$I(a,\eta,R) \equiv \int_0^\infty dx \frac{a}{(a-i\epsilon)^2+x^2}\frac{(-\eta)}{(-\eta-i\epsilon)^2+x^2}$$
$$\times e^{-2Rx}\frac{x^4}{R^2}\left[1+\frac{2}{Rx}+\frac{5}{(Rx)^2}\right.$$
$$\left.+\frac{6}{(Rx)^3}+\frac{3}{(Rx)^4}\right], \quad (A1)$$

which models the plain Casimir-Polder interaction as well as wave function-type corrections thereto, and

$$J(a,\eta,R) \equiv \int_0^\infty dx \frac{a}{(a-i\epsilon)^2+x^2}\frac{\partial}{\partial\eta}\frac{(-\eta)}{(-\eta-i\epsilon)^2+x^2}$$
$$\times e^{-2Rx}\frac{x^4}{R^2}\left[1+\frac{2}{Rx}+\frac{5}{(Rx)^2}\right.$$
$$\left.+\frac{6}{(Rx)^3}+\frac{3}{(Rx)^4}\right], \quad (A2)$$

which models energy-type corrections to the Casimir-Polder interaction. Our choices for the numerical values of the parameters are

$$\eta = 10^{-3}, \quad (A3a)$$
$$a = 1, \quad (A3b)$$
$$\epsilon = 10^{-6}. \quad (A3c)$$

These values are adapted to the investigation of the quasidegenerate contributions to the interatomic interaction, where a plays the role of the energy of a transition between quantum levels with different principal quantum numbers and η corresponds to the energy of a transition between quasidegenerate neighbors. These parameters and arguments are dimensionless. The transition from the $1/R^6$ short-range asymptotics to the $1/R^7$ long-range limit is clearly displayed in Fig. 1, while the intermediate $1/R^5$ regime for J is discernible in Fig. 2.
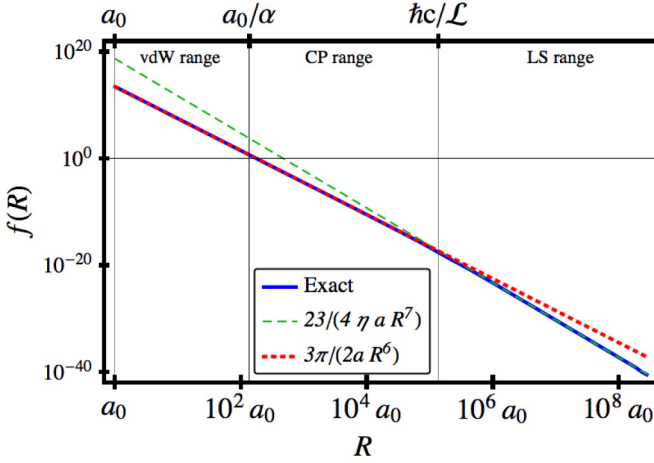
FIG. 1. Numerical illustration of the model integral (A1) in its asymptotic regions, for the parameters given in Eq. (A3).
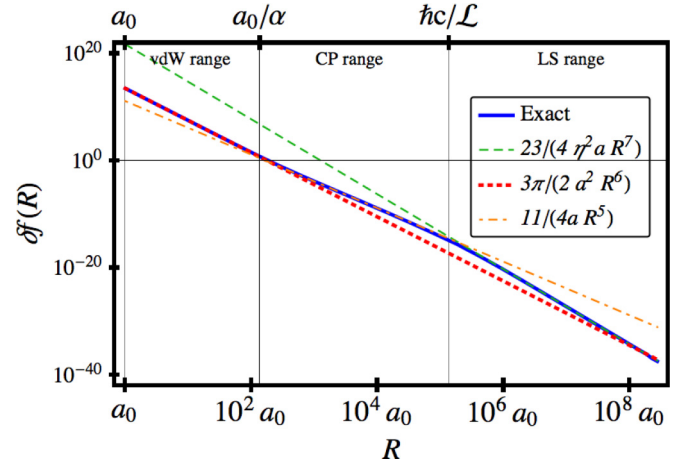

FIG. 2. Same as Fig. 1 for the model integral (A2).

APPENDIX B: DETAILS ON DIRAC-δ CORRECTIONS TO THE VAN DER WAALS INTERACTION

Here we present some details on how the numerical results (78) and (79) were obtained. We recall that for the $2S$-$1S$ system, δD_6 is given by

$$\delta D_6(2S;1S) = \frac{3}{\pi}\frac{\hbar}{(4\pi\epsilon_0)^2}\int_0^\infty d\omega[\delta_{2S}\alpha_{1S(2S)}(i\omega)\alpha_{2S(1S)}(i\omega) + \alpha_{1S(2S)}(i\omega)\delta_{2S}\alpha_{2S(1S)}(i\omega)], \tag{B1}$$

where the corrected polarizabilities read

$$\delta_{2S}\alpha_{1S(2S)}(\omega) = \frac{e^2}{3}\sum_\pm\langle 1S|\vec{r}\frac{1}{(H-E_{\overline{1S2S}}-i\epsilon\pm\hbar\omega)^2}\vec{r}|1S\rangle\frac{1}{2}\langle 2S|\delta V|2S\rangle \equiv \delta_{2S}\alpha_{1S(2S)}^{(E)}(\omega), \tag{B2a}$$

because we perturb only the $2S$ energy, and

$$\delta_{2S}\alpha_{2S(1S)}(\omega) = \frac{e^2}{3}\sum_\pm\langle 2S|\vec{r}\frac{1}{(H-E_{\overline{1S2S}}-i\epsilon\pm\hbar\omega)^2}\vec{r}|2S\rangle\frac{1}{2}\langle 2S|\delta V|2S\rangle + \frac{2e^2}{3}\sum_\pm\langle 2S|\vec{r}\frac{1}{H-E_{\overline{1S2S}}-i\epsilon\pm\hbar\omega}\vec{r}|\delta 2S\rangle$$

$$= \delta_{2S}\alpha_{2S(1S)}^{(E)}(\omega) + \delta_{2S}\alpha_{2S(1S)}^{(\psi)}(\omega). \tag{B2b}$$

Here the (E) superscript refers to the contribution from the energy correction and the (ψ) superscript refers to the contribution from the wave-function correction. It can be checked that the two summands in

$$\delta D_6^{(E)}(2S;1S) = \frac{3}{\pi}\frac{\hbar}{(4\pi\epsilon_0)^2}\int_0^\infty d\omega\big[\delta_{2S}\alpha_{1S(2S)}^{(E)}(i\omega)\alpha_{2S(1S)}(i\omega) + \alpha_{1S(2S)}(i\omega)\delta_{2S}\alpha_{2S(1S)}^{(E)}(i\omega)\big] \tag{B3}$$

contribute equally. This can be traced back to the integral identity (23). The easiest way to compute the energy correction to a polarizability is to notice that

$$\langle nS|\vec{r}\frac{1}{(H-E-i\epsilon+\hbar\omega)^2}\vec{r}|mS\rangle = -\frac{1}{\hbar}\frac{\partial}{\partial\omega}\langle nS|\vec{r}\frac{1}{H-E-i\epsilon+\hbar\omega}\vec{r}|mS\rangle, \tag{B4}$$

which is just the ω derivative of a typical P matrix element. To see that the summands in the integrand on the right-hand side of (B3) contribute equally, however, one rather notices that

$$\langle nS|\vec{r}\frac{1}{(H-E-i\epsilon+\hbar\omega)^2}\vec{r}|mS\rangle = \frac{\partial}{\partial E}\langle nS|\vec{r}\frac{1}{H-E-i\epsilon+\hbar\omega}\vec{r}|mS\rangle \tag{B5}$$

and the equality follows from (23). In the end, we obtain

$$\delta D_6^{(E)}(2S;1S) = 49.733\,193\,536\alpha^2 a_0^6 E_h. \tag{B6}$$

It is considerably harder to compute the contribution to the van der Waals coefficient from the wave-function correction

$$\delta D_6^{(\psi)}(2S;1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\alpha_{1S(2S)}(i\omega)\delta_{2S}\alpha_{2S(1S)}^{(\psi)}(i\omega). \tag{B7}$$

The first step is to obtain the correction (73) to the $2S$ wave function, from which we deduce

$$\delta P_{2S}^{(\psi)}(\omega) = \frac{e^2 a_0^2}{mc^2}\left[-\frac{8}{9}\frac{\tau^2 Q(\tau)}{(1-\tau)^7(1+\tau)^8} + \frac{4096\tau^9(-2+\tau+7\tau^2)}{3(\tau-1)^6(1+\tau)^5}\ln\left(\frac{2\tau}{1+\tau}\right) + \frac{512\tau^7(1+\tau^2)}{(1-\tau)^5(1+\tau)^5}\right.$$

$$\times {}_2F_1\left(1,-2\tau;1-2\tau;-\frac{1-\tau}{1+\tau}\right) - \frac{512\tau^7 R(\tau)}{9(1-\tau)^7(1+\tau)^7}\,{}_2F_1\left(1,-2\tau;1-2\tau;\left(\frac{1-\tau}{1+\tau}\right)^2\right)$$

$$+ \frac{32\,768}{3}\frac{\tau^{10}(-1+4\tau^2)}{(-1+\tau)^2(1+\tau)^{10}}\sum_{k=0}^{\infty}\left(\frac{-1+\tau}{1+\tau}\right)^k\frac{\partial_2\,{}_2F_1(-k,4;4;\frac{2}{1+\tau})}{(2+k-2\tau)}\right], \tag{B8}$$

where

$$Q(\tau) = -123 - 123\tau + 801\tau^2 + 801\tau^3 - 2124\tau^4 - 1932\tau^5 + 4002\tau^6 + 11\,234\tau^7 + 3661\tau^8$$

$$- 20\,979\tau^9 + 2285\tau^{10} + 9645\tau^{11} + 26\,314\tau^{12} + 3402\tau^{13} \tag{B9}$$

and

$$R(\tau) = -3 + 113\tau^2 - 193\tau^4 + 371\tau^6 + 96\tau^2(1-\tau^2)(1-4\tau^2)\ln\left(\frac{2\tau}{1+\tau}\right). \tag{B10}$$

Furthermore,

$$\tau = \left(1 + \frac{8\hbar\omega}{\alpha^2 mc^2}\right)^{-1/2}. \tag{B11}$$

We can then easily deduce $\delta_{2S}\alpha_{2S(1S)}^{(\psi)}(\omega)$ from (B8) via

$$\delta_{2S}\alpha_{2S(1S)}^{(\psi)}(\omega) = \delta_{2S}P_{2S(1S)}^{(\psi)}(\omega) + \delta_{2S}P_{2S(1S)}^{(\psi)}(-\omega), \tag{B12}$$

where $\delta_{2S}P_{2S(1S)}^{(\psi)}(\omega)$ has the same expression as (B8), with τ replaced by

$$t_{\text{eff}} = \left(1 + \frac{16\hbar\omega}{5\alpha^2 mc^2}\right)^{-1/2}. \tag{B13}$$

From all of this we obtain

$$\delta D_6^{(\psi)}(2S;1S) = 318.181\,412\,174\alpha^2 a_0^6 E_h. \tag{B14}$$

We now recall that for the $2S$-$1S$ system, δM_6 is given by

$$\delta M_6(2S;1S) = \frac{3}{\pi}\frac{\hbar}{(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\delta_{2S}\alpha_{\overline{1S2S}}(i\omega)\alpha_{\overline{1S2S}}(i\omega), \tag{B15}$$

where the corrected mixed polarizability reads

$$\delta_{2S}\alpha_{\overline{1S2S}}(\omega) = \sum_\pm \langle 1S|\vec{r}\frac{1}{(H - E_{\overline{1S2S}} - i\epsilon \pm \hbar\omega)^2}\vec{r}|2S\rangle\frac{e^2}{3}\frac{1}{2}\langle 2S|\delta V|2S\rangle + \frac{e^2}{3}\sum_\pm\langle 1S|\vec{r}\frac{1}{H - E_{\overline{1S2S}} - i\epsilon \pm \hbar\omega}\vec{r}|\delta 2S\rangle$$

$$= \delta_{2S}\alpha_{\overline{1S2S}}^{(E)}(\omega) + \delta_{2S}\alpha_{\overline{1S2S}}^{(\psi)}(\omega). \tag{B16}$$

Here again the (E) subscript refers to the contribution from the energy correction and the (ψ) subscript refers to the contribution from the wave-function correction. We again compute

$$\delta M_6^{(E)}(2S;1S) = \frac{6}{\pi}\frac{\hbar}{(4\pi\epsilon_0)^2}\int_0^\infty d\omega\,\delta_{2S}\alpha_{\overline{1S2S}}^{(E)}(i\omega)\alpha_{\overline{1S2S}}(i\omega) \tag{B17}$$

by using (B4). For that we need

$$P_{\overline{1S2S}}(\omega) = \frac{e^2 a_0^2}{E_h}\frac{512\sqrt{2}t_{\text{eff}}^2}{729(-1+t_{\text{eff}}^2)^2(-4+t_{\text{eff}}^2)^3}\left[128 - 272t_{\text{eff}}^2 + 120t_{\text{eff}}^4 + 253t_{\text{eff}}^6 + 972t_{\text{eff}}^7 + 419t_{\text{eff}}^8\right.$$

$$\left. - 1944t_{\text{eff}}^7\,{}_2F_1\left(1,-t_{\text{eff}};1-t_{\text{eff}};\frac{1-t_{\text{eff}}}{1+t_{\text{eff}}}\frac{2-t_{\text{eff}}}{2+t_{\text{eff}}}\right)\right], \tag{B18}$$

with t_{eff} given by (B13). In the end, we obtain

$$\delta M_6^{(E)}(2S;1S) = 12.556\,663\,547\alpha^2 a_0^6 E_h. \tag{B19}$$

Finally, we calculate the wave-function contribution to the mixing coefficient for the Dirac-δ correction

$$\delta M_6^{(\psi)}(2S;1S) = \frac{6}{\pi} \frac{\hbar}{(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta_{2S} \alpha_{\overline{1S2S}}^{(\psi)}(i\omega) \alpha_{\overline{1S2S}}(i\omega). \tag{B20}$$

From (73) we deduce

$$
\begin{aligned}
\delta P_{1S\underline{2S}}^{(\psi)}(\omega) = \frac{e^2 a_0^2}{mc^2} \Bigg[& -\frac{128\sqrt{2}\tau^2 S(\tau)}{2187(1-\tau^2)^4(1-4\tau^2)^3} - \frac{2048\sqrt{2}\tau^2 T(\tau)}{729(1-\tau)^3(1+\tau)^2(1-4\tau^2)^2} \ln\left(\frac{2\tau}{1+\tau}\right) \\
& -\frac{2048\sqrt{2}\tau^2(1+2\tau^2)U(\tau)}{729(1-\tau^2)^2(1-4\tau^2)^3} \ln\left(\frac{3\tau}{1+\tau}\right) + \frac{1024\sqrt{2}\tau^7(1+\tau^2)}{(1-\tau^2)^2(1-4\tau^2)^3} \, _2F_1\left(1,-2\tau;1-2\tau;-\frac{1-2\tau}{1+2\tau}\right) \\
& +\frac{1024\sqrt{2}\tau^7 R(\tau)}{9(1-\tau^2)^4(1-4\tau^2)^3} \, _2F_1\left(1,-2\tau;1-2\tau;-\frac{1-\tau}{1+\tau}\frac{1-2\tau}{1+2\tau}\right) \\
& +\frac{65\,536\sqrt{2}}{3}\frac{\tau^{10}}{(-1+\tau)(1+\tau)^5(1+2\tau)^4}\sum_{k=0}^{\infty}\left(-\frac{1-2\tau}{1+2\tau}\right)^k \frac{\partial_2 \, _2F_1(-k,4;4;\frac{2}{1+\tau})}{(2+k-2\tau)} \Bigg],
\end{aligned}
\tag{B21}
$$

with τ given by (B11), and $R(\tau)$ is defined in Eq. (B10). The function $S(\tau)$ is given as

$$
\begin{aligned}
S(\tau) = {} & -157 + 2436\tau^2 - 13\,326\tau^4 + 5832\tau^5 + 58\,868\tau^6 + 225\,504\tau^7 \\
& -283\,245\tau^8 + 99\,144\tau^9 - 431\,184\tau^{10} + 695\,952\tau^{11} + 200\,048\tau^{12},
\end{aligned}
\tag{B22}
$$

while $T(\tau)$ reads

$$T(\tau) = 2 - 2\tau - 15\tau^2 + 15\tau^3 + 15\tau^4 - 15\tau^5 + 268\tau^6 + 1676\tau^7 \tag{B23}$$

and $U(\tau)$ is

$$U(\tau) = -2 + 27\tau^2 - 129\tau^4 + 50\tau^6. \tag{B24}$$

We can then easily deduce $\delta_{2S}\alpha_{\overline{1S2S}}^{(\psi)}(\omega)$ from (B21) via

$$\delta_{2S}\alpha_{\overline{1S2S}}^{(\psi)}(\omega) = \delta_{2S}P_{1S2S}^{(\psi)}(\omega) + \delta_{2S}P_{1S2S}^{(\psi)}(-\omega), \tag{B25}$$

where again $\delta_{2S}P_{1S2S}^{(\psi)}(\omega)$ has the same expression as (B21), with τ replaced by t_{eff} [see (B13)]. From all of this we obtain

$$\delta M_6^{(\psi)}(2S;1S) = -70.652\,014\,640\,\alpha^2 a_0^6 E_h. \tag{B26}$$

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