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

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

1. Introduction

The long-range interaction of identical atoms, one of which is in an excited state, constitutes an interesting physical problem [1,2]. This is mainly due to energetic degeneracies connected with the "exchange" of the states among the two atoms. For *nS*–1*S* interactions (atomic hydrogen), this problem has recently been investigated in [3]. It was found that the interesting oscillatory $1/R^2$ long-range tails [4–10] are numerically suppressed and become dominant only for excessively large interatomic distances, in a region where the absolute magnitude of the interaction terms is numerically insignificant. Indeed, the Casimir–Polder regime of a $1/R^7$ interaction is never reached for systems with at least one atom in an excited state [9,10].

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

$$H_{\mathrm{vdW}} = \frac{1}{4\pi\epsilon_0} \frac{\beta_{ij}\, d_{Ai}\, d_{Bj}}{R^3}\,, \qquad \beta_{ik} = \delta_{ik} - 3\frac{R_i\, R_k}{R^2}\,, \tag{1}$$

where $\vec{R} = \vec{R}_A - \vec{R}_B$, $R = |\vec{R}|$ $\hat{R} = \vec{R}/R$. Furthermore, $\vec{d}_A = e\,\vec{r}_A$ is the electric dipole moment operator for atom *A*, and $\vec{d}_B$ is the same for atom *B* ($\vec{r}_i$ with $i = A, B$ is the electron coordinate relative to the atomic nucleus). States of the form, e.g., $|6P\rangle_A\,|1S\rangle_B$ are energetically degenerate with respect to states of the form $|1S\rangle_A\,|6P\rangle_B$, and are coupled by the van der Waals Hamiltonian. For the 2*S*–2*P* system, this problem has been analyzed in [12], on the basis of nonrelativistic Schrödinger theory. However, in order to evaluate the distance-dependent frequency shift of hyperfine-resolved transitions, one has

to invoke a more sophisticated analysis, which has recently been performed in [11]. A complete rediagonalization of the total Hamiltonian, comprising Lamb shift, fine-structure and hyperfine effects, becomes necessary.

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

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

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

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

2. General Formalism

The total Hamiltonian is:

$$H = H_{\text{LS},A} + H_{\text{LS},B} + H_{\text{HFS},A} + H_{\text{HFS},B} + H_{\text{FS},A} + H_{\text{FS},B} + H_{\text{vdW}} \, , \tag{3}$$

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

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

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

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

Here, $i = A, B$ denotes either atom, while α is the fine-structure constant and m_e is the electron mass. The momentum operators for the atomic electrons are denoted as $\vec{p}_i$, while $\vec{L}_i$ is the orbital angular momentum operator. The (dimensionless) spin operator for electron i is $\vec{S}_i$, while $\vec{I}_i$ is the spin operator for proton i. The CODATA (Committee on Data for Science and Technology) values (see [18]) for the electronic and protonic g factors are $g_s \simeq 2.002\,319$ and $g_p \simeq 5.585\,695$. The Bohr magneton is $\mu_B \simeq 9.274\,010 \times 10^{-24}$ Am^2, while $\mu_N \simeq 5.050\,784 \times 10^{-27}$ Am^2 is the nuclear magneton. The expression for H_{LS} in Equation (4b) follows the Welton approximation [19], which is sufficient for our purposes of calculating long-range interaction coefficients.

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

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

$$1S_{1/2}(F = 0) : n = 1,\, \ell = 0,\, J = \frac{1}{2},\, F = 0, \tag{5a}$$

$$1S_{1/2}(F = 1) : n = 1,\, \ell = 0,\, J = \frac{1}{2},\, F = 1, \tag{5b}$$

$$6P_{1/2}(F = 0) : n = 6,\, \ell = 1,\, J = \frac{1}{2},\, F = 0, \tag{5c}$$

$$6P_{1/2}(F = 1) : n = 6,\, \ell = 1,\, J = \frac{1}{2},\, F = 1. \tag{5d}$$

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

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

$$\left| n = 1, \ell = 0, J = \frac{1}{2}, F = 0, F_z = 0 \right\rangle = -\frac{|+\rangle_p\,|-\rangle_e - |-\rangle_p\,|+\rangle_e}{\sqrt{2}}\,|1,0,0\rangle_e, \tag{6a}$$

$$\left| n = 1, \ell = 0, J = \frac{1}{2}, F = 1, F_z = 0 \right\rangle = \frac{|+\rangle_p\,|-\rangle_e + |-\rangle_p\,|+\rangle_e}{\sqrt{2}}\,|1,0,0\rangle_e, \tag{6b}$$

$$\left| n = 1, \ell = 0, J = \frac{1}{2}, F = 1, F_z = \pm 1 \right\rangle = |\pm\rangle_p\,|\pm\rangle_e\,|1,0,0\rangle_e, \tag{6c}$$

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

$$\left| n = 6, \ell = 1, J = \tfrac{1}{2}, F = 0, F_z = 0 \right\rangle = \quad \frac{1}{\sqrt{3}}|+\rangle_p\,|+\rangle_e\,|6,1,-1\rangle_e - \frac{1}{\sqrt{6}}|+\rangle_p\,|-\rangle_e\,|6,1,0\rangle_e$$
$$+ \frac{1}{\sqrt{3}}|-\rangle_p\,|-\rangle_e\,|6,1,1\rangle_e - \frac{1}{\sqrt{6}}|-\rangle_p\,|+\rangle_e\,|6,1,0\rangle_e. \tag{7}$$

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

$$\left| n = 6, \ell = 1, J = \tfrac{1}{2}, F = 1, F_z = 0 \right\rangle = \quad -\frac{1}{\sqrt{3}}|+\rangle_p\,|+\rangle_e\,|6,1,-1\rangle_e + \frac{1}{\sqrt{6}}|+\rangle_p\,|-\rangle_e\,|6,1,0\rangle_e$$
$$+ \frac{1}{\sqrt{3}}|-\rangle_p\,|-\rangle_e\,|6,1,1\rangle_e - \frac{1}{\sqrt{6}}|-\rangle_p\,|+\rangle_e\,|6,1,0\rangle_e, \tag{8}$$

and:

$$\left| n = 6, \ell = 1, J = \frac{1}{2}, F = 1, F_z = \pm 1 \right\rangle = \mp \frac{1}{\sqrt{3}}\,|\pm\rangle_p\,[|\pm\rangle_e\,|6,1,0\rangle_e - \sqrt{2}\,|\mp\rangle_e\,|6,1,\pm 1\rangle_e]. \tag{9}$$

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

3. $6P$–$1S$ Interaction

3.1. Orientation

We need to diagonalize the Hamiltonian given in Equation (3), in a quasi-degenerate basis, composed of two atoms, the first being in a $6P$ state, the second being in a substate of the $1S$

hyperfine manifold. Retardation does not need to be considered. For the manifolds composed of the $(6P)_A(1S)_B$ and $(1S)_A(6P)_B$ states, with all hyperfine levels resolved, we obtain the following total multiplicities when all $6P_{1/2}$ and $6P_{3/2}$ states are added into the basis (see also Table 1): $g(F_z = \pm3) = 2$, $g(F_z = \pm2) = 10$, $g(F_z = \pm1) = 22$, $g(F_z = 0) = 28$. The multiplicities are the sums of the multiplicities in the $6P_{3/2}$–$1S$ and the $6P_{1/2}$–$1S$ system.

Table 1. Multiplicities in the $6P_{1/2}$–$6P_{3/2}$–$1S$ system. One might wonder why $F_z = \pm3$ is possible for $F = 2$. The answer is that $F = 2$ here refers to the total angular momentum (electron orbital plus electron spin plus nuclear spin) of one of the atoms, while $F_z = \pm3$ refers to the angular momentum projection of the sum of the total angular momenta of both electrons.

	$F_z = 0$	$F_z = \pm1$	$F_z = \pm2$	$F_z = \pm3$
$(J = \frac{3}{2}, F = 2)$	8	8	6	2
$(J = \frac{3}{2}, F = 1)$	8	6	2	0
$(J = \frac{3}{2})$	16	14	8	2
$(J = \frac{1}{2}, F = 1)$	8	6	2	0
$(J = \frac{1}{2}, F = 0)$	4	2	0	0
$(J = 1/2)$	12	8	2	0
$(J = \frac{1}{2}) + (J = \frac{3}{2})$	28	22	10	2

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

$$\mathcal{H} \equiv \frac{\alpha^4}{18} g_p \frac{m_e}{m_p} m_e c^2 = h\,59.21498\,\text{MHz}\,, \quad \mathcal{L}_2 \equiv h\,1057.845(9)\,\text{MHz}\,, \tag{10a}$$

$$\mathcal{L}_6 \equiv h \times \frac{1}{27} \times 1057.845(9)\,\text{MHz}\,, \qquad \mathcal{F} \equiv \frac{\alpha^4 m_e c^2}{864} = h\,405.529\,\text{MHz}\,, \tag{10b}$$

$$\mathcal{V} \equiv 3\,\frac{e^2}{4\pi\epsilon_0}\frac{a_0^2}{R^3} = \frac{3\,E_h}{\rho^3}\,, \qquad \mathcal{W} \equiv \frac{2^{15} \times 3^5 \times 5^7}{7^{17}}\frac{e^2}{4\pi\epsilon_0}\frac{a_0^2}{R^3} = \frac{2^{15} \times 3^5 \times 5^7}{7^{17}}\frac{E_h}{\rho^3}\,, \tag{10c}$$

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

$$\mathcal{H} = \alpha^3 E_h\,C_{\mathcal{H}}\,, \qquad \mathcal{L}_n = \alpha^3 E_h\,C_{\mathcal{L},n}\,, \qquad \mathcal{F} = \alpha^3 E_h\,C_{\mathcal{F}}\,, \tag{11}$$

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

$$\frac{\mathcal{V}^2}{T_1\mathcal{H} + T_2\mathcal{L}_n + T_3\mathcal{F}} = \frac{9}{T_1\,C_{\mathcal{H}} + T_2\,C_{\mathcal{L},n} + T_3 C_{\mathcal{F}}}\frac{E_h}{\alpha^3\,\rho^6}\,, \tag{12}$$

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

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

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

$$|a\rangle = |6P_{1/2}^{F=1}(F_z = \mu)\rangle = |6, 1, \tfrac{1}{2}, 1, \mu\rangle, \qquad |b\rangle = |6P_{3/2}^{F=1}(F_z = \mu)\rangle = |6, 1, \tfrac{3}{2}, 1, \mu\rangle, \qquad \mu = -1, 0, 1. \quad (13)$$

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

$$H_{\text{HFS+FS}} = \begin{pmatrix} D & X \\ X & -D + \mathcal{F} \end{pmatrix}, \qquad D = g_p \frac{\alpha^4 m_e^2 c^2}{1944\, m_p}, \qquad X = -g_p \frac{\alpha^4 m_e^2 c^2}{3888\, \sqrt{2}\, m_p}. \quad (14)$$

Here, g_p is the proton g factor, while D is a diagonal matrix element and X is the off-diagonal element given above. The eigenvalues of $H_{\text{HFS+FS}}^{F_z=1}$ are given by:

$$\mathcal{E}_+ = -D + \mathcal{F} + \frac{X^2}{\mathcal{F} - 2D} + \mathcal{O}(X^4), \qquad \mathcal{E}_- = D - \frac{X^2}{\mathcal{F} - 2D} + \mathcal{O}(X^4). \quad (15)$$

The second-order shift in the eigenvalues, $\Delta = X^2/(\mathcal{F} - 2D)$, is numerically equal to $1.412\,129 \times 10^{-13} E_h$, where $E_h = \alpha^2 m_e c^2$ is the Hartree energy. For simplicity, we thus define the parameter:

$$\Delta = 1.412\,129 \times 10^{-14}, \qquad \frac{\Delta \cdot E_h}{h} = 92.9137\,\text{Hz}. \quad (16)$$

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

3.2. States with $F_z = 3$

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

$$|\phi_1\rangle = |(1, 0, \tfrac{1}{2}, 1, 1)_A\, (6, 1, \tfrac{3}{2}, 2, 2)_B\rangle, \quad |\phi_2\rangle = |(6, 1, \tfrac{3}{2}, 2, 2)_A\, (1, 0, \tfrac{1}{2}, 1, 1)_B\rangle. \quad (17)$$

Here, we have ordered the basis vectors in ascending order of the quantum numbers, starting from the last member in the list. The Hamiltonian matrix evaluates to:

$$H_{F_z=3} = \begin{pmatrix} \dfrac{1081}{180}\mathcal{H} + \mathcal{F} & \dfrac{2^{15} \times 3^5 \times 5^7}{7^{17}}\mathcal{V} \\[2ex] \dfrac{2^{15} \times 3^5 \times 5^7}{7^{17}}\mathcal{V} & \dfrac{1081}{180}\mathcal{H} + \mathcal{F} \end{pmatrix}. \quad (18)$$

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

$$E_\pm = \frac{1081}{180}\mathcal{H} + \mathcal{F} \mp \frac{2^{15} \times 3^5 \times 5^7}{7^{17}}\mathcal{V}, \qquad |u_\pm\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle \pm |\phi_2\rangle\right). \quad (19)$$

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

3.3. Manifold $F_z = 2$

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

$$|\psi_1\rangle = |(1, 0, \tfrac{1}{2}, 0, 0)_A (6, 1, \tfrac{3}{2}, 2, 2)_B\rangle, \qquad |\psi_2\rangle = |(1, 0, \tfrac{1}{2}, 1, 0)_A (6, 1, \tfrac{3}{2}, 2, 2)_B\rangle, \tag{20a}$$

$$|\psi_3\rangle = |(1, 0, \tfrac{1}{2}, 1, 1)_A (6, 1, \tfrac{1}{2}, 1, 1)_B\rangle, \qquad |\psi_4\rangle = |(1, 0, \tfrac{1}{2}, 1, 1)_A (6, 1, \tfrac{3}{2}, 1, 1)_B\rangle, \tag{20b}$$

$$|\psi_5\rangle = |(1, 0, \tfrac{1}{2}, 1, 1)_A (6, 1, \tfrac{3}{2}, 2, 1)_B\rangle, \qquad |\psi_6\rangle = |(6, 1, \tfrac{1}{2}, 1, 1)_A (1, 0, \tfrac{1}{2}, 1, 1)_B\rangle, \tag{20c}$$

$$|\psi_7\rangle = |(6, 1, \tfrac{3}{2}, 1, 1)_A (1, 0, \tfrac{1}{2}, 1, 1)_B\rangle, \qquad |\psi_8\rangle = |(6, 1, \tfrac{3}{2}, 2, 1)_A (1, 0, \tfrac{1}{2}, 1, 1)_B\rangle, \tag{20d}$$

$$|\psi_9\rangle = |(6, 1, \tfrac{3}{2}, 2, 2)_A (1, 0, \tfrac{1}{2}, 0, 0)_B\rangle, \qquad |\psi_{10}\rangle = |(6, 1, \tfrac{3}{2}, 2, 2)_A (1, 0, \tfrac{1}{2}, 1, 0)_B\rangle. \tag{20e}$$

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

$$\mathcal{H} = \begin{pmatrix} \mathcal{F} - \frac{3239\mathcal{H}}{180} & 0 & 0 & 0 & 0 & -\sqrt{3}\mathcal{W} & \sqrt{6}\mathcal{W} & 0 & 0 & 0 \\ 0 & \frac{1081\mathcal{H}}{180} + \mathcal{F} & 0 & 0 & 0 & \sqrt{3}\mathcal{W} & \sqrt{\frac{3}{2}}\mathcal{W} & \frac{3\mathcal{W}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & \frac{649\mathcal{H}}{108} & -\frac{\mathcal{H}}{216\sqrt{2}} & 0 & -2\mathcal{W} & -\sqrt{2}\mathcal{W} & \sqrt{6}\mathcal{W} & -\sqrt{3}\mathcal{W} & \sqrt{3}\mathcal{W} \\ 0 & 0 & -\frac{\mathcal{H}}{216\sqrt{2}} & \frac{647\mathcal{H}}{108} + \mathcal{F} & 0 & -\sqrt{2}\mathcal{W} & -\mathcal{W} & \sqrt{3}\mathcal{W} & \sqrt{6}\mathcal{W} & \sqrt{\frac{3}{2}}\mathcal{W} \\ 0 & 0 & 0 & 0 & \frac{1081\mathcal{H}}{180} + \mathcal{F} & \sqrt{6}\mathcal{W} & \sqrt{3}\mathcal{W} & -3\mathcal{W} & 0 & \frac{3\mathcal{W}}{\sqrt{2}} \\ -\sqrt{3}\mathcal{W} & \sqrt{3}\mathcal{W} & -2\mathcal{W} & -\sqrt{2}\mathcal{W} & \sqrt{6}\mathcal{W} & \frac{649\mathcal{H}}{108} & -\frac{\mathcal{H}}{216\sqrt{2}} & 0 & 0 & 0 \\ \sqrt{6}\mathcal{W} & \sqrt{\frac{3}{2}}\mathcal{W} & -\sqrt{2}\mathcal{W} & -\mathcal{W} & \sqrt{3}\mathcal{W} & -\frac{\mathcal{H}}{216\sqrt{2}} & \frac{647\mathcal{H}}{108} + \mathcal{F} & 0 & 0 & 0 \\ 0 & \frac{3\mathcal{W}}{\sqrt{2}} & \sqrt{6}\mathcal{W} & \sqrt{3}\mathcal{W} & -3\mathcal{W} & 0 & 0 & \frac{1081\mathcal{H}}{180} + \mathcal{F} & 0 & 0 \\ 0 & 0 & -\sqrt{3}\mathcal{W} & \sqrt{6}\mathcal{W} & 0 & 0 & 0 & 0 & \mathcal{F} - \frac{3239\mathcal{H}}{180} & 0 \\ 0 & 0 & \sqrt{3}\mathcal{W} & \sqrt{\frac{3}{2}}\mathcal{W} & \frac{3\mathcal{W}}{\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{1081\mathcal{H}}{180} + \mathcal{F} \end{pmatrix}. \tag{21}$$

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

Of particular interest are second-order van der Waals shifts within the ($F_z = 2$) manifold. We have the quantum numbers J, F and F_z at our disposal. A weighted average over the possible values of F, namely $F = 1$ and $F = 2$, keeping $J = 1/2, 3/2$ and $F_z = +2$ fixed, leads to the result:

$$\langle E(6P_{1/2}, F_z = 2)\rangle_F = \left(-\Delta - \frac{1.138\,49 \times 10^3}{\rho^6}\right) E_h, \tag{22a}$$

$$\langle E(6P_{3/2}, F_z = 2)\rangle_F = \left(\frac{1}{4}\Delta + \frac{2.846\,23 \times 10^2}{\rho^6}\right) E_h. \tag{22b}$$

The weighted average vanishes,

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

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

Table 2. Second-order van der Waals shifts for $6P_J$ hydrogen atoms interacting with ground-state hydrogen atoms. Entries marked with a long hyphen (—) indicate unphysical combinations of F and F_z values. We denote the scaled interatomic distance by $\rho = R/a_0$ and give all energy shifts in atomic units, i.e., in units of the Hartree energy $E_h = \alpha^2 m_e c^2$. Recall that $F_z = F_{z,A} + F_{z,B}$. The results still involve an averaging over the quantum numbers of the spectator atom; e.g., the results for $J = 3/2$, $F = 2$ and $F_z = 2$ involve and averaging over the second-order shifts of the states $|\Psi_9\rangle$ and $|\Psi_{10}\rangle$ given in Equation (20e). We define Δ in Equation (16).

	$F_z = 0$	$F_z = \pm 1$	$F_z = \pm 2$	$F_z = \pm 3$
$(J = 3/2, F = 2)$	$\dfrac{1.077\,95 \times 10^5}{\rho^6}$	$\dfrac{8.759\,49 \times 10^4}{\rho^6}$	$\dfrac{8.068\,60 \times 10^4}{\rho^6}$	0
$(J = 3/2, F = 1)$	$\Delta - \dfrac{1.065\,90 \times 10^5}{\rho^6}$	$\Delta - \dfrac{1.157\,80 \times 10^5}{\rho^6}$	$\Delta - \dfrac{2.409\,19 \times 10^5}{\rho^6}$	—
$(J = 1/2, F = 1)$	$-\Delta + \dfrac{9.994\,77 \times 10^3}{\rho^6}$	$-\Delta + \dfrac{3.520\,47 \times 10^4}{\rho^6}$	$-\Delta - \dfrac{1.138\,49 \times 10^3}{\rho^6}$	—
$(J = 1/2, F = 0)$	$-\dfrac{2.239\,99 \times 10^4}{\rho^6}$	$-\dfrac{1.086\,54 \times 10^5}{\rho^6}$	—	—

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

We would like to list some of the 22 states in the $F_z = 1$ manifold in order of ascending quantum numbers, $|\Psi_1\rangle = |(1, 0, \frac{1}{2}, 0, 0)_A (6, 1, \frac{1}{2}, 1, 1)_B\rangle$, $|\Psi_2\rangle = |(1, 0, \frac{1}{2}, 0, 0)_A (6, 1, \frac{3}{2}, 1, 1)_B\rangle$, $|\Psi_3\rangle = |(1, 0, \frac{1}{2}, 0, 0)_A (6, 1, \frac{3}{2}, 2, 1)_B\rangle$, $|\Psi_4\rangle = |(1, 0, \frac{1}{2}, 1, -1)_A (6, 1, \frac{3}{2}, 2, 2)_B\rangle$, and so on, up to $|\Psi_{21}\rangle = |(6, 1, \frac{3}{2}, 2, 1)_A (1, 0, \frac{1}{2}, 1, 0)_B\rangle$ and $|\Psi_{22}\rangle = |(6, 1, \frac{3}{2}, 2, 2)_A (1, 0, \frac{1}{2}, 1, -1)_B\rangle$. We refer to Table 2 for the averaged second-order van der Waals shifts in the $F_z = 0$, $F_z = +1$, $F_z = +2$ and $F_z = +3$ manifolds. The Hamiltonian matrix for the $F_z = -3$ manifold is identical to that of $F_z = +3$. The $F_z = -2$ manifold has identical diagonal entries to that of $F_z = +2$, while some off-diagonal entries are different. The same is true of the $F_z = \pm 1$ manifolds. Yet, we have checked that the distance-dependent Born–Oppenheimer energy curves for $F_z = \pm 2$ and $F_z = \pm 1$ are alike.

3.5. Second-Order Energy Shifts

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

$$\langle E(6P_{1/2}, F = 0)\rangle_{F_z} = -\frac{6.552\,65 \times 10^4}{\rho^6} E_h, \tag{24a}$$

$$\langle E(6P_{1/2}, F = 1)\rangle_{F_z} = \left(-\Delta + \frac{2.074\,42 \times 10^4}{\rho^6}\right) E_h, \tag{24b}$$

$$\langle E(6P_{3/2}, F = 1)\rangle_{F_z} = \left(\Delta - \frac{1.335\,73 \times 10^5}{\rho^6}\right) E_h, \tag{24c}$$

$$\langle E(6P_{3/2}, F = 2)\rangle_{F_z} = \frac{8.080\,28 \times 10^4}{\rho^6} E_h. \tag{24d}$$

Comparing to Table 2, this average would correspond to an average over the entries in the different rows, for given F (for the multiplicities, see Table 1).

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

$$\langle E(6P_{1/2}, F_z = 0) \rangle_F = \left(-\frac{2}{3}\Delta - \frac{8.034\,54 \times 10^2}{\rho^6} \right) E_h \,, \tag{25a}$$

$$\langle E(6P_{1/2}, F_z = \pm 1) \rangle_F = \left(-\frac{3}{4}\Delta - \frac{7.597\,33 \times 10^2}{\rho^6} \right) E_h, \tag{25b}$$

$$\langle E(6P_{1/2}, F_z = \pm 2) \rangle_F = \left(-\Delta - \frac{1.138\,49 \times 10^3}{\rho^6} \right) E_h \,, \tag{25c}$$

and:

$$\langle E(6P_{3/2}, F_z = 0) \rangle_F = \left(\frac{1}{2}\Delta + \frac{6.025\,91 \times 10^2}{\rho^6} \right) E_h \,, \tag{26a}$$

$$\langle E(6P_{3/2}, F_z = \pm 1) \rangle_F = \left(\frac{3}{7}\Delta + \frac{4.341\,33 \times 10^2}{\rho^6} \right) E_h \,, \tag{26b}$$

$$\langle E(6P_{3/2}, F_z = \pm 2) \rangle_F = \left(\frac{1}{4}\Delta + \frac{2.846\,23 \times 10^2}{\rho^6} \right) E_h \,, \tag{26c}$$

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

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

$$\langle E(6P_{1/2}) \rangle_{F, F_z} = \left(-\frac{3}{4}\Delta - \frac{8.234\,74 \times 10^2}{\rho^6} \right) E_h \,, \tag{27a}$$

$$\langle E(6P_{3/2}) \rangle_{F, F_z} = \left(\frac{3}{8}\Delta + \frac{4.117\,37 \times 10^2}{\rho^6} \right) E_h \,. \tag{27b}$$

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

4. 6P–2S Interaction

4.1. Selection of the States

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

A priori, we have $4 + 8 + 4 + 4 + 4 = 24$ one-atom states in the $6P_{1/2}$–$6P_{3/2}$–$(6S;2P_{1/2})$–$2S$ system, which amounts to $24^2 = 576$ states for the two atoms, and the Hamiltonian matrix would have $576^2 = 331{,}776$ entries. In order to remain within the quasi-degenerate basis, we should select only those two-atom states composed of an S and a P state and only those where the principal quantum numbers add up to $2 + 6 = 8$. These selection rules drastically reduce the number of states in the basis, according to Table 3. Furthermore, the total Hamiltonian (3) commutes with the total angular momentum $\vec{F}$. From the $6P_{1/2}$–$6P_{3/2}$–$2S$ system, we obtain multiplicities of 28, 22, 10 and 2, for the

manifolds with $F_z = 0$, $F_z = \pm 1$, $F_z = \pm 2$ and $F_z = \pm 3$. By the addition of the $(6S, 2P_{1/2})$ states, we end up with multiplicities of 40, 30, 12 and 2, for the manifolds with $F_z = 0$, $F_z = \pm 1$, $F_z = \pm 2$, and $F_z = \pm 3$.

Table 3. Multiplicities in the $6P_{1/2}$–$6P_{3/2}$–$(6S;2P_{1/2})$–$2S$–$1S$ system. The entries in the first seven rows refer to the $6P_{1/2}$–$6P_{3/2}$–$2S$ system and are the same as those for the $6P_{1/2}$–$6P_{3/2}$–$1S$ system given in Table 1. The eighth row gives the number of added $(6S, 2P_{1/2})$ states, which complete the basis of the quasi-degenerate basis. Finally, we end up with multiplicities of 40, 30, 12 and 2 for $F_z = 0, \pm 1, \pm 2, \pm 3$, respectively (ninth row).

	$F_z = 0$	$F_z = \pm 1$	$F_z = \pm 2$	$F_z = \pm 3$
$(J = \frac{3}{2}, F = 2)$	8	8	6	2
$(J = \frac{3}{2}, F = 1)$	8	6	2	0
$(J = \frac{3}{2})$	16	14	8	2
$(J = \frac{1}{2}, F = 1)$	8	6	2	0
$(J = \frac{1}{2}, F = 0)$	4	2	0	0
$(J = 1/2)$	12	8	2	0
$(J = \frac{1}{2}) + (J = \frac{3}{2})$	28	22	10	2
$(6S, 2P_{1/2})$ States	12	8	2	0
Total # of States	40	30	12	2

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

4.2. Second-Order Energy Shifts

For the states within the individual (J, F, F_z) manifolds, the averaged second-order energy shifts of the $6P_J$–$2S$ reference levels are given in Table 4. As a function of J and F, an averaging over the magnetic quantum numbers F_z leads to the results:

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

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

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

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

These results are obtained from the entries in Table 4, using the weighting factors from Table 3 for averaging over the rows.

Table 4. Average second-order van der Waals shifts for $6P_J$ hydrogen atoms interacting with $2S$ metastable atoms. Entries marked with a long hyphen (—) indicate unphysical combinations of F and F_z values. We denote the scaled interatomic distance by $\rho = R/a_0$ and give all energy shifts in atomic units, i.e., in units of the Hartree energy $E_h = \alpha^2 m_e c^2$. The notation Δ is defined in Equation (16).

	$F_z = 0$	$F_z = \pm 1$	$F_z = \pm 2$	$F_z = \pm 3$
$(J = 3/2, F = 2)$	$\dfrac{3.942\,40 \times 10^{10}}{\rho^6}$	$\dfrac{3.283\,90 \times 10^{10}}{\rho^6}$	$\dfrac{1.773\,16 \times 10^{10}}{\rho^6}$	0
$(J = 3/2, F = 1)$	$\Delta + \dfrac{3.492\,69 \times 10^{10}}{\rho^6}$	$\Delta + \dfrac{2.635\,84 \times 10^{10}}{\rho^6}$	$\Delta + \dfrac{8.531\,51 \times 10^{9}}{\rho^6}$	—
$(J = 1/2, F = 1)$	$-\Delta + \dfrac{4.262\,61 \times 10^{10}}{\rho^6}$	$-\Delta + \dfrac{3.744\,79 \times 10^{10}}{\rho^6}$	$-\Delta + \dfrac{2.375\,05 \times 10^{10}}{\rho^6}$	—
$(J = 1/2, F = 0)$	$\dfrac{3.871\,53 \times 10^{10}}{\rho^6}$	$\dfrac{3.536\,58 \times 10^{10}}{\rho^6}$	—	—

One can also average over the possible orientations of F, namely $F = J \pm \frac{1}{2}$, for given J and F_z. This amounts to an averaging over the first two entries in the columns (for $J = 1/2$) and the third and fourth entry (for $J = 3/2$) in every column of Table 4. The results of the latter procedure are:

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

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

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

and:

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

$$\langle E(6P_{3/2}, F_z = \pm 1)\rangle_F = \left(\frac{3}{7}\Delta + \frac{3.006\,16 \times 10^{10}}{\rho^6}\right) E_h \,, \tag{30b}$$

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

$$\langle E(6P_{3/2}, F_z = \pm 3)\rangle_F = 0 \,. \tag{30d}$$

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

$$\langle E(6P_{1/2})\rangle_{F,F_z} = \left(-\frac{3}{4}\Delta + \frac{3.692\,87 \times 10^{10}}{\rho^6}\right) E_h \,, \tag{31a}$$

$$\langle E(6P_{3/2})\rangle_{F,F_z} = \left(\frac{3}{8}\Delta + \frac{2.632\,037 \times 10^{10}}{\rho^6}\right) E_h \,. \tag{31b}$$

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

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

5. Time Dependence and Oscillatory Terms

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

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

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

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

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

Additionally, in [5,7,8,25], time-dependent effects have been studied in the context of retarded van der Waals interactions for non-identical atoms. A comparison to formulas given in [7,8] , and [5,25], is in order. First, one should observe that the second-order shifts investigated in [7] diverge in the limit of identical atoms, i.e., for the case of the "interatomic detuning" $\Delta_{AB} \to 0$. Furthermore, the energy shifts given in Equations (6) and (7) of [8] diverge, because (in the notation of [8]) one has $\mathcal{U}_{ijpq} \propto \mu_i^A \mu_j^A \mu_p^B \mu_q^B / \Delta_{AB}$ where $\mathcal{U}_{ijpq}$ is a tensor that enters the calculation of the energy shift, and the μ_i are the dipole moment operators of non-identical atoms A and B. For the case of perfect degeneracy, we thus have to calculate one-photon rather than two-photon exchange (in the non-retardation approximation). This has been done here and in our recent work [11]. We find, in full analogy to the discussion in [11], that the average first-order shifts of the hyperfine-resolved levels, in the first-order of the van der Waals Hamiltonian, vanish.

The interaction with the quantized modes of the radiation field (which mediate the van der Waals interaction) is "switched on" at distance R and time $t = 0$ in [7,8]. We here refrain from a discussion of the relevance of this approximation. Otherwise, the interatomic interaction energy increases as the atoms approach each other from infinity to a finite distance R. We only explore the consequences of

the results reported in [7,8]. Let $|\Psi\rangle = |6P\rangle_A|1S\rangle_B$ denote a specific state within the 6P–1S hyperfine manifold, and let $|\Psi'\rangle = |1S'\rangle_A|6P'\rangle_B$ denote a different state, displaced by an energy shift of order:

$$\Delta_{\mathrm{HFS}} \sim \Delta_{AB} \sim \mathcal{H}\,. \tag{33}$$

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

$$\Gamma \ll \hbar\Omega \ll \Delta_{AB}\,, \tag{34}$$

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

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

$$\cos\left(\frac{2(E_{6P} - E_{1S})R}{\hbar c} + \frac{\Delta_{AB}T}{\hbar}\right)\,, \tag{35}$$

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

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

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

6. Conclusions

In this paper, we have studied the van der Waals interaction of excited 6P hydrogen atoms with ground-state 1S and metastable 2S atoms. Within our hyperfine-resolved basis, in order to obtain reliable estimates of the van der Waals interaction coefficients, one needs to consider all off-diagonal

matrix elements of the van der Waals interaction Hamiltonian. Specifically, for hydrogen, the nuclear spin $I = \frac{1}{2}$ needs to be added to the total electron angular momentum J, resulting in states with the total angular momentum $F = J \pm \frac{1}{2}$ of electron + nucleus. The explicit construction of the hyperfine-resolved states is discussed in Section 2. For the $6P$–$1S$ system, one needs to include both the $6P_{1/2}$, as well as the $6P_{3/2}$ states in the quasi-degenerate basis, because the $6P$ fine-structure frequency is commensurate with the $1S$ hyperfine transition splitting (see Section 3). The matrix elements of the total Hamiltonian involve the so-called hyperfine-fine-structure mixing term (see Section 3), which couples the $6P_{1/2}(F = 1)$ to the $6P_{3/2}(F = 1)$ levels (see Equation (14)).

The explicit matrices of the total Hamiltonian (3) in the manifolds with $F_z = 3, 2$ are described in Sections 3.2 and 3.3. Due to mixing terms of first order in the van der Waals interaction between degenerate states in the two-atom system, the leading term in the van der Waals energy, upon rediagonalization of the Hamiltonian matrix, is of order $1/R^3$ for the $6P$–$1S$ interaction, but it averages out to zero over the magnetic projections. The phenomenologically important second-order shifts of the energy levels are given in Section 3.5, with various averaging procedures illustrating the dependence of the shifts on the quantum numbers and the dependence of the repulsive or attractive character of the interaction on the hyperfine-resolved levels.

The same procedure is applied to the $6P$–$2S$ interaction in Section 4, with the additional complication that virtual quasi-degenerate $(6S; 2P_{1/2})$ levels also need to be included in the basis. The treatment of the $6P$–$1S$ and $6P$–$2S$ long-range interactions reveals the presence of numerically large coefficients multiplying the $1/\rho^6$ interaction terms, due to the presence of quasi-degenerate levels. The interaction remains non-retarded over all phenomenologically relevant distance scales. The repulsive character of the $6P$–$2S$ interaction due to the quasi-degenerate virtual $(6S; 2P_{1/2})$ levels is obtained as a surprise conclusion from the current investigation.

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