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Energy of van der Waals and dipole-dipole interactions between atoms in Rydberg states

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The van der Waals coefficient $C_6(\theta; nlJM)$ of two like Rydberg atoms in their identical Rydberg states $|nlJM\rangle$ is resolved into four irreducible components called scalar R_{ss}, axial (vector) R_{aa}, scalar-tensor $R_{sT} = R_{Ts}$, and tensor-tensor R_{TT} parts in analogy with the components of dipole polarizabilities. The irreducible components determine the dependence of $C_6(\theta; nlJM)$ on the angle θ between the interatomic and the quantization axes of atoms. The spectral resolution for the biatomic Green's function with account of the most contributing terms is used for evaluating the components $R_{\alpha\beta}$ of atoms in their Rydberg series of doublet states of the low angular momenta (^2S, ^2P, ^2D, ^2F). The polynomial presentations in powers of the Rydberg-state principal quantum number n taking into account the asymptotic dependence $C_6(\theta; nlJM) \propto n^{11}$ are derived for simplified evaluations of irreducible components. Numerical values of the polynomial coefficients are determined for Rb atoms in their $n\,^2S_{1/2}$, $n\,^2P_{1/2,3/2}$, $n\,^2D_{3/2,5/2}$, and $n\,^2F_{5/2,7/2}$ Rydberg states of arbitrary high n. The transformation of the van der Waals interaction law $-C_6/R^6$ into the dipole-dipole law C_3/R^3 in the case of close dipole-connected two-atomic states (the Förster resonance) is considered and the dependencies on the magnetic quantum numbers M and on the angle θ of the constant $C_3(\theta; nlJM)$ are determined together with the ranges of interatomic distances R, where the transformation appears.

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I. INTRODUCTION

Highly excited atoms in their Rydberg states attract much attention as worthwhile candidates for designing high-performance quantum processors of extremely fast logic operations [1–3]. In absence of external fields, the energy of interaction between two neutral atoms A and B separated by a distance R, significantly exceeding the total linear dimension of interacting atoms $R_{LR} = 2(\langle r_A^2\rangle^{1/2} + \langle r_B^2\rangle^{1/2})$ (the Le Roy radius [4]), follows the van der Waals law: $\Delta E_{\text{vdW}} = -C_6/R^6$. The constant coefficient C_6 may be determined using the second-order perturbation theory for the dipole-dipole interaction between atoms. If spin effects may be neglected, the van der Waals constant for a pair of like atoms in their nS states $C_6(nS)$ is a scalar dependent on the energies and matrix elements of dipole transitions between S and P states (see, e.g., Ref. [5]):

$$C_6(nS) = 6\sum_{n_1,n_2} \frac{|\langle n_1P|d_z|nS\rangle|^2|\langle n_2P|d_z|nS\rangle|^2}{E_{n_1P} + E_{n_2P} - 2E_{nS}}, \qquad (1)$$

where the summation involves the complete set of two-atomic states $|n_1P\rangle|n_2P\rangle$, including integrations over continuum states $|\varepsilon_1P\rangle|\varepsilon_2P\rangle$ of both atoms with positive energies $\varepsilon_1 > 0$, $\varepsilon_2 > 0$. For $n > 20$ the major contribution to the sum provides the closest to nS states $n_{1(2)}P$ ($|n_{1(2)} - n| < 10$). The fractional contribution of the remaining terms (together with the integral over continuum) does not exceed 10^{-4}.

For high principal quantum number n the specific "resonance" effects appear when one or a few of the denominators of fractions in Eq. (1) achieve nearly zero value. In the case of n_1 and n_2 close to n, these resonance terms provide the principal contributions to the twofold sum and make the absolute value of $C_6(nS)$ so large that in a definite region of interatomic distances $R_{LR} < R < R_F$ the magnitude of ΔE_{vdW} becomes comparable or even exceeds that of the energy difference in the denominator (so-called "Förster defect" $\delta = E_{n_1} + E_{n_2} - 2E_n$ [1]). In this case (known in the literature as the "Förster resonance" [1,2,6,7]), the perturbation theory for isolated states may become inapplicable. Therefore, a perturbation theory for close-energy states should be used in the region of distances below R_F (the "Förster radius").

Detailed analysis on the basis of the data for quantum defects of Rb Rydberg states detects the indicated type of degeneracy for $38P_{3/2}$, $39D_{3/2}$, $43D_{5/2}$, and $58D_{3/2}$ states [8–17]. The energy of two atoms in these states is separated from the closest dipole-coupled two-atomic levels by an energy gap δ (the "resonance detuning") of only few megahertz, at least two orders smaller than the separation on the order of gigahertz from any other state. The energy of the resonance interaction is usually considered as the first-order dipole-dipole interaction energy of the R^{-3} dependence [3,9,16,17]. The van der Waals energy, estimated as the squared dipole-dipole energy divided by the detuning δ [17], corresponds to account of only a single resonance term in the infinite series of the second-order perturbation theory, presented on the right-hand side of Eq. (1). Evidently, this situation appears for large distances $R > R_F$, where the dipole-dipole energy is essentially smaller than δ.

In this paper, we determine the energy of asymptotic interaction with the use of the higher-order perturbation theory for close states [18]. The transformation between the van der Waals law $\Delta E_{\text{vdW}} = -C_6/R^6$ and the dipole-dipole law $\Delta E_{\text{d-d}} = C_3/R^3$ of the interaction-induced energy shift may be determined both qualitatively and quantitatively from the general equations, which take into account the variation of the resonance detuning caused by the interaction of atoms. As a numerical example, in Sec. V the case of close-energy two-atomic states of Rb atoms in their $43D_{5/2}$ states, only 8 MHz above the joint energy of $41F$ and $45P$ states [1], is considered in detail numerically.

For states of nonzero angular momentum, the constant C_6 is a tensor quantity [19] dependent on the magnetic quantum

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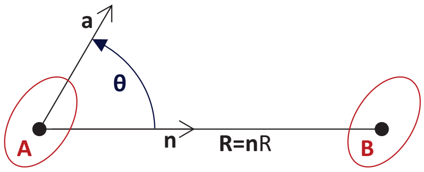

FIG. 1. Long-range-interacting atoms A and B in their identical Rydberg states, the radius vector $\mathbf{R} = \mathbf{n}R$ apart. The unit vector $\mathbf{n}$ points from A to B at the angle θ to the unit vector $\mathbf{a}$ along the axis of quantization for the total momenta $\mathbf{J}_{A(B)}$.

numbers and consequently on the relative orientation of the quantization and interatomic axes determined by the unit vectors **a** and **n**, respectively (see Fig. 1). In heavy alkali-metal atoms Rb and Cs the tensor properties of C_6 may arise also in $n\,^2S_{1/2}$ states due to considerable fine-structure splitting between $n_{1(2)}\,^2P_J$ states of the total momenta $J = 1/2$ and $3/2$, which should appear on the right-hand side of Eq. (1) and determine the double-axial (double-vector) component R_{aa} of the C_6 tensor (see Sec. III). Experimental investigations of the long-range interaction dependence on orientation of the interatomic axis were performed in [16] for Rb atoms in $32D$ states with the use of a static electric field providing resonant energy exchange with opposite-parity states $34(33)P$ and $n = 30(31)$ manifold.

The van der Waals interaction between two Rydberg atoms in identical states may shift Rydberg levels from resonance with a laser excitation radiation, thus prohibiting simultaneous excitation of nearby atoms [20]. This effect, called in the literature the "blockade effect," may be useful for processing quantum information (see, e.g., Ref. [2] and references therein). The shift of a Rydberg state $|nlJM\rangle$ is mainly determined by the C_6 constant which for highly excited states (usually for $n > 20$) is proportional to n^{11}. The dominant contribution to C_6 comes from the terms on the right-hand side of Eq. (1) with nearest to n values of the principal quantum numbers n_1,n_2, providing the smallest energy denominators and the largest values of the dipole-transition matrix elements. In this case of so-called "Förster resonance," the interaction between two atoms may transform from the usual van der Waals form $-C_6/R^6$ into the dipole-dipole interaction of the form C_3/R^3, which appears despite of absence of permanent electric-dipole moments in atoms. The situation is quite similar to a resonance for a frequency-dependent long-range susceptibility of ground-state atoms: the constant C_6 may be also enhanced by a laser radiation of a frequency corresponding to a two-atomic resonance on states of opposite parity [21], in analogy with the effect of the Förster-type resonance between opposite-parity Rydberg states $|nPnP\rangle - |nSn'F\rangle$ caused by the dipole-quadrupole interaction, which was observed experimentally for ultracold Cs atoms [22].

The states of the angular momenta $l > 4$ in many-electron atoms are similar to degenerate Rydberg states of a hydrogen atom. These states may be presented as superpositions of states with the momenta from $l = 5$ to $l = n - 1$. Therefore, atoms in these states have no definite parity and therefore possess a constant electric dipole, quadrupole, octupole, and higher-order (up to 2^{2n-2}-pole) negative- and positive-parity multipole moments [23]. So, the diagonal matrix elements of the first-order correction to energy include the dipole-dipole interaction, providing the most important contribution to the long-range interaction-induced shifts of energy levels, inversely proportional to the cube of the distance R: $\Delta E_{\text{d-d}} = C_3/R^3$. Evidently, the first-order matrix element also includes the dipole-quadrupole $\Delta E_{\text{d-q}} + \Delta E_{\text{q-d}} = C_4/R^4$, dipole-octupole, quadrupole-quadrupole $\Delta E_{\text{d-o}} + \Delta E_{\text{o-d}} + \Delta E_{\text{q-q}} = C_5/R^5$, and other higher-multipole terms of dispersion interaction [24]. However, since the increase of multipolarity accompanies corresponding increase of the $1/R$ power, the account of the indicated terms for $R > R_{LR}$ may introduce only small corrections to the energy of interaction. The coefficients C_3 are determined by products of electric-dipole moments of the given Rydberg states (each proportional to the square of the principal quantum number) and depend on the orientation of the dipole-moment vectors relative to the interatomic axis. For $|nlJM\rangle$ states of $l < 5$ in many-electron atoms the permanent electric dipole moments and all 2^q-pole moments of odd q are zero. The first-order interaction energy does not vanish for $nP_{3/2}$ states and for states of the angular momenta $l > 1$. The lowest order in $1/R$ term corresponds to the interaction of the electric quadrupole moments: $\Delta E^{(1)} = C_5/R^5$, where the tensor constant $C_5 \propto n^8$ depends on the magnetic quantum numbers M and on the relative orientation of the interatomic and quantization axes.

The n dependence of the van der Waals constant C_6 is essentially stronger, thus providing the principal contribution to the long-range interaction. Therefore, we consider in this paper analytical properties of the van der Waals energy $\Delta E_{\text{vdW}} \propto n^{11}/R^6$ determining asymptotic (both in n and R) interaction of atoms in identical Rydberg states with low angular momenta $l \leqslant 3$.

The structure of the paper is as follows. In Sec. II, the basic equations are presented for the energy of long-range interaction between two Rydberg-state atoms. The formulas are derived from the first-order and higher-order perturbation theory for the interaction operator resolved in power series of R^{-1}, the inverse distance between two Rydberg-state atoms. Rigorously speaking, the value of van der Waals constant C_6 for highly excited atoms is complex with the imaginary part determining the rate of the interaction-induced ionization [14,25]. The relations between the real and imaginary parts of the constant C_6 are discussed at the end of Sec. II. The dependence of the interaction between atoms in identical Rydberg states on the magnetic quantum number M and on the orientation of the interatomic axis is described in Sec. III in terms of the irreducible parts of C_6. Equations for the components of C_6 are presented in terms of the second-order radial matrix elements for doublet Rydberg states $|nlJM\rangle$ of low angular momentum l. In Sec. IV, asymptotic approximations are proposed for tensor components of C_6 determining its dependence on relative orientations of interatomic and quantization axes. Coefficients of asymptotic polynomials in powers of the principal quantum number are determined numerically on the basis of standard curve fitting polynomial procedures for nS, nP, nD, and nF states of highly excited Rb atoms. The case of close two-atomic states with the difference of energies in the denominator of Eq. (1) comparable or smaller in magnitude than ΔE_{vdW} is considered in detail in Sec. V.

The possibility of transformation of the van der Waals law into the law of the dipole-dipole interaction is discussed and corresponding ranges of the distance R, where this effect may be observable, are determined explicitly.

Numerical calculations of atomic dipole and multipole transition amplitudes were performed with the use of the Fues' model potential (FMP) approximation [18,26]. In this approach, all details of individual atomic structure (relativistic, spin-orbit, etc. effects) are taken into account in the parameters of analytical presentations for the Rydberg-state wave functions derived on the basis of currently most reliable data for atomic energy levels. The magnetic interactions of atoms are at least four orders smaller in magnitudes than corresponding electric-multipole interactions and therefore are omitted in the long-range two-atomic Hamiltonian. Our considerations assume absence of all external fields, such as stray electric or magnetic fields, thermal (blackbody) radiation, etc., which could mix and therefore perturb Rydberg states. An external field would induce electromagnetic moments in such easily polarizable systems as Rydberg atoms, thus violating individual properties of states, in particular, depriving of definite values of state angular momenta parities. Therefore, in what follows, all external perturbations on atomic states are neglected.

Atomic units $e = m = \hbar = 1$ are used throughout the paper, unless otherwise specified.

II. GENERAL FORMULAS

The operator of electrostatic interaction between two neutral atoms A and B may be presented in the form of asymptotic series of interaction between 2^L-pole electric moments

$$\hat{\mathbf{Q}}^{A(B)}_{L\mu} = \sum_{i=1}^{Z_{A(B)}} r_i^L \mathbf{C}_{L\mu}(\mathbf{n}_i), \tag{2}$$

which account for the contribution of each of Z^A (Z^B) electrons determined by its position vector $\mathbf{r}_i = r_i\mathbf{n}_i$ relative to the atomic nucleus ($\mathbf{n}_i$ is a unit vector, which points from the nucleus to the ith electron) [19]

$$\hat{V}_{AB}(\mathbf{R}) = \sum_{L_A=1}^{\infty}\sum_{L_B=1}^{\infty} \hat{V}_{L_AL_B}(\mathbf{R}). \tag{3}$$

A separate term of this sum is the operator of asymptotic interaction of electric 2^{L_A}–2^{L_B}-pole moments:

$$\hat{V}_{L_AL_B}(\mathbf{R}) = \frac{(-1)^{L_B}}{R^{L+1}}\sqrt{\frac{(2L)!}{(2L_A)!(2L_B)!}} \times \left[\mathbf{C}_L(\mathbf{n})\cdot\left\{\hat{\mathbf{Q}}^A_{L_A}\otimes\hat{\mathbf{Q}}^B_{L_B}\right\}_L\right],$$
$$L = L_A + L_B. \tag{4}$$

General notations of the quantum theory of angular momentum [27] are used here for scalar and tensor products. $\mathbf{C}_{L\mu}(\mathbf{n}_i) = \sqrt{4\pi/(2L+1)}\mathbf{Y}_{L\mu}(\mathbf{n}_i)$ is the modified spherical function of the vector $\mathbf{n}_i$ angular variables. The first term of the twofold series (3) $\hat{V}_{11}(\mathbf{R})$ describes the interaction between virtual electric dipole moments of atoms and determines in the first-order perturbation theory the dipole-dipole interaction of atoms in degenerate two-atomic states [9,16] and the van der Waals interaction in the second order for atoms in nondegenerate two-atomic states [17]. The modified spherical function $\mathbf{C}_L(\mathbf{n})$ determines the dependence of the $2^{L_A} - 2^{L_B}$-pole interaction on the angular variables of the unit vector $\mathbf{n} = \mathbf{R}/R$ which points from atom A to B. Thus, the energy of interaction between two atoms depends on the magnitude and orientation of the relative position vector $\mathbf{R}$. The orientational dependence finally transforms into the dependence on the angle $\theta = \cos^{-1}(\mathbf{n}\cdot\mathbf{a})$ between the vector $\mathbf{n}$ and a unit vector $\mathbf{a}$ pointing in the positive direction of the quantization axis for atomic total momenta $\mathbf{J}_{A(B)}$ (see Fig. 1). The presentation of the interaction operator (4) seems the most convenient since the variables of the "external" vector $\mathbf{R}$, collected in the tensor $\mathbf{C}_L(\mathbf{n})/R^{L+1}$, are separated from the "internal" variables of the interacting atoms, collected in the tensor $\{\hat{\mathbf{Q}}^A_{L_A}\otimes\hat{\mathbf{Q}}^B_{L_B}\}_L$. The components of the tensors may be written explicitly in terms of matrix elements of the operator $\hat{V}_{L_AL_B}(\mathbf{R})$.

It is useful to note that the dipole-dipole interaction operator is usually presented in terms of the electric-dipole operators $\hat{\mathbf{Q}}^{A(B)}_1 \equiv \hat{\mathbf{d}}^{A(B)}$ as follows:

$$\hat{V}_{11}(\mathbf{R}) = -\frac{\sqrt{6}}{R^3}[\mathbf{C}_2(\mathbf{n})\cdot\{\hat{\mathbf{d}}^A\otimes\hat{\mathbf{d}}^B\}_2] = \frac{(\hat{\mathbf{d}}^A\cdot\hat{\mathbf{d}}^B) - 3(\hat{\mathbf{d}}^A\cdot\mathbf{n})(\hat{\mathbf{d}}^B\cdot\mathbf{n})}{R^3}. \tag{5}$$

The first expression seems more convenient for analytical calculations and for analyzing explicitly the $\mathbf{R}$ dependence of the long-range interaction between atoms in Rydberg states. In particular, the determination of the dependence on the orientation of the vector $\mathbf{R} = R\mathbf{n}$, related to a fixed external axis, is distributed over numerous components of dot products in the second expression, which required laborious calculations of different dipole matrix elements already in the first-order perturbation theory [7,16,17,28]. In contrast, the $\mathbf{n}$ dependence is accumulated in a single factor $\mathbf{C}_2(\mathbf{n})$ of the first expression, which may be used straightforwardly not only in the first order, but also in the second and higher orders of perturbation theory.

In the first-order perturbation theory, the dipole-dipole interaction may contribute to the shift of energy levels in atoms A and B, but only in two cases: (i) if the states of interacting atoms represent a superposition of dipole-coupled states of opposite parity or (ii) if the states of *identical atoms* A and B are *dipole-coupled* ones [5]. For *identical atoms* in *identical states* of *definite parity* the contribution of dipole-dipole interaction (and of all odd-parity interactions, dipole-dipole, octupole-octupole, etc.) in the first-order perturbation theory for $\hat{V}_{AB}(\mathbf{R})$ vanishes. In this case, the even-parity interactions may become important for states of nonzero angular momenta. Aside from that, the higher multipolar interaction between atoms (quadrupole-quadrupole, etc.) should be taken into consideration in order to control applicability of the dipole-dipole approximation in higher orders of perturbation theory.

A. First-order perturbation theory for asymptotic interaction of two Rydberg atoms

The system of two identical infinitely separated atoms in their $|nlJM\rangle$ Rydberg states is a multiple degenerate state of the $(2J+1)^2$ multiplicity. Evidently, the operator of interaction (3) is not diagonal in the two-atomic system of eigenfunctions of different magnetic quantum numbers M. Nevertheless, the problem of evaluating the energy shift in a state of fixed magnetic quantum numbers does not aim at the search of the operator (3) eigenstates and eigenvalues. The principal challenge to the theory is to evaluate the magnitude of the interaction-induced shift which could forbid the simultaneous excitation of two atoms into identical Rydberg states. Therefore, the perturbation theory for a nondegenerate state may be used for determining this kind of detuning from the resonance excitation of the two-atomic system.

If the wave function $\langle \mathbf{r}_A,\mathbf{r}_B|AB\rangle$ (the Dirac's notations) determines the state of an isolated system of two noninteracting atoms A and B ($\langle \mathbf{r}_A,\mathbf{r}_B|AB\rangle = \langle \mathbf{r}_A|A\rangle\langle \mathbf{r}_B|B\rangle$) in their stationary states $\langle \mathbf{r}_{A(B)}|A(B)\rangle$ of principal quantum numbers $n_{A(B)}$, nonzero angular momenta $l_{A(B)} \geqslant 1$, and magnetic quantum numbers $m_{A(B)}$ [$|A(B)\rangle = |n_{A(B)}l_{A(B)}m_{A(B)}\rangle$], then the first-order energy shift

$$\Delta E_{AB}^{(1)} = \langle AB|\hat{V}_{AB}(\mathbf{R})|AB\rangle$$

of the perturbation theory for the interaction (3) gives a sum of terms describing contributions of even electric multipole moments $Q_{2L} = C_{l0\,2L0}^{l0}\langle nl|r^{2L}|nl\rangle$ (the odd-moment matrix elements vanish in states of definite parity) of the form

$$\Delta E_{AB}^{(1)}(\mathbf{R}) = \sum_{L_\mathrm{A}=1}^{l_A}\sum_{L_B=1}^{l_B} C_{l_Am_A\,2L_A0}^{l_Am_A} C_{l_Bm_B\,2L_\mathrm{B}0}^{l_Bm_B} \times \frac{(2L)!\,Q_{2L_A}^{A}Q_{2L_B}^{B}}{(2L_A)!\,(2L_B)!\,R^{2L+1}}\,P_{2L}(\mathbf{n}\cdot\mathbf{a}). \tag{6}$$

Here, $L = L_A + L_B$, as in Eq. (4), and common notations are used for the Clebsch-Gordan coefficients $C_{a\alpha\,b\beta}^{c\gamma}$ and Legendre polynomials $P_{2L}(\cos\theta) = \mathbf{C}_{2L\,0}(\theta,\varphi)$ [27]. Evidently, the principal contribution to the first-order interaction energy (6) comes from the lowest nonvanishing order in powers of $1/R$ determined by the electric quadrupolar moments $Q_2^{A(B)}$. The next term, described by the interaction of $Q_2^{A(B)}$ and $Q_4^{B(A)}$ moments, is on the order of n^4/R^2 of the $Q_2 - Q_2$ term. This ratio, equivalent to the ratio of the mean-squared radius of the Rydberg-electron orbit $\langle nl|r^2|nl\rangle \propto n^4$ and the squared distance R between atoms, is sufficiently small to ensure applicability of the long-range approximation (3), (4) for the interaction between atoms in the region of $R > R_{LR} \approx 6n^2$, where the principal contribution to the first-order energy (6) comes from the term $2L_A = 2L_B = 2$, which depends on the distance as R^{-5}. The number of terms in the right-hand side of (6) is $N_{AB} = l_A l_B$, so the first-order energy (6) vanishes ($N_{AB} = 0$), if one of the atoms is in its nS state ($l_{A(B)} = 0$). For both atoms in their nP states $N_{AB} = 1$, hence only $Q_2 - Q_2$ term remains in the right-hand side of (6) an estimate for which may be written as $\Delta E_{AB}^{(1)} \propto n^8/R^5$. For $n = 100$ the long-range approximation holds at $R > 5\times 10^4$ a.u. $\approx 2.6\,\mu$m. At this distance, $\Delta E_{AB}^{(1)} < 1$ GHz. However, the shift (6) will vanish in the nodes of the polynomial $P_4(\mathbf{n}\cdot\mathbf{a})$ at the angles between the vectors $\mathbf{n}$ and $\mathbf{a}$, equal to $\theta = 30.6^\circ, 70.1^\circ, 109.9^\circ$, and 149.4°. Also, $\Delta E_{AB}^{(1)}(\mathbf{R})$ vanishes after averaging over orientations of the vector $\mathbf{R}$ or after averaging over orientations of the total momentum $\mathbf{J}_{A(B)}$ (over magnetic quantum numbers $M_{A(B)}$) of the atom $A(B)$.

B. Higher-order perturbation theory for the asymptotic interaction

In the second-order perturbation theory, the shift of the two-atomic energy is determined by the matrix element

$$\Delta E_{AB}^{(2)}(\mathbf{R}) = -\langle AB|\hat{V}_{AB}(\mathbf{R})G'_{AB}(\mathbf{r}_A,\mathbf{r}_B;\mathbf{r}'_A,\mathbf{r}'_B)\hat{V}_{AB}(\mathbf{R})|AB\rangle \tag{7}$$

with two dispersion-interaction operators (3) and a reduced two-atomic Green's function which accounts for the sums over bound states and integrals over continua of noninteracting atoms [26,29,30]:

$$G'_{AB}(\mathbf{r}_A,\mathbf{r}_B;\mathbf{r}'_A,\mathbf{r}'_B) = {\sum_{n_1,n_2}}' \frac{\langle \mathbf{r}_A|n_1\rangle\langle n_1|\mathbf{r}'_A\rangle\langle \mathbf{r}_B|n_2\rangle\langle n_2|\mathbf{r}'_B\rangle}{E_{n_1}+E_{n_2}-E_A-E_B-i0}. \tag{8}$$

The summation spreads over the complete basis of eigenvectors

$$|n_i\rangle \equiv |n_il_iJ_iM_i\rangle \quad (i = 1,2)$$

of the Hamiltonian of noninteracting atoms $\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$, except for the eigenvector $\langle \mathbf{r}_A,\mathbf{r}_B|AB\rangle$, corresponding to the eigenvalue $E_A + E_B = E_{AB}$, the total energy of infinitely separated atoms. Evidently, $\Delta E_{AB}^{(2)} \neq 0$, independently of the values of angular momenta $l_{A(B)}$, since the Green's function contains all states and allows for arbitrary second-order multipolar transitions between states conforming to the parity conservation law. Therefore the second-order shift (7) involves infinite series of terms arising from the resolution in powers of $1/R$ for the interaction operator (3):

$$\Delta E_{AB}^{(2)}(\mathbf{R}) = -\sum_{q=0}^{\infty}\frac{C_{6+2q}^{(2)}(\mathbf{n})}{R^{6+2q}}. \tag{9}$$

Here, the infinite sum accounts for all virtual multipole moments of atoms A and B in the operators $\hat{V}_{L_AL_B}(\mathbf{R})$ from $L_{A(B)} = 1$ up to infinity. It should be kept in mind that the sum of the multipolar indexes $L_\Sigma^{A(B)} = L_{A(B)} + L'_{A(B)}$ should be an even number, if the bound states of atoms $\langle \mathbf{r}_1|A\rangle$, $\langle \mathbf{r}_2|B\rangle$ have definite parities. Hence, the shift $\Delta E_{AB}^{(2)}(\mathbf{R})$ of the second-order perturbation theory is resolved in even powers of the parameter $1/R$. Tensor components of coefficients $C_{6+2q}^{(2)}(\mathbf{n})$ include functions dependent on orientation of the interatomic axis $\mathbf{n}$.

The principal contribution to $\Delta E_{AB}^{(2)}(\mathbf{R})$ comes from the lowest order in $1/R$ term, so $\Delta E_{AB}^{(2)}(\mathbf{R}) \approx -C_6^{(2)}(\mathbf{n})/R^6$. The van der Waals constant $C_6^{(2)}(\mathbf{n})$ describes the second-order interaction of virtual electric dipole moments of atoms A and B. The next term $-C_8^{(2)}(\mathbf{n})/R^8$ is determined by the dipole-quadrupole interaction, which for high-n states is on the order of n^4/R^2 in comparison with the first nonvanishing term. The general relation $|C_{6+2(q+q')}^{(2)}/C_{6+2q}^{(2)}| \propto n^{4q'}$, $q' = 0,1,2\ldots$, holds for coefficients. So, the relation $n^2/R < 1$ ensures convergence of the series (9).

The third and higher orders of the perturbation theory for the dispersion interaction of ground-state atoms were already considered in the 1980s (see, for example [21,29,31] and references therein). Numerical data were calculated for coefficients determining asymptotic resolution of the third- and fourth-order dispersion interaction energy for neutral hydrogen and alkali-metal atoms in their ground states. Corrections to the energy of asymptotic interaction between hydrogen atoms up to the 10th order of perturbation theory were calculated in [32]. Specific properties of Rydberg atoms stimulate the analysis of higher-order terms of perturbation theory in the interaction (3).

The third-order energy shift involves matrix elements with three operators (3) and two Green's functions G'_{AB} [31,32]. Corresponding asymptotic resolution involves only odd powers of $1/R$, starting for states of definite parity from $1/R^{11}$, and may be written as follows [31,32]:

$$\Delta E^{(3)}_{AB}(\mathbf{R}) = \sum_{q=0}^{\infty} \frac{C^{(3)}_{11+2q}(\mathbf{n})}{R^{11+2q}}, \tag{10}$$

where the coefficients $C^{(3)}_{11+2q}(\mathbf{n})$ may be resolved in tensor components dependent on the direction of the interatomic axis $\mathbf{n}$.

The fourth-order perturbation theory will present the asymptotic interaction-induced energy $\Delta E^{(4)}_{AB}(\mathbf{R})$ in terms of a superposition of the fourth-order matrix elements and product of the first-order energy (6) with the third-order matrix element and the product of second-order energy (9) with the second-order matrix element of the product of two Green's functions (8) between two operators (3) [32]. Each term of the fourth-order superposition effectively includes four operators $\hat{V}_{AB}(\mathbf{R})$ and three Green's functions. The asymptotic resolution of the fourth-order energy may be written as a series in even powers of $1/R$ similar to (9), starting from $1/R^{12}$ [31,32].

Generally speaking, the energy of asymptotic interaction between neutral atoms in their bound states with definite orbital quantum numbers may be presented as an infinite series of terms $\Delta E^{(N)}_{AB}(\mathbf{R})$ of the Nth-order perturbation theory for the energy of asymptotic interaction (3):

$$\Delta E_{AB}(\mathbf{R}) = \sum_{N=1}^{\infty} \Delta E^{(N)}_{AB}(\mathbf{R}). \tag{11}$$

In its turn, each term of these series may be resolved in power series of an inverse interatomic distance $1/R$:

$$\Delta E^{(N)}_{AB}(\mathbf{R}) = (-1)^{N+1} \sum_{q=q_0}^{\infty} \frac{C^{(N)}_{3N+2q}(\mathbf{n})}{R^{3N+2q}}, \tag{12}$$

where q runs positive integer numbers starting from $q_0 = 0$ for even N, $q_0 = 1$ for odd N.

Thus, the series (11) finally transforms into power series of $1/R$:

$$\Delta E_{AB}(\mathbf{R}) = \sum_{s=s_0}^{\infty} \frac{C^{tot}_s(\mathbf{n})}{R^s}, \tag{13}$$

where the coefficients $C^{tot}_s(\mathbf{n})$ are the sums of corresponding coefficients $C^{(N)}_s(\mathbf{n})$ of resolutions (12) for different orders N of the perturbation theory:

$$C^{tot}_s(\mathbf{n}) = \sum_{k=1}^{[(s+1)/6]} C^{(2k-1)}_s(\mathbf{n}) \quad \text{for odd } s \geqslant 5, \tag{14}$$

$$C^{tot}_s(\mathbf{n}) = -\sum_{k=1}^{[s/6]} C^{(2k)}_s(\mathbf{n}) \quad \text{for even } s \geqslant 6, \tag{15}$$

where the notation $[a]$ is used for the integer part of a positive number a.

Comparison between the coefficients $C^{(N)}_{3N+2q}/C^{(N)}_{3N} \propto n^{4q}$ within one and the same order N of perturbation theory detects the condition for convergence of the series in $1/R$ (12) at $n^4/R^2 \ll 1$. Whereas the condition of convergence of the series (11), determined by the ratio of the terms of the order $N+2$ and N, where the lowest order (in R^{-1}) terms are taken into account, is slightly stronger:

$$\left|\Delta E^{(N+2)}_{AB}(\mathbf{R})/\Delta E^{(N)}_{AB}(\mathbf{R})\right| \propto n^{14}/R^6 \ll 1.$$

Simultaneously, comparison of terms from the Nth and $(N+2k)$th order of equal powers $s = 3N + 2q = 3(N+2k) + 2q'$ of $1/R$ (where $q' = q - 3k$)

$$\left|C^{(N+2k)}_s(\mathbf{n})/C^{(N)}_s(\mathbf{n})\right| \propto n^{2k}, \quad k = 1,2,\ldots,[q/3]$$

demonstrates negligible contributions of the lower-order perturbation-theory terms into the constant C^{tot}_s of the asymptotic resolution (13). This regularity follows from the asymptotic nature of the interaction operator (3) and was observed already for ground-state hydrogen atoms [32] but for rather remote terms of $s \geqslant 30$ in the series (13).

It is important to note different signs in the right-hand sides of Eqs. (15) and (14) for even- and odd-order sums of coefficients $C^{(N)}_s(\mathbf{n})$ determining the resultant resolution (13) in powers of $1/R$ for the long-range interaction energy. This rule follows from the signs of the highest-order matrix elements in corresponding expressions of the perturbation theory. In particular, $C^{tot}_s(\mathbf{n}) = C^{(1)}_s(\mathbf{n})$ for $s = 5,7,9$ and $C^{tot}_s(\mathbf{n}) = -C^{(2)}_s(\mathbf{n})$ for $s = 6,8,10$. In what follows, we confine our considerations mainly to the second-order corrections described by $C^{(2)}_6$ for which we use the notation C_6, thus omitting superscripts.

C. Van der Waals ionization of Rydberg atoms

Evidently, the cooperative energy of two atoms is always sufficient to put the Rydberg electron of the atom $B(A)$ into continuum while the electron of the atom $A(B)$ falls down to a lower-energy state $E_{n_{1(2)}} < E_A + E_B$. In this case, the integral over continuum of the atom $B(A)$ in the Green's function (8) has a singularity at the energy $\varepsilon_{B(A)} = E_A + E_B - E_{n_{1(2)}} > 0$. According to Sokhotski theorem, the imaginary part of the Green's function is given by the sum of products of corresponding bound-state and continuum radial functions:

$$\begin{aligned}
&\mathrm{Im}\{G_{AB}(\mathbf{r}_A,\mathbf{r}_B;\mathbf{r}'_A,\mathbf{r}'_B)\}\\
&\quad = \pi \sum_{n_1} \langle \mathbf{r}_A|n_1\rangle\langle n_1|\mathbf{r}'_A\rangle\langle \mathbf{r}_B|\varepsilon_2\rangle\langle \varepsilon_2|\mathbf{r}'_B\rangle\\
&\qquad + \pi \sum_{n_2} \langle \mathbf{r}_B|n_2\rangle\langle n_2|\mathbf{r}'_B\rangle\langle \mathbf{r}_A|\varepsilon_1\rangle\langle \varepsilon_1|\mathbf{r}'_A\rangle,
\end{aligned} \tag{16}$$

where $\varepsilon_{2(1)} = E_A + E_B - E_{n_{1(2)}} > 0$ is the energy of a state from atom $B(A)$ positive-energy continuum. So, the second-order energy (7) of interaction between two Rydberg atoms and constants of corresponding resolution (12) are complex values, the imaginary parts of which determine the rate of ionization for one of the atoms accompanied by simultaneous deexcitation of another one with transition to lower-energy levels [14].

This effect is analogous to an autoionization process of two-electron excited states in many-electron atoms, if the energy of the two-electron excitation exceeds the single-electron ionization potential. Also, the van der Waals interaction-induced ionization of Rydberg atoms may be compared with the so-called "Penning ionization" of an atom of a low ionization potential by a metastable atom of rather high excitation energy, which was considered in [29] as a result of the long-range interaction between inert-gas atoms in metastable states and ground-state alkali-metal atoms.

The imaginary parts of constant factors C_s of the resolution (13) are rather small in comparison with real parts $\mathrm{Re}\{C_s\}$. They appear already in the second-order perturbation theory from the imaginary part of the two-atomic Green's function (16) in the integral over continuum of atom $A(B)$ at the energy $\varepsilon_{A(B)} = E_{AB} - E_{n_{2(n_1)}} > 0$. Simple estimates for the van der Waals constant demonstrate that the ratio between the imaginary and real parts of C_6 may be determined as

$$\frac{\mathrm{Im}\{C_6\}}{\mathrm{Re}\{C_6\}} \propto n^{-p}, \tag{17}$$

where the exponent p varies from 10 to 3 in the region of the principal quantum numbers from $n \approx 10$ to $n \geqslant 1000$, thus maintaining the imaginary part of the van der Waals energy 9 to 10 orders smaller in absolute value than the real part in all the indicated regions of states. So, small values of $\mathrm{Im}\{C_6\}$ allow to neglect the broadening of Rydberg levels, caused by the long-range interaction-induced ionization. Therefore, we confine ourselves to calculating only real parts of the van der Waals constants.

An opposite to the long-range case of Rydberg-Rydberg autoionization was considered in [33] for a system of two Rydberg atoms, separated at distances $R \leqslant R_{LR}$, where the ionization rate increases almost exponentially with the overlap of Rydberg orbits.

III. IRREDUCIBLE COMPONENTS OF VAN DER WAALS CONSTANTS

A. C_6 dependence on the relative orientation of the quantization and interatomic axes

The general equation for the van der Waals constant describing the interaction of two identical atoms, both in one and the same Rydberg state, say $|n_A l_A J_A M_A\rangle = |n_B l_B J_B M_B\rangle \equiv |nlJM\rangle$, may be derived on the basis of an equation for the van der Waals constant determining the long-range interaction of two arbitrary (identical or different) atoms in their arbitrary (also identical or different) excited states [19]. Thus, the van der Waals constant for the like Rydberg-state atoms may be presented as a function of the magnetic quantum numbers M and of the angle θ between the unit vectors of interatomic $\mathbf{n}$ and quantization $\mathbf{a}$ axes (see Fig. 1), as follows:

$$\begin{aligned} C_6(\theta; nlJM) = {} & R_{ss} - \frac{M^2}{12J^2}(3\cos^2\theta - 2)R_{aa} \\ & + \frac{3M^2 - J(J+1)}{2J(2J-1)}(3\cos^2\theta - 1)R_{sT} \\ & + \frac{3}{2}\left[\frac{3M^2 - J(J+1)}{2J(2J-1)}\right]^2 \\ & \times (9\cos^4\theta - 8\cos^2\theta + 1)R_{TT}. \end{aligned} \tag{18}$$

The symmetry relation $C_6(\theta) = C_6(\pi - \theta)$ is seen from this equation. The first term on the left-hand side is independent of orientations of the quantization and interatomic axes. In averaging over orientations of the interatomic axis, the third term on the right-hand side disappears, while the dependence on the magnetic quantum numbers remains:

$$\begin{aligned} \overline{C}_6(nlJM) \equiv \int_\Omega C_6(\theta)\frac{d\Omega}{4\pi} = {} & R_{ss} + \frac{M^2}{12J^2}R_{aa} \\ & + \left[\frac{3M^2 - J(J+1)}{2J(2J-1)}\right]^2 \frac{R_{TT}}{5}. \end{aligned} \tag{19}$$

Also, assuming orientations of angular momenta being independent (this may occur as a result of the Rydberg-state excitation by unpolarized radiation) and averaging over the magnetic quantum numbers of one of the pairwise interacting atoms, all the θ-dependent terms disappear. So, the mean value of the van der Waals constant averaged over magnetic quantum numbers M_A and M_B independently (corresponding to free orientations of the angular momenta $\mathbf{J}_A$ and $\mathbf{J}_B$ of interacting atoms) is independent of the angle θ:

$$\langle C_6 \rangle \equiv \frac{1}{(2J+1)^2} \sum_{M_A M_B} C_6(nlJ; M_A M_B) = R_{ss}.$$

In addition, there are a number of orientational symmetry relations, which may be useful for determining separately the irreducible components. For example, the R_{aa} component of the van der Waals constant (18) disappears for a state of the total momentum $J \geqslant 1$ and its projection $M = 0$. For arbitrary $M \neq 0$, the component R_{aa} disappears at the angle $\theta = \cos^{-1}(\sqrt{2/3})$ and in a linear combination of the C_6 coefficients of the form

$$M_1^2 C_6(\theta; M_2) - M_2^2 C_6(\theta; M_1) = (M_1^2 - M_2^2)\left\{R_{ss} - \frac{J+1}{2J-1}R_{sT}P_2(\cos\theta) + \left[\frac{J^2(J+1)^2}{9} - M_1^2 M_2^2\right]R_{TT}K_J(\cos\theta)\right\}, \tag{20}$$

where $P_2(x) = (3x^2 - 1)/2$ is the Legendre polynomial

$$K_J(x) = \frac{27\{[P_2(x)]^2 - x^2/2\}}{2J^2(2J-1)^2}.$$

In particular, for $M_1 = 1$ and $M_2 = 0$ the right-hand side of Eq. (20) coincides with that of (18) where $M = 0$. For $J = 3/2$, $M_1 = 1/2$, $M_2 = 3/2$, Eq. (20) reads as

$$9C_6\left(\theta; \tfrac{3}{2}, \tfrac{1}{2}\right) - C_6\left(\theta; \tfrac{3}{2}, \tfrac{3}{2}\right) = 8R_{ss} - 10R_{sT}P_2(\cos\theta) + 8R_{TT}K_{3/2}(\cos\theta). \tag{21}$$

The component R_{sT} disappears at $\theta = \cos^{-1}(1/\sqrt{3})$ and is eliminated from the value of the van der Waals constant (19) averaged over orientations of the interatomic axis. The angular-dependent factor $K_J(\cos\theta)$ disappears together with the component R_{TT} at the angles $\theta_\pm = \cos^{-1}[(4 \pm \sqrt{7})/9]$ and in $\langle C_6\rangle$ after averaging over independent magnetic quantum numbers (together with R_{aa} and R_{sT}).

On the other hand, for states of the total momentum $J \geqslant 2$ only the component R_{TT} determines completely linear combinations of three van der Waals coefficients of the form

$$\begin{aligned} S_J(\theta) &\equiv \left(M_1^2 - M_2^2\right)C_6(\theta; JM_3) + \left(M_2^2 - M_3^2\right)C_6(\theta; JM_1) + \left(M_3^2 - M_1^2\right)C_6(\theta; JM_2) \\ &= -\left(M_1^2 - M_2^2\right)\left(M_2^2 - M_3^2\right)\left(M_3^2 - M_1^2\right)R_{TT}K_J(\cos\theta), \end{aligned} \tag{22}$$

where M_1, M_2, and M_3 are three different values of the magnetic quantum number available for a given value of the total momentum J.

In particular, for $nD_{5/2}$ states of the total angular momentum $J = 5/2$ and its projections $|M_1| = 1/2, |M_2| = 3/2, |M_3| = 5/2$, Eq. (22) reads as

$$S_{5/2}(\theta) = 2C_6\left(\theta; \tfrac{5}{2}, \tfrac{1}{2}\right) - 3C_6\left(\theta; \tfrac{5}{2}, \tfrac{3}{2}\right) + C_6\left(\theta; \tfrac{5}{2}, \tfrac{5}{2}\right) = \tfrac{81}{100}R_{TT}(9\cos^4\theta - 8\cos^2\theta + 1). \tag{23}$$

This combination at $\theta = 0$ is twice that of $\theta = \pi/2$:

$$S_{5/2}(\theta = 0) = 2S_{5/2}(\theta = \pi/2) = 1.62R_{TT}.$$

We consider below doublet states (spin $S = 1/2$ and total angular momentum $J = l \pm 1/2$) of the Rydberg series of alkali-metal atoms. In this case, the irreducible parts R_{ss}, R_{aa}, R_{sT}, R_{TT} may be presented in terms of the second-order radial matrix elements with two-atomic Green's functions $g_{l_1,J_1;l_2,J_2}(r_A,r_B;r'_A,r'_B)$:

$$\rho_{l_1,J_1;l_2,J_2} = \langle nlJ|\langle nlJ|r_Ar_B\, g_{l_1,J_1;l_2,J_2}\, r'_Ar'_B|nlJ\rangle|nlJ\rangle. \tag{24}$$

Corresponding equations may be written as follows:

$$\begin{aligned} R_{ss} = {}& \frac{1}{24J^2(J+1)^2}[(J+1)^2(2J-1)^2\rho_{l-1,J-1;l-1,J-1} + \rho_{l\pm1,J;l\pm1,J} + J^2(2J+3)^2\rho_{l+1,J+1;l+1,J+1} \\ & + 2(J+1)(2J-1)\rho_{l-1,J-1;l\pm1,J} + 2J(J+1)(2J-1)(2J+3)\rho_{l-1,J-1;l+1,J+1} + 2J(2J+3)\rho_{l\pm1,J;l+1,J+1}], \end{aligned} \tag{25}$$

$$\begin{aligned} R_{aa} = {}& \frac{3}{8J^2(J+1)^4}[(J+1)^4(2J-1)^2\rho_{l-1,J-1;l-1,J-1} + \rho_{l\pm1,J;l\pm1,J} + J^4(2J+3)^2\rho_{l+1,J+1;l+1,J+1} + 2(J+1)^2 \\ & \times(2J-1)\rho_{l-1,J-1;l\pm1,J} - 2J^2(J+1)^2(2J-1)(2J+3)\rho_{l-1,J-1;l+1,J+1} - 2J^2(2J+3)\rho_{l\pm1,J;l+1,J+1}], \end{aligned} \tag{26}$$

$$\begin{aligned} R_{sT} = R_{Ts} = {}& \frac{-(2J-1)}{24J^2(J+1)^3}[(J+1)^3(2J-1)\rho_{l-1,J-1;l-1,J-1} - \rho_{l\pm1,J;l\pm1,J} + J^3(2J+3)\rho_{l+1,J+1;l+1,J+1} \\ & -(J-2)(J+1)\rho_{l-1,J-1;l\pm1,J} + J(J+1)(4J^2+4J+3)\rho_{l-1,J-1;l+1,J+1} - J(J+3)\rho_{l\pm1,J;l+1,J+1}], \end{aligned} \tag{27}$$

$$\begin{aligned} R_{TT} = {}& \frac{(2J-1)^2}{24J^2(J+1)^4}[(J+1)^4\rho_{l-1,J-1;l-1,J-1} + \rho_{l\pm1,J;l\pm1,J} + J^4\rho_{l+1,J+1;l+1,J+1} - 2(J+1)^2\rho_{l-1,J-1;l\pm1,J} \\ & - 2J^2\rho_{l\pm1,J;l+1,J+1} + 2J^2(J+1)^2\rho_{l-1,J-1;l+1,J+1}]. \end{aligned} \tag{28}$$

Different terms on the right-hand sides of these equations correspond to different dipole-allowed angular-momentum channels, some properties of which were discussed, in particular, for Rb and Cs atoms in [1].

For states of $J = |M|$ (orbit in the plane perpendicular to the quantization axis), the orientation-dependent factors $\sin^2\theta$ appear in several terms of the C_6 constant and the contribution to C_6 of the radial matrix elements $\rho_{l-1,J-1;l-1,J-1}$ and $\rho_{l-1,J-1;l\pm1,J}$ disappears at $\theta = 0$. For example,

$$C_6|_{J=|M|=5/2}(\theta = 0) = \tfrac{4}{12\,005}(10\rho_{l\pm1,J;l\pm1,J} + 465\rho_{l+1,J+1;l+1,J+1} + 162\rho_{l\pm1,J;l+1,J+1} + 2058\rho_{l-1,J-1;l+1,J+1}). \tag{29}$$

B. Numerical evaluations of irreducible components of the van der Waals constant C_6 for Rydberg atoms

The radial part of the Green's function (8) in the radial matrix elements (24) may be presented as a spectral expansion in a Hilbert subspace of two-atomic states of fixed orbital l_1,l_2 and total J_1,J_2 angular momenta, as follows:

$$g_{l_1,J_1;l_2,J_2}(r_Ar_B;r'_Ar'_B) = \sum_{n_1,n_2} \frac{\langle r_A|n_1l_1J_1\rangle\langle n_1l_1J_1|r'_A\rangle\langle r_B|n_2l_2J_2\rangle\langle n_2l_2J_2|r'_B\rangle}{E_{n_1l_1J_1}+E_{n_2l_2J_2}-E_A-E_B-i0}, \tag{30}$$

where the sum performs over a complete set of radial eigenfunctions of isolated atoms A and B. The substitution of Eq. (30) for the Green's function turns the right-hand side of the radial matrix element (24) into the twofold infinite sum over complete set of states, including continua, of products of the radial parts of the first-order dipole-transition amplitudes of atoms A and B.

The principal contributions to the second-order matrix element come from the terms with closest principal quantum numbers of the intermediate states n_1,n_2 to that of the Rydberg state n and, simultaneously, of the lowest absolute values of the energy differences for both atoms $\delta_{n_{1(2)}} = E_{n_{1(2)}l_{1(2)}J_{1(2)}} - E_{A(B)}$ in the denominator. The most important of these contributions corresponds to opposite signs of the energy differences δ_{n_1} and δ_{n_2}, so that the absolute value of the energy defect

$$\delta = \delta_{n_1} + \delta_{n_2} \tag{31}$$

is at least one order smaller than the magnitudes of the separate differences $\delta_{n_{1(2)}}$. The contribution of remaining terms of the spectral resolution in (30) exponentially decreases with the increase of the absolute values of the differences between the principal quantum numbers $n_{A(B)} - n_{1(2)}$ (see, for example, Sec. 51 of Ref. [5]). Numerical calculations of the radial matrix elements reveal rather rapid convergence of the series over bound states. The convergence accelerates with the increase of the principal quantum number n of Rydberg states. Therefore, the account of terms from the region of $|n_{1(2)} - n| \leqslant 8$ ensured significant accuracy of calculated result for the matrix element (24) already for $n = 20$ (with the fractional uncertainty of the contribution from the residual sum over infinite number of bound states and integral over continuum, remaining below 10^{-4}–10^{-5}).

The Fues' model potential approach in the single-electron approximation for atomic wave functions (see, for example, [26,29–31]) gives analytical presentation for the radial matrix element

$$\begin{aligned}\langle n\,l\,J\,|\,r\,|n'l'J'\rangle &= \frac{\Gamma(b)}{4Z}\left(\frac{2\nu}{\nu+\nu'}\right)^{\lambda'+2}\left(\frac{2\nu'}{\nu+\nu'}\right)^{\lambda+2}\sqrt{\frac{(c)_{n_r}(c')_{n'_r}}{n_r!n'_r!\Gamma(c)\Gamma(c')}}\\ &\quad\times F_2\left(b;\,-n_r,-n'_r;c;c';\frac{2\nu'}{\nu+\nu'},\frac{2\nu}{\nu+\nu'}\right),\end{aligned} \tag{32}$$

where $b = \lambda + \lambda' + 4$, $c = 2\lambda + 2$, $c' = 2\lambda' + 2$; the usual notations for the Γ function and the Pochhammer symbol $(a)_n = \Gamma(a+n)/\Gamma(a)$ are used [34]. Here, n_r is the radial quantum number, which numbers the states of a given nlJ series and relates the effective principal quantum number $\nu = 1 + n_r + \lambda$ and the effective angular momentum λ; Z is the net charge of residual ion ($Z = 1$ for a neutral atom).

F_2 is the generalized hypergeometric function (Appel function) of five parameters and two variables, which may be calculated in terms of the Gauss hypergeometric functions ${}_2F_1$. The precision of evaluation of the hypergeometric functions rapidly decreases with the growth of n_r, due to the strong cancellation of digits in corresponding sums of sign-alternating terms. The transformation [34]

$$\begin{aligned}F_2(\alpha;-n_r,-n'_r;\gamma,\gamma';x,y) &= \sum_{p=0}^{\min(n_r,n'_r)}\frac{(\alpha)_p}{p!}\frac{(-n_r)_p(-n'_r)_p}{(\gamma)_p(\gamma')_p}(xy)^p\,{}_2F_1(\alpha+p,p\\ &\quad -n_r;\gamma+p;x){}_2F_1(\alpha+p,p-n'_r;\gamma'+p;y)\end{aligned} \tag{33}$$

turns out to be the most useful for Rydberg states because the last few terms [$p \sim \min(n_r,n'_r)$] are of one and the same sign and provide the main contribution to the sum.

The model-potential parameters of the radial matrix element (32) are determined from the most precise data for the energy levels of atoms and ions available, in particular, from the Internet resources [35]. The basic role for evaluating the model-potential parameters plays the so-called quantum defect $\mu_{nlJ} = n - \nu_{nlJ}$ of the energy level, which determines the difference between the principal quantum number n and the effective principal quantum number $\nu_{nlJ} = Z/\sqrt{-2E_{nlJ}}$ determined from the value of the $|nlJ\rangle$-state energy. Since available data for energies in every series of states are confined to a finite number of levels, the quantum defect allows to extend the information on the energies and therefore on the wave-function parameters, up to $n \to \infty$. The data for quantum defects from [8] (S and D states), [10,11] (P states), and [12] (F states) were used for determining the model-potential parameters of the Rydberg-state wave functions and the two-atomic frequencies (31) according to the relation

$$\mu_{lJ}(n) = \mu_{lJ}^{(0)} + \frac{\mu_{lJ}^{(2)}}{\left(n-\mu_{lJ}^{(0)}\right)^2}. \tag{34}$$

The parameters $\mu_{lJ}^{(0,2)}$ are constant values for nlJ series of states with fixed orbital l and total J momenta and different principal quantum numbers n. Meanwhile, the absolute values of $\mu_{lJ}^{(0,2)}$ rapidly vanish with the increase of the angular momentum l.

The states of rather high absolute values of the magnetic quantum numbers $m_{A(B)}$ and, consequently, of high angular momenta ($l_{A(B)} \geqslant |m_{A(B)}| \geqslant 5$) are equivalent to degenerate states of hydrogen atoms (spin-orbit effects neglected). These states have no definite parity and therefore possess both even and odd permanent electric multipole moments, which can also contribute to the sum (13) [23]. The electric dipole moments point along the quantization axis and may be written in terms of the parabolic quantum numbers n_1,n_2 [5] and the unit vector $\mathbf{a}$, as

$$\mathbf{d} = -\tfrac{3}{2}n(n_1-n_2)\mathbf{a}. \tag{35}$$

So, the dipole-dipole interaction (5) of two Rydberg atoms in their identical manifold states of $n > l \geqslant 5$, with fixed parabolic quantum numbers $|nn_1n_2\rangle$, determines the long-range energy shift, which for $R > R_{LR}$ may be written as

$$\Delta E_d = \langle nn_1n_2|\hat{V}_{11}|nn_1n_2\rangle = \frac{C_3(nn_1n_2;\theta)}{R^3},$$

where the coefficient

$$C_3(nn_1n_2;\theta) = \tfrac{9}{4}n^2q^2(1-3\cos^2\theta)$$

demonstrates the interaction-induced shift and splitting of the Rydberg manifold proportional to squared product of the principal n and dipole $q = n_1 - n_2$ quantum numbers. The orientational dependence is proportional to the second-order Legendre polynomial

$$P_2(\cos\theta) = (3\cos^2\theta - 1)/2,$$

as is usual for the interaction of two permanent electric dipole moments (35), parallel to each other and pointing at the angle θ relative the separation vector $\mathbf{R}$.

Some numerical data for the van der Waals constants of the two-atomic states with identically excited Rb atoms in their $nD_{5/2\,M}$ states of $n = 42{,}43{,}44$ are presented on Fig. 2 as the functions of the orientation angle θ for the magnetic quantum numbers $|M| = 1/2$ [Fig. 2(a)] and $|M| = 5/2$ [Fig. 2(b)]. The θ dependence of C_6 for $|M| = 3/2$ states is nearly similar and the absolute values are intermediate between those presented on Figs. 2(a) and 2(b). The magnitudes of negative (repulsive) values of C_6 for $43D_{5/2}$ states exceed those of the $42D_{5/2}$ and $44D_{5/2}$ states by more than one order. This property is due to the resonance behavior of the spectrum of two-atomic $(n+2)P$, nD, and $(n-2)F$ states: the difference between the energy of two atoms in $43D_{5/2}$ states and the total energy of one atom in the $45P_{3/2}$ and another one in $41F_{7/2}$ state $\delta = E_{45P_{3/2}} + E_{41F_{7/2}} - 2E_{43D_{5/2}} \approx -8.75$ MHz is about two orders smaller in magnitude than the difference from the energies of the other closest dipole-coupled two-atomic states. Therefore, the interaction of Rb atoms in $43D_{5/2}$ states in a definite region of interatomic distances $R_{LR} < R < R_F$, where $R_{LR} \approx 0.5\ \mu$m and $R_F \approx 7\ \mu$m, should be considered on the basis of the perturbation theory for close states (see Sec. V of this paper). In the region above the “Förster radius” $R > R_F$ the interaction-induced shift is essentially smaller than the “resonance detuning” δ and the usual perturbation theory for nondegenerate states is applicable with the van der Waals constants $C_6(43D_{5/2\,M})$ presented in Fig. 2. The curves for the constants of the neighbor states $C_6(42D_{5/2\,M})$ and $C_6(44D_{5/2\,M})$ are plotted for comparison and in order to demonstrate similar θ dependencies of the interaction energies of Rb atoms in $nD_{5/2\,M}$ states. The negative values of the C_6 constants for $n = 42{,}43$ correspond to repulsion between atoms. The positive values of $C_6(44D_{5/2\,M})$ determine attraction. It is important to note that the van der Waals interaction does not vanish in the indicated Rydberg states for all orientations of the total angular momenta (determined by the magnetic quantum numbers M) and for all orientations of the interatomic axis (determined by the angles θ).

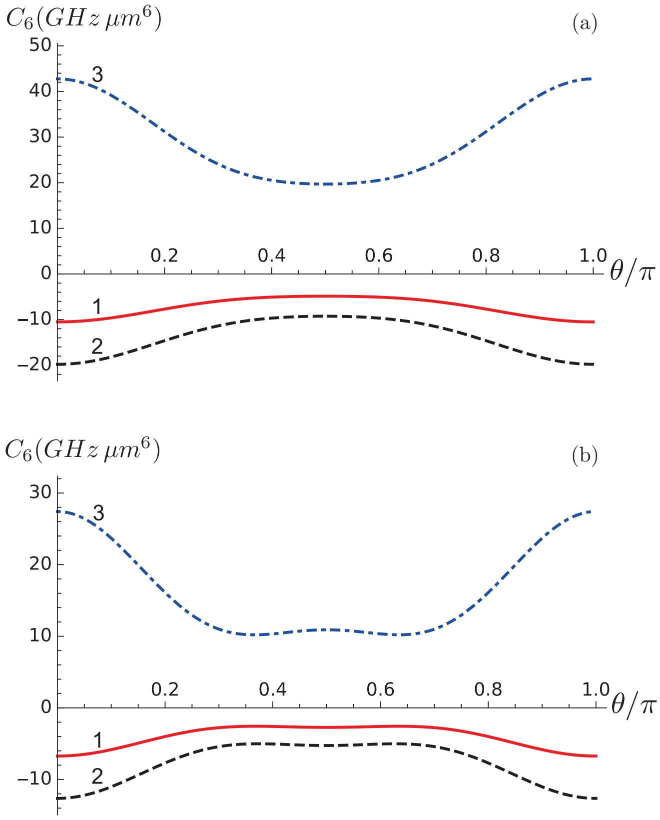

FIG. 2. Dependence of the van der Waals coefficients C_6 on the angle θ between the interatomic and quantization axes for the Rb $nD_{5/2\,M}$ states of the magnetic quantum numbers: $|M| = 1/2$ (a), $|M| = 5/2$ (b). Curves 1 and 3 correspond to the principal quantum numbers $n = 42$ and 44. Curves 2 give the values of $0.1 \times C_6$ for the states $43D_{5/2\,M}$.

IV. ASYMPTOTIC PRESENTATION OF C_6 FOR RYDBERG-STATE RUBIDIUM ATOMS

The presentation of the calculated data for the van der Waals constant and its tensor components (25)–(28) may be reduced to tabulating numerical values of a few constants determining an asymptotic dependence of the calculated values on the principal quantum number of a Rydberg state.

Results of numerical calculations reveal general regularities in the dependence of C_6 on the Rydberg-state quantum numbers. First of all, we start from the dependence (34) of the quantum defects $\mu_{lJ}(n)$ of different nlJ series used for determining energies and their differences (31) in the spectral resolution of the Green’s function (30). For Rydberg series in Rb atoms, the energy defect (31) is a monotonically decreasing function of n. In the series of states of the angular momenta $l \neq 0$, the defect δ for the most contributing states may tend to zero and change its sign between “resonance” states of the principal quantum numbers $n_{\rm res}$ and $n_{\rm res} \pm 1$. This situation appears for the C_6 components of P, D, and F states.

Nevertheless, the basic behavior of the van der Waals constant and its components as a function of the principal quantum number of a pair of identical Rydberg atoms is nearly one and the same, which may be presented in a general asymptotic form, as follows:

$$C_6(nlJ) = A(lJ)n^{11}\left[1 + \frac{a^{(1)}(lJ)}{n} + \frac{a^{(2)}(lJ)}{n^2} + \cdots\right]. \qquad (36)$$

However, the coefficients $A(lJ)$ and $a^{(i)}(lJ)$ in the right-hand side of this equation depend on the magnetic quantum numbers M and on the angle θ of the interatomic axis orientation. Therefore, it is more convenient to use the asymptotic series of the form (36) for the M- and θ-independent irreducible components (25)–(28) of the van der Waals constant (18).

The asymptotic series in parentheses of Eq. (36) may be truncated to a polynomial in the inverse powers of the principal quantum number. Numerical calculations demonstrate, that for $n \geqslant 30$, the third-order polynomial $\Pi_3(1/n)$ in powers of n^{-1} evaluates the components of C_6 with uncertainties below 1%. Therefore, we confine ourselves to the asymptotic equation

$$R_{\alpha\beta}(nlJ) = A_{\alpha\beta}(lJ)n^{11}\Pi_3(1/n), \qquad (37)$$

where the subscripts s, a, T should substitute for α and β to denote corresponding components of C_6 (R_{ss}, R_{aa}, R_{sT}, and R_{TT}). The third-order polynomial

$$\Pi_3(x) = 1 + a^{(1)}_{\alpha\beta}(lJ)x + a^{(2)}_{\alpha\beta}(lJ)x^2 + a^{(3)}_{\alpha\beta}(lJ)x^3$$

tends asymptotically (for $n \to \infty$) to the unit $\Pi_3(0) = 1$. The coefficients $a^{(i)}_{\alpha\beta}(lJ)$, $i = 1,2,3$, may be determined from a standard curve polynomial fitting procedure (see, for example, [36,37]). Thus, the most important part of dependence on the principal quantum number of the C_6 components is determined by the factor n^{11} with the amplitudes $A_{ss}(lJ)$, $A_{aa}(lJ)$, $A_{sT}(lJ)$, and $A_{TT}(lJ)$. Separate terms of the polynomial $\Pi_3(1/n)$ account for the lower powers (n^{10}, n^9, n^8), the fractional contribution from which gradually disappears, when $n \to \infty$.

In the case of resonances, where the energy defect (31) of the most contributing states changes its sign, the asymptotic Eq. (37) may be generalized, as follows:

$$R_{\alpha\beta}(nlJ) = \frac{A_{\alpha\beta}(lJ)}{\left[n - \tilde{n}^{(1)}_{\alpha\beta}(lJ)\right]\left[n - \tilde{n}^{(2)}_{\alpha\beta}(lJ)\right]}\, n^{13}\Pi_3\left(\frac{1}{n}\right), \qquad (38)$$

where $\tilde{n}^{(1,2)}_{\alpha\beta}(lJ)$ are empirical values, practically independent of the subscripts $\alpha\beta$ between the principal quantum numbers $n_{1(2)} = n_{\rm res}$ and $n_{\rm res} \pm 1$ of two states in the lJ series, for which energy defects δ have opposite signs. Equation (38) is written for two possible resonances, which appear for $|nD_{3/2}\rangle$ states. In the case of only one resonance $\tilde{n}^{(2)}_{\alpha\beta}(lJ) = 0$. If no resonances occur in the δ dependence on the Rydberg-state principal quantum number n, then $\tilde{n}^{(1)}_{\alpha\beta}(lJ) = \tilde{n}^{(2)}_{\alpha\beta}(lJ) = 0$, as in the case of $|nS_{1/2}\rangle$ and $|nP_{1/2}\rangle$ series of Rb states (see Table I).

Numerical values of the factor $A_{\alpha\beta}(lJ)$, resonance parameters $\tilde{n}^{(1,2)}_{\alpha\beta}(lJ)$, and polynomial coefficients $a^{(1,2,3)}_{\alpha\beta}(lJ)$ of the asymptotic presentation (38) for irreducible components of the van der Waals constants of Rb atoms in identical Rydberg states $|nlJM\rangle$ are listed in Table I.

Quite different from (38) asymptotic approximations to the long-range interaction of atoms were presented in Ref. [38] where the interatomic potentials in two-atomic molecules were discussed. In particular, the dependence on the principal quantum numbers n for the van der Waals constant, together with the basic term of c_0n^{11} for $ns{-}ns$ and $np{-}np$ asymptotic states, involved also the terms c_1n^{12} and c_2n^{13}, which begin to dominate already at $n > 50$ for all symmetries of biatomic molecules, thus giving a wrong n dependence for C_6 of highly excited Rydberg atoms. For the $np{-}np$ asymptotic state of the molecular symmetries ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$, an additional resonance-type term $c_{-1}n^{11}/(n - 29.5)$ appears. Also, for the $nd{-}nd$ states, the c_1n^{12} terms are involved with additional resonance terms $c_{-1}n^{11}/(n - 35.14)$. Equation (38) and the data of Table I demonstrate that the positions of resonances, presented in Ref. [38], differ from those determined by currently most reliable data on quantum defects [8,10–12] and energy levels [35].

Evidently, the polynomial approximations to C_6 of Ref. [38] may work only in a narrow region of n between 30 and 90 and become wrong for $n > 100$. However, the basic target of studies in Ref. [38] was the long-range molecular potentials. So, the individual atomic states were not addressed there. In addition, the data for the quantum defects were not yet so detailed as in our days. Therefore, the polynomial approximations of Ref. [38] could not account for either the current data on the Förster-type resonances or the fine structure of Rydberg states.

Numerical values for coefficients C_6 determined from Eqs. (18)–(28) and from the data of Table I demonstrate a good agreement with the approximation for $|A\rangle = |B\rangle = |nS_{1/2}\rangle$ states presented in Ref. [38] inside the region of $30 \leqslant n \leqslant 95$. It is impossible to compare the results for P and D states because the data of Table I account for the fine-structure splitting and for the relative orientation of the quantization and interatomic axes, which were hidden in the molecular symmetries of the data [38]. Also, our numerical results demonstrate a satisfactory agreement with the data of Ref. [17] for the dependence of the van der Waals constant on orientation of the interatomic axis (on the angle θ) for the interaction of Rb atoms in their $60D_{5/2}$ Zeeman substates. The origin of small discrepancies may be caused by some difference of the newest data for the quantum defects of P, D, and F states, used in our calculations, from those used in Ref. [17], which were not so detailed and accurate in 2007 as currently available data.

The negative asymptotic value of $R_{ss}(nS_{1/2}) = -70.9493n^{11}$ indicates the repulsive van der Waals interaction between nS-state atoms, nearly independent of the interatomic orientation (of the angle θ) determined by the asymptotic constant $R_{aa}(nS_{1/2}) = -8.3147n^{11}$. The repulsive interaction remains up to infinite principal quantum numbers of $|nS_{1/2}\rangle$ states.

For states $nP_{3/2}$, $nD_{5/2}$, and $nF_{5/2,7/2}$, the singularities appear in the vicinity of $\tilde{n}_{\alpha\beta}(P_{3/2}) \approx 38$, $\tilde{n}_{\alpha\beta}(D_{5/2}) \approx 43$, and $\tilde{n}_{\alpha\beta}(F_{5/2,7/2}) \approx 91$, correspondingly. The component R_{ss} provides the basic contribution to the constant C_6, as follows from Eq. (18). Since the values of R_{ss} are positive for all $|nlJ\rangle$ series presented in Table I for $J \geqslant 3/2$, the van der Waals interaction of atoms in states of $n < \tilde{n}$ is repulsive ($C_6 < 0$), while for $n > \tilde{n}$ the interaction becomes attractive ($C_6 > 0$). This property seems rather general, but the dependence on the magnetic quantum number and on the angle θ seen explicitly in the right-hand side of Eq. (18) may cause some deviations from this regularity. In particular, the series of states $nP_{3/2}$

TABLE I. The coefficients (in atomic units) of approximations for the irreducible parts of van der Waals constant C_6 of Rb atoms in their identical Rydberg states $|nlJM\rangle$.

$R_{\alpha\beta}(nl_J)$	$A_{\alpha\beta}(lJ)$ (a.u.)	$\tilde{n}^{(1)}_{\alpha\beta}(lJ)$	$\tilde{n}^{(2)}_{\alpha\beta}(lJ)$	$a^{(1)}_{\alpha\beta}(lJ)$	$a^{(2)}_{\alpha\beta}(lJ)$	$a^{(3)}_{\alpha\beta}(lJ)$
$R_{ss}(nS_{1/2})$	−70.9493	0	0	−58.1774	1483.95	−15315.5
$R_{aa}(nS_{1/2})$	−8.31468	0	0	−86.5096	2941.02	−36108.9
$R_{ss}(nP_{1/2})$	−0.72910	0	0	−192.969	4250.76	−67452.7
$R_{aa}(nP_{1/2})$	27.4073	0	0	−16.4848	75.5419	3929.00
$R_{ss}(nP_{3/2})$	6.49104	38.0528	0	−6.79382	−289.414	3761.25
$R_{aa}(nP_{3/2})$	112.333	38.0528	0	−36.4838	552.365	−3521.18
$R_{sT}(nP_{3/2})$	−8.32662	38.0528	0	−21.0358	130.272	35.0750
$R_{TT}(nP_{3/2})$	10.1141	38.0528	0	−29.3512	360.584	−1924.71
$R_{ss}(nD_{3/2})$	40.3517	39.5728	58.4180	−84.9677	1336.23	17955.6
$R_{aa}(nD_{3/2})$	−206.652	39.5513	58.4180	−85.1857	1366.57	17228.2
$R_{sT}(nD_{3/2})$	−20.0634	39.6145	58.4181	−82.9888	1177.92	21554.6
$R_{TT}(nD_{3/2})$	6.45440	39.5728	58.4180	−82.5907	1146.66	22261.3
$R_{ss}(nD_{5/2})$	32.9534	43.1113	0	−44.2979	307.619	−5245.68
$R_{aa}(nD_{5/2})$	−204.812	43.1139	0	−45.7028	369.796	−5524.51
$R_{sT}(nD_{5/2})$	−21.4608	43.1133	0	−44.6768	322.812	−5277.76
$R_{TT}(nD_{5/2})$	9.57341	43.1209	0	−44.4747	306.531	−5000.21
$R_{ss}(nF_{5/2})$	30.5200	90.8537	0	−90.2408	−43.3648	2488.29
$R_{aa}(nF_{5/2})$	177.092	90.8537	0	−90.3121	−44.2493	2404.11
$R_{sT}(nF_{5/2})$	−10.2820	90.8537	0	−90.2957	−36.3784	2523.22
$R_{TT}(nF_{5/2})$	3.55565	90.8537	0	−90.4571	−20.7632	2561.81
$R_{ss}(nF_{7/2})$	30.4162	90.7199	0	−90.1068	−43.2921	2479.81
$R_{aa}(nF_{7/2})$	195.089	90.7199	0	−90.1811	−43.9872	2396.60
$R_{sT}(nF_{7/2})$	−11.9271	90.7199	0	−90.1622	−36.1657	2514.51
$R_{TT}(nF_{7/2})$	4.79304	90.7199	0	−90.3280	−19.9966	2553.14

holds this regularity only for states of the magnetic quantum number $M = \pm 1/2$. The states of $M = \pm 3/2$ demonstrate significant departure from the indicated property for $\theta = 0$ (the interatomic axis points along the quantization axis, which for $|M| = J$ is perpendicular to the Rydberg-electron orbit). So, the repulsive interaction of Rb atoms remains at small angles θ for all $nP_{3/2}M = 3/2$ states ($n > 39$). The following regularity holds here: the greater n the greater is the region of the "repulsive angles" $\theta < \theta_0$. In particular, $\theta_0 \approx 12.6^\circ$, 28.8°, and 32.5° for $n = 39$, $n = 100$, and for all $n > 3000$, respectively.

The singularities correspond to vanishing of the difference between the two-atomic energies. In particular,

$$\delta = E_{nS_{1/2}} + E_{(n+1)S_{1/2}} - 2E_{nP_{3/2}} \approx 0,$$

which changes its negative sign at $n \leqslant 38 < \tilde{n}_{\alpha\beta}(P_{3/2}) \approx 38.053$ for positive at $n \geqslant 39 > \tilde{n}_{\alpha\beta}(P_{3/2})$, achieving its minimal absolute value at $n = 38$. For $|M| = 3/2$, the contribution of the radial matrix element with this singularity disappears at $\theta = 0$ together with the singularity in C_6 dependence on the principal quantum number n.

The "resonance" increase of $C_6(38P_{3/2M})$ for Rb atoms may result in transition from the van der Waals interaction energy of the form $-C_6/R^6$ to a specific form of the dipole-dipole energy described by a function $C_3(\theta)/R^3$. However, this dependence on R holds only in a region of interatomic distances confined from below and from above to the region $R_{\min} < R < R_{\max}$, where $R_{\min}$ and $R_{\max}$ depend on the energy defect (31) and on the matrix elements of the dipole transitions to the resonance states. In addition, the angular dependence of $C_3(\theta)$ does not obey the law of the Legendre polynomial $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$, characteristic of the interaction between constant dipoles, and depends on the total angular momentum J and magnetic M quantum numbers of the Rydberg state $|nlJM\rangle$, as is discussed in the next section.

For $nD_{3/2}$ states the singularities appear near $n = 39$ and 58. In both cases, an evidence appears of anomalous dependence of the C_6 constant on the principal quantum number in the vicinity of these numbers. However, the attractive nature of the van der Waals interaction for states of the principal quantum number $n < \tilde{n}^{(1)}_{\alpha\beta} \approx 39.6$ remains also attractive for $n \geqslant 40$ and becomes repulsive only for states of $n \geqslant 55$, up to $n = 58$. For $39D_{3/2}$ state of the magnetic quantum number $M = \pm 3/2$ the sign of the van der Waals constant depends on the angle θ, changing from repulsion ($C_6 < 0$) in the region of $0.1\pi < \theta < 0.3\pi$ to attraction ($C_6 > 0$) at $\theta < 0.1\pi$ and $\theta > 0.3\pi$ with maximum at $\theta = \pi/2$.

The singularity in the $nD_{5/2}$ series of states appears for the state of $n = 43$. However, the sign of $C_6(\theta; nD_{5/2})$ does not change, remaining negative for $n \leqslant 43$ and positive for $n \geqslant 44$ (see Fig. 2) independently of θ.

The numerical data of Table I provide rather accurate values of the van der Waals constant, which agree with the most reliable data of the literature. In particular, the fractional departure of the tabulated data from the experimental data for C_6 values of Rb atoms in their $nD_{3/2M}$ states [39], does not exceed 6% for $n = 53$ and falls down to about 3% for $n = 62$ and 82.

V. DEGENERATE PERTURBATION THEORY FOR ASYMPTOTIC INTERACTION BETWEEN RYDBERG ATOMS

If the perturbation-theory condition $|\Delta E_{\text{vdW}}/\delta| \ll 1$ does not hold for one of the energy splitting $\delta = E_2 - E_1$ between the energies $E_1 \equiv E_{AB} = E_A + E_B = 2E_n$ of the initial two-atomic state $\langle \mathbf{r}_1\mathbf{r}_2|1\rangle = \langle \mathbf{r}_1\mathbf{r}_2|AB\rangle = \langle \mathbf{r}_1|n\rangle\langle \mathbf{r}_2|n\rangle$ and $E_2 = E_{n_1} + E_{n_2}$ of an intermediate state $\langle \mathbf{r}_1\mathbf{r}_2|2\rangle = \langle \mathbf{r}_1|n_1\rangle\langle \mathbf{r}_2|n_2\rangle$ in the sum determining the two-atomic Green's function (8), then the perturbation theory for close states should be applied. Evidently, for identical individual states $|A\rangle = |B\rangle = |nlJM\rangle$ of the interacting atoms in the two-atomic state $|1\rangle$, the single-atomic states $\langle \mathbf{r}_1|n_1l_1J_1\rangle$ and $\langle \mathbf{r}_2|n_2l_2J_2\rangle$ will be different in the close state $\langle \mathbf{r}_1,\mathbf{r}_2|2\rangle = \langle \mathbf{r}_1|n_1l_1J_1\rangle\langle \mathbf{r}_2|n_2l_2J_2\rangle$. In the state $|2\rangle$, the sum over the magnetic quantum numbers M_1 and M_2 is performed as is assumed in equation for the Green's function (8), therefore, the momenta projections are not even mentioned there.

The interchange of individual states between atoms corresponds to a third close state $\langle \mathbf{r}_1,\mathbf{r}_2|3\rangle = \langle \mathbf{r}_1|n_2l_2J_2\rangle\langle \mathbf{r}_2|n_1l_1J_1\rangle$, equal in energy to that of the state $\langle \mathbf{r}_1,\mathbf{r}_2|2\rangle$ and also involved in the complete set of two-atomic states of the Green's function resolution (8). Therefore, the close-state subspace includes at least three different two-atomic states $|1\rangle$, $|2\rangle$, and $|3\rangle$, the last two are the states of equal energies $E_3 = E_2 = E_{n_1} + E_{n_2}$. The states $|2\rangle$ and $|3\rangle$ may be joined in a pair of alternative resonance states $|\pm\rangle = (|2\rangle \pm |3\rangle)/\sqrt{2}$. However, the state $|-\rangle$ does not interact with the initial state $|1\rangle$ and provides no contribution into the resonance enhancement of C_6 (the "dark state"), so in what follows, we accept the close-state basis of the states $|1\rangle$, $|2\rangle$, $|3\rangle$.

In this case, the energy of interaction between Rydberg-state atoms ΔE may be determined in arbitrary orders of the operator (3) from the solution to the third-order equation

$$\det||W_{ij} + (\varepsilon_i - \Delta E)\delta_{ij}|| = 0, \tag{39}$$

which is equivalent to the diagonalization of the 3×3 matrix (here, δ_{ij} is the Kronecker symbol, for brevity the argument $\mathbf{R}$ of the matrix elements is omitted) [18,40]:

$$W_{ij} = \langle i|\hat{V}_{AB}(\mathbf{R})\{1 + G'_{\overline{E}}[\hat{V}_{AB}(\mathbf{R}) - \Delta E]\}^{-1}|j\rangle, \tag{40}$$

where $i,j = 1,2,3$ corresponding to the close states, which are withdrawn from the twofold spectral summation of the Green's function (8). The interaction-induced shift $\Delta E = E - \overline{E}$ refers to the Green's function energy, which may be taken as the mean energy of the close states $\overline{E} = (E_1 + E_2 + E_3)/3$ [18]. However, since we look for the shift $\Delta E = E - E_1$ of the energy level E_1 and the energies of the other two levels are identical, $E_2 = E_3$, it is convenient to put $\overline{E} = E_1$. Then, the shifts $\varepsilon_i = E_i - \overline{E}$ of Eq. (39) $\varepsilon_1 = 0$ and $\varepsilon_2 = \varepsilon_3 = \delta$ determine the three solutions $\Delta E_{1(2,3)} = \varepsilon_{1(2,3)}$ to the cubic equation for infinitely separated atoms ($R \to \infty$, where the matrix elements W_{ij} vanish).

The formal resolution in power series of the interaction $\hat{V}_{AB}(\mathbf{R})$ for the matrix element (40)

$$W_{ij} = \sum_{k=1}^{\infty} W_{ij}^{(k)} \tag{41}$$

allows derivation of corresponding series for the van der Waals energy [32]

$$\Delta E = \sum_{k=1}^{\infty} E^{(k)}. \tag{42}$$

As follows from the resolution (3), each term of the matrix element series (41) and the terms of the series for energy (42) may be resolved in powers of $1/R$.

So, in the first order ($k = 1$) we have a sum of finite number of terms, which includes only allowed multipole transitions between initial and final states of atoms A and B, just similar to the first-order shift (6) for the isolated state $|AB\rangle$,

$$W_{ij}^{(1)} = \langle i|\hat{V}_{AB}(\mathbf{R})|j\rangle = \sum_{q=q_1}^{L_\Sigma+1} \frac{w_{ij}^{(1)}(q,\mathbf{n})}{R^q}, \tag{43}$$

where $L_\Sigma = l_A(i) + l_A(j) + l_B(i) + l_B(j)$ is the sum of all angular momenta of both atoms in their initial $|i\rangle$ and final $|j\rangle$ states ($i,j = 1,2,3$). The starting index q_1 also depends on the angular momenta of the two-atomic states $|i\rangle$ and $|j\rangle$. If the states $|i\rangle$ and $|j\rangle$ are dipole coupled for both atoms ($\Delta l_{A(B)} = |l_{A(B)}(i) - l_{A(B)}(j)| = 1$), then the summation in the nondiagonal matrix element (43) starts from $q_1 = 3$. Otherwise, if the states are dipole coupled for only one of the atoms and for another one the quadrupole transition is allowed, then $q_1 = 4$; if the dipole transitions are forbidden and quadrupole transitions are allowed for both atoms, then the sum for the first-order matrix element (43) starts from the quadrupole-quadrupole term, as in the resolution for the first-order energy (6), determined by the diagonal element $W_{ii}^{(1)}$, where the minimal power is $q_1 = 5$.

The second-order term of the resolution (41) may be presented as series of infinite number of terms

$$W_{ij}^{(2)} = -\langle i|\hat{V}_{AB}(\mathbf{R})G'_{\overline{E}}\hat{V}_{AB}(\mathbf{R})|j\rangle = \sum_{q=q_2}^{\infty} \frac{w_{ij}^{(2)}(q,\mathbf{n})}{R^q}, \tag{44}$$

where the sum for diagonal matrix elements $W_{ii}^{(2)}$ performs over even powers of $1/R$, starting from $q_2 = 6$. The parity and starting value q_2 of the power q for nondiagonal matrix elements $W_{12}^{(2)} = W_{13}^{(2)}$ depends on the relation between parities of the individual single-atomic states in the initial $|1\rangle$ and final $|2\rangle$, $|3\rangle$ two-atomic states. In the case of opposite parities for one of the two atoms, $q_2 = 7$ and the sum (44) involves only odd indices q. In the case of opposite parities of states for both atoms, the sum starts from $q_2 = 8$ and includes only even powers q. However, we confine ourselves to the most interesting case of dipole-coupled close states $|1\rangle$ and $|2\rangle$ ($|3\rangle$), therefore, the account for only first-order dipole term $W_{12}^{(1)} \propto 1/R^3$ is sufficient.

With the use of only the lowest-order matrix elements (43) and (44) and the identities

$$W_{12}^{(1)} = W_{21}^{(1)} = W_{13}^{(1)} = W_{31}^{(1)},$$

$$W_{22}^{(2)} = W_{33}^{(2)}, \quad W_{23}^{(2)} = W_{32}^{(2)},$$

the solutions to Eq. (39) may be presented, as

$$\begin{aligned}\Delta E_{1,2} \equiv \Delta E_{\pm} &= W_{11}^{(2)} + \frac{\Delta(\mathbf{R})}{2} \pm \sqrt{\left[\frac{\Delta(\mathbf{R})}{2}\right]^2 + 2\left|W_{12}^{(1)}\right|^2},\\ \Delta E_3 &= \delta + W_{22}^{(2)} - W_{23}^{(2)},\end{aligned} \tag{45}$$

where $\Delta(\mathbf{R}) = \delta - W_{11}^{(2)} + W_{22}^{(2)} + W_{23}^{(2)}$ is the van der Waals shifted resonance energy defect. The solution ΔE_3 corresponds to the interaction-induced splitting of completely degenerate states $|2\rangle$ and $|3\rangle$. Simultaneously, $\Delta E_2 = \Delta E_+ = \delta + W_{22}^{(2)} + W_{23}^{(2)}$ and $\Delta E_1 = \Delta E_- = W_{11}^{(2)}$ would describe correspondingly the second solution to the interaction-induced splitting of states $|2\rangle$ and $|3\rangle$ and the shift of energy of an isolated state $\langle \mathbf{r}_1\mathbf{r}_2|1\rangle$ in absence of interaction of the initial state $|1\rangle$ with the close states $|2\rangle$ and $|3\rangle$ [setting $W_{12}^{(1)} \equiv 0$ and assuming $\Delta(\mathbf{R}) > 0$; in case of a negative value of the energy defect $\Delta(\mathbf{R})$, the solutions ΔE_+ and ΔE_- should interchange]. It should be noted that the degeneracy, related with the transposition of single-atomic states, should be taken into account in calculating the van der Waals interaction between differently excited identical atoms [5].

The diagonal matrix elements are rapidly vanishing functions of the interatomic distance, as is seen from their asymptotic dependencies both in the first order $W_{ii}^{(1)} \propto n^8/R^5$ and in the second order $W_{ii}^{(2)} \propto n^{11}/R^6$. So, for large distances $R > n^3$ the main contribution to $\Delta(\mathbf{R})$ comes from the R-independent two-atomic difference of energies δ. In particular, for $n \approx 50$ states and $|\delta| > 100$ MHz, the fractional difference between $\Delta(\mathbf{R})$ and δ is below 10% at $R > 10\ \mu$m. The nondiagonal matrix element $W_{12}^{(1)} \propto n^4/R^3$ is also a rapidly vanishing function of the distance R, so in the indicated region of $R > n^3$ the inequality holds $|\Delta(\mathbf{R})|^2 \gg 8|W_{12}^{(1)}|^2$ and the approximate solutions to Eq. (39) are assuming [$\Delta(\mathbf{R}) > 0$]

$$\begin{aligned}\Delta E_1 &\equiv \Delta E_- = W_{11}^{(2)} - \frac{2\left|W_{12}^{(1)}\right|^2}{\Delta(\mathbf{R})}\big(\lim_{R\to\infty} \Delta E_1 \to \varepsilon_1 = 0\big);\\ \Delta E_2 &\equiv \Delta E_+ = \Delta(\mathbf{R}) + W_{11}^{(2)} + \frac{2\left|W_{12}^{(1)}\right|^2}{\Delta(\mathbf{R})}\\ &\quad\times\big(\lim_{R\to\infty} \Delta E_2 \to \varepsilon_2 = \delta\big),\end{aligned} \tag{46}$$

which describe the van der Waals shifts of the upper $|1\rangle$ and one of the lower ($|2\rangle$ and $|3\rangle$) two-atomic states, respectively. Evidently, the fraction with doubled square of the first-order nondiagonal element $W_{12}^{(1)}$ in the numerator restitutes the omitted terms in the reduced Green's function of the second-order matrix elements of the perturbation theory for nondegenerate states.

In an opposite case of $8|W_{12}^{(1)}|^2 \gg |\Delta(R)|^2$, when the splitting δ between close levels may be neglected, the principal contribution is given by the second term of the under-root expression of Eq. (45). Then, the two solutions (45) are

$$\Delta E_{\pm} \approx \pm\sqrt{2}\left|W_{12}^{(1)}\right|\left\{1 + \frac{[\Delta(\mathbf{R})]^2}{16\left|W_{12}^{(1)}\right|^2}\right\} + W_{11}^{(2)} + \frac{\Delta(\mathbf{R})}{2}. \tag{47}$$

This case is characteristic of the so-called Förster resonance, when the van der Waals power-6 dependence $\Delta E = -C_6/R^6$ may transform into the power-3 dependence $\Delta E = C_3/R^3$ [1,6], determined by the first-order nondiagonal matrix element $W_{12}^{(1)}$. Actually, this kind of resonance for close states $|1\rangle$, $|2\rangle$, and $|3\rangle$ is completely equivalent to a two-atomic resonance in the electromagnetic susceptibilities of two asymptotically interacting atoms in a frequency-dependent external field [21]. However, both $|W_{12}^{(1)}|$ and $|\Delta(R)|$ are R-dependent functions, therefore, the inequality $8|W_{12}^{(1)}|^2 \gg |\Delta(R)|^2$ breaks down both for small distances, where $|W_{12}^{(1)}|/|\Delta(R)|$ vanishes as $\propto R^3$ when $R \to 0$, and for large distances, where $|W_{12}^{(1)}|/|\Delta(R)|$ vanishes as $\propto R^{-3}$ when $R \to \infty$ [with account of only the lowest-order terms of (41) and (43)]. So, the range of the distance R, where the relation (47) holds, is restricted both from below and from above. Moreover, the dependence of the matrix element on the orientation of the interatomic vector $\mathbf{R}$ (on the angle θ) follows a function somewhat similar to the square-root dependence of Eq. (18) for the resonance part of $C_6(\theta)$ and may be presented, as follows:

$$W_{12}^{(1)}(R,\theta) = \frac{d^{AB}}{R^3}\mathcal{Z}_{J_1;J_2}^{J,M}(\theta), \tag{48}$$

where the reduced matrix element of the dipole-dipole interaction $d^{AB} \equiv \langle 1\|\mathbf{Q}_1^A\mathbf{Q}_1^B\|2\rangle$ is put in a factor and the sum was performed over magnetic quantum numbers M_1,M_2 of the resonant two-atomic state $|2\rangle = |n_1l_1J_1M_1\rangle|n_2l_2J_2M_2\rangle$ in calculating the term $\left|W_{12}^{(1)}(R,\theta)\right|^2$ of Eq. (45). So, Eqs. (47) and (48) make evident explicitly the existence of a Förster-type dipole-dipole energy shift

$$\Delta E_{\pm} = \pm\frac{C_3(M,\theta)}{R^3}, \tag{49}$$

but only in a restricted region of the distances. This region could be extended in the case of exact resonance, $\delta = 0$, when Eqs. (47) and (49) and corresponding condition $8|W_{12}^{(1)}|^2 \gg |\Delta(R)|^2$ hold in the region $R > R_{LR}$ up to $R \to \infty$. That is why different methods of reducing the energy defect in external static and radio-frequency fields are used for detailed studies of the spatial dependence of the Förster interaction [7,9,24,28,41].

The M- and θ-dependent factor $C_3(M,\theta)$ may be presented explicitly from Eqs. (47) and (48):

$$C_3(M,\theta) = \sqrt{2}|d^{AB}|\mathcal{Z}_{J_1;J_2}^{J,M}(\theta), \tag{50}$$

where the notations are introduced:

$$\begin{aligned}\mathcal{Z}_{J_1;J_2}^{J,M}(\theta) = \Bigg\{&\frac{2}{3(2J+1)^2} + \left[\frac{2M}{(2J)_3}\right]^2\frac{X_1X_2}{2}(2 - 3\cos^2\theta)\\ &+ \frac{[3M^2 - J(J+1)](Y_1+Y_2)}{3(2J+1)(2J-1)_5}(1 - 3\cos^2\theta)\\ &+ \left[\frac{3M^2 - J(J+1)}{(2J-1)_5}\right]^2\\ &\times Y_1Y_2(1 - 8\cos^2\theta + 9\cos^4\theta)\Bigg\}^{1/2},\end{aligned} \tag{51}$$

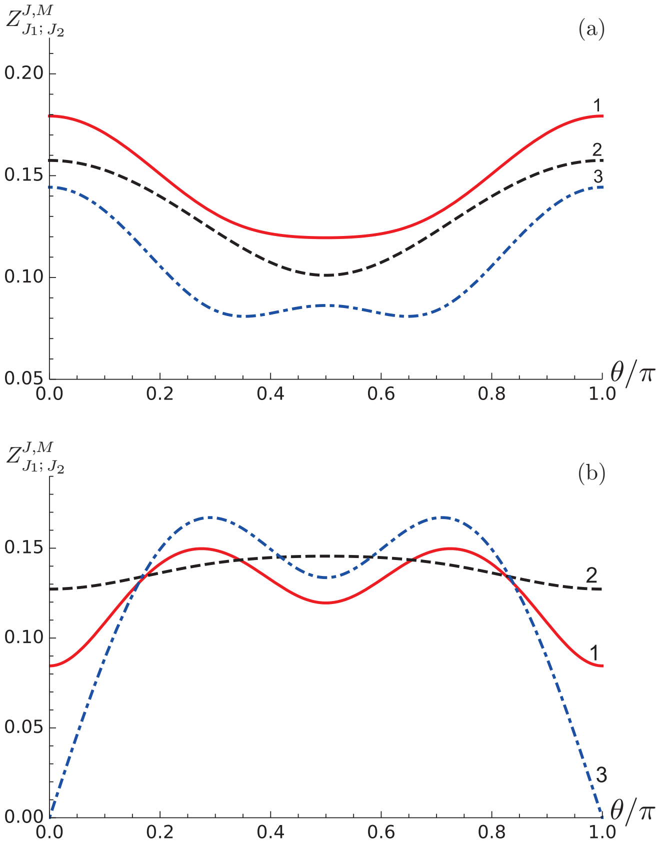

FIG. 3. The angle-dependent factor $\mathcal{Z}^{5/2,M}_{J_1;3/2}(\theta)$ of the first-order matrix element (48) for the dipole-dipole resonance between two-atomic states: $2 \times (nD_{5/2,M}) \to n_1F_{J_1} + n_2P_{3/2}$; (a): $J_1 = 7/2$, (b): $J_1 = 5/2$; $|M| = 1/2$ (curves 1), $|M| = 3/2$ (2), $|M| = 5/2$ (3).

where $X_{1(2)} = J(J+1) + 2 - J_{1(2)}(J_{1(2)} + 1)$ and $Y_{1(2)} = 3X_{1(2)}(X_{1(2)} - 1) - 8J(J+1)$. In contrast to the electrostatic energy of two independent dipoles, the shift (49) does not vanish either in averaging over the orientations of the interatomic axis or in averaging of the angular-momentum orientations (over magnetic quantum numbers M). It is important to remind that the summation over the magnetic quantum numbers of the states $|2\rangle$ and $|3\rangle$ was performed in determining the squared matrix element $|W^{(1)}_{12}(R,\theta)|^2$ of the under-root expression of Eq. (45) since all Zeeman substates have equal energies and therefore were introduced into the subspace of close states $|1\rangle$ and $|2\rangle$.

In Fig. 3, the plots of the factors (a) $\mathcal{Z}^{5/2,M}_{7/2;3/2}(\theta)$ and (b) $\mathcal{Z}^{5/2,M}_{5/2;3/2}(\theta)$ are presented, determining the angular dependence for the first-order matrix element (48) of the dipole-dipole transition between the two-atomic state $|1\rangle = \langle \mathbf{r}_1|nD_{5/2M}\rangle\langle \mathbf{r}_2|nD_{5/2M}\rangle$ of like alkali-metal atoms and the state $|2\rangle = \langle \mathbf{r}_1|n_1F_{7/2,5/2}\rangle\langle \mathbf{r}_2|n_2P_{3/2}\rangle$ for different magnetic quantum numbers $M = 1/2, 3/2$, and $5/2$. An evident difference between the angular dependencies for the fine-structure substates $J = 5/2$ and $7/2$ of the n_1F_J resonance is seen explicitly. However, at $\theta = 0$ the factor $Z(\theta)$ for $J = 7/2$ exceeds that for $J = 5/2$, remaining somewhat about 0.12–0.14 and almost equal to one another for $\theta \neq 0$.

As follows from the data of Table I, the asymptotic interaction of two Rb atoms in their $nP_{3/2}$, $nD_{3/2,5/2}$, and $nF_{5/2,7/2}$ Rydberg states may be suitable for observation of the biatomic resonance in the region of $n \approx \tilde{n}$, where the absolute values of the energy defects (31) are extremely small, ensuring the principal contribution of corresponding terms from the Green's function spectral expansion to the irreducible components of C_6. However, the region of distances R, where the nondiagonal term of the under-root expression of Eq. (45) exceeds essentially the first term, seems to be rather narrow. So, the R^{-3} energy-shift dependence of Eq. (49) may be expected but only in these narrow regions of distances. The dependence on the orientation of the interatomic axis does not follow that of dipole-dipole interaction described by the Legendre polynomial $P_2(\cos\theta)$.

The case of two Rb atoms in their $|43D_{5/2}M = 1/2, 3/2, 5/2\rangle$ states with the lowest absolute value of the Förster energy defect among the nearest states: $\delta(43D_{5/2}) = E(41F_{5/2(7/2)}) + E(45P_{3/2}) - 2E(43D_{5/2}) \approx -6.1(-8.7)$ MHz, where $\delta(nD_{5/2})$ changes its sign from negative to positive in transition from $n = 43$ to 44 state. Numerical data of Table I may be used for evaluating the second-order matrix element $W^{(2)}_{11} = -\tilde{C}_6(43D_{5/2}M)/R^6$, where $\tilde{C}_6(43D_{5/2}M) = C_6(43D_{5/2}M) - (C_3(M,\theta))^2/\delta$ is the van der Waals constant determined with the reduced Green's function. The data for the second-order diagonal $W^{(2)}_{22}$ and nondiagonal $W^{(2)}_{23}$ matrix elements calculated in the model-potential approach are as follows (in atomic units):

$$\begin{aligned} W^{(2)}_{22} &= W^{(2)}_{33} = -32\tilde{R}_{ss}/R^6 = 1.845 \times 10^{20}/R^6; \\ W^{(2)}_{23} &= 2.786 \times 10^{17}/R^6. \end{aligned} \tag{52}$$

The sum over Zeeman substates eliminates the contribution of the R_{aa}, R_{sT}, R_{TT} components of the $\tilde{C}_6 = C_6(41F_{7/2} - 45P_{3/2}) - 2(W^{(1)}_{12}R^3)^2/\delta$ for the interaction between Rb atoms in their $41F_{7/2}$ and $45P_{3/2}$ states, leaving behind only the $32\tilde{R}_{ss}(41F_{7/2} - 45P_{3/2})$ term. Evaluation of the radial matrix elements of the dipole-dipole transition matrix element factor (48),

$$\begin{aligned} d^{AB} &= -\sqrt{\frac{288}{35}}\langle 43D_{5/2}|r_A|41F_{7/2}\rangle\langle 43D_{5/2}|r_B|45P_{3/2}\rangle \\ &= 5.373 \times 10^6 \text{ a.u.} \end{aligned} \tag{53}$$

allows to determine the dispersion-interaction induced shifts (45)–(47).

The above-mentioned difference between resonance detuning due to the fine structure of $41F_J$ state ($J = 5/2, 7/2$) does not compensate for the difference between the factor of integration over angular variables $\sqrt{72/175}$ for $J = 5/2$, approximately 4.5 times smaller than the factor $\sqrt{288/35}$ for $J = 7/2$ of Eq. (53). Meanwhile, corresponding radial matrix elements coincide up to the fifth or sixth decimal place. In addition, the θ-dependent factors $\mathcal{Z}^{5/2,M}_{7/2;3/2}(\theta)$ and $\mathcal{Z}^{5/2,M}_{5/2;3/2}(\theta)$ do not display any essential difference (compare respective plots on Fig. 3) and even may strengthen the domination of the contribution from the $41F_{7/2}$ state, specifically, in the vicinity of $\theta \approx 0$. So, the contribution of the resonance on $41F_{5/2}$ state into the energy (45) constitutes less than 5% of the

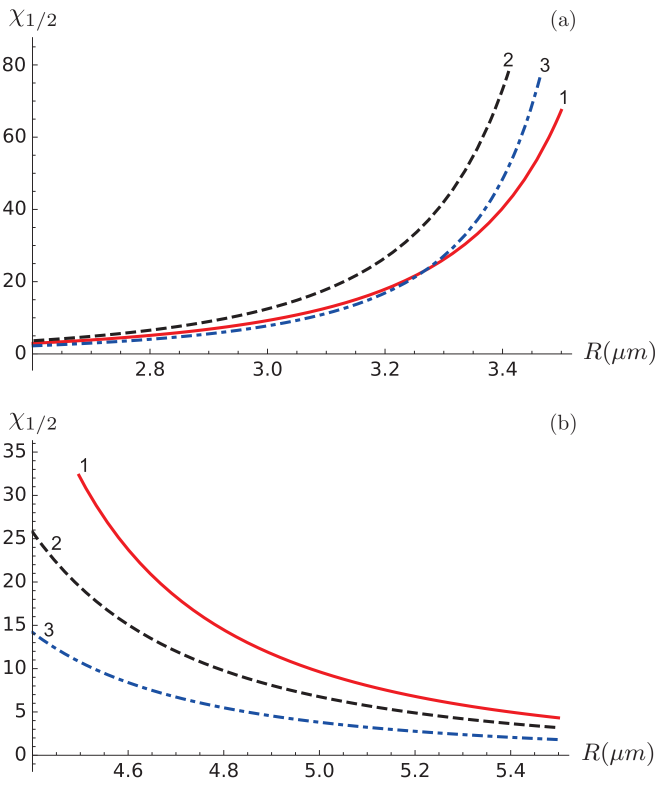

FIG. 4. Dependence of the ratio for the under-root terms of Eq. (45) $\chi_{1/2}(R,\theta) = 8|W_{12}(R,\theta)/\Delta(R,\theta)|^2$ on the interatomic distance R of Rb atoms in their $43D_{5/2,M=1/2}$ states at the angles $\theta = 0$ (curves 1), $\theta = \pi/6$ (2), and $\theta = \pi/2$ (3). Two regions, where $\chi_{1/2}(R,\theta) > 10$, are separated by a gap of singularity: (a) gives the region of $2.6\ \mu\text{m} < R < 3.5\ \mu\text{m}$ and in (b) the region of $4.4\ \mu\text{m} < R < 5.5\ \mu\text{m}$ is presented. Between these regions (for $3.5\ \mu\text{m} < R < 4.5\ \mu\text{m}$) $\chi_{1/2}(R,\theta)$ tends to infinity due to the node of the R-dependent Förster energy defect $\Delta(R,\theta) = 0$ at $R \approx 3.88\ \mu\text{m}$, which is practically independent of θ.

contribution from the $41F_{7/2}$ state and may be neglected in our considerations.

The R dependence of the ratio $\chi_{1/2}(R,\theta) = 8|W_{12}^{(1)}(R,\theta)/\Delta(R,\theta)|^2$ of the under-root terms of Eq. (45), presented in Fig. 4, allows to evaluate the region of the interatomic distances R, where the van der Waals dependence of the energy level $43D_{5/2\,M=1/2}$ shift $\Delta E_{\text{vdW}} = -C_6/R^6$ turns into the dipole-dipole shift $\Delta E_{\text{d-d}} = C_3/R^3$. As is seen from the figure, in the region of $2 < R < 5\ \mu\text{m}$, the absolute value of the matrix element $W_{12}^{(1)}$ of transition between two-atomic states $|1\rangle$ and $|2(3)\rangle$ exceeds essentially that of the distance-dependent biatomic energy detuning $\Delta(R)$ [the first term of the under-root expression of Eqs. (45)], which vanishes at $R \approx 3.9\ \mu\text{m}$. The ratio depends on the angle between the quantization and interatomic axes, achieving its maximal values at the condition $\Delta(\mathbf{R}) \approx 0$.

In states of the magnetic quantum numbers $M = 3/2, 5/2$ the θ dependence of the R region, where the inequality $\chi(R,\theta) \gg 1$ holds, is stronger since the first-order matrix element decreases in comparison with the case of $M = 1/2$. The region of the dipole-dipole interaction between Rydberg atoms is restricted by the finite value of the energy defect δ between dipole-coupled two-atomic energy levels: the smaller is $|\delta|$, the wider is the region of interatomic distances, where the first-order dipole-dipole law of interaction between atoms (49) holds. Therefore, different methods of extending the region of the Förster dipole-dipole interaction were developed and confirmed experimentally with the use of static or radio-frequency electric fields for reducing the magnitude of the energy defect δ [7,9,24,28,41]. However, consecutive theoretical considerations of the external-field-induced Förster resonance with account of simultaneous actions of the field and the long-range interaction of Rydberg atoms are still missing in the literature. The solution to this problem may be based on the use of the higher-order perturbation theory for the atom-field and atom-atom interactions on the straightforward analogy to the case of ground-state atoms in a field [21]. Corresponding susceptibilities of the two-atomic system would describe the energy shift dependence on the amplitude of external field, on the distance between atoms, and on the relative orientation of the interatomic $\mathbf{R}$ and external field vectors.

Outside the Förster region, the energy of interaction between Rydberg atoms follows the van der Waals law $\Delta E_{\text{vdW}} = -C_6/R^6$. Numerical evaluations demonstrate that the contribution to the long-range interaction-induced shift of $43D_{5/2}$-state energy levels of Rb atoms from all the remaining "nonresonant" terms of the two-atomic basis for the Green's function (8) within the "Förster region of distances" $2\ \mu\text{m} < R < 5\ \mu\text{m}$ is more than three orders of magnitude smaller than the contribution of the resonance terms. Outside this region (for $R > 5\ \mu\text{m}$), this shift follows the law of the usual van der Waals equation $\Delta E_{\text{vdW}} = -C_6/R^6$ with the constant C_6 of Eq. (18) where the asymptotic Eq. (38) and the numerical data of Table I may be used for determining irreducible components (25)–(28).

VI. SUMMARY AND CONCLUSIONS

For Rydberg levels of very high principal quantum numbers n, the absolute value of the energy splitting δ between the biatomic dipole-coupled states gradually decreases with the increase of the principal quantum numbers n and may become smaller than the magnitude of the van der Waals interaction energy $\Delta E_{\text{vdW}} = -C_6/R^6$ at the interatomic distances outside the Le Roy sphere $R > R_{LR}$. In this case, the region of applicability of the perturbation theory for isolated levels extends outside the "Förster sphere" $R > R_F > R_{LR}$, of the "Förster radius" R_F. In the region of the distances R between R_{LR} and R_F the perturbation theory for close states should be applied, as is presented in Sec. V.

The asymptotic approximations (37) and (38) to the constants of van der Waals interaction, together with numerical data of Table I, enable rather simple and reliable evaluations of irreducible components for the van der Waals constant $C_6(\theta; nlJM)$, which allow for the detailed description of the long-range interaction dependence on orientations of interatomic and quantization axes. In addition, the data of the table include information on the location of the Förster resonances within the S, P, D, and F series of Rydberg states in Rb atoms. The calculated numerical data presented in Sec. IV may be used in experimental investigations for quantitative evaluations of the asymptotic interaction energies of Rb atoms in their Rydberg states. Also, the empirical values $\tilde{n}^{(1,2)}_{\alpha\beta}(lJ)$ from the numerical data of Table I provide information on the principal quantum numbers of states within a given lJ series, for which the probability and the ranges of the Förster resonance region are the greatest. The values of irreducible parts of C_6, determined from the tabulated data and the data on the energy defect δ, derived from the most reliable databases on atomic energy levels, currently available in the literature, may serve for evaluating the "Förster radius" R_F, which usually exceeds approximately one order the Le Roy radius R_{LR}.

The method used in this paper may be also applied to describing numerically the influence of static or oscillating electric field on the long-range interaction [21] between Rydberg atoms (see Ref. [42]). The data for evaluations of static polarizabilities and hyperpolarizabilities of Rydberg states in alkali-metal atoms presented in Ref. [43] may be useful in this case. However, the higher-order perturbation theory for interaction between two Rydberg atoms and interaction of each atom with external field is required in solving this problem.

In the case of an ensemble of atoms separated from each other by approximately equal distances, the influence of nonadditive three- and many-body forces (see, e.g., Refs. [15,44–46]) should be also taken into account. These forces may introduce an additional asymmetry and affect the usual two-body van der Waals interaction of atoms even in their spherically symmetric S states.

In summary, the results in the field of theoretical studies on the long-range interaction of Rydberg-state atoms, presented in this paper, are as follows:

(i) The general relations (18)–(29) for the resolution of the van der Waals constant C_6 for two identical atoms in their doublet Rydberg states into irreducible components describing the dependence on the relative orientation of the angular momenta (on the magnetic quantum numbers) and the inter-atomic axis.

(ii) The asymptotic presentation (38) of the irreducible components (25)–(28) of C_6 in terms of polynomials in powers of the Rydberg-state principal quantum number n with polynomial coefficients presented in Table I for $S_{1/2}$, $P_{1/2,3/2}$, $D_{3/2,5/2}$, and $F_{5/2,7/2}$ series of Rydberg states of Rb atoms; correct asymptotic dependence extends high-precision evaluations of C_6 to arbitrary high principal quantum numbers n and arbitrary orientations of the angular momenta and interatomic axis.

(iii) Equations (44)–(51) for the interaction-induced shift and splitting of close two-atomic states, derived in the second-order perturbation theory for nearly degenerate states.

(iv) The radius R_F for the "Förster resonance" region of interatomic distances $R < R_F$, where the energy of the long-range interaction exceeds that of the "Förster resonance energy defect δ" for infinitely separated atoms and the van der Waals interaction law $\Delta E_{\mathrm{vdW}} = -C_6/R^6$ of the region $R > R_F$ transforms into the dipole-dipole law $\Delta E_{\mathrm{d\text{-}d}} = C_3/R^3$ of the region $R < R_F$ (see Fig. 4 and the last paragraph of Sec. V).

It is important to note that the use of the perturbation theory for close states implies that the energy defect is at least one order of magnitude smaller than the smallest defect for any other pair of biatomic states. Therefore, the numerical data were presented on the most appropriate example of the Rb states $43D_{5/2}$, with the energy approximately 8 MHz above that of the dipole-connected two-atomic state $41F_{7/2} + 45P_{3/2}$ (the Förster resonance detuning). Also, two Rb atoms in their $38P_{3/2}$ states have joint energy only 4.6 MHz above the joint energy of one atom in $38S_{1/2}$ and another one in $39S_{1/2}$ states. Two Rb atoms, both in their $58D_{3/2}$ states have energy approximately 7 MHz above the two-atomic state $56F_{5/2} + 60P_{3/2}$. In these cases, the contributions of all other dipole-connected states may be neglected since their energy detuning is at least one order of magnitude greater while corresponding transition matrix elements are smaller.

The considerations presented here for the Rydberg series of states in Rb atoms may be also applied to the low-angular-momenta series of Na, K, and Cs atoms. To this end, however, the high-precision information on the quantum defects is required, without which the search for the Förster-type resonances in the two-atomic Rydberg spectra is impossible.

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