Asymptotic approximations to the energy of dispersion interaction between rubidium atoms in Rydberg states

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Abstract
Irreducible components determining the dependence of the van der Waals coefficient $C_6(n|JM)$ on the angle $\theta$ between the interatomic and the quantisation axes of two Rb atoms in their identical Rydberg states $|n|JM\rangle$ are evaluated with account of the most contributing terms of the spectral resolution for the bi-atomic Green’s function. Asymptotic polynomials in powers of the Rydberg-state principal quantum number $n$ are derived for the $C_6$ irreducible components. Numerical values of the polynomial coefficients are determined for Rb atoms in their $^2S_{1/2}$, $^2P_{1/2,3/2}$, $^2D_{3/2,5/2}$ and $^2F_{3/2,7/2}$ 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 two-atomic states (the Förster resonance) is considered. Numerical values, the dependences on the magnetic quantum numbers $M$ and on the angle $\theta$ of the constant $C_3$ are determined together with the ranges of interatomic distances $R$, where the interaction law $R^{-6}$ transforms into the law of $R^{-3}$.

1. 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 $R_{LR} = 2\sqrt{(r_A^2 + r_B^2)}$ (the Le Roy radius [4]), follows the van der Waals law $\Delta E_{vdW} = -C_6/R^6$. The constant coefficient $C_6$ may be determined from the second-order perturbation theory for the dipole–dipole interaction of atoms. If spin effects may be neglected, the van-der-Waals constant $C_6(nS)$ is a scalar number dependent on the energies and matrix elements of dipole transitions between S- and P-states (see, e.g. [5]):

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

(1)

where the summation involves the complete set of two-atomic states $|n_1P\rangle |n_2P\rangle$, including integrations over states of continuum $|\xi_1P\rangle |\xi_2P\rangle$ of both atoms with positive energies $\xi_1 > 0$, $\xi_2 > 0$.

The distribution of the P-state energies $E_{n\sigma\sigma}$, both above and below the energy of the nS-state, makes calculation of the two-fold sum rather complicated. The terms of the closest to $n$ values of $n_1$ and $n_2$ may have the largest magnitudes, but the alternating signs. In the sum of the opposite-sign terms several digit numbers may be cancelled out, thus reducing the precision of calculations. For high principal quantum number $n$ the specific ‘resonance’ effects appear when one or a few of the denominators of fractions in (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 two-fold sum and make the absolute value of $C_6(nS; nS)$ so large that in a definite region of interatomic distances $R_{LR} < R < R_{tt}$ the magnitude of $\Delta E_{vdW}$ becomes comparable or even exceeds that of the energy difference in the denominator. 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 $R_0$ (the ‘Förster radius’). So the resonance states should be removed from the Green’s function Hilbert space (from the sum over $n_1n_2$ in (1) and considered as a separate subspace of degenerate states where the interaction operator should be diagonalized. The reduced Green’s function will appear in higher-order matrix elements of the interaction [8]. The second-order diagonal matrix elements are added to the detuning $\delta = E_{n_1} + E_{n_2} - 2E_0$ of the two-atomic states of infinitely separated atoms. The corresponding sum becomes the distance-dependent detuning $\Delta(R)$, which for a definite $R = R_0$ may vanish, thus enhancing the role of the non-diagonal element of the $R^{-3}$ dependence and consequently enhancing the long-range interaction energy in the above indicated region of distances (see section 5). Thus, at $R \approx R_0$ the opposite-parity states of each atom may be mixed, creating the degenerate state with large permanent electric dipole moment similar to those produced with the use of electric and/or magnetic field [9].

Detailed analysis on the basis of the data for quantum defects of Rb Rydberg states detects the indicated type of degeneracy for 38P3/2, 39D3/2, 43D5/2 and 58D3/2 states [10–19]. The energy of two atoms in these states is separated from the closest dipole-coupled two-atomic levels by an energy gap $\delta$ 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, 11, 18, 19]. The van-der-Waals energy, estimated as the squared dipole–dipole energy divided by the independent of the interatomic distance $R$ detuning $\delta$ [19], 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 equation (1). Evidently, this situation appears inevitably for large distances $R > R_0$, where the dipole–dipole energy is essentially smaller than $\delta$. The resonance-term estimate for the $C_6$ value holds only, if the contribution of non-resonant terms to the infinite summation in (1) is inessential.

In this paper, we determine the energy of asymptotic interaction with the use of the higher-order perturbation theory for close states [8]. The transformation between the van-der-Waals law $\Delta E_{vdW} = -C_6/R^6$ and the dipole–dipole law $\Delta E_d = C_4/R^8$ 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 section 5 the case of close-energy two-atomic states of Rb atoms in their 38P3/2 states, only 4 MHz above the joint energy of 39S- and 38S-states [1], is considered in detail numerically.

For states of nonzero angular momentum the constant $C_6$ is a tensor quantity [20] dependent on the magnetic quantum numbers and consequently on the relative orientation of the quantisation and interatomic axes determined by the unit vectors $\mathbf{a}$ and $\mathbf{n}$ respectively (see figure 1). In heavy alkaline-metal atoms Rb and Cs the tensor properties of $C_6$ may arise also in $n^{2}S_{1/2}$ states due to considerable fine-structure splitting between $n_1(2)^{2}P_J$ states of the total momenta $J = 1/2$ and $J = 3/2$, which should appear on the right-hand side of equation (1) and determine the double-axial (double-vector) component $R_{aa}$ of the $C_6$ tensor (see section 3). Experimental investigations of the long-range interaction dependence on orientation of the interatomic axis were performed in [18] 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 states of angular momenta $l$ values from 5 to $n - 1$.

The van-der-Waals interaction between two Rydberg atoms in identical states is the principal object under considerations of this paper. This interaction may shift Rydberg levels from resonance with a laser excitation radiation, thus prohibiting simultaneous excitation of nearby atoms [21]. This effect, called in the literature the ‘blockade effect’ (see e.g. [2] and references therein), may be useful for processing quantum information. The shift of a Rydberg state $\lvert n lJM \rangle$ is mainly determined by the $C_6$ constant which for highly excited states (usually for $n > 20$) is proportional to $n^{11}$. The principal contribution to $C_6$ comes from the terms in the right-hand side of equation (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 \( C_d / R^3 \), 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 \( C_d \) may be also enhanced by a laser radiation of a frequency corresponding to a two-atomic resonance on states of opposite parity [22], on analogy with the effect of the Förster-type resonance between opposite-parity Rydberg states \( |npnp⟩ \leftrightarrow |nsnf⟩ \) caused by the dipole–quadrupole interaction, which was observed experimentally for ultracold Cs atoms [23].

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 \( 2^{n-2} \)) negative- and positive-parity multipole moments [24]. 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 \( R \): \( \Delta E_{d-d} = C_d / R^3 \). Evidently, the first-order matrix element also includes the dipole–quadrupole, \( \Delta E_{d-q} + \Delta E_{q-d} = C_4 / R^4 \), dipole–octupole, quadrupole–quadrupole, \( \Delta E_{d-o} + \Delta E_{o-d} + \Delta E_{q-q} = C_6 / R^6 \), and other higher-multipole terms of dispersion interaction [25]. However, since the increase of multipolarity accompanies corresponding increase of the \( 1 / R^2 \) power, the account of the indicated terms for \( R > R_{12} \) may introduce only small corrections. The coefficients \( C_d \) 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 \( n|lM⟩ \) states of \( l < 5 \) in many-electron atoms the permanent electric dipole moments and all \( 2^n \)-pole moments of odd \( q \) zero. The first-order interaction energy does not vanish for \( nP_3/5 \) 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: \( \Delta E^{(1)} = C_4 / R^3 \), where the tensor constant \( C_4 \) depends on the magnetic quantum numbers \( M \) and on the relative orientation of the interatomic and quantisation axes. For identical Rydberg states of atoms \( C_d \) is proportional to \( n^6 \).

The \( n \)-dependence of the van-der-Waals constant \( C_6 \) determining the second-order energy \( \Delta E_{vdW} \) is essentially stronger, thus providing the principal contribution to the long-range interaction, enabling extremely sensitive control of the blockade effect and finally, ensuring high-efficiency logic operations with the use of Rydberg atoms. Therefore we consider in this paper analytical properties of the van-der-Waals energy \( \Delta E_{vdW} \propto n^6 / R^6 \) determining asymptotic (both in \( n \) and \( R \)) interaction of atoms in identical Rydberg states with low angular momenta \( l \leq 3 \).

The structure of the paper is as follows. In section 2, the basic equations are presented for the energy of long-range interaction between two Rydberg-state atoms. The formulae are derived from the first-order and higher-order perturbation theory for the interaction operator resolved in power series of \( 1 / R \), 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 imaginary part determining the rate of the interaction-induced ionisation [16, 26]. The relations between the real and imaginary parts of the constant \( C_6 \) are discussed at the end of section 2.

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 section 3 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 \( n|lM⟩ \) of low angular momentum \( l \).

In section 4, asymptotic approximations are proposed for tensor components of \( C_6 \) determining its dependence on relative orientations of interatomic and quantisation 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 \( s^−, P^−, D^− \) and \( nF \)-states of highly excited Rb atoms.

The case of close two-atomic states with the difference of energies in denominator of equation (1) (so called ‘Förster defect’ \( \delta = E_{n} + E_{n} - 2E_{n} \) [1]) comparable or smaller in magnitude than \( \Delta E_{vdW} \) is considered in detail in section 5. 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 appear, are determined explicitly.

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

2. General formulae

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

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\[ \mathbf{Q}_{L\mu}^{(A)} = \sum_{i=1}^{Z_{A}} r_{i}^{A} \mathbf{C}_{L\mu}(\mathbf{r}_{i}), \]  
(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 \( (\mathbf{n}_{i} \text{ is a unit vector, which points from the nucleus to the } i\text{th electron}) \) [20]

\[ \hat{V}_{AB}(\mathbf{R}) = \sum_{L_{A}=-L}^{L_{A}} \sum_{L_{B}=-L}^{L_{B}} \hat{V}_{L_{A}L_{B}}(\mathbf{R}). \]  
(3)

A separate term of this sum is the operator of asymptotic interaction of electric \( 2l_{A} - 2l_{B} \)-pole moments:

\[ \hat{V}_{L_{A}L_{B}}(\mathbf{R}) = \left( -\frac{1}{R^{1+l_{A}}} \right)^{\frac{(2L)!}{(2L_{A})!(2L_{B})!}} (\mathbf{C}_{L}(\mathbf{n}) \cdot [\mathbf{Q}_{L_{A}}^{A} \otimes \mathbf{Q}_{L_{B}}^{B}]) , \quad L = L_{A} + L_{B}. \]  
(4)

General notations of the quantum theory of angular momentum [27] are used here for scalar and tensor products. \( \mathbf{C}_{L}(\mathbf{n}) = \sqrt{4\pi / (2L + 1)} Y_{L}^{\mu}(\mathbf{n}) \) is the modified spherical function of the vector \( \mathbf{n} \) angular variables. The first term of the two-fold series (3) \( \hat{V}_{1}(\mathbf{R}) \) 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 [11, 18] and the van-der-Waals interaction in the second order for atoms in non-degenerate two-atomic states [19].

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 \( \mathbf{a} \) and a unit vector \( \mathbf{a} \) pointing in the positive direction of the quantisation axis for atomic total momenta \( J_{AB} \) (see figure 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 \( \mathbf{C}_{L}(\mathbf{n}) / R^{l_{A}+1} \), are separated from the ‘internal’ variables of the interacting atoms, collected in the tensor \( [\mathbf{Q}_{L_{A}}^{A} \otimes \mathbf{Q}_{L_{B}}^{B}] \). The components of the tensors are determined explicitly in matrix elements of the operator \( \hat{V}_{L_{A}L_{B}}(\mathbf{R}) \), according to selection rules for angular momenta.

It is useful to note, that the dipole–dipole interaction operator is usually presented in terms of the electric-dipole operators \( \hat{d}_{A}(\mathbf{R}) \), as follows

\[ \hat{V}_{1}(\mathbf{R}) = -\frac{\sqrt{6}}{R^{3}} (\mathbf{C}_{2}(\mathbf{n}) \cdot (\hat{d}^{A} \otimes \hat{d}_{B}^{B})) = \frac{(\hat{d}^{A} \cdot \hat{d}^{B}) - 3(\hat{d}^{A} \cdot \mathbf{n})(\hat{d}^{B} \cdot \mathbf{n})}{R^{3}}. \]  
(5)

The first expression seems more convenient for analytical calculations and for analysing 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, 18, 19, 28]. In contrast, the \( \mathbf{n} \)-dependence is accumulated in a single factor \( \mathbf{C}_{L}(\mathbf{n}) \) 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 identical atoms A and B are in different but dipole-coupled states [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 non-zero angular momenta. Besides 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.

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

The system of two identical infinitely separated atoms in their \( |nJM\rangle \) 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 non-degenerate 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 non-interacting 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 $n_{\alpha(\beta)}$, non-zero angular momenta $l_{\alpha(\beta)} \geq 1$, and magnetic quantum numbers $m_{\alpha(\beta)}$

\[
\langle \alpha(\beta) | = | n_{\alpha(\beta)} l_{\alpha(\beta)} m_{\alpha(\beta)} \rangle, \]

then the first-order energy shift

\[
\Delta E^{(1)}_{\alpha \beta}(R) = \langle \alpha | V_{\alpha \beta}(R) | \beta \rangle
\]

of the perturbation theory for the interaction (3) gives a sum of terms describing contributions of even electric multipole moments $Q_{2L} = \sum_{L=0}^{2L=0} (nL^2i^2mL^2i^2) \langle (2L+1)| \rangle \sum_{L=0}^{2L=0} Q_{2L}^2 \frac{Q_{2L}^2}{(2L+1)!} R^{2L+1} P_{2L}(n \cdot a).
\]

Here $L = L_A + L_B$, as equation (4), and common notations are used for the Clebsch–Gordan coefficients $C_{mLm_A, mB}^{m}.\text{Legendre polynomial} \quad P_2(\cos \theta) = C_2 \phi(\theta, \phi) [27] \text{and matrix elements} \quad Q_{2L}^{AB} \quad \text{Evidently, the principal contribution to the first-order interaction energy (6) comes from the lowest non-vanishing order in powers of} \quad 1/R \text{determined by the electric quadrupolar moments} \quad Q_{2L}^{AB}. \quad \text{The next term, described by the interaction of} \quad Q_{2L}^{AB} \quad \text{and} \quad Q_{2L}^{AB}, \text{is on the order of} \quad n^4/R^2 \text{of the} \quad Q_2 \quad \text{term. This ratio, equivalent to the ratio of the mean-squared radius of the Rydberg-electron orbit} \quad \langle nL^2 i^2 \rangle \propto n^2 \text{and the squared distance} \quad R \text{between atoms, is sufficiently small to ensure applicability of the long-range approximation (3) and (4) for the interaction between atoms in the region of} \quad R > R_{AB} \approx 5n^2, \text{where the principal contribution to the first-order energy (6) comes from the term} \quad 2L_A = 2L_B = 2, \text{which depends on the distance as} \quad R^{-2}. \quad \text{The number of terms in the right-hand side of (6) is} \quad N_{AB} = l_A l_B, \text{so the first-order energy (6) vanishes} \quad (N_{AB} = 0), \text{if one of the atoms is in its} \quad nS-\text{state} \quad (l_A = 0). \text{For both atoms in their} \quad nP-\text{states} \quad N_{AB} = 1, \text{hence only} \quad Q_2 \quad \text{term remains in the right-hand side of (6)} \text{an estimate for which may be written as} \quad \Delta E^{(1)} \propto n^4/R^2. \quad \text{For} \quad n = 100 \text{the long-range approximation holds at} \quad R > 5 \times 10^4 \text{a.u.} \approx 2.6 \mu \text{m. At this distance,} \quad \Delta E^{(1)} < 1 \text{GHz. However, the shift (6) will vanish in the nodes of the polynomial} \quad \mathcal{P}_2(n \cdot a) \text{at the angles between the vectors} \quad \mathbf{n} \text{and} \quad \mathbf{a}, \text{equal to} \quad \theta = 30.6^\circ, 70.1^\circ, 109.9^\circ \text{and} 149.4^\circ. \quad \text{Also} \quad \Delta E^{(1)} \text{vanishes after averaging over orientations of the vector} \quad \mathbf{R} \text{or after averaging over orientations of the total magnetic quantum numbers} \quad M_{AB} \text{of the atom} \quad \alpha(\beta).\]

### 2.2. Second-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

\[
\Delta E^{(2)}_{\alpha \beta}(R) = -\langle \alpha | V_{\alpha \beta}(R) C_{\alpha \beta}^{AB}(\mathbf{r}_A, \mathbf{r}_B; \mathbf{r}_A', \mathbf{r}_B') \mathcal{V}_{\alpha \beta}(R) | \beta \rangle
\]

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 non-interacting atoms [29–31]:

\[
C_{\alpha \beta}^{AB}(r_A, r_B; r'_A, r'_B) = \sum_{n_1, n_2} E_{n_1} + E_{n_2} - E_{A} - E_{B} - i \epsilon 0 \frac{\langle \alpha | n_1 | \beta \rangle \langle n_1 | r'_A \rangle \langle n_2 | r'_B \rangle}{E_{n_1} + E_{n_2} - E_{A} - E_{B} - i \epsilon 0}.
\]

The summation spreads over the complete basis of eigenvectors

\[
| \eta_i \rangle \equiv | n_i l_i | M_i \rangle, \quad (i = 1, 2)
\]

of the Hamiltonian of non-interacting atoms $\hat{H}_{\alpha \beta} = \hat{H}_A + \hat{H}_B$, except for the eigenvector $| \eta_1 \rangle$, corresponding to the eigenvalue $E_{A} + E_{B} = E_{\alpha \beta}$, the total energy of infinitely separated atoms. Evidently, $\Delta E^{(2)}_{\alpha \beta} = 0$, independently of the values of angular momenta $l_{\alpha(\beta)}$, since the Green’s function contains all states and allows 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):

\[
\Delta E^{(2)}_{\alpha \beta}(R) = -\sum_{q=0}^{\infty} \frac{C_{\alpha \beta}^{(2+2q)}(n)}{R^{2q+2}}
\]

Here the infinite sum accounts for all virtual multipole moments of atoms A and B in the operators $\mathcal{V}_{\alpha \beta}(L_{\alpha \beta} \mathcal{R}(R)$ from $L_{\alpha \beta} = 1 \text{up to infinity. It should be kept in mind that the sum of the multipolar indexes}

$C_{\alpha \beta}^{\ell}(n) \propto n^{2q'} \text{q'} = 0, 1, 2 \ldots \text{holds for coefficients. So, the ratio} \quad n^2/R < 1 \text{ensures convergence of the series (9).}
2.3. Higher-order perturbation theory for the asymptotic interaction

Higher-order perturbation theory for the dispersion interaction of ground-state atoms was already considered in 1980s (see, for example [22, 30, 32] and references therein). Numerical data were calculated for coefficients determining asymptotic resolution of the third-order and fourth-order dispersion interaction energy for neutral hydrogen and alkali-metal atoms. Corrections to the energy of asymptotic interaction between ground-state hydrogen atoms up to the tenth order of perturbation theory were calculated in [33]. Specific properties of Rydberg atoms, in particular, the increase of contributions from higher multipole interactions already in the second order term \( \Delta E^{(2)}_{\mathrm{AB}}(R) \) stimulate the analysis of higher-order terms of perturbation theory in the asymptotic interaction (3).

The third-order energy shift involves matrix elements with three operators (3) and two Green’s functions \( G_{\mathrm{AB}} [32, 33] \):

\[
\Delta E^{(3)}_{\mathrm{AB}}(R) = \langle \mathrm{AB} | \hat{\nabla}_{\mathrm{AB}}(R) G'_{\mathrm{AB}} \hat{\nabla}_{\mathrm{AB}}(R) G_{\mathrm{AB}} \hat{\nabla}_{\mathrm{AB}}(R) | \mathrm{AB} \rangle - \Delta E^{(1)}_{\mathrm{AB}}(R) \langle \mathrm{AB} | \hat{\nabla}_{\mathrm{AB}}(R) (G'_{\mathrm{AB}})^2 \hat{\nabla}_{\mathrm{AB}}(R) | \mathrm{AB} \rangle.
\]

(10)

Corresponding asymptotic resolution involves only odd powers of \( 1/R \), starting for states of definite parity from \( 1/R^3 \), and may be written as follows [32, 33]:

\[
\Delta E^{(3)}_{\mathrm{AB}}(R) = \sum_{q=0}^{\infty} \frac{c_{11}^{(3)}(n)}{R^{1+2q}},
\]

(11)

where the coefficients \( c_{11}^{(3)}(n) \) may be resolved in tensor components dependent on the direction of the interatomic axis \( n \).

By analogy with (7) and (10), the fourth order perturbation theory will present the asymptotic interaction-induced energy \( \Delta E^{(4)}_{\mathrm{AB}}(R) \) in terms of a superposition of the fourth-order matrix elements and products of the first-order energy (6) with the third-order matrix element and the second-order energy (9) with the second-order matrix element of the product of two Green’s functions (8) between two operators (3). Each term of the superposition effectively includes four operators \( \hat{\nabla}_{\mathrm{AB}}(R) \) and three Green’s functions [32, 33]. 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 \( 1/R^5 \). 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 \( \Delta E^{(N)}_{\mathrm{AB}}(R) \) of the \( N \)th-order perturbation theory for the energy of asymptotic interaction (3):

\[
\Delta E_{\mathrm{AB}}(R) = \sum_{N=1}^{\infty} \Delta E^{(N)}_{\mathrm{AB}}(R).
\]

(12)

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

\[
\Delta E^{(N)}_{\mathrm{AB}}(R) = (-1)^{N+1} \sum_{q=q_0}^{\infty} \frac{c_{N}^{(N)}(n)}{R^{N+2q}},
\]

(13)

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

Thus the series (12) finally transforms into power series of \( 1/R \):

\[
\Delta E_{\mathrm{AB}}(R) = \sum_{s=s_0}^{\infty} \frac{c_s^{\text{tot}}(n)}{R^s},
\]

(14)

where the coefficients \( c_s^{\text{tot}}(n) \) are the sums of corresponding coefficients \( c_s^{(N)}(n) \) of resolutions (13) for different orders \( N \) of the perturbation theory:

\[
c_s^{\text{tot}}(n) = \sum_{k=1}^{\lfloor s/6 \rfloor} c_s^{(2k)}(n), \quad \text{for even } s = 6, 8, 10 \ldots ;
\]

(15)

\[
c_s^{\text{tot}}(n) = \sum_{k=1}^{\lfloor (s+1)/6 \rfloor} c_s^{(2k-1)}(n), \quad \text{for odd } s = 5, 7, 9 \ldots ,
\]

(16)

where the notation \( \lfloor a \rfloor \) is used for the integer part of a positive number \( a \).

The first-order energy (6) does not vanish only for states with non-zero angular momenta \( l_{\mathrm{AB}} \geq 1 \), and is also described by equation (13), where the infinite series of the right-hand side in the case of \( N = 1 \) turns into a sum of finite number of terms, truncated at the maximal value of \( q_{\text{max}} = l_1/l_2 \). For \( N \geq 2 \) the series (13) are infinite and may involve terms of equal powers of \( 1/R \) in different orders \( N \) of perturbation theory.

Comparison between the coefficients \( c_{N+2q}^{(N)} / c_N^{(N)} \propto n^{4q} \) within one and the same order \( N \) of perturbation theory detects the condition for convergence of the series in \( 1/R \) (13) at \( n^4/R^2 \ll 1 \). Whereas the condition of convergence of the series (12), 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:
Simultaneously, comparison of terms from the Nth and \((N + 2k)\) th order of equal powers
\[ s = 3N + 2q = 3(N + 2k) + 2q' \text{ of } 1/R \text{ (where } q' = q - 3k) \]
\[
|C_s^{(N+2k)}(n) / C_s^{(N)}(n)| \propto n^{2k}, \quad k = 1, 2, \ldots, [q/3],
\]
demonstrates negligible contributions of the lower-order-perturbation-theory terms into the constant \(C_s^{\text{tot}}\) of the asymptotic resolution (14). This regularity follows from the asymptotic nature of the interaction operator (3) and was observed already for ground-state hydrogen atoms [33] but for rather remote terms of \(s \geq 30\) in the series (14).

It is important to note different signs in the right-hand sides of equations (15) and (16) for even- and odd-order sums of coefficients \(C_s^{(N)}(n)\) determining the resultant resolution (14) 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 (compare (7) and (10)). In particular, \(C_s^{\text{tot}}(n) = C_s^{(1)}(n)\) for \(s = 5, 7, 9\) and \(C_s^{\text{tot}}(n) = -C_s^{(2)}(n)\) for \(s = 6, 8, 10\). In what follows, we confine our considerations mainly to the second-order corrections described by \(C_s^{(2)}\) for which we use the notation \(C_6\), omitting superscripts.

### 2.4. Van-der-Waals ionisation of Rydberg atoms

Evidently, the cooperative energy of two atoms is always sufficient to put the Rydberg electron of the atom A into continuum while the electron of the atom A(B) falls down to a lower-energy state \(E_{n_{(1d)}} < E_A + E_B\). In this case the integral over continuum of the atom A(B) in the Green’s function (8) has a singularity at the energy \(E_{n_{(1d)}} = E_A + E_B - E_{n_{(1d)}} > 0\). 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 wave functions:

\[
\text{Im} \left[ C_{AB}(r_A, r_B; r_A', r_B') \right] = \pi \sum_{n_{1}(E_{n_{1}} < E_A + E_B)} \langle n_1 | r_A \rangle \langle r_A | n_1 \rangle \langle r_B | \varepsilon_2 \rangle \langle \varepsilon_2 | r_B' \rangle \\
+ \pi \sum_{n_{2}(E_{n_{2}} < E_A + E_B)} \langle n_2 | r_A \rangle \langle r_A | n_2 \rangle \langle r_B | \varepsilon_1 \rangle \langle \varepsilon_1 | r_B' \rangle,
\]

where \(\varepsilon_{1(1)} = E_A + E_B - E_{n_{(1d)}} > 0\) is the energy of a state from atom A(B) positive-energy continuum. So the second-order energy (7) of interaction between two Rydberg atoms and constants of corresponding resolution (13) are complex values, the imaginary parts of which determine the rate of ionisation for one of the atoms accompanied by simultaneous de-excitation of another one with transition to lower-energy levels [16].

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 ionisation potential. Also, the van-der-Waals interaction-induced ionisation of Rydberg atoms may be compared with the so-called ‘Penning ionisation’ of an atom of a low ionisation potential by a metastable atom of rather high excitation energy, which was considered in [30] as a result of the long-range interaction between inert-gas atoms in metastable states and ground-state alkali atoms. The rate of that radiation-less ionisation was estimated as rather low and rapidly vanishing with distance (at least, as \(R^{-12}\), since the first-order dipole transition between metastable and ground states is strictly forbidden).

The imaginary parts of constant factors \(C_s\) of the resolution (14) are rather small in comparison with real parts \(\text{Re} \{ C_s \}\). They appear already in the second-order perturbation theory from the imaginary part of the two-atomic Green’s function (17) in the integral over continuum of atom A(B) at the energy \(E_{n_{(1d)}} = E_A + E_B - E_{n_{(1d)}} > 0\). Simple estimates for the van-der-Waals constant demonstrate that the ratio between the imaginary and real parts of \(C_s\) may be determined as

\[
\frac{\text{Im} \{ C_s \}}{\text{Re} \{ C_s \}} \propto n^{-p},
\]

where the exponent \(p\) varies from 10 to 3 in the region of the principal quantum numbers from \(n \approx 10\) to \(n \gg 1000\), thus maintaining the imaginary part of the van-der-Waals energy 9–10 orders smaller in absolute value than the real part in all the indicated region of states. So small values of \(\text{Im} \{ C_s \}\) allow to neglect the broadening of Rydberg levels, caused by the long-range interaction-induced ionisation. 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 [34] for a system of two Rydberg atoms, separated at distances \(R \lesssim R_{LR}\), where the ionisation rate increases almost exponentially with the overlap of Rydberg orbits.
3. Irreducible components of van-der-Waals constants

3.1. \( C_6 \) dependence on the relative orientation of the quantisation 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 \([n\ell_j,l_j,M_j] = [n\ell_k,l_k,M_k] \equiv [n|M] \), 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 [20]. 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 \( \theta \) between the unit vectors of interatomic and quantisation axes (see figure 1), as follows:

\[
C_6(\theta) = R_{st} - \frac{M^2}{12J^2}(3\cos^2\theta - 2)R_{sat} + \frac{3M^2 - J(J + 1)}{2J(2J - 1)}(3\cos^2\theta - 1)R_{ST}
\]

\[
+ \frac{3}{2}\left(\frac{3M^2 - J(J + 1)}{2J(2J - 1)}\right)^2(9\cos^4\theta - 8\cos^2\theta + 1)R_{TT}.
\]

(19)

We consider below the case of doublet states (spin \( S = 1/2 \) and total angular momentum \( J = l \pm 1/2 \)). The irreducible parts \( R_{ss}, R_{sat}, R_{ST}, R_{Ts}, R_{TT} \) may be presented as

\[
R_{ss} = \frac{1}{24J^2(J + 1)^2}[\langle J + 1 \rangle^2(2J - 1)^2\rho_{l-1,J-1,l-1,J-1} + \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1}]
\]

\[
+ \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1},
\]

(20)

\[
R_{sat} = \frac{3}{8J^2(J + 1)^2}[\langle J + 1 \rangle^4(2J - 1)^2\rho_{l-1,J-1,l-1,J-1} + \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1}]
\]

\[
+ \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1},
\]

(21)

\[
R_{ST} = R_{Ts} = \frac{2J - 1}{24J^2(J + 1)^2}[\langle J + 1 \rangle^2(2J - 1)\rho_{l-1,J-1,l-1,J-1} + \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1}]
\]

\[
+ \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1},
\]

(22)

\[
R_{TT} = \frac{(2J - 1)^2}{24J^2(J + 1)^4}[\langle J + 1 \rangle^4\rho_{l-1,J-1,l-1,J-1} + \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1}]
\]

\[
+ \rho_{l+1,l+1,J+1,J+1} + \rho_{l+1,l+1,J+1,J-1} + \rho_{l+1,l+1,J-1,J+1} + \rho_{l+1,l+1,J-1,J-1}.
\]

(23)

Here the notations are used

\[
\rho_{l\ell_1,l\ell_2,M} = \langle n|M|n|M|n\ell_1,n\ell_2,\ell_1,\ell_2|n|M\rangle
\]

(24)

for the radial matrix elements with two-atomic radial Green’s function \( g_{l\ell_1,l\ell_2} \). These terms correspond to different angular-momentum channels, some properties of which were discussed, in particular, for Rb and Cs atoms in [1].

The results for states of \( J = |M| \) (orbit in the plane perpendicular to the quantisation axis) turn out to be interesting due to the orientation-dependent factors \( \sin^2\theta \) arising in several terms of the \( C_6 \) constant. As can be seen from (20) to (23), the contribution to \( C_6 \) of the radial matrix elements \( \rho_{l-1,J-1,l-1,J-1} \) and \( \rho_{l-1,J-1,l+1,J+1} \) disappears in this case at \( \theta = 0 \). For example,

\[
C_6|J=|M|=1/2,\theta=0 = \frac{2}{81}(2\rho_{l+1,l+1,J+1,J+1} + 11\rho_{l+1,l+1,J+1,J-1} + 14\rho_{l+1,l+1,J-1,J+1}),
\]

(25)

\[
C_6|J=|M|=3/2,\theta=0 = \frac{4}{1875}(3\rho_{l+1,l+1,J+1,J+1} + 63\rho_{l+1,l+1,J+1,J-1} + 125\rho_{l+1,l+1,J-1,J+1} + 34\rho_{l+1,l+1,J-1,J-1}),
\]

(26)

\[
C_6|J=|M|=5/2,\theta=0 = \frac{4}{12005}(10\rho_{l+1,l+1,J+1,J+1} + 465\rho_{l+1,l+1,J+1,J-1} + 2058\rho_{l+1,l+1,J-1,J+1} + 162\rho_{l+1,l+1,J-1,J-1}).
\]

(27)

Some numerical data for the van-der-Waals constants of the two-atomic states with identically excited Rb atoms in their \( nP_{3/2,M} \) states with \( n = 37, 38, 39 \) are presented on figure 2 as the functions of the orientation
angle $\theta$ for the magnetic quantum numbers $|M| = 1/2$ (plot (1)) and $|M| = 3/2$ (plot (2)). The negative (repulsive) values of $C_{\theta}$ for $38P_{1/2}$ states exceed by more than one order in magnitude those of the $37P_{1/2}$ and $39P_{1/2}$ states. This property follows from the resonance behaviour of the spectrum of two-atomic $C_{\theta}$-states from the total energy of the $3M(\pm 3M = \pm 3)\rangle$ of the neighbour states is at least one order smaller than the magnitudes of the differences of the interaction energies of Rb atoms in $3P_{1/2}$ states in a definite region of interatomic distances $R_{R} < R < R_{L}$, where $R_{R} \approx 0.5 \mu m$ and $R_{L} \approx 7 \mu m$, should be considered on the basis of the perturbation theory for close states (see below section 5). In the region above the ‘ Förster radius’ $R > R_{L}$ the interaction-induced shift is essentially smaller than the ‘resonance detuning’ $\delta$ and the usual perturbation theory for non-degenerate states is applicable with the van-der-Waals constants $C_{\theta}(3P_{1/2, M})$ presented in figure 2 as functions of the angle $\theta$. The curves for the constants of the neighbour states $C_{\theta}(37P_{1/2, M})$ and $C_{\theta}(39P_{1/2, M})$ are also plotted in order to demonstrate similar $\theta$-dependences of the interaction energies of Rb atoms in $nP_{1/2, M}$ states. The negative values of the $C_{\theta}$ constants for $n = 37, 38$ correspond to repulsion between atoms. The positive values of $C_{\theta}(39P_{1/2, M})$ determine attraction. For $M = \pm J$ states (orbits in the plane perpendicular to the quantisation axis) the interaction vanishes at $\theta = 0, \pi$, as seen in plot (2). The absolute value of $C_{\theta}(38P_{1/2, M})$ more than one order exceeds those for $n = 37, 39$, since the resonance energy defect $|\delta|$ is the smallest for $n = 38$ states.

### 3.2. Numerical evaluations of irreducible components of the van-der-Waals constant $C_{\theta}$ for Rydberg atoms

The radial part of the Green’s function (8) in the radial matrix elements (24) may be presented as a spectral resolution

$$g_{l_{1}l_{2}l_{3}}, l_{1}l_{2}l_{3} = \sum_{n_{1}n_{2}} \frac{(\lambda | n_{1}l_{1}J_{1}| \lambda ) (\lambda | n_{2}l_{2}J_{2}| \lambda ) (\lambda | n_{3}l_{3}J_{3}| \lambda )}{E_{n_{1}l_{1}J_{1}} + E_{n_{2}l_{2}J_{2}} - E_{\lambda} - i \cdot 0},$$

where the summation is performed over a complete set of radial eigenfunctions of isolated atoms A and B in a Hilbert subspace of bound and continuum states of fixed values of the orbital and total angular momenta. The substitution of equation (28) 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 $n_{i}$, $n_{j}$ to that of the Rydberg state $n$ and simultaneously, of the lowest absolute values of the energy differences for both atoms $\delta_{n_{i}n_{j}} = E_{n_{i}l_{i}J_{i}h_{i}} - E_{n_{j}l_{j}J_{j}h_{j}}$ in the denominator. The most important of these contributions correspond to opposite signs of the energy differences $\epsilon_{i(2)n}$ so that the absolute value of the energy defect

$$\delta = \delta_{n_{i}} + \delta_{n_{j}}$$

is at least one order smaller than the magnitudes of the differences $\delta_{n_{i}n_{j}}$. The contribution of remaining terms of the spectral resolution in (28) rapidly decreases with the increase of the absolute values of the differences between

*Figure 2. Dependence of the van-der-Waals coefficients $C_{\theta}(nP_{1/2, M})$ (in the units of G Hz $\mu m^6$) on the angle $\theta$ between the interatomic and quantisation axes for the Rb $nP_{1/2, M}$ states of the magnetic quantum numbers: (1) $M = 1/2$ and (2) $M = 3/2$, of the principal quantum numbers $n = 37$ (curves a), $n = 38$ (curves b, which give the values of $C_{\theta}(38P_{1/2, M})/10$) and $n = 39$ (curves c).*
the principal quantum numbers. Numerical calculations for the radial matrix elements reveal rather rapid convergence of the series over bound states. Therefore, the account of terms from the region of \( |n| > 8 \) ensures significant accuracy of calculated result for the matrix element (with the fractional uncertainty of the residual infinite sum and integral below \( 10^{-4} - 10^{-5} \)).

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

\[
\langle n l J | r | n'l'J' \rangle = \frac{\Gamma(\lambda + \lambda' + 4)}{4Z} \times \left( \frac{2\nu}{\nu + \nu'} \right)^{\lambda'+2} \left( \frac{2\nu'}{\nu + \nu'} \right)^{\lambda+2} \frac{(2\lambda + 2)n!n!_n(2\lambda' + 2)n!'_n}{\Gamma(2\lambda + 2)\Gamma(2\lambda' + 2)} \times F_2 \left( \lambda + \lambda' + 4; -n_r, -n'_r; 2\lambda + 2, 2\lambda' + 2; \frac{2\nu'}{\nu + \nu'}, \frac{2\nu}{\nu + \nu'} \right),
\]

(30)

where the usual notations for the \( \Gamma \) function and the Pochhammer symbol \( (a)_n = \Gamma(a + n) / \Gamma(a) \) are used [35]. Here \( n \) is the radial quantum number, \( \nu = 1 + n_r + \lambda \) is the effective principal quantum number, \( Z \) is the net charge of residual ion (\( Z = 1 \) for a neutral atom).

The generalised hypergeometric function (Appell function) \( F_2 \) of five parameters and two variables, may be calculated in terms of the Gauss hypergeometric functions \( _2F_1 \). But the precision of evaluation of the hypergeometric functions rapidly decreases with the growth of \( n \), due to the strong cancelation of digits in corresponding sums of sign-alternating terms. The transformation [35]

\[
F_2(\alpha; -n_r, -n'_r; \gamma, \gamma'; x, y) = \sum_{p = 0}^{\min(n_r, n'_r)} \frac{(\alpha)_p(-n_r)_p(-n'_r)_p}{p!(\gamma)_p(\gamma')_p} \times (xy)^{p} _2F_1(\alpha + p, p - n_r; \gamma + p; x) _2F_1(\alpha + p, p - n'_r; \gamma' + p; y)
\]

(31)

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

The model-potential parameters of equation (30) are determined from the most precise data for the energy levels of atoms and ions available, in particular, from the Internet resources [36]. 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 \( |nlf| \)-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 [10] (S- and D-states), [12, 13] (P-states) and [14] (F-states) were used for determining the model-potential parameters of the Rydberg-state wave functions and the two-atomic frequencies (29) according to the relation

\[
\mu_{nlJ}(n) = \mu_{nlJ}^{(0)} + \frac{\mu_{nlJ}^{(2)}}{(n - \mu_{nlJ}^{(0)})^2}.
\]

(32)

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

The states of rather high quantum numbers \( m_{A(B)} \) and consequently, of high angular momenta \( l_{A(B)} \geq |m_{A(B)}| \geq 5 \) 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 (14) [24]. The electric dipole moments point along the quantisation axis and may be written in terms of the parabolic quantum numbers \( n_1, n_2 \) [5] and the unit vector \( \mathbf{a} \), as

\[
d = -\frac{3}{2} n(n_1 - n_2) \mathbf{a}.
\]

(33)

So, the dipole–dipole interaction (5) of two Rydberg atoms in their identical manifold states of \( n > l \geq 5 \), with fixed parabolic quantum numbers \( |n_1 n_2| \), determines the long-range energy shift, which for \( R > R_{LR} \) may be written as
\[ \Delta E_d = \langle mn_1 n_2 | \tilde{V}_d | mn_1 n_2 \rangle = \frac{C_3(mn_1 n_2; \theta)}{R^3}, \]

where the coefficient
\[ C_3(mn_1 n_2; \theta) = \frac{9}{4} n^2 q^2 (1 - 3 \cos^2 \theta) \]
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 (33), parallel to each other and pointing at the angle \( \theta \) relative the separation vector \( R \).

4. Asymptotic presentation of \( C_6 \) for Rydberg-state Rb atoms

The presentation of the calculated data for the van-der-Waals constant and its tensor components (20)–(23) may be reduced to tabulating numerical data for 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 the van-der-Waals constant and its tensor components on 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:

\[ C_6(nl) = A(l) n l^4 \left(1 + \frac{a^{(1)}(l)}{n} + \frac{a^{(2)}(l)}{n^2} + \frac{a^{(3)}(l)}{n^3} + \ldots\right). \]  

(34)

However, the coefficients \( A(l) \) and \( a^{(i)}(l) \) in the right-hand side of this equation depend on the magnetic quantum numbers \( M \) and on the angle \( \theta \) of the interatomic axis orientation. Therefore, it is more convenient to use the asymptotic series of the form (34) for the \( M \) - and \( \theta \)-independent irreducible components (20)–(23) of the van-der-Waals constant (19).

The asymptotic series in parentheses of equation (34) may be truncated to a polynomial in the inverse powers of the principal quantum number. Numerical calculations demonstrate, that for \( n \geq 30 \), the third-order polynomial \( P_3(1/n) \) in powers of \( n^{-1} \) evaluates the components of \( C_6 \) with uncertainties below 1\%. Therefore, we confine ourselves to the asymptotic equation

\[ R_{\alpha\beta}(nl) = A_{\alpha\beta}(l) n^{l^4} P_3(1/n), \]  

(35)

where the subscripts \( s, a, T \) should substitute for \( \alpha \) and \( \beta \) to denote corresponding components of \( C_6 \) \( (R_{ssa}, R_{saa}, R_{stT} \) and \( R_{Tst}) \). The third-order polynomial

\[ P_3(x) = 1 + a^{(1)}(l)x + a^{(2)}(l)x^2 + a^{(3)}(l)x^3 \]
tends asymptotically (for \( n \to \infty \)) to the unit, \( P_3(0) = 1 \). The coefficients \( a^{(i)}(l) \), \( i = 1, 2, 3 \) may be determined from a standard curve polynomial fitting procedure (see for example [37, 38]). Thus, the most important part of dependence on the principal quantum number of the \( C_6 \) components is determined by the factor \( n^{l^4} \) with the amplitudes \( A_{ss}(l), A_{aa}(l), A_{stT}(l) \) and \( A_{Tst}(l) \). Separate terms of the polynomial \( P_3(1/n) \) account for the lower powers \( n^{l^4}, n^n, n^8 \), the fractional contribution from which gradually disappears, when \( n \to \infty \).

In the case of ‘resonances’, where the energy defect (29) of the most contributing states changes its sign, the asymptotic equation (35) may be generalised, as follows:

\[ R_{\alpha\beta}(nl) = \frac{A_{\alpha\beta}(l)}{(n - \bar{n}^{(1,2)}_{\alpha\beta}(l))(n - \bar{n}^{(2,3)}_{\alpha\beta}(l))} n^{l^4} P_3(1/n), \]  

(36)

where \( \bar{n}^{(1,2)}_{\alpha\beta}(l) \) are empirical values, practically independent of the subscripts \( \alpha \beta \) between the principal quantum numbers \( n_{l(1)} = n_{\alpha\beta} \) and \( n_{\alpha\beta} \pm 1 \) of two states in the \( l \) series, for which energy defects \( \delta \) have opposite signs. Equation (36) is written for two possible resonances, which appear for \( |n D_{l/2} \rangle \) states. In the case of only
one resonance $\tilde{n}^{(2)}_{\alpha\beta}(I) = 0$. If no resonances occur in the $n$ dependence on the Rydberg-state principal quantum number $n$, then $\tilde{n}^{(1)}_{\alpha\beta}(I) = \tilde{n}^{(2)}_{\alpha\beta}(I) = 0$, as in the case of $|nS_{1/2}\rangle$ and $|nP_{1/2}\rangle$ states (see table 1).

Numerical values of the factor $A_{\alpha\beta}(I)$, resonance parameters $\tilde{n}^{(1,2,3)}_{\alpha\beta}(I)$ and polynomial coefficients $a_{\alpha\beta}^{(1,2,3)}(I)$ of the asymptotic presentation (36) for irreducible components of the van-der-Waals constants of Rb atoms in identical Rydberg states $|n\ell M\rangle$ are listed in table 1.

Quite different from (36) asymptotic approximations to the long-range interaction of atoms were presented in [39] where the inter-atomic 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 $c_6n^{14}$ for $ns$–$ns$ and $np$–$np$ asymptotic states, involved also the terms $c_1n^{12}$ and $c_2n^{10}$, which begin dominate already at $n > 50$ for all symmetries of bi-atomic 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 $1\Sigma^+_u$ and $3\Sigma^+_u$ an additional 'resonance'-type term $c_\ast n^{11}/(n - 29.5)$ appears. Also, for the $nd$–$nd$ states, the $c_1n^{12}$ terms are involved with additional 'resonance' terms $c_\ast n^{11}/(n - 35.14)$. As is seen from equation (36) and the data of table 1, the resonances from [39] differ from those presented as the values of $\tilde{n}^{(2,3)}_{\alpha\beta}(I)$ determined from currently most reliable data on quantum defects [10, 12–14] and energy levels [36].

Evidently, the polynomial approximations to $C_6$ of [39] may work only in a narrow region of $n$ between 30 and 100 and become wrong for $n > 100$. However, the basic target of studies in [39] 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 [39] could not account for neither the current data on the Förster-type resonances, nor the fine structure of Rydberg states.

The van-der-Waals coefficients (19) may be written also as the resolution in powers of the geometric factor $\cos^2(\theta)$, as follows

$$C_6(\theta) = B_{6\ell M}^{(0)} + B_{6\ell M}^{(2)}\cos^2(\theta) + B_{6\ell M}^{(4)}\cos^4(\theta),$$  
(37)

where the $\theta$-independent coefficients $B_{6\ell M}^{(k)}$ ($k = 0, 2, 4$) may be presented as combinations of the irreducible parts $R_{ss}$, $R_{ss}$, $R_{TT}$ and $R_{TT}$ together with corresponding $M$-dependent factors. In particular,
where the notations are used

\[ U_{JM} = \frac{3M^2 - J(J + 1)}{2(J - 1)\, 2}. \]

Finally, the coefficients \( B^{(k)}_{nlM} \) may be written as combinations of the two-atomic radial matrix elements (24), for which the asymptotic presentations of the form (36) also hold.

Numerical values for coefficients \( C_6 \) determined from equations (19), (35)–(37) and from the data of table 1 demonstrate a good agreement with the approximation for \(|A| = |B| = |nS_{1/2}\) - states presented in (39) for \(30 \leq n \leq 95\). It is impossible to compare the results for P- and D-states, because the data of table 1 accounts for the fine-structure splitting and for the relative orientation of the quantisation and inter-atomic axes, which were hidden in the molecular symmetries of the data (39). Also, our numerical results demonstrate a satisfactory agreement with the data of [19] for the dependence of the van-der-Waals constant on orientation of the interatomic axis (on the angle \(\theta\)) 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 [19].

The negative asymptotic value of \( B^{(nS_{1/2} 2)/21/2} \) indicates the repulsive van-der-Waals interaction between \(nS\)-state atoms, nearly independent of the interatomic orientation (of the angle \(\theta\)) determined by the asymptotic constant \( B_{nS_{1/2} 21/2} = 2.08n^4 \). The repulsive interaction remains up to infinite principal quantum numbers of \( |nS_{1/2}\) - states.

For states \(nP_{3/2} \), \( nD_{5/2} \) and \( nF_{5/2} \) the singularities appear in the vicinity of \( \tilde{n}_{a,\beta}(P_{3/2}) \approx 38 \), \( \tilde{n}_{a,\beta}(D_{5/2}) \approx 43 \) and \( \tilde{n}_{a,\beta}(F_{5/2}) \approx 91 \), correspondingly. The component \( R_{\alpha} \) provides the basic contribution to the constant \( C_6 \) as follows from equation (19). Since the values of \( R_{\alpha} \) are positive for all \(|nlJ\) - series presented in table 1 for \( J \geq 3/2 \), 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 \(\theta\) seems explicitly in the right-hand side of equation (19) may cause some deviations from this regularity. In particular, the series of states \( nP_{3/2} \) holds this regularity only for states of the magnetic quantum number \( M = \pm 1/2 \). The states of the magnetic quantum numbers \( M = \pm 3/2 \) demonstrate significant departure from the indicated property for \( \theta = 0 \) (the interatomic axis points along the quantisation axis, which for \(|M| = J\) is perpendicular to the Rydberg-electron orbit). The constant \( C_6 \) for \( \theta = 0 \) equals to the sum of coefficients \( B_{nP_{3/2} M = 3/2}^{(n)} \) (equation (37)). This sum is \( 3 \)–\( 4 \) orders smaller than the positive coefficient \( B_{nP_{3/2} M = 3/2}^{(n)} \) which differs from the absolute value of the sum of two negative coefficients \( B_{nP_{3/2} M = -3/2}^{(n)} \) in the third or fourth digit number. This effect follows from the drop-out of the radial matrix element \( P_{1\pm,1\pm,1\pm,1\pm} \) from the right-hand side of equation (19) at \( \theta = 0 \). So the repulsive interaction of Rb atoms remains at small angles \( \theta \) for all \( nP_{3/2} \) 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, \( \theta_0 \approx 12.6^\circ \), \( 28.8^\circ \) and \( 32.5^\circ \) 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 \( n \leq 38 < \tilde{n}_{a,\beta}(P_{3/2}) \approx 38.053 \) for positive at \( n \geq 39 > \tilde{n}_{a,\beta}(P_{3/2}) \), achieving its minimal absolute value at \( n = 38 \). According to the equation (26) 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 \( n \). This effect is confirmed by the asymptotic values of coefficients of the resolution (37) following from the data of table 1: each coefficient \( B_{nP_{3/2} M = 3/2}^{(n)} \) more than three orders exceeds in magnitude the sum \( \sum_{M} B_{nP_{3/2} M = 3/2}^{(n)} \) (determining the value of \( C_6 (\theta = 0) \)).

The 'resonance' increase of \( C_6 (38P_{3/2}M) \) 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 \( R_{\min (max)} \) depend on the energy defect (29) and on the matrix elements of the dipole transitions to the resonance states. Besides that, the angular dependence of \( C_3 (\theta) \) does not obey the law of the Legendre polynomial \( P_j (\cos \theta) = (\cos^2 \theta - 1)/2 \), characteristic of the interaction.
between constant dipoles, and depends on the total angular momentum \( J \) and magnetic \( M \) quantum numbers of the Rydberg state \( |nJ\rangle \), as is discussed in the next section.

For \( nD_{3/2} \) states the singularities appear near \( n = 39 \) and \( n = 58 \). 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 \( n < \tilde{n}^{(3)}_{\text{c}} \approx 39.6 \) remains also attractive for \( n \geq 40 \) and becomes repulsive only for states of \( n \geq 55 \), 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 \( \theta \), changing from repulsion (\( C_6 < 0 \)) at \( \theta < 0.24\pi \) to attraction (\( C_6 > 0 \)) at \( \theta > 0.24\pi \).

The numerical data of table 1 provides 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 \( nD_{3/2} \) states [40], does not exceed 6% for \( n = 53 \) and falls down to about 3% for \( n = 62 \) and \( n = 82 \).

5. Close-state perturbation theory for asymptotic interaction between Rydberg atoms

If the perturbation-theory condition \(|\Delta E_{\text{vdW}}/\theta| \ll 1\) does not hold for one of the energy splitting \( \delta = E_2 - E_1 \) between the energies \( E_1 \equiv E_{AB} = E_A + E_B = 2E_r \) of the initial two-atomic state \( |r_f \rangle \) and \( E_2 \equiv E_{mn} = E_m + E_n \), of an intermediate state \( |r_i \rangle |n_f \rangle = |r_i \rangle n_f \rangle |r_i \rangle n_f \rangle \) 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 \( |A\rangle = |B\rangle = |nJM\rangle \) of the interacting atoms in the two-atomic state \( |1\rangle \), the single-atomic states \( |r_i \rangle n_f \rangle \) and \( |r_i \rangle |n_f \rangle \) will be different in the close state \( |r_i \rangle n_f \rangle |r_i \rangle n_f \rangle \). The interchange of individual states between atoms corresponds to a third close state \( |r_i \rangle n_f \rangle |r_i \rangle n_f \rangle \) equal in energy to that of the state \( |r_i \rangle n_f \rangle \) and also involved in the complete set of two-atomic states of the Green’s function (8) resolution. Therefore, the close-state subspace includes at least three different two-atomic states \( |1\rangle, |2\rangle, |3\rangle \), the last two are the states of equal energies \( E_3 = E_2 = E_{nm} + E_{nm}. \) 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 states \(|2\rangle \) and \(|3\rangle \) the magnetic quantum numbers \( M \) are not fixed, therefore the summation should be performed over all dipole-coupled to \(|1\rangle \) Zeeman substates as is assumed in the sum of equation (8) for the Green’s function.

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

\[
\text{det}[W_{ij} + (\varepsilon_i - \Delta E) \delta_{ij}] = 0, \tag{39}
\]

which is equivalent to the diagonalization of the \( 3 \times 3 \) matrix (here \( \delta_{ij} \) is the Kronecker symbol, for brevity the argument \( \mathbf{R} \) of the matrix elements is omitted) [8, 41]:

\[
W_{ij} = \langle i| \hat{V}_{AB} (\mathbf{R}) \{1 + G_2^{\mathbf{R}} [\hat{V}_{AB} (\mathbf{R}) - \Delta E] \}^{-1}\} | j\rangle, \tag{40}
\]

where \( i, j = 1, 2, 3 \) corresponding to the close states, which are withdrawn from the two-fold spectral summation of the Green’s function (8). The interaction-induced shift \( \Delta E = E - E_r \) refers to the Green’s function energy, which may be taken as the mean energy of the close states \( E = (E_1 + E_2 + E_3)/3 \) [8]. 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 \( E = E_1 \). Then the shifts \( \varepsilon_i = E_i - E \) of equation (39) \( \varepsilon_0 = 0 \) 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 \( R \rightarrow \infty, \) where the matrix elements \( W_{ij} \) vanish.

The formal use of the resolution (3) in power series of \( 1/R \) for the interaction \( \hat{V}_{AB} (\mathbf{R}) \) in 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 [33]

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

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 also 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 $|AB\rangle$

$$W_{ij}^{(1)} = \langle i|\hat{V}_{AB}(R)|j\rangle = \sum_{q=4}^{L_{SC}} \frac{w_{ij}^{(1)}(q, n)}{R^q}, \quad (43)$$

where $L_{SC} = l_0(i) + l_0(j) + l_0(i) + l_0(j)$ 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 ($\Delta l_{AB} = |l_{AB}(i) - l_{AB}(j)| = 1$), then the summation in the non-diagonal 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

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

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 non-diagonal matrix elements $W_{ij}^{(2)} = W_{ji}^{(2)}$ depends on the relation between parities of the individual single-atomic states in the initial $|i\rangle$ and final $|j\rangle$, [2], [3] 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]), therefore the account of only first-order dipole term $W_{12}^{(1)} \propto 1/R^3$ is sufficient.

With account of the lowest-order matrix elements (43) and (44) and the identities $W_{12}^{(1)} = W_{21}^{(1)} = W_{13}^{(1)} = W_{31}^{(1)}$, $W_{22}^{(1)} = W_{23}^{(1)}$, $W_{23}^{(2)} = W_{23}^{(2)}$, the solutions to equation (39) may be presented, as

$$\Delta E_{1,2} \equiv \Delta E_+ = W_{11}^{(2)} + \frac{\Delta(R)}{2} \pm \frac{1}{2} \sqrt{\left(\Delta(R)\right)^2 + 8W_{12}^{(1)}},$$

$$\Delta E_3 = \delta + W_{22}^{(2)} + W_{23}^{(2)}, \quad (45)$$

where $\Delta(R) = \delta - W_{12}^{(1)} + W_{22}^{(1)} + W_{23}^{(1)}$ is the van-der-Waals-shifted resonance energy defect. The solution $\Delta E_3$ corresponds to the interaction-induced splitting of completely degenerate states [2] and [3]. Simultaneously, $\Delta E_2 = \Delta E_+ = \delta + W_{22}^{(2)} + W_{23}^{(2)}$ would describe the second solution to the interaction-induced splitting of states [2] and [3] in absence of interaction with the initial state $|1\rangle$ (putting $W_{12}^{(1)} \equiv 0$ and assuming $\Delta(R) > 0$). It should be noted, that this kind of degeneracy of the two-atomic states, related with the transposition of states, should be taken into account in calculating the van-der-Waals interaction between identical atoms in different states [5]. For $W_{12}^{(1)} \equiv 0$ the solution $\Delta E_1 \equiv \Delta E_+ = W_{11}^{(2)}$ (here the upper (lower) sign of $\Delta E_+$ corresponds to positive (negative) value of the energy defect $\Delta(R)$) determines the shift of energy of an isolated state $|i, e_1\rangle$ (in absence of close states [2] and [3]).

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

$$\Delta E_1 \equiv \Delta E_+ = W_{11}^{(2)} \approx \frac{2|W_{12}^{(1)}|^2}{\Delta(R)}, \quad \left(\lim_{R \to \infty} \Delta E_1 \to \epsilon_1 = 0\right);$$

$$\Delta E_2 \equiv \Delta E_+ = \Delta(R) + W_{22}^{(2)} + \frac{2|W_{12}^{(1)}|^2}{\Delta(R)}, \quad \left(\lim_{R \to \infty} \Delta E_2 \to \epsilon_2 = \delta\right), \quad (46)$$

which describe the van-der-Waals shifts of the upper [1] and one of the lower [2] and [3] two-atomic states, respectively. Evidently, the fraction with doubled square of the first-order non-diagonal element $W_{12}^{(1)}$ in the numerator restitutes the omitted terms in the reduced Green’s function of the second-order diagonal elements in the case of perturbation theory for states [1], isolated from [2] and [3].

In an opposite case of $8|W_{12}^{(1)}|^2 \gg |\Delta(R)|^2$, when the splitting $\delta$ between close levels may be neglected, the principal contribution is given by the second term of the under-root expression of equation (45). Then the two solutions (45) are
\[ \Delta E_{\pm} \approx \pm \sqrt{2} |W_{11}^{(1)}| \left[ 1 + \frac{(\Delta(R))^2}{16 |W_{12}^{(1)}|^2} \right] + W_{11}^{(2)} + \frac{\Delta(R)}{2}. \] (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 \( \Delta E = C_3/R^3 \), determined by the first-order non-diagonal matrix element \( W_{12}^{(1)} \). Actually, this kind of 'resonance' for close states \([1], [2]\) and \([3]\) is completely equivalent to a two-atomic resonance in the electromagnetic susceptibilities of two asymptotically interacting atoms in a frequency-dependent external field \([22]\). 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 \( \propto R^2 \) 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 \( \theta \)) follows a function somewhat similar to the square-root dependence of equation (19) for the resonance part of \( C_6(\theta) \) and may be presented, as follows

\[ W_{12}^{(1)}(R, \theta) = \frac{d^{AB}}{R^3} Z_{j_1;j_2}^{LM}(\theta), \] (48)

where the reduced matrix element of the dipole–dipole interaction \( d^{AB} \equiv \langle 1||Q^A Q^B||2 \rangle \) is put in a factor and the sum was performed over magnetic quantum numbers \( M_1, M_2 \) of the resonant two-atomic state \( |2 \rangle = |n_1 h_1 J_1 M_1 \rangle |n_2 h_2 J_2 M_2 \rangle \) in calculating the term \( |W_{12}^{(1)}(R, \theta)|^2 \) of equation (45). So, equations (47) and (48) make evident explicitly the existence of a Förster-type dipole–dipole energy shift

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

but only in a restricted region of the distances. This region could be extended in the case of exact resonance, \( \delta = 0 \), when the equations (47), (49) and corresponding condition \( 8 |W_{12}^{(1)}|^2 \gg |\Delta(R)|^2 \) holds in the region \( R > R_{12} \) 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 \([7, 11, 12, 25, 28, 42]\).

The \( M \)- and \( \theta \)-dependent factor \( C_3(M, \theta) \) may be presented explicitly from equations (47) to (48):

\[ C_3 = \sqrt{2} |d^{AB}| Z_{j_1;j_2}^{LM}(\theta), \] (50)

where the notations are introduced:

\[ Z_{j_1;j_2}^{LM}(\theta) = \left\{ \frac{2}{3(2J + 1)^2} \left[ X_{J_1} X_{J_2} \left( 2 - 3 \cos^2 \theta \right) \right] + \frac{2M^2}{(2J + 1)} \frac{X_{J_1} X_{J_2}}{2} \left[ Y_{2J}(1 - 3 \cos^2 \theta) \right] \right\}^{1/2}. \] (51)

Here \( X_{J_1} = Y_{J_1}(J_1 + 1) - 2 J_1(J_1 + 1) + 1 \) and \( Y_{2J}(x) = 3 X_{2J}(x(2J + 1) - 1) - 8 J(J + 1) \). In contrast to the electrostatic energy of two independent dipoles, the shift (49) does not vanish neither in averaging over the orientations of the interatomic axis, nor in averaging of the angular-momentum orientations (over magnetic quantum numbers \( M \)). It is important to note, that the summation over the magnetic quantum numbers of the states \([2]\) and \([3]\) in determining the squared matrix element \( |W_{12}^{(1)}(R, \theta)|^2 \) of the under square root expression of equation (45) was carried out, since all the Zeeman substates of the resonant states \([2]\) and \([3]\) have equal energies and therefore were excluded from the complete Hilbert space of the Green’s function \((8)\) resolution and introduced into the close-state subspace.

In figure 5, the plots of the factor \( Z_{j_1;j_2}^{LM}(\theta) \) are presented for different cases of the dipole resonances between two-atomic states of alkali atoms

\[ \langle \mathbf{r}_1 | \mathbf{r}_2 | 1 \rangle = \langle \mathbf{r}_1 | nLJM \rangle \langle \mathbf{r}_2 | nLJM \rangle \]

and

\[ \langle \mathbf{r}_1 | \mathbf{r}_2 | 2(3) \rangle = \langle \mathbf{r}_1 | \mathbf{r}_2 | nL_1 J_1 M_1 \rangle \langle \mathbf{r}_2 | \mathbf{r}_1 | nL_2 J_2 M_2 \rangle. \]

As follows from the data of table 1, 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 bi-atomic ‘resonance’ in the region of \( n \approx \tilde{n} \), where the absolute values of the energy defects (29) 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 non-diagonal term of the under-root expression of equation (45) exceeds essentially the first term, seems to be rather narrow. So the \( R^{-3} \) energy-shift dependence of equation (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, i.e. the Legendre polynomial \( P_2(\cos \theta) \), as is seen from the figure 3, where the angle-dependent factors \((51)\) are presented for the ‘resonance’ interaction between two atoms in their \( nP_{3/2} M \) with different projections of the total momentum \( M = \pm 1/2 \) and \( M = \pm 3/2 \) and for the interaction of two atoms in \( nD_{5/2} M = 3/2 \)-states \((1)\). In particular, for \( |M| = 3/2 \) the \( \theta \) dependence of the non-diagonal element is determined by the function \( Z_{1/2,3/2}^{(1)}(\theta) = 3/8 \sin^2 \theta \), vanishing at \( \theta = 0, \pi \) since the radial matrix element, which includes the resonance transition \( |nP_{3/2} M| nP_{3/2} M \rightarrow |nS_{1/2} M| (n = 1) S_{1/2} M \), disappears in the van-der-Waals constant (see equation \((26)\)).

In plot (2) of figure 3 the \( \theta \)-dependences are also presented for the factor \( Z \) of the matrix elements of the dipole transitions between close two-atomic states \( |1| = |nD_{5/2} M| \) \( nD_{5/2} M \) and \( |2(3)| = |(n + 2) P_{3/2} M| (n - 2) P_{3/2} M \).

The most interesting is the case of two Rb atoms in their \( 38P_{3/2} M = 1/2, 3/2 \) states with the lowest absolute value of the Förster energy defect among the nearest states \( |nP|: \delta (38P_{3/2} M) = E(39S_{1/2} M) + E(38S_{1/2} M) - 2E(38P_{3/2} M) \approx -4.62 \text{ MHz} \), where \( \delta (nP_{3/2} M) \) changes its sign from negative to positive in transition from \( n = 38 \) to \( n = 39 \) state. Numerical data of table 1 may be used for evaluating the second-order matrix element \( W_{11}^{(2)} = -C_6(38P_{3/2} M)/R^6 \), where \( C_6 = C_6(38P_{3/2} M) = C_6(38P_{3/2} M) - 2(W_{11}^{(2)})^2/\delta \) is the van-der-Waals constant determined with the reduced Green’s function. The data for the second-order diagonal \( W_{11}^{(2)} \) and non-diagonal \( W_{13}^{(2)} \) matrix elements calculated in the model-potential approach are as follows (in atomic units):

\[
W_{22}^{(1)} = W_{33}^{(2)} = -\hat{R}_{11}/R^6 = 5.144 \times 10^{18}/R^6; \quad W_{23}^{(2)} = 4.097 \times 10^{18}/R^6.
\]

The sum over Zeeman substates eliminates the contribution of the \( R_{nm} \) components of the \( \tilde{C}_6 = C_6 \) \( 38S - 39S \) \(-2(W_{11}^{(2)})^2/\delta \) for the interaction between Rb atoms in their \( 38S_{1/2} M = 39S_{1/2} M \) states, leaving behind only the \( \hat{R}_{11} \) term. Evaluation of the radial matrix elements of the factor

\[
d_{AB}^{(1)} = \frac{4}{3} \langle 38P_{3/2} | R_{nm} | 38S_{1/2} \rangle \langle 38P_{3/2} | R_{nm} | 39S_{1/2} \rangle = -2.544 \times 10^6 \text{ a.u.}
\]

for the dipole–dipole transition matrix element \((48)\) allows to determine the dispersion-interaction induced shifts \((45)-(47)\). The \( R \)-dependence of the ratio \( \chi (R, \theta) = 8|W_{11}^{(1)}(R, \theta)|/\delta (R, \theta)|^2 \) of the under-root terms of equation \((45)\), presented in figure 4, allows to evaluate the region of the interatomic distances \( R \), where the van-der-Waals dependence of the energy level \( 38P_{3/2} M = 1/2 \) shift \( \Delta E = -C_6/R^6 \) turns into the dipole–dipole shift \( \Delta E = C_3/R^4 \). As is seen from the figure, in the region of \( 1 < R < 5,5 \mu m \), the absolute value of the matrix element \( W_{11}^{(2)} \) of transition between two-atomic states \((1)\) and \((2(3))\) exceeds essentially that of the distance-dependent bi-atomic energy detuning \( \Delta (R) \) (the first term of the under-root expression of equations \((45)\)), which vanishes at \( R \approx 2.61 \mu m \). The ratio depends on the angle between the quantisation and interatomic axes, achieving its maximal values at \( \theta = 0 \).
In states of the magnetic quantum number $M = 3/2$ the $\theta$-dependence of the $R$-region, where the inequality $\chi(R, \theta) \gg 1$ holds, is yet stronger since the first-order matrix element $W^{(1)}_{12}(R, \theta = 0) \equiv 0$, and the region of the energy-shift dependence (49) at $\theta = 0$ does not exist. For $\theta = \pi/6$ this region is reduced to the interval $1.8 < R < 3.7 \mu$m; for $\theta = \pi/2$ the inequality $\chi(R, \theta) \gg 1$ holds in the region of $1.2 < R < 5.8 \mu$m, which coincides with the region of $\chi(R, \theta = 0) \gg 1$ for the states $M = 1/2$. So, the region of the dipole–dipole interaction between Rydberg atoms is restricted by the finite value of the energy defect $\delta$ 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 $\delta$ [7, 11, 25, 28, 42]. 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–interaction on the straightforward analogy to the case of ground-state atoms in a field [22]. 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 38P$_{3/2,M=1/2}$-state energy levels of Rb atoms from all the remaining ‘non-resonant’ terms of the two-atomic basis for the Green’s function (8) within the ‘Förster region of distances’ $1 \mu$m $< R < 6 \mu$m is more than 3 orders of magnitude smaller than the contribution of the resonance terms. Outside this region (for $R > 6 \mu$m) this effect follows the law $R^{-6}$ of the usual van-der-Waals equation with the constant $C_6$ determined by equation (19), by the asymptotic equation (36) for irreducible components (20)–(23) and by the numerical data of table 1.

6. Conclusion

For Rydberg levels of very high principal quantum numbers $n$ the absolute value of the energy splitting $\delta$ between the bi-atomic 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 for the perturbation theory for isolated levels extends to $R > R_F > R_{LR}$, where $R_F$ is the ‘Förster radius’. In the region of the distances $R$ between $R_{LR}$ and $R_F$ the perturbation theory for close states should be applied, as discussed in section 5.
The asymptotic approximations (35) and (36) to the constants of van-der-Waals interaction, together with numerical data of table 1, enable rather simple and reliable evaluations of irreducible components for the van-der-Waals constant, with account for the dependence on orientations of interatomic and quantisation axes. In addition, the data of the table includes information on the location of the Förster resonances within the series of Rydberg states in Rb atoms. The information of section 5 may be useful for quantitative determinations of the asymptotic interaction energies of Rb atoms in their Rydberg states. Also, the empirical values $\bar{a}_{\text{FL}-s}^c (j)$ from the numerical data of table 1 provide information on the principal quantum numbers of states within a given $l$-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 data of table and the data on the energy defect $\delta$ determined from the most precise data of 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 [22] between Rydberg atoms (see [43]). The data for evaluations of static polarizabilities and hyperpolarizabilities of Rydberg states in alkali atoms presented in [44] 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 non-additive three- and many-body forces (see e.g. [17, 45–47]) 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 novel results in the field of theoretical studies of the long-range interaction of Rydberg-state atoms, presented in this paper, are as follows:

(i) the general equations (19)–(27) 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 (36) of the irreducible components (20)–(23) of $C_6$ in terms of polynomials in powers of the Rydberg-state principal quantum number $n$ with polynomial coefficients presented in table 1 for $S_{1/2}, P_{1/2}^{1/2}, D_{3/2, 5/2}^{1/2}$ and $F_{5/2, 7/2}^{1/2}$-series of Rydberg states of Rb atoms;

(iii) the interaction-induced shift and splitting of equations (44)–(51) for close-energy two-atomic states, determined within 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’ for infinitely separated atoms and the van-der-Waals interaction law $\Delta E_{\text{vdW}} = -C_6/R^6$ of the region $R > R_F$ transforms into the dipole–dipole law $\Delta E_{d-d} = C_7/R^5$ of the region $R < R_F$ (see figure 4 and the last paragraph of section 5).

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 bi-atomic states. Therefore, the numerical data were presented on the most appropriate example of the Rb states $38P_{3/2}$. Similar data may also be obtained for other close bi-atomic states, such as $2 \times 43D_{3/2}$, with the energy above that of the dipole-connected two-atomic state $41F_{5/2} + 45P_{3/2}$ (the Förster resonance detuning) by approximately $-6$ MHz. Also, two Rb atoms in their $58D_{3/2}$ states have energy approximately 7 MHz above the two-atomic state $56F_{5/2} + 60P_{3/2}$. In both 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 are required, without which the search for the Förster-type resonances in the two-atomic Rydberg spectra is impossible.

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