

Resonance dispersion interaction of alkali metal atoms in Rydberg states

A.A. Kamenski, S.N. Mokhnenko, V.D. Ovsyannikov

Abstract. With the use of second-order perturbation theory in the long-range interatomic interaction for the degenerate states of two Rydberg atoms we have obtained a general formula for the dependence of atomic interaction energy on the interatomic distance R in the presence of the Förster resonance. Inside of the ‘Förster sphere’ ($R < R_F$) this dependence transforms to the formula for electric dipole interaction energy $\Delta E_{d-d} = C_3/R^3$ and for $R > R_F$ it transforms to the formula for the van der Waals interaction energy $\Delta E_{vdW} = -C_6/R^6$. The van der Waals constant C_6 is represented as an expansion in terms of irreducible components which define the dependence on the interatomic axis orientation relative to the quantisation axis of projections M of the total angular momentum J . The numerical values of the irreducible components of tensor C_6 were calculated for rubidium atoms in the same Rydberg states $|nLJM\rangle$ with large quantum numbers n . We present the calculated resonance interaction energy of two rubidium atoms in the states $|43D_{5/2M}\rangle$, whose total energy exceeds by only 8 MHz the total energy of one of the atoms in the state $|45P_{3/2M}\rangle$ and of the other in the state $|41F_{7/2M}\rangle$.

Keywords: atom, Rydberg states, interatomic interaction, van der Waals constant, Förster resonance.

1. Introduction

Rydberg atoms are promising candidates for performing logical operations in quantum information processing devices [1–3]. The function of quantum information carriers may be fulfilled by bound states which are primarily highly excited Rydberg states. The existing laser radiation sources permit exciting specific states with prescribed quantum numbers. The efficiency of excitation and of the possibility of quantum coding is determined by the effect of interatomic interaction, which changes the energy spectrum of an individual atom.

The interaction energy shifts a Rydberg energy level and suppresses the radiative transition probability almost completely. In the absence of external fields, the interaction energy of atoms A and B in states $|n_A\rangle$ and $|n_B\rangle$ of certain parity located at a rather long distance R from each other [$R > R_{LR}$, where $R_{LR} = 2(\langle n_A|r_A^2|n_A\rangle^{1/2} + \langle n_B|r_B^2|n_B\rangle^{1/2})$ is the Le Roy radius [4], which is the total linear dimension of the atoms] is described by the van der Waals formula $\Delta E_{vdW} = -C_6/R^6$. The

van der Waals constant C_6 for S states is a scalar quantity, which is found from the general formula of second-order perturbation theory in the dipole interatomic interaction operator and may be represented as a series in the complete set of discrete spectrum states and the integral over the continuum spectrum states of a diatomic system [5]:

$$C_6(n_A S; n_B S) = 6 \sum_{n_1, n_2} \frac{|\langle n_1 P | \hat{d}_z^A | n_A S \rangle|^2 |\langle n_2 P | \hat{d}_z^B | n_B S \rangle|^2}{\omega_{n_1}^A + \omega_{n_2}^B}, \quad (1)$$

where $\hat{d}_z^{A(B)}$ is the electric dipole moment operator and

$$\omega_{n_1(2)}^{A(B)} = \frac{E_{n_1(2)P}^{A(B)} - E_{n_A(B)S}^{A(B)}}{\hbar}$$

is the dipole transition frequency between the states of the atom A(B). The main contribution to the sum of series (1) is made by the states $|n_{1(2)P}\rangle$, which are closest in energy to the states $|n_{A(B)S}\rangle$. That is why the series converges rather fast, its convergence improving with increasing principal quantum numbers of the $|n_{A(B)S}\rangle$ states, so that in the calculation of the sum it would be sufficient to include only several terms corresponding to the states $|n_{1(2)P}\rangle$ with energies both higher and lower than the energy $E_{n_{A(B)S}}^{A(B)}$. With increasing principal quantum numbers of the Rydberg states $|n_A\rangle$ and $|n_B\rangle$ the matrix elements in the numerator of the fraction in the right-hand side of expression (1) grow proportionally to the squares $n_A^2(n_B^2)$. In this case, the transition frequencies decreases as: $\omega_{n_1}^A \propto 1/n_A^3$, $\omega_{n_2}^B \propto 1/n_B^3$. As a result, the absolute value of the constant C_6 rapidly increases. In particular, for similar atoms in the same state ($n_A = n_B = n$) $|C_6| \propto n^{11}$.

Rydberg states $|n_A\rangle$ and $|n_B\rangle$ may have nonzero orbital, $l_{A(B)} \neq 0$, and total, $J_{A(B)} \neq 0$, angular momenta, whose directions [defined by the direction of the quantisation axis and the projections $M_{A(B)}$ of the total angular momenta], in the most general case, may not coincide with the direction of the interatomic axis defined by the radius-vector \mathbf{R} and the corresponding unit vector $\mathbf{n} = \mathbf{R}/R$. In this case, the van der Waals constant depends not only on the magnetic quantum numbers of bound atomic states but also on the relative orientation of the axes (on the angle θ between the radius-vector \mathbf{R} and the direction of quantization axis defined by the unit vector \mathbf{a} ; Fig. 1). In the general case these dependences are defined by five irreducible C_6 tensor components (see Section 4 below).

Given in Section 2 are explicit expressions for the long-range atomic interaction operator ($R > R_{LR}$). We write out formulas for the interaction energy in the first and second orders of the perturbation theory and determine the terms of asymptotic (in parameter $R_{LR}/R \ll 1$) series that describe the main contribution to the energy.

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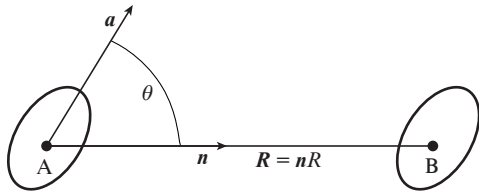


Figure 1. Rydberg atoms A and B in identical states separated by a distance $R = nR$. The unit vector \mathbf{a} aligned with the quantisation axis of the projections of the total angular momentum $\mathbf{J}_{A(B)}$ makes an angle θ with the unit vector \mathbf{n} directed from atom A to atom B.

Section 3 presents the general formulas for the dependence of the van der Waals constant on the direction of the radius-vector $\mathbf{R} = nR$. We give expressions for the irreducible C_6 tensor components in the form of combinations of diatomic radial matrix elements of dipole moment operators. Asymptotic formulas are found for approximate estimates of the C_6 tensor components for Rydberg atoms in the same states.

Using second-order perturbation theory for closely spaced levels, in Section 4 we obtain general formulas for the interaction energy of atoms in the states that have close-in-energy dipole-bound diatomic states. Unless otherwise stated, advantage is everywhere taken of the atomic system of units: $e = m = \hbar = 1$.

2. Perturbation theory for the long-range interaction of atoms in nondegenerate states

2.1. Asymptotic atomic interaction operator

The electrostatic interaction operator $\hat{V}_{AB}(\mathbf{R})$ between two distant ($R > R_{LR}$) neutral atoms A and B may be represented in the form of an asymptotic series of interaction operators $\hat{V}_{L_A L_B}(\mathbf{R})$ between 2^{λ} -pole electric moments

$$\hat{Q}_{\lambda\mu}^{A(B)} = \sum_{i=1}^{Z_{A(B)}} r_{A(B)i}^{\lambda} C_{\lambda\mu}(n_{A(B)i}), \quad (2)$$

which account for the contribution of each of $Z_A(Z_B)$ electrons described by its radius-vector $r_{A(B)i} = r_{A(B)i} n_{A(B)i}$ [$n_{A(B)i}$ is the unit vector directed from the nucleus of the atom A(B) to the i th electron]:

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

An individual term of this sum is the interaction operator of 2^{L_A} -pole and 2^{L_B} -pole electric moments of atoms A and B:

$$\hat{V}_{L_A L_B}(\mathbf{R}) = \frac{(-1)^{L_B}}{R^{L_A+1}} \sqrt{\frac{(2L)!}{(2L_A)!(2L_B)!}} \times (C_L(\mathbf{n})\{\hat{Q}_{L_A}^A \otimes \hat{Q}_{L_B}^B\}_L), \quad L = L_A + L_B. \quad (4)$$

Here use is made of the universally accepted notation of the quantum theory of the angular momentum for scalar and tensor products [6]; $C_{L\mu}(\mathbf{n}) = \sqrt{4\pi/(2L+1)} Y_{L\mu}(\mathbf{n})$ is a modified spherical function, which defines the dependence of the interaction of 2^{L_A} -pole and 2^{L_B} -pole moments on the angular variables of the vector $\mathbf{n} = \mathbf{R}/R$ (Fig. 1); and $Y_{L\mu}(\mathbf{n})$ is a spher-

ical function. The first term $\hat{V}_{11}(\mathbf{R})$ of double series (3) defines the dipole–dipole interaction of atoms in degenerate diatomic states in the first order of the perturbation theory and the van der Waals interaction for atoms in nondegenerate diatomic states in the second order of the perturbation theory.

Eventually the dependence on the orientation of vector \mathbf{R} is transformed to the dependence on the angle $\theta = \cos^{-1}(\mathbf{n}\mathbf{a})$ between the vector \mathbf{n} and the unit vector \mathbf{a} (Fig. 1). Expression (4) for the interaction operator appears to be most convenient, because all variables of the ‘external’ vector \mathbf{R} are contained in the tensor $C_L(\mathbf{n})/R^{L+1}$, which is separated from ‘internal’ variables of the interacting atoms contained in tensor $\{\hat{Q}_{L_A}^A \otimes \hat{Q}_{L_B}^B\}_L$. The components of these tensors appear explicitly in the matrix elements of the operator $\hat{V}_{L_A L_B}(\mathbf{R})$ in accordance with selection rules for angular momenta.

The dipole–dipole interaction operator may be expressed in terms of electric dipole operators $\hat{Q}_1^{A(B)} \equiv \hat{d}^{A(B)}$ in two ways:

$$\hat{V}_{11}(\mathbf{R}) = \begin{cases} -\frac{\sqrt{6}}{R^3} (C_2(\mathbf{n})\{\hat{d}^A \otimes \hat{d}^B\}_2), \\ \frac{(\hat{d}^A \hat{d}^B) - 3(\hat{d}^A \mathbf{n})(\hat{d}^B \mathbf{n})}{R^3}. \end{cases} \quad (5)$$

The former expression is better suited for practical calculations. The dependence on the orientation of the vector $\mathbf{R} = R\mathbf{n}$, which is distributed over the numerous components of scalar products in the latter expression, requires labourious calculations of different dipole matrix elements even in the first order of the perturbation theory, making energy calculations in the second and higher orders extremely cumbersome. By contrast, the former expression is convenient to use in high orders of the perturbation theory, since the \mathbf{n} dependence is confined in the single factor $C_2(\mathbf{n})$ alone.

In the first order of the perturbation theory the dipole–dipole interaction can make a contribution to a shift of energy levels in atoms A and B in the following cases:

- 1) when the states of interacting atoms are superpositions of dipole-bound states of opposite parity; and
- 2) when the identical atoms A and B are in different states with an allowed dipole transition between them.

For similar atoms in identical states of certain parity the contribution of the dipole–dipole interaction (and of all odd interactions: dipole, octupole, etc.) in the first-order perturbation theory in $\hat{V}_{AB}(\mathbf{R})$ is equal to zero. In this case, the interactions of even multipole moments may become significant for the states with nonzero angular momenta. Furthermore, higher multipole interactions between atoms (quadrupole–quadrupole, etc.) should be taken into account so as to verify the applicability of dipole–dipole approximation in higher orders of the perturbation theory.

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

To determine the interaction energy in the system of two highly excited Rydberg atoms in the first-order perturbation theory in interatomic interaction it is sufficient to calculate the matrix element of operator (3). Let the wave function $\langle r_A, r_B | AB \rangle$ (in Dirac’s notation) define the state of an isolated system of two noninteracting atoms A and B ($\langle r_A, r_B | AB \rangle = \langle r_A | A \rangle \langle r_B | B \rangle$) in their stationary states $\langle r_{A(B)} | A(B) \rangle$ with principal quantum numbers $n_{A(B)}$, nonzero angular momenta $l_{A(B)} \geq 1$, and magnetic quantum numbers $m_{A(B)}$ ($|A(B)\rangle =$

$|n_{A(B)} l_{A(B)} m_{A(B)}\rangle$). Then the first-order interaction energy $\Delta E_{AB}^{(1)} = \langle AB | \hat{V}_{AB}(\mathbf{R}) | AB \rangle$ is determined by the total contribution of even electric multipole moments $Q_{2L} = C_{l_0 2L 0}^{l_0} \times \langle n | r^{2L} | n \rangle$ (the matrix elements with odd momenta are equal to zero in states of specific parity):

$$\Delta E_{AB}^{(1)}(\mathbf{R}) = \sum_{L_A=1}^{l_A} \sum_{L_B=1}^{l_B} C_{l_A m_A 2L_A 0}^{l_A m_A} C_{l_B m_B 2L_B 0}^{l_B m_B} \times \frac{(2L)! Q_{2L_A}^A Q_{2L_B}^B}{(2L_A)!(2L_B)! R^{2L+1}} P_{2L}(\mathbf{n}\mathbf{a}). \quad (6)$$

Here, like in Eqn (4), $L = L_A + L_B$ and advantage is taken of the commonly accepted notation C_{acbp}^{cy} for Clebsch–Gordan coefficients and Legendre polynomials $P_{2L}(\cos\theta) = C_{2L 0}(\theta, \varphi)$. Evidently the main contribution to the first-order interaction energy (6) is made by the term of the lowest nonvanishing order in $1/R$ defined by the electric quadrupole moments $Q_2^{A(B)}$. The next term, which describes the interaction of the moments $Q_2^{A(B)}$ and $Q_4^{B(A)}$ is a quantity of order n^4/R^2 of the quadrupole–quadrupole term. This ratio, which is equivalent to the ratio of the mean-square radius $\langle n | r^2 | n \rangle \propto n^4$ of the Rydberg electron orbit and the squared interatomic distance R , is rather small in the applicability domain of the long-range approximation (3), (4) in the interaction at a distance $R > R_{LR} \approx 5n^2$. Therefore, the main contribution to the first-order energy (6) is made by the term with $2L_A = 2L_B = 2$, which is proportional to R^{-5} . In the right-hand side of expression (6) the number of terms is $N_{AB} = l_A l_B$, and therefore the energy (6) turns to zero ($N_{AB} = 0$) when one of the atoms is in an nS state ($l_{A(B)} = 0$). When both atoms are in nP states, $N_{AB} = 1$, and only the quadrupole–quadrupole term remains in the right-hand side of expression (6), which may be estimated by the formula $\Delta E_{AB}^{(1)} \propto n^8/R^5$. For $n = 100$, the applicability condition for the long-range approximation is fulfilled for $R > R_{LR} \approx 5 \times 10^4 \text{ au} \approx 2.6 \mu\text{m}$. At this separation distance $\Delta E_{AB}^{(1)} < 1 \text{ GHz}$. However, the shift (6) will vanish at the nodes of the polynomial $P_4(\mathbf{n}\mathbf{a})$ for angles θ between vectors \mathbf{n} and \mathbf{a} equal to 30.6° , 70.1° , 109.9° , and 149.4° . The energy $\Delta E_{AB}^{(1)}$ also vanishes after averaging over the orientations of radius-vector \mathbf{R} or orbital momentum $\mathbf{l}_{A(B)}$ (on averaging over magnetic quantum numbers $m_{A(B)}$ of the atom A(B)).

The states with sufficiently large absolute values of magnetic quantum numbers $m_{A(B)}$ and therefore high angular momenta ($l_{A(B)} \geq |m_{A(B)}| \geq 5$) are equivalent to degenerate states of a hydrogen atom. These states do not possess specific parity and possess both even and odd permanent electric multipole moments [7], which can also make a nonzero contribution to the sum (6).

2.3. Second-order perturbation theory for asymptotic interaction of atoms in nondegenerate states

In the second order of the perturbation theory the diatomic-state energy shift

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

is defined by the matrix element with two dispersion interaction operators (3) and reduced diatomic Green's function, which comprises the sums over bound spectrum states and the integrals over the continuum states of noninteracting atoms:

$$G'_{AB}(\mathbf{r}_A, \mathbf{r}_B; \mathbf{r}'_A, \mathbf{r}'_B) = \sum_{n_1, n_2} \frac{\langle \mathbf{r}_A | n_1 \rangle \langle n_1 | \mathbf{r}'_A \rangle \langle \mathbf{r}_B | n_2 \rangle \langle n_2 | \mathbf{r}'_B \rangle}{E_{n_1} + E_{n_2} - E_A - E_B - i0}. \quad (7)$$

Summation is performed over the complete eigenvector basis $|n_i\rangle \equiv |n_i l_i J_i M_i\rangle$ ($i = 1, 2$) of the Hamiltonian $\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$ of noninteracting atoms, with the exception of the eigenvector $\langle \mathbf{r}_A, \mathbf{r}_B | AB \rangle$, which corresponds to the eigenvalue $E_A + E_B = E_{AB}$ for the total energy of infinitely separated atoms (this is indicated by the primed summation sign). There are numerous methods for calculating higher-order matrix elements with diatomic Green's functions based on the separation of infinite summation for the atom A from that for the atom B. For this purpose the diatomic functions may be written in the form of convolution of the imaginary parts of the complex energies of monoatomic Green's functions [8, 9] with the use of their Sturmian representation [10]. The use of Laguerre orbitals turned out to be most efficient in the calculation of higher orders of the van der Waals interaction for the ground-state hydrogen atoms [11]. For diatomic Green's function with the total energy of two Rydberg states, the representation in terms of expansion in the eigenstates of noninteracting atoms (7) turns out to be most convenient, because the main contribution to the double sum is made by the terms nearest in energy to the state $\langle \mathbf{r}_A, \mathbf{r}_B | AB \rangle$. In practice, from six to eight terms from each sum with E_{n_1} (E_{n_2}) lower and higher than E_A (E_B) provide a precision of at least five decimal places in the determination of the matrix elements.

It is evident that $\Delta E_{AB}^{(2)} \neq 0$ independently of the values of the angular momenta $l_{A(B)}$, because Green's function contains all states and allows arbitrary second-order multipole transitions between states in accordance with the parity conservation law. Consequently, the correction to the second-order energy comprises an infinite series of terms arising in the expansion of the interaction operator (3) in powers of $1/R$ [11]:

$$\Delta E_{AB}^{(2)}(\mathbf{R}) = - \sum_{q=0}^{\infty} \frac{C_{6+2q}^{(2)}(\mathbf{n})}{R^{6+2q}}. \quad (8)$$

Here the infinite sum takes into account all virtual multipole moments of atoms A and B in operators $\hat{V}_{L_A L_B}(\mathbf{R})$: from $L_{A(B)} = 1$ to infinity. The shift $\Delta E_{AB}^{(2)}(\mathbf{R})$ in the second order of the perturbation theory is expanded in a series in even powers of the parameter $1/R$. Coefficients $C_{6+2q}^{(2)}(\mathbf{n})$ depend on the orientation of the interatomic axis \mathbf{n} . The main contribution to $\Delta E_{AB}^{(2)}(\mathbf{R})$ is made by the term of lowest order in $1/R$, so that $\Delta E_{AB}^{(2)}(\mathbf{R}) \approx -C_6^{(2)}(\mathbf{n})/R^6$, where the van der Waals constant $C_6^{(2)}(\mathbf{n})$ describes the second-order interaction of the virtual electric dipole moments of atoms A and B. From the general relation $|C_{6+2(q+q')}^{(2)}/C_{6+2q}^{(2)}| \propto n^{4q'}$ ($q' = 0, 1, 2, \dots$) between the coefficients of series (8) there follows an inequality $n^2/R < 1$, which defines the convergence domain of series (8) and is fully consistent with the inequality $R > R_{LR}$ given above.

3. Perturbation theory for asymptotic interaction of Rydberg atoms in states with close energy values

When the applicability condition $|\Delta E_{vdw}/\delta| \ll 1$ of the perturbation theory is not fulfilled for the energy difference $\delta = E_2 - E_1$ in the expression for diatomic Green's function (7) $E_1 \equiv E_{AB} = E_A + E_B = 2E_n$ of the initial diatomic 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 $E_2 \equiv E_{n_1 n_2} = E_{n_1} + E_{n_2}$ of the intermediate state $\langle \mathbf{r}_1, \mathbf{r}_2 | 2 \rangle = \langle \mathbf{r}_1 | n_1 \rangle \langle \mathbf{r}_2 | n_2 \rangle$, and use should be made

of the perturbation theory for close levels. For identical states of interacting atoms, $|A\rangle = |B\rangle = |nJM\rangle$, in the diatomic state $|1\rangle$ the monoatomic states $\langle r_1 | n_1 l_1 J_1 \rangle$ in the energetically close diatomic state $\langle r_1, r_2 | 2 \rangle = \langle r_1 | n_1 l_1 J_1 \rangle \langle r_2 | n_2 l_2 J_2 \rangle$ should be different. The permutation of individual atomic states corresponds to the third close state $\langle r_2, r_1 | 3 \rangle = \langle r_2 | n_1 l_1 J_1 \rangle \langle r_1 | n_2 l_2 J_2 \rangle$ energetically equivalent to the state $\langle r_1, r_2 | 2 \rangle$, which is also present in the expansion of Green's function (7). Consequently the subspace of close states comprises at least three different diatomic states – $|1\rangle$, $|2\rangle$, and $|3\rangle$ – the last two being of equal energy, $E_3 = E_2 = E_n + E_m$. The states $|2\rangle$ and $|3\rangle$ may be united in a pair of alternative resonance states, $|\pm\rangle = (|2\rangle \pm |3\rangle)/\sqrt{2}$. However, the $|- \rangle$ state does not interact with the initial state $|1\rangle$ (a 'dark' state) and does not make a contribution to the resonance increase in C_6 . That is why the basis consisting of the three vectors – $|1\rangle$, $|2\rangle$, and $|3\rangle$ – is most convenient. Vectors $|2\rangle$ and $|3\rangle$ contain the sum of states with all possible magnetic quantum numbers M , and therefore in the calculation of the matrix elements

$$W_{12}^{(1)} = W_{21}^{(1)} = W_{13}^{(1)} = W_{31}^{(1)}, \quad W_{22}^{(2)} = W_{33}^{(2)}, \quad W_{23}^{(2)} = W_{32}^{(2)} \quad (9)$$

of operator (3) summation should be performed over all Zeeman sublevels dipole-coupled to state $|1\rangle$, like in the full set of states for Green's function (7). In this case, the interaction energy ΔE between Rydberg atoms may be determined in an arbitrary order of the perturbation theory in interaction (3) by solving equation

$$\det \| W_{ij} + (\varepsilon_i - \Delta E) \delta_{ij} \| = 0, \quad (10)$$

which is equivalent to the diagonalisation procedure of a 3×3 matrix (here, δ_{ij} is the Kronecker delta) with the elements

$$W_{ij} = \langle i | \hat{V}_{AB}(\mathbf{R}) \{ 1 + G'_E [\hat{V}_{AB}(\mathbf{R}) - \Delta E] \}^{-1} | j \rangle, \quad (11)$$

where $i, j = 1, 2, 3$ correspond to close states separated out from series (7) to the three-vector subspace. The interaction-induced shift $\Delta E = E - \bar{E}$ relates to Green's function energy, for which it is convenient to choose $\bar{E} = E_1$. Then, the shifts $\varepsilon_i = E_i - \bar{E}$ in Eqn (10) ($\varepsilon_1 = 0$ and $\varepsilon_2 = \varepsilon_3 = \delta$) define three solutions $\Delta E_i = \varepsilon_i$ of the cubic equation for infinitely separated atoms (for $R \rightarrow \infty$, when the matrix elements W_{ij} tend to zero). Using expansion (3) of the interaction operator $\hat{V}_{AB}(\mathbf{R})$ in powers of $1/R$, for each term of the perturbation theory series

$$W_{ij} = \sum_{k=1}^{\infty} W_{ij}^{(k)}, \quad \Delta E = \sum_{k=1}^{\infty} E^{(k)} \quad (12)$$

it is possible to obtain the corresponding expansions in powers of the parameter $1/R$ for the matrix elements and energy in expression (11). In this case, in the first order ($k = 1$) we have the sum of a finite number of terms which describe only the allowed transitions between the initial and final states of atoms A and B, similarly to the sum for the first-order energy (6) for the isolated state $|AB\rangle$:

$$W_{ij}^{(1)} = \langle i | \hat{V}_{AB}(\mathbf{R}) | j \rangle = \sum_{q=q_1}^{L_{\Sigma}+1} \frac{w_{ij}^{(1)}(q, \mathbf{n})}{R^q}, \quad (13)$$

where $L_{\Sigma} = l_A(i) + l_A(j) + l_B(i) + l_B(j)$ is the sum of angular moments of both atoms in their initial ($|i\rangle$) and final ($|j\rangle$) states ($i, j = 1, 2, 3$). The starting power value q_1 also depends on the

angular momenta of the diatomic states $|i\rangle$ and $|j\rangle$. When these states are dipole-coupled for both atoms ($\Delta l_{A(B)} = |l_{A(B)}(i) - l_{A(B)}(j)| = 1$), summation for a nondiagonal element of expression (13) starts with $q_1 = 3$. When the states are dipole-coupled only for one of the atoms and only a quadrupole transition is allowed for the other one, then $q_1 = 4$; when dipole transitions are forbidden and quadrupole transitions are allowed for both atoms, then summation for the first-order matrix element of expression (13) starts with the quadrupole–quadrupole term and $q_1 = 5$, like in the expansion (6) for the first-order energy defined by the diagonal matrix element $W_{ii}^{(1)}$.

The second-order term in the expansion for the matrix element in series (12) may be represented in the form of a series:

$$W_{ij}^{(2)} = -\langle i | \hat{V}_{AB}(\mathbf{R}) G'_E \hat{V}_{AB}(\mathbf{R}) | j \rangle = \sum_{q=q_2}^{\infty} \frac{w_{ij}^{(2)}(q, \mathbf{n})}{R^q}, \quad (14)$$

which contains even powers of $1/R$, beginning with $q_2 = 6$, for diagonal matrix elements $W_{ii}^{(2)}$. The parity and starting value of power q_2 for nondiagonal matrix elements $W_{12}^{(2)} = W_{13}^{(2)}$ depend on the relation between the parities of individual monoatomic states in the initial ($|1\rangle$) and final ($|2\rangle$, $|3\rangle$) diatomic states. We restrict ourselves to the most interesting case of dipole-coupled close states $|1\rangle$ and $|2\rangle$, $|3\rangle$, which permits taking into account only the first-order matrix element $W_{12}^{(1)} \propto 1/R^3$.

With allowance for the matrix elements of the lowest non-vanishing orders in expressions (13) and (14) and for identities (9), the solutions of the secular equation (10) may be represented as

$$\Delta E_{1,2} \equiv \Delta E_{\pm} = W_{11}^{(2)} + \frac{\Delta(\mathbf{R})}{2} \pm \frac{1}{2} \sqrt{\Delta^2(\mathbf{R}) + 8 |W_{12}^{(1)}|^2}, \quad \Delta E_3 = \delta + W_{22}^{(2)} - W_{23}^{(2)}, \quad (15)$$

where $\Delta(\mathbf{R}) = \delta - W_{11}^{(2)} + W_{22}^{(2)} + W_{23}^{(2)}$ is the interatomic-distance-dependent splitting of close energy levels with the account for their van der Waals shift up to second-order of the perturbation theory in $\hat{V}_{AB}(\mathbf{R})$ inclusively. The solutions $\Delta E_2 = \Delta E_+ = \delta + W_{22}^{(2)} + W_{23}^{(2)}$ and ΔE_3 determine the splitting of completely degenerate states $|2\rangle$ and $|3\rangle$ induced by the interaction (3), (4) [under the assumption that $W_{12}^{(1)} \equiv 0$ and $\Delta(\mathbf{R}) > 0$]. It is pertinent to note that the degeneracy of the diatomic states which differ by permutation of the monoatomic states of identical atoms should be taken into consideration in the calculation of the van der Waals interaction energy. For $W_{12}^{(1)} \equiv 0$ the solution $\Delta E_1 = \Delta E_- = W_{11}^{(2)}$ defines the energy shift of the isolated state $\langle r_1, r_2 | 1 \rangle$ [in this case, the states $|2\rangle$ and $|3\rangle$ are included in Green's function (7)].

Diagonal matrix elements decrease rapidly with increasing interatomic distance, as is clear from their asymptotic dependences $W_{ii}^{(2)} \propto n^{11}/R^6$. That is why for long distances ($R > n^3$) the main contribution to $\Delta(\mathbf{R})$ is made by the energy difference δ between diatomic states, which is independent of R . In particular, for the states with $n \approx 50$ and $|\delta| > 100$ MHz the difference between $\Delta(\mathbf{R})$ and δ does not exceed 10% even for $R > 10 \mu\text{m}$. The first-order nondiagonal matrix element $W_{12}^{(1)} \propto n^4/R^3$ also decreases with R . Therefore, the inequality $8 |W_{12}^{(1)}|^2 \ll |\Delta(\mathbf{R})|^2$ holds in the indicated region of $R > n^3$ and approximate solutions of Eqn (10), which describe the van der

Waals shifts of the diatomic states, may be written in the form [assuming that $\Delta(\mathbf{R}) > 0$]

$$\Delta E_1 \equiv \Delta E_- = W_{11}^{(2)} - \frac{2|W_{12}^{(1)}|^2}{\Delta(\mathbf{R})} \xrightarrow{R \rightarrow \infty} 0, \quad (16)$$

$$\Delta E_2 \equiv \Delta E_+ = \delta + W_{22}^{(2)} + W_{23}^{(2)} - \frac{2|W_{12}^{(1)}|^2}{\Delta(\mathbf{R})} \xrightarrow{R \rightarrow \infty} \varepsilon_2 = \delta.$$

Here, the fraction with the doubled square of the first-order nondiagonal matrix element $W_{12}^{(1)}$ in the numerator is responsible for the restoration of the terms in reduced Green's function which correspond to states $|2\rangle$ and $|3\rangle$ and which are present in non-reduced Green's function of the matrix elements in the second-order perturbation theory for the isolated state $|1\rangle$.

In the opposite case, $8|W_{12}^{(1)}|^2 \gg |\Delta(\mathbf{R})|^2$, when the splitting δ between close levels may be neglected, the main contribution is made by the second term in the radicand of Eqn (15). In this case, the two solutions are of the form

$$\Delta E_{\pm} \approx \pm\sqrt{2}|W_{12}^{(1)}| \left[1 + \frac{\Delta^2(\mathbf{R})}{16|W_{12}^{(1)}|^2} \right] + W_{11}^{(2)} + \frac{\Delta(\mathbf{R})}{2}. \quad (17)$$

This case corresponds to the so-called Förster resonance, when the power-six van der Waals dependence $\Delta E_{\text{vdW}} = -C_6/R^6$ may turn into a power-three dependence $\Delta E_{\text{d-d}} = C_3/R^3$ determined by the first-order non-diagonal matrix element $W_{12}^{(1)}$. Since $|W_{12}^{(1)}|$ and $|\Delta(\mathbf{R})|$ depend differently on R , the inequality $8|W_{12}^{(1)}|^2 \gg |\Delta(\mathbf{R})|^2$ is violated both at short range, where $|W_{12}^{(1)}|/|\Delta(\mathbf{R})|$ tends to zero proportionally to R^3 for $R \rightarrow 0$, and at long range, where $|W_{12}^{(1)}|/|\Delta(\mathbf{R})|$ tends to zero proportionally to R^{-3} for $R \rightarrow \infty$. Therefore, the range of distances R in which relation (17) holds is limited both from above and from below. In this case, the dependence of the matrix element on the orientation of the interatomic vector \mathbf{R} (on the angle θ) may be represented in the form

$$W_{12}^{(1)}(R, \theta) = \frac{d^{\text{AB}}}{R^3} Z_{J_1; J_2}^{(JM)}(\theta), \quad (18)$$

where $d^{\text{AB}} = \langle 1 || \hat{\mathbf{d}}^{\text{A}} \hat{\mathbf{d}}^{\text{B}} || 2 \rangle$ is the reduced matrix element of dipole-dipole interaction. In the calculation of the factor $|W_{12}^{(1)}(R, \theta)|^2$ of the second term of the radicand in expression (15), the summation was performed over magnetic quantum numbers M_1, M_2 of resonance diatomic states $|2(3)\rangle = \langle r_{\text{A(B)}} | n_{1} J_1 M_1 \rangle \times \langle r_{\text{B(A)}} | n_2 J_2 M_2 \rangle$. Expressions (17) and (18) make evident the existence of the dipole-dipole (Förster) dependence of the energy shift on the separation distance

$$\Delta E_{\pm} = \pm \frac{C_3(M, \theta)}{R^3} \quad (19)$$

in some ranges of interatomic distances $R_{\text{LR}} < R < R_{\text{F}}$ limited above by the Förster radius. This region may be extended to infinity in the case of exact resonance ($\delta = 0$), when Eqns (17) and (18) and the corresponding condition $8|W_{12}^{(1)}|^2 \gg |\Delta(\mathbf{R})|^2$ hold up to $R \rightarrow \infty$. That is why different methods were employed for lowering the magnitude of energy defect $|\delta|$ in external static and time-dependent monochromatic fields [12, 13] to achieve the resonance distance dependence (19). The dependence of coefficient $C_3(M, \theta) = \sqrt{2} \times |d^{\text{AB}}| Z_{J_1; J_2}^{(JM)}(\theta)$ on the magnetic quantum number M and the angle θ is contained in the dependence of the factor:

$$Z_{J_1; J_2}^{(JM)}(\theta) = \left\{ \frac{2}{3(2J+1)^2} + \left[\frac{2M}{(2J)_3} \right]^2 \frac{X_1 X_2}{2} (2 - 3 \cos^2 \theta) + \frac{[3M^2 - J(J+1)](Y_1 + Y_2)}{3(2J+1)(2J-1)_5} (1 - 3 \cos^2 \theta) + \left[\frac{3M^2 - J(J+1)}{(2J-1)_5} \right]^2 Y_1 Y_2 (1 - 8 \cos^2 \theta + 9 \cos^4 \theta) \right\}^{1/2}, \quad (20)$$

where $X_{1(2)} = J(J+1) + 2 - J_{1(2)}(J_{1(2)} + 1)$ and $Y_{1(2)} = 3X_{1(2)} \times (X_{1(2)} - 1) - 8J(J+1)$. Unlike the electrostatic energy of two independent dipoles, the shift (19) does not vanish either on averaging over the orientations of interatomic axis or on averaging over the orientations of angular momenta (over magnetic quantum numbers M). It is significant that the summation over the magnetic quantum numbers of states $|2\rangle$ and $|3\rangle$ was performed in the determination of the squared matrix element $|W_{12}^{(1)}(R, \theta)|^2$ in the radicand of Eqn (15), because all Zeeman sublevels of resonance states $|2\rangle$ and $|3\rangle$ possess the same energy and were therefore excluded from the complete Hilbert space of Green's function expansion (7) and introduced into the subspace of close states.

The domain of separation distances R in which the second term of the radicand in Eqn (15) is significantly greater than the first one is rather small. That is why the dependence of energy shift (15) proportional to R^{-3} occurs only in a limited region of interatomic distances. The dependence of expression (20) on the interatomic axis orientation is significantly different from the corresponding dependence for the dipole-dipole interaction, which is proportional to the Legendre polynomial $P_2(\cos \theta)$, as is evident in Fig. 2.

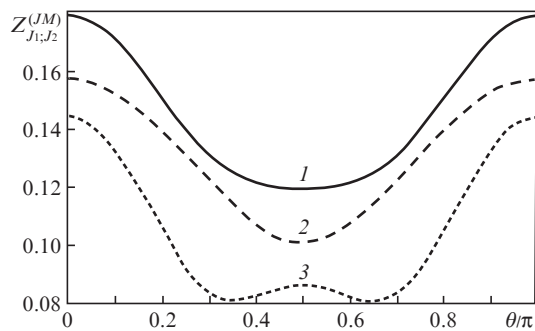


Figure 2. Factor $Z_{J_1; J_2}^{(JM)}(\theta)$ as a function of the angle $\theta = \arccos(na)$ for the resonance interaction of two atoms in the state $|1\rangle = \langle r_1 | n D_{5/2, M} \rangle \times \langle r_2 | n D_{5/2, M} \rangle$ with magnetic quantum numbers $M = (1) 1/2, (2) 3/2$ and $(3) 5/2$ in conditions of resonance for the diatomic states $|2(3)\rangle = \langle r_1(r_2) | n_1 P_{3/2} \rangle \langle r_2(r_1) | n_2 F_{7/2} \rangle$.

4. Irreducible components of van der Waals constant and dependence of C_6 on the interatomic axis orientation

Each coefficient in expansion (8) depends on the orientations of the total angular momentum (on magnetic quantum numbers) and the interatomic axis. These dependences may be expressed with the use of irreducible components defined only by the states of interacting particles. In particular, the van der

Waals constant for similar atoms in identical states, $|n_A l_A J_A M_A\rangle = |n_B l_B J_B M_B\rangle \equiv |n l J M\rangle$, may be represented as a function of magnetic quantum numbers and angle θ between the unit vectors of the interatomic axis \mathbf{n} and quantisation axis \mathbf{a} :

$$C_6(\theta) = C_6^{(2)}(\theta) = R_{ss} - \frac{M^2}{12J^2}(3\cos^2\theta - 2)R_{aa} + \frac{3M^2 - J(J+1)}{2J(2J-1)}(3\cos^2\theta - 1)R_{sT} + \frac{3}{2} \left[\frac{3M^2 - J(J+1)}{2J(2J-1)} \right]^2 (9\cos^4\theta - 8\cos^2\theta + 1)R_{TT}. \quad (21)$$

In this expansion the irreducible components R_{ss} , R_{aa} , $R_{sT} = R_{Ts}$, and R_{TT} of tensor C_6 may be represented as linear combinations of second-order diatomic radial matrix elements

$$\rho_{l_i J_i l_j J_j} = \langle n l J | \langle n l J | r_A r_B g_{l_i J_i l_j J_j} r'_A r'_B | n l J \rangle | n l J \rangle,$$

where $g_{l_i J_i l_j J_j}$ is the radial part of Green's function (7). The coefficients in these combinations are integrals over the angular variables of Rydberg electrons.

For the states with $J = |M|$ (the orbit is in the plane perpendicular to the quantisation axis), a factor $\sin^2\theta$ appears at some of radial matrix elements in expression (21). For this reason, in particular, the contribution of the radial matrix elements $\rho_{l-1, J-1; l-1, J-1}$ and $\rho_{l-1, J-1; l\pm 1, J}$ to C_6 vanishes for $\theta = 0$ and expression for C_6 becomes significantly simpler. For instance,

$$C_6|_{J=|M|=1/2, \theta=0} = \frac{2}{81}(2\rho_{l\pm 1, J; l\pm 1, J} + 11\rho_{l+1, J+1; l+1, J+1} + 14\rho_{l\pm 1, J; l+1, J+1}).$$

The results of numerical calculations of the van der Waals constants for diatomic states with similarly excited Rb atoms in the states $nD_{5/2, M}$ with $n = 42, 43$, and 44 are given in Fig. 3 as functions of angle θ for magnetic quantum numbers $|M| = 1/2$ and $5/2$.

5. Conclusions

The long-range dispersion interaction of identical atoms in the same states with the existence of energetically close dipole-coupled diatomic states may lead to a transition from the van der Waals interaction (C_6/R^6) to a dipole one (C_3/R^3). This rule holds true in the interatomic distance region in which the distance-dependent splitting of the close levels is much smaller than the non-diagonal matrix element of the dipole-dipole interaction. Along with dipole-coupled states, multipole-coupled states may also change their distance dependences if their energy separation is far less than the energy separation of dipole-coupled states. Calculations performed in our work suggest that the interatomic distance domain in which the dipole interaction type related to approximate relation (17) is realised depends significantly on the energy difference δ . This region may be characterised by the Förster radius R_F , which

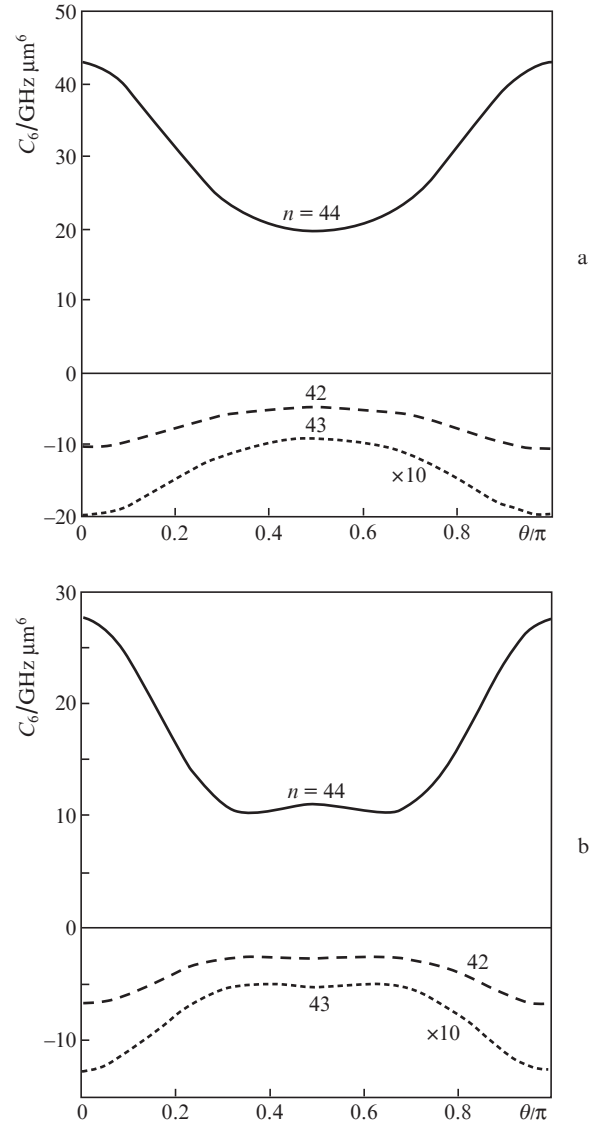


Figure 3. Van der Waals constant C_6 as a function of angle θ for the $nD_{5/2, M}$ states with principal quantum numbers $n = 42, 43$ and 44 and magnetic quantum numbers $|M| =$ (a) $1/2$ and (b) $5/2$.

tends to infinity for $\delta \rightarrow 0$. In particular, two Rb atoms in the same $43D_{5/2}$ state may interact by the $\Delta E_{d-d} = C_3/R^3$ law in the 2-to-10 μm interatomic distance domain owing to the proximity of their energies to the atomic energies in the states $45P_{3/2}$ and $41F_{7/2}$. In this case, the interaction energy depends significantly on the orientation of interatomic axis (on the angle θ) relative to the quantisation axis of the total atomic momenta.

The dependences of the van der Waals constant on the interatomic axis direction are described with the use of irreducible components calculated in a single-electron approximation employing the spectral decomposition of diatomic Green's function.

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