Interatomic interactions and thermally induced shifts and broadenings of energy levels of atoms in circular Rydberg states

A.A. Kamenski, V.D. Ovsiannikov, I.L. Glukhov

Abstract. **Analytical expressions are obtained for the constants determining the energy of the long-range (at large distances exceeding the LeRoy radius $R_{LR} \approx 4n^2$) polarisation interaction of the multipole electric moments of two atoms in identical Rydberg states with large principal (n) and maximum orbital (l) and magnetic (m) quantum numbers ($|m| = l = n - 1$). Asymptotic expansions in powers of n are found for the components of the van der Waals interaction tensor, which determine the dependence of the dispersion energy on the orientation of the interatomic axis. The spontaneous and thermally induced broadenings of the energy levels of circular states are represented analytically as functions of the principal quantum number and temperature. It is found that analytical formulae for the sum of spontaneous and thermally induced line widths in the region of high temperatures and large principal quantum numbers (assuming $n^3 k_B T \gg 1$) do not contain a temperature-independent contribution of the spontaneous part of the broadening. Closed analytical expressions are also obtained for the Farley–Wing function and for the n- and T-dependent corrections to the asymptotic behaviour of the thermally induced shift.**

Keywords: atom, Rydberg states, interatomic interaction, Van der Waals constant, thermal radiation, shift, width of energy levels.

1. Introduction

The infinite set of Rydberg atom/ion states is of considerable interest for the implementation of quantum methods of ultrafast computation and information processing [1–3]. The currently existing sources of laser radiation make it possible not only to cool atoms deeply and to hold them in electromagnetic traps, but also to excite these atoms into precisely defined states with given quantum numbers. In this case, the states with small orbital angular momenta l have a specific energy structure characteristic of atomic particles of each specific chemical element, and states with large angular momenta, in particular, circular states with the maximal angular momentum $l = n - 1$ for a fixed principal quantum number n, are practically similar for all atoms. This is because the Rydberg electron with large orbital angular momentum is held in a stationary state by a field that almost coincides with the field of a point charge. The main quantitative characteristic of the energy of a single-electron state in an atom is the

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quantum defect. For states with $l > 5$, it differs little from zero, regardless of the structure of the residual ion of any chemical element. Therefore, highly excited circular states with a maximum projection of the orbital angular momentum onto a preferred direction (the quantisation axis) are identical to the corresponding state of the hydrogen atom described by the Coulomb wave functions. This circumstance allows considering the Rydberg circular states of all atoms based on the quantum theory of the motion of an electron in a Coulomb field. Thus, all the results of calculations of the energy of pair interaction of two neutral atoms, spontaneous and thermally induced widths, as well as thermal radiation-induced shifts of energy levels of circular Rydberg states presented in this paper are valid and can be used for any atoms and ions of almost all chemical elements.

The efficiency of controlling quantum transitions in Rydberg states can be significantly limited (or, on the contrary, enhanced) by the influence of interatomic forces and effects of interaction with external electromagnetic fields that change the energy spectrum of bound states of atomic particles. Therefore, information about the change in the energy spectrum induced by these effects is of considerable interest for the development of quantum technologies using atoms in highly excited states. In particular, the interatomic interaction shifts the energy levels of Rydberg states, almost completely blocking the possibility of radiative excitation of atoms surrounding one of the atoms of the ensemble, already excited by resonant radiation. Such an effect, in the literature referred to as the Rydberg blockade, seems promising, e.g., for designing quantum logic gates [2].

In addition to interatomic interaction, a significant impact on the energy levels of Rydberg atoms can be due to the ubiquitous thermal radiation of the environment, referred to as black body radiation (BBR), in the spectral distribution of which there are not only the frequencies of resonance transitions between bound states of atoms, but also frequencies exceeding the ionisation threshold. The interaction with photons having such frequencies stimulates the induced processes of decay, excitation, and ionisation, leading to an additional broadening of the energy levels in comparison with their natural width. In addition, the interaction of the atom with the BBR causes a dynamic Stark level shift, to which photons give their contribution at all frequencies, including nonresonant frequencies that do not affect the broadening.

This paper presents the results of quantum-mechanical calculations of the quantitative characteristics of the most important phenomena affecting the structure of circular Rydberg atomic states. Section 2 presents the first-order perturbation theory of interatomic interaction for quantitative calculations of the energy of a long-range polarisation multi-

pole–multipole interaction of atoms at large distances $R > R_{LR}$ (where $R_{LR} \approx 4n^2$ is the LeRoy radius [4]). In Section 3, the energy of the dispersion interaction of virtual dipole moments arising in the intermediate states of the matrix elements in the second-order perturbation theory is calculated. For the van der Waals constant $C_6(n,\theta)$, which describes the most important contribution of $\Delta E_{vdW}(n,\theta,R) = -C_6(n,\theta)/R^6$ to the energy of dispersion interaction, the asymptotic dependence on the principal quantum number of the circular state is determined for the tensor $C_6(n,\theta)$ components. Analytical expressions are obtained for the coefficients of the expansion of $C_6(n,\theta)$ in powers of $\cos\theta$, where the angle θ determines the direction of the interatomic axis relative to the orbital angular momentum of the atom.

Section 4 presents analytical expressions for the spontaneous width and thermally induced broadening of the energy levels of highly excited circular states. An exponential decrease in the contributions to the broadening from excitations of high bound states and transitions to the continuous spectrum (ionisation) is demonstrated. An explicit expression is obtained for the total level width, which takes into account the contributions of all spontaneous and thermally induced transitions. The correction to the well-known Gallagher–Cooke formula [5, 6] is calculated, which is proportional to the square of the ratio of the energy of transitions between adjacent bound states $|E_n - E_{n\pm1}| \approx Z^2/n^3$ to the BBR thermal energy $k_B T$. In Section 5, the energy shift of the Rydberg circular state in the field of the BBR is calculated. An analytical expression for the Farley–Wing function $\mathcal{F}(y)$ is found in the form of an alternating series of odd powers of the argument y, which makes it possible to determine the numerical value of $\mathcal{F}(y)$ with a given accuracy in a wide range of numerical values of y.

Below in the text of the paper, unless otherwise specified, the atomic system of units $e = m = \hbar = 1$ is used, in which the velocity of light numerically coincides with the reciprocal of the fine structure constant, $c = \alpha^{-1} = 137.036$, the BBR temperature is expressed in kelvins, the Boltzmann constant k_B is determined by the ratio $1/T_a$ of atomic unit of energy to atomic unit of temperature $T_a = 315776$ K.

2. Polarisation interaction of atoms

2.1. Asymptotic interaction operator

The operator $\hat{V}_{AB}$ of electrostatic interaction of two neutral atoms A and B in states with nonzero orbital angular momenta L_A and L_B at large distances, $R > R_{LR}$, can be represented as a sum

$$\hat{V}_{AB}(R) = \sum_{L_A = 1}^{\infty} \sum_{L_B = 1}^{\infty} \hat{V}_{L_A L_B}(\boldsymbol{R}) \tag{1}$$

of operators of interaction of electric moments with multipolarity 2^λ

$$\hat{Q}_{\lambda\mu}^{A(B)} = \sum_{i=1}^{Z_{A(B)}} r_{A(B)i}^\lambda C_{\lambda\mu}(\boldsymbol{n}_{A(B)i}). \tag{2}$$

Here, the contribution of each of $Z_A(Z_B)$ electrons, described by its radius-vector $\boldsymbol{r}_{A(B)i} = r_{A(B)i}\boldsymbol{n}_{A(B)i}$ relative to the nucleus ($\boldsymbol{n}_{A(B)i}$ is the unit vector directed from the nucleus to the ith electron) of the atom A(B). Each term in sum (1) is an opera-

tor of the interaction of electric moments of atoms A and B with the multipolarity 2^{L_A} and 2^{L_B}:

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

$$L = L_A + L_B. \tag{3}$$

Here we use the conventional notation of the quantum theory of angular momentum for scalar and tensor products [7]; and $C_{L\mu}(\boldsymbol{n}) = \sqrt{4\pi/(2L+1)}\, Y_{L\mu}(\boldsymbol{n})$ is a modified spherical function that determines the dependence of the multipole interaction on the angular variables of the vector $\boldsymbol{n} = \boldsymbol{R}/R$, directed from atom A to atom B (Fig. 1).
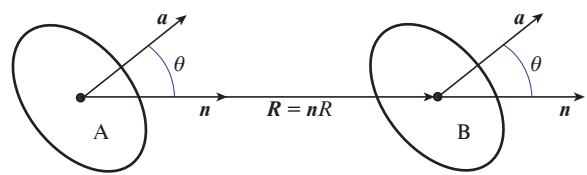
Figure 1. Atoms in similar circular states with maximum magnetic and orbital quantum numbers, $l = |m| = n - 1$, at a distance R from each other. The angle between the interatomic axis and the quantisation axis (the unit vectors $\boldsymbol{n}$ and $\boldsymbol{a}$, respectively) is θ.

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

In the first-order perturbation theory with respect to interaction (1), (3), the energy shift in the system of two atoms $\Delta E_{AB}^{(1)} = \langle AB|\hat{V}_{AB}(\boldsymbol{R})|AB\rangle$ is determined by the sum of the contributions of the even electric multipole moments $Q_{2L} = C_{l02L0}^{l0}\langle nl|r^{2L}|nl\rangle$ (in fixed parity states, the matrix elements of odd moments are zero). Let the wave function $\langle \boldsymbol{r}_A, \boldsymbol{r}_B|AB\rangle = \langle \boldsymbol{r}_A|A\rangle\langle \boldsymbol{r}_B|B\rangle$ determine the state of the system consisting of two noninteracting atoms A and B in their stationary states $\langle \boldsymbol{r}_{A(B)}|A(B)\rangle = \langle \boldsymbol{r}_{A(B)}|n_{A(B)}l_{A(B)}m_{A(B)}\rangle$ with the principal quantum numbers $n_{A(B)}$, angular momenta $l_{A(B)} \geqslant 1$, and magnetic quantum numbers $m_{A(B)}$. Then

$$\Delta E_{AB}^{(1)}(R) = \sum_{L_A = 1}^{l_A} \sum_{L_B = 1}^{l_B} C_{l_A m_A 2L_A 0}^{l_A m_A} C_{l_B m_B 2L_B 0}^{l_B m_B}$$

$$\times \frac{(2L)! Q_{2L_A}^A Q_{2L_B}^B}{(2L_A)!(2L_B)! R^{2L+1}} P_{2L}(\boldsymbol{na}). \tag{4}$$

Here, as in Eqn (3), $L = L_A + L_B$ and we use the generally accepted notation for the Clebsch–Gordan coefficients $C_{a\alpha b\beta}^{c\gamma}$ and Legendre polynomials $P_{2L}(\cos\theta) = C_{2L0}(\theta,\varphi)$. The even parity of polynomials corresponds to the fact that energy (4) is independent of the choice of direction on the interatomic axis:

$$\Delta E_{AB}^{(1)}(\boldsymbol{R}) = \Delta E_{AB}^{(1)}(-\boldsymbol{R}).$$

The calculation for the circular state using the Coulomb wave functions yields the dependence on the principal quantum number $n \geqslant 2$ and the interatomic distance $\boldsymbol{R}$ for the first

nonvanishing term of the expansion in powers of $1/R$, which corresponds to the quadrupole–quadrupole interaction

$$\Delta E_{2-2}(n, \boldsymbol{R}) = \frac{3}{2} n^4 (n^2 - 1)^2 \frac{P_4(\cos\theta)}{R^5}. \tag{5}$$

For states with $n \geqslant 3$ in sum (4) the following term appears, which determines the interaction energy of quadrupole and hexadecapole electric moments $Q_2^{A(B)}$ and $Q_4^{B(A)}$:

$$\Delta E_{2-4}(\boldsymbol{R}) + \Delta E_{4-2}(\boldsymbol{R})$$
$$= -\frac{45}{8} n^6 (n^2 - 1)^2 (n^2 - 4) \frac{P_6(\cos\theta)}{R^7}. \tag{6}$$

This energy is of the order of $4n^4/R^2$ with respect to the quadrupole–quadrupole term (5). This ratio, which is equivalent to the ratio of the mean square of the orbit radius of the Rydberg electron $\langle n|r^2|n\rangle \propto n^4$ to the square of the distance R between the atoms, is sufficiently small when $R > R_{LR} \approx 4n^2$. The next term of the order $1/R^9$, corresponding to hexadecapole–hexadecapole and quadrupole–2^6-pole interactions,

$$\Delta E_{4-4}(\boldsymbol{R}) + 2\Delta E_{2-6}(\boldsymbol{R})$$
$$= \frac{35}{32} n^8 (n^2 - 1)^2 (n^2 - 4)(17n^2 - 108) \frac{P_8(\cos\theta)}{R^9}, \tag{7}$$

is about $12n^8/R^4$ relative to the energy $\Delta E_{2-2}(\boldsymbol{R})$. Thus, in the region of interatomic distances $R > R_{LR}$, shifts (5)–(7) form a decreasing sequence, so that the main contribution to the first-order energy (4) is given by term (5), corresponding to $L_A = L_B = 1$.

The number of terms on the right-hand side of Eqn (4) is determined by the number of contributions to $\Delta E_{AB}^{(1)}$ from the interaction energy of even electric moments with multipolarity 2^{2q}, where $q = 1, 2, \ldots, l = n - 1$. In this case, the maximum order of the multipole moment of the circular state is 2^{2n-2}, and the corresponding power of R in the denominator of the fraction in Eqn (4) is $4n - 3$. The condition of applicability of the long-range approximation for $n = 100$ is satisfied when $R > R_{LR} \approx 4 \times 10^4$ a.u. ≈ 2.12 microns. At this distance, the value of $\Delta E_{AB}^{(1)} < 1$ GHz. Such a detuning is quite enough to reduce the probability of resonant excitation of the Rydberg state by five to six orders of magnitude. It should be borne in mind that the individual terms of shift (4) disappear at the nodes of the polynomials $P_{2L}(na)$. It should also be noted that $\Delta E_{AB}^{(1)}$ completely disappears after averaging over orientations of the radius vector $\boldsymbol{R}$.

3. Dispersion interaction of atoms in circular states

3.1. The second-order perturbation theory for interatomic interaction

In the second order of perturbation theory, the shift of the diatomic energy

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

$$= -\sum_{L_1 L_2 L'_1 L'_2}^{\infty} \frac{\varepsilon_{L_1 L_2 L'_1 L'_2}(\boldsymbol{n})}{R^{L+L'+2}} \tag{8}$$

is determined by a matrix element with two interaction operators (1) and a reduced diatomic Green function, which includes sums over bound states and integrals over the states of the continuous spectrum of noninteracting atoms:

$$G'_{AB}(\boldsymbol{r}_A, \boldsymbol{r}_A; \boldsymbol{r}'_A, \boldsymbol{r}'_A) = \sum_{n_1, n_2}' \frac{\langle \boldsymbol{r}_A|n_1\rangle\langle n_1|\boldsymbol{r}'_A\rangle\langle \boldsymbol{r}_B|n_2\rangle\langle n_2|\boldsymbol{r}'_B\rangle}{E_{n_1} + E_{n_2} - E_A - E_B - i0}. \tag{9}$$

The infinitely small imaginary value in the denominator of the fraction denotes the rule for circumventing singularities on the real energy axis.

The Green function (9) substituted in Eqn (8) takes into account the matrix elements of all virtual multipole transitions from $L_{A(B)} = 1$ to infinity with the same parity of $L_{A(B)}$ and $L'_{A(B)}$ in both operators $\hat{V}_{L_A L_B}(\boldsymbol{R})$ of the second-order matrix element. Therefore, the shift $\Delta E_{AB}^{(2)}(\boldsymbol{R})$ decomposes into a series (8) in even powers of the parameter $1/R$. The main contribution to $\Delta E_{AB}^{(2)}(\boldsymbol{R})$ comes from the term of the first nonvanishing order in $1/R$, i.e., $\Delta E_{AB}^{(2)}(\boldsymbol{R}) \approx -C_6^{(2)}(\boldsymbol{n}) \times R^{-6}$, where the van der Waals constant $C_6^{(2)}(\boldsymbol{n}) = \varepsilon_{1111}(\boldsymbol{n})$ determines the interaction of virtual electric dipole moments of atoms A and B. From the general relation between the coefficients of the series, the inequality $n^2/R < 1$ follows, determining the region of convergence of series (8), which is consistent with the inequality $R > R_{LR}$ for the first-order correction (4).

After integrating over angular variables of Rydberg electrons, the van der Waals constant can be represented as a polynomial in powers of the cosine of the angle θ between the quantisation axis and the interatomic axis (Fig. 1) [8]:

$$C_6(n, \theta) = B_0(n) + B_2(n)\cos^2\theta + B_4(n)\cos^4\theta. \tag{10}$$

The coefficients $B_k(n)$ of polynomial (10) are linear combinations of diatomic radial matrix elements of the second order dependent on n and having the form [8]

$$\rho_{l'l''} = \langle AB|r_A r_B g_{l'l''}^{AB}(r_A r_B; r'_A r'_B) r'_A r'_B|AB\rangle. \tag{11}$$

3.2. Asymptotic dependence of the van der Waals constant on the principal quantum number of the Rydberg circular state

The explicit form of combinations of matrix elements (11), which determine the irreducible components of the van der Waals interaction tensor (10), can be obtained using standard methods of the quantum theory of angular momentum [7]. The most efficient tool for numerical calculations of $\rho_{l'l''}$ is the spectral decomposition of the radial Green function $g_{l'l''}^{AB}(r_A r_B; r'_A r'_B)$ in the complete set of vectors in the subspace of diatomic states with orbital angular momenta $l' = l \pm 1$ and $l'' = l \pm 1$, similar to the decomposition of the Green function (9). Then the matrix element (11) can be expressed as sums over the discrete spectrum states and integrals over the continuous atomic spectra:

$$\rho_{l'l''} = \sum_{n' > l' + 1} \sum_{n'' > l'' + 1} \frac{|\langle n'l'|r|nl\rangle\langle n''l''|r|nl\rangle|^2}{E_{n'} + E_{n''} - 2E_n - i0}. \tag{12}$$

Numerical calculations of these matrix elements show that the terms of the series for the states of the discrete spectrum rapidly decrease with increasing differences $n' - n$ and $n'' - n$. When $n \gg 1$, the contribution of the discrete spectrum states with $n' - n > 10$ and $n'' - n > 10$ becomes pro-

portional to $\exp(-2n)$ for each of the two series (12) and does not affect the result of summation up to the fifth or sixth decimal digit. Similarly, the contribution of the integrals over the states of the continuous spectrum of both atoms is small, too. As the calculation shows, the van der Waals constant is positive for circular states with $n < 6$, which corresponds to van der Waals attraction, and negative for $n = 6$ and all $n \geqslant 8$ regardless of the angle θ, which corresponds to the repulsion of atoms in circular states with the indicated principal quantum numbers. The sign of the constant $C_\perp(n = 7) = C_6(n = 7, \theta = \pi/2)$ changes from negative to positive with increasing angle θ from zero to $\pi/2$ with a node at $\theta_0 = 34.17°$, for which the van der Waals interaction disappears, turning into repulsion for $\theta < \theta_0$ and into attraction for $\theta > \theta_0$. Figure 2 shows the dependence on n for the transverse, $C_\perp(n) = C_6(n, \theta = \pi/2)$, and longitudinal, $C_\parallel(n) = C_6(n, \theta = 0)$ components of the van der Waals constant normalised to the asymptotic dependence $C_6(n,\theta) \propto n^{12}$ in the region of small values of the principal quantum numbers of circular states $(4 \leqslant n \leqslant 14)$.
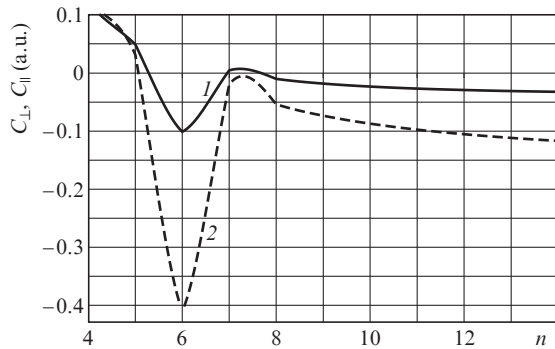
Figure 2. Van der Waals constants (*1*) $C_\perp = C_6(n, \theta = \pi/2)/n^{12}$ and (*2*) $C_\parallel = C_6(n, \theta = 0)/n^{12}$ normalised to the asymptotic dependence $C_6(n,\theta) \propto n^{12}$.

According to the 'Bethe rule' [9], the maximum values of the dipole matrix elements in the right-hand side of Eqn (12) $\langle n + 1l + 1|r|nl \rangle \approx \langle n - 1l - 1|r|nl \rangle \approx n^2$ correspond to the adjacent values of the principal and orbital quantum numbers $n \pm 1$ and $l \pm 1$, simultaneously decreased or increased by unity with respect to the quantum numbers of the circular state. Therefore, the main contribution to sum (12) is made by the intermediate states $|n' = n \pm 1l' = l \pm 1\rangle$ and $|n'' = n \pm 1l'' = l \pm 1\rangle$ close to $|nl\rangle$. For $n \gg 1$, the approximate equality $E_{n-1} + E_{n+1} - 2E_n \approx -3/n^4$ holds true. Thus, the matrix elements with $l' = l \pm 1$, $l'' = l \mp 1$, i.e., $\rho_{l+1l-1} = \rho_{l-1l+1} \approx -2n^{12}/3$ have the largest numerical absolute values. These values make the main contribution to the expansion coefficients of the van der Waals constant (12). Asymptotic values of the irreducible parts

$$B_0 \approx -n^{12}/24, \quad B_2 \approx n^{12}/4, \quad B_4 \approx -3n^{12}/8 \qquad (13)$$

determine the dependence of $C_6(n,\theta)$ on the principal quantum number $n \gg 1$ and the angle θ of the form

$$C_6(n,\theta) = -\frac{n^{12}}{24}(1 - 3\cos^2\theta)^2 + O(n^{11}). \qquad (14)$$

The expression in parentheses, which depends on the direction of the interatomic axis, vanishes at the 'magic' value of the angle $\theta = \theta_m \approx 54.7°$, which satisfies the condition $\cos^2\theta_m = 1/3$. Note that the angle θ_m corresponds to the node of the Legendre polynomial $P_2(\cos\theta_m) = 0$. In this case, the absolute value of the constant $C_6(n,\theta_m)$ decreases significantly, remaining proportional to n^{11} (Fig. 3).
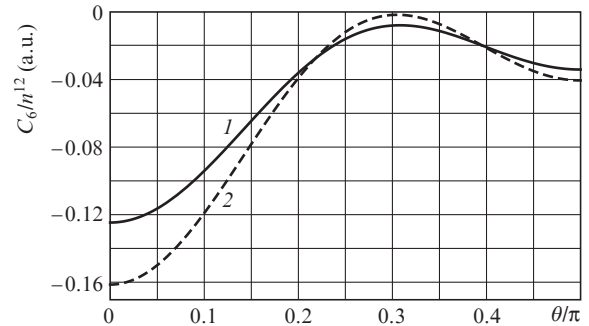
Figure 3. Dependences of the van der Waals constant on the angle θ for circular states from the shell with $n = $ (*1*) 16 and (*2*) 100. Near the magic angle $\theta_m = 0.31\pi$, the absolute value of the constant decreases by n times, which corresponds to the transition from the asymptotics of $C_6 \propto n^{12}$ to the asymptotic behaviour of $C_6 \propto n^{11}$.

To determine the value of $C_6(n,\theta_m)$ in the vicinity of angles $\theta \approx \theta_m$, one can use the expansion of the coefficients of polynomial (10) in powers of n, taking into account the terms of the 11th, 10th, 9th, etc. powers of n. These expansions can be obtained from the corresponding expressions for the amplitudes and transition energies summed in expressions (8), (9) and (12). Analytical calculations allow expressions (13) to be written with the terms proportional to n^{11} and n^{10} taken into account in the form [8]

$$B_0 \approx -\frac{n^{12}}{24}\left(1 - \frac{3}{n} + \frac{33.2}{n^2}\right), \quad B_2 \approx \frac{n^{12}}{4}\left(1 - \frac{6}{n} + \frac{14.5}{n^2}\right),$$

$$B_4 \approx -\frac{3n^{12}}{8}\left(1 - \frac{5}{n} - \frac{0.79}{n^2}\right). \qquad (15)$$

Experimental observation of the above dependences of the van der Waals constant on the direction of the interatomic axis seems possible when ultracold atoms are placed in a dc electric or magnetic field, which not only specifies the direction of the quantisation axis, but also significantly increases the lifetime of circular Rydberg states [1]. The practical implementation of this possibility is favoured by a higher degree of dependence of the constant C_6 ($C_6 \propto n^{12}$) on n, as compared to the dependence on n for the shifts in electric and magnetic fields, determined by the polarisability $\alpha_n \propto n^6$ for the quadratic Stark effect and by the Zeeman effect, linear in the magnetic quantum number $|m| = n - 1$, respectively.

4. Natural and thermally induced width of the circular state energy level

4.1. Natural width

The spontaneous width of the circular state $|nl\rangle$ energy level is determined by the probability of a dipole radiative transition

to the nearest state $|n' = n - 1 l' = l - 1\rangle$ with the emission of a photon with the frequency $\omega_{nn'} = E_n - E_{n'} \approx Z^2/n^3$. Here and below, Z is the charge of the residual ion equal to unity for a neutral atom. The general expression for the probability of a dipole radiative transition [9] after integrating over angular variables and summing over polarisation directions of a spontaneously emitted photon and over the projections of the orbital angular momentum of the Rydberg electron final state can be presented as

$$\Gamma_n^{\mathrm{sp}} = \frac{4\omega_{nn-1}^3(n-1)}{3c^3(2n-1)} |\langle n - 1 l - 1 | r | nl\rangle|^2. \qquad (16)$$

Substituting the expressions for the frequency $\omega_{nn-1} = Z^2 \times (2n-1)/[2n^2(n-1)^2]$ and the radial matrix element $\langle n - 1 l - 1 | r | nl\rangle$ into the right-hand side of Eqn (16), we obtain

$$\Gamma_n^{\mathrm{sp}} = \frac{4Z^4}{3c^3 n^3 (n-1)(2n-1)} \left[\frac{4n(n-1)}{(2n-1)^2}\right]^{2n-1}. \qquad (17)$$

As seen from this expression, the natural width of the Rydberg circular state $\Gamma_n^{\mathrm{sp}} \approx 2Z^4/(3c^3 n^5) \approx 2.6 \times 10^{-7} Z^4/n^5$ is approximately n^2 times smaller than the widths $\Gamma_n^{\mathrm{sp}} \approx 1.3 \times 10^{-7} f(n,l) \times Z^4/(n^3 l^2)$ of states with small orbital angular momenta $l = 1, 2, \ldots$, which facilitates the 'survival' and the possibility of practical use of states with maximum orbital momenta from a hydrogen-like shell with a fixed n. The factor $f(n,l)$ smoothly depends on l, almost coinciding with the unity, $f(n,l) \approx 1$, for small l, and slowly increasing with the growth of l, so that for large values of the orbital angular momentum $f(n,l) \to 2$ when $l \to n \gg 1$ [9, 10]. Rydberg states possess a high sensitivity to weak external fields, including the field of environment blackbody radiation (BBR). Therefore, when determining the frequencies and widths of the lines of radiative transitions from Rydberg states, it is necessary to take into account the interaction of the atom with the field of the BBR.

4.2. BBR-induced transitions into bound states

Thermal radiation induces temperature-dependent shifts and broadenings of atomic levels, which can be identified with the real and imaginary parts of the Stark energy. In the temperature ranges that are interesting for practical use, for estimating the Stark energy of the interaction of an atom with a thermal radiation field, it is sufficient to restrict ourselves to effects, quadratic in the field strength E, due to the polarisability of atomic levels. Because of the randomness of the directions and polarisations of the thermal radiation acting on the atom, this energy

$$\Delta E_{nl}^{\mathrm{BBR}} = \varepsilon_{nl}^{\mathrm{BBR}} - \mathrm{i}\frac{\Gamma_{nl}^{\mathrm{BBR}}}{2} = -\int_0^\infty \frac{E^2(\omega, T)}{4} \alpha_{nl}^{\mathrm{s}}(\omega)\,\mathrm{d}\omega \qquad (18)$$

is determined only by the scalar part of the dipole dynamic polarisability tensor [11], which can be represented as a superposition of second-order radial matrix elements [12]:

$$\alpha_{nl}^{\mathrm{s}}(\omega) = \frac{1}{3(2l+1)}$$
$$\times \sum_{l'=l\pm1} l_> \langle nl | r' [g_{l'}^{E_{nl}+\omega+\mathrm{i}0}(r';r) + g_{l'}^{E_{nl}-\omega+\mathrm{i}0}(r';r)] r | nl\rangle. \qquad (19)$$

Here $l_> = (l + l' + 1)/2$ is the larger of the two angular momenta l and l'. The real and imaginary parts of the radial

Green function can be extracted from the spectral expansion over the complete set of free atom states using the Sokhotski relation for the resonant terms:

$$g_{l'}^{E_{nl}\pm\omega+\mathrm{i}0}(r';r) = \sum_{n'} \langle r' | n' l'\rangle \langle n' l' | r\rangle$$
$$\times \left[\mathcal{P}\left(\frac{1}{E_{n'l'} - E_{nl} \mp \omega}\right) + \mathrm{i}\pi\delta(E_{n'l'} - E_{nl} \mp \omega)\right] \qquad (20)$$
$$+ \int_0^\infty \langle r' | \varepsilon l'\rangle \langle \varepsilon l' | r\rangle \left[\mathcal{P}\left(\frac{1}{\varepsilon - E_{nl} \mp \omega}\right) + \mathrm{i}\pi\delta(\varepsilon - E_{nl} \mp \omega)\right]\mathrm{d}\varepsilon.$$

Together with the sum over the states of the discrete spectrum, the integral over the continuous spectrum of atomic states with positive energy $\varepsilon > 0$ and orbital angular moment l' is also present here. Then the real part of the Stark energy (18) is presented as the principal value of the integral over the frequency of thermal radiation, denoted by the symbol $\mathcal{P}$.

Using the Planck distribution for the energy density of thermal radiation, the square of the electric field strength at the frequency ω can be presented as

$$E^2(\omega T) = \frac{8\omega^3}{\pi c^3 \{\exp[\omega/(k_B T)] - 1\}}. \qquad (21)$$

The imaginary part of energy (18) is determined by the total probability of radiative transitions induced by thermal radiation from the circular state to the states of discrete and continuous spectra. The frequencies of such transitions are determined by the arguments of the Dirac δ-functions in the right-hand side of Eqn (20). In particular, the term corresponding to the radiative decay and zeroing the argument of the Dirac δ-function at the thermal photon frequency $\omega = E_{nl} - E_{n-1 l-1} = \omega_{nn-1}$ appears in the Green function $g_{l'}^{E_{nl}-\omega+\mathrm{i}0}(r';r)$ with the orbital moment $l' = l - 1$. In this case, the probability of thermally induced decay

$$\Gamma_n^{\mathrm{d}} = \Gamma_n^{\mathrm{sp}} \bar{n}(\omega_{nn-1}, T) \qquad (22)$$

differs from probability (17) of spontaneous transition to a circular state from a neighbouring shell with $n' = n - 1$ by the factor

$$\bar{n}(\omega_{nn-1}, T) = \frac{1}{\exp[\omega_{nn-1}/(k_B T)] - 1}, \qquad (23)$$

that determines the number of thermal photons (occupation number or population) of the Planck distribution at the frequency $\omega_{nn-1} \approx Z^2/n^3$. Function (23) can be considered as the relative probability of the induced radiative decay of a bound state of an atom with a transition to a lower energy level: $R_n^{\mathrm{d}}(T) = \Gamma_n^{\mathrm{d}}(T)/\Gamma_n^{\mathrm{sp}} = \bar{n}(\omega_{nn-1}, T)$. An important feature of this function of the principal quantum number and temperature at $\omega_{nn-1}/(k_B T) \approx Z^2/(n^3 k_B T) \ll 1$ is the inverse proportionality to the square of the charge of the residual ion. Therefore, the relative decay rate $R_n^{\mathrm{d}}(T) \propto 1/Z^2$ of highly excited ion states is reduced by a factor of Z^2 in comparison with the similar characteristic of neutral atoms.

The asymptotic (for $n^3 k_B T/Z^2 \gg 1$) expression for the probability of thermally induced decay can be written in the form

$$\Gamma_n^{\mathrm{d}}(T) = \frac{2Z^2 k_B T}{3c^3 n^2} \left\{1 - \frac{1}{2n}Q_5(1/n) - o(1/n^7) + \frac{1}{12}\left(\frac{Z^2}{n^3 k_B T}\right)^2 \times\right.$$

$$\times\left[1 + \frac{5}{2n} + \frac{35}{8n^2} + \frac{157}{24n^2} + \frac{3433}{384n^4} + \frac{14753}{1280n^5} + o(1/n^6)\right]\right\} - \frac{\Gamma_n^{\text{sp}}}{2},$$
(24)

where

$$Q_5(x) = 1 + \frac{3}{4}x + \frac{5}{12}x^2 + \frac{35}{192}x^3 + \frac{91}{1920}x^4 - \frac{451}{23040}x^5$$

is a polynomial of the fifth order. The expansion in powers of $1/n$ in the first term in brackets proportional to temperature arises as a result of the product of the asymptotic expansions of the spontaneous width (17) and the transition frequency $\omega_{nn-1} = Z^2(2n-1)/[2n^2(n-1)^2]$. The temperature-independent term $-\Gamma_n^{\text{sp}}/2$ appears due to the series expansion of population (23) in powers of the exponent argument: $(\exp x - 1)^{-1} = 1/x - 1/2 + x/12 - x^3/720 + \ldots$.

In contrast to decay with emission of a photon and atomic transition (both spontaneous and induced) to a state with lower energy, an atom exposed to the thermal radiation can also absorb thermal photons and experience induced transitions to bound states with higher energy. Such states with $n' > n$ and orbital angular momenta $l' = l \pm 1$ are present in the expansion of the Green function $g_{l'}^{E_{nl}+\omega+\text{i}0}(r';r)$ (20). The delta functions of the imaginary part select from the integral (18) the frequencies of thermal radiation photons that coincide with the frequencies of transitions of the atom to the upper bound states: $\omega = \omega_{n'n} = E_{n'} - E_n$. Thus, the total probability of excitations takes the form

$$\Gamma_n^{\text{e}}(T) = \frac{4}{3c^3(2l+1)} \sum_{n',\, l'=l\pm 1}^{E_{n'l'} \geq E_n} \frac{l_> \omega_{n'n}^3 |\langle n'l'|r|nl\rangle|^2}{\exp[\omega_{n'n}/(k_{\text{B}}T)] - 1},$$
(25)

where the summation spans the entire infinite set of bound states with the principal quantum numbers $n' \geq n+1$ and orbital angular momenta $l' = n, n-2$. Analytical expressions for radial matrix elements of transitions to states with $n' = n + p$ ($p = 1, 2, \ldots$)

$$|\langle n+p\, l+1|r|nl\rangle|^2 = 4n^2 \frac{(p+1)(2n+p-1)}{p(2n+p)}$$
(26)

$$\times |\langle n+p\, l-1|r|nl\rangle|^2 = \frac{p^{2p-3}n^2(n+p)^2(2n)^p}{p!(2n+p)^{2p-1}Z^2}\left[\frac{4n(n+p)}{(2n+p)^2}\right]^{2n+2}$$

show that for $n \gg 1$ the terms of the series in (25) with the intermediate angular momentum $l' = l+1$ are approximately $4n^2(p+1)/p$ times the corresponding terms of the series with $l' = l-1$, in accordance with the Bethe rule [9]. In this case, the next term in both series (for $l' = l \pm 1$) is approximately $2n/p$ times smaller than the previous one, so that the series in Eqn (25) converges rapidly for all values of temperature T. In particular, for $n = 5$ to determine the probability of excitation with the accuracy to the fifth decimal point it is sufficient to take into account the terms of the series with $n' \leq 30$; to obtain the accuracy to the seventh digit, it is enough to take into account 150 terms in the sum over n'. For $n = 10$ and the required accuracy of the fifth and seventh digits, it is enough to take into account the contributions from the terms with $n' < 26$ and $n' < 85$, respectively. For $n = 100$, it suffices to take into account no more than five and seven terms that determine the sum of the series in Eqn (25) with relative errors of 10^{-5} and 10^{-7}, respectively. This acceleration of con-

vergence is associated with the rapid decrease in the radial matrix elements of the dipole transition $|n\rangle \to |n' = n + p\rangle$, whose dependence on the principal quantum number of the circular state for large values of n and p ($n' = n + p \gg n \gg 1$) becomes proportional to $\exp(-2n)$:

$$|\langle n'\, l+1|r|nl\rangle|^2 \approx 4n^2 |\langle n'\, l-1|r|nl\rangle|^2$$

$$\approx \frac{|\langle \varepsilon = 0\, l+1|r|nl\rangle|^2}{n'^3}Z^2,$$
(27)

where

$$|\langle \varepsilon = 0\, l+1|r|nl\rangle|^2 \approx \frac{2^{2(n+2)}n^{9/2}}{\sqrt{\pi}\, Z^4}\exp(-2n)$$
(28)

is the matrix element of the threshold ionisation transition to the zero-energy continuum state. For the same reason, the contribution $\Gamma_n^{\text{ion}}(T)$ of the probability of ionisation transitions to the continuous spectrum states to the total probability of excitations of states with energy $E_{\text{exc}} > E_n$ becomes exponentially small [10], and at $n > 10$ does not affect the first seven decimal digits of the value that determines the total width $\Gamma_n^{\text{tot}}(T) = \Gamma_n^{\text{sp}}(T) + \Gamma_n^{\text{d}}(T) + \Gamma_n^{\text{e}}(T) + \Gamma_n^{\text{ion}}(T)$ of the circular Rydberg state.

Using analytical expressions for the radial matrix elements (26) and the transition frequencies $\omega_{n'n}$, we can obtain the asymptotic representation similar to (24) for the probability of thermally induced excitation (25) in the form

$$\Gamma_n^{\text{e}}(T) = \frac{2Z^2 k_{\text{B}}T}{3c^3 n^2}\left\{1 + \frac{1}{2n}Q_5(1/n) - o(1/n^7) + \frac{1}{12}\left(\frac{Z^2}{n^3 k_{\text{B}}T}\right)^2\right.$$

$$\times\left[1 + \frac{7}{2n} + \frac{65}{8n^2} + \frac{383}{24n^2} + \frac{11015}{384n^4} + \frac{62527}{1280n^5} + o(1/n^6)\right]\right\} - \frac{\Gamma_n^{\text{sp}}}{2}.$$
(29)

Formulae (24) and (29) show that in the total probability $\Gamma_n^{\text{tot}}(T)$ of spontaneous and thermally induced transitions, the temperature-independent component Γ_n^{sp} disappears, leaving only temperature-dependent terms. Moreover, in the sum $\Gamma_n^{\text{d}}(T) + \Gamma_n^{\text{e}}(T)$, the polynomial $Q_5(1/n)$ also disappears, leaving the coefficient of the term proportional to the temperature to be strictly equal to unity. Thus, if the condition $Z^2/(n^3 k_{\text{B}}T) \ll 1$ is satisfied and the exponentially small probability of thermally induced ionisation is not taken into account, the total width of the circular Rydberg energy level can be presented as

$$\Gamma_n^{\text{tot}}(T) = \Gamma_n^{\text{sp}}(T) + \Gamma_n^{\text{d}}(T) + \Gamma_n^{\text{e}}(T)$$

$$= \frac{4Z^2 k_{\text{B}}T}{3c^3 n^2}\left\{1 + \frac{1}{12}\left(\frac{Z^2}{n^3 k_{\text{B}}T}\right)^2\left[1 + \frac{3}{n} + \frac{25}{4n^2} + \frac{45}{4n^3}\right.\right.$$

$$\left.\left. + \frac{301}{16n^4} + \frac{483}{16n^5} + o(1/n^6)\right]\right\}.$$
(30)

Here all terms of the expansion of the matrix elements (26) and the frequencies $\omega_{n'n}$ in powers of the small parameter $1/n \ll 1$ up to $1/n^7$, as well as of the exponents present in Eqns (23) and (25) for thermally induced widths in powers of the small argument $\eta = Z^2/(n^3 k_{\text{B}}T)$ up to η^3 are taken into account. At $T = 100$ K and $n = 15$, the second term in the brackets in

Eqn (30) does not exceed 0.1 for a neutral atom ($Z = 1$), and its contribution decreases proportionally to η^2. Thus, for $\eta < 1$, the total (spontaneous and thermally induced) width of the energy level of the circular state coincides with the asymptotic expression $\Gamma_n^{\mathrm{BBR}}(T) = 4Z^2 k_B T/(3c^3 n^2)$ for the thermally induced width [5, 6] with a relative accuracy of the order of $\eta^2/12$.

4.3. Ionisation of the circular state induced by BBR

The imaginary part of the integral over the continuous spectrum energy in expression (20) for the radial Green function $g_{l'=l\pm1}^{E_{nl}+\omega+\mathrm{i}0}$ at the frequency $\omega > |E_{nl}|$ is a product of the wave functions of the continuum states with the energy $\varepsilon = E_{nl} + \omega$:

$$\mathrm{Im}[g_{l'}^{E_{nl}+\omega+\mathrm{i}0}(r';r)] = \pi\langle r|\varepsilon l'\rangle\langle \varepsilon l'|r'\rangle. \tag{31}$$

This product corresponds to the imaginary part of the dynamic polarisability (19), which determines the ionisation cross section of the state $|nl\rangle$ by photons of thermal radiation:

$$\sigma_{nl}(\omega) = \frac{4\pi\omega}{c}\mathrm{Im}[\alpha_{nl}(\omega)] = \frac{4\pi^2\omega}{3c(2l+1)}\sum_{l'=l\pm1}l_>|\langle\varepsilon l'|r|nl\rangle|^2. \tag{32}$$

Thus, the ionisation component of the thermally induced broadening can be presented as

$$\Gamma_{nl}^{\mathrm{ion}}(T) = \int_{|E_{nl}|}^{\infty}\sigma_{nl}(\omega)\frac{cE^2(\omega,T)}{8\pi\omega}\mathrm{d}\omega, \tag{33}$$

where the fraction in the integrand determines the flux of the BBR photon number density [13].

The results of numerical calculations for Rydberg states with small orbital angular momenta $l \ll n$ (for S-, P-, D- and F-states of alkali metal atoms [13]) show that the asymptotic dependence of the ionisation component of the thermally induced broadening $\Gamma_{nl}^{\mathrm{ion}}(T) \propto n^{-7/3}$ on the principal quantum number is remarkably different from the dependences on n of the total probability of thermally induced transitions $\Gamma_{nl}^{\mathrm{d}}(T) + \Gamma_{nl}^{\mathrm{e}}(T) \propto n^{-2}$ to the states of the discrete spectrum. For states with large values of the orbital angular momentum, $1 \ll l \le n-1$, the difference between the contributions to the thermally induced broadening from transitions to the continuum and discrete spectrum states increases substantially.

For transitions from highly excited circular states with $n \gg 1$ to the states of continuous spectrum, one can get simple analytical expressions that demonstrate the exponential decrease in matrix elements with the growth of n:

$$|\langle\varepsilon l' = l+1|r|nl\rangle|^2 = 4n^2|\langle\varepsilon l' = l-1|r|nl\rangle|^2$$

$$\approx \sqrt{\frac{n}{\pi}}\left(\frac{4n^2}{Z^2}\right)^2\frac{2^{2n}}{\Omega^{7/2+n}}\exp\left(-2n\frac{\arctan\sqrt{\Omega-1}}{\sqrt{\Omega-1}}\right), \tag{34}$$

where $\Omega = \omega/|E_n|$ is the energy of an ionising photon in units of binding energy. The exponential decrease in the matrix elements is 'transferred' to the ionisation cross section $\sigma_n(\omega) \propto \exp(-2n)$ [10] and then to the ionisation width (33). Therefore, the contribution of $\Gamma_{nl}^{\mathrm{ion}}(T)$ to thermal broadening $\Gamma_{nl}^{\mathrm{BBR}}(T)$ turns out to be smaller than the errors of numerical calculations of the probabilities of decay (24) and excitations of bound states (29) already at $n > 5$.

5. Thermally induced shift of the circular state energy

The real part of the energy shift (18) after substituting expressions (19)–(21) into the integrand in the right-hand side of Eq. (18) can be represented as

$$\varepsilon_{nl}^{\mathrm{BBR}}(T) = -\frac{2}{3\pi c^3(2l+1)}\sum_{l'=l\pm1}l_>\mathcal{P}$$

$$\times\int_0^{\infty}\left\{\sum_{n'}\frac{2\omega_{n'n}|\langle n'l'|r|nl\rangle|^2}{\omega_{n'n}^2-\omega^2} + \int_0^{\infty}\frac{2(\varepsilon+|E_{nl}|)|\langle\varepsilon l'|r|nl\rangle|^2}{(\varepsilon+|E_{nl}|)^2-\omega^2}\mathrm{d}\varepsilon\right\}$$

$$\times\frac{\omega^3\mathrm{d}\omega}{\exp[\omega/(k_B T)]-1}. \tag{35}$$

The integration over the frequency of thermal radiation in this expression is conveniently represented in the form of the Farley–Wing function, introduced in Ref. [6]:

$$\mathcal{F}(y) = -2y\mathcal{P}\int_0^{\infty}\frac{x^3\mathrm{d}x}{(x^2-y^2)(\exp x-1)}. \tag{36}$$

Using this function, the energy shift (35) can be written as

$$\varepsilon_{nl}^{\mathrm{BBR}}(T) = -\frac{2}{3\pi c^3(2l+1)}(k_B T)^3\sum_{l'=l\pm1}l_> \tag{37}$$

$$\times\left[\sum_{n'}|\langle n'l'|r|nl\rangle|^2\mathcal{F}\left(\frac{\omega_{n'n}}{k_B T}\right) + \int_0^{\infty}\langle\varepsilon l'|r|nl\rangle|^2\mathcal{F}\left(\frac{\varepsilon+|E_{nl}|}{k_B T}\right)\mathrm{d}\varepsilon\right].$$

The arguments in the function $\mathcal{F}$ here are determined by the energy ratios of discrete–discrete and discrete-continuous transition energies to the thermal energy of the BBR.

Function (36) is the Cauchy principal value for the integral having a pole singularity of the logarithmic type. It is a smooth odd function of its argument that automatically takes into account the singularities of the integrals over the frequency of thermal radiation and over the states of the continuous spectrum in Eqn (20). Using the transformation of the integrand, function (36) can be presented in the form, for which a closed analytical expression exists [14]:

$$\mathcal{F}(y) = -\pi^2 y/3 - 2y^3\mathrm{Re}[\Phi(\mathrm{i}y)], \tag{38}$$

where

$$\Phi(z) = \int_0^{\infty}\frac{x\mathrm{d}x}{(x^2+z^2)(\exp x-1)}$$

$$= \frac{1}{2}\left[\ln\left(\frac{z}{2\pi}\right) - \frac{\pi}{z} - \psi\left(\frac{z}{2\pi}\right)\right]; \quad \mathrm{Re}\,z > 0;$$

$\psi(x) = \mathrm{d}\{\ln[\Gamma(x)]\}/\mathrm{d}x$ is the logarithmic derivative of the gamma function. Putting $z = \pm\mathrm{i}|y| + \delta$ for $\delta \to +0$, we obtain

$$\mathcal{F}(y) = -\frac{\pi^2}{3}y - \left\{\ln\left(\frac{|y|}{2\pi}\right) - \mathrm{Re}\left[\psi\left(\mathrm{i}\frac{|y|}{2\pi}\right)\right]\right\}y^3. \tag{39}$$

To determine the real part of the function ψ in this expression, it is possible to use the expansion in series [15]

$$\mathrm{Re}\left[\psi\left(\mathrm{i}\frac{|y|}{2\pi}\right)\right] = -\gamma + \frac{y^2}{4\pi^2}\sum_{k=1}^{\infty}\frac{1}{k[k^2 + y^2/(4\pi^2)]}, \qquad (40)$$

where $\gamma = 0.5772156649$ is the Euler constant. Expanding the terms of this series in powers of the ratio $y^2/(4\pi^2 k^2)$ and performing summation over k, we obtain the formal expansion of the Farley–Wing function into a power series in odd powers of the argument:

$$\mathcal{F}(y) = -\frac{\pi^2}{3}y - \left[\ln\left(\frac{|y|}{2\pi}\right) + \gamma\right]y^3 + \frac{y^5}{4\pi^2}\sum_{p=0}^{\infty}\zeta(2p+3)\left(-\frac{y^2}{4\pi^2}\right)^p, \qquad (41)$$

where $\zeta(s) = \sum_{k=1}^{\infty}k^{-s}$ is the Riemann zeta function [14, 15]. The formal radius of convergence of the alternating series in Eqn (41) is determined by the inequality $|y| < 2\pi$.

When $|y| > 5$ the exponential function in the denominator of the integrand in Eqn (36) significantly reduces the contribution to the integral from the singularity point $x = y$ and from the entire region $x > y$. In this connection, to estimate the integral, it suffices to expand the integrand in a series in powers of the ratio $x^2/y^2 < 1$ and use analytical expressions of improper integrals of each term. As a result, we obtain an asymptotic expansion of function (36) in odd powers of the inverse argument, which can be represented as

$$\mathcal{F}(y) = 2\sum_{p=0}^{\infty}\frac{(2p+3)!\,\zeta(2p+4)}{y^{2p+1}}$$
$$= \frac{2\pi^4}{15y}\left[1 + \frac{10}{21}\left(\frac{2\pi}{y}\right)^2 + \frac{1}{2}\left(\frac{2\pi}{y}\right)^4 + \frac{30}{33}\left(\frac{2\pi}{y}\right)^6 + \ldots\right]. \qquad (42)$$

The presence of factorial in the terms of this series indicates its asymptotic character. Since all the terms in this expansion are positive, the maximum accuracy for estimating $\mathcal{F}(y)$ at a given y can be provided by $N_{max} < |y|/2$ terms. Numerical estimates show that the four terms in the series, written out explicitly in Eqn (42), determine the value of function (36) with an accuracy of six decimal places in the region $|y| > 30$.

Attention should be paid to the substantial quantitative and qualitative differences in the procedures and results of numerical calculations of the sums of an infinite series over the states of the discrete spectrum and the integrals over the continuous spectrum in Eqn (37). A detailed analysis of the contributions of discrete states and the continuum to the sum of oscillator strengths, the sum of oscillator strength moments, and to thermally induced shifts of states with small orbital angular momenta is presented in [10, 12, 16]. For circular states with large n, the contribution of the continuous spectrum is determined by the exponentially small matrix elements (34) of the ionisation transition. Therefore, taking into account the integral over the continuous spectrum practically does not change the result of the calculation of shift (37), obtained only by summing up several terms of the series over the states of the discrete spectrum.

For the shift, as well as for the broadening of the energy levels of the Rydberg circular state, we can offer a polynomial approximation that significantly expands the range of use of the asymptotic approximation $\varepsilon_n^{\mathrm{BBR}}(T) = \pi(k_B T)^2/(3c^3)$ [6], which determines shift (37) with an accuracy of up to three or four decimal places, provided that $1/\eta = n^3 k_B T/Z^2 > 100$.

An expression applicable for smaller values of the principal quantum number n and temperature T can be obtained using the polynomial approximation [12]

$$\varepsilon_n^{\mathrm{BBR}}(T) = \varepsilon_0\left(\frac{T}{300\ \mathrm{K}}\right)^2(a_0^{(\varepsilon)} + a_1^{(\varepsilon)}x + a_2^{(\varepsilon)}x^2), \qquad (43)$$

where $\varepsilon_0 = \pi(k_B 300\ \mathrm{K})^2/(3c^3) = 2416.65$ Hz is the asymptotic (for $n^3 k_B T > 100$) thermally induced shift value at room temperature $T = 300$ K. The argument of the quadratic polynomial in Eqn (43) can be presented as a combined parameter

$$x = \sqrt{\frac{2|E_n|}{k_B T}} = \frac{Z}{n\sqrt{k_B T}}.$$

To determine the coefficients $a_i^{(\varepsilon)}$, we used the method of polynomial interpolation of the results of numerical calculation of the energy shift (43) with $n = 15$, 60 and 150 for temperatures $T = 100$, 300 and 1000 K. This dependence can be approximated by the polynomial

$$a_i^{(\varepsilon)}(T) = \sum_{j=0}^{2}\frac{b_{ij}^{(\varepsilon)}}{(k_B T)^j}, \quad i = 0, 1, 2, \qquad (44)$$

in which the coefficients $b_{ij}^{(\varepsilon)}$ are constants, the numerical values of which are presented in Table 1.

Table 1. The coefficients $b_{ij}^{(\varepsilon)}$ of polynomial approximations (43) and (44) for thermally induced shifts of the energy levels of circular Rydberg states (35).

i	$b_{i0}^{(\varepsilon)}$	$b_{i1}^{(\varepsilon)}$	$b_{i2}^{(\varepsilon)}$
0	1	1.085×10^{-7}	-1.726×10^{-10}
1	1.165×10^{-4}	7.287×10^{-9}	5.234×10^{-10}
2	-3.145×10^{-4}	-2.675×10^{-7}	-3.109×10^{-10}

6. Conclusions

The results of the analytical calculations of the shifts and broadening of the energy levels of circular states obtained in this paper provide important information about the effect of interatomic interactions and interactions with BBR on the spectral characteristics of highly excited Rydberg atoms. The choice in circular states is due to the possibility of analytical calculations of the interatomic interaction constants, as well as thermally induced broadening and a shift in the energy levels of states with large principal quantum numbers. The proportionality to the 12th power of the principal quantum number is demonstrated for the components of the van der Waals constant, which determine the dependence of the long-range interaction on the orientation of the interatomic axis.

The probability of ionisation of circular states by the BBR field appears to be exponentially small. For states with $n > 10$, the ionisation contribution to the broadening of the energy levels does not exceed 10^{-6} of the contribution of thermally induced transitions to the bound states. The temperature-independent terms of the probabilities of induced BBR transitions arising from the expansion in powers of small parameters $1/n$ and $\eta = Z^2/(n^3 k_B T)$ completely compensate for the contribution of the spontaneous width Γ_n^{sp} to the total width (30). Therefore, for large values of the parameter $1/\eta = n^3 k_B T/Z^2$ in the expression for the total width of the energy level of the circular state, only the terms that are directly proportional to temperature and inversely proportional to its integer powers, remain. In this case, the coefficient of the term linear in T, i.e., $4Z^2 k_B T/(3c^3 n^2)$, is exactly equal to unity and has no corrections depending on n. The second nonvanishing

term in brackets in Eqs (30), which determines the total width $\Gamma_n^{\text{tot}}(T)$, is proportional to the parameter η^2 multiplied by the asymptotic series in the parameter $1/n$, and contributes a correction proportional to $\eta^2/12$ to the unit coefficient.

Along with hydrogen-like atoms and ions, all multielectron atoms have circular states. Therefore, the results of the calculations are applicable to almost any atom or ion of any chemical element.

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