

Broadening of energy levels of Rydberg states with small orbital angular momenta in ions of group IIb by ambient thermal radiation

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Abstract. We present the derivation of simple analytical expressions for calculating the widths of Rydberg states with small orbital angular momenta in Zn^+ , Cd^+ , Hg^+ ions of group IIb of the periodic system of elements induced by blackbody radiation (BBR) at ambient temperatures from 100 to 3000 K. The probabilities of radiative transitions from excited nS , nP , nD and nF states to all dipole-accessible states of ions are calculated. The wave functions of the quantum defect (QD) method for the initial and final states of the Rydberg electron are used to calculate the amplitudes of transitions between bound states. The dependences of the probabilities of induced decays and excitations on the BBR temperature, the principal and orbital quantum numbers of the Rydberg ion are determined. Analytical expressions are derived for numerical estimates of the contributions of the probabilities of thermally induced decays and excitations to the width of the Rydberg energy level. The numerical values of the coefficients of interpolation polynomials representing asymptotic expansions in powers of the principal quantum number n for the relative probabilities of decays and excitations of Rydberg states with large values of n and small orbital angular momenta $l = 0, 1, 2, 3$ are calculated.

Keywords: atom, ion, group IIb, Rydberg states, blackbody radiation, decay probability, excitation, quantum defect method.

1. Introduction

Ions in highly excited Rydberg states are considered promising objects of research aimed at designing new frequency standards in the optical and microwave ranges [1–5], as well as highly efficient devices for processing quantum information [6–8]. Atoms and ions in Rydberg states are highly sensitive to external fields and can be used for precision measurement of the ambient thermal radiation temperature [referred to as blackbody radiation (BBR) in the literature] directly in the region of localisation of Rydberg particles [9], for measuring weak fields [10], as well as for metrological measurements of RF radiation characteristics [11]. Well-developed methods of laser excitation of high-energy states make Rydberg states with arbitrary values of the principal (n) and orbital (l) quantum numbers of a valence electron experimentally accessible [12–14].

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Ions of group II of the periodic system of elements attract the attention of researchers not only due to the availability of pure substances, but also due to the simplicity of the one-electron optical spectrum, which resembles the spectrum of alkali metal atoms and allows using the one-electron approximation to calculate the characteristics of interaction with external electromagnetic fields. The structure of the excitation energy spectrum of an external (valence) electron is described with good accuracy by the Rydberg formula, which uses the concept of a quantum defect. Based on the Rydberg formula, the semiempirical methods of Fues model potential (FMP) and quantum defect (QD) have been developed. They are widely used in numerical calculations, in which one-electron wave functions are represented as modified wave functions of a hydrogen-like atom, making it possible to obtain analytical expressions for susceptibilities and amplitudes of electromagnetic transitions in atoms and ions [15]. When calculating the characteristics of the interaction of group IIb ions with the BBR field in this work, we use the QD method, in which the numerical values of quantum defects are determined from the most reliable tables of energy levels [16, 17]. For levels with large principal quantum numbers, for which no data are available in the literature, the determination of quantum defects is based on asymptotic expressions with the parameters that can be found in Refs [18, 19]. A comparison of numerical results obtained by the QD method (QDM) with theoretical and experimental literature data for the excited state lifetimes of Zn^+ , Cd^+ , and Hg^+ ions confirms the applicability of this method for calculating the amplitudes of radiative transitions from Rydberg states. As an example, such a comparison is given in Table 1 for Zn^+ ions.

Table 1 shows the lifetimes in an ion completely isolated from the environment. Obviously, under real conditions an atomic ion can experience the effect of various external fields, in particular those that keep particles in a given localisation region [1], as well as residual laboratory fields and other stationary and variable fields. The influence of each specific field on the structure of the ion spectrum is an individual problem, the solution of which makes it possible to exclude, compensate, or take into account the effect in each specific case [2–8].

In the present paper, we consider the influence of the ubiquitous ambient BBR field on the shift and broadening of the Rydberg energy levels of a singly ionised atom from group IIb of the periodic table of elements. The numerical values of the probabilities of thermally induced transitions from the Rydberg states of the S, P, D, and F series of ions to the states of the discrete spectrum with both emission (decay) and absorption (excitation) of BBR photons are calculated. The obtained data were used to calculate the coefficients of cubic approximation polynomials describing the asymptotic depen-

Table 1. The lifetimes (in nanoseconds) of the excited nS , $nP_{3/2}$, $nD_{5/2}$ and $nF_{7/2}$ states of the Zn^+ ion, calculated in the QD approximation, in comparison with the data of the FMP method [19], the information system [17] and with the range of values of the most reliable theoretical and experimental data given in [20, 21].

State	QDM	FMP	[17]	Theory	Experiment
5S	2.594	3.24	1.7	1.4–2.5	1.7–3.9
6S	4.845	5.66	3.6	3.58–4.7	–
7S	8.858	9.89	7.3	–	–
8S	14.63	16.0	–	–	–
4P _{3/2}	2.049	2.04	2.6	1.91–3.1	1.81–3.5
5P _{3/2}	14.89	16.9	16.7	15.9–18.6	15.0–19.0
6P _{3/2}	59.9	55.0	46.9	46.9–67.9	–
7P _{3/2}	209.9	64.6	–	–	–
8P _{3/2}	155.2	266.9	–	–	–
4D _{5/2}	1.32	1.43	1.5	1.21–1.39	1.3–4.55
5D _{5/2}	3.25	3.45	3.7	3.25–3.75	4.9–5.9
6D _{5/2}	6.44	6.73	8.9	6.6–7.56	8.0–9.8
7D _{5/2}	11.2	11.8	17.0	11.48	15.2–18.8
8D _{5/2}	17.7	18.6	–	–	–
4F _{7/2}	4.79	4.97	4.3	4.2–4.8	4.35–7.2
5F _{7/2}	9.86	9.91	9.4	8.53–9.5	–
6F _{7/2}	17.2	17.0	17.3	17.11–18.8	–
7F _{7/2}	27.9	27.2	–	–	–

dences of the probabilities of thermally induced broadening of Rydberg energy levels. These calculations are motivated by the fact that the asymptotic formulae obtained in the early 1980s [22–24] provide good agreement with the results of exact numerical calculations only for very large values of the principal and orbital quantum numbers ($n > 30$, $n - l \ll n$) [24]. In addition, the difference in the functional dependences on the charge Z of the residual ion for spontaneous and thermally induced broadening [25] can significantly increase the contribution of the BBR effects in ions compared to neutral atoms. Analytical expressions for the corrections to the asymptotic broadening formula were obtained in [25, 26] for Rydberg states with large values of the orbital angular momentum. For states with small l , the present work uses the possibility of obtaining approximation formulae based on the results of exact calculations.

In Section 2, we present an asymptotic expression for the Stark energy of interaction of a Rydberg ion with a BBR field [22–26], which explicitly contains the quadratic dependence of the real part (shift) and the linear dependence of the imaginary part (broadening) on temperature. Moreover, the imaginary part of the energy is proportional to the square of the ratio of the charge Z of the residual ion (here $Z = 2$) to the principal quantum number n of the Rydberg state. The possibilities and applicability limits of quantitatively estimated corrections to these expressions, obtained in an analytical form in Refs [25, 26] for states with large orbital angular momenta, are discussed, as well as the possibilities of estimates by interpolating the results of numerical calculations performed in this work.

Section 3 discusses the procedure for calculating the amplitudes of spontaneous dipole transitions with emission of photons, which are used to calculate the probabilities of spontaneous transitions of ions from highly excited states with large values of the principal quantum numbers to states with lower energies. The total probabilities of spontaneous transitions Γ_{nl}^{sp} are converted into numerical values of spontaneous lifetimes $\tau_{nl}^{sp} = 1/\Gamma_{nl}^{sp}$. The results obtained are used

to determine the coefficients of a cubic polynomial approximating τ_{nl}^{sp} with the asymptotic dependence on the principal quantum number taken into account: $\tau_{nl}^{sp} \propto n^3$ [18]. The approximation parameters are shown in Table 2 below.

In Sections 4 and 5, we calculated the probabilities of stimulated emissions and excitations of a Rydberg atom, accompanied by radiative transitions to lower and higher bound states with emission and absorption of photons, respectively, under the action of BBR. Approximation formulae for the total probabilities of emissions and absorptions of the same form are chosen. The coefficients of the approximating polynomials are determined from the numerical values of the probabilities calculated within the QD approximation for Rydberg states with principal quantum numbers n in the range 15–400 of each of the selected series with orbital angular momenta $l = 0, 1, 2, 3$.

Numerical estimates show that in the considered BBR temperature range from 100 to 3000 K, the relative contribution of ionisation transitions to the states of the continuous spectrum to the width of the Rydberg energy level does not exceed 1%–2% and rapidly decreases with increasing n . Thus, the main cause of thermally induced broadening of high levels is transitions to states of the discrete spectrum. The approximating expressions obtained in Sections 3–5 provide detailed information on the ratio of the probabilities of thermally induced emissions and excitations as a function of the BBR temperature and on the principal quantum numbers of Rydberg levels with small orbital angular momenta ($l \leq 3$).

2. Thermally induced shift and width of the Rydberg energy level

The analytical expressions presented in Refs [25, 26] for corrections to the asymptotic formulae for energy level broadening and shifts of Rydberg states of atoms [22–24] turned out to be inapplicable to states with small orbital momenta ($l < 10$). When deriving formulae for these corrections, we used the expansion of the Planck formula for the number density distribution of thermal photons in powers of the parameter $z = \omega/k_B T$. Hereinafter, the atomic system of units $e = m = \hbar = 1$ is used, in which the speed of light numerically coincides with the inverse fine structure constant, $c = \alpha^{-1} = 137.036$; the temperature is expressed in kelvins; the Boltzmann constant is determined by the ratio of the atomic energy unit to the atomic temperature unit, $k_B = 1/T_a$; and $T_a = 315776$ K. The coefficients of expansion in powers of $\omega/k_B T$ turn out to be proportional to the sums of the oscillator strength moments of electric dipole transitions $f_{n'l'm',nlm}^{(q)} = 2\omega_{n'n}^{1+q} |\langle n'l'm' | r_\mu | nlm \rangle|^2$ from the initial state $|nlm\rangle$ into all dipole-accessible states $|n'l'm'\rangle$ of the Rydberg electron [25, 26]:

$$S_{nlm}^{(q)} = \frac{1}{3} \sum_{n'l'm'\mu} f_{n'l'm',nlm}^{(q)}. \quad (1)$$

The sums of the moments $S_{nlm}^{(q)}$ with $q = 0, 1$ determine asymptotic expressions of the real $[\varepsilon_0(T)]$ and imaginary $[T_0(T)]$ parts for the Stark interaction energy of the atom with the BBR field [22–26]

$$\mathcal{E}_{nl}^{BBR}(T) \approx \varepsilon_0(T) - i \frac{T_0(T)}{2} = \frac{\pi(k_B T)^2}{3c^3} - i \frac{2Z^2 k_B T}{3c^3 n^2} =$$

$$= \left[2416.65 \left(\frac{T}{300} \right)^2 - i5397.9 \frac{TZ^2}{n^2} \right] [\text{Hz}]. \quad (2)$$

Analytical expressions for the corrections to Eqn (2) depending on the quantum numbers n , l and on the temperature T are also determined by the sums of moments (1) with positive exponents q . In this case, $S_{nl}^{(q)}$ with even values of q determine the corrections to the real part

$$\text{Re}[\mathcal{E}_{nl}^{\text{BBR}}(T)] = \varepsilon_{nl}(T) = \varepsilon_0(T) + \varepsilon_1(T) + \varepsilon_2(T) + \dots, \quad (3)$$

where $\varepsilon_0(T) = \pi(k_B T)^2 / (3c^3)$ is the asymptotic value of the shift, represented explicitly in expression (2). A similar expansion for the broadening can be written as

$$\text{Im}[\mathcal{E}_{nl}^{\text{BBR}}(T)] = \Gamma_{nl}^{\text{tot}}(T) = \Gamma_0(T) + \Gamma_1(T) + \Gamma_2(T) + \dots, \quad (4)$$

where the asymptotic value $\Gamma_{nl}^{\text{tot}}(T) \approx \Gamma_0(T) = 2k_B T \times S_{nl}^{(1)} / c^3$ is also presented explicitly in Eqn (2). The subsequent terms are proportional to the ratios of sums (1) with odd exponents to odd degrees of temperature: $\Gamma_q(T) \propto S_{nl}^{(2q+1)} \times (k_B T)^{(1-2q)}$, where $q = 1, 2, 3, \dots$ [25, 26]. Taking into account the explicit dependence of sums (1) on the quantum numbers of the Rydberg state, the ratio of the subsequent terms of sums (3) and (4) at large values of the principal quantum number ($n \gg n_0$, where n_0 corresponds to the lowest energy level of the series with a given orbital angular momentum $l > q > l$) can be represented as

$$\frac{\varepsilon_{q+1}}{\varepsilon_q} \propto \frac{\Gamma_{q+1}}{\Gamma_q} \propto \left(\frac{Z^2}{l^3 k_B T} \right)^2, \quad (5)$$

each term $\Gamma_q(T)$ in (4) decreasing proportionally to $1/n^3$ with increasing n . Thus, expansions (3) and (4) formally represent the first terms of asymptotic expansions in powers of the parameter $Z^4 / (l^3 k_B T)^2$ of the real and imaginary parts of the energy of the Stark interaction of a Rydberg atom with the BBR field. For states with small orbital angular momenta ($l < p$, $p = 2, 3, \dots, 10$), the sums $S_{nl}^{(2p)}$ and $S_{nl}^{(2p+1)}$ become infinite. For states with $l > p$, ratios (5) become small only at temperatures sufficiently high to make the sequence of terms in expansions (3) and (4) decrease. Therefore, the use of two or three terms in these expansions to estimate the corrections to the asymptotic expressions ε_0 and Γ_0 at room or close to room temperatures is possible only for states with large orbital angular momenta, $l > 10$ [26].

To calculate the numerical values of the corrections ε_i , Γ_i ($i = 1, 2, 3, \dots$) to the energy of states with small orbital angular momenta, a different approach should be used, based on general formulae for the energy of the Stark interaction of an atom with the BBR field. From the results of calculations using these formulae, one can obtain simple approximate expressions that make it possible to assess quickly and accurately the probabilities of stimulated emissions and absorptions, which determine the broadening of the energy levels of stationary states. Asymptotic expressions for group IIb ions are determined by the method of approximating polynomials previously used for group IIa ions [27, 28].

The general expression for the total probability of induced radiative transitions from the state $|nlm\rangle$ under the influence of the BBR can be represented as [19, 29]

$$\Gamma_{nl}^{\text{BBR}}(T) = \frac{4}{3c^3} \sum_{n'l'm'\mu} \frac{|\omega_{n'n}|^3 |\langle n'l'm' | r_\mu | nlm \rangle|^2}{\exp[\omega_{n'n} / (k_B T)] - 1} =$$

$$= \frac{2}{3c^3(2l+1)} \sum_{n'l'} \frac{l_{>} |f_{n'l'}^{(2)}|}{\exp[\omega_{n'n} / (k_B T)] - 1}. \quad (6)$$

Here $l_{>} = (l + l' + |l - l'|) / 2$ is the larger of the two values l and l' ; the summation applies to all states $|n'l'm'\rangle$ from the complete set of states of the atom/ion, including integration over states of the continuous spectrum with positive energy. The last expression in Eqn (6) was obtained after summing over m' and μ and contains only the radial part of the dipole transition amplitude $f_{n'l'}^{(2)} = 2\omega_{n'n}^3 |\langle n'l' | r | nl \rangle|^2$. Numerical calculations show that the contribution of thermally induced transitions to the continuous spectrum states from the Rydberg state with an orbital angular momentum $l \leq 3$ and a principal quantum number n ranging from 15 to 400 for practically interesting temperatures $T < 1000$ K does not exceed 1%–2%. Therefore, in this study, the effect of thermally induced ionisation on the broadening of the energy level of the Rydberg state is not taken into account. Then probability (6) can be decomposed into two components, $\Gamma_{nl}^{\text{BBR}}(T) = \Gamma_{nl}^{\text{dec}}(T) + \Gamma_{nl}^{\text{exc}}(T)$, corresponding to the total probability of decays and excitations with emission and absorption of the BBR photons, respectively. In this case, $\Gamma_{nl}^{\text{dec}}(T)$ is determined by the sum of terms in Eqn (6) corresponding to the energy of final states lower than the energy of the initial state, $E_{n'l'} < E_{nl}$, and $\Gamma_{nl}^{\text{exc}}(T)$ is determined by the sum over all states of the discrete spectrum with energy $E_{n'l'} > E_{nl}$.

3. Spontaneous width and lifetime of the Rydberg state

The spontaneous width Γ_{nl}^{sp} of the energy level of the state $|nl\rangle$ is the total probability of dipole radiative transitions to the states $|n'l' = l \pm 1\rangle$ with energy $E_{n'l'} < E_{nl}$. The expression for Γ_{nl}^{sp} coincides with the corresponding expression for $\Gamma_{nl}^{\text{dec}}(T)$, in which the density of the number of states (population) of BBR photons $p^{\text{BBR}}(T) = \{\exp[\omega / (k_B T)] - 1\}^{-1}$ is replaced with the temperature-independent density of the number of states of spontaneous photons $p^{\text{sp}} = 1$. For a circular Rydberg state with the angular momentum $l = n - 1$, the transition from which is possible only to a single lower state with $n' = n - 1$, $l' = l - 1$ (also circular), one can obtain a closed analytical expression for Γ_{nl}^{sp} [25, 30]. This is because the wave functions of circular states are hydrogen-like. For states with small orbital angular momenta, it is necessary to use approximate wave functions. However, due to simple analytical expressions for the QD and FMP functions, numerical calculations are quite accessible for modern computer facilities, and the data obtained are in satisfactory agreement with theoretical and experimental data available in the literature for the natural lifetimes $\tau_{nl}^{\text{sp}} = 1 / \Gamma_{nl}^{\text{sp}}$ of excited states.

Calculations for highly excited states with principal quantum numbers n in the range 15–400 for all Rydberg series with $l = 0, 1, 2, 3$ give numerical values of the lifetimes, which are in good agreement with the asymptotic dependence $\tau_{nl}^{\text{sp}} = \tau_l^{(0)} n^3$, where the numerical factor $\tau_l^{(0)}$ is independent of the principal quantum number constant for series of states with the angular momentum l . To improve the accuracy of the asymptotic approximation and extend the domain of its applicability, a correcting factor can be introduced in the form of a cubic polynomial in powers of the inverse principal quantum number, which tends to unity in the limit $n \rightarrow \infty$, so that

$$\tau_{nl}^{\text{sp}} = \tau_l^{(0)} n^3 \left(1 + \frac{\tau_l^{(1)}}{n} + \frac{\tau_l^{(2)}}{n^2} + \frac{\tau_l^{(3)}}{n^3} \right). \quad (7)$$

Coefficients $\tau_l^{(i)}$ ($i = 0, 1, 2, 3$) are determined by the polynomial approximation method for the calculated τ_{nl}^{sp} values of a particular series of Rydberg states with a fixed orbital angular momentum l . Table 2 presents the values of the factor $\tau_l^{(0)}$ (in nanoseconds) and coefficients $\tau_l^{(i)}$ obtained here using the QD approximation for the series of Rydberg states S, $P_{3/2}$, $D_{5/2}$, and $F_{7/2}$ with the maximum total angular momentum $J = l + 1/2$ of group IIb ions.

The numerical values of the parameters $\tau_l^{(i)}$ ($i = 0, 1, 2, 3$) given in Table 2 ensure the accuracy of reproduction of the numerical data of the calculations described above with a relative error of less than 5% in the range of values of the principal quantum number $15 < n < 500$. For $nP_{3/2}$, $nD_{5/2}$, and $nF_{5/2}$ states of Zn^+ , and $nD_{5/2}$ states of Cd^+ , as well as $nP_{3/2}$ and $nD_{5/2}$ states of Hg^+ , the error does not exceed 1% in the region $12 < n < 1500$. The data in Table 2 can be useful for further studies of the properties of Rydberg states with small orbital angular momenta in Zn^+ , Cd^+ , and Hg^+ ions.

Table 2. Parameters of asymptotic approximation (7) for lifetimes $\tau_l^{(0)}$ and coefficients $\tau_l^{(i)}$ of the cubic polynomial for excited nS , $nP_{3/2}$, $nD_{5/2}$, and $nF_{7/2}$ states of ions of group IIb.

Ion	Series	$\tau_l^{(0)}/\text{ns}$	$\tau_l^{(1)}$	$\tau_l^{(2)}$	$\tau_l^{(3)}$
Zn^+	nS	0.059834	5.0513	-278.95	2287.3
	$nP_{3/2}$	0.12734	19.759	135.91	15507.1
	$nD_{5/2}$	0.048834	-1.9724	1.5145	-32.55
	$nF_{7/2}$	0.0843346	0.63229	-42.252	400.23
Cd^+	nS	0.0661534	1.5551	-292.84	2681.4
	$nP_{3/2}$	0.347681	11.859	-15.322	-666.88
	$nD_{5/2}$	0.047934	-3.3985	-6.1472	32.364
	$nF_{7/2}$	0.111851	40.157	-1138.0	8958.7
Hg^+	nS	0.0869103	3.1597	-449.73	4194.1
	$nP_{3/2}$	0.0903141	-1.9110	-58.046	153.10
	$nD_{5/2}$	0.0412015	-7.6834	36.613	-138.76
	$nF_{7/2}$	0.134523	33.325	-933.48	7221.4

4. BBR-induced transitions from the Rydberg state

From Table 2, it can be seen that the natural lifetime of the Rydberg state with $n = 100$ ranges from 34 to 127 μs , depending on the orbital angular momentum of the ion. For $n = 450$, the lifetime is 3–12 ms. However, the ubiquitous ambient thermal radiation can significantly reduce the lifetime of an atom in a highly excited state and even induce photoionisation [21–23]. Interaction with BBR leads to broadening of atomic levels, given by the total probability (6) of induced radiative transitions. The terms corresponding to the transitions from the Rydberg state $|nlm\rangle$ to the states $|n'l'm'\rangle$ with lower energies, $E_{n'l'} < E_{nl}$, represent the total probability of thermally induced decay transitions

$$\Gamma_{nl}^{\text{dec}}(T) = \frac{2}{3c^3(2l+1)} \sum_{\substack{n'l' = l \pm 1 \\ (E_{n'l'} < E_{nl})}} \frac{l > |f_{n'l'nl}^{(2)}|}{\exp[\omega_{n'n} / (k_B T)] - 1}, \quad (8)$$

where each term differs from the probability of the corresponding spontaneous transition by the factor

$$p^{\text{BBR}}(\omega_{n'n}, T) = \frac{1}{\exp[\omega_{n'n} / (k_B T)] - 1}, \quad (9)$$

determining the Planck distribution for the number density of thermal photons (population) at the frequency $\omega_{n'n} = E_{nl} - E_{n'l'}$. Thus, function (9) can be considered as the relative (with respect to the spontaneous) rate of the stimulated radiative transition. Obviously, this function has the maximum value for the minimum exponent in the denominator. At a fixed temperature, this minimum corresponds to the frequency of transition to a state neighbouring in energy, at which the exponent is $\omega_{n'n} / (k_B T) \approx \eta \equiv Z^2 / (n^3 k_B T)$. If $\eta \ll 1$, then the population (9) becomes proportional to the product $n^3 T$: $p^{\text{BBR}}(\omega_{n'n}, T) \approx n^3 k_B T / Z^2$. Note that this value is Z^2 -fold suppressed for ions in comparison with $p^{\text{BBR}}(\omega_{n'n}, T)$ for neutral atoms. This estimate of the photon number corresponds to taking into account only the dominant term in the expansion in powers of the exponent of the right-hand side of expression (9). Nevertheless, it indicates the possibility of obtaining a sufficient approximation formula for probability (8). More informative can be an approximation for the relative probability $R_{nl}^{\text{dec}}(T) = \Gamma_{nl}^{\text{dec}}(T) / \Gamma_{nl}^{\text{sp}}$, which directly reflects the relative contribution of thermally induced transitions to the broadening of the energy level in comparison with spontaneous broadening. Taking into account the major influence of the probabilities of induced transitions to neighbouring energy states on the probability $\Gamma_{nl}^{\text{dec}}(T)$, as well as the asymptotic behaviour of the lifetime (7), we can write an approximate expression that effectively takes into account all terms on the right-hand side of (8), in the form of a fraction

$$R_{nl}^{\text{dec}}(T) = \frac{(Z/n)^2 P_{nl}^{\text{dec}}(x)}{D_n(T)}, \quad (10)$$

whose numerator is a cubic polynomial

$$P_{nl}^{\text{dec}}(x) = \sum_{i=0}^3 a_i^{\text{d}}(T) x^i. \quad (11)$$

The argument $x = 200 / (nT^{1/3}) \propto \eta^{1/3}$ of the polynomial disappears at $nT^{1/3} \rightarrow \infty$, and the coefficients $a_i^{\text{d}}(T)$ ($i = 0, 1, 2, 3$) depend on temperature. Thus, $P_{nl}^{\text{dec}}(0) = a_0^{\text{d}}(T)$ becomes a T -dependent quantity as $n \rightarrow \infty$ ($x \rightarrow 0$). The denominator $D_n(T) = \exp[Z^2 / (n^3 k_B T)] - 1$ determines the density of the BBR photon number at frequencies $\omega \approx Z^2 / n^3$ of transitions to the nearest states, which make the main contribution to sum (8). The factor $(Z/n)^2$ in the numerator of the fraction in Eqn (10) takes into account the difference in the dependences of the asymptotic probabilities of thermally induced $[\Gamma_{nl}^{\text{dec}}(T)]$ and spontaneous $(\Gamma_{nl}^{\text{sp}})$ transitions on the charge of the ionic core Z and on the principal quantum number at $n \rightarrow \infty$. To determine the coefficients $a_i^{\text{d}}(T)$, one can use the method of polynomial interpolation of the function $\Gamma_{nl}^{\text{dec}}(T)$, calculated at specific temperatures in a certain range of numerical values of the principal quantum number. The obtained values of $a_i^{\text{d}}(T)$ at particular values of temperature T can also be used to determine their dependence on temperature using the interpolation by a cubic polynomial of the form

$$a_i^{\text{d}}(T) = Q_i^{\text{d}}(y) = \sum_{j=0}^3 b_{ij}^{\text{d}} y^j, \quad (12)$$

where $y = (100/T)^{1/3}$; $i = 0, 1, 2, 3$; b_{ij}^{d} are constant coefficients depending only on the orbital angular momentum l . The argument of the polynomial $Q_i^{\text{d}}(y)$ is chosen so that at high

temperatures it becomes a temperature-independent constant, $Q_i(y) \xrightarrow{T \rightarrow \infty} b_{i0}^d = a_i^d(\infty)$. A similar condition $P_{nl}^{\text{dec}}(x) \xrightarrow{n^3 T \rightarrow \infty} a_0^d(\infty) = b_{00}^d$ is used when choosing the coefficients of polynomial (11). Double interpolation is due to the dependence of the probability $\Gamma_{nl}^{\text{dec}}(T)$ on three quantities n , T , and l . The dependence of $\Gamma_{nl}^{\text{dec}}(T)$ on the orbital angular momentum leads to the need to determine separate sets of coefficients b_{ij}^d for each value of l . Thus, to find the numerical values of the relative probability $R_{nl}^{\text{dec}}(T)$ for the given values of the principal and orbital quantum numbers and the BBR temperature, it is sufficient to have a matrix of coefficients b_{ij}^d for a specific series of states with a fixed orbital angular momentum l .

5. Excitations from the Rydberg state induced by the BBR

The second part of the sum in expression (6) determines the total probability of excitations of the states $|n'l'\rangle$ with energies $E_{n'l'} > E_{nl}$:

$$\Gamma_{nl}^{\text{exc}}(T) = \frac{2}{3c^3(2l+1)} \sum_{\substack{n'l' = l \pm 1 \\ (E_{n'l'} > E_{nl})}} \frac{l > |f_{n'l'nl}^{(2)}|}{\exp[\omega_{n'l'nl}/(k_B T)] - 1}. \quad (13)$$

Similar to $\Gamma_{nl}^{\text{dec}}(T)$, the main contribution to this sum comes from terms with $n' - n \ll n$. Despite the infinite number of bound states with $n' > n$, due to the rapid decrease of the radial amplitudes of the electric dipole transition $\langle n'l' \pm 1|r|nl\rangle$, the contribution of an infinite number of states with $n' - n \gg 1$ turns out to be significantly smaller than the contribution of the states $|n'l'\rangle$ close in energy to the state $|nl\rangle$ with $n' - n \ll n$. Thus, the asymptotic dependences $\Gamma_{nl}^{\text{exc}}(T)$ and $\Gamma_{nl}^{\text{dec}}(T)$ at large values of n and T are virtually the same. Therefore, the approximate expression for the relative probability of excitation $R_{nl}^{\text{exc}}(T) = \Gamma_{nl}^{\text{exc}}(T)/\Gamma_{nl}^{\text{sp}}$ can be written similarly to Eqn (10) in the form

$$R_{nl}^{\text{exc}}(T) = \frac{(Z/n)^2 P_{nl}^{\text{exc}}(x)}{D_n(T)}, \quad (14)$$

where $P_{nl}^{\text{dec}}(x)$ is replaced with the polynomial

$$P_{nl}^{\text{exc}}(x) = \sum_{i=0}^3 a_i^e(T) x^i$$

with the same argument as in Eqn (11), $x = 200/(nT^{1/3})$, and the coefficients $a_i^e(T)$ are determined by the method of polynomial interpolation of the numerical values of the total probability (13) of the BBR-induced excitations, calculated at a fixed temperature T , similarly to the coefficients $a_i^d(T)$ (12) for the total probability of thermally induced transitions. In this case, the coefficients b_{ij}^d of the polynomial $Q_i^d(y)$ are replaced with the corresponding coefficients b_{ij}^e of the polynomial $Q_i^e(y)$ represented by the expansion in powers of the parameter $y = (100/T)^{1/3}$ similar to expansion (12).

6. Results of numerical calculations and their discussion

The results of numerical calculations using Eqns (8) and (13) with the QD method wave functions for the probabilities of radiative transitions, both spontaneous and induced by BBR with temperatures of 100–3000 K, for a series of Rydberg S, P, D, and F states with principal quantum numbers from $n = n_0$ to $n = 400$ in Zn^+ , Cd^+ , Hg^+ ions, were interpolated and presented in the form of approximating expressions (10) and (14). Coefficients of cubic polynomials (11) and (12) were obtained by polynomial interpolation of numerical values of probabilities for states with $n = 15, 40, 80$, and 120 at temperatures $T = 100, 300, 1000$, and 2000 K. Tables 3–5 present numerical values of the coefficients b_{ij}^d and b_{ij}^e , which determine the relative probabilities of thermally induced transitions in accordance with Eqns (10) and (14).

It should be noted that the coefficients b_{00}^d and b_{00}^e for each series of states allow estimating the ratio of the total probabilities of induced transitions from sufficiently high Rydberg states with the stimulated emission (decays) and absorption (excitation) at a sufficiently high temperature of the BBR. In particular, for cadmium ions, the probabilities of

Table 3. Coefficients of polynomials (12) approximating the total probabilities of BBR-induced decays (10) b_{ij}^d and excitations (14) b_{ij}^e of the series of Rydberg states with small orbital angular momenta ($l \leq 3$) in Zn^+ ions.

Series	i	b_{i0}^d	b_{i1}^d	b_{i2}^d	b_{i3}^d	b_{i0}^e	b_{i1}^e	b_{i2}^e	b_{i3}^e
S	0	4.3472	-0.02559	0.1021	-0.0060	0.6807	-0.1303	0.2763	-0.1888
	1	2.0671	-9.282	9.083	-3.493	1.639	-3.930	3.706	-1.042
	2	-20.07	69.54	-84.79	35.33	-0.1474	0.1080	0.6471	-0.8913
	3	15.732	-60.10	78.01	-33.58	-0.0288	0.4046	-0.7939	0.6084
$P_{3/2}$	0	4.2744	0.0083	-0.0100	0.0060	5.4406	-0.2504	0.6237	0.4415
	1	-2.9950	4.4292	-5.8494	2.4580	21.579	-56.19	59.78	-21.82
	2	18.317	-64.96	80.79	-33.77	21.063	-69.00	87.62	-40.71
$D_{5/2}$	0	1.6196	-0.00296	0.06123	-0.0210	2.0159	0.2875	-0.5680	0.3251
	1	-0.35352	-1.574	1.468	-0.5401	-3.8145	9.000	-8.307	2.655
	2	0.90718	-3.191	4.602	-2.060	7.6057	-25.63	28.40	-10.81
$F_{7/2}$	0	-0.99104	4.226	-5.891	2.639	-4.5544	17.04	-20.87	8.549
	0	4.2861	-0.0441	0.1074	-0.0269	2.2144	0.3765	-0.7373	0.4083
	1	-6.3532	11.19	-13.15	5.254	-1.0887	1.504	0.5937	-1.021
	2	7.3282	-24.58	31.58	-13.40	4.1727	13.41	12.09	-3.667
	3	-3.1643	12.64	-17.05	7.480	-2.4772	8.654	-9.331	3.398

Table 4. The same as in Table 3 for the series of Rydberg states with small orbital angular momenta ($l \leq 3$) in Cd⁺ ions.

Series	i	b_{i0}^d	b_{i1}^d	b_{i2}^d	b_{i3}^d	b_{i0}^e	b_{i1}^e	b_{i2}^e	b_{i3}^e
S	0	3.9271	-0.02767	0.05198	0.02910	1.6834	-0.0245	0.0595	-0.0412
	1	4.6613	-15.64	16.93	-6.781	1.750	-4.560	4.918	-1.648
	2	-25.149	86.21	-105.32	43.94	-9.148	31.86	-39.37	16.143
	3	17.175	-65.02	83.88	-35.97	7.1839	-27.95	36.72	-15.84
P _{3/2}	0	6.5008	-1.1653	2.455	-1.657	18.810	5.288	-9.598	4.786
	1	4.1867	-8.419	2.432	2.820	45.76	-143.3	190.8	-84.88
	2	15.987	-60.20	82.41	-39.78	24.813	-48.39	-7.069	23.06
	3	-10.248	42.27	-57.95	27.25	-37.377	107.17	-98.24	29.71
D _{5/2}	0	1.7392	-0.6652	0.1331	-0.07014	1.92994	0.2453	-0.4732	0.2552
	1	-0.59293	-0.2874	-0.09792	0.1836	-1.2535	2.369	-1.150	-0.03023
	2	-0.013664	-0.3767	1.402	-0.9033	2.3044	-7.101	5.796	-1.531
	3	-0.37448	1.930	-3.011	1.485	-1.7177	5.821	-6.168	2.225
F _{7/2}	0	7.34136	-0.1123	0.5234	-0.1636	1.75329	0.4078	-0.7624	0.3136
	1	28.9338	-83.765	89.66	35.03	15.8697	-43.27	50.94	-20.67
	2	-128.997	445.31	-547.3	228.2	-35.559	124.7	-160.5	68.48
	3	102.548	-394.17	514.07	-221.67	23.475	-92.44	124.04	-54.325

Table 5. The same as in Table 3 for the series of Rydberg states with small orbital angular momenta ($l \leq 3$) in Hg⁺ ions.

Series	i	b_{i0}^d	b_{i1}^d	b_{i2}^d	b_{i3}^d	b_{i0}^e	b_{i1}^e	b_{i2}^e	b_{i3}^e
S	0	3.8357	-0.002076	0.02964	0.04075	3.23202	0.2186	-0.4271	0.2610
	1	10.0336	-29.502	32.69	-13.10	5.0746	-14.101	16.81	-7.171
	2	-41.8764	144.6	-178.0	74.41	-27.342	95.96	-120.95	51.44
	3	29.2278	-112.6	146.8	-63.32	21.0187	-82.52	109.3	-47.67
P _{3/2}	0	2.11065	-0.07759	0.1647	-0.08750	4.59111	1.0002	-1.912	1.023
	1	-1.71419	4.057	-5.331	2.341	1.44581	-7.655	14.466	-7.738
	2	2.65271	-9.4865	12.67	-5.654	1.8896	-1.6956	-9.480	7.762
	3	-1.9035	7.429	-9.952	4.446	-6.113	19.135	-18.808	6.088
D _{5/2}	0	1.4831	-0.05220	0.1071	-0.05723	1.6690	0.2271	-0.4403	0.2443
	1	-0.89544	0.71389	-1.068	0.5266	-1.59713	3.339	-2.369	0.4661
	2	0.893183	-3.271	4.749	-2.234	2.61188	-8.149	7.429	-2.265
	3	-0.78603	3.233	-4.494	2.057	-1.68374	5.6632	-6.077	2.205
F _{7/2}	0	8.55152	-0.1059	0.4409	-0.08208	2.28538	0.6151	-1.116	0.4624
	1	29.3827	-85.16	91.00	-35.72	17.9806	-49.84	59.54	-24.35
	2	-121.997	418.5	-513.4	214.2	-36.4184	129.6	-169.6	73.02
	3	93.7923	-359.5	468.4	-201.9	23.2105	-93.32	127.3	-56.29

decays from S states are approximately twice, and from F states, four times higher than the probabilities of excitations. For P states, the picture is the opposite: excitations are almost three times more likely than decays. For D states, the probabilities of excitation and decay are practically the same. The corresponding broadening of Rydberg levels is determined by the total probability of all induced and spontaneous decays and excitations and can be written in the form

$$\begin{aligned} \Gamma_{nl}^{\text{tot}}(T) &= \Gamma_{nl}^{\text{sp}} + \Gamma_{nl}^{\text{dec}}(T) + \Gamma_{nl}^{\text{exc}}(T) \\ &= \Gamma_{nl}^{\text{sp}} [1 + R_{nl}^d(T) + R_{nl}^e(T)]. \end{aligned} \quad (15)$$

Note that for small values of the parameter η [$\eta = Z^2 \times (n^3 k_B T)^{-1} \ll 1$] in the expansion of the Planck distribution in powers of the exponent in expression (6) for $\Gamma_{nl}^{\text{BBR}}(T) = \Gamma_{nl}^{\text{dec}}(T) + \Gamma_{nl}^{\text{exc}}(T)$, a temperature-independent term appears, which completely compensates for Γ_{nl}^{sp} [25, 26]. Nevertheless,

to calculate the approximation polynomials in (10) and (14) exact expressions (8) and (13) were used.

7. Conclusions

The results obtained in this paper provide important information about the relative probabilities of thermally induced excitations and decays of the Rydberg states of IIb ions in the BBR field. The numerical values of the coefficients presented in Tables 3–5 make it possible to estimate the rates of decays with a transition to lower levels and excitations with a transition to states with higher energy from Rydberg states with small orbital angular momenta.

Along with the probabilities of individual processes of spontaneous decay and induced decays and excitations, the total width of the Rydberg level can be estimated from the quantitative data in Tables 2–5. If we represent the asymptotics for the thermally induced width (6) in the form $\Gamma_{nl}^{\text{BBR}}(T) = \gamma_l Z^2 T/n^2$, then from the expression $\Gamma_0(T) = 4Z^2 \times$

$k_B T / (3c^3 n^2)$ for the imaginary part of the Stark energy (2) we obtain the factor $\gamma_l = 4k_B / (3c^3) = 67833.1 \text{ K}^{-1} \text{ s}^{-1}$, independent of the orbital angular momentum l . For the series of Rydberg S, P, D, and F states of group IIb ions considered in this work, the factors l can be expressed through the numerical values of the coefficients $\tau_{nl}^{(0)}$ and b_{00}^d, b_{00}^e from Tables 2–5: $\gamma_l = 791.7004(b_{00}^d + b_{00}^e) / \tau_l^{(0)}$. These constants essentially depend on l .

For example, for Hg^+ ions, the numerical values of the factors (in $\text{K}^{-1} \text{ s}^{-1}$) are as follows: $\gamma_0 = 64382.6$, $\gamma_1 = 58748.1$, $\gamma_2 = 60568.6$, and $\gamma_3 = 63777.7$. This difference in the asymptotic values of $\Gamma_{nl}^{\text{BBR}}(T)$ and their lower values compared to $\Gamma_0(T)$ for Rydberg states with small orbital angular momenta l in neutral atoms were noted in the results of numerical calculations in Refs [24, 29]. The proportionality to the square of the residual ion charge Z for $\Gamma_{nl}^{\text{BBR}}(T)$ was first written explicitly in [30]. In this paper, a general expression is obtained in terms of the coefficients of the asymptotic polynomials (7), (11), (12), and (14) for the correction factor γ_l , which determines the dependence of the asymptotics of $\Gamma_{nl}^{\text{BBR}}(T)$ on the orbital angular momentum of the Rydberg state.

The relative contribution of ionisation processes to the broadening of Rydberg energy levels at a fixed temperature does not exceed 1%–2% and decreases rapidly with increasing principal quantum number. For this reason, the ionisation of the Rydberg levels of the BBR was not considered in this work. Nevertheless, the numerical values of the ionisation probability and their dependences on the principal and orbital quantum numbers of Rydberg states may be of special interest and can be calculated using semiempirical methods of the one-electron approximation similar to calculations for group IIa ions [27, 28].

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