Distribution of the radiative lifetimes over the excited states of atoms and ions

N.N. Bezuglov, E.N. Borisov, and Ya.F. Verolainen

Leningrad State University

(Submitted May 18, 1990; resubmitted June 14, 1990) Usp. Fiz. Nauk **161**, 3–29 (January 1991)

The empirical regularities in the variation of the radiative lifetimes τ_k of excited states of atoms are reviewed. A quasiclassical theory of radiation damping processes is constructed. The formalism of quantization of the natural width $A_k = \tau_k^{-1}$ of the excited states of atoms and ions is presented. The question of how to describe the serial dependences for a perturbed series is investigated. It is demonstrated that the radiation emission of atomic systems is sharply reduced when the classical factors in the radiative processes are suppressed. Schemes are proposed for extrapolating lifetimes from the lower terms of a series to the upper Rydberg states, right up to the continuum. Recommended values of τ_k for group I, II, and VIII atoms are given in a form that is convenient for inclusion in a computerized data base.

INTRODUCTION

Extensive numerical data, obtained by both experimental and computational methods, on the radiative lifetimes τ_k of the excited states of atoms and ions have now been accumulated in the literature. As new information on τ_k appeared steps were taken to interpret it with the help of different empirical rules. The dependences of τ_k on the principal quantum number *n* and the effective quantum number n^* ,¹⁻³ on the energy gap $\Delta \varepsilon$ between the levels of the same spectral series,⁴ and on the effective charge (z^*) of the atomic core⁵ were determined. A number of analytical relations describing the distribution of τ_k as a function of *n* were proposed for hydrogen-like states.

The serial behavior is interesting because it permits determining the most reliable values in a set of values of τ_k obtained by different methods and also often to predict τ_{μ} for states that have not been studied.⁶ Much more complete and accurate values of the atomic constants, including the radiation constants, are now required. This is because new fundamental and applied problems in atomic physics and spectroscopy, plasma physics, quantum electronics, plasma chemistry, and astrophysics must now be solved for a wide range of conditions. In this connection, the problem of creating a compilation of recommended constants (lifetimes) which have been evaluated by experts remains urgent. In this review the existing published data on τ_k for group I, II, and VIII atoms are systematized, different theoretical methods (formulas) for calculating τ_k are compared, and a novel quasiclassical theory for determining τ_k is developed. All this makes it possible to compare the results obtained by different authors, to analyze these results critically in order to determine omissions, to find a method for determining the most reliable values, and finally to compile recommended values of the lifetimes of group I, II, and VIII atoms. In Secs. 2 and 3, which are devoted to applications of the theory of radiation processes, the atomic system of units (a.u.) is mainly employed.

1. EMPIRICAL DISTRIBUTIONS OF THE RADIATIVE LIFETIMES OVER THE EXCITED STATES OF ATOMS AND IONS

The first serial rule was apparently established back in 1928 by A. Cooper in an investigation of the oscillator strengths $f(n,l \rightarrow n',l')$ of the hydrogen atom: $f(n,l \rightarrow n',l+1) \sim (n')^{-3}$. Later Bethe and Salpeter⁷ discovered that for the hydrogen atom the lifetimes τ_k of the levels having the same orbital quantum number *l* are proportional to n^3 .

N. P. Penkin and L. N. Shabanova also observed that $A_{ki} \sim (n^*)^{-3}$, where A_{ki} is the probability of a radiative transition from the level k to the level i, in the principal series for the Rydberg states of group II atoms.⁸ In 1975 it was reported in Refs. 1–3, virtually simultaneously and independently, that τ is a power-law function of n^* for different series of excited states of neon, mercury, and sodium atoms. Power-law dependences, whose empirical form is given by the relation

$$\tau_{\mathbf{k}} = \tau_{\mathbf{0}, l} \left(n^* \right)^{\alpha_l}, \tag{1.1}$$

were later observed for a large number of series of atoms and ions. Here $\tau_{0,l}$ and α_l are constants for a given series of levels with fixed orbital quantum number l; the symbol k incorporates all quantum numbers of a level in a series, but some quantum numbers are dropped, for example, $k = \{n, l, m\}$ or $k = \{n, l, \}$ or k = n. Another empirical law, proposed in Ref. 4,

$$\tau_{\mathbf{k}} = B \left(\Delta E_{\mathbf{k}} \right)^{-\beta_{l}},\tag{1.2}$$

relates the radiative lifetimes with the energy difference $\Delta E_k = \varepsilon_{k+1} - \varepsilon_k$ for adjacent states in the series. It is convenient to represent the dependences (1.1) and (1.2) graphically on a logarithmic scale, in which the dependences are straight lines. Figures 1 and 2 show several examples of such plots.

The practical utility of the relation (1.1) has been

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0038-5670/91/010001-15\$01.00

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FIG. 1. Power-law dependences (1.1) of the radiative lifetimes (τ) as functions of the effective principal quantum number (n^*) for a number of series of excited states. The exponent (α_i) takes on values between 2.7 and 4.3.



FIG. 2. Power-law dependences (1.2) of the radiative lifetimes (τ) on the energy splitting (ΔE) for several series of excited states of the neon atom.

pointed out before. For this reason, in the last few years the parameters $\tau_{0,l}$ and α_l have been determined for a number of atomic series by the method of least squares. The value of α_l is usually close to three, but both smaller and larger values are often observed. For example, for the series presented in Fig. 1 α_l varies from 2.8 (Cs) to 4.3 (Ne $np[3/2]_2$). Even for different series of the same atom α_l can fluctuate from 3 to 4.3 (Ne $ns'[1/2]_0$ and $np[3/2]_2$) (see Fig. 1). In Sec. 4 the serial laws (1.1) and (1.2) are employed for analyzing lifetimes and for discussing their range of application and correspondingly the possibilities of using them to extrapolate τ_k to highly excited states.

2. FORMULAS FOR CALCULATING THE RADIATIVE LIFETIMES τ_k

The main difficulty in interpreting the experimental results on lifetimes theoretically is that the probability $A_k = \tau_k^{-1}$ of radiative decay of the excited level k has a complicated structure. The radiative width consists of individual probabilities $A_{k\bar{k}}$ of the emission of a photon at the frequencies $\omega_{k\bar{k}} = (\varepsilon_k - \varepsilon_k)/\hbar$ in optical transitions $k \rightarrow \tilde{k}$:

$$\boldsymbol{\tau}_{\boldsymbol{k}}^{-1} \equiv \boldsymbol{A}_{\boldsymbol{k}} = \sum_{\boldsymbol{k}} \boldsymbol{A}_{\boldsymbol{k}\boldsymbol{k}}, \quad \boldsymbol{A}_{\boldsymbol{k}\boldsymbol{k}} = 2\omega_{\boldsymbol{k}\boldsymbol{k}}^{2}l^{2} (mc^{3})^{-1} f_{\boldsymbol{k}\boldsymbol{k}}. \tag{2.1}$$

Quite complete representations of the oscillator strengths $f_{k\bar{k}}$ as a function of the quantum numbers of the states k and

 \tilde{k} are now available,⁹⁻¹⁵ but the problem of obtaining approximate analytical expressions for the oscillator strengths nonetheless remains an important element of many theoretical studies¹³⁻²¹ concerned with lifetimes τ_k . Thus in Ref. 20 a very accurate approximation of $f_{k\bar{k}}$ is presented for hydrogen-like and alkali atoms, using the method of Bates and Damgaard (see, for example, Ref. 22). In Ref. 21 an approximate method is given for calculating the product $\langle \omega_{k\bar{k}}^2 f_{k\bar{k}} \rangle$, in which the summation in Eq. (2.1) over the components of the multiplet structure of the initial k and final \tilde{k} electronic terms is performed. In Ref. 16 the quasiclassical formulas of quantum mechanics²³ are used to estimate the oscillator strengths for the hydrogen atom. S. P. Gorslavskiĭ et al.¹⁴ and R. A. Gantsev¹⁵ made a detailed investigation of the overlap integrals of the radial wave functions appearing in $f_{k\bar{k}}$, starting both from the asymptotic limits for $f_{k\bar{k}}$ and from the general correspondence rules.¹⁵

The next step in the analytical description of A_k is to perform the summation in Eq. (2.1) over the lower states \tilde{k} . This can be done in several ways. For example, in Refs. 14– 16 the summation over the principal quantum number \tilde{n} of the levels of the hydrogen atom is replaced by an integral over \tilde{n} ; this is justified for the Rydberg states $(n \ge 1)$. The resulting expression for A_k , written in universal notation, has the following form (in atomic units)

$$A_{n_1 l} = \frac{z^4 \alpha}{n^3} \frac{G(n, l)}{L^2}, \quad \alpha = \frac{4}{\sqrt{3}\pi c^3}.$$
 (2.2)

Here z is the charge of the atomic core and c is the velocity of light (c = 137 a.u.). According to Refs. 14 and 16 the function G(n, l) is a constant: $G_{14} = 1$ (Ref. 14) and $G_{16} = \pi/2\sqrt{3}$ (Ref. 16). According to Ref. 16 L = l + 0.5 and according to Ref. 14 L = l. In Ref. 11 it is suggested that the "academic correction" $l \rightarrow l + 0.5$ be introduced into the formula for $A_{n,l}$ given in Ref. 14. This so-called Langer's correction arises in the quasiclassical theory because of the singularity of the centrifugal repulsive potential at the origin.²³ The accuracy of the representation (2.2) with $L_{14} \Rightarrow L_{111} = l + 0.5$ can be judged from the curves in Fig. 3a (l > 0).

The suggestion that the lifetime is a cubic function of the principal quantum number was first made in Ref. 7 without any indication of the character of the behavior of τ_k as a function of the orbital quantum number *l*. The specific dependence in the form (2.2) with L = l was proposed in Refs. 13–14. In Ref. 14 the relation (2.2) with G(n, l) = 1 was derived analytically whereas in Ref. 13 the dependence $A_{n,l} \sim L^{-2}$ was arrived at empirically. In Ref. 15, where the results of a number of investigations (see Ref. 10) on radiative processes involving hydrogen-like atoms are generalized, formulas are derived for the probabilities $A_n^{(l-l')}$ of radiative transitions to lower levels with a fixed value of the orbital quantum number. In the notation of Eq. (2.2)

$$A_{n}^{(l \to l-1)} = \frac{z^{4}\alpha}{n^{3}} \frac{G^{(l \to l-1)}}{l(l+1/2)}, \quad A_{n}^{(l \to l+1)} = \frac{z^{4}\alpha}{n^{3}} \frac{G^{(l \to l+1)}}{(l+1/2)(l+1)},$$
(2.3)

$$G^{(l \to l \mp 1)} = \left(1 \pm \frac{\pi \sqrt{3}}{6}\right), \qquad A_{n, l} = A_n^{(l \to l - 1)} + A_n^{(l \to l + 1)}.$$
(2.4)

According to Eqs. (2.3) and (2.4) the total probability $A_{n,l}$ has the form of Eq. (2.2) with $L_{[15]}^2 = l(l+1)$ and $G_{[15]} = 1 + \{\pi/[4\sqrt{3}(l+0.5)]\}$. The ordinate axes on the right in Fig. 3 refer to the straight lines (l = 0, 1, 2, 3), which describe the relations (2.3) and (2.4).

Under the conditions of an equilibrium distribution of the populations of the atoms the probability of radiative decay $\langle A_n \rangle$, averaged over an entire set l < n of degenerate states $|n, l\rangle$ with energy ε_n , is of interest:

$$\langle \tau_n \rangle^{-1} \equiv \langle A_n \rangle = \sum_{l=0}^{n-1} (2l+1) A_{n,l} \cdot n^{-2}, \quad \varepsilon_n = -\frac{z^2}{2n^2}.$$

In the limit of Rydberg states $\langle A_n \rangle$ reduces to the following asymptotic form:¹³⁻¹⁵

$$\langle A_n \rangle = 8z^4 (\sqrt{3}\pi c^3)^{-1} \ln (1,414n) n^{-5},$$
 (2.5)

which corrects the previously widely employed empirical formula of Bethe $\langle A_n \rangle \sim n^{-4.5}$.⁷

In Ref. 17 E. S. Chang used the technique of direct summation of Eq. (2.1) over \tilde{k} to establish the lower limit for the probability $A_{n^*,l}$ of radiative decay of the state n^* , *l*. Toward this end, he appeals to the sum rules,^{22,23} which enabled him to express Eq. (2.1) over the entire energy spectrum \tilde{k} of the



FIG. 3. Comparison of calculations of the probability $A_{n,l}$ of radiative decay according to the formula (2.2) (solid lines in Fig. 3a) with a quantum mechanical calculation²⁴ (the symbols Δ , +, $\mathbf{0}$, $\mathbf{0}$) for the hydrogen atom. The solid curves l-3 in Fig. 3a are plots of the functions G(n, l) from Refs. 13, 14, 5, 16, 17, and 18, respectively; the curve 0' describes the function $20G_s$ (see Eq. (3.32)). The dashed curves were constructed using the relation (3.26) taking into account corrections for the singularity of the Coulomb potential. The ordinate axes on the right refer to the straight lines l = 0, 1, 2, and 3, constructed according to the formulas of Ref. 15.

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electrons (discrete plus continuous) in terms of the wave function $|k\rangle$ of the starting radiating state k. In the case of a single electron in a centrally symmetric force field with the potential U(r) there occur transitions in which the orbital quantum number of the electron changes by one unit: $\tilde{l} \rightarrow l \pm 1$. According to Bethe's rule (Ref. 7, see also Ref. 15), however, downwards transitions to states with $\tilde{l} = l - 1$ occur with overwhelming probability, so that $A_{n^*,l} \approx A_{n^*}^{(l-l-1)}$. The criteria for Bethe's rule to be applicable in individual optical transitions $(l, n \rightarrow \tilde{l}, \tilde{n})$ were formulated in Refs. 14 and 15. They reduce to the requirement that there be a large gap between the energy of the states (l, n) and (\tilde{l}, \tilde{n}) . It is clear from the relations (2.3) and (2.4), according to which $A_n^{(l-l-1)}/A_n^{(l-l+1)} \approx 21$, in the total probability $A_{n,l}$ transitions into a state with $\tilde{l} = l - 1$ predominate. In the quasiclassical model of the emission of a photon upwards transitions (including also into the continuum) with $\tilde{l} = l - 1$ are unlikely (inverse Bethe rule). For this reason, the sum for

$$A_{n^{\bullet}}^{(l \rightarrow l-1)} = \sum_{\vec{n} < n} A_{n^{\bullet}l, \vec{n}^{\star}, l-1}$$

can be extended to all states \tilde{n} :

$$A_{n^*}^{(l \to l-1)} \approx A_{n^*, \infty}^{(l \to l-1)} \equiv \sum_{\tilde{n} < n} + \sum_{\tilde{n} > n}$$

The oscillator strengths (2.1) for upwards transitions change sign,²⁵ so that the second sum in $A_{n^{\bullet},\infty}^{(l-l-1)}$ is less than zero, and we have the following sequence of estimates:

$$\equiv \frac{l+1}{l+0.5} \frac{l}{r} \frac{dU}{dr} - \frac{2l}{2l+1} \cdot \frac{1}{2} \hat{\Delta} U(r), \qquad (2.7)$$

where $|n^*l\rangle$ is the wave function of the radiating state (n^*, l) and $\hat{\Delta}$ is the Laplacian. The derivation of the last equality in Eq. (2.6) for the probability $A_{n^*,\infty}^{(l-l-1)}$ is based on both the possibility of writing the matrix element $\langle n^*l | r | n^*l \rangle$ in three different forms²² and the fact that the set of radial wave functions $|n^*l\rangle$ is complete. In the case of the hydrogen atom $U(r) = -r^{-1}$ and $F(r) = F_1(r) = (l+1) \cdot l/(l+0.5)$ r^{-3} ; the radial integral in Eq. (2.6) is well known,²² so that $A_{n,\infty}^{(l-l-1)}$ reduces to the form Eq. (2.2), where $L_{[17]} = l + 0.5$ and $G_{[17]} = \pi/(2\sqrt{3})$. One can see from Fig. 3a that the curve 2 corresponding to $A_{n,\infty}^{(l-l-1)}$ (2.6) is indeed the lower limit of the probability of radiative transitions.

The inequality (2.6) indicates (though indirectly) that there exists a relation between the probability A_{n+l} of radiative decay and the wave function $|n*l\rangle$ of the radiating state. This connection is revealed more fully in Refs. 5, 18, and 19, where the total probability of radiative processes is determined in the quasiclassical limit in terms of the classical trajectory $r_{cl}(t)$ of the electron. In Ref. 5, in analyzing the lifetimes N. I. Afanas'eva and P. F. Gruzdev used the expression for the rate of decay of the angular momentum L(t) of a radiating electron:²⁶

$$\frac{\Delta \mathbf{L}}{\Delta t} = -\frac{2}{3c^2} \left\langle r^{-1} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\mathrm{cl}} \mathbf{L}; \qquad (2.8)$$

here the symbol $\langle \rho \rangle_{cl}$ means that the function $\rho(r)$ is averaged over the trajectory r_{cl} :

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$$\langle \rho \rangle_{\rm cl} = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} \rho \left(r_{\rm cl}(t) \right) dt \equiv T_{\rm r}^{-1} \int_{0}^{T_{\rm r}} \rho \left(r_{\rm cl}(t) \right) dt.$$
 (2.9)

We note that in Eq. (2.8) the characteristic time scale Δt over which the parameters of the electron orbit change is significantly longer than the period of the radial motion T_r . In the process of a radiative transition the absolute magnitude L of the orbital angular momentum L changes essentially by -1 unit (see above, Bethe's rule in the discussion of Eq. (2.6)). Then the transition time $\tau = \Delta t$ can be found from Eq. (2.8) by setting $\Delta |\mathbf{L}| = -1$:

$$\boldsymbol{\tau}^{-1} = A_{n^{\bullet}l}^{(L)} = \frac{1}{\Delta t} = \frac{2}{3c^3} \left\langle \frac{L}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\mathrm{cl}} ; \quad L = l + 0.5.$$
(2.10)

In the quasiclassical analysis angular momentum L, equal to (l + 0.5), is assigned to an electron with the orbital quantum number $l.^{23}$ For the Coulomb field $\langle r^{-3} \rangle_{cl} = z^3 n^{-3} L^{-3},^{22}$ and the expression (2.10) reduces to the representation (2.2) with L = l + 0.5 and $G_{151} = \pi/2\sqrt{3}$. We also note that the formulas (2.10) are identical (to within a factor) to the formula (2.6) with $F(r) \equiv F_1(r)$ (2.7). From here it follows that the function F_1 (2.7) determines the rate of decay of the orbital angular momentum of the electron.

A systematic quasiclassical description of radiative decay processes is given in Refs. 18, 19, and 27. The description is based on Feynman's formalism.²⁸ In this formalism a quantum system of N charged particles, subject to self-action as a result of electromagnetic fluctuations (zero-point oscillations) of the physical vacuum, is treated as a Hamiltonian system. The dynamics of this system is described with the help of the principle of least action for a complex Hamiltonian. Correspondingly, the total energy $E_k = \varepsilon_k - \varepsilon_k$ $(i\hbar A_k/2)$ of the atomic system acquires a purely imaginary correction, owing to the emission of light by the excited states. In Ref. 18 a unique relation between a set of k classical trajectories and the energy spectrum E_k is established with the help of multidimensional quantization rules. As a result, the natural width A_k , being the imaginary part of the total energy E_k , and the energy ε_k emerge together as characteristics of only the emitting state k. We emphasize that in this approach there are no individual transitions between excited levels, and to determine $\tau_k = A_k^{-1}$ it is not necessary to know the wave functions of all lower-lying states. From the formal standpoint the energy E_k is the diagonal matrix element of a complex Hamiltonian, so that the quasiclassical computational scheme is highly accurate. The quasiclassical theory of the radiative lifetime and applications of this theory are presented in Sec. 3. Here we give the results concerning the calculation of A_{nl} for the Coulomb field: A_{nl} has a representation of the type (2.2), where the function $G(n,l) \equiv G_{\rm H} (L/n)$ is given by the relation (3.18). Figure 3a shows $G_{\mu}(p)$ as a function of the parameter p = (l + 0.5)/n, where l > 0 (solid curve 3). The reasons why the deviation of the quasiclassical calculation (curve 3, in Fig. 3a) from the quantum-mechanical calculation (the points in Fig. 3a) is small are discussed below. The case of the s series requires a special analysis (Sec. 3.6) and is presented in Fig. 3b. One can see that the quasiclassical formula (3.30) with (3.32), which also is of the form (2.2), describes well (solid curve) the results of the quantum-mechanical

calculation²⁴ (circles) of A_k for the s states of the hydrogen atom.

3. SINGLE-CHANNEL THEORY FOR DETERMINING RADIATIVE LIFETIMES τ_k

The investigation of serial regularities entails a search for the analytical properties of the lifetimes as functions of the position of an energy level within a series. It is convenient to seek the solution of the problems arising here by analogy to the quantum-defect theory,¹² since by virtue of the nature of the effective quantum number n^*

$$E_{k} = \varepsilon_{k} - \frac{iA_{k}}{2} = -\frac{z^{2}}{2n_{c}^{*i}}, \quad n_{c}^{*} = n - \mu(E_{k}), \quad (3.1)$$

the fact that the total energy E_k of the level k is complex means that the quantum defect μ acquires a small imaginary correction:

$$i \operatorname{Im} \mu(e_{k}) = n^{*3} z^{-2} \left(1 + z^{2} n^{*-3} \frac{\partial \mu}{\partial e_{k}} \right) \cdot \frac{i A_{k}}{2} .$$
 (3.2)

The relation (3.2) is obtained by regarding the definition (3.1) as an equation for the imaginary part of E_k .

3.1. Notation and assumptions

We shall describe the serial regularities on the basis of the formalism of quantization of the radiative width A_k .¹⁸ In analyzing real atomic systems we shall confine our attention to the single-channel (single-electron) approximation (SCA). Photons are emitted as a result of transitions of one outer (optical) electron without a change in the state of the atomic core. Due to the interaction with the core electrons the optical electron moves in some effective central potential U(r) which is asymptotically Coulombic $U(\mathbf{r}) \simeq -z/r$ as $r \rightarrow \infty$. An individual term k of the series is characterized by three quantum numbers $k = \{m, l, n, \}$: azimuthal, orbital, and radial, respectively. The parameters of the classical orbit **r**, of the electron—the energy ε , the orbital angular momentum L, the period of the radial motion T_r , and the rotation of the orbit by an angle $\Delta \theta$, over the period T_r-are all uniquely fixed for the excited state k by the potential U(r) and the Einstein-Brillouin-Keller (EBK) multidimensional quantization rules:29-31

$$|\mathbf{L}| = l + 0.5, \quad l > 0, \quad \mathbf{L} = 0, \quad l = 0,$$

$$U_{ett}(r) = U(r) + \frac{L^2}{2r^2}, \quad (3.3)$$

$$S_{\rm r} = 2 \int_{0}^{\infty} (2\varepsilon - 2U_{\rm eff}(r))^{1/2} \, \mathrm{d}r, \quad S_{\rm r}(\varepsilon, L) = 2\pi \left(n_{\rm r} + \frac{1}{2}\right), \tag{3.4}$$

$$n^{*} = n_{\rm r} + l + 1 - \mu \equiv n - \mu,$$

$$\Delta \theta_{\rm r} = -\frac{\partial S_{\rm r}}{\partial L}, \quad T_{\rm r} = \frac{\partial S_{\rm r}}{\partial \varepsilon}; \qquad (3.5)$$

here S, is the action for the one-dimensional radial motion of the electron in a potential U_{eff} (3.3); the centrifugal parameter $L = |\mathbf{L}|$ is equal to l + 0.5 in the quasiclassical limit (Langer's correction²³). In what follows we shall require several representations for the period T, which are convenient for analyzing the behavior of the period within a series:

$$T_{\mathbf{r}} = 2\pi \frac{\Delta n_{\mathbf{r}}}{\Delta \varepsilon} = 2\pi n^{*3} z^{-2} \left(1 + z^2 n^{*-3} \frac{\partial \mu}{\partial \varepsilon} \right), \quad \varepsilon = -\frac{z^3}{2n^{*3}}.$$
(3.6)

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In the expression for T, the first equality follows from Eq. (3.5) and the Bohr-Sommerfeld selection rule $\Delta S_r = 2\pi\Delta n_r$, in Eq. (3.4) and the second equality is obtained from the first one by replacing Δn_r , by $\Delta n^* + \Delta \mu$ and using the relation $\partial \varepsilon / \partial n^* = z^2 n^{*-3}$ (see Eq. (3.6)).

When the single-channel approximation is applicable the general relation between A_k and the classical trajectories of motion assumes the form¹⁹

$$A_{k} = \bar{I} \left(A_{k}^{(cl)} - A_{k}^{(q)} \right), \quad A_{k}^{(q)} = \frac{e^{s}}{3m^{2}c^{s}} - \frac{1}{T_{r}} \int_{0}^{r} \hat{\Delta} U \left(\mathbf{r}_{t} \right) dt,$$

$$A_{k}^{(cl)} = \frac{2e}{\hbar} - \frac{1}{T_{r}} \int_{0}^{T_{r}} \frac{d\mathbf{r}_{t}}{dt} \mathbf{A}(t) dt,$$

$$\mathbf{A}(t) = \frac{e}{3\pi c^{3}m} P \int_{-\infty}^{\infty} \nabla U \left(\mathbf{r}_{t} \right) \frac{dt}{t-t};$$
(3.8)

here A is the vector potential of self-action. The factor \overline{I} takes into account the Fermi statistics of the electrons in the atom and depends on the type of coupling between the orbital and spin angular momenta of the electrons in configurations between which the transition of the optical electron occurs.²² In the case of alkali atoms and ions similar to them $\overline{I} = 1$. We note that the integrand in Eq. (3.8) is a periodic function (with period T_r) of the variable t. This reduces the average over the interval T as $T \to \infty$ to an average over T_r . The second term $A_k^{(q)}$ in Eq. (3.7) is of a quantum mechanical nature; because of this term the probability of radiative decay of the ground and metastable states of the atomic system is equal to zero.

The relation (3.7) makes it possible to interpret formally the previously obtained fact that the quantum defect (3.2) acquires an imaginary part. Comparing Eq. (3.2) and Eq. (3.6), we obtain

$$Im \mu = \frac{T_r}{2} \frac{A_k}{2\pi} \,. \tag{3.9}$$

In accordance with Eq. (3.8) it turns out that Im $\mu = \text{Im }\Delta S(r_{T_r})/(2\pi)$. Thus the imaginary part of the quantum defect is equal to (to within 2π) the complex change in phase, which increases over the period T_r in the wave function as a result of the interaction of the excited state k with the zero-point state of the quantum electromagnetic field. This situation agrees with the role of μ in quantum mechanics, when the quantum defect acquires an additional (as compared with the Coulomb case) increase in phase as a result of the interaction of the optical electron with the core electrons.^{12,23}

We call attention to an important property of the quasiclassical formula (3.7): This formula describes well the radiative lifetimes for nonsingular potentials, even in the region of small quantum numbers. Indeed, in this case the trajectories \mathbf{r}_t lie in a neighborhood of the minimum of the potential $U(\mathbf{r})$, where $U(\mathbf{r})$ can be replaced by a quadratic function. The total action $S_{\rm at} + J - \tilde{J}_{\rm q}$, which determines the dynamics of the electrons, also becomes a quadratic functional of \mathbf{r}_t , and for this reason Eq. (3.7) gives the exact result.²⁸ Thus, for example, for a three-dimensional oscillator with the potential $U(r) = \omega^2 r^2/2$ there follows from Eq. (3.7) the relation

$$A_{k} = \frac{2\omega^{3}}{3c^{3}} \left[(2n_{r} + l + 1, 5) - 1, 5 \right], \qquad (3.10)$$

which is identical to the quantum-mechanical relation. According to Eq. (3.10) in the ground state $(l = n_r = 0)$ the quantum correction $A_k^{(q)}$ (the term 1.5 in brackets) completely compensates the classical part $A_k^{(cl)}$ of the radiative width A_k .

3.2. Leading terms in the expansion of $\boldsymbol{A}_{\boldsymbol{k}}$ in powers of the energy $\boldsymbol{\epsilon}$

To expand Eq. (3.7) in a series in powers of ε it is convenient to introduce into the integrand the explicit dependence on the energy ε . To this end we define a polar coordinate system (θ, r) in the plane of motion of the electron and we replace the time integration variables (t, \tilde{t}) in Eqs. (3.7) and (3.8) by radial variables:

$$t(r) = \int_{r_{\pi}}^{r} \frac{\mathrm{d}r}{v_{\varepsilon}(r)}, \quad \theta(r) = L \int_{r_{\pi}}^{r} \frac{\mathrm{d}r}{r^{2}v_{\varepsilon}(r)},$$
$$v_{\varepsilon}(r) = (2\varepsilon - 2U_{\mathrm{eff}}(r))^{1/2}, \quad (3.11)$$

where v_{r} is the radial velocity and $r_{1}(r_{r})$ is the left (right) turning point. The following fact makes it difficult to determine the analytical structure of $A_k(\varepsilon)$. The contours of integration over the variables $r(\tilde{r})$ (Γ -from the left turning point to the right turning point and back, $\tilde{\Gamma}$ -infinite collection of Γ), appearing in Eqs. (3.7) and (3.8), as well as $r_{\rm Lr}$ depend on ε . In order to eliminate this dependence, we shall transform $\Gamma(\overline{\Gamma})$ into cycles $C(\overline{C})$ in the planes of the complex variables (r, \tilde{r}) by making a cut connecting the branch points r_1 , r_r of the analytic function $v_{\varepsilon}(r)$ (3.11). The cycles C in the complex planes can be deformed into other contours Γ_c so that Γ_c and $\widetilde{\Gamma}_c$ would not have points in common and would not be connected with the turning points. In contrast to Γ , the position of Γ_c can be fixed when $r_n \to \infty$ as $\varepsilon \to 0$. We call attention to the fact that when the contours Γ and $\tilde{\Gamma}$ are disconnected it is necessary to pass through the principal value singularities of the function $P(t(r) - t(r))^{-1}$ (3.8) at the points $r = \tilde{r}$; this leads³² to the appearance of an additional *r*-local term $A_k^{(L)}$ in Eq. (3.7):

$$A_{k} = \vec{I} \left(\operatorname{Re} A_{xc}^{(c)} + A_{k}^{(L)} - A_{k}^{(q)} \right),$$
$$A_{k}^{(L)} = \frac{2}{3c^{3}} \frac{1}{T_{r}} \int_{0}^{T_{r}} \frac{dU(r)}{dr} \frac{L}{r} dt; \qquad (3.12)$$

here $A_{kc}^{(cl)}$ is given by a double integral of the type (3.8), which is taken along the contours Γ_c and $\tilde{\Gamma}_c$. The latter lie in the planes of the complex variables r, \tilde{r} , respectively, and envelop the cut from the left. In finite regions (r, \tilde{r}) all integrands can be expanded in a series in powers of ε together with the velocity v_{ε} ; this introduces into A_k (3.12) terms of the type $\Sigma c_m \varepsilon^m$. The coefficients c_m depend on the details of the behavior of the potential near the atomic core. Because of the long-range Coulomb tail -z/r the double integration over (r, \tilde{r}) at infinity results in the appearance in $A_{kc}^{(cl)}$ (3.12) of a specific term logarithmic in ε ; this term is determined only by the turning angle $\Delta \theta_r$. Omitting the details of the proof, we shall give the leading terms in the expansion of A_k in powers of $\varepsilon \sim (n^*)^{-2}$:

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$$\tau_{k}^{-1} = A_{k} = \alpha z^{2} \frac{2\pi I}{T_{r}} \frac{G}{L^{2}},$$

$$G = C_{0} - \frac{D_{1}}{5} \frac{L^{2}}{n^{*2}} \frac{\ln(n^{*2}/L^{2})}{1 - p^{2}} + \frac{C_{1}L^{2}}{n^{*2}} + O(p^{4}),$$

$$p = \frac{L}{L^{*}}, \quad D_{1} = \cos(\Delta \theta_{r}) \left(-\frac{9\sqrt{3}}{2} \right) \sin^{2} \frac{\Delta \theta_{r}}{2},$$
(3.13)

$$Im \mu = \alpha z^2 \frac{I}{2L^2} G.$$
(3.14)

We note that the relation (3.13) agrees with the representation (2.2) for the probability of radiative decay of excited states of a hydrogen atom. The parameter p in Eq. (3.14)determines whether or not the expansion (3.13) can be continued from the highly excited states of the given series of levels to lower states. The critical value n_{cr}^* is determined from the equality $p^4(n_{cr}^*) = G(n_{cr}^*)$; for $n^* > n_{cr}^*$ terms $O(p^4)$ in Eq. (3.13) can be neglected. In what follows (see Sec. 4) we shall construct, based on the relation (3.13), an extrapolation scheme which will make it possible to obtain in the single-channel approximation, based on several lowerlying states of a fixed l series, τ_k for all terms in the series right up to the continuum. In this case the parameter C_0 for a slow thermal l electron will determine the cross section for photorecombination on the corresponding ion core.

In the case of hydrogen-like atoms and ions the result (3.13) can be made much more accurate (see Ref. 19):

$$G_{\rm H} = 1 + \frac{1}{5} \frac{p^2 \ln p^2}{1 - p^2} \left(1 + \frac{39}{56} p^2 \right) + 0.122p^2 + O(p^4), \quad p = \frac{L}{n} .$$
(3.15)

For Keplerian orbits the turning angle $\Delta \theta_r = 2\pi$,²⁹ and according to Eq. (3.14) $D_1 = 1$ for all series. We note that the structure of the logarithmic term in Eq. (3.13) was written in accordance with Eq. (3.15). We also call attention to the fact that in Eq. (3.14) the functions G and μ (3.9) are equal to one another to within a factor. In other words, the representation (3.13) determines the behavior of the imaginary part of the quantum defect for small ε .

3.3. Low-lying excited states

There exists another (unphysical) value $p_0 \sim 1$, when $G(p_0)$ has a simple form. Setting formally in Eq. (3.4) $n_r = -0.5$ we obtain $S_r = 0$. The energy of the electron $\varepsilon(n_r = -0.5) \equiv \varepsilon_0$ is equal to the minimum of the effective potential $U_{\text{eff}}(r_0) = \min U_{\text{eff}}$, and the electron itself, having reached the bottom of the potential well U_{eff} , moves in a circular orbit of radius r_0 with the frequency of revolution $v_{\theta}^{(0)} = L/(2\pi r_0^2)$ around the center of force. The left and right turning points merge with one another and the cut of the analytic function (3.11) vanishes, so that the probability $A_{kc}^{(c)}$ (3.12) is equal to zero. Rewriting Eq. (3.12) in accordance with the definition (2.9)

$$\frac{A_{k}}{I} = \frac{2}{3c^{3}} \left\langle \frac{L}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\mathrm{cl}} - \frac{1}{3c^{3}} \left\langle \hat{\Delta}U(r) \right\rangle_{\mathrm{cl}} + A_{\mathrm{xc}}^{(\mathrm{cl})} (3.16)$$

and setting $\langle \rho \rangle_{cl} = \rho(r_0)$ on the circular orbit $r = r_0$, we obtain

$$G\left(\varepsilon_{0}\right) = \frac{\pi}{4\sqrt{3}} \frac{L^{2}}{1 + \left[z^{2}/(L - \mu_{0})^{3}\right]\partial\mu/\partial\varepsilon_{0}} \frac{1}{(L - \mu_{0})^{3}} \\ \times \left[\left(2L + 1\right)\left(\frac{\Delta\theta_{r}^{(0)}}{2\pi}\right)^{2} - 1\right].$$
(3.17)

In deriving Eq. (3.17) we used the relation $\omega_r = U_{\text{eff}}''(r_0) = U_0'' - 3L^2r_0^{-4}$ between the frequency $v_r = \omega_r/2\pi$ of the radial motion and the second derivative of the potential U_0'' at the bottom of the well; from here follows the relation $\Delta U(r_0) = \omega_r^2 - \omega_\theta^2$. The energy ε_0 lies below the energy of the first level of the series $\varepsilon(n_r = 0)$, and the values of the functions at ε_0 (the index "0" in Eq. (3.17)) is found by analytic continuation from above. For the Coulomb field $\mu = 0$, $p(n_r = -0.5) = 1$, i.e., $G_H(p = 1) = \pi/2\sqrt{3}$. We note that the expansion of G_H (3.15) can be continued up to the value p = 1 by choosing appropriately the coefficient C_1 in Eq. (3.13). For example, the function \widetilde{G}_H , obtained by joining the top (3.13) and bottom (3.17) of the *l* series of the hydrogen atom,

$$G_{\rm H}(p) = 1 + 0.2p^2 (\ln p^2) (1 - p^2)^{-1} + 0.110p^2,$$
 (3.18)

describes $G_{\rm H}$ for $0 \le p \le 1$ to within one-tenth of one percent.

The foregoing example of the vanishing of $A_{kc}^{(cl)}$ (3.16) models the general situation when the vector $\mathbf{A}(t)$ in Eq. (3.8) becomes a simple *r*-local function: The radial motion must be slow compared with the angular motion: $v_{\theta} > v_r$, or $\Delta \theta_r > 2\pi$. In this case the trajectory $\mathbf{r}_{cl}(t)$ is a spiral with relatively "frozen" and almost harmonic circular motion with frequency $\omega_{\theta} = L/r^2$. Operating on the harmonic time-dependent function $\exp(i\omega_{\theta}t)$ with the integral operator from Eq. (3.8) multiplies the function by $i\pi$,³² so that $\mathbf{v} \cdot \mathbf{A}(t) = |\mathbf{v}| \cdot \pi dU/dr$. Since $|\mathbf{v}| = v_{\theta} = L/r$ the probability A_k (3.7) reduces to (3.16) with $A_{kc}^{(cl)} = 0$.

3.4. Criteria for satisfaction of Bethe's rule

Interesting physical consequences can be extracted from the three equivalent formulations obtained above:

$$A_{k}^{(\text{cl})} \approx A_{k}^{(L)} \equiv \frac{2}{3c^{3}} \left\langle \frac{L}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\text{cl}} , A_{kc}^{(\text{cl})} \approx 0, \quad \beta \equiv \frac{\Delta \theta_{r}}{2\pi} > 1$$
(3.19)

Comparing Eq. (3.16) with Eq. (2.6) shows that they are identical (to within insignificant factors ~ 1) if Eqs. (3.19) are satisfied and the quantum-mechanical averages are replaced by classical averages (2.9): $\langle k | F | k \rangle \sim \langle F \rangle_{cl}$ (Ref. 23). In other words, Eqs. (3.19) must be regarded as criteria for satisfaction of Bethe's rules as applied to the total probabilities of radiative transitions. The results of Ref. 16 make it possible to give the conditions (3.19) a more obvious interpretation: In the quasiclassical limit, when the probability of downwards transitions in which l changes by -1 is overwhelming (Bethe's rule), the emission of light is controlled by the Franck-Condon principle. The emitted photon with frequency ω_{ph} carries away energy equal to the energy difference $\Delta U_{\rm eff}$ between the initial and final values of $U_{\rm eff}$ at the transition point r: $\omega_{\rm ph}(r) = U_{\rm eff}^{(l)} - U_{\rm eff}^{(l-1)} = l/r^2 = \omega_{\theta}$ (see Eq. (3.3)), i.e., in the case when Bethe's rule holds the angular frequency of the electron motion is equal to the frequency of the emitted photon. The circular motion predominates over the radial motion in the vicinity of the left turning point r_1 , where ω_{θ} assumes its maximum value and where the main advance of the angle $\Delta \theta$, occurs. For this reason the satisfaction of Eqs. (3.19) is controlled by the spread Δr of the carriers of the integrands in the classical average $\langle ... \rangle_{cl}$ around r_l . If $\Delta r \ll r_l$, then photon emission is most likely to occur near r_1 at large frequencies. Transitions in the



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FIG. 4. The ratio of the total probabilities $A_{n_r}^{(l-l\pm1)}$ of radiative transitions with a fixed change in the orbital quantum number l by +1 $(l \rightarrow l + 1)$ or -1 $(l \rightarrow l - 1)$ for the potential U_{α} (3.20). The radial quantum number n, for the excited state of an l series is plotted along the abscissa axis; the value of the parameter β , determining the rotation $\Delta \theta$, of the electron orbit $(\Delta \theta_r = 2\pi\beta)$, is given on each curve. For the solid lines l = 3, for the dashed lines l = 4 (top line) and l = 1 (bottom line).

first few n_0 terms (~1) in the series (l-1) make the main contribution to the sum A_k in Eq. (2.1) $(k = \{l, n_r\})$. In the opposite case $(\Delta r \gg r_1)$ the emission probability and the photon frequency are distributed comparatively uniformly over r and ω : $n_0 \gg 1$. The smallness of the parameter β (3.19) (Bethe's rule does not work) is correlated with the fact that almost all terms in the series for A_k in Eq. (2.1) are of the same order of magnitude. Figures 4 and 5 illustrate this result for the example of the quantum-mechanical calculation of the total probabilities of radiative transitions $A_k^{(l-l\pm 1)}$ in the case of an electron moving in a force field with the model potential

$$U_{\alpha}(r) = -\frac{1}{r} + \frac{\alpha}{2r^2}, U_{\text{eff}} = -\frac{1}{r} + \frac{L_{\text{eff}}^2}{2r^2}, L_{\text{eff}} = (L^2 + \alpha)^{1/2}, \beta = L (L^2 + \alpha)^{-1/2}.$$
(3.20)



FIG. 5. The photon emission spectrum of the ninth level $(n_r = 8)$ of the *p* series for the potential U_a (3.20) for different values of the parameter β . The relative probabilities $A_{n_r \to n_r}^{(l_r-1)}/A_{n_r}^{(l_r-1-1)}$ of the radiative transitions with a fixed upper level $(n_r = 8, l = 1)$ are plotted along the ordinate axis. The area under the curves is normalized to unity.

The function U_{α} differs from the Coulomb function in that it contains a centrifugal term of the type in Eq. (3.3). The quantity L_{eff} in Eq. (3.20) is the effective centrifugal parameter for radial motion; the orbit rotates by the angle $\Delta \theta_r = 2\pi L / L_{\text{eff}}$, irrespective of the energy of the electron. The points in Fig. 4 give the branching ratio $W_k = A_k^{(l-l-1)} / A_k^{(l-l+1)} (k = n_r)$ for the first few levels of the f series (l = 3) and several values of α . The curves in Fig. 5 show the relative contribution of the partial transition probabilities $A_{n_r - \hat{n}_r}^{(1-0)} / A_{n_r}^{(1-0)}$ for the ninth level $(n_r = 8)$ of the *p* series for different β (3.20). One can see that, in accordance with Eq. (3.19), as β decreases Bethe's rule ceases to be satisfied (see Fig. 4), and in addition the spectrum of the light emitted by the atom is broadened at the same time (see Fig. 5).

Note that the change in the serial number has little effect on the behavior and vertical position of the curves in Fig. 4. The latter fact can be explained based on the physical meaning of the representation (3.19) for the probability $A_k^{(cl)}$. We have pointed out that $(-A_k^{(L)})$ in Eq. (2.10) gives the rate of change of the classical angular momentum of the electron owing to the radiation reaction forces. If $A_k^{(L)}$ (3.19) is greater than zero, then as the electron moves along its orbit the value of l decreases, the transitions $l \rightarrow l - 1$ are preferred, and $W_k \ge 1$. In the opposite situation, $A_k^{(L)} < 0$, on the basis of the classical approximation photon emission results in an increase of l and correspondingly $W_k < 1$. The rate $A_k^{(L)}$ in Eq. (3.19) for the potential U_{α} given in Eq. (3.20) is described by a simple relation of the type of Eq. (3.13), where $G^{(L)}$ consists of two terms:

$$G^{(L)} = C_0^{(L)} + \frac{C_1^{(L)}}{n^{*2}}, \quad C_0^{(L)} = \frac{\pi}{2\sqrt{3}} \beta^3 [1 + 1, 5(\beta^2 - 1)],$$
(3.21)

$$C_1^{(L)} = -\frac{\pi}{3\sqrt{3}} \beta^3 (\beta^3 - 1), \quad n^* = n_r + L_{eff} + 0.5. \quad (3.22)$$

It is obvious that for Rydberg states the coefficient C_0 determines the efficiency of radiation processes. It is obvious from Eq. (3.21) that for $\beta = \beta_0 = 1/\sqrt{3} = 0.57$ the rate of change of L changes sign. For $\beta > \beta_0$ the rate is $(-A_k^{(L)}) < 0$, i.e., here $W_k \ge 1$. For $\beta < \beta_0$ the rate is $(-A_k^{(L)}) > 0$ and $W_k \sim 1$. One can see from Fig. 4 that the value β_0 of the parameter β is indeed critical for satisfaction of Bethe's rule (curves with $\beta = 0.5$ and 0.35).

We note that the structure of the emission spectrum in Fig. 5 agrees well with the results of Refs. 14 and 15. When downwards transitions with a large change in energy predominate ($\beta > 0.7$) the emission channel in which *l* decreases is preferred (see Fig. 4). If mainly soft photons are emitted, i.e., transitions between close levels are preferred (curve with $\beta = 0.6$ in Fig. 5), then Bethe's rule is no longer satisfied (see Fig. 4).

3.5. Corrections to the quasiclassical formulas

The singularity of the Coulomb potential U = -z/r at the origin of the coordinate system results in the appearance of singularities in the integrands $\Delta U(r)$ and $\mathbf{v} \cdot \mathbf{A}$ in the representations (3.7) and (3.8). In this situation the quasiclassical averages can differ from the quantum-mechanical averages so that corrections must be introduced into the classical Bohr-Sommerfeld quantization scheme. Here we shall employ a device introduced by Langer, who substantially improved the accuracy of the quasiclassical formulas by redefining the effective quantum number of the state.

In the investigation of the analytical properties of the nonlocal vector potential $\mathbf{A}(t)$ in Eq. (3.8), as before, it is useful to transfer the contour of integration over \tilde{t} into the complex plane (see Sec. 3.2). It turns out that A separates into two terms $\mathbf{A}(t) = \operatorname{Re} \mathbf{A}_{c} + \mathbf{A}_{s}(r)$, corresponding to the first two terms of the formula (3.12):

$$A_{k} = 2 \operatorname{Re} \langle \mathbf{v} \mathbf{A}_{c} \rangle_{c1} + 2 \langle \mathbf{v} \mathbf{A}_{s} \rangle_{c1} - (3c^{3})^{-1} \langle \widehat{\Delta} U \rangle_{c1} ,$$

$$\mathbf{v} \mathbf{A}_{s} = L \frac{dU}{dr} \frac{1}{3c^{s}r} . \qquad (3.23)$$

The *r*-local potential $\mathbf{A}_{s}(t)$ absorbs the main singularity of $\mathbf{A}(t)$: the term $\mathbf{A}_{c}(t)$, like also $\mathbf{A}(t)$, is nonlocal, but it is finite in the complex region of *r* near the point r = 0. For this reason, the classical average $\langle \mathbf{v} \cdot \mathbf{A}_{c} \rangle_{cl}$ describes well the quantum-mechanical average. Conversely, the function $f_{s} = \mathbf{v} \cdot \mathbf{A}_{s}(r)$ in Eq. (3.23) has a r^{-3} divergence, so that $\langle f_{s} \rangle_{cl}$ and $\langle f_{s} \rangle_{q} = \langle k | f_{s} | k \rangle$ give somewhat different results:^{23,33}

$$\langle r^{-3} \rangle_{ci} = 2\pi z \, (T_r L^3)^{-1},$$

$$\langle r^{-3} \rangle_q = 2\pi z \, (T_r L^3)^{-1} \, L^2 \, (L^2 - 0.25)^{-1},$$

$$T_r = 2\pi n^3 z^{-2}.$$
(3.24)

In order to take this fact into account, in Eq. (3.23) $\langle ... \rangle_{cl}$ must be replaced by $\langle ... \rangle_{q}$:

$$A_{k} = 2 \left\langle \mathbf{v}\mathbf{A} - \frac{\mathcal{L}}{3c^{3}r} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\mathrm{cl}} \quad \widetilde{L} \rightarrow L$$
$$+ \frac{2\mathcal{L}}{3c^{3}} \left\langle \frac{1}{3r} \frac{\mathrm{d}U}{\mathrm{d}r} \right\rangle_{\mathrm{q}} - \frac{1}{3c^{3}} \left\langle \widehat{\Delta}U \right\rangle_{\mathrm{q}}$$
(3.25)

The first average in Eq. (3.25) is performed with a bounded function $(\mathbf{v} \cdot \mathbf{A} - \mathbf{v} \cdot \mathbf{A}_s)$, and it can be performed according to the quasiclassical scheme. The notation L indicates that L in Eq. (3.23) originates from the Keplerian orbit of the electron r_i in the variable t. In the regular case L = L. We emphasize that in the expression (3.25) only the outer quasiclassical average over t in Eq. (3.8) was corrected for the singularity; the inner average over t is in no way affected for the time being, though $\nabla U(t)$ diverges at $\tilde{r} = 0$. This difficulty is removed by redefining the angular momentum $L \rightarrow L_c$ of a single orbit $r_{i,i}$ in Eq. (3.8) so that the average $\langle \mathbf{v} \cdot \mathbf{A} \rangle_{\text{cll}\mathbf{L}_{a}}$ is equal to the quantum mechanical average when $\mathbf{v} \cdot \mathbf{A}$ is modeled by its r-local singular part $\mathbf{v} \cdot \mathbf{A}_{s} \sim r^{-3}$. Equating $\langle r^{-3} \rangle_{cl}$ (where $L \rightarrow L_c$) and $\langle r^{-3} \rangle_q$ from Eq. (3.24), we obtain $L_c = [1 - (0.25/L^2)]^{1/3} \cdot L$. The replacement $L \rightarrow L_c$ is necessary in order to improve the accuracy of the WKB approximation with respect to the "inner" variable \tilde{t} in A in Eq. (3.8). We note that the standard Langer correction $l \rightarrow L = l + 0.5$ (Ref. 23) takes into account the r^{-2} singularity of the centrifugal potential and is found from the requirement that for an arbitrary smooth function $F(r) \langle F \rangle_{q} = \langle F \rangle_{cl}^{33}$ In this connection the quasiclassical average in Eq. (3.25) over the "outer" variable t can be taken with the standard L; this is reflected in the first term of Eq. (3.25). Thus

$$A_{ln}^{(H)} = \frac{L}{L} A_{k}^{(cl)} - \frac{2}{3c^{3}} L \left\langle \frac{z}{r^{3}} \right\rangle_{cl} + \frac{2}{3c^{3}} L \left\langle \frac{z}{r^{3}} \right\rangle_{q},$$

$$L = L \left(1 - \frac{1}{4L^{3}} \right)^{1/3},$$
 (3.26)

where $A_{k}^{(cl)}$ is identical to the previously obtained expres-

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sions (3.13) and (3.18) for a Coulomb field. The factor L/L multiplying $A_k^{(cl)}$ redefines $L \rightarrow \tilde{L}$ for the "inner" variable of integration t from the double integral (3.8) into $A_k^{(cl)}$ of Eq. (3.26). One can see from Fig. 3a the degree (broken curves) to which the corrections (3.26) to the singularity of the Coulomb potential improve the accuracy of the quasiclassical formula (3.13) and (3.18).

3.6. Quantization of the radiative width of the s states

In a Coulomb field the s electron passes through the origin, where the potential and hence also the velocity of the electron become infinite. Near the nucleus the nonrelativistic approximation is not applicable, so that the double integral in Eq. (3.8) diverges because of the strong singularity of the acceleration $|\dot{\mathbf{v}}| = z/r^2$ at the Coulomb center. However outside the core $A_{k}^{(cl)}$ in Eq. (3.8) is meaningful, and it primarily determines the dependence of the probability A_k on the energy of the electron. For this reason, for s states it is natural to separate from $A_s(\varepsilon)$ the divergence in the form of parameters not defined by the theory and to find these parameters using a priori information (see below). In order to regularize A_s the rectilinear trajectory $r_{\epsilon}^{(s)}(t)$ of an s electron must be replaced by a curve $r_{\rho}(t)$ close to it. This curve must satisfy the requirement $r_{\rho}(t) \rightarrow r_{\varepsilon}^{(s)}(t)$ as $\rho \rightarrow 0$ (ρ is the regularization parameter) and it should not pass through the point r = 0. For $r_{\rho}(t)$ we shall take the orbits $r_{\rho,\epsilon}(t)$ of the altered Coulomb potential $U_k(r) \rightarrow U_{\rho}^{(i)}$ for a fixed class (i) of functions $U_{\rho}^{(i)}$; for example, possible functions are $U_{\rho}^{(1)} = -(z/r) + (\rho^2/2r^2), \quad U_{\rho}^{(2)} = -[zr/(r^2 + \rho^2)],$ etc. Another type of regularization is obtained by giving the Keplerian orbit a small angular momentum L; here $\rho = |L|$.

These examples have an important feature. For $r_{\rho,\varepsilon}(t)$ the Keplerian similarity rules for a change in scale $r \rightarrow r_{\delta} = \delta r$ of the spatial coordinate with a simultaneous redefinition of the regularization parameter ρ are satisfied:

$$t \to t_{\delta} = \delta^{3/2} t, \quad v \to v_{\delta} = \delta^{-1/2} v,$$

$$\varepsilon \to \varepsilon_{\delta} = \delta^{-1/2} \varepsilon; \quad \rho \to \rho_{\delta} = \delta^{1/2} \rho. \quad (3.27)$$

The relations (3.27) make it possible to find from the orbit $r_{\rho_{\delta},\epsilon_{\delta}}$ of the potential $U_{\rho_{\delta}}^{(i)}$ both the solution $r_{\rho,\epsilon}(t) = \delta^{-1} p_{\rho_{\delta},\epsilon_{\delta}}(t_{\delta})$ of Newton's equation for the potential $U_{\rho}^{(i)}$ and the main dynamic characteristics of the trajectories in this potential. From Eq. (3.27) and Newton's equations there follows the admissible class of functions $U_{\rho}^{(i)}(r)$ which regulate the Coulomb potential and preserve Kepler's laws (3.27):

$$U_{\rho}^{(i)}(\delta r) = \delta^{-1} U_{\delta^{1/2}\rho}^{(i)}(r),$$

$$U_{\rho}^{(i)}(r) \xrightarrow[r \to \infty]{} - \frac{z}{r}, \quad U_{\rho}^{(i)}(r) \xrightarrow[\rho \to 0]{} - \frac{z}{r}.$$
 (3.28)

We note that according to the integral representation (3.8), where $-\nabla U = (d^2/dt^2)r(t)$, to find $A_s^{(cl)}(\varepsilon, \rho)$ it is sufficient to know only the trajectories $r_{\rho}(t)$. For an orbit of the chosen type $|r_{\rho}| > 0$, so that the quantum part $A_s^{(q)}$ in Eq. (3.7) is identically equal to zero because of the inequality $\Delta U_k(r) = 4\pi z \delta^{(3)}(\mathbf{r})$, so that $A_s(\varepsilon) \equiv A_s^{(cl)}(\varepsilon)$ ($\delta^{(3)}$ is the three-dimensional Dirac δ -function).

Using the similarity rules (3.27) in the formula (3.8) gives the relation $A_s^{(cl)}(\varepsilon_{,\rho}) = \delta^{2.5}A_s^{(cl)}(\delta^{-1}\varepsilon_{,\delta}\delta^{1/2}\rho)$. This makes it possible, by selecting the scale factor $\delta = \rho^{-1/2}$, to

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reduce the number of variables on which A_s depends:

$$A_{s}(\boldsymbol{e}_{n}) = \rho^{-5} A_{s}^{(cl)}(\rho^{2}\boldsymbol{e}_{n}, 1).$$
(3.29)

It is clear that the problem of finding the lifetime of the s states reduces to an analysis of the dependence of $A_s^{(cl)}$ in Eq. (3.29) on the energy of the Rydberg electron $(\rho^2 \varepsilon_n \rightarrow 0)$ for a fixed potential $U_{\rho=1}^{(i)}(r)$, which as $r \rightarrow \infty$ decreases in the manner of a Coulomb potential (3.28). The expansion (3.13) obtained above completely determines the structure of the singular terms for s electrons. The substitution $\varepsilon_n \rightarrow \rho^2 \varepsilon_n$ in Eq. (3.29) corresponds to the transformation $n \rightarrow n/\rho$ in Eq. (3.13), so that for the hydrogen atom

$$A_{\mathbf{g}}(\varepsilon_{n}) = \frac{\alpha z^{4}}{n^{3}} G_{\mathbf{g}},$$

$$G_{\mathbf{g}} = \frac{C_{0}}{\rho^{-1}} \left(\frac{C_{0}}{\rho^{2}} + \frac{C_{1}}{n^{2}} + \frac{1}{5} \frac{\ln \rho^{2}}{n^{2}} - \frac{1}{5} \frac{\ln n^{2}}{n^{2}} + O\left(\frac{\rho^{2}}{n^{4}}\right) \right). \quad (3.30)$$

The values of the constants C_0 and C_1 depend on the specific form of the function $U_{\rho \equiv 1}^{(i)}$. It is obvious that the two parameters $\tilde{C}_0 = C_0/\rho^2$ and $\tilde{C}_1 = C_1 + (\ln \rho^2)/5$ diverge. It is reasonable to prescribe the nonsingular terms in the probability $A_s(\varepsilon_n)$ with the help of the terms of the function G_H/L^2 in Eq. (3.15) with $|\mathbf{L}| = 0.5$ which correspond to Eq. (3.30):

$$-\frac{1}{5} \frac{\ln n^{a}}{n^{a}} + O\left(\frac{p^{a}}{n^{4}}\right)$$
$$\rightarrow \frac{4}{5} \frac{p^{2} \ln p^{a}}{1 - p^{a}} \left(1 + \frac{39}{56} p^{2}\right) + O\left(p^{4}\right); \quad p = \frac{1}{2n}.$$
 (3.31)

The fact that the radial motion of s electrons can be described quasiclassically with the help of the effective potential $U_{\rm eff} = U + (L^2/2r^2)$ with L = 0.5 (Langer's correction) has already been mentioned above. In the case of nonsingular potentials this explains the fact that the $A_{L=0.5}(\varepsilon_n) = A_s(\varepsilon_n)$, which is easy to demonstrate for the example of a three-dimensional oscillator (3.10), if the co-factor in the brackets is rewritten in the form $2n_r + L - 0.5$. Including in Eq. (3.30) the regular terms (3.31) with L = 0.5 models the situation of regular force fields; the singularity of the Coulomb potential is reflected in Eq. (3.30) by the presence of the first three terms with constants $\tilde{C}_{0.1}$ which cannot be determined on the basis of the nonrelativistic approximation.

To find their values we shall use the fact that the 2s state of the hydrogen atom is metastable $(A_s (n = 2) = 0)$. This makes it possible to apply the condition for a minimum $\partial A_s / \partial \rho (n = 2) = 0$ to the imaginary part A_s of the total energy E_s (3.1).

The state with n = 2 is preferable over the ground state because it is closer to the Rydberg levels. Equating the derivative of the function G_s given in Eq. (3.30) with respect to ρ for n = 2 to zero gives $\tilde{C}_0 = C_0/\rho^2 = 1/5n^2 = 0.05$. The other unknown \tilde{C}_1 in Eq. (3.30) is specified by the condition A_s (n = 2) = 0, so that

$$G_{s}(p) = \frac{1}{20} \left[1 + 16p^{2} (\ln p^{2}) (1 - p^{2})^{-1} \times \left(1 + \frac{\epsilon_{9}}{56} p^{2} \right) + 33, 4p^{2} \right]; \quad p = \frac{1}{2n}. \quad (3.32)$$

The parameter p for $n \ge 2$ is small, and terms of order $O(p^4)$ can be dropped. In Fig. 3b the quasiclassical function $20G_s$ given by Eq. (3.32) (solid curve) is compared with its values

 $(20/\alpha)n^3A_s$ (circles) obtained from a quantum-mechanical calculation of the radiative width A_s for the s states of the hydrogen atom (Z = 1).

4. EXTRAPOLATION SCHEMES FOR FINDING τ_k OF HIGHLY EXCITED STATES OF ATOMS AND IONS

The Rydberg states of atoms, ions, and molecules are of great interest in connection with the development of laser spectroscopy as well as for practical applications, such as isotope separation, thermonuclear fusion, and detection of infrared and microwave radiation. For a number of reasons,^{6,34} however, the existing theoretical and experimental methods for studying atomic systems cannot give reliable information about the characteristics of highly excited states. In particular, there are virtually no data on the lifetimes of the Rydberg levels of atoms and ions. The lifetimes τ_k of states with principal quantum number up to 20 are known only for the helium atom and for atoms of alkali metals.^{35,36} As a result, it has been suggested in the scientific literature^{6,37-40} that different extrapolation schemes be employed to estimate the lifetimes of states with large n. Some analytical dependence $\tau_k = f_C(n^*)$ is selected to describe experimentally (or theoretically) the obtained values of τ_k within a fixed series of levels. The adjustable parameters C_{i} appearing in $f_{\rm C}$, are determined for the lower states, after which $f_{\rm C}(n^*)$ is extrapolated to the higher states of the series which have not been studied.

Practically all schemes mentioned are empirical, since the dependences $\tau(n^*)$ in them are obtained in a formal manner without rigorous proof of the analytical structure of $f_{\rm C}$. The functional form has been determined only in the simplest single-channel approximation (see Sec. 3.2). In other cases some arbitrariness must be admitted in choosing $f_{\rm C}$. As a result, both under the conditions of the single-channel approximation³⁹ and in approximations employing the multichannel quantum-defect theory for calculating τ_k (Refs. 37 and 40) the term logarithmic in the energy ~ $(\ln n^{*2})/n^{*2}$ (see Eq. (3.13)), which plays an important role for relatively weakly radiating states, was "lost." Here we shall demonstrate two extrapolation schemes. The first scheme²⁷ has been rigorously justified. It requires that the single-channel approximation be satisfied and it makes it possible to obtain the lifetimes of the Rydberg states right up to the continuum (Sec. 4.1). The second scheme^{6,38} supplements the first scheme under conditions when the singlechannel approximation breaks down, it is empirical (see Sec. 4.2) and it is based on an analysis of a large volume of data on τ_k .

4.1. Single-channel approximation

In this case the serial regularities are described by the relation (3.13), which we shall represent in the form (see Eq. (3.6))

$$\begin{aligned} \tau_{k}^{-1} &= \frac{\alpha z^{4}}{n^{\bullet 3}} \left[\frac{C_{0}}{(l+0.5)^{2}} + \frac{(\ln p^{3}) D_{1}}{n^{\bullet 2} (1-p^{2}) 5} + \frac{C_{1}}{n^{\bullet 2}} \right]; \\ p &= \frac{l+0.5}{n^{\bullet}} \cdot |p| < 1. \end{aligned}$$
(4.1)

The coefficient α (see Eq. (2.2)) is equal to $1.18 \cdot 10^{10} \text{ s}^{-1}$, and the parameters satisfy $\tilde{C}_{0,1} = \bar{I} \cdot C_{0,1}$ and $\tilde{D}_1 = \bar{I} \cdot D_1$. In Eq. (4.1) terms of order $O(p^4)$ have been dropped; the factor $(1 + \partial \mu / \partial n^*)^{-1}$ which is not significant under the conditions of the single-channel approximation (see below), has also been dropped. The value of p determines whether or not terms of order $O(p^4)$ can be dropped in the expansion (3.13). The applicability of Eq. (4.1) is determined exclusively by the applicability of the single-channel approximation for the given quantum state k. According to Refs. 18 and 19 the probability A_k is an individual characteristic of the excited level. For this reason the quantity τ_k is not sensitive to interconfigurational interaction, which can perturb the position of lower (or higher) states. A practical criterion for the single-particle approximation and thereby Eq. (4.1) to be satisfied is that the quantum defect μ , given in Eq. (3.5), must depend continuously on the energy ε along the series.⁴¹

According to Eq. (3.13) the lifetime τ_k is proportional to the period T_r given in Eq. (3.6). To two neighboring levels in a series there corresponds a unique change in the radial quantum number $(\Delta n_r = 1)$. The period T_r is equal to $2\pi/\Delta\varepsilon_k$, where $\Delta\varepsilon_k$ is the energy splitting between the state k and the nearest upper state, so that $\tau_k \sim \Delta\varepsilon_k^{-1}$. The correlation between the serial dependences of τ_k and $\Delta\varepsilon_k$ (Ref. 6) can be traced in the experimental data (see Figs. 1 and 2 and Sec. 4.2). We note that when the single-particle approximation holds the last equality for T_r in Eq. (3.6) predicts that T_r and τ_k are mainly cubic functions of n^* .

The expansion (4.1) contains three free parameters: $\widetilde{C}_{0,1}$ and \widetilde{D}_1 . Their values are found by the method of least squares, starting from the values of τ for several states; this makes it possible to reconstruct from Eq. (4.1) the radiative lifetimes of all higher levels of the series. The possibilities of such extrapolation can be judged from the curves in Fig. 6. The dots were constructed by calculating τ_k for the excited states of atoms of alkali metals,³⁶ for which the criterion of the single-channel approximation is satisfied. Initially the extrapolation (circles 1) was performed based on the first four levels of the series. The importance of monitoring (through the parameter p) the validity of dropping the term of order $O(p^4)$ in Eq. (3.13) for the lower states can be seen for the example of the D series. The values of $p = (l + 0.5)/n^*$ are given next to the first few curves. The deviations of the extrapolated values of τ_k from the true values decrease significantly, if the extrapolation is performed without the first few states with p > 0.87 (circles 2). The figure also shows the experimental data of Ref. 36 (crosses, first four levels). It is clear that the allowed error in τ_k (7p level of Na) strongly affects the accuracy of the predicted lifetimes (crosses following the fourth cross).

The coefficients \tilde{C}_0 and $\tilde{D}_1 = \tilde{I}D_1$ in Eq. (4.1) contain useful physical information about the scattering of slow thermal electrons by the corresponding ion core. The parameter D_1 in Eq. (3.14) makes it possible to estimate the classical scattering angle θ_r ($\varepsilon_k \rightarrow 0$), and the value of \tilde{C}_0 can be related with the partial cross section for radiative recombination $\sigma_r^{(I)}$. The situation arising here is typical for the quantum-defect theory, when a number of important properties of continuum states are determined from the spectroscopic data.¹² Indeed, the product $A_k T_r$, rewritten in the form

$$W^{(l)} = A_k T_r = 2\pi \alpha z^2 [[\bar{l}C_0 (l+0.5)^{-2} + O(p^2)],$$

$$p^2 = -2 (l+0.5)^2 \varepsilon_l z^{-2},$$
(4.2)

gives the probability $W^{(l)}$ of the emission of a photon by a Rydberg *l*-electron ($\varepsilon_l < 0$) during the period T_r . The proba-

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FIG. 6. Extrapolation of the radiative lifetimes τ_k from the lower levels of a series to highly excited states for alkali atoms. The extrapolation is performed with the help of the relation (4.1). The solid curves show the values of τ_k from Ref. 36; for the circles (1) the first four values of τ_k for the states with radial quantum number $n_r = 0$ -3 were taken as the initial values; for the circles (2) and crosses (experiment) the values for the states with $n_r = 1$ -4 were taken as the starting values for the extrapolation.

- **b**

TABLE I. The values of the coefficients C_0 , \tilde{D}_1 , and \tilde{C}_1 from the formula (4.1) for alkali-metal atoms and the helium atom. The error shown in parentheses refers to the last digit. a)

Atom	Series:	s	р	đ	r
Li		$\begin{array}{c} 0,0251(1) \\ 0,34(5) \\ -0,11(3) \end{array}$	0,069(1) 0,81(2) 0,1(1)	1, 12(1) 1, 1(5) 0, 05(9)	1,0088(4) 0,94(1) 0,094(3)
Na	$\begin{array}{c} C_0 \\ D_1 \\ C_1 \end{array}$	$\begin{array}{c} 0,01561(2) \\ -0,19(2) \\ -0,28(1) \end{array}$	0,0144(2) 0,10(2) 0,217(5)	0,567(1) 0,66(4) 0,39(1)	1;0380(2) 1,00(1) 0.087(1)
К	$ \begin{array}{c} C_0 \\ D_1 \\ C_1 \end{array} $	$\begin{array}{c} 0,0174(2) \\ 0,1(1) \\0,17(5) \end{array}$	0,051 (1) 0,48 (5) 0,19 (1)	$\begin{array}{c} 0, 18 (2) \\ 0, 19 (9) \\0, 1 (4) \end{array}$	1,290(2) 1,1(1) -0,23(2)
Rb	$ \begin{bmatrix} C_0 \\ D_1 \\ C_1 \end{bmatrix} $	$\begin{array}{c} 0,0171(1) \\ -0,12(3) \\ -0,29(2) \end{array}$	0,075 (2) 0,9 (1) 0,28 (3)	0,51 (4) 1,3 (3) -0,6 (1)	1,491(4) 1,1(2) -0,26(4)
Cs	$\begin{array}{c} C_0\\ D_1\\ C_1\end{array}$	$\begin{array}{c} 0,0175(1)\\ -0,11(3)\\ -0,31(2)\end{array}$	0,061 (1) 0,86 (5) 0,28 (2)	0,822 (3) 0,1 (1) -0,80 (3)	$\begin{array}{c} 1,6 (1) \\ -2 (2) \\ -1,0 (6) \end{array}$

b)

Helium atom	č,	\widetilde{D}_1			
1S 1P 1D 1F 3S 3P 3 F	$\begin{array}{c} 0,02344\ (2)\\ 3,224\ (2)\\ 0,976\ (2)\\ 1,009\ (1)\\ 0,0271\ (2)\\ 0,153\ (4)\\ 1,483\ (1)\\ 1,017\ (5) \end{array}$	0,96 (2) 0,8 (2) 0,90 (7) 0,88 (5) 0,8 (1) 0,9 (4) 1,07 (3) 1,1 (2)	$ \begin{vmatrix} 0,21 & (1) \\ -0,58 & (4) \\ 0,17 & (2) \\ 0,07 & (1) \\ 0,13 & (7) \\ -0,1 & (2) \\ -0,001 & (7) \\ 0,12 & (4) \end{vmatrix} $		

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bility $W^{(l)}$, continued with the help of Eq. (4.2) to positive energies $\varepsilon_l = v^2/2$, corresponds to a collision of the *l*-electron with the core and determines²³ the cross section $\sigma_r^{(l)} = [\pi(2l+1)/v^2]W^{(l)}$ for the radiative losses of the electron. Thus

$$\sigma_p^{(l)} = \alpha z^2 \cdot 4\pi^2 C_0 [v^2 (l+0,5)]^{-1}; \quad v < z (l+0,5)^{-1}. \quad (4.3)$$

The restriction in Eq. (4.3) on the electron velocity follows from the requirement (4.2) |p| < 1. The relations (4.2) and (4.3) also follow from the interpretation (3.9) of the product $A_k T_r = 4\pi \cdot \text{Im } \mu$ as the imaginary part of the quantum defect. According to Seaton¹² the defect μ , continued beyond the ionization limit, is proportional to the scattering phase of a slow thermal electron: $\delta_1 = \pi \mu$. The total probability $W_r^{(l)}$ of inelastic processes (in our case radiative) for the *l*-wave can be expressed in terms of the eigenvalues of the S_{l}^{23} $W_r^{(l)} = 1 - |S_l|^2$, scattering matrix where $S_l = \exp(2i\delta_l^{(n)})$ is given by the total scattering phase. Obviously, $|S_l|^2 = \exp(-4\pi \operatorname{Im} \delta_l)$, and $W_r^{(l)} = 1 - \exp(-4\pi \operatorname{Im} \delta_l)$ $(-A_kT_r) \simeq A_kT_r$, which agrees with Ref. 4.2.

The three numbers $\tilde{C}_{0,1}$ and \tilde{D}_1 in the expansion (4.1) contain complete information about the radiative constants of all levels in a given series. For the first four series of alkalimetal atoms and the helium atom the values of the coefficients $\tilde{C}_{0,1}$ and \tilde{D}_1 , obtained based on the data of Refs. 35 and 36, are given in Table I. Here the computational data on τ from Refs. 35 and 36 are described by Eq. (4.1) to within 5%. We recall that for the hydrogen atom $\tilde{C}_0 \equiv 1$ (see Eqs.

(3.13) and (3.15)), except for s states for which $\tilde{C}_0 = 0.0125$ (see Eqs. (3.13) and (3.32)). It is interesting that the emission of radiation by a Rydberg *l* electron decreases significantly when electrons with the same orbital quantum number *l* appear in the subshells of the core which are closest to it.

The example of alkali atoms shows that the formula (3.13) is applicable over a wide range. This is connected with the fact that for s, p, and d states the parameter p is small, even for the first few levels. Orbitals with large angular momentum (l>3), however, usually correspond to hydrogen-like states, for which, according to Eqs. (3.15) and (3.18), the terms $O(p^4)$ are not important.

4.2. Power-law serial dependences (SD)

These refer to empirical schemes and are based on the possibility of describing the extensive experimental and computational data on τ_k with the help of the relations (1.1) and (1.2).^{38,42} The dependence (1.1) can be used to estimate the lifetimes of Rydberg states by extrapolating it to states that have not been studied. In order that the estimates be reliable it is necessary to know 1) the constants $\tau_{0,i}$ and α_i as accurately as possible and 2) the range of values of n^* in which extrapolation is valid. The lowest states often do not conform to the serial dependences (see the plots for HeI in Fig. 7), so that information is required about τ_k for several of the low states in the series, where the values of $\tau_{0,i}$ and α_i are determined by the method of least squares. We propose



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FIG. 7. The serial behavior of the radiative lifetimes (τ) and energy splittings (ΔE) as functions of the effective principal quantum number (n^*) for a number of atoms. In each series a correspondence is observed between the form of the plots of the dependences $\Delta E(n^*)$ and $\tau(n^*)$.

finding the upper energy limit for the serial dependences by analyzing the spectroscopic data. It was pointed out above (Sec. 4.1) that the behavior of τ_k is correlated with the behavior of $\Delta \varepsilon_k$ as a function of n^* , where $\Delta \varepsilon_k$ is the energy gap between close-lying levels in the series: k and (k + 1). Analysis of a large number of series of excited states of group I, II, III, and VIII atoms revealed the existence of a dependence⁶ related with Eq. (1.1),

$$\Delta \varepsilon_{\mathbf{k}} = E_0 \ (n^*)^{-\beta} \tag{4.4}$$

with characteristic constants E_0 and β for each series of states. By virtue of the formulas (3.13) and (3.6) $\tau_k \sim G\Delta \varepsilon_k^{-1}$, i.e., the serial dependences (4.4) and (1.1) should be consistent with one another. Some typical examples of such a correspondence are presented in Figs. 7 and 8. The plots of the functions (1.1) and (4.4) on a logarithmic scale are straight lines; this is observed in Fig. 7 for the n^2D series of Na. For the n^{3} S series of HeI it is obvious that the n^{*} dependence of log τ corresponds to that of log $\Delta \varepsilon$ for all values of n^* , though at n = 7 both dependences become powerlaw functions. For the $n^2 P_{3/2}$ series of In and the $n^1 D_2$ series of BaI there is a local perturbation of the upper states with n = 10 and n = 25, respectively. But even in this case the curves of τ_k and $\nabla \varepsilon_k$ are correlated. Thus the form of the plot of $\Delta \varepsilon_k$ determines the region into which the serial dependence (1.1) can be extrapolated.

We shall formulate a method for estimating the radiative lifetimes of the Rydberg states. A plot of log τ_k as a function of log n^* is constructed for the most reliable values of τ_k for the lower levels and a plot of log $\Delta \varepsilon_k$ as a function of



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log n^* is constructed next to it. The energy splitting between the neighboring states $\Delta \varepsilon_k$ is assigned to the upper state. The region where the serial dependence (1.1) is valid (rectilinear sections) is determined by comparing the plots. The constants $\tau_{0,l}$ and α_l (1.1) are determined by the method of least squares from the points in this section. The plot of log $\Delta \varepsilon_k$ as a function of log n^* gives the range of values of n^* to which the extrapolation of the serial dependence (1.1) is valid.

The foregoing procedure was employed in Ref. 43 to estimate τ_k for the Rydberg states of the helium atom (n = 9-22). Values of the lifetimes of 40 states of the n^1P , n^1D , and n^3D series were obtained. Comparing our estimates with later calculations³⁵ showed that the estimate is accurate to within 10%. The method can be recommended for the middle Rydberg states (n < 20).

We note that for the unperturbed single-electron terms the lifetimes are described by the dependence (3.13):

$$\tau_{\mathbf{k}} = n^{*3} \tau_3(n^*), \quad \tau_3^{-1} \equiv \alpha z^4 \bar{I} G L^2 \left(1 + z^2 n^{*-3} \frac{\partial \mu}{\partial \varepsilon} \right). \tag{4.5}$$

As n^* increases the factor τ_3 becomes constant. The deviation of Eq. (4.5) from a cubic law is connected with changes in τ_3 only at the beginning of the series. The breakdown of the cubic dependence for Rydberg states could be caused by an energetically extended perturbation due to autoionization states and the continuum. In this case the power-law dependence (1.1) "corrects" the cubic dependence in the sense of giving the best approximation of the function $\tau_k(n^*)$. An example of an alternative description (see Table Ib) with the help of Eq. (1.1) for the helium atom is given in Ref. 35.

FIG. 8. The same as for Fig. 7. The systematic error can be seen to increase in some experimental results for cadmium and mercury as n^* increases.

TABLE II. The value of the constants $\tau_{0,l}$ (ns) and α_l from the formula (1.1) for group II and VIII atoms. The last column gives the region of applicability of the power-law dependence (1.1).

Atom	Series	τ _{0,1} , ns	αι	n	Atom	Series	τ _{0, l} , ns	α _l	n
MgI CaI SrI ZnI CaI HgI NeI		$\begin{array}{c} 4,22\ (3)\\ 0,54\ (1)\\ 0,430\ (8)\\ 0,213\ (7)\\ 0,667\ (12)\\ 0,315\ (9)\\ 0,266\ (5)\\ 0,409\ (4)\\ 1,53\ (1)\\ 0,340\ (7)\\ 1,64\ (2)\\ 1,50\ (3)\\ 1,18\ (2)\\ 1,07\ (1)\\ 0,670\ (8)\\ 0,510\ (5)\\ 0,860\ (7)\\ \end{array}$	$\begin{array}{c} 2,62\ (2)\\ 3,11\ (4)\\ 2.91\ (2)\\ 3,55\ (5)\\ 3,10\ (6)\\ 2,80\ (5)\\ 3,00\ (5)\\ 3\\ 3\\ 4,10\ (9)\\ 4,10\ (8)\\ 4,10\ (9)\\ 4,3\ (1)\\ 4,30\ (9)\\ \end{array}$	$\begin{array}{c} 4-15\\ 7-14\\ 5-11\\ 5-9\\ 6-11\\ 4-13\\ 5-10\\ 8-20\\ 5-12\\ 6-10\\ 5-12\\ 6-10\\ 5-12\\ 6-3\\ 9\\ 3-9\\ 3-9\\ 3-9\\ 3-6\\ \end{array}$	ArI	$\begin{array}{c} np'_i[3/2]_2\\ nd [1/2]_0\\ nd [7/2]_4\\ nd [7/2]_3\\ nd [3/2]_1\\ nd [5/2]_2\\ nd [5/2]_2\\ nd' [5/2]_3\\ nd' [3/2]_2\\ nd' [3/2]_3\\ nd' [3/2]_3\\ nf [3/2]_3\\ nf [1/2]_1\\ np [5/2]_3\\ np [5/2]_2\\ np [3/2]_2\\ np [3/2]_2\\ np [1/2]_0\\ \end{array}$	$\begin{array}{c} 1,38\ (1)\\ 0,450\ (5)\\ 0,590\ (6)\\ 0,590\ (6)\\ 0,590\ (7)\\ 0,590\ (7)\\ 0,590\ (7)\\ 0,490\ (4)\\ 0,330\ (5)\\ 0,180\ (1)\\ 1,08\ (2)\\ 0,520\ (9)\\ 3,47\ (3)\\ 4,58\ (5)\\ 2,95\ (3)\\ 2,24\ (3)\\ 1,82\ (2)\\ \end{array}$	$\begin{array}{c} 4,0 \ (1) \\ 3,4 \ (1) \\ 3,30 \ (9) \\ 3,50 \ (8) \\ 3,40 \ (9) \\ 3,30 \ (9) \\ 3,30 \ (9) \\ 3,30 \ (8) \\ 3,40 \ (7) \\ 3,60 \ (6) \\ 3,30 \ (9) \\ 3,0 \ (1) \\ 2,90 \ (9) \\ 2,90 \ (9) \\ 2,90 \ (9) \\ 2,90 \ (9) \\ 2,90 \ (9) \\ 3,0 \ (1) \\ 3,20 \ (8) \\ 3,1 \ (1) \\ 3,20 \ (8) \\ 3,1 \ (2) \end{array}$	$\begin{array}{c} 4-8\\ 5-10\\ 6-9\\ 5-9\\ 5-9\\ 3-9\\ 5-9\\ 3-10\\ 5-10\\ 7-10\\ 4-8\\ 5-9\\ 6-8\\ 5-8\\ 5-8\\ 5-8\\ 5-8\\ 5-8\\ 5-8\\ 5-8\\ 5$

5. RECOMMENDED VALUES OF THE RADIATIVE LIFETIMES OF THE EXCITED STATES OF GROUP IA, II, AND VIII ATOMS

An important problem in atomic spectroscopy is to construct a data base of standard values of the radiative lifetimes. Work on such a data base was begun in Ref. 38. Tables of recommended values of τ_k for resonance and metastable levels of a number of atoms appeared later.³⁹ Here we shall continue the work of collecting expertly evaluated information about τ_k for all atoms of the periodic system.

Values of τ_k for group I atoms are presented in Ref. 38. Subsequent publications³⁶ confirmed that the data given in Ref. 38, including the data based on analysis of serial distributions of the radiative lifetimes, are reliable (see Sec. 4.2). The values of τ_k obtained in Refs. 36 and 37 for alkali and helium atoms are described well by the single-electron dependences (4.1). The first levels of the *D* series of Na, Li, and Cs are exceptions; for them the parameter *p* is close to one (see Fig. 7). The values of the coefficients $\tilde{C}_{0,1}$ and \tilde{D}_1 from Eq. (4.1) are given in Table I. We recall that \tilde{C}_0 determines the partial photorecombination cross section (4.3).

Table II gives the recommended values of the radiative lifetimes in the form of the constants in the power-law dependences (1.1). We decided to describe the data on τ_k in this form because, first, it can be used to estimate rapidly τ_k for states which have not been studied and, second, it is convenient for constructing a computerized data base of the radiative lifetimes. The constants $\tau_{0,l}$ and α_l for the serial dependence (1.1) were calculated from the values of $\tau^{(rec)}$ for each state of the series which were obtained by statistical analysis of all currently published values of τ_k for a given state. The quantities $\tau_k^{(rec)}$ were taken to be the weighted-mean values

$$\tau_k^{(\text{rec})} = m^{-1} \sum_{i=1}^m \tau_k^{(i)}, \tag{5.1}$$

for *m* of the works considered. The results of measurements (calculations) of τ_k were ignored if they differed from the mean value obtained by more than 2σ (σ is the standard deviation). The values of τ_k presented without an error as well as the earliest results obtained by the same authors were ignored. Finally, τ_k were also not included in the average (5.1) if they did not correspond to the dependence (1.1)

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constructed from data of other works and confirmed by the power-law behavior of the function $\Delta \varepsilon_k(n^*)$ (see Eq. (4.4)).

CONCLUSIONS

The problems of systematizing the radiative lifetimes τ_k , together with experimental investigations, are largely connected with the development of theoretical ideas about quantum radiative decay processes. The nonlocal Hamiltonian formalism for describing the dynamics of radiating atomic systems and the resultant procedure for quantizing the radiative width may in the future be a suitable technical tool for calculating the values of τ_k . In this connection it would be useful to construct a systematic multichannel theory for determining τ_k . Analysis of quantum radiation friction forces in the irregular part of the spectrum of complex systems, when the interatomic interaction causes the classical trajectories of the motion to become chaotic,³⁰ should yield interesting results. An explanation of the fact that the lifetimes are consistently observed to have power-law dependences could be found here. In order to use these dependences to estimate the lifetimes of the Rydberg states it is necessary to have accurate information about the values of τ_k for the lower states. This in turn will stimulate new experimental investigations using modern methods.

This is a good point at which to outline briefly the current status of the problem of determining the most reliable values of the radiative lifetimes of the excited states of atoms. As we have already mentioned above, the construction of complete systematic tables of recommended values was begun by one of the authors of the review of Ref. 38, which is devoted to all group I atoms. This work was followed by publications on helium,43 group IIA atoms (Be, Mg, Ca, Sr, Ba),⁴⁴ and group IIB atoms (Zn, Cd, and Hg).⁴⁵ In 1984 two papers by Theodosiou on helium³⁵ and alkali-metal atoms (Li, Na, K, Rb, and Cs)³⁶ appeared; in these works the values of τ_k for all states (including f) up to n = 18-21were calculated theoretically with high accuracy. Comparing the values given in Refs. 35 and 36 with the most reliable experimental results allows us to recommend them as the most reliable values. The handbook of A. A. Radtsig and B. M. Smirnov was published in 1986.³⁹ In it the values of the radiative lifetimes of resonance, metastable, and some lower

states of 73 atoms are presented. In 1990 a review with a table of recommended values of τ_k for all inert gas atoms (He, Ne, Ar, Kr, and Xe) was published.⁵⁰ Reviews on τ_k for group III atoms (Sc, Y, La, Lu, B, Al, Ga, In, and Tl) and group VIB atoms (O, S, Se, and Te) is in press. Reviews on τ_k for group IV, V, and VII, iron-group, and lanthanide-group atoms will be published shortly. The publication of the latter reviews will complete the construction, to a first approximation, of complete systematic tables of the radiative lifetimes for all atoms.

We thank Yu. A. Tolmachev, A. I. Vasil'ev, E. A. Solov'ev, and V. P. Prosikhin for numerous discussions in which many aspects of the material presented in this review were elucidated.

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Translated by M. E. Alferieff

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