Nonadiabatic rotational coupling as a mechanism for quenching of Rydberg states by alkali metal atoms

V. M. Borodin and A. K. Kazanskiĭ

Leningrad State University

(Submitted 21 June 1988; revised 11 August 1988)
Zh. Eksp. Teor. Fiz. **95**, 1929–1940 (June 1989)

The quenching of nonhydrogenic Rydberg states by collisions with alkali metal ions is discussed on the assumption that the process is due to nonadiabatic transitions between Rydberg states with different principal quantum number *n*. The transitions are generated by the rotation of the internuclear axis and the interaction between the Rydberg electron and the alkali metal atom. It is shown that this mechanism leads to large (of the order of 1000 a.u.) cross sections that depend on the quantum number *n* (a shallow maximum is formed). The neighborhood of the point at which the relative velocity of the atoms is zero provides a significant contribution to the cross section. It is shown that the transitions are mostly due to the polarization coupling between the Rydberg electron and the alkali metal atom. The quenching cross sections are found to depend on the nature of the Rydberg atom, and there is a weak dependence on the gas temperature.

1. INTRODUCTION

The quenching cross sections of nonhydrogenic (S,P,D) Rydberg states of alkali metal atoms have been measured during the last decade for thermal collisions with atoms of the same type in the ground state. The measurements were made for both highly-excited partners with principal quantum number of the outermost electron $n \gtrsim 30$ (Ref. 1) and for relatively weakly excited atoms with $n \lesssim 15$ (Ref. 2). The theoretical description of processes with highly excited atoms, proposed in Refs. 3 and 4 and based either on the impulse approximation or on the binary theory of the formfactors, is entirely satisfactory for $n \gtrsim 30$, but is in conflict with experiment for lower *n*. Quenching reactions were not examined theoretically in a systematic way for $15 \lesssim n \lesssim 30$. This region is actually of particular interest because of the discovery of oscillations on the spectral characteristics of the quenching of *nS* and *nD* Rydberg states, i.e., level width and shift, in collisions between the alkali-metal Rydberg atoms and neutrals of the same kind. These oscillations have not, so far, received a satisfactory explanation. It is therefore interesting to consider whether oscillations of the type discussed in Refs. 5–7 occur in the cross sections for the quenching of the individual *S*, *P*, and *D* levels or, if there are no oscillations, whether the cross sections themselves exhibits a sharp peak in the required range of values of *n*.

We shall discuss nonadiabatic transitions due to the rotation of the internuclear axis and the radial motion of the atoms. Because of the high polarizability α of the neutral atom ($\alpha \approx 10^2$ a.u. for the alkali-metal atom), we find that, in the range $15 \lesssim n \lesssim 30$ that is of interest to us, the resonance kinematic condition

$$k\omega_{\text{orb}} = |\varepsilon_i - \varepsilon_f|, \tag{1}$$

associated with orbiting is satisfied, where ω_{orb} is the orbital frequency, ε_i and ε_f are the initial and final energies of the Rydberg electron, and *k* is the order of the resonance. It is readily verified that, for $15 \lesssim n \lesssim 30$, there are groups of definite final states that fall into resonance with the given initial state almost exactly. Hence we may expect that the transition probability may increase for these values of *n* and for impact parameters *s* for which (1) is satisfied. Unfortunately, these simple qualitative considerations cannot be made more specific to any great extent because, first, the high polarizability of the perturbing atom leads to a substantial modification of the Rydberg states and, second, nonadiabatic transitions can also occur for other configurations of heavy particles that differ from the resonant configurations satisfying (1). Nevertheless, the proposed mechanism can lead to substantial cross sections and therefore deserves consideration. The aim of this research was to formulate the problem and to perform approximate calculations that exhibit the basic features of this quenching mechanism.

2. DETERMINATION OF ADIABATIC STATES, ENERGY CURVES, AND MATRIX ELEMENTS

We shall assume that the motion of the heavy particles can be treated classically (although it may well happen that a more accurate description will be necessary in more accurate cross section calculations). The origin of coordinates will be placed in the nucleus of the charged core A^+, the *Z* axis will lie along the normal to the collision plane, and the *X* axis along the internuclear axis. The Hamiltonian for the Rydberg electron then takes the form (in atomic units)

$$\hat{H} = \hat{H}_0(\boldsymbol{\rho}) - \omega(s, R)\hat{L}_Z + \hat{V}(\boldsymbol{\rho}, \mathbf{R}) + \hat{H}_{inert}, \tag{2}$$

where $\mathbf{R}(t)$ is the vector connecting the two nuclei ($R_Y = R_Z = 0$), $\boldsymbol{\rho}$ is the position vector of the electron relative to A^+, $\hat{H}_0(\boldsymbol{\rho})$ is the Hamiltonian of the highly excited electron in the Rydberg atom $A^{**}(nl)$, $\hat{L}_Z$ is the *Z* component of the angular momentum of the electron, $\omega(s,R) = sv_\infty/R^2$ is the angular velocity of the internuclear axis, *s* is the impact parameter, v_∞ is the relative velocity of the atoms at infinity $\hat{V}(\boldsymbol{\rho},\mathbf{R})$ is the operator for the interaction between the electron in atom *B* and the dipole induced in it by the positive ion A^{+}[8,9]:

$$\hat{V}(\boldsymbol{\rho}, \mathbf{R}) = \hat{D} + \hat{V}_{eB}(|\boldsymbol{\rho} - \mathbf{R}|), \quad \hat{D} = -\alpha\mathbf{R}(\boldsymbol{\rho} - \mathbf{R})R^{-3}|\boldsymbol{\rho} - \mathbf{R}|^{-3}, \tag{3}$$

and $\hat{V}_{eB}$ describes the polarization interaction between the Rydberg electron and the isolated term *B*. The term $\hat{H}_{\text{inert}}$ is the effective potential energy operator associated with the fact that the coordinate frame is not inertial.[10] It takes the form of an interaction operator between the electron and the

0038-5646/89/061115-07$04.00

effective electric field, and is directly proportional to the acceleration of the heavy particles. Since this acceleration is inversely proportional to the mass of the core of A^+, and decreases with increasing $R(t)$, the term $\hat{H}_{\text{inert}}$ may be regarded as small, although its inclusion via perturbation theory presents no difficulty.

For a highly excited state with $15 \lesssim n \lesssim 30$, the wave function of the Rydberg electron occupies a large volume ($\rho \lesssim n^2$). However, the volume is large enough to enable us to consider the interaction between the Rydberg electron and the quasimolecular core A^+B as very small, so that we can use the impulse approximation. On the other hand, the volume is small enough to ensure that the usual adiabatic approximation should work. Hence we can take the eigenfunctions of the operator $\hat{H}_0(\boldsymbol{\rho}) - \omega(s,R)\hat{L}_Z$ as our basis. The interaction $\hat{V}(\boldsymbol{\rho},\mathbf{R})$ leads to the mixing of these states and to transitions between them. We must therefore evaluate the matrix elements of $\hat{V}(\boldsymbol{\rho},\mathbf{R})$ in this basis.

First, we must take into account the nonhydrogenic character of the states of the Rydberg electron. The simplest way of doing this is to introduce the effective (nonintegral) orbital quantum number l^* (Refs. 11 and 12) that is related to the quantum defect δ_l: $l^* = l + \delta$. We shall adopt this approach but, since the matrix elements that are significant for our analysis will be evaluated in the quasiclassical approximation, comparable results can also be obtained by taking the quantum deffect into account by other methods.

The interaction operator contains two terms, namely, the interaction of the Rydberg electron with the dipole induced in B and the polarization-type interaction between this electron and the atom B. Despite the apparent simplicity of the physical problem, the complexity of the calculation is determined by the high polarizability α of atom B. Allowance for the induced dipole is essentially simpler: all that needs to be done is to use the one-center expansion of the dipole interaction in terms of the Legendre polynomials,[9] and then proceed to states with electron angular momentum quantized along the internuclear axis:

$$\langle n_2 l_2 m_2 | \hat{D} | n_1 l_1 m_1 \rangle \equiv I_{n_1 l_1 m_1}^{n_2 l_2 m_2}$$

$$= \frac{\alpha}{R^2} \sum_{L,M} (-1)^{m_1} \frac{((2l_1+1)(2l_2+1))^{1/2}}{2L+1} C_{l_1 0 l_2 0}^{L0} C_{l_1 -m_1 l_2 m_2}^{LM}$$

$$\times D_{M0}{}^{L}\left(0, \frac{\pi}{2}, \frac{\pi}{2}\right) \Big\{ (L+1)$$

$$\times \int_0^R F_{n_1 l_1}(\rho)\, \rho^{L+2}/R^{L+2} F_{n_2 l_2}(\rho)\, d\rho$$

$$- L \int_R^\infty F_{n_1 l_1}(\rho)\, R^{L-1}/\rho^{L-1} F_{n_2 l_2}(\rho)\, d\rho \Big\} \qquad (4)$$

where m_1, m_2 are the components of the angular momentum of the Rydberg electron along the Z axis, $C_{l_1 m_1', l_2 m_2'}^{LM'}$, $D_{M'M''}^{L}(0,\pi/2,\pi/2)$ are the Clebsch–Gordan coefficients and the Wigner function,[13] and $F_{nl}(\rho)$ is the radial wave function of the Rydberg electron that can be taken in the following form in the range $l^2/2 \ll R \ll n^2$, $n \gg 1$, $\rho \ll n^2$ in which we are interested:

$$F_{nl}(\rho) = \left[\frac{2}{\rho (n^*)^3} \right]^{1/2} J_{2l^*+1}((8\rho)^{1/2}) \qquad (5)$$

where n^* is the effective principal quantum number. After evaluating the asymptotic behavior of the integrals in (4) with R (see Appendix), we obtain

$$I_{n_1 l_1 m_1}^{n_2 l_2 m_2} = (-1)^{m_1+1} \frac{2^{1/2} \alpha \cos[\pi (l_2^* - l_1^*)]}{\pi (n_1^* n_2^*)^{3/2} R^{5/2}}$$

$$\times \sum_{L,M} \frac{((2l_1+1)(2l_2+1))^{1/2}}{(2L+3)(2L-1)}$$

$$\times C_{l_1 0 l_2 0}^{L0} C_{l_1 -m_1 l_2 m_2}^{LM} D_{M0}{}^{L}\left(0, \frac{\pi}{2}, \frac{\pi}{2}\right). \qquad (6)$$

Much more complicated is the evaluation of the contribution of the polarization interaction between the Rydberg electron and atom B:

$$\Pi_{n_1 l_1 m_1}^{n_2 l_2 m_2} \equiv \langle n_2 l_2 m_2 | \hat{V}_{eB} | n_1 l_1 m_1 \rangle$$

$$= \sum_{L,M} [(2l_1+1)(2l_2+1)/4\pi(2L+1)]^{1/2}$$

$$\times (-1)^{m_1} C_{l_1 0 l_2 0}^{L0} C_{l_1 -m_1 l_2 m_2}^{LM} D_{M0}{}^{L}\left(0, \frac{\pi}{2}, \frac{\pi}{2}\right)$$

$$\times \int F_{n_1 l_1}(\rho)\, \hat{V}_{eB}(\rho_1)\, F_{n_2 l_2}(\rho)\, Y_{L0}(\theta, \varphi)\, d^3\rho_1, \qquad (7)$$

where $\boldsymbol{\rho}_1 = \boldsymbol{\rho} - \mathbf{R}$, θ and φ are the angular coordinates of the Rydberg electron in the system attached to the core of A^+. Integration with respect to the angles is simplified if we use the approximation $\theta \ll 1$ that is directly associated with the short range of the polarization interaction (see Appendix):

$$\Pi_{n_1 l_1 m_1}^{n_2 l_2 m_2} \approx (-1)^{m_1} ((2l_1+1)(2l_2+1))$$

$$\times {}^{1/2} D_{-m_1 0}^{l_1}\left(0, \frac{\pi}{2}, \frac{\pi}{2}\right) D_{m_2 0}^{l_2}\left(0, \frac{\pi}{2}, \frac{\pi}{2}\right)$$

$$\times \Big[F_{n_1 l_1}(R) F_{n_2 l_2}(R) \sum_{k=0}^{\infty} (4k+1)$$

$$\times \int_0^\infty j_{2k}(p_{n_1 l_1}(R)\rho_1)\, \hat{V}_{eB}(\rho_1)\, j_{2k}(p_{n_2 l_2}(R)\rho_1)\, \rho_1^2\, d\rho_1$$

$$+ F_{n_1 l_1}^{(1)}(R) F_{n_2 l_2}^{(1)}(R) \sum_{k=0}^{\infty} (4k+3)$$

$$\times \int_0^\infty j_{2k+1}(p_{n_1 l_1}(R)\rho_1)\, \hat{V}_{eB}(\rho_1)\, j_{2k+1}(p_{n_2 l_2}(R)\rho_1)\, \rho_1^2\, d\rho_1 \Big], \qquad (8)$$

where

$$p_{nl}(R) = [-1/(n^*)^2 + 2/R - (l+1/2)^2/R^2]^{1/2}.$$

The basic problem now is to evaluate the radial integrals in (8). The point is that the effective interaction between the electron and atom B is not known, so that the evaluation cannot be carried out without some further simplifying assumptions (we shall not examine here the possibility or otherwise of *ab initio* calculations). We note, first, that these integrals are equal to the Born amplitude for the elastic scattering of electrons off the energy shell. Since in our case $n_1 \sim n_2$, $l_1 \sim l_2$, we have $p_{n_1l_1}(R) \sim p_{n_2l_2}(R)$, and the Born amplitude in (8) off the energy shell can be approximately replaced with the Born amplitude for the scattering of an electron with momentum

$$p_+(R) = (p_{n_1l_1}(R) + p_{n_2l_2}(R))/2$$

on the energy shell. Once the integrals in (8) have been expressed in terms of the partial scattering amplitudes, they can be naturally expressed in terms of the potential scattering phases $\delta_l(p_+)$.

In accordance with the definition of the pseudopotential,[15] the operator $\hat{V}_{eB}(\rho_1)$ is defined so that its expectation value evaluated over the basis states $|nLM\rangle$ gives the asymptotically correct value for the shift $\Delta\varepsilon_{nLM}$ of an isolated nonhydrogenic level. It follows from (8) that the radial integrals depend on l only via $p_{nl}(R)$ and are independent of M, so that we confine our attention to the case $M=0$, $L=0$.

There are at present several published expressions[8,16,17] for $\Delta\varepsilon_{nLM}$. The formula in Ref. 16 ($\sin\delta_l$ from Ref. 18 replaced with $\operatorname{tg}\delta_l$) leads to difficulties when the phase $\delta_l(p_+)$ passes through $\pi/2$. The evaluation of the matrix elements from the formulas given in Refs. 8 and 17 results in values of the same order. Since the result given in Ref. 8 leads to a simpler dependence of $\Pi^{n_2l_2m_2}_{n_1l_1m_1}$ on p_+, we have written the radial integrals in (8) with the aid of Ref. 8 in terms of the scattering phase (s-singlet and t-triplet) of an electron of momentum p_+ in the following form:

$$\int_0^\infty j_l(p_{n_1l_1}(R)\rho_1)\hat{V}_{eB}(\rho_1) \times j_l(p_{n_2l_2}(R)\rho_1)\rho_1^2\,d\rho_1 \to -\frac{\sin\delta_l^{(s,t)}(p_+)}{2p_+}. \qquad (9)$$

Substitution of (9) in (8) gives

$$\begin{aligned}\Pi^{n_2l_2m_2}_{n_1l_1m_1}(R;s,t) &= (-1)^{m_1+1}((2l_1+1)(2l_2+1))^{1/2} D^{l_1}_{-m_10}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\\ &\times D^{l_2}_{m_20}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\Big[F_{n_1l_1}(R)F_{n_2l_2}(R) \times\sum_{k=0}^{\infty}\left(2k+\frac{1}{2}\right)\sin\delta_{2k}^{(s,t)}(p_+)\\ &+F^{(1)}_{n_1l_1}(R)F^{(1)}_{n_2l_2}(R)\sum_{k=0}^{\infty}\left(2k+\frac{3}{2}\right)\sin\delta_{2k+1}^{(s,t)}(p_+)\Big]\frac{1}{p_+}.\end{aligned} \qquad (10)$$

As in the derivation of (6), we extract from $F_{n_1l_1}(R)F_{n_2l_2}(F)$ and $F^{(1)}_{n_1l_1}(R)$ $F^{(1)}_{n_2l_2}(R)$n the part that does not oscillate with R. This is done using (A.5) and substituting it in (10). The latter then assumes the form

$$\begin{aligned}\Pi^{n_2l_2m_2}_{n_1l_1m_1}(R;s,t) &\approx (-1)^{m_1}((2l_1+1)(2l_2+1))^{1/2} D^{l_1}_{-m_10}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\\ &\times D^{l_2}_{m_20}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\frac{\cos[\pi(l_1^*-l_2^*)]}{2^{1/2}\pi(n_1^*n_2^*)^{3/2}R^{3/2}}\\ &\times\left[-\sum_{l=0}^{\infty}\left(l+\frac{1}{2}\right)\frac{\sin\delta_l^{(s,t)}(p_+)}{p_+}\right], \quad l_i^*=l_i+\delta_{l_i}, \quad i=1,2.\end{aligned} \qquad (11)$$

When the sum over l is evacuated, the first l_0 phases ($0 \leqslant l \leqslant l_0-1$) can be taken from strong-coupling calculations,[18–20] while the phases with $l \geqslant l_0$ can be calculated in the Born approximation:

$$-\sum_{l=0}^{\infty}\left(l+\frac{1}{2}\right)\frac{\sin\delta_l^{(s,t)}(p_+)}{p_+} = -\sum_{l=0}^{l_0-1}\left(l+\frac{1}{2}\right)\frac{\sin\delta_l^{(s,t)}(p_+)}{p_+} - \frac{\alpha\pi p_+ l_0}{2(4l_0^2-1)}. \qquad (12)$$

We note that the use of the exact phases for $l<l_0$ means that we have indirectly taken into account both polarization and exchange scattering. In particular, the contribution of the low-lying ^3P resonance is taken into account in this way. We emphasize that the approach that we have adopted to the evaluation of the matrix elements is qualitative in character, and that *ab initio* calculations of these matrix elements would be very desirable. For sufficiently large R (e.g., for potassium, $R \gtrsim 17$ a.u.), when only elastic scattering of the Rydberg electron by atom B is possible ($p_+^2(R)/2$) is less than the excitation energy of the atom), and $l^2/2 \ll R$ and $(2R)^{1/2}/n<1$, the matrix element (11) assumes the following form after the substitution of (12) in (11) with $p_+(R) \approx (2/R)^{1/2} \equiv p$:

$$\begin{aligned}\Pi^{n_2l_2m_2}_{n_1l_1m_1}(R;s,t) &\approx (-1)^{m_1}((2l_1+1)(2l_2+1))^{1/2} D^{l_1}_{-m_10}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\\ &\times D^{l_2}_{m_20}\left(0,\frac{\pi}{2},\frac{\pi}{2}\right)\frac{\cos[\pi(l_1^*-l_2^*)]}{2^{1/2}\pi(n_1^*n_2^*)^{3/2}R^{3/2}}\\ &\times\left[-\sum_{l=0}^{l_0-1}\left(l+\frac{1}{2}\right)\frac{\sin\delta_l^{(s,t)}(p)}{p} - \frac{\alpha\pi p l_0}{2(4l_0^2-1)}\right].\end{aligned} \qquad (13)$$

The expression given by (12) can be evaluated with the help of the phases.[18–20] It is found that in the above range of values of R, for which (13) is valid, this expression can be approximated by a linear function of the momentum p:

$$-\sum_{l=0}^{l_0-1}\left(l+\frac{1}{2}\right)\frac{\sin\delta_l^{(s,t)}(p)}{p} - \frac{\alpha\pi p l_0}{2(4l_0^2-1)} = -c^{(s,t)}p - d^{(s,t)}$$

i.e., in our range of values of R, we can confine our attention to the first few terms in the Taylor expansion of (12).

We note that, for $|\delta l_1 - \delta_{l_2}| \approx 0.5$, the matrix elements (6), (11), and (13) are numerically small and a more careful evaluation of the radial integrals becomes necessary for the determination of $I^{n_2l_2m_2}_{n_1l_1m_1}, \Pi^{n_2l_2m_2}_{n_1l_1m_1}$.

An important point here is that both the above interactions are symmetric under reflection in the collision plane. Hence the only nonzero matrix elements are those evaluated between states of the same parity $l+m$. More than that, the matrix element (11), (13) between states with odd $l+m$ contains an additional small quantity because the electron wave function is then found to vanish in the collision plane and higher order terms have to be taken into account in the expansion of the spherical harmonic in (7) if a nonzero result is to be obtained.

3. DESCRIPTION OF TRANSITIONS

We now turn to the evaluation of the probabilities of nonadiabatic transitions. We shall use the two-level approximation (the multiplicity indices s, t will at times be neglected). For the adiabatic energy curves we take the diagonal elements of the Hamiltonian (2):

$$U^{d}_{nlm}(R;s,v_\infty) \equiv \langle nlm|\hat{H}|nlm\rangle = -\frac{1}{2(n^*)^2} - m\frac{sv}{R^2} + I^{nlm}_{nlm}(R) + \Pi^{nlm}_{nlm}(R). \tag{14}$$

These curves depend on the internuclear distance R and the impact parameter s, as well as the velocity v_∞. The crossing of such curves signifies that, for $R=R_t(s,v_\infty)$, the electron transition frequency is a multiple of the angular frequency $\omega(s,R_t = sv_\infty/R_t^2$ of the internuclear axis. The splitting of the adiabatic terms at $R=R_t$ is, as usual, given by the off-diagonal matrix elements of the operator $\hat{V}(\boldsymbol{\rho},\mathbf{R})$:

$$a \equiv I^{n_2l_2m_2}_{n_1l_1m_1} + \Pi^{n_2l_2m_2}_{n_1l_1m_1}. \tag{15}$$

The dynamics of nuclei in our range of internuclear distances is determined by the polarization interaction $-\alpha/2R^4$. The description of the transitions requires the establishment of a relationship between the transition point $R=R_t$ and the point $R=R_{st}$ at which the heavy particles stop. For $R_t > R_{st}$, the transitions can be described (qualitatively) in terms of the Landau–Zener approximation, and for $R_t < R_{st}$ we have tunneling transitions. From the standpoint of the dynamics of electron transitions, a special case arises when the transition point R falls into the neighborhood of the orbital radius R_{orb}, and the energy of relative motion of the heavy particles is equal to the height of the effective potential barrier. For a given collision velocity v_∞, orbiting occurs for a particular impact parameter $s_{\text{orb}} = (4\alpha/\mu v_\infty^2)^{1/4}$ (μ is the reduced mass of the atoms) and radius R_{orb} (orbital radius) given by $R_{\text{orb}} = s_{\text{orb}}/2^{1/2}$. The equation

$$U^{(d)}_{n_1l_1m_1}(R_{\text{orb}}, s_{\text{orb}}, v_\infty) = U^{(d)}_{n_2l_2m_2}(R_{\text{orb}}, s_{\text{orb}}; v_\infty)$$

gives the relation between $\{n_1l_1m_1\}$ and $\{n_2l_2m_2\}$ for which the coupling between electron motion and the rotation of the internuclear axis can be substantially amplified. It is clear that this equation is an improved version of (1).

In this paper, we present only approximate calculations of transition cross sections based on the Landau–Zener and Nikitin models.[21] The basic objection to these models (other than the nonlinear character of the terms in the neighborhood of the transition point R_t) is the substantial contribution of the stopping point R_{st} (a singular point of the nuclear motion) to the cross section. Existing models of transitions near the turning point are relatively complicated[21] and their validity in our problem is not beyond challenge. To improve on the approximate calculations of the probability of transitions between the chosen two states, we have to carry out a numerical integration of the equations for the strong coupling between two channels in the quantum-mechanical description of the dynamics of nuclear motion. Nevertheless, to obtain qualitative results, we shall confine our attention to two simple models.

Thus, the inelastic transition cross sections were calculated from the formula

$$\sigma = 2\pi\int_0^\infty s\bar{P}(s)\,ds, \tag{16}$$

where $\bar{P}(s)$ is the probability of the inelastic process. In the Landau–Zener model,

$$\bar{P}(s) = 2\exp(-q)[1-\exp(-q)], \tag{17}$$

where

$$q = 2\pi|a|^2(v_R F)^{-1}, \qquad F = \left|\frac{dU^{(d)}_{n_1l_1m_1}}{dR} - \frac{dU^{(d)}_{n_2l_2m_2}}{dR}\right|_{R=R_t},$$

$$v_R = \left(v_\infty^2 + \frac{\alpha}{\mu R_t^4} - v_\infty^2\frac{s^2}{R_t^2}\right)^{1/2}.$$

When we take into account the effect or orbiting on the transition probability, we use the Nikitin formula[21]

$$\bar{P}(s) = 2\exp(\pi\xi\cos\theta)\,\mathrm{sh}(\pi\xi(1-\cos\theta)/2) \times \mathrm{sh}(\pi\xi(1+\cos\theta)/2)\,\mathrm{sh}^{-2}(\pi\xi). \tag{18}$$

Here the parameters ξ and θ are chosen as follows:

$$\xi = 2(a^2+(\Delta\varepsilon)^2/4)^{1/2}/\omega, \quad \theta = \mathrm{arcctg}(\Delta\varepsilon/2a),$$

$$\omega = \frac{sv_\infty}{R_t^2}, \quad \Delta\varepsilon = \begin{cases} Fv_R/\omega, & R_{st} < R_t \\ -F/(R_{st}-R_t), & R_{st} > R_t \end{cases}. \tag{19}$$

The parameters of the Nikitin model are specified so that the results calculated from it become identical with the Landau–Zener results as R is allowed to depart from R_{st} ($R_t > R_{st}$), whereas for $R_t \approx R_{\text{orb}}$ we obtain the correct result for the transition probability, namely, $\bar{P}(s) \approx 0.5$. In contrast to the Landau–Zener model, the Nikitin model gives a nonzero result for $\bar{P}(s)$ at $R_t = R_{st}$, although this value is actually too high; for $R_t < R_{st}$, the probability $\bar{P}(s)$ falls rapidly with increasing $R_{st} - R_t$.

As an example, let us consider a collision between K** and K with energy $E = 0.045$ eV ($T = 520$ K according to Refs. 5 and 6). Using the results reported in Ref. 18, we find that $c^{(s)} = 48.006$, $d^{(s)} = 7.484$, $c^{(t)} = 16.374$, and $d^{(t)} = 16.825$. Figure 1 shows the level diagram for potassium. The calculation was performed for the $S\to P$ and $S\to D$ transitions. Unfortunately, in the former case, the matrix elements (6) and (13) are anomalously small because $\cos(\pi(\delta_s - \delta_p)) \approx 0$ (this rule obtains for all alkali metals), and the transitions are highly suppressed for $15 \lesssim n \lesssim 30$. Moreover, they must be calculated more accurately for a

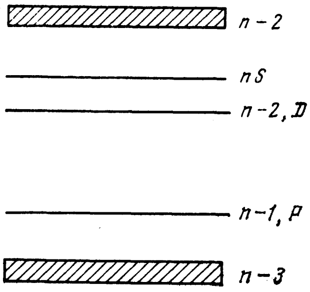

FIG. 1. Rydberg level scheme of the potassium atom. The shaded region shows the set of hydrodynamic states with $l \geqslant 3$.

correct description of the process, and the term $\hat{H}_{\text{inert}}$ that we discarded in (2) must be taken into account. Calculations performed for the $S \rightarrow P$ transitions do not therefore inspire much confidence, and will not be reproduced here. Much more reliable are calculations of cross sections for transitions from S to D $(m = -2)$ states $(|\cos(\pi(\delta_s - \delta_D))| \approx 1$. Figures 2a and b show the results for the singlet and triplet cases, obtained by discarding the interaction with the induced dipole. Figure 3 shows the cross sections obtained without the polarization interaction. It is clear that the Nikitin model gives higher cross sections than the Landau–Zener model. There is no significant difference between singlet and triplet scattering. Of the two interactions involving the Rydberg electron, namely, the interaction with the induced dipole and the polarization interaction with B, the latter is the dominant one.

The Landau–Zener model and the Nikitin model give very different results when they are used to describe transitions (see Fig. 2). We shall now consider some of the details in order to establish the origin of these differences. When the quenching cross section is calculated, it is convenient to take the independent variable to be the transition point R_t, and the impact parameter can be determined from

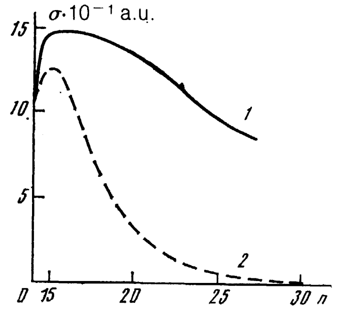

FIG. 3. Curves *1* and *2* show the cross sections for the transition $nS \rightarrow n-2, D(m = -2)$ in the K atom, calculated from Eqs. (18) and (17) without taking into account the polarization interaction of the Rydberg electron with the perturbed atom.

$$U^{(d)}_{nlm}(R_t,s) = U^{(d)}_{n_1 l_1 m_1}(R_t,s).$$

For fixed R_t, the impact parameter s is then found to decrease as n^{-3} with increasing n, and the parameter s_0 that corresponds to coincident transition and stopping points $R_t(s_0,n) = R_{st}(s_0)$, increases as $n^3 v_\infty/\delta$, where $\delta = |\delta_l - \delta_{l_1}|$. Although, as n increases, the point R_t may fall outside the classically allowed region for the Rydberg electron, this actually occurs for $n > \delta/v_\infty \sim 10^2$, i.e., for large n for which our model is definitely invalid (we are assuming that $(2s_0)^{1/2}/n < 1$). The characteristic parameter $-2\pi|a|^2F^{-1}$ that determines the transition behaves as $n^{-6}s^{-1}$ for large n and s, which leads to a Landau–Zener cross section that decreases with increasing n. Hence, for large n, the cross sections can be described by means of perturbation theory, which leaves us with the hope that it may be possible to reconcile the adiabatic and impulse approximations. This is a complicated question that will not be discussed any further here.

To understand the basic difference between the magnitudes of cross sections calculated on the basis of the different ways of describing transitions, we turn to Fig. 4 which shows the "partial" cross section

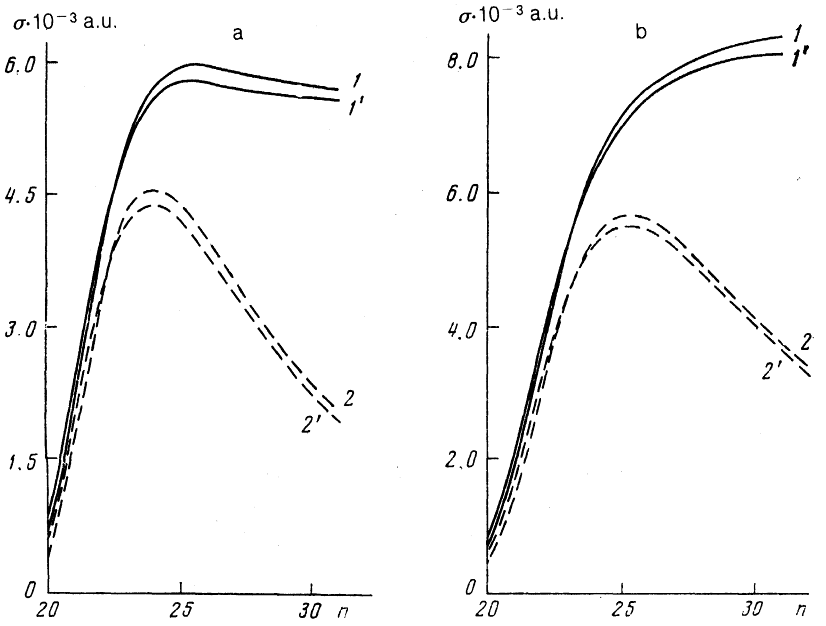

FIG. 2. Singlet and triplet cases (a and b, respectively): 1,2—cross sections calculated from the Nikitin formula (18) and the Landau–Zener formula (17) for the $nS \rightarrow n-2, D$ $(m = -2)$ transition $(b = -2)$ in the $K^{**}(nS)$ atom at 520 K; 1′,2′—the same cross sections calculated without taking into account the interaction between the Rydberg electron and the induced dipole.

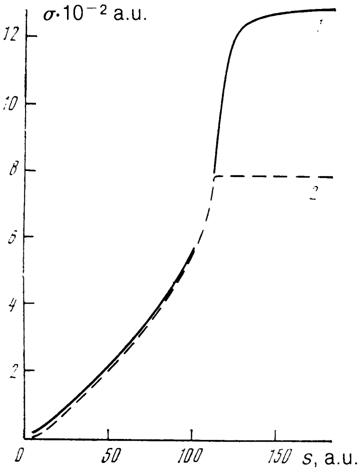

FIG. 4. Curves *1* and *2* show the "partial" cross sections $\tilde{\sigma}(S)$, calculated from Eqs. (18) and (17) for the triplet transition $28S\rightarrow 26D$ ($m=-2$) in the atom $K^{**}(28S)$.

$$\tilde{\sigma}(s)=\int_0^s \bar{P}(s)\,s\,ds$$

as a function of s for the triplet transition with $n=28$. It is clear that, for $R_t>R_{st}$, for which the transition point lies in the region that is classically allowed for the nuclei, curves 1 and 2 coincide, and this was used to determine the parameters of the Nikitin model (19). However, for $R_t<R_{st}$ ($s\geqslant s_0$), we consider the Landau–Zener probability to be identically zero, whereas in actual fact the transition probability is not zero. This was taken into account in our approximation, using the Nikitin model. Since the impact parameter ($s>s_0\gg 1$) is large, the neighborhood of the turning point provides a sizable contribution, so that the transition cross section calculated from the Nikitin formulas is larger than the Landau–Zener cross section. However, the results shown in Fig. 4 must not be taken too literally. As noted above, the Nikitin model overestimates the transition probability in our case for $R_t\lesssim R_{st}$. Moreover, for large R (small p), the linear approximation to the sum in (12) ceases to work. For example, the phase $\delta_1^{(t)}(p)$ exhibits a resonance,[18–20,22] and the characteristic Ramsauer minimum appears in the sum in (12) for triplet scattering, which was not taken into account in this approximation. Hence a transition to a slow reduction in $\sigma(n)$ with increasing n seems the most likely.

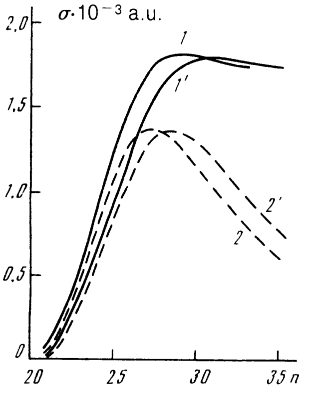

FIG. 5. Curves *1* and *2* show the cross sections for the singlet transitions $nS\rightarrow n-2, D$ ($m=-2$) in the system $Rb^{**}(nS)+K$, calculated from Eqs. (18) and (17), respectively, for $T=714$ K and mean velocity $v_\infty=3.06\cdot 10^{-4}$ a.u.; *1'*, *2'* show the corresponding results for $T=520$ K and $v_\infty=2.59\cdot 10^{-4}$ a.u.

Figure 5 shows the calculated $S\rightarrow D$ transition cross sections for the $Rb^{**}(nS)+K$ system. In this case, $|\cos(\pi(\delta_s-\delta_D))|\sim 1$, and for the same given temperature, the relative collision velocity for the pair $Rb^{**}+K$ is smaller than for $K^{**}+K$. Figure 5 shows the quenching sections for the same collision velocity as for $K^{**}+K$ (and, hence, different temperatures) and also for the same temperatures (different velocities). Only the singlet cross sections are considered because they are only slightly different from the cross sections for triplet transitions.

Comparison of Figs. 2 and 5 shows that the behavior of the $S\rightarrow D$ transitions is qualitatively similar, but the magnitude of the cross sections is significantly affected by the character of the Rydberg electron. This conclusion is in direct conflict with the conclusions derived from the impulse approximation (in which the transition cross section depends to a considerable extent on the perturbing atom), but agrees with experimental data.[5,6] It is important to note that our calculations show that the $S\rightarrow D$ transition cross section for the pair $K^{**}+K$ is greater than for $Rb^{**}+K$. The broadening cross sections measured in Ref. 5 are in a similar relationship. Our theory does not predict a significant temperature dependence. On the other hand, the experiments were performed at more or less constant temperature $T\approx 500$–550 K.

4. CONCLUSION

Our results must be regarded as a semiquantitative estimate of the partial cross section for the $S\rightarrow D$ transition that illustrates our mechanism. The analysis presented above shows that, despite its apparent simplicity, our problem is very complex, and has given rise to questions that require accurate numerical analysis. First, we must have a more accurate solution of the problem of transitions between nonlinear terms, especially near the turning point. This in turn involves the numerical solution of the problem of strong coupling of two channels with allowance for the quantum-mechanical motion of the nuclei. Particular attention must be paid at this point to the effect of the motion of the atoms during orbiting on the electron transitions. The $S\rightarrow P$ transition must be described more accurately [which involves the evaluation of the term representing the asymptotic behavior of matrix elements of the form indicated by (4) and (7)]. Another important requirement is the correct description of the scattering of a slow electron by atom B (choice of pseudopotential and extention beyond the linear approximation) when the sum (12) is evaluated.

Our discussion shows that the cross sections do not have features such as oscillations in n (or a sharp peak) for the $S\rightarrow D$ transition. Orbiting can give rise to an increase in the transition probability up to $W\sim 0.5$ at $R_{\rm orb}$. However, since the orbiting radius is relatively small, i.e., $R_{\rm orb}\approx 20$ a.u., the rotation effect is not expected to provide a large contribution to the transition cross section.

The authors are greatly indebted to V. S. Marchenko and I. I. Fabrikant for useful discussions.

APPENDIX

Consider the integral

$$I_< \equiv R^{-L-2} \int_0^R F_{n_1 l_1}(\rho)\rho^{L+2} F_{n_2 l_2}(\rho)\, d\rho. \tag{A1}$$

Substituting (5) into this expression, we obtain

$$I_< = 2(n_1^* n_2^*)^{-3/2} \int_0^1 J_{2l_1^*+1}((8Rx)^{1/2}) x^{L+1} J_{2l_2^*+1}((8Rx)^{1/2})\, dx.$$

For $R \gg l_{1,2}^2/2$, we replace the Bessel functions with their asymptotic forms and discard the rapidly oscillating term in the integrand. The integral (A1) can then be evaluated:

$$I_< \approx 2^{1/2}[\cos(\pi(l_2^* - l_1^*))]/[\pi(2L+3)(n_1^* n_2^*)^{3/4} R^{1/2}]. \tag{A2}$$

Similarly, for the second integral in (4) we obtain

$$I_> \approx 2^{1/2}[\cos(\pi(l_2^* - l_1^*))]/[\pi(2L-1)(n_1^* n_2^*)^{3/4} R^{1/2}]. \tag{A3}$$

This method of evaluation is exceedingly simple, but the same result can be obtained by the more rigorous quasiclassical method involving the Fourier components.[23,24] In particular, suppose that $n_1, n_2 \gg 1$, but $|n_1 - n_2|/n_1 \ll 1$ and $l_1 \sim l_2$. Then

$$I_> \approx \frac{R^{L-1}}{\pi(n_1^* n_2^*)^{3/2}} \times \int_{\rho_{1n_c^*}}^{2(n_c^*)^2} \frac{\cos[(n_1^* - n_2^*)t/(n_c^*)^3 + \pi\tilde{l}_-\tilde{l}_+/2\tilde{l}_c]\, d\rho}{\rho^L p_{n_c^*}(\rho)},$$

where n_c^* is the mean of n_1^* and n_2^* (the effective quantum number), $\tilde{l}_c$ is the mean of the angular momenta $\tilde{l}_1 = l_1^* + 1/2$ and $\tilde{l}_2 = l_2^* + 1/2$, $\tilde{l}_\pm = \tilde{l}_1 \pm \tilde{l}_2$,

$$p_{n_c^*}(\rho) = [-(n_c^*)^{-2} - \tilde{l}_c^2/\rho^2 + 2/\rho]^{1/2},$$

and $\rho_{1n_c}^*$ is the shortest distance to the ion A^+. Assuming that $\tilde{l}_c \approx \tilde{l}_+/2$, and using the classical parametrization of the Coulomb trajectory,[25] we obtain

$$I_> \approx \frac{R^{L-1}}{\pi(n_1^* n_2^*)^{3/2}(n_c^*)^{2L-1}} \times \int_{\xi_c}^{\pi} \frac{\cos[(n_1^* - n_2^*)(\xi - \sin\xi) + \pi\tilde{l}_-]}{(1-\cos\xi)^L} d\xi \tag{A4}$$

subject to the conditions $\tilde{l}_c^2 \ll 2(n_c^*)^2$, $R \gg \tilde{l}_c^2/2$, $\xi_c \equiv [(2R)^{1/2}/n_c^*] \ll 1$. Since ξ_c is a small parameter, we can write (A4) in the form

$$I_> \approx -\frac{R^{L-1}\sigma(\xi_c)}{\pi(n_1^* n_2^*)^{3/2}(n_c^*)^{2L-1}} \cos[(n_1^* - n_2^*)(\xi_c - \sin\xi_c) + \pi\tilde{l}_-],$$

where

$$\sigma(\xi) = \int (1-\cos\xi)^{-L} d\xi$$

$$= -2^{1-L} \sum_{k=0}^{L-1} C_{L-1}^k (2k+1)^{-1} \operatorname{ctg}^{2k+1}(\xi/2).$$

When $\xi_c \ll 1$

$$\sigma(\xi_c) \approx -\frac{2^{1/2}}{2L-1} \frac{(n_c^*)^{2L-1}}{R^{L-1/2}},$$

which gives (A3) for $I_>$. Thus the method of Fourier components enables us to specify more accurately the range of validity of (A2) and (A3):

$$l^2 \ll 2(n^*)^2,\quad R \gg l^2/2 \text{ and } (2R)^{1/2} < n^*.$$

Now consider the integral (7). Since, as $\rho \to \infty$, we have $U_{eB} \sim -\alpha/2\rho^4$, we may consider that U_{eB} is a short range potential, so that the main contribution to (7) is provided by the immediate neighborhood of the atom B. This enables us to replace $F_{nl}(\rho)$ in (7) with its quasiclassical representation[8]:

$$F_{nl}(\rho) \approx F_{nl}(R)\cos(p_{nl}(R)\boldsymbol{\rho}_1\boldsymbol{\tau}) + F_{nl}^{(1)}(R)\sin(p_{nl}(R)\boldsymbol{\rho}_1\boldsymbol{\tau}), \tag{A5}$$

where

$$p_{nl}(R) = [-(n^*)^{-2} + 2/R - (l^* + 1/2)^2/R^2]^{1/2}, \quad \boldsymbol{\tau} = \mathbf{R}/R,$$

$$F_{nl}^{(1)}(R) = p_{nl}^{-1}(R)\, \partial F_{nl}(\rho)/\partial\rho|_{\rho=R}.$$

Moreover, the short-range character of U_{eB} allows us to assume that $\theta \sim \rho/R \ll 1$ and replace the spherical harmonic in (7) with the approximate expression

$$Y_{L0}(\theta, \varphi) \approx [(2L+1)/4\pi]^{1/2} + O(\theta^2). \tag{A6}$$

Substituting (A5) and (A6) in (7), using the spherical harmonic expansion (A5), summing over L and M, and integrating with respect to the angles gives (8).

[1] M. Hugon, F. Gounand, P. R. Fornier, and J. Berlande, J. Phys. B **16**, 2531 (1983).

[2] R. F. Stebbings and F. B. Dunning (eds.), *The Rydberg States of Atoms and Molecules*, Cambridge University Press, 1983 [Russian transl., Mir, M., 1985].

[3] V. S. Lebedev and V. S. Marchenko, Zh. Eksp. Teor. Fiz. **91**, 428 (1986) [Sov. Phys.—JETP **64**, 251 (1986)].

[4] B. P. Kaulakis, Zh. Eksp. Teor. Fiz. **91**, 391 (1986) [Sov. Phys.—JETP **64**, 229 (1986)].

[5] H. Heinke, J. Lawrenz, K. Niemax, and K.-H. Weber, Z. Phys. A **312**, 329 (1983).

[6] D. C. Thompson, E. Weinberger, *et al.*, Phys. Rev. Lett. **35**, 690 (1987).

[7] B. P. Stoicheff and E. Weinberger, Phys. Rev. Lett. **44**, 733 (1980).

[8] B. M. Smirnov, *Asymptotic Methods in the Theory of Atomic Collisions* [in Russian], Atomizdat, Moscow, 1973, Chapters 2 and 3.

[9] W. E. Baylis, J. Chem. Phys. **51**, 2665 (1969).

[10] V. A. Smirnov, Opt. Spektrosk. **37**, 821 (1974) [Opt. Spectrosc. **37**, 498 (1974)].

[11] L. P. Rappoport, B. A. Zon, and N. L. Manakov, *The Theory of Multiphoton Processes in Atoms* [in Russian], Atomizdat, Moscow, 1978, Chap. 2.

[12] V. A. Kostelecky and M. M. Nieto, Phys. Rev. A **32**, 3243 (1985).

[13] D. A. Varshalovich, A. N. Moskalev, and V. K. Versonskii, *Quantum Theory of Angular Momentum* (Engl. transl. World Scientific, Singapore, 1987) [in Russian], Nauka, Leningrad, 1975, Chapters 4, 5, and 8.

[14] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Springer-Verlag, Berlin, 1957 [Russian transl., Fizmatgiz, M., 1960].

[15] J. M. Ziman, "The calculation of Bloch functions," Solid State Physics, **26**, 1 (1971) [Russian transl., Mir, M., 1973].

[16] G. K. Ivanov, Opt. Spektrosk. **37**, 636 (1974) [Opt. Spectrosc. **37**, 361 (1974)].

[17] E. A. Andreev, Theor. Chim. Acta B **30**, 191 (1973).

[18] E. M. Karule, J. Phys. B **5**, 2051 (1972).

[19] A. L. Sinfailam and R. K. Nesbet, Phys. Rev. A **7**, 1987 (1973).

[20] I. I. Fabrikant, Phys. Lett. A **58**, 21 (1976).

[21] E. E. Nikitin and S. Ya. Umanskiĭ, *Theory of Slow Atomic Collisions*, Springer, New York (1984), Chapters 5 and 6.

[22] I. I. Fabrikant, J. Phys. B **19**, 1527 (1986).

[23] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, 3rd ed., Pergamon Press, Oxford (1977) [Russian original, Nauka, Moscow, 1974, Sec. 48].

[24] A. B. Migdal, *Qualitative Methods in Quantum Theory*, Nauka, Moscow, 1975 (Engl. transl. Benjamin, Reading, MA, 1977).

[25] L. D. Landau and E. M. Lifshitz, *Mechanics*, 3rd ed., Pergamon Press, Oxford (1977) [Russian original, Nauka, Moscow, 1973, Sec. 15].

Translated by S. Chomet