Rydberg atoms of alkali metals in parallel electric and magnetic fields

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The Stark–Zeeman effect is analyzed for Rydberg atoms of alkali metals in parallel fields. The splitting is found in first-order perturbation theory as the spectrum of a five-diagonal secular matrix. A WKB formalism is developed for determining the eigenvectors of such matrices through an analysis of phase trajectories in the classical limit. Quantization rules for the eigenvalues are given. Explicit analytic expressions derived here describe the distortion of the Stark–Zeeman spectrum in comparison with that of the hydrogen atom in the quantum-defect approximation.

The Rydberg spectrum of the hydrogen atom in weak parallel electric and magnetic fields has several nontrivial features, the most prominent of which is the presence of three quite different types of states and of exponentially narrow quasicrossings of Stark–Zeeman levels, considered as functions of the electric field **F** and the magnetic field **H**. These quasicrossings occur at points at which the following relations hold:

$$5^{1/2}n\beta=0,\ 1,\ 2,\dots . \qquad (1)$$

The parameter β is a measure of the relative strength of the fields:

$$\beta=12c^2F/5n^2H^2. \qquad (2)$$

A semiclassical theory predicting these effects was presented in Refs. 1 and 2. The theory is based on a discrete analog of the WKB method, which is used to find the eigenvalues of the perturbation operator matrix in the basis of states belonging to a shell with the given principal quantum number n. These results were subsequently confirmed in Refs. 3 and 4, where Solov'ev's method of an equivalent diamagnetic operator[5] was used, and also in Ref. 6. Experimental tests of the theory have recently been carried out (e.g., Ref. 7).

A more complicated question is how fields $\mathbf{F}\|\mathbf{H}$ affect the Rydberg states of atoms other than hydrogen. The experiments which have been carried out to date have been on lithium[3,4] and barium[8] atoms. The splitting picture retains many of the features seen in the case of hydrogen. In particular, there are quasicrossings, whose positions agree with relation (1). However, since there is a core which distorts the Coulomb nature of the field acting on the valence electron, these quasicrossings turn out to be broad. The splitting picture in weak electric fields is not at all similar to that for hydrogen (we have previously studied[9] the limiting case of purely diamagnetic splitting for nonhydrogen atoms).

In the present paper we discuss a theory of the Stark–Zeeman effect for Rydberg levels of alkali metal atoms in weak, parallel, external electric and magnetic fields. The fields are assumed to be weak enough to ignore the mixing of states from different shells (with different values of n) but strong enough to break the coupling of the spin with the orbital motion (the legitimacy of ignoring the spin-orbit coupling in a study of the splitting of large-n states is discussed in Ref. 10). For simplicity we will be discussing for the most part the case of a lithium atom in a state with a magnetic quantum numer $m=0$, being guided by the experimental conditions of Ref. 3. These limitations are not of fundamental importance.

1. FORMULATION OF THE PROBLEM

The operator which represents the interaction of a valence electron of an alkali metal atom with an external electric field **F** and an external magnetic field **H**, both directed along the z axis, is

$$V=Fz+(H/2c)L_z+(H^2/8c^2)(x^2+y^2). \qquad (3)$$

It is to be understood that we are using the quantum-defect approximation; we are also using the atomic system of units. Since L_z is an integral of motion, equal to m, the splitting of the levels of shell n is determined in first-order perturbation theory for a group of nearly degenerate levels by the eigenvalues of the matrix of the perturbed Hamiltonian in the basis of unperturbed wave functions $|nlm\rangle$ with given n and m:

$$\mathcal{H}_{ll'}=E_{nl}^{(0)}\delta_{ll'}+\langle nlm|V|nl'm\rangle. \qquad (4)$$

Here $E_{nl}^{(0)}$ are the unperturbed energies of the alkali metal atom, which differ from the hydrogen energies $E_n^{(0)}=-(2n^2)^{-1}$ because of the quantum defect. The correct zeroth-approximation function is the linear combination

$$\Psi=\sum_{l=|m|}^{n-1}C_l|nlm\rangle. \qquad (5)$$

Matrix (4) has nonvanishing elements only for $|l-l'|\leqslant 2$; i.e., it is a five-diagonal matrix. The equation which determines the elements C_l of its eigenvectors is therefore a five-term recurrence relation. We will write it in a reduced form, referring the matrix elements in (4) to the energy

$$\Delta E_H=5n^4H^2/16c^2,$$

which is equal to the width of the quadratic Zeeman multiplet in the absence of an electric field.[1] The equation is

$$-p_lC_{l-2}+q_lC_{l-1}+(w_l-\varepsilon)C_l+q_{l+1}C_{l+1}-p_{l+2}C_{l+2}=0. \qquad (6)$$

Here we have introduced the following notation for the dimensionless quantities:

$$\begin{gathered}w_l=\frac{2}{5n^4}\langle nlm|x^2+y^2|nlm\rangle+\frac{E_{nl}^{(0)}-E_n^{(0)}}{\Delta E_H}\\ q_l=F\langle nl-1m|z|nlm\rangle/\Delta E_H,\\ p_l=-2\langle nl-2m|x^2+y^2|nlm\rangle/5n^4.\end{gathered} \qquad (7)$$

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The eigenvalues ε of five-term recurrence relation (6) are related to the energies of the Stark–Zeeman sublevels by

$$E=E_n^{(0)}+mH/2c+\varepsilon\Delta E_H.$$

We will be calling ε the "reduced energy," while the parameter β defined by (2) is the "reduced electric field."

The difference between the orbitals $|nlm\rangle$ and those of the hydrogen atom fades away rapidly with increasing l. As a measure of this difference we can use the quantum defect δ_l, which in the case of the lithium atom is 0.4 for s states, 0.05 for p states, and negligibly small for large-l states. In the case of highly excited Rydberg levels with large n, the overwhelming majority of the basis functions in expansion (5) are therefore essentially hydrogen orbitals, and the energies $E_{nl}^{(0)}$ at $l\geqslant 2$ are approximately equal to $E_n^{(0)}$. As a result, the overwhelming majority of the matrix elements in (7) are the same as the corresponding matrix elements of the problem for the hydrogen atom. With $m=0$, the latter are given by[11]

$$w_l=\left[1+\frac{1-3l(l+1)}{5n^2}\right]\frac{2(l^2+l-1)}{(2l-1)(2l+3)},$$
$$q_l=\left[1-\frac{l^2}{n^2}\right]^{1/2}\frac{2\beta l}{(2l+1)^{1/2}(2l-1)^{1/2}}, \qquad (8)$$
$$p_l=\left[\left(1-\frac{l^2}{n^2}\right)\left(1-\frac{(l-1)^2}{n^2}\right)\right]^{1/2}\frac{l(l-1)}{(2l-1)(2l+1)^{1/2}(2l-3)^{1/2}}.$$

2. CLASSICAL LIMIT

Recurrence relation (6) is analogous to a fourth-order ordinary differential equation. Like the latter, five-term recurrence relation (6) can be solved approximately by a quasiclassical method which is applicable at those values of the independent variable l for which the coefficients w_l, q_l, and p_l are smooth functions of l and vary slowly in each step of the five-term recurrence relation. A necessary condition here is that l satisfy the inequalities

$$l^2\gg 1,\quad n^2-l^2\gg 1.$$

Since the effect of the core is sensed only at very small values of l ($l=0$ and 1 for lithium), the quasiclassical picture of the motion of a valence electron will be the same for hydrogen and alkali metals (aside from the mixing phase near the point $l=0$; Sec. 4).

Formally treating l in (6) as a continuous variable, we introduce the "momentum" operator $\hat{\varphi}=-i\partial/\partial l$. Using the notation $p(l)=p_l$, $C(l)=C_l$, etc. and assuming $\exp(\pm i\hat{\varphi})C(l)=C(l\pm 1)$, we can rewrite the five-term recurrence relation as the equation $(\hat{\mathscr{H}}-\varepsilon)C(l)=0$, where

$$\hat{\mathscr{H}}=w(l)+[q(l)\exp(-i\hat{\varphi})+q(l+1)\exp(+i\hat{\varphi})]$$
$$-[p(l)\exp(-i2\hat{\varphi})+p(l+2)\exp(i2\hat{\varphi})]. \qquad (9)$$

In the classical limit, $\hat{\varphi}$ becomes the canonical momentum which is the conjugate of l, while $\hat{\mathscr{H}}$ becomes the Hamiltonian

$$\mathscr{H}=w(l)+2q(l+1/2)\cos\varphi-2p(l+1)\cos 2\varphi. \qquad (10)$$

Correspondingly, we have the canonical equations

$$l=\partial\mathscr{H}/\partial\varphi,\quad \varphi=-\partial\mathscr{H}/\partial l. \qquad (11)$$

These equations describe a slow evolution of the elements of the classical elliptical orbit of the valence electron under the influence of the external fields. The variable φ determines the orientation of the orbit here. In the case $m=0$ one can show that φ is the angle between the direction of the fields and that of the Runge–Lenz vector.

In the classical limit it is convenient to replace l by the variable $x=(l+\frac{1}{2})/n$, which is related to the eccentricity of the orbit, e, by $x=(1-e^2)^{1/2}$. Taking the limit $n\to\infty$, $x=\text{const}$, and retaining in the matrix elements w, p, q two orders in the "quasiclassical parameter" n^{-1}, we find an explicit expression for the Hamiltonian:

$$\mathscr{H}=1/2(1-3/5x^2)+2\beta(1-x^2)^{1/2}\cos\varphi-1/2(1-x^2)\cos 2\varphi. \qquad (12)$$

The trajectory of the image point in the x, φ phase plane is determined by the energy conservation law

$$\mathscr{H}(x,\varphi)=\varepsilon,$$

which is a quadratic equation for $\cos\varphi$. This trajectory consists thus generally of two branches:

$$\cos\varphi=[\beta\pm(1+\beta^2-4/5x^2-\varepsilon)^{1/2}]/(1-x^2)^{1/2}\equiv\zeta^{\mathrm{I,II}}(x) \qquad (13)$$

(branches I and II correspond to the $-$ and $+$, respectively).

To construct a WKB theory, it is important to know the position of the turning points on the x axis—the points at which the generalized velocity $\dot{x}$ vanishes. According to the canonical equation we have

$$\partial\mathscr{H}/\partial\varphi=2\sin\varphi(+4p\cos\varphi-q)=0.$$

This result means that one of the three following equalities must hold at the turning points x_t:

$$\cos\varphi=-1,\quad \cos\varphi=1,\quad \cos\varphi=q/4p,$$

When energy conservation is taken into account, one finds that these equalities are equivalent to the equations

$$\varepsilon=U^{\mathrm{I}}(x),\quad \varepsilon=U^{\mathrm{II}}(x),\quad \varepsilon=U^D(x),$$
$$U^{\mathrm{I,II}}=1/5x^2\pm 2\beta(1-x^2)^{1/2},\quad U^D=1+\beta^2-4/5x^2. \qquad (14)$$

The turning points are intersections of lines of constant energy with the plot of the function $U^{\mathrm{I,II},D}$ (Fig. 1). In this sense, functions (14) are analogous to a potential energy. It is easy to verify that the plots of U^{I} and U^{II} are the locus of turning points for motion along trajectory branches I and II, respectively. On the U^D curve, a change in the sign of the general-

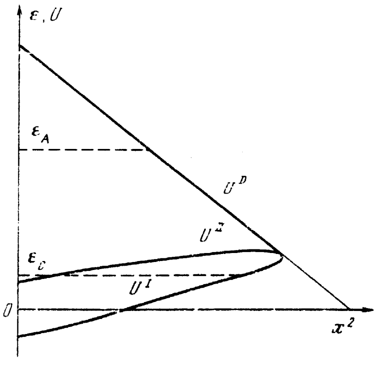

FIG. 1. Potential curves of Hamiltonian (10) for $\beta=0.05$. Classically, motion is allowed along both branches of the phase trajectory if $U^{\mathrm{II}}<\varepsilon<U^D$ but only along branch I if $U^{\mathrm{I}}<\varepsilon<U^{\mathrm{II}}$. In other cases, motion is classically forbidden.

ized velocity $\dot{x}$ is accompanied by a transition from branch I to II and back. On a given branch, the values of x which are allowed classically are those for which the corresponding function $\zeta(x)$ is real and lies between -1 and 1.

The motion along the x axis is an oscillation in an interval bounded on the left by the point $x=0$, which corresponds to the degeneration of the classical elliptical orbit into a straight line. The nature of the motion is qualitatively different at different energies: (a) At $\frac{1}{5}+5\beta^2<\varepsilon<1+\beta^2$, branches I and II form a unified phase trajectory, and the right-hand turning point lies on U^D (the energy ε_A in Fig. 1). (b) For $-2\beta<\varepsilon<2\beta$, only branch I of the trajectory is realized. The right-hand turning point lies on $U^{\rm I}$. (c) For $2\beta<\varepsilon<\frac{1}{5}+5\beta^2$ the phase trajectory consists of two unconnected branches. If $2\beta<\varepsilon<\frac{1}{5}$ (the energy ε_C), the motion along branch I (II) corresponds on the diagram in Fig. 1 to an oscillation of x between the point $x=0$ and the right-hand turning point $x_t^{\rm I}$ ($x_t^{\rm II}$). For $\frac{1}{5}<\varepsilon<\frac{1}{5}+\beta^2$, the motion along branch II is more complicated. All three regimes are realized if $\beta<\frac{1}{5}$. For $\frac{1}{5}<\beta<1$, only regimes (a) ($\varepsilon\in[2\beta, 1+\beta^2]$) and (b) $\varepsilon\in[-2\beta, 2\beta]$) remain. If $\beta>1$, only regime (b) is possible, and the reduced energy can take on values in the interval $[-2\beta, 2\beta]$.

3. WKB SOLUTIONS OF FIVE-TERM RECURRENCE RELATIONS

Branches I and II of the classical trajectory correspond to solutions of quantum-mechanical problem (6):

$$C_l^{(\lambda)}\approx A^{(\lambda)}(v_l^{(\lambda)})^{-1/2}\cos[nS^{(\lambda)}(x_0,x_l)+\vartheta^{(\lambda)}],\quad \lambda={\rm I, II}. \qquad (15)$$

Here x_l are the values of x at discrete points corresponding to integer values of l, and $v_l^{(\lambda)}$ and $S^{(\lambda)}$ are the classical velocity and the classical action at point x_l on the corresponding branch of the trajectory, given by

$$v_l^{(\lambda)}=\frac{\partial\mathscr{H}}{\partial\varphi}\bigg|_{\varphi=\varphi^{(\lambda)}(x_l)},\quad S^{(\lambda)}(x_0,x_l)=\int\limits_{x_0}^{x_l}\varphi^{(\lambda)}(x)\,dx,$$

$$\varphi^{(\lambda)}(x)=\arccos\zeta^{(\lambda)}(x).$$

Here A and ϑ are arbitrary constants. The solutions $C_l^{(\lambda)}$ satisfy five-term recurrence relation (6) with an accuracy to two orders in n^{-1}. This conclusion follows from the general theory of the WKB approximation; it can also be verified by direct substitution.

A general solution of the five-term recurrence relation containing four arbitrary constants is a superposition of the solutions $C_l^{\rm I}$ and $C_l^{\rm II}$. These solutions oscillate within "their own" classically allowed regions, in which the momentum $\varphi^{\rm I}$ or $\varphi^{\rm II}$ is real. To the right of the corresponding turning point, the cosine in (15) is replaced by the sum of an exponentially growing solution and a solution which is decreasing in magnitude. Physically permissible solutions should not contain growing terms. This condition determines the arbitrary constants in (15) to some extent, leading to joining conditions at the turning points. These conditions can be derived most simply by circumventing the turning points in the plane of the complex angular momentum l (see Ref. 12 for a description of a method in the case of three-term recurrence relations). Examining the turning point $x_t^{\rm I}$, one can show that a solution of type I, which decays exponentially at $x_l>x_t^{\rm I}$, should have the following form to the left of $x_t^{\rm I}$:

$$C_l^{\rm I}=A^{\rm I}(v_l^{\rm I})^{-1/2}\cos\{n[S^{\rm I}(x_l,x_t^{\rm I})-\pi x_t^{\rm I}]-\pi/4\}. \qquad (16)$$

Correspondingly, to the left of the point $x_t^{\rm II}$ we have a solution of type II which decays at $x_l>x_t^{\rm II}$:

$$C_l^{\rm II}=A^{\rm II}(v_l^{\rm II})^{-1/2}\cos[nS^{\rm II}(x_l,x_t^{\rm II})-\pi/4]. \qquad (17)$$

The joining conditions on the U^D curve relate the arbitrary constants in the solutions of types I and II. A combination of the solutions which decays at $x_l>x_t^D$ should have the following form at $x_l<x_t^D$:

$$\begin{aligned}C_l=A\{&\cos[nS^{\rm II}(x_l,x_t^D)+\pi/4+\chi](v_l^{\rm II})^{-1/2}\\&+\cos[nS^{\rm I}(x_l,x_t^D)-\pi/4+\chi](v_l^{\rm I})^{-1/2}\}\end{aligned} \qquad (18)$$

(A and χ are arbitrary quantities).

4. JOINING CONDITIONS AT SMALL ANGULAR MOMENTA; QUANTIZATION RULES

In our $m=0$ case, the left-hand boundary of the classically allowed intervals is at $l=0$, where we cannot use the WKB method (because of singularities in the angular parts of the matrix elements of the operators x^2+y^2 and z and also, in the case of alkali metals, because of the energy shifts in the diagonal elements of the secular matrix which are generated by the quantum defects—these energy shifts are not smooth functions of l). To derive a joining condition we make use of the circumstance that under the condition $l^2\ll n^2$, which allows us to ignore the difference between the factors in the square brackets in matrix elements (8) and unity, five-term recurrence relation (6) can be solved exactly. Its general solution can then be expressed in terms of the functions Q_l and the Legendre polynomials P_l:

$$C_l=\sum_{\lambda={\rm I,II}}(2l+1)^{1/2}[\alpha_P^{(\lambda)}P_l^{(\lambda)}(\zeta_0^{(\lambda)})+\alpha_Q^{(\lambda)}Q_l^{(\lambda)}(\zeta_0^{(\lambda)})] \qquad (19)$$

(the α are arbitrary constants). Serving as arguments of the functions P_l and Q_l are the values of the cosine of the angle φ at $x=0$:

$$\zeta_0^{(\lambda)}=\zeta^{(\lambda)}(0)=\beta\pm(1+\beta^2-\varepsilon)^{1/2}.$$

For $1\ll l^2\ll n^2$, approximation (19) and the the WKB approximation are both applicable. We write a general WKB solution of the five-term recurrence relation in the form

$$C_l=\sum_{\lambda={\rm I,II}}A^{(\lambda)}(v_l^{(\lambda)})^{-1/2}\cos\left[nS^{(\lambda)}(0,x_l)+\chi^{(\lambda)}-\frac{\pi}{4}\right] \qquad (20)$$

(A and χ are arbitrary). Under the condition $l^2\ll n^2$ we have

$$nS^{(\lambda)}(0,x_l)\approx(l+1/2)\varphi_0^{(\lambda)},$$

$$v_l^{(\lambda)}\approx v_0^{(\lambda)}=2(1+\beta^2-\varepsilon)^{1/2}.$$

Using the well-known asymptotic expressions for the Legendre functions at large values of their index, we find a relationship between the arbitrary constants in general solutions (19) and (20):

$$\begin{aligned}&A^{(\lambda)}=[(4/\pi)(\alpha_P^{(\lambda)})^2+\pi(\alpha_Q^{(\lambda)})^2]^{1/2}[2(1+\beta^2-\varepsilon)^{1/2}]^{1/2},\\&\operatorname{ctg}\chi^{(\lambda)}=(2/\pi)(\alpha_P^{(\lambda)}/\alpha_Q^{(\lambda)}),\qquad\lambda={\rm I, II}.\end{aligned} \qquad (21)$$

Solution (19) satisfies five-term recurrence relation (6) with $1 < l^2 \ll n^2$, while it generally does not satisfy the first two equations of the five-term recurrence relation. By requiring that (19) also satisfy the five-term recurrence relating in the cases $l = 0$ and 1, we find two restrictions on the four constants α in (19) and, by virtue of relationship (21), on the constants A and χ of the WKB solution. This will be the joining condition which we are seeking at small l. The results will be different in the cases of the hydrogen and lithium atoms.

a) Hydrogen atom

Expressions (8) for the matrix elements are also applicable for $l = 0$ and 1. The first two equations of the five-term recurrence relations are satisfied by Legendre polynomials but not by the Legendre functions. In a physically permissible solution we would thus have $\chi^{\mathrm{I}} = \chi^{\mathrm{II}} = 0$. On the other hand, the coefficients A^{I} and A^{II} in the WKB solution are not related by the boundary condition at the point $x = 0$.

Continuing WKB solution (20) rightward to the turning points, and using joining conditions (16) and (17), we find quantization conditions for the reduced energy ε. We will not analyze these conditions comprehensively here, since we ultimately obtain the same equations as in a parabolic basis.[2] A useful new result is the demonstration that it is possible to derive explicit expressions for the coefficients C_l of the wave function of a perturbed atom in a spherical basis. The physical meaning of C_l derives from the circumstance that these quantities determine the relative probabilities for transitions from low-lying levels of the hydrogen atom, weakly perturbed by external fields, to various Stark–Zeeman sublevels of shell n. For example, the oscillator strengths of a transition from the 1s level are proportional to C_1^2.

Here and below, we will also discuss the most interesting situation, in which the reduced electric field and the reduced energy satisfy the inequalities

$$\beta < {}^1/_5, \quad 2\beta < \varepsilon < {}^1/_5 + 5\beta^2. \tag{22}$$

Under these conditions, the classical phase trajectory consists of two uncoupled branches, with right-hand turning points x_t^{I} and x_t^{II} ($x_t^{\mathrm{I}} > x_t^{\mathrm{II}}$). Let us assume $x_l < x_t^{\mathrm{II}}$. The WKB solution then takes the form in (20) with vanishing phase shifts $\chi^{(\lambda)}$. If the amplitude A^{II} of component II in this solution is nonzero, we find the following equation from joining condition (17) at the point x_t^{II}:

$$S^{\mathrm{II}}(0, x_t^{\mathrm{II}}) = (N^{\mathrm{II}} + {}^1/_2)\pi, \tag{23}$$

where N^{II} is an integer.

In the region $x_t^{\mathrm{II}} < x_l < x_t^{\mathrm{I}}$, component II of the WKB solution is exponentially small and can be omitted. Continuing the remaining component (I), with amplitude A^{I}, to the turning point x_t^{I}, the imposing joining condition (16), we find

$$S^{\mathrm{I}}(0, x_t^{\mathrm{I}}) - \pi x_t^{\mathrm{I}} = \pi(N^{\mathrm{I}} + {}^1/_2), \tag{24}$$

where N^{I} is also an integer. Relations (23) and (24) are equations for the energy ε. In general, they are incompatible. Consequently, either condition (23) alone holds (in which case, the WKB function does not contain component I: $A^{\mathrm{I}} = 0$), or condition (24) alone holds (and we have $A^{\mathrm{II}} = 0$). As a result we find two independent series of energy levels (the levels of types I and II in Ref. 2). As the electric field β is strengthened, levels II rise, while levels I decrease approximately linearly at small values of β. This behavior was predicted in Ref. 13. Condition (1) determines the exceptional values of the electric field at which the levels of groups I and II cross. This condition follows from an identity which relates the action integrals in (23) and (24):

$$\pi x_t^{\mathrm{I}} - S^{\mathrm{I}}(0, x_t^{\mathrm{I}}) - S^{\mathrm{II}}(0, x_t^{\mathrm{II}}) = 5^{1/2}\beta\pi \tag{25}$$

(these integrals reduce to complete elliptic integrals). Actually, when the exponentially small corrections are taken into account, there is a quasicrossing of levels.

To completely determine the solution of the five-term recurrence relation, we must still determine the normalization coefficient A^{I} or A^{II}, depending on the particular type of level under consideration. As usual in the WKB approximation we have

$$A^{(\lambda)} = (2\omega^{(\lambda)}/\pi)^{1/2}, \quad \lambda = \mathrm{I}, \mathrm{II},$$

where $\omega^{(\lambda)}$ is the classical frequency, which can be expressed in terms of the period:

$$\frac{\pi}{\omega^{(\lambda)}} = \int_0^{x_t^{(\lambda)}} \frac{dx}{v^{(\lambda)}(x)}. \tag{26}$$

In reality, for a given energy the period does not depend on the index of the branch of the classical trajectory [as can be shown by differentiating identity (25) with respect to ε], so we have $\omega^{\mathrm{I}} = \omega^{\mathrm{II}}$. Using (21), we finally find the following result for $l^2 \ll n^2$:

$$C_l^{(\lambda)} \approx \frac{1}{2} \frac{[(2l+1)\omega]^{1/2} P_l(\zeta_0^{(\lambda)})}{(1+\beta^2-\varepsilon)^{1/4}}. \tag{27}$$

The quantity ω can either be calculated from (26) or be extracted from the approximate expressions for the energy [expression (28) in Ref. 2], since we have $\omega \approx \varepsilon_{N+1} - \varepsilon_N$.

We now assume that the electric field satisfies condition (1). In energy interval (22), the spectrum then consists of doublets with an exponentially close spacing (in terms of n). The components of the doublets correspond to wave functions which have the following coefficients in a spherical basis:

$$C_l^+ = (C_l^{\mathrm{I}} + C_l^{\mathrm{II}})/2^{1/2}, \quad C_l^- = (C_l^{\mathrm{I}} - C_l^{\mathrm{II}})/2^{1/2}. \tag{28}$$

If the electric field is weak ($\beta \ll 1$), one of these coefficients is far greater than the other. Specifically, for $\beta \ll 1$ we have

$$\zeta_0^{\mathrm{I}} \approx -\zeta_0^{\mathrm{II}}, \quad P_l(\zeta_0^{\mathrm{I}}) \approx (-1)^l P_l(\zeta_0^{\mathrm{II}}),$$

i.e., $C_l^{\mathrm{I}} \approx (-1)^l C_l^{\mathrm{II}}$. Accordingly, for even l the quantity $|C_l|^2$ reaches a maximum for the plus component at the quasicrossing point, while for the minus component it reaches a minimum, which is close to or even equal to zero (for $l = 0$). When l is odd, we find the opposite situation. An abrupt and nonmonotonic variation of the oscillator strengths for transitions to components of the Stark–Zeeman multiplet upon changes of this sort in the relative strengths of the fields was recently found in some nunerical calculations.[14] We see that the physical reason for this behavior is an interference of the components of types I and II of the atomic wave function.

b) Lithium atom

The first two equations in five-term recurrence relation (6) are "spoiled" by the presence of shifts $\varepsilon_{nl}^{(0)} \equiv (E_{nl}^{(0)} - E_{n}^{(0)})/\Delta E_H$ in the diagonal elements. If these equations are to be satisfied, solution (19) must contain not only Legendre polynomials but also Legendre functions. Joining solution (19) with WKB solution (20), we find that the phase shifts χ^{I} and χ^{II} in the latter are nonzero and are not determined unambiguously by the boundary condition at small l. The condition on the phase shifts is a rather complicated equation which relates χ^{I}, χ^{II}, and the energy. We will reproduce it here for the simplified case in which the field-induced splitting is large, and we can ignore the quantum defect for the p orbitals. Using the notation $\sigma \equiv (1+\beta^2-\varepsilon)^{1/2}$, we can then write the following relation for the phase shifts:

$$\operatorname{ctg}\chi^{\mathrm{II}} - \operatorname{ctg}\chi^{\mathrm{I}} = 2\Phi,$$

$$\Phi(\beta,\varepsilon) \equiv \frac{1}{\pi}\left[\frac{1}{2}\ln\frac{(\sigma+1)^2-\beta^2}{(\sigma-1)^2-\beta^2} + \frac{2\sigma}{\varepsilon_{n0}{}^{(0)}}\right]. \tag{29}$$

For the amplitudes we find $A^{\mathrm{I}}\sin\chi^{\mathrm{I}} + A^{\mathrm{II}}\sin\chi^{\mathrm{II}} = 0$.

The quantum defect of the s state is taken into account in (29) through the reduced splitting in a zero field, $\varepsilon_{n0}^{(0)}$. If we were to formally let $\varepsilon_{n0}^{(0)}$ go to zero, we would find $\Phi \to \infty$, and we would return to the case of the hydrogen atom. The opposite limit $\varepsilon_{n0}^{(0)} \to \infty$ corresponds to the so-called truncated-basis approximation[9,15] (in which it is assumed that the s state is essentially not mixed with other states of the shell under consideration by external fields, because of the large value of the quantum defect).

Continuing WKB solution (20) to the turning points x_t^{I} and x_t^{II}, we again find two quantization conditions in the energy interval $[2\beta, \frac{1}{5}]$:

$$\begin{aligned} n[S^{\mathrm{II}}(0, x_t{}^{\mathrm{II}}) - \pi x_t{}^{\mathrm{II}}] &= \pi(N^{\mathrm{II}} + {}^1/_2) - \chi^{\mathrm{II}}, \\ nS^{\mathrm{I}}(0, x_t{}^{\mathrm{I}}) &= \pi(N^{\mathrm{I}} + {}^1/_2) - \chi^{\mathrm{I}}. \end{aligned} \tag{30}$$

In contrast with the hydrogen case, these equations do not contradict each other, because of the additional degree of freedom associated with the phase shifts $\chi^{\mathrm{I,II}}$. Consequently, the two components associated with the different branches of the phase trajectory appear simultaneously in the WKB solution, with nonzero weights $A^{\mathrm{I,II}}$.

Adding Eqs. (30) and using (25), we find that, within an integer multiple of the π term, the sum $\chi^{\mathrm{I}} + \chi^{\mathrm{II}}$ is equal to $5^{1/2}\beta n\pi$. In the approximation of a zero quantum defect of the p state, this result leads to the following relation for the square amplitudes:

$$\begin{aligned} &[(A^{\mathrm{I}})^2 - (A^{\mathrm{II}})^2]/[(A^{\mathrm{I}})^2 + (A^{\mathrm{II}})^2] \\ &\quad = \pm\{1 + [\Phi\sin(5^{1/2}\beta n\pi)]^{-2}\}^{-1/2}. \end{aligned} \tag{31}$$

Some important physical consequences follow from this relation. An elementary analysis of the classical equations of motion, presented here and also in Ref. 2, shows that branches I and II of the trajectory correspond to elliptical orbits of the valence electron which are greatly stretched out respectively along and opposite the direction of the electric field. They correspond to quasiclassical quantum-mechanical states of types I and II with expectation values of the dipole-moment projection k_z which are opposite in sign. The value of $|d_z|$ is close to its maximum possible value $d_{\max} \approx (\frac{3}{2})n^2$. The resulant dipole moment of this stationary state of the alkali metal atom is the difference between the contributions of the I and II components. We can write the approximate expression

$$d_z/d_{\max} = [(A^{\mathrm{I}})^2 - (A^{\mathrm{II}})^2]/[(A^{\mathrm{I}})^2 + (A^{\mathrm{II}})^2].$$

As the reduced electric field β is varied, the relation between these contributions varies smoothly, so d_z is a smooth function of the electric field and does not reach the extreme value $d_{\max}$. This situation is strikingly different from that in the case of the hydrogen atom ($\Phi \to \infty$), in which d_z is approximately a step function (see Fig. 7 in Ref. 2).

We turn now to the energy spectrum. The phase difference $\vartheta \equiv \chi^{\mathrm{I}} - \chi^{\mathrm{II}}$ can be expressed in terms of ε and β with the help of relation (29) and with the help of the known sum of the phase shifts:

$$\vartheta = \arccos\frac{\Phi}{(1+\Phi^2)^{1/2}} \pm \arccos\frac{\Phi\cos(5^{1/2}n\beta\pi)}{(1+\Phi^2)^{1/2}}. \tag{32}$$

Subtracting one of equations (30) from the other, we find the quantization rules in their final form:

$$nS = (2N+1)\pi + \vartheta. \tag{33}$$

Here N is an integer quantum number. Corresponding to each value of N are two energy levels, which correspond to the + and − in (32). After integration by parts, the quantity

$$S \equiv S^{\mathrm{II}}(0, x_t{}^{\mathrm{II}}) - S^{\mathrm{I}}(0, x_t{}^{\mathrm{I}}) + \pi x_t{}^{\mathrm{I}}$$

can be reduced to the complete elliptic integral of the third kind:

$$S = \pi - \int_{-1}^{1}\left[1 - \frac{5\varepsilon}{2(z+{}^3/_2)} + \frac{25}{4}\frac{\beta^2}{(z+{}^3/_2)^2}\right]^{1/2}\frac{dz}{(1-z^2)^{1/2}}.$$

In the region of small β, in which we are interested here, the integral S and the function Φ depend only weakly on β. The behavior of the terms as functions of β is thus determined primarily by the oscillations in the angle ϑ which are associated with the phase of the cosine in (32) (in this phase, β is multiplied by the large parameter n). Figure 2 shows the

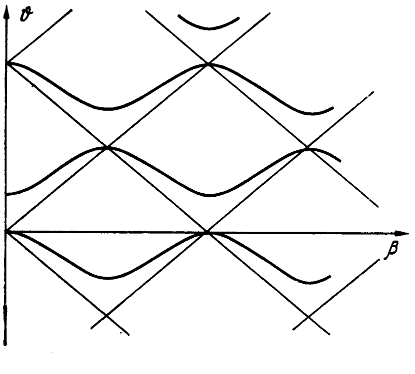

FIG. 2. The angle on the right side of quantization condition (33) as a function of the reduced electric field ($\varepsilon = 0.1$). Straight thin and heavy lines—hydrogen atom and lithium atom in the truncated-basis approximation.

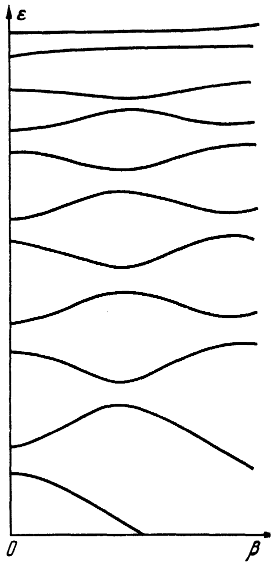

FIG. 3. Reduced Stark–Zeeman levels of the lithium atom versus the reduced electric field (truncated-basis approximation).

β dependence of the right side of (33) for $\varepsilon = 0.1$ for both signs in the definition of the angle ϑ. Shown here are limiting cases: the hydrogen limit (the grid of thin straight lines) and the approximation of a truncated basis (the heavy lines).

In the case of the hydrogen atom, the right side of (33) does not depend on the energy. The lines corresponding to different values of N and different signs in (32) cross under condition (1). As a result, we have the exponentially narrow quasicrossings which we have already mentioned. In the case of lithium, the existence of a quantum defect causes a pronounced broadening of the quasicrossings. In addition, the energy dependence of the right side of (33) has the consequence that the quasicrossings occur not exactly under condition (1) and not simultaneously for different pairs of levels. For highly excited shells, however, the shift of the quasicrossings along the β scale is negligible.

Under condition (1) we have $\vartheta = 0$ for one pair of quasicrossing levels and $\vartheta = \pm 2$ arctan Φ for the other. The meaning here is that one of the levels is not shifted with respect to the corresponding pair in the case of the hydrogen atom, while the other is shifted, by

$$\pm \frac{2 \operatorname{arcctg} \Phi}{n \partial S / \partial \varepsilon} \approx \pm \frac{\omega \operatorname{arcctg} \Phi}{\pi} .$$

Here ω is the classical frequency given by (26). This expression determines the distance between levels at the quasicrossings.

A comparison of the results found through the use of the quasiclassical quantization rule in (33) and a direct numerical solution of the perturbation-theory equations has demonstrated that the WKB approximation is highly accurate (at $n = 30$, the error does not exceed 10^{-4}). Figure 3 shows a plot of the terms calculated in the truncated-basis approximation. This diagram agrees satisfactorily with the experimental picture.[3] Estimates show that the differences can be explained for the most part in terms of a mixing of states from neighboring shells—a factor which we have ignored here.

5. CONCLUSION

Until a significant n mixing is observed, the splitting of the Rydberg levels in parallel external fields can be described highly accurately by the one-dimensional WKB approximation. The interaction of the electron with the core, which causes a marked change in the picture of the spectrum, is of a fundamentally nonclassical nature. In the discrete version of the WKB method which we are using, however, the incorporation of the core field reduces to a renormalization of the joining condition in the region of small angular momenta. As a result it becomes possible to explain the characteristic picture of oscillating Stark–Zeeman levels with broad quasicrossings which is typical of nonhydrogen atoms. The distances between levels at the quasicrossing points can be expressed analytically in terms of the quantum defects of the atom.

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