Doubly excited states of a two-electron atom. The quadrupole approximation

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A perturbation theory is constructed for the highly excited states of a two-electron atom under conditions when the multipole expansion of the interelectron potential is applicable. The new procedure is used to calculate the first nonzero correction, first found by Nikitin and Ostrovskiĭ, to the energy. This correction only partially lifts the Coulomb degeneracy. It is shown that, in the quadrupole approximation, the degeneracy is completely lifted, except for a specific twofold degeneracy (quasidegeneracy) for some of the states, which is lifted by nonperturbative quantum effects. The indicated quasidegeneracy for some of the states leads to the possibility of their exhibiting the linear Stark effect in weak fields. The effective quadrupole-approximation Hamiltonian, the semiclassical quantization of which yields the energy levels, is found.

1. INTRODUCTION

The doubly excited states of atoms have in recent years found numerous applications in most diverse areas of experimental physics and technology, primarily in isotope separation and fine frequency tuning of lasers. This has made the problem of a more accurate computation of the spectrum of doubly excited atoms a pressing one.

Below we shall be concerned with only those states in which the principal quantum numbers of the excited electrons are connected by the inequality $n \ll N$ (we shall henceforth call these electrons the inner and the outer electron). In this case the interelectron interaction potential $|R_\mu - r_\mu|^{-1}$ can be expanded in a series in powers of the ratio r/R of the distances of the inner and outer electrons from the nucleus, i.e., in a multipole series. The terms of the multipole series decrease rapidly (the 2^l-pole term V_l is of the order of n^{2l}/N^{2l+2}), which allows us to limit ourselves to only the first few terms.

In spite of the considerable number of papers devoted to the doubly excited states of atoms, no consistent theory has so far been constructed which allows us to compute the corrections to the spectrum in the quadrupole approximation (i.e., the corrections of order n^4/N^6). The need to achieve this accuracy in the computation of the spectrum is due to the fact that (as will be shown below) it is precisely in the n^4/N^6-order approximation that the degeneracy is completely lifted.

There are fundamental obstacles to the construction of a rigorous quantum perturbation theory for the doubly excited states, and this to a considerable extent limits what we can learn about the spectrum. Indeed, the unperturbed spectrum is imbedded in the continuum, so that the individual eigenvalues are not isolated (besides, they are multiply degenerate). When the perturbation (say, V_1) is switched on, the discrete spectrum dissolves in the continuum, so that there are, strictly speaking, no perturbed eigenvalues.

But at the physical level of rigor the problem of the spectrum is quite interesting, since, for example, the cross section for electron scattering by ions (with one excited electron) exhibits relatively narrow peaks corresponding to autoionizing states. In view of this various attempts have been made to compute the spectrum outside the bounds of quantum perturbation theory. In particular, Leopold and Percival and a number of other researchers[1–3] have developed a classical perturbation theory for the quadrupole approximation. But because of the fact that these authors constructed the perturbation theory only in first order, they did not find that contribution to the energy which is quadratic in the dipole term V_1, and which, as will be seen below, is comparable in order of magnitude to the contribution from the quadrupole term V_2.

The spectrum was computed within the framework of the dipole approximation in a series of papers[4–8] by Nikitin and Ostrovskiĭ. They also investigated the symmetry properties of the states. It follows from their results that, in the leading order n^2/N^4, the energy does not contain a correction due to the dipole term, and they computed the first nonzero correction, which is of order n^3/N^5, and which partially lifts the degeneracy (from the Coulomb multiplicity n^2N^2 down to the multiplicity $2(n-m)2L$, where m is the magnetic quantum number of the inner electron and L is the orbital angular momentum of the outer electron).

Our problem is to compute the correction to the spectrum in the next order n^4/N^6. This correction completely lifts the degeneracy in terms of the quantum numbers of the inner electron, leaving only 2Λ-fold degeneracy in terms of the component M of the total angular momentum Λ. For some of the states, however, there remains an additional twofold quasidegeneracy (see Sec. 4).

The approach developed by us is based on the perturbation theory for highly excited states. This theory was recently developed for systems with multiple classical degeneracy by Kazantsev and Pokrovskiĭ.[9] Following this theory, we shall consider the purely classical case, when not only the outer, but also the inner electron is highly excited, and has a large orbital angular momentum (i.e., when $n \gg 1$, $l \gg 1$). These conditions, together with the conditions $N \gg n$, $L \gg l$, guarantee the applicability of the classical perturbation theory for both the inner and outer electrons.

The requirement that $L \gg l \gg 1$ may at first glance appear to be artificial. But as has been shown by a number of auth-

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ors,[4,6,10] it is precisely such states that are stable against autoionization, and have an exponentially small decay probability. Therefore, it makes sense to formulate the spectrum problem precisely for such states.

Since such states cannot be obtained through optical excitation, the question of the methods of their production requires special examination. We indicate here one method that, from our point of view, is the most promising. It is described in detail in Ref. 11, and consists in the following. First a weak electric field is adiabatically applied to the atomic system. Then the field is suddenly rotated through 90°, and suddenly switched off after a Stark period has elapsed. As a result, the states with high principal quantum numbers acquire large orbital angular momenta.

We carry out the computations for an arbitrary effective atomiccore charge Z, limited only by the inequalities $1+n/N<Z<N/n$, which, together with the requirement that $L\gg l$, allow us to estimate the relative magnitudes of the various contributions to the correction to the energy in terms of only the ratio n/N of the principal quantum numbers (no additional small parameter arises).

2. CLASSICAL PERTURBATION THEORY IN THE CASE OF MULTIPLE DEGENERACY

Let us first formulate the perturbation theory for highly excited systems in the action-angle variables.[9,12] First of all, since Λ and M are integrals of the total Hamiltonian, the two angle variables, Φ_Λ and Φ_M, conjugate to them will not enter into the effective Hamiltonian (in any approximation). The phase Φ_M, moreover, is a constant, since the degeneracy in M is maintained. The phase w conjugate to n is the fastest angle variable, the corresponding frequency being equal to $\omega=Z^2/n^3$. The next fastest phase is the phase W conjugate to N; it varies with frequency $\Omega=(Z-1)^2/N^3$. The phases w and W correspond respectively to the inner- and outerelectron motions along unperturbed Coulomb orbits. The remaining action-angle variables pertain to the slow motions in the system (the variation of the orbit parameters).

As the action variables we choose the components of the Runge-Lenz vector $\mathbf{a}$ and the orbital angular momentum $\mathbf{l}$ of the inner electron along the total angular momentum $\mathbf{\Lambda}$ of the system, and as the angle variables we choose the variables canonically conjugate to these components:

$$k=\mathbf{a}\mathbf{\Lambda}/\Lambda\leftrightarrow\varphi,\quad m=\mathbf{l}\mathbf{\Lambda}/\Lambda\leftrightarrow\psi. \tag{1}$$

As will be shown below, $\mathbf{l}\cdot\mathbf{\Lambda}$ is also an invariant of the effective Hamiltonian for the quadrupole approximation, and therefore the phase ψ does not enter into this Hamiltonian.

As shown in Refs. 4–8, the first nonzero correction ε_2 to the energy is of the order of n^3/N^5. This part of the energy does not depend on the variable k. The correction ε_3 computed by us below is of the order of n^4/N^6. From this we obtain the estimates given below for the characteristic frequencies

$$\omega_m\sim\partial\varepsilon/\partial m\sim n^2/N^5,\quad \omega_k\sim\partial\varepsilon/\partial k\sim n^3/N^6$$

of the slow motions of the inner electron. These frequencies are much lower than the frequency, $\sim\partial V_1/\partial n\sim n/N^4$, obtained in the preceding approximation for the slow inner-electron motion. The frequency ω_k is of the same order as, while the frequency ω_m is significantly higher than, the libration frequency ω_L of the outer electron.

Thus, the following frequency hierarchy obtains:

$$\omega/\Omega\sim(N/n)^3,\ \Omega/\omega_m\sim(N/n)^2,\ \omega_m/\omega_k\sim(N/n)^1,\ \omega_k/\Omega_L\sim(N/n)^0. \tag{2}$$

From this it follows that the naive adiabatic approximation, in which the inner-electron terms are computed for a fixed position of the outer electron, is not valid. The reason for this is that the orbital motion of the outer electron is faster than the libratory motion of the inner electron. This is a characteristic feature of the Coulomb problem with threefold classical degeneracy of the frequencies (for the unperturbed Hamiltonian). The correct adiabatic approximation consists in the following: we shall, after carrying out the averaging over the fast orbital motions of the two electrons, consider the effective Hamiltonian describing the variation of the parameters of the inner electron's orbit for frozen outer-electron orbit parameters.

To construct the perturbation theory, we represent the Hamiltonian of the two-electron atom in the form of a sum of the unperturbed system's Hamiltonian (the noninteracting-electron approximation), to which we attribute the major part of the interelectron interaction $1/R$, and the perturbation potential V:

$$H=H_0+h_0+V,\quad H_0=\frac{P^2}{2}-\frac{Z-1}{R},\quad h_0=\frac{p^2}{2}-\frac{Z}{r}, \tag{3}$$

$$V(r_\mu,\ R_\nu)=1/|R_\mu-r_\mu|-1/R, \tag{4}$$

where r_μ, p_μ, R_μ, and P_μ are the coordinates and momenta of the electrons. Let us expand the perturbing potential in a multipole series

$$V=\sum_{l=1}^{\infty}V_l,$$

limiting ourselves to the dipole and quadrupole terms:

$$V_1=r_\mu\frac{R_\mu}{R^3},\quad V_2=r_\mu r_\nu\frac{3R_\mu R_\nu-\delta_{\mu\nu}R^2}{2R^5}. \tag{5}$$

The classical perturbation theory is based on the solution of the Hamilton-Jacobi equation by the iteration method. This equation in the action-angle variables has the following form:

$$H\equiv H_0\left(N+\frac{\partial S}{\partial W}\right)+h_0\left(n+\frac{\partial S}{\partial w}\right)$$
$$+V\left(N+\frac{\partial S}{\partial W},n+\frac{\partial S}{\partial w},\Lambda,k+\frac{\partial S}{\partial\varphi},m\,|\,W,w,\varphi\right)=E \tag{6}$$

(the Hamiltonian depends on five action and three angle variables).

We shall seek the expressions for the action S and the energy E in the form of series in powers of n/N:

$$S=\sum_{j=1}^{\infty}S_j,\quad E=E_0+\sum_{j=1}^{\infty}\varepsilon_j,\quad E_0=-\frac{Z^2}{2n^2}-\frac{(Z-1)^2}{2N^2}. \tag{7}$$

The correction ε_j is of the order of n^{j+1}/N^{j+3}. We shall seek the solution for S_j by the method of approximate separation of the variables:

$$S_j(W,\ w)=S_j(W)+s_j(w|W), \tag{8}$$

where $S_j(W)$ is the action's slowly oscillating part, which depends only on W, while $s_j(w|W)$ is the rapidly oscillating part, which depends largely on w and weakly on W. Let us demonstrate the method of solving Eq. (6) by carrying out the first iteration. The subsequent iterations can be carried out in much the same way. For the first iteration, it is sufficient to limit ourselves in the potential V to the dipole term. We obtain the following equation:

$$H_1=\Omega\frac{\partial S_1}{\partial W}+\omega\frac{\partial s_1}{\partial w}+V_1(N,n,\Lambda,k,m|W,w,\varphi)=\varepsilon_1. \tag{9}$$

Let us introduce a notation for the average over the phase w:

$$\langle V\rangle_w\equiv\frac{1}{2\pi}\int_0^{2\pi}V\,dw$$

and one for the part that oscillates with varying w: $V^w\equiv V-\langle V\rangle_w$ (and similarly for W).

To carry out the subsequent calculations, we must introduce Coulomb parametrizations of the coordinates and momenta of the electrons:

$$r_\mu=\frac{n}{Za}[(n\cos\xi-a)a_\mu+\sin\xi\varepsilon_{\mu\nu\lambda}l_\nu a_\lambda],$$

$$p_\mu=\frac{Z}{an(n-a\cos\xi)}(-n\sin\xi a_\mu+\cos\xi\varepsilon_{\mu\nu\lambda}l_\nu a_\lambda),$$

$$R_\mu=\frac{N}{(Z-1)A}[(N\cos\Xi-A)A_\mu+\sin\Xi\varepsilon_{\mu\nu\lambda}L_\nu A_\lambda],$$

$$P_\mu=\frac{Z-1}{AN(N-A\cos\Xi)}(-N\sin\Xi A_\mu+\cos\Xi\varepsilon_{\mu\nu\lambda}L_\nu A_\lambda),$$

where ξ and Ξ are the eccentric anomalies of the inner and outer electrons and $\varepsilon_{\mu\nu\lambda}$ is the completely antisymmetric tensor. Let us average (9) over w. Then the term containing s_1 vanishes, and we obtain the equation

$$\Omega\frac{\partial S_1}{\partial W}+\langle V_1\rangle_w=\varepsilon_1. \tag{9'}$$

Averaging (9') over W, we find

$$\varepsilon_1=\langle\langle V_1\rangle_w\rangle_W=0 \tag{10}$$

(the average over W is equal to zero since it is proportional to the average force exerted on the outer electron by the nucleus). Thus, there is no correction of order n^2/N^4 to the energy.

Separating out in (9') the W-oscillating part, we find

$$S_1(W)=-\frac{1}{\Omega}\int^W\langle V_1\rangle_w{}^W dW'. \tag{11}$$

A simple calculation yields

$$S_1=\frac{\hat a_\mu P_\mu}{(Z-1)},\quad \hat a_\mu\equiv-\frac{3n}{2Z}a_\mu. \tag{12}$$

The quantity S_1 is of the order of n^2/N. Separating out in Eq. (9) the w-oscillating part (the rapid oscillations), we obtain in similar fashion

$$s_1(w|W)=-\frac{1}{\omega}\int^w V_1{}^w dw'. \tag{13}$$

From the calculations we find

$$s_1=\frac{n^2}{2Z^2}\left(2p_\mu r^2-r_\mu r_\lambda p_\lambda+\frac{5}{2Z}n\varepsilon_{\mu\nu\lambda}l_\nu a_\lambda\right)\frac{R_\mu}{R^3}. \tag{14}$$

The rapidly oscillating part s_1 of the action is of order (n^5/N^4) of magnitude significantly lower than that of S_1.

The first nonzero correction (of order n^3/N^5) to the energy is given by the second iteration. This correction is quadratic in the dipole term, and has the form

$$\varepsilon_2^{dd}=\left\langle\frac{\partial\overline{V}_1}{\partial k}\frac{\partial S_1}{\partial\varphi}\right\rangle_w, \tag{15}$$

where we have introduced the notation $V_1\equiv\langle V_1\rangle_w$. The correction ε_2^{dd} can be represented in the form of a Poisson bracket averaged over the variables of the inner electron:

$$\varepsilon_2^{dd}={}^1/_2\langle\{\overline{V}_1,\ S_1\}_{in}\rangle_W. \tag{15'}$$

Evaluating the Poisson bracket in terms of the coordinate-momentum variables (which is much simpler than the direct evaluation in terms of the action-angle variables), we find

$$\varepsilon_2^{dd}=-\frac{1}{2}\left(\frac{3n}{2Z}\right)^2(\mathrm{lL})\frac{(Z-1)^2}{N^3L^3}. \tag{15''}$$

To obtain the final expression, we must go over in (15'') from L_μ to Λ_μ, since in the order n^4/N^6 (which is of interest to us) L_μ is not conserved.

This correction, which was first found by Nikitin and Ostrovskiĭ by an entirely different method,[4-8] effects a partial lifting of the degeneracy. But there still remains substantial—$2(n-m)(2L)$–fold—degeneracy, which is lifted by the next-order corrections to the energy. (There remains only the trivial 2Λ–fold degeneracy and, for some of the states, a twofold degeneracy.)

3. COMPUTATION OF THE CORRECTION TO THE ENERGY IN THE QUADRUPOLE APPROXIMATION

The correction ε_3, which is of the order of n^4/N^6, to the effective Hamiltonian corresponds to the quadrupole approximation, and is made up of three terms: the first order in the quadrupole interaction and the second and third orders in the dipole interaction.

The contribution to the effective Hamiltonian from the quadruple term is obtained by carrying out the following elementary averaging:

$$\varepsilon_3{}^q=\langle\langle V_2\rangle_w\rangle_W=\langle r_\mu r_\nu\rangle_w\left\langle\frac{3R_\mu R_\nu-\delta_{\mu\nu}R^2}{2R^5}\right\rangle_W$$

$$=-\frac{3}{2}\left(\frac{n}{2Z}\right)^2\frac{(Z-1)^3}{N^3L^3}\left(\frac{5(\mathbf{aL})^2}{L^2}-\frac{(\mathrm{lL})^2}{L^2}-2a^2+\frac{n^2}{3}\right). \tag{16}$$

The computation of the higher-order contributions from the dipole term, which are of the same order of magnitude as n^4/N^6, is significantly more complicated. The correction that is quadratic in the dipole term assumes, after a number of transformations, a form similar to that of the formula (15), with the difference that the Poisson bracket is averaged over the variables of the outer electron:

$$\varepsilon_3{}^{dd}={}^1/_2\langle\{\overline{V}_1S_1\}_{ext}\rangle_W. \tag{17}$$

The calculation yields

$$\varepsilon_3^{dd}=\frac{1}{2}\hat{a}_\mu\hat{a}_\nu\left\langle\left\{\frac{R_\mu}{R^3},\frac{P_\nu}{(Z-1)}\right\}_{ext}\right\rangle_w$$
$$=-\frac{1}{4}\left(\frac{3n}{2Z}\right)^2\frac{(Z-1)^2}{N^3L^3}\left(\frac{3(\mathbf{aL})^2}{L^2}-a^2\right). \quad (18)$$

The correction of third order in the dipole term has the form

$$\varepsilon_3^{ddd}=\left\langle\frac{\partial\overline{V}_1}{\partial k}\frac{\partial S_2}{\partial\varphi}\right\rangle_w+\frac{1}{2}\left\langle\frac{\partial^2\overline{V}_1}{\partial k^2}\left(\frac{\partial S_1}{\partial\varphi}\right)^2\right\rangle_w, \quad (19)$$

where S_2 is given by the expression

$$S_2=-\frac{1}{\Omega}\int^W\left(\frac{\partial\overline{V}_1}{\partial k}\frac{\partial S_1}{\partial\varphi}-\varepsilon_2^{dd}\right)dW'. \quad (20)$$

Here ε_2 is given by the formula (15″), and the expression for S_1 is taken from (11). The quantity S_2 is of the order of n^3/N^2.

The expression for the correction of third order in the dipole term can be represented in the form of a double Poisson bracket:

$$\varepsilon_3^{ddd}=\frac{1}{3}\langle\{\{\overline{V}_1,S_1\}_{int},S_1\}_{int}\rangle_W. \quad (21)$$

The calculation yields

$$\varepsilon_3^{ddd}=\frac{1}{3}\{\hat{a}_\nu,\{\hat{a}_\lambda,\hat{a}_\mu\}\}\left\langle\frac{R_\mu}{R^3}\frac{P_\nu P_\lambda}{(Z-1)^2}\right\rangle_w \quad (22)$$
$$=-\left(\frac{3n}{2Z}\right)^3(Z-1)^2\frac{\mathbf{aA}}{4N^4L^3}.$$

The correction ε_3^{ddd}, (22), to the effective Hamiltonian does not, in the order under consideration by us, make a contribution to the energy, the result of its addition to ε_2^{dd}, (15″), amounting to a slight redefinition of the quantum numbers k and m.

In the formulas obtained, we must go over from the orbital angular momentum L_μ of the outer electron to the total angular momentum Λ_μ. This is due to the fact that the action variables of the inner electron should be defined as the components of the Runge-Lenz vector and the orbital angular momentum of this electron along the system's total angular momentum vector, and not along the time-varying outer electron's orbital angular momentum vector. We shall indicate the corrections obtained as a result of such a transition by a tilde.

As a result of this transition, the correction ε_2^{dd} makes a contribution to $\tilde{\varepsilon}_3^{dd}$:

$$\varepsilon_2^{dd}\to\tilde{\varepsilon}_2^{dd}+\delta\tilde{\varepsilon}_3^{dd}.$$

For the accuracy required by us, it is sufficient to simply replace L_μ by Λ_μ in the correction of first order in the quadrupole term and in the correction of second order in the dipole term. Thus, the expression for the effective Hamiltonian in the quadrupole approximation has the form

$$\mathcal{H}_3=-\frac{Z^2}{2n^2}-\frac{(Z-1)^2}{2N^2}+\tilde{\varepsilon}_2+\tilde{\varepsilon}_3\equiv H_0+h_0+\mathcal{H}_{eff}. \quad (23)$$

Let us give the final formulas:

$$\tilde{\varepsilon}_2=-\frac{9(Z-1)^2}{8Z^2}\frac{n^2}{N^3}\frac{\mathbf{l\Lambda}}{\Lambda^3}, \quad (24)$$

$$\tilde{\varepsilon}_3=-\frac{3n^2(Z-1)^2}{16Z^2N^3\Lambda^5}\Big[(9+10(Z-1))(\mathbf{a\Lambda})^2$$
$$+(18-2(Z-1))(\mathbf{l\Lambda})^2$$
$$+(3-4(Z-1))a^2\Lambda^2-\left(6-\frac{2}{3}(Z-1)\right)n^2\Lambda^2\Big]. \quad (25)$$

The expression for the part $\tilde{\varepsilon}_3$ of the effective Hamiltonian is the new result. As has been shown by Solov'ev,[13] a Hamiltonian of similar form (with different coefficients) arises in the problem of the Rydberg atom in a magnetic field. In our problem the total angular momentum plays the same role as the external magnetic field in the above-cited paper.

4. SEMICLASSICAL QUANTIZATION OF THE EFFECTIVE HAMILTONIAN. THE DENSITY OF STATES

The effective Hamiltonian $\mathcal{H}_{\text{eff}}=\tilde{\varepsilon}_2+\tilde{\varepsilon}_3$ found in the preceding section has $\mathbf{l}\cdot\mathbf{\Lambda}$ as an invariant, and this makes its quantization within the framework of the semiclassical approximation possible. Using the definition (1) of the action variables (i.e., of the quantum numbers) k and m, as well as the semiclassical formula for a^2:

$$a^2=\frac{1}{2}(n^2+k^2-m^2+q^2\cos 2\varphi),$$
$$q^2=(k^4-2k^2(n^2+m^2)+(n^2-m^2)^2)^{1/2}, \quad (26)$$

we obtain the following semiclassical expression for the effective Hamiltonian:

$$\mathcal{H}_{eff}(N,n,\Lambda,k,m|\varphi)=\tilde{\varepsilon}_2(m)+\tilde{\varepsilon}_3(m,k|\varphi), \quad (27)$$
$$\tilde{\varepsilon}_2=-\frac{9(Z-1)^2}{8Z^2}\frac{n^2m}{N^3\Lambda^2},$$
$$\tilde{\varepsilon}_3=-\frac{3n^2(Z-1)^2}{32Z^2N^3\Lambda^3}\Big[(21+16(Z-1))k^2+33m^2$$
$$+(3-4(Z-1))q^2\cos 2\varphi$$
$$-\left(9+\frac{8}{3}(Z-1)\right)n^2\Big]. \quad (28)$$

The effective Hamiltonian does not, in accordance with the fact that m is an adiabatic invariant, depend on the phase ψ conjugate to m. This allows us to reduce the problem of the semiclassical quantization of this Hamiltonian to a one-dimensional problem for any fixed m. To solve this problem, let us separate out the k- and φ-dependent part of the Hamiltonian:

$$\tilde{\varepsilon}=c(\varkappa k^2+q^2\cos 2\varphi), \quad (29)$$
$$c=\frac{3(4(Z-1)-3)(Z-1)^2}{32Z^2}\frac{n^2}{N^3\Lambda^3},\quad \varkappa=\frac{21+16(Z-1)}{3-4(Z-1)}.$$

A similar Hamiltonian arises in the problem of the Rydberg atom in a magnetic field, as was first shown by Solov'ev.[13] Its spectrum is investigated in detail in Refs. 9, 14, and 15. In view of this, we shall not dwell on its quantization, limiting ourselves to the listing of the results. The energy levels are determined from the Bohr-Sommerfeld quantization rule:

$$\int_{k_1}^{k_2}\varphi\,dk=s\pi+k_2\varphi(k_2)-k_1\varphi(k_1). \tag{30}$$

Here s is a new action variable (quantum number), k_1 and k_2 are the turning points, and $\varphi(k)$ is found from (29), where $\tilde{\varepsilon}$ should in the process be regarded as a parameter. The most computationally convenient characteristic is the density of states $\rho(\tilde{\varepsilon})\equiv\partial s/\partial\tilde{\varepsilon}$. The general formula for it is the following:

$$\rho(\tilde{\varepsilon})=\frac{1}{\pi}\int_{k_1}^{k_2}\frac{dk}{|\partial\tilde{\varepsilon}/\partial\varphi|}=\frac{1}{2\pi|c|}\int_{k_1}^{k_2}\frac{dk}{[q^4-(\tilde{\varepsilon}/c-\varkappa k^2)^2]^{1/2}}. \tag{31}$$

The classically admissible region of motion is bounded by two curves, which are the loci of the turning points:

$$\tilde{\varepsilon}_{\pm}=c(\varkappa k^2\pm q^2). \tag{32}$$

There exists a unique value of Z (equal to 7/4) at which the classically allowed region in the plane of the variables k and $\tilde{\varepsilon}$ degenerates into a curve as a result of the vanishing of the coefficient of $\cos 2\varphi$ in the effective Hamiltonian. At this value of Z the classical quantization degenerates into the trivial identity $s\equiv k$.

The coincidence of the "correct" action variable s with the original variable k is approximately realized in the vicinity of the point $Z=7/4$. For the He atom ($Z=2$) the deviation of s from k can, in a sense, be considered to be insignificant for the majority of the states, since the classically allowed region is very narrow.

The roots of the denominator in the formula (31) can be disposed in two different ways: the first case (I) corresponds to two real and two complex conjugate roots ($k_-^2<0<k_+^2$); in the second case (II) all the four roots are real ($0<k_-^2<k_+^2$). Let us give the explicit form of the roots:

$$k_{\pm}^2=\left[\frac{\tilde{\varepsilon}}{c}\varkappa-n^2-m^2\pm D^{1/2}\right](\varkappa^2-1)^{-1},$$

$$D=4n^2m^2-\frac{2\tilde{\varepsilon}}{c}\varkappa(n^2+m^2)+\varkappa^2(n^2-m^2)^2+\left(\frac{\tilde{\varepsilon}}{c}\right)^2.$$

The case I is realized at all $\tilde{\varepsilon}$ for $m>m_c$, as well as at $\tilde{\varepsilon}>\tilde{\varepsilon}_c$ for $m<m_c$. Here

$$\tilde{\varepsilon}_c=|c|(n^2-m^2),\quad m_c=(|\varkappa|-1)^{1/2}(|\varkappa|+1)^{-1/2}n.$$

The case II is realized at $\tilde{\varepsilon}<\tilde{\varepsilon}_c$ for $m<m_c$. In the case I the trajectories are symmetric and the states are nondegenerate, while in the case II the trajectories are concentrated in the region $k>0$, or in the region $k<0$, and the corresponding states are doubly degenerate (here we ignore the quantum tunneling effect (which lifts the degeneracy) in view of the fact that it is exponentially small everywhere except in a small neighborhood of the point $\tilde{\varepsilon}_c$). Because of the fact that $\varkappa$ for $Z=2$ is large (equal to 37), in the He case $m_c=(18/19)^{1/2}n\approx n$, and the doubly degenerate states constitute a significant fraction of the states at virtually all values of m. At $m=0$ this fraction is approximately equal to 6/7.

In conclusion of this section, let us give the formulas for the density of states. In the case I

$$\rho(\tilde{\varepsilon})=\frac{1}{\pi|c|}\frac{1}{(k_+^2+|k_-|^2)^{1/2}}K\left[\frac{k_+}{(k_+^2+|k_-|^2)^{1/2}}\right]. \tag{33}$$

In the case II

$$\rho(\tilde{\varepsilon})=\frac{1}{\pi|c|k_+}K\left[\frac{(k_+^2-k_-^2)^{1/2}}{k_+}\right], \tag{34}$$

where $K(k)$ is the complete elliptic integral of the first kind. Notice the logarithmic singularity in the density of states for $m<m_c$ at the point $\tilde{\varepsilon}=\tilde{\varepsilon}_c=|c|(n^2-m^2)$. The presence of a specific twofold quasidegeneracy makes possible the observation of the linear Stark effect, to which the following section is devoted.

5. POLARIZABILITY IN A WEAK ELECTRIC FIELD

As noted above, a significant fraction of the trajectories are k-symmetric, to which fact corresponds the twofold degeneracy in the energy of the corresponding states. In a sufficiently weak electric field we can, as a result of the existence of symmetric inner-electron states, detect the linear Stark effect in a background of the quadratic effect (due largely to the outer electron), which is of the order of $\mathscr{E}^2N^6$. The set of quantum numbers chosen by us corresponds to a basis in which the components a_μ and l_μ along Λ_μ simultaneously have definite values. The averages of the operators r_λ and $-(3n/2Z)a_\mu\Lambda_\mu\Lambda_\lambda/\Lambda^2$ over the states $|nN\Lambda Mms\rangle$ are equal.

The energy shift in a weak electric field $\mathscr{E}_\mu$ is found from the formula

$$\delta_{\mathscr{E}}\varepsilon=-\frac{3n}{2Z\Lambda^2}\langle a_\mu\rangle_\chi\Lambda_\mu\Lambda_\nu\mathscr{E}_\nu. \tag{35}$$

In a state with a definite component of the total angular momentum Λ_ν along the axis $\mathscr{E}_\nu$, specifically, in a state with $M=\Lambda_\nu\mathscr{E}_\nu/\mathscr{E}$, the dipole moment is equal to

$$d=\frac{3n}{2Z\Lambda^2}\langle a_\mu\rangle_\chi\Lambda_\mu M=\frac{3n}{2Z\Lambda}\langle k\rangle_\chi M. \tag{36}$$

Here the averaging is over the phase χ:

$$\langle k\rangle_\chi\equiv\frac{1}{2\pi}\int_0^{2\pi}kd\chi=\frac{\omega_k}{2\pi}\int\frac{kdk}{|\partial\tilde{\varepsilon}/\partial\varphi|},$$

where $\omega_k=1/\rho(\tilde{\varepsilon})$ is the frequency with which the parameters of the inner-electron orbit vary as a result of the action of only the part $\tilde{\varepsilon}(k,\varphi)$ of the effective Hamiltonian.

The computation of the average $\langle k\rangle_\chi$ is elementary. As a result we find

$$d=\frac{3}{8Z\rho(\tilde{\varepsilon})|c|(\varkappa^2-1)^{1/2}}\frac{nM}{\Lambda}. \tag{37}$$

It can be seen from this formula that the polarizability is inversely proportional to the density of states $\rho(\tilde{\varepsilon})$. The linear Stark effect predicted by us pertains to electric fields in the range

$$n^5/N^7\ll n^2\mathscr{E}\ll n^4/N^6, \tag{38}$$

and is stronger than the quadratic effect involving the outer electron. The quadratic Stark effect, which is $\propto\mathscr{E}^2N^6$, is stronger than the linear effect in the following range of electric field intensities:

$$n^3/N^5\gg n^2\mathscr{E}\gg n^4/N^6 \tag{39}$$

and is comparable to it when $n^2\mathscr{E} \sim n^4/N^6$. In the strongest fields, i.e., when $n^2\mathscr{E} \gtrsim n^3/N^5$, the linear Stark effect again predominates. It should be noted that the linear Stark effect for doubly excited atoms was predicted by Nikitin and Ostrovskiĭ[4-8] on the basis of a dipole-approximation analysis. The effect predicted by them pertains to fields in the range (39), in which the quadratic Stark effect involving the outer electron is significantly stronger than the linear effect involving the inner electron. The linear Stark effect in the intensity range (39) occurs in all the states, whereas the case investigated by us extends to the region (38) of significantly weaker fields, and occurs in approximately three fourths of the states.

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