Perturbation theory for highly-excited states

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The quasiclassical perturbation theory is considered for the discrete spectrum when the variables can be separated in the unperturbed system. The analysis is largely confined to classically degenerate systems. Approximate wave functions, energy levels, and matrix elements of physical quantities are found. Highly-excited states of the hydrogen atom in a magnetic field are examined as a specific application of the theory. The density of states and the polarizability of this system are investigated in the case where the classical perturbation theory is valid. It is shown that the hydrogen atom exhibits paraelectric properties in the longitudinal direction and dielectric properties in the transverse direction.

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The procedure involving averaging over fast variables is well known in classical mechanics. It is used when the unperturbed system has separable variables. The general classical perturbation theory was developed by Born and Pauli[1] with allowance for degeneracy in frequency. When a system is classically nondegenerate, the action variables of the unperturbed Hamiltonian are adiabatic invariants, i.e., they are approximately conserved when the perturbation is turned on (see, for example, Ref. 2). In the case of degeneracy, not all the action variables are adiabatic invariants, and some of them vary slowly. The conjugate angle variables are also slowly varying. If we average the Hamiltonian over the fast angle variables, we obtain the Hamiltonian in the slow variables, i.e., the problem is reduced. A rigorous justification of the averaging procedure has been given by Bogolyubov and Mitropol'skiĭ.[3]

The present paper is devoted to the development of a perturbation theory for highly-excited quantum-mechanical states in the discrete spectrum. Classically degenerate systems will be of primary interest. Approximate wave functions, energy levels, and matrix elements of physical quantities will be found.

The Rydberg atom in an external field is the most interesting object to which general methods can be applied. Highly-excited atoms with $n \sim 30$–50 in an external magnetic field (quadratic Zeeman effect) have been investigated experimentally and theoretically by Zimmerman *et al.*[4,5] and Delande and Gay.[6] They found that variation of the magnetic field was accompanied by the quasicrossing of levels, but level repulsion was very small and decreased with increasing n. Additional symmetry was therefore proposed for the problem.[4–6] Solov'ev[7] applied classical perturbation theory to the problem and found a new adiabatic invariant and the energy levels. The spectrum of the hydrogen atom with allowance for the quadratic Zeeman effect was subsequently investigated by various methods by Herrick,[8] Bergou *et al.*,[9] [1)] and Delos *et al.*[12] Bergou *et al.*[9] noted the absence of the linear Stark effects for all states except for roughly one-third of states with $m/n < 1/\sqrt{5}$.

However, the wave functions of the new states and their physical characteristics were not determined. It will be shown below that the average potential energy of the perturbation is a new constant of motion, and expressions will be found for the quasiclassical wave functions and polarizabilities of states.

1. FORMULATION OF THE PROBLEM. ONE-DIMENSIONAL CASE

We shall take the Hamiltonian for the system in the form of the sum

$$H=H_0+V, \tag{1}$$

where the variables in H_0 are separable and V is small in comparison with H_0. Let us introduce the action and angle variables for the Hamiltonian H_0. They will be denoted by $n_1, n_2, \dots, n_s$ and $w_1, w_2, \dots, w_s$. The wave functions $\psi_{n_1,n_2,\dots,n_s}$ corresponding to integers $n_1, n_2, \dots, n_s$ have the simple form

$$\psi_{\mathbf{n}}=(2\pi)^{-s/2}e^{i\mathbf{n}\mathbf{w}}; \quad \mathbf{n}=n_1, n_2, \dots, n_s, \quad \mathbf{w}=w_1, w_2, \dots, w_s. \tag{2}$$

The Schrödinger equation is then conveniently written in the n-representation:

$$(E-E_{\mathbf{n}}^{(0)})c_{\mathbf{n}}=\sum_{\mathbf{n}'} V_{\mathbf{n}}^{\mathbf{n}'} c_{\mathbf{n}'}, \tag{3}$$

where $V_n^{n'}$ are the matrix elements of the perturbation, c_n are the amplitudes of the corresponding states, and $E_n^{(0)}$ are the energy levels of the Hamiltonian H_0.

For highly-excited states in which all the quantum numbers n_i are large, the perturbation matrix elements are equal to the Fourier components of the classical potential to within $1/n$:

$$V_{\mathbf{n}}^{\mathbf{n}'}=\frac{1}{(2\pi)^s}\int V(w)e^{i\mathbf{v}\mathbf{w}}\,dw, \tag{4}$$

where $\nu_i = n_i - n_i'$. It is implied that the function V is expressed in terms of the action and angle variables. We shall now develop a method for finding the amplitudes c_n when $V \ll E$.

We begin with a simple one-dimensional case. We shall suppose that the state is a wave packet in n-space with its center at n_0. We now introduce the new variable $\nu = n - n_0$ and write c_ν instead of $c_{n_0+\nu}$ assuming that $\nu \ll n_0$. Equation (3) then assumes the much simpler form

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$$\sum_{\nu'} V_{\nu-\nu'} c_{\nu'} = (\varepsilon - \omega\nu) c_\nu; \qquad \varepsilon = E - E_n^{(0)}, \tag{5}$$

where $\omega = \partial E_n^{(0)}/\partial n$ is the frequency of the classical motion. To solve (5), it is convenient to use the w-representation in which (5) assumes the form

$$V(w)\psi(w) = \left(\varepsilon + i\omega\frac{d}{dw}\right)\psi(w); \qquad \psi(w) = \sum_\nu c_\nu e^{i\nu w}. \tag{6}$$

This has the following elementary solution:

$$\psi(w) = \psi(0)\exp\left\{-\frac{i}{\omega}\int_0^w [V(w') - \varepsilon]\, dw'\right\}. \tag{7}$$

By definition, $\psi(w)$ is a periodic function of w with period 2π. The periodicity condition imposes a restriction on the possible values of ε:

$$\varepsilon = \langle V\rangle_w + l\omega,$$

where the angle brackets indicate averaging over w and l is an arbitrary integer that can be set equal to zero, since the choice of the center of the packet, n_0, is arbitrary. The amplitudes c_ν can be found with the aid of the inverse Fourier transformation

$$c_\nu = \frac{\psi(0)}{2\pi}\int_0^{2\pi}\exp\left[-\frac{i}{\omega}\int_0^w \tilde V(w')\, dw' - i\nu w\right] dw;$$

$$\tilde V(w) = V(w) - \langle V\rangle_w. \tag{8}$$

This expression for the amplitudes c_ν and the expression for the energy

$$\varepsilon = \langle V(w)\rangle \equiv V_{n_0}{}^{n_0} \tag{9}$$

together provide the complete solution of the above problem in the one-dimensional case. It is natural to normalize the amplitude c_ν so that the sum of the squares of its moduli is equal to unity. By Parseval's theorem,

$$\sum_\nu |c_\nu|^2 = \frac{1}{2\pi}\int_0^{2\pi} |\psi(w)|^2\, dw = |\psi(0)|^2.$$

We shall assume henceforth that $\psi(0) = 1$.

We now note that the energy ε is determined by the average value of the classical perturbation or, in other words, by the diagonal matrix element, whatever the value of the perturbation-theory parameter V/ω, provided $V \ll n_0\omega \sim E$. This result is in agreement with the corresponding note in Landau and Lifshitz.[10]

It is instructive to consider how all the perturbation-theory approximations for the energy tend to zero except the first. We begin with the second approximation:

$$\delta\varepsilon^{(2)} = \sum_n{}' \frac{|V_{n_0}{}^n|^2}{E_{n_0}^{(0)} - E_n^{(0)}} \cong \sum_\nu{}' \frac{|V_\nu|^2}{\nu\omega}. \tag{10}$$

The numerator in this expression is an even function of ν, whereas the denominator is an odd function of this variable. This ensures that the sum tends to zero to within terms $O(V/E)$. The same argument is valid for any term of even order. To see how terms of odd order tend to zero, let us consider the third-order contribution

$$\delta\varepsilon^{(3)} = \sum_{n_1,n_2}{}'' \frac{V_{n_0}^{n_1} V_{n_1}^{n_2} V_{n_2}^{n_0}}{(E_{n_0}^{(0)} - E_{n_1}^{(0)})(E_{n_0}^{(0)} - E_{n_2}^{(0)})} \cong -\sum_{\nu_1,\nu_2}{}'' \frac{V_{\nu_1} V_{\nu_2} V_{-\nu_1-\nu_2}}{\nu_1\nu_2\omega^2}. \tag{11}$$

The sum in this expression has the form of a contraction and can therefore be written in the form of an integral with respect to w:

$$\delta\varepsilon^{(3)} = \frac{1}{2\pi\omega^2}\int_0^{2\pi}\left[\int_0^w \tilde V(w')\, dw'\right]^2 \tilde V(w)\, dw. \tag{12}$$

The integrand in this expression is the total derivative of a periodic function. The integral is therefore equal to zero.

These considerations do not, of course, apply to the amplitudes c_ν, which depend essentially on the perturbation theory parameter V/ω. In the limiting case where $V/\omega \ll 1$, the equation given by (8) yields the results of quantum perturbation theory, whereas, for $V/\omega \gg 1$, we obtain a wave packet of width[2)]

$$\Delta\nu = (V_{max} - V_{min})/\omega. \tag{13}$$

Let us now find the next correction to the energy level. There are two sources of correction of this kind. Firstly, we must take into account the quadratic terms in the expansion for the energy $E_{n_0+\nu}^{(0)}$ in powers of ν. Secondly, we must take into account the fact that n and w do not commute in the perturbation energy.

The general form of the Hermitian operator $V(w,\hat n)$ that is a periodic function of w with period 2π is:

$$V(w,\hat n) = \sum_{k=-\infty}^{\infty} e^{ikw} V_k(\hat n + k/2), \qquad V_{-k} = V_k^+.$$

The matrix elements of this operator are given by the following expression to within $1/n$:

$$V_{n_0+\nu}^{n_0+\nu'} \cong V_{\nu'-\nu}(n_0) + \frac{\nu+\nu'}{2}\frac{\partial}{\partial n}[V_{\nu'-\nu}(n)]\big|_{n=n_0}.$$

The corrected equation for $\psi(w)$ is

$$V(w,n)\psi(w) + \frac{1}{i}\frac{\partial}{\partial w}\left[\frac{\partial V}{\partial n}\psi\right] - \frac{1}{2i}\frac{\partial^2 V}{\partial w\,\partial n}\psi$$

$$= \left(\varepsilon + i\omega\frac{\partial}{\partial w} + \frac{1}{2}\frac{d\omega}{dn}\frac{\partial^2}{\partial w^2}\right)\psi.$$

We now seek ψ in the form $\psi = \psi_0 e^{i\chi}$, where ψ_0 is the solution of the zeroth approximation, given by (7). For χ, we obtain the equation

$$\omega\chi = \frac{1}{2}\frac{\partial}{\partial n}\int \frac{\tilde V^2 - \langle V^2\rangle_w}{\omega}\, dw + \frac{1}{\omega}\frac{\partial\langle V\rangle_w}{\partial n}\int \tilde V\, dw + \frac{i}{2}\frac{\partial\tilde V}{\partial n}, \tag{14}$$

and the energy correction is

$$\delta\varepsilon = -\frac{\partial}{\partial n}\left[\frac{\langle\tilde V^2\rangle_w}{2\omega}\right]. \tag{15}$$

All the terms in (14) are small in comparison with the phase $\psi_0(w)$ [see Eq. (7)]. Moreover, the last two terms are of the order of the quantities $V/n\omega \sim V/E \ll 1$ and are therefore unimportant. The first term is of the order of $V^2/n\omega^2$ and, in general, it is not small but changes only the phase of the wave function. Thus, only the quadratic correction to the energy turns out to be important.

2. MULTIDIMENSIONAL SYSTEMS IN THE NONDEGENERATE CASE

We now examine the case of a classically nondegenerate system. This means that the frequency ratios are irrational numbers. For simplicity, we confine our attention to the case of two degrees of freedom because the more general situation does not introduce anything essentially new. The Schrödinger equation, obtained under the same assumptions as before, has the form

$$\sum V_{\nu_1-\nu_1',\nu_2-\nu_2'}c_{\nu_1'\nu_2'}=(\varepsilon-\nu_1\omega_1-\nu_2\omega_2)\,c_{\nu_1\nu_2}. \qquad (16)$$

Transforming from the amplitudes $c_{v_1v_2}$ to their Fourier transforms $\psi(w_1,w_2)$, we obtain

$$V(w_1, w_2)\psi(w_1, w_2)=\left(\varepsilon+i\omega_1\frac{\partial}{\partial w_1}+i\omega_2\frac{\partial}{\partial w_2}\right)\psi(w_1, w_2). \qquad (17)$$

We shall seek the function $\psi(w_1,w_2)$ in the form

$$\psi(w_1, w_2)=\exp\,[iS(w_1, w_2)].$$

The equation for S that ensues from (17) is

$$\omega_1\frac{\partial S}{\partial w_1}+\omega_2\frac{\partial S}{\partial w_2}=\varepsilon-V(w_1, w_2). \qquad (18)$$

The function $\psi(w_1,w_2)$ is a period function of its arguments with period 2π. When any of the arguments w_i changes by 2π, the function $S(w_1,w_2)$ can only change by $2\pi l_i$, where l_i is an integer. The number l_i can be set equal to zero, as before, by suitably choosing the center of the packet $n_1{}^0,n_2{}^0$. The left-hand side of (18) is then a periodic function with zero mean. The right-hand side should have the same properties. Consequently,

$$\varepsilon=\langle V(w_1, w_2)\rangle_{w_1, w_2}. \qquad (19)$$

As in the previous case, this first approximation of quantum perturbation theory is valid when the condition $V\ll E$ for the validity of the classical perturbation theory is satisfied.

The solution of (18) that is identical with the result of the classical perturbation theory for the action S (see, for example, Ref. 1) is

$$S_0=\sum{}'\frac{V_{\nu_1\nu_2}}{\nu_1\omega_1+\nu_2\omega_2}\exp[i(\nu_1w_1+\nu_2w_2)]$$

$$=\int\limits_{-\infty}^{0}e^{\lambda t}[V(w_1+\omega_1t, w_2+\omega_2t)-\langle V\rangle_{w_1,w_2}]dt \quad (\lambda\to0). \qquad (20)$$

This solution implies that the small denominators $v_1\omega_1+v_2\omega_2$ appear with small weights $V_{v_1v_2}$. When this is not so, the variable $v_1\omega_1+v_2\omega_2$ must be regarded as slow. This situation either corresponds to classical degeneracy or is close to it (see Sec. 6).

The expression for the correction in the next approximation to the energy is

$$\delta\varepsilon=\frac{1}{2}\frac{\partial\omega_1}{\partial n_1}\left\langle\left(\frac{\partial S_0}{\partial w_1}\right)^2\right\rangle+\frac{1}{2}\frac{\partial\omega_2}{\partial n_2}\left\langle\left(\frac{\partial S_0}{\partial w_2}\right)^2\right\rangle$$

$$+\frac{\partial\omega_1}{\partial n_2}\left\langle\frac{\partial S_0}{\partial w_1}\frac{\partial S_0}{\partial w_2}\right\rangle+\left\langle\left(\frac{\partial\tilde{V}}{\partial n_1}\frac{\partial S_0}{\partial w_1}+\frac{\partial\tilde{V}}{\partial n_2}\frac{\partial S_0}{\partial w_2}\right)\right\rangle,$$

where S_0 is given by (20).

3. DOUBLY DEGENERATE SYSTEM

Consider a system with two degrees of freedom. We assume that, by virtue of symmetry, the frequencies of classical motion associated with the Hamiltonian H_0 are equal for all the values of the action variables n_1, n_2. This means that the energy levels $E^{(0)}_{n_1,n_2}$ actually depend only on the sum $n=n_1+n_2$. In classical motion, the variable $w=\frac{1}{2}(w_1+w_2)$, which is the conjugate of n, varies rapidly, whereas $\Phi=(w_1-w_2)/2$, the conjugate of $k=n_1-n_2$, varies slowly when the perturbation V is turned on. It is natural to transform to these variables, and describe the quantum state by the amplitudes c_{nk}. As before, we assume that the wave packet is sufficiently narrow in n but, of course, this is not true of the variable k which, even in classical motion, varies within a wide range of the order of n. Let us take the center of the packet in n at n_0 and, instead of $c_{n_0+v,k}$, write $c_{v,k}$, as before. In the leading approximation, the Schrödinger equation then assumes the form

$$\sum_{\nu',k'}V_{\nu-\nu',k-k'}c_{\nu',k'}=(\varepsilon-\nu\omega)\,c_{\nu,k}. \qquad (21)$$

where, as in Sec. 1, $\omega=\partial E^{(0)}_n/\partial n\,\big|_{n=n_0}$ is the classical (doubly degenerate) frequency of the motion and $V_{v,-x}$ are the Fourier components of the perturbation potential $V(w,\Phi)$ with n_0 and k as parameters. We now transform in (21) to the mixed (w,k)-representation and, to achieve this, multiply both sides of the equation by $e^{iv\omega}$ and sum over ν. The result is

$$\sum_{k'}V_{k-k'}(w)c_{k'}(w)=\left(\varepsilon+i\omega\frac{\partial}{\partial w}\right)c_k(w),$$

$$c_k(w)=\sum_{\nu}c_{\nu k}e^{i\nu w}. \qquad (22)$$

We shall seek $c_k(w)$ in the form

$$c_k(w)=\exp\,[iS_k(w)].$$

Dividing both sides of (22) by $c_k(w)$, and taking into account the fact that the principal contribution to the sum on the left-hand side of (22) is provided by terms with $|k'-k|\ll k$, we obtain

$$V(w, \Phi_k)=\varepsilon+\omega\frac{\partial S_k(w)}{\partial w}\qquad \Phi_k=\frac{\partial S_k(w)}{\partial k}, \qquad (23)$$

where $V(w,\Phi)=\Sigma_{\varkappa}V_{\varkappa}(w)e^{-i\varkappa\Phi}$.

Equation (23) is none other than the approximate Hamilton–Jacobi equation in the (w,k)-representation.

The solution of (23) can be found by approximate separation of variables. In particular, we write $S_k(w)$ in the form of the sum of two terms

$$V(w, \Phi)=\sum_{\varkappa}V_{\varkappa}(w)e^{-i\varkappa\Phi}.$$

of which the first, $S_1(w|k)$, depends on w and is a slowly-varying function of k, so that $\partial S_1/\partial k\ll1$, whereas the second,

$$S_k(w)=S_1(w\,|\,k)+S_2(k),$$

$S_2(k)$, is independent of w and is a rapidly-varying function of k. To within quantities of the order of $1/n$, we then have

$$\Phi_k=\partial S_2/\partial k,\quad \partial S_k(w)/\partial w=\partial S_1/\partial w. \tag{24}$$

Substituting this in (23), and subtracting terms that are independent of w, we obtain

$$\langle V(w,\ \Phi_k)\rangle_w\equiv V_0(\Phi_k)=\varepsilon, \tag{25}$$

where, as before, the angle brackets indicate averaging over w. Equation (25) defines Φ_k as a function of k and, consequently, $S_2(k)$ as a function of k and ε. The remaining terms give the equation for S_1:

$$\omega\partial S_1/\partial w=-\tilde{V}(w,\ \Phi_k)=-V(w,\ \Phi_k)+V_0(\Phi_k). \tag{26}$$

The solution of this equation is precisely the same as for the one-dimensional system:

$$S_1=-\frac{1}{\omega}\int\tilde{V}(w,\Phi_k)\,dw.$$

In principle, the same constant α can be added to the right-hand side of (25) and (26). However, since $c_k(w)$ is periodic, it follows that this constant must be equal to $l\omega$, where l is an arbitrary integer. This integer can be set equal to zero by suitably choosing the center n_0 of the packet.

Equation (25) has real solutions in a certain range of classically allowed values of k. Suppose k_1, k_2 define the boundaries of this region. The Bohr-Sommerfeld quantization condition

$$\int\limits_{k_1}^{k_2}\Phi_k\,dk=(s+{}^1/_2)\pi+k_2\Phi_{k_2}-k_1\Phi_{k_1} \tag{27}$$

determines the energy levels as functions of the new quantum number s.

In the simplest case, where

$$V_0(\Phi)=a(k)+b(k)\cos p\Phi$$

(p is an integer), we obtain the three-term recurrence relations used by Sazonov[13] and Braun.[14] They were used in Ref. 9 to investigate the splitting of highly-excited states of the hydrogen atom in a magnetic field within the framework of perturbation theory. We emphasize that the results obtained here are valid throughout the region $V\ll E$, and not only in the region $V\ll\omega$, in which perturbation theory is valid.

Let us consider the correction to the above result in the next order in V/E. Corrections for the fact that $\hat{n}$ and w do not commute, and for the quadratic term in the expansion of E_{n_0+v} in powers of v, were actually examined in Sec. 1. They retain their form in the present case if $V(w)$ in (14) and (15) is replaced with $V(w,\Phi_k)$.

As already noted, these corrections reduce to a slight change in the energy and an addition to the phase of the wave function or, in other words, to $S_1(w,k)$. With the precision indicated above, the effective potential is

$$V_{eff}(\Phi_k)=\langle V(w,\Phi_k)\rangle_w-\frac{1}{2}\frac{\partial}{\partial n}\frac{\langle\tilde{V}^2\rangle_w}{\omega}. \tag{28}$$

All that remains is to consider the corrections to $S_2(k)$. These corrections arise, above all, because k and Φ do not commute and because of the term in the expansion of $S_2(k+\varkappa)-S_2(k)$ that is quadratic in $\varkappa$. The result is

$$c_k(w)=\frac{1}{(|\partial V_0/\partial\Phi_k|)^{1/2}}\exp\left\{iS_1(w,k)+i\sum^{k}\Phi_k^{(0)}\right\}, \tag{29}$$

where

$$S_1=-\frac{1}{\omega}\int\left[\tilde{V}(w)-\frac{1}{2}\frac{\partial}{\partial n}\widetilde{(\tilde{V}^2/\omega)}\right]dw.$$

The physical significance of the pre-exponential factor in (29) is quite clear. The derivative $\partial V_0/\partial\Phi$ is the particle velocity in k-space, since $V_0(\Phi)$ plays the role of energy and Φ the role of momentum. Thus, the factor $(\partial V_0/\partial\Phi_k)^{-1/2}$ ensures that the number of particles is conserved, i.e., the flux is the same at all points in k-space. The dependence on w in $c_k(w)$ can be isolated in the form of the phase factor

$$c_k(w)=\psi(w\,|\,k)\bar{c}_k,$$

so that the function $\psi(w|k)$ is normalized by the usual condition

$$\frac{1}{2\pi}\int\limits_0^{2\pi}|\psi(w|k)|^2\,dw=1.$$

In the v-space, the packet has a finite width described by (13), where $V_{\max,\min}$ must be interpreted as the extrema of $V(w,\Phi_k)$ in w for fixed Φ_k.

From (25) and (27), we can readily find a simple formula for the level density $\rho(\varepsilon)$ for fixed n:

$$\rho(\varepsilon)=\frac{\partial s}{\partial\varepsilon}=\frac{1}{\pi}\int\limits_{k_1}^{k_2}\frac{dk}{|\partial V_0/\partial\Phi_k|}=\frac{1}{\pi}\int\limits_{\Phi_1}^{\Phi_2}\frac{d\Phi}{|\partial V_0/\partial k|}. \tag{30}$$

This is identical with the reciprocal frequency Ω^{-1} of the slow motion.

All the results obtained so far are, essentially, purely classical. The distinguishing feature of our approach appears in the region in which classical results are invalid, i.e., for small values of the new quantum number s. In this region, motion in the fast variable w is, as before, quasiclassical, but the slow variable Φ is fundamentally quantum-mechanical. This region lies near the absolute maximum or minimum of the function $V_0(\Phi,k)$. To be specific, let us suppose that the values of Φ and k at this point are both zero. For simplicity, we confine our attention to a function $V_0(\Phi,k)$ that is even in Φ. Near the above points, we then have the approximate result

$$V_0(\Phi,\ k)=a\Phi^2+bk^2,$$

where $a\sim V$, $b\sim V/n^2$ and we have assumed that $V_0(0,0)=0$. To describe the quantum states, we must regard Φ and k as operators satisfying canonical commutation relations. The complete wave function in this approximation takes the form of the product $\psi(w,\Phi)=\psi_1(\Phi)\psi_2(w,\Phi)$, where $\psi_1(\Phi)$ is the oscillator wave function and

$$\psi_2(w,\ \Phi)=\exp\left[-\frac{i}{\omega}\int\tilde{V}(w,\ \Phi)\,dw\right].$$

Thus, near the extrema we obtain the standard quantum oscillator equation for the slow motion. We emphasize that this approximate analysis is valid for low-lying excited states of the oscillator and for the ground state. In particular, for the ground state, we have

$$\varepsilon_0=(ab)^{1/2}\sim V/n, \quad \Delta k\sim n^{1/2}, \quad \Delta\Phi\sim 1/n^{1/2},$$

which justifies the harmonic approximation. This approximation is valid for $s\ll n$ and smoothly goes over into the quasiclassical approximation for $1\ll s\ll n$.

Thus, we can now formulate the following rule: the slow-motion Hamiltonian is the perturbation $\langle V(w,\hat{\Phi},\hat{k})\rangle_w$ averaged over the fast phase w. This is, in fact, the quantum-mechanical generalization of the classical method of averaging over a rapidly-varying variable.

We note in conclusion that, to the accuracy to which the above approximation is valid, the question of the order of the operator $\hat{\Phi}$ and $\hat{k}$ in the average Hamiltonian does not arise.

4. MULTIPLY DEGENERATE SYSTEMS

Suppose that the energy of a system with m degrees of freedom depends only on the sum $n=n_1+n_2+\dots+n_m$. The frequencies of all the motions are then equal, and we can introduce a "fast" classical phase

$$w=\sum_1^m w_i/m$$

and the slow phases $\Phi_r (r=1,\dots,m-1)$, having defined them, for example, as being w_r-w_m. The corresponding adiabatic invariants are the k_r. The equation for the wave function in the (w,k)-representation is identical with (22) if k is taken to be the $(m-1)$-dimensional vector with integer components $k_1,k_2,\dots,k_{m-1}$. Approximate separation of variables leads to the Schrödinger equation with the average Hamiltonian

$$V_0(\hat{\Phi},k)\psi(k)=\varepsilon\psi(k),$$

just as in the case of two-fold degeneracy. In the classical limit, the problem reduces to quantization along closed classical trajectories Γ:

$$\oint_\Gamma \Phi_k\,dk=2\pi s.$$

The trajectories Γ themselves are determined with the aid of the Hamiltonian $V_0(\Phi,k)$.

Near a known classical trajectory, we can construct a coordinate system in which the variables can be approximately separated by the methods developed in the theory of the parabolic equation (see the book by Babich and Buldyrev[16]).

5. MATRIX ELEMENTS

In applications, one often has to evaluate matrix elements of different physical quantities. This can be done in a relatively general form. We begin with the case of one degree of freedom. Within the framework of classical mechanics, the quantity under investigation, $A(w,n)$, can be expanded into a Fourier series:

$$A(w,n)=\sum_\nu A_\nu(n)e^{i\nu w}.$$

It is convenient to use the w-representation. By definition, the required matrix element $\langle n_0'|A|n_0\rangle$ is then given by

$$\langle n_0'|A|n_0\rangle=\int_0^{2\pi}\psi_{n_0'}(w)\psi_{n_0}^*(w)A(w,n_0)e^{i(n_0'-n_0)w}\,dw$$

$$=\int_0^{2\pi}A(w,n_0)\left[1-i(n_0'-n_0)\int^w\frac{\partial}{\partial n_0}\left(\frac{\tilde{V}(w')}{\omega}\right)dw'\right]e^{i(n_0'-n_0)w}\,dw. \tag{31}$$

The term of the relative order of V/E becomes important when the main term in (31) becomes equal to zero. The average of A over the state n_0

$$\langle n_0|A|n_0\rangle=A_0(n_0),$$

is equal to the average over the classical state, and is a special case of (31).

We now turn to the case of two-fold degeneracy. In this case, we must find the matrix elements of A which, in the classical limit, is a function of w and Φ and of their conjugates n and k. It can be expanded into a Fourier series:

$$A(w,\Phi|n,k)=\sum_{\nu,\varkappa}A_{\nu\varkappa}(n,k)e^{i(\nu w+\varkappa\Phi)}.$$

The matrix elements in which we are interested can now be written down in the form of integrals:

$$\langle n_0's'|A|n_0s\rangle$$

$$=\frac{1}{2\pi}\int_0^{2\pi}dw\sum_{k,k'}\psi_{n_0s}^*(w,k)\psi_{n_0's'}(w,k')A_{k'-k}(w|n_0k)e^{i(n_0'-n_0)w},$$

where

$$A_\varkappa(w|n,k)=\sum_\nu A_{\nu\varkappa}(n,k)e^{i\nu w}$$

and $\psi_{n_0s}(w,k)$ is the wave function in the (w,k)-representation, which is equal to $c_k(w)$, given by (22). The subscripts n_0 and s are new quantum numbers defining the state (see Sec. 3). Using the results of Sec. 3 for the wave function $\psi_{n_0s}(w,k)$, we obtain the following intermediate result:

$$\langle n_0's'|A|n_0s\rangle$$

$$=\int_{k_1}^{k_2}A_{n_0'-n_0}(\Phi_k|n_0k)\exp\left[i\frac{\partial S_2}{\partial s}(s'-s)+i\frac{\partial S_2}{\partial n}(n_0'-n_0)\right],$$

$$A_\nu(\Phi|n,k)=\sum_\varkappa A_{\nu\varkappa}(n,k)e^{i\varkappa\Phi}, \tag{32}$$

where we have omitted all but the leading term. In particular, we have omitted the correction included in (31). If necessary, this correction can readily be reinstated. We now introduce the new variable

$$\chi=\frac{\partial S_2}{\partial s}=\Omega\int\frac{dk}{|\partial V_0/\partial\Phi|}, \quad \Omega=[\rho(\varepsilon)]^{-1}, \tag{33}$$

where the density of states $\rho(\varepsilon)$ is given by (30) and Λ is the frequency of slow motion. The variable χ plays the role of the phase in the slow motion. If we use (25) and (27), we can express $\partial S_2/\partial n$ in terms of χ:

$$\frac{\partial S_2}{\partial n}=\rho(\varepsilon)\left(\frac{\partial\varepsilon}{\partial n}\chi-\int\frac{\partial V_0}{\partial n}d\chi\right).$$

The matrix element given by (32) can now be rewritten in the following form with the aid of the variable χ:

$$\langle n_0's'|A|n_0s\rangle=\frac{1}{2\pi}\int_0^{2\pi}d\chi A_{n_0'-n_0}(\Phi|n,k)$$

$$\exp\left\{i(s'-s)\chi+i(n_0'-n_0)\rho(\varepsilon)\left[\chi\frac{\partial\varepsilon}{\partial n}-\int\frac{\partial V_0}{\partial n}d\chi\right]\right\}. \tag{34}$$

It is implied that Φ has been determined with the aid of (25) and (33) as a function of χ. Equation (34) solves our problem in the case of two-fold degeneracy.

Let us suppose, for example, that the operator A is a small addition to the Hamiltonian (1). The energy correction that is of the first order in A is then equal to the diagonal matrix element. It is often important to be able to evaluate the energy correction of the second order in A. We shall do this for the one-dimensional case:

$$\delta\varepsilon_A^{(2)}=\sum_{n_0'}\frac{|\langle n_0'|A|n_0\rangle|^2}{E_{n_0}^{(0)}-E_{n_0'}^{(0)}}\approx-\sum_{\nu}{}'\frac{|A_\nu|^2}{\omega\nu+{}^1/_2(d\omega/dn)\nu^2}$$

$$\approx-\frac{1}{2}\frac{\partial}{\partial n}\frac{\langle|\tilde{A}(w)|^2\rangle_w}{\omega}.$$

Thus, to calculate the second-order correction, we must evaluate the average of $|\tilde{A}^2(w)|$.

In the case of two-fold degeneracy, a similar procedure yields

$$\delta\varepsilon_A^{(2)}\cong\frac{1}{2}\sum_{\nu,\sigma}{}'\left\{\frac{|A_{\nu,\sigma}|^2}{(\omega\nu+\Omega\sigma)^2}\left(\frac{d\omega}{dn}\nu^2+\frac{\partial\Omega}{\partial s}\sigma^2+2\frac{\partial\Omega}{\partial n}\sigma\nu\right)\right.$$

$$\left.-\left(\nu\frac{\partial}{\partial n}+\sigma\frac{\partial}{\partial s}\right)\frac{|A_{\nu,\sigma}|^2}{\omega\nu+\Omega\sigma}\right\},$$

where $\Omega=\partial\varepsilon/\partial s\sim V/n$ is the frequency of the slow motion. Since the "fast" frequency ω is greater than the "slow" frequency Ω by a factor approximately equal to E/V, we need only retain the terms with $\nu=0$ in the above sum. This finally yields the following expression for the correction:

$$\delta\varepsilon_A^{(2)}=-\frac{1}{2}\frac{\partial}{\partial s}\left[\frac{\langle\tilde{A}_0^2(\Phi)\rangle_\chi}{\Omega}\right]$$

$$=-\frac{1}{2\pi}\frac{\partial}{\partial s}\left[\int_{k_1}^{k_2}|\tilde{A}_0^2(\Phi)|\frac{dk}{|\partial V_0/\partial\Phi|}\right], \tag{35}$$

where $A_0(\Phi)$ is the harmonic of $A(w,\Phi)$ of zero order in w.

6. RANDOM DEGENERACY

It was assumed in Secs. 3 and 4 that equal frequencies for all values of the action variables n_1, n_2, ... were a consequence of additional symmetry of the system. The best known example is the hydrogen atom, whose symmetry group is O_4 (see Ref. 15). We shall now consider random degeneracy, i.e., the coincidence of two frequencies for particular values of the quantum numbers. Generalizing a little, we assume that the condition $q\bar{\omega}_1=p\bar{\omega}_2$ is satisfied for some values $n_i=\bar{n}_i$, where p, q are mutually primitive integers and $\bar{\omega}_i=\partial E^{(0)}/\partial n_i$ are frequencies taken at $n_i=\bar{n}_i$. Our problem is to investigate quantum states centered near $\bar{n}_i$. We shall confine our attention to the case of two variables, since the other variables are unimportant. Let us introduce the new action variables

$$n=pn_1+qn_2,\quad k=-qn_1+pn_2. \tag{36}$$

The energy levels $E_{n,k}^{(0)}$ of the Hamiltonian H_0 will be expanded near $(\bar{n},\bar{k})$, where $\bar{n}=p\bar{n}_1+q\bar{n}_2$, $\bar{k}=-q\bar{n}_1+p\bar{n}_2$:

$$E_{n,k}^{(0)}=E_{\bar{n},\bar{k}}^{(0)}+\omega\nu+\frac{1}{2}\frac{\partial^2E_{n,k}^{(0)}}{\partial k^2}\bigg|_{\bar{n},\bar{k}}\varkappa^2,$$

where $\nu=n-\bar{n}$, $\varkappa=k-\bar{k}$,

$$\omega=(p\bar{\omega}_1+q\bar{\omega}_2)/(p^2+q^2)=\partial E/\partial n|_{\bar{n}\bar{k}}.$$

To be specific, we shall suppose that $\partial^2E^{(0)}/\partial k^2|_{\bar{n}\bar{k}}>0$. The Schrödinger equation is then conveniently written in the representation of w,Φ which are conjugates of n and k:

$$w=\frac{pw_1+qw_2}{p^2+q^2},\qquad\Phi=\frac{-qw_1+pw_2}{p^2+q^2},$$

$$V(w,\Phi|\bar{n},\bar{k})\psi(w,\Phi) \tag{37}$$

$$=\left(\varepsilon+i\omega\frac{\partial}{\partial w}+\frac{1}{2}\frac{\partial^2E^{(0)}}{\partial k^2}\frac{\partial^2}{\partial\Phi^2}\right)\psi(w,\Phi),$$

where

$$\psi(w,\Phi)=\sum_{\nu,\varkappa}c_{\nu\varkappa}e^{i(\nu w+\varkappa\Phi)},$$

$$V(w,\Phi|\bar{n},\bar{k})=\sum_{\nu,\varkappa}V_{\nu\varkappa}(\bar{n},\bar{k})e^{i(\nu w+\varkappa\Phi)}.$$

Equation (37) is none other than the parabolic equation introduced by M. A. Leontovich and V. A. Fock into diffraction theory, and which has since been widely used in the theory of wave propagation (see, for example, the book by Babich and Buldyrev[16]). We note that Eq. (22) is the difference analog of the parabolic equation.

The slight difference as compared with the previous analysis is that we are now using an expansion about the point $\bar{n}_i$ rather than the center of the packet. When, in classical mechanics, the system passes through resonance, the variable Φ varies slowly and w rapidly near resonance. The variable n is then the adiabatic invariant, and k varies slowly. However, when k has changed by a sufficiently large amount, the resonance condition is violated, and we should see a return to the resonance value $\bar{k}$. In quantum mechanics, a stationary state is established instead of the oscillations, in which the characteristic value $\varkappa$ is greater than ν. The wave function $\psi(w,\Phi)$ should therefore vary with w much more rapidly than with Φ. Let us write the solution of (37) in the form

$$\psi(w,\Phi)=\exp\{-iS(w,\Phi)+i\nu_0w\}\bar{\psi},\qquad S=\frac{1}{\omega}\int^w\bar{V}\,dw,$$

where, as before, $\bar{V}(w,\Phi)=V(w,\Phi)-\langle V(w,\Phi)\rangle_w$. We then obtain the following equation for $\bar{\psi}$:

$$\frac{1}{2}\frac{\partial^2 E}{\partial k^2}\frac{\partial^2\bar{\psi}}{\partial\Phi^2}+(\bar{\varepsilon}-V_0(\Phi))\bar{\psi}=-i\omega\frac{\partial\bar{\psi}}{\partial w}+$$
$$+i\frac{\partial^2 E}{\partial k^2}\left[\frac{\partial^2 S}{\partial\Phi^2}\bar{\psi}+2\frac{\partial S}{\partial\Phi}\frac{\partial\bar{\psi}}{\partial\Phi}-i\left(\frac{\partial S}{\partial\Phi}\right)^2\bar{\psi}\right], \qquad (38)$$

where $\bar{\varepsilon}=\varepsilon-\omega v_0$. It is readily seen that $\partial S/\partial\Phi\sim\partial^2 S/\partial\Phi^2\sim V/\omega$. It will be shown later that $\partial\bar{\psi}/\partial\Phi\ll n\bar{\psi}$. Hence, the term containing the brackets in (38) is negligible. As a result, we have the one-dimensional Schrödinger equation for the w-independent wave function:

$$\frac{1}{2}\frac{\partial^2 E}{\partial k^2}\frac{\partial^2\bar{\psi}}{\partial\Phi^2}+(\bar{\varepsilon}-V_0(\Phi))\bar{\psi}=0. \qquad (39)$$

The motion in Φ can also be exclusively quantum-mechanical.

The admissible values of $\bar{\varepsilon}$ are restricted by the condition for the validity of our approximation: $\bar{\varepsilon}\ll E$. When $V_0 n^2/E\lesssim 1$, the ground-state energy in (39) is $\varepsilon_0\sim E/n^2$. When $V_0 n^2/E\gg 1$, the ground and low-lying excited states are oscillatory so that $\bar{\varepsilon}_0\approx\min V_0(\Phi)$ and the oscillation frequency is $\Omega\sim(VE)^{1/2}/n$. The characteristic interval of variation of k is then

$$\Delta k\sim(Vn^2/E)^{1/2}\sim(Vn/\omega)^{1/2}.$$

It is clear that $\Delta k\gg\Delta n\sim V/\omega$, which we have, in fact, assumed.

When $V_0 n^2/E\gg 1$ and $\bar{\varepsilon}\gg V$, the phase of the function $\bar{\psi}(\Phi)$ can be expanded in powers of V_0. The result is the approximate formula given by (20) for the nondegenerate case of a packet centered on v_0:

$$\varkappa_0=[2\bar{\varepsilon}(\partial^2 E/\partial k^2)^{-1}]^{1/2}.$$

Since the width of the packet in k is of the order of $(Vn/\omega)^{1/2}$, and the width in Φ is therefore of the order of $(Vn/\omega)^{-1/2}$, stochastic phenomena, which take place in an exponentially narrow layer near the separatrices, do not appear to play a significant role for the quantum states. On the other hand, the vanishing of the frequency $\Omega=\partial E/\partial k$ signifies a higher density of states. Since random resonances in a nonlinear system can be encountered at any point in the spectrum, the density of states is a very strange function of energy. This problem requires careful investigation.

7. THE HYDROGEN ATOM IN A MAGNETIC FIELD

The Hamiltonian for this system is:

$$H=H_0+V,\quad H_0=p^2/2-1/r,\quad V={}^1/_8\omega_c^2\rho^2, \qquad (40)$$

where we are using the atomic system of units in which $\hbar=m=e=1$, $\omega_c=\mathscr{H}/c$ is the cyclotron frequency, and ρ is the component of the radius vector perpendicular to the magnetic field. The term $m\omega_c/2$ has been omitted from (40), where m is the component of the orbital angular momentum along the z axis, since the inclusion of this term is a trivial matter. The azimuthal quantum number m is, as before, a strictly conserved quantity.

Let us now transform to the parabolic coordinates ξ,η (see, for example, Ref. 10). It is well known that, in the Keppler problem, the variables are separable in the parabolic set of coordinates. Instead of the original variables ξ,η and the conjugate momenta, we can introduce the angle variables w_1, w_2 and the respective conjugate action variables (quantum numbers) n_1, n_2. The Hamiltonian H_0 can then be expressed in terms of n_1 and n_2 alone:

$$H_0=-1/2(n_1+n_2+m)^2.$$

We thus have before us the case of two-fold degeneracy[3] that was examined in a general form in Sec. 2. According to the general recipe, we must transform to the quantum numbers $n=n_1+n_2$, $k=n_1-n_2$ and the corresponding angle variables $w=(w_1+w_2)/2$ and $\Phi=(w_1-w_2)/2$, and then use them to separate fast and slow motions. The following parametrization is convenient in calculation:

$$\xi=n(n+k-r_+\cos u),\quad \eta=n(n-k-r_-\cos v),$$
$$r_\pm=[(n\pm k)^2-m^2]^{1/2}. \qquad (41)$$

The phase variables w and Φ are related to the parameters u and v as follows:

$$\Phi=(u-v)/2,\quad \psi=(u+v)/2, \qquad (42)$$
$$w=\psi-\gamma\sin(\psi+\alpha), \qquad (43)$$

where

$$\operatorname{tg}\alpha=\frac{r_+-r_-}{r_++r_-}\operatorname{tg}\Phi,$$
$$\gamma^2=\frac{1}{4n^2}(r_+^2+r_-^2+2r_+r_-\cos 2\Phi). \qquad (44)$$

We must now average $\rho^2=\xi\eta$ over w:

$$\langle\xi\eta\rangle_w=\frac{1}{2\pi}\int_0^{2\pi}\xi\eta\,dw=\frac{1}{2\pi}\int_0^{2\pi}\xi\eta[1-\gamma\cos(\psi+\alpha)]d\psi.$$

In the last equation we used (43). Using the parametrization defined by (41) together with (42)–(44), we obtain

$$\langle\xi\eta\rangle_w=n^2({}^3/_2n^2-{}^3/_2k^2-{}^1/_2m^2+r_+r_-\cos 2\Phi). \qquad (45)$$

This result is in agreement with accurate evaluations of the matrix elements of V, performed by Clark[17] and Bergou *et al.*[9] The energy levels are determined by (25) which, in the present case, assumes the form

$$V_0(\Phi)={}^1/_8\omega_c^2n^2({}^3/_2n^2-{}^3/_2k^2-{}^1/_2m^2+r_+r_-\cos 2\Phi)=\varepsilon, \qquad (46)$$

and the quantization rule (27), in which we must now substitute

$$\Phi_k=\frac{1}{2}\arccos\frac{\varepsilon'+{}^3/_2k^2}{r_+r_-},\qquad \varepsilon'=\frac{8\varepsilon}{\omega_c^2n^2}-\frac{3}{2}n^2+\frac{1}{2}m^2. \qquad (47)$$

The turning points k_1, k_2 are determined by setting the argument of the arccosine equal to ± 1.

The expressions (46) and (47) were obtained in Ref. 9 within the framework of quantum perturbation theory $(\omega_c{}^2n^7\ll 1)$. As we have already shown (see Secs. 1 and 2), the range of their validity is much broader and is determined by the condition $\omega_c{}^2n^6\ll 1$ alone. This is why our energy spectrum is identical with that found earlier by Solov'ev.[7] However, it is important to note that Solov'ev used a different representation (spherical set of coordinates and the adiabatic invariants associated with it). In this representation, the quantized phases are written in the form of hyperelliptic integrals (the roots of polynomials of degree eight are integrated). These integrals become the ordinary elliptic integrals in

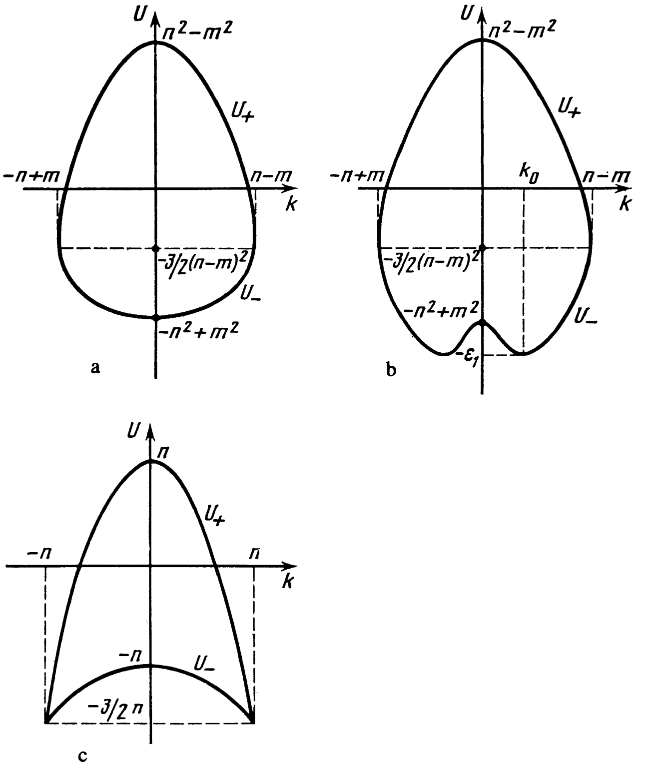

FIG. 1. Branches of the effective potential $U_\pm$ as a function of k: a) $n<m\sqrt{5}$, b) $n>m\sqrt{5}$, c) $m=0$. Here $\varepsilon_1 = -3/2(n^2+m^2)+nm\sqrt{5}$.

the representation that we have used. In particular, the integral given by (47) is transformed into a complete elliptic integral of the third kind. The density of states looks simpler still:

$$\rho(\varepsilon)=\frac{\partial s}{\partial \varepsilon}=\frac{8K(\lambda)}{\pi\omega_c{}^2n^2R},\qquad \lambda^2=\frac{1}{2}\left(1-\frac{2(n^2+m^2)+3\varepsilon'}{R^2}\right), \tag{48}$$

where $K(\lambda)$ is the complete elliptic integral and

$$R^2=2\{[{}^3/_2(n^2+m^2)+\varepsilon']^2-5n^2m^2\}^{1/2}.$$

We now wish to emphasize that the two-fold degeneracy of the frequencies is lifted in the corresponding classical problem and, as shown in Sec. 3, in addition to the "old" adiabatic invariants m, n, we have a further approximately conserved quantity that arises in a very general way. This is the average $\langle V(w,\Phi)\rangle_w$, evaluated over w, or the corresponding action variable s. There are no other additional conservation laws.

We shall now reproduce some of the results given in Ref. 9 and needed in the discussion below. The equations for the turning points are

$$\varepsilon'=-{}^3/_2k^2\pm r_+r_-=U_\pm(k).$$

These curves are shown in Fig. 1 for different values of the ratio m/n. When $m/n>1/\sqrt{5}$, there are two series of states corresponding to the upper and lower branches of the curve, and all the states are symmetric in k. This means, in particular, that the dipole moment of such oscillations is zero. The values of the angles $\Phi_{\pm k_0}$ at the turning points $\pm k_0$ are equal, and are both zero or $\pi/2$. Asymmetric states with nonzero dipole moments appear for $m/n<1/\sqrt{5}$. They correspond to energies $\varepsilon'<-n^2+m^2$. The corresponding states are doubly degenerate. This degeneracy is, of course, removed in the course of quantum tunneling, and slightly split doublets of even and odd states appear. As usual, the splitting is exponentially small and can be neglected even in relatively weak electric fields. The number of asymmetric states for $n=0$ is

$$\left(1-\frac{2}{\pi}\operatorname{arctg}2\right)n\approx 0{,}29n.$$

Let us examine in greater detail the behavior of the density of states in different regions. The formula given by (48) is valid for any n and m and for energies in the range $-(n^2-m^2)\leqslant\varepsilon'\leqslant n^2-m^2$. When $m/n>1/\sqrt{5}$, this interval covers the entire range of allowed energies. When $m/n<1/\sqrt{5}$, the density in the region of asymmetric states

$$-{}^3/_2(n^2+m^2)+\sqrt{5}nm\leqslant\varepsilon'\leqslant -n^2+m^2$$

is found from the equation (where we have taken two-fold degeneracy into account)

$$\rho(\varepsilon)=\frac{16K(1/\lambda)}{\pi\omega_c{}^2n^2\{R^2-[2(n^2+m^2)+3\varepsilon']\}^{1/2}}. \tag{49}$$

The density of states (48) and (49) becomes logarithmically infinite for $\varepsilon'=-n^2+m^2(\lambda=1)$.

8. STARK EFFECT

It is shown in Ref. 9 that, when a weak additional field $\mathscr{E}\ll\mathscr{H}^2n^2/c^2$ is applied in the same direction as the magnetic field, the Stark effect is always quadratic for states with $m/n>1/\sqrt{5}$ and is linear for states with $m/n<1/\sqrt{5}$ and $\varepsilon'<-n^2+m^2$. We shall now confirm this result by directly evaluating the dipole moment, and we shall demonstrate that its magnitude is inversely proportional to $\rho(\varepsilon)$.

According to the general formulas in Sec. 3, we must evaluate the average of the coordinate z over the fast variable w and the slow variable χ. Using the parametrization defined by (41), we have

$$z={}^1/_2(\xi-\eta)=n[k-{}^1/_2(r_+\cos u-r_-\cos v)]. \tag{50}$$

Let us begin with averaging over w:

$$\langle z\rangle_w=nk-\frac{n}{4\pi}\int_0^{2\pi}[r_+\cos(\psi+\Phi)-r_-\cos(\psi-\Phi)]$$

$$\times[1-\gamma\cos(\psi+\alpha)]d\psi.$$

Using (44), we obtain

$$\langle z\rangle_w={}^3/_2nk. \tag{51}$$

The next step is to evaluate

$$\langle z\rangle_{w,\chi}=\frac{1}{2\pi}\int_0^{2\pi}\langle z\rangle_w d\chi=\frac{3n\Omega}{2\pi}\int_{k_1}^{k_2}\frac{kdk}{|\partial V_0/\partial\Phi|} \tag{52}$$

[see (32) for $s'=s$, $n_0'=n_0$ and (33)]. If the limits of integration are symmetric in k, the average $\langle z\rangle_{w,\chi}$ vanishes, since Φ_k are even functions of k. Hence, a nonzero result emerges only for the asymmetric trajectories. According to (46),

$$\frac{\partial V_0}{\partial \Phi}=\frac{\omega_c{}^2 n^2}{4} r_+ r_- \sin 2\Phi_k=\frac{\omega_c{}^2 n^2}{4}\left[r_+{}^2 r_-{}^2-\left(\varepsilon'+\frac{3}{2}k^2\right)^2\right]^{1/2}.$$

The integral in (52) can be evaluated in an elementary manner, and we find that

$$\langle z\rangle_{w,\chi}=\frac{3\pi n\{R^2-[2(n^2+m^2)+3\varepsilon']\}^{1/2}}{8K(1/\lambda)}=\frac{6[\rho(\varepsilon)]^{-1}}{\omega_c{}^2 n}. \tag{53}$$

The quantity $\mathscr{E}\langle z\rangle_{w,\chi}$ is equal to the Stark level shift.

Thus, the magnetic field annuls the linear Stark effect for most of the states. However, states that can be obtained from the ground state by moderately multiple excitation with lasers have small m and, as we have already pointed out, approximately one-third of them are asymmetric. The connection between the density of states $\rho(\varepsilon)$ and the linear Stark effect [Eq. (53)] can be verified experimentally.

The linear Stark effect is absent when $-n^2+m^2 \leqslant \varepsilon' \leqslant n^2-m^2$. When the electric and magnetic field are parallel, the energy correction $\delta\varepsilon_{\parallel}^{(2)}$ can be evaluated by direct utilization of (35).

In the general case, the result is very unwieldy but, for the physically interesting case where $m \ll n$, it becomes much simpler and assumes the form

$$\delta\varepsilon_{\parallel}^{(2)}=\frac{9\mathscr{E}^2}{\omega_c{}^2}\left(1-\frac{4}{5}\frac{E(\lambda)}{K(\lambda)}\right), \tag{54}$$

where $E(\lambda)$ is the complete elliptic integral of the second kind.

When the electric and magnetic fields are perpendicular, the formula given by (35) cannot be used directly because the perturbation operator $A=\mathscr{E}x$ produces a change in the azimuthal quantum number by ± 1. However, proceeding by analogy, we can show that the level shift in the transverse Stark effect is

$$\delta\varepsilon_{\perp}^{(2)}=\frac{1}{\omega_c{}^2}\left\{\frac{\partial}{\partial s}\left[\Omega\left\langle\left\langle\frac{\partial A^+}{\partial\chi}\right\rangle_w^2\right\rangle_\chi\right]\frac{\partial^2\varepsilon}{\partial m^2}\langle\langle A^+\rangle_w{}^2\rangle_\chi\right\}$$
$$-\frac{1}{\omega_c}\frac{\partial}{\partial m}\langle\langle A^+\rangle_w{}^2\rangle,\quad A^+={}^1/{}_2\mathscr{E}(\xi\eta)^{1/2}. \tag{55}$$

Specific calculations will be performed only for $m/n \ll \omega_c n^3$. The last term in (55) can then be neglected, and the result has the form (see Appendix)

$$\delta\varepsilon_{\perp}^{(2)}=-\frac{9}{32}\frac{\mathscr{E}^2 n^6}{(1+4\lambda^2)}\left\{9-4\lambda^2-\frac{E(\lambda)}{K(\lambda)}\left[\frac{2(16\lambda^4+6\lambda^2+3)}{1+4\lambda^2}\right.\right.$$
$$\left.\left.+\frac{4}{(1+4\lambda^2)^{1/2}K(\lambda)}\int_0^\lambda j(\lambda')K(\lambda')\,d\lambda'\right]\right\}, \tag{56}$$

where

$$j(\lambda)=\lambda(7-8\lambda^2-64\lambda^4)(1+4\lambda^2)^{-3/2}.$$

Figures 2 and 3 show graphs of the functions $\rho(\varepsilon)$, $\delta\varepsilon_{\parallel}^{(2)}$, and $\delta\varepsilon_{\perp}^{(2)}$.

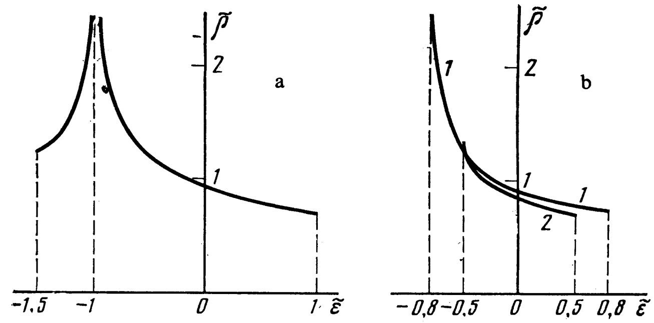

FIG. 2. Graph of density of states. $\tilde{\rho}=\rho\omega_c{}^2 n^2/16$, $\tilde{\varepsilon}=\varepsilon'/n^2$: a—$m=0$, b—$m/n=1/\sqrt{5}$ (curve 1) and $m/n=1/\sqrt{2}$ (curve 2).

9. DISCUSSION

Thus, for highly-excited discrete states, we can use a theory close to the classical perturbation theory, which was developed in Ref. 1. When the unperturbed system allows the use of separation of variables, one can identify simple rules for finding the level shifts produced by the perturbation, and the matrix elements of physical quantities. The case of classically degenerate frequencies is of particular interest in connection with the problem of the hydrogen atom. We have used the theory given above to solve the problem of highly-excited states of the hydrogen atom in an external magnetic field. The condition for the validity of the above results is the criterion for the validity of classical perturbation theory, namely, $\omega_c n^3 \ll 1$. The quantization rules, expressed by (47), are equivalent to those obtained earlier by Solov'ev[7] by a different method. The energy levels are characterized by the three quantum numbers n, m, and s, of which only s is a new specific number. The level shift in the magnetic field can be written in the form

$$\varepsilon=\omega_c{}^2 n^4 f(m/n, s/n).$$

The explicit form of the function f is given in the Appendix. It is clear that, when the magnetic field is varied, levels corresponding to different n and s (but constant m) will cross. The repulsion of these levels is a consequence of the nonconservation of adiabatic invariants. It is well known from classical mechanics (see Ref. 20, Sec. 51) that these invariants vary as $\sim e^{-\mathrm{const}(E/V)}$. The exponentially small repulsion of the levels due to the classical nonconservation of the adiaba-

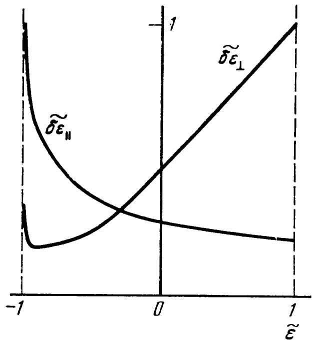

FIG. 3. Longitudinal and transverse energy shift in an electric field (quadratic Stark effect) for $m=0$. $\tilde{\delta\varepsilon}_{\parallel}=\delta\varepsilon_{\parallel}\frac{\omega_c{}^2}{9\mathscr{E}^2}$, $\tilde{\delta\varepsilon}_{\perp}=-\delta\varepsilon_{\perp}\frac{32}{27n^6\mathscr{E}^2}$, $\tilde{\varepsilon}=\varepsilon'/n^2$.

tic invariant must be compared with the quantum-mechanical tunneling effect, which is of the order of $e^{-\text{const}\, n}$. The latter was examined by Solov'ev.[7] It is clear that the arguments of these exponentials are of the same order of magnitude when the perturbation V approaches ω, i.e., when the condition for a level crossing is satisfied. Thereafter, the classical effect becomes more important for $V \gg \omega$. Thus, the classical estimate for the repulsion of levels, $e^{-\text{const}(E/V)}$, is valid throughout the region in which the levels can cross. For given m and n, the addition to the Coulomb energy lies between limits defined by

$$-n^2+m^2 \leqslant \varepsilon' \leqslant n^2-m^2, \qquad m/n > 1/\sqrt{5},$$
$$-{}^3/_2(n^2+m^2)+nm\sqrt{5} \leqslant \varepsilon' \leqslant n^2-m^2.$$

The magnetic field leads to the symmetrization of the wave function and to the vanishing of the dipole moment for all states with $m/n > 1/\sqrt{5}$ and states with $m/n < 1/\sqrt{5}$ and $\varepsilon' > -n^2+m^2$. The Stark effect has interesting features when the electric field is small, i.e., $\mathscr{E} < \omega_c{}^2 n^2$. When $\omega_c n^3 \sim 1$ and $n \sim 50$, we have $\mathscr{E} < n^{-4} \sim 10^2\ V \cdot \text{cm}^{-1}$.

The linear level shift $\mathscr{E}\langle z\rangle_{w,\chi}$, given by (53), appears in asymmetric states. Its magnitude is of the order of n^2 and is independent of the magnetic field.

Symmetric states are characterized by the polarizability defined by (54) and (56). The transverse polarizability is independent of the magnetic field and is of the order of $\sim n^6$. The longitudinal polarizability is inversely proportional to the square of the magnetic field, and depends only on the ratios m/n and s/n. Thus, the transverse polarizability is smaller than the longitudinal polarizability by the factor $\omega_c{}^2 n^6 \ll 1$. Moreover, they have different signs: the atom has paraelectric and dielectric properties in the longitudinal and transverse directions, respectively.

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APPENDIX

To find $\partial^2\varepsilon/\partial m^2$, we use the formula for the density of states, given by (48). Integration with respect to the energy then gives

$$\int\limits_{\varepsilon}^{\varepsilon_0} \rho(\varepsilon)\, d\varepsilon = \pi s, \qquad \varepsilon_0 = {}^1/_{16}\omega_c{}^2 n^2(5n^2-3m^2).$$

Taking the derivative with respect to m^2 for fixed s, we obtain

$$\frac{\partial\varepsilon}{\partial(m^2)}\rho(\varepsilon) = \frac{\partial\varepsilon_0}{\partial(m^2)}\rho(\varepsilon_0) - \frac{8}{\pi\omega_c{}^2 n^2}\int\limits_0^{\lambda} d\lambda' K(\lambda') \frac{\partial}{\partial(m^2)}\left(\frac{\partial\varepsilon}{\partial\lambda'}\frac{1}{R}\right).$$

We have thus replaced integration with respect to ε by integration with respect to λ. As $m^2 \to 0$, this gives the expression used in (56).

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1) Bergou *et al.*[9] used the quasiclassical procedure for solving the three-term relations discussed by Sazonov[13] and Braun.[14]

2) This relation was obtained in a paper by Shuryak,[11] devoted to the time-dependent quasiclassical perturbation theory.

3) In reality, the frequency of Coulomb motion is triply degenerate (including azimuthal motion). Since the azimuthal quantum number m is strictly conserved, we need only consider two degrees of freedom.

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[1] M. Born and W. Pauli, Z. Phys. **10**, 137 (1922); W. Pauli, Papers on Quantum Theory [Russian transl., Nauka, Moscow, 1975].

[2] L. D. Landau and E. M. Lifshitz, Mekhanika (Mechanics), Nauka, Moscow, 1973 [English transl. by Pergamon Press, 1975].

[3] N. N. Bogolyubov and Yu. M. Mitropol'skiĭ, Asimptoticheskie metody v teorii nelineĭnykh kolebaniĭ (Asymmetric Methods in the Theory of Nonlinear Oscillations), Nauka, Moscow, 1974.

[4] J. C. Castro, M. L. Zimmerman, R. G. Hulet, and D. Kleppner, Phys. Rev. Lett. **45**, 1780 (1980).

[5] M. L. Zimmerman, M. M. Kash, and D. Kleppner, Phys. Rev. Lett. **45**, 1092 (1980).

[6] D. Delande and J. C. Gay, Phys. Lett. A **82**, 393, 399 (1981).

[7] E. A. Solov'ev, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 278 (1981) [JETP Lett. **34**, 265 (1981)].
Zh. Eksp. Teor. Fiz. **82**, 1762 (1982) [Sov. Phys. JETP **55**, 1017 (1982)].

[8] D. R. Herrick, Phys. Rev. A **26**, 323 (1982).

[9] A. P. Kazantsev, V. L. Pokrovsky, and J. Bergou, Preprint KFKI, 1983, 01.

[10] L. D. Landau and E. M. Lifshitz, Kvantovaya Mekhanika (Quantum Mechanics), Nauka, Moscow, 1974 (English transl. by Pergamon Press, 1975).

[11] É. V. Shuryak, Zh. Eksp. Teor. Fiz. **71**, 2039 (1976) [Sov. Phys. JETP **44**, 1070 (1976)].

[12] J. B. Delos, S. H. Knudson, and D. N. Noid, Phys. Rev. Lett. **50**, 583 (1983).

[13] V. N. Sazonov, Teor. Mat. Fiz. **35**, 361 (1978).

[14] P. A. Braun, Teor. Mat. Fiz. **37**, 355 (1978).

[15] V. A. Fock, Izv. Akad. Nauk SSSR Ser. Fiz. **2**, 169 (1935); Z. Phys. **98**, 145 (1935).

[16] V. M. Babich and V. S. Buldyrev, Asimptoticheskie metody v zadachakh difraktsii korotkikh voln (Asymptotic Methods in Problems of Short-Wave Diffraction), Nauka Moscow, 1972.

[17] C. W. Clark, Phys. Rev. A **24**, 605 (1981).

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