

Quasiclassical perturbation theory for the helium atom and heliumlike ions

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A quasiclassical perturbation theory in the interelectron interaction is developed for equivalent electrons ($n_1 = n_2$, where n_i is the quantum number of the i th electron) with zero total angular momentum. The application of this theory to other states of a heliumlike system is considered.

1. INTRODUCTION

The problem of quasiclassical quantization of nonintegrable systems is of great fundamental and applied significance. Study of this problem contributes to a more complete understanding of the relation between classical and quantum mechanics. Quasiclassical quantization methods can also compete with the laborious quantum calculations for highly excited states, where a large number of basis functions must be invoked. In most quasiclassical calculations performed so far of the energies of nonintegrable systems make use of the Einstein-Brillouin-Keller (EBK) quantization procedure (see, e.g., Percival's review¹). It is assumed in this procedure that the system moves in phase space over s -dimensional tori (the dimensionality of the phase space is $2s$), and this assumption limits primarily the range in which the procedure is valid. The existence of invariant tori was rigorously proven only for systems close enough to integrable (the Kolmogorov-Arnol'd-Moser theory²). The quasiclassical bound states are selected in the EBK quantization procedure by quantizing the simplified action over all the topologically independent contours on the invariant tori.

From the standpoint of practical applications in the theory of atoms and molecules, great interest attaches to extension of the EBK procedure to calculations of the spectra of charged-particle systems. The simplest nontrivial examples of such systems are the helium atom and heliumlike molecules, for which, however, no investigations were made even of a semiclassical perturbation theory in the electron-electron interaction. The quantum analog of such a perturbation is treated in many works (see, e.g., the review by Nikitin and Ostrovskii³). Its use is more justified for heliumlike ions with large nuclear charge, but even for the helium atom this approach turns out to be most fruitful for the classification of states and for investigation of the spectrum structure. At present, however, there is no satisfactory theory that leads to a simple and well-founded picture. The reason is that even the perturbation matrix elements cannot be calculated analytically and one cannot see from the very outset any substantial simplifications compared with the general scheme of perturbation theory in the degenerate case. To obtain simpler qualitative results, additional approximations are introduced in perturbation, such as the dipole approximation for electron-electron interaction. This is in fact the aim of the quasiclassical approach developed in the present paper. In addition, the results of quasiclassical perturbation theory are the starting point for the calculation of the

spectra of heliumlike systems in quasiclassical approximation outside the framework of perturbation theory, by the method of adiabatic turning-on of the electron-electron interaction.⁴

A distinguishing feature of classical perturbation theory for heliumlike systems is the presence of random degeneracy in the unperturbed state (by random degeneracy is meant, as usual, commensurability of the oscillation periods for two or several coordinates; this commensurability is present not always, but only if initial conditions are given). The general scheme of developing a perturbation theory for random degeneracy is described in Born's book,⁵ where it is also shown that nonstandard quantization conditions arise in this situation. Modification of the quasiclassical approximation in the presence of random degeneracy was considered from the standpoint of modern theory by Kazantsev and Pokrovskii⁶.

The first attempts to develop a quasiclassical perturbation theory for helium were made even in the old Bohr theory.⁵ According to the then employed heuristic concepts, only the simplest symmetric trajectories were considered. Those results are therefore not suitable for the development of a consistent quasiclassical approximation. Some aspects of the use of a quasiclassical approach to the helium atom were considered recently in Refs. 7–9. Leopold *et al.*⁷ compared the diagonal matrix elements of the electron-electron interaction in a spherical hydrogenlike basis with mean values of this interaction on the corresponding unperturbed classical trajectories. These averaged-interaction values were then incorrectly taken to be the first-order corrections to the energy. In fact, neither in quantum nor in classical mechanics are unperturbed states with fixed values of the angular momentum of each electron correct zeroth-approximation states. In the degenerate case the first problem of perturbation theory is in fact to find a correct, and independent of the type of perturbation, combination of degenerate states in quantum mechanics, or a correct ensemble of unperturbed classical trajectories in classical mechanics. This problem was not treated in Refs. 7–9. A quasiclassical analog of the Hileras variational method was developed in Ref. 8, while a singlet-triplet splitting of the energy levels was considered in Ref. 9 in the framework of a model quasiclassical approach.

In this paper we develop a quasiclassical perturbation theory for equivalent electrons ($n_1 = n_2$, where n_i is the principal quantum number of the i th electron) with zero total angular momentum, and discuss the application of this

charge equal to unity we have $\mu = Z^{-1}$, therefore the condition for validity of the perturbation theory is $Z > 1$. The pair of equations in (1) is standard in the elliptic-element-variation method.¹¹ Equations (2) describe the change of the delay time τ for a small exchange of energy between the electrons near random resonance: $d\tau/dt = (T_1 - T_2)/T$.

It is possible to eliminate the small parameter μ from Eqs. (1) and (2) by changing from ΔE to $\varepsilon = \mu^{-1/2}\Delta E$ and introducing new variables $s_1 = \mu t$ and $s_2 = \mu^{1/2}t$ for the first and second pairs of equations, respectively. It follows hence that the rate of change of τ and ε is of the order of $\mu^{1/2}$, and that of l and θ of the order of μ , i.e., l and θ vary infinitely slowly compared with τ and ε as $\mu \rightarrow 0$. In addition, the energy transfer ΔE is always small, on the order of $\mu^{1/2}(\Delta E = \mu^{1/2}\varepsilon)$. The change of the parameters E_1 and E_2 in the electron-electron interaction should therefore be neglected, and these arguments of V will hereafter be omitted.

Since the characteristic frequencies are different, the variables are adiabatically separated in first-order perturbation theory and the problem reduces to a simultaneous solution of two one-dimensional problems (1) and (2). The most sensitive to the exclusion of the electron-electron interaction are the parameters τ and ε . They change by finite amounts in a time on the order of $\mu^{-1/2}$, during which l and θ can be regarded as constant. On the other hand, the motion in terms of the variable ξ has a high frequency compared with τ . Replacing, in accord with the method of secular equations, the interaction V in (2) by the value

$$V_1(\tau; l, \theta) = \frac{1}{T} \int_0^\tau V(\xi(t); l, \theta, \tau) dt \quad (3)$$

averaged over ξ , we obtain in the first-order approximation the equations of motion for τ and ε :

$$\frac{d\varepsilon}{ds_2} = -\frac{\partial V_1}{\partial \tau}, \quad \frac{d\tau}{ds_2} = \frac{3}{E_0} \varepsilon. \quad (4)$$

Equations (4) describe one-dimensional motion with an effective Hamiltonian

$$h(\varepsilon, \tau; l, \theta) = \frac{3}{2E_0} \varepsilon^2 + V_1(\tau; l, \theta), \quad (5)$$

in which τ and ε play the role of the coordinate and momentum, while l and θ are for the time being fixed arguments. Since τ and $\tau + T$ are physically equivalent, the potential $V_1(\tau)$ can be formally continued periodically past the interval $\theta \leq \tau < T$. It takes in this interval the shape of a symmetric potential well (see Fig. 2) and diverges logarithmically at the end points of the interval

$$V_1(\tau) \sim \begin{cases} \text{const} \cdot \ln \tau, & \tau \rightarrow 0 \\ \text{const} \cdot \ln(T - \tau), & \tau \rightarrow T \end{cases}$$

The motion as a function of τ constitutes oscillations between the turning points τ_1 and τ_2 . The $\varepsilon(\tau)$ dependence is obtained from the condition that the effective Hamiltonian (5) is conserved over time intervals $\Delta t \sim \mu^{-1/2}$:

$$h(\varepsilon, \tau; l, \theta) = q(l, \theta). \quad (6)$$

For time intervals of the order of μ^{-1} and longer account must be taken of the changes of l and θ . These will lead to changes of the separation constant $q(l, \theta)$. Since the rate of

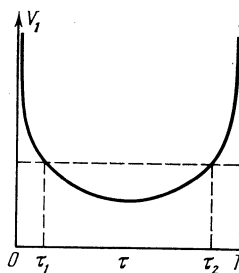


FIG. 2. Effective potential as a function of τ .

change of l and θ . These will lead to changes of the separation constant $q(l, \theta)$. Since the rate of change of l and θ is small compared with the frequency of the oscillations in τ , the quantity

$$\alpha = \int_{\tau_1}^{\tau_2} \varepsilon(\tau) d\tau = \int_{\tau_1}^{\tau_2} \left\{ \frac{2E_0}{3} (q - V_1(\tau; l, \theta)) \right\}^{1/2} d\tau \quad (7)$$

is an adiabatic invariant and is conserved for finite change of l and θ . Relation (7) determines the dependence of q on the variables l and θ and on the integral of motion α .

The equations of motion for l and α are obtained by averaging the electron-electron interaction in (1) both over the unperturbed motion and over the oscillations in τ :

$$\frac{dl}{ds_1} = -\frac{\partial V_2}{\partial \theta}, \quad \frac{d\theta}{ds_1} = \frac{\partial V_2}{\partial l}, \quad (8)$$

where

$$V_2(l, \theta) = \frac{1}{Q} \int_0^Q V_1(\tau(s_2); l, \theta) ds_2, \quad (9)$$

and $Q\mu^{-1/2}$ is the period of the oscillations in τ . The effective Hamiltonian for the Hamilton equations of motion (8) is the averaged interaction (9), while θ and l are the canonically conjugate coordinate and momentum of this one-dimensional problem. The dependence of l on θ is obtained from the condition for the conservation of V_2 on the trajectory:

$$V_2(l, \theta) = \beta. \quad (10)$$

The motion as a function θ constitutes oscillations in the interval $\theta_m < 0 < 2\pi - \theta_m$ (see Fig. 1). $l(\theta)$ vanishes at the turning points. The amplitude $\chi_m = (\pi - \theta_m)/2$ of the oscillations depends on β . The trajectory of the entire system is thus uniquely determined by the integrals of motion α and β and by the quantum numbers $L = L_2 = 0$ and $n_1 = n_2 = n$.

3. QUANTIZATION CONDITIONS

Turning-on the electron-electron interaction lifts the degeneracy partially on account of the motion with respect to the variable τ . The trajectories in phase space are no longer closed curves but coil themselves on a two-dimensional torus S_τ . The lifting of the degeneracy is partial, since the complete invariant tori are three-dimensional in this problem and are obtained in the next order of the adiabatic expansion of the motion in terms of θ . A condition for quantization in the major radius of the torus S_τ was present also in the unperturbed problem, and was used in fact to determine

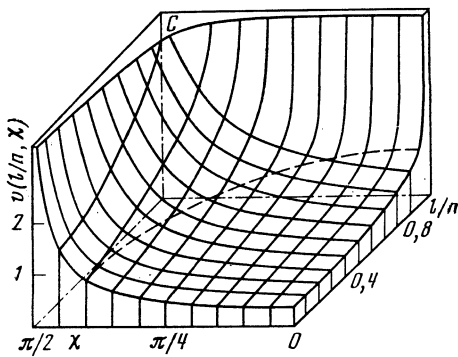


FIG. 3. Effective Hamiltonian in terms of $\theta(\chi = (\pi - \theta)/2)$. The dashed curve shows the function $l(\chi)$ for $\chi_m = 2\pi/5$, $q = 0.61$.

the quantum numbers n_1 and n_2 . In the EBK procedure, motion with respect to the variable τ corresponds formally to the condition of quantization over a closed contour C around the minor radius of the torus S_1 :

$$I_\tau = \oint_C \mathbf{p}_1 \cdot d\mathbf{r}_1 + \oint_C \mathbf{p}_2 \cdot d\mathbf{r}_2 = 2\pi(s + 1/2), \quad (11)$$

where the Morse index $1/2$ takes into account the phase shift at the turning points τ_1 and τ_2 . This quantization method, however, cannot be used for the variable τ (Refs. 5 and 6). To demonstrate the violation of the standard EBK procedure, we express I_τ in terms of the adiabatic invariant α :

$$I_\tau = 2\mu^{1/2}\alpha. \quad (12)$$

This relation is obtained by using the explicit expressions for the coordinates and momenta of the Kepler problem¹² with account taken of the changes of ΔE and τ in accordance with Eqs. (4). Expressing I_τ in terms of the adiabatic invariant α is legitimate, since it ensures preservation of the condition of quantization in τ for finite changes of l and θ . A fundamental contradiction arises, however. It follows from (12) that I_τ becomes an infinitely small quantity of order $\mu^{1/2}$ as $\mu \rightarrow 0$. On the other hand, to satisfy the quantization condition (11) the minimum value of I_τ should equal π . This contradiction is the consequence of the random degeneracy and will set in for arbitrary states of a heliumlike system, since the electron periods are always commensurate in the unperturbed state. In addition, as $\mu \rightarrow 0$ the penetrability of the barrier between the neighboring potential wells of the periodic potential $V_1(\tau)$ also tends to zero, another violation of the applicability of Bohr-Sommerfeld condition (11).

The EBK procedure is thus not suitable for motion as a function of τ and more complicated quantization methods are necessary here. According to the general scheme for developing a quasiclassical perturbation theory, the Bohr-Sommerfeld condition must be replaced in the presence of random degeneracy by a Schrödinger equation in terms of the corresponding variable.⁶ Motion as a function of τ is replaced by an effective Hamiltonian of standard form (5); the momentum canonically conjugate to the variable τ is ΔE [see Eqs. (2)], so that the Schrödinger equation takes the form

$$\left[-\frac{3}{2E_0} \frac{d^2}{d\tau^2} + \mu V_1(\tau; l, \theta) \right] \Psi(\tau) = \bar{V}_2(l, \theta) \Psi(\tau). \quad (13)$$

The boundary condition for the wave function $\Psi(\tau)$ is the periodicity condition $\Psi(0) = \Psi(T)$. The analysis, in Ref. 6, of this perturbation-theory variant did not take into account two important circumstances. First, only the ground state has a physical meaning in (13), inasmuch as ΔE is finite at $\mu = 0$ for the remaining states, and they do not go over into the solutions of the unperturbed problem as $\mu \rightarrow 0$. Second, according to the initial formulation of the problem, it is meaningful to solve (13) only in first-order perturbation theory. Obviously \bar{V}_2 is zero for the ground state, and the corresponding wave function is constant and equal to $\Psi_0 = T^{-1/2}$. The first-order correction

$$\bar{V}_2(l, \theta) = \int_0^T \Psi_0^2(\tau) V_1(\tau; l, \theta) d\tau \quad (14)$$

is a supplementary integral of motion and serves as an effective Hamiltonian in the variable θ . Comparison of (9) and (14) shows that on going to the modified perturbation theory the classical averaging in the calculation of the effective Hamiltonian is replaced by quantum-mechanical averaging which, as can be easily verified, coincides again with the classical one but for the nondegenerate case:

$$\bar{V}_2(l, \theta) = \frac{1}{T} \int_0^T V_1(\tau; l, \theta) d\tau = \frac{1}{T^2} \int_0^T \int_0^T \frac{dt_1 dt_2}{|\mathbf{r}_1(t_1) - \mathbf{r}_2(t_2)|}. \quad (15)$$

This leads to the important conclusion that in classical mechanics the quasiclassical approximation eliminates the difference between the nondegenerate and random-degenerate motions, and both situations are described by the same EBK procedure for the nondegenerate case. This eliminates, in particular, the problem discussed in Ref. 6, that of the irregular behavior of the energy-level density near random resonances, a problem we now see to be the result of an incomplete analysis of the quasiclassical perturbation theory.

The dependence of l on θ is determined from the condition that the integral of motion $\bar{V}_2(l, \theta)$ be conserved on the trajectory. Using the explicit expressions for the Kepler trajectory¹² we can show that \bar{V}_2 satisfies the scaling condition

$$\bar{V}_2(l, \theta) = (Z/n^2) v(l/n, \theta). \quad (16)$$

The numerically obtained universal function $v(x, y)$ is shown in Fig. 3. Owing to the scaling property (16), the transcendental equation that yields the dependence of l on θ ,

$$v(l/n, \theta) = w = \text{const}, \quad (17)$$

does not contain the nuclear charge and depends on n only in the form of the ratio l/n .

Quasiclassical quantization in the variable $\chi \equiv (\pi - \theta)/2$ is the same as considered in Ref. 13 for a hydrogen atom in a magnetic field, when the component of the angular momentum in the magnetic-field direction is zero. As indicated in Ref. 13, it is necessary in this case to take into account the following circumstance. The total quasiclassical state is made up of an ensemble of trajectories having a common symmetry axis z (see Fig. 1) and making different angles with this axis. Condensation of the trajectories (caus-

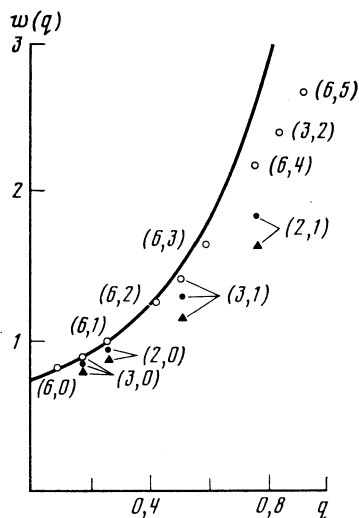


FIG. 4. Reduced correction to the unperturbed-state energy: \circ —first order of quantum perturbation theory, \blacktriangle —exact values for He (Ref. 14), \bullet —exact values for B^{+++} (Ref. 14). The parentheses contain the state quantum numbers (n, k) .

tic) on the z axis ($\chi = 0$) takes place in such an ensemble and is of purely geometric origin. Taking into account the caustic at ($\chi = 0$) and the turning point at $\chi = \chi_m$, the condition for quantization in χ takes the form¹³

$$\int_0^{\chi_m} l(\chi) d\chi = \frac{\pi}{2} \left(k + \frac{1}{2} \right), \quad k=0, 1, \dots, n-1. \quad (18)$$

The values of k are bounded from above, since $l \leq n$ and $\chi < \pi/2$; the number of states here is n , as it should be. The quantization condition (18) is made unique by the scaling property (16) in the following manner. Since (17) contains the combination $\nu = l/n$, we divide both sides of (18) by n :

$$\int_0^{\chi_m} \nu(\chi) d\chi = \frac{\pi}{2} q, \quad q = \frac{2k+1}{2n} \quad (0 < q < 1). \quad (19)$$

Inverting the transcendental equation (17) we get ν as a function of the angle χ and the constant w ; the maximum angle χ_m is determined from the equation $\nu(\chi_m; w) = 0$ and depends only on w . It follows that the quantized values of w depend only on the reduced quantum number q . In first-order perturbation theory, the correction $E^{(1)}$ to the energy is equal to the averaged perturbation \bar{V}_2 . Taking (16) and (17) into account, it reduces to the form ($\mu = 1$)

$$E^{(1)} = (Z/n^2) w(q). \quad (20)$$

Figure 4 shows a plot of $w(q)$ and also the corrections, recalculated in accordance with the scaling property (20), to the unperturbed energy in first-order perturbation theory for helium²⁾ and obtained by exact calculation for He and B^{+++} . It can be seen from the figure that the agreement with calculation improves with increasing nuclear charge. The discrepancy between quasiclassical and quantum theory becomes noticeable only at $q > 1/2$. It is attributable to the fact that as $q \rightarrow 1$ the turning point χ_m approaches the singular point $\chi = \pi/2$ (see Fig. 3). In this case the quantization condition (18) must be replaced by the standard-equation

method, in which simultaneous account is taken of the turning point and the singular point at $\chi = \pi/2$.

The quasiclassical approximation is valid, generally speaking, when the quantum numbers are large, i.e., $n \gg 1$ and $k \gg 1$. The second restriction is of no importance here. The motion as a function of θ , with which the quantum number is connected, constitutes oscillations in a potential well replaceable at $k \ll n$ by an oscillator well for which the exact and quasiclassical level positions are the same. This explains the good agreement between the quasiclassical and the quantum corrections at small k (see Fig. 4). The general condition $E^{(0)} \gg V$ for the validity of quasiclassical perturbation theory¹⁰ takes, when account is taken of (20), the form $Z \gg \omega(q) \approx 1$. To estimate the order of magnitude of the second-order correction $E^{(2)}$ of the quasiclassical perturbation theory we use the expression⁵

$$E^{(2)} = -\frac{\partial}{\partial n} \left[\frac{\langle V^2 \rangle}{2} T \right],$$

which, albeit obtained for the one-dimensional case, can be expected to describe correctly the dependence of $E^{(2)}$ on the principal quantum number and on the charge. We get then in our case $E^{(2)} \approx n^{-2}$, which can be neglected under the condition $E^{(1)}/E^{(2)} \approx Z \gg 1$ which coincides with the obtained restriction on the nuclear charge.

4. CLASSIFICATION OF STATES

One of the main purposes of various approximate approaches used in atomic theory is to find simple approximate classification systems for the spectra and the states. In the approximation considered above, the states are specified by the quantum numbers L, L_z, n_1, n_2 , and k , with $n_1 = n_2$ and $L = L_z = 0$. What is new in this set is the quantum number k connected with the integral of motion $\bar{V}_2(l, \theta)$. A natural sequel to this approach would be a quantum-mechanical investigation of \bar{V}_2 so as to obtain, using the symmetry group $O(4) \times O(4)$ of the unperturbed problem, the correct zeroth-order approximation wave functions, as was done in Ref. 13 for the hydrogen atom in a magnetic field. This, however, is an unrealistic task for lack of an explicit expression for $\bar{V}_2(l, \theta)$. This makes it necessary to obtain approximate expressions $\Lambda(l, \theta)$ that would be, on the one hand conserved to the utmost in first-order perturbation theory, and on the other simple enough for a group-theoretical approach.

For the case $n_1 \sim n_2$ and $L \sim 1$, the following approximate two operators that commute with each other were chosen in Refs. 15 and 16 from heuristic considerations as the approximate integrals of motion:

$$\begin{aligned} \Lambda &= A_1^2 + A_2^2 - 2A_1 A_2, \\ Q &= L(A_1 - A_2), \end{aligned} \quad (21)$$

where

$$A_i = \frac{n}{Z} \left\{ \frac{1}{2} ([l_i p_i] - [p_i l_i]) - Z \frac{\mathbf{r}_i}{r_i} \right\} \quad (22)$$

is the Runge-Lenz operator of i th electron.

At $L = 0$ the operator Q is an exact integral of the motion and vanishes. For this case we can track directly in our approach the variation of Λ as the elliptic electron trajectory-

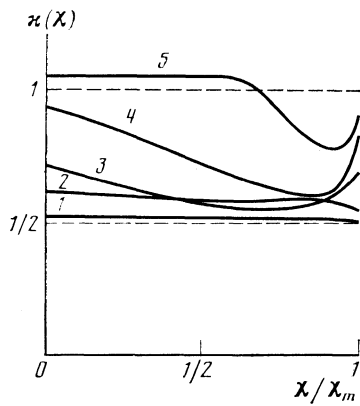


FIG. 5. Plot of κ versus χ for certain values of q : 1— $\chi_m = \pi/40$, $q = 0.003$; 2— $\chi_m = \pi/8m$, $q = 0.065$; 3— $\chi_m = \pi/4$, $q = 0.25$; 4— $\chi_m = 3\pi/8$, $q = 0.53$; 5— $\chi_m = 9\pi/20$, $q = 0.8$.

ies evolve under the influence of the perturbation and estimate the extent to which the choice of a simplified integral of motion in this form is justified. In classical mechanics, the \mathbf{A}_i are connected with $l(\chi)$ by the relation $A_1^2 = A_2^2 = n^2 - l^2(\chi)$, and the angle between \mathbf{A}_1 and \mathbf{A}_2 is equal to $\pi - 2\chi$. Let us consider an equation of more general form

$$\tilde{\Lambda}_x = \Lambda_x (1 + \kappa \cos 2\chi_m)^{-1}, \quad \Lambda_x \equiv A_1^2 + A_2^2 - 2\kappa \mathbf{A}_1 \mathbf{A}_2. \quad (23)$$

To verify that the quadratic form (23) is a suitable simplified integral of motion we can track either the variation, on the trajectory, of Λ_x at a fixed κ or, conversely, of κ at a fixed Λ_x . We use the second variant. The quadratic form $\tilde{\Lambda}_x$ to the value at the point χ_m , we get

$$\kappa(\chi) = l^2(\chi) [(n^2 - l^2(\chi)) \cos 2\chi - n^2 \cos 2\chi_m]^{-1}. \quad (24)$$

Figure 5 shows the numerically calculated κ for several values of q . It shows that κ is conserved at small q and that $\kappa \rightarrow 1/2$ as $q \rightarrow 0$. At $q \approx 1$ we have $l \approx n$ at all χ except in a small vicinity of χ_m , and $\cos 2\chi_m \approx -1$ (this situation is illustrated by curve 3 of Fig. 3). It follows therefore from (24) that $\kappa \approx 1$ in this region. On the other, we have the nonnormalized expression $\Lambda_x \approx (n^2 - l^2) \approx 0$ everywhere except in a small vicinity of χ_m . At the turning point itself $l = 0$ and to ensure smallness of Λ_x at this point we must put also $\kappa \approx 1$. Thus, the integral of motion (23) can be used for the lower ($q \approx 0$) and upper ($q \approx 1$) energy levels of the given multiplet $\{n_1 = n_2 \equiv n, L = 0\}$, i.e., the correct zeroth-ap-

proximation functions in the quantum perturbation theory are the eigenfunctions of the operator $\hat{\Lambda}_x = \hat{A}_1^2 + \hat{A}_2^2 - 2\kappa \hat{\mathbf{A}}_1 \cdot \hat{\mathbf{A}}_2$ with $\kappa \approx 1/2$ for the lower energy levels and $\kappa \approx 1$ for the upper. In a basis of two-electron wave functions with zero total angular momentum

$$\Phi_l(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{(2l+1)^{1/2}} \sum_{m=-l}^l (-1)^m \varphi_{n_1 m}(\mathbf{r}_1) \varphi_{n_2 -m}(\mathbf{r}_2)$$

the nonzero matrix elements of the operator Λ_x are

$$\langle \Phi_l | \hat{\Lambda}_x | \Phi_l \rangle = 2[n^2 - 1 - l(l+1)],$$

$$\langle \Phi_l | \hat{\Lambda}_x | \Phi_{l-1} \rangle = -2\kappa \frac{l(n^2 - l^2)}{(4l^2 - 1)^{1/2}}$$

and the equation for the eigenfunctions $\hat{\Lambda}_x \Psi_k = \lambda_k \Psi_k$ reduces to three-term recurrence relations for the coefficients $g_l = \langle \Psi_k | \Psi_l \rangle$, in the form

$$\frac{l(n^2 - l^2)}{(4l^2 - 1)^{1/2}} g_{l-1} + \frac{1}{2\kappa} [\lambda_k - 2(n^2 - 1 - l(l+1))] g_l + \frac{(l+1)[n^2 - (l+1)^2]}{[(2l+1)(2l+3)]^{1/2}} g_{l+1} = 0. \quad (25)$$

The problem can be solved exactly for $\kappa = 1$ (Refs. 15 and 16); in this case $\lambda_k = 4(n-k)(n-k-1)$ and the coefficients g_l are expressed in terms of the Wigner 6_j symbol

$$g_l = (-1)^{k+n+1} [(2k+1)(2l+1)]^{1/2} \times$$

$$\times \begin{pmatrix} \frac{n-1}{2} & \frac{n-1}{2} & k \\ 2 & 2 & l \end{pmatrix}.$$

For other values of κ the solution (25) can be obtained only numerically. The next and first-order perturbation-theory values of g_l obtained from the recurrence relations (25) are listed in Table I. The value $\kappa = 0.65$ for the lower level was taken from the numerical calculation for $q = 1/6$; the classical value in this case is $\Lambda_x = 1.21 n^2$ and is conserved and the trajectory accurate to 1%. It can be seen from the table that a good result is obtained for the upper level at $\kappa = 1$ and for the lower at $\kappa = 0.65$, while both variants overestimate g_0 and underestimate g_2 for the middle level.

We have considered above a quasiclassical perturbation theory for equivalent electrons ($n_1 = n_2$) with zero total angular momentum. This case is simplest from the standpoint of calculations and is at the same time of great physical interest,

TABLE I. Comparison of the correct zeroth-approximation functions (Ref. 3) with the eigenfunctions of the operator Λ_x at $n_1 = n_2 = 3$ and $L = 0$.

	g_0	g_1	g_2	
$k=2$	[3]	0.331	-0.586	0.739
	$\kappa=1$	0.333	-0.577	0.744
	$\kappa=0.65$	0.188	-0.428	0.885
$k=1$	[3]	-0.519	0.541	0.662
	$\kappa=1$	-0.577	0.500	0.645
	$\kappa=0.65$	-0.584	0.676	0.450
$k=0$	[3]	0.788	0.603	0.125
	$\kappa=1$	0.744	0.645	0.167
	$\kappa=0.65$	0.789	0.601	0.122

being the fullest manifestation of the electron correlation. A change to the case $n_1 \neq n_2$, $L = 0$ changes nothing, generally speaking in the foregoing analysis, except that in the calculation of the averaged perturbation (15) the integration with respect to t_1 and t_2 is over different periods. It is doubtful, however, whether a direct application of this approach at $n_1 \neq n_2$, is useful. First, it is natural to take into account here in the perturbation theory, from the very outset, the screening of the nuclear charge for the outer electron. The screening can be included in trivial fashion in the foregoing perturbation-theory scheme, but the difference between the quantum numbers, together with the screening, can lead to a significant difference between the electron periods. It is physically more justified in this case to use the adiabatic separation of the variables, associated with the small parameter (at $n_1 < n_2$)

$$\gamma = T_1/T_2 = n_1^3 (Z-1)^2 / n_2^3 Z^2,$$

and not Z^{-1} (for example, $\gamma < 1/32$ for all singly excited states of helium). The most important circumstance that makes this approach inadequate for a classification of states with $n_1 \neq n_2$ is the lack of a method for calculating the exchange singlet-triplet level splitting that is comparable with the first-order correction. Thus, for helium states with $n_1 = 1$ and $n_2 = 2$ there we have one singlet state and one triplet state with respective energies $E_s = -2.146$ and $E_t = -2.175$ (Ref. 17), whereas their common unperturbed energy is $E_0 = -2.125$. For equivalent electrons ($n_1 = n_2$) all the states with $L = 0$ are singlet and there is no need to take exchange interaction into account.

The case $L \neq 0$ differs fundamentally from $L = 0$. At $L \neq 0$ the problem can be reduced, after separating the angle variables connected with the angular momentum, to a four- rather than to a three-dimensional one as at $L = 0$ (Ref. 11). After averaging over ξ_1 and ξ_2 we get therefore a two-dimensional effective Hamiltonian and there is no complete separation of the variables in first order of perturbation theory. The non-integrability leads to an important qualitative result, viz., the distribution of the distance between multiplet energy levels with given n_1, n_2 , and $L \neq 0$ has in first-order perturbation

theory a Landau-Wigner-Dyson distribution, whereas the same distribution with $L = 0$ has a Poisson distribution for integrable systems (see, e.g., Ref. 18). This points to the absence of a sufficiently universal classification of the states with $L \neq 0$. In some particular cases, for example, $n_1 \ll n_2$ or $L \gg 1$, approximate integration is possible and such cases have been investigated.³

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¹The atomic system of units is used in this article.

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¹I. C. Percival, *Adv. Chem. Phys.* **1**, 36 (1977).

²V. I. Arnol'd, *Mathematical Methods of Classical Mechanics* [in Russian], Nauk, 1979.

³S. I. Nikitin and V. N. Ostrovskii, *Fiz. Molekul* **8**, 3 (1980).

⁴E. A. Solov'ev, *Zh. Eksp. Teor. Fiz.* **75**, 1261 (1978) [*Sov. Phys. JETP* **48**, 635 (1978)].

⁵M. Born, *Lectures on Atomic Mechanics* [Russ. Transl.], ONTI, 1934 [Probably: *Mechanics of the Atom*, Bell, London, 1927].

⁶A. P. Kazantsev and V. L. Pokrovskii, *Zh. Eksp. Teor. Fiz.* **85**, 1917 (1983) [*Sov. Phys. JETP* **48**, 1114 (1983)].

⁷J. G. Leopold, I. C. Percival, and A. S. Tworkowski, *J. Phys.* **B13**, 1028 (1980).

⁸J. G. Leopold and I. C. Percival, *J. Phys.* **B13**, 1037 (1980).

⁹P. V. Coveney and M. S. Child, *ibid.* **B17**, 319 (1984).

¹⁰L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Nonrelativistic Theory)*, Pergamon, 1985.

¹¹L. A. Pars, *Treatise on Analytical Dynamics*, Wiley, 1965.

¹²L. D. Landau and E. M. Lifshitz, *Mechanics*, Pergamon, 1969.

¹³E. A. Solov'ev, *Zh. Eksp. Teor. Fiz.* **82**, 1762 (1982) [*Sov. Phys. JETP* **55**, 1017 (1982)].

¹⁴L. Lipsky, R. Anania, and J. M. Connelly, *Atomic and Nuclear Data Tables* **20**, 127 (1977).

¹⁵C. E. Wulfman, *Chem. Phys. Lett.* **23**, 370 (1975).

¹⁶O. Simanoglu and D. R. Herrick, *J. Chem. Phys.* **62**, 886 (1975).

¹⁷H. A. Bethe and E. A. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Springer, 1958.

¹⁸E. B. Bogomol'nyi, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 55 (1985). [*JETP Lett.* **41**, 65 (1985)].

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