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Adiabatic theory for the doubly excited asymmetric states of the helium atom

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In the asymmetric (or planetary) doubly excited states of the helium atom, one of the electrons is excited much more than the other. The motion of the electrons is strongly correlated: both of them reside mostly on the same side of the atomic nucleus. An adiabatic theory for such states is based on the approximate separation of rapid and slow motion. The rapid motion is that of the inner electron along its elliptic orbit. The parameters of the orbit (eccentricity and the aphelion vector) slowly evolve in time. The other slow motion is the radial vibrations of the outer electron. The effective Hamiltonian is constructed as the average of the exact Hamiltonian over the rapid motion. In the quadratic approximation two types of slow motion are separated and reduced to two harmonic oscillators. The unexpected feature is that the ratio of the related frequencies is very simple: 1:2. The ratio is changed when the outer electron is replaced by the particle with an arbitrary mass. The slow motions are quantized and the series of the energy levels are obtained. In the case of infinite mass of the outer particle, the potential curves of the quasimolecule are calculated. The present purely analytic results are compared with the numerical data.

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I. INTRODUCTION

In the asymmetric doubly excited states of the two-electron atom, one of the electrons is excited much more than the other. These states are sometimes referred to also as the planetary atom states.

In the present paper we develop the adiabatic theory for the asymmetric states of the special type, namely with the maximal localization of both electrons on the same side of the nucleus. Generally, for the asymmetric states, it is natural to use the long-range multipole expansion of the interaction between the electrons, which are localized in different regions of space. The leading term of expansion is the dipole interaction (apart from the trivial monopole term). The bibliography on the dipole approximation is quite extensive and can be found in Ref. [1]. For the special type of asymmetric states considered here, the dipole picture is particularly appealing. The outer electron is *attracted* by the Coulomb potential of the nucleus, which is screened by the inner electron. The inner-electron distribution is asymmetric being shifted towards the outer electron. Its long-range potential is described as *repulsive* dipole. Hence, the total potential seen by the outer electron has a minimum. Actually the dynamics of the correlated electron motion is rather complicated including strong exchange by the orbital momentum between the electrons [1].

For the asymmetric states under consideration, the large-scale precise quantum calculations by the complex coordinate rotation method were carried out recently by Richter and co-workers [2,3]. The classical electron trajectories were also calculated and visualized. Using the well-known Gutzwiller [4] quantization procedure, Richter and co-workers [2,3] obtained the Rydberg series in the form

$$E_{nk\tilde{l}}=\frac{S^2}{[n+\frac{1}{2}+2(k+\frac{1}{2})\gamma_1+(\tilde{l}+\frac{1}{2})\gamma_2]^2} . \tag{1.1}$$

The parameters S, γ_1, and γ_2 were related with the properties of the periodic classical electron trajectory; n, k, and $\tilde{l}$ are integer quantum numbers. The Rydberg series of type (1.1) converging to the energy zero (which corresponds to the double electron escape) are usually referred to as the Wannier resonances. They were discussed by a number of authors [5–7].

The dipole picture [1,8–10] leads to the Rydberg series of the form

$$E_{n_2 n_r \gamma}=-\frac{Z^2}{2n_2^2}-\frac{(Z-1)^2}{2(n_1-\delta_\gamma)^2} , \tag{1.2}$$

where Z is the charge of the nucleus and δ_γ is the quantum defect. As the principal quantum number of the outer electron n_1 increases, the series converges to the level of the residual ion with the principal quantum number n_2. The quantum number γ distinguishes the series with the same limit. The series of the form (1.2) were discussed also by a number of authors [11,12] without resort to the dipole approximation. Experimentally the states of this type with various n_2 (up to 6) were observed in the helium atom [12]. We mention also the recent experiments [13,14] with the rare earth atoms, where the additional effect of the non-Coulomb core is important.

Our analysis [9,10] have shown that the results of the numerical calculations [2,3] in fact agree better with the Rydberg series of the form (1.2) than with (1.1). For the quantitative estimate of the quantum defect δ_γ (or, more exactly, of the related parameter $1_{\mathrm{eff}\gamma}$) we have used the dipole approximation for the electron-electron interaction and accounted also for the quadrupole correction.

The precision of this simple approximation is not high, although it is sufficient for the states classification and the semiquantitative analysis of the electron correlation pattern.

The applicability of the dipole approximation for the electron-electron interaction is justified by the localization of the outer electron at large distance as compared with the extension of the inner-electron orbit. Numerically the ratio of the characteristic dimensions is about 2.7 for the heluim atom (Sec. III).

Additionally, the dipole approximation (as it was employed in Refs. [1,9,10]) assumes also the adiabaticity intrinsic in the asymmetric states. Namely, the characteristic frequency for the inner-electron motion exceeds that of the outer electron. The ratio of the frequencies proves to be about 13 for the helium atom (see Sec. IV). Hence, the related applicability criterion is satisfied much better than for the dipole approximation.

In the present paper, we drop the dipole approximation and develop a purely adiabatic classical and semiclassical theory. In the classical picture, the inner electron moves rapidly along the elliptic orbit. The energy of the inner electron averaged over this rapid motion is an adiabatic invariant: It is conserved in time in the first order over the adiabaticity parameter.

The remaining system coordinates vary slowly. As shown in Secs. II and III, the Hamiltonian $\langle H \rangle$ averaged over the rapid motion possesses a stationary point. In this configuration, the orbit of the inner electron is squeezed into the straight line segment; it corresponds to zero orbital momentum. The outer electron resides at some fixed distance from the nucleus. The same trajectory appeared in Refs. [2,3] (see, in particular, the figure of Richter and Wintgen in Ref. [2]), where the classical motion was quantized using the Gutzwiller [4] scheme. The numerical analysis generated the parameters entering Eq. (1.1). We are considering the vicinity of the same classical trajectory using the adiabatic approach, which allows us to construct a purely analytical scheme. Both the classical motion and its quantization are described. An adiabatic and analytical treatment seems to be conceptually important. Indeed, the general Gutzwiller quantization procedure ignores the presence of rapid and slow components in the motion, which defines the physical specifics of the system under consideration. The adiabatic theory provides a new outlook on the nature of the same quantum states and leads to some new conclusions.

The expansion of $\langle H \rangle$ over the small deviations from the stationary configuration does not contain the linear terms. In the quadratic approximation, the motion is described as a superposition of two slow harmonic vibrations with frequencies of the same order of magnitude: (i) oscillations of the outer-electron separation from the nucleus r_1 (Sec. III) and (ii) oscillations of the angle between the outer-electron and the aphelion of the inner-electron orbit (Sec. IV). The momentum canonically conjugate to the latter coordinate is the one-electron orbital momentum.

The harmonic oscillations are easily quantized (Sec. V). The structure of the Hamiltonian testifies in favor of the Rydberg series of the form (1.1). In Sec. VI, we analyze in more detail the spectrum domain where the Rydberg series (1.1) and (1.2) do not differ much. For these levels, the semiclassical formula obtained by Richter and coworkers [2,3] is in very good agreement with the precise quantum calculations of the same authors. Our results are compared with these of Refs. [2,3] and with the simple dipole approximation.

We discuss also the analogous problem with the outer electron substituted by the particle with an arbitrary mass. In particular, in the limit of infinite mass we come to the problem of a single electron in the field of two space-fixed Coulomb centers (Sec. VII). The latter was used by Richter and co-workers [2,3] in the adiabatic calculations for the helium atom. Although this approach is well justified when the outer particle is an antiproton [15], in the case of electron [2] it seems to be too crude. Section VIII contains some concluding discussion.

II. STATIONARY CONFIGURATION FOR THE HELIUM ATOM

The helium atom Hamiltonian we cast in the form

$$H=\tfrac{1}{2}p_{1r}^2-\frac{l_1^2}{2r_1^2}-\frac{Z}{r_1}+\frac{1}{r_{12}}+h_{20}\ , \tag{2.1}$$

where

$$h_{20}=\tfrac{1}{2}p_2^2-\frac{Z}{r_2} \tag{2.2}$$

is the Hamiltonian of the inner electron, $\mathbf{r}_1=\{x_i,y_i,z_i\}$ is the ith electron coordinate, $\mathbf{p}_i$ is the related momentum, p_{ir} is its radial component, l_i is the orbital momentum, and Z is the nucleus charge. The electrons are treated as distinguishable particles (in the asymmetric states they are located mostly in different regions of space). We consider primarily the S states of the atom ($l_1=-l_2$) where the classical electron motion is confined to the plane ($z_i=0$).

Our first step is the averaging of H over the rapid motion of the inner electron. As discussed in the Introduction, it implies replacement of h_{20} by the constant energy E_{20}, which can be parameterized as $E_{20}=-Z^2/(2n_2^2)$. In quantum mechanics, n_2 has the meaning of the inner-electron principal quantum number, which is "good" in the present approximation.

The nontrivial averaging is that of the electron-electron interaction potential $1/r_{12}$. It is convenient to introduce the rotating frame $(X',Y',Z'=Z)$ with the X' axis directed along the principal axis of the unperturbed elliptic orbit of the inner electron. The parametric equations of motion along the elliptic orbit (in terms of Kepler eccentric anomaly ζ) are universally known:

$$\begin{gathered} x_2'=\frac{n_2^2}{Z}(e-\cos\zeta)\ ,\quad y_2'=\frac{n_2^2}{Z}\frac{l_2}{n_2}\sin\zeta\ , \\ t=\frac{T_0}{2\pi}(\zeta-e\sin\zeta)\ , \end{gathered} \tag{2.3}$$

where T_0 is the period and e is the orbit eccentricity:

$e=\sqrt{1-l_2^2/n_2^2}$. In the space-fixed frame, the inner electron has the coordinates

$$\begin{aligned} x_2 &= x_2'\cos\Phi_2 - y_2'\sin\Phi_2 \ , \\ y_2 &= x_2'\sin\Phi_2 + y_2'\cos\Phi_2 \ , \end{aligned} \tag{2.4}$$

where Φ_2 is the azimuthal angle of the orbit aphelion. The orbit parameters Φ_2 and l_2 depend on time describing the slow evolution of the inner-electron orbit due to the electron-electron interaction. The azimuthal angle of the ith electron in the space-fixed frame will be designated as φ_i.

We will carry out the averaging of $1/r_{12}$ in the vicinity of the stationary configuration. The latter is described in the Introduction and corresponds to $l_2=0$ (i.e., $y_2'=0$, $\varphi_1=\Phi_2=0$) and some fixed value of r_1, which will be defined in Sec. III. For simplicity it is assumed that in the stationary configuration the vector $\mathbf{r}_1$ lies along the X axis. The expansion of $1/r_{12}$ is obtained using Eq. (2.4) and the trivial relations $x_1=r_1\cos\varphi_1$, $y_1=r_1\sin\varphi_1$. Only the terms quadratic in small y_2', φ_1, and Φ_2 are retained:

$$\frac{1}{r_{12}} = \left[\frac{1}{r_{12}}\right]_1 + \left[\frac{1}{r_{12}}\right]_2 + \left[\frac{1}{r_{12}}\right]_3 , \tag{2.5}$$

$$\left[\frac{1}{r_{12}}\right]_1 = \frac{1}{r_1 - x_2'} , \tag{2.6}$$

$$\left[\frac{1}{r_{12}}\right]^2 = -\frac{y_2'^2 + r_1 x_2' \varphi_{12}^2}{2(r_1 - x_2')^3} , \tag{2.7}$$

$$\left[\frac{1}{r_{12}}\right]_3 = \frac{r_1 y_2' \varphi_{12}}{(r_1 - x_2')^3} , \quad \varphi_{12} = \varphi_1 - \Phi_2 \ . \tag{2.8}$$

The term (2.8) is linear in y_2'. Hence, being averaged over the rapid motion it gives zero, as is straightforwardly seen from Eqs. (2.3). Therefore, this term does not appear in the subsequent analysis. In the stationary configuration ($y_2'=0$) only the term (2.6) in the right hand side of (2.5) contributes. The term (2.7) is important when the motion in the vicinity of this configuration is considered.

III. RADIAL MOTION OF THE OUTER ELECTRON IN THE ADIABATIC THEORY

The averaging of the Hamiltonian (2.1) over the rapid motion implies the replacement of the electron-electron interaction potential $1/r_{12}$ by

$$\left\langle \frac{1}{r_{12}} \right\rangle \equiv \frac{1}{T_0} \int_0^{T_0} \frac{1}{r_{12}} dt \ . \tag{3.1}$$

The basic integral required for this and subsequent (Sec. IV) calculations is known:

$$\int_0^{2\pi} \frac{\cos nx \, dx}{1 + b\cos x} = \frac{2\pi}{\sqrt{1-a^2}} \left[\frac{\sqrt{1-b^2}-1}{b}\right]^n . \tag{3.2}$$

We start with the averaging of the first term in the right hand side of the expression (2.5). The integration gives the result

$$\left\langle \frac{1}{r_{12}} \right\rangle_1 \equiv \frac{1}{T_0} \int_0^{T_0} \frac{1}{r_1 - x_2'} dt = \frac{Z}{n_2^2} \left[\frac{a+e}{\sqrt{1-a^2}} - e\right] , \tag{3.3}$$

where

$$a = \frac{1}{Zr_1/n_2^2 - e} \ . \tag{3.4}$$

The average (3.3) varies with r_1 (via the parameter a) and also with the variation of the form of the inner-electron orbit (via its eccentricity e). In this Section, we are interested in the former dependence (the corrections due to the orbit evolution are considered in Sec. IV). Therefore, we take the expression (3.3) for $e=1$; it will be designated as $\langle 1/r_{12} \rangle_{\mathrm{rad}}$. This potential gives the averaged electron-electron interaction under the additional condition that the inner electron moves along the elliptical orbit squeezed into the interval of line. The related averaged Hamiltonian for the radial motion of the outer electron is

$$H_{\mathrm{rad}} = \tfrac{1}{2}p_{1r}^2 - \frac{Z}{r_1} + \left\langle \frac{1}{r_{12}} \right\rangle_{\mathrm{rad}} = \tfrac{1}{2}p_{1r}^2 + V(r_1) \ , \tag{3.5}$$

with the effective potential $V(r_1)$

$$V(r_1) = \frac{Z}{n_2^2} \left[\left[1 - \frac{2}{Z}\frac{n_2^2}{r_1} \right]^{-1/2} - 1 - \frac{n_2^2}{r_1} \right] . \tag{3.6}$$

The structure of the interaction becomes particularly simple in the long-range asymptote

$$V(r_1) = \frac{Z-1}{r_1} + \frac{3n_2^2}{2Zr_1^2} + O(r_1^{-3}) \ , \tag{3.7}$$

where the first term corresponds to the interaction of the outer electron with the nucleus screened by the inner electron. The second term describes the outer-electron interaction with the permanent dipole, which corresponds to the inner-electron motion in the stationary (squeezed ellipse) configuration. It is worthwhile to note that in the quantum-mechanical description of the inner electron, this term should be replaced by $3n_2(n_2-1)/(2Zr_1^2)$, i.e., the dipole moment is somewhat less than in the classical limit. This is due to the fact that in the quantum mechanics the inner-electron distribution cannot be stretched into the line, but is somewhat spread around the axis of the electric field created by the outer particle. In other words, the angular oscillations considered in the Sec. IV cannot be eliminated completely due to the uncertainty relation (see also Sec. VII).

The effective potential (3.6) has a weak (square root) repulsive singularity at the point $r_{1s}=2n_2^2/Z$ where the electron-electron collision becomes possible.

The minimum of the potential (3.6) lies at the point $r_1=r_{10}$:

$$r_{10} = \alpha n_2^2 \ , \quad \alpha = \frac{2}{Z}(1 - Z^{-2/3})^{-1} \ , \tag{3.8}$$

$$V(r_{10}) = -\frac{Z^2}{2n_2^2}(1 - 3Z^{-2/3} + 2Z^{-1}) \ . \tag{3.9}$$

Note that for $Z=1$ (i.e., for the H^- ion isoelectronic to the helium atom) the effective potential becomes purely repulsive and the minimum disappears.

The presence of the Coulomb term in the asymptote (3.7) shows that the energy levels form a Rydberg series. The series is convergent to the eigenvalues E_{20} of the inner-electron Hamiltonian h_{20}, i.e., to the energy levels of the residual ion. This conclusion coincides with that drawn by us before [9,10], and differs from the results by Richter and co-workers [2,3].

Now we consider the lowest members of the series. The corresponding wave functions are located primarily in the vicinity of the potential minimum r_{10}. The quadratic approximation for the Hamiltonian H_{rad} reads

$$H_{\text{rad}} = H'_{\text{rad}} + V(r_{10}) , \quad H'_{\text{rad}} = \tfrac{1}{2}p_{1r}^2 + \tfrac{1}{2}k(r_1 - r_{10})^2 , \tag{3.10}$$

where

$$k \equiv \frac{\partial^2 V}{\partial r_1^2} = \frac{3Z^{2/3}}{16 n_2^6}(Z - Z^{1/3})^4 . \tag{3.11}$$

In this approximation, the outer-electron radial motion corresponds to harmonic oscillations with the frequency

$$\omega_{\text{rad}} = \sqrt{k} = \frac{\sqrt{3}}{4} n_2^{-3} Z^{1/3}(Z - Z^{1/3})^2 . \tag{3.12}$$

It is instructive to consider the characteristic numerical values of the parameters for the helium atom ($Z=2$). The parameter $\alpha = 2.7024$ is essentially the ratio of the characteristic dimensions of the inner-electron and outer-electron orbits. As discussed in the Introduction, this parameter governs the applicability of the dipole approximation. The other parameters are

$$V(r_{10}) = -0.220\,24 n_2^{-2} , \quad \omega_{\text{rad}} = 0.298\,81 n_2^{-3} . \tag{3.13}$$

Note that $V(r_{10})$ is small compared with the unperturbed energy of the inner electron $[|V(r_{10})|/E_{20} \approx 0.1]$. This relation is important for the justification of the present approximation. Table I demonstrates that the radial frequency ω_{rad} is in good agreement with the energy separation between the numerically calculated quantum energy levels.

IV. ANGULAR ELECTRON CORRELATIONS IN THE ADIABATIC THEORY

When the averaging of the electron-electron interaction (2.5) is carried out, the terms responsible for the angular correlations come from (i) the averaging of the term (2.7) and (ii) the difference between the expression (3.2) for $\langle 1/r_{12} \rangle_1$ and its value for $e=1$ designated above as $\langle 1/r_{12} \rangle_{\text{rad}}$. In the quadratic approximation, only the terms linear in $e - 1 \approx l_2^2/(2n_2^2)$ or in φ_{12}^2 are retained.

The averaging of (2.7) gives

$$\langle 1/r_{12} \rangle_2 = -\tfrac{1}{2}I_1 l_2^2 - \tfrac{1}{2}I_2 \varphi_{12}^2 , \tag{4.1}$$

$$I_1(r_1) \equiv \frac{1}{T_0}\int_0^{T_0} \frac{1}{(r_1 - x'_2)^3}\left[\frac{y'_2}{l_2}\right]^2 dt , \tag{4.2}$$

$$I_2(r_1) \equiv \frac{1}{T_0}\int_0^{T_0} \frac{r_{10}x'_2}{(r_1 - x'_2)^3} dt , \tag{4.3}$$

where x'_2 is defined by Eq. (2.3) with $e=1$. In (4.1), one should use the integrals (4.2) and (4.3) calculated for $r_1 = r_{10}$. However, at first we will carry out the integration for arbitrary r_1 (these results are used in the discussion of the potential curves, Sec. VII). The necessary integrals are obtained from (3.2) by taking derivative over the parameter b. The calculations are quite cumbersome but the final result looks simple:

$$I_1(r_1) = \frac{Z}{2n_2^4}\left[\frac{a_0^3 + 3a_0^2 - 2}{2(1 - a_0^2)^{3/2}} + 1\right] , \tag{4.4}$$

$$I_2(r_1) = \frac{3Z^2}{2n_2^4} r_1 a_0^3 \frac{(1 + a_0)^2}{(1 - a_0^2)^{5/2}} . \tag{4.5}$$

The r_1 dependence enters here via $a_0(r_1)$:

$$a_0 = \frac{1}{Zr_1/n_2^2 - 1} . \tag{4.6}$$

The calculation of the second contribution to the angular correlations is straightforward:

$$\langle 1/r_{12} \rangle_1 - \langle 1/r_{12} \rangle_{\text{rad}} = \frac{Z}{n_2^2}\left[1 - \frac{1 + a_0^3}{(1 - a_0^2)^{3/2}}\right]\frac{1_2^2}{2n_2^2} . \tag{4.7}$$

In the present context the sum of the contributions (4.1) and (4.7) can be named the angular-dependent part of $\langle 1/r_{12} \rangle$:

$$\langle 1/r_{12} \rangle_{\text{ang}} = -\tfrac{1}{2}k'_1 l^2 - \tfrac{1}{2}k_2 \varphi_{12}^2 , \tag{4.8}$$

$$k'_1(r_1) = \frac{3Za_0^2}{2n_2^4}\frac{1 + a_0}{(1 - a_0^2)^{3/2}} , \quad k_2(r_1) = I_2(r_1) . \tag{4.9}$$

As discussed in Sec. II, in our case $l_1 = -l_2$; we intro-

TABLE I. The classical frequency of the radial vibrations ω_{rad} compared with the energy separation ΔE [3] between the lowest levels in the Rydberg series: $\{n,k,\overline{T}\} = \{n_2 - 1,0,0\}$ and $\{n,k,\overline{T}\} = \{n_2 - 1,0,1\}$ for the helium atom.

n_2	4	5	7	8	9
ΔE	0.0040	0.002	7.8×10^{-4}	5.3×10^{-4}	3.76×10^{-4}
ω_{rad}	0.0047	0.0024	8.7×10^{-4}	5.8×10^{-4}	4.09×10^{-4}
$\dfrac{\Delta E - \omega_{\text{rad}}}{\omega_{\text{rad}}}$,%	16	16	10	8	6

duced the notation $l^2 \equiv l_1^2 = l_2^2$.

The effective Hamiltonian for the slow angular motion $H_{\rm ang}$ is obtained as a sum of (4.8) and the term $l_1^2/(2r_1^2)$ in the helium atom Hamiltonian (2.1). All contributions should be calculated at the stationary point $r_1 = r_{10}$, which leads to the compact expressions

$$H_{\rm ang} = -\tfrac{1}{2}k_1 l^2 - \tfrac{1}{2}k_2 \varphi_{12}^2 \ , \tag{4.10}$$

$$k_1' = \tfrac{3}{8} n_2^{-4}(Z - Z^{1/3})^2 \ , \tag{4.11}$$

$$k_1 \equiv k_1' - \alpha^{-2} n_2^{-4} = \tfrac{1}{8} n_2^{-4}(Z - Z^{1/3})^2 \ , \tag{4.12}$$

$$k_2 = \tfrac{3}{8} Z^{2/3} n_2^{-2}(Z - Z^{1/3})^2 \ . \tag{4.13}$$

The Hamiltonian (4.10) is of the type $-\frac{1}{2}p^2 - \frac{1}{2}\omega^2 q^2$, i.e., it differs only by the sign from the standard harmonic oscillator Hamiltonian $\frac{1}{2}p^2 + \frac{1}{2}\omega^2 q^2$. Obviously the spectra of both Hamiltonians also differ only by the sign. (Note that we do not meet here the Hamiltonian of the parabolic potential barrier $\frac{1}{2}p^2 - \frac{1}{2}\alpha^2 q^2$.) The Hamiltonians of this form appear very frequently in a large variety of quantum problems reducible to the three-term recursion relations (see the recent review by Braun [16] and Refs. [1,17]). The "upside down" oscillator Hamiltonians arise also in the description of the vibrational spectra of polyatomic molecules. The analysis of local and normal modes and the dynamical barrier picture could be mentioned here [18,19].

The role of canonically conjugate coordinate q and momentum p in (4.10) are played by l and φ_{12} (or vice versa) and the frequency is

$$\omega_{\rm ang} = (k_1 k_2)^{1/2} = \frac{\sqrt{3}}{8} n_2^{-3} Z^{1/3}(Z - Z^{1/3})^2 \ . \tag{4.14}$$

The numerical values of the parameters for the helium atom are $k_1 = 0.068\,464/n_2^3$, $k_2 = 0.326\,04/n_2^3$, and $\omega_{\rm ang} = 0.149\,406/n_2^3$.

The pair of conjugate coordinate and momentum is the same as in the dipole approximation [1]. Physically the oscillations imply the exchange by the orbital momentum between the inner and outer electron under the constraint $l_1 + l_2 = 0$. When $l = |l_1| = |l_2|$ is maximal, the elliptical inner-electron orbit has minimal eccentricity, and the angle φ_{12} is zero. As φ_{12} increases with time, the orbit eccentricity increases also, i.e., l decreases. As φ_{12} reaches its maximum value, l turns zero, i.e., the orbit is squeezed into the straight line segment. After that $|l|$ increases again, but the sign of l is changed (that implies that the sense of the inner-electron circulation along its elliptical orbit is reversed).

Comparing the expressions (3.12) and (4.14), we obtain an unexpected result. The ratio of the frequencies for the radial and angular vibrations proves to be an integer: $\omega_{\rm rad}{:}\omega_{\rm ang} = 2{:}1$. This implies the resonances in the classical mechanics and the additional degeneracies in the quantum description. Both these frequencies are much less than the typical frequency of the orbital motion $\omega_{\rm orb} = Z^2/n_2^3$. In particular, for the helium atom, we have $\omega_{\rm orb}/\omega_{\rm rad} = 13.4$. This large parameter governs applicability of the present adiabatic approximation.

V. QUANTIZATION

As a summary of Sec. III and IV, the present adiabatic approach generates the effective Hamiltonian for the lowest members of the Rydberg series

$$\langle H \rangle = -\frac{Z_{\rm eff}^2}{2n_2^2} + H'_{\rm rad} + H_{\rm ang} \ . \tag{5.1}$$

Here the effective charge is defined by the relation

$$Z_{\rm eff}^2 = Z^2 - 2n_2^2 V(r_{10}) \ . \tag{5.2}$$

It should be stressed that this form is applicable only to the bottom of the Rydberg series; for the highly excited states, $Z_{\rm eff}$ is replaced by Z in agreement with (1.1). (See also the discussion in Sec. III.)

The second and third terms in (5.1) are essentially the Hamiltonians of the harmonic oscillators in the radial and angular motion, respectively. The quantization of the oscillatory motion is trivial:

$$E_{n_2 n_r n_a} = -\frac{Z_{\rm eff}^2}{2n_2^2} + \omega_{\rm rad}(n_r + \tfrac{1}{2}) - \omega_{\rm ang}(n_a + 1) \ , \tag{5.3}$$

where n_r and n_a are nonnegative integer quantum numbers. We took into account that the angular vibrations correspond to the two-dimensional oscillator. Note also the sign "minus" in the last term, which is related with the form of the Hamiltonian (4.10) discussed above.

In particular, for $Z = 2$ the expression (5.3) reads

$$E_{n_2 n_r n_a} = -\frac{2.220\,24}{n_2^2} + \frac{0.298\,81}{n_2^3}(n_r + \tfrac{1}{2}) - \frac{0.149\,41}{n_2^3}(n_a + 1) \ . \tag{5.4}$$

The interpretation of the formulas (5.3) and (5.4) requires some additional discussion. The straightforward analysis shows (see also Ref. [1]) that the relation $l_1^2 = l_2^2$ in quantum mechanics holds not only for S states, but also for P^e states. In the dipole approximation [1], the P^e levels lie approximately halfway between S levels. This alternating structure is retained in the present approach. Bearing in mind also that the unexcited n_a mode should correspond to the S state, we conclude that even n_a give S levels, whereas odd n_a produce P^e states.

VI. APPROXIMATIONS FOR THE ENERGY SPECTRUM

The formula (5.4) can be compared with the expansion of the expression (1.1). At fist we assume that $n = n_2 - 1$ [9,10]. Taking the numerical coefficients for helium from the papers by Richter and co-workers [2,3] ($S = 1.491\,50$, $\gamma_1 = 0.461\,64$, $\gamma_2 = 0.0676$), one obtains

$$E_{nk\tilde{l}} = -\frac{2.224\,57}{n_2^2} + \frac{2.224\,57}{n_2^3} + \frac{0.300\,98}{n_2^3}(\tilde{l} + \tfrac{1}{2}) + \frac{4.1078}{n_2^3}(k + \tfrac{1}{2}) \ . \tag{6.1}$$

The formula (5.4) corresponds to $Z_{\text{eff}}=2.1073$. The formula (6.1) gives a very close value $Z_{\text{eff}}=2.1093$; note that in both cases one has "antiscreening" since $Z_{\text{eff}}>Z$. Using the Gutzwiller [4] quantization procedure, Richter and co-workers [2,3] have expressed Z_{eff} via the action S along the classical periodic trajectory. In the present approach, practically the same numerical value is obtained via the sum of the energy parameters (5.2) (the unperturbed energy of the inner electron E_{20} and the depth $V(r_{10})$ of the potential well for the outer electron).

For the n_r mode in (5.4) and the $\tilde{l}$ mode in (6.1), the frequencies practically coincide. This sustains interpretation of the $\tilde{l}$ mode as the radial excitation [9,10].

At the same time there is the large difference in the frequencies associated with the n_a mode in (5.4) and the k mode in (6.1). Moreover, bearing in mind the numerical values of the parameters, from the formula (1.1) we see that the typical frequency for the k mode is very close to that of the n mode. In other words, the motion associated with the k mode is not slow.

The underlying reason for this is easy to understand. There are two natural possibilities to choose the angular variables for the planetary states of the helium atom. The angle between the electron vectors (for the plane motion $\varphi_1-\varphi_2$, see Sec. II) is the rapid variable. The related frequency is close to the frequency of the inner-electron orbital motion; it corresponds to the k mode. The adiabatic separation of the dynamic variables cannot be carried out in these coordinates. This corresponds to the approach adopted by Richter and co-workers [2,3] who obtained Eq. (1.1) without resort to the separation of rapid and slow motion.

The alternative choice of the angular variable is suggested in the present paper: It is the angle between the outer-electron vector and the aphelion of the inner-electron orbit $\varphi_{12}=\varphi_1-\Phi_2$ (2.8). It is a slow variable well decoupled from the rapid orbital motion.

Closer correspondence between (1.1) and the present results can be achieved if one refines the relation between the quantum numbers introduced by Richter and co-workers [2,3] and in the present approach. Note that our previous study [9,10] in fact was confined to the states with the unexcited angular mode (since Richter and co-workers [2,3] have published the results of the precise quantum calculations only for this case). For $k\neq 0$, we suggest the following relation: $n_2=n+k-1$, $n_r=\tilde{l}$, $n_a=2k$. Then the expansion of the expression (1.1) gives the formula, which differs from (6.1) in the last term only:

$$E_{nk\tilde{l}}=-\frac{2.224\,57}{n_2^2}+\frac{0.300\,98}{n_2^3}(\tilde{l}+\tfrac{1}{2}) -\frac{0.170\,67}{n_2^3}(2k+1)\ . \qquad (6.2)$$

Bearing in mind that for S states n_a is even (see discussion above) we see that the expressions (5.4) and (6.2) are in a good quantitative correspondence concerning the angular mode (related with the last terms in the right hand side). However, it is worthwhile to note that for the radial excitation mode the agreement is appreciably better.

The result of the dipole approximation discussed in Ref. [9] can be also presented in the form similar to (5.4) and (6.2):

$$E_{n_2 n_r N'}=-\frac{2.32}{n_2^2}+\frac{0.512}{n_2^3}(n_r+\tfrac{1}{2}) -\frac{0.169\,33}{n_2^3}(2N'+1)\ . \qquad (6.3)$$

(We have used here the approximate expression (4) of Ref. [9].) The angular frequency in (6.3) is quite close to that in Eq. (5.4) and especially to that in Eq. (6.2). However, the radial frequency differs appreciably. The reason is quite evident: The dipole approximation is quite crude near the minimum of the effective potential $r_1=r_{10}$. It can be used only for the states classification and semiquantitative analysis [9]. Accounting for the quadrupole correction [10] somewhat improves the situation, but the convergence proves to be quite slow. On the contrary, the present treatment does not resort to the multipole expansion and generates the effective potential (3.6), which includes contribution of a large number of multipoles. Therefore, it is much more efficient quantitatively.

VII. TRANSITION TO THE QUASIMOLECULAR SYSTEM

The present theory is easily generalized to the case when the outer electron is replaced by a particle with an arbitrary mass m_1. The frequency of the radial vibrations is simply multiplied by the factor $m_1^{-1/2}$. For the angular oscillations, the situation is somewhat more complicated. In the expression $k_1\equiv k_1'-\alpha^{-2}n_2^{-4}$ only the second term should be multiplied by the same factor. As a corollary, we see that 2:1 ratio of the radial and angular vibrations is specific for the (nonexotic) atom when the outer particle is an electron ($m_1=1$). As m_1 increases from 1 to ∞, the ratio $\omega_{\text{rad}}:\omega_{\text{ang}}$ varies from 2:1 to $2:\sqrt{3}$.

The case $m_1\rightarrow\infty$ is particularly important, since it corresponds to the inner electron placed in the field of the nucleus and the space-fixed outer particle. The present theory allows one to calculate the r_1 dependent potential curves for this quasimolecular system.

In the potential curves analysis, the radial vibrations do not appear. The angular vibrations correspond to the oscillations of the inner-electron orbit in the field of the space-fixed charge with the frequency $\omega_{\text{ang}}'=\sqrt{k_1'k_2}$. In the asymptotic limit of large n_2, the relative role of these vibrations is negligible and the potential curve coincides with $V(r_1)$ [see Eq. (3.6)]. (Note that the separated atom limit of the potential curve is chosen as a zero of the energy here.) This potential curve has minimum at $r_1=r_{10}$. The similar minimum was obtained previously in the numerical calculations of the potential curves [3,15]. The results were employed in the tentative analysis of the bound states of antiproton in the matter [15].

If the angular oscillations are taken into account, the potential curves are given by the sum

$$W_{n_a}(r_1)=V(r_1)-\omega_{\text{ang}}'(r_1)(n_a+1)\ , \qquad (7.1)$$

where ω'_{ang} should be calculated via r_1 dependent k'_1 and k_2 (4.9): $\omega'_{\text{ang}}=(k'_1k_2)^{1/2}$. In particular, the large-r_1 asymptote of this potential curve is

$$W_{n_a}(r_1)=\frac{Z-1}{r_1}+\frac{3n_2(n_2-n_a-1)}{2Zr_1^2}+O(r_1^{-3}) , \qquad (7.2)$$

It describes *exactly* the charge-dipole interaction in contradistinction to the formula (3.7) (see the subsequent discussion in the Sec. III).

The analytical potential curves in the present approximation are compared with the numerical data [3] in Figs. 1 and 2 where we replace r_1 by R (which is the notation conventional for the quasimolecular system). It should be stressed that we show only the region of the potential minimum and the inner wall since the long-range outer wall is reproduced quite well already in the simplest dipole approximation (3.7). Figure 1 shows the potential curves in the case $n_a=0$. For the inner wall, the dipole approximation underestimates the repulsion, whereas the simplest approximation (3.6) overestimates it. (Note that the curve $n_2^2V(R)$ is a universal (n_2 independent) function of n_2.) The potential $W_0(R)$ agrees with the numerical data [3] much better. For $n_2=10$, it reproduces even the height of the potential maximum. However, this accidental agreement disappears for higher n_2.

The effect of the angular mode excitation is demonstrated by Fig. 2. Richter *et al.* [3] noted that for $n_a=1$ (in our notations) the minimum on the potential curve exists for $n_2 \geq 16$. Our results agree with this conclusion. The minimum is absent in the case $n_2=14$ but appears for $n_2=18$, where it is somewhat deeper than for the exact adiabatic potential curve.

Richter and co-workers [2,3] analyzed the asymmetric atomic states in terms of the potential curves obtained for the space-fixed atomic electron. The apparent advantage of this approach lies in the fact that the two-center Coulomb problem is well studied and, in particular, the efficient computer codes are available. Although such an approach is well justified for the heavy outer particle (such as an antiproton), for the electron it leads to appreciable error in the treatment of the angular vibrations. Indeed, it corresponds to the replacement of angular frequency ω_{ang} in the proper adiabatic treatment by ω'_{ang}, which is larger by the factor $3^{1/2}$. The physical reason is easy to understand. For the atom the angular motion of the outer particle is important and enters as a constituent part in the construction of the effective Hamiltonian (4.10) [via the term $l_1^2/(2r_1^2)$]. Namely, this term governs the difference between ω_{ang} and ω'_{ang}. It implies exchange by the orbital momentum between the inner and the outer electrons. The space-fixed outer particle destroys the spherical symmetry of the system and can be considered as an unlimited source of the angular momentum for the inner electron.

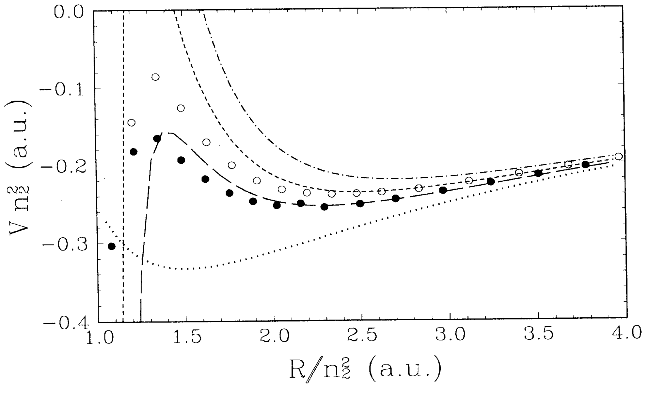

FIG. 1. The potential curves describing the interaction of $He^+(n_2)$ with the unit negative charge (antiproton) in the reduced variables. The separated atoms energy is chosen as energy zero. The dotted curve is the approximate dipole-charge interaction (3.7); the dash-dotted curve is the universal (n_2 independent) approximation (3.6). The analytic potential curves $W_0(R)$ (7.1) account for the zero vibrations ($n_a=0$) in the electron angular mode for $n_2=10$ (the long-dashed curve) and $n_2=18$ (the short-dashed curve). The results of the numerical calculations [3] are shown by the closed ($n_2=10$) and empty ($n_2=18$) circles.

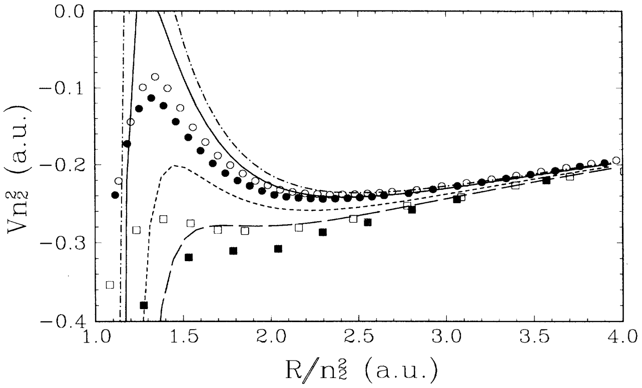

FIG. 2. Same as Fig. 1, but showing also the result of the angular mode excitation. The solid and the dashed-dotted curves show $W_0(R)$ for the unexcited angular mode ($n_a=0$) in the cases $n_2=14$ and $n_2=18$, respectively. The potentials $W_1(R)$ for the excited angular mode ($n_a=1$) are given by the short-dashed and long-dashed curves, respectively. The results of the numerical calculations [3] are presented by the closed ($n_2=10$) and empty ($n_2=18$) circles for $n_a=0$ and by the closed ($n_2=10$) and empty ($n_2=18$) squares for $n_a=1$.

VIII. DISCUSSION AND CONCLUSION

Previously the adiabatic approach to the doubly excited states was related with the hyperspherical representation [20] where it proved to be very effective although the underlying physical reasons are not easy to understand. In the present study, the adiabatic ideas are applied to the case of highly asymmetric excitation. In this case, the adiabaticity parameter has a lucid meaning.

In many aspects the present paper can be considered as an extension of our previous studies in the dipole approximation [1,9,10]. We drop the most restrictive assumption, the dipole approximation itself, but some important qualitative features of the dynamics are retained.

It would be interesting to extend the adiabatic treatment to the higher-L doubly excited states. In the present paper, we have obtained (Sec. V) the energies of P^e states as a by-product in our treatment of S states. Generally, for the states with $L > 0$, the associated classical motion is nonplanar and that makes the analysis considerably more difficult.

The integer (2:1) ratio of the radial and angular frequencies of the oscillations (Sec. IV) is an intriguing point. This extremely simple result is obtained in the present treatment via quite extensive calculations. It implies the classical resonances and the additional degeneracy of the levels in quantum mechanics. The latter can be considered tentatively as some residual part of high $[O(4)\times O(4)]$ symmetry of the two-electron atom with the electron-electron interaction being switched off. Alternatively, one can try to concatenate the present situation with the famous 2:1 Fermi resonance in polyatomic molecules. Physically the situation looks very different since there is no net Coulomb forces between the atoms in molecules. The molecules with the Fermi resonances are not necessarily asymmetrical as the planetary atomic states under consideration. However, it could be that all such specific features in fact are not important. Indeed, recently Xiao and Kellman [21] used the catastrophe theory to relate the appearance of the 2:1 or 1:1 resonances with the general structure of the system phase space. The analysis of these interesting problems is beyond the scope of the present paper.

In principle, 2:1 resonance could imply an efficient mixing of the radial and angular modes by the weak perturbations omitted in the present approximation. The fact that the contributions from the radial and angular excitations to the energy (5.4) differ in sign could be particularly important in this context.

However, it seems that in practice the mixing is not very important. This is testified by the good agreement between the energy levels obtained from Eq. (5.4) and the results of the quantum calculations. The tentative reason could lie in the strong anharmonicity effects. For the radial excitation, the anharmonicity is manifested as the transition from the serial form (5.3) to (1.2) as n_r increases. For the angular mode, the anharmonicity is more important. This can be seen, for instance, from Fig. 2, which shows that the excitation of the angular mode changes the shape of the potential curve very significantly.

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