Theory of two- and three-electron autoionizing states

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The wave functions, energies, and widths of high-lying autoionizing states are calculated and systematized for strongly correlated electron motion in two- and three-electron atoms. The energies of the states are "molecular" and the Auger decay widths decrease exponentially with increasing excitation. The autoionizing states have a simple interpretation as quasistationary states in a potential well formed by a spherically symmetric barrier, whereas such a representation is not possible if one-electron wave functions are employed.

1. INTRODUCTION

Our understanding of the electron shell structure in multielectron atoms is based on the assumption that the electrons can be regarded as independent in the lowest order of approximation. This requires that the electron-electron (*e-e*) interaction be weak enough so that perturbation theory applies. The opposite is encountered for the electron states when the *e-e* interaction is strong and the shell structure may be expected to break down. Such states are by no means rare—they occur when the orbital velocity of the electrons is low, and in high-lying states containing at least two electrons, and are observed for the outermost electrons in the ground states of multielectron atoms, electrons in excited autoionizing states, etc. It is known that the properties of doubly excited helium cannot be correctly described if one starts from the assumption that the electrons are independent.[1,2] In this case the *e-e* interaction is not weak, and the lack of a shell structure makes it necessary to adopt other schemes for classifying these states.[1,4] It was suggested in Refs. 4–6 that the energies and quantum numbers for doubly excited states of two-electron atoms can be found by drawing an analogy with a linear rotating triatomic molecule consisting of two electrons separated by an atomic nucleus. This molecular interpretation is also supported, e.g., by numerical calculations[7] of the wave functions for several autoionizing states in He and He-like ions, where such an electron localization was observed. There is much current interest in the possible existence of a new class of autoionizing states in two-electron atoms in which the electrons are localized on opposite sides of the nucleus (this work has been reviewed in Ref. 8). For three-electron systems, symmetry considerations suggest that states should exist in which the electrons are localized near the vertices of an equilateral triangle. This idea is also strongly supported by the recent solution[10] of the classical Lagrangian equations of motion for the three-body problem[9]; these solutions predict that localization of the above type should occur when a nucleus and two or more moving electrons interact via the Coulomb force. However, the quantum mechanical techniques proposed thus far for solving two- and three-electron problems are for the most part phenomenological. In the present paper we find for the Schrödinger equation for two- and three-electron atoms and ions solutions which describe such a collective electron motion. A method is proposed for calculating and systematizing the wave functions, energies, and widths of the states.

2. METHOD

We consider a two-electron atom with both electrons highly excited. The electron velocities are assumed small and nearly equal. In this case the *e-e* interaction is strong and must be treated exactly, and the electrons in the stationary states tend to lie on opposite sides of their orbit. The center of mass (CM) of the two-electron system must lie near the nucleus of the atom, and since the electron orbits are large, the CM will either move more slowly than the electrons (like the center of mass of a long dumbbell) or move adiabatically. Let the coordinates of the mass center of the *e-e* pair and of the relative motion be $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, respectively, where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons. In these variables the wave function of the entire three-particle system satisfies the equation

$$\left(-\frac{1}{4}\frac{\partial^2}{\partial \mathbf{R}^2}-\frac{\partial^2}{\partial \mathbf{r}^2}-\frac{Z}{|\mathbf{R}-\mathbf{r}/2|}-\frac{Z}{|\mathbf{R}+\mathbf{r}/2|}+\frac{1}{r}-E\right) \times \Psi(\mathbf{R},\mathbf{r})=0, \tag{1}$$

where Z is the charge of the nucleus (which lies at the coordinate origin) and we employ atomic units. We fix $\mathbf{R}$ and introduce a complete set of states whose wave functions $\phi_{\mathbf{R}}^{(n)}(\mathbf{r})$ are solutions of the equation

$$\left(-\frac{\partial^2}{\partial \mathbf{r}^2}-\frac{Z}{|\mathbf{R}-\mathbf{r}/2|}-\frac{Z}{|\mathbf{R}+\mathbf{r}/2|}+\frac{1}{r}-\varepsilon_n(\mathbf{R})\right)\varphi_{\mathbf{R}}^{(n)}(\mathbf{r})=0. \tag{2}$$

We can then express the solution of (1) as a sum

$$\Psi(\mathbf{R},\mathbf{r})=\sum_{n}\varphi_{\mathbf{R}}^{(n)}(\mathbf{r})C_n(\mathbf{R}). \tag{3}$$

If we assume that the CM moves adiabatically, we get the lowest-order equation

$$\left(-\frac{1}{4}\frac{\partial^2}{\partial \mathbf{R}^2}+\varepsilon_n(\mathbf{R})-E\right)C_n(\mathbf{R})=0 \tag{4}$$

for the coefficients $C_n(\mathbf{R})$ by the standard method. We will use the assumption that $|\mathbf{R}|$ is small to calculate $\varepsilon_n(\mathbf{R})$; then up to terms $\sim (R/r)^4$ we find that

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$$\frac{Z}{|\mathbf{R}-\mathbf{r}/2|}+\frac{Z}{|\mathbf{R}+\mathbf{r}/2|}\approx 4\frac{Z}{r}+\frac{8Z\mathbf{R}^2}{r^3}\left[3\frac{(\mathbf{rR})^2}{(rR)^2}-1\right]. \quad (5)$$

We can now apply perturbation theory to the unperturbed equation (2) with $\mathbf{R}=0$:

$$\left(-\frac{\partial^2}{\partial\mathbf{r}^2}-\frac{4Z-1}{r}\right)\varphi_0^{(n)}(\mathbf{r})=\varepsilon_n(0)\varphi_0^{(n)}(\mathbf{r}). \quad (6)$$

Here $n\equiv n, l, m$ are the principal quantum number, the orbital momentum, and its projection on $\mathbf{R}$, respectively. Then

$$\varepsilon_n(\mathbf{R})=\varepsilon_n(0)+\frac{2Z(4Z-1)^3(3m^2-l^2-l)}{n^3(l+1)(l+1/2)l(2l+3)(2l-1)}\mathbf{R}^2$$

$$\equiv\varepsilon_n(0)+\alpha_n\mathbf{R}^2. \quad (7)$$

We have $\alpha_n>0$ if $3m^2>l(l+1)$, which we will assume in what follows. To lowest order, the equations of motion of the CM for the two-electron system have the same form as the equations for a three-dimensional oscillator. The energies of the high-lying two-electron states are thus "molecular" (see Refs. 6, 8):

$$E_{nN}=\varepsilon_n(0)+(N+3/2)\sqrt{\alpha_n};\quad N=0, 1, 2\ldots, \quad (8)$$

where N is the principal quantum number of the oscillator. The state wave functions are expressible as products $C_n(\mathbf{R})\varphi_0^{(n)}(\mathbf{r})$, where C_n is the wave function for the oscillatory motion of the CM near the nucleus [Eq. (4)], and $\varphi_0^{(n)}$ describes the relative motion of the electron pair in the Coulomb field of a nucleus of charge $4Z-1$ [Eq. (6)]. We note that the zero-order functions $\phi_0^{(n)}(\mathbf{r})$ are regular, just as in Ref. 11, where two closely spaced nuclei in a diatomic molecule were considered. We can therefore take the quantization axis of the orbital momentum in (6) to lie along $\mathbf{R}$, which ensures that the potential (7) is binding. The three-center problem (2) can be solved numerically to calculate more accurate wave functions and "terms" $\varepsilon_n(\mathbf{R})$.

3. ANALYSIS OF THE APPROXIMATIONS

We first give some elementary arguments to support the approximations which we have made above.

1. The condition $\alpha_n>0$ for the existence of a binding potential in (7), needed for the motion of the CM of the electron pair to be bounded near $R=0$, is satisfied if $3m^2>l(l+1)$.

2. The condition for the CM of the electron pair to lie near the nucleus, viz., $\overline{(R^2)}^{1/2}\ll a_n$, where

$$\overline{(\mathbf{R}^2)}^{1/2}\sim 1/2(N+3/2)(\alpha_n)^{-1/2}$$

is the rms deviation of the CM from the equilibrium position; $\alpha_n\sim 2n^2(4Z-1)^{-1}$ is the size of the Coulomb orbit for $l\sim n\gg 1$. We have $\alpha_n\sim(4Z)^4/4n^6$ for $|m|\approx l\sim n\gg 1$, since $4Z-1\approx 4Z$ for $Z\geqslant 2$ (hereafter $|m|\approx l\sim n\gg 1$ always means $l-|m|\ll l\sim n\gg 1$). We thus get the condition

$$n^{1/2}\gg 1/2(N+3/2)^{1/2} \quad (9)$$

for $\overline{R^2}$ to be small.

3. We expect that the CM of the electron pair will move adiabatically if its velocity

$$\overline{(\mathbf{V}^2)}^{1/2}\sim[1/2(N+3/2)]^{1/2}\alpha_n^{1/4}$$

is much less than the velocity $\overline{(\mathbf{V}^2)}^{1/2}\approx(4Z-1)n^{-1}$, of the relative motion in the Coulomb field. This again leads to inequality (9) for $|m|\approx l\sim n\gg 1$. Thus in any case we must assume that $n\gtrsim 10$ in order for our treatment to be valid.

4. There are also further constraints due to the finite depth of the potential well $\varepsilon_n(\mathbf{R})$ in which the CM of the electron pair moves. Our simple treatment requires that N be small in order for the potential $\varepsilon_n(\mathbf{R})$ to remain harmonic. However, this constraint is found to be weaker than (9).

Now that we have seen that our analysis requires at any rate for $|m|\sim l\sim n\gg 1$, we can proceed to a more rigorous justification of the following two assumptions: a) Eq. (2) can be solved by perturbation theory; b) the equation for the coefficients $C_n(\mathbf{R})$ in expansion (3) can be solved in the adiabatic approximation. We note at the outset that the detailed behavior of the matrix elements for $|m|\sim l\sim\gg 1$ is crucial for the validity of these assumptions.

a) Expansion (5) is valid for $\overline{(\mathbf{R}_2)}^{1/2}\ll\alpha_n$, where (9) holds. The matrix elements of the perturbation

$$V=\frac{4Z}{r}-\frac{Z}{|\mathbf{R}-\mathbf{r}/2|}-\frac{Z}{|\mathbf{R}+\mathbf{r}/2|}\approx -8Z\frac{\mathbf{R}^2}{r^3}\left[3\frac{(\mathbf{Rr})^2}{R^2r^2}-1\right] \quad (10)$$

can be expressed as a product of radial $r_{nn'}^{-3}$ and angular $\Omega_{nn'}$ parts:

$$V_{nn'}=-8Z\mathbf{R}^2r_{nn'}^{-3}\Omega_{nn'},\qquad n\equiv(n,l,m),$$

where

$$r_{nn'}^{-3}=(\varphi_0^{(n)}(\mathbf{r}), r^{-3}\varphi_0^{(n')}(\mathbf{r})),$$

$$\Omega_{nn'}=2(4\pi/5)^{1/2}\langle lm|Y_{20}|l'm'\rangle.$$

According to our choice of $\{\varphi_0^{(n)}(\mathbf{r})\}$ as the regular zero-order basis set, the Z axis points along R. We have $\Omega_{nn'}\neq 0$ for $l'=l, l\pm 2$ and $m'=m$. For $l\sim n$ and $l-|m|\ll l$ we have

$$\Omega_{l,l}\sim 1,\quad \Omega_{l,l\pm 2}\sim(l^2-m^2)/l^2\ll 1,$$

$$r_{n+2,l+2;n,l}^{-3}\sim R_{n-2,l-2;n,l}^{-3}\sim r_{n,l;n,l}^{-3}\sim(4Z-1)^3/8n^6,$$

and the remaining radial matrix elements can all be neglected for $n\gg 1$, $l\sim n$. For example, for $|n-n'|=\Delta n\ll n$ we have

$$r_{n+\Delta n,l;n,l}^{-3}\sim(2n)^{-1/2\Delta n}r_{n,l;n,l}^{-3}\ll r_{n,l;n,l}^{-3},$$

etc. Therefore,

$$|V_{nn'}|_{n\neq n'}\sim\left|8Z\overline{\mathbf{R}^2}\frac{(4Z-1)^3}{8n^6}\Omega_{nn'}\right|\ll\frac{4Z-1}{2n^3}, \quad (11)$$

where the right-hand side is the spacing of the levels for the unperturbed Coulomb case (6) (the reduced mass is equal to 0.5 atomic units). We can thus solve Eq. (2) by perturbation theory if we take the $\varphi_0^{(n)}(\mathbf{r})$ in (6) as the zero-order basis set. Indeed, as in Ref. 11, the perturbaton (10) has the property that $V_{n,lm;n,l\pm 2,m}=0$ because $r_{n,l;n,l\pm 2}=0$, while the other elements are small so that the perturbation theory corrections to $\varphi_0^{(n)}(\mathbf{r})$ are small. Finally, the highest-order terms of the expansion in powers of R/r, not accounted for in (10), give a negligible contribution; for instance, $\overline{R^4/r^5}_{nn'}\lesssim 1/n^4$, etc.

b) In order for the adiabatic approximation to be valid we must have[12]

$$B_{nn'}\equiv|\langle C_{nN}(\mathbf{R})|\Lambda_{nn'}|C_{n'N'}(\mathbf{R})\rangle|\ll|E_{nN}-E_{n'N'}|, \quad (12)$$

where $n\neq n'$, N and N' are arbitrary, the $C_{nN}(R)$ are solutions of Eq. (4), and

$$\Lambda_{nn'}=\int d^3r\varphi_{\mathbf{R}}^{(n)}(\mathbf{r})\{\nabla_{\mathbf{R}}{}^2\varphi_{\mathbf{R}}^{(n')}(\mathbf{r})+2(\nabla_{\mathbf{R}}\varphi_{\mathbf{R}}^{(n')}(\mathbf{r}))\nabla_{\mathbf{R}}\}.$$

We have already seen that the solutions $\phi_{\mathbf{R}}^{(n')}$ of Eq. (2) appearing in this formula can be found by perturbation theory:

$$\varphi_{\mathbf{R}}^{(n)}(\mathbf{r})=\varphi_0^{(n)}(\mathbf{r})-8Z\mathbf{R}^2\sum_{n'\neq n}\frac{r_{nn'}^{-3}\Omega_{nn'}}{\varepsilon_n(0)-\varepsilon_{n'}(0)}\varphi_0^{(n')}(\mathbf{r}).$$

This leads to the result

$$B_{nn'}\ll(4Z-1)^2/2n^3\leqslant|E_{nN}-E_{n'N'}| \quad (13)$$

so that the inequaltiy that ensures the validity of the adiabatic approximation is satisfied. We have thus used the specific properties of the states with $|m|\approx l\sim n\gg 1$ to show that the adiabatic approximation is valid if the CM motion is slow compared to the relative motion of the electrons in the Coulomb field, rather than the frequencies of the motions (this result is similar to the conditions that the perturbation theory considered in Ref. 13 be applicable to highly excited states). We emphasize that even though the oscillator mass (2 a.u.) is not much greater than the reduced mass (0.5 a.u.), the parameters in the potential (7) are such that the oscillator (CM) velocity is much less than the relative velocity in the Coulomb field.

4. SYSTEMATIZATION, WAVE FUNCTIONS, AND ENERGY

In order to find the two-electron states with a prescribed total momentum K and projection M, we use spherical coordinates to rewrite (4) as

$$\frac{1}{4}\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_n(\mathbf{R})}{\partial R}\right)-\frac{(\mathbf{K}-\mathbf{L})^2}{R^2}C_n(\mathbf{R})\right]$$

$$+(\varepsilon_n(\mathbf{R})-E)C_n(\mathbf{R})=0, \quad (14)$$

where $\mathbf{L}$ is the angular-momentum operator of the relative motion (6). In accord with the analogy between the adiabatic approximation used in Sec. 2 and the corresponding approximation in the theory of diatomic molecules, we write Λ for the projection of the total angular momentum on the moving axis $\mathbf{R}$ and let $\Lambda=m$ be the projection of $\mathbf{L}$ on $\mathbf{R}$. According to the theory of diatomic molecules,[14] the wave functions of the high-lying autoionizing states with specified total angular momentum K and its projection Λ and M are given by (see Ref. 6)

$$\Phi(\mathbf{R},\mathbf{r})=\varphi_0^{(nlm)}(\mathbf{r})\rho_{nlmn_r K}(R)i^K\left(\frac{2K+1}{4\pi}\right)^{1/2}D_{mM}^K(\varphi,\theta,0). \quad (15)$$

Here ρ is the radial part of the oscillator-motion wave function (14), n_r is the corresponding radial quantum number, and the D are the Wigner squared angular momentum functions. Since $l\sim n\gg 1$ in our case, we can assume that the operator has for the functions (15) a definite value:

$$P^2=(\mathbf{K}-\mathbf{L})^2=K(K+1)+l(l+1)-2m^2,$$

and since $K\geqslant|m|$ we have $P^2\geqslant 2l$. The energies corresponding to the states (15) are given by

$$E=\varepsilon_n(0)+\alpha_n^{1/2}(2n_r+P+{}^3/_2), \quad n\equiv(n,l,m). \quad (16)$$

We can thus describe the high-lying autoionizing two-electron states in terms of the wave functions (15), energies (16), and quantum numbers n, l, m, n_r, K, and M, where $n\gg 1$, $l\sim n$, $l-|m|\ll l$, $K\geqslant|m|$, $-K\leqslant M\leqslant K$. Condition (9) can then be rewritten as

$$n^{1/2}\gg{}^1/_2(2n_r+P+{}^3/_2)^{1/2}, \quad P\geqslant(2l)^{1/2}, \quad (17)$$

which [like (9)] imposes constraints on the values $N=2n_r+P$, and hence also on n_r and on the total angular momentum K, at a fixed $n\gg 1$.

5. PROBABILITY OF AUGER DECAY

Perturbation theory cannot be used to calculate the Auger decay probabilities because the *e-e* interaction is not weak. However, we can use the above technique to describe the autoionizing states in a simple way as quasistationary states in the well produced by a spherically symmetric barrier. To do this we continue the expansion (10) up to terms $\sim(R/r)^6$; we then find that

$$\varepsilon_n(\mathbf{R})=\varepsilon_n(0)+\alpha_n\mathbf{R}^2-\beta_n\mathbf{R}^4, \quad (18)$$

where for $|m|\approx l\sim n\gg 1$

$$\alpha_n=\frac{(4Z)^4}{4n^6}, \quad \beta_n=\frac{3}{16}\frac{(4Z)^6}{n^{10}}, \quad 4Z-1\approx 4Z.$$

The "term" $\varepsilon_n(\mathbf{R})$ thus represents a well with a barrier through which the CM of the electron pair penetrates when an Auger transition occurs and escapes to infinity. If we multiply the probability of penetrating through the barrier by the incident particle flux, we find the estimate

$$\Gamma_n=\frac{1}{2\sqrt{2}}\frac{(4Z)^2}{n^3}\exp\left(-\frac{2^3}{3^2}n\right) \quad (19)$$

for the widths of the autoionizing states. Under the assumptions for which our treatment is valid, the other quantum numbers have little influence on Γ_n. The Auger decay probability thus drops as n increases.

6. COLLECTIVE THREE-ELECTRON STATES

We will find for the Schrödinger equation for a three-electron atom solutions that correspond to the motion of three electrons localized near the vertices of an equilateral triangle centered near the atomic nucleus. We let $\mathbf{r}_i$, $i=1,2,3$, be the position vectors on the electrons and define the operator T as T_0I, where T_0 is a 60° rotation about a fixed spatial axis passing through the coordinate origin (i.e., through the nucleus); I is the inversion operator about the plane normal to the rotation axis. The change of variables

$$\mathbf{x}=\mathbf{r}_1+T\mathbf{r}_2, \quad \mathbf{y}=\mathbf{r}_1+T^{-1}\mathbf{r}_3, \quad \mathbf{z}=\mathbf{r}_1-T\mathbf{r}_2-T^{-1}\mathbf{r}_3,$$
$$\alpha=\mathbf{x}+\mathbf{y}, \quad \beta=\mathbf{x}-\mathbf{y}, \quad \gamma=\mathbf{z} \quad (20)$$

leads to the expression

$$K=-\frac{1}{2}\sum_{i=1}^{3}\frac{\partial^2}{\partial \mathbf{r}_i^2}=-\frac{1}{2}\left(3\frac{\partial^2}{\partial\gamma^2}+6\frac{\partial^2}{\partial\alpha^2}+2\frac{\partial^2}{\partial\beta^2}\right) \quad (21)$$

for the kinetic energy operator of the electrons. The potential

$$V=-\sum_{i=1}^{3}\frac{Z}{r_i}=-3Z\left(|\gamma+\alpha|^{-1}+\left|\gamma-\frac{3}{2}\beta-\frac{1}{2}\alpha\right|^{-1}+\left|\gamma+\frac{3}{2}\beta-\frac{1}{2}\alpha\right|^{-1}\right) \quad (22)$$

describes the interaction between the electrons and the nucleus, of charge Z. The *e-e* interaction operator is given by

$$U=\frac{1}{2}\sum_{i\neq j}^{3}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$
$$=\left|\frac{\gamma}{3}+\frac{T}{3}\gamma-\frac{1}{6}\alpha-\frac{T}{6}\alpha+\frac{1}{2}\beta-\frac{T}{2}\beta\right|^{-1}+\left|\frac{1}{3}\gamma+\frac{T}{3}\gamma+\frac{1}{3}\alpha-\frac{T}{6}\alpha+\frac{T}{2}\beta\right|^{-1}+\left|\frac{1}{3}\gamma+\frac{T}{3}\gamma+\frac{T}{3}\alpha-\frac{1}{6}\alpha-\frac{1}{2}\beta\right|^{-1}. \quad (23)$$

For definiteness we consider an equilateral triangle which is oriented in space so that the first three changes in (20) lead to $|x|\ll|z|$ and $|y|\ll|z|$; this is the analog of the condition for $\mathbf{R}/r$ to be small in Sec. 2. In addition, we assume that the vectors α and β are nearly parallel to the fixed rotation axis, and that γ nearly lies in the plane of rotation, i.e.,

$$T\alpha\approx-\alpha,\quad T\beta\approx-\beta,\quad \gamma+T\gamma\approx\sqrt{3}\,T_0^{1/2}\gamma. \quad (24)$$

We will discuss these approximations and their limitations more fully below. If we expand the potential energy $W=V+U$ (regarded as a function of α,β,γ) in powers of the small quantities α/γ and β/γ [cf. (5)], we get

$$W\approx-\frac{a}{\gamma}-b\frac{\beta^2}{\gamma^3}\left[3\frac{(\gamma\beta)^2}{\gamma^2\beta^2}-1\right]-c\frac{\alpha^2}{\gamma^3}\left[3\frac{(\alpha\gamma)^2}{\alpha^2\gamma^2}-1\right], \quad (25)$$

$$a=3(3Z-\sqrt{3}),\quad b=\frac{9}{4}(3Z-\sqrt{3}),\quad c=\frac{3}{4}(3Z-\sqrt{3}).$$

We can now solve the exact three-electron equation

$$\left[-\frac{3}{2}\frac{\partial^2}{\partial\gamma^2}-3\frac{\partial^2}{\partial\alpha^2}-\frac{\partial^2}{\partial\beta^2}+W(\alpha,\beta,\gamma)-E\right]\Psi(\alpha,\beta,\gamma)=0 \quad (26)$$

by proceeding as in Sec. 2. First we fix α and β and find a complete set of solutions of the equation

$$\left[-\frac{3}{2}\frac{\partial^2}{\partial\gamma^2}+W(\alpha,\beta,\gamma)-\varepsilon_n(\alpha,\beta)\right]\varphi_{\alpha,\beta}^{(n)}(\gamma)=0 \quad (27)$$

in terms of which we can write

$$\Psi(\alpha,\beta,\gamma)=\sum_n C_n(\alpha,\beta)\varphi_{\alpha,\beta}^{(n)}(\gamma). \quad (28)$$

Under the assumption that α and β vary slowly compared with γ, we get the equation

$$\left[-\frac{3}{2}\frac{\partial^2}{\partial\gamma^2}-\frac{\partial^2}{\partial\beta^2}+\varepsilon_n(\alpha,\beta)-E\right]C_n(\alpha,\beta)=0 \quad (29)$$

for the coefficients $C_n(\alpha,\beta)$ in the standard lowest-order adiabatic approximation. Equation (27) can be solved by applying perturbation theory to the unperturbed Coulomb equation

$$\left[-\frac{3}{2}\frac{\partial^2}{\partial\gamma^2}-\frac{a}{\gamma}-\varepsilon_n(0,0)\right]\varphi_{0,0}^{(n)}(\gamma)=0, \quad (30)$$

which follows from (27) by setting $\alpha=\beta=0$. Here $n\equiv n, l, m$ are the same Coulomb quantum numbers as in Sec. 2, and the perturbation

$$\Delta W=W(\alpha,\beta,\gamma)-W(\alpha=0,\beta=0,\gamma)=W(\alpha,\beta,\gamma)+a/\gamma$$

is given by (25). Since the orbital quantization axis for (30) is parallel to $\alpha/\alpha\approx\beta/\beta$ and the regular zero-order functions are the same as in Sec. 2, we find that

$$\varepsilon_n(\alpha,\beta)=\varepsilon_n(0,0)+p_n\beta^2+q_n\alpha^2, \quad (31)$$

where as in (7)

$$p_n=\frac{1}{3}q_n=\frac{16}{9}\frac{ba^3(3m^2-l^2-l)}{n^3(l+1)(l+1/2)l(2l+3)(2l-1)}. \quad (32)$$

The solutions of (29) with the potential (31) are expressible as products of the solutions of the equations for two three-dimensional oscillators:

$$\left(-\frac{3}{2}\frac{\partial^2}{\partial\alpha^2}+q_n\alpha^2-E_1\right)A_n(\alpha)=0,\qquad \left(-\frac{\partial^2}{\partial\beta^2}+p_n\beta^2-E_2\right)B_n(\beta)=0. \quad (33)$$

Here E_1 and E_2 are the oscillator energies. The energies of the three-electron states are therefore given by

$$E=\varepsilon_n(0,0)+E_1+E_2=\varepsilon_n(0,0)+\left(N_1+\frac{3}{2}\right)q_n^{1/2}+\left(N_2+\frac{3}{2}\right)p_n^{1/2}, \quad (34)$$

where N_1 and N_2 are the principal quantum numbers of the oscillators (33). The corresponding wave functions of the three-electron states are products of the wave functions of the unperturbed Coulomb problem (30) and the wave functions of oscillators (33).

We will now discuss the above approximations. An analysis shows that the conditions

$$3m^2>l(l+1),\quad l-|m|\ll l\sim n\gg 1,$$
$$n^{1/2}\gg 1/2(N_i+3/2)^{1/2},\quad i=1,2,$$

will ensure that p_n and q_n in (31) are positive, that the expansion (25) is valid, that (27) can be solved by perturbation theory, and that the adiabatic approximation can be assumed in (28) for the coefficients $C_n(\alpha,\beta)$. These relations are the same as were found in Secs. 2 and 3. Considering in addition the specific assumptions made in solving the three-electron problem, we note that for $|m|\approx l\sim n\gg l$ and $|M-m|\ll|m|$, the Wigner D-functions for each oscillator [see (15)] contain the factor $\cos^p(\theta/2)$, where $p\sim n$ and $\theta\leqslant\pi$. Here $\cos^n(\theta/2)\sim\exp(-n\theta^2/4)$, i.e., the axes α and

β lie in a narrow cone of angle $\theta \sim 1/2n^{1/2}$ and are therefore parallel in this approximation. To the same accuracy, the Coulomb orbits (30) are localized in the plane normal to α; this is because the angular parts of the wave functions contain the factor $\sin^q \theta_\gamma$, where $q \sim n$ (for $|m| \approx l \sim n$), θ_γ is the angle between γ and α, and

$$\sin^n \theta_\gamma = \cos^n (\theta_\gamma - \pi/2) \sim \exp(-n(\theta_\gamma - \pi/2)^2).$$

The vector γ is therefore almost perpendicular to $\alpha/\alpha \approx \beta/\beta$, so that the approximations (24) are valid. To within the same approximation, it is immaterial whether α/α or β/β is chosen as the quantization axis for the orbital momentum in (30); this is because a rotation of the quantization axis from α to β will change the angular part of the wave function (30) by[15] $\Delta\varphi \sim \Delta l^{1/2} \theta_\gamma^2 \sim \varphi / l^{1/2} \ll \varphi$ for $|m| \approx l \sim n \gg 1$.

We have shown that the Auger decay probability drops as the degree of excitation of an atom in a highly correlated state increases, so that population inversion may occur. The three-electron states are equally likely to decay with ejection of a single electron or with ejection of a pair of highly correlated electrons. Since an ejected electron pair can be regarded formally as a Bose particle, induced (stimulated) electron-pair emission should be possible.

7. CONCLUSION

The results derived above become exact in the limit $n \to \infty$. Our analysis thus shows that even though the electron orbits have large radii in highly excited states ($n \gtrsim 10$), they can by no means always be regarded as moving independently. In fact, in states with large l and m, when the electrons move along circular orbits and "in a single direction," the e-e interaction determines the character of the motion. The motion constitutes small deviations from rotation of a long dumbbell with center near the atomic nucleus in the case of two electrons, and small deviations from rotation of an equilateral triangle centered near the nucleus for a three-electron system. However, if the motions of the electron mass-center system are not small, the behavior can be treated qualitatively by assuming that the electrons move independently.

The wave functions found above describe strongly correlated electron motion and can also be used to calculate multiparticle decays of autoionizing states.[16] Like the corresponding solutions[10] for classical mechanics, our computational scheme can be generalized to apply to high-lying states of n electrons.

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