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Doubly excited states with zero angular momentum and electrons in opposite directions

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$L=0$ doubly excited states, whose mean value of the interelectronic angle is close to π, are studied within the O(4,2) group-theoretical framework. It is conjectured that the energies of these resonances correspond in the limit of large excitation of both electrons to those of the Hamiltonian $H=p^2/2+p'^2/2-Z/r-Z/r'+1/(r+r')$ in a space where both particles have fixed value, to be denoted f, for their angular momenta ($l=l'=f$). The choice for the fixed value f is not important in the limit of infinite principal quantum numbers. In other cases, f must remain smaller than or of the order of the square root of the lowest principal quantum numbers of both electrons. The initial problem with three degrees of freedom thus could be reduced, insofar as energies of resonances are concerned, to a problem with only two degrees of freedom in the limit of large excitation of both electrons. It is of course obvious that the state vectors of the above Hamiltonian with $l=l'=f$ are totally inadequate for describing real two-electron atomic states with interelectronic angles close to π. However, the coefficients of the expansion of these unphysical states with respect to specified Sturmian vectors with $l=l'=f$ approximate the coefficients of the real two-electron states with respect to different specified Sturmian vectors; the latter Sturmian vectors have a large distribution over different values of l ($=l'$).

I. INTRODUCTION

Doubly excited states of two-electron atoms have aroused interest in the recent past. For a general view on the subject see, e.g., Ref. [1–7]. The present work focuses on states with total orbital angular momentum L equal to zero and with mean values of the interelectronic angle θ_{12} close to π. A classification scheme initially based on the O(4) group and on the hyperspherical analysis of the problem has been proposed [3]. According to this scheme, each state is designated by the notation (see Ref. [3]) ${}_n(K,T)_N^{A\,2S+1}L^{\pi}$. These quantum numbers can also be introduced within a molecular approach where the interelectronic distance is used as an adiabatic coordinate [8]. Within this classification, the states of interest for the present paper are those with $L=0$ and K maxima ($K=N-1$).

A general formulation which relies upon the O(4,2) group-theoretical approach to the subject [9, 10] is outlined in Sec. II. The bases used for describing two-electron states depend on two arbitrary scaled factors β,β', and on six quantum numbers [see Eq. (14) below]:

$$|(n,n',J_1,J_2,L,M)\beta,\beta'\rangle\ .$$

For $J_1=J_2$, the parity of the vectors of Eq. (14) is related to the angular momentum through the relation $\pi=(-1)^L$. The spin S has to be taken into account by symmetrizing ($S=0$) or antisymmetrizing ($S=1$) the previous basis vectors. The attention is then focused on the states with zero total angular momentum. For $L=0$ only three quantum numbers n,n',J remain independent since J_1 and J_2 then must have the same value, to be denoted J.

The key point of this paper is to note that for $L=0$ and large n,n' values, the vectors characterized by maximum value of J [$J=(n+n'-2)/2$], to be denoted $|(n,n')\beta,\beta'\rangle$ [see Eq. (16)], correspond to mean values of the interelectronic angle close to π for n,n' large enough [see Eq. (A15) of the Appendix] and that the two-electron problem can approximately be studied inside the subspaces generated by these vectors $|(n,n')\beta,\beta'\rangle$.

This approximation is first checked (Sec. III) in the case of two noninteracting electrons, a problem whose exact solution is, of course, known. It is found that the hydrogenic spectrum is exactly obtained. It is shown that an appropriate choice for the scaled parameters β,β' allows one to obtain an arbitrarily chosen hydrogenlike state as an exact eigenvector of the approximate problem. The other eigenvectors remain good in the vicinity of the chosen hydrogenlike solution and become worse far from it. A measure of "how good" is provided by the $1/r$ overlap with the hydrogenlike solutions. The case of two interacting electrons is then considered in Sec. IV. It is conjectured that the energies of the resonance associated with $L=0$ states whose electrons are almost in opposite directions correspond to those of the Hamiltonian

$$H=\tfrac{1}{2}p^2-Z/r+\tfrac{1}{2}p'^2-Z/r'+1/(r+r') \tag{1}$$

in the space where each particle has fixed angular momentum ($l=l'=f$). The common value f must remain smaller or of the order of the square root of the smallest principal quantum number of each electron.

Clearly, only the energies of the resonances associated to the above model are relevant for the real physical atoms. It is, of course, obvious that the state vectors of the above Hamiltonian with $l=l'=f$ fixed are totally inadequate for describing real two-electron atomic states with interelectronic close to π. The requirement that the electrons of the real atomic states be in almost opposite directions implies that both are sufficiently excited but does not necessarily require that their degree of excitation be comparable. Stated otherwise, intrashell and intershell resonances are both concerned by the present approach provided the smallest degree of excitation of the two electrons is sufficiently large.

II. GENERAL FORMULATION

It is known [11] that the Lie algebra o(4,2) is realized by the following 15 generators:

$$\mathbf{l}=\mathbf{r}\times\mathbf{p}\ , \tag{2}$$

$$\mathbf{a}(\beta)=\exp(-\beta)[\tfrac{1}{2}\mathbf{r}p^2-\mathbf{p}(\mathbf{r}\cdot\mathbf{p})]-\tfrac{1}{2}\exp(\beta)\mathbf{r}\ , \tag{3}$$

$$\mathbf{b}(\beta)=\exp(-\beta)(\tfrac{1}{2}\mathbf{r}p^2-\mathbf{p}(\mathbf{r}\cdot\mathbf{p}))+\tfrac{1}{2}\exp(\beta)\mathbf{r}\ , \tag{4}$$

$$\mathbf{g}=r\mathbf{p}\ , \tag{5}$$

$$t_1(\beta)=\tfrac{1}{2}[\exp(-\beta)rp^2-\exp(\beta)r]\ , \tag{6}$$

$$t_2=\mathbf{r}\cdot\mathbf{p}-i=rp_r\ , \tag{7}$$

$$t_3(\beta)=\tfrac{1}{2}[\exp(-\beta)rp^2+\exp(\beta)r]\ . \tag{8}$$

These generators are Hermitian with respect to the so-called $1/r$ scalar product defined by

$$\langle e|f\rangle\equiv\int d^3r(1/r)e^*(\mathbf{r})f(\mathbf{r})\ . \tag{9}$$

It is emphasized that the $1/r$ scalar product is always implicit in the "bra ket" notation throughout this paper and that, when two electrons are considered, the element of integration is $(d^3r/r)(d^3r'/r')$. The β dependence of the generators corresponds to a unitary transformation generated by t_2. For example,

$$\mathbf{a}(\beta)\equiv\exp(i\beta t_2)\mathbf{a}(0)\exp(-i\beta t_2)\ . \tag{10}$$

The physical meaning of this transformation is a change of length scale by a factor $\exp(\beta)$. The generators **l** and **g** commute with t_2 and therefore these seven generators are β independent. The notation $t_2(\beta)$ or t_2 will therefore be used indifferently in what follows. We also introduce the non-Hermitian generators

$$t_\pm(\beta)\equiv t_1(\beta)\pm it_2\ . \tag{11}$$

A unitary irreducible representation (UIR) of O(4,2) is obtained (see, e.g., Ref. [12]) if these 15 generators act on the scaled hydrogenic states $|(n,l,m),\beta\rangle$ defined in terms of the hydrogenlike states $|Z,n,l,m\rangle$ for nuclear charge Z, by

$$|(n,l,m)\beta\rangle=Z^{-1/2}n\exp\{i[\beta+\ln(n/Z)]t_2\}|Z,n,l,m\rangle\ . \tag{12}$$

The hydrogenlike states introduced above are normalized with respect to the usual scalar product of quantum mechanics. The space of the UIR is spanned by all the $|(n,l,m),\beta\rangle$. These states, also called Sturmian states, are orthonormal with respect to the $1/r$ scalar product:

$$\langle(n_j,l_j,m_j),\beta|(n_k,l_k,m_k),\beta\rangle=\delta_{m_jm_k}\delta_{l_jl_k}\delta_{n_jn_k}\ . \tag{13}$$

The action of each of the 15 o(4,2) generators [Eqs. (2)–(8)] on these states can be found in Ref. [12] and is, of course, β independent since both operators and vectors have been transformed by the same unitary transformation. A suitable basis for two-electron states is then [13, 14, 9, 10]:

$$\begin{aligned}|(n,n',J_1,J_2,L,M)\beta,\beta'\rangle&\\ \equiv\sum_{l,l'}&|(n,l,n',l',L,M)\beta,\beta'\rangle\\ &\times[(2l+1)(2l'+1)(2J_1+1)(2J_2+1)]^{1/2}\\ &\times(-1)^{l'}\begin{Bmatrix}\frac{1}{2}(n-1) & \frac{1}{2}(n'-1) & J_1\\ \frac{1}{2}(n-1) & \frac{1}{2}(n'-1) & J_2\\ l & l' & L\end{Bmatrix}\ .\end{aligned} \tag{14}$$

These states are eigenvectors of $t_3(\beta)$, $t_3'(\beta')$, $[\mathbf{a}(\beta)-\mathbf{a}'(\beta')]^2$, L^2, and $\mathbf{L}\cdot[\mathbf{a}(\beta)-\mathbf{a}'(\beta')]$, with respective eigenvalues n,n',

$$\{2[J_1(J_1+1)+J_2(J_2+1)]-L(L+1)\}\ ,$$

$$[J_1(J_1+1)]-[J_2(J_2+1)]\ .$$

The explicit action of $t_1(\beta)$ on these states is given by Eq. (74) of Ref. [10]. Within the phase convention [15] of Eq. (14), the action of the permutation operator P_{12} is

$$\begin{aligned}P_{12}|(n,n',J_1,J_2,L,M)\beta,\beta'\rangle&\\ =(-1)^L&|(n',n,J_2,J_1,L,M)\beta',\beta\rangle\ .\end{aligned} \tag{15}$$

Turning now to the special case $L=0$, J_1,J_2 maximum, and defining

$$|(n,n')\beta,\beta'\rangle\equiv|(n,n',J_1=\tfrac{1}{2}(n+n'-2),J_2=\tfrac{1}{2}(n+n'-2),L=0,M=0)\beta,\beta'\rangle\ , \tag{16}$$

one obtains from Eq. (74) of Ref. [10]

$$t_-(\beta)|(n,n')\beta,\beta'\rangle=(n-1)[(n+n'-1)/(n+n'-2)]^{1/2}|(n-1,n')\beta,\beta'\rangle\ , \tag{17}$$

$$\begin{aligned}t_+(\beta)|(n,n')\beta,\beta'\rangle=&\,n[(n+n')/(n+n'-1)]^{1/2}|(n+1,n')\beta,\beta'\rangle\\ &+(n'-1)/\{[(n+n'-1)(n+n'-2)]\}^{1/2}\\ &\times|(n+1,n',J_1=(n+n'-3)/2,J_2=J_1,L=0,M=0)\beta,\beta'\rangle\ .\end{aligned} \tag{18}$$

For n,n' large enough, it is seen [right-hand side of Eq. (18)] that the coefficient in front of the last vector is small with respect to the one in front of the first vector. It is therefore very tempting to approximate $t(\beta)$ by $\tau(\beta)$ defined by

$$\tau_3(\beta)=t_3(\beta)\ , \tag{19}$$

$$\tau_-(\beta)|(n,n')\beta,\beta'\rangle=[n(n-1)]^{1/2}|(n-1,n')\beta,\beta'\rangle\ , \tag{20}$$

$$\tau_+(\beta)|(n,n')\beta,\beta'\rangle=[n(n+1)]^{1/2}|(n+1,n')\beta,\beta'\rangle\ . \tag{21}$$

The action of $\tau(\beta)$ on the two-electron states $|(n,n')\beta,\beta'\rangle$ corresponds to the action of $t(\beta)$ on the one-electron states with zero angular momentum, $|(n,l=0,m=0),\beta\rangle$ Namely, one has

$$\tau_\pm(\beta)|(n,l,m)\beta\rangle=c(l,\pm n)|(n\pm 1,l,m)\beta\rangle\ ,$$

with

$$c(l,n)=[(n+l+1)(n-l)]^{1/2}\ .$$

The approximation of the coefficients $n-1$ and n appearing in Eqs. (17) and (18) by the functions $c(l,\mp n)$ remains good provided l remains smaller or of the order of $\sqrt{n}$. We choose the case $l=0$ in Eqs. (20) and (21) and this choice is retained throughout this paper. This choice is purely arbitrary if one considers the limit of infinite principal quantum numbers. In that limit, any fixed value f for l in $c(l,\mp n)$ still leads to a good approximation and corresponds to a limit eccentricity of one for the Kepler orbits. It is, however, adapted to choose a small value for f in order to determine the lowest energy from which the Hamiltonian (1) becomes a good approximation for determining resonance energies. We choose $f=0$ but this choice is not crucial and, for example, the difference of the resonance energies of the Hamiltonian (1) in the space $f=0$ and $f=1$ will rapidly become negligible when the degree of excitation rises. From now on we always consider the case $l=l'=0$ but it should be recalled that this value is not of any fundamental importance.

The most important property of this approximation is that the subspace spanned by the vectors of Eq. (16) remains invariant under the action of the operators $\tau(\beta)$. Moreover, the operator $\tau_j(\beta)$ $(j=1,2,3)$ are Hermitian with respect to the $1/r$ scalar product. More precisely, the three equations (19)–(21) correspond to a positive discrete UIR of su(1,1) [16] characterized by the eigenvalue zero of the Casimir operator

$$\tau_3^2(\beta)-\tau_1^2(\beta)-\tau_2^2(\beta)=0\ . \tag{22}$$

It should be noted that the approximation is β dependent. This means that we are free to choose an arbitrary value for β. It is, however, very important to realize that different values of the pair β,β' correspond to different two-electron subspaces: The two-electron subspace spanned by all the vectors $|(n,n')\beta,\beta'\rangle$ (β,β' fixed) is different from the two-electron subspace spanned by all vectors $|(n,n')\alpha,\alpha'\rangle$ (α,α' fixed) if the pair β,β' is different from the pair α,α'. The sentence "the operators $t(\beta),t'(\beta')$ are replaced by the operators $\tau(\beta),\tau'(\beta')$" means in particular that we are working in the β,β'-dependent two-electron subspace generated by the vectors of Eq. (16).

The approximation will first be tested in Sec. III for the case of two noninteracting electrons, a problem whose exact solution is the hydrogenlike one. The approximation will then be considered for the real two-electron problem in Sec. IV. It will be seen that in both cases the spectrum does not depend on the particular values chosen for the pair β,β'.

III. TEST OF THE APPROXIMATION FOR TWO NONINTERACTING ELECTRONS

The Schrödinger equation for two noninteracting electrons can be written in terms of the generators t [see Eqs. (6) and (8)]:

$$\begin{aligned}\{e^{-\beta'}[t'_3(\beta')-t'_1(\beta')][t_3(\beta)(e^{\beta}-2\varepsilon e^{-\beta})\\ +t_1(\beta)(e^{\beta}+2\varepsilon e^{-\beta})-2Z]\\ +e^{-\beta}[t_3(\beta)-t_1(\beta)][t'_3(\beta')(e^{\beta'}-2\varepsilon' e^{-\beta'})\\ +t'_1(\beta')(e^{\beta'}+2\varepsilon' e^{-\beta'})-2Z]\}|\Psi\rangle=0\ ,\end{aligned} \tag{23}$$

with the total energy E separated according to

$$E=\varepsilon+\varepsilon' \tag{24}$$

and β,β' arbitrary. The bounded eigenvectors are given by the Eq. (14) where $\beta=\ln(Z/n)$, $\beta'=\ln(Z/n')$, and the corresponding eigenvalues are

$$E=Z^2[-1/(2n^2)-1/(2n'^2)]\ . \tag{25}$$

We now arbitrarily fix two integer values to be denoted n_0 and n'_0 and define

$$\begin{aligned}\beta_0&\equiv\ln(Z/n_0)\ ,\\ \beta'_0&\equiv\ln(Z/n'_0)\ .\end{aligned} \tag{26}$$

We then consider the exact Schrödinger equation for two independent electrons [Eq. (23)] with these fixed values for β and β'. We replace in this equation $t(\beta_0)$, $t'(\beta'_0)$ by $\tau(\beta_0)$, $\tau'(\beta'_0)$. Using the relation

$$\begin{aligned}\exp[-i\alpha\tau_2(\beta_0)]\tau_3(\beta_0)\exp[i\alpha\tau_2(\beta_0)]\\ =\cosh(\alpha)\tau_3(\beta_0)+\sinh(\alpha)\tau_1(\beta_0)\ ,\end{aligned} \tag{27}$$

the replaced Schrödinger equation takes the form

$$\begin{aligned}\{n'_0(-8\varepsilon)^{-1/2}[\tau'_3(\beta'_0)-\tau'_1(\beta'_0)]e^{-i\ln(\alpha)\tau_2(\beta_0)}[\tau_3(\beta_0)-n_0e^{\alpha}]e^{i\ln(\alpha)\tau_2(\beta_0)}\\ +n_0(-8\varepsilon')^{-1/2}[\tau_3(\beta_0)-\tau_1(\beta_0)]e^{-i\ln(\alpha')\tau'_2(\beta'_0)}[\tau'_3(\beta'_0)-n'_0e^{\alpha'}]e^{i\ln(\alpha')\tau'_2(\beta'_0)}\}|\Phi\rangle=0\ ,\end{aligned} \tag{28}$$

where

$$e^{\alpha} \equiv (-2\varepsilon)^{-1/2} Z/n_0 \tag{29}$$

and the same for variables with a prime superscript. The spectrum of τ_3, τ'_3 is the set of positive integers. The energy eigenvalues corresponding to Eq. (28) are then exactly the hydrogenlike ones [see Eq. (25)]. This can also be seen as follows: Since the action of $\tau(\beta_0), \tau'(\beta'_0)$ on the vectors $|(n,n')\beta,\beta'_0\rangle$ is the same as the action of $t(\beta_0), t'(\beta'_0)$ on the vectors

$$|(n,l=0,m=0),\beta_0\rangle|(n',l'=0,m'=0),\beta'_0\rangle ,$$

Eq. (28) corresponds, insofar as energies of the resonances are concerned, to the eigenvalue equation

$$(\tfrac{1}{2}p^2 - Z/r + \tfrac{1}{2}p'^2 - Z/r' - E)|\Psi\rangle = 0 , \tag{30}$$

restricted to the subspace where both particles have zero angular momentum ($l = l' = 0$). It is emphasized that the energy eigenvalues are independent of the values of β, β'. The corresponding eigenvectors, to be denoted $|n,n_0,n',n'_0\rangle$, are given by

$$|n,n_0,n',n'_0\rangle \equiv \exp[i\ln(n_0/n)\tau_2(\beta_0) + i\ln(n'_0/n')\tau'_2(\beta'_0)]|(n,n')\beta_0,\beta'_0\rangle . \tag{31}$$

These vectors are exact eigenvectors of the replaced Schrödinger equation [Eq. (28)] and will be called replaced eigenvectors in the following. These replaced eigenvectors have a large distribution over the values of l ($=l'$) since they are constructed from the vectors $|(n,n')\beta,\beta'_0\rangle$ defined by Eq. (16). The mean values of l^2 for the vector of Eq. (16) is explicitly given by Eq. (A16) of the Appendix where the total angular momentum L has to be taken equal to zero. It is seen that the replaced eigenvector is the hydrogenlike one for the special case $n = n_0, n' = n'_0$. The replaced eigenvectors will now be compared to the hydrogenlike ones in the general case by considering the $1/r$ overlaps, to be denoted X, between them:

$$\begin{aligned} X(n,n',n_0,n'_0) &\equiv \langle n,n_0,n',n'_0|(n,n')\ln(Z/n),\ln(Z/n')\rangle \\ &= \langle (n,n')\beta_0,\beta'_0|\exp[i\ln(n/n_0)\tau_2(\beta_0)]\exp[i\ln(n'/n'_0)\tau'_2(\beta'_0)] \\ &\quad \times \exp[-i\ln(n/n_0)t_2]\exp[-i\ln(n'/n'_0)t'_2]|(n,n')\beta_0,\beta'_0\rangle . \end{aligned} \tag{32}$$

This expression does not depend on the charge Z. X represents the cosine of the angle, measured with respect to the $1/r$ scalar product, between the hydrogenlike vector [Eq. (16) where $\beta = \ln(Z/n), \beta' = \ln(Z/n')$] and the replaced eigenvector [Eq. (31)]. It is seen from Eq. (31) and Eqs. (19)–(21) that the expansion of the replaced eigenvectors in terms of the vectors $|(n,n')\beta_0,\beta'_0\rangle$ involves only SU(1,1) representation functions [16], to be denoted δ, as defined in Ref. [17]:

$$|n,n_0,n',n'_0\rangle = \sum_{n_1,n'_1} \delta^{-1}_{n_1 n}\left[\ln\left[\frac{n}{n_0}\right]\right]\delta^{-1}_{n'_1 n'}\left[\ln\left[\frac{n'}{n'_0}\right]\right]|(n_1,n'_1)\beta_0,\beta'_0\rangle . \tag{33}$$

The problem therefore reduces to the calculation of

$$Y \equiv \langle (n_1,n'_1)\beta_0,\beta'_0|\exp[-i\ln(n/n_0)t_2 - i\ln(n'/n'_0)t'_2]|(n,n')\beta_0,\beta'_0\rangle . \tag{34}$$

Y can be calculated from Eq. (14) and the explicit expression of $9j$ coefficients [18]. One obtains

$$\begin{aligned} Y &= [(n_1+n'_1-1)(n+n'-1)]^{1/2} \\ &\quad \times \sum_l (2l+1)e(n_1,l)e(n'_1,l)e(n,l)e(n',l) \\ &\quad \times \delta^{-l-1}_{n_1 n}(\ln(n/n_0))\delta^{-l-1}_{n'_1 n'}(\ln(n'/n'_0)) , \end{aligned} \tag{35}$$

where

$$e(n,l) \equiv (n-1)![(n-l-1)!(n+l)!]^{-1/2} . \tag{36}$$

The overlaps X thus can be expressed in term of SU(1,1) representation functions. From the symmetry property

$$\delta^{\gamma}_{\mu'\mu}(\beta) = (-1)^{\mu'-\mu}\delta^{\gamma}_{\mu'\mu}(-\beta) , \tag{37}$$

it is seen that the overlap $X(n,n',n_0,n'_0)$ is invariant by the transformation of n_0 into n^2/n_0 (the same holds for variables with a prime superscript). Algorithms for the numerical evaluation of the SU(1,1) representation functions have been described elsewhere [17]. Numerical results are reported in Fig. 1, where $X(n,n,n_0,n_0)$ is plotted as a function of n for the three cases $n_0 = 3$, 10, 20. It is seen in this figure that the decrease of the scalar product when n moves away from n_0 rapidly slows down as n_0 increases. Stated otherwise, for fixed values of $n - n_0$, the angles between the replaced eigenvectors and the hydrogenlike ones decrease to zero as n_0 goes to infinity.

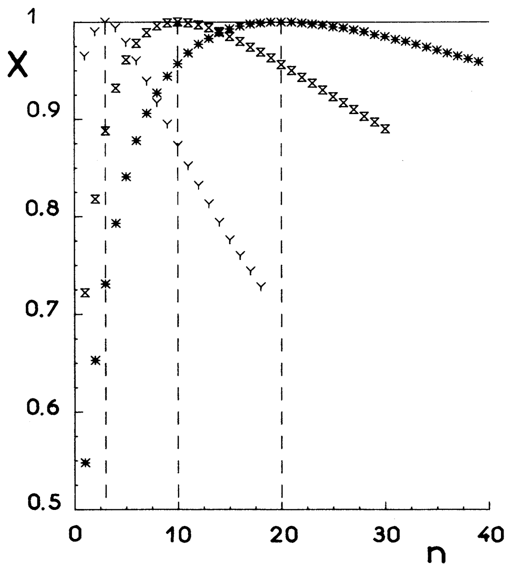

FIG. 1. $X(n,n,n_0,n_0)$: Cosine of the angle with respect to the $1/r$ scalar product between the two-electron hydrogenlike states and the replaced two-electron states (see text). This cosine is plotted as a function of n for three different values of n_0: Y, $n_0=3$; $\mathtt{x}$, $n_0=10$; $*$, $n_0=20$.

IV. THE REAL CASE OF TWO INTERACTING ELECTRONS

It is clear from Eq. (A15) of the Appendix that the mean value of the interelectronic angle is closed to π for those vectors of Eq. (14) which have J maximum,

$$J_1=J_2=(n+n'-2)/2 \ ,$$

provided that n and n' are sufficiently large. The action of $\mathbf{r}\cdot\mathbf{r}'$ on these vectors will therefore be compared with the action of $-rr'$. From Eqs. (3), (4), (6), and (8) one has

$$-e^{\beta+\beta'}rr' = -t_3(\beta)t_3'(\beta')+t_3(\beta)t_1'(\beta') + t_1(\beta)t_3'(\beta')-t_1(\beta)t_1'(\beta') \ , \tag{38}$$

$$e^{\beta+\beta'}\mathbf{r}\cdot\mathbf{r}'=\mathbf{a}(\beta)\cdot\mathbf{a}'(\beta')-\mathbf{a}(\beta)\cdot\mathbf{b}'(\beta') -\mathbf{b}(\beta)\cdot\mathbf{a}'(\beta')+\mathbf{b}(\beta)\cdot\mathbf{b}'(\beta') \ . \tag{39}$$

From the commutation relation

$$[t_2,a_j(\beta)]=ib_j(\beta) \ , \tag{40}$$

it is seen that $\mathbf{r}\cdot\mathbf{r}'$ can be expressed in terms of the operator t,t' and of

$$\mathbf{a}(\beta)\cdot\mathbf{a}'(\beta')=-1+\tfrac{1}{2}\{t_1^2(\beta)+t_2^2+t_1'^2(\beta') +t_2'^2-[\mathbf{a}(\beta)-\mathbf{a}(\beta')]^2\} \ . \tag{41}$$

From the further relation

$$[\mathbf{a}(\beta)-\mathbf{a}(\beta')]^2|(n,n')\beta,\beta'\rangle =[t_3(\beta)+t_3'(\beta')-2][t_3(\beta)+t_3'(\beta')]|(n,n')\beta,\beta'\rangle \ , \tag{42}$$

it is seen that the action of $\mathbf{r}\cdot\mathbf{r}'$ on the vectors $|(n,n')\beta,\beta'\rangle$ can be expressed in terms of the operators $t(\beta),t'(\beta')$ only. We then proceed as in Sec. III, i.e., we approximate $t(\beta)$ by $\tau(\beta)$ [see Eqs. (19)–(21)] and one finally obtains, within this approximation only,

$$\mathbf{a}(\beta)\cdot\mathbf{a}'(\beta')|(n,n')\beta,\beta'\rangle \simeq[-\tau_3(\beta)\tau_3'(\beta')+\tau_3(\beta)+\tau_3'(\beta')-1]|(n,n')\beta,\beta'\rangle \ . \tag{43}$$

For n and n' sufficiently large, one has

$$-nn'\{1-(1/n')-(1/n)+[1/(nn')]\}\simeq -nn' \tag{44}$$

and therefore

$$\mathbf{a}(\beta)\cdot\mathbf{a}'(\beta')|(n,n')\beta,\beta'\rangle \simeq -\tau_3(\beta)\tau_3'(\beta')|(n,n')\beta,\beta'\rangle \ . \tag{45}$$

It is then easy to show that within the above approximations the actions of $\mathbf{r}\cdot\mathbf{r}'$ and of $-rr'$ on the vectors $|(n,n')\beta,\beta'\rangle$ coincide.

The procedure for the study of the real case of two-electron atoms having total angular momentum zero and electrons almost in opposite directions is now summarized. First, one chooses two values for β and β', to be denoted β_0 and β_0'. The Schrödinger equation is then formulated in terms of the operators $t(\beta_0),t'(\beta_0')$. As in Sec. III, these operators are replaced by $\tau(\beta_0),\tau'(\beta_0')$. This corresponds to working only in the subspace generated by the vectors $|(n,n')\beta_0,\beta_0'\rangle$. With the further approximation given by Eq. (44), the initial Schrödinger equation is equivalent, insofar as the energies of the resonances are concerned, to the study of the Hamiltonian given by Eq. (1) in the subspace where both particles have zero angular momentum ($l=l'=0$). The eigenvalues are therefore independent of the initial choice β_0,β_0' for β,β'. Once again, it is of course obvious that the state vectors of the Hamiltonian of Eq. (1) with $l=l'=0$ are totally inadequate for describing real two-electron atomic states with interelectronic close to π. However, the coefficients of the expansion of the eigenvectors of the Hamiltonian of Eq. (1) in the basis

$$|(n,l=0,m=0),\beta_0\rangle|(n',l'=0,m'=0),\beta_0'\rangle$$

are also the coefficients of the expansion of the real two-electron problem in the basis $|(n,n')\beta_0,\beta_0'\rangle$ [Eq. (16)]. The mean values of l^2 for these basis vectors [Eq. (16)] are clearly different from zero, as can be seen from Eq. (A16) of the Appendix where the total angular momentum L has to be taken equal to zero. One can expect in view of the results obtained in Sec. III that the eigenvectors associated with energy eigenvalues close to

$$-\exp(2\beta_0)/2-\exp(2\beta_0')/2$$

should represent good eigenvectors, provided their expansion in the basis $|(n,n')\beta_0,\beta_0'\rangle$ is sufficiently localized in an interval centered on the vector basis with

$$n=Z\exp(-\beta_0),\quad n'=Z\exp(-\beta_0') .$$

The size of this interval should increase rapidly with the degree of excitation. The initial choice for β_0,β_0' thus depends on the particular eigenvector to be studied.

V. REMARKS AND PROSPECTS

The words eigenvalue and eigenvector in the above sentences have to be considered in a large sense since doubly excited states are not true eigenstates of the Hamiltonian but are resonances. Thus, "eigenvalue" should be interpreted as resonance positions and "eigenvector" as an autoionizing state. Numerical calculations of the position and width of these resonances can be performed using a large number of different specific methods (Feshbach projection methods, complex coordinates methods, etc.). A study of the Hamiltonian of Eq. (1) by these methods within the subspace characterized by $l=l'=0$ is beyond the scope of the present paper. We only briefly discuss here a perturbative approach which should be of interest as Z increases. Neglecting exchange effects, the mean value of $1/(r+r')$ for two noninteracting electrons both with zero angular momentum can be obtained for large n,n' on the basis of classical mechanics. The classical probability density is inversely proportional to the velocity associated with a rectilinear Coulombic motion and, therefore,

$$\begin{aligned}\langle 1/(r+r')\rangle &= [Z/(\pi^2 n^3 n'^3)]\int_0^{2n^2}dr\int_0^{2n'^2}dr'[(2/r)-(1/n^2)]^{-1/2}(r+r')^{-1}[(2/r')-(1/n'^2)]^{-1/2}\\ &= Z\{\tfrac{1}{2}s-[(2/nn')+d\arcsin(d/s)]/\pi\}\ ,\end{aligned}\tag{46}$$

where

$$\begin{aligned}s&\equiv(1/n^2)+(1/n'^2)\ ,\\ d&\equiv(1/n^2)-(1/n'^2)\ .\end{aligned}\tag{47}$$

For the intrashell case ($n=n'$), one obtains

$$\langle 1/(r+r')\rangle = Z[1-(2/\pi)]/(n^2)\ ,\tag{48}$$

a result previously obtained by Dmitrieva and Plindov [20]. These authors then [21] have shown that a double Rydberg formula,

$$\begin{aligned}E&=-(\{Z-\tfrac{1}{2}[1-(2/\pi)]\}/n)^2\\ &\simeq -(Z/n)^2+\langle 1/(r+r')\rangle \quad \text{for } Z \text{ large enough}\ ,\end{aligned}$$

approximately reproduces the positions of lower edge intrashell resonances for n large enough. This seems to support the fact that the Hamiltonian of Eq. (1) with $l=l'=0$ should be relevant for the study of the energies of these resonances. Our present work indicates that the initial problem with three degrees of freedom (the internal coordinates which describe the geometry of the three-particle system) could well be reduced to a problem with two degrees of freedom only [Eq. (1) and $l=l'=0$]. It would be of particular interest to check this conjecture by the numerical computation of the position of the intrashell resonances associated to the Hamiltonian of Eq. (1) in the space where $l=l'=0$ and compare the results as n increases with the lower edge resonances associated with the real two-electron problem. The first 15 $L=0$ lower edge resonance positions have recently been computed [22] with a method which takes the interelectronic axis as adiabatic coordinate. Comparison with double Rydberg formula (see, e.g., Ref. [23]) would also be of interest. For previous works on the Hamiltonian given by Eq. (1), see, e.g., Refs. [24,25].

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APPENDIX: MEAN VALUES OF $\cos(\theta_{12})$ AND l^2

The quantum-mechanical mean value $\langle O\rangle$ of an operator O in an arbitrary state is given within our notations [see Eq. (9) and below]:

$$\langle O\rangle=\langle\Psi|rr'O|\Psi\rangle/\langle\Psi|rr'|\Psi\rangle\ .\tag{A1}$$

For the vectors given by Eq. (14), one obtains from Eqs. (6)–(8) and from the fact that the diagonal element of t_1,t_1' are zero:

$$\langle O\rangle=[1/(nn')]\langle(n,n',J_1,J_2,L,M)\beta,\beta'|[t_3(\beta)-t_1(\beta)][t_3'(\beta)-t_1'(\beta')]O|(n,n',J_1,J_2,L,M)\beta,\beta'\rangle\ .\tag{A2}$$

When the operator on the right-hand side of Eq. (A2) is a polynomial function of the O(4,2) generators of the two electrons, the calculation can be made algebraically. Two cases will now be considered: $O=\cos(\theta_{12})$ and $O=l^2$. These operators commute with t_2,t_2' and thus Eq. (A2) becomes independent of β,β' and these scaling factors will therefore be dropped out in the sequel. One thus obtains

$$\langle\cos(\theta_{12})\rangle=\langle(n,n',J_1,J_2,L,M)|(\mathbf{b}-\mathbf{a})\cdot(\mathbf{b}'-\mathbf{a}')|(n,n',J_1,J_2,L,M)\rangle/(nn')\ ,\tag{A3}$$

$$\langle l^2\rangle=\langle(n,n',J_1,J_2,L,M)|(t_3-t_1)(t_3'-t_1')l^2|(n,n',J_1,J_2,L,M)\rangle/(nn')\ .\tag{A4}$$

As

$$l^2=t_3^2-t_1^2-t_2^2 \tag{A5}$$

and as odd powers of t_1, or t'_1, or $\mathbf{b}$ or $\mathbf{b}'$ give zero contribution [12], one obtains

$$\langle\cos(\theta_{12})\rangle=\langle(n,n',J_1,J_2,L,M)|\mathbf{a}\cdot\mathbf{a}'|(n,n',J_1,J_2,L,M)\rangle/(nn') , \tag{A6}$$

$$\langle l^2\rangle=n^2-\langle(n,n',J_1,J_2,L,M)|t_1^2+t_2^2|(n,n',J_1,J_2,L,M)\rangle . \tag{A7}$$

From Eq. (41) it is seen that the only nontrivial part remains the calculation of the matrix element of

$$t_1^2+t_2^2=t_+t_-+t_3 . \tag{A8}$$

This problem is solved as the action of t_+,t_- is known from Eq. (74) of Ref. [10]. One obtains

$$\begin{aligned}\langle(n,n',J_1,J_2,L,M)|t_1^2+t_2^2|(n,n',J_1,J_2,L,M)\rangle\\ =n+\{1/[4(2J_1+1)(2J_2+1)]\}\{f(j',j+J_1)f(j',j+J_2)f(L,J_1+J_2)/(J_1J_2)\\ +f(J_1-j,j')f(j',j+J_2)f(J_1-J_2,L)/[(J_1+1)J_2]\\ +f(j',j+J_1)f(J_2-j,j')f(J_2-J_1,L)/[J_1(J_2+1)]\\ +f(J_1-j,j')f(J_2-j,j')f(L,J_1+J_2+1)/[(J_1+1)(J_2+1)]\} ,\end{aligned} \tag{A9}$$

where

$$f(x,y)\equiv(y+x+1)(y-x) , \tag{A10}$$

$$j\equiv(n-1)/2 , \tag{A11}$$

$$j'\equiv(n'-1)/2 . \tag{A12}$$

For the intrashell cases $n=n'$, one obtains

$$\langle\cos(\theta_{12})\rangle=(n^2-1+\tfrac{1}{2}\{L(L+1)-3[J_1(J_1+1)+J_2(J_2+1)]\})/(2n^2) , \tag{A13}$$

$$\langle l^2\rangle=[2n^2-J_1(J_1+1)-J_2(J_2+1)+L(L+1)-2]/4 . \tag{A14}$$

Equation (A13) was previously obtained [19] on the basis of O(4) group-theoretical considerations. Turning now to the cases $J_1=J_2=(n+n'-2)/2$, one obtains

$$\langle\cos(\theta_{12})\rangle=-1+[(n-1)^2+(n'-1)^2+nn'-1+L(L+1)(n-1)(n'-1)/(n+n'-2)]/[nn'(n+n'-2)] , \tag{A15}$$

$$\langle l^2\rangle=(n-1)[n'-1+(n-1)L(L+1)/(n+n'-2)]/(n+n'-2) . \tag{A16}$$

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