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Radial and angular correlations of two excited electrons. IV. Comparison of configuration-interaction wave functions with the group-theoretical basis functions

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Doubly-excited-state basis (DESB) functions of Herrick and Sinanoğlu are compared with the large-scale configuration-interaction (CI) wave functions of Lipsky *et al.*, and with the adiabatic channel functions in hyperspherical coordinates. It is shown that DESB functions will represent those states where the mean value of θ_{12} is large. Owing to the absence of intershell correlations, and a consequent underestimation of radial correlations, the DESB functions give excessive concentrations near $\theta_{12}=0$ for other, less sharply correlated in angle, states.

I. INTRODUCTION

Since the identification of doubly excited states of He (Ref. 1) in 1963, it has been recognized that understanding these states requires careful examination of the correlation of two excited electrons.[2] The independent-particle model, which forms the basis for almost all areas of microscopic physics, no longer suffices as first-order description of these states. Because of the relative simplicity of the two-electron Hamiltonian, many variational approaches have been proposed and applied to the study of doubly excited states. The predictions of energies and widths from these calculations often accord well with existing observations.[3] On the other hand, very few approaches addressed the problem of providing a first-order description of doubly excited states.

In the past few years, two methods of addressing the nature of correlations of two excited electrons emerged. One approach represents the two-electron wave functions in hyperspherical coordinates in the adiabatic approximation.[4] This method stresses the adiabatic evolution of electron correlations as the hyperradius of the system varies and relates the properties of doubly excited states to the pattern of radial and angular correlations. In the first two papers of this series,[5] such correlation patterns have been displayed graphically for $^{1,3}S^e$ states of two-electron systems. The systematics for other angular momentum states was addressed in a recent paper.[6]

Another first-order approach which also addresses the general characters of doubly excited states is the algebraic method described by Herrick and Sinanoğlu.[7] Two quantum numbers K and T were introduced. In the (K,T) representation, it was shown that the Hamiltonian on the (N,n) subspace, where N and n are the principal quantum numbers of the inner and the outer electrons, respectively, is nearly diagonal. The corresponding doubly excited states in the (K,T) representation are called doubly-excited-state basis (DESB) functions. These functions are regarded as a first-order approximation for describing doubly excited states. Such states are then labeled in terms of quantum number K,T,N,n, together with the usual L, S, and π.

The two schemes above both address the classification of doubly excited states. For first-order approximations to doubly excited states, it is important to recognize the degree to which major features of such states are adequately incorporated. Thus, we compare the correlation features of the simple first-order theory with those of more accurate calculations. Such comparisons were made in paper III of this series where the correlation patterns calculated from the adiabatic approximation were found to resemble closely those obtained from the configuration-interaction (CI) method in regions where charge densities are *not* small. We also established in that paper that hyperspherical coordinates provide a natural system for such a comparison.

In this paper we examine the correlation features built into the DESB functions. In this connection we note that DESB functions are equivalent to approximate CI functions in that only intrashell correlations within a given (N,n) subspace are included, while conventional CI includes intershell correlations between (N,n) subspaces. The restriction emphasizes angular correlations and, as we will show, underrepresents radial correlations.

In Sec. II we present a brief description of the three approximation methods used for doubly excited states. The comparisons are presented in Sec. III. In Sec. IV we discuss the general characteristics of DESB functions as a first-order approximation to doubly excited states.

II. METHODS OF CALCULATIONS

In this paper we compare wave functions of doubly excited states calculated from the three approximations: (a) the configuration-interaction results of Lipsky *et al.*,[8] (b) the DESB functions of Herrick and Sinanoğlu,[7] and (c) the adiabatic approximation in hyperspherical coordinates. In paper III, we compared (a) and (c) for $^{1,3}S^e$ states of He. It was illustrated there that the comparison is best achieved by comparing the wave functions in hyperspherical coordinates.

The CI wave functions are given by

$$\psi_\gamma = \sum_i C_i \psi_i(\vec{r}_1, \vec{r}_2) , \tag{1}$$

where

$$\psi_i = | n_1 l_1 n_2 l_2 L S \pi M_L M_S \rangle \tag{2}$$

is the properly symmetrized two-electron basis functions constructed from the product of hydrogenic functions. We rewrite (1) in hyperspherical coordinates in the form

$$\psi_\gamma = F_\gamma(R)\Phi_\gamma(R;\Omega) , \tag{3}$$

where $\Omega \equiv (\alpha, \hat{r}_1, \hat{r}_2)$ denotes the five angles and R is the hyperradius. Requiring $\Phi_\gamma(R;\Omega)$ to be normalized to unity on the surface $R(\Omega)$=const serves to define $F_\gamma(R)$ uniquely.

The DESB functions are also written in the form of Eq. (1) except that the summation includes only possible pairs of (l_1, l_2) with n_1 and n_2 fixed. Thus in the DESB functions, n_1 and n_2 are good quantum numbers, where $n_1 = N$ denotes the principal quantum number of the inner electron and $n_2 = n$ the principal quantum number of the outer electron.

The angular momentum quantum numbers l_1 and l_2 are replaced by a pair of new quantum numbers (K,T). The DESB states are labeled by $\gamma \equiv \{n,N,K,T,L,S,\pi,M_L,M_S\}$. We say that DESB functions include intrashell correlations. To see the degree of correlations included in the DESB functions, we also rewrite these functions in the form of Eq. (3).

The method of calculating doubly excited states in hyperspherical coordinates in the adiabatic approximation has been described previously.[5] These functions are expressed as $F^n_\mu(R)\Phi_\mu(R;\Omega)$ where μ is the channel index and n denotes the quantum number of the radial function $F(R)$. With all the wave functions expressed in the form $F(R)\Phi(R;\Omega)$ from the three approximations, it is possible to compare $F(R)$ and $\Phi(R;\Omega)$ separately from the three approaches.

III. RESULTS

A. Radial functions

In Fig. 1 we show $F(R)$ for the three functions of He $^1P^o$ states which were called $2s3p \pm 2p3s$, $2p3d$ states by Cooper *et al.*[2] These states were called (2,3*a*), (2,3*b*), and (2,3*c*) by Lipsky *et al.* and have (K,T)=(0,1), (1,0), and (−1,0), respectively, according to Herrick and Sinanoğlu. From Fig. 1, we have the following observations:

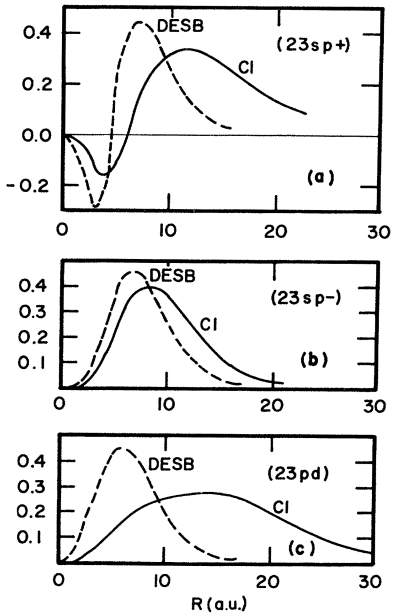

FIG. 1. Radial wave function $F(R)$ for (a) $23sp+$ $^1P^o$, (b) $23sp-$ $^1P^o$, and (c) $23pd$ $^1P^o$ states of helium calculated from the DESB functions of Herrick and Sinanoğlu (Ref. 7), from the configuration-interaction (CI) wave functions of Lipsky *et al.* (Ref. 8).

(i) The $23sp+$ state has a node in $F(R)$. It occurs at R=4.5 according to DESB and at R=6.0 according to the other two approaches. The DESB $F(R)$ is more localized at small R while the results from the two other approaches are more diffuse and agree with each other.

(ii) The $23sp-$ state is the lowest state of the "−" channel (or the 2*b* channel of Lipsky *et al.*) and has no node in $F(R)$. It is not as diffuse and the DESB prediction agrees well with both the CI and adiabatic approximations.

(iii) The $23pd$ state is the lowest state of the "*pd*" channel (or the 2*c* channel of Lipsky *et al.*) and has no node in $F(R)$. The state is very diffuse and deviates greatly from the very localized DESB function.

In Fig. 2 we show the comparison of $F(R)$ between CI and DESB functions for the lowest state of each of the He $^1S^e$ channels that lie below the $He^+(N=3)$ thresholds. These three states are designated as (3,3*a*), (3,3*b*), (3,3*c*) by Lipsky *et al.* with (K,T)=(2,0), (0,0), and (−2,0), respectively. The first two states are localized and CI and DESB predictions agree. The (3,3*c*) state is very diffuse and the DESB prediction is quite inaccurate.

B. Radial and angular correlations

A more direct comparison of correlations included in the three approaches is to show the surface charge-density plots. For the adiabatic approximation in hyperspherical coordinates, it was shown in I and II that these surface charge-density plots vary smoothly with R. The major

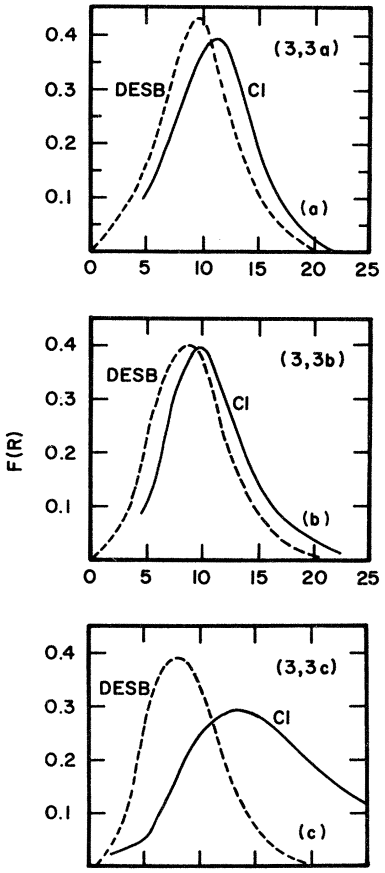

FIG. 2. Similar to Fig. 1 but for (a) $(3,3a)\ ^1S^e$, (b) $(3,3b)\ ^1S^e$, and (c) $(3,3c)\ ^1S^e$ states of helium.

variation at large R is the decrease of charge density in the neighborhood of $\alpha=45°$. In paper III we compared the corresponding plots from the CI calculations of Lipsky *et al.* In these works only $^{1,3}S^e$ states are compared.

For $^{1,3}S^e$ states, it is straightforward to express $|\Phi_\mu(R;\Omega)|^2$ on (α,θ_{12}) plane. For $L\neq 0$ states, $\Phi_\mu(R;\Omega)$ contains information describing the overall rotation of the atom. We define surface charge densities for these states by averaging over the rotations. Thus we define

$$\rho(R;\alpha,\theta'_{12})=\int d\hat{r}_1 d\hat{r}_2 \delta(\cos\theta_{12}-\cos\theta'_{12})\,|\Phi(R;\Omega)|^2\,. \tag{4}$$

In Fig. 3 we compare ρ's for the $23sp+\ ^1P^o$ of He at $R=4$, 10, and 14 from the three approaches. Both the DESB and adiabatic functions show a distribution more peaked near small θ_{12} than does the CI, although the differences appear minor except for DESB functions at $R=4$. Here the DESB distribution differs completely from the adiabatic and CI distributions. At $R=14$ the CI shows the least concentration near $\theta_{12}=0$, the adiabatic functions slightly more, and the DESB functions significantly more.

In Fig. 4 we compare the ρ's for the $23sp-\ ^1P^o$ state of He at $R=6$ and 10. This state has a large charge concentration for $\theta_{12}\sim\pi$ but there is little charge density for

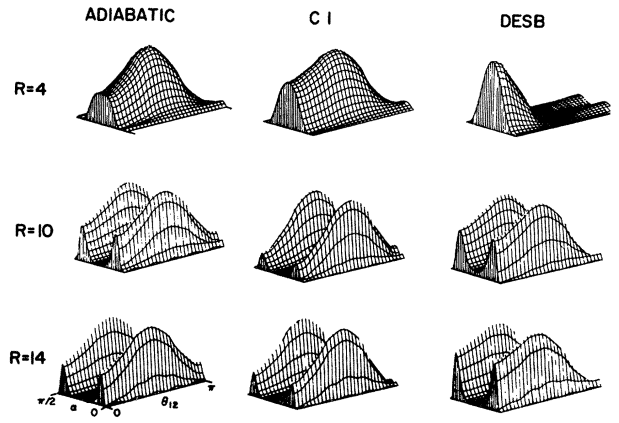

FIG. 3. Comparison of surface charge-density plots of $23sp+\ ^1P^o$ states of helium at $R=4$, 10, and 14. The three theoretical approaches are: adiabatic approximation hyperspherical coordinates, large-scale CI, and DESB functions. Note that DESB functions do not agree with the other two approaches very well at $R=4$. The orientation of each plot is identical to the one labeled at the lower-left corner.

$\alpha\sim 45°$. This is a characteristic of "$-$" states. All three approaches agree, as do the corresponding $F(R)$'s.

In Fig. 5 we compare the ρ's for $23pd\ ^1P^o$ state between DESB and CI calculations. Because the radial functions $F(R)$ in the two approaches are quite different we display ρ's corresponding to different R values, i.e., at values of R where $F(R)$ is near the maximum and two other R values on either side of the peak. Although the general θ_{12} dependence appears to be similar, there are important differences in the α dependence. The CI calculations show that $\rho(\alpha,\theta_{12})$ is always small for $\alpha\sim 45°$ for all the values of R shown, consistent with the results from the adiabatic approximation (not shown); the DESB functions, on the other hand, predict pronounced charge density for $\alpha\sim 45°$. The limited basis set included in the DESB functions thus describe the qualitative behavior of θ_{12} angular correlations, but radial correlations are not adequately described. Similar density plots for $(3,3a)\ ^1S^e$ and $(3,3b)\ ^1S^e$ states are shown in Figs. 6 and 7, respectively. We notice that the agreement between DESB and CI results is quite good for $(3,3a)\ ^1S^e$ and not so good for $(3,3b)\ ^1S^e$. The discrepancies between the two approaches

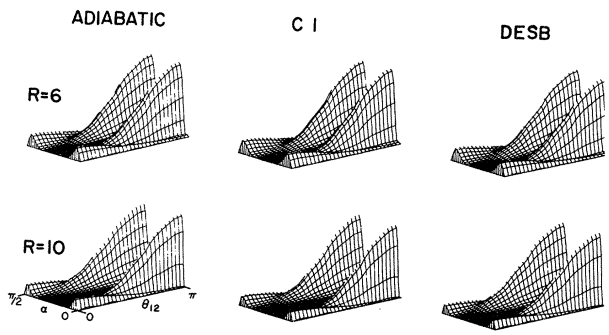

FIG. 4. Similar to Fig. 3 except for $23sp-\ ^1P^o$ at $R=6$ and 10.

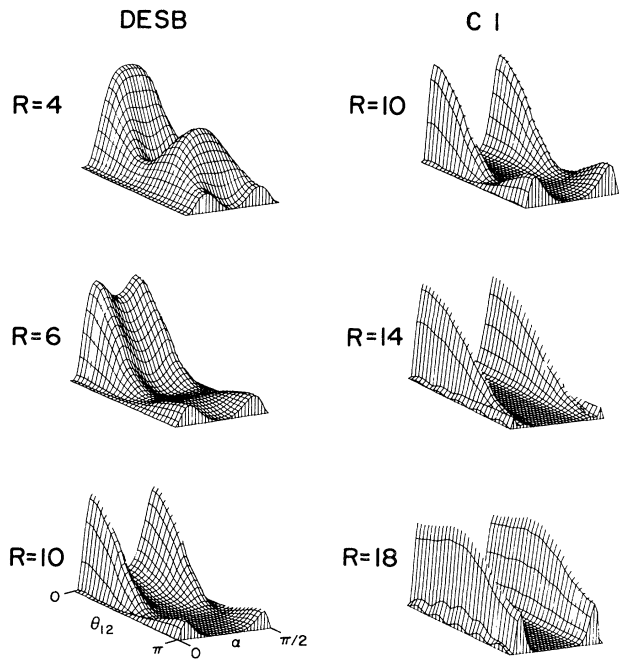

FIG. 5. Similar to Fig. 3 but for $23pd\ ^1P^o$. Only DESB and CI functions are shown. Note that the graphs are shown at different values of R.

are so large for (3,3c) $^1S^e$ state that we do not present the comparison.

IV. DISCUSSIONS AND CONCLUSIONS

In Sec. III we compared the wave functions of doubly excited states calculated from three different approaches in hyperspherical coordinates. The adiabatic approximation gives results quite close to those obtained in the large-scale CI calculations, consistent with our conclusion in paper III. The DESB functions of Herrick and Sinanoğlu,[7] from which quantum numbers (K,T) are defined, are typically more compact than the CI functions. In addition, some DESB functions are too concentrated near $\theta_{12}=0$. Most importantly, however, the corresponding Φ_μ's do not vary slowly with R and thus do not correspond to the adiabatic hyperspherical function $\Phi_\mu(R;\Omega)$.

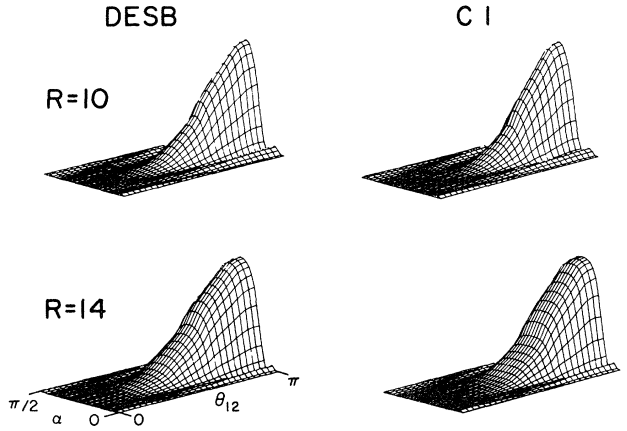

FIG. 6. Similar to Fig. 3 except for (3,3a) $^1S^e$ state.

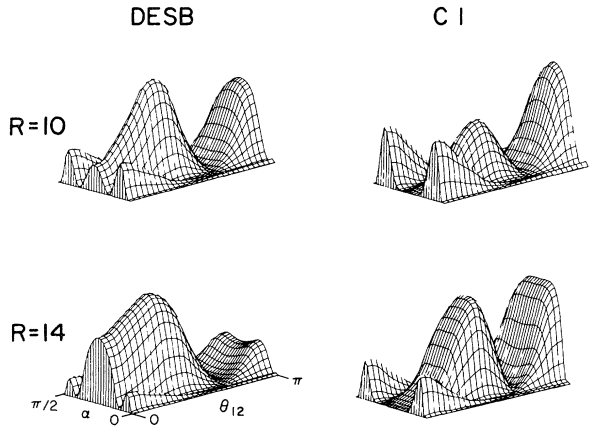

FIG. 7. Similar to Fig. 3 except for (3,3b) $^1S^e$ state.

This is particularly noticeable for the $23sp+\ ^1P^o$, $23pd\ ^1P^o$, (3,3b) $^1S^e$, and (3,3c) $^1S^o$ states. Alternatively, the $23sp-\ ^1P$ and the (3,3a) $^1S^e$ DESB functions agree well with both the adiabatic and CI functions (see Figs. 4 and 6). These two functions are concentrated near $\theta_{12}=\pi$ and thus minimize electron-electron repulsion. It appears that the DESB prescription accurately represents those states whose distributions minimize the electron-electron repulsion, but are increasingly inaccurate for other states. The degree of inaccuracy correlates with the tendency of the angular distributions to peak away from the $\theta_{12}=\pi$ region.

It was argued in Ref. 7 that accurate doubly excited states can be constructed as linear superpositions of states with common (K,T) but varying n_1,

$$|nNKTLS\pi M_L M_S\rangle=\sum_{n_1} a_{n_1}|n_1 NKTLS\pi M_L M_S\rangle\ , \quad (5)$$

i.e., (N,K,T) can be treated as approximate good quantum numbers. Such superpositions allow for screening and, with the exception of the $23pd\ ^1P$ and (3,3c) ^1S series, bring the calculated DESB energies into modest agreement with the full CI results of Lipsky *et al.*[8] Such superpositions may alter the α distributions, however, because K and T are chosen to diagonalize an operator which describes the θ_{12} correlations, the corresponding distributions in θ_{12} should be largely unaltered by the superposition of Eq. (5). Accordingly, some (K,T) mixing is needed to bring the DESB functions into close accord with the full CI functions.

Our comparisons show that the (K,T) mixing is smallest for the $23sp-\ ^1P$ and the (3,3a) ^1S series, but is most pronounced in the $23pd\ ^1P$ and (3,3c) ^1S series. This feature was already noticed by Herrick and Sinanoğlu.[7] We can understand the consequences of such mixing from the $F(R)$ curves for the $23pd\ ^1P$ series. Note that the wave function is kept out of the small-R region. This is understood as the effect of the high generalized angular momentum barrier for this series. Macek,[9] in his investigation of the doubly excited states noted that while the $2pnd$ series contained admixtures of the $2nsp+$ and $2nsp-$, this mixture occurred with alternating signs so that the wave functions canceled near the nucleus. This effect is readily understood in the adiabatic approxima-

tion but has no counterpart in the DESB classification. Figure 2 shows that the effects of the generalized angular momentum barrier are also absent from the DESB $(3,3c)$ ^1S functions. Again, this is substantiated by the marked disagreement between the quantum defects calculated by Herrick and Sinanoğlu[7] ($n^*=4.304$) and those of Lipsky[10] and co-workers ($n^*=3.786$).

The DESB functions reproduce some of the features of the full CI functions; in particular, they represent well those states in which the two electrons are on opposite sides of the nucleus. It is noteworthy that these are precisely the states which dominate at the threshold for double electron escape. The DESB functions do not, however, incorporate the generalized angular momentum barrier and appear to give excessive concentrations of many of the eigenfunctions near $\theta_{12}=0$.[11] Since the DESB functions diagonalize an operator which does not commute with the Hamiltonian, it is unclear why they give accurate representations for some series but not others. Varying degrees of (K,T) mixing are needed to reproduce the hyperspherical results, but the systematics of such mixing can, at present, only be extracted with full CI calculations.

ACKNOWLEDGMENTS

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