Radial and angular correlations of two excited electrons. III. Comparison of configuration-interaction wave functions with adiabatic channel functions in hyperspherical coordinates

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Wave functions for doubly excited states of helium $^{1,3}S^e$ states calculated in the configuration-interaction (CI) method are examined in hyperspherical coordinates. It is shown that these wave functions are essentially identical to the wave functions calculated in the adiabatic approximation except in regions where the charge density is vanishingly small. This comparison establishes the *connection* between the classification of doubly excited states based upon the adiabatic approximation in hyperspherical coordinates and the classification of Herrick and Sinanoglŭ which is based upon the approximate CI wave functions. It is also shown that states calculated from the CI method which have similar quantum defects have the same correlation patterns except in regions where the charge density is small. This establishes the approximate channel classification of doubly excited states as implied in the adiabatic approximation in hyperspherical coordinates.

I. INTRODUCTION

In the last few years, many properties of doubly excited states of H^- and He have been studied by examining their wave functions in hyperspherical coordinates.[1-7] In these studies, an adiabatic approximation similar to the Born-Oppenheimer approximation in molecular physics has often been used. If the hyper-radius is denoted by R and the five angles are denoted collectively by Ω, in the adiabatic approximation the wave function for the nth excited state in a given channel μ is expressed as $F_\mu^n(R)\Phi_\mu^{ad}(R;\Omega)$. By assigning a single angular function $\Phi_\mu^{ad}(R;\Omega)$ to all the states within a given channel μ, this approach emphasizes that states belonging to the same channel have similar correlation patterns. Earlier studies have illustrated that this is a good approximation for doubly excited states. In recent studies,[1,8] the correlation patterns for $^{1,3}S^e$ states have been examined graphically by displaying $|\Phi_\mu^{ad}(R;\Omega)|^2$ on the (α,θ_{12}) plane. These studies revealed that different channels exhibit very distinct correlation patterns.

While these earlier works have shown the usefulness of the adiabatic approximation in elucidating many important characteristics of electron correlations in doubly excited states, two important questions are still not adequately investigated: (1) How good is the adiabatic approximation? (2) Do the wave functions calculated in the adiabatic approximation in hyperspherical coordinates resemble wave functions calculated using conventional approaches?

The validity of the adiabatic approximation is often "justified" by the simple argument that the kinetic energy associated with the motion in R is much smaller than that associated with Ω. It can also be argued from the relatively accurate eigenenergies for doubly excited states calculated in this approximation. However, these explanations are often not very satisfactory in view of the more"apparent" explanations in molecular physics. In the Born-Oppenheimer approximation, the wave functions of molecules are expressed as the product of electronic and vibrational wave functions. This quasiseparability is conventionally attributed to the fact that the mass m of the electron is much less than the mass M of the nucleus with the result that the vibrational motion of the nuclei is adiabatic in comparison with the faster electronic motion. Such an explanation is not substantially supported by the actual size of the nonadiabatic coupling terms. These terms are proportional to $(m/M)^{1/4}\sim\frac{1}{6}$, while the precise calculations[9,10] for low-lying states of H_2^+ and H_2 indicated that nonadiabatic effects are only of the order 10^{-5}. Therefore there are other underlying dynamical factors for the validity of adiabatic approximation in molecular physics. In the case for the approximate separability of wave functions in hyperspherical coordinates, the "mass ratio" between the R and Ω motion is unity. Nevertheless, eigenener-

gies of doubly excited states calculated in the adiabatic approximation agree quite well with other theoretical calculations and with experiments. It might also be noted that the adiabatic approximation has also been used in the study of hydrogen atoms in a strong magnetic field.[11] The mass ratio in this case is also unity.

In this article we will illustrate the *dynamical* origin of the quasiseparability of low-lying doubly excited states. We will show that the configuration-interaction (CI) wave functions of Lipsky *et al.*[12] exhibit approximate separability if their wave functions are expressed in hyperspherical coordinates. We will show that wave functions computed in the two approaches are nearly identical in the important regions where the probability density is large, but deviations do occur in regions where the probability density is small.

The present study also serves to illustrate the connection between the classification of doubly excited states by Herrick and Sinanoglŭ[13] with the classification based upon the adiabatic approximation in hyperspherical coordinates. Doubly excited states classified in the group-theoretical method by Herrick and Sinanglŭ are approximate CI wave functions. The graphical display of the more accurate CI wave functions of Lipsky *et al.* in hyperspherical coordinates serves to compare the two classification schemes. On the other hand, the adiabatic approximation in hyperspherical coordinates also emphasizes the similarity of correlation patterns of states belonging to the same channel. Such a concept is absent in the group-theoretical approach. The CI and other better wave functions have also been displayed graphically[8] in terms of the conventional coordinates (r_2,θ_{12}) with fixed r_1. In those works the similarity of the states belonging to the same channels had not been illustrated.

II. METHODS OF CALCULATIONS

The methods of calculating doubly excited states in hyperspherical coordinates in the adiabatic approximation have been described previously.[14] For each set of quantum numbers $\{L,S,\pi\}$, the wave function for the nth excited states in channel μ is expressed as $F_\mu^n(R)\Phi_\mu^{\rm ad}(R;\Omega)$. In this approximation, $\Phi_\mu^{\rm ad}(R;\Omega)$ is obtained by solving a partial differential equation in Ω with R treated as parameters. The eigenvalues $U_\mu(R)$ are then used to calculate the radial wave functions $F_\mu^n(R)$. These radial wave functions $F_\mu^n(R)$ have very simple nodal structure—the lowest state within each μ is nodeless and the higher states have increasing number of nodes and extend to higher values of R.

Adiabatic approximation was not assumed in the conventional approaches for calculating doubly excited states. Most of these calculations are variational in nature in that the wave functions of doubly excited states are expanded in a truncated basis set. For example, in the CI approach of Lipsky *et al.*, the wave functions are expressed as

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

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 wave function constructed from the product of hydrogenic wave functions. For doubly excited states of helium with given L, S, π, M_L, and M_S, ψ_i is constructed from the $|n_1 l_l m_1\rangle$ and $|n_2 l_2 m_2\rangle$ hydrogenlike wave functions of He^+. The CI coefficients C_i are obtained by diagonalizing the two-electron Hamiltonian in a chosen truncated basis. The accuracy of this approach and other similar approaches is limited by the flexibility of the chosen basis set. This type of calculation gives the energy E_γ and wave function ψ_γ without correlating the properties of different doubly excited states within a certain energy range. States with nearly identical quantum defects are assigned to belong to the same channels.

The CI wave functions are often expressed in terms of the spherical coordinates (r_1,ϕ_1,θ_1) and

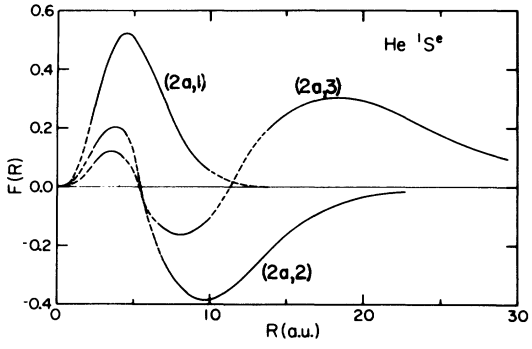

FIG. 1. R-weighted radial wave functions [see Eq. (3) of the text] of the three lowest CI states of the $\mu=2a$ channel for $^1S^e$ symmetry of helium atoms. The curves are shown in solid lines in regions where the angular part of the CI wave function has large overlap integral (>0.95) with the adiabatic channel function. If the overlap integral is small (<0.95), the curves are shown in dashed lines (see text).

(r_2,ϕ_2,θ_2) of the two electrons. For $^{1,3}S^e$ states, the CI wave functions for the nth state of channel μ can be rewritten in hyperspherical coordinates as

$$\psi_\mu^n = \sum_i C_i \psi_i(\vec{r}_1,\vec{r}_2)$$

$$\equiv \bar{F}_\mu^n(R)\Phi_\mu^n(R;\alpha,\theta_{12}) \,. \tag{3}$$

By requiring that $\Phi_\mu^n(R;\alpha,\theta_{12})$ be normalized on the hyperspherical surface $R=$const, this equation serves to define $\bar{F}_\mu^n(R)$ and $\Phi_\mu^n(R;\alpha,\theta_{12})$ uniquely. In (3), we do not assume that Φ_μ^n behave identically for different n states within the same channel μ, nor do we assume that Φ_μ^n evolve adiabatically with R. In the next section, we compare $\Phi_\mu^n(R;\alpha,\theta_{12})$ with $\Phi_\mu^{\rm ad}(R;\alpha,\theta_{12})$.

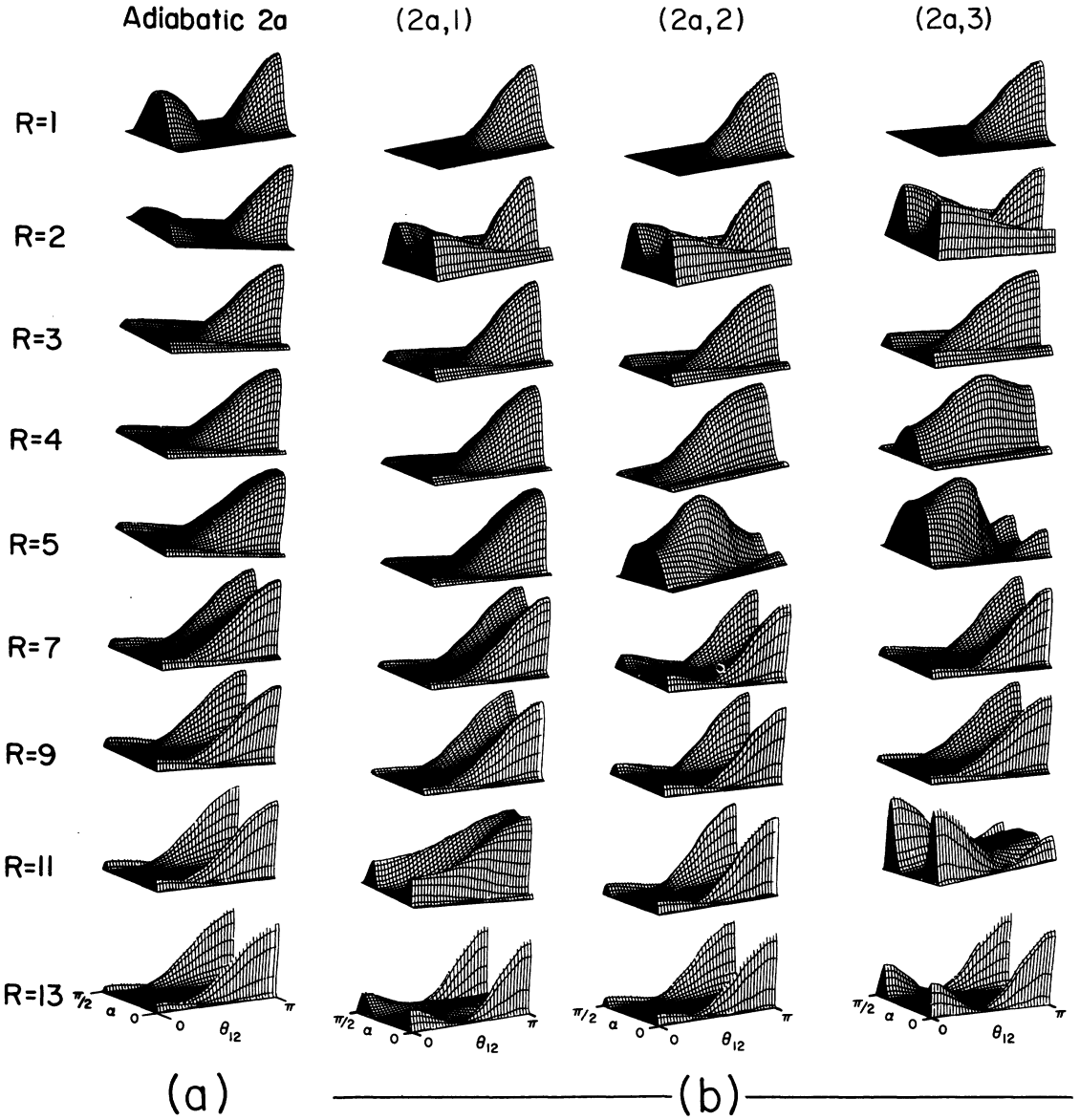

FIG. 2. Comparison of the adiabatic channel function with the angular part of the CI wave functions of the $\mu=2a$ channel for $^1S^e$ state of helium. Shown along the first column are the surface charge-density plots at selected values of R calculated in the adiabatic approximation. The surface charge-density plots for the three lowest CI states of the $\mu=2a$ channel are shown along each column. Notice that the CI results agree with the adiabatic ones at values of R where $|F_{2a}^n(R)|$ is large (as shown in Fig. 1).

III. RESULTS AND DISCUSSION

We first examine $^1S^e$ doubly excited states of helium that converge to the $He^+(N=2)$ thresholds. There are two channels converging to this limit. In the notation of II, these two channels are identified as $[N,\lambda]=[2,1]$ and $[2,2]$. In the notation of Lipsky *et al.*, these two channels are identified as $\mu=2a$ and $2b$. For our purpose here, the states are identified as $(2a,n)$ and $(2b,n)$ with $n=1$ corresponding to the lowest state of each channel.

The R-weighted radial wave functions $\bar{F}^n_\mu(R)$ [cf, Eq. (3)] calculated in the CI approximation are shown in Fig. 1 for the $n=1$, 2, and 3 states of the $2a$ channel. These functions behave like typical radial wave functions computed from a given local potential with the number of radial nodes n_R given by $n_R=n-1$. These nodal behaviors are similar to the radial wave functions calculated in the adiabatic approximation.[4(c),14] In Fig. 1 the R-weighted radial wave function for each state n is plotted partly in solid lines and partly in dashed lines in order to illustrate the degree of overlap between $\Phi^n_{2a}(R;\alpha,\theta_{12})$ and $\Phi^{ad}_{2a}(R;\alpha,\theta_{12})$ at fixed values of R. If the overlap is greater than 0.95, then in that region $\bar{F}^n_{2a}(R)$ is shown in solid lines. If the overlap is less than 0.95, then that region is shown in dashed lines. We notice that the overlap is large (>0.95) if $|\bar{F}^n_{2a}|$ is large. In other words, the angular wave functions Φ^n_μ calculated from the CI approximation differ from the adiabatic ones only when $|\bar{F}^n_{2a}(R)|$ is small. This occurs at small and at large values of R and for R near the nodal points of the radial functions.

To illustrate the comparison in greater detail, in Fig. 2 we show the surface charge-density plots of $|\Phi^{ad}_{2a}|^2$ and $|\Phi^n_{2a}|^2$ on the (α,θ_{12}) plane for $n=1$, 2, and 3 at $R=1$, 2, 3, 4, 5, 7, 9, 11, and 13 a.u. Each graph is normalized to the same maximum height. Except for a few graphs to be discussed below, there is a general agreement between the adiabatic channel function and the angular functions calculated in the CI approximation. In other words, we observe the channel characters of CI wave functions when these wave functions are expressed in hyperspherical coordinates. We also observe the adiabatic evolution of these functions in certain ranges of R even though quasiseparability was *not* assumed *a priori* in the CI calculation.

In Fig. 2 we also notice some discrepancies among the surface plots at the same R. At $R=1$ and 2 a.u. the plots from the CI calculation for the three states are identical to each other but differ from the ones calculated in the adiabatic approximation. At $R=3$ a.u., $|\bar{F}^n_{2a}(R)|$ is large for all three states, and all four graphs are identical. This shows that at this value of R the angular wave functions from the CI calculation for states belonging to the same channel agree with the adiabatic channel function. For the higher values of R shown, except for $R=11$ and 13 a.u., the angular functions for the state $(2a,1)$ ble the corresponding ones from the adiabatic calculation. The large discrepancies between the adiabatic and the CI's $(2a,1)$ state at $R=11$ and 13 a.u. are most likely due to the truncation of the basis set in the CI calculation. The rapid variation of the angular function in the CI calculation here does not appear plausible since at such large values of R the two electrons stay away from each other, and a drastic redistribution of charge density is not expected. Since the radial wave function is very small in this range of R, this limitation in the CI expansion has essentially no effect on the eigenenergy determined. For the states $(2a,2)$ and $(2a,3)$, we notice that there are substantial discrepancies with the adiabatic ones at $R=5$ and 7 a.u. In particular, at $R=5$ a.u., the shape is not even similar. For the state $(2a,3)$ we notice additional discrepancies at $R=11$ and 13 a.u. All these discrepancies occur at values of R where R is close to the nodal points of the radial wave functions where the volume charge density $|\bar{F}^n_{2a}(R)\Phi^n_{2a}(R;\alpha,\theta_{12})|^2$ is small.

The R-weighted radial wave functions for the three $^1S^e$ doubly excited states $(2b,1)$, $(2b,2)$, and $(2b,3)$, of helium are shown in Fig. 3. Similar to Fig. 1, the radial wave functions are shown in solid lines if the overlap integral of $\Phi^n_{2b}(R;\alpha,\theta_{12})$ with $\Phi^{ad}_{2b}(R;\alpha,\theta_{12})$ at that R is greater than 0.95 and in dashed lines if the overlap is less than 0.95. We notice that the overlap is small when $|\bar{F}^n_{2b}(R)|$ is small.

Surface plots of $|\Phi^{ad}_{2b}(R;\alpha,\theta_{12})|^2$ and $|\Phi^n_{2b}(R;\alpha,\theta_{12})|^2$ for $n=1$, 2, and 3 are shown in Fig. 4 for several values of R. We again notice that the CI results agree very well with the results from the adiabatic approximation whenever the *magnitude* of the radial wave function is large, and

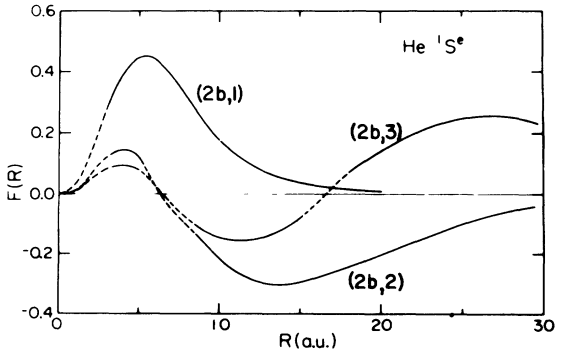

FIG. 3. Similar to Fig. 1 except for the $\mu=2b$ channel of $^1S^e$ states.

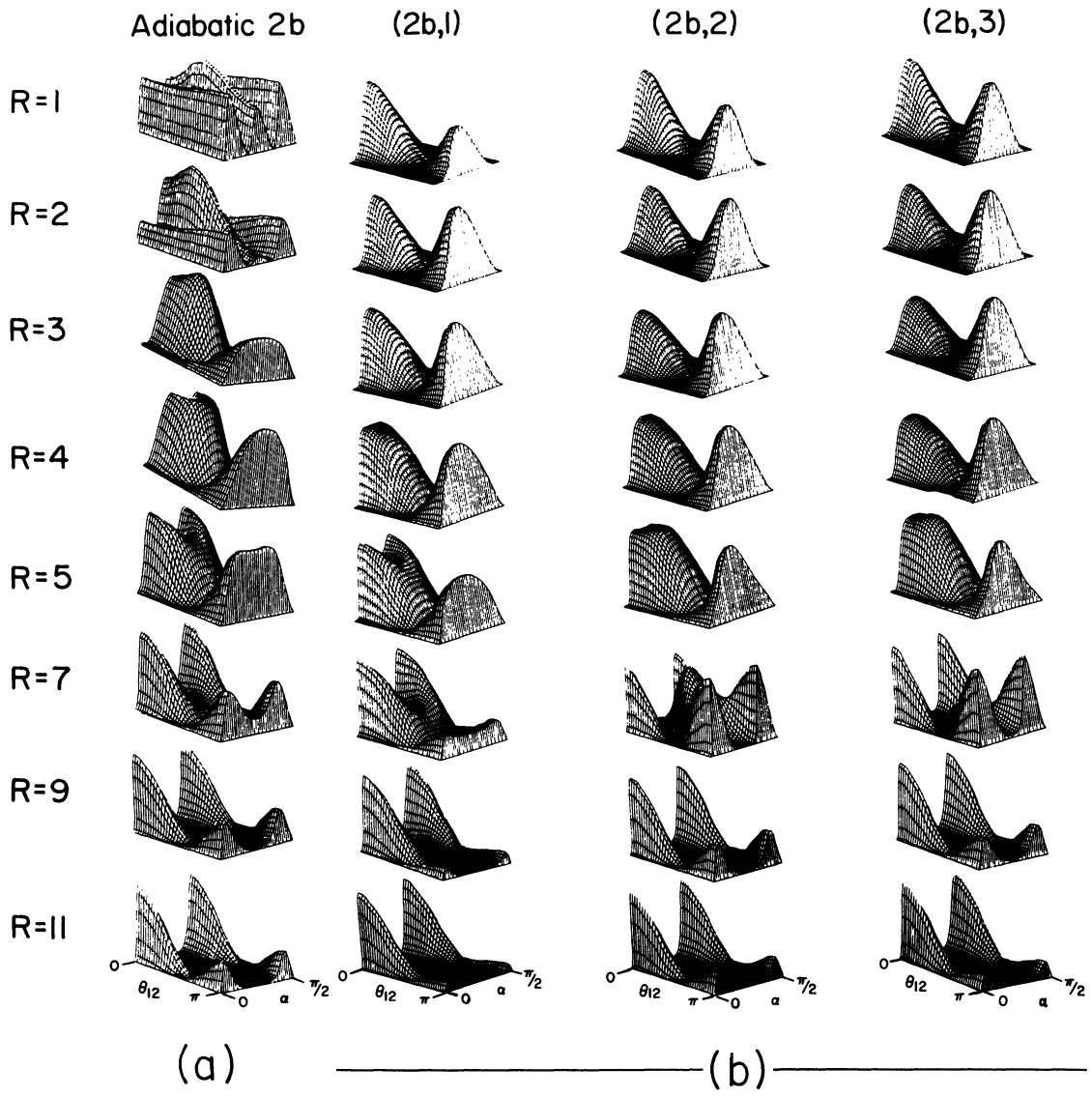

FIG. 4. Similar to Fig. 2 except for the $\mu=2b$ channel of $^1S^e$ states.

discrepancies occur when the magnitude of the radial wave function is small.

The above conclusion is not limited to $^1S^e$ states only. In Fig. 5 we show the radial wave functions of the first three states of the $\mu=2a$ and $2b$ channels of helium $^3S^e$ states. Each radial wave function is shown in solid lines if the overlap of the angular function with the adiabatic channel function is greater than 0.95 and in dashed lines if the overlap is less than 0.95. We notice again that the overlap is small whenever the magnitude of the radial wave function is small.

To show the great variety of correlation patterns for other high-lying doubly excited states, we illustrate in Fig. 6 the radial wave functions for the lowest state of the $\mu=3a$, $3b$, $3c$, and $4a$ channels for the $^1S^e$ states of helium calculated from the CI method. Notice that none of the radial wave functions shows any nodes. The corresponding surface charge densities for each state are shown in Fig. 7 at values of R where the radial wave functions are near the maximum. These correlation patterns are similar to the ones displayed in I calculated in the adiabatic approximation.

IV. CONCLUSIONS

The comparison shown in this article clearly established the quasiseparability of doubly-excited-states wave functions in hyperspherical coordinates.

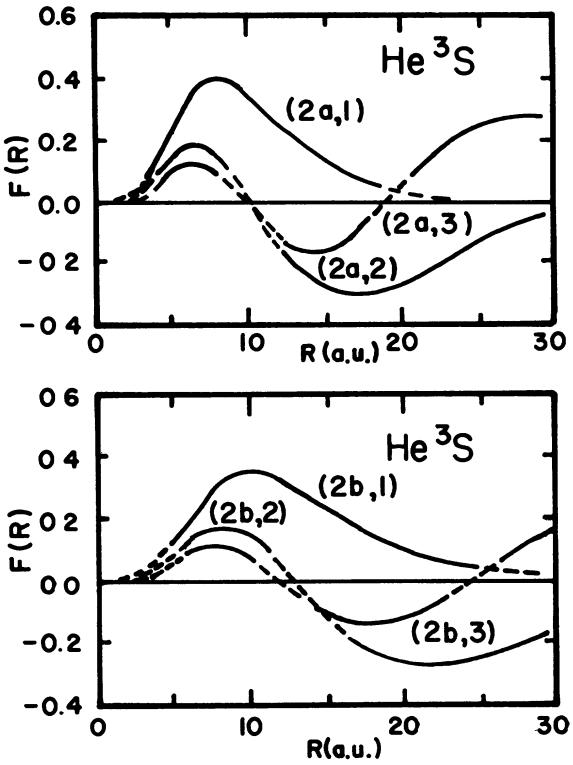

FIG. 5. Similar to Fig. 1 except for the $\mu=2a$ and $\mu=2b$ channels of $^3S^e$ states of helium.

States belonging to the same channel were shown to have angular wave functions similar to the adiabatic channel function for that channel except at regions of R where the volume charge density is small. This general agreement is expected to be true for other similar or other more elaborate variational wave functions and true for doubly excited states of other L, S, and π.

The question of which approximation gives more accurate results is more difficult to answer. The quasiseparability in the adiabatic approximation forces R and Ω motion to decouple at all values of

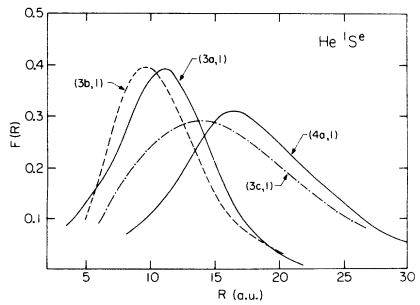

FIG. 6. R-weighted radial wave functions for the lowest state of $\mu=3a$, 3b, 3c, and 4a channels of $^1S^e$ states of helium calculated from the CI approximation.

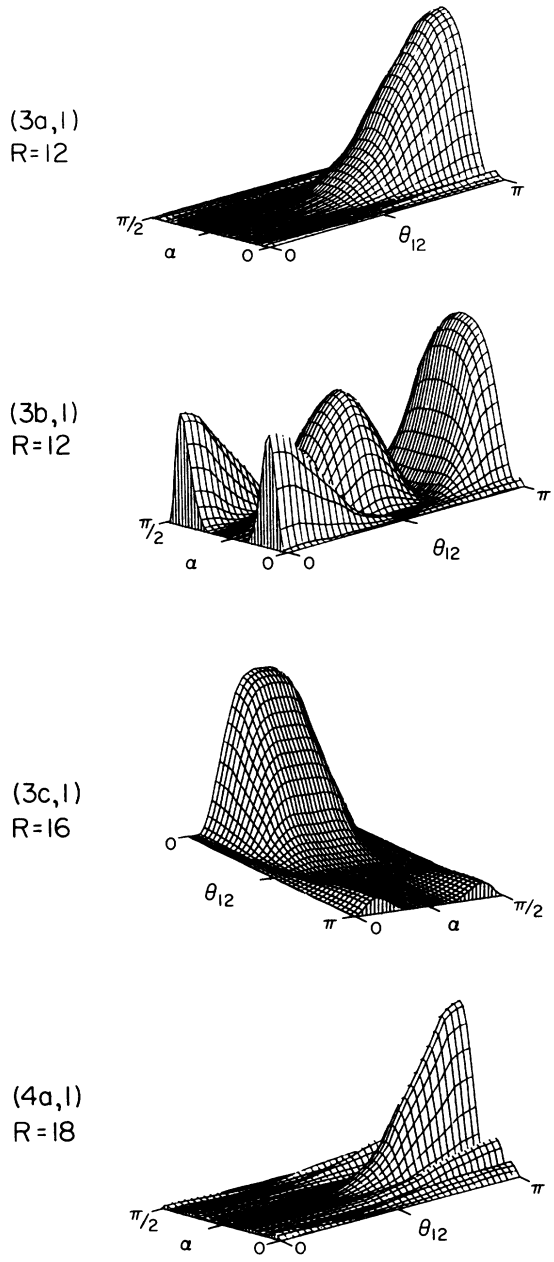

FIG. 7. Correlation patterns of several doubly excited $^1S^e$ states of helium calculated from the CI approximation. The surface charge densities are shown at the selected values of hyperradius R indicated.

R. While this appears to be quite reasonable in the larger-R region, as can be seen from the size of the nonadiabatic coupling terms, such separability is known to be invalid at small R. The Fock expansion illustrates that the wave functions contain terms involving $\ln R$ at small R and are not separable in R and Ω. Adiabatic approximation also does not guarantee smooth variation of the channel functions

at small R, as can be seen in Figs. 2 and 4 at $R=1$ and 2 a.u. Thus we tend to believe that adiabatic approximation does not represent the wave functions in the small-R region very well. To represent this region more accurately, a Fock expansion is necessary. On the other hand, these small-R regions do not have significant effects on the channel characters of the states.

The validity of CI approximation is also questionable in certain regions of R. It is not expected that CI approximation is very accurate in the small-R region. The basis set used in the calculation by Lipsky *et al.* does not allow much flexibility for $r_1, r_2 \leq 1$ a.u. It also does not have the $(\ln R)$-type terms in the expansion. The validity of the CI wave functions in the region where $|\bar{F}_\mu^n(R)| \sim 0$ is also open to question. How much of the CI results in Figs. 2 and 4 are due to the artifact of basis truncation is not clear without a systematic study. In the CI or other variational calculations, the accuracy of the wave functions in the region of small volume charge densities is determined by the flexibility of variational parameters. Since these regions do not have much effect on the variationally determined energies, the wave functions in these regions are not expected to be very accurately determined.

We have not and do not intend to pursue the detailed comparisons of wave functions calculated using various approximations. Instead, we conclude that adiabatic approximation does provide a first-order approximation to the channel classification of doubly excited states. Wave functions from other accurate theoretical calculations should also exhibit quasiseparability if expressed in hyperspherical coordinates. Such quasiseparability is often hidden in the numerical calculations without being exploited. One exception is the classification scheme proposed by Herrick and Sinanoglŭ[13] where doubly excited states are classified in terms of an approximate SO(4) symmetry group. Their wave functions are equivalent to approximate CI wave functions. Although angular correlations are explicitly included in their wave functions, radial correlations are only approximately accounted for in their approach.[15]

In summary, we have shown that the CI wave functions for doubly excited states exhibit quasiseparability in hyperspherical coordinates except in regions where the volume charge density is small and where the radial function $|F_\mu^n(R)| \sim 0$. We have also shown that the angular functions calculated from the CI approximation are essentially identical to the adiabatic channel functions in the important regions of R where $|F_\mu^n(R)|$ is not small. We thus conclude that wave functions of doubly excited states exhibit channel characters which can be unraveled in studying the wave functions in hyperspherical coordinates in the adiabatic approximation.

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[15]I am indebted to Dr. J. Macek for this point. Intershell radial correlation is included in the large CI calculation of Lipsky *et al.* (Ref. 12) but not in the limited CI calculation of Herrick and Sinanoglŭ (Ref. 13).