Inherent Nodal Structures in Doubly-Excited Intrashell States of Atoms *

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Quantum mechanical systems are strongly constrained by symmetry. Consequently, inherent nodal surfaces are imposed on the wave functions. In this paper, the inherent nodal surfaces existing in the doubly-excited intrashell states of atoms have been investigated. The decisive effect of these surfaces on low-lying states has been demonstrated. The feature of the spectra has been explained.

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The important role of symmetry in nature is well-known. A number of laws or constraints based on symmetry have been discovered, they govern the evolution of basic physical processes in nature.[1-5] In quantum mechanical systems, owing to the invariance of the Hamiltonian with respect to symmetric operations (rotation, space inversion, and particle permutation), the eigenstates are classified according to a set of quantum numbers. These numbers specify the transformation property of the wavefunctions under symmetric operation. On the other hand, the feature of an eigenstate depends on how the wavefunction is distributed in the coordinate space. More specifically, in which domain is the wave function distributed, and whether nodal surfaces are contained in the wave function. Would the domain of distribution and the nodal structure of a wave function be affected by the transformation property inherent in the wave function? This problem was first investigated in Ref. 6. Owing to the requirement that specific transformation property must be possessed, a very strong constraint is found to be imposed on the wave function.[6] This constraint is embodied by the existence of a special type of nodal surfaces, the so-called inherent nodal surfaces (INS). In this paper, we shall study how the INS affect the spatial distributions of the wavefunctions of the doubly excited intrashell states of atoms, and how the low-lying spectrum is thereby decisively affected.

Let A be a point in a multi-dimensional coordinate space. Evidently, A is associated with geometric configurations. Let O_i be a combined symmetric operation e.g., a rotation together with a particle permutation. In some cases, one may find a set of O_i (i from 1 to m) to leave A invariant; i.e., $O_iA = A$. Let Ψ be an eigenstate, $\hat{O}_i$ the operator acting on Ψ so that $\hat{O}_i\Psi(A) = \Psi(O_iA)$. When A is invariant to O_i, we have

$$\hat{O}_i\Psi(A) = \Psi(A). \tag{1}$$

Owing to the inherent transformation property of Ψ, Eq. (1) always can be rewritten as a set of homogeneous linear algebra equations (as we shall see). It is well-known that a set of homogeneous equation does not always have non-zero solutions. If there is not a non-zero solution fulfilling all the m set of equations, Ψ must be zero at A. This is the origin of the INS.

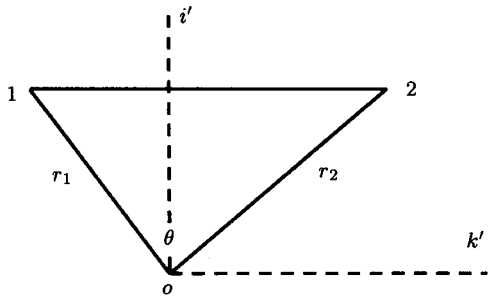

Fig. 1. Body-frame for a two-electron atomic system.

Let us now consider a two-valence-electron atom, the degrees of freedom of the inner core are not taken into account. Let $\boldsymbol{r}_i$ be the position vector of the i-th electron originating from the nucleus. Let i'-j'-k' be a body-frame (Fig. 1) with k' parallel to $\boldsymbol{r}_2 - \boldsymbol{r}_1$, and j' normal to the plane of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Let $R^{\hat{n}}_{\delta}$ denote an operator of rotation about the $\hat{n}$ axis by the angle δ (in degree), p_{ij} denotes an interchange of $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$, P denotes a space inversion. When $r_1 = r_2$, the two electrons and the nucleus form an isosceles triangle (IST) with the electrons at the base. This geometric configuration is invariant to the operators

$$O_1 = PR^{j'}_{180} \tag{2a}$$

and

$$O_2 = R^{i'}_{180}p_{12}. \tag{2b}$$

Let F_M be the spatial function of an eigenstate with total orbital angular momentum L, parity Π, and total spin S, M is the Z-component of L. It can be expanded as

$$F_M(12) = \sum_Q D^L_{QM}(-\gamma, -\beta, -\alpha)F_Q(1'2'), \tag{3}$$

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where D^L_{QM} is the Wigner function, α, β, γ are the Euler angles, Q is the components of L along the k'-axis, The notations $F_M(12)$ and $F_Q(1'2')$ denote that the coordinates are relative to a fixed frame and to the body-frame, respectively. F_Q is called a Q-component, these components span a representation of the rotation group, space inversion group, and permutation group. Hence, how the F_Q are transformed under the operators O_1 and O_2 is prescribed. The invariance of an IST to O_1 leads to a set of $2L+1$ homogeneous equations:

$$\Pi(-1)^{L+Q}F_{\bar{Q}}(\mathrm{IST}) = F_Q(\mathrm{IST}), \tag{4}$$

where (IST) denotes that the coordinates form an IST. The invariance to O_2 leads to

$$(-1)^{L+S}F_{\bar{Q}}(\mathrm{IST}) = F_Q(\mathrm{IST}). \tag{5}$$

Owing to Eqs. (4) and (5), an F_Q is nonzero at an IST only if

$$(-1)^S = \Pi(-1)^Q, \quad \text{if} \quad Q \neq 0, \tag{6}$$

or

$$(-1)^S = (-1)^L = \Pi, \quad \text{if} \quad Q = 0. \tag{7}$$

Otherwise, a nodal surface emerges at IST configurations so that the F_Q cannot access the IST. In this case we say that the F_Q is IST-inaccessible. This nodal surface arises purely from symmetry, it is just the above mentioned INS.

If $r_1 = r_2$ and $\theta = 180°$ (cf. Fig. 1), the shape is called a dumbbell. This shape is very favorable because the Coulomb repulsion is minimized. The dumbbell is invariant to O_1, O_2, and

$$O_3 = R^{k'}_{\delta}, \tag{8}$$

where δ is an arbitrary angle. Evidently, an F_Q can be nonzero at a dumbbell shape only if $Q = 0$ and if Eq. (7) holds.

The INS existing in the F_Q is summarized in Table 1. In this table '×' implies that the associated Q-component of a specific $^{2S+1}L^{\Pi}$ state is IST-inaccessible or r_1 is not allowed to be equal to r_2, therefore this component will be abandoned by the intrashell states where the configurations with $r_1 \simeq r_2$ are important; A samble '★' implies that the component is IST-accessible but dumbbell-inaccessible, in this component a nodal line exists at the dumbbell shape. This nodal line would invoke a swing mode (a variation of θ left and right around $\theta = 180°$ as an equilibrium shape). Hence, the component with '★' contains an excited mode of motion. The components associated with a blank block are inherent-nodeless, where the distribution of wavefunction does not constrained by symmetry at all, thereby the energy can be minimized. These components are called the inherent-nodeless components, they are superior for binding and will be pursued by low-lying states. Thus, three types of Q-components, namely the ×−component, the ★−component, and the inherent nodeless component are found.

Let the lowest one of a series of $^{2S+1}L^{\Pi}$ states be called a first-state, this state will do its best to lower the energy. Hence, if an inherent-nodeless component is contained, the first-state would be dominated by this superior component. From Table 1 we have the following predictions on the intrashell first-states.

(i) For the S states, only the $^1S^{\mathrm{e}}$ is allowed because all the others are composed of the ×−components (a fact already known but now explained in a new way).

(ii) For the P states, the $^3P^{\mathrm{o}}$ would be the lowest (due to containing an inherent-nodeless component), the $^1P^{\mathrm{o}}$ and $^3P^{\mathrm{e}}$ would be higher and close in energy (due to both having the ★−component with $|Q| = 1$). The $^1P^{\mathrm{e}}$ can not be an intrashell states due to containing only the ×-components.

(iii) For the D states, the $^1D^{\mathrm{e}}$ would be dominated by the inherent-nodeless component and would be the lowest. The $^1D^{\mathrm{e}}(2)$ (the second-state) would be dominated by the $|Q| = 2$ component, in this way the requirement that a second-state must be orthogonal to the first-state is obviously realized. In our choice of the body frame, for the $|Q| = L$ component the plane of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ is essentially parallel to L, resulting in having a smaller moment of inertia, and therefore a larger collective rotation energy E_{rot}. Hence, although the pair $^1D^{\mathrm{e}}(2)$ and $^3D^{\mathrm{o}}$, and the pair $^1D^{\mathrm{o}}$ and $^3D^{\mathrm{e}}$ would all be dominated by the ★-components, the former pair would be higher because their ★-components have $|Q| = L$. Therefore we predict that the latter pair $^1D^{\mathrm{o}}$ and $^3D^{\mathrm{e}}$ would be the second lowest. For both pairs the two partner states would be close in energy.

Table 1. Inherent nodal structures in the $|Q|$-components of a two-electron atom.

$^{2S+1}L^{\Pi}$	$Q=0$	$^{2S+1}L^{\Pi}$	$Q=0$	$\lvert Q\rvert=1$	$^{2S+1}L^{\Pi}$	$Q=0$	$\lvert Q\rvert=1$	$\lvert Q\rvert=2$
$^1S^{\mathrm{e}}$		$^1P^{\mathrm{e}}$	×	×	$^1D^{\mathrm{e}}$		×	★
$^3S^{\mathrm{o}}$	×	$^3P^{\mathrm{o}}$		×	$^3D^{\mathrm{o}}$	×	×	★
$^1S^{\mathrm{o}}$	×	$^1P^{\mathrm{o}}$	×	★	$^1D^{\mathrm{o}}$	×	★	×
$^3S^{\mathrm{e}}$	×	$^3P^{\mathrm{e}}$	×	★	$^3D^{\mathrm{e}}$	×	★	×

Table 2. Energies of $n = 3$ intrashell states of the helium atom in units of eV, E_{a} is from Ref. 7, and E_{b} is from Ref. 8.

	$^1S^{\mathrm{e}}$	$^1S^{\mathrm{e}}$	$^3P^{\mathrm{o}}$	$^1P^{\mathrm{o}}$	$^3P^{\mathrm{e}}$	$^1D^{\mathrm{e}}$	$^1D^{\mathrm{o}}$	$^3D^{\mathrm{e}}$	$^1D^{\mathrm{e}}$	$^3D^{\mathrm{o}}$
E_{a}	−9.63	−8.58	−9.55	−9.11	−9.16	−9.36	−8.94	−8.87	−8.56	−8.57
E_{b}			−9.51	−9.13	−9.12	−9.38	−8.93	−8.85	−8.59	−8.59

Table 3. Energies (in cm^{-1}) of $n = 2$ intrashell states of the berylliummlike atoms (ions) in units of cm^{-1}, the data are from Ref. 9.

	$^1S^e$	$^1S^e(2)$	$^3P^o$	$^1P^o$	$^3P^e$	$^1D^e$
Be	0	71499	21980	42565	59696	56432
B^+	0	127662	37340	73397	98919	102362
C^{++}	0	182520	52338	102351	137403	145875

To check the predictions, two typical spectra of helium atom from theoretical calculation[7,8] are given in Table 2 (the data from other sources are qualitatively the same). Three spectra of the beryllium-like atoms (ions) from experimental data[9] are given in Table 3. These tables in general confirm the above predictions. Thus the low-lying spectra are decisively affected by the INS. Incidentally, in the case of Table 2 both electrons are excited while in the case of Table 3 both electrons are not excited. Evidently, in the latter case the effect of the core is more serious. It is recalled that in the above analysis the effect of the core has been omitted, hence the analysis would be less valid in the latter case. In fact, the data in Table 2 support the analysis strongly, but the data in Table 3 do not. Although the ordering of levels in Table 3 is the same as predicted, but the nearly-degeneracy of the pair $^1P^e$ and $^3P^e$ is not explicit.

There are two noticeable points in Table 1. (i) Each $^{2S+1}L^{\Pi}$ series has a superior $|Q|$-component, this component would be dominant in the first-states. This fact leads to approximate conservation of $|Q|$ for the first-states. (ii) Different states may be dominated by the same type components with the same Q. This fact leads to the existence of the well-known rotor series and the T-doubling (the nearly degeneracy of a pair of states having the same L and belonging to the same rotor-series).[10] For example, the $^1S^e$, $^3P^o$, and $^1D^e$ first-states form a band dominated by the inherent-nodeless component with $Q = 0$. The $^1P^o$, $3P^e$, $^1D^o$, and $^3D^e$ first-states form a band dominated by $\star$-components with $|Q| = 1$. Nonetheless, the conservation of $|Q|$ is questionable for higher states.

The above analysis supports strongly the $(K,T)^A$ classification scheme.[10–13] In fact, the physics underlying this scheme now becomes more lucid. For example, why $|Q|$ is nearly conserved? what is the origin of the rotor series? what is the origin of the T-doubling? And so on, all these questions can be easily explained based on the inherent nodal structure. It is noted that the base of the $(K,T)^A$ scheme is the $O(4)$ dynamical symmetry of the hydrogen-like atoms. Thereby an $O(4)\otimes O(4)$ representation with the quantum numbers K and T has been introduced for the doubly-excited states (where '$\otimes$' denotes the outer product). Alternatively, the analysis of this paper is based on the inherent nodal structures which are imposed by the symmetry of the $O(3) \times S_2$ group (where '$\times$' denotes the direct product, and S_2 is the permutation group). Thus, it is interesting to see that two ways of analysis based on different symmetry lead to consistent results.

Furthermore, the generalization of the procedure of analysis to other few-body systems is straight forward. In each case, the existence of the INS should be identified to make sure the accessibility of a few most important regular shapes, then the states can be classified based on the inherent nodal structures. In particular, the inherent-nodeless components are particularly important, they are the main building blocks to constitute the low-lying states.

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