

LETTER TO THE EDITOR

Identification and visualization of the collective normal modes of intrashell triply excited states of atoms

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Abstract

We identify the elementary normal modes of the collective motion of three electrons in intrashell triply excited states of atoms. By modelling the atom as consisting of three electrons on the surface of a sphere with the nucleus at the centre, we analysed the calculated wavefunctions in the body-fixed frame. Using contour surfaces in appropriate coordinates, the nodal surfaces and the normal modes of the collective motion of the three electrons can be visualized. Three elementary normal modes and their excited modes are identified, thus allowing the new classification of intrashell triply excited states.

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

Since the beginning of quantum mechanics, the basic conceptual framework for describing the structure of a many-electron atom is the independent electron model. In the past few decades, it has been well established that the independent electron model fails to describe multiply excited states. For the simpler doubly excited states, alternative equivalent descriptions have been found [1–4] and a new set of approximate quantum numbers have been obtained. In all of these descriptions, the motion of the two electrons is treated together and the correlation of the two electrons is understood as analogous to the bending vibrations and the symmetric or antisymmetric stretch motion of a floppy linear triatomic molecule. It is fair to say that the basic properties of correlations in doubly excited states are now well understood.

As a natural extension, the next major step is to understand the correlated motion of triply excited states of an atom. Experimentally, triply excited states have been explored recently at synchrotron radiation facilities [5, 6] and in experiments involving collisions of multiply charged ions with atoms, molecules, and surfaces [7]. Calculations based on the *R*-matrix method [8] or the general configuration mixing method [9–11] have been able to give a very accurate description of individual triply excited states. However, the nature of how the three electrons are correlated is still not understood and there is no global knowledge of these states. Unless the basic normal modes of the collective motion of the three electrons are delineated, classification of triply excited states in terms of a new set of quantum numbers is not possible.

Various aspects of electron correlations in selected triply excited states have been examined in the past, by partial display of the calculated wavefunctions [12, 13]. In our recent works [14, 15] we have solved the three-electron atomic Hamiltonian in hyperspherical coordinates

and examined the correlations of triply excited states of Li. Since these triply excited states lie above both the singly and the doubly excited states, the analysis has been limited only to the lowest eight $2l2l'2l''$ intrashell states. We have found that these eight states can be separated into three groups, and each group is characterized by a certain normal mode of a symmetric top.

To elucidate other possible normal modes, triply excited states such as those in the higher $3l3l'3l''$ manifold have to be examined. A full hyperspherical calculation of these states would, however, be too tedious and too complicated since these states lie further above the $2lnl'ml''$ ($n, m \geq 2$) triply excited states. We have thus studied the correlation of $3l3l'3l''$ triply excited states of a model atom where the three electrons are confined to the surface of a sphere, with the nucleus at the centre. For the $2l2l'2l''$ states, the density distributions obtained using this model are similar to those obtained from the full solution using hyperspherical coordinates when the three electrons are at the same distance from the nucleus [15].

The model Hamiltonian (in atomic units) we used is

$$H = \frac{1}{2r^2} \sum_{i=1}^3 \hat{\ell}_i^2 - \frac{3Z}{r} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1)$$

where $\hat{\ell}_i$ is the angular momentum operator of each electron with respect to the nucleus, Z is the nuclear charge, $\mathbf{r}_i$ is its position vector from the centre: $\mathbf{r}_i = r\hat{\mathbf{r}}_i$. In the present calculation, we set $Z = 2$ and $r = 6.326$ au to simulate the intrashell states of He^- in the $N = 3$ manifold [12]. The eigenstates of the Hamiltonian (1) are labelled by the good quantum numbers L , S , and π —the total orbital angular momentum, the total spin, and the parity, respectively. The total wavefunction must be antisymmetric under exchange of any two electrons and can be written as

$$\psi = \sum_{S_{12}} \Phi_{LM}^{S, S_{12}}(\Omega) \chi_{S_{12}}^S \quad (2)$$

where $\Omega = \{\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3\}$ denotes, collectively, the six spherical angles of the three electrons in the laboratory-fixed frame and $\chi_{S_{12}}^S = [\{\chi(1)\chi(2)\}^{S_{12}}\chi(3)]^S$ is the coupled spin function of the three electrons with intermediate spin S_{12} . The eigenfunctions $\Phi_{LM}^{S, S_{12}}(\Omega)$ are obtained by diagonalizing a basis of $[\{Y_{l_1}(\hat{\mathbf{r}}_1)Y_{l_2}(\hat{\mathbf{r}}_2)\}^{l_{12}}Y_{l_3}(\hat{\mathbf{r}}_3)]^{LM}$ which is the coupled orbital angular momentum eigenstate for the three electrons. To obtain accurate eigenenergies and eigenfunctions, the maximum value of each l_i has been set to 7 in the calculation.

The wavefunctions thus obtained are expressed in the laboratory-fixed frame. Since we are interested in the internal shape of the model atom, the overall rotation of the three electrons with respect to the laboratory-fixed frame must be removed. Thus we analyse the wavefunction in the body-fixed frame. Following Watanabe and Lin [12] and Bao *et al* [13], the body-fixed frame z -axis is chosen to be perpendicular to the plane of the three electrons (the σ plane, see figure 1). This plane makes an angle θ with respect to the nucleus. The shape of the triangle of the three electrons on the σ plane is specified by two angles, η and ϕ . Here, 2η is the angle between electrons 1 and 2, choosing along the arc including electron 3, and ϕ is the angle between electron 3 and the line bisecting electrons 1 and 2. The ranges of the internal angles are $(0 \leq \theta \leq \pi, 0 \leq \eta \leq \pi, -\eta \leq \phi \leq \eta)$.

The wavefunction in the laboratory-fixed frame $\Phi_{LM}^{S, S_{12}}(\Omega)$ can be expressed in terms of the body-fixed frame wavefunction $\varphi_{LQ}^{S, S_{12}}(\Omega_I)$ by the general rotation,

$$\Phi_{LM}^{S, S_{12}}(\Omega) = \sum_{Q=-L}^L \varphi_{LQ}^{S, S_{12}}(\Omega_I) D_{QM}^{(L)}(\omega) \quad (3)$$

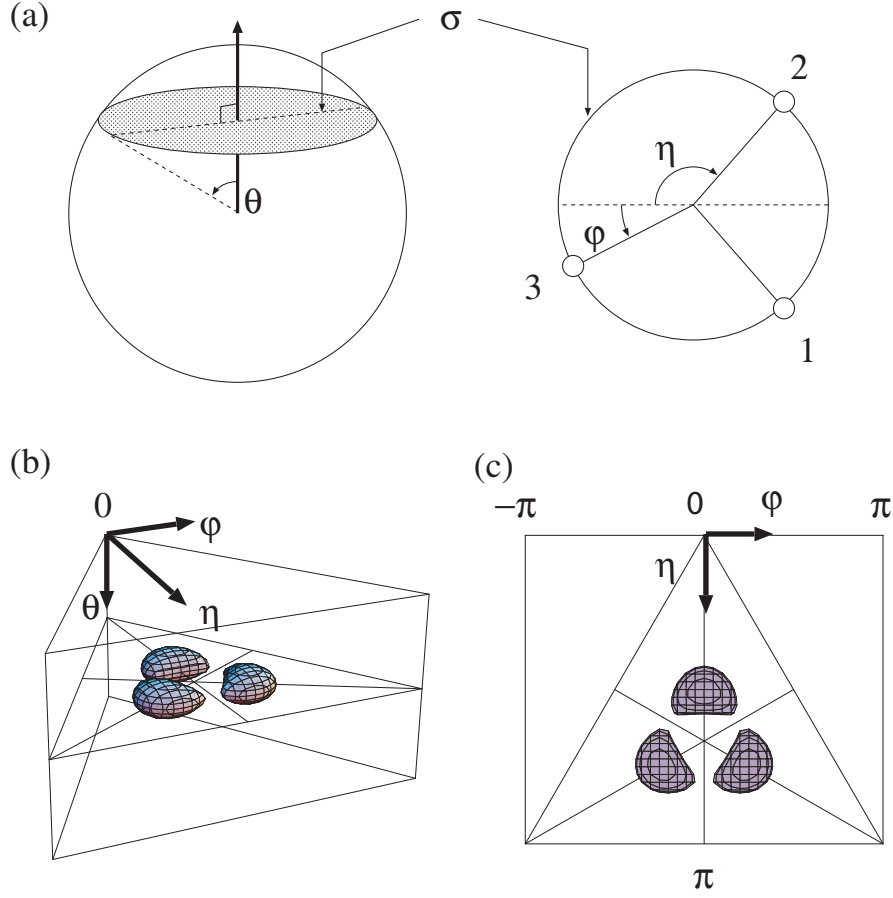


Figure 1. (a) Definition of the three internal angles used to describe the relative positions of the three electrons on a sphere. (b) Side view and (c) top view of the contour surface plots of the distribution of the three-electron shape density $\rho_T(\theta, \eta, \phi)$. The ranges of the internal angles are $(0 \leq \theta \leq \pi, 0 \leq \eta \leq \pi, -\eta \leq \phi \leq \eta)$.

where $D_{QM}^{(L)}(\omega)$ is the rotation matrix; Q and M are the azimuthal components of L in the body-fixed frame and in the laboratory-fixed frame, respectively. Here ω represents the three Euler angles defining the orientation of the body-fixed frame with respect to the laboratory-fixed frame, and Ω_I is the set of three angles $\{\theta, \eta, \phi\}$ defined in figure 1. From the symmetry properties of the rotation matrix, the Q and $-Q$ components of the body-fixed frame wavefunctions are identical except for a phase factor. Thus, we need to examine the $Q \geq 0$ components only. We define $T = |Q|$ and $0 \leq T \leq L$. For each rotational component wavefunction, one can define the density distribution, or the shape density, averaged over the Euler angles,

$$\rho_T(\Omega_I) = \sum_{S_{12}} |\varphi_{LQ}^{S, S_{12}}(\Omega_I)|^2 \quad (4)$$

where the summation is over the intermediate spin S_{12} and over $Q = +T$ and $-T$ if T is nonzero. For a rigid body, T is a good quantum number. If the three electrons are highly correlated, its shape density $\rho_T(\Omega_I)$ would be quite localized, and the summation over Q in

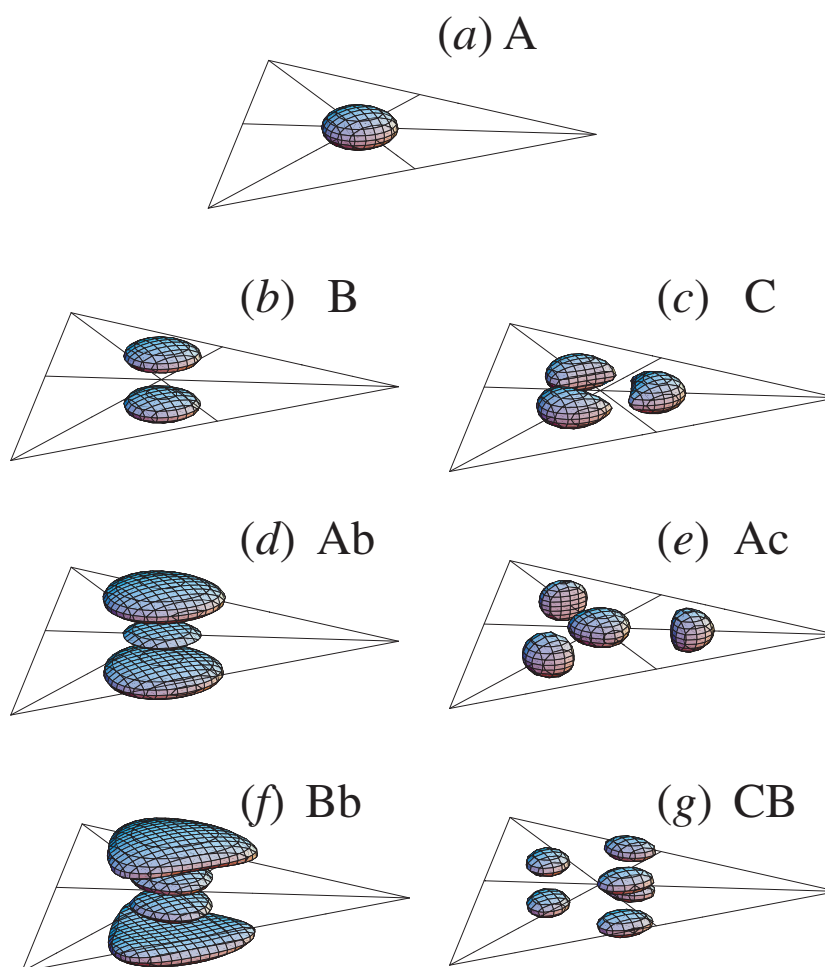


Figure 2. Representative contour surfaces of the shape densities illustrating the different normal modes of the collective motion of the three electrons.

equation (3) would be dominated by a single T -component. In such a case, this T can be used as an approximate quantum number. Furthermore, the shape density of such a localized function of three variables can be visualized by displaying the contour surfaces. As an example, figure 1(b) is a contour surface where the shape density is at 60% of the maximum. A contour surface of higher density would fit inside the surface shown.

We can now identify the basic normal modes of the collective motion of the three electrons in $3/3l'3l''$ triply excited states. They are extracted from the dominant T -components of the shape densities among the states examined. The first three normal modes have contour surfaces as shown in figures 2(a), (b) and (c). We will use A, B and C to designate these normal modes. These contour surfaces have been found already in the $2/2l'2l''$ triply excited states [14].

In figure 2(a), the maximum density occurs when the three electrons form a coplanar equilateral triangle with the nucleus at the centre, i.e. at $(\theta = \pi/2, \eta = 2\pi/3, \phi = 0)$ in the figure, which is the intersection of the three diagonals. There are no nodal surfaces in this mode. It follows that states dominated by this mode would have lower energies. We further

note that the potential energy is smallest when the three electrons form a coplanar equilateral triangle. The lowest ${}^4P^e$ state is represented by this mode. We have counted all 14 states in the $3/3/3/3''$ manifold, represented by this mode, altogether. These 14 states, each further identified by an approximate T , form a rotational multiplet similar to the rotational levels of an oblate symmetric top (not shown). Using a familiar molecular example, the model atom in the A-mode has a shape similar to the planar BF_3 molecule.

In figure 2(b), the shape density vanishes at the equatorial plane $\theta = \pi/2$, that is, this plane is a nodal surface. Above or below this plane the three electrons prefer to form an equilateral triangle. Thus in the B-mode, the model atom resembles an ammonia molecule NH_3 where the wavefunction vanishes when the plane of the three H atoms coincides with the N atom. The lowest ${}^4S^o$ state is represented by such an example. In this mode there is a fixed nodal surface at $\theta = \pi/2$, thus the internal energy of this B-mode is higher than that of the A-mode.

In figure 2(c), the maximum of the shape density occurs at the equator plane, but the equilateral triangle configuration is not allowed. This is identified as the C-mode, and the $T = 1$ component of the lowest ${}^4P^o$ state exhibits this mode. In the C-mode, the three electrons cannot form an equilateral triangle, so that the potential energy is higher. We emphasize that the B- and C-modes have inherent internal nodal surfaces imposed by the quantum symmetry [12, 13] and that their rotational level structure differs from that of the A-mode.

Among the eight $2/2/2/2''$ triply excited states, four were identified to belong to the A-mode, two to the B-mode, and two to the C-mode [14]. There are 64 intrashell $3/3/3/3''$ triply excited states, and we have identified additional excited normal modes. In figure 2(d) we have the Ab-mode; and in figure 2(e) the Ac-mode. It has been found that the rotational level structure of these two groups follows the pattern of the A-mode. In the Ab-mode, there is an antinode at the coplanar equilateral triangle configuration, but two nodal surfaces perpendicular to the internal θ -axis can be seen. Since there is one nodal plane perpendicular to the θ -axis for the B-mode, the two nodal planes in this case can be considered as an excited B-mode. We use small letters to designate excited modes such that the Ab-mode involves an excited B-mode in combination with the rotational level structure of the A-mode. Similarly in the Ac-mode, a maximum occurs at the coplanar equilateral triangle configuration, but this maximum is separated from the other three 'islands' by additional nodal surfaces perpendicular to the η - ϕ plane. (More explicit exhibitions of the nodal surfaces can be seen in figure 3.) Note that the three lowest ${}^4P^e$ states are described by the A-, Ab-, and Ac-modes, respectively.

We have also identified a Bb-mode as shown in figure 2(f). The rotational level structure of this group follows the pattern of the B-mode. The shape density has a nodal surface at the equator characteristic of the B-mode and two other nodal planes perpendicular to the θ -axis, thus the mode is designated as the Bb-mode. The second ${}^4S^o$ state is characterized by this mode. Recall that the first ${}^4S^o$ state is characterized by the B-mode. This shows that ${}^4S^o$ intrashell triply excited states are characterized by the vibrational excitation of the σ plane with respect to the nucleus.

We have also identified a CB-mode as shown in figure 2(g). In this mode, the shape density consists of two sets of three 'islands', as in the C-mode of figure 2(c), one set above the equator plane and one set below the equator plane, but the equatorial plane is a nodal surface characteristic of the B-mode. The nodal surfaces in this example are from conditions imposed by quantum symmetry, and thus we use both capital letters to designate this mode. Note that these Ab-, Ac-, Bb-, and CB-modes have more nodal surfaces, and states characterized by these modes would have higher internal vibrational energies.

In the normal modes identified in figure 2 the T -component shape densities are relatively localized such that a contour surface can be used to display the characteristic shape of the positions or the correlation of the three electrons. For the higher excited states, we have found

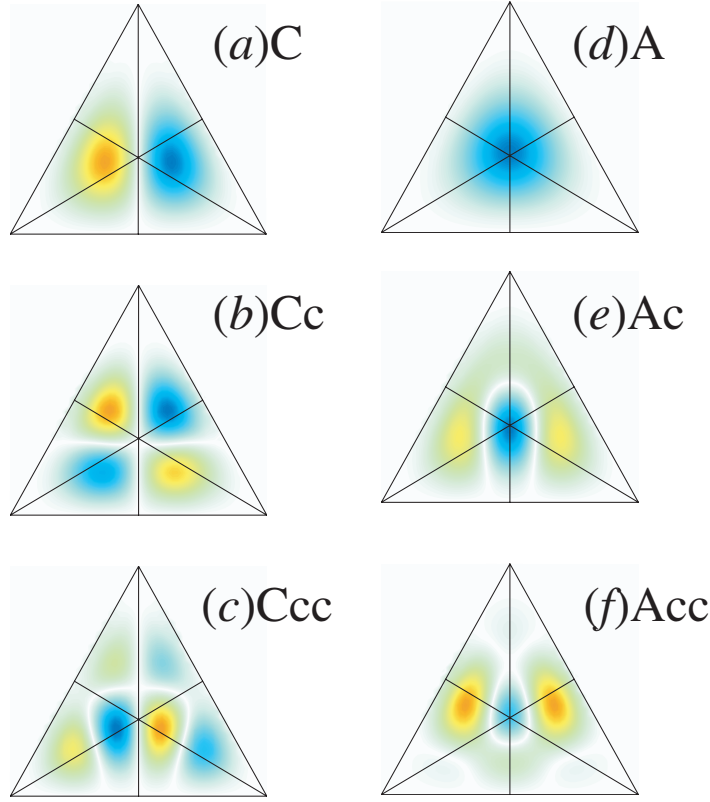


Figure 3. (a)–(c) Density plots of the partial wavefunctions of the three $^2S^e$ states. (d)–(f) Density plots of the imaginary part of the $Q = 1$ component of the internal wavefunctions of the 1st, 4th, and 6th $^2P^o$ states. The plots are for $\theta = \pi/2$ and for the triplet components of the wavefunctions, see text.

density distributions that are more diffuse. These diffuse functions are not easily represented by single contour surfaces. However, it is still possible to address the degree of excitation in terms of nodal surfaces. In figures 3(a)–(c) we show the internal wavefunctions $\varphi_{LQ}^{S,S_{12}}(\Omega_I)$ of the lowest three $^2S^e$ states in the $N = 3$ manifold. Only the triplet components ($S_{12} = 1$) are shown since the singlet components are related to the triplet components according to the S_3 permutation group. Also, only the real part of the function is shown since the imaginary part is identically zero. These three states are identified with the C-, Cc-, and Ccc-modes, respectively. In figure 3, all the wavefunctions are shown on the equatorial plane. Clearly the number of nodal lines increases by one in going from the C-mode to the Cc-mode, and from the Cc-mode to the Ccc-mode. Note that the nodal line can be in ϕ (figure 3(a)), in η (figure 3(b)), or in the combination of ϕ and η (figure 3(c)). The Hamiltonian is not separable in these angular coordinates, so the nodal lines are not straight lines in the figures.

A clearer exhibition of the nodal structure of the Ac- and Acc-modes can also be seen by displaying the wavefunctions at the equator plane. We compare the $Q = 1$ component of the 1st, 4th, and 6th $^2P^o$ states (there are seven such intrashell states in the $N = 3$ manifold) in figures 3(d), (e) and (f). They belong to the A-, Ac-, and Acc-modes, respectively. The triplet component wavefunction has both a real part and an imaginary part. The real part has one more nodal surface than the imaginary part, and thus its component weight is smaller. We

only show the imaginary part. For the A-mode, there are no nodal lines for the imaginary part. For the Ac-mode, the imaginary part has one nodal line and the maximum is at the equilateral triangle configuration, which is characteristic of the A-mode. For the Acc-mode, the imaginary part acquires one additional nodal line as compared to the Ac-mode. Thus, even though the wavefunctions for these higher excited states are not localized and cannot be easily visualized by single contour surface plots, they can still be identified by the number of nodal surfaces in their component wavefunctions.

We have found that the dominant T -component for each of the 64 intrashell $3/3l'/3l''$ triply excited states can be identified with one of the modes presented in figures 2 and 3. For the lower states, the body-fixed frame wavefunction is dominated by a single T -component in general. For the higher states the admixture of other T -components is not small, but a dominant T -component can still be recognized. A detailed analysis of the admixture of T -components and the classification of all 64 states will be presented elsewhere.

In summary, we have identified all the normal modes of the 64 intrashell $3/3l'/3l''$ triply excited states of a model atom where the three electrons are confined to the surface of a sphere. Using collective coordinates, the shape densities of the three electrons are calculated and visualized. We have identified three basic modes, A, B and C, where the B- and C-modes have inherent internal nodal surfaces imposed by the quantum symmetry. These nodal surfaces are the consequence of requiring that each state be characterized by well-defined L , S , and π and that the wavefunction be antisymmetric under the exchange of any two electrons. For the $3/3l'/3l''$ triply excited states we have also identified additional excited normal modes. We have found the Ab-, Ac-, Bb-, Cc-, CB-, Ccc-, and Acc-modes, where each small letter represents one additional excitation of the corresponding mode. Even though each triply excited state is not represented by a single mode only, the dominant mode of each state can be used to designate the state, and serve to classify intrashell triply excited states. By comparing the classification of $2/2l'/2l''$ and $3/3l'/3l''$ triply excited states, clearly intrashell triply excited states for the higher manifolds are similarly classified except that higher excited normal modes will appear.

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