

## Pyramidal atoms: Berylliumlike hollow states

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Based on the idea that four excited electrons arrange themselves around the nucleus in the corners of a pyramid in order to minimize their mutual repulsion, we present an analytical model of quadruply excited states. The model shows excellent comparison with *ab initio* results and provides a clear physical picture of the intrinsic motion of the four electrons. The model is used to predict configuration-mixing fractions and spectra of these highly correlated states.

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Describing electron correlations in terms of simple physical pictures requires an understanding of the interelectronic interaction that goes beyond numerical diagonalization of the Hamiltonian of the system. The study of electron-electron correlation in multiply excited states has contributed a lot to this understanding and in the 1980s, group theoretical [1,2], molecular adiabatic [3], and hyperspherical [4] approaches led to an understanding of doubly excited states in terms of approximate quantum numbers associated with angular and radial correlations. In the 1990s, advances in light sources stimulated research on triply excited hollow states in Li (see Ref. [5] for a recent review). In particular, theoretical models referred to as the three-electron ionization ladder [6,7], the normal mode analysis [8–10], and the symmetric rotor [11–13] confirmed the appealing physical picture for the lowest-lying triply excited states that the three electrons be arranged in an equilateral triangle coplanar with the nucleus situated in the center, and identified the magnetic quantum number with respect to the body-fixed  $z$  axis as approximately conserved.

Current interest in multiply excited states is strongly stimulated by further development of synchrotron radiation sources and free-electron lasers providing unprecedented brightness in the UV and XUV and therefore ready access to the spectral region of interest. Access to hollow lithium states [5] makes studies of quadruply excited states a natural next step in this development. So far there are no experiments and only very few theoretical studies on these systems. One work [14] considered the lowest-lying quadruply excited  $5S^o$  state in Be by multiconfigurational Hartree-Fock calculations, while two other works [15,16] presented a classification scheme based on symmetry considerations. Hence, in view of experimental advances, it seems timely to aim at a better understanding in the form of physical images, including geometry, symmetry considerations, and electronic motion for highly correlated four-electron systems. Here we shall concentrate on intrashell states with the electrons confined to the same shell. These states are interesting since the dominant configurations of the lowest-lying quadruply excited berylliumlike states are intrashell states.

Figure 1 shows the thresholds in Be, the lowest  $3P^e$  quadruply excited resonance state, and an inset of the physical picture on which our model is based. We note that while two and three electrons are confined to a line and a plane, respectively, the extent of four randomly placed electrons is three-

dimensional. Furthermore, the electron-electron correlations are expected to be stronger when more electrons interact. Therefore, research on these states opens new possibilities to test theoretical approximations for correlated electron motion.

We consider the Coulombic system of four electrons moving in the field of a point-like nucleus of charge  $Z$  corresponding to the nonrelativistic Hamiltonian

$$\hat{H} = \sum_{j=1}^4 \left( \frac{-\hbar^2}{2\mu} \nabla_j^2 - \frac{Ze^2}{r_j} \right) + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (1)$$

where  $\mu$  is the reduced electron mass and  $e$  is the electron charge. The electron-electron interaction complicates the problem since the potential is not diagonal in a basis of antisymmetrized products of single-electron configurations. Consequently, single-electron quantum numbers are not conserved and the eigenfunctions are represented as superpositions of configurations. Our model accounts for the electron-electron interaction by assuming the wave function to be a product of carefully chosen one-electron states. Furthermore,

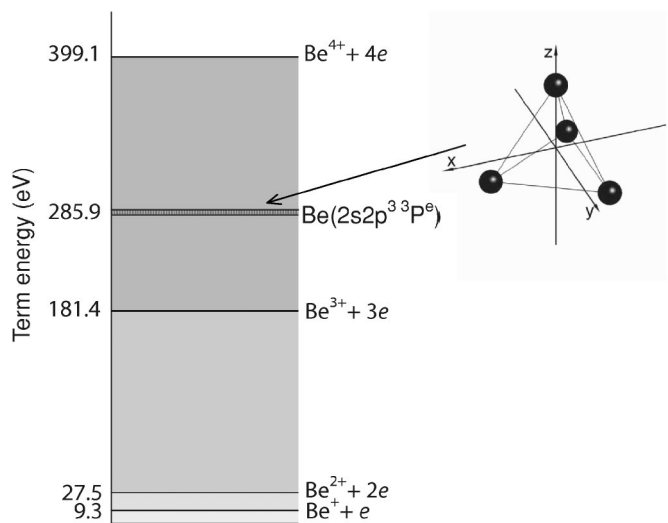


FIG. 1. Thresholds and the lowest quadruply excited  $3P^e$  state in Be. The inset to the right shows, in the body-fixed frame, the physical picture on which our model is based. The nucleus is located in the origin and the circles denote the electrons.

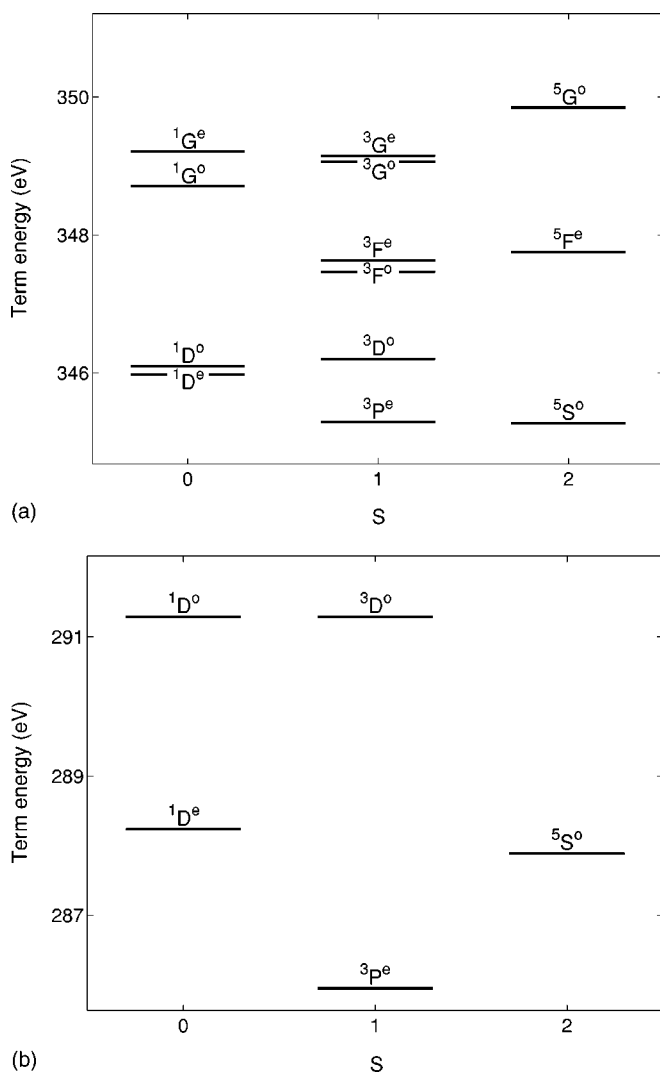


FIG. 2. Energy levels for pyramidal intrashell states in Be. (a)  $n=3$  states with  $L \leq 4$  (b)  $n=2$  states.

the ansatz for the wave function must be supplemented to take into account basic quantum symmetries (parity, spin, etc.)

The Coulomb repulsion between the four electrons is minimized when they are placed at the vertices of a regular

tetrahedron (see Fig. 1). In this configuration, the interaction between any electron and the remaining three is represented by a repulsive electric field along the direction  $\xi$  of the electron considered with respect to the nucleus. Hence, the Hamiltonian in Eq. (1) can be approximated by a sum of hydrogenic Hamiltonians perturbed by weak external electric fields causing only intrashell transitions. The eigenstates of the hydrogenic Hamiltonian perturbed by a weak external electric field are the polarized Stark states  $|nkm\rangle$ , described by the principal, parabolic, and azimuthal quantum numbers denoted  $n$ ,  $k$ , and  $m$ , respectively [17]. The wave function therefore splits up into a product of one-electron states, which is the simplest possible way to represent a many-particle wave function. Thus, the basic idea in the model is that the electron interaction tends to stabilize the electrons in individual Stark states (see Refs. [18,19] for two- and [11] three-electron cases). The parabolic quantum number  $k$  may be associated with the electric dipole moment of the atom through the relation  $p_z = (3/2Z)enk$  [17]. Hence, the largest energy shift and thus the lowest-lying state for each  $n$  is obtained when the Stark states are maximally polarized along  $\xi_i$ ,  $|n, k=n-1, m=0\rangle_{\xi_i}$ . The ansatz for the wave function is therefore

$$|Y_R\rangle = |nn-10\rangle_{\xi_1} |nn-10\rangle_{\xi_2} |nn-10\rangle_{\xi_3} |nn-10\rangle_{\xi_4}, \quad (2)$$

with  $\xi_j$  the direction of the  $j$ th electron with respect to the nucleus. Quantum numbers in kets without a subscript refer to quantization along the  $z$  axis, so that the electron on this axis is represented by the state  $|nn-10\rangle$ . The other three states,  $|nn-10\rangle_{\xi_q}$ ,  $q=1,2,3$ , are related to it via rotations  $|nn-10\rangle_{\xi_q} = \mathbf{R}(q2\pi/3, \Phi, 0)|nn-10\rangle = e^{-iq(2\pi/3)\hat{L}_z} e^{-i\Phi\hat{L}_y} |nn-10\rangle$ , with  $\Phi = 109.5^\circ$  the interelectron angle as seen from the nucleus (see Fig. 1).

The wave function  $|Y_R\rangle$  is anisotropic since the electrons are oriented. As a consequence of this break of rotational symmetry,  $|Y_R\rangle$  is not an eigenstate of  $\hat{L}^2$  and  $\hat{L}_z$ . On the contrary, the rotational average over Euler angles  $\omega = (\alpha, \beta, \gamma)$ ,

TABLE I. Configuration-mixing fractions in Be for the most important intrashell configuration states of  $5S^o$  symmetry. SR denotes predictions within the present symmetric rotor model, and MCHF denotes multi-configurational Hartree-Fock calculations [14].

Configuration	$n=3$		$n=4$		$n=5$		$n=6$	
	SR	MCHF	SR	MCHF	SR	MCHF	SR	MCHF
$sp^3$	0.94	0.90	0.81	0.76	0.67	0.66	0.55	0.59
$spd^2$	0.063	0.084	0.15	0.18	0.20	0.21	0.23	0.23
$sd^2f$			0.013	0.0081	0.039	0.040	0.068	0.053
$p^2df$			0.022	0.032	0.057	0.058	0.091	0.078
$pdf^2$			0.0014	0.0025	0.0085	0.0081	0.021	0.017
$d^3f$			0.0022	0.0025	0.0097	0.0064	0.021	0.012

$$|Y_R^{LMMI\pi}\rangle = \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin\beta D_{MM_I}^L(\omega)^* |Y_R\rangle_\omega, \quad (3)$$

is so [12]. Here  $\pi$  denotes the parity and  $M_I$  is the magnetic quantum number with respect to the body-fixed  $z$  axis. In molecular theory this is an important quantum number specifying the rotational state of the molecule. Since the Hamiltonian is spin independent, the total wave function is simply a product of the spatial function  $|Y_R^{LMMI\pi}\rangle$  and a spin function  $|\chi_{M_s}^{S_{12}S_{34}S}\rangle$ . The spin function specifies the total spin  $S$  of the four electrons and its projection  $M_s$  which are both conserved quantities. The indices  $S_{12}$  and  $S_{34}$  refer to the intermediate spins arising from coupling the spins of the first and second and of the third and fourth electrons, respectively. The total wave function is obtained by antisymmetrizing the product state  $|Y_R^{LMMI\pi}\rangle|\chi_{M_s}^{S_{12}S_{34}S}\rangle$ , as

$$|\Psi_{R,S_{12}S_{34}}^{LMMI\pi,SM_s}\rangle = A[|Y_R^{LMMI\pi}\rangle|\chi_{M_s}^{S_{12}S_{34}S}\rangle], \quad (4)$$

where  $A$  is the four-particle antisymmetrization operator. The final expression for the four-electron state is  $|\Psi_R^{LMMI\pi,SM_s}\rangle = N \sum_{i=\{S_{12}S_{34}\}} |\Psi_{R,i}^{LMMI\pi,SM_s}\rangle$ , with  $N$  being a normalization constant. The possible values of intermediate spins  $S_{12}$  and  $S_{34}$  are determined by  $\vec{S} = \vec{S}_{12} + \vec{S}_{34}$  added as angular momentum operators.

Our model provides an analytical expression for the wave function describing quadruply excited intrashell states of the four-electron atom and gives a simple physical image of the atomic states. To test the quality of the model, configuration-mixing fractions are compared with *ab initio* results. We expand the ansatz in the spherical basis

$$|\Psi_R^{LMMI\pi,SM_s}\rangle = \sum_{\bar{l}\bar{\mu}\bar{m}_s} c(\bar{l}\bar{\mu}\bar{m}_s, LMMI\pi, SM_s) \prod_{i=1}^4 |l_i \mu_i m_{si}\rangle$$

$[\bar{p} = (p_1, p_2, p_3, p_4), p = (l, \mu, m_s)]$  with  $|\Psi_R^{LMMI\pi,SM_s}\rangle$  being normalized such that  $\sum_{\bar{l}\bar{\mu}\bar{m}_s} |c(\bar{l}\bar{\mu}\bar{m}_s, LMMI\pi, SM_s)|^2 = 1$ . The configuration-mixing fractions specifying the  $l$  mixing between several multiplet states are defined as

$$P_{\bar{l}_c}^{LMI\pi S} \equiv \sum_{\bar{l} \in \bar{l}_c} \sum_{\bar{\mu}\bar{m}_s} |c(\bar{l}\bar{\mu}\bar{m}_s, LMMI\pi, SM_s)|^2, \quad (5)$$

where  $\bar{l}_c = (l_1 l_2 l_3 l_4)_c$  denotes the  $l$ -configuration regardless of permutation, e.g.,  $(sppp)_c = \{sppp, pspp, ppsp, ppps\}$ . For  $n=2$  the pyramidal states are shown in Fig. 2(b). The mixing fractions for  ${}^3P^e$  and  ${}^1D^e$  are 0.9  $s^2p^2$  and 0.1  $p^4$ . The other terms have only a single configuration ( $sp^3$ ). Table I shows a comparison between the mixing fractions predicted within the model and from multiconfigurational Hartree-Fock calculations [14]. The model not only predicts the trend in the mixing fractions, but actually compares very well with the configurational calculations. The convincing agreement in the predictions shows that our four-electron model accounts for the strong electron-electron correlations within the quadruply excited intrashell states. Table II shows configuration-mixing fractions for all terms with  $L \leq 4$  within the  $n=3$  shell for which the pyramidal shape is accessible [15,16]. The

TABLE II. Configuration-mixing fractions for pyramidal states in Be for the  $n=3$  shell with  $L \leq 4$ .

Term	Configuration	$S=0$	$S=1$	$S=2$
$2S+1S^o$	$sp^3$			0.9375
	$spd^2$			0.0625
$2S+1D^o$	$s^2pd$	0.5265	0.1529	
	$sp^3$	0.2632	0.6878	
	$p^3d$	0.1504	0.0983	
	$spd^2$	0.0501	0.0546	
	$pd^3$	0.0097	0.0065	
$2S+1F^o$	$s^2pd$		0.6490	
	$spd^2$		0.2163	
	$p^3d$		0.1217	
	$pd^3$		0.0129	
$2S+1G^o$	$p^3d$	0.8010	0.5659	
	$spd^2$	0.1424	0.4024	1.0000
	$pd^3$	0.0566	0.0316	
$2S+1P^e$	$s^2p^2$		0.6082	
	$sp^2d$		0.2027	
	$p^4$		0.1521	
	$p^2d^2$		0.0174	
	$s^2d^2$		0.0135	
	$sd^3$		0.0058	
	$d^4$		0.0003	
$2S+1D^e$	$s^2p^2$	0.6204		
	$p^4$	0.1551		
	$sp^2d$	0.1477		
	$p^2d^2$	0.0443		
	$s^2d^2$	0.0295		
	$sd^3$	0.0022		
	$d^4$	0.0008		
$2S+1F^e$	$sp^2d$		0.7829	0.9643
	$s^2d^2$		0.1392	
	$p^2d^2$		0.0706	
	$sd^3$		0.0058	0.0357
	$d^4$		0.0016	
$2S+1G^e$	$sp^2d$	0.4165	0.7692	
	$s^2d^2$	0.2777		
	$p^2d^2$	0.2752	0.1795	
	$sd^3$	0.0278	0.0513	
	$d^4$	0.0028		

mixing fractions are seen to be strongly spin dependent. As a consequence of Pauli statistics, some configurations are even forbidden for accessible terms. Furthermore, there is a notable difference between the mixing fractions for quadruply excited states and those for triply excited states [12]: Contrary to triply excited states, the mixing fractions for quadruply excited intrashell states do not depend on  $M_I$ . This re-

flects the three-dimensional symmetry of the regular tetrahedron (spherical top) compared to two-dimensional symmetry of an equilateral triangle (symmetric top).

The energy of a state within the symmetric rotor model is given by  $\langle \Psi_R^{LM_I\pi S} | \hat{H} | \Psi_R^{LM_I\pi S} \rangle$ , i.e.,

$$E_n^{LM_I\pi S} = 4E_n + \sum_{i < j} \langle \Psi_R^{LM_I\pi S} | \frac{e^2}{r_{ij}} | \Psi_R^{LM_I\pi S} \rangle, \quad (6)$$

with  $r_{ij} = |r_i - r_j|$ . Here  $E_n$  is the Bohr energy and the last term is the electron-electron interaction energy. The equality follows from the fact that the Stark states are eigenstates of the single-particle part of the Hamiltonian of Eq. (1).

Figure 2 shows the energies predicted within our model for the pyramidal states within  $n=2$  and for  $L \leq 4$  within the  $n=3$  shell. The energy increases with increasing  $L$ . Furthermore, we see the tendency that the energy increases with increasing spin  $S$ , contrary to the behavior in ground state configurations, where the term with the largest possible value of  $S$  for a given  $L$  has the lowest energy (Hund's rules). Finally, the energy levels split up for different parities since different parities require different configurations. We note that if the system is considered from a molecular viewpoint, the  $M_I$  independence of the configuration-mixing fractions is expected since the rotational energy of the spherical top molecule reads  $E = (1/2I)L(L+1)$ , with  $I = \sum_i m r_i^2$  being the moment of inertia of the molecule. However, the  $L$  scaling does not follow this relation and it is clear from Eq. (6) that rotational-like structure in excited atomic states is not asso-

ciated with the kinetic energy term as in a molecule, but is exclusively due to the electron-electron interaction. The term  $\langle \Psi_R^{LM_I\pi S} | e^2/r_{ij} | \Psi_R^{LM_I\pi S} \rangle$  scales linearly with the nuclear charge  $Z$ , due to the scaling of the matrix element of  $1/r_{ij}$ . On the contrary, the spherical top model predicts a  $Z^2$  scaling of the energies due to the scaling of the moment of inertia.

In summary, we constructed an analytical wave function for quadruply excited states corresponding to the case wherein the four excited electrons are in the corners of a pyramid. By comparison with *ab initio* calculations, we confirmed the accuracy of the model and, hence, the appealing physical image of the correlated motion of the four electrons. We predicted configuration mixing fractions for a number of states and generally found that a labeling of states in terms of single configurations is insufficient. Finally, we calculated the spectrum of pyramidal states within the second and third principal shells and compared with the expectations obtained when viewing the system as a molecular-like spherical rotor.

We propose to address pyramidal states by dipole-allowed light absorption transferring a fraction of the Be ground state population to the singly excited  $\text{Be}(1s1s2s2p^1P^o)$  state by resonant laser excitation (5.277 eV). A synchrotron or a free-electron laser source could then subsequently scan through the region of quadruply excited pyramidal states of  $^1D^e$  symmetry. A similar two-color technique was successfully applied on triply excited states in Li [20].

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