

LETTER TO THE EDITOR

Symmetry and low-lying intrashell states of three-valence-electron atoms

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Abstract. The low-lying intrashell states of three-valence-electron atoms are examined via an analysis of the geometric and quantum mechanical symmetry. It is shown that the morphology and the energy ordering of these states are essentially determined by the symmetry, not by the details of dynamics.

Symmetry is decisive in determining the structure and properties of microscopic systems. In this letter, we examine intrashell states of three-electron atoms as well as the ground state and low-lying states of boron (or aluminium) atom as examples to show how their structures are essentially determined by symmetry. For the convenience of discussion, in what follows M (the z -component of L) = L , M_S (the z -component of S) = $\frac{1}{2}$ are assumed. Thus, we have L essentially lying along the z -axis, and among the three valence electrons, two are spin-up and one spin-down. If we made another choice of M , the difference is only in the overall geometry. For atoms such as boron and aluminium, the status of the core electrons is trivial and we shall concentrate only on the three valence electrons. We exclude spin interactions such that each state has well defined quantum numbers L , S and parity π where L and S are the orbital and spin angular momentum, respectively.

In determining the stability and the internal structure of a microscopic system, there are two basic factors (Bao and Ruan 1994) to consider.

(a) Low-lying states pursue configurations associated with better geometric symmetry. These configurations are associated with the valleys of the total potential energy in the multi-dimensional coordinate space and thus lower binding and better stability are achieved. In the meanwhile, the wavefunctions would prefer to be smoothly distributed (without nodes to reduce average kinetic energy) around these favorable configurations as their most probable shapes.

(b) For a given quantum mechanical symmetry $^{2S+1}L^\pi$, there are specific inherent nodal surfaces (INS) appearing in the multidimensional coordinate space (as shown later), where the wavefunctions must be zero. If a wavefunction is evenly distributed on both sides of and close to the surface, the system would be induced to undergo a specific mode of motion by crossing the surface back and forth repeatedly. In this sense, the existence of a nodal surface implies the existence of a specific mode. In order to have this mode not invoked, the distribution of the wavefunctions will prefer not to be close to the INS.

In what follows, only the lowest states of every $^{2S+1}L^\pi$ symmetry are considered. The first task is the search for the INS. Once the structure of the INS is clear, we shall study how

the low-lying states choose the most probable shape and the most preferred orientation, so that the binding is optimal and at the same time the wavefunction is distributed sufficiently far away from the INS. Then the main features of the low-lying states would be clear.

Let the plane of the three valence electrons be denoted by σ . If σ contains the origin (where the core is), it is called a coplanar structure. It is evident that the geometric symmetry of an isosceles triangle (including the equilateral triangle as a special case) is better than an irregular triangle. A coplanar isosceles triangle is even better, because when the electrons move on a sphere, they would be farther away from each other in coplanar structure, resulting in weaker Coulomb repulsion. Hence, the coplanar isosceles triangle (CIST) configuration is chosen as the starting point of analysis. The two spin-up electrons are hereafter denoted by e_1 and e_2 . In $S = \frac{1}{2}$ states, since electrons with different spin polarities play different role in structure (Bao 1992a) while the electrons with the same polarity (in our case, the two up-electrons) play equal role, it is natural to assign e_1 and e_2 to be at the base of the isosceles triangle. However, in $S = \frac{3}{2}$ states, which pair of electrons stay at the base is irrelevant.

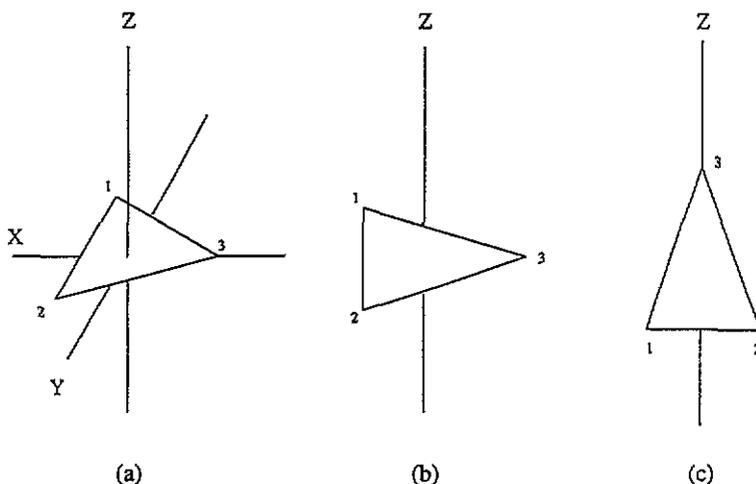


Figure 1. Different orientations of the CIST configurations for intrashell states.

If the σ -plane of the CIST is roughly parallel to the xy plane, it is called a lying CIST (figure 1(a)); if σ is roughly parallel to the z -axis, it is called an upstanding CIST (figure 1(b) and (c)). Evidently, the orientation relative to the z -axis is in fact relative to L . For a lying CIST and an upstanding CIST, the moment of inertia of the former relative to the z -axis is in general considerably larger than the latter. Hence, when L is fixed, the lying one rotates more slowly and would be lower in energy. In fact, this phenomenon holds definitely in two-electron atoms. For example, the energy (theoretical) of the lowest ${}^3P_1^o$ intrashell state ($N = 3$) of helium is -9.496 eV, while that of the corresponding ${}^3P_1^e$ state is -9.134 eV; the plane formed by r_1 and r_2 in the former was found to be lying (Bao 1994), while the latter is upstanding (Bao 1993).

However, not all the states with specific L , S and π can have the most favourable lying CIST configuration because of the symmetry constraints.

(i) In any lying coplanar configuration, a space inversion is equivalent to a rotation by 180° about the z -axis. Hence, an INS appears in this configuration in all the $\pi(-1)^L = -1$ states. This INS would cause the whole σ plane to shift back and forth across the origin

resulting in instability (it is called a d oscillation in Bao (1992b), where d is the distance from the origin to σ). Accordingly, only the $\pi(-1)^L = +1$ states may pursue the lying CIST as their most probable shape.

(ii) A rotation about the height of any CIST by 180° is equivalent to an interchange of r_1 and r_2 . The former operation causes no effect in $L = 0$ states, while the latter causes an extra (-1) factor (since e_1 and e_2 are spin-parallel). Hence, $L = 0$ states are not allowed to possess CIST configurations.

(iii) In $S = \frac{3}{2}$ states, any horizontal configuration (σ being parallel to the xy plane) would be seriously affected by an INS of a horizontal equilateral triangle where a rotation by 120° about the z -axis is equivalent to a cyclic permutation of r_1 , r_2 and r_3 . The rotation causes an extra $e^{i2\pi L/3}$ factor, while the permutation causes no effect in $S = \frac{3}{2}$ states. Thus an INS appears unless $L = 0, 3, \dots$

From the above analysis, point (i) would exclude the $\pi(-1)^L = -1$ states from the candidates of pursuing lying CIST structures, point (ii) would exclude the $L = 0$ states and point (iii) would exclude $S = \frac{3}{2}$ states when $L = 1, 2, 4, 5, \dots$. Thus only $2P^0$, $2D^e$, $4F^0$, ... states can survive. Among them, since a larger L implies a stronger collective rotation, it is deduced that the ground state would be the $2P^0$ state. This deduction coincides with experimental findings and is consistent with the shell model for a three-valence electron atom with configuration such as $2s^2 2p^2 P^0$. The lowest triply excited state of He^- is also known to be a $2P^0$ state.

Let us next examine which states may pursue an upstanding CIST configuration. Firstly, with r_{12} (the base of the CIST) being parallel to the z -axis (figure 1(b)). It is noticed that:

(iv) for an isosceles triangle (coplanar or non-coplanar) with its base parallel to the z -axis, a space inversion is equivalent to a rotation by 180° about the z -axis together with an interchange of the two particles at the base vertexes. In this case the interchange provides a (-1) factor. Hence, an INS appears in this configuration in all the $\pi(-1)^L = +1$ states. This INS would cause e_3 (at the top of the isosceles triangle) to undergo a swing motion (Bao 1992a) resulting in instability. Accordingly, only the $\pi(-1)^L = -1$ states may pursue this configuration as their most probable shape.

(v) Let us examine a latent effect of the equilateral triangle configuration. This effect was first discovered by Watanabe and Lin (1987). Here a simpler verification is given. Let us define a body frame (i', j', k') so that k' is normal and points to σ , and the angular coordinates of e_1 , e_2 and e_3 read $(\theta, -\phi)$, (θ, ϕ) and (θ, ϕ'') , respectively. Then an eigenstate can be expanded as

$$\Psi_{LMS} = \sum_Q D_{QM}^L(-\mathcal{R}) (\phi_Q^1(1'2'3') \chi_S^1(123) + \phi_Q^0(1'2'3') \chi_S^0(123)) \quad (1)$$

where \mathcal{R} denotes a rotation from the fixed frame to the body frame; $(1'2'3')$ are spatial coordinates observed in the body frame, and

$$\chi_S^e(123) = [(\xi(1)\xi(2))_s \xi(3)]_S \quad (2)$$

where $\xi(i)$ is a spin state.

Since Ψ_{LMS} should be antisymmetrized, it must be invariant under a cyclic permutation of the electrons. In the spatial part, if the electrons form an equilateral triangle, then a cyclic permutation is equivalent to a rotation by 120° about the k' -axis resulting in an extra $e^{i2\pi Q/3}$ factor.

On the other hand in the spin part, when $S = \frac{1}{2}$ we have

$$\begin{aligned} \chi_{1/2}^1(231) &= -\frac{1}{2}\chi_{1/2}^1(123) - \frac{1}{2}\sqrt{3}\chi_{1/2}^0(123) \\ \chi_{1/2}^0(231) &= \frac{1}{2}\sqrt{3}\chi_{1/2}^1(123) - \frac{1}{2}\chi_{1/2}^0(123). \end{aligned} \quad (3)$$

Thus we have

$$e^{i2\pi Q/3} \left(-\frac{1}{2}\phi_Q^1 + \frac{1}{2}\sqrt{3}\phi_Q^0 \right) = \phi_Q^1 \quad e^{i2\pi Q/3} \left(-\frac{1}{2}\sqrt{3}\phi_Q^1 - \frac{1}{2}\phi_Q^0 \right) = \phi_Q^0. \quad (4)$$

These two equations imply that

$$(1 + 2\cos \frac{2}{3}\pi Q) \phi_Q^s = 0 \quad (s = 0 \text{ or } 1). \quad (5)$$

Hence, in the $S = \frac{1}{2}$ states, the $Q = 0, \pm 3, \pm 6, \dots$ components are prohibited to have equilateral triangle structures.

In the $S = \frac{3}{2}$ states, obviously we have

$$\chi_{3/2}^1(231) = \chi_{3/2}^1(123) \quad \chi_{3/2}^0 \equiv 0. \quad (6)$$

Instead of equation (5) we have

$$(1 - e^{i2\pi Q/3})\phi_Q^1 = 0. \quad (7)$$

Hence, in the $S = \frac{3}{2}$ state, only the $Q = 0, \pm 3, \pm 6, \dots$ components are allowed to have equilateral triangle structures; otherwise, an INS would appear at equilateral triangle configuration resulting in instability.

(vi) For any coplanar structure, a space inversion is equivalent to a rotation by 180° about the k' -axis. From equation (1) it is clear that only those Q -components fulfilling the condition $\pi(-1)^Q = +1$ are allowed to have coplanar structures (Watanabe and Lin 1987). In particular, since $L = 0$ states have only $Q = 0$ component, odd-parity $L = 0$ states cannot have coplanar structures.

From the above analysis, point (iv) would exclude the $\pi(-1)^L = +1$ states from the candidates of pursuing the CIST as shown in figure 1(b), point (vi) would exclude the odd-parity $L = 0$ states. Thus the rest are the ${}^2{}^4P^e$ and ${}^2{}^4D^o, \dots$ states. Furthermore, in the ${}^2P^e$ states, the $Q = \pm 1$ component is excluded by (vi), while the $Q = 0$ component is excluded by (v), thus the ${}^2P^e$ states are excluded. In the ${}^4D^o$ states, the $Q = 0$, and ± 2 components are excluded by (vi), while the $Q = \pm 1$ component is excluded by (v), thus the ${}^4D^o$ states are excluded. Finally, the survivals are the ${}^4P^e$ and ${}^2D^o, \dots$ states.

Secondly, let us examine which states may pursue the upstanding CIST configuration with r_{12} being normal to the z -axis (figure 1(c)). In this case, a rotation by 180° about the z -axis is equivalent to an interchange of r_1 and r_2 ; thus this configuration is allowed only in $L = \text{odd}$ states. Besides, points (v) and (vi) hold evidently in this case. Accordingly, among $L \leq 2$ states, only the ${}^2P^o$ and ${}^4P^e$ are allowed to pursue this configuration.

Since the ${}^2P^o$ state is allowed to possess both the lying and upstanding CIST configurations (figure 1(a) and (c)); the σ -plane may incline and, accordingly, r_{12} may leave the plane but remains normal to the z -axis; as a result, the angle between the normal of σ and the z -axis is quite arbitrary. Since the r_{12} of upstanding CIST in the ${}^4P^e$ state is allowed to be parallel or normal to the z -axis (figure 1(b) and (c)); the σ -plane may roll about its normal; as a result, the angle between r_{12} and the z -axis is quite arbitrary. In other words, these two states have more choices in their orientation.

In summary, the above ${}^2P^o, {}^4P^e, {}^2D^e, {}^2D^o$ states are the only survivals (among all $L \leq 2$ states) which possess the CIST structure and do not contain nodal surfaces (by skillfully selecting the preferred orientation), thus they have lower energies. Among them, the two P states should be the lower due to smaller L , and the ${}^2P^o$ should be the lowest

owing to its lying CIST. Between the two D states, the ${}^2D^e$ should be lower in energy, also because of its lying CIST structure. Since no nodal surface is involved, all of these states have a gentle internal motion which is a small oscillation around the equilibrium CIST shape. From the above analysis, the S states must contain internal nodal surfaces. However, they do not contain collective rotation, and thus the energies of the S states may end up to be near or even lower than D states.

Let us check how this prediction compares with experimental data. For the triply excited states of He^- , the known resonances for the $n = 2$ intrashell states are at 57.22, 57.42 and 58.28 eV from the ground state of helium for ${}^2P^o$, ${}^4P^e$ and ${}^2D^e$ states, respectively (Smith *et al* 1974, Gosselin and Marmet 1990, Nicolaides *et al* 1993 and references therein). The positions of other resonances are less clear. Similarly, the lowest three $n = 2$ intrashell states of C^+ also follow the increasing order for $2s^22p^2 P^o$, $2s2p^2 {}^4P^e$ and $2s2p^2 {}^2D^e$ states, but the ${}^2S^e$ state is lower in energy than the ${}^2D^o$ state. The latter is a demonstration that a state with nodal surfaces but lower rotational energy can have lower total energy than a state with no nodal surfaces but higher rotation energy. The same energy ordering can be found also for Al and Si^+ (Moore 1949). It is interesting to note that the present analysis of energy ordering does not assign any orbital configuration to each state. We comment that for Al, the ${}^2D^e$ state is assigned to have the configuration $3s^23d$, while for Si^+ it is assigned to have configuration $3s3p^2$. From the shell model viewpoint, it is known that these two states interact strongly (Lin 1974), but the present energy ordering scheme does not assign such orbital configurations.

Although we are talking about an atomic system, however, neither the dynamical equation (Schrödinger equation) nor the details of dynamics (the interaction, the masses, etc) were invoked. Since only symmetry is used in the discussion, the results and the methods of analysis are expected to be quite general. It is clearly established that the main feature of each low-lying state (including L , S , π and the morphology) is completely determined by symmetry. Accordingly, the similarity of different systems is expected to be widely established in nature.

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References

- Bao C G 1992a *Z. Phys. D* **22** 557
- 1992b *J. Phys. B: At. Mol. Opt. Phys.* **25** 3725
- 1993 *Sci. China A* **36** 1186
- 1994 *Sci. China* in press
- Bao C G and Ruan W Y 1994 *Few-Body Systems* in press
- Gosselin R N and Marmet P 1990 *Phys. Rev. A* **41** 1335
- Lin C D 1974 *Astrophys. J.* **187** 385
- Moore C E 1949 *Atomic Energy Levels* (NBS Circular No 467) (Washington, DC: US Govt Printing Office) p 124
- Nicolaides C A, Piangos N A and Komninos Y 1993 *Phys. Rev. A* **48** 3578
- Smith A J *et al* 1974 *J. Phys. B: At. Mol. Phys.* **7** L496
- Watanabe S and Lin C D 1987 *Phys. Rev. A* **36** 511