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Geometry of the three-electron ionization ladder and its corresponding spectrum

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We have computed correlated wave functions for a special class of $^4S^\circ$ triply excited states of Li that exhibit strong localization at the corners of an equilateral triangle as the three-electron ionization threshold is approached. Starting from this finding, we have derived the corresponding spectral formula $-E_n = C[n(n-1)]/r_n^2$, with $r_n \sim n^2$ for $n \geq 3$. C is dependent on the solid angle of the pyramid only for low n , acquiring a θ_n -independent value of 3.36 for $n \geq 12$, where θ_n is the angle formed by the position vectors of any pair of electrons. The above simple formula characterizes other many-electron ionization ladders as well and, for large n , scales like the Bohr formula for the hydrogenic spectra.

I. INTRODUCTION

The possibility of predicting from first principles the properties of multiply excited states (MES) and their quantitative influence on spectroscopy is an interesting, as well as a challenging field of research. A related polyelectronic theory and a variety of applications have been presented in a series of publications (e.g., Refs. 1-4 and references therein). This approach is based on the state-specific choice and computation of a physically meaningful, suitably orthogonalized, self-consistently obtained zeroth-order multiconfigurational solution and on the additional incorporation of localized and multichannel asymptotic correlation via energy minimization, K -matrix, and complex scaling methods.

In a recent publication³ we examined the case of the simultaneous excitation of three electrons in Li. By applying our state-specific approach, we computed correlated wave functions of a particular class of triply excited states (TES) that constitute a "ladder" leading to the three-electron ionization threshold. These wave functions were shown to exhibit strong geometrical localization with the following characteristics:

$$|\mathbf{r}_1|_n = |\mathbf{r}_2|_n = |\mathbf{r}_3|_n, \quad (1a)$$

and

$$90^\circ \leq \theta_{12} = \theta_{23} = \theta_{31} \equiv \theta_n \leq 120^\circ. \quad (1b)$$

The angle θ_n , formed by the position vectors of any pair of electrons, is given by Eq. (2) (see Ref. 3), and has the

property that as the energy (n) increases it tends to 120°

$$\begin{aligned} \langle \cos \theta_n \rangle &= \langle \cos \theta_{12} \rangle \\ &= \int_{-1}^1 d(\cos \theta_{12}) \rho(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \cos \theta_{12}, \end{aligned} \quad (2)$$

where $\rho(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ represents the angular probability density for an electron pair.³

In this paper, the quantum mechanical prediction of conditions (1) is used as a starting point for the derivation of a simple formula for the energy spectrum of the three-electron ionization ladder (THEIL).

II. THEORY AND RESULTS

The geometrical localization of the THEIL wave functions points to a system with the geometry of a rotating oblate symmetric top (OST).⁵ The spectrum of the atomic OST can be written as

$$E_{J^{\text{eff}}} = A \frac{J^{\text{eff}}(J^{\text{eff}} + 1)}{r^2} - B \frac{K^2}{r^2}, \quad (3)$$

$$K = -J^{\text{eff}}, \dots, 0, \dots, J^{\text{eff}},$$

where A and B are positive, \hat{J}^{eff} is the effective angular momentum, K is the projection along the threefold symmetry axis, and r is the distance from the nucleus to the electron.

According to the theory of Ref. 3, the THEIL states are described very well by an intrashell ($n_1 = n_2 = n_3 = n$)

zeroth-order multiconfigurational wave function whose orbitals are obtained self-consistently and which corresponds to the lowest energy of the intrashell manifold. The lowest energy condition is a consequence of the expectation that if there exists a hyperridge analogous to that of the Wannier ridge for doubly excited states,² this should correspond to the solution for which interelectronic correlations are minimized.

These wave functions satisfy the virial theorem, $\langle E \rangle = -\langle T \rangle$. Therefore, by making the correspondence between the THEIL spectrum as a function of n with that of an effective OST as a function of J^{eff} , we choose those values of J^{eff} and K which maximize Eq. (2). This means that

$$K=0 \text{ and } J^{\text{eff}}=J_{\text{max}}^{\text{eff}}, \quad (4)$$

where $J_{\text{max}}^{\text{eff}}$ is to be determined by the nature of the problem. The hydrogenic characteristics of the THEIL electrons—albeit with modifications due to dynamical screening and interelectronic interactions—allows us to write for the total angular momentum in terms of hydrogenic quantum numbers

$$J_{\text{max}}^{\text{eff}}(J_{\text{max}}^{\text{eff}}+1) = \alpha l_{\text{max}}^h(l_{\text{max}}^h+1) = \alpha(n-1)n, \quad (5)$$

where α is a proportionality constant and n is the principal hydrogenic quantum number.

By combining Eqs. (3)–(5), we obtain for the spectrum of the THEIL states

$$-E_n = C \frac{n(n-1)}{r_n^2}, \quad (6)$$

which is the same as that of the Wannier two-electron ionization ladder (TEIL).⁶

In Eq. (6), the quantities E_n and r_n have been computed from first principles up to $n=5$ as the expectation values over the multiconfiguration Hartree-Fock correlated wave functions.³ For this work we extended the computations to the $n=6$ shell. It is important to note that if one considered hydrogenic basis sets for constructing the intrashell vectors, neither E_n nor r_n would be meaningful.

The radii r_n incorporate mainly the effect of the concerted motion of the three electrons. As if it turns out from the results of our computation, they satisfy

$$r_n \sim n^2, \quad n \geq 3, \quad (7)$$

remarkably accurately (Table I, column 4).

The coefficient C is n dependent for low n due to the θ_n dependence of the geometry [see Eq. (1b) and Ref. 3]. However, the angle θ_n tends to 120° very rapidly (Table I, column 5) and so extrapolation shows that for $n \geq 12$, C

TABLE I. Computed data for the Li^4S° three-electron ionization ladder pertinent to the present theory. The energies E_n^* (in a.u.) and the radii r_n (a.u.) are computed from multiconfigurational Hartree-Fock wave functions for each n , the smallest n corresponding to $2p^3$. The energies E_n are computed from Eq. (6) using the fact of Eq. (7) (see column 4) and the smooth convergence of C to a θ_n independent (n independent) value of 3.36 for $n \geq 12$. The theory for the computation of the angle θ_n is given in Ref. 3. No experimental or other theoretical results exist for these states.

n	$-E_n^*$	r_n	r_n/n^2	θ_n [Eq. (2)]	C [Eq. (6)]	$-E_n$ [Eq. (6)]
2				90°		
3	0.9973	5.04	0.56	99.5°	4.22	
4	0.5801	8.96	0.56	105.2°	3.88	
5	0.3776	14.01	0.56	110.1°	3.71	
6	0.2650	20.21	0.56	113.7°	3.61	
7					3.52	0.196
8					3.47	0.151
9					3.43	0.120
10					3.40	0.098
11					3.38	0.081
12					3.36	0.068

is a true constant $C_{n \text{ large}} = 3.36$.

Table I contains the results which have emerged from the present theory and that of Ref. 3. The E_n^* are computed as expectation values. Using Eq. (6) the corresponding C_n are obtained. Extrapolation of C_n and the aforementioned behavior of r_n [Eq. (7)] then allows the prediction of the E_n for all n . We give the values of $n=7-12$.

III. CONCLUSION

It has become possible to compute correlated wave functions and their properties for a special class of triply excited states of Li which define a hyperridge for the three-electron threshold ionization. Accounting for the strong electron localization which they exhibit and based on the relevant properties, we have deduced from first principles a formula for their energy spectrum. Should it become possible in the future to compute and analyze geometrical properties of correlated wave functions for quadruply excited states, a four-electron ionization ladder might be discovered with geometries of the symmetric top. In that case, again the same spectral formula would be valid.⁷ For large n , this formula reduces to the Bohr form for hydrogenic spectra.⁶

¹C. A. Nicolaides, Phys. Rev. A **6**, 2078 (1972).

²Y. Komninos and C. A. Nicolaides, J. Phys. B **19**, 1701 (1986).

³Y. Komninos, M. Chrysos, and C. A. Nicolaides, Phys. Rev. A **38**, 3182 (1988).

⁴C. A. Nicolaides, Y. Komninos, M. Chrysos, and G. Aspromallis, in *Atoms in Strong Fields*, edited by C. A. Nicolaides, C. Clark, and M. Nayfeh (Plenum, New York, 1990).

⁵C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*

(McGraw-Hill, New York, 1955), Chap. 3.

⁶C. A. Nicolaides, M. Chrysos, and Y. Komninos, J. Phys. B **21**, L73 (1988); Phys. Rev. A **39**, 1523 (1988).

⁷For the prolate symmetric top [B of Eq. (2) is negative] maximization of the energy E_J of Eq. (3) implies that $K=J_{\text{max}}$. The corresponding spectrum for the lowest energy intrashell states is $E_n = C[n(n-1)/r_n^2](1+D/n)$, where C and D can be obtained as in the present work.