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Li^- resonances: The two-electron ionization ladder of ^1S symmetry

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We predict the ^1S two-electron ionization ladder (TEIL) of Li^-, for $n=3$–9. This special class of resonances can be observed via electron-lithium scattering experiments. In conjunction with our previous work on such doubly excited states, we conclude that the TEIL spectrum as $n\rightarrow\infty$ is determined essentially by the rigid-rotor correlated motion of the two valence electrons. It appears that no core-induced, quantum-defect concept is necessary to explain the spectrum.

I. INTRODUCTION

We have recently presented[1] a general theory of *ab initio* many-electron calculations of the wave functions, energies, and oscillator strengths of a special class of doubly excited states (DES's) which seem to lead smoothly to the Wannier state at $E=0$ (i.e., where the free electrons are characterized by $\mathbf{r}_1=-\mathbf{r}_2$). This class has been named the two-electron ionization ladder (TEIL).

A different way of looking at these problems has been developed over the last two decades within the formalism of hyperspherical coordinates by Macek, Fano, Rau, Lin, Greene, and others (see Refs. 1–5, and references therein).

Predictions of TEIL's have been made for H^-, He, Li^+, and He^- for ^1S, ^2S, and $^1P^\circ$ symmetries.[1] In the case of the free-electron system He^-, there have been accurate measurements of the resonance spectrum for high-n states by Buckman *et al.*[6] Our recent calculations,[1(c)] which are purely quantum mechanical and account for electron correlation, constitute the first theoretical verification of the experimental assignments.

In this Brief Report, we present our predictions for the ^1S TEIL of Li^-, which can be verified by electron-lithium scattering experiments. The importance of the Li^- system for such work lies in the following two facts.

(1) It is a truly polyelectronic system ($N>3$). The quantitative, first-principles treatment of *high-lying* DES's in such systems—especially in negative ions—has not been achieved before.

(2) It represents a natural step in the sequence of TEIL's, $H^-(nl^2\,{}^1S)$ (coreless), $He^-(nl^2\,{}^2S)$ ($1s$ core), $Li^-(nl^2\,{}^1S)$ ($1s^2$ core). It is borne out by our calculations that, indeed, as n increases, the TEIL energy spectra of the three ions show a remarkable convergence toward each other. This fact raises questions as to whether the conventional notions of quantum defect are applicable in representing such series of DES's. On the other hand, it appears that a general geometrical interpretation of the TEIL energy spectra can be developed which leads to the formula

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

where the value of n starts from the third or fourth TEIL state. A is characteristic of the atom and r_n is the average radius defined in Ref. 1. In the case of He^-, where there exist accurate experimental results,[6] this formula is verified for $A=2.48$.

II. REVIEW OF BASIC CHARACTERISTICS OF THE THEORY

The requirements for the quantum theory and computation of highly excited atomic and molecular states are quite demanding. Over the years we have developed an integrated approach for the systematic quantitative treatment of a variety of such states.[7–11] According to this theory, the approximate solution for each state is obtained in terms of its own, optimized zeroth-order and correlation function spaces.

Zeroth-order vector

Crucial for DES's is the concept and the efficient computation of a realistic *zeroth-order* vector. We have shown that it is numerically feasible, accounting for a variety of convergence difficulties, to compute such a zeroth-order bound wave function within the multiconfigurational Hartree-Fock (MCHF) theory, which accounts for the concerted motion of electrons in a self-consistent field. Numerical as well as analytic methods have been used, and the wave functions are obtained subject to constraints of radial nodes and of orbital and configurational orthogonality which permits the exclusion of open channels and the possibility of convergence to lower states of the same symmetry.

The fact that the theory of DES's is based on a MCHF zeroth-order wave function has a number of advantages. For example, the total energies are already very good with small MCHF functions.[10(c)] Furthermore, some physically interesting characteristics of DES's can be shown to appear already at this level.[10(c)] For the high part of the Wannier TEIL, the corresponding suitably orthogonalized MCHF functions constitute an excellent approximation to the accurately correlated TEIL wave functions.[1] Finally, in cases of polyelectronic atoms, the *self-consistent, long-range interaction* between the large orbitals as well as between them and the core orbitals are automatically taken into account. Thus the use of the suitably calculated zeroth-order, N-electron MCHF solution allows for general studies of highly excited states without any conceptual difficulty or computational bottlenecks.

Localized correlation

Going beyond MCHF, the remaining localized electron correlation is added variationally and the overall calculation yields wave functions that are compact and easy to apply. The most important correlation effects can be identified *a priori* and computed systematically.

Asymptotic correlation

For the prediction of the TEIL energy spectrum and wave-function characteristics, only the zeroth-order vector W_n^0 and the localized correlation X_n are needed. The asymptotic correlation, which represents discrete-continuum and continuum-continuum interactions, cannot affect the properties which are calculated in this work significantly and it is not computed. This is because the TEIL states are localized at a region of configuration space ($r_1=r_2$, $\theta_{12}=\pi$), where the open channels have small amplitude.

III. CALCULATION OF THE Li-($1s^2nl^2\,{}^1S$) TEIL RESONANCES ($n=3$–9)

In the case of Li^-, the zeroth-order multiconfigurational Hartree-Fock functions W_n^0 (Ref. 1) were calculated analytically. The results are the same as those of the numerical MCHF for low n. However, for high n only the analytic method converges. The $1s^2$ orbitals were calculated once and then were kept frozen for all W_n^0. The variational, self-consistent optimization of the valence orbitals was carried out under special orthogonality conditions to specific orbitals in order to exclude open channels or convergence to lower states.[7,8,10] The latter orbitals were obtained from independent Hartree-Fock calculations on Li($1s^2nl$) configurations.

Having obtained the W_n^0, the second step of the overall calculation concerns the localized correlation so that the total energies can be obtained accurately. Only the valence pair was treated, even though the aim is indeed the presentation of an energy spectrum which is verifiable directly, without any use of semiempirical fitting. The justification for this approach is the following.

(1) Given W_n^0, the intershell correlation ($1snl$) is extremely small for high n. Thus pair and triple virtual excitations involving one $1s$ electron are negligible.

(2) The correlation of the $1s^2$ pair (about 1.1 eV) is, to a very good approximation, the same in the Li^- TEIL states and in the $\text{Li}^+(1s^2)$ ion. Since we are interested in the *difference* of total energies, i.e., in the distance of the TEIL states from the two-electron ionization threshold, we need only subtract the HF energy of the $\text{Li}^+(1s^2\,{}^1S)$ state from the TEIL energies with an uncorrelated (i.e., a HF) $1s^2$ core. Thus the physically relevant energies which we computed were

$$\Delta E_n = E_{\text{HF}}(\text{Li}^+(1s^2)) - E(W_n') \ , \tag{1}$$

where

$$E(W_n') \equiv E(W_n^0) + E_n^{\text{corr}} \ \text{(valence only)} \ . \tag{2}$$

This reliable simplification of the overall calculation of the observable spectrum is a result of the character of the present theory. It is evident that larger atoms can be subjected to a similar analysis from first principles. In doing so, the treatment of the core and of the core-valence interactions will vary according to the electronic structure of the polyelectronic atom and the type of TEIL under investigation.

The results of our calculations are shown in Tables I–III. Conditional probability plots, similar to those defined and computed earlier,[1] have shown again the expected localization of the valence electrons on the Wannier ridge.

IV. FORMULA FOR THE TEIL SPECTRUM OF SMALL ATOMS

There are two properties which are computed accurately in our theory: the energy E_n of each TEIL state and the corresponding average radius r_n. These have been defined in Ref. 1.

Another property which emerges from our conditional probability plots, where the position of one electron is kept fixed at r_n, is the fact that the two electrons are strongly localized on opposite sides of the nucleus with $r_1=r_2=r_n$. Thus this system is equivalent to an *effective* particle-on-a-sphere system.

Given the above, and assuming that for these high-lying states the square of the angular momentum of the TEIL electrons is proportional to that of hydrogenic orbitals, we have shown[12] that for the small atomic systems we have examined thus far, when $n>5$ (so that the valence electrons satisfy $\theta_{12}=\pi$ sufficiently well),

$$E_n = A\frac{n(n-1)}{r_n^2} \ . \tag{3}$$

A is a proportionality constant, characterizing the atomic state. It turns out that it varies very little from system

TABLE I. Energy distance, in eV, of the $\text{Li}^-\,{}^1S$ TEIL states from the $\text{Li}^+(1s^2)$ two-electron ionization threshold. The first column corresponds to the zeroth-order, analytic MCHF, W_n^0, and the second to the correlated, W_n. As n increases, $\Delta E(W_n^0)\rightarrow\Delta E(W_n)$. This fact removes the necessity of carrying out complete calculations for high n (see Ref. 1). Therefore, after $n=5$, only the $\Delta E(W_n^0)$ are computed.

n	$\Delta E(W_n^0)$	$\Delta E(W_n)$
3	2.269	2.285
4	1.205	1.213
5	0.753	0.755
6	0.517	
7	0.376	
8	0.287	
9	0.227	

TABLE II. Average values (in a.u.) of $\langle r_1 \rangle_n \approx \langle r_2 \rangle_n = \langle r \rangle_n$ for the valence pair of the Li^- ^1S TEIL. For reasons of comparison, we also report the TEIL radii of H^- ^1S and He^- ^2S obtained from the calculations of Ref. 1 (but not presented there). The small difference in the r_n for He^- between this set and that of Ref. 12 is due to an improved calculation as regards the multidimensional optimization of the nonlinear parameters of the virtual functions. The energies are insensitive to such modifications. However, the r_n are sensitive, since as n increases the TEIL functions become very diffuse.

n	$\mathrm{H}^-(nl^2)$	$\mathrm{He}^-(1snl^2)$	$\mathrm{Li}^-(1s^2nl^2)$
3	16.3	14.2	13.3
4	28.7	26.5	25.8
5	44.9	42.6	41.8
6	66.5	62.9	62.0
7	90.9	87.0	86.9
8	120.1	114.7	114.9
9	152.0	144.1	144.0

TABLE III. Comparison of $\Delta E(W_n)$ (in eV) [see Eqs. (1) and (2) and Table I] for the TEIL's of $\mathrm{H}^-(nl^2\,{}^1S)$, $\mathrm{He}^-(1snl^2\,{}^2S)$ (from Ref. 1), and $\mathrm{Li}(1s^2nl^2\,{}^1S)$ (this work). As n increases, these energies converge toward each other, regardless of the different cores.

	Komninos *et al.* [Ref. 1(c)]		This work
n	H^-	He^-	Li^-
3	1.885	2.156	2.285
4	1.088	1.180	1.213
5	0.706	0.745	0.755
6	0.493	0.511	0.517
7	0.366	0.375	0.376
8	0.282	0.287	0.287
9	0.224	0.227	0.227
10		0.184	

to system.[12] In fact, once the regularity as a function of n sets in for each ion, it can be obtained from a *single* calculation at a particular n (i.e., the theory does not require least-square fitting). On the other hand, one must remember that, according to Eq. (3), E_n is very sensitive to the value of r_n, which must, therefore, be computed very accurately.

In the present case of Li^-, $A=2.45$. When this value is substituted in Eq. (3) and use of the calculated r_n is made (Table II), the resulting energies are in excellent agreement with those calculated from first principles (Table I).

Since the concept of quantum defect on energies must refer to a *coreless,* zeroth-order system, and since, as Tables II and III show, the TEIL of Li^- agrees quantitatively with those of H^- and He^-, it appears that, for high enough n, one cannot determine a quantum defect for these DES's. Therefore it might be useful to examine further the related suggestions and interpretations of the double-Rydberg formulas (for example, Refs. 5, 13, and 14).

V. CONCLUSION

The present results constitute the first prediction of a specific part of the resonance spectrum which can in principle manifest itself in electron-lithium scattering, just as in the case of e-He scattering.[6]

The methods and arguments which were presented here are general enough so that they can be used to justify similar calculations in larger systems. An important physical result which has come out of the present and our previous work is that, for relatively high n, the behavior of the TEIL pair of valence electrons behaves quantitatively similarly, regardless of the existence or not of a core. Furthermore, their rigid-rotor characteristics can be used to deduce Eq. (3), which is readily verifiable and can be used to explain the Rydberg-like formulas used earlier in the study of DES's.[12-14]

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[1] (a) Y. Komninos and C. A. Nicolaides, J. Phys. B **19**, 1701 (1986); (b) C. A. Nicolaides and Y. Komninos, Phys. Rev. A **35**, 999 (1987); (c) Y. Komninos, M. Chrysos, and C. A. Nicolaides, J. Phys. B **20**, L791 (1987).

[2] A. R. P. Rau, J. Phys. (Paris) Colloq. **43**, 211 (1982).

[3] C. D. Lin, Phys. Rev. A **26**, 2305 (1982).

[4] U. Fano, Rep. Prog. Phys. **46**, 97 (1983).

[5] J. Macek and J. M. Feagin, J. Phys. B **18**, 2161 (1985).

[6] S. J. Buckman, P. Hammond, F. H. Read, and G. C. King, J. Phys. B **16**, 4039 (1983); S. J. Buckman and D. S. Newman, *ibid.* **20**, L711 (1987).

[7] C. A. Nicolaides, Phys. Rev. A **6**, 2078 (1972); C. A. Nicolaides and D. R. Beck, Int. J. Quantum. Chem. **14**, 435 (1978); J. Chem. Phys. **66**, 1982 (1977).

[8] Y. Komninos, G. Aspromallis, and C. A. Nicolaides, Phys. Rev. A **27**, 1865 (1983); C. A. Nicolaides and G. Aspromallis, J. Phys. B **16**, L251 (1983).

[9] C. A. Nicolaides and Th. Mercouris, Phys. Rev. A **32**, 3247 (1985); **36**, 390 (1987).

[10] (a) Y. Komninos and C. A. Nicolaides, Phys. Rev. A **33**, 1995 (1986); (b) Y. Komninos and C. A. Nicolaides, Z. Phys. D **4**, 301 (1987); (c) Y. Komninos, N. Makri, and C. A. Nicolaides, Z. Phys. D **2**, 105 (1986).

[11] C. A. Nicolaides, in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules,* edited by C. E. Dykstra (Reidel, Dordrecht, 1984), p. 161.

[12] C. A. Nicolaides, M. Chrysos, and Y. Komninos, J. Phys. B **21**, 73 (1988).

[13] A. R. P. Rau, J. Phys. B **16**, L699 (1983).

[14] C. D. Lin and S. Watanabe, Phys. Rev. A **35**, 4499 (1987).