

Wannier two-electron ionization ladder of $^1P^o$ symmetry in H^- , He, and Li^+

Cleanthes A. Nicolaides and Yannis Komninos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vas. Constantinou Ave., Athens 116/35, Greece

(Received 9 June 1986)

We have developed a systematic approach for identifying *a priori* and computing accurately wave functions of a special class of doubly excited states which seem to lead in a regular way to the Wannier state at the two-electron ionization threshold. As an application, we present a variety of new and experimentally verifiable results for the $^1P^o$ symmetry in H^- , He, and Li^+ .

I. INTRODUCTION

A fundamental problem of atomic and molecular physics in the field of electronic structure and excitation dynamics has been the quantitative understanding of multiply excited states, or, more specifically, of doubly excited states (DES's).

For the Coulomb Hamiltonian, DES's may correspond to bound discrete states, quasibound autoionizing states, or to free scattering states.

The question of the rigorous methodology for the proper quantum-mechanical description of the wave function of two free electrons in the field of a positive ion (with or without structure) is still open.^{1,2} Related to it are the results at the classical³ level on the qualitative behavior of the cross section^{2,4} for the two-electron ionization at threshold and, accepting Wannier's arguments,² the results at the WKB-like level.^{2,4} Most of the earlier activity in this field has been reviewed recently.⁵⁻⁸

In the case of low-lying bound or quasibound DES's, there has been considerable progress in the rigorous, quantum-mechanical description of their wave functions and their properties (energies, widths, excitation transition probabilities). Representative papers from different schools can be found in Refs. 9-15. It is left up to the reader to evaluate the advantages and limitations as regards generality and accuracy of the various approaches.

This paper presents the first quantum-mechanical results on the wave functions and on the photoexcitation transition probabilities of a special class of DES's, which we have called the Wannier two-electron ionization ladder (TEIL). The basic property of the TEIL states is that they seem to lead to the so-called Wannier state at $E=0$, i.e., to the state where the two electrons leave the atom simultaneously in opposite directions. The theory and method of the *a priori* identification and systematic calculation of the Wannier TEIL is described in detail elsewhere.¹⁸ Here, we review briefly its important characteristics and present the first quantitative properties of the Wannier TEIL of $^1P^o$ symmetry in H^- , He, and Li^+ , expressed in terms of conditional probability plots, of calculated energies and photoabsorption oscillator strengths, of fitted Rydberg-like formulas, and of average radii of the positions of the two electrons as a function of the quantum number n .

II. THE WANNIER TEIL

The progress which has been made on the so-called Wannier problem (e.g., Refs. 1-8, 16, 17, 19, and 20) has not yet been able to provide rigorous quantum-mechanical, many-electron explanations and the concepts and information currently employed are either classical or vague or semiquantitative. It is thus evident that a many-electron quantitative treatment of aspects of this problem might provide a new view to it. Our approach has been formulated around the following question:

Out of the infinity of DES's of any symmetry in any atom, how can one identify *a priori* and compute without any approximation the true wave functions of only that class of states which, for small but negative total energies, have the same distinct characteristics of the Wannier state (at $E=0$) and therefore, by virtue of smoothness and continuity, lead to it?

Given the above statement of the problem we have developed a general theory for the calculation of the Wannier TEIL which is implemented in three steps.¹⁸

(a) We accept that one of Wannier's results from classical mechanics, i.e., that at $E=0$, $\hat{r}_1 = -\hat{r}_2$ must also hold in the quantum-mechanical case for the special class of DES's mentioned above. This hypothesis leads to the conceptual choice of the *zeroth-order* representation. More specifically, according to the *state-specific* theory of DES's,¹⁴ the *zeroth-order multiconfigurational* vector is

TABLE I. Total energies (in a.u.) of the Wannier TEIL of $^1P^o$ symmetry in H^- , He, and Li^+ . The calculations involve a multiconfigurational Hartree-Fock zeroth-order vector W_n^0 , with all the configurations of each shell n , to which the remaining correlation is added variationally.

n	H^-	He	Li^+
3	-0.062 386	-0.335 694	-0.829 753
4	-0.037 351	-0.194 871	-0.476 859
5	-0.024 624	-0.126 743	-0.308 552
6	-0.017 434	-0.088 984	-0.215 760
7	-0.013 017	-0.065 871	-0.159 051
8	-0.010 086	-0.050 714	-0.122 208
9	-0.008 045	-0.040 247	-0.096 812
10		-0.032 718	-0.078 597

TABLE II. Expansion coefficients of the W_n^0 zeroth-order functions for $n=7, 8,$ and 9 .

Atom Coeff.	$n=7$			$n=8$			$n=9$		
	H ⁻	He	Li ⁺	H ⁻	He	Li ⁺	H ⁻	He	Li ⁺
C_{sp}	0.3307	0.3672	0.3839	0.2913	0.3250	0.3398	0.2609	0.2909	0.3053
C_{pd}	0.6289	0.6624	0.6769	0.5846	0.6225	0.6376	0.5447	0.5837	0.6007
C_{df}	0.5926	0.5724	0.5598	0.6030	0.5946	0.5891	0.6013	0.6025	0.6001
C_{fg}	0.3517	0.2985	0.2727	0.4091	0.3605	0.3375	0.4502	0.4100	0.3896
C_{gh}	0.1396	0.0966	0.0804	0.1946	0.1470	0.1266	0.2454	0.1967	0.1754
C_{hi}	0.0321	0.0172	0.0130	0.0653	0.0395	0.0308	0.0993	0.0674	0.0552
C_{ik}				0.0136	0.0064	0.0044	0.0295	0.0161	0.0118
C_{kl}							0.0057	0.0024	0.0015

constructed in terms of configurations with orbitals in the same shell ($n_1=n_2$). In order to minimize the (negative) electron correlation, the physically relevant zeroth-order vector must correspond to the lowest root of the matrix formed by the possible configurations of each symmetry at each n . (For example, consider the $^1P^\circ$ symmetry of He. For $n=4$, only the $4s4p$, $4p4d$, and $4d4f$ configurations constitute the basis set.)

(b) The zeroth-order vector for each shell, W_n^0 , is computed self-consistently via numerical (for low-lying) or analytic (for high-lying) multiconfigurational Hartree-Fock (MCHF) theory with orthogonality constraints to core orbitals. Thus, relaxation and the concerted motion of the two electrons in the field of an *arbitrary* core (and not just a bare nucleus or zero angular momentum ion) is taken into account rigorously and systematically.

(c) The remaining electron correlation X_n , corresponding to each W_n^0 , is added variationally by keeping the virtual orbitals orthogonal to the appropriate core orbitals.¹⁴ Thus, the total wave function for the Wannier DES at each shell n is given by

$$W_n = W_n^0 + X_n. \quad (1)$$

The quantum-mechanical version of the Wannier condition $-\hat{\tau}_1 = \hat{\tau}_2$ is, in terms of the operators for the radial distance and the angle between the position vectors,

$$\langle r_1 \rangle \approx \langle r_2 \rangle, \quad (2a)$$

$$\langle \theta_{12} \rangle \approx \pi. \quad (2b)$$

In order to translate this into practical wave-mechanical language with many-electron, correlated wave functions,

TABLE III. Average radii of the electrons in the Wannier TEIL (in a.u.). These values fit Eq. (5).

n	H ⁻	He	Li ⁺
3	16.96	7.36	4.61
4	29.33	13.02	8.29
5	45.49	20.42	13.09
6	65.12	29.78	18.89
7	88.66	40.92	25.95
8	117.21	53.91	34.25
9	147.77	68.58	44.31
10		84.92	54.95

we have conceptualized the problem in terms of *conditional probability distributions*²¹⁻²⁴ and have introduced the definitions

$$\langle r_1 \rangle = \int \int \rho(r_1, r_2) r_1 dr_1 dr_2, \quad (3a)$$

$$\langle r_2 \rangle = \frac{\int \rho(\langle r_1 \rangle, r_2) r_2 dr_2}{\int \rho(\langle r_1 \rangle, r_2) dr_2}, \quad (3b)$$

where $\rho(r_1, r_2)$ is the exact electron density of the state of interest and $\rho(\langle r_1 \rangle, r_2)$ is the density that results if r_1 is fixed at the average value $\langle r_1 \rangle$ and the angular dependence on \hat{r}_1 is integrated.

Our choice and calculation of the Wannier TEIL wave functions lead to solutions for which the expectation values (3a) and (3b) indeed satisfy Eq. (2a) and which, with increasing n , tend to satisfy Eq. (2b). [Here, it is important to note that the Eqs. (3) are not imposed on the wave functions. Instead, they are evaluated after the calculation, which is based on the previously mentioned steps (a)–(c), and serve to confirm the hypothesis that our choice of the Wannier TEIL indeed satisfies conditions (2).] Furthermore, the MCHF zeroth-order vectors become a better approximation to the exact wave functions as n increases, a fact which justifies the use of Rydberg-like formulas for the TEIL and which implies that the anticipated smoothness is setting in already at about $n=8-10$ (see Ref. 18 and below).

III. RESULTS

The results for the Wannier TEIL of $^1P^\circ$ symmetry of H⁻, He, and Li⁺ which we present here are as follows.

TABLE IV. Oscillator strengths from the ground 1S state to the Wannier TEIL.

n	H ⁻	He	Li ⁺
3	2.3×10^{-5}	4.2×10^{-5}	2.3×10^{-5}
4	9.0×10^{-9}	2.1×10^{-6}	1.3×10^{-6}
5	2.7×10^{-10}	2.2×10^{-7}	1.4×10^{-7}
6	2.2×10^{-9}	3.4×10^{-8}	3.0×10^{-8}
7	1.1×10^{-9}	6.7×10^{-9}	6.8×10^{-9}
8	4.8×10^{-10}	1.7×10^{-9}	1.4×10^{-9}
9	1.5×10^{-10}	6.3×10^{-10}	4.8×10^{-10}
10		2.3×10^{-10}	1.8×10^{-10}

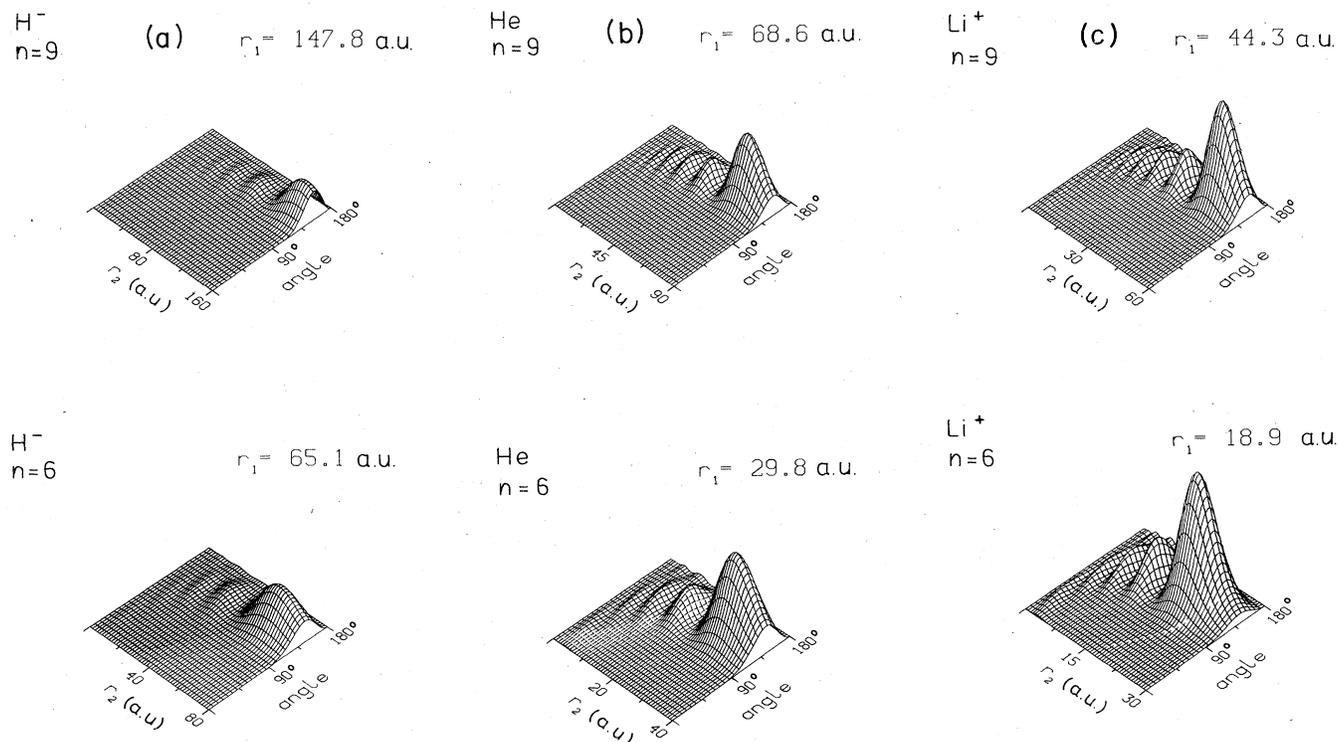


FIG. 1. Conditional probability plots with the position of the one electron fixed at the average value r_n (Table III). (a) H^- , (b) He, (c) Li^+ . The TEIL wave functions show a wave-front-like behavior, moving with n toward $\theta_{12}=180^\circ$, the angle which is predicted classically for the two electrons with $L=0$ emitted at $E=0$.

(a) The computed energy spectrum and the concomitant Rydberg-like formulas

$$E_n = -\frac{(Z-\sigma)^2}{(n+\mu)^2}, \quad (4)$$

where n is the principal quantum number. Such formulas have been examined recently from a different point of view.²⁵ We have found that σ is essentially Z independent while μ goes as $\sim 0.3/Z$. More specifically, our calculations yield for H^- , $\sigma=0.161$, $\mu=0.354$; for He, $\sigma=0.162$, $\mu=0.160$; and for Li^+ , $\sigma=0.168$, $\mu=0.101$. The computed energies until $n=10$ are presented in Table I.

(b) The coefficients of the MCHF wave functions for $n=7-9$ W_n^0 , i.e., for each zeroth-order description of the states constituting the Wannier TEIL. These are given in Table II. Since the W_n^0 approximate the exact W_n with good accuracy, the expansion coefficients offer a good picture of the structure of the wave functions.

(c) The values produced by Eqs. (3) using the W_n wave functions. As predicted by the theory, $\langle r_1 \rangle \approx \langle r_2 \rangle \approx r_n$. These r_n are presented in Table III. Apart from their quantitative value in interpreting the behavior of electrons along the Wannier TEIL, such numbers might prove useful for "molecular" models of the spectra of DES's.²⁶ Based on the hydrogenic formula for the average value of r , we have fit the values of Table III to the formula

$$r_n = \frac{1.7}{Z-0.08} (n-0.1Z)^2. \quad (5)$$

(d) The photoabsorption oscillator strengths from the ground state $1S$ to the Wannier TEIL. The results of Table IV were obtained with the velocity formula which was more stable. We believe that, in spite of their very small size, these numbers, together with the energy spectrum [Table I and Eq. (4)], will form the basis for the systematic experimental and theoretical understanding of the excitation dynamics of the Wannier TEIL.

(e) The conditional probability density plots (see Fig. 1), with one coordinate fixed at the average value r_n , which show how the localization around $\langle r_1 \rangle \approx \langle r_2 \rangle$ and $\langle \theta_{12} \rangle \approx \pi$ increases as a function of n , with a node at π due to the symmetry of the $1P^\circ$ wave function.

IV. CONCLUSION

We have produced definitive results which demonstrate the existence and some basic properties of a special class of doubly excited states of $1P^\circ$ symmetry in H^- , He, and Li^+ , which seem to lead smoothly to the Wannier state at the two-electron ionization threshold. The methodology of the present theory is extendable to many-electron systems in a straightforward way. It remains to be seen whether the wave functions of the DES's in larger atoms, where a core is coupled to the two excited electrons, have similar properties.

In a separate publication,²⁷ we have employed the Wannier TEIL's of $1S$ symmetry in H^- , He, and Li^+ in order to derive the angular distribution of the simultaneously emitted electrons at $E=0$.

- ¹P. L. Altick, *J. Phys. B* **16**, 3543 (1983); **18**, 1841 (1985).
- ²A. R. P. Rau, *Phys. Rev. A* **4**, 207 (1971).
- ³G. H. Wannier, *Phys. Rev.* **90**, 817 (1953); **100**, 1180 (1955).
- ⁴R. Peterkop, *J. Phys. B* **4**, 513 (1971).
- ⁵A. R. P. Rau, in *Electronic and Atomic Collisions*, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (Elsevier, Amsterdam, 1984), p. 711.
- ⁶H. Klar, in *Electronic and Atomic Collisions*, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (Elsevier, Amsterdam, 1984), p. 767.
- ⁷G. G. M. Heideman, in *Electronic and Atomic Collisions*, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (Elsevier, Amsterdam, 1984), p. 743.
- ⁸J. Feagin, in *Electronic and Atomic Collisions*, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (Elsevier, Amsterdam, 1984), p. 777.
- ⁹T. F. O'Malley and S. Geltman, *Phys. Rev. A* **137**, 1344 (1965); E. Holøien and J. Midtdal, *J. Chem. Phys.* **45**, 2209 (1966); L. Lipsky and A. Russek, *Phys. Rev.* **141**, 59 (1966); I. Eliezer and Y. I. Pan, *Theor. Chim. Acta* **16**, 63 (1970).
- ¹⁰P. G. Burke and A. J. Taylor, *Proc. Phys. Soc. London* **88**, 549 (1966).
- ¹¹J. Macek, *J. Phys. B* **1**, 831 (1968); C. D. Lin, *Phys. Rev. A* **10**, 1986 (1974); **27**, 22 (1983).
- ¹²Y. K. Ho, *Phys. Rep.* **99**, 1 (1983).
- ¹³C. A. Nicolaides and Th. Mercouris, *Phys. Rev. A* **32**, 3247 (1985); C. A. Nicolaides and E. Adamides, *ibid.* **27**, 1691 (1983); C. A. Nicolaides and D. R. Beck, *Int. J. Quantum Chem.* **14**, 457 (1978); *Phys. Lett.* **65A**, 11 (1978).
- ¹⁴C. A. Nicolaides, *Phys. Rev. A* **6**, 2078 (1972); G. Aspromallis, Y. Komninos, and C. A. Nicolaides *J. Phys. B* **17**, L151 (1984).
- ¹⁵D. E. Ramaker and D. M. Schrader, *Phys. Rev. A* **9**, 1980 (1974); Y. Komninos, G. Aspromallis, and C. A. Nicolaides, *ibid.* **27**, 1865 (1983); G. Aspromallis, C. A. Nicolaides, and Y. Komninos, *J. Phys. B* **18**, L545 (1985); Y. Komninos and C. A. Nicolaides, *Phys. Rev. A* **34**, 1995 (1986).
- ¹⁶U. Fano, *Rep. Prog. Phys.* **46**, 97 (1983).
- ¹⁷A. R. P. Rau, *J. Phys. (Paris) Colloq.* **43**, C-211 (1982); *At. Phys.* **9**, 491 (1984).
- ¹⁸Y. Komninos and C. A. Nicolaides, *J. Phys. B* **19**, 1701 (1986).
- ¹⁹S. Cvejanovic and F. H. Read, *J. Phys. B* **7**, 1841 (1974).
- ²⁰F. H. Read, *Aust. J. Phys.* **35**, 475 (1982).
- ²¹K. E. Banyard and G. K. Taylor, *Phys. Rev. A* **10**, 1972 (1974).
- ²²D. R. Beck and C. A. Nicolaides, *Int. J. Quantum Chem. Symp.* **10**, 119 (1976).
- ²³G. S. Ezra and R. S. Berry, *Phys. Rev. A* **28**, 1974 (1983).
- ²⁴Y. Komninos, N. Makri, and C. A. Nicolaides, *Z. Phys.* **D2**, 105 (1986).
- ²⁵J. Macek and J. M. Feagin, *J. Phys. B* **18**, 2161 (1985).
- ²⁶D. R. Herrick and R. D. Polliak, *J. Phys. B* **13**, 4533 (1980); *Phys. Rev. A* **21**, 418 (1980).
- ²⁷Y. Komninos, M. Chrysos, and C. A. Nicolaides (unpublished).