

dc-field tunneling of polyelectronic atoms and of negative ions: Computations based on models and on *ab initio* theory

Spyros I. Themelis and Cleanthes A. Nicolaidis

*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48 Vassileos Constantinou Avenue, 116 35 Athens, Greece*

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We have computed the dc-field-induced tunneling rates for H^- , He, Li, and Li^- by applying two methods. The first used *ab initio* theory, which not only produces reliable results but also allows the systematic analysis of the effects of electronic structure, of the multichannel continuum, and of field-induced mixings. The second used previously published formulas derived from semiclassical models. Comparison shows large quantitative differences, especially for strong fields and for He, where the electrons are equivalent. However, for H^- , Li, and Li^- , the plots of the widths on a logarithmic scale as a function of the field strength yield similar shapes.

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Tunneling of electrons due to the application of an external dc or low-frequency laser field is a phenomenon which has attracted experimental and theoretical interest since the early 1960s [1–12]. Although it has proven possible to develop and apply rigorous theory in the case of one-electron atoms ([13] and references therein), for many-electron atoms and ions the computation of tunneling rates has been carried out by the use of approximate, semiclassical, or semiempirical formulas based on models [1,3,4,6,7,11]. It is only recently [14] that results from *ab initio* theory and computation have been published, on the prototypical He and Li atoms. This theory is obviously three dimensional and polyelectronic, and applicable to atomic as well as molecular states.

In the absence of a first-principles quantum-mechanical theory and method of computation of field-induced tunneling rates (FITR's), current and previous work on low-frequency laser-induced ionization (e.g., [7–12]) has been utilizing the formulas of Perelomov and co-workers [3,4] (also used by Ammosov, Delone, and Krainov [7]) in the context of the "quasistatic" approximation [8–12]. As regards the use of purely static fields for the experimental determination of FITR's in polyelectronic atoms and ions, it appears that this is an open field. This reality has left the aforementioned models, until now, as the only source of quantitative information on FITR's.

Given the above, the present investigation was undertaken in order to produce results from *ab initio* theory on two negative ions of different electronic structures, the H^- and the Li^- , and, in conjunction with our previous ones on the neutral atoms He and Li [14], to compare with the values which we have computed using the models of Perelomov and co-workers [3,4] for neutral atoms and of Guschina and Nikulin [6] for negative ions (i.e., for a short-range potential). Such a test would provide guidelines for future use of these structureless models in polyelectronic atoms and negative ions.

For the *ab initio* theory and formalism, the reader is referred to recent papers from this institute [13–18]. It is electronic-structure oriented and shows how to incorpo-

rate systematically to all orders the effects of the interelectronic interactions and of the external field. The aim is to compute a state-specific complex eigenvalue of a non-Hermitian full Hamiltonian matrix \underline{H} , constructed from the sum of two suitably chosen function spaces Q and P . This eigenvalue represents the energy shift Δ and width Γ (i.e., the FITR), due to the external dc field. In the present application to H^- and Li^- , the Q space was one dimensional, consisting of a compact but well-correlated state-specific wave function for the field-free states Ψ_0 :

$$\Psi_0 = \Phi_{\text{MCHF}} + X_{\text{loc}} \quad (1)$$

For H^- , the numerical multiconfigurational Hartree-Fock (MCHF) function Φ_{MCHF} was $0.967(1s^2) + 0.217(2s^2) + 0.114(2p^2)$, while X_{loc} consisted of 12 doubly excited configurations with virtual orbitals up to $l=4$, whose Slater-type radials were optimized variationally. The energy of this Ψ_0 is $E_0 = -0.527484$ a.u., of sufficient accuracy when compared with the exact H^- energy, $E_{\text{ex}} = -0.527751$ a.u.. Similarly, for Li^- , $\Phi_{\text{MCHF}} = 0.933(1s^2 2s^2) + 0.360(1s^2 2p^2)$, while X_{loc} represented only L -shell correlation and was expanded in terms of 12 doubly excited, variationally optimized configurations. The corresponding energy was -7.455430 a.u., implying an L -shell correlation energy of 0.0272 a.u.. A numerically implemented coupled cluster calculation [19] gave an L -shell correlation energy of 0.0270 a.u.

The P space is multidimensional and involves \mathcal{L}^2 representations of the multichannel Rydberg and, especially, continuous spectrum. For H^- ,

$$P = \{1s\epsilon s, 1s\epsilon p, 1s\epsilon d, \dots\}, \quad (2)$$

where $1s$ is exact and ϵl is expanded in terms of complex Slater-type orbitals (STO's):

$$\epsilon l(r, \theta) = \sum_n a_n \varphi_{nl}(r, \theta), \quad (3)$$

$$\varphi_{nl} = r^{n+l} e^{-\alpha r} e^{-i\theta} \quad (4)$$

The parameters α and θ are optimized until a stable eigenvalue of \underline{H} corresponding to the Ψ_0 vector is found. We used a basis of $10s$, $10p$, $8d$, $6f$, and $4g$ complex STO's, with the parameter α varied between 0.4 and 0.7. Higher thresholds of the form $2s\epsilon l$, $2p\epsilon l$, etc., were not included since their contribution is negligible due to small coupling matrix elements and large energy differences.

On the contrary, for Li^- the final state must include two thresholds, the $1s^2 2s^2 S$ and the $1s^2 2p^2 P^o$, which are coupled through the field. This final-state open-shell effect was shown to be important in a previous nonperturbative study of multiphoton ionization and of nonlinear polarization of Li^- , with or without a dc field [15–17]. Each of the two thresholds was symmetry coupled to its own basis set of complex STO's. Between them, these two sets are nonorthonormal. The symmetry-adapted configurations that were used are

$$P = \{ 1s^2 2s\epsilon s^1 S, 1s^2 2p\bar{\epsilon} p^1 S, 1s^2 2s\epsilon p^1 P^o, \\ 1s^2 2p\bar{\epsilon} s^1 P^o, 1s^2 2p\epsilon d^1 P^o, 1s^2 2s\epsilon d^1 D, \\ 1s^2 2p\epsilon p^1 D, 1s^2 2p\epsilon f^1 D, 1s^2 2s\epsilon f^1 F^o, \\ 1s^2 2p\epsilon d^1 F^o \} .$$

The bar indicates the different basis set. We used $7s$, $7\bar{s}$, $7p$, $7\bar{p}$, $6d$, and $4f$ complex STO's having the form (4). The parameter α was varied between 0.3 and 0.5. The convergence of the calculation with respect to the function space was checked carefully. We found that doubly excited configurations did not change the results significantly.

The results of these calculations are shown in Figs. 1–3 for H^- , Li^- , and Li (solid line) and in Table I for He. Due to its structure, the $\text{Li}^- 1S$ state has a larger FITR than the $\text{H}^- 1S$ state. The FITR has an exponential growth for small values of the field strength F and a saturation for larger F values, characteristic of a quasilinear dependence (observe the log scale on the axis of $\Gamma/2$). We note that very small tunneling rates are not reliably obtainable due to the singular behavior

$$\Gamma(F) \underset{F \rightarrow 0}{\sim} g(F) \exp(-\alpha/F) .$$

We now turn to the calculation of FITR's from the model formulas produced in the pioneering work of Refs. [1,3,4,6]. For negative ions in an s state, Guschina and Nikulin [6] concluded that the complex energy \mathcal{W} of the field-dressed state is the solution of the transcendental equation

$$\sqrt{2\pi} \left(\frac{F^2}{2} \right)^{1/6} \{ \text{Ai}'(z) \text{Bi}'(z) - z \text{Ai}(z) \text{Bi}(z) \\ + i [\text{Ai}'^2(z) - z \text{Ai}^2(z)] \} + a_0 = 0 , \quad (5)$$

where $\text{Ai}(x)$, $\text{Bi}(x)$ are the Airy functions, F is the field strength, $z = -(2/F^2)^{1/3} \mathcal{W}$, $a_0 = \sqrt{2|\lambda_0|}$, and λ_0 is the binding energy of the electron. When F is small, the ex-

TABLE I. Field-induced tunneling widths for the ground state of He calculated from Eq. (7) and from the *ab initio* polyelectronic theory. The discrepancy is large for all field strengths. Numbers in square brackets denote powers of 10.

F (a.u.)	Γ (a.u.)	
	Model	<i>ab initio</i>
0.0600	5.98[−11]	8.24[−7]
0.0625	1.73[−10]	9.30[−7]
0.0650	4.59[−10]	1.05[−6]
0.0675	1.13[−9]	1.19[−6]
0.0700	2.62[−9]	1.36[−6]
0.0725	5.73[−9]	1.68[−6]
0.0750	1.19[−8]	1.88[−6]

pression for the tunneling rate deduced from Eq. (5) is [1,6]

$$\Gamma(F) \cong \frac{F}{2a_0} \exp \left[-\frac{2}{3} \frac{a_0^3}{F} \right] . \quad (6)$$

Our results are given in Figs. 1 and 2. Compared to the *ab initio* theory, in the case of H^- the model underestimates the FITR by a factor of about $\frac{1}{2}$. A significant discrepancy is observed for the polarizability, which comes out to be 82.7 a.u. compared to the accurate value of 206.4 ± 2.5 a.u. [20]. The situation is worse for Li^- , where the results are six or seven times smaller than our calculations. Also, the estimated polarizability from the model is 121.3 a.u. compared with the *ab initio* value of 748 a.u. given by Nicolaides, Mercouris, and Aspromallis [17].

As regards the model results on the atoms He and Li, these are contained in Table I for He and in Fig. 3 for Li. They were obtained using the semiclassical formula for an s state [3,4]:

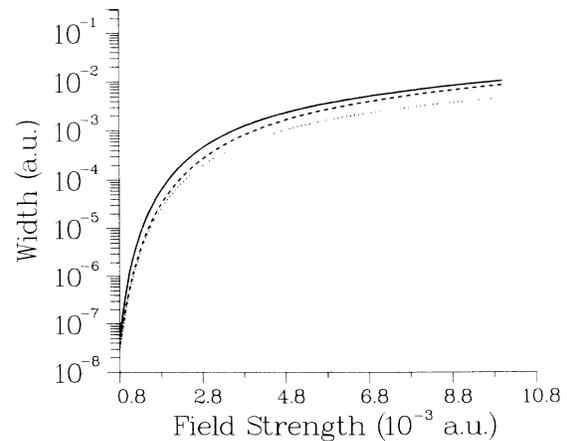


FIG. 1. Field-induced tunneling widths for H^- (log scale) calculated in this work from *ab initio* polyelectronic theory (solid line), the transcendental equation (5) (dotted line), and the asymptotic approximation (6) (dashed line). Note the increasing difference between the last two curves as F increases.

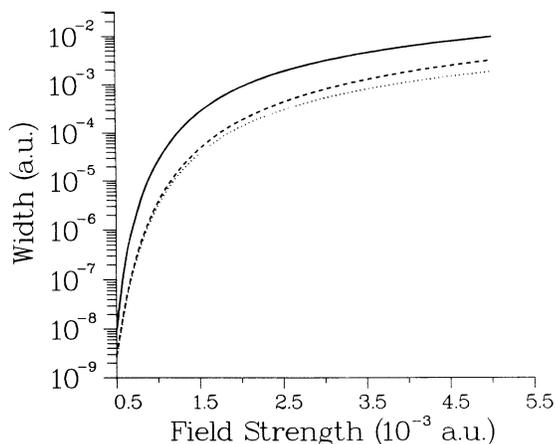


FIG. 2. As in Fig. 1 but for Li^- .

$$\Gamma = c_n^2 E_p \left\{ \frac{2}{F} (2E_p)^{3/2} \right\}^{2n^*-1} \exp \left\{ -\frac{2}{3} \frac{(2E_p)^{3/2}}{F} \right\}, \quad (7)$$

where E_p is the ionization potential, $n^* = Z^* / \sqrt{2E_p}$, Z^* is the effective charge of the escaping electron, and c_n^* is a constant computed by Ammosov, Delone, and Krainov [7].

Comparison of the *ab initio* with the model results shows that for He, where we have equivalent electrons, the difference is very large (orders of magnitude) for the whole range of the field strength, and leads to different exponential dependences. This is why it was thought unnecessary to present a comparative graph. For Li, which is essentially a modified one-electron system, there is better agreement for small field strengths. However, for larger field strengths the discrepancy increases, as expected by the fact that the exponential dependence of Eq. (7) need not be accurate.

In summary, we have presented *ab initio* results for the

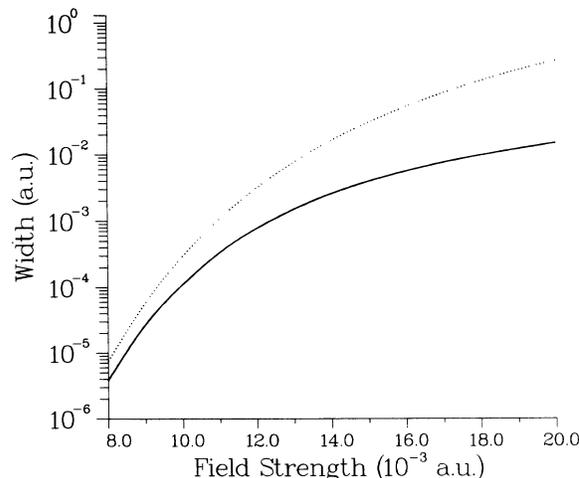


FIG. 3. Field-induced tunneling widths for the ground state of Li calculated from *ab initio* polyelectronic theory (solid line) and from Eq. (7) (dotted line). As F increases, the model results are inaccurate by orders of magnitude.

FITR's of H^- , He, Li, and Li^- obtained from a polyelectronic theory accounting for electronic structure and electron correlation in the field-dressed states, and have compared them with results from the application of models for the approximate description of tunneling in neutral atoms and in negative ions. We conclude that the shapes of the plot of the widths on a log scale as a function of the field strength for negative ions or for modified one-electron atoms are similar. However, in general the quantitative information contains inaccuracies which increase with the complexity of electronic structure in initial and in final states and with field strength. It would be useful if accurate experimental values became available, especially for the negative ions where the field strengths can be obtained in the laboratory without difficulty.

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