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Theory and computation of electric-field-induced tunneling rates of polyelectronic atomic states

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It is shown how to obtain efficiently quantum-mechanical tunneling rates (and energy shifts) induced by electric fields for arbitrary polyelectronic states. The problem is formulated as one of solving nonperturbatively a complex-eigenvalue matrix equation, constructed in terms of two separately optimized multidimensional function spaces, Q and P. The theory is demonstrated on two prototypical ground states, He $1s^2\,{}^1S$ and Li $1s^2 2s\,{}^2S$, as well as on the Li $1s^2 2p\,{}^2P^\circ$ excited levels ($M_L=0,\pm1$). For example, for field strengths $F=3.86\times10^7$–3.86×10^8 V/cm the He ${}^1S$ tunneling rates range from 5.79×10^7 to 7.75×10^{10} s^{-1}.

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I. FIELD-INDUCED TUNNELING RATES FOR POLYELECTRONIC STATES

The LoSurdo-Stark effect has a history spanning most of this century. It refers to the shifting and broadening of atomic and molecular states under the influence of an external electric field. As regards the near-zero-field energy shift and its breakdown into linear and nonlinear polarizabilities, its study has defined a whole field of experimental and theoretical research covering one-electron as well as many-electron systems, and a huge amount of related information is available, albeit of varying quality (e.g., see Refs. [1–8] and references therein).

On the other hand, our knowledge of the dynamics of this phenomenon, i.e., of the energy broadening due to field-induced tunneling (FIT), is limited to systems which are treated quantum mechanically or semiclassically as monoelectronic, such as the hydrogen atom, high-lying Rydberg levels, or negative ions [6–27]. For example, for the H atom there is an accumulation of methods and results on the tunneling rates (energy widths) of the ground and of the excited states [15–27]. Most of the theories are specific to the hydrogenic system (e.g., use of parabolic coordinates). A few, such as those of Refs. [26,27] are formulated in such a way so as to be computationally implementable for many-electron states.

Recent work has shown that it is possible to compute FIT rates (FITR's) using polyelectronic, electronic structure dependent methods [27–30]. The first applications involved the ground states of the negative ions H$^-$ and Li$^-$ [28,29] as well as multiply excited states (MES) [30]. For the ground states, the formal complexity is reduced due to the nonexistence of discrete states of the same spin. However, consideration of neighboring bound states does become necessary in MES of negative ions [30]. On the other hand, in negative ions the core of the final state is neutral and more easily polarizable than an ionic one. This implies that the theory must incorporate the important couplings of low-lying excited states of the neutral system, thus adding intriguing complexity to the problem. This has been done in the case of the strongly correlated Li$^-$ $1s^2 2s^2\,{}^1S$ [28], where the mixing of the final core states Li $1s^2 2s\,{}^2S$ and $1s^2 2p\,{}^2P^\circ$ is important and results in observable physical effects (see Fig. 2 of Ref. [28]).

It follows from the above that for ordinary ground or low-lying excited states of *neutral* atoms or molecules, the subject of FITR's remains *terra incognita.* How large are such quantities, what magnitude of field strengths is necessary to make them observable, what is their dependence on electronic structure and angular momentum, and how can one compute them from first principles?

This paper presents results of many-electron computations of FIT rates in neutrals, in an attempt to provide answers to the above questions. Apart from the basic physics, knowledge of such quantities could prove useful for the understanding and modeling of phenomena where electric fields are created, such as discharges. We considered three prototypical atomic states: The two-electron He $1s^2\,{}^1S$ and the three-electron Li $1s^2 2s\,{}^2S$ and $1s^2 2p\,{}^2P^\circ$. The last two are connected by an electric dipole transition. Possible measurement of the linewidth variation as a function of field strength would produce information on FITR's, provided the variation of the radiative channel due to the field-induced mixing of states is accounted for. (See Ref. [8] for a measurement and calculation of the energy shift of the Li D_1 line.)

II. THEORY

The system "neutral atom plus dc field" constitutes an electronic structure dependent many-electron problem whose solution to good accuracy can be achieved as follows. Upon application of the field, the discrete spectrum changes into a resonance spectrum whose states correspond to the solutions of the complex-eigenvalue Schrödinger equation (CESE) [27]

$$(H-z_0)\Psi=0\ , \tag{1}$$

where

$$H=H_A+\sum_i^N \mathbf{F}\cdot\mathbf{r}_i \tag{2}$$

and

$$z_0=E_0+\Delta(F)-\frac{i}{2}\Gamma(F) . \tag{3}$$

H_A is the free-atom Hamiltonian and $\mathbf{F}$ represents the external electric field. The shift Δ and the width Γ are functions of the field strength. E_0 is the energy of H_A in the state of interest.

Since Ψ represents a nonstationary state decaying into the electronic continuum, it satisfies a special asymptotic boundary condition that makes it unnormalizable [27]. Nevertheless, the solution of Eq. (1) is feasible in terms of function spaces which are square integrable, provided the transformation $\rho=re^{i\theta}$ is applied [27]. This coordinate rotation was used on the Hamiltonian operators for the computation of the LoSurdo-Stark ground-state resonance of the H atom and the solution was achieved by direct diagonalization of the non-Hermitian Hamiltonian on a large square-integrable basis set [19]. However, for decaying states of many-electron systems, the brute-force diagonalization approach is unrealistic, just like it is for the much "simpler" many-electron problem corresponding to the stationary states of the conventional real eigenvalue Schrödinger equation.

In a series of papers ([27–32] and references therein) it has been shown how state-specific electronic structure theory, based on Hartree-Fock (HF) or multiconfiguration HF zeroth-order functions, can be combined with methods accounting for the peculiarities of decaying states, in order to treat reliably a number of nonstationary phenomena in atoms and molecules. For the general case of an N-electron system with a discrete and a continuous spectrum, we divide the total function space into two multidimensional parts, Q: $\{\Phi_i\}$ and P: $\{\chi_i\}$. The Q space is fixed by considering judiciously the electronic structure and spectrum of the system under study, in conjunction with the dipole form of the perturbation. Its elements are state-specific correlated or uncorrelated wave functions of the significant states which make up the Hamiltonian matrix H.

The P space is not fixed. It contains parametrized [β is defined as the nonlinear parameter, see Eq. (5)] virtual configurations with real as well as complex orbitals representing contributions from the multichannel high Rydberg and scattering states. It is the variational optimization of this space via diagonalization of $\underline{H}$ (see below) that allows the fine tuning of the concerted effect of field-induced state mixing and of electron correlation and leads to the determination of the energy width and shift of the perturbated state [Eq. (3)].

Having thus defined the Q and P spaces, we construct the complex symmetric "dressed" matrix of the atom plus field Hamiltonian

$$\underline{H}=\begin{bmatrix} H_{QQ} & H_{QP} \\ H_{PQ} & H_{PP} \end{bmatrix} \tag{4}$$

which is diagonalized repeatedly until the stability conditions

$$\left.\frac{\partial z}{\partial\beta}\right|_{z=z_0}=0 , \quad \left.\frac{\partial z}{\partial\theta}\right|_{z=z_0}=0 \tag{5}$$

are satisfied for the root of $\underline{H}$ [Eq. (4)] whose overlap with the unperturbed reference function is maximum. The parameter β is the nonlinear parameter of the Slater orbitals in the P space (see below).

III. APPLICATION TO THE He $1s^2\,{}^1S$, Li $1s^22s\,{}^2S$, and $1s^22p\,{}^2P^\circ$ STATES

Let us first consider the He $1s^2\,{}^1S$ state. If understanding and efficiency for the general polyelectronic problem is to go along with sufficient accuracy, it is necessary to incorporate only that part of the radial and angular correlation which contributes to the overall nature of the wave function and to its outer region the most. Hence, based on the accumulated knowledge on the problem of He electron correlation, in order to define the reference vector, $i=0$, we computed a six-term numerical multiconfigurational Hartree-Fock (MCHF) wave function [33]

$$\begin{aligned}\Phi_0({}^1S)=0.996(1s^2)-0.062(2s^2)+0.063(2p^2)\\ -0.007(3s^2)+0.010(3p^2)-0.012(3d^2) ,\end{aligned} \tag{6}$$

$$E_{\mathrm{MCHF}}=-2.901\,84 \text{ a.u.}$$

The remaining Φ_i ($i\neq0$) in the Q space of the He $1s^2\,{}^1S$ are chosen according to the following syllogism. The two valence electrons are correlated in the ground state mainly as in Eq. (6), where the $1s^2$ character is overwhelming. In other words, the Fermi sea (FS) (i.e., the set of orbitals making up the important zeroth-order configurations) is given reliably by the $1s$ orbital only. Nevertheless, in order to push the level of accuracy and also in order to demonstrate how our ideas can be applied to arbitrary states, most of which have multiconfigurational Fermi seas, in this application we have included the $2s$ and $2p$ orbitals into the He ${}^1S$ Fermi sea. Following this choice, the Φ_i ($i\neq0$) configurations in Q were chosen as the singly excited $1snl$, $n=2,3$ $l=0,1,2$, as well as the Fermi-sea-induced doubly excited $2s2p$ and $2p3d\,{}^1P^\circ$. Because convergence was good enough, we did not enlarge computation by including doubly excited states of ${}^1D$ or ${}^1S$ symmetry. However, we point out that such states ought to be more important in heavier atoms, where they are found much lower in energy than in He (~57–60 eV), and carry larger oscillator strengths.

The case of Li has different characteristics. Its spectral and polarization properties are dominated by the single valence electron. Therefore, the portion of Q space which contributes the most to the physics of tunneling over a large range of field strengths is formed by uncorrelated Hartree-Fock configurations representing the ground together with discrete Rydberg states:

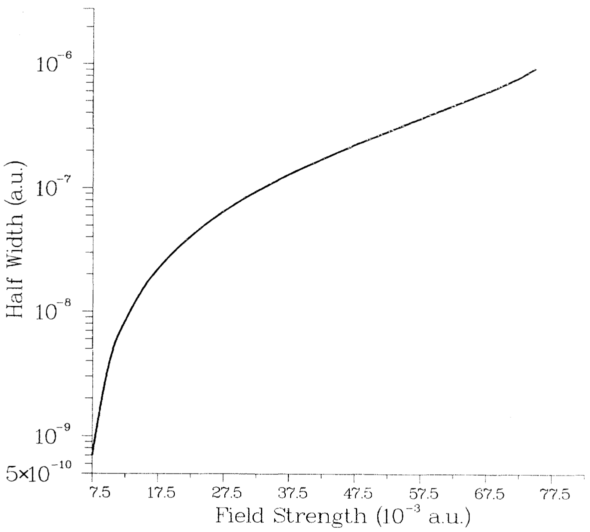

FIG. 1. Calculated quantum-mechanical tunneling half-widths of the helium ground state over a range of applied static fields. The axis of $\Gamma/2$ is on a logarithmic scale.

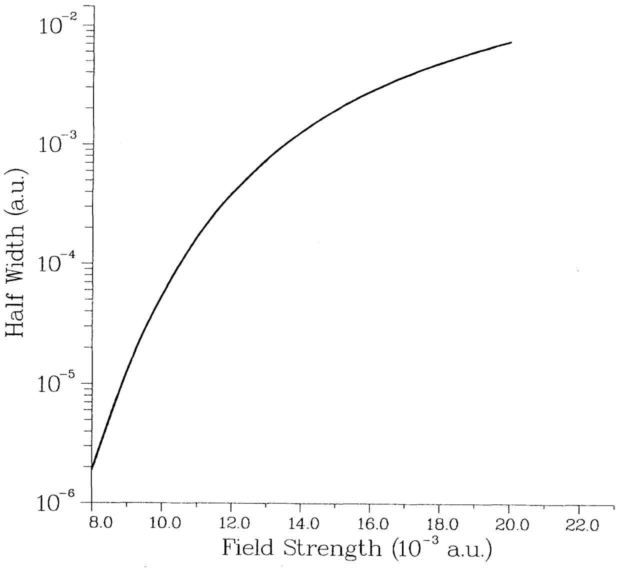

FIG. 2. Half-widths of the lithium ground state calculated over a range of applied static fields.

TABLE I. Field-induced energy shift Δ, half-width $\Gamma/2$, and corresponding tunneling rate,R, for the LoSurdo-Stark effect of the helium ground state [R (sec^{-1})]$=4.136\times10^{16}$ [Γ (a.u.)] [F(V/cm)]$=5.14\times10^{9}$ [F(a.u.)].

F (a.u.)	F (V/cm)	$-\Delta$ (a.u.)	$\Gamma/2$ (a.u.)	R (s^{-1})
0.0025	1.29×10^{7}	4.34×10^{-6}		
0.0050	2.57×10^{7}	1.74×10^{-5}		
0.0075	3.86×10^{7}	3.91×10^{-5}	7.0×10^{-10}	5.79×10^{7}
0.0100	5.14×10^{7}	6.95×10^{-5}	3.8×10^{-9}	3.14×10^{8}
0.0125	6.43×10^{7}	1.09×10^{-4}	8.50×10^{-9}	7.03×10^{8}
0.0150	7.71×10^{7}	1.56×10^{-4}	1.47×10^{-8}	1.22×10^{9}
0.0175	9.00×10^{7}	2.13×10^{-4}	2.21×10^{-8}	1.83×10^{9}
0.0200	1.03×10^{8}	2.78×10^{-4}	3.09×10^{-8}	2.55×10^{9}
0.0225	1.16×10^{8}	3.52×10^{-4}	4.09×10^{-8}	3.38×10^{9}
0.0250	1.29×10^{8}	4.35×10^{-4}	5.23×10^{-8}	4.32×10^{9}
0.0275	1.41×10^{8}	5.26×10^{-4}	6.49×10^{-8}	5.37×10^{9}
0.0300	1.54×10^{8}	6.27×10^{-4}	7.89×10^{-8}	6.52×10^{9}
0.0325	1.67×10^{8}	7.36×10^{-4}	9.43×10^{-8}	7.80×10^{9}
0.0350	1.80×10^{8}	8.54×10^{-4}	1.11×10^{-7}	9.20×10^{9}
0.0375	1.93×10^{8}	9.80×10^{-4}	1.30×10^{-7}	1.07×10^{10}
0.0400	2.06×10^{8}	1.12×10^{-3}	1.50×10^{-7}	1.24×10^{10}
0.0425	2.18×10^{8}	1.26×10^{-3}	1.72×10^{-7}	1.43×10^{10}
0.0450	2.31×10^{8}	1.41×10^{-3}	1.97×10^{-7}	1.63×10^{10}
0.0475	2.44×10^{8}	1.58×10^{-3}	2.24×10^{-7}	1.85×10^{10}
0.0500	2.57×10^{8}	1.75×10^{-3}	2.54×10^{-7}	2.10×10^{10}
0.0525	2.70×10^{8}	1.93×10^{-3}	2.87×10^{-7}	2.38×10^{10}
0.0550	2.83×10^{8}	2.12×10^{-3}	3.25×10^{-7}	2.68×10^{10}
0.0575	2.96×10^{8}	2.32×10^{-3}	3.66×10^{-7}	3.03×10^{10}
0.0600	3.08×10^{8}	2.52×10^{-3}	4.12×10^{-7}	3.41×10^{10}
0.0625	3.21×10^{8}	2.74×10^{-3}	4.65×10^{-7}	3.85×10^{10}
0.0650	3.34×10^{8}	2.97×10^{-3}	5.26×10^{-7}	4.35×10^{10}
0.0675	3.47×10^{8}	3.20×10^{-3}	5.96×10^{-7}	4.93×10^{10}
0.0700	3.60×10^{8}	3.45×10^{-3}	6.79×10^{-7}	5.62×10^{10}
0.0725	3.73×10^{8}	3.70×10^{-3}	7.84×10^{-7}	6.48×10^{10}
0.0750	3.86×10^{8}	3.97×10^{-3}	9.38×10^{-7}	7.75×10^{10}

TABLE II. Field-induced energy shift, half-width, and corresponding tunneling rate for the LoSurdo-Stark effect of the lithium ground state.

F (a.u.)	F (V/cm)	$-\Delta$ (a.u.)	$\Gamma/2$ (a.u.)	R (s^{-1})
0.001	5.14×10^{6}	8.31×10^{-5}		
0.002	1.03×10^{7}	3.33×10^{-4}		
0.003	1.54×10^{7}	7.63×10^{-4}		
0.004	2.06×10^{7}	1.35×10^{-3}		
0.005	2.57×10^{7}	2.11×10^{-3}		
0.006	3.08×10^{7}	3.04×10^{-3}		
0.007	3.60×10^{7}	4.15×10^{-3}		
0.008	4.11×10^{7}	5.44×10^{-3}	1.9×10^{-6}	1.57×10^{11}
0.009	4.63×10^{7}	6.94×10^{-3}	1.35×10^{-5}	1.12×10^{12}
0.010	5.14×10^{7}	8.65×10^{-3}	5.50×10^{-5}	4.55×10^{12}
0.011	5.65×10^{7}	1.06×10^{-2}	1.68×10^{-4}	1.17×10^{13}
0.012	6.17×10^{7}	1.27×10^{-2}	3.90×10^{-4}	3.22×10^{13}
0.013	6.68×10^{7}	1.50×10^{-2}	7.57×10^{-4}	6.26×10^{13}
0.014	7.20×10^{7}	1.75×10^{-2}	1.29×10^{-3}	1.06×10^{14}
0.015	7.71×10^{7}	2.00×10^{-2}	1.98×10^{-3}	1.64×10^{14}
0.016	8.22×10^{7}	2.26×10^{-2}	2.82×10^{-3}	2.34×10^{14}
0.017	8.74×10^{7}	2.52×10^{-2}	3.81×10^{-3}	3.15×10^{14}
0.018	9.25×10^{7}	2.79×10^{-2}	4.90×10^{-3}	4.05×10^{14}
0.019	9.77×10^{7}	3.05×10^{-2}	6.12×10^{-3}	5.06×10^{14}
0.020	1.03×10^{8}	3.31×10^{-2}	7.45×10^{-3}	6.16×10^{14}

$$\Phi_0(^2S)=1s^22s\ ,\quad \Phi_0(^2P^\circ)=1s^22p\ ,\quad \Phi_{i\neq0}\colon\ 1s^2nl\ ,\qquad n=2,3,4,\ l=0,1,2,3\ .$$

These account for valence electron excitations induced by the interelectronic interactions (e.g., $2s\leftrightarrow3s$) and by the electric field (e.g., $2s\leftrightarrow2p\leftrightarrow3d\leftrightarrow4f$). Core or core-valence excitations are not expected to affect the results significantly.

The P space consisted of virtual configurations $1skl$ and $1s^2kl$, where the coordinate of (kl) is complex, $\rho=re^{-i\theta}$. The cores, He^+ $1s$ and Li^+ $1s^2$, were computed separately, while the (kl) had the convenient Slater form $(kl)=\rho^{n+l-1}e^{-\beta\rho}$, with $9s,9p,7d,6f,5g,5h,5i,5k,4l,4m$ functions for He and for Li, which were kept orthogonal to each other but not to the bound HF orbitals. The nonlinear parameter β is optimized according to Eq. (5).

TABLE III. Field-induced energy shift, half-width, and corresponding tunneling rate for the LoSurdo-Stark effect of the $1s^22p\ ^2P^\circ(M_L=0)$ level of the lithium atom.

F (a.u.)	F (V/cm)	$-\Delta$ (a.u.)	$\Gamma/2$ (a.u.)	R (s^{-1})
0.0005	2.57×10^{6}	1.70×10^{-5}		
0.0008	4.11×10^{6}	4.38×10^{-5}		
0.0010	5.14×10^{6}	6.88×10^{-5}	3.23×10^{-8}	2.67×10^{9}
0.0013	6.68×10^{6}	1.18×10^{-4}	8.59×10^{-8}	7.10×10^{9}
0.0015	7.71×10^{6}	1.58×10^{-4}	1.28×10^{-7}	1.06×10^{10}
0.0018	9.25×10^{6}	2.31×10^{-4}	2.22×10^{-7}	1.84×10^{10}
0.0020	1.03×10^{7}	2.89×10^{-4}	2.85×10^{-7}	2.36×10^{10}
0.0022	1.13×10^{7}	3.54×10^{-4}	3.45×10^{-7}	2.85×10^{10}
0.0025	1.29×10^{7}	4.69×10^{-4}	4.42×10^{-7}	3.65×10^{10}
0.0027	1.39×10^{7}	5.57×10^{-4}	5.67×10^{-7}	4.69×10^{10}
0.0030	1.54×10^{7}	7.09×10^{-4}	8.40×10^{-7}	6.95×10^{10}
0.0032	1.64×10^{7}	8.26×10^{-4}	1.18×10^{-6}	9.76×10^{10}
0.0035	1.80×10^{7}	1.03×10^{-3}	2.34×10^{-6}	1.93×10^{11}
0.0037	1.90×10^{7}	1.19×10^{-3}	4.09×10^{-6}	3.38×10^{11}
0.0040	2.06×10^{7}	1.47×10^{-3}	1.01×10^{-5}	8.35×10^{11}
0.0045	2.31×10^{7}	2.07×10^{-3}	7.30×10^{-5}	6.04×10^{12}
0.0050	2.57×10^{7}	2.87×10^{-3}	2.74×10^{-4}	2.27×10^{13}
0.0055	2.83×10^{7}	3.84×10^{-3}	7.33×10^{-4}	6.06×10^{13}
0.0060	3.08×10^{7}	4.92×10^{-3}	1.57×10^{-3}	1.30×10^{14}
0.0065	3.34×10^{7}	5.90×10^{-3}	2.70×10^{-3}	2.23×10^{14}
0.0070	3.60×10^{7}	6.77×10^{-3}	4.22×10^{-3}	3.49×10^{14}

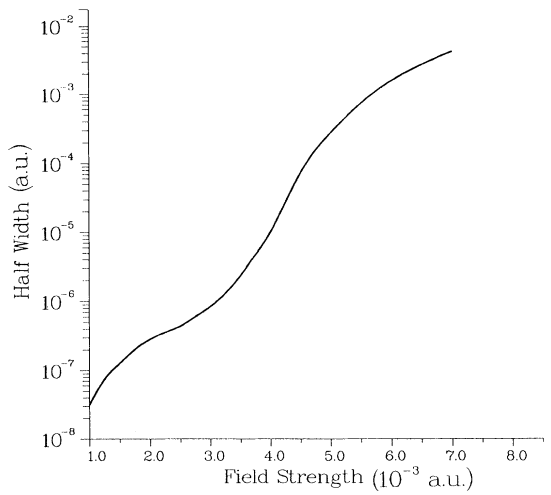

FIG. 3. Half-widths of the $1s^22p\,^2P^o(M_L=0)$ level of the lithium atom calculated over a range of applied static fields.

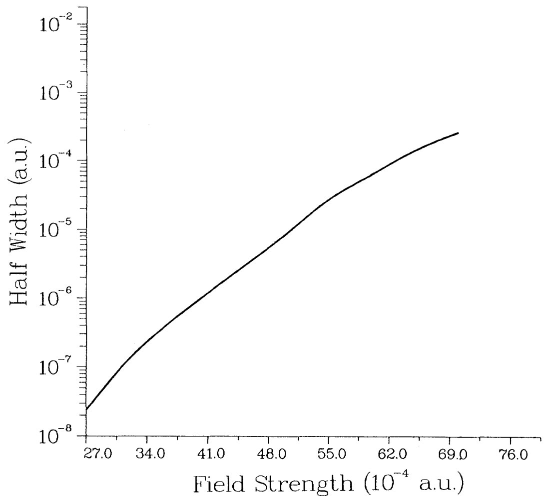

FIG. 4. Half-widths of the $1s^22p\,^2P^o(M_L=\pm1)$ state of the lithium atom calculated over a range of applied static fields. Note the difference between these results and those of Fig. 3.

IV. RESULTS

The results of our computations are presented in Tables I–IV and in Figs. 1–4. Energy widths as well as shifts are presented. The tunneling rates (R) for the Li states are much larger than those of the He ground state for the same field strengths. For example, for $F=0.020$ a.u. the He ^1S rate is 2.55×10^9 s^{-1}, while that of the Li $1s^22s\,^2S$ state is 6.16×10^{14} s^{-1}. Similarly, the Li $^2P^o$ levels are field ionized faster than the Li ^2S ground state.

If individual state measurements of ion or electron emission could be made, the tunneling rates could be obtained directly. If $^2P^o$-^2S linewidth or lifetime variation measurements were made, these would be dominated by the broadening of the $^2P^o$ state. The field strengths required for FITR's of about 3.7×10^7 s^{-1} (radiation transition rate of the Li $^2P^o$ state) or larger, are probably difficult to handle in the laboratory at the present time. On the other hand, calculations for smaller fields do not exhibit reliable convergence, since the corresponding

TABLE IV. Field-induced energy shift, half-width, and corresponding tunneling rate for the LoSurdo-Stark effect of the $1s^22p\,^2P^o(M_L=\pm1)$ level of the lithium atom.

F (a.u.)	F (V/cm)	$-\Delta$ (a.u.)	$\Gamma/2$ (a.u.)	R (s^{-1})
0.0005	2.57×10^6	1.70×10^{-5}		
0.0008	4.11×10^6	4.35×10^{-5}		
0.0010	5.14×10^6	6.81×10^{-5}		
0.0013	6.68×10^6	1.15×10^{-4}		
0.0015	7.71×10^6	1.54×10^{-4}		
0.0018	9.25×10^6	2.22×10^{-4}		
0.0020	1.03×10^7	2.75×10^{-4}		
0.0022	1.13×10^7	3.33×10^{-4}		
0.0025	1.29×10^7	4.31×10^{-4}		
0.0027	1.39×10^7	5.05×10^{-4}	2.40×10^{-8}	1.98×10^9
0.0030	1.54×10^7	6.27×10^{-4}	6.99×10^{-8}	5.78×10^9
0.0032	1.64×10^7	7.16×10^{-4}	1.34×10^{-7}	1.11×10^{10}
0.0035	1.80×10^7	8.62×10^{-4}	3.01×10^{-7}	2.49×10^{10}
0.0037	1.90×10^7	9.67×10^{-4}	4.90×10^{-7}	4.05×10^{10}
0.0040	2.06×10^7	1.14×10^{-4}	9.63×10^{-7}	7.96×10^{10}
0.0045	2.31×10^7	1.46×10^{-4}	2.88×10^{-6}	2.38×10^{11}
0.0050	2.57×10^7	1.84×10^{-4}	8.62×10^{-6}	7.13×10^{11}
0.0055	2.83×10^7	2.29×10^{-4}	2.73×10^{-5}	2.26×10^{12}
0.0060	3.08×10^7	2.80×10^{-4}	6.37×10^{-5}	5.27×10^{12}
0.0065	3.34×10^7	3.36×10^{-4}	1.43×10^{-4}	1.18×10^{13}
0.0070	3.60×10^7	3.98×10^{-4}	2.61×10^{-4}	2.16×10^{13}

FITR's rapidly become very small. We note that the same occurs even in the case of hydrogen [15–26], the reason being the exponential times a power series dependence of the width on the field strength, F, as F goes to zero [15,20,21].

V. CONCLUSION

The present many-electron theory and computations break away from the half-century-old study of the one-electron atom [6,15–26] and demonstrate the feasibility of obtaining from first principles (FITR's) of polyelectronic states of neutral systems over a broad range of field strengths. The foundations of the theory of the resonances of the LoSurdo-Stark effect can be found in [27] while the implementation (separation into Q and P spaces, each containing physically different wave functions) herein shows how states with closed- or open-shell electronic structures can be treated with economy and accuracy.

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