Quantum-mechanical versus semiclassical calculations of dc-field-induced tunneling rates of Li $1s^2 2s\ ^2S$, $1s^2 2p\ ^2P^o$, and $1s^2 3d\ ^2D$

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(Received 5 October 1998)

The dc-field-induced tunneling rates for Li $1s^2 2s\ ^2S$, $1s^2 2p\ ^2P^o$, and $1s^2 3d\ ^2D$ states were computed from our previously published nonperturbative, many-electron quantum-mechanical theory. The results are compared to those obtained using formulas derived from one-electron semiclassical models. For small values of the field strength, the results exhibit the same behavior. However, quantitative as well as qualitative differences are observed for strong fields. [S1050-2947(99)04103-7]

PACS number(s): 32.60.+i, 31.15.Ar

When an atomic state is subjected to an external dc field, its energy is shifted and broadened, the latter being the result of field-induced tunneling (FIT). This is the LoSurdo-Stark effect. The quasidiscrete spectrum of the *N*-electron Hamiltonian containing the perturbing electric dipole operator consists of quasibound resonances corresponding to the discrete as well as to the resonance states of the free-atom Hamiltonian. The dc-field-induced resonance eigenfunctions have complex eigenvalues and special boundary conditions as a result of the appropriate mixing of bound and scattering basis wave functions [1]. Work from this institute has shown (see Refs. [1–5] and reference therein) how the regularization of these eigenfunctions by the transformation $r \rightarrow \rho = re^{i\theta}$, first proposed by Dykhne and Chaplik [6] in the case of short-range potentials, and the subsequent diagonalization of a complex eigenvalue matrix equation constructed in terms of suitably chosen, state-specific square-integrable *N*-electron, symmetry-adapted configurations of real and complex coordinates, reduce the many-electron problem (*N*-electron atom plus electric field) to systematic computational steps that can be handled in a practical way for arbitrary structures of polyelectronic atoms.

In a recent paper, Fisher, Maron, and Pitaevskii [7] reported applications of the WKB approximation to the calculation of FIT rates (FITR) of Li states (one electron outside a core) and C states (equivalent electrons). As regards the treatment of the many-electron problem through the expressions of Ref. [7], it seems to us that further analysis and computation as well as measurements are needed in order to acquire a good understanding of the meaning and accuracy of the assumptions and approximations used in Ref. [7]. On the other hand, the treatment of pseudo one-electron systems, such as the $1s^2 2s\ ^2S$, $1s^2 2p\ ^2P^o$, and $1s^2 3d\ ^2D$ states examined in Refs. [4,7], via a one-electron expression, is justifiable conceptually in the context of the WKB approach, in which case only the question of quantitative accuracy as a function of field strengths, is raised.

Fisher, Maron, and Pitaevskii [7] compared their Li FITR results with our earlier ones [3,4]. A strong discrepancy, of orders of magnitude, was observed in Li $1s^2 2p\ ^2P^o$ for field strengths (F) below 22 MV/cm and on the order of magnitude of Li $1s^2 2s\ ^2S$ for field strengths above 75 MV/cm. (For the $1s^2 3d\ ^2D$ state, they reported agreement with our

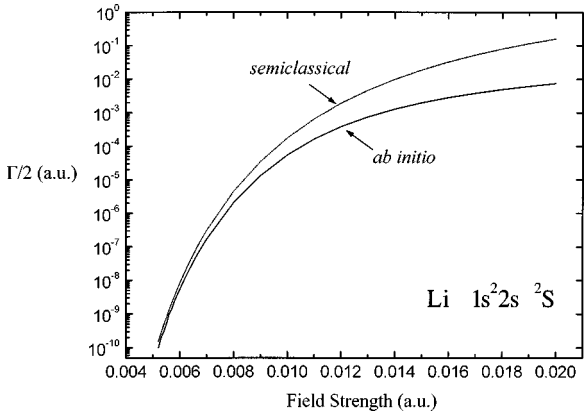

FIG. 1. Field-induced tunneling half-width for Li $1s^2 2s\ ^2S$, calculated from the present *ab initio* theory and from the formula of the WKB approximation.

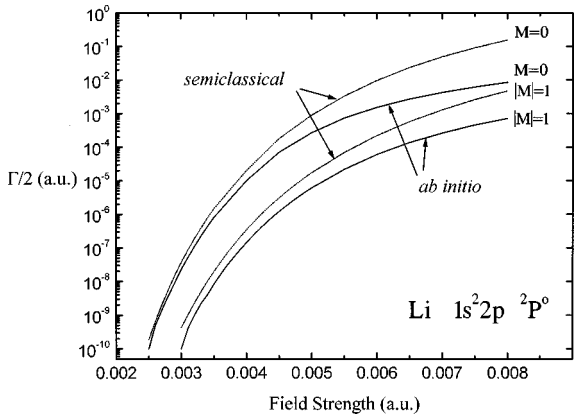

FIG. 2. Field-induced tunneling half-width for Li $1s^2 2p\ ^2P^o$, $M=0$ and Li $1s^2 2p\ ^2P^o$, $|M|=1$ states calculated from the present *ab initio* theory and from the formula of the WKB approximation.

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TABLE I. Field-induced tunneling width for Li $1s^2 2s\ ^2S$ calculated from the present *ab initio* theory and from the semiclassical approach of Ref. [7]. The difference between the two calculations increases with increasing field strength.

F (a.u.)	$\Gamma_{\text{ab initio}}/2$ (a.u.)	$\Gamma_{\text{WKB}}/2$ (a.u.)
0.0010		2.620×10^{-67}
0.0030		3.407×10^{-20}
0.0050		4.786×10^{-11}
0.0051	$<10^{-10}$	8.800×10^{-11}
0.0052	$\sim1.\times10^{-10}$	1.579×10^{-10}
0.0053	$2.\times10^{-10}$	2.770×10^{-10}
0.0054	$3.\times10^{-10}$	4.756×10^{-10}
0.0055	$5.\times10^{-10}$	8.000×10^{-10}
0.0056	1.0×10^{-9}	1.320×10^{-9}
0.0057	1.4×10^{-9}	2.138×10^{-9}
0.0058	2.4×10^{-9}	3.405×10^{-9}
0.0060	5.4×10^{-9}	8.226×10^{-9}
0.0062	1.19×10^{-8}	1.873×10^{-8}
0.0065	3.50×10^{-8}	5.828×10^{-8}
0.0067	6.78×10^{-8}	1.171×10^{-7}
0.0070	1.693×10^{-7}	3.085×10^{-7}
0.0080	2.062×10^{-6}	4.495×10^{-6}
0.0090	1.332×10^{-5}	3.504×10^{-5}
0.0100	5.498×10^{-5}	1.768×10^{-4}
0.0110	1.639×10^{-4}	6.517×10^{-4}
0.0120	3.831×10^{-4}	1.901×10^{-3}
0.0150	1.966×10^{-3}	1.870×10^{-2}
0.0180	4.918×10^{-3}	7.979×10^{-2}
0.0200	7.469×10^{-3}	1.598×10^{-1}

result for $F=4$ MV/cm (Ref. [7], p. 2217). They stated that our ''numerical calculations have been performed by solving the time-dependent Schrödinger equation using a truncated basis of Hartree-Fock (HF) functions,'' and offered an explanation for the discrepancy by attributing it to the insufficiency of the HF functions at large radii (Ref. [7], p. 2217).

In view of these new results and their interpretation, we repeated our quantum-mechanical calculations using larger and better optimized function spaces. (Incidentally, our approach [3,4] does not solve the time-dependent Schrödinger equation, as is stated in Ref. [7]). It turns out that our earlier calculations, which had used slightly smaller and less well-optimized Q (bound states) and P (high-lying Rydberg and scattering states) spaces due to computer power limitations, led to wrongly converged results for small field values in the case of the Li $1s^2 2p\ ^2P^o$ state. The new results, reported below, agree with the WKB results at small-F values. However, the reason for the previous discrepancy, which is an object of discussion in Ref. [7], is not related to the hypothesized inaccuracy of the HF radials at large distances. Rather, the reason is, simply, that the set of virtual orbitals of the P space was not large and flexible enough. We point out that, because of the (near) exponential dependence of the FITR on F, as F becomes smaller the FITR acquires very small values very rapidly. As with every theory of a phenom-

TABLE II. (a) As in Table I for Li $1s^2 2p\ ^2P^0, M=0$. The differences between the *ab initio* and the WKB calculations are comparable to those of Table I. (b) As in (a) for Li $1s^2 p\ ^2P^0$, $|M|=1$.

F (a.u.)	$\Gamma_{\text{ab initio}}/2$ (a.u.)	$\Gamma_{\text{WKB}}/2$ (a.u.)
	(a)	
0.0005		7.695×10^{-69}
0.0015		7.245×10^{-20}
0.0020	$<10^{-10}$	6.160×10^{-14}
0.0025	$\sim1.\times10^{-10}$	1.917×10^{-10}
0.0026	$5.\times10^{-10}$	6.514×10^{-10}
0.0027	1.4×10^{-9}	2.013×10^{-9}
0.0028	3.7×10^{-9}	5.717×10^{-9}
0.0029	9.1×10^{-9}	1.505×10^{-8}
0.0030	2.27×10^{-8}	3.703×10^{-8}
0.0031	5.13×10^{-8}	8.569×10^{-8}
0.0032	1.101×10^{-7}	1.876×10^{-7}
0.0033	2.243×10^{-7}	3.906×10^{-7}
0.0034	4.357×10^{-7}	7.768×10^{-7}
0.0035	8.110×10^{-7}	1.482×10^{-6}
0.0040	1.061×10^{-5}	2.236×10^{-5}
0.0045	6.897×10^{-5}	1.772×10^{-4}
0.0050	2.692×10^{-4}	8.984×10^{-4}
0.0055	7.267×10^{-4}	3.301×10^{-3}
0.0060	1.520×10^{-3}	9.548×10^{-3}
0.0065	2.678×10^{-3}	2.301×10^{-2}
0.0070	4.204×10^{-3}	4.814×10^{-2}
0.0075	6.102×10^{-3}	8.998×10^{-2}
0.0080	8.383×10^{-3}	1.536×10^{-1}
	(b)	
0.0005		1.474×10^{-71}
0.0015		4.164×10^{-22}
0.0020		4.720×10^{-16}
0.0025	$<10^{-10}$	1.837×10^{-12}
0.0030	$\sim1.\times10^{-10}$	4.257×10^{-10}
0.0031	$4.\times10^{-10}$	1.018×10^{-9}
0.0032	1.0×10^{-9}	2.300×10^{-9}
0.0033	2.2×10^{-9}	4.939×10^{-9}
0.0035	8.3×10^{-9}	1.987×10^{-8}
0.0037	2.94×10^{-8}	6.837×10^{-8}
0.0040	1.422×10^{-7}	3.427×10^{-7}
0.0042	3.614×10^{-7}	8.782×10^{-7}
0.0045	1.199×10^{-6}	3.056×10^{-6}
0.0050	6.108×10^{-6}	1.721×10^{-5}
0.0055	2.181×10^{-5}	6.956×10^{-5}
0.0060	5.994×10^{-5}	2.195×10^{-4}
0.0065	1.353×10^{-4}	5.732×10^{-4}
0.0070	2.625×10^{-4}	1.291×10^{-3}
0.0075	4.524×10^{-4}	2.586×10^{-3}
0.0080	7.109×10^{-4}	4.710×10^{-3}

TABLE III. Quantum-mechanical and WKB field-induced energy widths for the ground state of the hydrogen atom. All values are in a.u.

F	$\Gamma_{\text{this work}}$	Γ' [10]	Γ_{WKB}
0.03	1.120×10^{-8}	1.118×10^{-8}	1.489×10^{-8}
0.04	1.949×10^{-6}	1.944×10^{-6}	2.889×10^{-6}
0.05	3.858×10^{-5}	3.85×10^{-5}	6.478×10^{-5}
0.10	7.270×10^{-3}	7.27×10^{-3}	2.545×10^{-2}
0.15	3.001×10^{-2}	2.98×10^{-2}	1.566×10^{-1}
0.20	6.059×10^{-2}	6.2×10^{-2}	3.567×10^{-1}

enon produced by weak perturbation, the small-F regime is expected to be well accounted for by a formula involving only one matrix element of the operator, coupling initial and final states. On the other hand, the theory of Refs. [3,4] is nonperturbative, involving a multitude of couplings and searching for an accurate imaginary part of a complex eigenvalue. It follows that the numerical requirements on function spaces, matrix elements accuracies, and parameter optimization become rather stringent when computing very small FITRs by the all orders nonperturbative approach [1–5].

The present calculation used a Q space which contained numerical HF wave functions for all states $1s^2nl\ ^2L$, $n=2,\ldots,5$, $l=0,\ldots,n-1$. In order to account for core polarization effects on the dipole matrix elements, we employed the replacement [8,9]

$$\vec{r}\rightarrow\vec{r}_{\text{eff}}=\vec{r}\left\{1-\frac{\alpha_c}{r^3}w_3(r/r_c)\right\}, \tag{1}$$

where α_c is the polarizability of the core $1s^2$ of Li^+ ($\alpha_c=0.1883$ a.u.), and r_c is an effective core radius (1.426 a.u.). $w_3(x)=1-e^{-x^3}$ is a cutoff function.

The P space contained configurations where the εl orbitals have $l\leqslant7$. We used ten complex Slater-type orbitals (STO's) with $l=0$, ten STO's with $l=1$, ten STO's with $l=2$, eight STO's with $l=3$, six STO's with $l=4$, four STO's with $l=5$, four STO's with $l=6$, and two STO's with $l=7$. The form of each complex STO is $r^{n+l+1}e^{-\beta re^{-i\theta}}$. The optimal value of β (common to all STO's) was 0.25, for which the complex eigenvalue was stable for a wide range of θ values.

The results for the $1s^22s\ ^2S$ and $1s^22p\ ^2P^o$, $M=0$ and $1s^22p\ ^2P^o$, $|M|=1$ states of Li are presented in Tables I and II and in Figs. 1 and 2. The results of the WKB formula used in Ref. [7] are also presented in the same tables and figures. Although the trends of the variation of the width $\Gamma(F)$ as a function of the field intensity, F, are the same, as the field strength increases, the disagreement between the quantum-mechanical and WKB values grows. We point out that this behavior also characterizes the purely hydrogenic potential. This is shown in Table III, where we present *ab initio* results produced by us [1] and also by Ivanov [10] for the FITR of H $1s$, together with the WKB result of the simple formula [11]

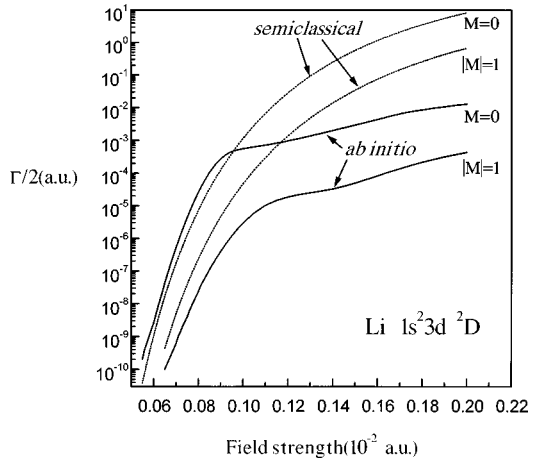

FIG. 3. Field-induced tunneling half-width for Li $1s^23d\ ^2D$, $M=0$ and Li $1s^23d\ ^2D$, $|M|=1$ states calculated from the present *ab initio* theory and from the formula of the WKB approximation.

$$\Gamma_H(F)=\frac{4}{F}e^{-2/3F}. \tag{2}$$

The trends for the case of the $1s^23d\ ^2D$ $|M|=0$ and 1, states show a greater discrepancy for large fields. (The results produced here are almost identical with those given in Ref. [4]). Figure 3 presents our results for the $1s^23d\ ^2D$, $M=0$ and $1s^23d\ ^2D$, $|M|=1$ states, together with the results of the WKB formula. Fisher, Maron, and Pitaevskii did not give values for the parameters in this case, and so we used the formulae proposed by Ilkov, Decker, and Chin [12]. The observed difference between the *ab initio* theory and the semiclassical formula is due to the mixing of the states of different L which becomes significant for strong fields. Such mixings cannot be accounted for by the WKB formula. The positive-energy shift for these two states causes their strong interaction with higher-lying Rydberg states and the concomitant ''anomaly'' in the $\Gamma(F)$. Therefore, in cases of such wave-function mixings, (e.g., in excited states), the one-electron-based semiclassical formulas are liable to produce even qualitatively erroneous results for $\Gamma(F)$ as a function of F.

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