# Green-function approach to the theory of tunneling ionization

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# Green's function approach to the theory of tunneling ionization

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## Abstract

We solve the problem of tunneling ionization of a multielectron atom in a static electric field by using the Green's function for the Stark-Coulomb problem. This allows us to incorporate the outgoing-wave boundary conditions at infinity. The interaction of the active electron with the atomic residue is described either by a model potential or by the $l$-dependent pseudopotential which prevents virtual transitions to orbitals occupied by inner electrons. The method works well in the broad range of electric fields including the region above the classical ionization threshold (the barrier-suppression region). Calculations of ionization of Ar demonstrate a noticeable difference between the model potential approach and the pseudopotential approach, but both sets of results agree with experimental data.

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## I. INTRODUCTION

Quantum tunneling is one of fundamental problems in physics. In the area of atomic and molecular physics tunneling is usually associated with ionization of atoms and molecules in external electric fields. Tunneling is the first stage of processes which involve rescattering, such as two-electron nonsequential ionization [1] and high-order harmonic generation [2].

Although in general we are interested in tunneling in alternating (ac) fields, in the limit of small frequencies, or high intensities, when the Keldysh parameter [3] is small, the problem can be described in terms of ionization in a static (dc) field [4]. For ionization of the hydrogen atom, this problem can be solved with an arbitrary accuracy [5] due to separability of the corresponding Hamiltonian in parabolic coordinates. For many-electron atoms the situation is different. Even in the approximation of one active electron (occupying the highest atomic orbital), the exact formulation of the problem presents big challenges. These challenges are usually associated with incorporation of the proper (outgoing-wave) boundary conditions at infinity. Most of the methods used so far for tunneling ionization are based on additional approximations. The most popular among them is the PPT theory based on the semiclassical work of Smirnov and Chibisov [6] and Perelomov *et al* [4]. Later this theory was used in Ref. [7], and has been often called by the acronym ADK since then. This theory assumes that the region of atomic field dominance and electric field dominance do not overlap. Apparently this assumption breaks down for higher fields. Indeed, calculations with more accurate methods show that whereas ADK equation works well for weak fields, it overestimates the actual ionization rate by a factor of 2 to 3 near the classical ionization threshold. At fields above this threshold, called the barrier-suppression region, the ADK theory is not supposed to work at all. Nevertheless, many authors used the ADK equation in this region as a suitable extrapolation formula. Tong and Lin [8] suggested an empirical modification of this formula which introduces an exponential factor suppressing the difference between the ADK formula and exact calculations as the field grows. The problem with this extrapolation is that the suppression factor decreases with the electric field $F$ whereas theoretical considerations [9, 10] suggest that in the barrier-suppression region the ionization rate should grow linearly with $F$. Another improvement of the ADK theory based on the partial Fourier-transform approach was recently developed by Murray *et al* [11].

A more accurate method developed for electron ionization in the presence of an ac field is the explicit numerical solution of the time-dependent Schrödinger equation using a finite-difference representation for the wave function [12]. For multielectron atoms model potentials, representing the effective field due to the nucleus and other electrons, are introduced. The Schrödinger equation is solved with the outgoing-wave boundary conditions. However, these conditions are difficult to implement computationally, particularly in the case of a static field [13]. An additional complication is that the resulting Hamiltonian is non-self-adjoint [14].

Another method widely used in dc and ac ionization problems is the complex scaling [15]. However, its implementation also contains numerical difficulties as there is no complete mathematical theory for the application of complex scaling to time-dependent problems [14]. Although in the present paper we are dealing with the problem of the static-field ionization, its results can be used in the adiabatic theory of ionization in ac fields [16, 17].

Several other theories are based on semiclassical propagation of the electron wave function from the inner region dominated by the atomic field to the outer region dominated by the electric field. This can be accomplished, for example, by the complex-time method [18–20]. This method, due to its semiclassical character, fails close to the classical ionization threshold.

Apparently we need an one-electron theory of ionization in a static field which can give the answer with an arbitrary accuracy, similar to that developed for the hydrogen atom [5, 21]. Recently such a theory was developed by Batishchev *et al* [22]. It is based on the solution of equations involving nonadiabatic coupling between parabolic channels caused by deviation of the atomic potential from a pure Coulomb potential. The authors have calculated ionization rates and the transverse momentum distribution of ionized electrons for rare-gas atoms.

In the present paper we develop an alternative method incorporating the correct boundary condition by using the Green's function for the electron in the superposition of the Coulomb and electric fields. A similar method was used before for calculations of the decay rate of negative ions in electric fields [23] and for calculations of molecular Rydberg states [24, 25]. We calculate the ionization rate for Ar atoms in a wide range of electric fields and compare the results with the ADK theory and its empirical modification [8]. Atomic units (a.u.) are used throughout the paper.

# II. THEORY

## A. Basic equations

We approximate the problem by the one-electron Hamiltonian with the potential [26]

$$V(\mathbf{r}) = U(\mathbf{r}) + Fz, \tag{1}$$

where $F$ is the force on the electron due to the external field (directed along the negative $z$ axis), and $U(\mathbf{r})$ is a one-electron potential describing electron interaction with the rest of the atom. Generally it is a nonlocal operator whose form is [27]

$$U(\mathbf{r}) = \sum_{lm} |Y_{lm}\rangle U_l(r) \langle Y_{lm}|, \tag{2}$$

where $U_l(r)$ is a partial potential for a specific value of the angular momentum $l$.

We divide now the whole space into two regions separated by a spherical surface of radius $r_0$ that should be chosen such that at $r > r_0$ the equation

$$U(\mathbf{r}) = -\frac{Z}{r}$$

is valid with a good accuracy. Here $Z$ is the charge of the ion residue. In particular, for ionization of neutral atoms $Z = 1$.

At $r < r_0$ we seek the solution of the Schrödinger equation in the form

$$\psi_m(\mathbf{r}) = \sum_{ll'} A^m_{l'} \frac{\chi^m_{ll'}(r)}{r} Y_{lm}(\hat{\mathbf{r}}), \tag{3}$$

where $m$ is the conserved projection of the angular momentum on the $z$ axis. (To simplify notations from now on we drop index $m$ from $\psi$, $\chi$ and $A$). In the radial function $\chi_{ll'}(r)$ the first index lists different channels, and the second different solutions. The unknown coefficients $A_{l'}$ are determined from the boundary conditions at $r \to \infty$.

The radial functions $\chi_{ll'}(r)$ satisfy the following set of coupled equations

$$\left[\frac{d^2}{dr^2} + 2E - \frac{l'(l'+1)}{r^2} - 2U_{l'}(r)\right] \chi_{l'l}(r) - 2F \sum_{l''} (z)_{l'l''} \chi_{l''l}(r) = 0 \tag{4}$$

which are solved by numerical integration. The function $\psi(\mathbf{r})$ should be matched with the external solution satisfying the outgoing-wave boundary condition. This can be achieved by writing a Kirchhoff-type integral equation [23]

$$\int [G(\mathbf{r},\mathbf{r}')\nabla_r \psi(\mathbf{r}) - \psi(\mathbf{r}) \nabla_r G(\mathbf{r},\mathbf{r}')] d\hat{\mathbf{r}} = 0, \tag{5}$$

where $r' < r$, $G(\mathbf{r}, \mathbf{r}')$ is the Green's function for electron motion in the superposition of the Coulomb field and the external field (or the Stark Green's function), corresponding to the outgoing-wave boundary condition, and the integration is performed over the surface of the sphere of radius $r$. Alternatively, if $r' > r$, we have

$$\int [G(\mathbf{r}, \mathbf{r}')\nabla_r \psi(\mathbf{r}) - \psi(\mathbf{r})\nabla_r G(\mathbf{r}, \mathbf{r}')] d\hat{\mathbf{r}} = 2\psi(\mathbf{r}'). \tag{6}$$

This representation can be used for calculation of the electron flux distribution in the position and momentum space at $r' \gg r_0$.

Projecting Eq. (5) on the spherical harmonic $Y_{l'm}(\hat{\mathbf{r}}')$ and taking the limit $r = r_0$, $r' \to r_0 - 0$, we obtain a system of homogeneous algebraic equations for the coefficients $A_l$

$$\sum_l A_l M_{l''l} = 0 \tag{7}$$

where

$$M_{l''l} = \sum_{l'} \left[ \langle l''m|G|l'm\rangle \frac{du_{l'l}}{dr} - \langle l''m|\frac{\partial G}{\partial r}|l'm\rangle u_{l'l} \right] \tag{8}$$

where $r = r_0$, $r' = r_0 - 0$, $u_{l'l}(r) = \chi_{l'l}(r)/r$. The eigenenergy $E$ is found as a solution of the equation

$$\det M_{l''l} = 0. \tag{9}$$

Because of the outgoing-wave boundary condition, the energy $E$ is complex and is represented in the form

$$E = E_0 + \Delta - i\frac{\Gamma}{2} \tag{10}$$

where $E_0$ is the unperturbed energy of the stationary state, $\Delta$ is the energy shift, and $\Gamma$ is the decay width which is the same as the ionization rate in a.u. At weak fields

$$\Delta = -\frac{1}{2}\alpha F^2 \tag{11}$$

where $\alpha$ is the dipole polarizability of the atom.

Like in any theory requiring matching of the internal and external wavefunctions, the matching radius $r_0$ enters the calculations, but the physical results should not depend on it. In our case the matching radius should be such that at $r > r_0$ the atomic potential $U(r)$ is pure Coulombic. On the other hand, $r_0$ should not be too large, otherwise the expansion (3) is converging too slowly. In practical calculations for Ar we varied $r_0$ between 4.5 and 7 a.u. without noticeable change of the result for $\Gamma$.

### B. Green's function

In the parabolic coordinates $\xi = r + z$, $\eta = r - z$, $\phi = \tan^{-1}(y/x)$ the Stark Green's function [28] has the form

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi} \sum_{\beta m} \frac{g_\beta^Z(\eta, \eta')}{(\eta\eta')^{1/2}} \frac{u_\beta(\xi) u_\beta(\xi')}{(\xi\xi')^{1/2}} e^{im(\phi-\phi')} \tag{12}$$

where $\beta$, $u_\beta(\xi)$ are eigenvalues and eigenfunctions of the equation

$$\left( \frac{d^2}{d\xi^2} + \frac{1-m^2}{4\xi^2} + \frac{\beta}{\xi} - \frac{F}{4}\xi + \frac{E}{2} \right) u_\beta(\xi) = 0, \tag{13}$$

and $g_\beta^Z(\eta, \eta')$ is the Green's function for the motion along the $\eta$ coordinate satisfying the equation

$$\frac{d^2 g_\beta^Z(\eta)}{d\eta^2} + \left( \frac{1-m^2}{4\eta^2} + \frac{Z-\beta}{\eta} + \frac{F}{4}\eta + \frac{E}{2} \right) g_\beta^Z(\eta) = 2\delta(\eta - \eta'). \tag{14}$$

$g_\beta^Z(\eta, \eta')$ can be calculated as

$$g_\beta^Z(\eta, \eta') = \frac{2 v_\beta^+(\eta_>) v_\beta^r(\eta_<)}{W(v_\beta^r, v_\beta^+)} \tag{15}$$

where $\eta_<$, $\eta_>$ are lesser or greater of $\eta$, $\eta'$, $v_\beta^+(\eta)$ is the solution of the corresponding homogeneous equation satisfying the outgoing-wave boundary condition, $v_\beta^r(\eta)$ is the solution regular at the origin, and $W(v_\beta^r, v_\beta^+)$ is the constant Wronskian of these two solutions. The function $v_\beta^+(\eta)$ at $\eta \to \infty$ behaves as

$$v_\beta^+(\eta) \sim \mathrm{Bi}(-x) + i\mathrm{Ai}(-x)$$

where

$$x = \left( \eta + \frac{2E}{F} \right) \left( \frac{F}{4} \right)^{1/3}$$

and Ai, Bi are standard regular and irregular Airy functions. This form of $v_\beta^+(\eta)$ guarantees the outgoing-wave (or Siegert) boundary condition.

Because of the invariance of the Eqs. (13), (14) under transformation $m \to -m$, the sum in Eq. (12) can be limited to $m \geq 0$ by the replacement

$$\exp[im(\phi - \phi')] \to (2 - \delta_{m0}) \cos[m(\phi - \phi')].$$

However, even after this reduction, the sum in Eq. (12) converges slowly, therefore we use the closure procedure in the form

$$G(\mathbf{r}, \mathbf{r}') = G^{(0)}(\mathbf{r}, \mathbf{r}') + \Delta G(\mathbf{r}, \mathbf{r}') \tag{16}$$

where $G^{(0)}(\mathbf{r},\mathbf{r}')$ is the Green's function without inclusion of the Coulomb field, and $\Delta G(\mathbf{r},\mathbf{r}')$ is a correction that can be written as

$$\Delta G(\mathbf{r},\mathbf{r}') = \frac{1}{2\pi}\sum_{\beta m\geq 0} \frac{g^Z_\beta(\eta,\eta') - g^0_\beta(\eta,\eta')}{(\eta\eta')^{1/2}} \frac{u(\xi)u(\xi')}{(\xi\xi')^{1/2}}(2-\delta_{m0})\cos[m(\phi-\phi')]. \tag{17}$$

This sum converges very rapidly, and for most fields of our interest one term is sufficient. The Green's function $G^{(0)}(\mathbf{r},\mathbf{r}')$ is known in a closed analytical form [29]

$$G^{(0)}(\mathbf{r},\mathbf{r}') = -\frac{1}{2|\mathbf{r}-\mathbf{r}'|}(f_1 f_2' - f_1' f_2) \tag{18}$$

where $f_1$, $f_2$ are Airy functions defined as

$$f_1 = \mathrm{Ai}(\zeta_0 - \zeta_1) \qquad f_2 = \mathrm{Bi}(\zeta_0-\zeta_2) + i\mathrm{Ai}(\zeta_0-\zeta_2) \tag{19}$$

$$\zeta_0 = -2E/(2F)^{2/3} \qquad \zeta_{2,1} = \frac{1}{2}(2F)^{1/3}(z+z' \pm |\mathbf{r}-\mathbf{r}'|) \tag{20}$$

and the primed symbols in Eq. (18) indicate derivatives with respect to the arguments of the Airy functions. Again, like in Eq. (15) the choice of the specific Airy function for $f_2$ guarantees the outgoing-wave boundary conditions.

Since both $G$ and $G^{(0)}$ are singular at $\mathbf{r}'\to\mathbf{r}$, we introduce the regular Green's function $G_r$

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{2\pi|\mathbf{r}-\mathbf{r}'|} + G_r(\mathbf{r},\mathbf{r}'). \tag{21}$$

$G_r$ can be calculated as

$$G_r(\mathbf{r},\mathbf{r}') = G_r^{(0)}(\mathbf{r},\mathbf{r}') + \Delta G(\mathbf{r},\mathbf{r}') \tag{22}$$

where $\Delta G$ is given by Eq. (17).

### C. Final equations

After substitution of Eqs. (21), (22) into Eq. (8), all singular terms can be evaluated analytically. Expanding the $1/|\mathbf{r}-\mathbf{r}'|$ term in spherical harmonics, we obtain for $r=r'$

$$\left\langle l'm \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| lm \right\rangle = \frac{4\pi}{(2l+1)r}\delta_{ll'}$$

and

$$\left\langle l'm \left| \frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| lm \right\rangle = -\frac{4\pi(l+1)}{(2l+1)r^2}\delta_{ll'}.$$

The required derivative of the Green's function $G^{(0)}(\mathbf{r},\mathbf{r}')$ can be also obtained in an analytical form. Writing

$$\frac{\partial}{\partial r}G^{(0)}(\mathbf{r},\mathbf{r}') = \frac{1}{2}\left[s(\mathbf{r},\mathbf{r}') + \frac{1}{\pi}\right]\frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2|\mathbf{r}-\mathbf{r}'|}\frac{\partial}{\partial r}s(\mathbf{r},\mathbf{r}')$$

where

$$s(\mathbf{r},\mathbf{r}') = -f_1 f_2' + f_1' f_2,$$

as defined in Eqs. (18)-(20), we find first

$$\frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|} = -\frac{1}{2r|\mathbf{r}-\mathbf{r}'|}, \qquad r = r'.$$

To find the derivative of $s(\mathbf{r},\mathbf{r}')$, we use the equations

$$f_1'' = (\zeta_0 - \zeta_1)f_1, \qquad f_2'' = (\zeta_0 - \zeta_2)f_2,$$

following from the Airy equation, and

$$\frac{\partial}{\partial r}(\zeta_2 + \zeta_1) = (2F)^{1/3}\cos\theta, \qquad \frac{\partial}{\partial r}(\zeta_2 - \zeta_1) = (2F)^{1/3}\left(\frac{1-\cos\theta_{12}}{2}\right)^{1/2}$$

where $\theta_{12}$ is the angle between $\mathbf{r}$ and $\mathbf{r}'$.

Finally

$$\frac{\partial}{\partial r}(f_1' f_2 - f_1 f_2') = (2F)^{1/3}\left(\frac{1-\cos\theta_{12}}{2}\right)^{1/2} h(\mathbf{r},\mathbf{r}')$$

where

$$h(\mathbf{r},\mathbf{r}') = \frac{(2F)^{1/3}}{4r}[-f_1' f_2' + \zeta_0 f_1 f_2 - \frac{1}{2}(2F)^{1/3} r(3\cos\theta + \cos\theta')f_1 f_2], \tag{23}$$

and we obtain the following equation for the matrix $M_{l'l}$ convenient for calculations

$$rM_{l'l} = \sum_{l''}\left\langle l'm\left|\frac{d\chi_{l''l}}{dr}(G_r^{(0)} + \Delta G) - \chi_{l''l}\left[\frac{1}{2r}G_r^{(0)} + h + \frac{1}{r}\Delta G + \frac{\partial \Delta G}{\partial r}\right]\right| l''m\right\rangle \tag{24}$$
$$+\frac{1}{\pi r(2l'+1)}\left[\frac{d\chi_{l'l}}{dr} + \frac{l'}{r}\chi_{l'l}\right]$$

where all quantities are calculated at $r = r' = r_0$.

### D. Analytical continuation

To solve Eq. (9) we need to calculate the $M$ matrix for complex energies. This means evaluation of the solution set $\chi_{ll'}$ and the Green's function for complex $E$. To avoid related complications, as a first step towards solution of the problem, we use the method of analytical continuation. That is, we calculate det$M$ for several real energies close to the unperturbed energy $E_0$ and approximate the results by a polynomial

$$\det M = \sum_n c_n (E - E_0)^n. \tag{25}$$

The complex energy is obtained as an appropriate zero of this polynomial. We first tried this method for the zero-range potential problem [30] and the hydrogen-atom problem. In the former case we obtained an excellent agreement between the method of analytical continuation and the direct solution of the corresponding transcendental equation in the complex plane. In the hydrogen atom case we obtained a very good agreement with the results of Damburg and Kolosov [5, 21] for the ground and excited states.

Calculations for the Ar atom showed that the procedure is very stable below the field $F_c$ corresponding to the classical ionization limit. In this region even the linear approximation for det$M$ produces correct results. However, the procedure becomes unstable for higher fields and requires averaging over several calculations involving different approximations for det$M$. With such an average we are able to perform calculations for ionization of the Ar atom (ionization potential 0.579 a.u., $F_c = 0.084$ a.u.) for fields up to 0.2 a.u. For stronger fields more direct methods based on calculation of the solution set $\chi_{ll'}(r)$ and the Green's function for complex energies are necessary.

### E. Atomic potentials

Since many calculations of strong-field ionization incorporate the single active electron model, it is customary to introduce a model central-field potential $U(r)$ representing the field of the nucleus and the effective field of the other electrons [31]. At small distances this potential behaves as $-Z_N/r$, where $Z_N$ is the nuclear charge. Tong and Lin [8], using the density-functional theory for rare-gas atoms, obtained effective potentials which were used by other authors [32] for laser ionization calculations. Model potentials were also used for calculation of static-field ionization [22]. However, this type of the potential does not take into account the Pauli exclusion principle preventing the active electron from transitions to lower states occupied by inner electrons. As a result, in the presence of an external field, the electron can be involved in virtual transitions to lower states. This reduces the dipole polarizability of the atom and can make it even negative leading to the wrong sign of the Stark shift according to Eq. (11).

To avoid such a spurious effect, we need to use a pseudopotential containing a repulsive core which prevents formation of states with energies lower than that of the highest occupied orbital. In the case of Ar, for example, the lowest state generated by the pseudopotential should have the $p$ symmetry and no nodes, in contrast to the actual $3p$ orbital having one node. The excited state should have the $s$ symmetry, also with no nodes, in contrast to the $4s$ orbital with three nodes. Obviously such a potential should be dependent on the angular momentum $l$ and can be represented in the form (2). The repulsive core due to the Pauli exclusion principle can be modelled as [33, 34]

$$U_{rep}(r) = \frac{B}{r^n} e^{-\beta r}$$

where $n$ is an integer, and $B$, $\beta$ fit parameters. In the present paper we have chosen the following form of the partial potential $U_l(r)$

$$U_l(r) = -\frac{Z_n}{r} e^{-\alpha r} + \frac{B}{r^3} e^{-\beta * r} - \frac{Z}{r}. \tag{26}$$

The parameter $Z_n$ not necessarily equals the nuclear charge, since at low energies the electron does not penetrate deeply into the atomic core. Therefore all the parameters in Eq. (26), except $Z$, are considered as $l$-dependent fitting parameters which should reproduce the main features of the corresponding bound state: binding energy, expectation value of $r$, $\langle r \rangle$, and the shape of the atomic orbital outside the atomic core.

TABLE I: Pseudopotential parameters for Ar. Expectation values of $r$ for the $4s$ and $3p$ orbitals are calculated with the present pseudopotential and the model potential of Tong and Lin [8].

| $l$ | $Z_n$ | $\alpha$ | $B$ | $\beta$ | $\langle r \rangle$ | $\langle r \rangle$ (model) |
|---|---|---|---|---|---|---|
| 0 | 2.3 | 2.2 | 5.215 | 0.50 | 4.940 | 4.977 |
| 1 | 10.0 | 1.2 | 1.709 | 0.50 | 1.536 | 1.665 |
| $\geq 2$ | 2.3 | 2.2 | 0. | – | – | – |

Table I presents the list of parameters and expectation values of $\langle r \rangle$ for the $4s$ and $3p$ orbitals calculated with the present pseudopotential and the model potential of Tong and Lin [8]. At $l \geq 2$ the exact form of the potential is not important because of the dominance of the centrifugal barrier, therefore we use the same parameters for all $l$ exceeding 1.

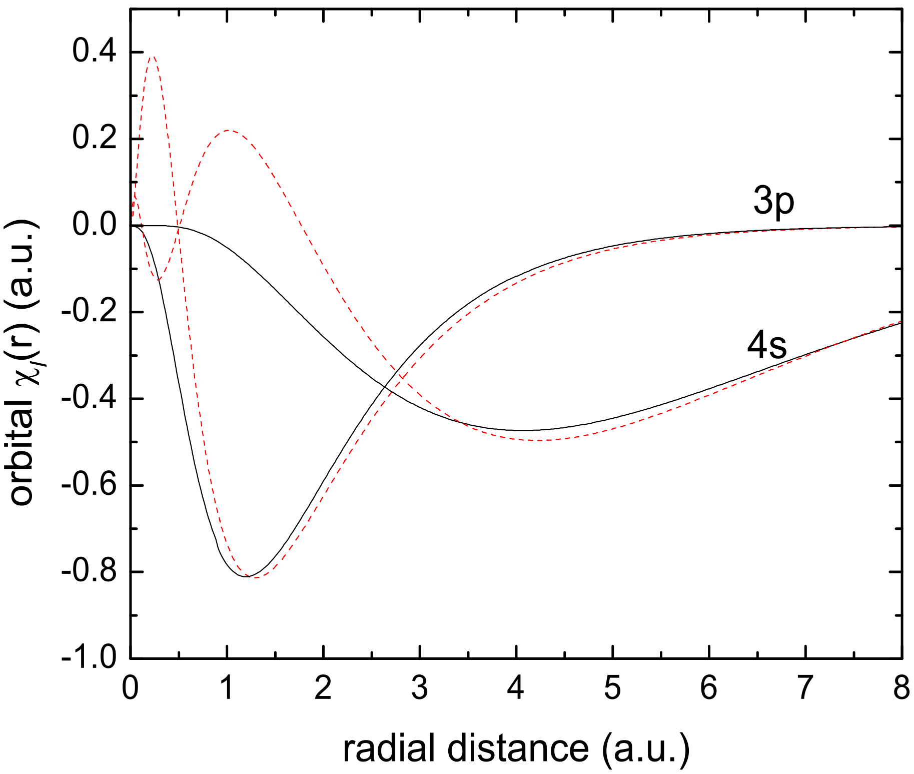

FIG. 1: (Color online). Ar $3p$ and $4s$ orbitals. Black solid curves: pseudoorbitals. Red dashed curves: orbitals calculated with the model potential of Tong and Lin [8].

In Fig. 1 we present $3p$ and $4s$ orbitals $\chi(r) = ru(r)$ for Ar calculated for the model potential of Tong and Lin [8] and compare them with $p$ and $s$ pseudo-orbitals. The node of the $3p$ orbital is located at the distance $r = 0.50$ a.u. from the nucleus and should not influence the tunneling process. However, the different shapes of the $s$ orbitals and the existence of lower $s$ (mainly $3s$) orbitals in the model potential make the static polarizability and the Stark shift quite different. Calculations show that the Ar polarizability calculated with the model potential is 1.95 a.u., whereas that calculated with the pseudopotential is about 6.5 a.u. However, even the latter is substantially lower than the actual polarizability of Ar, 11.1 a.u. The disagreement is apparently due to the one active electron approximation used in the present calculations.

### F. Asymptotic coefficient

An important characteristic of an atomic orbital is the coefficient $C_l$ appearing in the asymptotic behavior of the orbital

$$u_l(r) \sim C_l r^{Z/\kappa-1} e^{-\kappa r}, \quad \kappa = (-2E)^{1/2}. \tag{27}$$

In particular the ADK ionization rate is proportional to $C_l^2$. This asymptotic value is actually achieved at very large distances well beyond the core of the atom. To demonstrate this, in Fig. 2 we plot the quantity

$$C_1(r) = u_l(r) r^{-Z/\kappa+1} e^{\kappa r} \tag{28}$$

as a function of $r$ for two types of orbitals, one obtained from the model potential, and the other from the pseudopotential. Both approach their asymptotic values very slowly and don't reach them even at $r = 14$ a.u. This creates a problem in application of the ADK theory. Indeed, the original tunneling theory [6] assumes that the asymptotic behavior (27) is reached in the region where the electric field can still be neglected as compared to the Coulomb field. Apparently such an assumption can be made only for distances $r < (Z/F)^{1/2}$, or $r < 5$ a.u. if $Z = 1$, $F = 0.04$ a.u. To fix this deficiency one may suggest that $C_l(r)$ should be taken not at $r = \infty$ but at $r = (Z/F)^{1/2}$. However, this suggests that $C_l$ grows with $F$ that contradicts the semiempirical extrapolation formula of Tong and Lin [8].

In what follows, when comparing our results with the ADK theory, we will be using the value of the coefficient $C_1$ for Ar following from the model potential of Tong and Lin [8], $C_1 = 2.44$ a.u., but because of the aforementioned inconsistency, it is not clear what is the accuracy of the obtained ADK rate.

## III. AR IONIZATION RATES

In Fig. 3 we present the ionization rate for the $3p_0$ orbital of Ar as a function of the electric field in the field range close to the classical ionization threshold, $F_c = 0.084$ a.u., and above it up to $F = 0.2$ a.u. The ionization rate for the $3p_1$ orbital is significantly smaller and is not included in the present calculation. To simplify the comparison with other theories, we do not multiply the rate by the occupation number 2 for the $3p_0$ orbital, although this is actually necessary to obtain the correct magnitude of the ionization rate

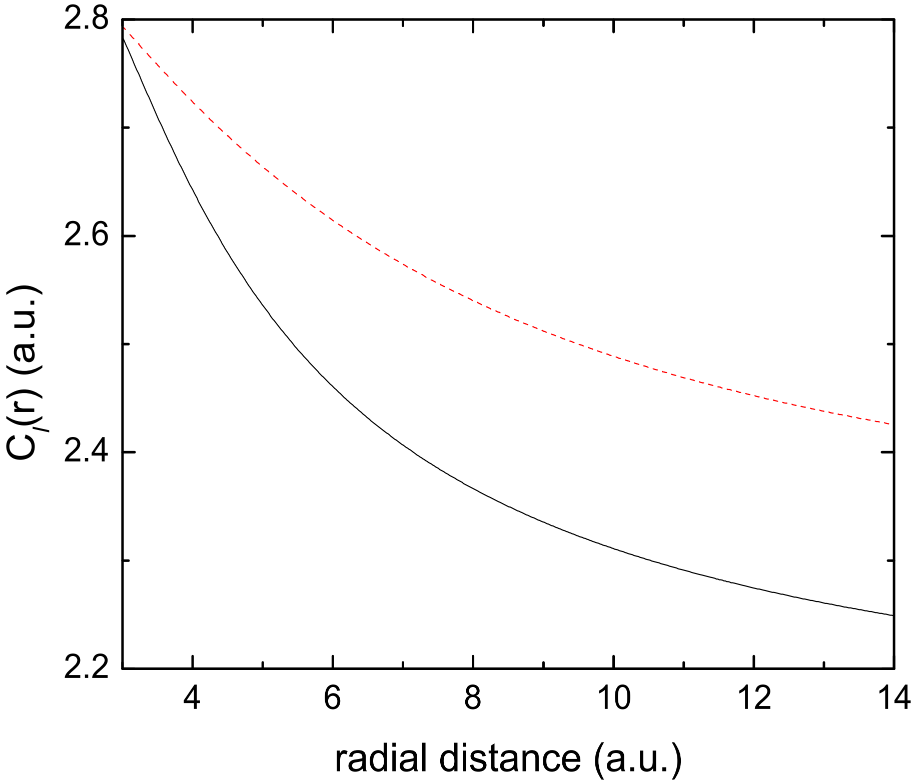

FIG. 2: (Color online). The function $C_l(r)$, Eq. (28), for the Ar $3p$ orbital. Black solid curves: pseudopotential calculation. Red dashed curves: model potential calculation.

[35]. For comparison with the ADK formula we use its modification proposed by Damburg and Kolosov [5] who suggested to use the Stark-shifted energy when calculating the decay width by the asymptotic formula. Since for the ground state the Stark shift is negative, this modification reduces the ionization rate and improves agreement with more accurate calculations. When calculating the Stark shift we used Eq. (11) with the actual polarizability of Ar, $\alpha = 11.1$ a.u., although the present calculations give a lower effective polarizability, as discussed in the previous section. In addition, at high fields the perturbation theory for the Stark shift is not supposed to work. Still, the Damburg-Kolosov modification overestimates the ionization rate by a factor of 5 at $F = 0.16$ a.u. whereas the original ADK formula overestimates the ionization rate by a factor of 8.

Results of the calculations with the model potential of Tong and Lin are very close to

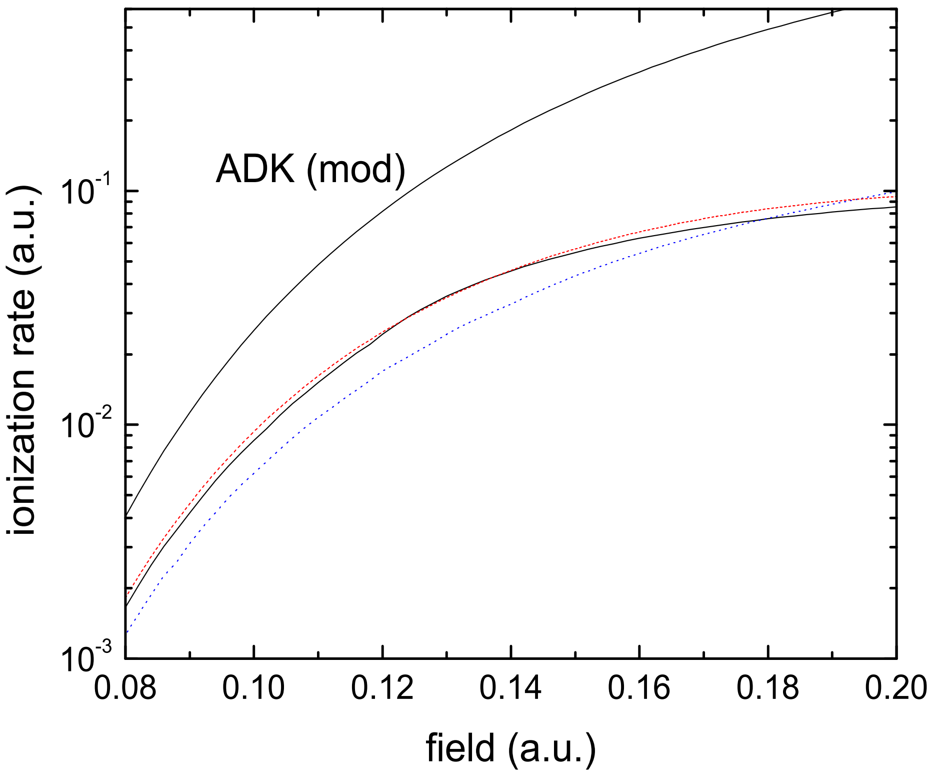

FIG. 3: (Color online). Ionization rates for the $3p_0$ orbital of Ar. Lower black curve: calculation with the model potential of Tong and Lin [8]. Blue dotted curve: calculation with the pseudopotential. Red dashed curve: semiempirical formula of Tong and Lin. Upper black curve 'ADK (mod)': ADK theory with the Stark-shifted energy.

their semiempirical formula. The calculations with the pseudopotential, corresponding to a higher polarizability of Ar, produce a lower rate at lower fields. However, the rate grows faster with $F$ at $F > 0.12$ a.u. and starts to exceed the model-potential rate at $F = 0.18$ a.u. The difference, however, is substantially smaller than the difference between the ADK rate and the numerical rate. The fact that the pseudopotential rate is lower than the model potential rate at low fields, can be explained by higher effective polarizability which makes the Stark-shifted state to lie lower.

Batishchev *et al* [22] calculated ionization rates for rare-gas atoms in a broad range of fields up to 1 a.u. Their method incorporates nonadiabatic coupling between parabolic channels

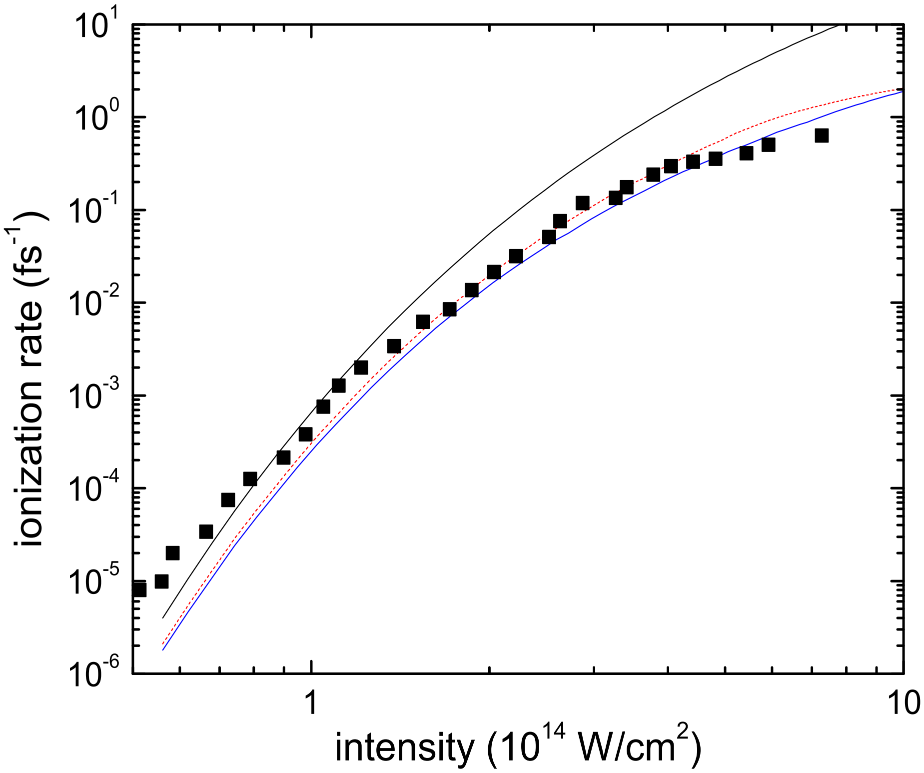

FIG. 4: (Color online). Ar ionization rate in fs$^{-1}$ as a function of the laser intensity. Blue solid curve: calculation with the pseudopotential. Red dashed curve: calculation with the model potential of Tong and Lin [8]. Black solid curve: ADK theory. Squares: experimental ionization probability of Guo *et al* [36] normalized to the rate calculated with the model potential at $I = 2 \times 10^{14}$ W/cm$^2$.

and employs model potentials [31]. We find good agreement with their results for Ar in the range of fields considered in the present paper. We also note that our pseudopotential results demonstrate linear growth with $F$ for $F > 0.15$ a.u. that is consistent with the theoretical prediction for hydrogen [9, 10]. However, in the model potential approach the linear regime is reached at substantially higher fields. This is confirmed by calculations of Batishchev *et al* [22] which demonstrate the linear behavior at $F > 0.5$ a.u. In this connection we should emphasize the limited range of validity of the semiempirical extrapolation formula [8] which, in contrast to the linear growth, predicts exponential suppression at higher fields.

To compare results of static-field ionization theory with experiments performed with ac fields, the static ionization rate $\Gamma$ has to be converted into the ac rate $\Gamma_{dyn}$ according to the equation [4, 7]

$$\Gamma_{dyn} = \sqrt{\frac{3F}{\pi\kappa^3}}\Gamma.$$

In Fig. 4 we compare the dependence of the ionization rate on the laser intensity with experimental ionization probability measured by Guo *et al* [36] with the Ti:sapphire laser of wavelength 800 nm and pulse duration 30 fs. Since the experimental results are relative, we normalize them to the theoretical value, obtained with the model potential, at the intensity $I = 2 \times 10^{14}$ W/cm$^2$. Note that in this figure the ionization rate incorporates the occupation number (2) of the $2p_0$ orbital. This factor is necessary to obtain the correct absolute value of $\Gamma$ [35]. The overall agreement is very good except the low-intensity region below $I = 10^{14}$ W/cm$^2$ where the Keldysh parameter exceeds 1 and the the static-field approximation starts to fail. Note that the classical ionization threshold corresponds to the intensity $I = 2.48 \times 10^{14}$ W/cm$^2$.

Regarding the high-intensity region, we should note that whereas at low laser intensities the ionization probability $w$ is proportional to the ionization rate $\Gamma$, at higher intensities the probability should be calculated as [8]

$$w = 1 - \exp[-\int \Gamma(F(t))dt] \tag{29}$$

where $F(t)$ is the laser field amplitude as a function of time. For a 30-fs laser pulse the saturation, i.e. deviation from $w \propto \Gamma$, is reached at about $I_s = 3 \times 10^{14}$ W/cm$^2$. This can be seen from the figure showing that the experimental probability is growing slower than the theoretical rate at $I > I_s$ where Eq. (29) should be used. Spatial effects can play role too [37]. However, a detailed comparison with experiments is not a primary purpose of the present paper, and Fig. 4 serves just illustrative purposes.

It is interesting that even at the low intensity $I = 0.56 \times 10^{14}$ W/cm$^2$, corresponding to $F = 0.04$ a.u., the ADK result exceeds the present result by the factor 1.9. For the hydrogen-atom problem the asymptotic ("ADK") formula gives

$$\Gamma^{as} = \frac{4}{F}e^{-2/(3F)}$$

whereas the exact result for $F = 0.04$ a.u. is $\Gamma = 0.389 \times 10^{-5}$ a.u. [5], therefore $\Gamma^{as}/\Gamma = 1.485$. Although for both atoms at lower fields numerical results converge to corresponding asymptotic values, apparently this convergence for Ar is slower than for hydrogen. This difference can be explained by the uncertainty in determination of the asymptotic coefficient $C_l$ for multielectron atoms, as discussed in Sec. II F: for the hydrogen atom the asymptotic form of the $1s$ orbital is exact and valid in the whole space, whereas for a complex atom like Ar the asymptotic form is reached only at large $r$ where the electric-field effects are substantial even for the field as small as 0.04 a.u.

Otobe *et al* [13] calculated the Ar ionization rate as a function of intensity in the range of intensities between $0.3\times10^{14}$ and $1.4\times10^{14}$ W/cm$^2$ using the absorbing boundary conditions. Surprisingly, their ionization rates exceed the ADK rates in the whole range of covered intensities. This overestimate of the ionization rate is probably due to spherical symmetry of their absorption potential which does not correspond to the parabolic symmetry of the problem. Comparison with the semiclassical results obtained by the complex time method [20, 35] shows a good agreement with the present calculations at $F < F_c$. However, this method fails when $F$ is close to $F_c$.

## IV. CONCLUSION

Incorporation of outgoing-wave boundary condition in calculations of the static-field ionization rates often presents a big challenge to theory. In the present paper we have proposed a method based on the use of the Green's function in the superposition of the laser and the Coulomb fields. It works below as well as above the classical ionization limit. Our method is an alternative to a recently developed theory [22] based on inclusion of nonadiabatic coupling between parabolic channels by employing the slow-variable discretization method [38]. In addition to calculation of complex energies of the quasistationary (Siegert) states, Batishchev *et al* [22] calculated the transverse momentum distribution of the ionized electrons. The present method also allows this calculation by using Eq. (6) for the wavefunction at $r' \gg r_0$.

Both methods are in principle exact in the sense that for a given atomic potential ionization rate can be calculated with an arbitary accuracy. However, the present method is able to incorporate $l$-dependent pseudopotentials for description of the electron-atom interaction. Our method is computationally less demanding for weaker fields (below about $2F_c$). However, for stronger fields the method of analytical continuation employed in the present paper becomes unstable, and calculations of the Green's function directly at complex energies becomes necessary.

A generalization of the present method to tunneling ionization of molecules with arbitrary orientation with respect to the static field is straightforward. Since for not very weak fields the Keldysh characteristic time

$$\tau = \frac{\sqrt{-2E}}{F}$$

is significantly shorter than the rotational period, the approximation of the fixed molecular orientation can be used. If molecules are randomly oriented, the fixed-nuclei result can be averaged over molecular orientations, see, for example, [35, 39] and references therein.

A more challenging task is the extension of the present method to time-dependent laser fields. For inclusion of the rescattering effect, the time-dependent Green's function (or what can be called the Coulomb-Volkov propagator) should be incorporated. The basic idea was presented by Popov [18], but his basic equations contain a simplified form of the propagator, not including the Coulomb field. In this case, according to Feynman [40], the propagator is simplified significantly. Such a propagator corresponds to the very commonly used strong field approximation. The Coulomb effect has been treated in the form of a correction to the action functional [18, 19]. For a more accurate inclusion of the Coulomb field in the propagator semiclassical methods [41, 42] can be applied.

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