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Tunnel ionization of atoms and molecules: How accurate are the weak-field asymptotic formulas?

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Weak field asymptotic formulas for the tunnel ionization rate of atoms and molecules in strong laser fields are often used for the analysis of strong field recollision experiments. We investigate their accuracy and domain of validity for different model systems by confronting them to exact numerical results, obtained by solving the time dependent Schrödinger equation. We find that corrections that take the dc-Stark shift into account are a simple and efficient way to improve the formula. Furthermore, analyzing the different approximations used, we show that error compensation plays a crucial role in the fair agreement between exact and analytical results.

Keywords: Tunnel ionization, Strong field physics, Analytic formulas

I. INTRODUCTION

The interaction between an atom or a molecule and an electric field can give rise to various phenomena depending on the considered time and energy scales. At low frequencies (typically infrared radiation) and high intensities (10^{13} W cm⁻² and beyond), the ionization of the system by a laser can no longer be described by the absorption of one or several photons as depicted by perturbation theory. In such conditions, the laser field strongly distorts the atomic potential so that electrons can escape through tunnel effect. This phenomenon was first modeled by Keldysh [1] in the 60's and was then intensively investigated since it represents the first step of highly non-linear recollision driven processes such as High Harmonic Generation (HHG) [2, 3], or non-sequential multiple ionization [4]. Beyond their fundamental importance, these recollision processes have been identified in the last 10 years as central for the design of cutting edge spectroscopies merging Angström and attosecond resolutions, see [5, 6] and references therein.

As for many non-linear processes, the only way to accurately describe tunnel ionization is to numerically solve the Time Dependent Schrödinger Equation (TDSE). However, because of its high numerical cost, this method can only be used for small systems, i.e. an atom with one or two electrons. The description of larger and more complex systems such as molecules is very delicate and requires some approximations: Single Active Electron approximation and frozen nuclei [7–9], Strong Field Approximation [10, 11] or low dimensionality [12]. On the other hand, one may rely on approximate models such as the Lewenstein model [13] or quantitative rescattering theory [6]. These models have the advantage to yield analytical formulas and developments that are easier to handle than numerical simulations. Moreover, they allow to decompose each strong field process into different steps, e.g. the celebrated three-step model for HHG [2, 14], which provides valuable physical pictures and insights. In this framework, tunnel ionization is the universal first step of all recollision processes, and is also the main source of their non-linearity, hence its central importance in strong field physics.

For all the reasons we just cited, approximate analytical for-

mulas, see [15, 16] for more complete reviews, are often preferred to numerical simulations for the analysis and interpretation of experimental results. The most frequently used of these formulas rely on the adiabatic approximation. Among them are the ones derived by Perelomov *et al.* (PPT) [17] or Ammosov *et al.* (ADK) [18] for atoms, and extended to molecules by Tong *et al.* (Mo-ADK) [19, 20] and Kjeldsen and Madsen [21], but also more advanced analytical works like the ones performed by Tolstikhin *et al.* [22, 23]. However, these analytical PPT, ADK and Mo-ADK formulas have a limited accuracy as was extensively shown recently by Lai *et al.* [24]. In fact, they are asymptotically exact when the Keldysh parameter [1] vanishes, and are directly deduced from the ionization rate in a static electric field. Consequently, their accuracy strongly depends on the computation of the static ionization rate.

This static rate is called asymptotic because it is asymptotically exact when the electric field F goes to zero, i.e. $F \rightarrow 0$. It was obtained at first order for the Hydrogen atom by Landau and Lifshitz (LL) [25] and extended to any atom by Smirnov and Chibisov (SC) [26]. Using more advanced analytical development based on Siegert states, Tolstikhin *et al.* have recently achieved an asymptotic development of the ionization rate at higher orders for atoms [27–29], and molecules [30–32] including nuclear motion in the Born Oppenheimer approximation [12, 33]. At the same time, Manakov *et al.* performed a derivation for negative atomic [34] and molecular ions [35].

A more empirical and much more direct approach has been developed for molecules. It consists in a correction of the asymptotic SC (or ADK, which is equivalent) rate by taking into account the Stark shift up to second order of perturbation theory [8, 36, 37]. However, this correction has been used in a rather inconsistent way considering the development made by LL [25] and SC [26].

In this work, we show that if one adds consistently the DC-Stark shift in the derivation of the Landau formula, then the Stark shift correction only appears in the argument of the dominant exponential term. Moreover, we show that for highly polarizable molecules, second order perturbation theory can become insufficient to compute the correct shape of the Stark shift, with great consequences on the ionization rate. Finally, we show that, at working laser intensities ($\gtrsim 10^{12}$ W.cm⁻²), the asymptotic condition that the electric field is small is in fact not fulfilled. Nonetheless relatively good quantitative re-

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sults are obtained when using the asymptotic formulas compared to TDSE calculations because of error compensation.

In this paper, we use a one-dimensional model for which the TDSE can be easily solved numerically. Then we confront our TDSE results to the analytical models to test their accuracy. As the ionization of the hydrogen atom in a static field reduces to a one-dimensional problem (through a change to parabolic coordinates), we believe that our results are most general and will help to get physical insights that can be extended to the three-dimensional case.

The article is organized as follows. In section II we present the numerical methods, and the analytical formulas. Section III contains our results for atoms and diatomic molecules. Then, a detailed analysis of the Landau approximations and their ranges of validity is given in section IV and in the appendix. Atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$) are used throughout this article unless stated otherwise.

II. METHODS

We model a one-dimensional atom by an electron trapped in a Coulomb like potential well. To avoid numerical difficulties at the origin we use a standard soft Coulomb potential [38]

$$V_0(x) = -\frac{Z}{\sqrt{a^2 + x^2}}, \quad (1)$$

where the parameters Z and a can be adjusted to control the shape of the potential and notably its ground state energy. We also model one-dimensional diatomic molecules by the sum of two shifted soft Coulomb wells

$$V_0(x) = -\frac{Z/2}{\sqrt{a^2 + (x + R/2)^2}} - \frac{Z/2}{\sqrt{a^2 + (x - R/2)^2}}, \quad (2)$$

where R is the internuclear distance. This can be seen, to some extent, as a simple benchmark model for three-dimensional diatomic molecules that would be previously aligned along the direction of the electric field.

The TDSE describing the evolution of the system writes, in length gauge,

$$i\frac{\partial\psi}{\partial t}(x, t) = \left(-\frac{1}{2}\frac{\partial^2}{\partial x^2} + V_0(x) + xF(t)\right)\psi(x, t), \quad (3)$$

where ψ is the electronic wave function and $F(t)$ is the electric field. The initial state is taken as the ground state of the system, numerically calculated on a grid [39]. The wave function is then propagated on the same grid by a Crank-Nicolson algorithm [40]. We take a box of size 500 a.u. with a step $\Delta x = 5 \times 10^{-2}$ a.u. and a time step of 6.3×10^{-3} a.u.. To ensure an adiabatic transition from a zero field to a finite value F , the electric field is slowly brought to a constant value, with a sine square turn on, for $\simeq 10^4$ a.u. In order to avoid non-physical reflections at the boundaries of the computation box, a mask type absorber [41] of width 200 a.u. is used. The ionization probability is computed as

$$W(t) = 1 - \sum_{\varphi_i \in \text{bound states}} |\langle \varphi_i | \psi(t) \rangle|^2. \quad (4)$$

From this probability we deduce the ionization rate

$$\Gamma_{\text{TDSE}} = -\frac{d \ln(1 - W)}{dt}, \quad (5)$$

which is time independent as soon as the electric field reaches its plateau. The results obtained by this method are considered as *exact*, and used in the following as a reference to test the accuracy of analytical formulas for the ionization rate.

In a very low static electric field ($|F| \ll (2I_p)^{3/2}$), the asymptotic ionization rate is given in three dimensions by Smirnov and Chibisov (SC) [26]. The same formula adapted to our one-dimensional system reads:

$$\Gamma_{\text{SC}} = |B|^2 \sqrt{2I_p} \left(\frac{4I_p}{|F|}\right)^{\frac{2Z}{\sqrt{2I_p}}} \exp\left(-\frac{2(2I_p)^{3/2}}{3|F|}\right), \quad (6)$$

where I_p is the ionization potential of the *atom* and B is the asymptotic coefficient of the atomic ground state φ_0 , i.e. following [26],

$$\varphi_0(x) \underset{\pm\infty}{\sim} B |x|^{\frac{Z}{\sqrt{2I_p}}} e^{-\sqrt{2I_p}|x|}. \quad (7)$$

Though there exist approximate formulas for this asymptotic coefficient, such as the one used in the ADK rate, or numerical tabulations for several atoms and ions (see [16] and references therein), we computed it numerically for our systems to get the most accurate value.

The previous formula involve the field free ionization potential I_p . However, the presence of the field perturbs the energy levels of the system, and therefore the effective ionization potential, since it couples the bound states to the continuum. We computed this energy shift, or dc-Stark shift, using the R-box method [42] to get the *corrected* ionization potential $\tilde{I}_p(F) = I_p + \Delta I_p(F)$ as a function of the electric field. From the second derivative of $\Delta I_p(F)$ we could then deduce the polarizability of the atomic ground state. If this Stark shift remains small, $\Delta I_p \ll I_p$, then it is possible to take it into account in the analytical calculations of the ionization rate to obtain a corrected formula

$$\tilde{\Gamma}_{\text{SC}} = |B|^2 \sqrt{2I_p} \left(\frac{4I_p}{|F|}\right)^{\frac{2Z}{\sqrt{2I_p}}} \exp\left(-\frac{2(\tilde{I}_p)^{3/2}}{3|F|}\right), \quad (8)$$

where the ionization potential I_p is replaced by its *corrected* value $\tilde{I}_p(F)$ in the exponential factor *only*. The detailed calculations to get this formula is given in appendix.

Though the *exact* value of the Stark shift can be computed for our simple systems, it is not the case in general. It is therefore useful to consider approximate expansions for ΔI_p that will be detailed in the following section.

III. RESULTS

A. Atoms

We consider here a model atom with the parameters set to $Z = 1$ and $a = 1.1545$, with an ionization potential

$I_p = 0.594$ a.u.. We first confront the analytical uncorrected SC rate Γ_{SC} (6) to our exact TDSE results, then we will test the corrected rate $\tilde{\Gamma}_{SC}$ (8). From Figure 1 (a), we can see that

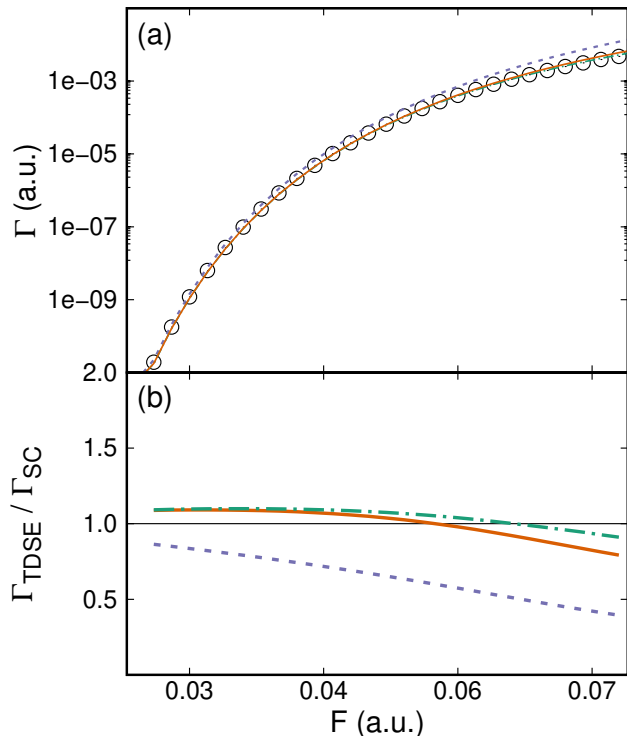


FIG. 1. (Color online) Tunnel ionization of the atomic system (section III.A). (a) Ionization rate as a function of the electric field. Black circles for the reference value Γ_{TDSE} (5), dotted purple line for the SC analytical formula Γ_{SC} (6), dash-dotted green line for the modified SC formula $\tilde{\Gamma}_{SC}$ (8) corrected with the *exact* \tilde{I}_p and solid orange line for the same modified SC formula but with the 2PT approximation $\tilde{I}_p^{(2PT)}$ (9). (b) Ratio of the numerical to analytical ionization rates. Dotted purple line for $\Gamma_{TDSE} / \Gamma_{SC}$, dash-dotted green line for $\Gamma_{TDSE} / \tilde{\Gamma}_{SC}$ computed with the *exact* \tilde{I}_p , and solid orange line for $\Gamma_{TDSE} / \tilde{\Gamma}_{SC}$ computed with the 2PT approximation $\tilde{I}_p^{(2PT)}$.

although it is derived for an asymptotically weak field $|F| \rightarrow 0$ the uncorrected SC formula (dashed red line) gives the correct behavior for the ionization rate compared to the TDSE results (black crosses). This observation remains true on a large range of field values corresponding to eight orders of magnitude of Γ values. It is however difficult to appreciate the accuracy of the formula because of the logarithmic scale. This is why we show the ratio of the exact numerical results Γ_{TDSE} to the analytical ones on Figure 1 (b). It becomes clear on this figure that the analytical formula Γ_{SC} (red crosses) can only be trusted up to $\simeq 10\%$ in the best case. As expected from an asymptotic rate, the accuracy decreases with increasing fields, and the difference with the TDSE result exceeds 100% for fields larger than 6.5×10^{-2} a.u., which corresponds to intensities larger than 1.5×10^{14} W cm $^{-2}$. It is therefore very delicate to use this formula for quantitative predictions of ionization rates at finite (nonzero) fields.

To check the validity of the corrected formula $\tilde{\Gamma}_{SC}$ (8), we

computed the Stark shift of this atomic system. As can be seen on Figure 2 it is very well approximated by second order perturbation theory (2PT):

$$\tilde{I}_p^{(2PT)} = I_p + \alpha F^2, \quad (9)$$

where $\alpha = 4.06$ a.u. for this system. Then we compare the modified SC rate $\tilde{\Gamma}_{SC}$ (8) computed either with the *exact* \tilde{I}_p (dotted blue line) or with the 2PT correction $\tilde{I}_p^{(2PT)}$ (solid green line) to the TDSE results (black crosses) on Figure 1 (a) and (b). We see that both versions of $\tilde{\Gamma}_{SC}$ are closer to the the TDSE results than the uncorrected Γ_{SC} , indicating that the Stark shift correction systematically reduce the error made by the SC formula. Moreover we see in the lower panel that in both cases (*exact* and 2PT corrections) the exact to analytical ratio is flat, which indicates that the behavior predicted by this corrected formula is very close to the *exact* one.

As a result, the corrected formula $\tilde{\Gamma}_{SC}$ can be used on a large range of field values with a relatively constant error of $\simeq 10\%$. Furthermore, we see that the rate corrected with the 2PT approximation $\tilde{I}_p^{(2PT)}$ is in very good agreement with the one corrected with the *exact* \tilde{I}_p . This justifies the use of the 2PT approximation to compute the ionization rate. We have checked that the general behavior described here is insensitive to the values of the atomic parameters Z and a .

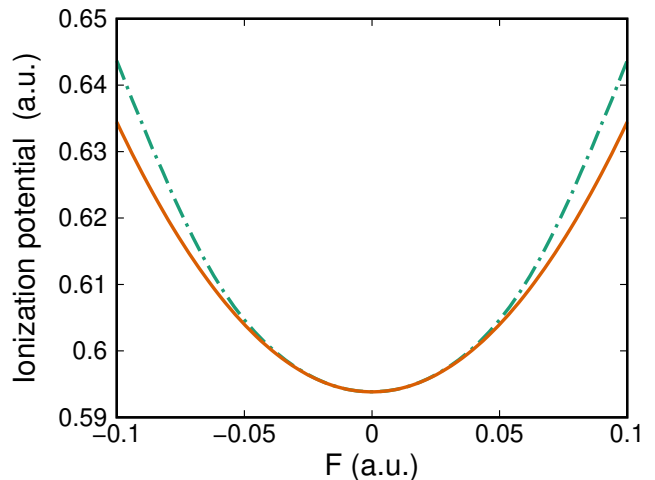


FIG. 2. (Color online) Stark shift of an atomic system (section III.A). Corrected ionization potential as a function of the electric field: dash-dotted green line for the numerical results and solid orange line for second order perturbation theory $\tilde{I}_p^{(2PT)}$ (9).

B. Diatomic molecules

In the case of homonuclear diatomic molecules, the behavior of the Stark shift is very sensitive to the interatomic bond length. This is because the energy gap between the ground and first excited states, $\Delta E = E_1 - E_0$ decreases when the bond length increases. If this gap gets small, such that $\Delta E \lesssim \Delta I_p$,

then the Stark shift becomes linear and one has to use degenerate perturbation theory (DPT) to compute the corrected ionization potential. This reads, at first order:

$$\tilde{I}_p^{(\text{DPT})} = -\frac{E_0 + E_1}{2} + \frac{1}{2} \sqrt{(E_1 - E_0)^2 + 4|\langle \varphi_0 | x | \varphi_1 \rangle|^2 F^2}. \quad (10)$$

To compare numerically the two different versions of perturbation theory, we consider two different molecular systems S_1 and S_2 with the same asymptotic behavior ($Z = 1$) and the same ionization potential $I_p = 0.573$ a.u. but two different bond lengths. For the first system S_1 we take $a = 1$, $R = 2.2$ a.u. and obtain a field free energy gap of $\Delta E = 0.260$ a.u., whereas for the second one S_2 we take $a = 0.6925$, $R = 4.0$ a.u. and get $\Delta E = 0.117$ a.u. We show their dressed *exact* ionization potential \tilde{I}_p and the two different perturbation theories $\tilde{I}_p^{2\text{PT}}$ and \tilde{I}_p^{DPT} on Figure 3. We notice quantitative differences: it is remarkable on Figure 3 (a) that in the first case 2PT (solid blue line) gives a better agreement with numerical results (red crosses), while in the second case, we see on Figure 3 (b) that DPT (dotted black line) is more adequate. This clearly illustrates that second order approximation of the Stark shift can be ill-fitting and has to be considered with care, especially for molecules.

We now use the two different Stark shift perturbation expansions (2PT and DPT) to obtain two different corrected ionization rate formulas $\tilde{\Gamma}_{\text{SC}}$ (8) and we compare them to our exact numerical results Γ_{TDSE} on Figure 4. The results for the smaller molecule (Figure 4 (a) and (b)) are quite similar to the ones obtained for the atom. The error made by the uncorrected rate (dashed red line in the upper panel, and red crosses in the lower panel) increases with the field and becomes rapidly too large for quantitative applications. The corrected rate $\tilde{\Gamma}_{\text{SC}}$ is closer to the exact one, especially for high fields. In this case, the 2PT (solid green line and green X's) and DPT (dotted blue line and blue dots) corrections give similar results, which is consistent with the results of Figure 3 (a).

However, in the case of the larger molecule shown on Figure 4 (c) and (d), the uncorrected formula (dashed red line and red crosses) fails to predict the right value of the rate. It is wrong by a factor of two for a field value corresponding to an intensity of $\simeq 5 \times 10^{13} \text{ W cm}^{-2}$ and the error is even larger at higher intensities. Besides, the corrected formula using 2PT (solid green line and green X's) does not reduce the error at all. The only formula that predicts the right order of magnitude on a broad range of field values is the formula that uses the DPT correction (dotted blue line and blue dots).

Here we only present the case of symmetric molecules, for which there is no permanent dipole moment. Nevertheless in the case of polar molecules, the Stark shift correction is crucial for the description of tunnel ionization. In that case the ionization rate becomes anisotropic, and by considering only the uncorrected formula (6), one would intuitively state that ionization preferentially occurs in the direction of the maximum of the electronic density. However, as is detailed in [8], the Stark shift has an opposite contribution which enhances ionization in the direction of the permanent dipole moment. When one considers the two contributions, we find (data not

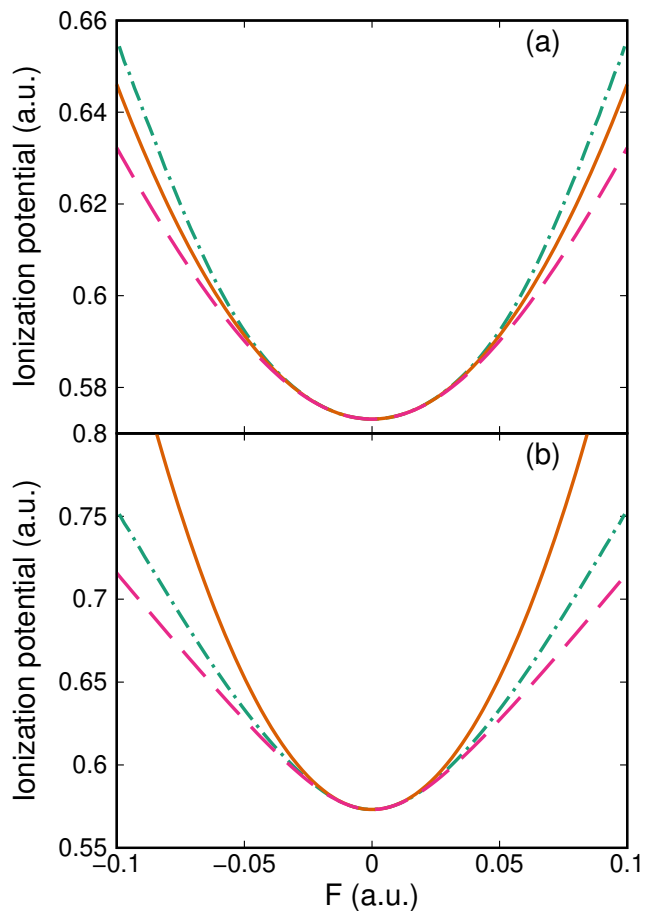


FIG. 3. (Color online) Stark shift of molecules S_1 (a) and S_2 (b) (section III.B). Corrected ionization potential as a function of the electric field: dash-dotted green line for the numerical results, solid orange line for second order perturbation theory $\tilde{I}_p^{2\text{PT}}$ (9) and dashed pink line for degenerate perturbation theory \tilde{I}_p^{DPT} (10). Upper panel: S_1 , lower panel: S_2 .

shown), in accordance with the results of [8], that it is actually the Stark shift anisotropy that controls the ionization anisotropy. Therefore, the Stark shift correction is in that case mandatory even to reproduce the *qualitative* behavior of a polar molecule.

In conclusion to sections A and B, extreme care has to be taken when the uncorrected SC formula is used to predict the ionization rate of a system, especially in the presence of a particularly strong field. If one can compute the polarizability of the ground state and therefore correct the ionization potential, the accuracy of the analytical rate may be improved. Nevertheless, this correction is not universal: if the energy levels of the system are too close to each other, degenerate perturbation theory should be used instead.

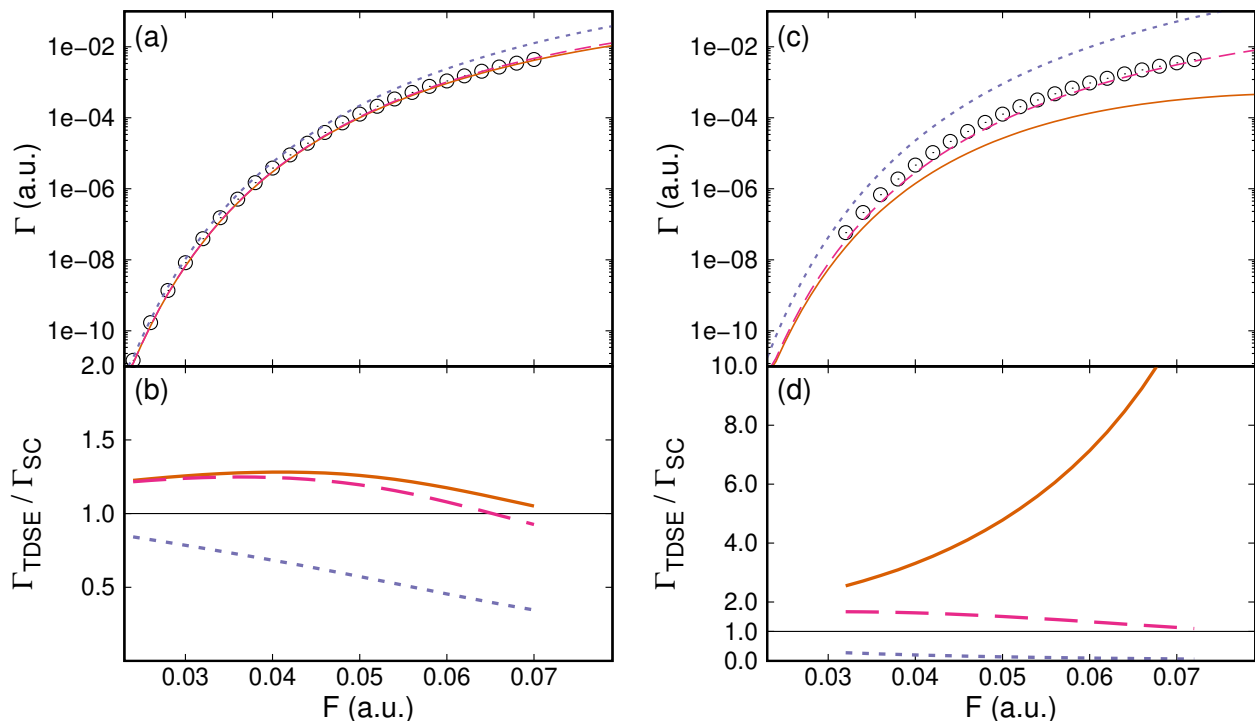


FIG. 4. (Color online) Tunnel ionization of molecules S_1 and S_2 (section III.B). Upper panels: ionization rate as a function of the electric field of S_1 (a) and S_2 (c). Black circles for the reference value Γ_{TDSE} (5), dotted purple line for the SC analytical formula Γ_{SC} (6), dashed pink line for the modified SC formula $\tilde{\Gamma}_{\text{SC}}$ (8) corrected with the DPT approximation of \tilde{I}_p and solid orange line for the same modified SC formula but with the 2PT approximation of \tilde{I}_p . Lower panel: ratio of the numerical to analytical ionization rates of S_1 (b) and S_2 (d).

IV. ERROR ANALYSIS

In the previous section we have seen that while the Stark shift correction can improve the accuracy of the analytical rate, discrepancies with *exact* TDSE results remain. In order to identify the origin of the error, we analyze all the approximations that are made to establish the ionization rate (see appendix) by gradually introducing them in approximate evaluations of the ionization rate. Then we analyze the error resulting from each of these approximations to determine which one of our hypothesis is not fulfilled.

To obtain the analytical expression $\tilde{\Gamma}_{\text{SC}}$ given in (8), we compute the electronic density flux far from the atomic potential, i.e. at a point $x \rightarrow -\infty$, out of the wave function $\psi(x)$ corresponding to the ground state dressed by the electric field. The wave function is not available for most of the practical cases, which is why we use the semi-classical approximate expression of the wave function. However, this approximation only gives the wave function up to a constant normalization factor, i.e. C in (11). The computation of this factor C supposes a choice of normalization, of which the absolute value of the rate will depend. The choice of Landau and Lifshitz in [25] and Smirnov and Chibisov in [26] is to connect the semi-classical wave function with the ground state φ_0 of the unperturbed system. To this end, we divide the space into three different intervals, as illustrated in Figure 5, and then use continuity conditions at the frontiers x_1 and x_0 , where x_1 is the external turning point i.e. $p(x_1) = 0$ where

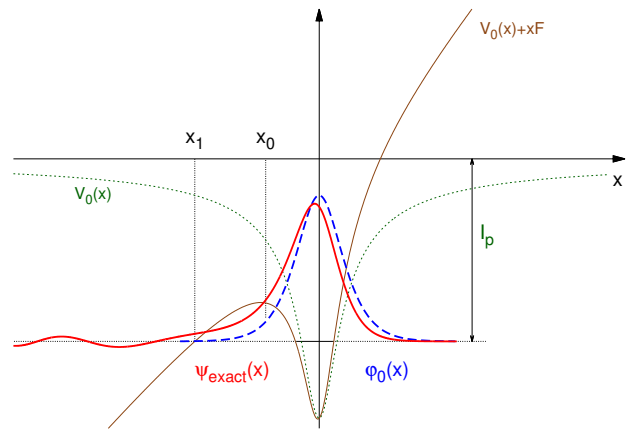


FIG. 5. (Color online) Schematic view of tunnel ionization of the atomic system described in section III A in a field $F = 6 \times 10^{-2}$ a.u.. Solid red line: exact wave function $\psi_{\text{exact}}(x)$ dressed by the electric field and dashed blue line: exact ground state $\varphi_0(x)$ of the unperturbed system (both computed by inverse iteration [39]). See text and appendix.

$p(x) = \sqrt{2(\tilde{I}_p + V_0(x) + xF)}$ is the classical action, and x_0 is any point inside the barrier. At the right of the point x_0 we approximate the wave function by the ground state φ_0 of the unperturbed system. At the left of x_0 we use the semi-

classical approximation to get two different expression for the wave functions in the two regions of space $x < x_1$ and $x_1 < x \leq x_0$. We refer the interested reader to the appendix for more details.

The first approximation we use is the semi-classical approximation in the regions of space *inside* the potential barrier and far from the atomic core. It is justified as long as the spatial variations of the De Broglie wavelength of the electron are small [25], which can be written as

$$\frac{1}{|p|^2} \left| \frac{dp}{dx} \right| \ll 1. \quad (11)$$

If we use only this approximation, we find the following expression for the ionization rate

$$\Gamma_1 = |\psi(x_0)|^2 |p(x_0)| \exp\left(-2 \int_{x_1}^{x_0} |p(x)| dx\right), \quad (12)$$

To evaluate the validity of the hypothesis in (11) the left-hand side quantity Γ_1 is computed numerically in the case of the atomic system of section III A. For this, the exact wave function $\psi(x_0)$ dressed by the field is computed numerically (e.g. by inverse iteration [39] or Runge-Kutta propagation), and then normalized by

$$\int_{x_1}^{+\infty} |\psi(x)|^2 dx = 1. \quad (13)$$

This choice of normalization is consistent the way LL and SC build their approximate wave function. Note that it is also consistent with the approximation in equation (36) of [27]. The numerical Γ_1 is shown as red connected triangles on Figure 6 for a field $F = 2.5 \times 10^{-2}$ a.u., which corresponds to an intensity of 2.2×10^{13} W.cm². In these conditions $x_1 = -22.05$ a.u.. We see that if we choose x_0 in the range between 5 and 15 a.u., then the semi-classical approximation gives results very close to the TDSE rate. Also, the rate Γ_1 is almost independent of the choice of the arbitrary parameter x_0 , which is consistent with the fact that the ionization rate should not depend on x_0 at all. We remark that a different choice of normalization for ψ would only scale Γ_1 by a constant factor which would thus still be independent of the arbitrary parameter x_0 .

The second hypothesis is that there exists an interval \mathcal{I} *inside* the barrier where the wave function ψ can be approximated by the ground state φ_0 of the *unperturbed* atomic potential. According to [25, 26], this is justified if the interaction with the electric field is very small i.e. $|x_0 F| \ll I_p$ if $x_0 \in \mathcal{I}$. By replacing the exact wave function $\psi(x_0)$ by $\varphi_0(x_0)$ in the expression of Γ_1 (12), we obtain the rate Γ_2 which corresponds to the expression (A5) given in appendix. We plotted Γ_2 as a solid yellow line in Figure 6. We immediately see the huge difference between Γ_1 and Γ_2 . First Γ_2 departs from Γ_1 and from the TDSE results, which indicates that the approximation $\psi(x_0) \simeq \varphi(x_0)$ is not justified, whatever the value of x_0 . Moreover Γ_2 strongly depends on the unphysical parameter x_0 , which is non satisfactory.

The third hypothesis is that $|x_0|$ is very large, such that $|V_0(x_0)| \ll I_p$. This allows to use the asymptotic form of

the atomic ground state (7). It also allows to neglect $V_0(x_0)$ in the expression of $|p(x_0)|$, and to expand $p(x)$ in powers of $V_0(x)/(xF + \tilde{I}_p)$ as we did in (A8). We insert all this in (A5) to get

$$\Gamma_3 = |\psi(x_0)|^2 \sqrt{2\tilde{I}_p(1+\eta)} e^{-2\mathcal{K}}, \quad (14)$$

where

$$\mathcal{K} = \frac{(2\tilde{I}_p)^{3/2}}{3F} (1+\eta)^{3/2} - \frac{Z}{\sqrt{2\tilde{I}_p}} \ln\left(\frac{1+\sqrt{1+\eta}}{1-\sqrt{1+\eta}}\right), \quad (15)$$

and where we defined

$$\eta = \frac{x_0 F}{\tilde{I}_p}. \quad (16)$$

This is shown as a dashed blue line in Figure 6. We see that, as long as $x_0 > 4$ a.u., there is almost no difference between Γ_3 and Γ_2 , which indicates that the hypothesis $|V_0(x_0)| \ll I_p$ is justified.

Finally, the last approximation uses again that $|x_0 F| \ll I_p$, i.e. that $\eta \ll 1$, to make the expansion (A9) and to neglect $x_0 F$ in $|p(x_0)|$. This last step gives the SC formula of (8), which is plotted with a dash-dotted green line in Figure 6. We observe a dramatic difference between $\tilde{\Gamma}_{SC}$ and Γ_3 , which indicates that, again, the condition $\eta \ll 1$ is not fulfilled, whatever the value of x_0 , for a field of 2.5×10^{-2} a.u.. However it is remarkable that the error made by this last approximation almost perfectly compensates the error made by the approximation $\psi(x_0) \simeq \varphi(x_0)$ so that the SC formula eventually gives results relatively close to the *exact* TDSE computations.

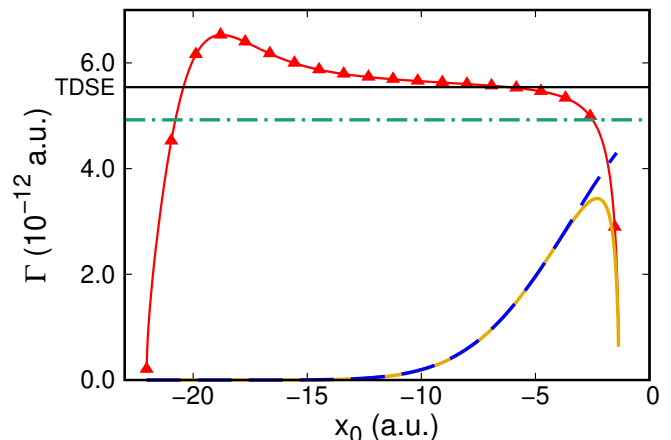


FIG. 6. (Color online) Ionization rate as a function of x_0 (see text) for an electric field $F = 2.5 \times 10^{-2}$ a.u.. The red connected triangles corresponds to Γ_1 given in (12), the solid yellow line Γ_2 given in (A5), the dashed blue line Γ_3 (14) and the dash-dotted green line $\tilde{\Gamma}_{SC}$ given in (6). The horizontal black line indicates the *exact* value obtained in TDSE simulations.

We did the same analysis for a much weaker field value $F = 2 \times 10^{-3}$ a.u., which corresponds to an intensity of

$1.4 \times 10^{11} \text{ W.cm}^2$. In these conditions $x_1 = -295.23 \text{ a.u.}$. As can be seen in Figure 7, at this field value the ionization rate is of order of magnitude 10^{-182} a.u. which drastically highlights the extreme non-linearity of the process. It is well below any practical application, and obviously below the numerical accuracy of TDSE simulations, which is why we have no reference TDSE value for this value of F . Nevertheless, this academic case constitute a severe test of the approximations relying on the weak influence of the external field on the electron at the position x_0 . We find that the conclusions concerning the relative roles of the approximations are exactly the same as the ones obtained with $F = 2.5 \times 10^{-2} \text{ a.u.}$. Indeed, we see on Figure 7 that the two rates Γ_1 and Γ_2 are very different from one another, and that Γ_2 still exhibits a strong x_0 dependency. Therefore the approximation that there exists a point x_0 that is at the same time very large, i.e. $|V_0(x_0)| \ll I_p$, and very small, i.e. $|x_0 F| \ll I_p$, is never justified, even for a field value as small as $F = 2 \times 10^{-3} \text{ a.u.}$

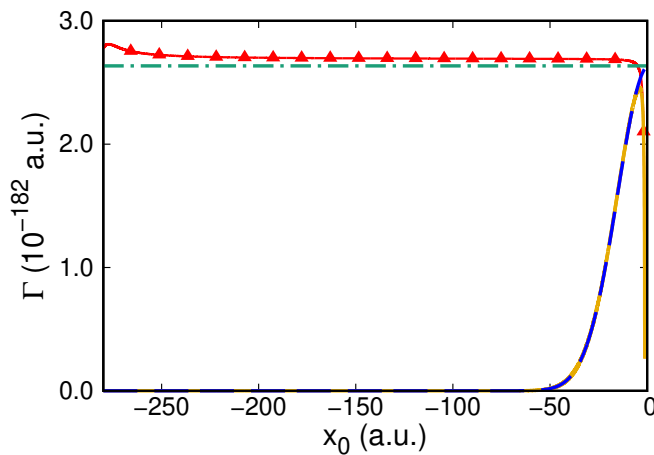


FIG. 7. (Color online) Same as in Figure 6 for an electric field of $F = 2 \times 10^{-3} \text{ a.u.}$. The TDSE value is not displayed because it lies below the numerical accuracy of the simulation.

Indeed, for these two conditions to be fulfilled at the same time, the electric field has to be much smaller than the condition one often finds in the literature [17, 26]:

$$F \ll (2I_p)^{3/2}. \quad (17)$$

For example in the case of hydrogen ($I_p = 0.5 \text{ a.u.}$), $(2I_p)^{3/2} = 1$ and the inequality (17) is fulfilled for the two field values used in Figure 6 and Figure 7. However, the expansion in (A9) is, in this case, justified if

$$e^{-\frac{2}{3F}(1-2|x_0|F)^{3/2}} \simeq e^{-\frac{2}{3F}} e^{2|x_0|}, \quad (18)$$

which will hold if the third term of the expansion is negligible, i.e.

$$e^{-2|x_0|^2 F} \simeq 1. \quad (19)$$

As we have $|x_0| \gg 1$, we actually need $F \leq 10^{-4} \text{ a.u.}$ for (19) to be true. This means that the hypotheses of the Landau and SC derivation are verified if the intensity is below

10^8 W cm^{-2} , which corresponds to a meaningless tunnel ionization rate of about $\Gamma \lesssim 10^{-2891}$! However, once again, thanks to the error compensation evidenced with the stronger field as well as with the weaker one (see Figure 6 and 7), the Landau rate gives semi-quantitative results for intensities up to $10^{12} - 10^{13} \text{ W cm}^{-2}$. The use of this formula for finite values of the electric field has therefore more empirical than theoretical foundations.

V. CONCLUSION

We computed the tunnel ionization rate in a static electric field for different symmetric systems using both the standard analytical formulas and *exact* numerical solution of the time dependent Schrödinger equation. By comparing the two approaches we found that the standard rate derived by Smirnov and Chibisov [26] only yields qualitative trends in the best cases. We demonstrated that we can correct this formula by taking into account the Stark shift, and we derived a consistent formula where the Stark shift correction only appears in the argument of the dominant exponential term. We tested this formula for an atomic and two different homonuclear diatomic molecules and showed that the correction systematically improves the accuracy of the ionization rate. We proved that if the energy gap between the two first bound states remains big enough compared to the Stark shift, then second order perturbation theory is sufficient to compute the Stark shift, implying that one only needs to know the permanent dipole moment and polarizability of the system under study. However, we showed that for highly polarizable systems, second order perturbation theory is a very bad approximation for the Stark shift and therefore a very bad correction of the ionization rate. In these cases, one has to consider degenerate perturbation theory.

The main conclusion of this work is that the hypotheses used for the Landau derivation of the tunnel ionization rate are unjustified at working intensities to model quantitatively atoms and molecules interacting with strong laser fields. We showed that the accuracy of the Landau formula is difficult to predict since it originates from the compensation of different approximations. Consequently, all the dynamical formulas that are based on this static rate (ADK), or asymptotically equal to it in the limit of a zero frequency electric field (e.g. the rate derived by Perelomov et al. [17]), should be handled with care when used for quantitative applications.

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Appendix A: On the corrected Smirnov and Chibisov ionization rate

In this Appendix we establish the formula (8) taking into account the Stark shift. We follow the procedure of [25, 26], but adapted to our one dimensional case. To recover the three dimensional rate, one only needs to integrate the formula over the two remaining variables, as it is done in [25, 26].

We consider the same system as described in section II, in presence of a very weak static electric field $F \ll (2I_p)^{3/2}$. We note $\tilde{I}_p = I_p + \Delta I_p$ the *corrected* ionization potential that include the Stark shift ΔI_p . For weak electric field, the Stark shift can be treated through perturbation theory, and $\Delta I_p \ll I_p$. For a symmetric potential, the choice of sign of the electric field is irrelevant and we choose F positive, therefore ionization occurs in the region of space where x is negative.

We define a point x_0 *inside* the potential energy barrier such that $|V_0(x_0)| \ll I_p$ and $|x_0 F| \ll I_p$, and we note

$$\eta = \frac{x_0 F}{\tilde{I}_p}. \quad (\text{A1})$$

For $x \leq x_0$ we use the quasi-classical expression of the wave function:

$$\psi(x) = \begin{cases} \frac{C}{\sqrt{p}} \exp\left(i \int_x^{x_1} p(x') dx' - \frac{i\pi}{4}\right), & x < x_1 \\ \frac{C'}{\sqrt{|p|}} \exp\left(\int_{x_1}^x |p(x')| dx'\right), & x_1 < x \leq x_0 \end{cases} \quad (\text{A2})$$

where $p(x) = \sqrt{2(-\tilde{I}_p - V_0(x) - xF)}$ is the classical action, and x_1 is the external turning point i.e. $p(x_1) = 0$. Using the connecting formulas in [25], we find the relations between C and C' , and thus the wave function *inside* the barrier

$$\psi(x) = \frac{C}{\sqrt{|p|}} \exp\left(\int_{x_1}^x |p(x')| dx' + \frac{i\pi}{2}\right), \quad x_1 < x \leq x_0. \quad (\text{A3})$$

Using $|x_0 F| \ll I_p$, $\psi(x_0)$ can be approximated by the *unperturbed* ground state $\varphi_0(x_0)$ of the system. This determines the constant C and thus the final expression for $\psi(x)$ *outside* the barrier as

$$\begin{aligned} \psi(x) &= \varphi_0(x_0) \frac{\sqrt{|p(x_0)|}}{\sqrt{p(x)}} \exp\left(-\int_{x_1}^{x_0} |p(x')| dx'\right) \\ &\times \exp\left(i \int_x^{x_1} p(x') dx' - \frac{3i\pi}{4}\right), \quad x < x_1. \end{aligned} \quad (\text{A4})$$

The ionization rate Γ is given by the opposite of the probability flux at a point x with $|x| \gg |x_1|$ (where $x, x_1 < 0$)

$$\Gamma = -\text{Im}(\psi^* \frac{d\psi}{dx}) \quad (\text{A5})$$

$$= |\varphi_0(x_0)|^2 |p(x_0)| \exp\left(-2 \int_{x_1}^{x_0} |p(x')| dx'\right). \quad (\text{A6})$$

In the preexponential factor we take $|p(x_0)| \simeq \sqrt{2\tilde{I}_p}$, and in the exponential we keep the first two terms of the expansion in powers of $V_0(x)/(xF + \tilde{I}_p)$

$$|p(x)| = \sqrt{2(xF + \tilde{I}_p)} + \frac{V_0(x)}{\sqrt{2(xF + \tilde{I}_p)}} + O\left(\frac{V_0(x)^2}{(xF + \tilde{I}_p)^{3/2}}\right) \quad (\text{A7})$$

which, after integration gives

$$\begin{aligned} \int_{x_1}^{x_0} |p(x)| dx &= \frac{(2\tilde{I}_p)^{3/2}}{3F} (1 + \eta)^{3/2} \\ &- \frac{Z}{\sqrt{2\tilde{I}_p}} \ln\left(\frac{1 + \sqrt{1 + \eta}}{1 - \sqrt{1 + \eta}}\right) + O\left(\frac{Z^{3/2} F^{1/2}}{I_p^{3/2}}\right). \end{aligned} \quad (\text{A8})$$

For exhaustivity reasons, we have kept the factors in front of the powers of F in the $O(F^\alpha)$. We use $\eta \ll 1$ to make the expansion

$$\begin{aligned} \int_{x_1}^{x_0} |p(x)| dx &= \frac{(2\tilde{I}_p)^{3/2}}{3F} + x_0 \sqrt{2\tilde{I}_p} \\ &\underbrace{- \frac{Z}{\sqrt{2\tilde{I}_p}} \ln\left(\frac{4}{\eta} + O(1)\right)}_{\mathcal{A}} \\ &\underbrace{+ O\left(\frac{x_0^2 F}{\sqrt{I_p}}\right) + O\left(\frac{Z^{3/2} F^{1/2}}{I_p^{3/2}}\right)}_{\mathcal{B}}. \end{aligned} \quad (\text{A9})$$

First, we will see why we *can* neglect ΔI_p in terms \mathcal{A} and \mathcal{B} , and then we will see why we *must* do it. As ΔI_p can be treated by perturbation theory we have $\Delta I_p = O(x_0 F)$ when $F \rightarrow 0$. Then we use $\Delta I_p \ll I_p$ to make the expansion

$$\mathcal{A} = x_0 \sqrt{2I_p} + \frac{2x_0 \Delta I_p}{\sqrt{2I_p}} \quad (\text{A10})$$

$$= x_0 \sqrt{2I_p} + O\left(\frac{x_0^2 F}{\sqrt{I_p}}\right) \quad (\text{A11})$$

and remark that the second term can just be inserted in the $O(x_0^2 F / \sqrt{I_p})$ term in (A9). We also expand term \mathcal{B} as

$$\begin{aligned} \mathcal{B} &= \frac{Z}{\sqrt{2I_p}} \ln\left(\frac{4I_p}{|x_0|F} + \frac{4\Delta I_p}{|x_0|F} + O(1)\right) \\ &+ \frac{Z\Delta I_p}{(2I_p)^{3/2}} \ln\left(\frac{4I_p}{|x_0|F} + O(1)\right). \end{aligned} \quad (\text{A12})$$

First we have $4\Delta I_p / (|x_0|F) = O(1)$, and we remark that for $X \gg 1$, we have $\ln(X) = o(X^\epsilon)$ for any $\epsilon > 0$, this gives

$$\mathcal{B} = \frac{Z}{\sqrt{2I_p}} \ln\left(\frac{4I_p}{|x_0|F} + O(1)\right) + o\left(\frac{Z(x_0 F)^{1-\epsilon}}{I_p^{3/2-\epsilon}}\right) \quad (\text{A13})$$

If we choose $\epsilon < \frac{1}{2}$, we can insert this $o\left(Z(x_0 F)^{1-\epsilon}/I_p^{\frac{3}{2}-\epsilon}\right)$ in the $O\left(Z^{\frac{3}{2}}F^{\frac{1}{2}}/I_p^{\frac{3}{2}}\right)$ term in (A9). We thus see that we can consistently neglect all terms that contain ΔI_p in (A9) except for the first term $(2\tilde{I}_p)^{\frac{3}{2}}/3F$. We can now insert (A9) in (A5) to get

$$\Gamma = |\varphi_0(x_0)|^2 |x_0|^{-\frac{2Z}{\sqrt{2I_p}}} e^{2|x_0|\sqrt{2I_p}} \sqrt{2I_p} \left(\frac{4I_p}{F}\right)^{\frac{2Z}{\sqrt{2I_p}}} \times \exp\left(-\frac{2(2\tilde{I}_p)^{\frac{3}{2}}}{3F}\right). \quad (\text{A14})$$

Finally we use $|V_0(x_0)| \ll I_p$ to replace $\varphi_0(x_0)$ by its asymptotic form, i.e. (7), and notice that

$$|\varphi_0(x_0)|^2 |x_0|^{-\frac{2Z}{\sqrt{2I_p}}} e^{2|x_0|\sqrt{2I_p}} \xrightarrow{x_0 \rightarrow \infty} |B|^2 \quad (\text{A15})$$

to get the final expression

$$\tilde{\Gamma}_{\text{SC}} = |B|^2 \sqrt{2I_p} \left(\frac{4I_p}{|F|}\right)^{\frac{2Z}{\sqrt{2I_p}}} \exp\left(-\frac{2(2\tilde{I}_p)^{3/2}}{3|F|}\right). \quad (\text{A16})$$

The reason why we *must* neglect ΔI_p in terms \mathcal{A} and \mathcal{B} appears more clearly. Indeed, if one kept \tilde{I}_p instead of I_p then the simplification (A15) would not work anymore, and the final formula for the ionization rate would depend on the unphysical quantity x_0 . To avoid such an inconsistency, it is thus necessary to neglect the Stark shift as we have done. For the term in the dominant exponential, there is no such requirement, and one may keep the corrected ionization potential \tilde{I}_p .

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- [1] L. V. Keldysh, Sov. Phys. JETP **20**, 1307 (1965).
[2] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[3] P. Salières, A. L’Huillier, P. Antoine, and M. Lewenstein, Adv. At. Mol. Opt. Phys. **41**, 83 (1999).
[4] A. Becker, R. Dörner, and R. Moshhammer, J. Phys. B: At. Mol. Opt. Phys. **38**, S753 (2005).
[5] S. Haessler, J. Caillat, and P. Salières, J. Phys. B: At. Mol. Opt. Phys. **44**, 203001 (2011).
[6] C. D. Lin, A.-T. Le, Z. Chen, T. Morishita, and R. Lucchese, J. Phys. B: At. Mol. Opt. Phys. **43**, 122001 (2010).
[7] S. Petretti, Y. V. Vanne, A. Saenz, A. Castro, and P. Decleva, Phys. Rev. Lett. **104**, 223001 (2010).
[8] M. Abu-samha and L. B. Madsen, Phys. Rev. A **82**, 043413 (2010).
[9] M. Awasthi, Y. V. Vanne, A. Saenz, A. Castro, and P. Decleva, Phys. Rev. A **77**, 063403 (2008).
[10] D. B. Milosevic, Phys. Rev. A **74**, 063404 (2006).
[11] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A **71**, 023411 (2005).
[12] J. Svensmark, O. I. Tolstikhin, and L. B. Madsen, Phys. Rev. A **91** (2015), 10.1103/PhysRevA.91.013408.
[13] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L’huillier, and P. B. Corkum, Phys. Rev. A **49**, 2117 (1994).
[14] M. Y. Kuchiev, JETP lett. **45**, 404 (1987).
[15] S. V. Popruzhenko, J. Phys. B: At. Mol. Opt. Phys. **47**, 204001 (2014).
[16] V. S. Popov, Physics-Uspekhi **47**, 855 (2004).
[17] A. M. Perelomov, V. S. Popov, and M. V. Terent’ev, Sov. Phys. JETP **23**, 924 (1966).
[18] M. V. Ammosov, N. B. Delone, and V. P. Krařnov, Sov. Phys. JETP **64**, 1191 (1986).
[19] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. A **66**, 033402 (2002).
[20] Z. X. Zhao, X. M. Tong, and C. D. Lin, Phys. Rev. A **67**, 043404 (2003).
[21] T. K. Kjeldsen and L. B. Madsen, J. Phys. B: At. Mol. Opt. Phys. **37**, 2033 (2004).
[22] O. I. Tolstikhin, T. Morishita, and S. Watanabe, Phys. Rev. A **81**, 033415 (2010).
[23] O. I. Tolstikhin and T. Morishita, Phys. Rev. A **86**, 043417 (2012).
[24] Y. H. Lai, J. Xu, U. B. Szafruga, B. K. Talbert, X. Gong, K. Zhang, H. Fuest, M. F. Kling, C. I. Blaga, P. Agostini, and L. F. DiMauro, Phys. Rev. A **96**, 063417 (2017).
[25] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-relativistic Theory* (Pergamon Press, 1962).
[26] B. M. Smirnov and M. I. Chibisov, Sov. Phys. JETP **22**, 23 (1966).
[27] P. A. Batishchev, O. I. Tolstikhin, and T. Morishita, Phys. Rev. A **82**, 023416 (2010).
[28] V. H. Trinh, O. I. Tolstikhin, L. B. Madsen, and T. Morishita, Phys. Rev. A **87** (2013), 10.1103/PhysRevA.87.043426.
[29] S. Ohgoda, O. I. Tolstikhin, and T. Morishita, Phys. Rev. A **95**, 043417 (2017).
[30] O. I. Tolstikhin, T. Morishita, and L. B. Madsen, Phys. Rev. A **84**, 053423 (2011).
[31] L. Hamonou, T. Morishita, and O. I. Tolstikhin, Phys. Rev. A **86**, 013412 (2012).
[32] V. H. Trinh, V. N. T. Pham, O. I. Tolstikhin, and T. Morishita, Phys. Rev. A **91** (2015), 10.1103/PhysRevA.91.063410.
[33] O. I. Tolstikhin and T. Morishita, Phys. Rev. A **95**, 033410 (2017).
[34] N. L. Manakov, M. V. Frolov, A. F. Starace, and I. I. Fabrikant, J. Phys. B: At. Mol. Opt. Phys. **33**, R141 (2000).
[35] S. V. Borzunov, N. L. Manakov, A. F. Starace, and M. V. Frolov, JETP **112**, 725 (2011).
[36] L. Holmegaard, J. L. Hansen, L. Kalthøj, S. Louise Kragh, H. Stapelfeldt, F. Filsinger, J. Küpper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, and L. Bojer Madsen, Nat. Phys. **6**, 428 (2010).
[37] A. Rupenyan, P. M. Kraus, J. Schneider, and H. J. Worner, Phys. Rev. A **87**, 033409 (2013).
[38] Q. Su and J. H. Eberly, Phys. Rev. A **44**, 5997 (1991).
[39] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes 3rd Edition: The Art of Scientific Computing*, 3rd ed. (Cambridge University Press, New York, NY, USA, 2007).
[40] J. Crank and P. Nicolson, in *Mathematical Proceedings of the Cambridge Philosophical Society*, Vol. 43 (Cambridge Univ Press, 1947) pp. 50–67.

- [41] J. L. Krause, K. J. Schafer, and K. C. Kulander, *Phys. Rev. A* **45**, 4998 (1992).
- [42] C. H. Maier, L. S. Cederbaum, and W. Domcke, *J. Phys. B: At. Mol. Opt. Phys.* **13**, L119 (1980).