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Empirical formula for static field ionization rates of atoms and molecules by lasers in the barrier-suppression regime

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Abstract

We propose an empirical formula for the static field ionization rates of atoms and molecules by extending the well-known analytical tunnelling ionization rates to the barrier-suppression regime. The validity of this formula is checked against ionization rates calculated from solving the Schrödinger equation for a number of atoms and ions. The empirical formula retains the simplicity of the original tunnelling ionization rate expression but can be used to calculate the ionization rates of atoms and molecules by lasers at high intensities.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With the advent of intense femtosecond laser pulses in the last two decades, many interesting nonlinear optical phenomena including high harmonic generation, attosecond pulse generation, above threshold ionization, as well as the femtosecond timing of the break up of molecules have emerged. Central to the understanding of these phenomena is the ready evaluation of the ionization rates on the laser intensities. While accurate calculations of these rates based on solving the time-dependent Schrödinger equation within the single-active electron (SAE) model is quite feasible these days, simple analytical expression based on the tunnelling ionization(TI) such as the Ammosov–Delone–Krainov (ADK) theory (Perelomov *et al* 1966, Ammosov *et al* 1986) is known to be much more useful. The ADK theory (we will not attempt to distinguish the ADK rate from the static tunnelling ionization rate since they are simply related), which is based on the WKB approximation to the static field ionization rate, is valid when the laser photon energy is much less than the ionization energy and when the atomic level is much below the top of the effective one-dimensional potential barrier for an atom in the electric field. For short pulses at higher intensity that are easily available today, ionization

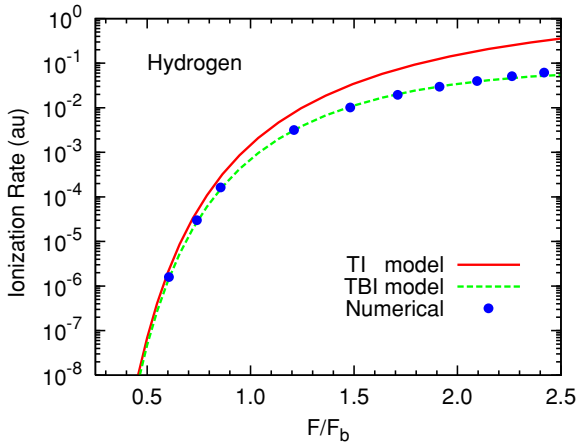

Figure 1. Ionization rates of hydrogen atoms in a static electric field. The field strength is defined in units of the critical field F_b, see equation (1).

can occur in the so-called barrier-suppression region, near or above the top of the potential barrier. In the barrier-suppression regime, the ADK theory does not work. Figure 1 shows the ionization rates calculated using the ADK model (solid line) and the comparison with the rates calculated from solving the Schrödinger equation using the complex scaling method (Scrinzi *et al* 1999) (filled circles). It is clear that the ADK rates significantly overestimate the numerically calculated static ionization rates when the scaled field strength is near or above 1.0 (the barrier-suppression regime) for hydrogen atoms. Our goal in this paper is to find an empirical formula that can extend the ADK rates from the tunnelling ionization region to the near- and over-the-barrier regime. With the implementation of an empirical correction factor, the ionization rates, based on the single-active electron model, can be analytically obtained from the ADK rates, not only for atoms, but also for molecules. For the latter, in combination with the molecular tunnelling ionization theory (Tong *et al* 2002), the dependence of the ionization rates on the alignment or the internuclear separation can be easily calculated for any laser intensities. These rates are needed in order to study the break up of molecules, either in the sequential or non-sequential double ionization regimes (Legare *et al* 2003, Alnaser *et al* 2004, Voss *et al* 2004). Similarly these simple expressions of analytical ionization rates can be used to study the multiple ionization of atoms and molecules in the so-called sequential ionization regime.

There have been several attempts (Krainov 1997, Posthumus *et al* 1997, Bauer and Mulser 1999) to extend the tunnelling ionization (TI) model to the barrier-suppression ionization (BSI) regime. Krainov (1997) did so by deriving a new expression involving Airy functions. The new formula improves the ionization rate near the BSI region but the discrepancies with the exact calculations are still quite large. Further attempts by Bauer and Mulser (1999) did not find a simple formula. These authors further concluded that other proposed approximate or empirical expressions do not give correct ionization rates when compared to those from solving the time-dependent Schrödinger equation directly.

In this paper, we will attempt to obtain an empirical formula for the static ionization rate which is valid from the TI to BSI regimes. The ionization rate for any atoms in a static electric field can be solved 'exactly' in the single-active electron model by the complex scaling method (Scrinzi *et al* 1999). The empirically derived expression will be used to check against results

from such calculations. We will use $W_{\rm TBI}$ to denote the resulting expression as the analytical formula gives the ionization rates covering from the TI to BSI regimes. We will show that by using only one empirical parameter the resulting $W_{\rm TBI}$ agrees with the numerically calculated rates to better than 50% over the whole intensity region for the atoms and molecules we have tested. For the rest of this paper, the TBI formula and the test of its validity are given in section 2, followed by a short conclusion in section 3.

2. The empirical static ionization rates in the tunnelling and barrier-suppression regimes

2.1. Static ionization rates

According to the static ionization theory in the tunnelling regime for atoms (Perelomov *et al* 1966, Ammosov *et al* 1986) and molecules (Tong *et al* 2002), the ionization rate is proportional to $\exp(-2\kappa^3/3F)$ where $\kappa = \sqrt{2I_{\rm p}}$, with $I_{\rm p}$ being the ionization energy. The tunnelling ionization rate was derived using perturbation theory where the unperturbed atomic energy is below the top of the potential barrier from the combined atomic potential and the electric field potential. At the critical field

$$F_{\rm b} = \frac{\kappa^4}{16Z_{\rm c}}, \tag{1}$$

the unperturbed atomic energy level lies on the top of the potential barrier. Above this critical field, we enter the barrier-suppression region and the tunnelling ionization rate based on the perturbation theory would overestimate the exact ionization rate. This is reflected by the exponential growth in the error of the tunnelling ionization rate as compared to the numerically calculated one seen in figure 1 . To remedy this error in the barrier-suppression region but to maintain the simplicity of the tunnelling ionization formula, we proposed a modified formula of the form

$$W_{\rm TBI}(F) = W_{\rm TI}(F)\,{\rm e}^{-\alpha(Z_{\rm c}^2/I_{\rm p})(F/\kappa^3)}. \tag{2}$$

Here, $W_{\rm TI}(F)$ is the usual ADK rates for atoms, which is expressed as

$$W_{\rm TI}(F) = \frac{C_l^2}{2^{|m|}|m|!}\frac{(2l+1)(l+|m|)!}{2(l-|m|)!}\frac{1}{\kappa^{2Z_{\rm c}/\kappa-1}}\left(\frac{2\kappa^3}{F}\right)^{2Z_{\rm c}/\kappa-|m|-1}{\rm e}^{-2\kappa^3/3F}. \tag{3}$$

In the above equation, l and m are the usual angular momentum quantum numbers of the valence electron(s) of the atom, C_l measures the amplitude of the electron wavefunction in the tunnelling region. The latter is derived from the ground-state wavefunction calculated from the model potential, see table II of (Tong *et al* 2002). Note that the exponential correction factor in equation (2) is expressed in terms of scaled field strength and scaled ionization energy, with an empirical parameter α to be obtained by fitting the formula to the ionization rates calculated for a number of atoms and ions within the single-active electron (SAE) approximation. For atomic hydrogen where the atomic potential is exact, the numerically calculated ionization rate over a large region of the scaled field $(F/F_{\rm b})$ can be nicely fitted by this empirical expression, $W_{\rm TBI}(F)$, with $\alpha = 6$, see the dashed line in figure 1.

To test the range of α for different atoms and ions within the SAE model, we approximate the atomic potential in the form of

$$V(r) = -\frac{Z_{\rm c} + a_1\,{\rm e}^{-a_2 r} + a_3 r\,{\rm e}^{-a_4 r} + a_5\,{\rm e}^{-a_6 r}}{r}. \tag{4}$$

Here, $Z_{\rm c}$ is the charge seen by the active electron asymptotically. The a_i's are obtained by fitting the numerical potential calculated from the self-interaction free density functional theory

Table 1. Atomic parameters used in the model potential.

Target	Z_c	a_1	a_2	a_3	a_4	a_5	a_6
H	1.0	0.000	0.000	0.000	0.000	0.000	0.000
He	1.0	1.231	0.662	−1.325	1.236	−0.231	0.480
Ne	1.0	8.069	2.148	−3.570	1.986	0.931	0.602
Ar	1.0	16.039	2.007	−25.543	4.525	0.961	0.443
Rb	1.0	24.023	11.107	115.200	6.629	11.977	1.245
Ne^+	2.0	8.043	2.715	0.506	0.982	−0.043	0.401
Ar^+	2.0	14.989	2.217	−23.606	4.585	1.011	0.551

Table 2. The α parameter used in equation (2) for atoms and atomic ions. The critical field strength and the ionization potential (in au) are also listed.

	Rb	H	He	Ar^+	Ne^+	Ar	Ne
α	6.0	6.0	7.0	8.0	8.0	9.0	9.0
F_b	0.006	0.063	0.204	0.129	0.2845	0.084	0.157
I_p	0.154	0.500	0.904	1.016	1.506	0.579	0.793

(Tong and Chu 1997a). We further fine tune a_3 to make the ionization potential calculated from the model potential in good agreement with the measured one. Finally, the model potential parameters for different atoms and ions used in the present calculations are tabulated in table 1. With the model potential fixed, accurate ionization rates for the one-electron system can be calculated accurately using the complex scaling method (Scrinzi *et al* 1999, Chu and Chu 2001).

In table 2, we show the fitted parameter α, together with the critical top-of-the-barrier field strength, F_b, and the ionization energy, I_p, of a few atoms and ions. To assess quantitatively the accuracy of the rates calculated using W_{TI} and W_{TBI}, we define the error by

$$\text{Error} = \frac{W_m(F) - W_{\text{exact}}(F)}{W_{\text{exact}}(F)}. \tag{5}$$

Here m stands for TI or TBI and W_{exact} stands for the rate calculated numerically. From figure 2, it is clear that the TI model works well for small-scaled field but the errors grow exponentially as the field strength becomes larger than the critical field F_b. It is also clear that targets with lower binding energies show faster growth in error. For a scaled field of 2, the error from the TI model can be as high as a factor of 20 for the cases examined. In contrast, the error from the TBI model remains small and stays nearly the same from the tunnelling region to the barrier-suppression region. This shows clearly that the empirical correction factor introduced in equation (2) is quite good. From table 2, we further note that the fitted parameter α ranges from 6.0 to 9.0, covering binding energies from 0.15 to 1.5 au. Based on table 2, we suggest that one chooses $\alpha = 6.0$ for electrons ionized from the s-wave and $\alpha = 9.0$ for ionization from the higher partial waves. With such choices the TBI rates agree with the numerically calculated ionization rates within 50%.

The empirical TBI model can be readily applied to the ionization of molecules in the BSI region if one uses the MO-ADK theory (Tong *et al* 2002) for the TI rates for molecules. In figure 3 we show the static ionization rate from the ground electronic state of H_2^+ at the equilibrium distance, for static field parallel to the internuclear axis. In this case, the ionization rate can also be calculated 'exactly' numerically. The numerical results, shown in figure 3 as filled circles, are shown to be well reproduced by the TBI model in the high field region with

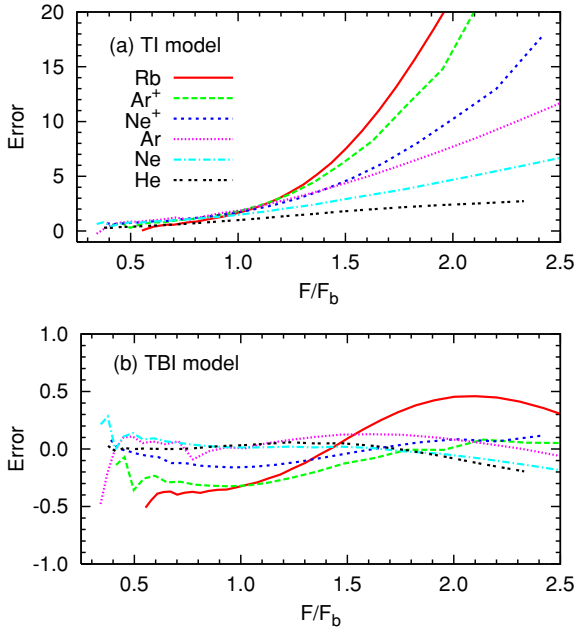

Figure 2. Comparison of ionization rates using (a) the tunnelling ionization model and (b) the tunnelling and barrier ionization model, with the rates solved numerically in the single-active electron approximation for Rb, He, Ne, Ar atoms and Ne^+, Ar^+ atomic ions.

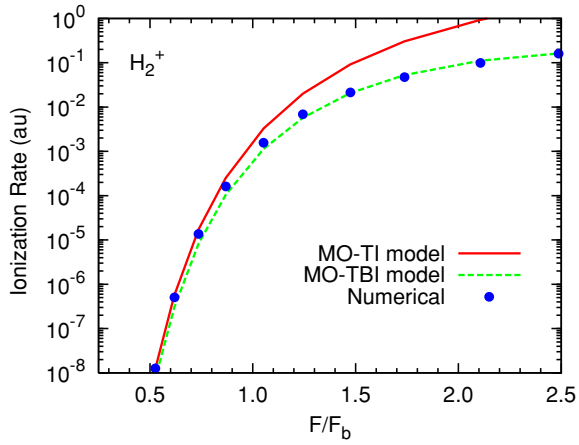

Figure 3. Static ionization rates of H_2^+ molecular ions at the equilibrium distance of the ground potential curve. The electric field is parallel to the molecular axis.

$\alpha = 6$. For other molecules or arbitrary alignment of the molecules, there are no accurate static ionization rates available for further comparison. In view of the success of the MO-ADK model in explaining the ionization dynamics of many molecules (Wells *et al* 2002, Benis *et al* 2004, Litvinyuk *et al* 2003, Alnaser *et al* 2004) in the tunnelling ionization region, we believe that the TBI model can be used for these molecules in the higher intensity region.

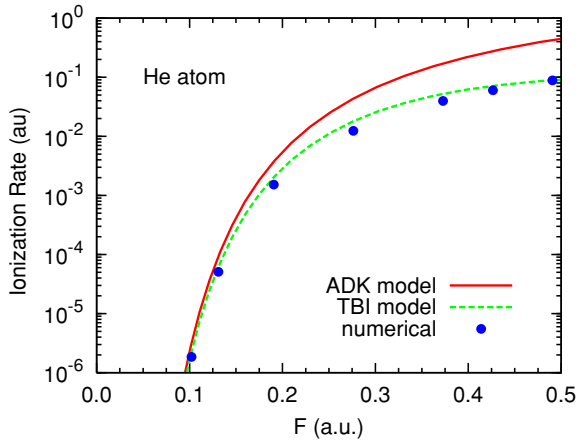

Figure 4. Static ionization rates per electron for He atom. Data for the numerical results are taken from Scrinzi *et al* (1999) where electron–electron correlation was included in the calculation.

So far, we have only presented the comparison of the TBI model with the 'exact' numerical results within the single-active electron model. How good is the single-active electron model? Is many-electron effect important? Figure 4 shows the comparison of the predicted static ionization rates using the TBI model with the 'exact' numerical results calculated by Scrinzi *et al* for He using the complex scaling method where electron correlation was accounted for. The TBI predicted static ionization rates are in good agreement with the 'exact' results over the whole range of laser intensities. The TBI results do show a significant improvement over the ADK model in the over-the-barrier ionization regime ($F > 0.2$ au). We conclude that electron–electron correlation does not affect the tunnelling ionization rates for He in any significant way.

2.2. Ionization probability by a laser pulse

From the static field ionization rate one can calculate the total ionization probability by a laser pulse as

$$P = 1.0 - \mathrm{e}^{-\int_{-\infty}^{\infty} W_m[|F(t)|]\,\mathrm{d}t}. \tag{6}$$

Within this model the ionization probability is not sensitive to the laser frequency. Consider the ionization of atomic hydrogen by a Gaussian pulse of duration of 25 fs of wavelength 800 nm, and of 1064 nm, respectively. The ionization probabilities at the end of the pulse have been calculated as a function of the peak laser intensity by solving the time-dependent Schrödinger equation (Tong and Chu 1997b), as shown in figure 5. Using equation (6), we also calculated the ionization probability using the TI or TBI rates. From figure 5, it is clear that the probability calculated using TBI rates agree much better with the results from the numerical calculations, especially for wavelength of 1064 nm. The probability calculated from the TI model predicts much larger ionization probability at higher intensities. Based on the two curves in figure 4 the saturation intensity calculated from the TI model is $2.75I_0$ ($I_0 = 10^{14}$ W cm^{-2}) while from the TBI model is $4.40I_0$. Here, the saturation intensity is defined at which the total ionization probability is 98%. This is somewhat different from the one used by Hankin *et al* (2001). Discrepancies between the TBI model and the simulated ones from 800 nm laser (open circles) are attributed to the multi-photon contribution. If we

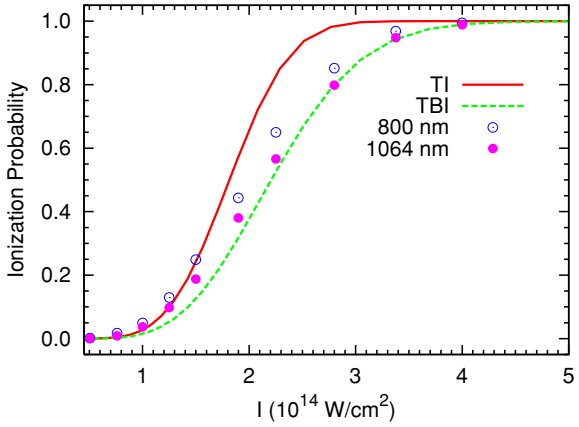

Figure 5. Ionization probabilities of hydrogen atoms in a 25 fs pulsed laser with varying peak intensities.

use long wavelength (1064 nm) (filled circles), the results are closer to the static TBI model's prediction.

2.3. Limitation of the TBI model

The proposed TBI model is an empirical extension of the tunnelling ionization theory to the barrier-suppression regime of an atom or molecule in a static electric field. When it is applied to ionization of atoms or molecules by a laser pulse, it is expected to be valid when the laser interaction can be approximated in the static limit. Thus, the theory is expected to work better for lasers of longer wavelength (see figure 5) or for targets of higher ionization energy. Since the parameter was fitted to accurate numerical ionization rates for atoms within the single-active electron approximation, the TBI rate can be expected to work only when the many-electron effect is small. If the single ionization rate for a many-electron system can be accurately determined experimentally, or calculated accurately by solving the time-dependent many-electron Schrödinger equation, then the comparison of the TBI rate with these data would shed some light on the significance of many-electron effect in the ionization of atoms and molecules by intense lasers. Unfortunately, such accurate rates are not available either from experiment or from theory. We comment that many-electron effect has been discussed in terms of dynamic screening, which tends to be more significant at the higher laser intensity region. In fact, in a recent paper, Smits *et al* (2004) examined the saturation intensity of a number of transition metal atoms. By comparing the saturation intensity from their measurements with the saturation intensity predicted by the ADK model, they found that the experimental saturation intensity is a factor of 2–5 larger than the one predicted based on the ADK model. However, based on figure 5, it is clear that the saturation intensity based on the ADK model tends to be too small. It would be tempting to use the present TBI model to estimate the saturation intensity for their measured systems from which the size of the many-electron effect can be deduced. However, the conclusion from such an exercise is still not very meaningful since the transition metal atoms all have relatively low binding energies, and the validity of the TI and TBI models is not certified. More accurate quantitative evaluation of the many-electron effect for the ionization rates by intense lasers probably should be deduced first for the rare gas atoms where the tunnelling ionization theory is known to work in the TI regime.

3. Summary and conclusions

In summary, we have proposed a simple empirical formula to extend the tunnelling ionization model into the barrier-suppression regime. The proposed empirical formula can provide accurate ionization rates for atoms and molecules in the intense laser field under the single-active electron approximation. The theory can be used to study multiple ionization of atoms, the dissociation and the ionization dynamics of molecules by intense lasers beyond the usual tunnelling ionization regime. It probably can also be used in the modelling of laser–solid interactions where such ionization rates are needed (Bauer *et al* 1998). On the other hand, the present empirical theory has not taken into account many-electron effects since such information is rarely available so far (Tong and Chu 1998, 2001).

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