LETTER TO THE EDITOR

Tunnel ionization of open-shell atoms


View the article online for updates and enhancements.
LETTER TO THE EDITOR

Tunnel ionization of open-shell atoms

Z X Zhao and T Brabec

Physics Department and Center for Research in Photonics, University of Ottawa, 150 Louis Pasteur, Ottawa, ON K1N 6N5, Canada

Received 15 September 2006, in final form 2 October 2006
Published 27 October 2006
Online at stacks.iop.org/JPhysB/39/L345

Abstract
A generalized ADK (Ammosov–Delone–Krainov) theory for ionization of open-shell atoms is compared to ionization experiments performed on the transition metal atoms V, Ni, Pd, Ta and Nb. Our theory is found to be in good agreement for V, Ni, Pd and Ta, whereas conventional ADK theory overestimates ionization by orders of magnitude. The key to understanding the observed ionization reduction is the angular momentum barrier. Our analysis shows that the determination of the angular momentum barrier in open-shell atoms is nontrivial. The Stark shift is identified as the second dominant effect responsible for ionization suppression. Finally, these two effects cannot explain the Nb data. An analysis of the electron spins suggests that Pauli blocking might be responsible for the suppression of tunnelling in Nb.

Atoms and molecules exposed to intense laser fields follow a three-step process: (i) the valence electron is tunnel ionized, (ii) the free electron is accelerated and quivers in the laser field and (iii) the electron can return to its parent ion and collide with it. Recently methods [1, 2] were suggested that use this three-step process to resolve the electronic and vibrational dynamics in the parent system on an attosecond time and Ångstrom length scale. During recollision, electron diffraction and high harmonic generation take place from which a snapshot of the parent system can be retrieved. First proof of principle experiments exists [1, 2]. If these methods can be generalized to make movies of the microscopic dynamics in complex systems, they will undoubtedly trigger a major breakthrough in material sciences. For the retrieval algorithms to work, the electronic wavepacket created during tunnel ionization must be known. This presents a strong motivation to study and understand the physical mechanisms underlying the tunnel ionization of complex systems.

Tunnel ionization theory was developed in several seminal works [3–5]. All of these theories are based on the single-active electron (SAE) approximation, where only the weakest bound electron interacts with the laser field, and on the quasistatic approximation that is valid in the long wavelength limit. The most commonly used tunnelling theories are ADK (Ammosov–Delone–Krainov) [4] and MO-ADK (molecular-ADK) theory [5], which are in
good agreement with the experiments in noble gases and small molecules [6–8]. There is an ongoing discussion about the validity of ADK and Keldysh-type theories in the transition region between the long and short wavelength limits, where both tunnel ionization and multi-photon ionization channels can exist [9–11]. Our work relies on the quasistatic approximation and therewith focuses on parameter ranges, where tunnel ionization dominates.

Theoretical predictions from ADK theory for more complex systems often overestimate experimentally measured ionization yields by orders of magnitude [12–15]. Recently, a quasi-analytical multi-electron theory of tunnel ionization was developed [16], revealing that multi-electron effects have to be accounted for in complex materials. This theory opens the door to explore the new multi-electron physics associated with tunnel ionization in complex systems.

In this letter, we develop the theory of [16] further to analyse the tunnel ionization of the transition metal atoms vanadium (V), nickel (Ni), palladium (Pd), tantalum (Ta) and niobium (Nb). They are significantly more complex than noble gas atoms due to an open d shell and large angular and spin momenta. ADK theory overestimates ionization in transition metal atoms by orders of magnitude [15]. Our work reveals the following new findings.

(i) We find good agreement with V, Ni, Pd and Ta experiments. This further corroborates the applicability of the theoretical framework, developed here and in [16], to general complex systems.

(ii) The first major effect responsible for the suppression of ionization is found to be the angular momentum barrier. The single electron angular momentum $l$ is defined in the asymptotic limit of the valence electron far away from the ion core. In contrast to electron and x-ray photon scattering, being determined by the electronic structure close to the ion core, tunnel ionization is determined by the asymptotic part of the wavefunction. Due to the complexity of open-shell atoms, determination of $l$ is not as straightforward as in noble gases, but requires a careful analysis. This offers novel insight into the structure and complexity of the asymptotic wavefunction of transition metal atoms. The second dominant contribution to the suppression of tunneling comes from an increase of the ionization potential caused by the Stark shift. This is in agreement with recent investigations of $H_2$, where the Stark effect was shown to reduce tunnel ionization [17].

(iii) The two effects discussed in (ii) cannot explain the strong ionization reduction found in Nb. An analysis of the spins of s- and d-orbital electrons suggests that the reduction of tunnel ionization in Nb might be caused by Pauli blocking, an effect central to many-body physics.

(iv) Starting from the quasi-analytical multi-electron theory of [16], a generalized multi-electron ADK/MO-ADK theory is derived, which includes correction factors accounting for the multi-electron effects and angular momentum barrier.

Our analysis begins with the tunnel ionization rate in atomic units from [16],

$$w_m = \frac{\Delta l (m+1)}{(2\kappa)^{2|m+1|} |m|!} \left( \sum_l B_{lm} e^{-\kappa} \right)^2,$$

(1)

where $l$ and $m$ refer to the angular momentum and magnetic quantum numbers of the field-free asymptotic wavefunction of the weakest bound valence electron that is matched with the wavefunction of the tunnelling electron. Note that equation (1) corrects a misprint in equation (8) of [16] with respect to the position of $\sum_l$. The general orientation of the system with regard to the laser electric field is accounted for by $B_{lm} = \sum_m \mathcal{D}^{l}_{m,m}(R) Q_{lm} C_{lm}^*$. Where $Q_{lm}$ is the normalization constant of the spherical harmonics [4, 16]. The rotation matrix $\mathcal{D}^{l}_{m,m}$ rotates the coordinate system by the Euler angle, indicated here by the change of the
ionization potential of the weakest bound electron are given by

\[ V(z) = -\frac{Z}{z} + \frac{\beta_s E}{z^2} - \frac{\beta_n}{2z^4} + \frac{l(l+1)}{2z^6}. \]  

The electric field \( E \) is assumed to point along the \( z \)-direction, \( Z \) is the charge of the residual ion after ionization and \( \beta = \beta_n \) and \( \beta_s = \beta_{n-1} \) refer to the polarizability of the \( n \)-electron system along the \( z \)-direction before and after ionization [16]. The Stark shifted [17] and the field-free ionization potential of the weakest bound electron are given by \( \kappa^2/2 = I_p - (\beta - \beta_s) E^2/2 \) and \( I_p \), respectively. The four terms in equation (2) represent the barrier coming from the Coulomb potential, the laser polarization, the image charge and the angular momentum, respectively.

The last three terms are not accounted for in ADK/MO-ADK theory. Note that in general the polarizability is a tensor. We take only the dominant contribution along the laser electric field into account. Further, as the contribution of the image charge term to the asymptotic wavefunction is weak, \( l \) is well defined and approximately conserved in the field-free limit. In this limit, \( \sum \beta_m = Q_m C_{lm} \). Further, in addition to the image charge there is also a monopole–quadrupole interaction term (\( \propto 1/r^3 \)). This term is found to be more than one order smaller than the terms in equation (2) and is therefore omitted.

Finally, the lower integration limit \( z_0 \) is the point at which the laser dressed, tunnelling wavefunction is matched to the field free, asymptotic ground state, see [16]. Matching has to be done at a field-free point. As complex systems are highly polarizable, the polarization field cancels the laser field at a point \( a \), where \( \beta_a E/a^3 - a E \approx 0 \). The solution of this equation gives \( z_0 = a = \beta_a^{1/3} \). Due to shielding the inner part of the system, \( z \leq a \), is approximately field free. In a metallic sphere, the matching point lies on the surface.

In atoms the total ionization rate \( w \) is obtained from equation (2) by summing over all possible ionization channels. This is done by representing the multi-electron atomic ground state \( (L, M) \) as a sum over tensor products of the ionic ground state \( (L', M') \) and the escaping electron \((l, m)\) and by summing over \( M, M', m \). The weight of the individual tensor products to the atomic ground state is given by the \( 3j \) symbols and \( w = \sum_{M, M', m} w_m(L', l, l; M', M, M) \). We assume that the \( M / M' \) states are energetically close and therewith uniformly populated, and that the ionization rate is weakly dependent on \( M / M' \). Then, the summation over \( M \) and \( M' \) can be performed and results in \( w = 1/(2l + 1) \sum_m w_m \).

When \( V(z) \ll \kappa^2/2 \) for \( z_0 < z < z_1 \) is fulfilled, the square root in \( p_{z=0} \) can be Taylor expanded. In this limit, all the integrals can be solved analytically and contact can be made between equation (1) and ADK/MO-ADK theory. The calculation is fairly involved; details will be given in a longer paper. The generalized ADK/MO-ADK ionization rate is given by

\[ w_m = w_o \left( \frac{E}{2\kappa^4} \right)^{\alpha} \quad \alpha = \frac{l(l+1)E}{\kappa^3} + \frac{2\beta_s E^2}{\kappa^5} - \frac{5\beta_a E^3}{2\kappa^7}, \]  

where \( w_o \) refers to the conventional ADK/MO-ADK ionization rate,

\[ w_o = \frac{|\hat{C}_{lm} Q_{lm}|^2}{2|m||m'|\kappa^{2/\kappa-1}} \left( \frac{2\kappa^3}{E} \right)^{2.5/\kappa-|m|-1} \exp \left(-\frac{2\kappa^3}{3E} \right). \]  

The ADK/MO-ADK matching coefficient in equation (4) is related to the matching coefficient in equation (1) by \( \hat{C}_{lm} = C_{lm} e^{z_0(\beta_{n-1} - \beta_n)E} \). The atomic ionization rate is determined by \( w = 1/(2l + 1) \sum_m w_m \). The three correction terms in \( \alpha \) come from the angular momentum barrier, the laser polarization barrier and the image charge term, respectively. The \( l \)-barrier
**Table 1.** Table for the transition metal elements V, Ni, Pd, Ta and Nb, containing the total charge of the nucleus, configuration, total spin and angular momentum, polarizability (Å³) of neutral and singly charged ion, ionization potential $I_p$ and the angular momentum $l$ of the tunnelling electron. The plus subscript refers to singly charged ions and their properties throughout the letter. The polarizability is calculated by using density functional theory in the local density approximation [19]; $\beta$ agrees with published data, see http://webbook.nist.gov; for $\beta^+$ no data are available for comparison. The configuration data are taken from http://physics.nist.gov/PhysRefData/Handbook/index.html.

<table>
<thead>
<tr>
<th>Z</th>
<th>Neutral</th>
<th>Ion</th>
<th>$I_p$ (eV)</th>
<th>$l$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conf. $^{2S+1}L_J$</td>
<td>$\beta$</td>
<td>Conf. $^{2S+1}L_J$</td>
<td>$\beta^+$</td>
</tr>
<tr>
<td>V</td>
<td>23 $3d^34s^2$</td>
<td>$^4F_{5/2}$</td>
<td>12.4</td>
<td>3d$^4$</td>
</tr>
<tr>
<td>Ni</td>
<td>28 $3d^84s^2$</td>
<td>$^3F_4$</td>
<td>6.8</td>
<td>3d$^9$</td>
</tr>
<tr>
<td>Pd</td>
<td>46 $4d^{10}$</td>
<td>$^1S_0$</td>
<td>4.8</td>
<td>4d$^9$</td>
</tr>
<tr>
<td>Ta</td>
<td>73 $5d^36s^2$</td>
<td>$^4F_{5/2}$</td>
<td>13.1</td>
<td>5d$^6$</td>
</tr>
<tr>
<td>Nb</td>
<td>41 $4d^55s$</td>
<td>$^6D_{5/2}$</td>
<td>15.7</td>
<td>4d$^4$</td>
</tr>
</tbody>
</table>

is not contained in the ADK/MO-ADK theory. The $l$ dependence in ADK/MO-ADK theory comes from the spherical harmonics and the matching coefficient. In the limit of $l = 0$ and small polarizability, equation (3) reduces to the conventional ADK/MO-ADK ionization rate, $w_m = w_0$. A comparison of equation (3) with equation (1) shows excellent agreement for the transition metal atoms investigated here. Therefore, we use equations (3)–(4) throughout the latter. The applicability of (3) for complex molecules will be investigated in future work.

A key to understanding tunnel ionization in transition metal atoms is the knowledge of the angular momentum $l$ of the asymptotic wavefunction of the weakest bound valence electron. Quantum chemistry codes have been used to determine $l$ for small molecules and noble gas atoms [4, 18]. As Hartree–Fock (HF) is sufficient to model these systems, the asymptotic wavefunction can be obtained from the highest occupied molecular orbital. We find that this method is also applicable to Pd and gives $l = 2$, see the discussion below. This allows us also to extract $\tilde{C}_{lm}$ for Pd from the numerical analysis and to compare it with the ADK matching coefficient [4], as determined by quantum defect theory. The ADK matching coefficient is commonly used to calculate the tunnel ionization of atoms. The numerical result is found to be smaller by a factor of 1.2. This difference is insignificant and corroborates the validity of quantum defect theory. Hence, the ADK matching coefficient is used for all the other transition metal atoms, where a numerical determination is not possible.

For the other transition metals, we have performed a configuration interaction (CI) analysis. The configurations are constructed from combinations of parent ion orbitals with a given $L'S'$ and all valence electron orbitals that give the total $LS$ term of the neutral ground state specified in table 1. Our analysis of the transition metal atoms starts with vanadium. The CI calculation shows that the ground state consists of 94% of the $3d^44s^2$ configuration while the ground and the first excited configuration of the V ion are dominated by $3d^4$ and $3d^34s$, respectively. The $3d^4$ ion ground state times a $d$-valence electron represents the asymptotic limit of the $3d^5$ excited state of neutral V. Angular momentum conservation excludes $l = 0$. Similarly, the $3d^44s$ first excited ion state times an $s$-electron represents the asymptotic limit of the $3d^34s^2$ ground state of neutral V. As the two configurations are not exact eigenstates of the transition metal Hamiltonian, there is coupling between the configurations, as a result of which the ground state undergoes a reconfiguration as a function of the (valence electron) distance from the ion core. At a certain distance the ground and excited configuration energies cross, and the coupling between the configurations results in an avoided crossing. At this
avoided crossing the V ground state changes from $3d^34s^2$ close to the ion core to $3d^5$ far away from the ion core. As pointed out in [9], this reconfiguration requires additional energy that is expected to inhibit ionization.

CI does not account for this reconfiguration. It is known that CI, and all other quantum chemistry codes relying on energy minimization, has great difficulties modelling the asymptotic part of the electronic wavefunction. The reason is that variational optimization works well for the high probability parts of the wavefunction close to the ion core, however it is insensitive to the exponentially small asymptotic parts. Due to the complex nature of the wavefunction, we exploit qualitative arguments to identify the correct value of $l$. Quantitatively more accurate ways, including the $R$-matrix method [20], will be explored in a longer paper to obtain exact expressions for the asymptotic wavefunction.

Tunnelling theory assumes that the residual ion is in its ground state after ionization. When an excited state is populated after ionization, which is termed shake-up [21], the ionization potential increases by the energy difference between ion excited and ground state, $\Delta I$. In transition metal atoms $\Delta I \approx 0.3 - 1$ eV is small, so that the shake-up channel might be important. From the discussion above we find that $l = 0$ for the shake-up channel in V. Whereas it would be surprising when tunnel ionization leaves ions dominantly in an excited state, due to the complexity of the problem it also cannot be rigorously ruled out. The $l = 0$ shake-up channel is excluded based on the fact that $l = 2$ explains the experimentally observed ionization suppression very well. We suggest an experiment to corroborate our conclusion. The first excited state in transition metal atoms is non-dipole allowed and therewith metastable. Therefore, the population of the ion states after ionization can be probed by exciting dipole allowed transitions and measuring fluorescence or the loss experienced by the probing laser. For example, in $V^+$ the lowest dipole allowed transitions from the $3d^5$ ground state and the first excited (metastable) $3d^34s$ state can be probed, with transition energies of $\approx 4.5$ eV and $4$ eV, respectively.

For $l = 2$, our theory is in good agreement with the experimental data of [15]. In figure 1, the ionization yield $\int w[E(t)] \, dt$ is plotted versus the laser peak intensity. For pulse
parameters and the shape of the laser electric field $E(t)$ see the figure caption. Our theory (full line) explains the difference between experiment (empty circles) and ADK theory (dashed line). Half of the difference is due to the $l$-barrier which is not accounted for in ADK/MO-ADK theory. As $\beta_s$ is small, the role of the laser polarization induced barrier is insignificant. The other half of the difference is accounted for by the Stark shift, which reduces ionization by increasing the ionization potential. The large Stark effect arises from the big difference in polarizabilities $\beta$ and $\beta_+$. As the Stark effect increases with laser intensity, its effect is most pronounced at high intensities. Therefore, the ionization yield rises gradually and reproduces the shape of the experimental curve, in contrast to the abrupt rise predicted by ADK/MO-ADK theory. Switching off the $l$-barrier shows that the Stark effect requires the $l$-barrier to suppress ionization effectively. Without the $l$-barrier ionization would be shifted to lower intensities, where the role of the Stark effect is insignificant.

Part of the large discrepancy between ADK/MO-ADK theory and experiment might arise from the fact that ADK/MO-ADK overestimates tunnel ionization in the above barrier limit. The Coulomb barrier is suppressed at an electric field $E_{bs} = I_p^2/4$, which corresponds to a laser intensity of $7 \times 10^{13}$ W cm$^{-2}$ in V. Hence, barrier suppression in V occurs before ADK/MO-ADK theory shows that significant ionization takes place. In H and He, ADK/MO-ADK theory overestimates above the barrier ionization rates by a factor of 2–4 [22, 23], which is by far not enough to explain the difference in figure 1. In transition metals the magnitude of the overestimation is unknown. Nevertheless, we believe that barrier suppression is not the dominant factor responsible for the difference between ADK/MO-ADK theory and experiment. Significant ionization usually takes place around the intensity at which the barrier is suppressed. In V, ionization becomes dominant in the range between $4 \times 10^{13}$ W cm$^{-2}$ and $7 \times 10^{13}$ W cm$^{-2}$, which is a factor of 5–10 larger than the barrier suppression intensity. It appears to be counterintuitive that ionization should only start at intensities so much higher than the barrier suppression intensity. In our opinion, the large difference points to the fact that ADK/MO-ADK theory, which is exclusively based on the Coulomb barrier, underestimates the true tunnelling barrier. This is corroborated by our theory, equation (2). Due to $l$-barrier and Stark shift, the tunnelling barrier is not suppressed over the laser intensity range used in figure 1.

For Ni, Ta and Pd, we get similarly good agreements as for V, see figure 1. Ni undergoes a ground-state reconfiguration similar to V, following the same argument as for V and using $l = 2$. In Pd, the CI calculation gives $l = 2$. In Ta, we did not find a ground-state reconfiguration, and our simple analysis would indicate $l = 0, 2$ for the fundamental ionization channel. As we cannot decide which of the channels is dominant, $l = 2$ is used as an ad hoc assumption to explain the experiments. We feel that this is justified by the complexity of the problem and by the lack of rigorous tools for the calculation of the asymptotic ground-state wavefunction.

Finally, for Nb we could not get agreement with experimental data. The possible CI channels are $l = 0, 2, 4$. We have performed calculations for $l = 0, 2, 4$. The ionization rate depends only weakly on $l$. We use $l = 0$ in figure 1. We conclude that the $l$-barrier is not responsible for the observed ionization suppression. Further, ionization due to dimers and higher clusters was excluded experimentally [24].

A spin analysis of the s- and d-electrons shows that the spins of the tunnelling and bound electrons are all parallel in Nb. In all other transition metal atoms the spins of the bound electrons are parallel; however the tunnelling spin points in the opposite direction. Therefore, in V, Ni, Pa and Ta, the exchange effect between tunnelling and bound electrons is zero. In contrast to that, the tunnelling electron in Nb feels the exchange effect with the bound electrons. The exchange effect makes it harder for the tunnelling electron to pass the other
open-shell electrons and to escape. In the language of many-body physics this is termed Pauli blocking. Based on the fact that none of the other mechanisms can explain the Nb experiments, we speculate that Pauli blocking is responsible for the observed ionization suppression. A quantitative proof will require a generalization of the current ionization theory to account for the exchange effect, which will be subject to future work.

References

[3] Smirnov B M and Chibisov M I 1966 The breaking up of atomic particles by an electric field and by electron collisions Sov. Phys.—JETP 22 585
[22] Bauer D and Mulser P 1999 Exact field ionization rates in the barrier-suppression regime from numerical time-dependent Schrödinger-equation calculations Phys. Rev. A 59 569
[24] Rayner D 2006 Private communication