Theory of Tunnel Ionization in Complex Systems

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A quasianalytical theory of tunnel ionization is developed that is applicable to general complex systems, such as large molecules. Our analysis reveals strong deviations from conventional tunnel ionization theories, dependent upon the system’s geometry, angular momentum, and polarizability. A comparison of our theory with recent C60 ionization experiments yields reasonable agreement.

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Intense femtosecond laser fields are an important tool for the measurement and coherent control of microscopic processes in complex materials [1]. Tunnel ionization often plays a key role in these processes, making a thorough understanding of ionization essential.

Ionization in noble gas atoms and diatomic molecules is well reproduced by conventional tunnel ionization theories, such as ADK (Ammosov-Delone-Krainov) and MOADK (molecular-ADK) [2–4]. These are based on the single active electron (SAE) approximation, where only the weakest bound valence electron interacts with the laser. Recent investigations [5,6] showed that the SAE approximation fails for large molecules. Since a full numerical solution of systems with more than two electrons is beyond reach [7], there is a demand for an ionization theory that can handle complex materials.

This demand is met by our Letter. A tunnel ionization theory applicable to complex systems is developed. The Letter is organized in three parts.

First, a long-range multielectron strong-field (LMS) ansatz is introduced. Starting from the multielectron Schrödinger equation, a single-electron equation for the tunneling electron is derived. Our analysis generalizes SAE theories [2–4] and puts them on a solid theoretical footing. The LMS approach takes into account the long-range interaction between tunneling and core electrons and proves that it can be accounted for by the system polarizability [6]. Further, it solves the long-standing issue of why the laser induced Stark shift does not affect tunneling and reveals how bound electron reconfiguration takes place during tunnel ionization.

In the second part, the obtained equation is solved analytically along the lines of ADK theory, yielding expressions for the ionization rate and momentum distribution of the electron wave packet born in the continuum. In contrast to previous theories, our analysis also takes account of the angular momentum barrier. We find that the width and shape of the momentum distribution in complex materials show strong deviations from ADK theory.

In the last part, our theory is applied to C60 2+ with Z = 1–9. Comparing ionization probabilities and momentum distributions with recent experiments [6] shows reasonable agreement and corroborates the validity of our approach. Finally, our analysis of C60 shows that the angular momentum of the highest occupied molecular orbital (HOMO) imprints a signature on the momentum distribution of tunnel ionized electrons that can be used to study ultrafast electronic reconfiguration dynamics in complex materials.

Tunnel ionization takes place in the quasistatic limit [3]; i.e., the laser remains constant during the tunneling process. Therefore, our derivation starts from the time-independent, n-electron Schrödinger equation (in atomic units),

\[ -I_n \Psi_n = \left[ \sum_{j=1}^{n} (H_j - \mathbf{r}_j \cdot \mathbf{E}) + V_{ee}^n \right] \Psi_n, \]

where \( H_j = T_j + V_j \) denotes the field free single-electron Hamiltonian of the jth electron with \( T_j = -(1/2)\nabla_j^2 \), and \( V_j \) the attractive potential due to the nuclei with total charge m. The second term in (1) represents the electron laser dipole interaction with \( \mathbf{E} = -\mathbf{z}E \). The repulsive interaction potential of the n electrons is \( V_{ee}^n = \Sigma_{k<j}^n 1/|\mathbf{r}_k - \mathbf{r}_j| \). The charge of the parent ion before and after ionization is \( Z = m - n \) and \( Z = m - n + 1 \), respectively. Finally, the laser dressed wave function and total energy of the n-electron ground state are denoted by \( \Psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) \) and \( I_n \), respectively. Second order perturbation theory yields \( I_n = I_n - (1/2)\beta_n E^2 \) with \( I_n \) the field free total energy and \( \beta_n \) the polarizability tensor component along \( \mathbf{E} \).

Equation (1) is solved by using our LMS ansatz \( \Psi_n(\mathbf{r}_n, \mathbf{r}) = \Psi_{n-1}(\mathbf{r}_n, \mathbf{r}) \otimes \Psi_f(\mathbf{r}) \), where \( \Psi_{n-1} \) is the ground state of the ionized system in the combined fields of laser and escaping electron, and \( \Psi_f \) denotes the wave function of the tunneling electron. For convenience, the ionizing electron is assigned the coordinate \( \mathbf{r} = \mathbf{r}_n \), and \( \mathbf{r}_r = (\mathbf{r}_1, \ldots, \mathbf{r}_{n-1}) \) refers to the residual bound electrons. The neglect of antisymmetrization between tunneling and core electrons in the LMS ansatz is valid asymptotically for \( |\mathbf{r}| \gg |\mathbf{r}_r| \), as the overlap integrals between tunneling and bound electrons become negligible. Further, \( V_{ee}^n \) can be
expanded to second order in \( |r| \), yielding \( V_{ee}^n = V_{ee}^{n-1} + (n-1)/|r| + \sum_j \frac{n-1}{r_j} \cdot d \). Here, \( V_{ee}^{n-1} \) denotes the interaction between the \( n-1 \) core electrons. The second and third terms represent the monopole and dipole interaction between tunneling and core electrons, with \( d = (r/|r|^3) \approx \kappa d \) and \( d = 1/z^2 \).

The LMS ansatz is conceptually equivalent to the Born-Oppenheimer approach, which is used to decouple the motion of nuclei and electrons in molecules. It relies on the assumption that the bound electrons follow adiabatically changes induced by the tunneling electron. This assumption excludes the nonadiabatic population of excited bound states. Under the barrier the electron wave function follows adiabatically the laser and thus creates an electric field with laser frequency \( \omega \). The adiabatic approximation is valid as long as the change of the field created by the tunneling electron is slow as compared to the transition frequency between ground and first excited states of the residual ion, i.e., \( \omega < \omega_{n-1} \).

Following the Born-Oppenheimer derivation [8], Eq. (1) can be decoupled into two equations, separating \( \Psi_{n-1} \) and \( \Psi_t \). The bound electron part satisfies

\[
-I_{n-1} \Psi_{n-1} = \left[ \sum_{j=1}^{n-1} (H_j - z E_j) + V_{ee}^{n-1} \right] \Psi_{n-1},
\]

where \( I_{n-1} = I_{n-1} - (1/2)\beta_{n-1}E_j^2 \) is the total energy of the electronic ground state of the ionized medium dressed by the combined laser and tunneling electron field, \( E_j = E - d \). The total energy of the field free electronic state is \( I_{n-1} \), and \( \beta_{n-1} \) is the polarizability.

The equation for the tunneling electron is

\[
-(I_n - I_{n-1}) \Psi_t = \left( T - \frac{Z}{|r|} - zE \right) \Psi_t.
\]

The second term on the right-hand side contains the monopole contributions of the ions and bound electrons. The first term, \( \langle \Psi_{n-1} | T | \Psi_{n-1} \rangle \), contains an integration over \( d^2r \). The kinetic operator is applied with respect to \( r \), yielding \( \nabla^2 \Psi_{n-1} \Psi_t = \Psi_{n-1} \nabla^2 \Psi_t + 2 \nabla \Psi_{n-1} \nabla \Psi_t + \Psi_t \nabla^2 \Psi_{n-1} \). Similar to Born-Oppenheimer theory, the second and third terms can be neglected [8]. Perturbation theory shows they contribute to higher order multipole terms.

The energy difference in (3) can be written as \( I_n - I_{n-1} = I_p + (1/2)(\beta_{n-1}E_j^2 - \beta_{n-1}E_j^2) \) with \( I_p = I_n - I_{n-1} \) the field free ionization potential of the HOMO. As the change in polarizability due to the removal of a single electron is generally small, \( \beta_{n-1} \approx 0 \), the laser induced Stark effect cancels. This answers the long-standing question of why the laser induced Stark shift does not affect tunnel ionization. Setting \( \beta = \beta_{n-1} \) gives \( I_n - I_{n-1} = I_p + \Delta I_p \) with \( \Delta I_p = -2\beta E/z^2 + \beta/z^4 \). The first and second terms are due to the laser induced dipole and the image charge of the tunneling electron, respectively.

With the above approximations Eq. (3) becomes

\[
I_p \Psi_t = \left( \frac{1}{2} \nabla^2 - V(r) + zE \right) \Psi_t,
\]

\[
V(r) = -\frac{Z}{|r|} + \frac{2\beta E}{z^2} - \frac{\beta}{z^4}.
\]

Equation (4) is the first main result of this Letter, generalizing ADK/MDK-ADK theory to describe complex materials. The interaction between core and ionizing electrons is accounted for by \( \beta \).

Conventional SAE theories do not describe the reconfiguration of the remaining bound electrons during tunnel ionization. Our analysis reveals the following picture. The potential barrier modification in (4) can also be interpreted as a change in binding energy of the tunneling electron by \( \Delta I_p \). Because the total energy \( I_n \) has to remain conserved during ionization, the residual bound electron energy \( I_{n-1} \) must undergo a Stark shift by \( -\Delta I_p \), see (2). As a result of the coupling caused by energy conservation, the residual electron core reconfigures into its new ground state following adiabatically the motion of the leaving electron.

For a charged sphere of radius \( a \) the polarization terms in (4) agree asymptotically with the classical, electrostatic expression \( 2\beta E/z^2 - Z/z - \beta/[z^2(1 - (a/z)^2)] \). Close to the molecule surface the dipole approximation fails and the classical image charge terms differ. Quantum mechanically, both terms show deviation close to the surface (\( \approx 1 \text{ Å} \)). Guided by the following picture, we neglect these changes in a first order approximation. The integrated area under the potential curve determines the exponent of the tunneling rate. When the tunneling barrier is large, the contributions close to the surface present only a small part of the integrated area. Only close to the barrier suppression intensity do the near field contributions dominate the tunneling exponent. However, in this range the tunneling exponent goes to zero, and errors in the exponent (exp[O(0)] = 1) have little weight.

In the second part of the Letter, Eq. (4) is solved to determine ionization in complex materials. In standard ionization theory [2-4] the (angular momentum-) \( l \)-barrier \( (l + 1/2)^2/r^2 \) is neglected. As complex systems can have large \( l \) values, this effect must be accounted for. Quasically classically the angular momentum \( l(l + 1) \) has to be substituted by \( (l + 1/2)^2 \) [9]. We solve (4) in two limits: near the surface, where laser field effects are weak and the \( l \) barrier is most pronounced, and far from the surface, where the laser field dominates and the \( l \) barrier is negligible. The two solutions are connected in the intermediate area.

The solution close to the surface starts from spherical coordinates, \( r = |r|, \theta, \phi \). As only parts of the wave function in a narrow cone along the laser electric field, \( \theta = 0 \), contribute to tunnel ionization, the solution can be greatly simplified. Using \( \cos(\theta) = 1 \), angular and radial parts of Eq. (4) are decoupled and the solution can be written as \( \Psi_t = \sum_r C_{r \ell} Y_{r \ell}(\theta, \phi) F_r(r) \). The spherical har-
monics are approximated by the leading term

$$Y_{lm} = \frac{Q_{lm}}{\sqrt{2\pi^2} |m|!} \sin^{|m|} \theta e^{i m \phi},$$

$$Q_{lm} = (-1)^m \sqrt{(2l+1)(l+|m|)!} \frac{(2l+1)(l+|m|)!}{2(l-|m|)!}.$$

The resulting equation for $F_1(r)$ is solved by the Wentzel-Kramers-Brillouin method, and $\Psi_z$ is Fourier transformed to the coordinate system $z, p, \varphi$ by using the smallness of the laser field. Here, $p$ and $\varphi$ determine the momentum transversal to $\hat{z}$. Far from the surface, the angular momentum contribution is negligible, and Eq. (4) is solved directly for $\Psi_z(z, p, \varphi)$.

Matching of the two solutions gives

$$\Psi_z = \sum A_j \sqrt{\frac{2^{|m|} |m|!}{\pi^2}} \exp \left( -\int_{z_0}^{z_1} p_z dz \right),$$

$$A_j = \sum_{m} \frac{C_{lm}^m P_{lm}^{|m|} \exp \left( \phi + \varphi/2 \right)}{2^{|m|} |m|!} \frac{\sqrt{\pi^2}}{2^{|m|} |m|!}$$

with $p_z = [\kappa^2 + p^2 + 2(V(z) + (l + 1/2)/z^2 - E_z)]^{1/2}$ the momentum along $\hat{z}$, and $\kappa^2 = 2I_p$. The integration limits $z_0$ and $z_1$ are the turning points at which $p_z = 0$. Here, we use $z_0 = a$. The coefficients $C_{lm}^m$ are determined in the following way. The field free ground state wave function [10] is calculated by a quantum chemistry code (e.g., density functional theory) and expanded in terms of spherical harmonics with coefficients renormalized so that the numerical $F_1(r = z_0) = 1$. It is sufficient to determine the $C_{lm}^m$ along a single direction, preferentially a molecular axis. Ionization along an arbitrary direction can be calculated by a rotation of the coordinate system by the Euler angle $\mathbf{R}$, keeping $E \parallel \hat{z}$ [4]. This determines $P_{lm}^m = \sum_{m'} D_{m'm}^m(\mathbf{R}) Q_{lm}$, with the rotation matrix $D_{m'm}^m$ given, e.g., in Ref. [11].

From Eq. (6) the tunneling current, $j_z = |\Psi_z|^2 p_z$, is

$$j_z = \sum_j \frac{|A_j|^2}{2\pi} \exp \left[ -2t - \left( \frac{p_z}{\Delta} \right)^2 \right].$$

Here, $t = \int_{z_0}^{z_1} p_z dz$, and $p_{z0} = p_z(p = 0)$. The exponent was expanded to first order in $p_z^2$, yielding the term with $1/\Delta^2 = \int_{z_0}^{z_1} 1/p_z dz$. We do not further evaluate the two integrals in (7), as they can be integrated numerically very efficiently. However, analytical integration is possible when $\kappa^2$ dominates $p_z$.

Equation (7) solves another long-standing issue: it determines the transversal momentum distribution of electrons born by tunnel ionization of molecules. We find the following differences between our approach and atomic ADK theory. First, the $1/e$ width is, in general, different from $\Delta^2 = E/k$ [3]. Second, because of the complex geometry of molecules, the momentum distribution can exhibit a much richer structure than a Gaussian dependence [3]. For $m \neq 0$, as for O$_2$, the momentum distribution exhibits a minimum at $p = 0$. If terms with different $m$ interfere in $A_j$, the electron wave packet loses its $\varphi$ symmetry.

Finally, the ionization rate is obtained by performing the integral $w = \int d\varphi \, dppj_z$, which gives

$$w = \sum_{lm} \frac{C_{lm}^2 \left| P_{lm}^m \right|^2 \left( \frac{2(l+1)}{2(m+1)l+1} \right)^{1/2}}{2\pi^2} \exp \left[ -2t \right].$$

The quasi-analytical solutions (7) and (8) present our second major result.

In the last part of the Letter we calculate tunnel ionization for C$_{60}$H$^+$ and compare it to recent experiments. We use the following parameters: $\beta = 80 \, \text{Å}^3$, outer radius of the shell surface $a = 4.7 \, \text{Å}$, shell center radius $a_c = 3.54 \, \text{Å}$, and ionization potentials as determined by the molecular capacitance model [6]. Density functional calculations show two different regimes. For $Z = 1, 2$, C$_{60}$ is close to spherically symmetric. The HOMO has $I_h$ symmetry and is characterized by $l = 5$, $m$ degenerate [12]. We obtain a weakly $Z$-dependent $C_{10}^Z = 0.15$. Note that (8) applies to a nondegenerate HOMO. In case of degeneracy, $w$ is averaged over the individual $m$ contributions, i.e., the $\Sigma_m$ in (8) is replaced by $1/(2l+1)\Sigma_m$. For $Z > 2$, C$_{60}$ undergoes a Jahn-Teller deformation resulting in $e_1$ HOMO states of the $D_{5d}$ group [12] with $l = 1$ the lowest spherical harmonic. Along the main axis of the molecule only $m = \pm 1$ contribute. Along all other directions $m = 0$ contributes, as determined by $D_{5d}^l$. Ionization is calculated by averaging over all directions. A comparison shows that $m = 0$ dominates ionization. We find $C_{10}^Z = 0.1$, again weakly $Z$ dependent.

In Fig. 1 the charge of C$_{60}$ is plotted versus a characteristic intensity $I_\theta$ that signifies the onset of strong ionization. The onset intensity is determined by calculating the ionization probability versus laser intensity. The linear regime of this graph is extended to the intensity axis. The point of intersection determines $I_\theta$. The squares denote the measured data from Ref. [6]. The circles and triangles denote calculations without and with the $l$ barrier, respectively. The good agreement of the triangles pointed up with experiment demonstrates the importance of the $l$ barrier for large $l$. For $l = 1$ the $l$ barrier is found to be negligible, and results without $l$ barrier are not shown. For $Z > 2$ the empty triangles pointed up and down refer to $I_h$ and $D_{5d}$ symmetry, respectively. As all electrons are stripped by one laser pulse within $\approx 70$ fs, it is not clear whether the system has time to undergo symmetry breaking from $I_h$ into $D_{5d}$. Physically both options are possible, dependent on whether the reconfiguration is driven by electrons or by nuclei. As both are in reasonable agreement with experiment, the relevant mechanism cannot be inferred from Fig. 1 alone.
There is, however, an indication that fast electronic transitions might be dominant. We suggest to use the momentum distribution of the ionized electron as a signature to identify the dominant \( l \) state. For \( l = 5 \) the \( m \neq 0 \) and the \( m = 0 \) contributions are comparable, resulting in a dip in the center of the momentum distribution. For \( l = 1 \) the momentum distribution is dominated by \( m = 0 \) and therefore is Gaussian, in agreement with experiments for \( \text{C}_{60}^{4+} \) [6]. An experimental confirmation of the predicted dip for \( Z \leq 2 \), where \( l = 5 \) is known to be dominant, will prove electronically driven symmetry breaking. Systematically decreasing the pulse duration will further allow one to time resolve the transition dynamics. Thus, our theory enables time-resolved pump-probe spectroscopy of ultrafast electronically driven reconfiguration processes, difficult to access otherwise.

In Fig. 2 the \( 1/\varepsilon \)-momentum distribution width is plotted versus peak intensity for \( \text{C}_{60}^{4+} \). Graphs 1 and 2 show \( \Delta \) as determined by Eq. (7) and by ADK theory, respectively. Whereas ADK theory predicts a slow increase of \( \Delta \) with intensity, graph 1 shows a rapid increase as a result of the shape of the tunneling barrier. The singularity is a result of the dipole approximation used for the near field potential. Inclusion of the electrostatically exact polarizability terms shows that the steep increase remains; however, the singularity levels off close to barrier suppression. The full square is the corresponding data point measured in [6]. Considering experimental uncertainties arising mainly from the measurement of the laser intensity, the agreement is reasonable. A laser intensity 50% larger than the experimentally specified one would yield very good agreement.

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[10] Inside the molecule the total electric field is weak. The polarized core field will cancel the laser field; this can also be inferred from the negligible laser induced Stark shift of the tunneling electron.