The electron tunneling from fullerene molecule in a weak electric field

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Abstract. We derive equations describing the electron tunneling ionization of the molecular orbitals without symmetry. The modified method of smooth matching the asymptotic wave functions with molecule's wave functions is suggested, to use the results of numerical calculations of the molecules in the GAUSSIAN. The spatial distribution of the current is considered for tunneling ionization the fullerene C60. We obtained the ionization probability of individual orbitals and spatial distribution of the electron currents at different values of the field, a distance to the screen and orientation of the fullerene.

1. Introduction

Tunneling ionization of atoms and molecules is determined by the behavior of the valence electron at large distances from the atomic nucleus. To simplify the problem, one often used one-dimensional models. The most common variant of this model is a well known the Fowler-Nordheim formula for metals with the Coulomb correction on the image-potential [1]. The heterogeneity of the studied structure is taken into account in such a model by semi-empirical correction factors [2, 3]. A simplified approach to the description of tunneling currents from individual atoms is based on an idea of the point source [4, 5]. It allows one to calculate the spatial distribution of the electron current for a simple [6] and complex emitters [7]. This approach is useful in describing the tunneling electron in negative ions [8] and electron photodetachment in the presence a constant electric field [9-11], but is not suitable for neutral atoms and molecules with the long-range Coulomb interaction. The consistent solution to the problem is based on the fact that at large distances from the nucleus the electron wave function satisfies the Schrödinger equation with the Coulomb potential and the potential of a uniform electric field. This asymptotic behavior of the potential allowed us to obtain an analytic solution to the problems of tunneling ionization of the hydrogen atom and hydrogen-like ions [12, 13].

In this paper we consider the spatial distribution of current in the tunneling ionization of fullerene C60 in a uniform electric field. Note that a strong external electric field leads to additional changes in the electronic structure of the fullerene [14, 15]. In any case, the current spatial nonuniformity arises from the distribution of the local electron density over different molecular orbitals.

2. The asymptotic model of the tunnel ionization in a weak electric field

We follow the general approach to the ionization of many-electron systems [16, 17] and use a number of approximations. The first is the approach of the frozen cores. The second is the idea that the
dynamics of each individual electron $j$ can be represented as a motion in a nonlocal potential $\hat{V}_j(r_j)$, in which the self-interaction is eliminated. This means that we considered atomic and molecular systems well described in the Hartree-Fock approximation, and the complete wave function can be represented as a product of antisymmetrised one-electron wave functions of the individual electrons. This means that the Hamiltonian $H$ of the whole electronic system can be written as a sum of single-particle Hamiltonians (in atomic units):

$$
H = \sum_{j=1}^{N} h_j, \quad h_j = -\frac{1}{2}\Delta_j + \hat{V}_j(r_j),
$$

where $N$ is number of electrons in the system. After projecting onto the space of the bound states of $N - 1$ electron, for the tunnel electron we obtain the equation

$$
\left( -\frac{1}{2}\Delta + \hat{V}(r) \right)\psi = E\psi.
$$

At a large distance from the center of orbitals we have

$$
\left. \hat{V}(r) \right|_{r\to\infty} = -\frac{1}{r} + F_z.
$$

In this region the asymptotic solution of the Schrödinger equation is factorized in the parabolic coordinate system [18].

In the inner atomic-molecular space, the quantum states are calculated numerically based on the method of molecular atom-like orbitals. The main difficulty of tunneling problem is to coordinate solutions within the molecule and asymptotically remote region. Implementation of this approach presupposes the existence an area in which both solutions are correct. However, the sample functions used in a well-known the GAUSSIAN program of the quantum chemistry simulation do not have the correct asymptotic behavior in the under-barrier region. The initial basis functions contain the usual separation of radial and angular coordinates. For a molecular orbital, the wave function in the coordinate system with the center in atom is written as

$$
\psi_{LM}(r, \theta, \varphi) = \sum_{LM} C_{LM} R_{\ell}(r) Y_{LM}(\theta, \varphi),
$$

where $Y_{LM}(\theta, \varphi)$ is spherical harmonic, $L$ and $M$ are the quantum numbers of the angular momentum and its projection to the selected axis, $r, \theta, \varphi$ are spherical coordinates, and the radial part at large $r$ decreases as the Gaussian distribution, that is, the asymptotic behavior is false. Therefore, convenient functions that meet the compatibility conditions are absent. One way to overcome this difficulty is the analytic continuation of numerical solution out of the area of their formal applicability [19] with the subsequent fitting the asymptotic in sub-barrier region. A special feature of our procedure is to coordinate the amplitudes of numerical and analytical asymptotic wave functions at the point of smooth matching solutions before entering the under-barrier region by continuation of the semiclassical asymptotic of the outgoing wave to this area. The advantage of this approach is the uniqueness of the asymptotic fitting and option to account for electric field action close to the inner turning point.
3. Separation of variables in the Schrödinger equation for hydrogen atom in parabolic coordinates

The Schrödinger equation for an electron with energy $E$ in the Coulomb attraction field and a uniform electric field of strength $F$ in parabolic coordinates takes the form

$$
\frac{4}{\xi + \eta} \left[ \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \psi}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left( \eta \frac{\partial \psi}{\partial \eta} \right) \right] + \frac{1}{\xi \eta} \frac{\partial^2 \psi}{\partial \phi^2} + 2 \left( E + \frac{2}{\xi + \eta} \frac{F}{2 (\xi - \eta)} \right) \psi = 0 ,
$$

(5)

where $x = \sqrt{\xi \eta} \cos \phi$, $y = \sqrt{\xi \eta} \sin \phi$, $z = 2^{-1} (\xi - \eta)$ are parabolic coordinates [18].

We are looking for a solution of equation (5) as a product of functions

$$
\psi = \Phi(\xi) X(\eta) e^{im\phi} (2\pi)^{-1/2} .
$$

(6)

Introducing variables $\Phi(\xi) = \phi(\xi) \xi^{-1/2}$ and $X(\eta) = f(\eta) \eta^{-1/2}$ we obtain two differential equations

$$
-\frac{1}{2} \frac{d^2 \phi}{d \xi^2} + U_1(\xi) \phi = \frac{E}{4} \phi ,
$$

(7)

$$
-\frac{1}{2} \frac{d^2 f}{d \eta^2} + U_1(\eta) f = \frac{E}{4} f .
$$

Effective potentials that are contained in the equation (7) are equal

$$
U_1(\xi) = -\frac{\beta_1}{2 \xi} + \frac{m^2 - 1}{8 \xi^2} + \frac{F \xi}{8} ,
$$

(8)

$$
U_1(\eta) = -\frac{\beta_2}{2 \eta} + \frac{m^2 - 1}{8 \eta^2} - \frac{F \eta}{8} ,
$$

with separation constants $\beta_1 + \beta_2 = 1$. Ionization occurs in the direction $z \to \infty$, which corresponds to the coordinate $\eta \to \infty$. External weak field has no significant effect on the function $\phi$. Therefore, as an approximate solution of the equation (7) we can take the well-known exact solution for $F = 0$ [16], which is expressed in terms of the generalized Laguerre polynomials:

$$
\phi_{mn}(\xi) = \kappa^{1/2} (\kappa \xi)^{m/2} e^{-\kappa/2} \left( \frac{n_m!}{(n + |m|)!} \right)^{1/2} L_{n_m}^{(m)}(\kappa \xi) ,
$$

(9)

$$
n_m = -(|m| + 1)/2 + n \beta_1 , \kappa = \sqrt{2 E} , E = -(2n^2)^{-1} .
$$

For the analysis of the second equation (7) we introduce variables $\rho = \kappa \eta$, $\tilde{F} = F/(4 \kappa^{3/2})$, $\beta = \beta_2/\kappa$, and obtain

$$
\left( \frac{d^2}{d \rho^2} + k^2(\rho) \right) f(\rho) = 0 ,
$$

(10)

$$
k^2(\rho) = \frac{1}{4} - \frac{m^2 - 1}{4 \rho^2} + \tilde{F} \rho + \frac{\beta}{\rho} .
$$
The asymptotic solution of the equation (10) is considered in [20]. Classical turning points are
\[ \rho_1 \sim 2\beta + (4\beta^2 - m^2 + 1) \frac{1}{2}, \quad \rho_2 \sim \left(4\bar{F}\right)^{1/2}. \]
In the interval between these points, the potential gradually transforms from the Coulomb potential into linear one. In the vicinity of each of the turning points the solution can be written as
\[
f_{i,z}(\rho) = \frac{1}{\sqrt{v_{i,z}(\rho)}} \left[ a_{i,z} \text{Ai}[v_{i,z}(\rho)] + b_{i,z} \text{Bi}[v_{i,z}(\rho)] \right],
\]
where
\[
v_i(\rho) = \left( \frac{3}{2} \int_0^{\rho} |k(\rho)| d\rho \right)^{2/3}, \quad \rho > \rho_i,
\]
and
\[
v_i(\rho) = -\left( \frac{3}{2} \int_0^{\rho} |k(\rho)| d\rho \right)^{2/3}, \quad \rho < \rho_i.
\]
To the left of the point \( \rho_1 \) and the right of the point \( \rho_2 \) the solution is oscillatory. In the interval \( \rho_1 < \rho < \rho_2 \) the solution is the sum of exponentially decreasing and increasing functions. To coordinate asymptotic we use the semiclassical approximation [18].

4. Ionization probability

The motion of the electron in the initial molecular orbitals splits into channels corresponding to certain states of the hydrogen atom [19]. The solution of the problem of electron tunneling at distance \( \rho \gg \rho_2 \) can be written as the sum over the channels with certain parabolic quantum numbers:
\[
f(\eta) = \eta^{-1/2} \sum \hat{A}_i \phi_i(\xi) e^{i\eta \theta}, \quad \nu = n, m.
\]
In the weak-field approximation coefficients \( \hat{A}_i \) are expressed in terms of coefficients of matching asymptotic of the exact and numerical solutions. The initial state \( \psi_0(r) \), projected onto the full set of functions \( \phi_{n,m}(\xi) e^{i\eta \theta} \), gives the result
\[
G_{n,m}(\theta, \eta) = \int_0^{2\pi} \int_0^\infty \phi_{n,m}(\xi) e^{i\eta \theta} \psi_0(r) d\xi d\varphi,
\]
where \( \theta \) is the angle between the direction of the electric field and the axis of quantization of the orbital angular momentum of an electron in the molecular orbital.

The known asymptotic behavior of the wave function of a tunnel electron (6) allows us to calculate the probability of ionization, using the current density \( j_z \) in the direction of the axis \( z \) through the orthogonal surface \( S \), in the form of
\[ \Gamma = \int j_z \, dS. \] (16)

Here, the current density for a large \( z \) can be written as
\[ j_z = i \left( \psi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \psi^*}{\partial z} \right) \approx i \frac{|\phi(|x|)|^2}{2\pi \xi \eta} \left( f^* \frac{\partial f}{\partial z} - f \frac{\partial f^*}{\partial z} \right). \] (17)

The probability of tunneling ionization depends on the barrier permeability \( P \). Calculating the integral between the turning points in the classically forbidden region of motion, we obtain 
\[ P = \exp \left( -\int \rho \, |k| \, dp \right) = \left( 4\beta F \right)^{\beta} \exp \left( -\frac{1}{3 \cdot 4F} \right). \] (18)

The matching of asymptotic behavior \( f_s(\eta) \) in the internal region of variable \( \eta < \eta_c \) can be done by equating the functions \( f_s(\eta) \) and \( G_s(\theta, \eta) \), and their derivatives [21].

The total probability of the electron ionization rate in the weak field limit is given by [19, 22]
\[ \Gamma(\theta) = \sum_{n_i}^{\infty} \sum_{m=0}^{\infty} \Gamma_{n_i, m}(\theta), \] (19)
where \( \Gamma_{n_i, m}(\theta) \) is partial ionization probability in the channel with parabolic quantum numbers \( n_i \) and \( m \). The partial current density at a large distance from the source is of form
\[ j_{z, n_i, m} = \frac{\kappa}{\pi \xi \eta} \frac{\phi_{n_i, m}(\xi) G_{n_i, m}(\theta, P_{n_i, m})}{\text{Ai}(v_i(\kappa P_{n_i, m})) \sqrt{\pi}} \left| \frac{v_i(\kappa P_{n_i, m})}{\text{Ai}(v_i(\kappa P_{n_i, m}))} \right|^2 P_{n_i, m}. \] (20)

It follows the expression for the partial probability
\[ \Gamma_{n_i, m}(\theta) = \frac{\kappa}{\pi} \left| \frac{v_i(\kappa P_{n_i, m})}{\text{Ai}(v_i(\kappa P_{n_i, m}))} \right|^2 P_{n_i, m}. \] (21)

5. Conclusions
We have examined the spatial effects in the tunneling ionization of multicenter systems depending on their structure. It is important to note that the position of the atomic centers and the shape of the molecular orbitals are manifested in the electron current distribution. At a great distance from the C_{60} fullerene molecule the distribution pattern of the tunnel current density tends to image a point source. To clarify the role of the many-electron structure of complex molecules and charge delocalization in the formation of interference effects in the emission current, more research is needed.

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