

Theory of tunneling ionization of molecules: Weak-field asymptotics including dipole effectsOleg I. Tolstikhin,¹ Toru Morishita,² and Lars Bojer Madsen³¹National Research Center “Kurchatov Institute,” Kurchatov Square 1, Moscow 123182, Russia²Department of Engineering Science, The University of Electro-Communications, 1-5-1 Chofu-ga-oka, Chofu-shi, Tokyo 182-8585, Japan³Lundbeck Foundation Theoretical Center for Quantum System Research, Department of Physics and Astronomy, Aarhus University, Denmark

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The formulation of the parabolic adiabatic expansion approach to the problem of ionization of atomic systems in a static electric field, originally developed for the axially symmetric case [*Phys. Rev. A* **82**, 023416 (2010)], is generalized to arbitrary potentials. This approach is used to rederive the asymptotic theory of tunneling ionization in the weak-field limit. In the atomic case, the resulting formulas for the ionization rate coincide with previously known results. In addition, the present theory accounts for the possible existence of a permanent dipole moment of the unperturbed system and, hence, applies to polar molecules. Accounting for dipole effects constitutes an important difference of the present theory from the so-called molecular Ammosov-Delone-Krainov theory. The theory is illustrated by comparing exact and asymptotic results for a set of model polar molecules and a realistic molecular ion HeH^{2+} in the $2p\sigma$ state.

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I. INTRODUCTION

An atom or molecule placed into a static electric field can be ionized. In weak fields, the ionization occurs by tunneling of an atomic electron through a potential barrier separating the potential well inside the atom from the asymptotic region. This is the tunneling regime. As the field grows, the barrier becomes lower, and in sufficiently strong fields, the electron can escape from the atom through a classically accessible window over the barrier. This is the overbarrier regime. The boundary between the two regimes naturally separates the weak- and strong-field cases. An essential element of the theory of field ionization in the time-independent framework consists in recognizing the fact that, in the presence of an external electric field, the atomic bound states turn into the complex-energy eigensolutions to the stationary Schrödinger equation satisfying the regularity and outgoing-wave boundary conditions. Such solutions in the general context were first introduced in [1] and are called Siegert states (SSs). In the weak-field case, the imaginary part of the energy eigenvalues is small, and the SSs originating from unperturbed bound states represent slowly decaying quasistationary states. As the field grows, the energy eigenvalues move deeper into the complex plane, and eventually the SSs lose their physical meaning as stationary states. All the characteristics of the ionized electrons, e.g., the ionization rate and the transverse momentum distribution (TMD) in the outgoing flux, can be expressed in terms of the properties of the SSs, so the study of the field ionization amounts to studying the SSs.

In addition to characterizing the ionization in a static electric field, the properties of the SSs determine the dynamics of ionization in the interaction of atoms and molecules with low-frequency laser pulses. It should be noted that the terminology commonly used in the time-dependent problem is different from the static case: the field is regarded as weak only if the laser-matter interaction can be treated perturbatively, while in the tunneling regime, it is referred to as “strong.” The tunneling regime of ionization by laser pulses is treated in the Keldysh theory [2,3] and strong-field approximation [4–7]. In spite of the name, these theories apply only in the weak-field

(in the static sense) case, which can be seen from the fact that the *weak-field asymptotics* of the ionization rate and TMD in a static field emerge in their formulation [3]. In the adiabatic theory of ionization of atoms by intense laser pulses, which was originally developed for a one-dimensional model [8] and is currently extended to the three-dimensional case [9], all parts of the theory, from the solution of the time-dependent Schrödinger equation to the photoelectron momentum distribution, are expressed in terms of the SS originating from the initial bound state. To implement the adiabatic theory, one must be able to construct the SS. This theory is uniform in terms of the amplitude of the laser field and applies to the tunneling as well as overbarrier regimes, provided that the SS is calculated exactly. Thus, both approximate analytical methods of constructing SSs in the weak-field case and exact numerical techniques required in the overbarrier regime are of interest for applications.

An efficient approach to constructing the SSs of atomic systems in a static electric field in the single-active-electron approximation based on the adiabatic expansion in parabolic coordinates was proposed recently [10]. Parabolic coordinates play a special role in the theory of field ionization because both the asymptotic Coulomb tail of the atomic potential and the interaction with the field allow separation of variables in this coordinate system [11]. This enables one to expand the SS eigenfunction in terms of adiabatic channels that are coupled by the non-Coulombic part of the potential in the atomic core and become uncoupled in the asymptotic region. The multichannel problem can then be efficiently solved numerically using the slow variable discretization method [12] in combination with the *R*-matrix propagation technique [13]. In Ref. [10], the parabolic adiabatic expansion approach was formulated and demonstrated by calculations for axially symmetric potentials, which correspond to atoms and linear molecules aligned along the direction of the electric field. One of the goals of this paper is to generalize the formulation of [10] to arbitrary potentials without any symmetry, that is, to arbitrarily oriented molecules. The numerical implementation of the generalized approach and its illustration by calculations

of the orientation dependence of the ionization rate of the hydrogen molecular ion will be presented elsewhere [14].

The parabolic adiabatic expansion approach [10] also provides a new theoretical framework for the asymptotic analysis of tunneling ionization in the weak-field limit (deep tunneling regime). It is well known that the standard perturbation theory can not yield the ionization rate; at the same time, the problem can be treated using asymptotic methods, as in the semiclassical approximation [11]. The application of asymptotic methods to this problem was pioneered by Oppenheimer [15] and Lanczos [16], but it took decades before the correct weak-field asymptotics of the ionization rate for the basic system of hydrogen in the ground state was obtained [11]. Later, similar results were obtained for a short-range potential [17], an arbitrary state in a central atomic potential [18,19], and an arbitrary state of the hydrogen atom [20,21]. These results pertaining to atoms constitute the foundation of the asymptotic theory of tunneling ionization. Their extension to molecules was initiated in [22], where the asymptotics of the ionization rate for a homonuclear model with two identical short-range potentials was obtained. Very recently, the results for this model in the heteronuclear case with two different short-range potentials were reported [23]. An attempt to extend the atomic results [18,19] to the general molecular case beyond model treatment was undertaken in Ref. [24]. The formulas for the ionization rate presented in Ref. [24] for axially symmetric molecules aligned along the direction of the field and arbitrarily oriented molecules were constructed by *analogy* with the atomic case rather than derived from the Schrödinger equation. As shown below, in addition to some inconsistency from the viewpoint of the asymptotic theory in the latter case, these formulas are lacking a very important physical factor: the possible existence of a permanent electric dipole moment of the molecule. Meanwhile, polar molecules are very abundant and correspondingly important. The role of the dipole effects in polar molecules was recognized in Ref. [23]. Recently, dipole effects have attracted much attention in experiment and theory on strong-field ionization [25–31] and high-order harmonic generation [32–35]. A wish to clarify the situation with molecules has prompted us to rederive the asymptotic theory of tunneling ionization on the basis of the parabolic adiabatic expansion approach. This is the main goal of this paper.

The paper is organized as follows. In Sec. II A, we generalize the formulation of the parabolic adiabatic expansion approach [10] to arbitrary potentials. The derivation of the weak-field asymptotics of the tunneling ionization rate is presented in Sec. II B. The resulting formulas are compared with previous theories in Sec. II C. The theory is illustrated by comparison of the asymptotic formulas with accurate numerical results in Sec. III. We first discuss the simplest case of atomic hydrogen in the ground state, then consider a set of model polar molecules, and then present the results for the molecular ion HeH^{2+} . Section IV concludes. The analysis of the behavior of the different quantities under translations of the origin of the coordinate system plays an important role in the present theory. The choice of the coordinate origin in the Schrödinger equation for the active electron is discussed in the Appendix.

II. THEORY

A. Adiabatic expansion in parabolic coordinates

We consider a molecule treated in the single-active-electron approximation interacting with an external static uniform electric field $\mathbf{F} = F\mathbf{e}_z$, $F \geq 0$. The stationary Schrödinger equation for the active electron reads (atomic units are used throughout the paper)

$$\left[-\frac{1}{2}\Delta + V(\mathbf{r}) + Fz - E\right]\psi(\mathbf{r}) = 0, \quad (1)$$

where the potential $V(\mathbf{r})$ describes the interaction with the frozen nuclei and all other electrons and the coordinate \mathbf{r} is measured from the center of mass of the molecule (see Appendix). The internuclear configuration and orientation of the molecule with respect to the field are represented by the shape of the potential $V(\mathbf{r})$ and can be arbitrary. The only assumption regarding $V(\mathbf{r})$ is

$$V(\mathbf{r})|_{r \rightarrow \infty} = -\frac{Z}{r}, \quad (2)$$

where Z is the total charge of the molecular ion. The direction of the field is kept fixed, so the flux of tunnel-ionized electrons is always directed toward $z \rightarrow -\infty$. We are interested in the solutions to Eq. (1) satisfying the regularity and outgoing-wave boundary conditions. Such solutions, called Siegert states, exist only for a discrete set of generally complex values of the electron's energy E . The goal of this section is to formulate a framework suitable for numerical construction and asymptotic analysis of the SSs. Here, we generalize the parabolic adiabatic expansion approach originally proposed in Ref. [10] for axially symmetric potentials, which corresponds to atoms or linear molecules aligned along the field, to any arbitrarily oriented molecules.

It is convenient to use parabolic coordinates defined by [11]

$$\xi = r + z, \quad 0 \leq \xi < \infty \quad (3a)$$

$$\eta = r - z, \quad 0 \leq \eta < \infty \quad (3b)$$

$$\varphi = \arctan \frac{y}{x}, \quad 0 \leq \varphi < 2\pi. \quad (3c)$$

We rewrite Eq. (1) in the form

$$\left[\frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} + \mathcal{B}(\eta) + \frac{E\eta}{2} + \frac{F\eta^2}{4}\right]\psi(\mathbf{r}) = 0, \quad (4)$$

where

$$\mathcal{B}(\eta) = \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{\xi + \eta}{4\xi\eta} \frac{\partial^2}{\partial \varphi^2} - rV(\mathbf{r}) + \frac{E\xi}{2} - \frac{F\xi^2}{4} \quad (5)$$

is an operator acting on functions of ξ and φ and depending on η as a parameter. For $F > 0$, this operator has a purely discrete spectrum, and η is the only variable that can go to infinity. The essence of the present approach consists in treating η as a *slow* variable, like the internuclear distance in the Born-Oppenheimer treatment of diatomic molecules [36] or hyperradius in hyperspherical treatments of three-body Coulomb systems [37,38] and chemical reactions [39,40]. We emphasize that such an approach merely provides a convenient *adiabatic* basis for expanding the solution to Eq. (4) and does not imply any approximations as long as all *nonadiabatic*

couplings are taken into account. The adiabatic basis is defined by the equation

$$[\mathcal{B}(\eta) - \beta_\nu(\eta)]\Phi_\nu(\xi, \varphi; \eta) = 0 \quad (6)$$

supplemented by the regularity boundary condition at $\xi = 0$ and periodic boundary condition in φ . Here, ν is a discrete multi-index enumerating the solutions. The eigenvalues $\beta_\nu(\eta)$ and eigenfunctions $\Phi_\nu(\xi, \varphi; \eta)$ of $\mathcal{B}(\eta)$ also depend on η as a parameter. For any η , the different eigenfunctions are orthogonal and we normalize them by

$$\langle \Phi_\nu | \Phi_\mu \rangle \equiv \int_0^\infty \int_0^{2\pi} \Phi_\nu(\xi, \varphi; \eta) \Phi_\mu(\xi, \varphi; \eta) d\xi d\varphi = \delta_{\nu\mu}. \quad (7)$$

Since the operator $\mathcal{B}(\eta)$ depends on E , the solutions to Eq. (6) are generally complex. Note, however, that there is no complex conjugation in Eq. (7): the operator $\mathcal{B}(\eta)$ is non-Hermitian but symmetric. Consider Eq. (6) in the asymptotic region $\eta \rightarrow \infty$. By using Eq. (2), one can see that $\mathcal{B}(\eta)$ ceases to depend on η as $\eta \rightarrow \infty$:

$$\mathcal{B} = \mathcal{B}(\eta)|_{\eta \rightarrow \infty} = \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{1}{4\xi} \frac{\partial^2}{\partial \varphi^2} + Z + \frac{E\xi}{2} - \frac{F\xi^2}{4}. \quad (8)$$

The same holds for the solutions to Eq. (6). Let us introduce the asymptotic adiabatic eigenvalues and eigenfunctions defined by

$$\beta_\nu = \beta_\nu(\eta)|_{\eta \rightarrow \infty}, \quad \Phi_\nu(\xi, \varphi) = \Phi_\nu(\xi, \varphi; \eta)|_{\eta \rightarrow \infty}, \quad (9)$$

or

$$(\mathcal{B} - \beta_\nu)\Phi_\nu(\xi, \varphi) = 0. \quad (10)$$

This equation allows separation of variables, so the asymptotic basis can be defined more explicitly. Because of the degeneracy of the spectrum of \mathcal{B} , the eigenfunctions of this operator are not defined uniquely. One possible set of the eigenfunctions is

$$\Phi_{n_\xi m}(\xi, \varphi) = \phi_{n_\xi |m|}(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}, \quad (11)$$

where $\phi_{n_\xi |m|}(\xi)$ and the corresponding eigenvalues $\beta_{n_\xi |m|}$ are defined by

$$\left[\frac{d}{d\xi} \xi \frac{d}{d\xi} - \frac{m^2}{4\xi} + Z + \frac{E\xi}{2} - \frac{F\xi^2}{4} - \beta_{n_\xi |m|} \right] \phi_{n_\xi |m|}(\xi) = 0, \quad (12a)$$

$$\phi_{n_\xi |m|}(\xi)|_{\xi \rightarrow 0} \propto \xi^{|m|/2}, \quad \phi_{n_\xi |m|}(\xi)|_{\xi \rightarrow \infty} = 0, \quad (12b)$$

$$\int_0^\infty \phi_{n_\xi |m|}(\xi) \phi_{n'_\xi |m|}(\xi) d\xi = \delta_{n_\xi n'_\xi}. \quad (12c)$$

Here, $m = 0, \pm 1, \pm 2, \dots$ is the azimuthal quantum number and $n_\xi = 0, 1, 2, \dots$ enumerates the different solutions to Eqs. (12) for a given value of $|m|$. The states $\Phi_{n_\xi \pm m}(\xi, \varphi)$ with nonzero m are degenerate since $\beta_{n_\xi |m|}$ does not depend

on the sign of m . Thus, in the general case, we have

$$\beta_\nu = \beta_{n_\xi |m|}, \quad (13a)$$

$$\Phi_\nu(\xi, \varphi) = \begin{cases} \Phi_{n_\xi 0}(\xi, \varphi), & m = 0 \\ c_{|m|\lambda} \Phi_{n_\xi |m|}(\xi, \varphi) + c_{|m|\lambda}^* \Phi_{n_\xi - |m|}(\xi, \varphi), & m \neq 0. \end{cases} \quad (13b)$$

The coefficients $c_{|m|\lambda}$ can be obtained by diagonalizing the matrix of $rV(\mathbf{r})$ in the subspace of the two degenerate states for $\eta \rightarrow \infty$, and $\lambda = 1, 2$ enumerates the eigenvectors of this matrix. Equations (13) show that in the asymptotic region the multi-index ν is given by

$$\nu = (n_\xi, |m|, \lambda). \quad (14)$$

By continuity, this classification of the solutions to Eq. (6) by asymptotic quantum numbers can be applied to all values of η . This specifies what will be meant by ν in the following.

The solution to Eq. (4) can be sought in the form

$$\psi(\mathbf{r}) = \eta^{-1/2} \sum_\nu f_\nu(\eta) \Phi_\nu(\xi, \varphi; \eta). \quad (15)$$

By substituting this expansion into Eq. (4), one obtains a set of ordinary differential equations defining the coefficient functions $f_\nu(\eta)$:

$$\left[\frac{d^2}{d\eta^2} + \frac{F\eta}{4} + \frac{E}{2} + \frac{\beta_\nu(\eta)}{\eta} + \frac{1}{4\eta^2} \right] f_\nu(\eta) + \sum_\mu \left[2P_{\nu\mu}(\eta) \frac{d}{d\eta} + Q_{\nu\mu}(\eta) \right] f_\mu(\eta) = 0, \quad (16)$$

where the matrices

$$P_{\nu\mu}(\eta) = \left\langle \Phi_\nu \left| \frac{\partial \Phi_\mu}{\partial \eta} \right. \right\rangle, \quad Q_{\nu\mu}(\eta) = \left\langle \Phi_\nu \left| \frac{\partial^2 \Phi_\mu}{\partial \eta^2} \right. \right\rangle \quad (17)$$

represent nonadiabatic couplings. Taking into account Eq. (9), these matrices vanish as $\eta \rightarrow \infty$. It is convenient to introduce a boundary of the *coupling* or *core* region η_c such that beyond this boundary, all coupling terms in Eq. (16) can be neglected within a desired accuracy. The uncoupled equations for $\eta > \eta_c$ can be written as

$$\left[\frac{d^2}{d\eta^2} + \frac{F\eta}{4} + \frac{E}{2} + \frac{\beta_\nu}{\eta} + O(\eta^{-2}) \right] f_\nu(\eta) = 0, \quad (18)$$

where the explicit form of the term $O(\eta^{-2})$ is immaterial for the following discussion. For $F > 0$, the outgoing-wave solutions to these equations satisfy

$$f_\nu(\eta)|_{\eta \rightarrow \infty} = f_\nu f(\eta), \quad (19a)$$

$$f(\eta) = \frac{2^{1/2}}{(F\eta)^{1/4}} \exp \left[\frac{iF^{1/2}\eta^{3/2}}{3} + \frac{iE\eta^{1/2}}{F^{1/2}} \right]. \quad (19b)$$

Importantly, this asymptotics does not depend on β_ν , and hence, apart from a constant coefficient f_ν , it is the same for all channels. By substituting Eq. (19a) into Eq. (15), we obtain

$$\psi(\mathbf{r})|_{\eta \rightarrow \infty} = \eta^{-1/2} f(\eta) \Phi(\xi, \varphi), \quad (20)$$

where

$$\Phi(\xi, \varphi) = \sum_\nu f_\nu \Phi_\nu(\xi, \varphi). \quad (21)$$

Thus, independently of the potential $V(\mathbf{r})$, the outgoing-wave solutions to Eq. (1) acquire a separable form in the asymptotic region in parabolic coordinates. Equation (16) must be solved subject to regularity boundary conditions at $\eta = 0$ and outgoing-wave boundary conditions (19) at $\eta \rightarrow \infty$. This is an eigenvalue problem. The real and imaginary parts of the eigenvalue E define the energy and ionization width of the SS:

$$E = \mathcal{E} - \frac{i}{2} \Gamma. \quad (22)$$

The eigenfunction is normalized by

$$\frac{1}{4} \int_0^\infty \int_0^\infty \int_0^{2\pi} \psi^2(\mathbf{r})(\xi + \eta) d\xi d\eta d\varphi = 1, \quad (23)$$

which formally coincides with the normalization condition for real bound states [11]. As can be seen from Eqs. (19b), (20), and (22), $\psi(\mathbf{r})$ exponentially grows as $\eta \rightarrow \infty$. Therefore, the integral in Eq. (23) should be regularized by deforming the integration path in η from the real semiaxis into a contour in the complex η plane (for more details, see [10]). We again note that there is no complex conjugation in Eq. (23), which is a general property of the theory of SSs [1,41–43].

The outgoing-wave boundary condition for Eq. (1) can be also written in the form [10]

$$\psi(\mathbf{r})|_{z \rightarrow -\infty} = \int A(\mathbf{k}_\perp) e^{i\mathbf{k}_\perp \mathbf{r}_\perp} g(z, k_\perp) \frac{d\mathbf{k}_\perp}{(2\pi)^2}, \quad (24)$$

where $\mathbf{r}_\perp = (x, y) = (r_\perp \cos \varphi, r_\perp \sin \varphi)$, $\mathbf{k}_\perp = (k_x, k_y) = (k_\perp \cos \varphi_k, k_\perp \sin \varphi_k)$, and

$$g(z, k_\perp) = e^{-i\pi/12} 2\pi^{1/2} (2F)^{-1/6} \text{Ai}(\zeta), \quad (25a)$$

$$\zeta = \frac{2e^{-i\pi/3}}{(2F)^{2/3}} \left[E - Fz - \frac{k_\perp^2}{2} \right]. \quad (25b)$$

Here, $\text{Ai}(x)$ is the Airy function [44]. The function $g(z, k_\perp)$ contains only an outgoing wave as $z \rightarrow -\infty$, and $A(\mathbf{k}_\perp)$ is the amplitude of the transverse momentum distribution of ionized electrons in the outgoing flux. From Eq. (24), we have

$$A(\mathbf{k}_\perp) = \frac{1}{g(z, k_\perp)} \int \psi(\mathbf{r}) e^{-i\mathbf{k}_\perp \mathbf{r}_\perp} d\mathbf{r}_\perp \Big|_{z \rightarrow -\infty}. \quad (26)$$

To calculate this integral, let us consider the asymptotics defined by

$$z \rightarrow -\infty, \quad r_\perp = O(|z|^{1/2}), \quad k_\perp = O(|z|^0). \quad (27)$$

In this limit, we have

$$\xi = \frac{r_\perp^2}{2|z|} + O(|z|^{-1}), \quad \eta = 2|z| + \frac{r_\perp^2}{2|z|} + O(|z|^{-1}). \quad (28)$$

By using Eqs. (19b) and (20), we obtain

$$\begin{aligned} & \frac{\psi(\mathbf{r})}{g(z, k_\perp)} \Big|_{z \rightarrow -\infty} \\ &= \frac{1}{|z|^{1/2}} \exp \left[\frac{ik_\perp^2 |z|^{1/2}}{(2F)^{1/2}} + \frac{iF^{1/2} r_\perp^2}{2|2z|^{1/2}} \right] \Phi \left(\frac{r_\perp^2}{2|z|}, \varphi \right). \end{aligned} \quad (29)$$

By substituting this into Eq. (26), the integral can be calculated using the steepest descent method. The only saddle point contributing to the integral is given by

$$\mathbf{r}_\perp = \frac{|2z|^{1/2}}{F^{1/2}} \mathbf{k}_\perp, \quad (30)$$

which agrees with Eq. (27). This saddle point has a simple physical meaning [10]: the coordinate of an ionized electron accelerated by the electric field at large times is $(\mathbf{r}_\perp, z) = (\mathbf{k}_\perp t, -Ft^2/2)$, independently of the initial conditions, which, after eliminating the time t , leads to Eq. (30). By calculating the integral in Eq. (26), we find

$$A(\mathbf{k}_\perp) = \frac{2^{3/2} \pi i}{F^{1/2}} \Phi \left(\frac{k_\perp^2}{F}, \varphi_k \right). \quad (31)$$

The TMD is thus given by

$$P(\mathbf{k}_\perp) \equiv |A(\mathbf{k}_\perp)|^2 = \frac{8\pi^2}{F} \left| \Phi \left(\frac{k_\perp^2}{F}, \varphi_k \right) \right|^2. \quad (32)$$

This formula generalizes a similar result obtained in Ref. [10] to arbitrary potentials $V(\mathbf{r})$.

The main quantities characterizing the Siegert state and related to observables are the complex eigenvalue E defining its energy \mathcal{E} and ionization width Γ [see Eq. (22)] and asymptotic coefficients f_ν in Eq. (19a) defining the TMD amplitude (31). It is instructive to discuss how these quantities depend on the position of the coordinate origin in Eq. (1). Consider a translation

$$\mathbf{r} \rightarrow \mathbf{r} + \mathbf{a}, \quad (33)$$

where \mathbf{a} is a constant vector. Equation (1) preserves its form under this transformation if one simultaneously substitutes $E \rightarrow E + Fa_z$. Thus, Γ does not depend on the position of the origin, but \mathcal{E} does. The invariance of Γ follows from the homogeneity of the field and is evident *a priori*; an uncertainty in the definition of \mathcal{E} is eliminated by the prescription to place the origin at the center of mass of the molecule (see the Appendix). In the asymptotic region $\eta \rightarrow \infty$, the transformation (33) amounts to $\eta \rightarrow \eta - 2a_z$, so the function (19b) remains unchanged. Taking into account that the channel functions in Eq. (21) depend only on the asymptotic behavior of the potential (2) and are also not affected by the transformation, one can see from Eq. (20) that the coefficients f_ν do not depend on the position of the origin and, hence, the TMD amplitude (31) does not either.

This completes the formulation of the present approach. The values of E and f_ν can be obtained by solving Eq. (16). An efficient numerical procedure to do this based on the slow variable discretization method [12] was developed in Ref. [10] for the case of axially symmetric potentials. An extension of this procedure to arbitrary potentials is in progress [14].

B. Weak-field asymptotics

An advantage of having an accurate numerical procedure to solve Eq. (16) is that this enables one to find E and f_ν for arbitrary values of the electric field F . Meanwhile, even approximate analytical results valid in the weak-field limit are of great interest for applications. In this section, we discuss the asymptotic solution of the above equations for $F \rightarrow 0$.

We begin with the unperturbed bound state. Let $E_0 < 0$ and $\psi_0(\mathbf{r})$ be the energy and normalized wave function of a bound-state solution to Eq. (1) for $F = 0$. We introduce the dipole moment of the active electron

$$\boldsymbol{\mu} = - \int \psi_0^*(\mathbf{r}) \mathbf{r} \psi_0(\mathbf{r}) d\mathbf{r}. \quad (34)$$

The function $\psi_0(\mathbf{r})$ can also be expanded in the form (15). We shall need its expansion only in the asymptotic region. Let $\beta_v^{(0)} = \beta_{n_\xi|m|}^{(0)}$, $\Phi_v^{(0)}(\xi, \varphi)$, and $\phi_{n_\xi|m|}^{(0)}(\xi)$ denote the asymptotic adiabatic eigenvalues, eigenfunctions, and the solutions to Eqs. (12), respectively, for $F = 0$ and $E = E_0$. From Eqs. (12), we obtain

$$\beta_{n_\xi|m|}^{(0)} = Z - \varkappa \left(n_\xi + \frac{|m| + 1}{2} \right), \quad (35a)$$

$$\phi_{n_\xi|m|}^{(0)}(\xi) = \varkappa^{1/2} s^{|m|/2} e^{-s/2} \tilde{L}_{n_\xi}^{(|m|)}(s), \quad s = \varkappa \xi \quad (35b)$$

where

$$\varkappa = \sqrt{2|E_0|} \quad (36)$$

and $\tilde{L}_n^{(\alpha)}(x)$ are the normalized generalized Laguerre polynomials [44]. The coefficients $c_{|m|\lambda}$ in Eq. (13b) do not depend on F , so $\Phi_v^{(0)}(\xi, \varphi)$ is given in terms of $\phi_{n_\xi|m|}^{(0)}(\xi)$ by the same Eq. (13b). By solving Eq. (18) for $F = 0$, $E = E_0$, and $\beta_v = \beta_v^{(0)}$, and retaining only the leading power of η for each channel, one finds

$$\psi_0(\mathbf{r})|_{\eta \rightarrow \infty} = \sum_v g_v \eta^{\beta_v^{(0)}/\varkappa - 1/2} e^{-\varkappa \eta/2} \Phi_v^{(0)}(\xi, \varphi). \quad (37)$$

Note that the bound-state solutions to Eq. (1) for $F = 0$ do not acquire as simple a separable form in the asymptotic region as the outgoing-wave solutions for $F > 0$ do [compare Eqs. (37) and (20)]. We assume that E_0 , $\boldsymbol{\mu}$, and the coefficients g_v in Eq. (37) are known; these are the properties of the unperturbed bound state needed for the following.

Now, we consider nonzero but weak fields; the exact condition when the field can be treated as weak will be given shortly. Let E and f_v refer to that particular SS that coincides with the unperturbed bound state for $F = 0$. Our goal is to obtain the leading-order terms in the asymptotics of E and f_v for $F \rightarrow 0$. Using perturbation theory, one finds

$$\mathcal{E} = E_0 - \boldsymbol{\mu}_z F + O(F^2). \quad (38)$$

The presence of the linear Stark shift in this expansion is a general property of polar molecules; this term is in the focus of this paper. The higher-order terms can be neglected in the leading-order approximation. It is well known [11] that all terms in the expansion (38) are real, i.e., perturbation theory enables one to find the real part \mathcal{E} of the energy of the SS, but does not yield the ionization width Γ . This is because Γ is exponentially small in F as $F \rightarrow 0$. The asymptotic expansions of Γ and f_v for $F \rightarrow 0$ have the form

$$a F^b e^{-c/F} [1 + O(F)], \quad (39)$$

where the coefficients a , b , and c defining the leading-order term are to be found. We note that, in the weak-field limit, Γ becomes related to the TMD $P(\mathbf{k}_\perp)$ and coefficients f_v . By omitting the derivation that is quite similar to the one presented in Ref. [10], we obtain

$$\Gamma = \int P(\mathbf{k}_\perp) \frac{d\mathbf{k}_\perp}{(2\pi)^2} + O(\Gamma^2) \quad (40a)$$

$$= \sum_v \Gamma_v + O(\Gamma^2), \quad \Gamma_v = |f_v|^2 \quad (40b)$$

where Γ_v is the partial width of the Siegert state corresponding to ionization into channel v . Thus, the problem of finding Γ reduces to finding the coefficients f_v . This can be done by matching the asymptotics of Eq. (15) for $F \rightarrow 0$ with Eq. (37) in a *matching* region where both asymptotics apply. The term with the electric field in Eq. (18) can be neglected for $\eta \ll \varkappa^2/F$. On the other hand, the asymptotics of the individual terms in Eq. (37) obtained from the uncoupled equation (18) become valid for $\eta \gg 4|\beta_v^{(0)}|/\varkappa^2$, provided that $4|\beta_v^{(0)}|/\varkappa^2 > \eta_c$. Thus, the matching region for channel v is determined by

$$4|\beta_v^{(0)}|/\varkappa^2 \ll \eta \ll \varkappa^2/F. \quad (41)$$

For this region to exist, we require

$$F \ll \frac{\varkappa^4}{4|\beta_v^{(0)}|} = \frac{\varkappa^3}{2|2Z/\varkappa - 2n_\xi - |m| - 1|}. \quad (42)$$

This is the condition of validity of the weak-field asymptotics of f_v obtained below.

We turn to deriving the asymptotics. Let us rewrite Eq. (18) in the form

$$\left[\frac{d^2}{d\eta^2} + p^2(\eta) \right] f_v(\eta) = 0, \quad (43)$$

where

$$p^2(\eta) = \frac{F\eta}{4} + \frac{E}{2} + \frac{\beta_v}{\eta} + O(\eta^{-2}). \quad (44)$$

We introduce a new variable

$$\eta = \frac{\varkappa^2 x}{F}, \quad x = \frac{F\eta}{\varkappa^2}. \quad (45)$$

Consider the limit

$$F \rightarrow 0, \quad \eta = O(F^{-1}), \quad x = O(F^0). \quad (46)$$

In this limit,

$$p^2(\eta) = \frac{\varkappa^2}{4} \left[x - 1 - \frac{2F}{\varkappa^2} \left(\mu_z - \frac{2\beta_v^{(0)}}{\varkappa^2 x} \right) + O(F^2) \right]. \quad (47)$$

Let η_t be the outer turning point defined by

$$p(\eta) = 0 \quad \rightarrow \quad \eta = \eta_t = \frac{\varkappa^2}{F} + O(F^0), \quad (48)$$

and $S(\eta)$ be the action

$$S(\eta) = \int_{\eta_t}^{\eta} p(\eta') d\eta'. \quad (49)$$

The asymptotics of the outgoing-wave solution to Eq. (43) in the limit (46) is given by

$$f_v(\eta) = \frac{C \exp[iS(\eta)]}{p^{1/2}(\eta)}, \quad (50)$$

where the coefficient C is to be found by comparing Eq. (50) with (19a). Equation (50) has a form of the standard semiclassical (WKB) asymptotics [11], but the physical origin of

the small parameter is different. This equation holds under the condition

$$\frac{d}{d\eta} \frac{1}{p(\eta)} \ll 1 \quad \rightarrow \quad |x-1| \gg \frac{F^{2/3}}{\varkappa^2}. \quad (51)$$

Taking into account Eq. (48), this means that it becomes valid at a sufficient distance from the turning point η_t . By substituting Eq. (47) into (49), for $x > 1$ we obtain

$$S(\eta) = \frac{\varkappa^3}{2F} \left[\frac{2}{3} (x-1)^{3/2} - \frac{2F}{\varkappa^2} \left(\mu_z (x-1)^{1/2} - \frac{2\beta_v^{(0)}}{\varkappa^2} \arctan(x-1)^{1/2} \right) + O(F^2) \right]. \quad (52)$$

In the asymptotic region $x \gg 1$, in the limit (46), we have

$$S(\eta) = \frac{\varkappa^3}{2F} \left[\frac{2}{3} x^{3/2} - x^{1/2} - \frac{2F}{\varkappa^2} \left(\mu_z x^{1/2} - \frac{\pi\beta_v^{(0)}}{\varkappa^2} \right) + O(F^2) \right] \quad (53a)$$

$$\rightarrow \frac{F^{1/2}\eta^{3/2}}{3} - \frac{\varkappa^2\eta^{1/2}}{2F^{1/2}} - \mu_z F^{1/2}\eta^{1/2} + \frac{\pi\beta_v^{(0)}}{\varkappa}. \quad (53b)$$

By substituting this into Eq. (50) and comparing with Eqs. (19), we find

$$C = f_v \exp \left[-\frac{i\pi\beta_v^{(0)}}{\varkappa} \right]. \quad (54)$$

Let us analytically continue Eq. (50) using Eqs. (47) and (52) from $x > 1$ to $x < 1$ through the upper half of the complex x plane, all the way staying inside the region (51). Assuming that condition (42) is fulfilled, there exists an interval $4F\beta_v^{(0)}/\varkappa^4 \ll x \ll 1$ corresponding to the matching region (41). In this interval, in the limit (46), we have

$$S(\eta) = \frac{i\varkappa^3}{2F} \left[-\frac{2}{3} + x - \frac{2F}{\varkappa^2} \left(\mu_z + \frac{\beta_v^{(0)}}{\varkappa^2} \ln \frac{x}{4} \right) + O(F^2) \right] \quad (55a)$$

$$\rightarrow -\frac{i\varkappa^3}{3F} + \frac{i\varkappa\eta}{2} - i\varkappa\mu_z - \frac{i\beta_v^{(0)}}{\varkappa} \ln \frac{F\eta}{4\varkappa^2}. \quad (55b)$$

By substituting this and Eq. (54) into Eq. (50), we obtain that in the matching region $f_v(\eta)$ is given by

$$f_v(\eta) = \frac{2^{1/2} f_v}{\varkappa^{1/2}} \left(\frac{F}{4\varkappa^2} \right)^{\beta_v^{(0)}/\varkappa} \times \exp \left[-\frac{i\pi}{4} - \frac{i\pi\beta_v^{(0)}}{\varkappa} + \varkappa\mu_z + \frac{\varkappa^3}{3F} \right] \eta^{\beta_v^{(0)}/\varkappa} e^{-\varkappa\eta/2}. \quad (56)$$

Comparing this with Eq. (37), we find

$$f_v = \frac{\varkappa^{1/2} g_v}{2^{1/2}} \left(\frac{4\varkappa^2}{F} \right)^{\beta_v^{(0)}/\varkappa} \times \exp \left[\frac{i\pi}{4} + \frac{i\pi\beta_v^{(0)}}{\varkappa} - \varkappa\mu_z - \frac{\varkappa^3}{3F} \right]. \quad (57)$$

This formula is the main result of the derivation. It gives the leading-order term in the asymptotic expansion (39) of f_v and holds under the condition (42).

By using Eq. (57), one can obtain the partial width $\Gamma_v = |f_v|^2$ for ionization into channel v . In practical calculations, however, the bound-state wave function is usually given as an expansion in terms of functions labeled by the azimuthal quantum number m , so it is convenient to rewrite Eq. (37) as

$$\psi_0(\mathbf{r})|_{\eta \rightarrow \infty} = \sum_{n_\xi=0}^{\infty} \sum_{m=-\infty}^{\infty} g_{n_\xi m} \eta^{Z/\varkappa - n_\xi - |m|/2 - 1} \times e^{-\varkappa\eta/2} \phi_{n_\xi |m|}^{(0)}(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}. \quad (58)$$

This corresponds to switching in the asymptotic region from the adiabatic basis (13b) to the one defined by Eqs. (11) and (12). The coefficients g_v with $\lambda = 1, 2$ [see Eq. (14)] can be expressed in terms of $g_{n_\xi \pm m}$ and the coefficients $c_{|m|\lambda}$ in Eq. (13b). It can be shown that $|g_{(n_\xi, |m|, 1)}|^2 + |g_{(n_\xi, |m|, 2)}|^2 = |g_{n_\xi m}|^2 + |g_{n_\xi - m}|^2$. Then, Eq. (40b) can be rewritten as

$$\Gamma = \sum_{n_\xi=0}^{\infty} \sum_{m=-\infty}^{\infty} \Gamma_{n_\xi m} + O(\Gamma^2), \quad (59)$$

where $\Gamma_{n_\xi m}$ is the partial width for ionization into channel (n_ξ, m) . By using Eq. (57), one obtains the leading-order term in the weak-field asymptotics of $\Gamma_{n_\xi m}$:

$$\Gamma_{n_\xi m} = \frac{\varkappa |g_{n_\xi m}|^2}{2} \left(\frac{4\varkappa^2}{F} \right)^{2Z/\varkappa - 2n_\xi - |m| - 1} \times \exp \left[-2\varkappa\mu_z - \frac{2\varkappa^3}{3F} \right]. \quad (60)$$

Note that all $\Gamma_{n_\xi m}$ have the same value of c in Eq. (39) and differ only in the powers b of F and coefficients a . This means that, for $F \rightarrow 0$, the error term $O(\Gamma^2)$ in Eq. (59) is smaller than not only Γ , that is, the sum of all partial widths, but also each of the partial widths $\Gamma_{n_\xi m}$. Hence, in principle, it is allowed, within the specified accuracy, to retain all channels in the sum (59). This fact indicates an interesting possibility of constructing a

generalized asymptotics of Γ , which would include all powers of F in the preexponential factor in Eq. (39). However, it should be understood that by retaining higher channels in Eq. (59), one must simultaneously retain higher terms in the expansion (39) of $\Gamma_{n_\xi m}$; Eq. (60) is not sufficient for this purpose. In the leading-order approximation, one must retain only the dominant channel that corresponds to the minimum values of n_ξ and $|m|$ present in the expansion (58). In the important case of axially symmetric potentials (atoms and linear molecules aligned along the field), the dominant channel for bound states with a given azimuthal quantum number m is $(n_\xi = 0, m)$. The leading-order term in the asymptotics of the total ionization width in this case is

$$\Gamma = \Gamma_{n_\xi=0, m}. \quad (61)$$

The coefficient g_{0m} needed to implement this formula is explicitly given by

$$g_{0m} = \sqrt{\frac{\varkappa^{|m|+1}}{|m|!}} \eta^{1+|m|/2-Z/\varkappa} e^{\varkappa\eta/2} \int_0^\infty \int_0^{2\pi} \xi^{|m|/2} \times e^{-\varkappa\xi/2-im\varphi} \psi_0(\mathbf{r}) \frac{d\xi d\varphi}{\sqrt{2\pi}} \Big|_{\eta \rightarrow \infty}. \quad (62)$$

Thus, to obtain Γ , one needs to know \varkappa , μ_z , and only one coefficient g_{0m} characterizing the unperturbed bound-state wave function. In the most general case, when the potential $V(\mathbf{r})$ does not have any symmetry (arbitrarily oriented multiatomic molecules), the dominant channel is $(n_\xi = 0, m = 0)$ and the total ionization width is given by

$$\Gamma = \Gamma_{n_\xi=0, m=0}. \quad (63)$$

The values of μ_z and g_{00} in this case depend on the orientation of the molecule with respect to the field implicitly contained in the potential $V(\mathbf{r})$ and wave function $\psi_0(\mathbf{r})$. As is seen from Eq. (60), Γ factorizes into a product of two factors, one of which, namely, $|g_{00}|^2 e^{-2\varkappa\mu_z}$, depends on the orientation of the molecule but does not depend on F , and the other depends only on F and \varkappa . This means that, in the weak-field limit, the dependence of Γ on the orientation of the molecule is the same for all F . In the same approximation, the TMD (32) in the general case (no symmetry) does not depend on the orientation of \mathbf{k}_\perp and is given by

$$P(\mathbf{k}_\perp) = \Gamma_{00} \frac{4\pi\varkappa}{F} \exp\left[-\frac{\varkappa k_\perp^2}{F}\right]. \quad (64)$$

Note that Eqs. (63) and (64) agree with Eq. (40a).

With explicit asymptotic formulas for \mathcal{E} , Γ , and f_v at hand, let us check whether these quantities depend on the position of the coordinate origin in Eq. (1) in the way that they should. One can see that, under a translation (33), the dipole moment (34) and coefficients in Eq. (37) undergo transformations $\boldsymbol{\mu} \rightarrow \boldsymbol{\mu} - \mathbf{a}$ and $g_v \rightarrow g_v e^{-\varkappa a_z}$. Thus, \mathcal{E} given by Eq. (38) changes as $\mathcal{E} \rightarrow \mathcal{E} + F a_z$. The right-hand side of Eq. (57) remains unchanged, so f_v , and hence $\Gamma_{n_\xi m}$ given by Eq. (60), do not depend on the position of the origin. All this agrees with conclusions drawn from Eq. (33) in the end of Sec. II A for arbitrary values of F , which confirms consistency of the asymptotic formulas.

Equations (60), (61), and (63) are of main interest for applications. As discussed below, an important difference of these formulas from previous theories is the presence of the term with the electronic dipole moment μ_z in the exponent. This term does not appear for atoms, except for a special case of hydrogen in excited states, but is an essential factor for polar molecules. Importantly, without this term, Eq. (60) would not be invariant under translations (33). One can notice that the two terms in the exponent in Eq. (60) coincide with the first two terms in the expansion of $-2\varkappa^3(F)/3F$ in powers of F , where $\varkappa(F) = \sqrt{2|\mathcal{E}|}$ and \mathcal{E} is given by Eq. (38). This partly justifies a physically motivated attempt to account for a linear Stark shift, so much important for polar molecules, by substituting $\varkappa(F)$ for \varkappa into the atomic ionization rate (see, e.g., [25,26]). However, such an *ad hoc* procedure can not ensure, of course, that some other parts of the formula should not be changed as well (see also the discussion in Ref. [28]). The present derivation guarantees that Eqs. (61) and (63) with $\Gamma_{n_\xi m}$ given by Eq. (60) give the leading-order term in the asymptotic expansion (39) of Γ .

C. Comparison with previous theories

The asymptotic theory of tunneling ionization of atoms and molecules in the weak-field case has a long history containing a number of fundamental results. Our discussion would be incomplete without comparing the formulas derived above with previous theories. The structure of the ionizing system in the present approach, i.e., whether we deal with an atom or molecule, how this molecule is oriented with respect to the field, etc., is described by the potential $V(\mathbf{r})$. The symmetry properties of the potential determine which channels are present in the expansion (58) and, hence, what is the dominant channel defining the leading-order term in the asymptotics of the ionization rate Γ . The hydrogen atom is a very special case in this sense since this is the only system for which Eq. (2) applies at all distances. As a consequence of the $O(4)$ symmetry of the Coulomb potential, the different adiabatic channels in our formalism for hydrogen (and hydrogen only) are exactly decoupled and, therefore, the weak-field asymptotics can be defined for each channel (n_ξ, m) separately. For all atoms other than hydrogen, the azimuthal quantum number m is still conserved, but there is a nonadiabatic coupling between channels with the different values of n_ξ . Hence, the leading-order contribution to Γ in this case comes from the channel $(n_\xi = 0, m)$. The same holds for linear molecules aligned along the field, when the potential $V(\mathbf{r})$ is axially symmetric about the direction of the field. As discussed above, in the most general case, for potentials without any symmetry, the dominant channel is $(n_\xi = 0, m = 0)$. Historically, these cases have been treated separately by the different authors. Since the present theory covers all these cases, we believe it is worthwhile to consider them in more detail.

1. Hydrogen in the ground state

The hydrogen atom in the ground $1s$ state is the first system for which a correct weak-field asymptotics of the ionization rate was obtained [11]. In this case, $Z = 1$, $\varkappa = 1$, $\mu_z = 0$, and $\psi_{1s}(\mathbf{r}) = e^{-r}/\sqrt{\pi}$. The dominant channel coincides with the

only channel present in the expansion (58) and corresponds to $(n_\xi, m) = (0, 0)$. From Eq. (62), we find $g_{00} = \sqrt{2}$. By inserting these values into Eq. (60), from Eq. (61) or (63), we obtain

$$\Gamma_{1s} = \frac{4}{F} \exp\left[-\frac{2}{3F}\right], \quad (65)$$

which coincides with the well-known result [11].

2. Hydrogen in excited states

The Schrödinger equation for hydrogen allows separation of variables in parabolic coordinates (ξ, η, φ) [11]. The different bound states are labeled by parabolic quantum numbers (n_1, n_2, m) , with $n = n_1 + n_2 + |m| + 1$ giving the principal quantum number. In this case, $Z = 1$, $\varkappa = 1/n$, and $\mu_z = -3n(n_1 - n_2)/2$. There is again only one channel in the expansion (58) with $(n_\xi, m) = (n_1, m)$. The bound-state wave functions are known analytically [11]. It can be shown that

$$\begin{aligned} \psi_{n_1 n_2 m}(\mathbf{r})|_{\eta \rightarrow \infty} &= \frac{(-1)^{n_2} \sqrt{2}}{n^{3/2} \sqrt{n_2! (n_2 + |m|)!}} \left(\frac{\eta}{n}\right)^{n_2 + |m|/2} \\ &\times e^{-\eta/2n} \phi_{n_1 |m|}^{(0)}(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}. \end{aligned} \quad (66)$$

By comparing this with Eq. (58), we find

$$g_{n_\xi m} = \frac{(-1)^{n_2} \sqrt{2}}{n^{n_2 + |m|/2 + 3/2} \sqrt{n_2! (n_2 + |m|)!}}. \quad (67)$$

Substituting all this into Eq. (60) gives

$$\begin{aligned} \Gamma_{n_1 n_2 m} &= \frac{1}{n^3 n_2! (n_2 + |m|)!} \left(\frac{4}{n^3 F}\right)^{2n_2 + |m| + 1} \\ &\times \exp\left[3(n_1 - n_2) - \frac{2}{3n^3 F}\right], \end{aligned} \quad (68)$$

in full agreement with another well-known result [20,21]. It can be often heard that the weak-field asymptotic formulas for ionization rate hold under the condition $F \ll \varkappa^3$, which for hydrogen amounts to $F \ll n^{-3}$. In this particular case, the condition of validity of Eq. (68) can be specified more precisely as $F \ll [8n^3(2n_2 + |m| + 1)]^{-1}$ [45], which, up to a factor of 4, coincides with Eq. (42).

For atoms, the presence of a linear Stark shift in Eq. (38) and the dipole term $-2\varkappa\mu_z = 3(n_1 - n_2)$ in Eqs. (60) and (68) is unique to hydrogen and is a consequence of the $O(4)$ symmetry. The states with the same n and $n_1 > n_2$ ($n_1 < n_2$) are stretched toward $z > 0$ ($z < 0$) and shifted up (down) in energy by the field. It is instructive to consider how this difference in the behavior of the energy is reflected in the ionization rates of the states. In the case $n_1 > n_2$ ($n_1 < n_2$), the term $3(n_1 - n_2)$ increases (decreases) the exponent in Eq. (68). This tendency agrees with the general belief that weaker bound states are easier to ionize. However, for sufficiently small F , the preexponential factor behaves oppositely and can overweigh the dipole term in the exponent. As a result, the states with $n_1 < n_2$ shifted down in energy may have larger ionization rate, contrary to what would be expected based on the behavior of the binding energy alone [see, e.g., Fig. 1 in Ref. [10] showing the rates for the $(n_1, n_2, m) = (1, 0, 0)$ and $(0, 1, 0)$ states]. Although this conclusion is reached for the very special and peculiar case of atomic hydrogen, it is generic to

polar molecules with a permanent dipole moment. We shall return to this point below.

3. General atomic case

In the general atomic case, the potential $V(\mathbf{r})$ differs from Eq. (2) at short distances, so the $O(4)$ symmetry of the Coulomb problem is broken. But, it is still spherically symmetric. The bound-state wave function is naturally expressed in the form $\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi)$. In the asymptotic region, it behaves as

$$\psi_{nlm}(\mathbf{r})|_{r \rightarrow \infty} = C_{nl} r^{Z/\varkappa - 1} e^{-\varkappa r} Y_{lm}(\theta, \varphi), \quad (69)$$

where C_{nl} is a constant. The direction of tunneling $z \rightarrow -\infty$ corresponds to $\theta = \pi$. Using [the phase convention for $Y_{lm}(\theta, \varphi)$ is adopted from [46,47]]

$$Y_{lm}(\theta, \varphi)|_{\theta \rightarrow \pi} = \frac{(-1)^l Q(l, m)}{|m|!} \left(\frac{\pi - \theta}{2}\right)^{|m|} \frac{e^{im\varphi}}{\sqrt{2\pi}}, \quad (70)$$

where

$$Q(l, m) = (-1)^{(|m| - m)/2} \sqrt{\frac{(2l + 1)(l + |m|)!}{2(l - |m|)!}}, \quad (71)$$

and noting that $\pi - \theta \rightarrow 2\sqrt{\xi/\eta}$ for $\eta \rightarrow \infty$ and $\xi = \text{const}$, we obtain

$$\begin{aligned} \psi_{nlm}(\mathbf{r})|_{\eta \rightarrow \infty} &= \frac{(-1)^l C_{nl} 2^{1 - Z/\varkappa} Q(l, m)}{\sqrt{\varkappa^{|m| + 1} |m|!}} \eta^{Z/\varkappa - |m|/2 - 1} \\ &\times e^{-\varkappa\eta/2} \phi_{0|m|}^{(0)}(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}. \end{aligned} \quad (72)$$

Thus, the dominant channel in this case is $(n_\xi, m) = (0, m)$. By comparing Eq. (72) with Eq. (58), or using Eq. (62), we find

$$g_{0m} = \frac{(-1)^l C_{nl} 2^{1 - Z/\varkappa} Q(l, m)}{\sqrt{\varkappa^{|m| + 1} |m|!}}. \quad (73)$$

Substituting this and $\mu_z = 0$ into Eqs. (60) and (61) yields

$$\Gamma_{nlm} = \frac{|C_{nl}|^2 Q^2(l, m)}{(2\varkappa)^{|m|} |m|!} \left(\frac{2\varkappa^2}{F}\right)^{2Z/\varkappa - |m| - 1} \exp\left[-\frac{2\varkappa^3}{3F}\right]. \quad (74)$$

In the non-Coulombic case, a weak-field asymptotics of the ionization rate was first obtained for the $1s$ state in a short-range potential [17]; the result agrees with Eq. (74). The result for the general atomic case (an arbitrary bound state in a central potential) was first obtained in Ref. [18]. The formula for the ionization rate given in Ref. [18] contains a misprint that was corrected in Ref. [19]. Later on, this result was reproduced by other authors [48] and became known as the Ammosov-Delone-Krainov (ADK) theory; a history of the problem is discussed in Refs. [3,49]. Equation (74) coincides with the original result [18,19]. As a special case, by substituting into Eq. (74) $Z = \varkappa = 1$, $l = m = 0$, and $C_{nl} = 2$, which corresponds to hydrogen in the ground state [11], one obtains Eq. (65).

4. Axially symmetric molecules aligned along the field

For axially symmetric molecules aligned along the direction of the field, the projection of the electronic angular momentum

m is still a good quantum number. The bound-state wave function is therefore labeled by m . In the asymptotic region, it is given by

$$\psi_m(\mathbf{r})|_{r \rightarrow \infty} = r^{Z/\varkappa-1} e^{-\varkappa r} \sum_l C_{lm} Y_{lm}(\theta, \varphi). \quad (75)$$

In contrast to the atomic case [see Eq. (69)], here we have a summation over the angular momentum l , which is a consequence of the breakdown of spherical symmetry. Proceeding as in the derivation of Eq. (72), we obtain

$$\begin{aligned} \psi_m(\mathbf{r})|_{\eta \rightarrow \infty} &= \frac{B_m 2^{1-Z/\varkappa}}{\sqrt{\varkappa^{|m|+1} |m|!}} \eta^{Z/\varkappa-|m|/2-1} \\ &\times e^{-\varkappa \eta/2} \phi_{0|m|}^{(0)}(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}, \end{aligned} \quad (76)$$

where

$$B_m = \sum_l (-1)^l C_{lm} Q(l, m). \quad (77)$$

Thus, the dominant channel is again $(n_\xi, m) = (0, m)$. By comparing Eq. (76) with (58), we find

$$g_{0m} = \frac{B_m 2^{1-Z/\varkappa}}{\sqrt{\varkappa^{|m|+1} |m|!}}. \quad (78)$$

Inserting this into Eqs. (60) and (61) gives

$$\Gamma_m = \frac{|B_m|^2}{(2\varkappa)^{|m|} |m|!} \left(\frac{2\varkappa^2}{F} \right)^{2Z/\varkappa-|m|-1} \exp \left[-2\varkappa \mu_z - \frac{2\varkappa^3}{3F} \right]. \quad (79)$$

This result should be compared with the so-called molecular Ammosov-Delone-Krainov (MO-ADK) formula [24]. An important difference stems from the presence of the electronic dipole moment μ_z in the exponent in Eq. (79). As shown above, without this term, Eq. (79) is not invariant under translations (33), and hence is not physically sensible. The present convention defining the phases in Eq. (77) differs from that in [24]. In our case, the orientation of the molecule is fixed parallel to the direction of the field $\mathbf{F} \parallel \mathbf{e}_z$; this determines the asymptotic coefficients C_{lm} in Eq. (75). The electron tunnels out in the direction $z \rightarrow -\infty$ opposite to that assumed in Ref. [24]. This explains an additional factor $(-1)^l$ in Eq. (77), which comes from the parity of spherical harmonics. Summarizing, Eq. (79) differs from the MO-ADK formula in the axially symmetric case [24] by a factor $\exp(-2\varkappa \mu_z)$.

For molecules without a permanent dipole moment, e.g., homonuclear diatomic molecules, $\mu_z = 0$ and this difference does not reveal itself. Even in this case, the present theory has an advantage in the representation that may be important in practical calculations. To implement Eq. (61), one needs to know only one coefficient g_{0m} given in terms of the molecular wave function $\psi_m(\mathbf{r})$ by Eq. (62). On the other hand, to implement the MO-ADK formula [24], one has to find C_{lm} for all values of l that contribute to the sum in Eq. (77).

5. General molecular case

In the most general case of an arbitrarily oriented multiatomic molecule, the potential $V(\mathbf{r})$ has no symmetry. A diatomic molecule placed at a nonzero angle with respect to the

direction of the field also belongs to this case. Let $\Omega = (\alpha, \beta, \gamma)$ denote collectively three Euler angles defining the rotation from the laboratory frame to a molecule-fixed frame [47]. The bound-state wave function of the molecule will be labeled by Ω . The generalization of Eq. (75) in this case reads

$$\begin{aligned} \psi_\Omega(\mathbf{r})|_{r \rightarrow \infty} &= r^{Z/\varkappa-1} e^{-\varkappa r} \sum_{lm'} C_{lm'} Y_{lm'}(\theta', \varphi') \\ &= r^{Z/\varkappa-1} e^{-\varkappa r} \sum_{lm'} C_{lm'} \sum_m \mathcal{D}_{mm'}^{(l)}(\Omega) Y_{lm}(\theta, \varphi), \end{aligned} \quad (80a)$$

$$(80b)$$

where θ' and φ' are the spherical angles of \mathbf{r} in the molecule-fixed frame and $\mathcal{D}_{mm'}^{(l)}(\Omega)$ is the Wigner rotation function [47]. In Eq. (80b), the summation over l and m' accounts for the breaking of spherical and axial symmetries in the molecule-fixed frame, and the summation over m is a consequence of the rotation between the frames. We follow the procedure of the previous sections and rewrite Eq. (80b) as

$$\begin{aligned} \psi_\Omega(\mathbf{r})|_{\eta \rightarrow \infty} &= \sum_m \frac{B_m(\Omega) 2^{1-Z/\varkappa}}{|m|!} \eta^{Z/\varkappa-|m|/2-1} \xi^{|m|/2} \\ &\times e^{-\varkappa(\xi+\eta)/2} \frac{e^{im\varphi}}{\sqrt{2\pi}}, \end{aligned} \quad (81)$$

where

$$B_m(\Omega) = \sum_{lm'} (-1)^l C_{lm'} \mathcal{D}_{mm'}^{(l)}(\Omega) Q(l, m). \quad (82)$$

Equation (81) requires an explanation. In contrast to Eqs. (72) and (76), which indeed give the leading-order term in the asymptotics of the bound-state wave function for $\eta \rightarrow \infty$, because of the summation over m , Eq. (81) contains also higher-order terms with smaller powers of η . The procedure that has led us to Eq. (81) is based on the expansion (70). It can be easily seen that retaining higher-order terms in this expansion would lead to the appearance of other terms with smaller powers of η in Eq. (81). However, these terms are not included, which introduces an inconsistency. Let us proceed keeping this inconsistency in mind. By expanding the right-hand side of Eq. (81) in terms of the complete asymptotic basis $\phi_{n_\xi|m|}^{(0)}(\xi) e^{im\varphi} / \sqrt{2\pi}$ and comparing with Eq. (58), we find

$$g_{n_\xi m} = \frac{\delta_{n_\xi 0} B_m(\Omega) 2^{1-Z/\varkappa}}{\sqrt{\varkappa^{|m|+1} |m|!}}. \quad (83)$$

The fact that only the coefficients with $n_\xi = 0$ turn out to differ from zero is a consequence of the inconsistency of Eq. (81). Inserting Eq. (83) into (60) yields a partial ionization rate for the channel $(n_\xi = 0, m)$

$$\begin{aligned} \Gamma_{n_\xi=0, m}(\beta, \gamma) &= \frac{|B_m(\Omega)|^2}{(2\varkappa)^{|m|} |m|!} \left(\frac{2\varkappa^2}{F} \right)^{2Z/\varkappa-|m|-1} \\ &\times \exp \left[-2\varkappa \mu_z - \frac{2\varkappa^3}{3F} \right]. \end{aligned} \quad (84)$$

This coincides with Eq. (79), where B_m is substituted by $B_m(\Omega)$. Although the coefficients $B_m(\Omega)$ depend on all three Euler angles Ω , from Eq. (82) and $\mathcal{D}_{mm'}^{(l)}(\Omega) = e^{-im\alpha} d_{mm'}^{(l)}(\beta) e^{-im'\gamma}$ [47], one can see that the rate (84) does

not depend on the angle α of rotation of the molecule about the laboratory z axis, that is, about the direction of the electric field. This is a consequence of the homogeneity and, hence, axial symmetry of the field.

In the general molecular case, the MO-ADK formula for the ionization rate reads [24]

$$\Gamma_{\text{MO-ADK}} = \sum_m \frac{|B_m(\Omega)|^2}{(2\mathcal{I})^{|m|} |m|!} \left(\frac{2\mathcal{I}^2}{F} \right)^{2Z/\mathcal{I} - |m| - 1} \exp \left[-\frac{2\mathcal{I}^3}{3F} \right]. \quad (85)$$

First of all, it should be noted that, as in the axially symmetric case, this formula does not account for a permanent dipole moment of the molecule. Let us temporarily forget about the dipole term and consider the case $\mu_z = 0$, when this important difference becomes immaterial. Then, $\Gamma_{\text{MO-ADK}}$ coincides with the sum of the partial rates (84) over m . This amounts to retaining in Eq. (59) only contributions from the channels with $n_\xi = 0$ and neglecting all channels with $n_\xi > 0$. As explained just below Eq. (60), there are higher-order terms in the expansion (39) of the partial rates (84), which are also neglected in Eq. (85). Retaining in Eq. (85) the terms with $m \neq 0$ and neglecting other terms with the same powers of F is not consistent from the viewpoint of the weak-field asymptotics. As can be seen from the derivation, this inconsistency of Eq. (85) in the part concerning the neglect of channels with $n_\xi > 0$ results from the inconsistency of Eq. (81). In the present theory, the leading-order term in the asymptotic expansion of the total ionization rate comes from the channel ($n_\xi = 0, m = 0$) and is given by Eq. (84) with $m = 0$. This coincides with Eq. (63), where the coefficient g_{00} is given in terms of the molecular wave function $\psi_\Omega(\mathbf{r})$ by Eq. (62) with $m = 0$. This result is valid under the condition (42), which guarantees that terms with $m \neq 0$ in Eq. (85) are much smaller than the leading-order term with $m = 0$. This circumstance reduces the effect of the inconsistency of Eq. (85) in the weak-field limit (see also the discussion in Sec. III B).

Returning to the dipole term, the present theory accounts for the possible existence of a permanent dipole moment of the molecule and, hence, applies also to polar molecules. The dipole term was not included in the original MO-ADK theory [24,50–52]. This term was also obtained for a heteronuclear two-short-range potential model [23]. Its importance was recently pointed out in the analysis of photoelectron angular distributions from polar molecules [26,29,30], and inspired by earlier work [53], insertion of the Stark-shifted energy into the atomic tunneling rate formula was used in the interpretation of a recent experiment on laser tunnel ionization from multiple orbital in HCl [25]. Also, the effect of the Stark shift and dipole moment was recently discussed in a model of high-order harmonic generation [32] and in strong-field ionization based on the solution of the time-dependent Schrödinger equation in the single-active-electron approximation [27].

III. ILLUSTRATIVE RESULTS AND DISCUSSION

Having an accurate numerical method to calculate the ionization rate, on the one hand, and asymptotic formulas

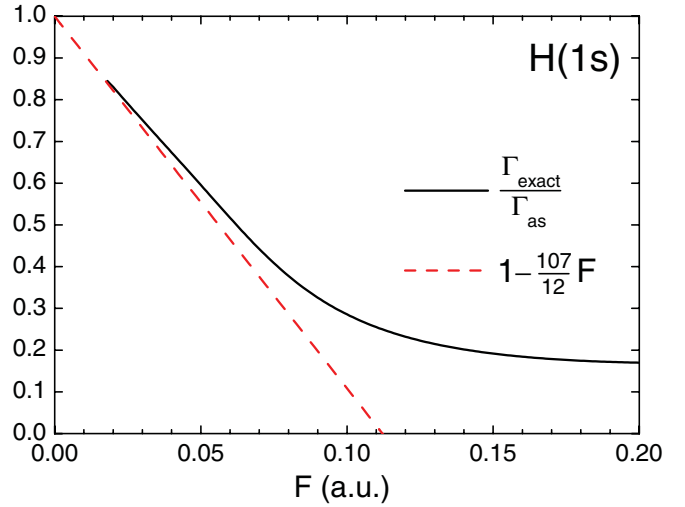


FIG. 1. (Color online) Solid line: the ratio of the exact ionization rate for atomic hydrogen in the ground state to the asymptotic results obtained from Eq. (65). Dashed line: the asymptotic expansion for this ratio up to the linear in F term [45].

applicable in the weak-field limit, on the other, in this section we scrutinize the theory by comparing the exact and asymptotic results. Before discussing polar molecules, it is worthwhile to begin with the simplest system: atomic hydrogen in the ground state. This example allows us to gauge the accuracy of the results and make several observations that apply to more general cases as well.

Figure 1 shows the ratio of the exact ionization rate of H(1s) calculated by the method developed in [10] to the weak-field asymptotic results obtained from Eq. (65). We note that, in order to gauge the accuracy at the level of relevance for the theory, a linear scale is needed; no difference can be seen when exact and asymptotic rates are plotted in a logarithmic scale. In particular, the ratio shown in Fig. 1 is a suitable characteristic; we will consider such ratios also in the molecular examples below. The solid curve in Fig. 1 is not continued to smaller F because of a limitation of our numerical procedure [10]: the rate is obtained from the imaginary part of the SS eigenvalue E [see Eq. (22)], and the procedure in double precision fails at sufficiently small F , when $\text{Im}E$ becomes by more ten orders of magnitude smaller than $\text{Re}E$. Despite this difficulty, we see that the solid curve in Fig. 1 approaches unity as F decreases. In the pure Coulomb potential, the different channels in our formalism are exactly decoupled, so there is only one contribution from the channel with $n_\xi = m = 0$ in Eq. (59). This means that a departure of the ratio shown in Fig. 1 from unity is entirely due to higher-order terms in the asymptotic expansion (39). Two higher-order terms in the expansion of Γ for H(1s) are known analytically [45]. The dashed line in Fig. 1 shows the analytical prediction of the ratio including the linear in F correction term. One can clearly see that the slope of the solid curve approaches that of the dashed curve as F decreases, as it should be. This linear dependence of the ratio on F in the weak-field limit confirms the structure of the asymptotic series (39) and demonstrates the accuracy of the present numerical procedure. Our first observation thus

concerns the presence and importance of higher-order terms in the expansion (39) of partial ionization rates. The discussion above should make it clear that it is inconsistent to include contributions from higher channels to the total ionization rate (59) without including higher-order corrections to the partial rate of the dominant channel.

We use this example also to discuss another inconsistency of approaches that attempt to account for the Stark shift of the energy of the state by amending the exponent in the tunneling rate by means of the substitution $-2\kappa^3/3F \rightarrow -2\kappa^3(F)/3F$ discussed in the end of Sec. II B. For H(1s), the energy (38) including the second-order Stark shift is $\mathcal{E} = E_0 - 9F^2/4$ [11]. By inserting the corresponding field-dependent value of $\kappa(F)$ into the tunneling exponent and expanding in F , for the coefficient of the linear in F term in the ratio shown in Fig. 1, one would obtain 9/2 instead of the exact value $107/12 \approx 8.92$ [45]. We may say that the second-order Stark shift accounts only for about one half of the correction to the rate, while the other half comes from a consistent inclusion of other terms of the same order in F , e.g., a field-induced distortion of the 1s state. Thus, our second observation is that the use of the Stark-shifted energy \mathcal{E} instead of the unperturbed one E_0 in the tunneling exponent is not sufficient to account for higher-order corrections in F .

Our third observation concerns the numerical accuracy of the asymptotic results. As can be seen from Fig. 1, the error of Eq. (65) reaches 10% already at $F = 0.01$, and at the most interesting field strengths for applications, around $F = 0.1$, Eq. (65) overestimates the ionization rate by a factor of 3. The weak-field asymptotic formulas for the tunneling rate are used in the Keldysh theory [3] and strong-field approximation [6,7] for the analysis of the strong-field ionization and high-order harmonic generation. It should be remembered that these formulas, at least in the leading-order approximation, work well quantitatively only in a very limited interval of F ; at larger F , one has to resort to exact numerical calculations.

After this preliminary discussion, we turn to examples in molecules. We consider diatomic molecules modeled by the potential

$$V(\mathbf{r}) = -\frac{Z_1}{\sqrt{(\mathbf{r} - \mathbf{r}_1)^2 + \epsilon}} - \frac{Z_2}{\sqrt{(\mathbf{r} - \mathbf{r}_2)^2 + \epsilon}}, \quad (86)$$

where Z_i and $\mathbf{r}_i = (z_i \sin \beta, 0, z_i \cos \beta)$, $i = 1, 2$, are the effective charges and positions of the nuclei measured from the center of mass of the molecule, β is one of the Euler angles in Eq. (80b) defining the orientation of the molecule with respect to the field, and ϵ is the softening parameter required in the present numerical procedure. For this model, $\mu_z = \mu \cos \beta$, with $\mu \mathbf{e}_z$ being the molecular dipole moment for $\beta = 0^\circ$. The ‘‘exact’’ results reported below are obtained by the method developed in Ref. [10] and, therefore, are restricted to the axially symmetric cases $\beta = 0^\circ$ and 180° , when the molecule is aligned along the field in two possible orientations. But, the asymptotic results for HeH^{2+} will be presented also for arbitrary values of β . We consider only σ states with $m = 0$, so the wave functions do not depend on the azimuthal angle φ . The bound-state energies E_0 and wave functions $\psi_0(\mathbf{r})$ needed to implement the asymptotic theory are obtained by diagonalizing the one-electron Hamiltonian with the potential (86)

using the direct product of two discrete variable representation (DVR) basis sets in spherical coordinates r and θ constructed from the Legendre polynomials [54]. A maximum radius of 30 a.u. is found to be sufficient to obtain accurate results for all the models considered. The dipole moment μ is then calculated from Eq. (34) using the DVR quadratures. The coefficient g_{00} in Eqs. (60) and (63) is obtained from $\psi_0(\mathbf{r})$ using Eq. (62) and a fitting procedure applied at sufficiently large values of η .

A. Model polar molecules

We first consider a set of three model polar molecules in the ground σ state. The nuclear charges in the molecules are $(Z_1, Z_2) = (0.8, 0.7)$, $(1, 0.5)$, and $(1.2, 0.3)$, so the total charge in all the cases is $Z_1 + Z_2 = 1.5$. The positions of the nuclei are defined by $(z_1, z_2) = (-0.5, 1.5)$, which correspond to the nuclear mass ratio $m_1/m_2 = 3$. We choose a relatively large softening parameter $\epsilon = 0.2$. The energies and dipole moments for the three models are $E_0 = -0.585\,217$, $-0.602\,833$, and $-0.641\,018$, and $\mu = -0.392\,723$, $-0.003\,249$, and $0.273\,680$, respectively. From the numerical viewpoint, these models present a rather simple case when both the field-free bound state and the corresponding SS in the presence of the field can be calculated very accurately. Such calculations are needed to analyze and illustrate the reliability of our exact method and asymptotic theory.

Figures 2 and 3 show the energy \mathcal{E} and ionization rate Γ , respectively, as functions of the field F for the three model molecules. For each of the models, the results are shown for two orientations of the molecule with $\beta = 0^\circ$ and 180° . The figures also display the first-order perturbation theory results from Eq. (38), for the energy in Fig. 2, and the asymptotic results from Eq. (63), for the rate in Fig. 3.

For the model in the upper panel of Fig. 2, the energy \mathcal{E} for $\beta = 0^\circ$ ($\beta = 180^\circ$) is shifted up (down) by the linear term in Eq. (38) because $\mu < 0$. For the model in the lower panel, $\mu > 0$, and the situation is inverted. In the middle panel, because of a very small value of μ , the linear term in Eq. (38) is negligible and the energies are shifted down by the second-order Stark shift. In all the cases, a deviation of the exact results from Eq. (38) becomes visible at fields about $F \simeq 0.02$. When the deviation sets in, the exact results are always lower than the prediction of the first-order perturbation theory (38), in accordance with the expectation inferred from the second-order Stark shift.

As seen from Fig. 3, for all three models, the ionization rate for the orientation with $\beta = 0^\circ$ is smaller than that for $\beta = 180^\circ$. This tendency is reproduced by the asymptotic formula (63). We note that, for the model in Figs. 2(a) and 3(a), the orientation with $\beta = 0^\circ$, the binding energy of which is decreased by the field, has a slightly smaller ionization rate than the orientation with $\beta = 180^\circ$, the binding energy of which is increased. This ordering of the magnitudes of the rates compared to that of the binding energies adds to the point already touched upon in the discussion in Sec. II C 2. Equations (60) and (63) show that the rate is determined by three main characteristics of the unperturbed bound state: the energy E_0 , the projection of the molecular dipole moment along the field μ_z , and the coefficient g_{00} in the asymptotics

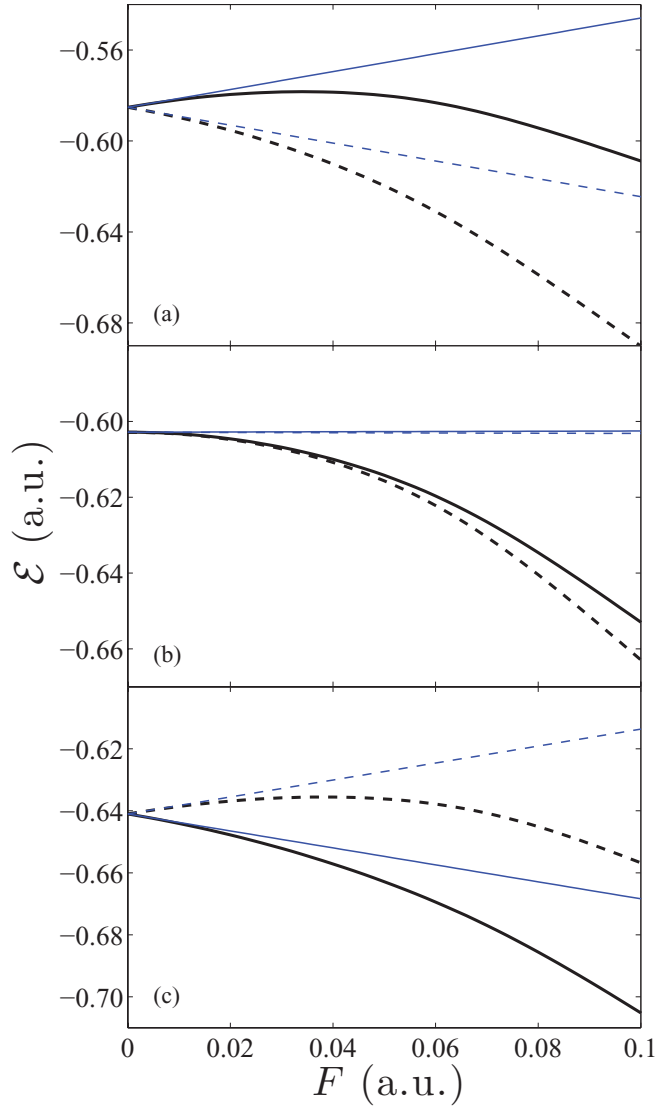


FIG. 2. (Color online) The energy of the ground σ state for three model polar molecules as a function of the field. (a) $(Z_1, Z_2) = (0.8, 0.7)$, $E_0 = -0.585\,217$, $\mu = -0.392\,723$; (b) $(Z_1, Z_2) = (1, 0.5)$, $E_0 = -0.602\,833$, $\mu = -0.003\,249$; (c) $(Z_1, Z_2) = (1.2, 0.3)$, $E_0 = -0.641\,018$, $\mu = 0.273\,680$. Solid (dashed) black curves: exact results for $\beta = 0^\circ$ ($\beta = 180^\circ$). Solid (dashed) blue curves: the corresponding first-order perturbation theory results [Eq. (38)].

of the molecular wave function (58). On the other hand, the energy (38) depends only on two of these characteristics E_0 and μ_z . So, it is clear that \mathcal{E} alone is not sufficient to predict Γ . Like in the case of excited hydrogen, the examples in Figs. 2 and 3 show that it is not always the change of the binding energy that dictates which orientation of the molecule with respect to the field ionizes easier. Thus, for the model in the upper panels of Figs. 2 and 3, the increase of the coefficient g_{00} when the orientation is changed from $\beta = 0^\circ$ to 180° overweighs the effect from the increase of the binding energy. At the same time, for the model in the lower panels, the behavior of the rates agrees with what is expected from the behavior of the binding energies.

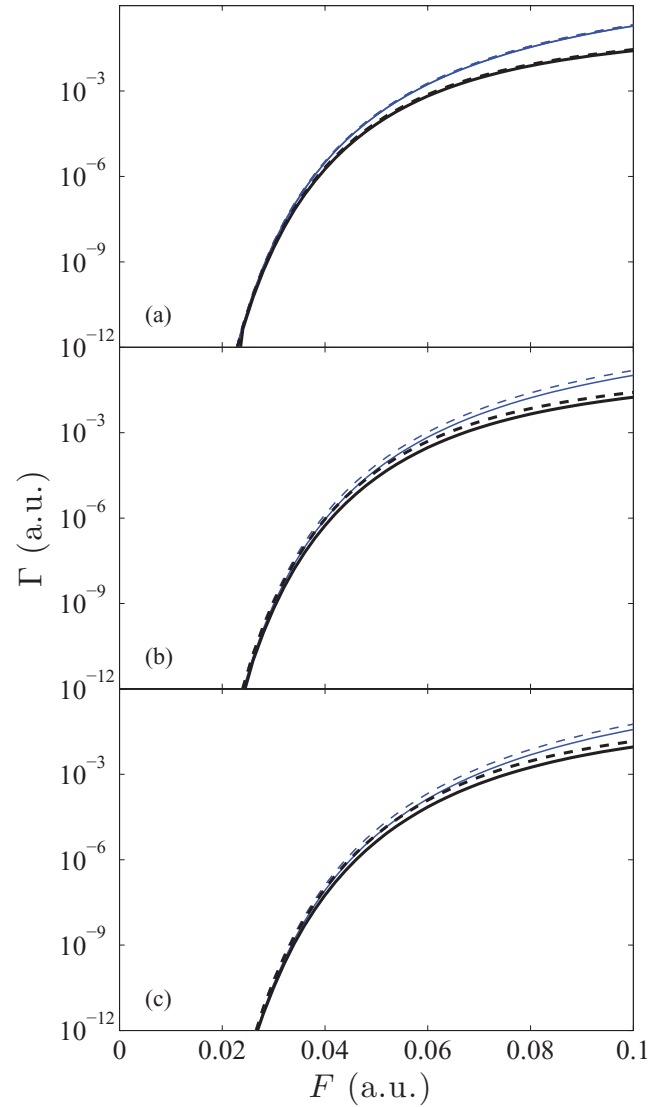


FIG. 3. (Color online) The ionization rate for the same models as in Fig. 2. Solid (dashed) black curves: exact results for $\beta = 0^\circ$ ($\beta = 180^\circ$). Solid (dashed) blue curves: the corresponding asymptotic results [Eq. (63)].

In Fig. 4, we show the ratios of the exact and asymptotic results for the ionization rates. Because of the limitation of our numerical procedure discussed above, these results can not be continued to smaller F . However, as is clear from the figure, for all three models and both orientations of the molecules, the ratios approach unity linearly as the field F decreases. One can see that the asymptotic theory always overestimates the rates, as in the case of atomic hydrogen (see Fig. 1; semiempirical procedures to correct the tunneling rates were discussed in Refs. [55,56]). These results pertaining to computationally involved molecular systems with strong couplings between the adiabatic channels provide an additional illustration of the accuracy of the present numerical method and confirm the consistency of the asymptotic theory. In particular, they demonstrate that the theory correctly accounts for the presence of the dipole moment of the model molecules. These are the main conclusions to be drawn from this section.

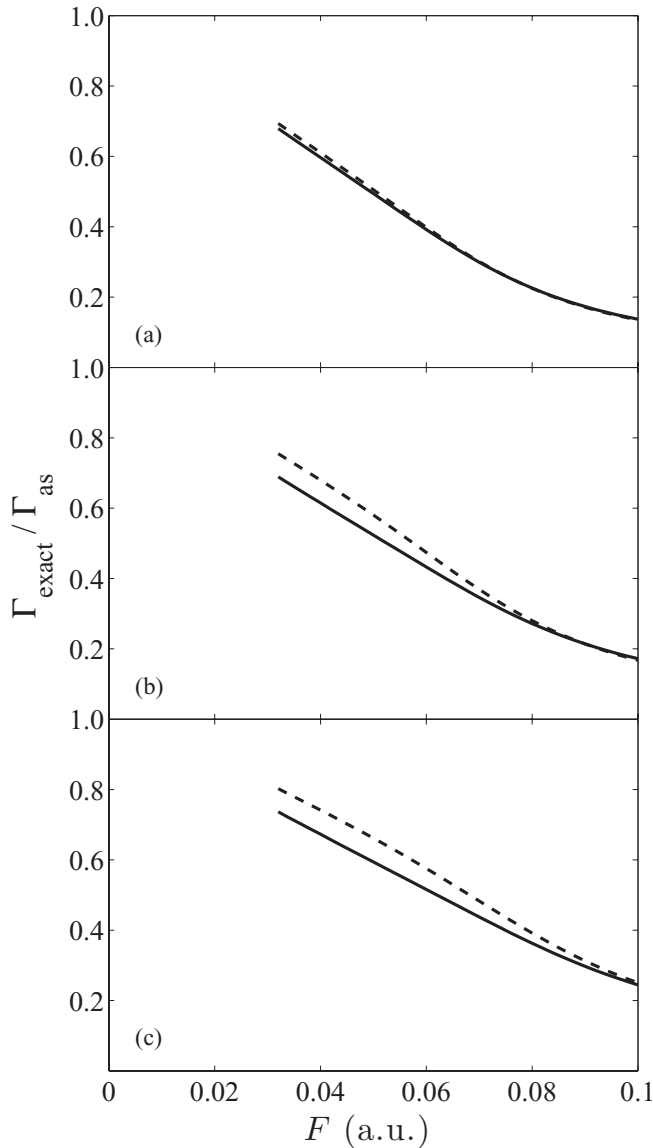


FIG. 4. The ratio of the exact and asymptotic ionization rates shown in Fig. 3. Solid (dashed) curves: $\beta = 0^\circ$ ($\beta = 180^\circ$).

B. Molecular ion HeH^{2+}

After having validated the theory by the comparison of the exact and asymptotic results for model molecules, we now turn to the analysis of a more realistic system. We consider a one-electron molecular ion HeH^{2+} in the first excited $2p\sigma$ state. This system has been considered previously in strong-field studies involving the solution of the time-dependent Schrödinger equation (see [57] and references therein). The ground electronic state of HeH^{2+} is known to be repulsive, but the Born-Oppenheimer potential for the first excited $2p\sigma$ state has a minimum at the internuclear distance $R = 3.89$ [58]. We fix this equilibrium value of the internuclear distance and model the molecule by Eq. (86) with the parameters $(Z_1, Z_2) = (2, 1)$ and $(z_1, z_2) = (-0.778, 3.112)$, which corresponds to the α -particle-to-proton mass ratio $m_1/m_2 = 4$. The softening parameter is chosen to be $\epsilon = 0.1$, smaller than in the previous section. The bound-state energy and dipole moment

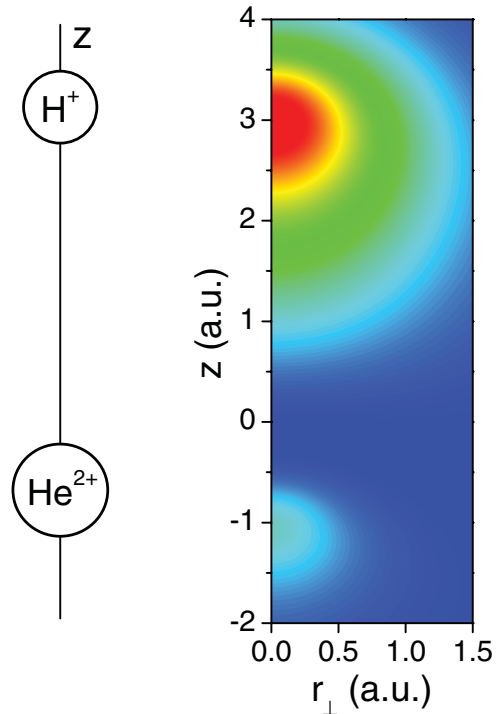


FIG. 5. (Color online) Schematic illustration of the orientation of the molecule HeH^{2+} for $\beta = 0^\circ$ and the electron density distribution (in arbitrary units) in the first excited $2p\sigma$ state for the equilibrium internuclear distance $R = 3.89$. The coordinate origin is at the center of mass, so the α particle and proton are placed at $\mathbf{r}_1 = (0, 0, -0.778)$ and $\mathbf{r}_2 = (0, 0, 3.112)$, respectively. For this system, $E_0 = -0.939749$ and $\mu = -2.202072$.

for this system are $E_0 = -0.939749$ and $\mu = -2.202072$, respectively. The exact energy of the $2p\sigma$ state for $R = 3.89$ is $E_0 = -1.045349$; the difference is due to the nonzero value of ϵ .

Figure 5 illustrates the orientation of the molecule for $\beta = 0^\circ$ and shows the electron density distribution in the $2p\sigma$ state as a function of z and $r_\perp = \sqrt{x^2 + y^2}$. One can see that the electron is almost completely localized near the proton and only weakly affected by the presence of the α particle. Figure 6 shows the energies, ionization rates, and the ratios of the exact and asymptotic results for the rates for two orientations of the molecule with $\beta = 0^\circ$ and 180° . We see that, for the present system, the orientation with $\beta = 0^\circ$, which becomes less bound in the presence of the field, has higher ionization rate. The asymptotic theory again overestimates the ionization rate, at least for sufficiently large values of F . The behavior of the ratios shown in the lower panel of Fig. 6 at smaller F differs from the previous cases (compare with Figs. 1 and 4). Although the ratios do approach unity as F decreases, this does not happen in that simple linear way as before. Unfortunately, we can not continue the curves to smaller F . If calculations for smaller F were possible, we would expect to see a linear trend. The difference in the behavior of the ratios may be due to the fact that now we consider an excited state, whereas in the previous models, we have dealt with the ground state. The more rapid variation of the ratios in the present case requires a more detailed investigation.

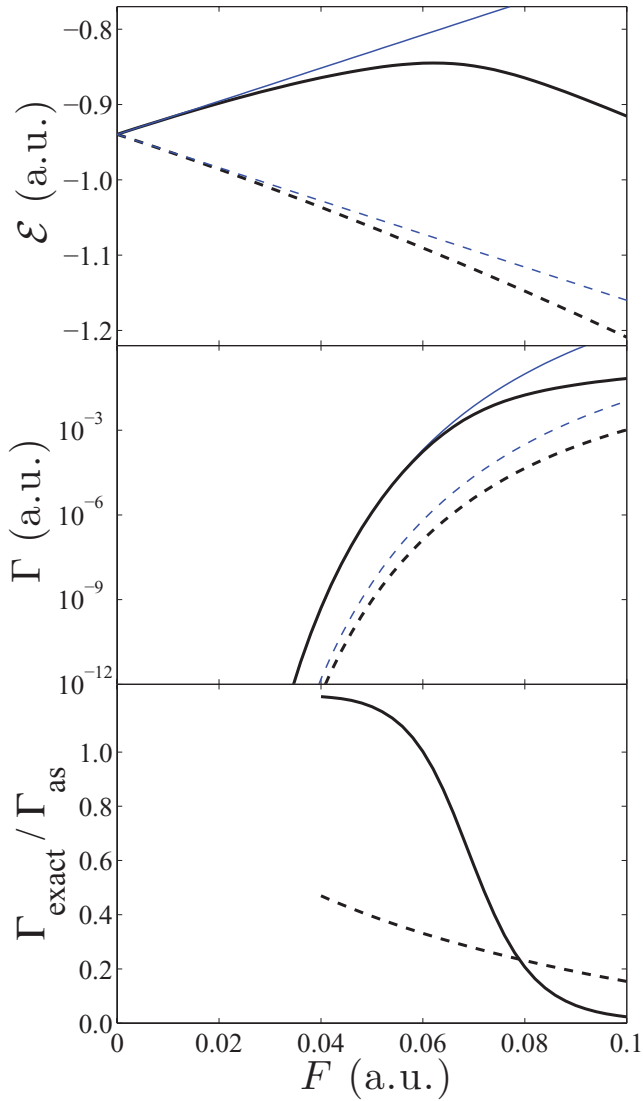


FIG. 6. (Color online) The energy (upper panel), ionization rate (middle panel), and the ratio of the exact and asymptotic results for the rate (lower panel) for $\text{HeH}^{2+}(2p\sigma)$. Solid (dashed) black curves: the exact results for $\beta = 0^\circ$ ($\beta = 180^\circ$). Solid (dashed) blue curves in the upper and middle panels: the corresponding first-order perturbation theory results for \mathcal{E} [Eq. (38)] and the asymptotic results for Γ [Eq. (63)], respectively.

We extend the analysis of the present system and consider also the dependence of the ionization rate on the orientation angle β . Although the exact results are available at the moment only for two axially symmetric orientations, $\beta = 0^\circ$ and 180° , the asymptotic results can be obtained from Eqs. (60) and (63) for any value of β . As follows from the discussion after Eq. (63), in the leading-order approximation of the asymptotic theory, the dependence of the ionization rate Γ on β factorizes from its dependence on F and is represented by the product

$$|g_{00}|^2 \exp(-2\kappa\mu \cos \beta), \quad (87)$$

where g_{00} given in terms of the rotated molecular wave function $\psi_\Omega(\mathbf{r})$ by Eq. (62) depends on β , but κ and μ do

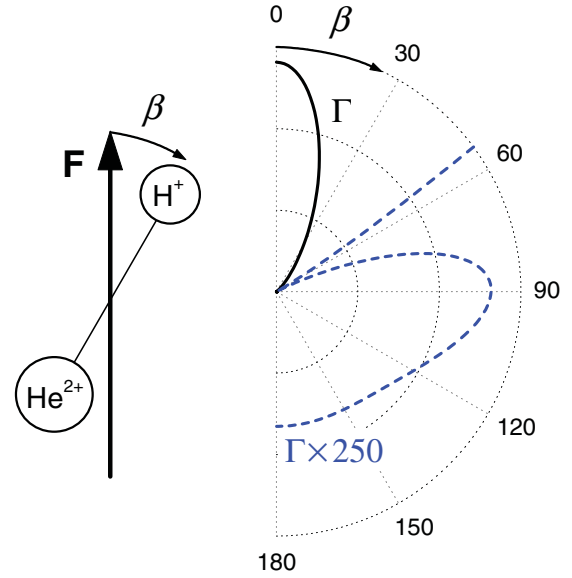


FIG. 7. (Color online) The definition of the angle β between the molecule HeH^{2+} and the electric field \mathbf{F} and the shape of the angular dependence of the weak-field asymptotics of the ionization rate in the $2p\sigma$ state (in arbitrary units). Solid black curve: the leading-order asymptotic results from Eq. (63) obtained by plotting the function (87). Dashed blue curve: the same results multiplied by 250.

not. In other words, in the interval of F where the asymptotic theory is valid, the orientation dependence of the ionization rate is independent of F and its shape is determined by the function (87). In Fig. 7, we show the shape of the dependence of Γ on β for $\text{HeH}^{2+}(2p\sigma)$. We see from the figure that the rate strongly peaks at $\beta = 0^\circ$. The function (87) decreases monotonically from $\beta = 0^\circ$ to $\beta = \beta_0 \simeq 61^\circ$, where it turns zero. Then, it increases up to $\beta \simeq 89^\circ$ and decreases again up to $\beta = 180^\circ$. The zero at $\beta = \beta_0$ results from a zero of g_{00} and reflects the fact that the unperturbed bound-state wave function has a nodal surface along this direction (see Fig. 5). The situation near $\beta = \beta_0$ returns us to the notion of the dominant channel in the leading-order approximation. As follows from Eq. (60), in the general case, the dominant channel is $(n_\xi, m) = (0, 0)$. However, if there is an additional parameter in the problem, like β in the present case, such that the coefficient g_{00} turns zero or becomes very small at a certain value of this parameter, then the contribution from the next to the leading-order channel must be included. For example, in the present case, near $\beta = \beta_0$ one must include also the channel $(n_\xi, m) = (0, 1)$. Since g_{00} linearly turns zero, the width of the interval of β near $\beta = \beta_0$, where the contribution from the channel $m = 1$ is not negligible compared to the channel $m = 0$ in the weak-field limit, is proportional to $F^{1/2}$ and tends to zero together with F . The relative role of the two partial contributions to the total rate as functions of F and β near $\beta = \beta_0$ for each particular system requires a special investigation. A work on these issues for neutral molecules of interest for applications is in progress.

Finally, in Fig. 8, we illustrate the last and the most informative element of the theoretical description of tunneling ionization: the transverse momentum distribution (TMD). We

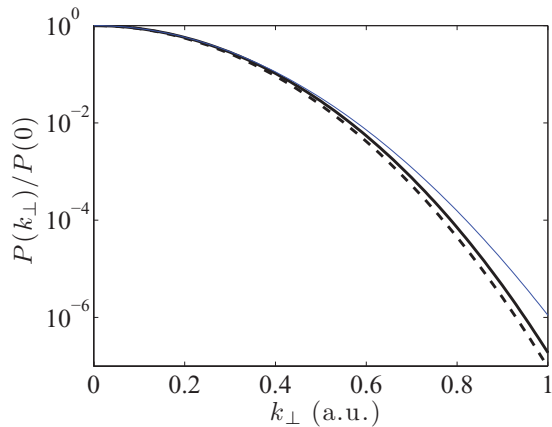


FIG. 8. (Color online) The transverse momentum distributions for tunneling ionization of $\text{HeH}^{2+}(2p\sigma)$ in the field $F = 0.1$. The distributions are normalized to their peak values at $k_{\perp} = 0$. Solid (dashed) black curve: the exact results for $\beta = 0^\circ$ ($\beta = 180^\circ$). Solid blue curve: the prediction of the asymptotic theory [Eq. (64)].

show the TMDs for electrons ionized from $\text{HeH}^{2+}(2p\sigma)$ in the field $F = 0.1$. The exact results were obtained by the method developed in Refs. [10] and, hence, are restricted to axially symmetric orientations of the molecule, $\beta = 0^\circ$ and 180° . The total ionization rates in these two cases differ by more than two orders of magnitude (see Fig. 6). To bring the TMDs to a common scale, we normalize them to their peak values at $k_{\perp} = 0$. The asymptotic results after such a normalization are given by the exponential factor in Eq. (64) and do not depend on β . As can be seen from the figure, both exact TMDs for $\beta = 0^\circ$ and 180° are slightly narrower than the prediction of the asymptotic theory. This fact can be readily explained within the present formalism. The exact TMD is given by Eq. (32). Its shape is determined by the function $\Phi(\xi, \varphi)$ defined in Eq. (21), where $\Phi_v(\xi, \varphi)$ are the eigenfunctions of the operator (8). After separation of variables in Eq. (10), one arrives at Eq. (12a). It can be seen that the field-dependent term in this equation acts to confine the motion in ξ ; it reduces the spatial extent of the solutions compared to the field-free case. Through the substitution $\xi \rightarrow k_{\perp}^2/F$ in Eq. (32), this leads to narrowing of the TMD. The difference between the exact TMDs for the two orientations of the molecule can not be explained in such general terms and depends on the details of the potential. We note that the Gaussian shape of the TMD (64) resulting from the asymptotic theory is essentially maintained in the exact results shown in Fig. 8. This is not generally true for other systems and stronger fields, as discussed in Ref. [10]. For larger values of F , when the contributions from higher channels become important, the shape of the TMD may qualitatively differ from the Gaussian centered at $k_{\perp} = 0$.

IV. CONCLUSION

In this work, we have generalized the formulation of the parabolic adiabatic expansion approach to the problem of ionization of atomic systems in a static electric field, originally developed for the axially symmetric case [10], to

arbitrary potentials. In particular, we have derived an exact expression (32) for the transverse momentum distribution of the ionized electrons in terms of the properties of the corresponding complex-energy Siegert eigenfunction. This opens a way to extend the numerical implementation of the method [10] to arbitrarily oriented molecules in the single-active-electron approximation [14]. The parabolic adiabatic expansion approach is used to rederive the asymptotic theory of tunneling ionization in the weak-field limit. In the atomic case, the resulting formulas for the ionization rate coincide with previously known results [11,17–21,48]. In addition, the present theory accounts for the possible existence of a permanent dipole moment of the unperturbed system and hence applies to polar molecules. It is shown that, without the dipole term, the asymptotic formulas for the ionization rate are not invariant under translations of the origin of the coordinate system and, hence, are not physically sensible. The account for dipole effects constitutes an important advantage of the present theory over the MO-ADK theory [24], which may have far-reaching consequences for numerous applications in the analysis of the ionization of polar molecules by intense laser pulses and in high-order harmonic generation. The present theory also has an advantage in the representation. For example, from Eqs. (60) and (63), one can readily see that the shape of the orientation dependence of the ionization rate in the weak-field limit does not depend on F and is determined by the function (87), where the coefficient g_{00} is an image of the bound-state wave function defined by Eq. (62). All this is not evident from the MO-ADK formula [24]. Hence, this work clarifies, in the weak-field limit, which information about molecular orbitals future experiments on time-resolved strong-field ionization may be able to extract. The theory is illustrated by calculations for several model polar molecules and a realistic molecular ion HeH^{2+} in the $2p\sigma$ state. The exact results for the energy and ionization rate obtained by the method developed in Ref. [10] are always in good agreement with the asymptotic results in the weak-field limit, which confirms the accuracy of the former and consistency of the latter.

The comparison of exact and asymptotic results is an important element of this study, which enables one to gauge the numerical accuracy of the asymptotic theory. One of the general conclusions that should be drawn is that the asymptotic formulas for the ionization rate work well quantitatively only for very small values of the field F . For example, even for $F = 0.1$, which corresponds to the field amplitude in a laser pulse with intensity $3.5 \times 10^{14} \text{ W/cm}^2$, the asymptotic theory overestimates the ionization rate of $\text{H}(1s)$ by a factor of 3. The present approach to the asymptotic theory of tunneling ionization allows an extension beyond the leading-order approximation. Such a development would be useful for applications to the laser-matter interaction problem in the situations where the exact results are not available.

ACKNOWLEDGMENTS

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APPENDIX: ON THE POSITION OF THE COORDINATE ORIGIN IN THE SINGLE-ACTIVE-ELECTRON APPROXIMATION FOR MOLECULES

Equation (1) raises a question: Where is the electron's coordinate \mathbf{r} measured from? Indeed, shifting the origin of \mathbf{r} results in changing the electron's energy E . Such an uncertainty in the definition of E is unphysical, of course. For consistency of presentation, here we address this issue. The uncertainty is eliminated by returning to the original many-body formulation of the problem. It is sufficient to consider a system of three particles as the simplest model of a molecule. Let m_i and q_i , $i = 1, 2, 3$, be the masses and charges of the particles, and \mathbf{r}_i be their coordinates in an inertial laboratory frame. Let particles interact with each other via pairwise potentials $V_{ij} = V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$ and form a bound state in the absence of the field. Then, the Schrödinger equation for the system in the presence of an electric field \mathbf{F} in the laboratory frame reads (we still use atomic units; m_i and q_i should be considered as dimensionless parameters)

$$\left[-\sum_i \frac{\Delta_i}{2m_i} + \sum_{i<j} V_{ij} - \mathbf{d}_L \mathbf{F} - E_L \right] \Psi_L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = 0, \quad (\text{A1})$$

where

$$\mathbf{d}_L = \sum_i q_i \mathbf{r}_i. \quad (\text{A2})$$

We first separate out the center of mass of the system. Let

$$M = \sum_i m_i, \quad Q = \sum_i q_i, \quad \mathbf{r}_{\text{c.m.}} = \frac{1}{M} \sum_i m_i \mathbf{r}_i. \quad (\text{A3})$$

We introduce the Jacobi coordinates

$$\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1, \quad \mathbf{r} = \mathbf{r}_3 - \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}, \quad (\text{A4})$$

and the corresponding reduced masses

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}, \quad \mu_{12,3} = \frac{(m_1 + m_2) m_3}{M}. \quad (\text{A5})$$

By substituting $E_L = \varepsilon + E_{\text{c.m.}}$ and

$$\Psi_L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \chi(\mathbf{r}_{\text{c.m.}}) \Psi_{\text{c.m.}}(\mathbf{r}, \mathbf{R}), \quad (\text{A6})$$

where $\chi(\mathbf{r}_{\text{c.m.}})$ satisfies

$$\left[-\frac{\Delta_{\text{c.m.}}}{2M} - Q \mathbf{r}_{\text{c.m.}} \mathbf{F} - \varepsilon \right] \chi(\mathbf{r}_{\text{c.m.}}) = 0, \quad (\text{A7})$$

we obtain

$$\left[-\frac{\Delta_{\mathbf{r}}}{2\mu_{12}} - \frac{\Delta_{\mathbf{r}}}{2\mu_{12,3}} + \sum_{i<j} V_{ij} - \mathbf{d}_{\text{c.m.}} \mathbf{F} - E_{\text{c.m.}} \right] \times \Psi_{\text{c.m.}}(\mathbf{r}, \mathbf{R}) = 0, \quad (\text{A8})$$

where

$$\mathbf{d}_{\text{c.m.}} = \mathbf{d}_L - Q \mathbf{r}_{\text{c.m.}} = \mathbf{d}_{12} + \mathbf{d}_{12,3} \quad (\text{A9})$$

and

$$\mathbf{d}_{12} = \mu_{12} \left(\frac{q_2}{m_2} - \frac{q_1}{m_1} \right) \mathbf{R}, \quad (\text{A10a})$$

$$\mathbf{d}_{12,3} = \mu_{12,3} \left(\frac{q_3}{m_3} - \frac{q_1 + q_2}{m_1 + m_2} \right) \mathbf{r}. \quad (\text{A10b})$$

Here, $E_{\text{c.m.}}$, $\Psi_{\text{c.m.}}(\mathbf{r}, \mathbf{R})$, and $\mathbf{d}_{\text{c.m.}}$ are the energy, wave function, and dipole moment operator of the three-body system in the center-of-mass frame. Note that $\mathbf{d}_{\text{c.m.}}$ is invariant under simultaneous translations of all particles, while \mathbf{d}_L is not if the total charge of the system Q is nonzero. Note also that, in this case, the center-of-mass frame is noninertial: it moves with a constant acceleration $Q\mathbf{F}/M$ with respect to the laboratory frame. Let particles 1 and 2 be neutral atoms, atomic ions, or bare nuclei, and hence they are heavy, and let particle 3 be an electron, so $m_3 = 1$ and $q_3 = -1$. By substituting

$$\Psi_{\text{c.m.}}(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}; \mathbf{R}) \Psi(\mathbf{R}) \quad (\text{A11})$$

and implementing the Born-Oppenheimer approximation [36], we obtain

$$\left[-\frac{\Delta_{\mathbf{r}}}{2\mu_{12,3}} + V(\mathbf{r}; \mathbf{R}) - \mathbf{d}_{12,3} \mathbf{F} - E(\mathbf{R}) \right] \psi(\mathbf{r}; \mathbf{R}) = 0, \quad (\text{A12})$$

where $V(\mathbf{r}; \mathbf{R}) = V_{13} + V_{23}$, and

$$\left[-\frac{\Delta_{\mathbf{R}}}{2\mu_{12}} + V_{12} + E(\mathbf{R}) - \mathbf{d}_{12} \mathbf{F} - E_{\text{c.m.}} \right] \Psi(\mathbf{R}) = 0. \quad (\text{A13})$$

The electronic energy $E(\mathbf{R})$ and wave function $\psi(\mathbf{r}; \mathbf{R})$ are the eigenvalue and eigenfunction of Eq. (A12) (supplemented by appropriate boundary conditions) for a given internuclear configuration \mathbf{R} . The actual configuration \mathbf{R}_0 for which Eq. (A12) is to be solved is determined by external with respect to the electron's dynamics factors and, hence, must be specified from outside the electronic subproblem. For example, in the present model, \mathbf{R}_0 is the equilibrium configuration determined by Eq. (A13). In the limit $m_1 \rightarrow \infty$, $m_2 \rightarrow \infty$, and $m_1/m_2 = \text{const}$, we have $\mu_{12,3} = 1$, $\mathbf{d}_{12,3} = -\mathbf{r}$, and $\mathbf{r} = \mathbf{r}_3 - \mathbf{r}_{\text{c.m.}}$. Then, Eq. (A12) reduces to Eq. (1). We thus conclude that the electron's coordinate \mathbf{r} in Eq. (1) should be measured from the center of mass of the molecule. It is clear that this conclusion applies to any polyatomic molecule treated in the single-active-electron approximation.

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