

Weak-field asymptotic theory of tunneling ionization in many-electron atomic and molecular systems

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The weak-field asymptotic theory of tunneling ionization in an external static uniform electric field [Tolstikhin *et al.*, *Phys. Rev. A* **84**, 053423 (2011)] is extended to many-electron atomic and molecular systems treated in the frozen-nuclei approximation. The leading-order term in the asymptotic expansion of the ionization rate Γ in the value of the field F for $F \rightarrow 0$ is obtained. The resulting formulas express Γ in terms of properties of the unperturbed system. The most essential difference from the one-electron case, through which the many-electron character of the present theory reveals itself, is that the structure factor for a given ionization channel, defining the dependence of the ionization rate into this channel on the orientation of the system with respect to the field, is determined by the corresponding Dyson orbital. The theory is illustrated by calculations for several few-electron systems. The asymptotic results are compared with accurate fully correlated calculations of tunneling ionization rates available in the literature.

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I. INTRODUCTION

The theoretical description of ionization of atomic and molecular systems by an external static uniform electric field is one of the fundamental problems in quantum mechanics. In sufficiently weak fields, the ionization occurs by tunneling of an electron through a potential barrier separating the region of its localization in an initial bound state from the asymptotic region where it can fly away from the system driven by the field. In this case the problem can be treated analytically. All the previous achievements in the theory of tunneling ionization can be summarized by stating that the ionization rate Γ as a function of the field F for $F \rightarrow 0$ is given by an asymptotic expansion of the form (atomic units $\hbar = m_e = |e| = 1$ are used throughout)

$$\Gamma = cF^b e^{-a/F} (1 + AF \ln F + BF^2 + \dots), \quad (1)$$

where the coefficients a , b , c, \dots do not depend on F and the dots indicate the existence of higher-order terms. This expansion applies in the interval $F \ll F_c$, where F_c is a boundary between the tunneling and over-the-barrier ionization regimes. Since the asymptotic expansion is unique and its structure is already established, the development of the theory reduces to finding the coefficients in Eq. (1), that is, to expressing them in terms of properties of the unperturbed system. This task turned out to be nontrivial, as seen from the history of its solution outlined below.

The theory was pioneered by Oppenheimer who considered tunneling ionization of a hydrogen atom in the ground state [1]. He showed that the exponent in Eq. (1) is twice the action accumulated by an electron under the barrier and obtained the coefficient $a = 2\kappa^3/3$, where $\kappa = \sqrt{2I_p}$ and I_p is the ionization potential. The argumentation of Ref. [1], and hence the result, has a classical origin and is believed to hold universally for all systems. However, the exponential factor is not sufficient for Eq. (1) to be quantitatively predictive. For applications, one needs to know the complete leading-order

term, including the power b of F and the coefficient c in the preexponential factor.

It took three decades to derive these coefficients for the simplest system of atomic hydrogen in the ground state [2]. This result was soon generalized to tunneling ionization from a bound state in an arbitrary spherically symmetric potential $V(r)$ [3] (a misprint in this paper was corrected in Ref. [4]). Such a potential can be used to model many-electron atoms in the single-active-electron approximation (SAEA). It was shown that $b = 1 + |m| - 2Z/\kappa$, where Z is the Coulomb charge in the asymptotic tail of $V(r)$ at $r \rightarrow \infty$ and m is the projection of the electron's angular momentum on the direction of the field, and c is determined by a coefficient appearing in the asymptotic tail of the unperturbed wave function. Thus b is insensitive to the details of the system, while c incorporates the effect of the structure of the initial bound state. Because of the Coulomb degeneracy, excited states of hydrogen require a special treatment. The correct zeroth-order eigenfunctions, which diagonalize the interaction with the field within the degenerate manifolds, coincide with parabolic states [2]. The leading-order term in Eq. (1) for these states was obtained in Refs. [5,6]. The analysis of the Coulomb potential was extended to the higher-order terms in Eq. (1) following the unity in the brackets. In this case the expansion contains only integer powers of F , thus $A = 0$. The value of B for any parabolic state of hydrogen was derived in Ref. [7]. The coefficients of a number of higher-order terms for the four lowest states were obtained in Ref. [8].

It took several more decades before the leading-order term in Eq. (1) was obtained for tunneling ionization from a bound state in a general potential $V(\mathbf{r})$ without any symmetry [9]. Such a potential can model many-electron molecules in the SAEA and the frozen-nuclei approximation (FNA). The weak-field asymptotic theory (WFAT) of tunneling ionization developed in Ref. [9] reproduces the results of Refs. [2,3,5,6] in appropriate particular cases. A qualitatively different feature of a general potential compared with the spherically symmetric

case [3] is that the unperturbed bound state may have a permanent dipole moment, and then the coefficient c involves an additional factor depending on the dipole. The dipole factor is also contained in the value of c obtained in Refs. [5,6], as it should be since the hydrogen atom generally has a nonzero dipole in excited parabolic states. Another difference in the general case is that c depends on the orientation of the potential $V(\mathbf{r})$ (that is, of a molecule modeled by this potential) with respect to the field. Since a and b do not depend on the orientation, the dependence on the orientation in the leading-order term in Eq. (1) factorizes from the dependence on the field. Thus each potential and state are characterized by a structure factor incorporating the orientation dependence and defining c . The techniques to calculate molecular structure factors in the SAEA and FNA were developed in Refs. [10,11]. The WFAT yields not only the leading-order term in Eq. (1), but also a regular procedure to derive the following terms. The approach of Ref. [9] enabled us to obtain the coefficients A and B of the first-order correction terms for a general potential [12], with the result for hydrogen [7] again emerging as a particular case. In the general case $A \neq 0$ and the expression for B contains the dipole polarizability in the initial state and a coefficient characterizing its distortion by the field, thus more structure information is involved. This completes a survey of the results available in the theory for one-electron systems. In addition, we mention studies of the one-center [13] and two-center [14,15] zero-range-potential models for which the problem of finding the ionization rate reduces to solving a transcendental equation and the asymptotic expansion (1) follows straightforwardly from this equation.

Although tunneling ionization of many-electron systems was discussed before [16,17], we are not aware of any theoretical results obtained from the unique perspective of the asymptotic expansion (1). In this paper, we extend the WFAT to many-electron systems. Namely, we derive the leading-order term in Eq. (1) for many-electron atoms and molecules treated in the FNA. The ionization rate is expressed in terms of properties of the unperturbed system in as general a form as the perturbation-theory result for the Stark shift of the energy of a state [2]. To avoid confusion with the terminology, we reserve the term WFAT for the general theoretical approach based on the expansion (1), the one-electron theory of Refs. [9–12] will be referred to as OE-WFAT, and the present many-electron theory will be called ME-WFAT. The FNA remains the only approximation regarding the system in the ME-WFAT. The effect of nuclear motion can be taken into account within the Born-Oppenheimer approximation [18–20]. However, it was recently realized that this approximation in the theory of tunneling ionization breaks down at sufficiently weak fields and, on the other hand, the WFAT expansion for the ionization rate of systems with active nuclei must be restructured to account for the appearance of an additional small parameter given by the electron-to-nuclear mass ratio [21]. The incorporation of nuclear motion into the WFAT is postponed to future studies.

The extension of the WFAT to many-electron systems is not only of fundamental interest, but is also timely and required for applications in strong-field physics and attoscience [22–24]. The initial step for a variety of processes in this research area is tunneling ionization in the field of an intense femtosecond laser pulse whose peak amplitude is still weak in the static-

field sense. At sufficiently low frequencies the adiabatic approximation applies [25], and then this step can be described by the ionization rate in a static field. The applications in laser-induced rescattering photoelectron spectroscopy [23,26] and high-order harmonic spectroscopy [24] require accurate ionization rates. Recently, the OE-WFAT was successfully applied in an analysis of experimental photoelectron spectra of C_2H_4 [27,28] and OCS [29], and other interesting applications are in progress [30]. The ME-WFAT accounting for many-electron effects in the tunneling step is highly relevant for strong-field physics.

The paper is organized as follows. In Sec. II the ME-WFAT is developed. In Sec. II A, the ionization rate is related to the imaginary part of the complex energy eigenvalue of a Siegert state (SS), which is a solution of the stationary Schrödinger equation satisfying outgoing-wave boundary conditions. After a brief discussion of the permutation symmetry issues (Sec. II B), the problem of constructing the SS is reformulated using the method of adiabatic expansion in parabolic coordinates [9,31,32] as a multichannel eigenvalue problem in one variable (Sec. II C). An important concept of ionization channels [9] is thus generalized to the many-electron case. The following derivation and argumentation in Secs. II D–II F are similar to that in Ref. [9]. The main difference is that the ionization rate into a given channel is now expressed in terms of the corresponding Dyson orbital. Dyson orbitals (or Dyson amplitudes) naturally arise in many-body theories [33,34]; more recent applications can be found, e.g., in Ref. [35]. The genealogical spin basis is introduced in Appendix A and used in Appendix B to clarify the space-spin structure of a Dyson orbital. In Sec. II G, some aspects of the implementation of the present theory and its relation to previous approaches are discussed. Illustrative calculations for H^- , He, H_2 , and Li are presented in Sec. III. The asymptotic results are compared with accurate fully correlated calculations of tunneling ionization rates available in the literature [18,36–39]. Section IV concludes the paper.

II. THEORY

A. Formulation of the problem

We consider a molecule (or an atom, as a particular case) treated in the FNA interacting with an external electric field. More specifically, we consider a system of N nonrelativistic electrons described by the coordinates \mathbf{r}_i , $i = 1, \dots, N$, interacting with each other, A nuclei with charges Z_a fixed in space at the positions \mathbf{N}_a , $a = 1, \dots, A$, and a static uniform electric field directed along the z axis of the laboratory frame, $\mathbf{F} = F\mathbf{e}_z$, $F \geq 0$. The Hamiltonian of the system is

$$H_N = \sum_{i=1}^N \left[-\frac{1}{2} \Delta_i - \sum_{a=1}^A \frac{Z_a}{|\mathbf{r}_i - \mathbf{N}_a|} + \sum_{j=1}^{i-1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + Fz_i \right]. \quad (2)$$

If one starts by considering a system with active nuclei, then to eliminate the motion of the system as a whole, which is irrelevant for the tunneling problem, the electronic coordinates \mathbf{r}_i must be measured from the center of mass [9]. The present assumption that the nuclei do not move should be viewed

as a consequence of the Born-Oppenheimer approximation applied in the center-of-mass frame. In this approximation, the center of mass of the system coincides with that of the nuclei, therefore nuclear masses implicitly appear in the formulation. The shape of the molecule and its orientation with respect to the field are determined by the vectors \mathbf{N}_a . The stationary Schrödinger equation describing the electrons reads

$$(H_N - E)\Psi(Q_N) = 0, \quad (3)$$

where $Q_N = (q_1, \dots, q_N)$, $q_i = (\mathbf{r}_i, \sigma_i)$, and $\sigma_i = \pm 1/2$ is the spin coordinate of the i th electron. We are interested in the solutions to Eq. (3) which are regular everywhere in $3N$ -dimensional configuration space spanned by the variables \mathbf{r}_i and have only outgoing waves in the asymptotic region. Equation (3) supplemented by these boundary conditions constitutes an eigenvalue problem, its solutions exist only for a discrete set of generally complex energies E and are called SSs in an electric field [9,12,31,32]. Among the SSs, we consider only *tunneling states* which turn into bound states for $F = 0$. It should be mentioned that there exists another type of SSs, *static-field-induced states* [40,41], which do not have counterparts in the absence of the field. The complex SS eigenvalue presented in the form

$$E = \mathcal{E} - \frac{i}{2} \Gamma \quad (4)$$

defines the energy \mathcal{E} and ionization rate Γ of the system in the state $\Psi(Q_N)$ as functions of the field F . One can expect that at weak fields E can be expressed in terms of properties of the unperturbed system. Indeed, the energy \mathcal{E} can be obtained using the standard perturbation theory as an expansion in powers of F [2]. However, perturbation theory does not enable one to find the ionization rate Γ which is exponentially small in F . The goal of this work is to extend the approach of Ref. [9] to many-electron systems and obtain the asymptotics of Γ for $F \rightarrow 0$ without making any approximations regarding the structure of the unperturbed system, apart from the FNA.

B. Permutation symmetry

The total wave function $\Psi(Q_N)$ must be antisymmetric with respect to permutations of any two electrons,

$$\begin{aligned} & \Psi(q_1, \dots, q_i, \dots, q_j, \dots, q_N) \\ &= -\Psi(q_1, \dots, q_j, \dots, q_i, \dots, q_N). \end{aligned} \quad (5)$$

It is well known that the necessity to satisfy this condition in the general case prevents one from separating the space and spin coordinates in Eq. (3). Since the permutation symmetry plays an important role in the derivation, it is helpful to recall some facts from the theory of many-electron systems [2,42,43]. For the following, we need to know how the solutions to Eq. (3) satisfying Eq. (5) depend on their space and spin arguments. Throughout the paper, we consider a solution characterized by given values of the total spin S and its projection M_S . Such a solution can be presented in the form

$$\Psi(Q_N) = \frac{1}{\sqrt{\tau_{NS}}} \sum_{\tau=1}^{\tau_{NS}} \psi_{\tau S}(\mathbf{R}_N) \chi_{\tau S M_S}(\Sigma_N), \quad (6)$$

where $\mathbf{R}_N = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ and $\Sigma_N = (\sigma_1, \dots, \sigma_N)$. The spin functions $\chi_{\tau S M_S}(\Sigma_N)$ in Eq. (6) are a basis of the corresponding irreducible representation of the symmetric group, the space functions $\psi_{\tau S}(\mathbf{R}_N)$ transform according to the conjugate representation, and τ_{NS} is the dimension of the representation,

$$\tau_{NS} = \frac{(2S+1)N!}{(N/2+S+1)!(N/2-S)!}. \quad (7)$$

The spin functions satisfy

$$[\mathbf{S}_N^2 - S(S+1)]\chi_{\tau S M_S}(\Sigma_N) = 0, \quad (8a)$$

$$[S_{Nz} - M_S]\chi_{\tau S M_S}(\Sigma_N) = 0, \quad (8b)$$

where

$$\mathbf{S}_N = \sum_{i=1}^N \mathbf{s}_i \quad (9)$$

and \mathbf{s}_i is the spin operator of the i th electron. We assume them to be real and orthonormal,

$$\chi_{\tau S M_S}^T \chi_{\tau' S' M'_S} = \delta_{\tau\tau'} \delta_{SS'} \delta_{M_S M'_S}. \quad (10)$$

Here and in the following, we treat functions of spin coordinates taken at the different values of these coordinates as components of a vector. For any two such functions A and B we use the notation

$$A^T B \equiv \sum_{\sigma_1, \sigma_2, \dots} A(\sigma_1, \sigma_2, \dots) B(\sigma_1, \sigma_2, \dots), \quad (11)$$

where T stands for transpose. A method to construct spin functions with the specified properties is described in Appendix A. The space functions are the degenerate (unless $\tau_{NS} = 1$) solutions to

$$(H_N - E)\psi_{\tau S}(\mathbf{R}_N) = 0. \quad (12)$$

For $F = 0$, they are assumed to be real (this is always possible to achieve for a bound state) and normalized by

$$\int \psi_{\tau S}^2(\mathbf{R}_N) dV_N = 1, \quad dV_N = d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (13)$$

Equations (10) and (13) lead to the normalization condition for the total wave function (6),

$$\int \Psi^T \Psi dV_N = 1. \quad (14)$$

The tunneling SSs are the analytic continuation in F of bound states of the unperturbed system, so the normalization condition for $F > 0$ remains the same. Note that there is no complex conjugation in Eqs. (13) and (14); this general property of the theory of SSs [9,12,31,32] can be simply explained by the fact that complex conjugation is not an analytic operation. We do not discuss here rotational symmetry of the space functions which is an important issue for atoms but does not apply in the general case of molecules.

C. Ionization channels

Our calculation of the ionization rate (see Sec. II E) is based on the consideration of the flux of outgoing electrons in the

asymptotic region of configuration space. In the weak-field limit, this flux is sharply localized in the directions where one of the z_i tends to $-\infty$ while all the other $3N - 1$ space coordinates remain finite. Each of these N directions corresponds to tunneling ionization of one of the electrons. We will see shortly that the part of the outgoing flux representing simultaneous tunneling ionization of more than one electrons is exponentially suppressed. In other words, in the weak-field limit tunneling ionization is a one-electron process. Taking into account Eq. (5), it is sufficient to consider tunneling of any one of the electrons. We choose the N th electron and simplify the notation for its coordinates,

$$\mathbf{r} \equiv \mathbf{r}_N, \quad \sigma \equiv \sigma_N, \quad q \equiv q_N. \quad (15)$$

Let H_{N-1} be the Hamiltonian of the remaining $(N - 1)$ -electron subsystem. From Eq. (2) we obtain

$$H_N = H_{N-1} - \frac{1}{2} \Delta + V(\mathbf{r}) + Fz, \quad (16)$$

where

$$V(\mathbf{r}) = - \sum_{a=1}^A \frac{Z_a}{|\mathbf{r} - \mathbf{N}_a|} + \sum_{i=1}^{N-1} \frac{1}{|\mathbf{r} - \mathbf{r}_i|}. \quad (17)$$

In the asymptotic region we have

$$V(\mathbf{r})|_{r \rightarrow \infty} = -\frac{Z}{r} + O(r^{-2}), \quad (18)$$

where Z is the total charge of the parent ion,

$$Z = \sum_{a=1}^A Z_a - N + 1. \quad (19)$$

The term $O(r^{-2})$ in Eq. (18) is immaterial for the derivation in the leading-order approximation for $F \rightarrow 0$. Equations (16) and (18) show that the ionized electron asymptotically moves under the influence of the external electric field and the Coulomb potential of the parent ion. The one-electron Schrödinger equation in this combined potential allows separation of variables in parabolic coordinates [2],

$$\xi = r + z, \quad 0 \leq \xi < \infty, \quad (20a)$$

$$\eta = r - z, \quad 0 \leq \eta < \infty, \quad (20b)$$

$$\varphi = \arctan \frac{y}{x}, \quad 0 \leq \varphi < 2\pi. \quad (20c)$$

To exploit this advantage of parabolic coordinates in the many-electron problem, following the approach of Ref. [9] we present Eq. (3) in the form

$$\left[\frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} + \mathcal{B}(\eta) + (E - H_{N-1}) \frac{\eta}{2} + \frac{F\eta^2}{4} \right] \Psi(Q_N) = 0, \quad (21)$$

where $\mathcal{B}(\eta)$ is the adiabatic Hamiltonian,

$$\begin{aligned} \mathcal{B}(\eta) = & \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{\xi + \eta}{4\xi\eta} \frac{\partial^2}{\partial \varphi^2} - rV(\mathbf{r}) \\ & + (E - H_{N-1}) \frac{\xi}{2} - \frac{F\xi^2}{4}, \end{aligned} \quad (22)$$

which depends on η as a parameter. Driven by the field, the ionized electron moves toward $z \rightarrow -\infty$, which corresponds to $\eta \rightarrow \infty$. Let us introduce the asymptotic Hamiltonian,

$$\begin{aligned} \mathcal{B} \equiv \mathcal{B}(\eta)|_{\eta \rightarrow \infty} = & \frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{1}{4\xi} \frac{\partial^2}{\partial \varphi^2} \\ & + Z + (E - H_{N-1}) \frac{\xi}{2} - \frac{F\xi^2}{4}. \end{aligned} \quad (23)$$

The eigenfunctions of this operator defined by

$$(\mathcal{B} - \beta_\nu) \Phi_{\nu M'_S}(Q_{N-1}, \xi, \varphi, \sigma) = 0 \quad (24)$$

are called the *ionization channels*. By separating variables in Eq. (24) we find

$$\Phi_{\nu M'_S}(Q_{N-1}, \xi, \varphi, \sigma) = \Psi_{n M'_S}(Q_{N-1}) \phi_\nu(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}} \chi_{M_S - M'_S}(\sigma), \quad (25)$$

where ν is a multiindex,

$$\nu = (n, n_\xi, m). \quad (26)$$

Here $\Psi_{n M'_S}(Q_{N-1})$ is a SS of the $(N - 1)$ -electron subsystem defined similarly to $\Psi(Q_N)$ by

$$(H_{N-1} - E_n) \Psi_{n M'_S}(Q_{N-1}) = 0 \quad (27)$$

supplemented by outgoing-wave boundary conditions and n is a complete set of quantum numbers identifying the SSs, including the total spin S' but excluding its projection M'_S ; it is convenient to treat M'_S separately. The different solutions to Eq. (27) satisfy

$$\int \Psi_{n M'_S}^T \Psi_{n' M'_S} dV_{N-1} = \delta_{nn'} \delta_{M'_S M'_S}. \quad (28)$$

The function $\phi_\nu(\xi)$ and the eigenvalue β_ν in Eq. (24) are defined by

$$\left[\frac{d}{d\xi} \xi \frac{d}{d\xi} - \frac{m^2}{4\xi} + Z + (E - E_n) \frac{\xi}{2} - \frac{F\xi^2}{4} - \beta_\nu \right] \phi_\nu(\xi) = 0, \quad (29a)$$

$$\phi_\nu(\xi)|_{\xi \rightarrow 0} \propto \xi^{|m|/2}, \quad \phi_\nu(\xi)|_{\xi \rightarrow \infty} = 0, \quad (29b)$$

$$\int_0^\infty \phi_{n n_\xi m}(\xi) \phi_{n n'_\xi m}(\xi) d\xi = \delta_{n n'_\xi}, \quad (29c)$$

where $m = 0, \pm 1, \pm 2, \dots$ is the azimuthal quantum number of the outgoing electron and $n_\xi = 0, 1, 2, \dots$ enumerates the different solutions to Eq. (29a) for given n and m . Finally, $\chi_{m_s}(\sigma)$ is a one-electron spin function [see Eq. (A3) in Appendix A], and Eq. (25) explicitly takes into account that for given M_S and M'_S the projection of the spin of the outgoing electron is $m_s = M_S - M'_S$. The solution to Eq. (21) is sought in the form

$$\Psi(Q_N) = \eta^{-1/2} \sum_{\nu M'_S} f_{\nu M'_S}(\eta) \Phi_{\nu M'_S}(Q_{N-1}, \xi, \varphi, \sigma). \quad (30)$$

Substituting this expansion into Eq. (21) and using Eqs. (28) and (29c), one can obtain a set of coupled equations for the unknown functions $f_{\nu M'_S}(\eta)$. For developing the weak-field

asymptotics, it is sufficient to consider these equations in the region $\eta = O(F^{-1})$ [9], where they take the form

$$\left[\frac{d^2}{d\eta^2} + \frac{F\eta}{4} + \frac{1}{2}(E - E_n) + \frac{\beta_v}{\eta} + O(\eta^{-2}) \right] f_{\nu M'_S}(\eta) = 0. \quad (31)$$

Here, again, the term $O(\eta^{-2})$ is immaterial in the leading-order approximation for $F \rightarrow 0$. Equations (31) for the different channels $\nu M'_S$ are decoupled; the coupling terms appear in the higher orders in η^{-1} and are contained in $O(\eta^{-2})$. The SSs are represented by the solutions to Eqs. (31) satisfying the outgoing-wave boundary condition [9],

$$f_{\nu M'_S}(\eta)|_{\eta \rightarrow \infty} = \frac{2^{1/2} f_{\nu M'_S}}{(F\eta)^{1/4}} \times \exp \left[\frac{i F^{1/2} \eta^{3/2}}{3} + \frac{i(E - E_n) \eta^{1/2}}{F^{1/2}} \right]. \quad (32)$$

The coefficient $f_{\nu M'_S}$ appearing here defines the amplitude of the outgoing wave in the ionization channel $\nu M'_S$. We have thus decomposed the outgoing flux into orthogonal (noninterfering) ionization channels, which is a key step in the derivation. As detailed in Sec. II E, the problem of calculating the ionization rate now reduces to finding the coefficients $f_{\nu M'_S}$.

D. Connection formula

In the weak-field limit, $f_{\nu M'_S}$ can be expressed in terms of a coefficient appearing in the asymptotics of the unperturbed bound-state wave function at $\eta \rightarrow \infty$. This relation is called the connection formula. It can be derived by constructing the asymptotic solution of Eq. (31) for $F \rightarrow 0$. To this end, all the quantities introduced in the previous section must be expanded in F . It should be noted that the expansions consist of power series parts and exponentially small terms. Since $f_{\nu M'_S}$ is itself exponentially small in F , we need to retain only the power series parts which can be found by means of perturbation theory [2]. Thus, e.g., the difference between E and \mathcal{E} can be neglected. Let $E_0^{(N)}$ and $\Psi_0^{(N)}(Q_N)$ be the solution to Eq. (3) for $F = 0$ representing the initial bound state of the N -electron system. For $F > 0$, the corresponding SS is given by

$$E = E_0^{(N)} - \mu_{0z}^{(N)} F + O(F^2), \quad (33a)$$

$$\Psi(Q_N) = \Psi_0^{(N)}(Q_N) + O(F), \quad (33b)$$

where $\mu_0^{(N)}$ is the dipole moment of the unperturbed system,

$$\mu_0^{(N)} = - \sum_{i=1}^N \int \Psi_0^{(N)T} \mathbf{r}_i \Psi_0^{(N)} dV_N. \quad (34)$$

For the $(N - 1)$ -electron subsystem we similarly have

$$E_n = E_n^{(N-1)} - \mu_{nz}^{(N-1)} F + O(F^2), \quad (35a)$$

$$\Psi_{nM'_S}(Q_{N-1}) = \Psi_{nM'_S}^{(N-1)}(Q_{N-1}) + O(F), \quad (35b)$$

where

$$\mu_n^{(N-1)} = - \sum_{i=1}^{N-1} \int \Psi_{nM'_S}^{(N-1)T} \mathbf{r}_i \Psi_{nM'_S}^{(N-1)} dV_{N-1}. \quad (36)$$

Equation (35b) requires a comment. The SSs $\Psi_{nM'_S}(Q_{N-1})$ with different n form a purely discrete set. Meanwhile, in the field-free case, it is more conventional to work with bound and continuum states. The bound states of the parent ion are recovered from the tunneling SSs $\Psi_{nM'_S}(Q_{N-1})$ in the limit $F \rightarrow 0$ and hence belong to the set of $\Psi_{nM'_S}^{(N-1)}(Q_{N-1})$. The continuum states are not given by any single one of these functions, but can be expanded in terms of them. We note that the static-field-induced states mentioned above [40,41], which do not have counterparts for $F = 0$, are also included in the set of $\Psi_{nM'_S}^{(N-1)}(Q_{N-1})$, but for them Eq. (35b) implies certain regularization. These mathematical subtleties concern the issue of completeness of the set of SSs. We do not discuss them in more detail here because the dominant contribution to the outgoing flux for $F \rightarrow 0$ comes from channels for which n corresponds to low-lying bound states of the ion. In the following, we assume that all the quantities on the right-hand sides of Eqs. (33) and (35) characterizing the unperturbed system are known. The solution to Eqs. (29) is given by

$$\beta_v = \beta_v^{(0)} + O(F), \quad (37a)$$

$$\phi_v(\xi) = \phi_v^{(0)}(\xi) + O(F), \quad (37b)$$

where [9]

$$\beta_v^{(0)} = Z - \varkappa_n \left(n_\xi + \frac{|m| + 1}{2} \right), \quad (38a)$$

$$\phi_v^{(0)}(\xi) = \varkappa_n^{1/2} (\varkappa_n \xi)^{|m|/2} e^{-\varkappa_n \xi / 2} \sqrt{\frac{n_\xi!}{(n_\xi + |m|)!}} L_{n_\xi}^{(|m|)}(\varkappa_n \xi). \quad (38b)$$

Here $L_n^{(\alpha)}(x)$ are the generalized Laguerre polynomials [44] and

$$\varkappa_n = \sqrt{2I_n}, \quad I_n = E_n^{(N-1)} - E_0^{(N)}, \quad (39)$$

where I_n is the field-free ionization potential in channel $\nu M'_S$. Substituting Eqs. (35b) and (37b) into Eq. (25), we obtain

$$\Phi_{\nu M'_S}(Q_{N-1}, \xi, \varphi, \sigma) = \Phi_{\nu M'_S}^{(0)}(Q_{N-1}, \xi, \varphi, \sigma) + O(F). \quad (40)$$

The unperturbed bound-state wave function can be expanded in terms of the unperturbed channels similarly to Eq. (30). By solving Eq. (31) for $F = 0$, we find that in the asymptotic region this expansion takes the form

$$\Psi_0^{(N)}(Q_N) \Big|_{\eta \rightarrow \infty} = N^{-1/2} \sum_{\nu M'_S} g_{\nu M'_S} \eta^{\beta_v^{(0)}/\varkappa_n - 1/2} e^{-\varkappa_n \eta / 2} \times \Phi_{\nu M'_S}^{(0)}(Q_{N-1}, \xi, \varphi, \sigma) [1 + O(\eta^{-1})]. \quad (41)$$

The coefficients $g_{\nu M'_S}$ here are given by

$$g_{\nu M'_S} = \hat{P}_v [\chi_{M_S - M'_S}^T \Upsilon_{nM'_S}], \quad (42)$$

where \hat{P}_v is a projection operator whose action on a function $\psi(\mathbf{r})$ is defined by

$$\hat{P}_v[\psi(\mathbf{r})] = \eta^{1/2 - \beta_v^{(0)}/\varkappa_n} e^{\varkappa_n \eta/2} \int_0^\infty \int_0^{2\pi} \phi_v^{(0)}(\xi) \times \frac{e^{-im\varphi}}{\sqrt{2\pi}} \psi(\mathbf{r}) d\xi d\varphi \Big|_{\eta \rightarrow \infty}, \quad (43)$$

and $\Upsilon_{nM'_S}(q)$ is the Dyson orbital [33,34],

$$\Upsilon_{nM'_S}(q) = N^{1/2} \int \Psi_{nM'_S}^{(N-1)T} \Psi_0^{(N)} dV_{N-1}. \quad (44)$$

To find $f_{vM'_S}$, one should substitute the solutions to Eqs. (31) satisfying Eq. (32) into Eq. (30) and match the resulting function in the region $1 \ll \eta \ll \eta_t$ with Eq. (41), where $\eta_t = 2I_n/F + O(F^0)$ is the turning point for Eq. (31). The derivation coincides with that given in Ref. [9], so we simply invoke the result obtained there. The connection formula reads

$$f_{vM'_S} = \frac{\varkappa_n^{1/2} g_{vM'_S}}{(2N)^{1/2}} \left(\frac{4\varkappa_n^2}{F} \right)^{\beta_v^{(0)}/\varkappa_n} \times \exp \left[\frac{i\pi}{4} + \frac{i\pi\beta_v^{(0)}}{\varkappa_n} - \varkappa_n \mu_n - \frac{\varkappa_n^3}{3F} \right] \times [1 + O(F \ln F)], \quad (45)$$

where

$$\mu_n = \mu_{0z}^{(N)} - \mu_{nz}^{(N-1)}. \quad (46)$$

This formula expresses the ionization amplitude $f_{vM'_S}$ in terms of the coefficient $g_{vM'_S}$ appearing in Eq. (41) and given by Eq. (42). Let us emphasize that in the present derivation we have retained in Eqs. (18), (31), (33), (35), and (37) only the terms needed to obtain the leading-order term in Eq. (45). For deriving the first-order correction terms $O(F \ln F)$ and $O(F)$ in Eq. (45) one would have to take into account the next-order term in the expansions [12].

It is worthwhile to indicate how the present formulation allows one to account for the possibility of multiple ionization. Simultaneous tunneling ionization of more than one electron is represented by the outgoing flux in the directions where two or more z_i simultaneously tend to $-\infty$. This does not happen in channels for which $\Psi_{nM'_S}^{(N-1)}(Q_{N-1})$ is a bound state of the parent ion. On the other hand, for continuum states, the value of $f_{vM'_S}$ is suppressed in comparison with ionization amplitudes into bound-state channels by the last term in the exponent in Eq. (45), because of a larger ionization potential I_n . There is also a possibility of sequential multiple ionization represented by the imaginary part of $E_n^{(N-1)}$ which is not accounted for by the expansion (35a). However, its effect on the value of $f_{vM'_S}$ is also exponentially small.

E. Ionization rate

We now turn to the calculation of the ionization rate. From Eqs. (3) and (4) we have

$$\Gamma \Psi^\dagger \Psi = \sum_{i=1}^N \nabla_i \mathbf{j}_i(\mathbf{R}_N), \quad (47)$$

where $\Psi^\dagger(Q_N) = \Psi^{*T}(Q_N)$ and

$$\mathbf{j}_i(\mathbf{R}_N) = \frac{-i}{2} [\Psi^\dagger(\nabla_i \Psi) - (\nabla_i \Psi^\dagger)\Psi]. \quad (48)$$

In the weak-field limit, the imaginary part of $\Psi(Q_N)$ is exponentially small in F and can be neglected on the left-hand side of Eq. (47), but not on its right-hand side. Substituting into Eq. (47) $\Psi^\dagger \Psi \approx \Psi^T \Psi$, integrating both sides over all \mathbf{r}_i , and using the normalization condition (13), we obtain

$$\Gamma = \sum_{i=1}^N \int_{S_i} \mathbf{e}_i \mathbf{j}_i(\mathbf{r}_i) dS_i \Big|_{r_i \rightarrow \infty}, \quad (49)$$

where $\mathbf{j}_i(\mathbf{r}_i)$ is the flux of the i th electron,

$$\mathbf{j}_i(\mathbf{r}_i) = \int \mathbf{j}_i(\mathbf{R}_N) d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N, \quad (50)$$

$\mathbf{r}_i \in S_i$, S_i is an expanding surface all points of which move away from the origin, \mathbf{e}_i is the outward-pointing unit normal vector to S_i , and dS_i is the area element of S_i . Equation (49) shows that in the weak-field limit the ionization rate coincides with the total flux of outgoing electrons, as one would expect on physical grounds. Let us introduce the one-electron density matrix,

$$\rho(\mathbf{r}, \mathbf{r}') = \int \Psi^\dagger(Q_{N-1}, \mathbf{r}, \sigma) \Psi(Q_{N-1}, \mathbf{r}', \sigma) dV_{N-1}. \quad (51)$$

Taking into account Eq. (5), we obtain

$$\mathbf{j}_i(\mathbf{r}) = \frac{-i}{2} (\nabla_{\mathbf{r}'} - \nabla_{\mathbf{r}}) \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}. \quad (52)$$

Hence the one-electron flux does not depend on the subscript i ,

$$\mathbf{j}_i(\mathbf{r}) = \mathbf{j}_N(\mathbf{r}) \equiv \mathbf{j}(\mathbf{r}), \quad (53)$$

and Eq. (49) can be presented in the form

$$\Gamma = N \int_S \mathbf{e} \mathbf{j}(\mathbf{r}) dS, \quad (54)$$

where $S \equiv S_N$ and $\mathbf{e} \equiv \mathbf{e}_N$. We choose S to be a surface of constant η at $\eta \rightarrow \infty$. The rest of the derivation is the same as in Ref. [9], the details can be found in Ref. [12]. By calculating the flux $\mathbf{j}(\mathbf{r})$ using Eq. (32), we find

$$\Gamma = \sum_{vM'_S} \Gamma_{vM'_S} + O(\Gamma^2), \quad \Gamma_{vM'_S} = N |f_{vM'_S}|^2. \quad (55)$$

Here $\Gamma_{vM'_S}$ is the partial rate for ionization into channel vM'_S and the error term $O(\Gamma^2)$ arises from the exponentially small contributions neglected in the derivation. Since $f_{vM'_S}$ is given by Eq. (45), and hence is assumed to be known, Eq. (55) is the result we sought.

This equation can be further simplified. In the expression for $\Gamma_{vM'_S}$ obtained by substituting Eq. (45), only the coefficient $g_{vM'_S}$ depends on M'_S , which enables one to perform the summation over M'_S in Eq. (55). To this end, we present the Dyson orbital (44) in the factorized form (see Appendix B)

$$\Upsilon_{nM'_S}(q) = v_n(\mathbf{r}) \chi_{S'M'_S, SM'_S}(\sigma). \quad (56)$$

The space function $v_n(\mathbf{r})$ here is expressed in terms of the space functions defining $\Psi_0^{(N)}(Q_N)$ and $\Psi_{nM'_S}^{(N-1)}(Q_{N-1})$ in the

form (6) by Eq. (B5) and the spin function is given by Eq. (B3). Substituting Eq. (56) into Eq. (42) and using Eq. (B6), we obtain

$$\Gamma = \sum_v (\delta_{S',S-1/2} + \delta_{S',S+1/2}) \Gamma_v + O(\Gamma^2), \quad (57)$$

where

$$\Gamma_v = |G_v|^2 W_v(F) [1 + O(F \ln F)] \quad (58)$$

is the total ionization rate into all spin-projection components of channel v . Here G_v is the structure factor,

$$G_v = e^{-\varkappa_n \mu_n} g_v, \quad (59)$$

where g_v is the asymptotic coefficient of the Dyson orbital given by

$$g_v = \hat{P}_v[v_n(\mathbf{r})], \quad (60)$$

and $W_v(F)$ is the field factor,

$$W_v(F) = \frac{\varkappa_n}{2} \left(\frac{4\varkappa_n^2}{F} \right)^{2Z/\varkappa_n - 2n_\xi - |m| - 1} \exp\left(-\frac{2\varkappa_n^3}{3F}\right). \quad (61)$$

This completes the derivation. Equations (57)–(61) expressing the asymptotics of Γ for $F \rightarrow 0$ in terms of the properties of the unperturbed system and its ion represented by Z , \varkappa_n , μ_n , and g_v are the main result of this work. We note that Eq. (58) has the form of Eq. (1). The leading-order term in this expansion looks similar to the corresponding partial rate for ionization into channel (n_ξ, m) in the one-electron problem [compare Eqs. (58)–(61) with Eq. (60) in Ref. [9]]. The many-electron character of the present theory reveals itself only in the different definitions of the quantities Z , \varkappa_n , μ_n , and g_v [whose counterparts in Ref. [9] are denoted by Z , \varkappa , μ_z , and $g_{n_\xi m}$, respectively], and the most essential difference is that the spatial part $v_n(\mathbf{r})$ of the Dyson orbital replaces in Eq. (60) the initial bound-state wave function in the one-electron case (denoted by $\psi_0(\mathbf{r})$ in Ref. [9]). We also note that the two factors in Eq. (59) separately depend on the origin of the electronic coordinates \mathbf{r}_i , but their product, and hence the partial ionization rate (58), is invariant with respect to a shift of the origin [9].

F. Dominant channel

To arrive at the final working formula for calculating the ionization rate within the ME-WFAT an additional consideration is needed. It should be understood that Eqs. (57) and (58) are asymptotic expansions in F . One cannot retain in these expansions terms which become smaller as $F \rightarrow 0$ than the error terms indicated. The error term in Eq. (57) is exponentially small in F and can always be neglected. But Eq. (58) is an expansion in powers of F and $\ln F$; the error term in this expansion for one channel can exceed the leading-order term for another channel. To determine which terms may be retained and which should be neglected, we note that the field factor (61) for channels with different sets of quantum numbers n defining the final state of the parent ion has different exponential factors, while for channels with the same n and different parabolic quantum numbers n_ξ and m it has different powers of F . For any positive a and b , $e^{-a/F} = o(F^b)$ as $F \rightarrow 0$. This means that in the present approximation, where

only the leading-order term in Eq. (58) is obtained, only the contribution from the *dominant* channel in the expansion for a given observable may be retained.

One can distinguish two possibilities. If only the total ionization rate Γ is observable, then the dominant channel corresponds to the smallest values of \varkappa_n [that is, of the ionization potential I_n ; see Eq. (39)] and parabolic quantum numbers n_ξ and $|m|$ present in the sum (57). However, we believe it is more sensible to assume that the partial rate for ionization into a given final state n of the parent ion defined by

$$\Gamma_n = \sum_{n_\xi=0}^{\infty} \sum_{m=-\infty}^{\infty} \Gamma_v \quad (62)$$

can be measured, provided that in this state $S' = S - 1/2$ or $S + 1/2$. Then the situation becomes quite similar to that in the one-electron problem [9]. The exponent in Eq. (61) is fixed now and the different terms in Eq. (62) in respect of their behavior for $F \rightarrow 0$ differ only by powers of F . The dominant channel in this case corresponds to the smallest n_ξ and $|m|$ present in Eq. (62). In the general (no symmetry) case, this is the channel with $n_\xi = m = 0$. The leading-order term in the asymptotics of Γ_n is then given by [see Eq. (26)]

$$\Gamma_n \approx |G_{n00}|^2 W_{n00}(F). \quad (63)$$

This is the working formula for molecules arbitrarily oriented with respect to the field. The dependence of Γ_n on the orientation, which is of main interest for applications [10,11], is contained in the structure factor G_{n00} . In the presence of a symmetry that may result in the vanishing of g_{n00} (this is the case for atoms and linear molecules aligned along the field in a state with nonzero projection of the orbital angular momentum) the dominant channel may have a nonzero value of the azimuthal quantum number m ; for more details see Refs. [9–11].

G. One-electron and single-active-electron approximations

The above equations express the ionization rate in terms of quantities determined by the exact wave functions of the unperturbed initial $\Psi_0^{(N)}(Q_N)$ and final $\Psi_{nM'_\xi}^{(N-1)}(Q_{N-1})$ states. However, accurate wave functions are available only for simplest few-electron systems. The approaches capable of calculating the electronic structure of many-electron atoms and molecules are usually based on some kind of one-electron approximation (OEA). For simplicity, we discuss only approaches in which many-electron wave functions are represented by a single Slater determinant. Below we indicate some difficulties in implementing the ME-WFAT in this approximation.

Let the initial state be represented by a Slater determinant composed of one-electron orbitals $\Psi_{n_i m_{s_i}}(q) = \psi_{n_i}(\mathbf{r}) \chi_{m_{s_i}}(\sigma)$, $i = 1, \dots, N$. Let ϵ_i be the corresponding one-electron energies defining the behavior of $\psi_{n_i}(\mathbf{r}) \propto \exp[-(-2\epsilon_i)^{1/2} r]$ at $r \rightarrow \infty$. Let $\Psi'_{n_i m_{s_i}}(q) = \psi'_{n_i}(\mathbf{r}) \chi_{m_{s_i}}(\sigma)$ and ϵ'_i , $i = 1, \dots, N - 1$, have the same meaning for the final state. First, we note that in the general case single-determinant wave functions are not eigenfunctions of the total spin [45]. And, on the other hand, not all states can be represented

by a single determinant; for example, the $1s2s\ ^1S$ state of He cannot be represented in this way. Thus not all initial and final states can be considered within the OEA. Second, single-determinant wave functions do not generally have the correct asymptotic behavior given by Eq. (41). As a result, the Dyson orbital (44) constructed from such functions does not have the correct asymptotic behavior either. Indeed, it can be seen that in the general case, when the initial $\Psi_{n_i m_{s_i}}(q)$ and final $\Psi'_{n_f m_{s_f}}(q)$ one-electron orbitals are different, the Dyson orbital $\Upsilon_{n M'_S}(q)$ is given by a linear combination of all $\Psi_{n_i m_{s_i}}(q)$ occupied in the initial state. Then, independently of the final state, the exponent in the asymptotics of $\Upsilon_{n M'_S}(q)$ at $r \rightarrow \infty$ is determined by the smallest ϵ_i which in general differs from the ionization potential for a given ionization channel. This inconsistency causes a problem in extracting the asymptotic coefficient (60). The situation is even worse in the Hartree-Fock (HF) approximation, since in this version of the OEA all one-electron orbitals $\Psi_{n_i m_{s_i}}(q)$ generally have the same exponent in the asymptotic tail determined by the first ionization potential [46,47]. This peculiarity of the HF method has led some authors to the conclusion that, independently of the orbital from which ionization occurs, the exponent in the field factor (61) must be determined by the first ionization potential, which results in a profound increase of ionization rates from inner orbitals by many orders of magnitude [48]. This conclusion is not supported by the present theory: the exponent in Eq. (61) is determined by the true ionization potential I_n for a given ionization channel, and ionization from inner orbitals is suppressed compared with that from outer orbitals, as can be expected on physical grounds. All this shows that the implementation of the ME-WFAT within the OEA is not straightforward. The development of the corresponding techniques on the basis of available codes for calculating atomic and molecular electronic structure is a direction for future studies.

The situation greatly simplifies if the initial $\Psi_{n_i m_{s_i}}(q)$ and final $\Psi'_{n_f m_{s_f}}(q)$ one-electron orbitals belong to the same orthonormal set. Physically, this corresponds to neglecting the relaxation of the final-state orbitals. In this approximation, the Dyson orbital (44) differs from zero only if the final state is obtained from the initial one by eliminating one electron, and then it coincides with the orbital $\psi_n(\mathbf{r})\chi_{m_s}(\sigma)$ of the eliminated electron. It can be seen that the space part in Eq. (56) in this case is $v_n(\mathbf{r}) = \sqrt{p_n}\psi_n(\mathbf{r})$, where $p_n = 1$ or 2 is the number of electrons in the initial state having the same $\psi_n(\mathbf{r})$ but different m_s . Thus, for $p_n = 1$, Eqs. (58)–(61) coincide with formulas defining the partial ionization rate for one electron initially bound in a state with the wave function $\psi_n(\mathbf{r})$ [9]. This corresponds to the SAEA. For $p_n = 2$, when both orbitals with $m_s = \pm 1/2$ for the same $\psi_n(\mathbf{r})$ are occupied in the initial state, the SAEA result for the ionization rate must be multiplied by 2, due to the summation over M'_S .

Another issue which is elucidated further by the present theory is the question of which dipole moment should appear in the structure factor (59) for a many-electron system. As shown in Ref. [9] and mentioned above, the very fact that the exponent with the dipole term originating from the linear Stark shift should appear in Eq. (59) follows immediately from the requirement that the ionization rate must be invariant with

respect to a shift of the origin of the electronic coordinates \mathbf{r}_i . The question about the dipole is critical, since the ionization rate depends exponentially on its value. Together with the orbital shape represented by the coefficient g_ν in Eq. (59), the value of the dipole determines, e.g., from which end the molecule ionizes most readily. For these reasons having an unambiguous theoretical prescription for estimating the dipole is important, also to resolve current disagreements between theory and experiment for CO [49–52]. In the literature, the study of tunneling ionization has typically so far been in some version of an OEA, possibly with some features of the many-electron system included. The initial state of the ionizing electron has, accordingly, been identified with an orbital, typically the least bound highest occupied molecular orbital (HOMO) but also, in the presence of nodal surfaces, with the next lower-lying orbitals denoted by HOMO-1 and HOMO-2 [53]. Three different ways to estimate the dipole of the initial state of the active electron (assumed to be the HOMO in the following) have been used. (i) One method uses the charge distribution of the HOMO to calculate the dipole [10,11,54–56]. This procedure is well justified in the strict SAEA, where all orbitals except the HOMO are fixed. In this approximation, the Dyson orbital reduces to the HOMO and the dipole of the ME-WFAT in Eq. (46) reduces to that defined by the charge distribution of the HOMO. (ii) Another method which has been used to estimate the dipole entering OEA models is to fit the energy of the HOMO for weak fields to the perturbation theory expansion similar to Eqs. (33a) and (35a) [57–60]. This approach yields the dipole of the HOMO with some multielectron effects included, since all electrons relax and re-adjust for each calculation performed at a given field F . (iii) Finally, in a series of papers the dipole of interest was obtained as the difference between the total dipole of the molecule and the dipole of the parent ion in the unrelaxed geometry [50,61–64]. This procedure was justified in Refs. [61–63] following an approach introduced in Ref. [17]. Equation (46) gives an answer to the question within the ME-WFAT: the dipole is given by the difference of the dipoles of the N - and $(N - 1)$ -electron systems. Within the present FNA, the latter should be calculated for the unrelaxed geometry of the nuclei.

III. ILLUSTRATIVE CALCULATIONS FOR FEW-ELECTRON SYSTEMS

We illustrate the theory by considering several few-electron systems. To confirm the validity of the theory, it is essential to compare the present asymptotic results with accurate calculations of the ionization rates of atoms and molecules in a static electric field. We are aware of only few such fully correlated calculations for systems containing more than one electron [18,36–39]. All these systems are discussed below.

In the following, we consider the total rate Γ_n of tunneling ionization from a given initial state $\Psi_0^{(N)}(Q_N)$ into all M'_S components of a given final state $\Psi_{n M'_S}^{(N-1)}(Q_{N-1})$. In all the cases, the dominant ionization channel corresponds to $n_\xi = m = 0$, so Γ_n is given by Eq. (63), and $\mu_{0z}^{(N)} = \mu_{n_z}^{(N-1)} = 0$, so $G_{n00} = g_{n00}$; see Eqs. (46) and (59). To implement Eq. (63), one needs to know the total charge of the parent ion Z , Eq. (19),

the parameter ν_n defined by the energies of the initial $E_0^{(N)}$ and final $E_n^{(N-1)}$ states, Eq. (39), and the asymptotic coefficient g_{n00} in the Dyson orbital defined by Eq. (60). The energies for the systems considered can be found in the literature, so the main goal of the present calculations is to obtain the coefficient g_{n00} . In each case, the initial and final states are explicitly defined; so, for brevity, we omit the subscripts in the notation g_{n00} and $W_{n00}(F)$.

A. Benchmark results for two-electron atoms H^- and He

We begin with two-electron atoms for which accurate bound-state wave functions can be constructed and thus the theory can be implemented as prescribed, without any approximations. For $N = 2$, the total spin S can take two values, 0 and 1. The corresponding irreducible representations of the symmetric group are one dimensional, $\tau_{2S} = 1$, and their spin basis functions are $\chi_{00}(\Sigma_2)$ and $\chi_{1M_S}(\Sigma_2)$, respectively [see Eqs. (A5) in Appendix A]. The initial state of a two-electron system has the form

$$\Psi_0^{(2)}(Q_2) = \psi_S(\mathbf{R}_2)\chi_{SM_S}(\Sigma_2), \quad (64)$$

where the space function satisfies $\psi_S(\mathbf{r}_1, \mathbf{r}_2) = (-1)^S \psi_S(\mathbf{r}_2, \mathbf{r}_1)$. The final state of the one-electron subsystem is $\Psi_n^{(1)}(q_1) = \psi_n(\mathbf{r}_1)\chi_{M_S}(\sigma_1)$. The space part of the Dyson orbital (56) is thus given by [see notation in Eq. (15)]

$$v_n(\mathbf{r}) = \sqrt{2} \int \psi_n(\mathbf{r}_1)\psi_S(\mathbf{R}_2)d\mathbf{r}_1. \quad (65)$$

We consider tunneling ionization from the only bound state of H^- and three lowest states of He, all states having the total orbital angular momentum $L = 0$. In all the cases, the final state is the ground $1s$ state; see Table I. Because of the rotational invariance of the initial and final states, the Dyson orbital (65) is a spherically symmetric function, $v_{1s}(\mathbf{r}) = v_{1s}(r)$. The two-electron wave functions were constructed in the form of an expansion in hyperspherical adiabatic basis [65] implemented in hyperspherical elliptic coordinates [66,67] by means of the slow variable discretization method [68]. This approach yields not only highly accurate energies of the bound states, see Table I, but also accurate wave functions with correct

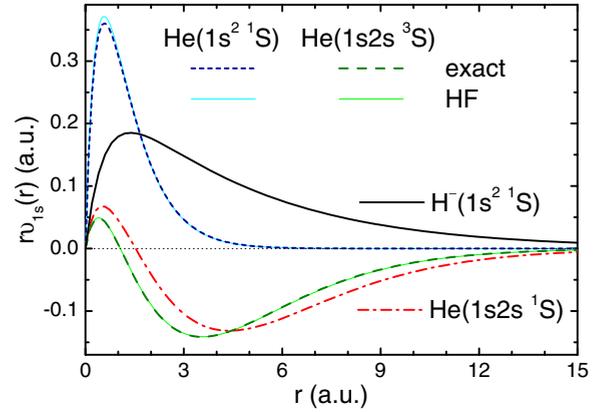


FIG. 1. (Color online) Dyson orbitals for H^- and three lowest states of He, see Table I, calculated with the present accurate two-electron wave functions. Thin solid lines: $1s$ HF orbital of $\text{He}(1s^2 1S)$ multiplied by $\sqrt{2}$ (cyan) and $2s$ HF orbital of $\text{He}(1s2s^3S)$ (light green) calculated using the program of Ref. [70].

asymptotic behavior. The wave functions and energies of the final one-electron states are known analytically. The Dyson orbitals calculated using these functions are shown in Fig. 1. The asymptotic coefficients g extracted from these orbitals by means of Eq. (60) are given in Table I. The error of these results should not exceed a unit in the last digit quoted.

Taking into account that accurate wave functions for many-electron systems are not available, and in future implementations of the theory one will have to resort to a OEA, it is instructive to compare the present benchmark results for two-electron atoms with the results obtained by the single-determinant HF method. For simplicity, we adopt an approximation in which the relaxation of the final-state orbitals is neglected. Then the Dyson orbital for $\text{He}(1s^2 1S)$ coincides with the $1s$ HF orbital for this state multiplied by $\sqrt{2}$ (the origin of this factor is explained in Sec. II G), and the Dyson orbital for $\text{He}(1s2s^3S)$ coincides with the $2s$ HF orbital for this state. The HF orbitals were calculated using the program of Ref. [70], the results are shown by thin solid lines in Fig. 1. The orbital energies defining the ionization potentials within the HF method are -0.917956 and -0.174256 , respectively.

TABLE I. Quantities needed to implement the ME-WFAT for the few-electron systems considered. $E_0^{(N)}$ and $E_n^{(N-1)}$ are energies of the initial and final states, respectively, obtained in the present calculations for H^- , He, and H_2^+ , analytically known for H and He^+ , adopted from^bRef. [69] for H_2 , and calculated by the HF method using the program of^dRef. [70] for Li and Li^+ . $E_{0,\text{exact}}^{(N)}$ and $E_{n,\text{exact}}^{(N-1)}$ are the corresponding energies from accurate variational calculations of^aRef. [71],^cRef. [72], and^eRef. [73]. g is the asymptotic coefficient in Eq. (63) obtained from the present accurate wave functions. g_{HF} is the coefficient obtained in the single-determinant unrelaxed HF approximation. The results for H_2 and H_2^+ are for the internuclear distance $R = 1.4009$, except for the energy from^eRef. [72] which is for $R = 1.4011$. All values are given in atomic units.

System	Initial state		System	Final state		g	g_{HF}
	$E_0^{(N)}$	$E_{0,\text{exact}}^{(N)}$		$E_n^{(N-1)}$	$E_{n,\text{exact}}^{(N-1)}$		
$\text{H}^-(1s^2 1S)$	-0.527 751 016	-0.527 751 017 ^a	$\text{H}(1s)$	-0.5		3.256	
$\text{He}(1s^2 1S)$	-2.903 724 376	-2.903 724 377 ^a	$\text{He}^+(1s)$	-2		2.932	2.99
$\text{He}(1s2s^1S)$	-2.145 974 015	-2.145 974 046 ^a	$\text{He}^+(1s)$	-2		-0.2602	
$\text{He}(1s2s^3S)$	-2.175 229 363	-2.175 229 378 ^a	$\text{He}^+(1s)$	-2		-0.3847	-0.380
$\text{H}_2(1s\sigma^{21}\Sigma_g^+)$	-1.888 275 ^b	-1.888 200 862 ^c	$\text{H}_2^+(1s\sigma)$	-1.283 941 230		2.73	2.71
$\text{Li}(1s^2 2s^2 S)$	-7.432 727 ^d	-7.478 060 323 ^e	$\text{Li}^+(1s^2 1S)$	-7.236 415 ^d	-7.279 913 413 ^e		0.474

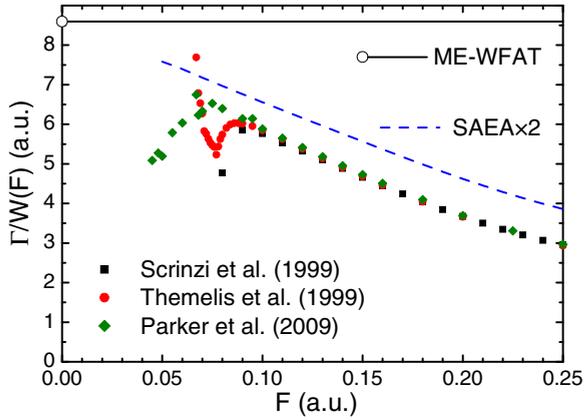


FIG. 2. (Color online) Ionization rate of He in the ground state divided by the field factor (61) for the dominant ionization channel $\text{He}(1s^2^1S) \rightarrow \text{He}^+(1s)$ with $n_\xi = m = 0$. Solid symbols: fully correlated calculations from Refs. [36–38]. Solid (black) line with an open circle at $F = 0$: present leading-order ME-WFAT results for ionization into the final state $\text{He}^+(1s)$, Eq. (63), given by a constant $g^2 = 8.595$; see Table I. Dashed (blue) line: SAEA results for ionization of one electron from the $1s$ state in the potential (66) calculated by the method of Ref. [31] and multiplied by 2.

The asymptotic coefficients g_{HF} extracted from the HF orbitals are given in Table I. The relative error of g_{HF} is less than 2% and similar in magnitude to the relative error of the ionization potentials. Thus for these two states of He the approximation considered works very well. This is encouraging for future applications of the theory on the basis of the HF method. However, as mentioned above, the state $\text{He}(1s2s^1S)$ cannot be represented by a single Slater determinant. Moreover, the $2s$ HF orbital for this state obtained with the program of Ref. [70] does not have the correct asymptotic behavior implied in Eq. (60), so we failed to extract the asymptotic coefficient from this orbital. The HF method also fails to describe the bound state of H^- .

The ionization rate of He in the ground state in a static electric field was calculated by the complex rotation method in the stationary framework [36,37] and by solving the time-dependent Schrödinger equation [38]. These references provide the total ionization rate Γ since the final state of the system is not resolved. The results are shown in Fig. 2. To eliminate a rapid variation of Γ by many orders of magnitude in the interval of F considered, and thus to facilitate the comparison of the different results, we show the rates divided by the field factor (61) for ionization into the final state $\text{He}^+(1s)$ in the dominant ionization channel with $n_\xi = m = 0$. The different calculations closely agree with each other at $F > 0.1$. At weaker fields, however, the results behave quite differently. We believe that they all are wrong at $F < 0.1$ because of the very small values of Γ . Indeed, $\Gamma \approx 2.9 \times 10^{-6}$ at $F = 0.1$ and rapidly decreases with F . It is difficult to treat such small values of Γ by any method; this problem was discussed in Refs. [9,12]. The ME-WFAT result for the ratio shown in Fig. 2 obtained from Eq. (63) is a constant g^2 ; see Table I. This constant is shown by the solid line in Fig. 2. We recall that Eq. (63) gives only the leading-order term in the asymptotic expansion of Γ for $F \rightarrow 0$. Including

the first-order correction terms, the ratio shown in Fig. 2 behaves as $g^2(1 + AF + BF \ln F)$; see Eq. (1) and Ref. [12]. Thus the ratio should almost linearly approach its limiting value g^2 as $F \rightarrow 0$. This is likely to be the case, as can be seen by extrapolating the results of Refs. [36–38] from the interval $F > 0.1$, where they are trustworthy, to $F = 0$. This establishes a consistency between the structure of the asymptotic expansion for Γ , the present value of g , and the results of Refs. [36–38], which eventually confirms the predictions of the ME-WFAT. To obtain a more convincing confirmation, one has to calculate the coefficients A and B of the first-order correction terms.

Within the SAEA, the ground state of He can be described by the potential seen by the active electron [74],

$$V_{\text{He}}(r) = -\frac{1 + \exp(-\alpha r)}{r}. \quad (66)$$

For $\alpha = 2.132405$, the energy of the $1s$ state in this potential is $E_{1s} = -0.903724$, so the ionization potential coincides with that of He; see Table I. We have calculated the ionization rate from the $1s$ state in this potential by the method developed in Ref. [31]. This rate multiplied by 2 (this factor is explained in Sec. II G) and divided by the field factor is shown by the dashed line in Fig. 2. The method of Ref. [31] also cannot treat too small values of Γ , so this line stops at $F = 0.05$. The SAEA results lie slightly higher than the results of fully correlated calculations [36–38]. However, being extrapolated to $F = 0$, they are consistent with the present value of g , which favorably characterizes the one-electron potential (66).

B. Two-electron molecule H_2

We next consider a two-electron molecule H_2 . The molecule is assumed to be aligned along the field, and we consider tunneling ionization from the ground state of H_2 to the ground $1s\sigma$ state of H_2^+ ; see Table I. The space-spin structure of the initial and final states is the same as for two-electron atoms. For the initial two-electron state, we adopt the 50-term variational wave function defined in Table VI of Ref. [69]. This wave function is for the internuclear distance $R = 1.4009$, which dictates the value of R used in the present calculations. The energy obtained in the same group with a similar in quality 54-term wave function for the equilibrium internuclear distance $R = 1.4011$ is -1.888195 [75], which is close to the best available variational result from Ref. [72]; see Table I. The final one-electron state was calculated using the program of Ref. [76]. This program returns virtually exact energies and wave functions for one-electron diatomic molecules. The Dyson orbital $v_{1s\sigma}(\mathbf{r})$ was calculated with these functions using Eq. (65). It has the same symmetry as the $1s\sigma$ orbital of H_2^+ . It is shown in Fig. 3 as a function of the distance r measured from the center of the molecule along the internuclear axis. Although the present two-electron wave function from Ref. [69] is good enough to yield rather accurate energy, it has incorrect behavior in the asymptotic region. This is understandable, because the exponents in the basis functions were chosen to minimize the energy which is insensitive to the asymptotic tail of the wave function. As a result, the tail of $v_{1s\sigma}(\mathbf{r})$ has the correct behavior with the exponent determined by the ionization potential in the region $r \lesssim 6$, but decays more rapidly at larger r . The

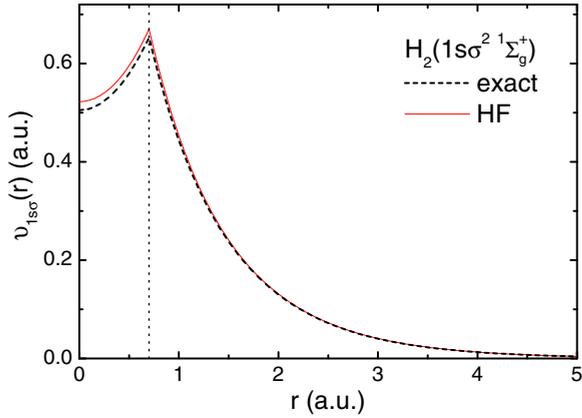


FIG. 3. (Color online) Dyson orbital for H_2 , see Table I, as a function of the distance r from the center of the molecule along the internuclear axis for the internuclear distance $R = 1.4009$. Dashed (black) line: results obtained with an accurate two-electron wave function from Ref. [69]. Thin solid (red) line: $1s\sigma$ HF orbital of $H_2(1s\sigma^2 1\Sigma_g^+)$ multiplied by $\sqrt{2}$ calculated using the program of Ref. [76]. Vertical dotted line at $r = R/2$ indicates the position of one of the nuclei.

coefficient g extracted from this orbital by means of Eq. (60) and a fitting procedure described in Ref. [11] applied in the interval $1 \leq r \leq 5$ is given in Table I. The error of this result should not exceed a unit in the last digit quoted.

In the single-determinant unrelaxed HF approximation, the Dyson orbital for $H_2(1s\sigma^2 1\Sigma_g^+)$ coincides with the $1s\sigma$ HF orbital for this state multiplied by $\sqrt{2}$. The HF results calculated using the program of Ref. [76] are also shown in Fig. 3. The asymptotic coefficient g_{HF} obtained in this approximation is given in Table I. The agreement between the accurate and HF results in the present case is as good as for He.

The ionization rate of H_2 in the ground state for the same orientation with respect to the field and a slightly different internuclear distance $R = 1.4$ was calculated by the complex rotation method in Ref. [18]. These results are compared in Fig. 4 with the prediction of the ME-WFAT. For the present value of g (see Table I), the ME-WFAT result for the ratio shown in the figure is consistent with what can be obtained by extrapolating the results of Ref. [18] to $F = 0$, which again confirms the present theory. The orientation dependence of the ionization rate of H_2 within the OE-WFAT calculated in the HF approximation was discussed in Ref. [10].

C. Three-electron atom Li

We finally discuss a three-electron atom Li. The total spin S of a three-electron system also can take only two values, $1/2$ and $3/2$. The irreducible representation corresponding to doublet states ($S = 1/2$) is two dimensional and its genealogical spin basis consists of $\chi_{0\frac{1}{2}M_S}(\Sigma_3)$ and $\chi_{1\frac{1}{2}M_S}(\Sigma_3)$; that for quartet states ($S = 3/2$) is one dimensional with a single basis function $\chi_{1\frac{3}{2}M_S}(\Sigma_3)$ [see Eqs. (A6) in Appendix A]. The doublet three-electron states have the form

$$\Psi_0^{(3)}(Q_3) = \frac{1}{\sqrt{2}} \sum_{S_2=0}^1 \psi_{S_2}(\mathbf{R}_3) \chi_{S_2\frac{1}{2}M_S}(\Sigma_3). \quad (67)$$

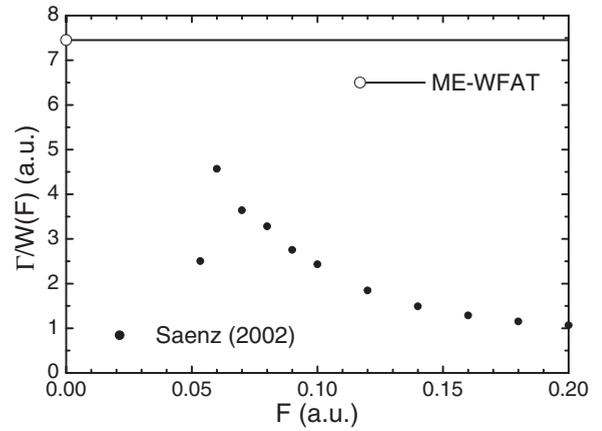


FIG. 4. Ionization rate of H_2 aligned along the field in the ground electronic state divided by the field factor (61) for the dominant ionization channel $H_2(1s\sigma^2 1\Sigma_g^+) \rightarrow H_2^+(1s\sigma)$ with $n_g = m = 0$. Solid circles: fully correlated calculations from Ref. [18] for the internuclear distance $R = 1.4$. Solid line with an open circle at $F = 0$: present leading-order ME-WFAT results for ionization into the final state $H_2^+(1s\sigma)$, Eq. (63), given by a constant $g^2 = 7.45$ calculated for $R = 1.4009$; see Table I.

The final state of the two-electron subsystem is $\Psi_{nM_S}^{(2)}(Q_2) = \psi_n(\mathbf{R}_2) \chi_{S'M_S'}(\Sigma_2)$, so the space part of the Dyson orbital (56) is given by

$$v_n(\mathbf{r}) = \sqrt{\frac{3}{2}} \int \psi_n(\mathbf{R}_2) \psi_{S'}(\mathbf{R}_3) dV_2. \quad (68)$$

We consider tunneling ionization from the ground state of Li to the ground state of Li^+ ; see Table I. In principle, accurate variational wave functions of Li are available in the literature; see Ref. [73] and references therein. However, as we have seen on the example of H_2 , such functions do not necessarily have the correct behavior in the asymptotic region required for extracting the coefficient g . We postpone the analysis of Li with more precise wave functions to future studies and restrict our treatment here to the single-determinant unrelaxed HF approximation which turned out to be rather accurate in the previous cases. In this approximation, the Dyson orbital for $Li(1s^2 2s^2 S)$ coincides with the $2s$ HF orbital for this state. This orbital is again calculated using the program of Ref. [70]. The corresponding asymptotic coefficient g_{HF} is given in Table I.

The ionization rate of Li in the ground state was calculated by the complex rotation method in Ref. [39]; the results are shown in Fig. 5. A linear extrapolation of these results to $F = 0$ seems to disagree with the prediction of the ME-WFAT obtained in the HF approximation. This disagreement can result from a more complicated nonmonotonic way of how the ratio shown in the figure approaches its limiting value as $F \rightarrow 0$; examples of such a behavior were met before [9,32]. But it can also reflect a deficiency of the HF approximation in the present case, or an inaccuracy of the results of Ref. [39]. To clarify this situation, the asymptotic coefficient g must be calculated with the use of more accurate wave functions.

An additional insight into the situation is provided by the SAEA. In this approximation, the ground state of Li can be

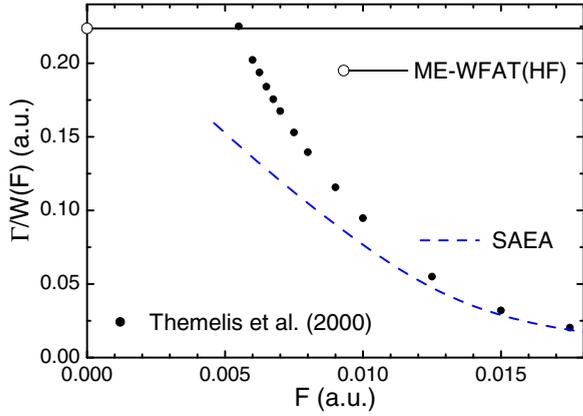


FIG. 5. (Color online) Ionization rate of Li in the ground state divided by the field factor (61) for the dominant ionization channel $\text{Li}(1s^2 2s^2 S) \rightarrow \text{Li}^+(1s^2 1S)$ with $n_\xi = m = 0$. Solid symbols: fully correlated calculations from Ref. [39]. Solid (black) line with an open circle at $F = 0$: present leading-order ME-WFAT results for ionization into the final state $\text{Li}^+(1s^2 1S)$, Eq. (63), obtained in the single-determinant unrelaxed HF approximation and given by a constant $g_{\text{HF}}^2 = 0.225$; see Table I. Dashed (blue) line: SAEA results for ionization of one electron from the $2s$ state in the potential (69) calculated by the method of Ref. [31].

described by the potential [77–79]

$$V_{\text{Li}}(r) = -\frac{1 + 2(1 + \beta r) \exp(-2\beta r)}{r} \quad (69)$$

with $\beta = 1.6559$. The $2s$ state in this potential has the energy $E_{2s} = -0.198141$, so the ionization potential within five digits coincides with that of Li; see Table I. We have calculated the ionization rate from the $2s$ state by the method of Ref. [31]; the results are shown by the dashed line in Fig. 5. There exist earlier calculations for this potential by the complex absorbing potential method [78] and B -spline approach [79]. The ionization rates obtained in these calculations are in close agreement with each other at $F = 0.015$, but rapidly diverge at weaker fields. Our calculations confirm the results of Ref. [79]. For example, for the weakest field $F = 0.0055$ considered there, the complex energy eigenvalues obtained in the different calculations are $-0.20061970 - i0.745 \times 10^{-8}$ [78] and $-0.20052299 - i0.38 \times 10^{-9}$ [79] and the present result is $-0.200619759 - i0.37844 \times 10^{-9}$. We believe that our result is correct in all digits. Thus the method of Ref. [78] works well for the real part of the energy, but fails at weak fields for the imaginary part, while the approach of Ref. [79] is not so accurate for the energy, but works much better for the ionization rate. As seen from Fig. 5, the SAEA results are consistent with the ME-WFAT result obtained in the HF approximation at $F \rightarrow 0$, and, on the other hand, agree with the results of Ref. [39] at stronger fields, but disagree with Ref. [39] at weaker fields. This, however, is not sufficient to judge which of the results reproduces the correct behavior of the ionization rate of Li at $F \rightarrow 0$.

IV. CONCLUSION

In this paper, we have extended the WFAT, originally developed for one-electron systems [9], to many-electron

atoms and molecules treated in the FNA. The total ionization flux is decomposed into ionization channels $\nu = (n, n_\xi, m)$ corresponding to a given state n of the parent ion and a given set of parabolic quantum numbers (n_ξ, m) of the ionized electron. The asymptotic expansion (58) of the partial rate Γ_ν for ionization into channel ν has the general form of Eq. (1). The leading-order term in this expansion is obtained and given by Eqs. (59)–(61). The results are expressed in terms of properties of the unperturbed system and its ion. In particular, the asymptotic coefficient (60) in the structure factor (59) is determined by the corresponding Dyson orbital. The theory is illustrated by calculations for several few-electron systems for which accurate wave functions can be constructed. The asymptotic results for the tunneling ionization rates of He and H_2 are consistent with the results of fully correlated calculations [18,36–38], but for Li there is an indication of disagreement with the results of Ref. [39]. The implementation of the theory on the basis of available quantum chemistry codes for electronic structure calculations with the help of the experience gained in Refs. [10,11] is a goal for future studies.

Since main applications of the ME-WFAT belong to strong-field physics, it is worthwhile to mention some unresolved problems. There is a class of small molecules where one-electron tunneling theories and strong-field ionization experiments disagree qualitatively. These molecules are therefore of immediate interest for application of the ME-WFAT. For CO_2 previous theories, including the OE-WFAT, fail to explain the measured [80,81] maximum in the ionization signal at the angle between the molecular axis and external field $\approx 45^\circ$, but systematically predict an angle 5° – 10° smaller (see Ref. [11] for a detailed discussion). For CO the OE-WFAT predicts that ionization occurs most likely when the field points from the O to the C end [11], which is opposite to what is observed experimentally [49–51]. For OCS the OE-WFAT tunneling rate peaks when the dipole of the HOMO (pointing from the S to the O end) has a component antiparallel with the field, i.e., when the electron leaves from the O end [11]. This is consistent with previous work on OCS in circularly polarized fields [61,63], but is in contrast with experiments in linearly polarized fields, where the ionization signal peaks when the molecular axis is perpendicular to the direction of the field [82]. In these three cases (CO_2 , CO, and OCS), one possible reason of the difference between experimental and theoretical results is many-electron effects, and then the ME-WFAT may resolve the discrepancies. Other possible sources of the disagreement within the adiabatic approximation [25] are the strong-field effects represented by the correction terms in Eq. (1), which can be accounted for by extending the ME-WFAT along the lines of Ref. [12], and the effects of nuclear motion [20,21]. Any remaining disagreement should then be associated with nonadiabatic effects caused by the temporal dependence of the field.

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APPENDIX A: GENEALOGICAL SPIN BASIS

The spin functions $\chi_{\tau S M_S}(\Sigma_N)$, $\tau = 1, \dots, \tau_{N_S}$, should form a real orthonormal basis of the irreducible representation corresponding to a given value of the total spin S of the N -electron system. Any such basis can be used in Eq. (6). A particular set of the spin functions can be constructed by adding the spins of individual electrons, one by one, in the order as the electrons are numbered [42]. We denote such functions by $\chi_{S_2 \dots S_{N-1} S M_S}(\Sigma_N)$, where S_n is the total spin of the first n electrons and $S_1 = 1/2$ is omitted from the notation because its value is fixed. In addition to Eqs. (8), these functions satisfy

$$[\mathbf{S}_n^2 - S_n(S_n + 1)]\chi_{S_2 \dots S_{N-1} S M_S}(\Sigma_N) = 0, \quad n = 1, \dots, N-1. \quad (\text{A1})$$

For this *genealogical* spin basis, the subscript τ in Eq. (6) enumerates all possible sets of the intermediate spins $S_2 \dots S_{N-1}$ and the orthonormalization condition (10) takes the form

$$\chi_{S_2 \dots S_{N-1} S M_S}^T \chi_{S'_2 \dots S'_{N-1} S' M'_S} = \delta_{S_2 S'_2} \dots \delta_{S_{N-1} S'_{N-1}} \delta_{S S'} \delta_{M_S M'_S}. \quad (\text{A2})$$

Let us introduce the one-electron spin functions $\chi_{m_s}(\sigma)$, $m_s = \pm 1/2$, defined by

$$\chi_{m_s}(\sigma) = \delta_{m_s \sigma}, \quad \chi_{m_s}^T \chi_{m'_s} = \delta_{m_s m'_s}. \quad (\text{A3})$$

Then the complete set of functions $\chi_{S_2 \dots S_{N-1}; S, M_S}(\Sigma_N)$ for an N -electron system can be obtained from the complete set of similar functions $\chi_{S_2 \dots S_{N-2}; S, M_S}(\Sigma_{N-1})$ for its $(N-1)$ -electron subsystem by means of the equations

$$\begin{aligned} & \chi_{S_2 \dots S_{N-2} S, S+1/2, M_S}(\Sigma_N) \\ &= \sqrt{\frac{S - M_S + \frac{1}{2}}{2S + 1}} \chi_{S_2 \dots S_{N-2} S, M_S+1/2}(\Sigma_{N-1}) \chi_{-\frac{1}{2}}(\sigma_N) \\ &+ \sqrt{\frac{S + M_S + \frac{1}{2}}{2S + 1}} \chi_{S_2 \dots S_{N-2} S, M_S-1/2}(\Sigma_{N-1}) \chi_{+\frac{1}{2}}(\sigma_N), \end{aligned} \quad (\text{A4a})$$

$$\begin{aligned} & \chi_{S_2 \dots S_{N-2} S, S-1/2, M_S}(\Sigma_N) \\ &= \sqrt{\frac{S + M_S + \frac{1}{2}}{2S + 1}} \chi_{S_2 \dots S_{N-2} S, M_S+1/2}(\Sigma_{N-1}) \chi_{-\frac{1}{2}}(\sigma_N) \\ &- \sqrt{\frac{S - M_S + \frac{1}{2}}{2S + 1}} \chi_{S_2 \dots S_{N-2} S, M_S-1/2}(\Sigma_{N-1}) \chi_{+\frac{1}{2}}(\sigma_N). \end{aligned} \quad (\text{A4b})$$

Applying these equations recursively in N , starting with $N = 2$, one can obtain all the spin functions for any N . For example, the two-electron functions $\chi_{S M_S}(\Sigma_2)$ are

given by

$$\chi_{00}(\Sigma_2) = \frac{1}{\sqrt{2}} [\chi_{+\frac{1}{2}}(\sigma_1) \chi_{-\frac{1}{2}}(\sigma_2) - \chi_{-\frac{1}{2}}(\sigma_1) \chi_{+\frac{1}{2}}(\sigma_2)], \quad (\text{A5a})$$

$$\chi_{1, \pm 1}(\Sigma_2) = \chi_{\pm \frac{1}{2}}(\sigma_1) \chi_{\pm \frac{1}{2}}(\sigma_2), \quad (\text{A5b})$$

$$\chi_{10}(\Sigma_2) = \frac{1}{\sqrt{2}} [\chi_{+\frac{1}{2}}(\sigma_1) \chi_{-\frac{1}{2}}(\sigma_2) + \chi_{-\frac{1}{2}}(\sigma_1) \chi_{+\frac{1}{2}}(\sigma_2)]. \quad (\text{A5c})$$

For the three-electron functions $\chi_{S_2 S M_S}(\Sigma_3)$ we obtain

$$\chi_{0\frac{1}{2}, \pm \frac{1}{2}}(\Sigma_3) = \chi_{00}(\Sigma_2) \chi_{\pm \frac{1}{2}}(\sigma_3), \quad (\text{A6a})$$

$$\begin{aligned} \chi_{1\frac{1}{2}, \pm \frac{1}{2}}(\Sigma_3) &= \pm \sqrt{\frac{2}{3}} \chi_{1, \pm 1}(\Sigma_2) \chi_{\mp \frac{1}{2}}(\sigma_3) \\ &\mp \frac{1}{\sqrt{3}} \chi_{10}(\Sigma_2) \chi_{\pm \frac{1}{2}}(\sigma_3), \end{aligned} \quad (\text{A6b})$$

$$\chi_{1\frac{3}{2}, \pm \frac{3}{2}}(\Sigma_3) = \chi_{1, \pm 1}(\Sigma_2) \chi_{\pm \frac{1}{2}}(\sigma_3), \quad (\text{A6c})$$

$$\begin{aligned} \chi_{1\frac{3}{2}, \pm \frac{1}{2}}(\Sigma_3) &= \frac{1}{\sqrt{3}} \chi_{1, \pm 1}(\Sigma_2) \chi_{\mp \frac{1}{2}}(\sigma_3) \\ &+ \sqrt{\frac{2}{3}} \chi_{10}(\Sigma_2) \chi_{\pm \frac{1}{2}}(\sigma_3). \end{aligned} \quad (\text{A6d})$$

APPENDIX B: SPACE-SPIN STRUCTURE OF A DYSON ORBITAL

The use of the genealogical spin basis in Eq. (6) enables one to clarify the space-spin structure of a Dyson orbital. Let $\Psi_{S M_S}(Q_N)$ be given by the right-hand side of Eq. (6), where $\tau = S_2 \dots S_{N-1}$. Let $\Psi_{S' M'_S}(Q_{N-1})$ has a similar form, where N , S , and M_S are substituted by $N-1$, S' , and M'_S , respectively, and the summation runs over all possible $\tau' = S'_2 \dots S'_{N-2}$. The Dyson orbital is defined by [we use the simplified notation of Eq. (15)]

$$\Upsilon(q) = N^{1/2} \int \Psi_{S' M'_S}^T \Psi_{S M_S} dV_{N-1}. \quad (\text{B1})$$

The advantage of the genealogical basis stems from the relation

$$\chi_{\tau' S' M'_S}^T \chi_{\tau S M_S} = \delta_{\tau' S', \tau} \chi_{S' M'_S, S M_S}(\sigma), \quad (\text{B2})$$

where

$$\begin{aligned} \chi_{S' M'_S, S M_S}(\sigma) &= \delta_{S', S-1/2} \left[\sqrt{\frac{S - M_S}{2S}} \delta_{M'_S, M_S+1/2} \chi_{-\frac{1}{2}}(\sigma) \right. \\ &+ \left. \sqrt{\frac{S + M_S}{2S}} \delta_{M'_S, M_S-1/2} \chi_{+\frac{1}{2}}(\sigma) \right] \\ &+ \delta_{S', S+1/2} \left[\sqrt{\frac{S + M_S + 1}{2S + 2}} \delta_{M'_S, M_S+1/2} \chi_{-\frac{1}{2}}(\sigma) \right. \\ &- \left. \sqrt{\frac{S - M_S + 1}{2S + 2}} \delta_{M'_S, M_S-1/2} \chi_{+\frac{1}{2}}(\sigma) \right]. \end{aligned} \quad (\text{B3})$$

Using Eq. (B2), we obtain $\Upsilon(q)$ in the factorized form

$$\Upsilon(q) = v(\mathbf{r})\chi_{S'M'_S, SM_S}(\sigma), \quad (\text{B4})$$

where

$$v(\mathbf{r}) = \sqrt{\frac{N}{\tau_{N-1, S'} \tau_{NS}}} \sum_{\tau=1}^{\tau_{NS}} \delta_{S'S_{N-1}} \int \psi_{\tau}(\mathbf{R}_{N-1}) \psi_{\tau S}(\mathbf{R}_N) dV_{N-1}. \quad (\text{B5})$$

The spin function (B3) has the property

$$\sum_{M'_S} (\chi_{M_S - M'_S}^T \chi_{S'M'_S, SM_S})^2 = \delta_{S', S-1/2} + \delta_{S', S+1/2}, \quad (\text{B6})$$

which facilitates the summation over M'_S in Eq. (55).

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