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Structure factors for tunneling ionization rates of molecules: General Hartree-Fock-based integral representation

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In the leading-order approximation of the weak-field asymptotic theory (WFAT), the dependence of the tunneling ionization rate of a molecule in an electric field on its orientation with respect to the field is determined by the structure factor of the ionizing molecular orbital. The WFAT yields an expression for the structure factor in terms of a local property of the orbital in the asymptotic region. However, in general quantum chemistry approaches molecular orbitals are expanded in a Gaussian basis which does not reproduce their asymptotic behavior correctly. This hinders the application of the WFAT to polyatomic molecules, which are attracting increasing interest in strong-field physics. Recently, an integral-equation approach to the WFAT for tunneling ionization of one electron from an arbitrary potential has been developed. The structure factor is expressed in an integral form as a matrix element involving the ionizing orbital. The integral is not sensitive to the asymptotic behavior of the orbital, which resolves the difficulty mentioned above. Here, we extend the integral representation for the structure factor to many-electron systems treated within the Hartree-Fock method and show how it can be implemented on the basis of standard quantum chemistry software packages. We validate the methodology by considering noble-gas atoms and the CO molecule, for which accurate structure factors exist in the literature. We also present benchmark results for CO₂ and for NH₃ in the pyramidal and planar geometries.

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I. INTRODUCTION

The release of an electron from a molecule caused by its interaction with the electric field of an intense laser pulse is the first step for a variety of strong-field phenomena [1]. The theory of this process is simplified by two approximations which hold for the majority of current strong-field experiments: the laser frequency is sufficiently low, so the ionization proceeds as if the field were static, and the field is sufficiently weak, so the electron is released by tunneling. Tunneling ionization rates of molecules in a static electric field are needed for many applications in strong-field physics. In particular, there is an increasing interest in considering polyatomic molecules like benzonitrile [2], *n*-butane and 1,3-butadiene [3], naphthalene [4,5], fenchone [6], toluene, *o*-xylene, and fluorobenzene [7].

A theory of tunneling ionization can be developed by seeking the ionization rate in the form of the asymptotic expansion in field strength. Such an approach was initiated in early studies of tunneling ionization from the Coulomb potential [8–12], zero-range potential [13], and arbitrary spherically symmetric atomic potentials [14]. In recent years the problem has attracted new interest due to its role in strong-field physics. The approach was generalized to arbitrary potentials without any symmetry [15], which made its application to molecules possible, and became known as the weak-field asymptotic theory (WFAT). The one-electron leading-order WFAT developed in Ref. [15] was extended to the first-order terms in the asymptotic expansion for the rate [16] and to many-electron systems in the leading-order approximation [17] and including the first-order terms [18,19]. This theory has been successfully applied to the analysis of strong-field ionization in a number of experiments [20–25].

Of main interest for applications in strong-field physics is the dependence of the ionization rate on the orientation

of a molecule with respect to the field. In the leading-order approximation of the WFAT, this dependence is determined by the structure factor of the ionizing molecular orbital [26]. The structure factor is expressed in terms of a local property of the asymptotic tail of the orbital [15,26]; we will call this formula the *tail representation* (TR) for the structure factor. In this paper, for definiteness, we assume that the electronic structure information needed for implementing the WFAT is calculated using the Hartree-Fock (HF) method. There exist efficient and accurate software packages solving the HF equations for atoms [27] and diatomic molecules [28] by grid methods in spherical and prolate spheroidal coordinates, respectively. Grid methods reproduce the correct asymptotic behavior of HF orbitals. As a consequence, the packages [27,28] have enabled systematic calculations of structure factors for atoms [29] and diatomic molecules [30] using the TR. However, in the general case of polyatomic molecules the HF equations are more efficiently solved using an expansion in terms of Gaussian-type orbitals (GTOs) [31,32]. In particular, this approach is implemented in the packages GAUSSIAN [33] and GAMESS [34]. The expansion in GTOs does not reproduce the correct asymptotic behavior of HF orbitals, because GTOs decay too fast. So, strictly speaking, GTO expansion approaches do not enable one to calculate molecular structure factors using the TR. This difficulty is essential, since it hinders the application of the WFAT to polyatomic molecules. We mention that it is common to other approaches to the theory of tunneling ionization in which the ionization rate is extracted from the asymptotic form of the ionizing orbital [35–38]. A technique to partially overcome the difficulty by optimizing the GTO basis, and thus improving the asymptotic behavior of the GTO expansion, was proposed and demonstrated for diatomic and triatomic molecules in Ref. [39]. However, the computational cost of the optimization rapidly grows with the number of

atoms, so the technique is not routinely feasible for larger molecules.

Recently, two of the authors have developed an integral-equation approach to the WFAT [40]. The WFAT expansion for the rate of ionization of one electron from an arbitrary potential has been rederived up to the first-order terms. The result coincides with the results of Refs. [15,16], of course, but different *integral representations* (IRs) for the coefficients in the expansion have been obtained. In particular, the IR for the structure factor has the form of a matrix element involving the ionizing orbital. The integral accumulates in the region of localization of the orbital and is not sensitive to its asymptotic behavior, so the IR is applicable even if the orbital is expanded in GTOs. This advantage of the IR over the TR was illustrated by calculations for helium.

The results of Ref. [40] open a possibility to turn the calculation of molecular structure factors into a routine procedure which can be implemented on the basis of standard quantum chemistry software packages. This will enable one to produce reliable data for any molecule. In the present paper we make a first step towards this goal. The paper is organized as follows. In Sec. II, we extend the IR for the structure factor [40] to many-electron systems treated within the HF method. The structure factor for an arbitrary orientation of a molecule is expressed in terms of a small number of integrals involving the ionizing orbital. In Sec. III, we show how these integrals can be calculated using the packages [33,34]. In Sec. IV, we first validate the methodology by comparing the present IR results with accurate TR results from the literature for noble-gas atoms and a diatomic molecule CO. We then consider a triatomic molecule CO₂ for which the IR improves the accuracy of previous TR calculations. Finally, we present benchmark results for NH₃, in the pyramidal and planar geometries, which has not been treated previously. In Sec. V, we summarize the results and indicate a direction for further development. As an instructive analytical model, in the Appendix we discuss the application of the IR to tunneling ionization from a zero-range potential [13].

II. THEORY

A. Tunneling ionization rate: Tail representation

Many-electron wave functions of atoms and molecules treated in the frozen nuclei approximation are in practical calculations often expressed in terms of a suitable set of one-electron orbitals defined by some effective generally nonlocal potentials [31,32]. This in particular is the case in the HF method. We consider tunneling ionization from such an orbital satisfying (atomic units are used throughout)

$$\left[-\frac{1}{2}\Delta + \hat{V}(\mathbf{r}) - E_0\right]\psi_0(\mathbf{r}) = 0. \quad (1)$$

This equation is written in a molecular frame (MF) defined implicitly by a given potential $\hat{V}(\mathbf{r})$ which depends on the positions of the nuclei. The potential is an operator of the form

$$\hat{V}(\mathbf{r})\psi_0(\mathbf{r}) = \int V(\mathbf{r},\mathbf{r}')\psi_0(\mathbf{r}')d\mathbf{r}'. \quad (2)$$

We assume that

$$\hat{V}(\mathbf{r})\psi_0(\mathbf{r})|_{r\rightarrow\infty} = \left[-\frac{Z}{r} - \frac{\mathbf{D}\cdot\mathbf{n}}{r^2} + O(r^{-3})\right]\psi_0(\mathbf{r}), \quad (3)$$

where Z is the total charge of the parent ion, $\mathbf{D}'$ is its dipole moment in the MF, and $\mathbf{n} = \mathbf{r}/r$. The electric field of strength F is assumed to point in the positive z direction of the laboratory frame (LF). The orientation of the molecule with respect to the field is specified by the three Euler angles (α, β, γ) defining a passive rotation $\hat{R}$ from the LF to the MF, where α is the angle of rotation around the laboratory z axis, β is the angle of rotation around the new y axis, and γ is the angle of rotation around the molecular z axis [41]. The rotation operator $\hat{R}$ is a matrix such that $\mathbf{v}' = \hat{R}\mathbf{v}$, where $\mathbf{v}$ and $\mathbf{v}'$ are columns representing the same vector in the LF and MF, respectively. By convention, all vectors characterizing the molecule in the MF are primed; this rule does not apply to electronic coordinates, but we always indicate explicitly which frame is used. The inverse rotation matrix is denoted by $\hat{R}^{-1}$; for example, the dipole moment of the parent ion in the LF is $\mathbf{D} = \hat{R}^{-1}\mathbf{D}'$. The field is axially symmetric in the LF, so the ionization rate does not depend on α and in the following we set $\alpha = 0$ [26].

Within the WFAT [15], the ionization rate is obtained as an asymptotic expansion in F with the coefficients determined by properties of the ionizing orbital. The total rate is given by

$$\Gamma(\beta, \gamma) = \sum_v \Gamma_v(\beta, \gamma), \quad (4)$$

where $\Gamma_v(\beta, \gamma)$ is the partial rate of ionization in parabolic channel $v = (n_\xi, m)$. The channels are defined by quantum numbers $n_\xi = 0, 1, \dots$ and $m = 0, \pm 1, \dots$ associated with parabolic coordinates (ξ, η, φ) in the LF [8]. The leading-order term in the asymptotic expansion of $\Gamma_v(\beta, \gamma)$ for $F \rightarrow 0$ is

$$\Gamma_v(\beta, \gamma) = |G_v(\beta, \gamma)|^2 W_v(F), \quad (5)$$

where $G_v(\beta, \gamma)$ is the structure factor,

$$G_v(\beta, \gamma) = e^{-\kappa\mu_z} g_v(\beta, \gamma), \quad (6)$$

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

$$W_v(F) = \frac{\kappa}{2} \left(\frac{4\kappa^2}{F}\right)^{2Z/\kappa - 2n_\xi - |m| - 1} \exp\left(-\frac{2\kappa^3}{3F}\right). \quad (7)$$

The parameter κ is determined by the ionization potential $|E_0|$ of the orbital,

$$\kappa = \sqrt{2|E_0|}, \quad (8)$$

and μ_z is the z component of the orbital dipole moment $\boldsymbol{\mu} = \hat{R}^{-1}\boldsymbol{\mu}'$ in the LF,

$$\mu_z = (-\mu'_x \cos \gamma + \mu'_y \sin \gamma) \sin \beta + \mu'_z \cos \beta, \quad (9)$$

where

$$\boldsymbol{\mu}' = - \int \psi_0^*(\mathbf{r}) \mathbf{r} \psi_0(\mathbf{r}) d\mathbf{r} \quad (10)$$

is the same vector in the MF. The remaining quantity $g_v(\beta, \gamma)$ is the asymptotic coefficient which appears in the expansion

of the orbital at $\eta \rightarrow \infty$ in the LF

$$\begin{aligned} \psi_0(\hat{\mathbf{R}}\mathbf{r})|_{\eta \rightarrow \infty} \\ = \sum_v g_v(\beta, \gamma) \eta^{Z/\kappa - n_\xi - |m|/2 - 1} e^{-\kappa\eta/2} \phi_v(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}} \end{aligned} \quad (11)$$

and is given by

$$\begin{aligned} g_v(\beta, \gamma) = \eta^{1+n_\xi+|m|/2-Z/\kappa} e^{\kappa\eta/2} \\ \times \int_0^\infty \int_0^{2\pi} \phi_v(\xi) \frac{e^{-im\varphi}}{\sqrt{2\pi}} \psi_0(\hat{\mathbf{R}}\mathbf{r}) d\xi d\varphi \Big|_{\eta \rightarrow \infty}, \end{aligned} \quad (12)$$

where $\phi_v(\xi)$ are the parabolic channel functions,

$$\phi_v(\xi) = \kappa^{1/2} (\kappa\xi)^{|m|/2} e^{-\kappa\xi/2} \sqrt{\frac{n_\xi!}{(n_\xi + |m|)!}} L_{n_\xi}^{(|m|)}(\kappa\xi), \quad (13)$$

and $L_n^{(\alpha)}(x)$ are the generalized Laguerre polynomials [42]. In the leading-order approximation only the dominant ionization channels having the lowest power of F in Eq. (7) should be retained in the sum (4). These are the channels with $n_\xi = 0$ and $m = \pm\bar{m}$, where the value of $\bar{m} \geq 0$ depends on the symmetry of the orbital [15]. In the general case $\bar{m} = 0$, but if $\psi_0(\mathbf{r})$ has a nodal line (e.g., π state of a linear molecule) or a nodal surface (e.g., odd state of a molecule with reflection symmetry), then $\bar{m} > 0$ for the corresponding orientations. In the leading-order approximation the total rate is

$$\Gamma(\beta, \gamma) = (2 - \delta_{\bar{m}0}) |G_{0\bar{m}}(\beta, \gamma)|^2 W_{0\bar{m}}(F). \quad (14)$$

It factorizes into the structure factor squared and the field factor for the dominant ionization channel $v = (0, \bar{m})$ which thus define its dependence on the orientation of the molecule with respect to the field and field strength, respectively [15,26].

Of main interest for applications in strong-field physics is the orientation dependence of the ionization rate. To predict this dependence one needs to calculate the structure factor $G_v(\beta, \gamma)$ for the dominant ionization channel, which requires knowledge of the corresponding asymptotic coefficient $g_v(\beta, \gamma)$. The structure factor is invariant under a shift of the coordinate frame, while the asymptotic coefficient is not [15]; this point is illustrated in the Appendix. One therefore should focus on $G_v(\beta, \gamma)$ as a primary property of the molecule, while $g_v(\beta, \gamma)$ is an auxiliary frame-dependent characteristic. However, since the two quantities differ by a factor known analytically [see Eq. (6)], and it is the calculation of the asymptotic coefficient which causes difficulties, in the following we discuss $g_v(\beta, \gamma)$.

Equation (12) expresses $g_v(\beta, \gamma)$ in terms of a local property of the asymptotic *tail* of the ionizing orbital $\psi_0(\mathbf{r})$, so we call it the TR for the asymptotic coefficient. If the orbital is expanded in GTOs, the right-hand side of Eq. (12) turns to zero at $\eta \rightarrow \infty$, and hence, strictly speaking, the TR is not applicable. In practical calculations one extracts $g_v(\beta, \gamma)$ from Eq. (12) at a finite η . Reliable results can be obtained only if there exists a plateau in the dependence of the right-hand side of Eq. (12) on η , where the function approaches its asymptotic value before vanishing due to too fast decay of GTOs, and Eq. (12) is applied at the plateau. Such a plateau does not generally appear (or is not sufficiently well pronounced) with

the use of standard non-species-optimized GTOs [31]. The optimization of the exponents defining the GTO basis enables one to systematically improve the asymptotic behavior of the GTO expansion, which eventually results in the appearance of a plateau [39]. However, the optimization is not feasible for large molecules. This difficulty may seem to be technical, but it prevents the application of the WFAT to polyatomic molecules and thus becomes essential. It is worth stressing that this difficulty is not specific to the WFAT, but also applies to other approaches to the theory of tunneling ionization [35–38].

B. Integral representation for the asymptotic coefficient

An alternative *integral* representation for $g_v(\beta, \gamma)$ was obtained in Ref. [40]. Let us introduce a reference function $\Omega_v(\mathbf{r})$ in the LF defined as a regular solution to

$$\left[-\frac{1}{2} \Delta - \frac{Z}{r} - E_0 \right] \Omega_v(\mathbf{r}) = 0 \quad (15)$$

given by

$$\Omega_v(\mathbf{r}) = f_v(\eta) \phi_v(\xi) \frac{e^{im\varphi}}{\sqrt{2\pi}}, \quad (16)$$

where

$$f_v(\eta) = -\frac{2\kappa^{|m|/2-a}\Gamma(a)}{|m|!} (\kappa\eta)^{|m|/2} e^{-\kappa\eta/2} M(a, 1 + |m|, \kappa\eta), \quad (17a)$$

$$a = 1 + n_\xi + |m| - Z/\kappa, \quad (17b)$$

and $M(a, b, x)$ is a confluent hypergeometric function [42]. The orbital energy E_0 defined by Eq. (1) does not generally coincide with any of the bound-state energies $-Z^2/2n^2$, $n = 1, 2, \dots$, of the reference hydrogenic Hamiltonian in Eq. (15), so the function $f_v(\eta)$ exponentially grows at $\eta \rightarrow \infty$:

$$f_v(\eta)|_{\eta \rightarrow \infty} = -\frac{2}{\kappa} \eta^{n_\xi+|m|/2-Z/\kappa} e^{\kappa\eta/2}. \quad (18)$$

Calculating the following integral in η by parts using Eqs. (11) and (18), we obtain

$$g_v(\beta, \gamma) = \int \Omega_v^*(\mathbf{r}) \left[\frac{1}{2} \Delta + \frac{Z}{r} + E_0 \right] \psi_0(\hat{\mathbf{R}}\mathbf{r}) d\mathbf{r}. \quad (19)$$

Taking into account Eq. (1), we can rewrite this as

$$g_v(\beta, \gamma) = \int \Omega_v^*(\mathbf{r}) \hat{V}_c(\hat{\mathbf{R}}\mathbf{r}) \psi_0(\hat{\mathbf{R}}\mathbf{r}) d\mathbf{r}, \quad (20)$$

where

$$\hat{V}_c(\mathbf{r}) = \hat{V}(\mathbf{r}) + \frac{Z}{r} \quad (21)$$

is the core potential having no Coulomb tail at $r \rightarrow \infty$ [see Eq. (2)]. We call Eq. (20) the IR for the asymptotic coefficient. This formula was obtained in Ref. [40] as a consequence of a more general relation—an integral representation for the exact ionization amplitude in channel v . The present derivation is simpler and more transparent. The equivalence of Eqs. (12) and (20) for an analytically tractable model is shown in the Appendix.

Equation (20) has the form of a matrix element of the core potential (21) between the reference function $\Omega_v(\mathbf{r})$ and the ionizing orbital. The exponential growth of $\Omega_v(\mathbf{r})$ at $\eta \rightarrow \infty$ [see Eq. (18)] in the integrand is compensated by the exponential decay of $\psi_0(\hat{R}\mathbf{r})$ [see Eq. (11)]. So the convergence of the integral at large η is determined by the asymptotic behavior of the core potential, and the integral does converge if $\hat{V}(\mathbf{r})$ satisfies Eq. (3) [40]. The integral is accumulated in the region of localization of the core potential and is not sensitive to the asymptotic behavior of the ionizing orbital outside this region. Hence the IR, Eq. (20), is applicable even if $\psi_0(\mathbf{r})$ is expanded in GTOs, and this constitutes its main advantage over the TR, Eq. (12).

We note that Eq. (19) gives another integral representation for $g_v(\beta, \gamma)$. Although Eqs. (19) and (20) are shown to be equivalent for an exact orbital $\psi_0(\mathbf{r})$ satisfying Eq. (11), they yield quite different results if the orbital does not have the correct asymptotic behavior. Indeed, the integral in Eq. (19) turns to zero if the orbital is approximated by a function for which the coefficients in the expansion in parabolic channels as functions of η decay at $\eta \rightarrow \infty$ faster than the coefficients in Eq. (11). This means that one cannot use Eq. (19) if the orbital is expanded in GTOs, while Eq. (20) remains applicable.

C. Partial-wave expansion

To implement Eq. (20), it is convenient to expand the reference function $\Omega_v(\mathbf{r})$ in spherical harmonics:

$$\Omega_v(\mathbf{r}) = \sum_{l=|m|}^{\infty} R_l^v(r) Y_{lm}(\theta, \varphi). \quad (22)$$

We adopt the phase convention for $Y_{lm}(\theta, \varphi)$ from Refs. [43,44]. As follows from Eq. (15), the radial functions $R_l^v(r)$ are regular solutions to

$$\left[-\frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} - E_0 \right] R_l^v(r) = 0 \quad (23)$$

and hence are given by

$$R_l^v(r) = \omega_l^v(\chi r)^l e^{-\chi r} M(l+1-Z/\chi, 2l+2, 2\chi r). \quad (24)$$

The coefficient ω_l^v here can be found as follows. On the one hand, from Eq. (24) we obtain

$$R_l^v(r)|_{r \rightarrow \infty} = \omega_l^v \frac{2^{-Z/\chi-l-1} (2l+1)!}{\Gamma(l+1-Z/\chi)} (\chi r)^{-Z/\chi-1} e^{\chi r}. \quad (25)$$

On the other hand, from Eq. (22) we have

$$R_l^v(r) = \int Y_{lm}^*(\theta, \varphi) \Omega_v(\mathbf{r}) \sin \theta d\theta d\varphi. \quad (26)$$

Calculating the asymptotics of the latter integral at $r \rightarrow \infty$ and comparing the result with Eq. (25), one obtains ω_l^v . This approach can be easily implemented for $n_\xi = 0$. Using Eqs. (16)–(18) and the asymptotics of $Y_{lm}(\theta, \varphi)$ at $\theta \rightarrow \pi$ given in Ref. [44], we find

$$\omega_l^{0m} = (-1)^{l+(|m|-m)/2+1} 2^{l+3/2} \chi^{Z/\chi-(|m|+1)/2} \times \sqrt{\frac{(2l+1)(l+|m|)!}{(l-|m|)!|m|!}} \frac{\Gamma(l+1-Z/\chi)}{(2l+1)!}. \quad (27)$$

One can similarly obtain ω_l^v for arbitrary n_ξ , although the derivation in the general case is more laborious. We do not discuss it here since only the case $n_\xi = 0$ is needed for Eq. (14).

To find the dependence of $g_v(\beta, \gamma)$ on the orientation angles β and γ using Eq. (20) one has to calculate the integral for a dense set of orientations. The advantage of the expansion (22) is that it enables one to describe this dependence analytically, simultaneously reducing the computational cost. The integrand in Eq. (20) is a function of the electron coordinate in the LF. Let us rewrite it in the MF:

$$g_v(\beta, \gamma) = \int \Omega_v^*(\hat{R}^{-1}\mathbf{r}) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r}. \quad (28)$$

The inverse rotation $\hat{R}^{-1}$ is defined by the Euler angles $(-\gamma, -\beta, 0)$. From Eq. (22) we obtain

$$\Omega_v(\hat{R}^{-1}\mathbf{r}) = \sum_{l=|m|}^{\infty} R_l^v(r) \sum_{m'=-l}^l Y_{lm'}(\theta, \varphi) D_{m'm}^l(-\gamma, -\beta, 0), \quad (29)$$

where $D_{mm'}^l(\alpha, \beta, \gamma) = e^{-im\alpha} d_{mm'}^l(\beta) e^{-im'\gamma}$ is the Wigner D -function [44]. Using the property $D_{m'm}^l(-\gamma, -\beta, 0) = d_{mm'}^l(\beta) e^{im'\gamma}$ and substituting Eq. (29) into Eq. (28), we obtain

$$g_v(\beta, \gamma) = \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l I_{lm'}^v d_{mm'}^l(\beta) e^{-im'\gamma}, \quad (30)$$

where

$$I_{lm'}^v = \int R_l^v(r) Y_{lm'}^*(\theta, \varphi) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r}. \quad (31)$$

Thus, having calculated the integrals (31) for a number of partial waves sufficient to achieve convergence in Eq. (30), one can easily calculate the asymptotic coefficient $g_v(\beta, \gamma)$, and hence the structure factor (6), for any orientation of the molecule. Equations (30) and (31) are the formulas to be implemented in calculations.

III. IMPLEMENTATION WITHIN THE HARTREE-FOCK METHOD

Equations (30) and (31) can be implemented on the basis of any approach to the electronic structure calculations formulated in terms of one-electron orbitals, such as the HF method or the density functional theory. In this section we discuss their implementation within the HF method. Aiming at developing the general procedure applicable to any molecule, we embed the discussion into the context of standard quantum chemistry software packages [33,34].

A. Hartree-Fock potential

We restrict the present treatment to closed-shell atoms and molecules with an even number of electrons N . Let $\psi_i(\mathbf{r})$, $i = 1, \dots, N/2$ denote the doubly occupied spatial HF orbitals for the system. The orbital $\psi_0(\mathbf{r})$, from which tunneling ionization is considered to occur, is one of the $\psi_i(\mathbf{r})$. The HF orbitals are known to have a special asymptotic behavior [45,46]. Namely, in the general case all $\psi_i(\mathbf{r})$ decay at $r \rightarrow \infty$ with the same exponent determined by the energy of the highest occupied

molecular orbital (HOMO). The exponent κ in Eq. (11), on the other hand, is assumed to be determined by the orbital energy E_0 [see Eq. (8)], which is consistent with Eq. (3). Thus, in the general case only the HOMO satisfies Eq. (11). In the following we assume that $\psi_0(\mathbf{r})$ is the HOMO, which is in any case of main interest for applications.

The HF equation for the HOMO has the form of Eq. (1), where

$$\hat{V}(\mathbf{r}) = - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}'_A|} + V_d(\mathbf{r}) + \hat{V}_{\text{ex}}(\mathbf{r}). \quad (32)$$

Here Z_A are nuclear charges, $\mathbf{R}'_A$ are their positions in the MF, and

$$V_d(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \int \frac{\psi_i^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (33)$$

and

$$\hat{V}_{\text{ex}}(\mathbf{r}) \psi_0(\mathbf{r}) = - \sum_{i=1}^{N/2} \psi_i(\mathbf{r}) \int \frac{\psi_i^*(\mathbf{r}') \psi_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (34)$$

represent the direct and exchange parts of the interelectron interaction, respectively. The potential (32) satisfies Eq. (3) with $Z = \sum_A Z_A - N + 1$, where the unity results from cancellation of the self-interaction terms in Eqs. (33) and (34), and

$$\mathbf{D}' = \left[\sum_A Z_A \mathbf{R}'_A - 2 \sum_{i=1}^{N/2} \int \psi_i^*(\mathbf{r}) \mathbf{r} \psi_i(\mathbf{r}) d\mathbf{r} \right] - \boldsymbol{\mu}', \quad (35)$$

where the expression in the square brackets is the total dipole moment of the molecule, including the nuclear contribution, and $\boldsymbol{\mu}'$ is the HOMO dipole defined in Eq. (10).

For atoms and diatomic molecules, the self-consistent HF equations can be accurately solved by grid methods [27,28]. Simultaneously with the HF orbitals, the solution also yields the potential (32). However, in this case it is easier to calculate structure factors using the TR, Eq. (12), because grid methods correctly reproduce the asymptotic tail of the orbitals. Such calculations are reported in Refs. [29,30]. For polyatomic molecules, the HF equations are more efficiently solved by basis set expansion methods [31,32]. In particular, GTO basis sets are used in standard packages [33,34]. We wish to show that in this case the IR, Eq. (20), remains applicable and yields reliable results. For implementing this formula by means of Eq. (30) one needs to calculate integrals (31) involving the potential (32).

B. GTO expansion

In GTO expansion approaches the integrals (31) can be calculated as follows. The HF orbitals $\psi_i(\mathbf{r})$ in the MF are obtained in the form

$$\psi_i(\mathbf{r}) = \sum_{\gamma} c_{i\gamma} \chi_{\gamma}(\mathbf{r} - \mathbf{R}'_{\gamma}), \quad (36)$$

where $\chi_{\gamma}(\mathbf{r} - \mathbf{R}'_{\gamma})$ is a GTO centered at $\mathbf{R}'_{\gamma}$, the subscript γ defines the central point $\mathbf{R}'_{\gamma}$ as well as the parameters of the GTO, and the coefficients $c_{i\gamma}$ are found by minimizing the total HF energy of the molecule. In different implementations of the

method different types of GTOs (spherical, solid, Cartesian, etc. [31]) may be used, so we do not specify their particular form here. To construct the matrix of the potential (32) one needs to calculate one- and two-electron integrals of the form

$$\int \frac{\chi_{\gamma_1}^*(\mathbf{r} - \mathbf{R}'_{\gamma_1}) \chi_{\gamma_2}(\mathbf{r} - \mathbf{R}'_{\gamma_2})}{|\mathbf{r} - \mathbf{R}'_{\gamma_3}|} d\mathbf{r} \quad (37)$$

and

$$\int \frac{\chi_{\gamma_1}^*(\mathbf{r} - \mathbf{R}'_{\gamma_1}) \chi_{\gamma_2}^*(\mathbf{r}' - \mathbf{R}'_{\gamma_2}) \chi_{\gamma_3}(\mathbf{r} - \mathbf{R}'_{\gamma_3}) \chi_{\gamma_4}(\mathbf{r}' - \mathbf{R}'_{\gamma_4})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (38)$$

This is done using well-developed quantum chemistry techniques available within standard packages [33,34]. The core potential (21) has the form of Eq. (32) with one additional artificial nuclei with charge $-Z$ located at the origin. This means that the same techniques can be used for calculating the integral in Eq. (20), provided that the function $\Omega_v(\mathbf{r})$ is also expanded in a GTO basis. Since Eqs. (30) and (31) rely on the partial-wave expansion (22), $\Omega_v(\mathbf{r})$ should be expanded in a spherical GTO basis [31], which amounts to expanding the radial functions in Eq. (22) in radial GTOs. This outlines the general idea of the present implementation.

C. Computational procedure

We now summarize our computational procedure. The sum over l in Eq. (30) is truncated at $l = L_{\text{max}}$. The radial functions $R_l^v(r)$ are approximated by the expansion

$$R_l^v(r) = \sum_{i=1}^{N_l} f_{li} R_l^{\text{GTO}}(\alpha_{li}, r), \quad (39)$$

where

$$R_l^{\text{GTO}}(\alpha, r) = \frac{2(2\alpha)^{3/4}}{\pi^{1/4}} \sqrt{\frac{2^l}{(2l+1)!!}} \left(\sqrt{2\alpha} r \right)^l \exp(-\alpha r^2) \quad (40)$$

is a normalized radial GTO [31]. We use even-tempered GTO basis sets with the exponents of the form $\alpha_{li} = \alpha_l \beta_l^i$ [32]. Equation (39) is considered as a fit applicable in the interval $0 \leq r \leq r_{\text{fit}}$. The coefficients f_{li} are found by minimizing the sum of squares of the difference between the exact $R_l^v(r)$ given by Eq. (24) and the right-hand side of Eq. (39) taken at sufficiently many equidistant points distributed over the fitting interval using a LAPACK routine [47]. Substituting Eq. (39) into Eq. (31), we obtain

$$I_{lm'i}^v = \sum_{i=1}^{N_l} f_{li} I_{lm'i}, \quad (41)$$

where

$$I_{lm'i} = \int R_l^{\text{GTO}}(\alpha_{li}, r) Y_{lm'}^*(\theta, \varphi) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r}. \quad (42)$$

The latter integrals can be reduced to a linear combination of integrals of the form of Eqs. (37) and (38), and hence can be easily calculated within standard packages [33,34]. Thus, Eqs. (41) and (42) enable one to obtain integrals

(31) algebraically, by combining quantities already available, without grid integration.

The procedure described above contains the parameters $L_{\max}$, r_{fit} , N_l , α_l , and β_l . These parameters should be properly chosen to ensure convergence of the asymptotic coefficient (30). The choice is dictated by the following. The fitting radius r_{fit} should be chosen first since the other parameters crucially depend on it. Its value is estimated by the radius of the region contributing to the integral (31). The latter is affected by the asymptotic behavior of the core potential (21) and the size of the ionizing orbital $\psi_0(\mathbf{r})$, and hence depends on the molecule. For a given r_{fit} , the value of $L_{\max}$ is determined by the requirement that the partial-wave expansion (22) should hold with sufficient accuracy at $r < r_{\text{fit}}$. Note, importantly, that $\Omega_v(\mathbf{r})$ is a universal function which only weakly depends on the molecule via Z and κ [see Eq. (15)], therefore $L_{\max}$ is essentially determined by r_{fit} and does not depend on details of the molecular structure. Although the functions $R_l^v(r)$ exponentially grow at large r [see Eq. (25)], in a finite interval $r < r_{\text{fit}}$ they can be accurately fitted by Eq. (39). The number of terms N_l in the fit is determined by r_{fit} and the accuracy required. The conflict between the growth of $R_l^v(r)$ and the decay of the GTO basis (40) has consequences. It reveals itself in the alternating signs of the coefficients f_{li} and their rapid growth with the increase of r_{fit} , which may result in the loss of accuracy in Eq. (41) because of inevitably finite accuracy of the integrals (42). This indeed happens for sufficiently large r_{fit} and is a weak point of the procedure. The parameters α_l and β_l defining the GTO exponents are chosen to keep the coefficients f_{li} within acceptable limits for a required accuracy of the fit (39).

The difficulty associated with large r_{fit} means that the present procedure is limited to relatively small molecules. To extend the implementation to large molecules would require one to calculate integrals (31) by grid methods; a work in this direction is in progress. Meanwhile, there is still room for optimization of the present procedure. The value of r_{fit} needed can be reduced by a proper choice of the origin of the MF, that is, by shifting the origin with respect to the molecule. We recall that the asymptotic coefficient is affected by such a shift, but the structure factor (6) remains invariant [15], so any coordinate frame can be used in the calculations. The integral (31) is accumulated in the region of localization of the core potential (21). The radius of this region, and hence r_{fit} , can be reduced by choosing a frame in which the dipole term in Eq. (2) vanishes. This is a frame where $\mathbf{D}' = \mathbf{0}$, so the total dipole moment of the molecule coincides with the dipole of the HOMO in Eq. (10). Such a coordinate frame is used in all calculations reported below.

Finally, let us discuss the case of a degenerate HOMO. Suppose for a given molecule that several orbitals $\psi_0^{(n)}(\mathbf{r})$, $n = 1, \dots, N_{\text{deg}}$, from the set of $\psi_i(\mathbf{r})$, have the same energy E_0 . The corresponding asymptotic coefficients we denote by $g_v^{(n)}(\beta, \gamma)$. There are cases where, due to symmetry of the molecule, only one of the $g_v^{(n)}(\beta, \gamma)$ differs from zero for a given ionization channel v . For example, π orbitals of linear molecules are doubly degenerate. One can construct such orthogonal linear combinations of the degenerate orbitals that for one of them the dominant channel is (0,0), while for the other it is (0,1) (such orbitals were denoted in Refs. [26,30,39] by (yz) and (xz),

respectively, which indicates the nodal plane). This means that for the latter orbital the asymptotic coefficient in the channel $v = (0,0)$ is identically zero. Meanwhile, standard packages [33,34] return arbitrary orthonormal linear combinations of the degenerate orbitals, unless one takes special care of this issue. The calculation of the only nonzero asymptotic coefficient for a given channel can be facilitated by noting that the sum

$$\sum_{n=1}^{N_{\text{deg}}} |g_v^{(n)}(\beta, \gamma)|^2 \quad (43)$$

is invariant under unitary transformations within the degenerate subspace. By calculating this sum one obtains the asymptotic coefficient of interest up to its sign; a smooth dependence on the orientation angles can then be restored by changing the sign through lines in the (β, γ) plane where the sum (43) turns to zero.

IV. RESULTS AND DISCUSSION

In this section, results are given for the structure factors for He, Ne, Ar, Kr, and Xe atoms and for CO, CO₂, and NH₃ molecules obtained with the IR for the asymptotic coefficient, Eq. (20). Where possible, the results are compared with data obtained with the TR of the asymptotic coefficient, Eq. (12). In the examples involving atoms, the comparison is with results from Ref. [29], where a numerical HF program with a grid representation of the radial coordinate was used and the tail of the HOMO was accurately represented. In the case of CO, the comparison is with data also obtained by the TR approach and a numerical grid-based HF code as described in Ref. [30]. These comparisons illustrate the convergence properties of the IR approach with respect to basis set size and maximum angular momentum $L_{\max}$ used in the fit, and validate the new approach, but also illustrate the difficulty of obtaining convergence with respect to r_{fit} (see Sec. III C). We also provide IR results for CO₂. For this molecule, the orientation dependent structure factor is compared with data from Ref. [39] obtained from the TR using a GTO basis set specifically optimized for CO₂. Finally, we show results for NH₃ in the pyramidal and planar geometries. These latter results form benchmark data for tunneling ionization with which other results in the literature [48] can be compared. Since in high-harmonic spectroscopy applications of the WFAT the phase of the structure factor is important [22–24], we emphasize that we show the structure factor and not its norm squared as in previous publications [26,30,39,49].

A. Atoms

Figure 1 shows the behavior of the radial function $R_1^{00}(r)$ [Eq. (24)]. The fit is generated by the procedure described in Sec. III C. In the figure, the dashed vertical black line denotes the position of the parameter r_{fit} used in the construction of the fit of the radial functions needed in Eq. (31) [see also Eq. (39)]. We see from the figure that the fit agrees with the exact function up to ~ 9 by using $r_{\text{fit}} = 8$. A good agreement would also be seen in the figure using $r_{\text{fit}} = 10$. For $r_{\text{fit}} > 8$, we do, however, face the problem that the coefficients f_{li} of Eq. (39) become very large and of alternating sign. Together

FIG. 1. Radial functions $R_l^{00}(r)$ in the partial-wave expansion (22) for noble-gas atoms Ne, Ar, Kr, and Xe (from top to bottom) with the HOMO of p symmetry. The exact functions (solid lines) are obtained from Eq. (24). The fits (dashed lines) are generated as described in Sec. III C with $r_{\text{fit}} = 8$ (this value is indicated by the vertical dotted line).

with inevitable numerical inaccuracies in the evaluation of the integrals in Eq. (42), this leads to an accumulation of errors in the evaluation of the sum in Eq. (41) and therefore in the asymptotic coefficient of Eq. (30). In the following, we therefore keep $r_{\text{fit}} \leq 8$.

We now turn to a discussion of the structure factor for the considered atoms. We use uncontracted polarization-consistent basis sets denoted by upc- n with $n = 1, 2, 3$, and 4 and systematically improved accuracy [50]. For He, the basis set compositions are $4s, 6s, 9s$, and $11s$, respectively [51]. For Ne, they are $7s4p, 10s6p, 14s9p$, and $18s11p$, respectively [50]. For Ar, they are $11s8p, 13s10p, 17s13p$, and $21s16p$, respectively [51]. For Kr, they are $12s10p7d, 16s13p9d, 20s16p11d$, and $24s19p13d$, respectively [52]. For Xe, they are $13s11p8d, 17s14p10d, 21s17p12d$, and $25s20p14d$, respectively. We also present results obtained with the most accurate near-HF basis set compositions, which for Ne, Ar, Kr, and Xe are $30s20p, 37s26p, 31s24p15d$, and $28s22p16d$, respectively. The Xe and near-HF basis sets have been explicitly optimized at the HF level in this paper; the other basis sets have been used in the form defined in the given references. In Table I, the numbers illustrate the behavior of G_{00} as a function of the basis set and the r_{fit} used. For each atom, the reference values for G_{00} from Ref. [29] are given. The results in the table show convergence to approximately two digits or more with respect to the basis set. The convergence with respect to r_{fit} is typically approximately one to two digits, except for He, where convergence is to three digits in both upc- n and r_{fit} . We emphasize that the upc-2 basis set, which is relatively small and therefore applicable for any molecule, is sufficient for two digit accuracy.

B. Molecules

We consider CO with the IR approach as an example of a polar diatomic molecule where accurate reference data obtained by the TR are available [30]. The other examples of

TABLE I. Convergence of the IR results for the structure factor G_{00} for the HOMO of noble-gas atoms with respect to the fit radius r_{fit} and basis set (see text). For each atom, the first line indicates the ionizing orbital, the HF value of κ [see Eq. (8)], and the TR result for G_{00} from Ref. [29]. All values are given in atomic units.

He, $1s, \kappa = 1.354\,958, G_{00} = 2.114$			
Basis / r_{fit}	4	5	6
upc-1	2.118	2.118	2.118
upc-2	2.116	2.116	2.116
upc-3	2.114	2.114	2.114
upc-4	2.114	2.114	2.114
Ne, $2p, \kappa = 1.304\,155, G_{00} = 2.406$			
Basis / r_{fit}	6	7	8
upc-1	2.350	2.350	2.350
upc-2	2.386	2.386	2.386
upc-3	2.395	2.396	2.396
upc-4	2.396	2.398	2.398
Near-HF	2.396	2.398	2.400
Ar, $3p, \kappa = 1.087\,215, G_{00} = 2.861$			
Basis / r_{fit}	6	7	8
upc-1	2.782	2.783	2.786
upc-2	2.800	2.802	2.806
upc-3	2.821	2.827	2.833
upc-4	2.824	2.831	2.841
Near-HF	2.824	2.832	2.843
Kr, $4p, \kappa = 1.023\,901, G_{00} = 2.940$			
Basis / r_{fit}	6	7	8
upc-1	2.786	2.784	2.781
upc-2	2.846	2.848	2.846
upc-3	2.864	2.870	2.872
upc-4	2.867	2.875	2.879
Near-HF	2.869	2.878	2.883
Xe, $5p, \kappa = 0.956\,337, G_{00} = 3.024$			
Basis / r_{fit}	6	7	8
upc-1	2.750	2.751	2.746
upc-2	2.888	2.891	2.886
upc-3	2.928	2.937	2.935
upc-4	2.947	2.962	2.965
Near-HF	2.949	2.965	2.970

CO₂ and NH₃ illustrate the usefulness of the IR approach with standard basis sets. For CO₂ and NH₃ reliable results cannot be obtained with the TR approach using standard quantum chemistry basis sets. Only with basis sets that are specifically optimized for each molecule in question, it is possible to extract a reliable value of the structure factor and hence the rate (see the discussion in Ref. [39]). For the three molecules considered, we use the IR approach with standard upc- n basis sets from Ref. [50]. We illustrate the convergence of the structure factor for CO with respect to basis set in Fig. 2 for fixed $r_{\text{fit}} = 7$ and $L_{\text{max}} = 6$. The figure shows a very fast convergence with respect to the basis set. Already the upc-2 results cannot be discriminated from the results obtained with the larger basis sets on the scale of the figure. Still we cannot fully converge to the very accurate reference value extracted from the HF orbital generated using the grid method x2DHF [28]. We have tried different values for r_{fit} , and indeed for $r_{\text{fit}} = 6$ the results are slightly different than the present $r_{\text{fit}} = 7$ results, indicating

FIG. 2. Dependence of the structure factor for the HOMO in CO of σ symmetry on the angle β between the internuclear axis and the electric field. The distance between the nuclei is $R = 2.132$ and the HOMO energy is $E_0 = -0.554923$ [30]. In the molecular frame where $\mathbf{D}' = \mathbf{0}$ the nuclear coordinates are $Z'_C = 0.603639$ and $Z'_O = 2.735639$ and the HOMO dipole is $\mu'_z = -0.1043$. Broken lines show the present IR results obtained with $r_{\text{fit}} = 7$ and $L_{\text{max}} = 6$. The figure illustrates their convergence with respect to the basis set used in the calculations. The notation upc- n ($n = 1, \dots, 4$) refers to standard basis sets from Ref. [50]. The solid line shows the TR results from Ref. [30] extracted from the HF orbital generated using a grid method X2DHF [28].

lack of convergence. We cannot increase r_{fit} further due to the difficulties discussed above and in Sec. III C.

Figure 3 illustrates the convergence of the results for the structure factor with L_{max} for a fixed $r_{\text{fit}} = 7$, and the upc-4 basis set. The figure shows that $L_{\text{max}} \sim 5-6$ gives acceptable results.

The results for CO_2 are given in Figs. 4 and 5. Figure 4 confirms the fast convergence with respect to basis set for fixed $r_{\text{fit}} = 7$ and $L_{\text{max}} = 6$. As for CO, the upc-2 results are converged on the scale of the figure. Figure 5 shows that the IR results are converged with $L_{\text{max}} \sim 4-6$ for fixed $r_{\text{fit}} = 7$ and the upc-3 basis set. In both Figs. 4 and 5, the reference TR values are from calculations using an optimized GTO basis [39]. In the case of CO_2 , calculations with $r_{\text{fit}} = 6$ confirmed

FIG. 3. Same as in Fig. 2, but illustrates the convergence of the IR results (broken lines) obtained with $r_{\text{fit}} = 7$ using the upc-4 basis set [50] with respect to the number of partial waves L_{max} in Eq. (30).

FIG. 4. Dependence of the structure factor for the degenerate HOMO in CO_2 of π symmetry on the angle β between the internuclear axis and the electric field. The HOMO energy is $E_0 = -0.544905$. In the molecular frame where $\mathbf{D}' = \mathbf{0}$ the nuclear positions are $Z'_O = \pm 2.19605$ and $Z'_C = 0$ and the HOMO dipole is $\mu'_z = 0$. Broken lines show the present IR results obtained with $r_{\text{fit}} = 7$ and $L_{\text{max}} = 6$. The figure illustrates their convergence with respect to the basis set used in the calculations. The notation upc- n ($n = 1, \dots, 3$) refers to standard basis sets from Ref. [50]. The solid line shows the TR results from Ref. [39] extracted from the HF orbital generated using an expansion in terms of the optimized opc-4 GTO basis set.

the convergence of the IR results, and we can hence conclude that these are more accurate than the TR reference data. The difference in the convergence of the CO and CO_2 results with r_{fit} is caused by the difference in the dipole, and higher-order terms in the multipole expansion [see Eq. (3)]. For CO the effect of these terms turns out to be stronger than for CO_2 .

As a final example of the usefulness of the present IR approach, we consider the example of NH_3 , which has not been considered before with the WFAT. Recently, there was some interest in imaging the umbrella motion in NH_3 by strong-field ionization [48]. In that work, ionization yields were obtained by frozen nuclei time-dependent Schrödinger equation (TDSE) model calculations as a function of the inversion coordinate. The ionization yield was considered for linearly polarized laser pulses with the polarization aligned

FIG. 5. Same as in Fig. 4, but illustrates the convergence of the IR results (broken lines) obtained with $r_{\text{fit}} = 7$ using the upc-3 basis set [50] with respect to the number of partial waves L_{max} in Eq. (30).

FIG. 6. Dependence of the structure factors G_{00} for the HOMO of NH_3 in planar (top panel) and pyramidal (bottom panel) geometries on the Euler angles β and γ . In the planar geometry, the nuclear positions are $\mathbf{R}'_N = (0,0,0)$, $\mathbf{R}'_H = (0,1.882\,129,0)$, $\mathbf{R}'_H = (1.629\,972, -0.941\,065,0)$, and $\mathbf{R}'_H = (-1.629\,972, -0.941\,065,0)$; the HOMO energy is $E_0 = -0.391\,564$; and its dipole is $\boldsymbol{\mu}' = \mathbf{0}$. In the pyramidal geometry, in the frame where $\mathbf{D}' = \mathbf{0}$, the nuclear positions are $\mathbf{R}'_N = (0,0,-0.862\,442)$, $\mathbf{R}'_H = (0,1.772\,461,-1.580\,782)$, $\mathbf{R}'_H = (1.534\,996,-0.886\,231,-1.580\,782)$, and $\mathbf{R}'_H = (-1.534\,996, -0.886\,231,-1.580\,782)$; the HOMO energy is $E_0 = -0.429\,608$; and its dipole is $\boldsymbol{\mu}' = (0,0,0.635\,392)$. In both cases, the calculations were done using the upc-2 basis set [50] with $r_{\text{fit}} = 7$ and $L_{\text{max}} = 6$. The β is the angle between the field direction, and the principal inertial axis of the molecule going through N and the γ is the angle of rotation around this axis.

along the inversion coordinate, i.e., along the C_3 symmetry axis of the molecule. The yield was found to be maximal for the planar geometry and to decrease with increasing magnitude of the inversion coordinate. The yield obtained with the frozen nuclei TDSE calculations for 1800-nm ten-cycle pulses with intensities 1×10^{13} – 6×10^{13} W/cm² was a factor of 5–8 higher for the planar than for the pyramidal geometry. Here we provide accurate tunneling reference data for the planar and the pyramidal geometries for *all* orientations of NH_3 with respect to the external field. Let us first consider the case with the field along the C_3 axis. In the planar case, we obtain the structure factor 1.105 for $(\beta, \gamma) = (0,0)$ deg. In the pyramidal case, we need to consider two geometries corresponding to the N atom either above or below the plane formed by the H atoms, and find structure factors 0.903 and 2.859 for $(\beta, \gamma) = (0,0)$ and $(180,0)$ deg, respectively. Combining these structure factor values with the field factors at 5×10^{13} W/cm² [see Eq. (5)], we find the ratios between the tunneling rates of the planar and the pyramidal geometries to be 12.5 and 1.25 at $(\beta, \gamma) = (0,0)$ and $(180,0)$ deg. In an oscillating field, the direction of the field

alternates, equivalent to $\beta = 0$ and 180 deg, and the average value of the ratio of the rates is ~ 6.9 , which can be compared with the ratio of ~ 5 – 8 (at 1×10^{13} – 6×10^{13} W/cm²) obtained from the frozen nuclei TDSE calculations reported in Ref. [48].

The results for the structure factor G_{00} for all orientations are shown in Fig. 6. For the planar case, the (β, γ) dependence follows from the dominating p_z character of the HOMO. We see from the top panel in Fig. 6 that the structure factor only depends weakly on the γ angle, i.e., on rotation around the C_3 axis. The behavior with respect to β reflects that the HOMO is having a node in the molecular plane. Because of the C_3 symmetry, the structure factor as a function of β is repeated in an identical manner over the three γ intervals, $\gamma \in [0; 120], [120; 240], [240; 360]$ deg.

For the pyramidal geometry, we again exploit the C_3 symmetry and focus on the variation in the structure factor in the lower panel of Fig. 6 with β and γ for $\gamma \in [0; 120]$ deg. The HOMO is an sp^3 hybrid orbital, which is p'_z like. This character explains that the structure factor vanishes for $\beta = 90$ deg. The difference in the variation over $\gamma \in [0; 60]$ and $[60; 120]$ deg reflects the detailed shape of the HOMO and its dipole moment.

V. CONCLUSION AND OUTLOOK

In this paper, we presented the IR approach for the description of tunneling ionization of atoms and molecules based on a mean-field Hartree-Fock description of the electronic structure. This approach allows the evaluation of the tunneling rate within the WFAT without the need for an accurate description of the asymptotic form of the ionizing orbital. The rate is expressed in terms of an integral that accumulates its contribution from the part of space where the core potential and the orbital from which ionization occurs have weight. For this reason, the IR approach is applicable for ionization out of orbitals obtained from standard quantum chemistry methodology based on an expansion in GTOs and can hence, in principle, be applied to any molecule. This is an advantage of the IR approach within the WFAT over other tunneling theories the evaluation of which is based on the asymptotic form of the ionizing orbital and suffers from the difficulty of representing the latter accurately. We validated the approach by comparison with atomic and molecular reference data. For NH_3 , we provided benchmark results for the tunneling rate for the pyramidal and planar geometries. For all atoms and molecules considered, we found that accurate results were obtained with uncontracted polarization-consistent basis sets of moderate size (upc-2 basis sets). This finding is important for the evaluation of tunneling rates for larger molecules, where the application of larger basis sets is numerically demanding.

As discussed in Sec. III C, the present implementation of the theory relies on expressing the analytical reference function $\Omega_v(\mathbf{r})$ of Eq. (16) in terms of a Gaussian fit. The integrals involved in the approach then all reduce to integrals involving GTOs and can be readily evaluated. Unfortunately, the fit of the function $\Omega_v(\mathbf{r})$ cannot be accurately extended to radial distances larger than $r \sim 7$. This restricts the application of the method in its current implementation to relatively small molecular systems, but also suggests that a more versatile implementation should circumvent the fitting

procedure. Indeed, the function $\Omega_v(\mathbf{r})$ is known analytically and can be easily evaluated at any point in space, and a direct grid-based evaluation of the integral in Eq. (20) should be possible. In practice the structure factor would be evaluated by a small number of integrals as described in Eqs. (30) and (31). In such a future implementation, the IR approach within the WFAT will allow the evaluation of tunneling rates for any molecular system, and this could become an integrated part of standard quantum chemistry packages.

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APPENDIX: ZERO-RANGE POTENTIAL

The zero-range potential (ZRP) model is instructive to illustrate the equivalence of the two formulas (12) and (20) for

the asymptotic coefficient, on the one hand, and the invariance of the structure factor (6) with respect to a shift of the origin of the coordinate frame used in Eqs. (12) and (20), on the other hand. Consider a ZRP located at $\mathbf{r} = \mathbf{a}$ (here we work in the LF). The ZRP is defined by a single parameter κ such that its action on the normalized bound-state solution of Eq. (1) is given by [53]

$$\hat{V}(\mathbf{r})\psi_0(\mathbf{r}) = -\sqrt{2\pi\kappa}\delta(\mathbf{r}'), \quad (\text{A1})$$

and the solution is

$$E_0 = -\frac{\kappa^2}{2}, \quad \psi_0(\mathbf{r}) = \sqrt{\frac{\kappa}{2\pi}} \frac{e^{-\kappa r'}}{r'}, \quad (\text{A2})$$

where $\mathbf{r}' = \mathbf{r} - \mathbf{a}$. From Eq. (12) we obtain

$$g_{00} = 2e^{-\kappa a_z}. \quad (\text{A3})$$

For this potential $Z = 0$, so from Eq. (16) we have

$$\Omega_{00}(\mathbf{r}) = -\sqrt{\frac{2}{\pi\kappa}} e^{-\kappa z}. \quad (\text{A4})$$

Substituting this and Eq. (A1) into Eq. (20) again gives Eq. (A3). For this model $\boldsymbol{\mu} = -\mathbf{a}$, so from Eq. (6) we obtain

$$G_{00} = 2. \quad (\text{A5})$$

Thus, the structure factor does not depend on the location of the ZRP. The rate formula following from Eq. (5) for $\nu = (0,0)$ using Eq. (A5) coincides with that obtained in Ref. [13].

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