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Structure factors for tunneling ionization rates of molecules: General grid-based methodology and convergence studies

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We present a general methodology for evaluating structure factors defining the orientation dependence of tunneling ionization rates of molecules, which is a key process in strong-field physics. The method is implemented at the Hartree-Fock level of electronic structure theory and is based on an integral-equation approach to the weak-field asymptotic theory of tunneling ionization, which expresses the structure factor in terms of an integral involving the ionizing orbital and a known analytical function. The evaluation of the required integrals is done by three-dimensional quadrature which allows calculations using conventional quantum chemistry software packages. This extends the applications of the weak-field asymptotic theory to polyatomic molecules of almost arbitrary size. The method is tested by comparison with previous results and illustrated by calculating structure factors for the two degenerate highest occupied molecular orbitals (HOMOs) of benzene and for the HOMO and HOMO-1 of naphthalene.

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I. INTRODUCTION

The nonlinear response of atoms and molecules to intense near-infrared or infrared femtosecond laser pulses is of fundamental interest in strong-field physics. The photon energy at these wavelengths is significantly less than the energy required for electronic excitations and the typical femtosecond timescale of the laser field variation is much larger than the attosecond timescale associated with the electronic motion. The interaction of an initially bound electron with a laser field at long wavelengths thus proceeds as if the field were static and equal to the instantaneous value of the laser field.¹ This adiabatic approximation has become increasingly relevant in recent years due to the development of new laser source technologies.² The effective potential felt by the electron in the instantaneous laser field at intensities of interest $\sim 10^{13} - 10^{14}$ W/cm² has a barrier through which the electron must tunnel to dissociate from the system. Tunneling ionization in an external electric field has thus played a key role in strong-field physics for more than 25 years;³⁻⁷ see also Ref. 8 and references therein.

The current interest in tunneling ionization is closely associated with its role in ultrafast spectroscopies aiming at extracting information of electronic and nuclear motion on the attosecond timescale. Tunneling ionization is for example the first step in modelling high-order harmonic spectroscopy, where the time from ionization to recombination is used to extract temporal information,⁹⁻¹⁴ and in laser-induced electron diffraction, where the ionized electron propagates in the field and rescatters to record a diffraction pattern of the parent ion, thereby allowing a monitoring of nuclear motion on the sub-femtosecond timescale.¹⁵⁻²⁰ Tunneling ionization is also the first step in strong-field holography, where holographic interference between a reference and a sig-

nal photoelectron wave allows the decoding of ultrafast dynamics.²¹⁻²⁸ The same applies to tunneling-ionization imaging of molecular photoexcitation, where the products of dissociation are recorded to detect changes occurring in the excited orbital.²⁹ For the successful extraction of the dynamics from these experimental techniques, accurate and reliable evaluation of tunneling ionization rates is needed, and this is a challenge, not least in view of the interest in polyatomic molecules.³⁰⁻³³ It is the purpose of the present work to present a general methodology, which overcomes this challenge and enables the evaluation of tunneling ionization rates for any molecule whose electronic structure can be described by standard quantum chemistry methods.

The laser field at the above indicated intensities is weak compared to a field where over-the-barrier ionization becomes accessible, and therefore tunneling ionization can be treated using the weak-field asymptotic theory (WFAT),³⁴ in which the ionization rate is obtained from an asymptotic expansion in the field strength. In the leading-order WFAT approximation, the rate factorizes into a structure factor squared and a field factor describing the dependence on the field strength and the orientation of the molecule with respect to the field.³⁵ The field factor determines the absolute value of the rate, which is usually not measurable experimentally, and the structure factor is the main interesting quantity for applications in strong-field physics. The structure factor is a molecular property that relates to tunneling ionization and it was in the original formulation of the WFAT³⁴ expressed in terms of local characteristics of the unperturbed ionizing orbital in the asymptotic region far from the nuclei. This *tail representation* (TR) method was in prior work implemented using basis set³⁵⁻³⁷ and grid-based^{38,39} approaches for the electronic structure calculations within the Hartree-Fock (HF) method. The WFAT

implemented using the TR was successfully applied to the analysis of strong-field ionization in a number of recent works.^{9,10,29,40–45}

Wave function methods for polyatomic molecules in almost all quantum chemistry programs employ an expansion in a basis set of Gaussian-type functions. Such methods, however, do in general not produce the correct exponential asymptotic behavior of molecular orbitals and this hinders the applications of the WFAT TR to polyatomic molecules. To resolve this difficulty, an integral-equation approach to the WFAT was developed.⁴⁶ In this *integral representation* (IR), the asymptotic coefficient defining the molecular structure factor is expressed as an integral involving the ionizing orbital and a known analytical function. The advantage is that this integral depends on the overall shape of the ionizing orbital and is not sensitive to details in its asymptotic behavior. In a previous paper,⁴⁷ we showed the implementation of the IR at the HF level of theory by expanding the known analytical function as a linear combination of Gaussian functions. This had the feature that the desired integral can be obtained by combining elementary integrals that can be calculated analytically by standard quantum chemistry software packages. While this approach was shown to work well for small molecules, it had limited numerical stability and was difficult to apply to large molecules.

In the present work, we develop a grid-based approach for calculating the integrals involved in the IR. Although this formally is only a different technical approach for integral evaluation, it leads to much better numerical stability and transforms the calculation of molecular structure factors into a routine procedure, thus making the application of WFAT to general polyatomic molecules possible. The paper is organized as follows. In Sec. II, we summarize the basic equations of the WFAT within the IR. In Sec. III, we describe the grid-based approach to the evaluation of the integrals. In Sec. IV, we illustrate the numerical performance of the method by discussing its convergence properties and accuracy compared to previous results. As examples of polyatomic molecules not treated previously within WFAT, we present benchmark results for structure factors of the two degenerate highest occupied molecular orbitals (HOMOs) of benzene and for the HOMO and HOMO-1 of naphthalene. Section V concludes the paper.

II. WEAK-FIELD ASYMPTOTIC THEORY

We consider tunneling ionization from a reference molecular orbital in a static uniform electric field. The orbital is a solution to an effective one-electron Schrödinger equation (atomic units are used throughout)

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

written in a molecular frame (MF). The generally nonlocal potential $\hat{V}(\mathbf{r})$ describes the interaction of a selected electron with the parent ion, its explicit form within the HF method is given Sec. III. We assume that

$$\hat{V}(\mathbf{r})|_{r \rightarrow \infty} = -\frac{Z}{r} - \frac{\mathbf{D}\mathbf{r}}{r^3} + O(r^{-3}), \quad (2)$$

where Z is the total charge of the parent ion (for tunneling ionization from a neutral molecule $Z = 1$) and $\mathbf{D}$ is its dipole moment in the MF. The ionizing 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.⁴⁸ The rotation operator $\hat{R}$ is a matrix such that $\mathbf{v}_{\text{MF}} = \hat{R}\mathbf{v}_{\text{LF}}$, where $\mathbf{v}_{\text{LF}}$ and $\mathbf{v}_{\text{MF}}$ are columns representing the same vector in the LF and MF, respectively. The ionization rate does not depend on α , so in the following we set $\alpha = 0$.

Within the WFAT, the total ionization rate is given by³⁴

$$\Gamma(\beta, \gamma) = \sum_{\nu} \Gamma_{\nu}(\beta, \gamma), \quad (3)$$

where $\Gamma_{\nu}(\beta, \gamma)$ are partial rates of ionization into parabolic channels enumerated by a multi-index

$$\nu = (n_{\xi}, m), \quad n_{\xi} = 0, 1, \dots, \quad m = 0, \pm 1, \dots, \quad (4)$$

consisting of parabolic n_{ξ} and magnetic m quantum numbers. The partial rates are obtained as asymptotic expansions in F for $F \rightarrow 0$. In the leading-order approximation they are given by

$$\Gamma_{\nu}(\beta, \gamma) = |G_{\nu}(\beta, \gamma)|^2 W_{\nu}(F), \quad (5)$$

where

$$G_{\nu}(\beta, \gamma) = e^{-\varkappa \mu_z} g_{\nu}(\beta, \gamma) \quad (6)$$

is the structure factor defining the dependence of the rate on the orientation of the molecule with respect to the ionizing field and

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

is the field factor defining its dependence on the field strength. All quantities needed to implement these formulas are determined by properties of the unperturbed orbital, namely, $\varkappa = \sqrt{-2E_0}$, μ_z is the z -component of the orbital dipole moment $\hat{R}^{-1}\boldsymbol{\mu}$ in the LF, where

$$\boldsymbol{\mu} = - \int \psi_0^*(\mathbf{r}) \mathbf{r} \psi_0(\mathbf{r}) d\mathbf{r} \quad (8)$$

is the same vector in the MF, and $g_{\nu}(\beta, \gamma)$ is a coefficient appearing in the asymptotic tail of $\psi_0(\mathbf{r})$ at $r \rightarrow \infty$. We emphasize that structure factors $G_{\nu}(\beta, \gamma)$, and therefore

also partial rates (5), are invariant under a shift of the coordinate origin,³⁴ while each of the two factors on the right-hand side of Eq. (6) is not. We will define our particular choice of origin in Sec. III. The structure factors are the primary quantities needed for applications, however, in the following we focus on the asymptotic coefficients $g_\nu(\beta, \gamma)$, since their calculation is the most challenging part in implementing Eq. (3).

The coefficients $g_\nu(\beta, \gamma)$ can be extracted from the asymptotic tail of $\psi_0(\mathbf{r})$, and this TR approach has been discussed in Refs. 34–39. An alternative approach to calculate $g_\nu(\beta, \gamma)$ based on the IR was developed in Ref. 46. In the IR, the asymptotic coefficients are given by integrals

$$g_\nu(\beta, \gamma) = \int \Omega_\nu^*(\hat{R}^{-1}\mathbf{r}) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where

$$\hat{V}_c(\mathbf{r}) = \hat{V}(\mathbf{r}) + \frac{Z}{r} \quad (10)$$

is a core potential. The function $\Omega_\nu(\mathbf{r})$ satisfies

$$\left[-\frac{1}{2}\Delta - \frac{Z}{r} - E_0 \right] \Omega_\nu(\mathbf{r}) = 0 \quad (11)$$

and is known analytically. It can be expanded in spherical harmonics,⁴⁷

$$\Omega_\nu(\mathbf{r}) = \sum_{l=|m|}^{\infty} \Omega_{lm}^\nu(\mathbf{r}), \quad (12)$$

where

$$\Omega_{lm}^\nu(\mathbf{r}) = R_l^\nu(r) Y_{lm}(\theta, \varphi) \quad (13)$$

and we recall that the channel multi-index ν defined in Eq. (4) includes m . The radial functions are given by

$$R_l^\nu(r) = \omega_l^\nu(\kappa r)^l e^{-\kappa r} M(l+1-Z/\kappa, 2l+2, 2\kappa r), \quad (14)$$

where $M(a, b, x)$ is a confluent hypergeometric function⁴⁹ and

$$\begin{aligned} \omega_l^\nu &= (-1)^{l+(|m|-m)/2+1} 2^{l+3/2} \kappa^{Z/\kappa-(|m|+1)/2-n_\xi} \\ &\times \sqrt{(2l+1)(l+m)!(l-m)! (|m|+n_\xi)! n_\xi!} \frac{l!}{(2l+1)!} \\ &\times \sum_{k=0}^{\min(n_\xi, l-|m|)} \frac{\Gamma(l+1-Z/\kappa+n_\xi-k)}{k!(l-k)! (|m|+k)! (l-|m|-k)! (n_\xi-k)!} \end{aligned} \quad (15)$$

is a normalization coefficient. Combining Eqs. (9) and (12) gives⁴⁷

$$g_\nu(\beta, \gamma) = \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l I_{lm'}^\nu d_{mm'}^l(\beta) e^{-im'\gamma}, \quad (16)$$

where

$$I_{lm'}^\nu = \int \Omega_{lm'}^{\nu*}(\mathbf{r}) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r} \quad (17)$$

and $d_{mm'}^l(\beta)$ is a Wigner function.⁴⁸ Note that the function $\Omega_\nu(\mathbf{r})$ exponentially grows in the asymptotic region, and hence $R_l^\nu(r)$ grow at $r \rightarrow \infty$, unless the orbital energy E_0 defined by Eq. (1) accidentally coincides with one of the eigenvalues of the Hamiltonian in Eq. (11) given by the hydrogenic energies $-Z^2/2n^2$, $n = 1, 2, \dots$. This growth is compensated by the decay of the orbital $\psi_0(\mathbf{r})$, so the integrals in Eqs. (9) and (17) converge.⁴⁶ Equations (16) and (17) are the working formulas for calculating the asymptotic coefficients. These equations hold in the case $E_0 \neq -Z^2/2n^2$, $n = 1, 2, \dots$. The methodology of evaluating the integrals (17) in this case within the HF method is discussed in the next section. The uncertainty arising in Eq. (17) when the orbital energy E_0 happens to be close to or coincides with one of the hydrogenic energies is treated in the Appendix.

III. NUMERICAL PROCEDURE

We will, in the present case, restrict ourselves to closed-shell systems described within the HF approximation but the extension to open-shell systems is straight-forward. The $\psi_i(\mathbf{r})$ denotes molecular orbitals with $\psi_0(\mathbf{r})$ being the ionizing orbital, usually the highest occupied molecular orbital (HOMO), N is the number of electrons, Z is the charge of the resulting ion upon ionization, N_{at} , Z_A and $\mathbf{R}_A$ denote the number of nuclei, nuclear charges and positions, respectively, while $\mathbf{r}$ and $\mathbf{r}'$ indicate electron coordinates.

The Hartree-Fock potential is given by

$$\hat{V}(\mathbf{r}) = - \sum_{A=1}^{N_{\text{at}}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + V_d(\mathbf{r}) + \hat{V}_{\text{ex}}(\mathbf{r}), \quad (18)$$

where

$$V_d(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \int \frac{\psi_i^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (19)$$

and

$$\hat{V}_{\text{ex}}(\mathbf{r}) \psi_0(\mathbf{r}) = - \sum_{i=1}^{N/2} \psi_i(\mathbf{r}) \int \frac{\psi_i^*(\mathbf{r}') \psi_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (20)$$

are the direct (Coulomb) and exchange parts of the interelectron interaction.

We have in previous work⁴⁷ shown that the convergence of the integral (9) can be accelerated if it is calculated with an origo chosen such that the dipole of the parent ion $\mathbf{D}$ equals zero, where

$$\mathbf{D} = \left[\sum_{A=1}^{N_{\text{at}}} Z_A \mathbf{R}_A - 2 \sum_{i=1}^{N/2} \int \psi_i^*(\mathbf{r}) \mathbf{r} \psi_i(\mathbf{r}) d\mathbf{r} \right] - \boldsymbol{\mu}. \quad (21)$$

Since the structure factor is origin independent, we define the origin by the condition $\mathbf{D} = \mathbf{0}$.

In our previous work,⁴⁷ we expanded the function $\Omega_{lm'}^\nu(\mathbf{r})$ as a linear combination of Gaussian functions, which had the appealing feature that all of the integrals in the Eq. (17) can be calculated by standard techniques employed for calculating the electronic wave function. As shown in our previous publication,⁴⁷ this procedure for handling the $\Omega_{lm'}^\nu(\mathbf{r})$ integration yields results identical to the TR for atoms and small molecules. The $\Omega_{lm'}^\nu(\mathbf{r})$ and Gaussian functions, however, have different asymptotic behaviors and this leads to numerical problems when trying to achieve a systematic convergence. Attempts of improving the least squares fit for the $\Omega_{lm'}^\nu(\mathbf{r})$ function leads to Gaussian exponents converging towards each other and resulting in fitting coefficients having large values of opposing sign. This in practice leads to numerical problems, as the final value of the integral of interest is calculated as a sum of large contributions with opposite signs, where incomplete cancellations due to numerical issues limit the accuracy of the final result.

In the present work we propose an alternative approach where the integrals (17) are evaluated by a three-dimensional grid-based integration, rather than being evaluated as a sum of analytic integrals arising from a fitting procedure of the $\Omega_{lm'}^\nu(\mathbf{r})$ function. As shown in the following, this leads to a computational efficient calculation of the asymptotic coefficient for any molecule where the corresponding wave function can be generated, and allows a systematic convergence in terms of the quality of the orbital basis set and of the numerical grid for evaluating the integrals (17).

The MOs are expanded in a linear combination of Gaussian functions with coefficients obtained by a standard self-consistent-field approach

$$\psi_i(\mathbf{r}) = \sum_{\alpha} c_{i\alpha} \chi_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}), \quad (22)$$

where the multi-index α defines the Gaussian type orbital (GTO) in terms of its exponent, angular momentum and origin (nuclear position), and all coefficients $c_{i\alpha}$ and GTOs are assumed to be real. Substituting Eq. (22) into Eqs. (19) and (20), and then into Eq. (17) the latter can be written as:

$$I_{lm'}^\nu = \int \Omega_{lm'}^{\nu*}(\mathbf{r}) \sum_{\gamma} \left[c_{0\gamma} \left(\frac{Z}{r} - \sum_{A=1}^{N_{\text{at}}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right) + \sum_{i=1}^{N/2} \sum_{\alpha} c_{i\alpha} \sum_{\beta} (2c_{i\beta}c_{0\gamma} - c_{0\beta}c_{i\gamma}) H_{\alpha\beta}(\mathbf{r}) \right] \chi_{\gamma}(\mathbf{r} - \mathbf{R}_{\gamma}) d\mathbf{r}. \quad (23)$$

where the matrix elements $H_{\alpha\beta}(\mathbf{r})$ are defined as

$$H_{\alpha\beta}(\mathbf{r}) = \int \frac{\chi_{\alpha}(\mathbf{r}' - \mathbf{R}_{\alpha}) \chi_{\beta}(\mathbf{r}' - \mathbf{R}_{\beta})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \quad (24)$$

and can be computed analytically by standard methods used in the calculation of the electron-nucleus interaction.⁵⁰

We used grid-based methods for calculating the integrals (23). A uniform three-dimensional grid in Cartesian coordinates is the simplest and was implemented for testing, but it is computationally inefficient, so the integrals in the present case are evaluated numerically by the standard Becke fuzzy cells integration scheme⁵¹

$$\int F(\mathbf{r}) d\mathbf{r} = \sum_{B=1}^{N_{\text{at}}} \int w_B(\mathbf{r}) F(\mathbf{r}) d\mathbf{r}, \quad (25)$$

where $w_B(\mathbf{r})$ denote smooth weighting functions of a point $\mathbf{r}$ corresponding to the B -th cell. Each integral on the right hand side of Eq. (25) is evaluated numerically using a spherical numerical grid centered on the B -th nucleus. The spherical grid is a unison of radial and angular grids: as the radial grid the Euler-Maclaurin scheme is used,⁵² while integration over polar and azimuthal angles is performed using Gauss-Legendre and Gauss-Chebyshev quadrature formulas, respectively. The quadratures are completely described by the numbers of grid points N_r , N_{θ} and N_{φ} , and R_{max} , the size of the region covered by the grid. The technique is the same as that used for numerically integrating the exchange-correlation energy in density functional theory.⁵³

The complete numerical integration of the integrals (17) has been implemented in the freely available program package GAMESS-US,⁵⁴ and the required modifications are available upon request.

IV. CONVERGENCE AND COMPARISON WITH PREVIOUS RESULTS

The implementation of the IR method discussed in Sec. III produces results that depend on three variables: the choice of the basis set for representing the orbitals, the grids for integrating the integrals on the right-hand side of the Eq. (25), and the L_{max} , the maximum angular momentum in the sums in Eqs. (12) and (16). We will in this section show the dependence of the calculated structure factors for the HOMO of several systems (He, Ne, Ar, and Kr atoms, CO, CO₂, benzene and naphthalene molecules) and compare to relevant reference values when available. The reference results for atoms and CO are obtained with the TR of the asymptotic coefficient using numerical grid-based HF programs described in Refs. 55 and 56, respectively. For the CO₂ molecule we compare the results to data obtained by the TR using a specifically optimized GTO basis set,³⁶ while the benzene and naphthalene results show how the present implementation can handle a more general class of polyatomic molecules. Since only one term in Eq. (12) contributes to the final structure factor for atoms, we show only the basis set convergence for these systems, while orbital, grid and L_{max} convergence is probed for CO and CO₂.

We have chosen the uncontracted polarization-consistent basis sets⁵⁷ for expanding the orbitals as these allows a systematic convergence towards the basis set limit. We have tested also the corresponding (uncontracted) augmented polarization-consistent (aug-pc) and the correlation-consistent (cc-pVXZ) basis sets, but the uncontracted polarization-consistent basis sets gave the best convergence.

A. Atoms

We consider the noble gas atoms He, Ne, Ar, and Kr using a sequence of uncontracted polarization-consistent basis sets denoted upc- n , $n = 1, 2, 3, 4$, where the polarization functions have been removed since they make no contribution for atoms. For He, the basis set compositions are $4s$, $6s$, $9s$, and $11s$, respectively.⁵⁸ For Ne, they are $7s4p$, $10s6p$, $14s9p$, and $18s11p$, respectively.⁵⁷ For Ar, they are $11s8p$, $13s10p$, $17s13p$, and $21s16p$, respectively.⁵⁸ For Kr, they are $12s10p7d$, $16s13p9d$, $20s16p11d$, and $24s19p13d$, respectively.⁵⁹ Table I shows the calculated structure factor G_{00} as a function of the basis set quality with the reference values from Ref. 39 given in the last column with the label "Exact". The deviation between the upc-4 and exact results is less than 1% for He, Ne, and Ar, and less than 2% for Kr. It is significant that even the upc-2 basis set, which is of triple-zeta quality, produces acceptable results, in contrast to the TR method which requires explicit optimized basis sets of upc-5 quality for achieving the same level of accuracy.

B. Molecules

Based on our previous work⁴⁷ we consider a polar diatomic molecule (CO) and a nonpolar triatomic molecule (CO₂). The orientation with respect to the electric field is for both molecules determined by the Euler angle β describing the angle between the direction of the external field and the molecular axis. Figure 1 shows the convergence of the structure factor for the CO molecule with respect to the basis set, where the reference data is taken from Ref. 38, obtained from very accurate HF results using a grid method in prolate spheroidal coordinates implemented in the program x2DHF.⁵⁶ For CO the angle $\beta = 0^\circ$ corresponds to the case when the field points from the C end to the O end. Figure 1 shows a systematic basis sets convergence and the upc-3 and upc-4 results are indistinguishable from the reference data on the scale of the figure. The stable convergence towards the limiting results is a significant advantage compared to the previous approach based on fitting of the function $\Omega_\nu(\mathbf{r})$,⁴⁷ where a stable convergence was problematic due to numerical issues.

Figure 2 shows the basis set convergence of the structure factor for CO₂, compared to the data obtained using

the TR method in connection with an explicit upc-4 optimized basis set, denoted opc-4.³⁶ As in the case of CO, the figure shows a fast convergence of the upc- n results, but the upc-4 results differ from the TR(opc-4) values. This illustrates the advantage of the IR approach over the TR formalism, as even an explicit optimized basis set of pc-4 quality leads to basis set deficiencies within the TR method. We emphasize that reliable structure factors for both the CO and CO₂ molecules are obtained with the present approach using the standard non-optimized upc-2 basis set.

The convergence of the structure factors for the both CO and CO₂ molecules with the respect to the number of partial waves $L_{\max}$ used in Eqs. (12) and (16) are given in the Figs. 3 and 4, respectively. The reference data in the figures for CO and CO₂ is taken from Refs. 38 and 36 as well, respectively. It is easily seen from the figures that in both cases the value $L_{\max} = 6$ is enough for convergence.

The convergence with respect to grid size was studied for the both CO and CO₂ molecule. As we indicated in the previous section, the integrals (23) are evaluated using the Becke integration scheme, where each integral on the right-hand side of the Eq. (25) is computed using a spherical numerical grid placed into its corresponding cell. The setup of the grids is determined by the number of grid points and the largest radial distance to a grid point. For the spherical grid, these parameters are the number of radial points N_r , number of angular points N_θ and N_ϕ , and the grid size $R_{\max}$. We set the grid size fixed, and considered several grids of different density of grid points. The calculation of the structure factors for the molecules considered using different grids were performed with the upc-4 basis set and $L_{\max} = 6$ partial waves. The results for CO and CO₂ molecules are shown in Figs. 5 and 6 and demonstrate fast convergence with respect to the number of grid points used. Taking the computational time for determining the wave function as the reference, the grid integration for the present systems increases the total computational time by less than a factor of three, and the calculation of molecular structure factors are thus feasible for any system where the wave function can be calculated.

To illustrate the merit of the present approach we apply it to benzene and naphthalene molecules, which are significantly larger than any other system considered so far with WFAT in both the TR and IR. Tunneling ionization of benzene is of interest in strong-field physics,⁶⁰ and a number of theoretical investigations were performed more than 10 year ago.^{61,62} Since the molecule is nonlinear, the dependence of its orientation with respect to the field is determined by two Euler angles β and γ . Figure 7 shows the orientation of benzene with respect to the field and the shapes of its doubly degenerate HOMO. The two degenerate HOMOs can be distinguished according to their nodal planes xz and yz , respectively. Benzene is a symmetric top molecules, and its plane can be aligned by circularly or elliptically polarized light. The rotation around the z -axis (the C_6 axis), can not be controlled, so

only the γ -averaged ionization rate is directly accessible in ionization experiments. At the time of the first strong-field experiments⁶⁰ and early theory,^{61,62} the interest was therefore in the behavior of the rate as a function of the angle β . However, to model the results of high-order harmonic spectroscopy experiments^{9,10} the full orientational dependence of the rate, i.e., structure factor is needed. Figure 8 shows the structure factor G_{00} for the two degenerate HOMOs of benzene as a function of the Euler angles using the upc-3 basis set. As a consequence of the results, the ionization rate averaged over the γ angle is maximized at $\beta = 52^\circ$ while its minima are reached at $\beta = 0^\circ$ and $\beta = 90^\circ$, i.e. along the nodal planes of the molecule, which is in qualitative agreement with earlier calculations.^{61,62}

Finally we consider the naphthalene molecule. This molecule has already been studied in a series of strong-field ionization experiments. For example, the role of dissociative ionization channels in the energy distributions^{63,64} and orientation dependence of the ionization yields⁶⁵ was studied. Effects of orbital nodal planes and their modifications by strong external fields were inferred from photoelectron momentum distributions³¹. Moreover, naphthalene was used to elucidate the role of the laser-induced dipole part of the cationic potential in facilitating the creation of low energy electrons^{30,66}, and finally the laser-induced dipole potential of naphthalene was shown to be crucial in explaining an angular shift in the peak of the photoelectron momentum distribution with respect to that expected from theory not accounting for such effects⁶⁷. In the modeling of such strong-field ionization experiments, accurate WFAT reference data are highly relevant and this is the reason why we consider naphthalene and supply such data in this work. Using an upc-4 basis set we obtain, ≈ -0.29003 and ≈ -0.31998 for the HOMO and HOMO-1 HF energies. These energies are so close that both orbitals contribute comparably to the ionization rate. Iso-contours of the HOMO and HOMO-1 orbitals of naphthalene are shown in Fig. 9. For the HOMO we observe a single nodal plane in the molecular plane and two nodal planes perpendicular to that plane. For the HOMO-1, we observe a single nodal plane in the molecular plane and two nodal planes perpendicular to that plane. Figure 10 shows the corresponding structure factors and for both orbitals the nodal planes are reflected in the angular behavior of the structure factors. For the HOMO, we observe a vanishing structure for $\beta = 0^\circ, 90^\circ$ and 180° and for $\gamma = 0^\circ, 90^\circ, 180^\circ, 270^\circ$ and 360° , while for the HOMO-1, we observe a vanishing structure factor for $\gamma = 90^\circ$ and 270° .

The converged results for the structure factors of benzene and naphthalene were obtained using the following grid parameters: the grid size $R_{\max} = 25$, the number of radial grid points $N_r = 30$, and the numbers of polar and azimuthal angle points $N_\theta = 15$ and $N_\varphi = 16$, respectively. The maximum angular momentum, $L_{\max}$, used in Eqs. (12) and (16) is a function of the size of the

molecule. The larger the molecule, the larger the $L_{\max}$ is needed for convergence. We found that $L_{\max} = 6$ is sufficient to obtain converged results for benzene, and $L_{\max} = 10$ is sufficient to obtain converged results for naphthalene.

We note that we would not be able to treat such large polyatomic molecules as benzene and naphthalene with the previous integration scheme described in Ref. 47. This illustrates the advantage of the present grid-based scheme which enables one to treat almost any molecule.

V. CONCLUSION

The molecular structure factor is within the weak-field asymptotic theory³⁴ a key quantity for describing tunneling ionization, and this is a molecular property analogous to other properties describing the interaction of a molecule with external fields, such as static and dynamic polarizability, magnetic susceptibility, photoionization cross section, etc. We have in the present work shown how molecular structure factors within its integral representation can be calculated within a general framework at the Hartree-Fock level of theory. We provided an efficient computational implementation and hence have made probably the last step on the way from the original theory³⁴ to a routine procedure for calculating molecular structure factors. This allows a calculation of the structure factor for any system where the wave function can be calculated, and therefore provides a tool for a range of applications in strong-field physics.

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Appendix: THE CASE $E_0 \approx -Z^2/2n^2$

Let $R_l(r)$ and $I_{lm'}$ denote the radial function (14) and the integral (17) with the normalization coefficient (15) omitted, that is, $R_l^\nu(r) = \omega_l^\nu R_l(r)$ and $I_{lm'}^\nu = \omega_l^\nu I_{lm'}$. Suppose the orbital energy E_0 coincides with one of the hydrogenic energies $-Z^2/2n^2$, $n = 1, 2, \dots$, so $Z/\kappa = n$. If for given ν , l , and n the condition $n \geq \max(l, n_\xi + |m|) + 1$ is satisfied, then the following problem arises. On the one hand, the normalization factor ω_l^ν turns to infinity, because the argument of at least one of the gamma functions in Eq. (15) is a nonpositive

integer. On the other hand, the hypergeometric function in Eq. (14) turns into a polynomial of finite degree, and hence $R_l(r)$ vanishes at $r \rightarrow \infty$. In this case, substituting Eqs. (10) and (1) into Eq. (17), integrating by parts, and taking into account that each partial-wave component (13) also satisfies Eq. (11), one obtains $I_{lm'} = 0$. Thus, Eq. (17) contains the uncertainty of the type $\infty \times 0$. Here we resolve this uncertainty. We mention that the uncertainty does not arise if $Z = 0$.

Consider the case when E_0 is close to one of the hydrogenic energies. The uncertainty appears in the product of the normalization factor ω_l' and the radial function $R_l(r)$ in Eq. (17). We substitute into these factors $E_0 = -Z^2/2n^2 + \delta$ and analyze the behavior of the integral in the limit $\delta \rightarrow 0$. The function $R_l(r)$ is the solution to the radial equation

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

satisfying the boundary condition

$$R_l(r)|_{r \rightarrow 0} = (\kappa r)^l. \quad (\text{A.2})$$

For $\delta \rightarrow 0$, it can be expanded in the form

$$R_l(r) = R_l^{(0)}(r) + \delta R_l^{(1)}(r) + O(\delta^2). \quad (\text{A.3})$$

The leading term $R_l^{(0)}(r)$ here is given by Eq. (14) upon omitting the factor ω_l' and substituting $\kappa = Z/n$. The function $R_l^{(1)}(r)$ can be obtained by differentiating $R_l(r)$ with respect to δ using Eq. (14) and then setting $\delta = 0$. However, in practical calculations it is easier to find it by solving the inhomogeneous equation

$$\left[-\frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + \frac{Z^2}{2n^2} \right] R_l^{(1)}(r) = R_l^{(0)}(r) \quad (\text{A.4})$$

subject to the boundary condition

$$R_l^{(1)}(r)|_{r \rightarrow 0} = -l \left(\frac{Z}{n} \right)^{l-2} r^l \quad (\text{A.5})$$

obtained by expanding Eq. (A.2). Substituting Eq. (A.3) into Eq. (17) gives

$$I_{lm'} = \int R_l^{(0)}(r) Y_{lm'}^*(\theta, \varphi) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r} + \delta \int R_l^{(1)}(r) Y_{lm'}^*(\theta, \varphi) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r} + O(\delta^2). \quad (\text{A.6})$$

Integrating the first term by parts, we obtain

$$I_{lm'} = \delta \left[\int R_l^{(0)}(r) Y_{lm'}^*(\theta, \varphi) \psi_0(\mathbf{r}) d\mathbf{r} + \int R_l^{(1)}(r) Y_{lm'}^*(\theta, \varphi) \hat{V}_c(\mathbf{r}) \psi_0(\mathbf{r}) d\mathbf{r} \right] + O(\delta^2). \quad (\text{A.7})$$

Thus, in the limit $\delta \rightarrow 0$ the value of $I_{lm'}$ turns to zero $\propto \delta$. On the other hand, as can be seen from Eq. (15), in this limit the coefficient ω_l' diverges $\propto 1/\delta$. Summarizing, the integral in Eq. (17) is a continuous function of δ having no singularities at $\delta = 0$. This resolves the uncertainty considered.

In practical calculations, the orbital energy E_0 never coincides with hydrogenic energies exactly, but may be rather close to one of them. For example, the energy of the doubly degenerate HOMO-1 in neutral benzene (the asymptotic charge is $Z = 1$) is ≈ -0.49506 and that of the HOMO-2 is ≈ -0.50120 , which is close to the hydrogenic energy -0.5 for $n = 1$. We have confirmed that in such cases the numerical scheme for calculating the integrals (17) described in the main text still converges, although denser grids covering larger regions of integration may be needed to obtain the converged result.

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FIGURES

Figure 1: 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 angle $\beta = 0^\circ$ describes the case, where the field points from C to O. The distance between the nuclei is $R = 2.132$ and the HOMO energy is $E_0 = -0.554923$.³⁸ Broken lines show the results obtained by the new method. 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. 57. The solid line shows the TR results from Ref. 38 extracted from the HF orbital generated using a grid method X2DHF.⁵⁶

Figure 2: 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 distance between the C and O nuclei is $R = 2.19605$ and the HOMO energy is $E_0 = -0.544905$. Broken lines show the results obtained by the new method. 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. 57. The solid line shows the TR results from Ref. 36 extracted from the HF orbital generated using an expansion in terms of the optimized pc-4 GTO basis set.

Figure 3: Same as in Fig. 1, but illustrates the convergence of the results (broken lines) obtained with the method using the upc-4 basis set⁵⁷ with respect to the number of partial waves $L_{\max}$ in Eq. (16).

Figure 4: Same as in Fig. 2, but illustrates the convergence of the results (broken lines) obtained with the method using the upc-4 basis set⁵⁷ with respect to the number of partial waves $L_{\max}$ in Eq. (16).

Figure 5: Convergence of the structure factor for the HOMO of CO as the function of the angle β with respect to the numerical grid used. Calculations were done using the same Becke integration scheme but with four different numerical grids placed in each cell. The grids differ by the number of grid points (N_r, N_θ, N_φ) and are denoted grid- n , $n = 1, 2, 3, 4$. The number of grid points are (15,7,10) for grid-1, (20,10,15) for grid-2, (40,20,30) for grid-3, and (60,30,45) for grid-4, respectively. Broken lines denote results obtained using these four grids with upc-4 basis set⁵⁷ and the number of partial waves $L_{\max} = 6$ used in Eq. (16). The solid line shows the TR results from Ref. 38.

Figure 6: Convergence of the structure factor for the HOMO of CO₂ as the function of the angle β with respect to the numerical grid used. Calculations were done using the same Becke integration scheme but with four different numerical grids placed in each cell. The grids differ by the number of grid points (N_r, N_θ, N_φ) and are denoted grid- n , $n = 1, 2, 3$. The number of grid points are (6,3,8) for grid-1, (10,5,12) for grid-2, and (20,10,20) for grid-3, respectively. Broken lines denote results obtained using these three grids with upc-4 basis set⁵⁷ and the number of partial waves $L_{\max} = 6$ used in Eq. (16). The solid line shows the TR results from Ref. 36 obtained using the optimized pc-4 basis set.

Figure 7: The orientation of the benzene molecule with respect to the electric field F . Axes x and z determine the MF of benzene, while the primed axis refers to the LF, in which the electric field F is directed along z' -axis. The rotation from the LF to the MF is specified by the Euler angles $(0, \beta, \gamma)$.⁴⁸ Iso-contours of two degenerate HOMOs of benzene are also shown in the figure. One of the HOMOs (a) has a nodal plane in the xz plane, the other HOMO (b) has a nodal plane in the yz plane in the MF. Both orbitals have common nodal plane xy . Visualization of the orbitals was performed with help of the molecular builder Avogadro v1.2.0.⁶⁸

Figure 8: Dependence on the Euler angles of the structure factors $G_{00}(\beta, \gamma)$ for the two degenerate HOMOs of benzene obtained with the new method using upc-3 basis set. The orbitals are denoted by their nodal planes as xz and yz , which correspond to the orbitals (a) and (b) in Fig. 7, respectively.

Figure 10: Dependence on the Euler angles of the structure factors $G_{00}(\beta, \gamma)$ for the HOMO and HOMO-1 of naphthalene obtained with the new method using upc-2 basis set.

Figure 9: The orientation of the naphthalene molecule with respect to the electric field F . Axes y and z determine the MF of benzene, while the primed axis refers to the LF, in which the electric field F is directed along z' -axis. The rotation from the LF to the MF is specified by the Euler angles $(0, \beta, \gamma)$.⁴⁸ Iso-contours of the HOMO (a) and HOMO-1 (b) of naphthalene are also shown in the figure. Visualization of the orbitals was performed with help of the molecular builder Avogadro v1.2.0.⁶⁸

TABLES

Table I: Convergence of the results obtained with the new method for the structure factor G_{00} for the HOMO of noble gas atoms with respect to the basis set. The notation upc- n ($n = 1, \dots, 4$) refers to standard basis sets from Ref. 57. The reference values of the structure factors denoted "Exact" are given from Ref. 39. All values are given in atomic units.

	upc-1	upc-2	upc-3	upc-4	Exact
He	2.122	2.116	2.114	2.114	2.114
Ne	2.341	2.387	2.396	2.398	2.406
Ar	2.783	2.804	2.830	2.839	2.861
Kr	2.775	2.853	2.881	2.889	2.940