AARHUS UNIVERSITY

Coversheet

This is the publisher's PDF (Version of Record) of the article.

This is the final published version of the article.

How to cite this publication:

Lun Yue, Sebastian Bauch, and Lars Bojer Madsen (2017). Electron correlation in tunneling ionization of diatomic molecules: An application of the many-electron weak-field asymptotic theory with a generalized-active-space partition scheme, *Physical Review A*, Volume 96, Issue 4, Oktober 2017, <https://doi.org/10.1103/PhysRevA.96.043408>

Publication metadata

Title:	Electron correlation in tunneling ionization of diatomic molecules: An application of the many-electron weak-field asymptotic theory with a generalized-active-space partition scheme
Author(s):	Lun Yue, Sebastian Bauch, and Lars Bojer Madsen
Journal:	<i>Physical Review A</i>
DOI/Link:	https://doi.org/10.1103/PhysRevA.96.043408
Document version:	<i>Publisher's PDF (Version of Record)</i>

©2017 American Physical Society

General Rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognize and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

If the document is published under a Creative Commons license, this applies instead of the general rights.

Electron correlation in tunneling ionization of diatomic molecules: An application of the many-electron weak-field asymptotic theory with a generalized-active-space partition scheme

Lun Yue,¹ Sebastian Bauch,² and Lars Bojer Madsen³¹*Institute for Physical Chemistry and Abbe Center for Photonics, Friedrich-Schiller University, 07743 Jena, Germany*²*Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, Leibnizstraße 15, 24098 Kiel, Germany*³*Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark*

(Received 26 June 2017; published 11 October 2017)

The many-electron weak-field asymptotic theory (ME-WFAT) for static tunneling ionization [O. I. Tolstikhin *et al.*, *Phys. Rev. A* **89**, 013421 (2014)] is applied to diatomic molecules. In the ME-WFAT, the dependence of the ionization rate on the molecular orientation with respect to the static field direction is determined by the structure factor, which in turn depends on the asymptotic tail of the Dyson orbital. We extract the latter by the time-dependent generalized-active-space configuration-interaction method [S. Bauch *et al.*, *Phys. Rev. A* **90**, 062508 (2014)], which takes into account electron correlation effects systematically. Results for the orientation-dependent structure factor are presented for H₂ and LiH. Compared to mean-field Hartree-Fock results, the inclusion of electron-electron correlation affects the structure factor, and hence the rate, even for these simple systems.

DOI: [10.1103/PhysRevA.96.043408](https://doi.org/10.1103/PhysRevA.96.043408)

I. INTRODUCTION

Tunneling ionization of atoms and molecules in a static uniform electric field is of fundamental importance. In strong-field physics and attoscience [1,2], tunneling ionization is the key process that triggers a host of other interesting phenomena such as high-harmonic generation [3] and electron rescattering [4]. For an oscillating laser field with sufficiently low frequency and high intensity, ionization can be regarded as a static-field tunneling problem wherein the field is equal to its instantaneous value. Historically, the static-field tunneling ionization problem has attracted considerable attention, starting with Oppenheimer's treatment of a hydrogen atom in the ground state [5,6] and followed by formulations of effective one-electron theories for atoms [7,8] and molecules [9]. Since in a multielectron system a valence-shell electron is energetically most favorable to tunneling, the single-active-electron approximation (SAEA) in tunneling theories is often well justified. However, with the gradual maturation of attoscience and the desire to accurately understand experimental observables, electron correlation effects in tunneling ionization of atoms are now being actively investigated [10–12]. In the case of molecules, the orientation and internuclear-distance dependences of tunneling ionization introduce further factors wherein electron correlation effects can have an effect, e.g., it is known that the mean-field Hartree-Fock (HF) approximation breaks down at nonequilibrium internuclear distances [13]. To address these challenges, the many-electron weak-field asymptotic theory (ME-WFAT) for tunneling ionization [14,15] was recently developed for arbitrary atoms and molecules in the fixed-nuclei approximation (FNA). The theory generalizes earlier tunneling theories based on the SAEA [5–9].

In the weak-field asymptotic theory (WFAT), the ionization rate is sought as an asymptotic expansion in the electric-field strength F [9,14]. To leading order in the asymptotic expansion, the ionization rate factorizes into an analytic F -dependent field factor and an F -independent structure factor. The latter is determined by the asymptotic tail of the field-free wave function, or alternatively by an integral formulation [16,17]. Thus, for molecules, to obtain the ionization rate

with respect to the molecular orientation in the static field, the calculation reduces to the calculation of the structure factor. The formulas in the WFAT are derived from first principles with the Schrödinger equation as the starting point and naturally include the effects of a permanent dipole moment. For a detailed comparison between the WFAT and the molecular Ammosov-Delone-Krainov (MO-ADK) formula [18], see Ref. [9].

The calculation of the structure factor from the asymptotic form of the wave function in the ME-WFAT provides a challenge. As already demonstrated for the one-electron WFAT, usage of standard quantum chemistry Gaussian basis sets to obtain the structure factor is made difficult by the slow convergence of the tail of the wave function with the number of primitive basis functions [19–21]: The calculation of the ground-state energy, which is the main objective in quantum chemistry, does not require an accurate treatment of the long-range behavior of the wave function. For diatomics in the HF approximation, an existing grid-based method in a prolate spheroidal basis, X2DHF [22], was shown to produce accurate long-range behavior [20,23]. For polyatomic molecules, the usage of a polarization-consistent basis was able to obtain structure factors in the HF approximation [20]. In the ME-WFAT, the calculation of the structure factor requires the asymptotic form of the Dyson orbital [14,24]. The only application of the ME-WFAT was on the simplest multielectron atoms H[−] and He [14,15,24] and the simplest multielectron molecule H₂ [14] aligned with the electric field. Strategies for application of the ME-WFAT on more complicated atomic systems were discussed in Ref. [24]. Thus, multielectron correlation effects, i.e., effects beyond the mean-field HF treatment, in static tunneling ionization of complex molecules in the framework of the ME-WFAT have not been discussed.

The recently developed time-dependent generalized-active-space configuration-interaction (TD-GASCI) method [25,26] for solving the time-independent Schrödinger equation (TISE) and time-dependent Schrödinger equation (TDSE) can take electron correlation effects into account systematically by consistent inclusion of more and more configurations (Slater

determinants) in the configuration-interaction expansion of the total wave function. For an efficient description of both bound and continuum states, the spatial volume used for the calculation is partitioned into an inner and an outer region: In the inner region, molecular orbitals are chosen as the single-particle basis, while in the outer region a finite-element discrete-variable representation (FE-DVR) [27] grid basis is employed. Different choices of the configuration space in the TD-GASCI method correspond to different levels of approximation: from the SAEA, configuration-interaction singles, to the full configuration interaction. The TD-GASCI method was recently employed to study electron correlation effects in enhanced ionization of model molecules [28] and strong-field ionization of full-dimensional LiH in a prolate spheroidal coordinate system [29]. In principle, the TD-GASCI method with its partially-grid-based basis should be a suitable candidate for the correct extraction of the asymptotic tail of the Dyson orbital, as well as a means to systematically include correlation effects in the ME-WFAT and hence in the tunneling rate.

In this work we study electron correlation effects in static tunneling ionization within the ME-WFAT, employing the TD-GASCI method to obtain the structure factor of the Dyson orbital. We present the orientation-dependent structure factors for H_2 and LiH and show that electron correlation has a non-negligible effect on tunneling ionization for these molecules. We note in passing that extensions of the WFAT to molecules beyond the FNA were considered in Refs. [30–34] and inclusion of first-order terms in the asymptotic expansion was treated in Refs. [15,35] in the FNA. These extensions will not be considered in this work. Very recently, the one-electron WFAT was reformulated into an integral-equation approach wherein the asymptotic tail of the wave function was not explicitly required [16,17].

This paper is organized as follows. In Sec. II we summarize the key formulas for the tunneling ionization rate and the structure factor within the ME-WFAT [14] and present a brief introduction of the TD-GASCI method [25,26] and the extraction of the Dyson orbitals and structure factors. In Sec. III we present and discuss results for the orientation-dependent structure factors for H_2 and LiH, taking into account different levels of electron correlation. Section IV summarizes this work.

II. THEORY

In this section we provide the most important formulas in the ME-WFAT, introduce the generalized-active-space partition schemes, and present the method used to calculate the Dyson orbitals. Consider a neutral N -electron (N assumed even) diatomic molecule initially in its ground state interacting with an external static electric field polarized along the $+z$ direction of the laboratory frame $\mathbf{F} = F\mathbf{e}_z$. Let $\mathbf{r}_i$ and $\bar{\mathbf{r}}_i = \hat{R}\mathbf{r}_i$ be the coordinates of the i th electron measured from the geometric center of the molecule in the laboratory and molecular frames, respectively, and $\hat{R}$ a rotation from the laboratory to the molecular frame. For diatomics, we choose the y axis to coincide with the $\bar{y}$ axis and the $\bar{z}$ axis to be the molecular symmetry axis. The orientation of the molecule is then determined by a single angle $\beta \in [0, \pi]$ between the z and

$\bar{z}$ axes, with $\hat{R}$ a rotation by β about the y axis. Henceforth we will use an overline to denote variables in the molecular frame. Atomic units are used throughout unless indicated otherwise.

A. Many-electron WFAT

The ionization rate Γ in the ME-WFAT to leading order in F was derived in parabolic coordinates (ξ, η, φ) and for diatomics is given by [14]

$$\Gamma(F, \beta) = \sum_{\nu M'_S} \Gamma_{\nu M'_S}(F, \beta), \quad (1)$$

with $\Gamma_{\nu M'_S}$ the ionization-channel-specific ionization rate. The ionization channel is characterized by the spin projection M'_S of the $(N-1)$ -electron ionic state and the multiple index $\nu \equiv (n, n_\xi, m)$, with n the ionic state label and (n_ξ, m) the parabolic quantum numbers of the outgoing electron. Since the initial N -electron ground state and the outgoing electron have spin projections $M_S = 0$ and $m_S = \mp 1/2$, respectively, we have $M'_S = \pm 1/2$, assuming no spin-orbit coupling. The two ionic states with the same n and different M'_S contribute equally to the ionization rate $\Gamma_\nu \equiv \Gamma_{\nu(1/2)} = \Gamma_{\nu(-1/2)}$ and the sum in Eq. (1) over M'_S can readily be performed, resulting in a factor of 2. The expression for Γ_ν in the weak-field limit is

$$\Gamma_\nu(F, \beta) = |G_\nu(\beta)|^2 W_\nu(F) [1 + O(F \ln F)], \quad (2)$$

with the structure factor

$$G_\nu(\beta) = e^{-\kappa_n \mu_n} g_\nu(\beta) = e^{-\kappa_n \mu_n} \lim_{\eta \rightarrow \infty} g_\nu(\beta, \eta) \quad (3)$$

given in terms of the asymptotic value of the structure function

$$g_\nu(\beta, \eta) = \eta^{1+n_\xi+|m|/2-Z/\kappa_n} e^{\kappa_n \eta/2} \times \int_0^\infty \int_0^{2\pi} \psi_\nu(\xi) \frac{e^{-im\varphi}}{\sqrt{2\pi}} \mathcal{D}(\mathbf{r}) d\varphi d\xi, \quad (4)$$

and the field factor

$$W_\nu(F) = \frac{\kappa_n}{2} \left(\frac{4\kappa_n^2}{F} \right)^{2Z/\kappa_n - 2n_\xi - |m| - 1} \exp\left(-\frac{2\kappa_n^3}{3F}\right). \quad (5)$$

In Eqs. (2)–(5), $\kappa_n = \sqrt{2(E_n^{(N-1)} - E_0^{(N)})}$ with $E_n^{(N-1)}$ and $E_0^{(N)}$ the energies of the $(N-1)$ -electron cationic state and the N -electron unperturbed molecule, respectively; $\mu_n = \mu_{0z}^N - \mu_{nz}^{N-1}$ the difference between the z component of the dipole moments of the unperturbed molecule and cationic state; Z the charge of the ion after the removal of a single electron, i.e., for ionization of a neutral system, $Z = 1$; ψ_ν a parabolic channel function

$$\psi_\nu(\xi) = \kappa_n^{1/2} (\kappa_n \xi)^{|m|/2} e^{-\kappa_n \xi/2} \sqrt{\frac{n_\xi!}{(n_\xi + |m|)!}} L_{n_\xi}^{|m|}(\kappa_n \xi), \quad (6)$$

with $L_n^\alpha(x)$ the generalized Laguerre-polynomials [36]; and $\mathcal{D}(\mathbf{r})$ the spatial representation of the Dyson orbital (see Sec. II C). To leading order in F , $\Gamma_\nu(F, \beta)$ in Eq. (2) thus factorizes into a β -dependent factor and an F -dependent factor. The field factor involving the exponential characteristic of tunneling in Eq. (5) is dominant for the smallest ionization potential, corresponding to ionization into the $(N-1)$ -electron ionic ground state with $n = 0$. In addition, for a given n , the

dominant contribution to Γ_v is determined by the power factor with the largest exponent, corresponding to $n_\xi = m = 0$. Thus, in this work, we assume

$$\Gamma(F, \beta) = 2|G_{000}(\beta)|^2 W_{000}(F), \quad (7)$$

with the orientation dependence of the tunneling ionization rate fully determined by the structure factor. The asymptotic tail of the Dyson orbital required for the structure factor in Eq. (3) [see Eq. (4)] is obtained with the TD-GASCI method discussed below.

B. The TD-GASCI method

The *ab initio* TD-GASCI method [25,26] for solving the TISE and the TDSE for a general N -electron system generalizes the GASCI concept from quantum chemistry [37] to time-dependent problems where an ionization continuum is involved. In the following we briefly recapitulate the key points of the method and discuss the procedure to obtain the Dyson orbitals and the structure factors. For more details on the implementation of the TD-GASCI method, we refer the readers to Refs. [25,26,29]. We note that while the TD-GASCI method was developed to treat time-dependent problems, we employ it here to find the initial ground states to be used as input in the ME-WFAT by relaxing of the wave function in imaginary time.

In the FNA, the time-independent diatomic N -electron Hamiltonian in the molecular frame reads

$$H = \sum_{i=1}^N h_i + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_A Z_B}{R}, \quad (8)$$

where the one-body contribution from the i th electron is

$$h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}/2|} - \frac{Z_B}{|\mathbf{r}_i + \mathbf{R}/2|}, \quad (9)$$

with $\mathbf{R}$ the internuclear vector pointing from nucleus A to nucleus B . In the TD-GASCI method, the ansatz for the N -electron wave function with total spin projection $M_S = 0$ is expanded in a basis of Slater determinants

$$|\Psi_0^{(N)}\rangle = \sum_{I \in \Omega_{\text{GAS}}^{(N)}} C_I |\Phi_I\rangle, \quad (10)$$

with $\Omega_{\text{GAS}}^{(N)}$ the space containing all the possible multiple indices I corresponding to a given generalized-active-space (GAS) partition [26]. The determinants in Eq. (10) are constructed from a $2N_b$ -dimensional single-particle spin-orbital basis $\{|\chi_{i\sigma}\rangle\}$, with $i \in [1, N_b]$ the spatial-orbital index and σ the spin projection. An example of a determinant could be $|\Phi_I\rangle = |\chi_{i_1\sigma_1}, \dots, \chi_{i_N\sigma_N}\rangle = \hat{a}_{i_1\sigma_1}^\dagger \cdots \hat{a}_{i_N\sigma_N}^\dagger |0\rangle$, where $|0\rangle$ is the vacuum state and $\hat{a}_{i\sigma}^\dagger$ ($\hat{a}_{i\sigma}$) is a creation (annihilation) operator that creates (annihilates) a particle in the spin orbital $|\chi_{i\sigma}\rangle$.

The spin orbitals are chosen on the spin-restricted form $|\chi_{i\sigma}\rangle = |\phi_i\rangle|\sigma\rangle$, with the same set of orbitals $|\phi_i\rangle$ for the two different spin projections. The spatial orbitals $\phi_i(\mathbf{r}) \equiv \langle \mathbf{r} | \phi_i \rangle$ are chosen from a mixed basis in prolate spheroidal coordinates (ζ, μ, φ) [29]. The underlying primitive basis functions used to construct the spatial orbitals are products between FE-DVR functions [27] for the ζ and μ coordinates

FIG. 1. The GAS partitions used in this work for the calculation of the Dyson orbitals. The spatial-orbital basis spaces of dimension N_b for the two different spins (with orbital energies denoted by ϵ_i) are assumed to be identical. Different spin-orbital subspaces are marked by different colors: all orbitals inside a gray subspace are frozen; all possible orbital excitations are allowed inside a blue subspace; a purple orbital space only allows single excitation from a blue subspace. The HF partition has all orbitals frozen, while $\text{CAS}^*(N_{\text{act}}, K)$ allows all possible excitations of N_{act} active electrons in a K -dimensional orbital space (see the text).

and $e^{im\varphi}$ for the φ coordinate. The convenient properties of the prolate spheroidal FE-DVR basis, especially for the efficient evaluation and storage of two-electron integrals, have been exploited extensively in the literature [38–40]. The orbital basis is split at a finite-element boundary $\zeta = \zeta_s$ into an inner region $\zeta < \zeta_s$ and an outer region $\zeta \geq \zeta_s$. The first $N/2$ spatial inner orbitals are chosen as the lowest $N/2$ HF orbitals obtained by solving the HF problem in the inner region. While the $N/2$ occupied HF orbitals are well localized, the unoccupied HF orbitals are very delocalized and not suitable for the construction of the basis in the inner region. Therefore, the rest of the inner orbitals are obtained by first solving the $(N-2)$ -electron HF problem and subsequently orthogonalizing on the lowest $N/2$ orbitals. As discussed in Refs. [26,29], such a choice is suitable for the description of the single-ionization problem, where a remaining electron moves in the effective potential of the $N-2$ other electrons. Note that any choice of the inner orbital basis can be made, but a good basis tailored to the problem at hand can dramatically reduce the orbital space required for a converged GAS partition. For the orbitals in the outer region, the primitive FE-DVR functions are used for a good description of the electronic continuum, as well as the asymptotic tail of the wave function required in the ME-WFAT.

The GAS partitions employed in this work are sketched in Fig. 1 for the examples of a four- and a three-electron system. The HF approximation, being a single-determinant approximation, has all electrons occupying the lowest-energy orbitals. The second GAS partition denoted by CAS in Fig. 1 refers to the complete-active space notation from

quantum chemistry [13,37]. Here $\text{CAS}^*(N_{\text{act}}, K)$ indicates that all possible configurations involving the excitation of N_{act} active electrons in a K -dimensional spatial-orbital space are taken into account and the asterisk denotes that all single excitations out of the active space are included. The ground state is obtained by imaginary-time propagation of the TD-GASCI TDSE with a short-iterative Arnoldi-Lanczos propagator [41,42].

C. Dyson orbitals

The Dyson spin orbital is given by the overlap between the N -electron ground state in Eq. (10) and the $(N-1)$ -electron ground state $|\Psi_{M'_S}^{(N-1)}\rangle = \sum_{J \in \Omega_{\text{GAS}}^{(N-1)}} B_J |\Phi_J\rangle$ with spin projection $M'_S = -m_S = \pm \frac{1}{2}$. For the calculation of $|\Psi_{M'_S}^{(N-1)}\rangle$ with the TD-GASCI method, the orbital basis from the N -electron problem is used. The choice of the GAS partitions for the N -electron problem and the $(N-1)$ -electron problem must be made consistently. An example is shown in Fig. 1: If we choose $\text{CAS}^*(2, K-1)$ for $|\Psi_0^{(N)}\rangle$, the corresponding suitable GAS partition for $|\Psi_{M'_S}^{(N-1)}\rangle$ is $\text{CAS}^*(1, K-1)$ (also known as configuration-interaction singles).

The explicit form of the Dyson orbital reads (see Sec. 1 of the Appendix for details)

$$|\mathcal{D}\rangle = \langle \Psi_{M'_S}^{(N-1)} | \Psi_0^{(N)} \rangle = \sum_{i=1}^{N_b} \sum_{m_S} d_{i,m_S} |\chi_{i,m_S}\rangle, \quad (11)$$

with d_{i,m_S} expressed in terms of the configuration-interaction (CI) coefficients of the N - and $(N-1)$ -electron wave functions

$$d_{i,m_S} = \sum_{k=1}^N (-1)^k \sum_{\sigma_1, \dots, \sigma_{N-1}} \sum_{\substack{j_1 < \dots < j_{k-1} < i \\ < j_k < \dots < j_{N-1}}} B_{j_1 \sigma_1, \dots, j_{N-1} \sigma_{N-1}}^* \times C_{j_1 \sigma_1, \dots, j_{k-1} \sigma_{k-1}, i m_S, j_k \sigma_k, \dots, j_{N-1} \sigma_{N-1}}. \quad (12)$$

Since $d_{i,m_S} = d_{i,-m_S} \equiv d_i$, the spin-independent Dyson orbital in a spatial representation is

$$\mathcal{D}(\mathbf{r}) = \sum_{i=1}^{N_b} d_i \phi_i(\mathbf{r}). \quad (13)$$

Note that in the special case of the HF GAS partition, the Dyson orbital is just the highest occupied molecular orbital (HOMO) $\mathcal{D}(\mathbf{r}) = \phi_{N/2}(\mathbf{r})$.

D. Structure factors

As discussed in Sec. II A, the desired structure factor in the ionization rate of Eq. (7) is

$$G_{000}(\beta) = e^{-\kappa_0 \mu_0} \lim_{\eta \rightarrow \infty} g_{000}(\beta; \eta) \quad (14)$$

with the structure function from Eq. (4),

$$g_{000}(\beta; \eta) = \frac{1}{\sqrt{2\pi}} \eta^{1-Z/\kappa_0} e^{\kappa_0 \eta/2} \times \int_0^\infty \psi_{000}(\xi) \int_0^{2\pi} \mathcal{D}(\mathbf{r}) d\varphi d\xi \quad (15)$$

TABLE I. Norm of the Dyson orbitals, κ_0 , and $\bar{\mu}_0$ for the converged GAS partitions, for H_2 and LiH at their equilibrium internuclear distances. The dot in our notation $\text{CAS}^*(2, \cdot)$ is a placeholder for the converged number of spatial orbitals, i.e. $\text{CAS}^*(2, 80)$ -0 and $\text{CAS}^*(2, 160)$ -1 for H_2 , and $\text{CAS}^*(2, 120)$ -0 and $\text{CAS}^*(2, 180)$ -1 for LiH .

Partition	H_2 ($R = 1.4011$)			LiH ($R = 3.0139$)		
	$\langle \mathcal{D} \mathcal{D} \rangle$	κ_0	$\bar{\mu}_0$	$\langle \mathcal{D} \mathcal{D} \rangle$	κ_0	$\bar{\mu}_0$
HF	1.000	1.090	0	1.000	0.777	-1.188
$\text{CAS}^*(2, \cdot)$ -0	0.955	1.087	0	0.889	0.750	-1.004
$\text{CAS}^*(2, \cdot)$ -1	0.952	1.102	0	0.886	0.769	-1.018

and the z component of the dipole moment in the laboratory frame related to its value in the molecular frame

$$\mu_0 = \bar{\mu}_0 \cos \beta. \quad (16)$$

For details on the evaluation of the integral in Eq. (15) and the extraction of the structure factor, see Sec. 2 of the Appendix.

III. RESULTS AND DISCUSSION

In this section we extract as examples the β -dependent structure factors for H_2 and LiH , employing the procedure outlined in Sec. II. For each molecule we calculate the Dyson orbitals taking into account different amounts of electron correlation. The uncorrelated case is given by the HF approximation. The correlated case is denoted by $\text{CAS}^*(2, K)$ - $\bar{m}_{\text{max}}$ and includes configurations involving excitations of two active electrons in a K -dimensional spatial-orbital space and all possible single-excitations out of this space. The extension $\bar{m}_{\text{max}}$ in the CAS^* -notation denotes the maximum azimuthal quantum number employed in the prolate spheroidal primitive basis and K is an integer large enough for the structure function to be converged, i.e., so large that unphysical oscillations in the structure function have disappeared (see Secs. 3 and 4 in the Appendix). Note that the HF result is equivalent to $\text{CAS}(2, 1)$.

Table I shows $\langle \mathcal{D} | \mathcal{D} \rangle$, κ_0 , and $\bar{\mu}_0$ for the converged GAS partitions. Note that the Dyson orbitals are not necessarily normalized: The Dyson norms decrease in value when more correlation effects are taken into account [43]. In the case of perturbative extreme-ultraviolet ionization, the Dyson norms were used to predict the total ionization yields [44].

A. Structure factors for H_2

For HF and the converged CAS partitions, the β -dependent structure factors $G_{000}(\beta)$ for H_2 are shown in Fig. 2. First we notice that our HF result agrees very well with the previous result in Refs. [19,23], with maxima at $\beta = 0$ and $\beta = \pi$, i.e., when the molecule is aligned along the polarization direction of the electric field. As discussed in previous works (e.g., in [19]), this form of the structure factor and therefore the tunneling ionization rate is due to the HOMO being of σ symmetry, with the charge density elongated along the internuclear axis.

For the $\text{CAS}^*(2, 80)$ -0 case, the overall shape of the orientation-dependent structure factor is similar to the HF case, with a reduction in magnitude at $\beta = \pi/2$. The smaller

FIG. 2. Orientation-dependent structure factor calculated for H_2 for $R = 1.4011$ with different GAS partitions.

structure factor at $\beta = \pi/2$ can be explained as follows. For a specific molecular orientation and the field polarized along the $+z$ axis, ionization occurs predominantly along the $-z$ axis. This is seen in the WFAT by realizing that the limits $\eta \rightarrow \infty$ and $\xi \rightarrow 0$ [ψ_{000} in Eq. (6) attains a maximum at $\xi = 0$] correspond to the limits $z \rightarrow -\infty$ and $x, y \rightarrow 0$. Since the CI wave function must be normalized, the inclusion of configurations involving σ^* orbitals with $\bar{m} = 0$ and a nodal plane at $\bar{z} = 0$ will lead to less ionization at $\beta = \pi/2$ compared to the HF case. A more quantitative analysis can be made by considering the Dyson orbital with the asymptotic tail scaled out $\bar{r}^{1-Z/\kappa_0} e^{\kappa_0 \bar{r}} \mathcal{D}(\bar{\mathbf{r}})$, which in the limits $z \rightarrow -\infty$ and $x, y \rightarrow 0$ is approximately the integrand in Eq. (15). Thus, for a given molecular orientation β , looking in the direction $\bar{\theta} = \pi - \beta$ in the scaled Dyson orbital gives us an indication of the magnitude of the structure factor.

In Fig. 3(a) we show the difference between the HF and CAS*(2,80)-0 results for the scaled Dyson densities,

$$A(\bar{\mathbf{r}}) = \left| \bar{r}^{1-Z/\kappa_0^{\text{CAS}}} e^{\kappa_0^{\text{CAS}} \bar{r}} \mathcal{D}_{\text{CAS}}(\bar{\mathbf{r}}) \right|^2 - \left| \bar{r}^{1-Z/\kappa_0^{\text{HF}}} e^{\kappa_0^{\text{HF}} \bar{r}} \mathcal{D}_{\text{HF}}(\bar{\mathbf{r}}) \right|^2. \quad (17)$$

FIG. 3. Difference for the H_2 Dyson densities without the asymptotic tail [see Eq. (17)] in the $\bar{x}\bar{z}$ plane between (a) the HF result and CAS*(2,80)-0 and (b) the HF result and CAS*(2,160)-1. The two black circles indicate the positions of the two nuclei.

FIG. 4. Orientation-dependent structure factor calculated for LiH for $R = 3.0139$ with different CAS partitions. Solid lines show $|G_{000}(\beta)|^2$ and dash-dotted lines $|g_{000}(\beta)|^2$ in Eq. (3) excluding the dipole factor. The purple dashed line shows $\tilde{G}_{000}(\beta)$ from Eq. (18), with electron correlation only included in the dipole. At $\beta = 0$, Li is placed at $-R/2$.

This quantity is seen for large $\bar{r} = |\bar{\mathbf{r}}|$ to be positive along the molecular axis and negative perpendicular to the molecular axis. This is in qualitative agreement with Fig. 2, where $|G_{000}(\beta)|^2$ for CAS*(2,80)-0 is seen to be (slightly) larger than the HF result at $\beta = 0$ and smaller than the HF result at $\beta = \pi/2$.

In Fig. 2, the structure factor for the CAS*(2,160)-1 partition is consistently larger than that for the HF case at all β , with the largest increase at $\beta = 0$. This is consistent with Fig. 3(b), where $A(\bar{\mathbf{r}})$ is seen to be most positive along the internuclear axis. The inclusion of electron correlation thus has a non-negligible influence on the magnitude of the structure factor (and consequently the ionization rate) even for one of the simplest molecular systems, H_2 . It should be mentioned that at $\beta = 0$, our CAS*(2,160)-1 result does not coincide with that in Ref. [14], as shown in Fig. 2. A cause for this discrepancy could be the smaller interval used ($1 \leq r \leq 5$) in their fitting procedure for the extraction of the structure factor.

B. Structure factors for LiH

As an example of a multielectron polar molecule we consider the case of LiH . The orientation-dependent structure factors in Eqs. (3) and (14), with $|G_{000}(\beta)|^2$ including the dipole factor $e^{-\kappa_0 \mu_0}$ and $|g_{000}(\beta)|^2$ excluding the dipole factor, are presented in Fig. 4. We note that for the LiH calculation, the Li atom is placed at $\bar{z} = -R/2$ and the H atom at $\bar{z} = R/2$. In the HF case, $|g_{000}(\beta)|^2$ is largest at $\beta = \pi$, meaning that if the permanent dipole is (incorrectly) neglected, the molecule is most likely to ionize when the internuclear vector from Li to H is aligned antiparallel with the field polarization direction, with the electron tunneling out from the hydrogen end of the molecule. As the HOMO in LiH is localized at the hydrogen atom (see, e.g., Ref. [29]), this naive expectation is indeed consistent with $|g_{000}(\beta)|^2$. However, when the dipole factor is taken into account, the situation is seen to be reversed in Fig. 4, with $|G_{000}(\beta)|^2$ attaining a maximum at $\beta = 0$. Indeed,

FIG. 5. Difference for the LiH Dyson densities without the asymptotic tail [see Eq. (17)] in the $\bar{x}\bar{z}$ plane between (a) the HF result and CAS*(2,120)-0 and (b) the HF result and CAS*(2,180)-1. The two black circles indicate the positions of the two nuclei, with Li placed at $\bar{z} < 0$.

for $\beta = 0$ the dipole moment $\mu_0 = \bar{\mu}_0 = -1.188$ is negative (pointing in the $-\bar{z}$ direction), with the exponential factor $e^{-\kappa_0\mu_0}$ attaining its maximum. With increasing β , the dipole changes according to Eq. (16), until the dipole factor attains its minimum at $\beta = \pi$. Our HF result for LiH is again seen to agree with Ref. [23].

For the correlated cases, we assume that two electrons are frozen in the two lowest bound spin orbitals (see Fig. 1). Such partition schemes are suitable since tunneling ionization is mostly a valence-shell problem. For the correlated CAS*(2,120)-0 results in Fig. 4, the overall behavior is similar to the HF case. The structure coefficient $|g_{000}(\beta)|^2$ is slightly larger than the HF result at $\beta = 0$, while being quite smaller at $\beta = \pi$. These observations are consistent with $A(\bar{\mathbf{r}})$ plotted in Fig. 5(a). For $\beta = 0$, the electron tunnels out in the $-\bar{z}$ direction (or $\eta \rightarrow \infty$ and $\xi \rightarrow 0$), and indeed in Fig. 5(a) along this direction we see $A(\bar{\mathbf{r}})$ being slightly positive, implying a slightly larger-scaled Dyson density for CAS*(2,120)-0, which is consistent with the slightly larger value of $|g_{000}(0)|^2$ for CAS*(2,120)-0 in Fig. 4. In the $\bar{\theta} = \pi/2$ direction of Fig. 5(a), $A(\bar{\mathbf{r}})$ is slightly negative, resulting in the slightly smaller value of $|g_{000}(\pi/2)|^2$ for CAS*(2,120)-0. Along $\bar{\theta} = \pi$ in Fig. 5, $A(\bar{\mathbf{r}})$ is quite negative on the scale of the figure, in agreement with the significant smaller value of $|g_{000}(\pi)|^2$. Since $\bar{\mu}_0 = -1.004$ is less negative for CAS*(2,120)-0 compared to $\bar{\mu}_0 = -1.188$ for the HF case (see Table I), $|G_{000}(\beta)|^2$ is smaller for CAS*(2,120)-0 at $\beta = 0$.

With the inclusion of the π orbitals in CAS*(2,180)-1, it is seen in Fig. 4 that $|g_{000}(0)|^2$ is unchanged compared to CAS*(2,120)-0, while $|g_{000}(\pi)|^2$ is increased, which can be understood by considering $A(\bar{\mathbf{r}})$ along the $\bar{\theta} = \pi$ and $\bar{\theta} = 0$ directions in Fig. 5(b), respectively, and comparing them to Fig. 5(a). The μ_0 value for CAS*(2,180)-1 lies between the values for the HF case and CAS*(2,120)-0, resulting in $G_{000}(0)$ attaining a value between the HF result and CAS*(2,120)-0 as well.

Since the orientation-dependent dipole factor $e^{-\kappa_0\mu_0}$ in G_{000} is of exponential form, it often dominates over the factor g_{000} . This is the reason why in many previous works (see, e.g., [45,46]), the effects of the permanent dipole on the orientation-dependent tunneling problem have been discussed, but without

the stringent consideration of the prefactor g_v . In recent experimental works employing the WFAT [47–49], the factor g_v was obtained within a one-electron approach employing the HF orbitals, while the projected dipole $\bar{\mu}_n$ was obtained by an effective multielectron approach involving the fitting of field-shifted ionization potentials obtained from quantum chemistry calculations. The reason for such an approach was the difficulty in obtaining the asymptotic behavior of the Dyson orbital for the calculations of the correlated g_v , while the calculation of the dipole projection $\bar{\mu}_n$ did not present this difficulty. We now investigate the accuracy of such an application of WFAT, taking LiH as an example. In Fig. 4 we have plotted

$$|\tilde{G}_{000}(\beta)|^2 = |e^{-\kappa_0^{\text{HF}}\mu_0^{\text{CAS}}} g_{000}^{\text{HF}}(\beta)|^2, \quad (18)$$

i.e., with the electron correlation only included in the dipole moment μ_0^{CAS} calculated with CAS*(2,180)-1. Although the overall behavior is correct with the largest ionization rate at $\beta = 0$, the discrepancies with our most correlated ME-WFAT calculation, CAS*(2,180)-1, are quite significant at $\beta = 0$ and $\beta = \pi$ and even the HF result is closer to the correct correlated structure factor. The current considerations suggest that *ad hoc* inclusion of multielectron effects into the WFAT calculation does not always lead to a better quality structure factor. Our approach in the current work, in contrast, is able to include multielectron effects in the ME-WFAT consistently in a single framework, without the need to resort to different approximations for the calculation of g_{000} and $\bar{\mu}_0$.

IV. CONCLUSION AND OUTLOOK

We have investigated electron correlation effects in static tunneling ionization of diatomic molecules, by application of the many-electron weak-field asymptotic theory [14]. In the leading order of the theory, the field-molecule orientation dependence of the ionization rate depends only on the structure factor, which in turn requires an accurate treatment of the asymptotic tail of the correlated Dyson orbital. The time-dependent generalized-active-space configuration-interaction method [26] for the solution of the time-dependent and time-independent Schrödinger equation was shown to be suitable for the extraction of the required Dyson orbitals: The methodology can take into account electron correlations systematically, the asymptotic behavior of the Dyson orbitals are correctly treated due to the mixed primitive basis in the TD-GASCI method, the parameters required for the calculation of the structure factor are included consistently, and the second-quantized formulation of the TD-GASCI method automatically includes the antisymmetrization requirement of the wave function, which was shown in Ref. [50] to be of significance for the orientation-dependent ionization rate of molecules.

There are, however, limitations to our current numerical implementation of the method. In the current approach [26], the zeros of the CI matrix are identified and discarded while the remaining nonzero blocks are calculated and stored in a sparse matrix format. While this part of the calculation is parallelized for this work, in the largest GAS partition used for LiH, CAS*(2,180)-1, the CI matrix still has $\sim 7 \times 10^7$ nonzero elements, requiring ~ 246 GB of memory. Initiatives to resolve these issues have already been taken in the integral screened

configuration-interaction method [51], where the CI matrix does not need to be explicitly stored, and the CI matrix-vector multiplications can be performed efficiently.

Our calculated structure factors for H₂ and LiH reveal that electron correlation has a noticeable effect on the orientation dependence of the ionization rate. The deviation between the uncorrelated and correlated results was traced back to their respective Dyson orbitals with the asymptotic tail scaled out. Although the shape of the correlated orientation-dependent structure factor is similar to the uncorrelated case, with maxima and minima at the same orientation angles (see Figs. 2 and 4), our method for extraction of the Dyson orbitals is important for future studies wherein electron correlation is of significance. For example, the weights of the HF determinant in the full configuration-interaction (FCI) wave function for N₂ and C₂ at equilibrium R are 0.879 and 0.687, respectively [52], indicating strong electron correlations. Another relevant situation is tunneling ionization of molecules at internuclear distances R displaced from equilibrium. For example, for H₂ at $R = 4.0$, the weight of the restricted HF determinant in the FCI wave function is 0.74 [13], compared to 0.98 at equilibrium. Studies involving the correlated orientation-dependent ionization rates with the ME-WFAT and the TD-GASCI method at nonequilibrium internuclear distances are left for future studies.

ACKNOWLEDGMENTS

This work was supported by the Villum Kann Rasmussen (VKR) Center of Excellence, QUSCOPE - Quantum Scale Optical Processes. L.Y. acknowledges support from the German Research Foundation (Grant No. DFG-SPP-1840 “Quantum Dynamics in Tailored Intense Fields”). S.B. acknowledges the hospitality of L.B.M. and funding by the German BMBF in the frame of the Verbundprojekt No. FSP302. We thank Henrik R. Larsson for help with the prolate basis set. The calculations were performed at the Centre for Scientific Computing Aarhus.

APPENDIX: NUMERICAL DETAILS

In this appendix we provide some details on the evaluation of the Dyson orbitals and structure factors. The basis parameters used and the convergence of the structure functions with respect to the GAS partitions are also discussed for H₂ and LiH.

1. Evaluation of Dyson orbitals in the TD-GASCI method

Assuming that the ground states of the N -electron and $(N - 1)$ -electron systems are known,

$$\begin{aligned} |\Psi_0^{(N)}\rangle &= \sum_{I \in \Omega_{\text{GAS}}^{(N)}} C_I |\Phi_I\rangle, \quad |\Phi_I\rangle = \hat{a}_{i_1 \sigma_1}^\dagger \cdots \hat{a}_{i_N \sigma_N}^\dagger |0\rangle, \\ |\Psi_{M'_S}^{(N-1)}\rangle &= \sum_{J \in \Omega_{\text{GAS}}^{(N-1)}} B_J |\Phi_J\rangle, \quad |\Phi_J\rangle = \hat{a}_{j_1 \tau_1}^\dagger \cdots \hat{a}_{j_{N-1} \tau_{N-1}}^\dagger |0\rangle, \end{aligned} \quad (\text{A1})$$

the Dyson orbital is given by the overlap (we omit $\Omega_{\text{GAS}}^{(N)}$ and $\Omega_{\text{GAS}}^{(N-1)}$ in the notation for convenience)

$$\begin{aligned} |\mathcal{D}\rangle &= \langle \Psi_{M'_S}^{(N-1)} | \Psi_0^{(N)} \rangle = \sum_J \sum_I B_J^* C_I \langle \Phi_J | \Phi_I \rangle = \sum_J \sum_I B_J^* C_I \hat{a}_{j_{N-1} \tau_{N-1}} \cdots \hat{a}_{j_1 \tau_1} \hat{a}_{i_1 \sigma_1}^\dagger \cdots \hat{a}_{i_N \sigma_N}^\dagger |0\rangle \\ &= \sum_J \sum_I B_J^* C_I \sum_{k=1}^N (-1)^k \delta_{j_1 i_1} \delta_{\tau_1 \sigma_1} \cdots \delta_{j_{k-1} i_{k-1}} \delta_{\tau_{k-1} \sigma_{k-1}} \hat{a}_{i_k \sigma_k}^\dagger \delta_{j_k i_{k+1}} \delta_{\tau_k \sigma_{k+1}} \cdots \delta_{j_{N-1} i_N} \delta_{\tau_{N-1} \sigma_N} |0\rangle \\ &= \sum_{k=1}^N (-1)^k \sum_{\substack{j_1 < \cdots < j_{k-1} < i_k \\ < j_k < \cdots < j_{N-1}}} \sum_{\sigma_k} \sum_{\tau_1, \dots, \tau_{N-1}} B_{j_1 \tau_1, \dots, j_{N-1} \tau_{N-1}}^* C_{j_1 \tau_1, \dots, j_{k-1} \tau_{k-1}, i_k \sigma_k, j_k \tau_k, \dots, j_{N-1} \tau_{N-1}} \hat{a}_{i_k \sigma_k}^\dagger |0\rangle \\ &= \sum_{i=1}^{N_b} \sum_{m_S} d_{i, m_S} |\phi_{i, m_S}\rangle, \end{aligned} \quad (\text{A2})$$

with d_{i, m_S} given by Eq. (12). To obtain the fourth equality in Eq. (A2) we used Wick's theorem [53] to reduce the operator string, and to obtain the last equality we inserted the complete set $1 = \sum_{i, m_S} |\phi_{i, m_S}\rangle \langle \phi_{i, m_S}|$, where $|\phi_{i, m_S}\rangle$ is a spin-orbital ket with orbital index i and spin index m_S .

The numerical evaluation of the Dyson orbitals follows Eq. (A2): for all multiple indices J and I , the determinant overlap $\langle \Phi_J | \Phi_I \rangle$ is calculated, yielding only a nonzero result when all indices in $|\Phi_J\rangle$ are contained in $|\Phi_I\rangle$. If the remaining orbital and spin indices in I are i and m_S , respectively, the term

$B_J^* C_I$ (with a suitable factor ± 1) is added to the coefficient d_{i, m_S} . For the HF partition, the highest occupied molecular orbital from the HF calculation of the N -electron system is used.

2. Evaluation of structure factors

To perform the integral in Eq. (15) to obtain the structure functions, we need the Dyson orbital in the laboratory frame in parabolic coordinates. Numerically, a parabolic spatial quadra-

FIG. 6. Structure function squared $|g_{000}(0; \eta)|^2$ [Eq.(15)] calculated for H_2 with $R = 1.4011$ in different GAS partitions: $\bar{m}_{\max} = 0$ (top) and $\bar{m}_{\max} = 1$ (bottom). The inset is a close-up of the rectangular area.

ture grid $(\xi_i, \eta_j, \varphi_k)$ is first chosen such that the integration can be conveniently performed. We use Laguerre quadrature for the ξ coordinate and an equidistant grid for φ . The parabolic grid is transformed into Cartesian coordinates, which afterward is rotated into the molecular-frame Cartesian coordinates by

$$\begin{aligned}\bar{x} &= x \cos \beta - z \sin \beta, \\ \bar{z} &= z \sin \beta + x \cos \beta.\end{aligned}\quad (A3)$$

TABLE II. The TD-GASCI prolate spheroidal basis parameters used for H_2 with $R = 1.4011$. The dot in our notation $CAS^*(2, \cdot)$ is a placeholder for an arbitrary number. The extension -0 (-1) in a method denotes the magnetic quantum number $\bar{m}_{\max} = 0$ ($\bar{m}_{\max} = 1$) used in the prolate spheroidal primitive basis. In addition, N_μ is the number of DVR functions for the μ coordinate; ζ_{FE} gives the FE boundaries with the vertical line separating the inner and outer regions, with the dots representing equidistant finite elements in the outer region; and N_ζ is the number of ζ -coordinate DVR functions in each finite element. The total number of spatial orbitals in the inner region is 168 for $\bar{m}_{\max} = 0$ and 504 for $\bar{m}_{\max} = 1$.

Partition	N_μ	ζ_{FE}	N_ζ	$[\eta_{\min}, \eta_{\max}]$
HF	8	(1 2 4 7 11 15 19)	(4 6 7 8 8 8)	[10, 16]
$CAS^*(2, \cdot)-0$	8	(1 2 4 7 11 15.2 ... 32)	(4 6 7 8 8 ...)	[10, 20]
$CAS^*(2, \cdot)-1$	8	(1 2 4 7 11 15.2 ... 32)	(4 6 7 8 8 ...)	[10, 20]

FIG. 7. Structure function squared $|g_{000}(0; \eta)|^2$ calculated for LiH with $R = 3.0139$ in different CAS partitions: $\bar{m}_{\max} = 0$ (top) and $\bar{m}_{\max} = 1$ (bottom). The insets are close-ups of the rectangular areas.

Finally, the Cartesian grid is transformed into the corresponding prolate spheroidal grid, where the Dyson orbitals are evaluated as in Eq. (13) using the orbital basis $\phi_i(\mathbf{r})$ from the TD-GASCI method. With this procedure, we obtain the Dyson orbital in the parabolic quadrature grid $\mathcal{D}(\xi_i, \eta_j, \varphi_k)$, which is integrated according to Eq. (15) to obtain the structure function $g_{000}(\beta; \eta)$. The calculation of the Dyson orbital coefficients d_i , which is numerically the most time-consuming part, only needs to be performed once.

To take the limit $\eta \rightarrow \infty$ of the structure function in Eq. (15), we follow the approach employed in Refs. [20, 23]. We consider $g_{000}(\beta; \eta)$ as a function of $1/\eta$ with N_{fit} points in the interval $[1/\eta_{\max}, 1/\eta_{\min}]$ and fit it with a polynomial of degree N_{deg} ,

$$g_{000}(\beta; \eta) = \sum_{n=0}^{N_{\text{deg}}} c_n(\beta) \left(\frac{1}{\eta} \right)^n. \quad (A4)$$

The structure factor is then the coefficient $g_{000}(\beta) = \lim_{\eta \rightarrow \infty} g_{000}(\beta, \eta) = c_0(\beta)$. In this work, the choices $N_{\text{fit}} = 80$ and $N_{\text{deg}} = 2$ are used. The choices of $\eta_{\min}$ and $\eta_{\max}$ vary, as $g_{000}(\beta, \eta)$ can show unphysical nonmonotonic behavior at large η due to the choice of the primitive basis and different CAS partition schemes. The $\eta_{\max}$ must be chosen smaller than the distance corresponding to the onset of such behaviors.

TABLE III. The TDGASCI prolate spheroidal basis parameters used for LiH with $R = 3.0139$. The notation is the same as in Table II. The total number of spatial orbitals in the inner region is 192 for $\bar{m}_{\max} = 0$ and 576 for $\bar{m}_{\max} = 1$.

Method	N_{μ}	ζ_{FE}	N_{ζ}	$[\eta_{\min}, \eta_{\max}]$
HF	8	(1 2 4 7 11 15)	(6 7 7 8 8)	[10,20]
CAS*(2,-)-0	8	(1 2 4 7 11 15 19)	(6 7 7 8 8 ...)	[20,40]
CAS*(2,-)-1	8	(1 2 4 7 11 15 19)	(6 7 7 8 8 ...)	[10,17]

3. Complete-active-space convergence for H₂

In Fig. 6 we present for the orientation $\beta = 0$ the η -dependent structure functions for H₂ calculated with different GAS partitions. The prolate basis parameters and the η interval used for the fitting of the structure factors are given in Table II. The extension -0 (-1) in the notation of a CAS method denotes the maximum azimuthal quantum number $\bar{m}_{\max} = 0$ ($\bar{m}_{\max} = 1$) employed in the prolate spheroidal primitive basis. For $\bar{m}_{\max} = 0$ in the top panel, it is shown that for CAS*(2,20)-0 unphysical oscillations are seen at $\eta \approx 12$ due to the small CAS space used. For CAS*(2,40)-0, the unphysical oscillations are no longer present on the scale of the figure. For CAS*(2,80)-0, a sufficiently high number of diffuse orbitals are included in the calculation and the result is fully converged with respect to the CAS. To include more correlations in the TD-GASCI method, orbitals with higher azimuthal quantum number are

taken into account. The case $\bar{m}_{\max} = 1$ is shown in the bottom panel of Fig. 6. Again unphysical oscillations are present, with convergence observed for CAS*(2,140)-1 and CAS*(2,160)-1. Note that for $\bar{m}_{\max} = 0$, the largest possible CAS with our chosen primitive basis set is CAS*(2,168)-0, while for $\bar{m}_{\max} = 1$ it is CAS*(2,504)-1. Since the structure functions are converged for smaller CASs, as shown in Fig. 6, the TD-GASCI method allows the extraction of the structure factors with reduced computational effort compared to a full CAS calculation.

4. Complete-active-space convergence for LiH

In Fig. 7 we present the η -dependent structure functions for LiH in different CAS partitions, assuming that two electrons are frozen in the two lowest bound spin orbitals (see Fig. 1). The prolate basis parameters used for the calculations are given in Table III. For $\bar{m}_{\max} = 0$ in the top panel of Fig. 7, with increasing CAS, the unphysical oscillations decrease in amplitude and eventually disappear for CAS*(2,120)-1. For the $\bar{m}_{\max} = 1$ case in the bottom panel, the convergence is achieved at least up to $\eta = 17$ for CAS*(2,180)-1. A calculation for a larger CAS with our current employed version of the TD-GASCI code is not yet feasible due to the large memory requirement for the storage the sparse CI matrix, although progress has been made to circumvent this problem [51]. Nevertheless, the structure factor can still be extracted by fitting the interval $\eta \in [10,17]$ (see Table III), albeit with slightly less accuracy compared to previous fits.

- [1] F. Krausz and M. Ivanov, Attosecond physics, *Rev. Mod. Phys.* **81**, 163 (2009).
- [2] P. B. Corkum and F. Krausz, Attosecond science, *Nat. Phys.* **3**, 381 (2007).
- [3] T. Brabec and F. Krausz, Intense few-cycle laser fields: Frontiers of nonlinear optics, *Rev. Mod. Phys.* **72**, 545 (2000).
- [4] W. Becker, A. Lohr, and M. Kleber, Effects of rescattering on above-threshold ionization, *J. Phys. B* **27**, L325 (1994).
- [5] J. R. Oppenheimer, Three notes on the quantum theory of aperiodic effects, *Phys. Rev.* **31**, 66 (1928).
- [6] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Pergamon, Oxford, 1977).
- [7] B. M. Smirnov and M. I. Chibisov, The breaking up of atomic particles by an electric field and by electron collisions, *Zh. Eksp. Teor. Fiz.* **49**, 841 (1965) [*Sov. Phys. JETP* **22**, 585 (1966)].
- [8] A. M. Perelomov, V. S. Popov, and M. V. Terent'ev, Ionization of atoms in an alternating electric field, *Zh. Eksp. Teor. Fiz.* **50**, 1393 (1966) [*Sov. Phys. JETP* **23**, 924 (1966)].
- [9] O. I. Tolstikhin, T. Morishita, and L. B. Madsen, Theory of tunneling ionization of molecules: Weak-field asymptotics including dipole effects, *Phys. Rev. A* **84**, 053423 (2011).
- [10] Z. B. Walters and O. Smirnova, Attosecond correlation dynamics during electron tunneling from molecules, *J. Phys. B* **43**, 161002 (2010).
- [11] L. Torlina, M. Ivanov, Z. B. Walters, and O. Smirnova, Time-dependent analytical r -matrix approach for strong-field dynamics. ii. many-electron systems, *Phys. Rev. A* **86**, 043409 (2012).
- [12] L. Torlina, F. Morales, J. Kaushal, I. Ivanov, A. Kheifets, A. Zielinski, A. Scrinzi, H. G. Muller, S. Sukiasyan, M. Ivanov, and O. Smirnova, Interpreting attoclock measurements of tunneling times, *Nat. Phys.* **11**, 503 (2015).
- [13] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).
- [14] O. I. Tolstikhin, L. B. Madsen, and T. Morishita, Weak-field asymptotic theory of tunneling ionization in many-electron atomic and molecular systems, *Phys. Rev. A* **89**, 013421 (2014).
- [15] V. H. Trinh, O. I. Tolstikhin, and T. Morishita, First-order correction terms in the weak-field asymptotic theory of tunneling ionization in many-electron systems, *J. Phys. B* **49**, 195603 (2016).
- [16] A. I. Dnestryan and O. I. Tolstikhin, Integral-equation approach to the weak-field asymptotic theory of tunneling ionization, *Phys. Rev. A* **93**, 033412 (2016).
- [17] L. B. Madsen, F. Jensen, A. I. Dnestryan, and O. I. Tolstikhin, Structure factors for tunneling ionization rates of molecules: General Hartree-Fock-based integral representation, *Phys. Rev. A* **96**, 013423 (2017).
- [18] X. M. Tong, Z. X. Zhao, and C. D. Lin, Theory of molecular tunneling ionization, *Phys. Rev. A* **66**, 033402 (2002).
- [19] L. B. Madsen, O. I. Tolstikhin, and T. Morishita, Application of the weak-field asymptotic theory to the analysis of tunneling ionization of linear molecules, *Phys. Rev. A* **85**, 053404 (2012).

- [20] L. B. Madsen, F. Jensen, O. I. Tolstikhin, and T. Morishita, Structure factors for tunneling ionization rates of molecules, *Phys. Rev. A* **87**, 013406 (2013).
- [21] L. B. Madsen, F. Jensen, O. I. Tolstikhin, and T. Morishita, Application of the weak-field asymptotic theory to tunneling ionization of H₂O, *Phys. Rev. A* **89**, 033412 (2014).
- [22] J. Kobus, L. Laaksonen, and D. Sundholm, A numerical Hartree-Fock program for diatomic molecules, *Comput. Phys. Commun.* **98**, 346 (1996).
- [23] R. Saito, O. I. Tolstikhin, L. B. Madsen, and T. Morishita, Structure factors for tunneling ionization rates of diatomic molecules, *At. Data Nucl. Data Tables* **103–104**, 4 (2015).
- [24] I. Y. Tolstikhina, T. Morishita, and O. I. Tolstikhin, Application of the many-electron weak-field asymptotic theory of tunneling ionization to atoms, *Phys. Rev. A* **90**, 053413 (2014).
- [25] D. Hochstuhl and M. Bonitz, Time-dependent restricted-active-space configuration-interaction method for the photoionization of many-electron atoms, *Phys. Rev. A* **86**, 053424 (2012).
- [26] S. Bauch, L. K. Sørensen, and L. B. Madsen, Time-dependent generalized-active-space configuration-interaction approach to photoionization dynamics of atoms and molecules, *Phys. Rev. A* **90**, 062508 (2014).
- [27] T. N. Rescigno and C. W. McCurdy, Numerical grid methods for quantum-mechanical scattering problems, *Phys. Rev. A* **62**, 032706 (2000).
- [28] S. Chattopadhyay, S. Bauch, and L. B. Madsen, Electron-correlation effects in enhanced ionization of molecules: A time-dependent generalized-active-space configuration-interaction study, *Phys. Rev. A* **92**, 063423 (2015).
- [29] H. R. Larsson, S. Bauch, L. K. Sørensen, and M. Bonitz, Correlation effects in strong-field ionization of heteronuclear diatomic molecules, *Phys. Rev. A* **93**, 013426 (2016).
- [30] O. I. Tolstikhin, H. J. Wörner, and T. Morishita, Effect of nuclear motion on tunneling ionization rates of molecules, *Phys. Rev. A* **87**, 041401 (2013).
- [31] O. I. Tolstikhin and L. B. Madsen, Retardation Effects and the Born-Oppenheimer Approximation: Theory of Tunneling Ionization of Molecules Revisited, *Phys. Rev. Lett.* **111**, 153003 (2013).
- [32] J. Svensmark, O. I. Tolstikhin, and L. B. Madsen, Coulomb and dipole effects in tunneling ionization of molecules including nuclear motion, *Phys. Rev. A* **91**, 013408 (2015).
- [33] J. Svensmark, O. I. Tolstikhin, and L. B. Madsen, Theory of dissociative tunneling ionization, *Phys. Rev. A* **93**, 053426 (2016).
- [34] O. I. Tolstikhin and T. Morishita, Weak-field versus Born-Oppenheimer asymptotics in the theory of tunneling ionization of molecules, *Phys. Rev. A* **95**, 033410 (2017).
- [35] V. H. Trinh, O. I. Tolstikhin, L. B. Madsen, and T. Morishita, First-order correction terms in the weak-field asymptotic theory of tunneling ionization, *Phys. Rev. A* **87**, 043426 (2013).
- [36] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, 9th ed. (Dover, New York, 1972).
- [37] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. A. Jensen, Determinant based configuration interaction algorithms for complete and restricted configuration interaction spaces, *J. Chem. Phys.* **89**, 2185 (1988).
- [38] L. Tao, C. W. McCurdy, and T. N. Rescigno, Grid-based methods for diatomic quantum scattering problems: A finite-element discrete-variable representation in prolate spheroidal coordinates, *Phys. Rev. A* **79**, 012719 (2009).
- [39] X. Guan, K. Bartschat, and B. I. Schneider, Breakup of the aligned H₂ molecule by xuv laser pulses: A time-dependent treatment in prolate spheroidal coordinates, *Phys. Rev. A* **83**, 043403 (2011).
- [40] D. J. Haxton, K. V. Lawler, and C. W. McCurdy, Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules, *Phys. Rev. A* **83**, 063416 (2011).
- [41] T. J. Park and J. C. Light, Unitary quantum time evolution by iterative Lanczos reduction, *J. Chem. Phys.* **85**, 5870 (1986).
- [42] M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, The multiconfiguration time-dependent Hartree (MCTDH) method: A highly efficient algorithm for propagating wavepackets, *Phys. Rep.* **324**, 1 (2000).
- [43] C. M. Oana and A. I. Krylov, Dyson orbitals for ionization from the ground and electronically excited states within equation-of-motion coupled-cluster formalism: Theory, implementation, and examples, *J. Chem. Phys.* **127**, 234106 (2007).
- [44] M. Spanner, S. Patchkovskii, C. Zhou, S. Matsika, M. Kotur, and T. C. Weinacht, Dyson norms in XUV and strong-field ionization of polyatomics: Cytosine and uracil, *Phys. Rev. A* **86**, 053406 (2012).
- [45] H. Akagi, T. Otobe, A. Staudte, A. Shiner, F. Turner, R. Dörner, D. M. Villeneuve, and P. B. Corkum, Laser tunnel ionization from multiple orbitals in HCl, *Science* **325**, 1364 (2009).
- [46] L. Holmegaard, J. L. Hansen, L. Kalhøj, S. L. Kragh, H. Stapelfeldt, F. Filsinger, J. Kupper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, and L. Bojer Madsen, Photoelectron angular distributions from strong-field ionization of oriented molecules, *Nat. Phys.* **6**, 428 (2010).
- [47] P. M. Kraus, O. I. Tolstikhin, D. Baykusheva, A. Rupenyan, J. Schneider, C. Z. Bisgaard, T. Morishita, F. Jensen, L. B. Madsen, and H. J. Wörner, Observation of laser-induced electronic structure in oriented polyatomic molecules, *Nat. Commun.* **6**, 7039 (2015).
- [48] P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horn, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle, and H. J. Wörner, Measurement and laser control of attosecond charge migration in ionized iodoacetylene, *Science* **350**, 790 (2015).
- [49] S. G. Walt, N. Bhargava Ram, A. von Conta, O. I. Tolstikhin, L. B. Madsen, F. Jensen, and H. J. Wörner, Role of multi-electron effects in the asymmetry of strong-field ionization and fragmentation of polar molecules: The methyl halide series, *J. Phys. Chem. A* **119**, 11772 (2015).
- [50] V. P. Majety and A. Scrinzi, Dynamic Exchange in the Strong Field Ionization of Molecules, *Phys. Rev. Lett.* **115**, 103002 (2015).
- [51] L. K. Sørensen, S. Bauch, and L. B. Madsen, The integral screened configuration interaction method, *arXiv:1609.07757*.
- [52] O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, Excitation energies of H₂O, N₂ and C₂ in full configuration interaction and coupled cluster theory, *Chem. Phys. Lett.* **256**, 185 (1996).
- [53] G. C. Wick, The evaluation of the collision matrix, *Phys. Rev.* **80**, 268 (1950).