PHYSICAL REVIEW A **89**, 033412 (2014)

Application of the weak-field asymptotic theory to tunneling ionization of H_2O

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(Received 30 January 2014; published 12 March 2014)

The weak-field asymptotic theory of tunneling ionization in a static electric field is applied to H_2O. The orientation dependence of the ionization rate is studied. The use of polarization-consistent basis sets with up to heptuble-zeta accuracy and variationally optimized exponents improves the asymptotic form of the wave function and allows for an accurate extraction of the structure factor defining the ionization rate. The results are presented based on Hartree-Fock wave functions and density functional theory. The density functional theory reproduces closely the experimental vertical ionization potential. We find that the rate peaks at an angle of 81° between the field and molecular principal inertial axis through the O atom. The predictions for the orientation dependence of the rate are compared to available theoretical results.

DOI: 10.1103/PhysRevA.89.033412 PACS number(s): 32.80.Rm, 33.80.Rv, 42.50.Hz

I. INTRODUCTION

For more than two decades H_2O (D_2O) has served as a test example of the behavior of a nonlinear molecule in strong-field ionization studies. Initially, the investigations focused on ion yields as a function of laser intensity under radiation from a CO_2 (10.6 μm) laser pulse [1,2]. Later, ionization and dissociation pathways were identified in the multiphoton regime using 532-nm light [3]. Strong-field-induced geometry modifications were addressed in Coulomb explosion experiments [4], and the kinetic energy release spectra of H^+ in the breakup of H_2O under intense few-cycle pulses were shown to depend strongly on pulse duration [5]. Theoretically, the strong-field ionization of H_2O was studied with the molecular Ammosov-Delone-Krainov (MO-ADK) model [6] in Ref. [7], the molecular strong-field approximation (MO-SFA) [8,9] in Ref. [10], and by time-dependent density functional theory (DFT) [11], the time-dependent configuration-interaction singles and singles-doubles approach [12], and within the single-active-electron approximation (SAEA) to the time-dependent Schrödinger equation [13–16]. The results of these approaches disagree on which orientation of the molecular principal inertial axis through the O atom that maximizes the ionization yield with respect to the field direction. One of the purposes of the present work is to provide accurate reference data for tunneling ionization of H_2O using the weak-field asymptotic theory (WFAT) within the SAEA [17].

The WFAT describes tunneling ionization of atoms and molecules by an external static electric field F. To leading order in F and within the SAEA, the theory was developed and validated by calculations for model polar molecules and HeH^{2+} by the authors of Ref. [17]. The techniques for calculating the rate for general molecules in the frozen-nuclei approximation were developed by the authors of Refs. [18,19]. This basic theory was applied to the analysis of experimental photoionization spectra in Refs. [20–22]. In Ref. [23] the theory was extended to include the first-order correction terms in F. The comparison with exact results for atoms within the SAEA showed that these terms extend the region of applicability of the WFAT at the quantitative level toward stronger fields, practically up to the boundary between tunneling and over-the-barrier ionization regimes. Very recently, extensions of the WFAT to account for the effects of nuclear motion were considered [24,25] and a generalization to many-electron systems in the frozen-nuclei approximation was developed [26].

The WFAT expression for the ionization rate factors to the leading order in F into two terms. One term is the field factor that depends on the field and the vertical ionization potential of the system. The ionization potential difference between ionization into the cationic ground state and an excited state is typically several electron volts, and this leads to a strong preference for ionization into the cationic ground state. In the SAEA and Hartree-Fock approximation, this corresponds to ionization from the highest-occupied molecular orbital (HOMO), and the HOMO is taken as the active orbital in the rest of this work. The other term in the WFAT ionization rate expression is the structure factor that depends on the asymptotic form of the HOMO and its dipole moment, and this is what defines the orientation dependence. Hence, an accurate description of the tail of the HOMO is essential for a reliable evaluation of the tunneling dynamics.

Obtaining an accurate asymptotically correct (exponential) long-range behavior of the HOMO is difficult with standard quantum chemistry basis set methods. Standard basis sets employ Gaussian functions which individually have an incorrect long-range behavior. An expansion in a large set of Gaussian basis functions formally allows a description of an exponential decay, but the wave-function tail contributes energetically not enough to give proper weights to the long-ranged Gaussian functions in self-consistent field calculations [19]. Numerical grid-based HF calculations are possible for diatomic systems, and they are capable of providing an accurate description of the wave-function tail [18,27], and have been used in connection with WFAT to the leading order in F [18]. Grid-based calculations are, however, limited to diatomic systems, and for larger molecules it is necessary to resort to basis-set methods. In Ref. [19] a systematic study of the possibility for reproducing the asymptotic tail of the HOMO in calculations with Gaussian basis sets was performed for the linear molecules CO_2 and OCS. While standard basis sets lead to an unpredictable oscillating behavior, it was established that the explicit optimization of all basis-set exponents in connection with the polarization consistent (pc) basis sets up to pentuble zeta quality allowed a systematic improvement of the description of the tail region of the HOMO. In the present work, we extend the application of the WFAT to the nonlinear water molecule and extract the structure factors needed for the evaluation of the ionization rate from results with pc basis sets up to heptuble-zeta quality. We, in addition, compare the results obtained at the HF level to those from DFT, where in the latter case the HOMO energy can be tuned to match the experimental ionization energy.

The paper is organized as follows. In Sec. II, the formulas needed for the evaluation of the WFAT are summarized. In Sec. III the methodology is presented. In Sec. IV results are given for the structure factors, the associated structure coefficients and the orientation dependent rate. Section V concludes.

II. WEAK-FIELD ASYMPTOTIC THEORY

In this section, we summarize the formulas needed to evaluate the WFAT tunneling ionization rate from the HOMO to the leading order in F [17]. The formulas are also given in Ref. [18], and for the particular case of linear molecules in Ref. [19], but included here for completeness. We choose a geometry where the external electric field $\mathbf{F}$ is pointing in the positive direction of the z axis of the laboratory frame, so $\mathbf{F} = F\mathbf{e}_z$ with $F > 0$, while the molecule can be rotated with respect to the laboratory frame. Let $\mathbf{r}$ and $\mathbf{r}' = \hat{R}\mathbf{r}$ be the coordinates of the HOMO measured from the center of mass of the molecule in the laboratory and the molecular frame, respectively, where $\hat{R}$ describes a rotation between the two frames. The rotation is parameterized by the three Euler angles (α,β,γ), where α is the angle of rotation around the laboratory z axis $[(x,y,z) \to (x_1,y_1,z)]$, β is the angle of rotation around the intermediate y_1 axis $[(x_1,y_1,z) \to (x_1',y_1,z')]$, and γ is the angle of rotation around the molecular z' axis $[(x_1',y_1,z') \to (x',y',z')]$ [28]. Since the field is axially symmetric in the laboratory frame, the ionization rate does not depend on α, and can be assigned a fixed value $\alpha = 0$. The orientation of the molecule is therefore determined by the angles $\beta \in [0,\pi]$ and $\gamma \in [0,2\pi]$. The ionization rate can be obtained from the field-free orbital energy $E_0 < 0$, the orbital $\psi_0(\mathbf{r}')$, and the dipole moment $\boldsymbol{\mu}'$ of the HOMO in the molecular frame, where (atomic units are used throughout)

$$\boldsymbol{\mu}' = -\int \psi_0^*(\mathbf{r}')\mathbf{r}'\psi_0(\mathbf{r}')\,d\mathbf{r}'. \tag{1}$$

The corresponding orbital and dipole moments in the laboratory frame are $\psi_0(\hat{R}\mathbf{r})$ and $\boldsymbol{\mu} = \hat{R}^{-1}\boldsymbol{\mu}'$.

The ionization rates of atoms and molecules in the SAEA can be calculated numerically for arbitrary values of the field F by the method of adiabatic expansion in parabolic coordinates (ξ,η,φ) [17,23,29,30]. For weak fields the problem can be treated analytically by the WFAT. The region where the WFAT applies is defined by [23]

$$F \ll F_c \approx \frac{\varkappa^4}{8|2Z - \varkappa(2n_\xi + |m| + 1)|}, \tag{2}$$

with F_c the boundary between the tunneling and overbarrier regimes of ionization, $\varkappa = \sqrt{2|E_0|}$, Z the charge in the Coulomb tail of the one-electron potential, and (n_ξ,m) parabolic quantum numbers. The condition of Eq. (2) guarantees that the leading-order approximation in F is accurate [17,23,30].

The total ionization rate in the weak-field limit is given by [17]

$$\Gamma(\beta,\gamma) = \sum_{n_\xi=0}^{\infty}\sum_{m=-\infty}^{\infty}\Gamma_{n_\xi m}(\beta,\gamma) + O(\Gamma^2), \tag{3}$$

where $\Gamma_{n_\xi m}(\beta,\gamma)$ is the partial rate for ionization into a channel specified by (n_ξ,m). The asymptotics of $\Gamma_{n_\xi m}(\beta,\gamma)$ for $F \to 0$ has the form [17]

$$\Gamma_{n_\xi m}(\beta,\gamma) = \left|G_{n_\xi m}(\beta,\gamma)\right|^2 W_{n_\xi m}(F)[1 + O(F)], \tag{4}$$

where $G_{n_\xi m}(\beta,\gamma)$ is the structure factor

$$G_{n_\xi m}(\beta,\gamma) = \lim_{\eta\to\infty} G_{n_\xi m}(\beta,\gamma,\eta), \tag{5}$$

given by the asymptotic value of the structure function

$$G_{n_\xi m}(\beta,\gamma,\eta) = e^{-\varkappa\mu_z}\eta^{1+|m|/2-Z/\varkappa}e^{\varkappa\eta/2} \times \int_0^{\infty}\int_0^{2\pi}\phi_{n_\xi|m|}(\xi)\frac{e^{-im\varphi}}{\sqrt{2\pi}}\psi_0(\hat{R}\mathbf{r})\,d\xi\,d\varphi, \tag{6}$$

and $W_{n_\xi m}(F)$ is the field factor

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

Here μ_z is the z component of $\boldsymbol{\mu}$, and $\phi_{n_\xi|m|}(\xi)$ is a parabolic channel function

$$\phi_{n_\xi|m|}(\xi) = \varkappa^{1/2}(\varkappa\xi)^{|m|/2}e^{-\varkappa\xi/2}\sqrt{\frac{n_\xi!}{(n_\xi+|m|)!}}L_{n_\xi}^{(|m|)}(\varkappa\xi), \tag{8}$$

where $L_n^{(\alpha)}(x)$ are the generalized Laguerre polynomials [31]. Equation (4) shows that the partial rate $\Gamma_{n_\xi m}(\beta,\gamma)$ in the leading-order approximation factorizes into two factors, one of which depends only on the orientation angles β,γ and the other only on the field F. The orientation-dependent structure factor $G_{n_\xi m}(\beta,\gamma)$ is the most important characteristic and it can be extracted from the HOMO by the procedure described in Ref. [19]. The dependence on β and γ is contained in μ_z and $\psi_0(\hat{R}\mathbf{r})$ in Eq. (6). The field factor $W_{n_\xi m}(F)$ is a simple analytical function which depends on the molecule only via Z and $\varkappa$. We emphasize that $G_{n_\xi m}(\beta,\gamma)$, and hence $\Gamma_{n_\xi m}(\beta,\gamma)$, are invariant under translations of the coordinate origin of the HOMO [17], as they should be.

The different channels (n_ξ,m) have different powers of F in Eq. (7). For frozen nuclei, and in the leading-order approximation, where the correction $O(F)$ in Eq. (4) is neglected, one can retain only the dominant term in Eq. (3) which corresponds to the channel with the smallest values of

n_ξ and m. For H_2O the dominating channel is $(n_\xi,m) = (0,0)$. When nuclear motion is included, the WFAT restructures and for each electronic channel the channels associated with the nuclear degrees of freedom should be included in the expression for the rate [25].

The structure factor $G_{n_\xi m}(\beta,\gamma)$ for the dominant channel as a function of the orientation angles β and γ can be expanded in terms of an appropriate set of standard functions. This compresses the information needed for applications and facilitates the exchange between researchers. We first note that the bound-state wave function $\psi_0(\mathbf{r})$ can always be chosen to be real, which leads to Eq. (9)

$$G_{n_\xi,-|m|}(\beta,\gamma) = G^*_{n_\xi,|m|}(\beta,\gamma). \tag{9}$$

The structure factors $G_{n_\xi m}(\beta,\gamma)$ can, in the general case of nonlinear molecules, be expanded as in Eq. (10)

$$G_{n_\xi m}(\beta,\gamma) = \sum_{lm'} C^{(lm')}_{n_\xi m} Y_{lm'}(\beta,\gamma), \tag{10}$$

where

$$Y_{lm}(\beta,\gamma) = \Theta_{lm}(\beta)\,\frac{e^{im\gamma}}{\sqrt{2\pi}} \tag{11}$$

are spherical harmonics and $\Theta_{lm}(\beta)$ is given in terms of the associated Legendre polynomials $P_l^m(x)$ by

$$\Theta_{lm}(\beta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}\,P_l^m(\cos\beta). \tag{12}$$

We use the Condon-Shortley [32] phase convention for $\Theta_{lm}(\beta)$, i.e.,

$$\Theta_{l-m}(\beta) = (-1)^m \Theta_{lm}(\beta). \tag{13}$$

The structure factor for the dominant channel $G_{00}(\beta,\gamma)$ is real, leading to Eq. (14)

$$C^{(l-m')}_{00} = (-1)^{m'} C^{(lm')*}_{00}. \tag{14}$$

The *structure coefficients* $C^{(l)}_{n_\xi m}$ in the expansion of Eq. (10) can be tabulated for the molecules under investigation and used for calculating the structure factors $G_{n_\xi m}(\beta,\gamma)$. Given these coefficients, the application of the WFAT becomes straightforward.

III. METHODOLOGY

The asymptotic behavior of the HOMO $\psi_0(\hat{R}\mathbf{r})$ at large η is the key quantity for the application of WFAT [see Eqs. (5) and (6)]. Grid-based HF codes are limited to diatomic systems and we here employ a basis-set quantum chemistry approach using the pc basis sets. These basis sets have been designed and optimized for DFT, which have very similar basis-set requirements as HF, and are available in five different quality levels from (unpolarized) double zeta to (polarized) pentuble zeta quality (pc-n, $n = 0$–4) [33]. It has been shown that these basis sets are capable of reproducing grid-based numerical HF energies for diatomic systems to micro-Hartree accuracy [34]. In the present work we have extended the basis sets to hextuble and heptuble zeta quality (pc-5 and pc-6) which allow the calculation of total energies to nano-Hartree accuracy. All basis sets in the present work have been used in their uncontracted forms and variationally optimized with respect to all basis-set exponents. Analytical gradients of the HF or DFT energy with respect to basis function exponents have been calculated with the DALTON program [35]. Basis exponent optimizations have been done using a pseudo-Newton-Raphson method. The starting values were taken from the standard pc-n basis sets [33]. In Ref. [19] it was shown that this procedure greatly improves the asymptotic behavior of the wave function at the HF level of theory. Here, the methodology is furthermore extended to DFT, which can be tuned such that the HOMO energy matches the experimental ionization potential, which should ensure a more accurate asymptotic behavior than HF. We have here used a molecular specific Coulomb-attenuating method Becke three-parameter Lee-Yang-Parr (CAM-B3LYP) [36] DFT functional, which employs a range-separated exchange functional. The range-separated exchange functional switches from a Becke density functional to pure HF exchange as a function of the interelectronic distance using an error function as the interpolating function. The error function switching is controlled by a range parameter which we have chosen such that the DFT HOMO energy reproduces the experimental ionization potential [37].

IV. RESULTS AND DISCUSSION

We now turn to a discussion of our results. In all calculations the nuclei are frozen in the molecular fixed $y'z'$ plane at the positions H: $(x',y',z') = (0,1.43143164,-0.886665171)$, H: $(x',y',z') = (0,-1.43143164,-0.886665171)$, and O: $(x',y',z') = (0,0,0.221666765)$. The orientation of the molecule with respect to the laboratory-fixed z axis defined by the direction of the electric field is specified by the Euler angles β and γ (see Sec. II).

Table I shows the convergence of the HF and DFT HOMO energies and dipoles [Eq. (1)] as a function of the basis-set quality, pc-n ($n = 1,\ldots,6$). These quantities are converged to at least six digits with the optimized pc-6 basis set. The DFT result are tuned (see Sec. III) such that the HOMO energy reflects the experimental ionization potential. The asymptotic long-range behavior of any wave function within HF or DFT is determined by the HOMO energy. Because of the more

TABLE I. Convergence properties of the HF ($E^{\text{HF}}_{\text{HOMO}}$, $\boldsymbol{\mu}'^{\text{HF}}_{\text{HOMO}}$) and DFT ($E^{\text{DFT}}_{\text{HOMO}}$, $\boldsymbol{\mu}'^{\text{DFT}}_{\text{HOMO}}$) HOMO energies and dipoles for H_2O using optimized pc-n basis sets. $\hat{\mathbf{z}}'$ is a unit vector in the direction of the molecular z' axis through the O atom. The nuclei are fixed at H: $(x',y',z') = (0,1.43143164,-0.886665171)$; H: $(x',y',z') = (0,-1.43143164,-0.886665171)$; and O: $(x',y',z') = (0,0,0.221666765)$. The experimental ionization potentials are -0.4634 [40], -0.4630 [41], and -0.46386 [42].

pc-n	$E^{\text{HF}}_{\text{HOMO}}$	$E^{\text{DFT}}_{\text{HOMO}}$	$\boldsymbol{\mu}'^{\text{HF}}_{\text{HOMO}}$	$\boldsymbol{\mu}'^{\text{DFT}}_{\text{HOMO}}$
1	-0.5011915	-0.4524208	$-0.1756614\,\hat{\mathbf{z}}'$	$-0.1683711\,\hat{\mathbf{z}}'$
2	-0.5096242	-0.4631005	$-0.1505280\,\hat{\mathbf{z}}'$	$-0.1410246\,\hat{\mathbf{z}}'$
3	-0.5104304	-0.4641310	$-0.1454070\,\hat{\mathbf{z}}'$	$-0.1350633\,\hat{\mathbf{z}}'$
4	-0.5104643	-0.4641849	$-0.1455538\,\hat{\mathbf{z}}'$	$-0.1352472\,\hat{\mathbf{z}}'$
5	-0.5104686	-0.4641902	$-0.1455675\,\hat{\mathbf{z}}'$	$-0.1352648\,\hat{\mathbf{z}}'$
6	-0.5104687	-0.4641904	$-0.1455675\,\hat{\mathbf{z}}'$	$-0.1352644\,\hat{\mathbf{z}}'$

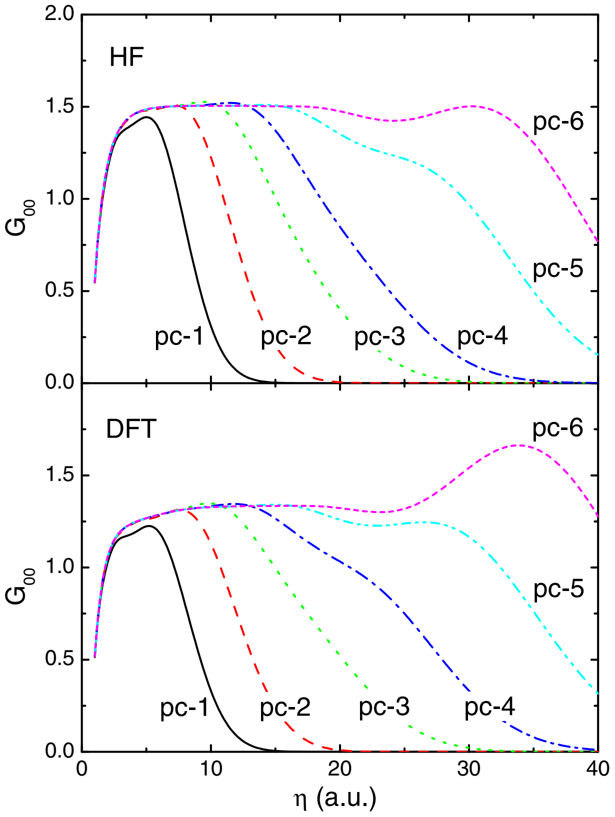

FIG. 1. (Color online) Structure function $G_{00}(\beta = 90^\circ, \gamma = 0^\circ, \eta)$ [Eq. (6)] for the HF and DFT HOMO of H_2O using optimized pc-n basis sets. The nuclei are fixed at the geometry given in the caption of Table I.

accurate HOMO energy, the DFT should be more accurate than the HF results.

We investigate in detail the asymptotic form of the HOMO determining the structure factor of the WFAT. Figure 1 shows the structure function $G_{00}(\beta = 90^\circ, \gamma = 0^\circ, \eta)$ as a function of η for the HF and DFT HOMO of H_2O for optimized basis sets of increasing quality. An accurate representation of the asymptotic form of the HOMO requires that G_{00} attains a constant value at large η as discussed in Sec. II. Figure 1 shows that an onset of a plateau is formed as the quality of the basis is increased, but also that the value of the plateau is different for HF and DFT. The decrease in the G_{00} function for large η values reflects the inadequacy of Gaussian-type basis functions for reproducing the (exact) exponential HOMO fall-off. As the quality of the basis set is improved, the correct exponential behavior is reproduced to increasingly larger η values. The exponent optimization becomes numerically very difficult for the largest pc-5 and pc-6 basis sets, and the small residual exponent gradient results in slight oscillations for large η values. The pc-5 and pc-6 results agree out to $\eta = 15$, and this is the value of η we use to determine the structure factor. We stress that standard basis sets without optimization do not display a plateau region as illustrated and discussed in detail in Ref. [19]. It is hence essential to use the present approach which optimizes the basis-set exponents for each molecule to obtain a reliable asymptotic form of the wave function. The structure factor G_{00} extracted in this way for each orientation can now be expanded in terms of the structure coefficients [Eq. (10)]. Table II gives the HF and DFT coefficients for future reference. As the DFT HOMO energy is tuned to match the experimental ionization potential, the DFT structure factors are the recommended values.

TABLE II. Structure coefficients [Eq. (10)] for the HOMO of H_2O obtained using Gaussian [43] and HF and DFT with an optimized pc-6 basis set. The coefficients are extracted at $\eta = 15$. The structure coefficients $C_{00}^{(lm')}$ are real and equal to zero for even m'. The nuclei are fixed at the geometry given in the caption of Table I. $a[b] = a^b$.

l/m'	1	3	5
	HF		
1	2.235		
2	1.601[−1]		
3	1.403[−2]	−4.087[−2]	
4	−3.718[−4]	−8.582[−3]	
5	−8.869[−5]	−6.330[−4]	4.095[−4]
	DFT		
1	1.984		
2	1.476[−1]		
3	1.211[−2]	−3.602[−2]	
4	−3.096[−4]	−7.053[−3]	
5	−7.430[−5]	−5.212[−4]	2.602[−4]

Figure 2 shows $|G_{00}(\beta,\gamma)|^2$, which according to Eq. (4), gives the orientation dependence of the WFAT ionization rate to leading order in F. The results using HF or DFT differ in absolute value, but the behavior of the results with β and γ is very similar. The figure shows that the molecule is most readily ionized for $\beta \simeq 81^\circ$, and $\gamma = 0^\circ$, 180°, or 360°. These geometries correspond to the cases when the HOMO of H_2O is almost along the field direction. In our geometry the HOMO is a p-like orbital with the p lobes perpendicular to the molecular $y'z'$ plane. When the orientation of the molecule is such that the nodal plane lies in the direction of the field, ionization from the HOMO is suppressed, and lower-lying orbitals contribute [38]. These contributions are suppressed by a factor of $F/(2\varkappa^2)$ and the contribution quickly decays away from the node [18,19]. The offset in the maximal ionization yield from the $\beta = 90^\circ$ geometry is due to the presence of a small dipole of the HOMO. For β slightly smaller than 90°, the dipole has a component antiparallel to the field direction, which lowers the ionization potential, while the major part of the p-like lobes is still in the direction of the field. The shift in the maximum away from 90° can thus be understood as a competition between a geometric charge density effect and the shift of the ionization potential, both of which are accounted for by the structure factor G_{00}.

The MO-ADK model [7] predicts a maximum in the rate at 80° (see Fig. 3 in Ref. [7]). The closeness of this result to our reference value of 81° is accidental since the MO-ADK model does not take into account the presence of the dipole of the HOMO (see Ref. [17] for a detailed discussion of the deficiencies of the MO-ADK model). In Ref. [13], the strong-field ionization of H_2O in 800-nm few-cycle laser pulses was investigated. The approach was a particular realization of the SAEA (see Refs. [14,39]), where all orbitals are evolved independently of each other (see also Ref. [15] for an application to high-order harmonic generation in H_2O). In

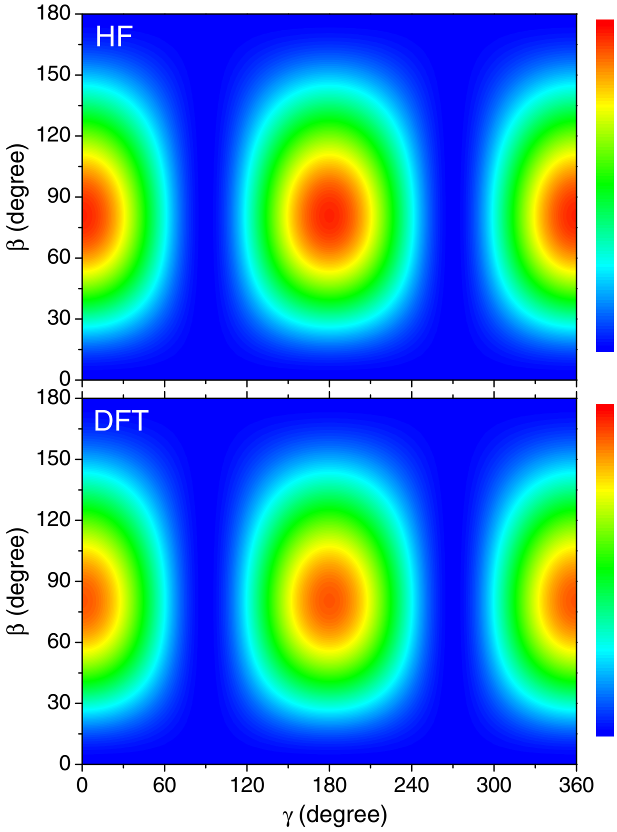

FIG. 2. (Color online) Norm squared of the structure factor $|G_{00}(\beta,\gamma)|^2$ [Eq. (5)] extracted at $\eta = 15$ as a function of γ and β for the HF and DFT HOMO of H_2O using the pc-6 basis set. The nuclei are fixed at the geometry given in the caption of Table I. The angle β represents the angle between the field direction and the principal inertial axis of the molecule going through O. The angle γ represents the angle of rotation around the molecular principle axis.

Ref. [13] it was found that the orbital shape is reflected in the orientation-resolved total ionization yield. In the results there is an indication of a small peak in the rate below 90° (see right panel in Fig. 6 in Ref. [13]), which is consistent with our work and the physical role of the HOMO dipole. Time-dependent DFT calculations have also been performed for H_2O by means of the Voronoi-cell finite difference method (TDVFD) [11]. The ionization probability from the HOMO was considered for $\beta \in [0; 90]$ in Fig. 9 in Ref. [11] and found to peak at 90° in contradiction with our findings. Finally, we mention that the ionization of H_2O by intense laser pulses was recently investigated within the MO-SFA at 800 nm and for a field strength of $F = 0.6$ [10]. That work found a maximal ionization probability from the HOMO for $\beta = 90^\circ$ (see Fig. 7(c) in Ref. [10]). This value can be understood from the geometry of the HOMO, and from the fact that the dipole of the HOMO was not accounted for by the authors of Ref. [10].

V. CONCLUSION

By using a hierarchical sequence of fully optimized basis sets, we show that it is possible to determine the asymptotic behavior of the wave function for the polyatomic water molecule in the form of the HOMO for HF and DFT wave functions with Gaussian basis functions for expanding the molecular orbitals, such that a useful accuracy can be obtained for extracting structure factors, and consequently determine the tunneling rate in the WFAT. The DFT approach is expected to provide the more accurate results because the HOMO energy can be tuned to match the experimental ionization potential, and thus provide the correct asymptotic form of the wave function. Within the SAEA, the present tunneling data provided for H_2O are of unprecedented precision. It will be interesting to see in the future if the inclusion of many-electron effects [26] has an impact on the tunneling ionization of H_2O.

ACKNOWLEDGMENTS

This work was supported by grants from the Danish Center for Scientific Computation, the Danish Natural Science Research Council, the Aarhus University Research Foundation, and an ERC-StG (Project No. 277767 - TDMET). O.I.T. thanks the Russian Foundation for Basic Research for the support through Grant No. 14-02-92110. T.M. acknowledges the support of Grants-in-Aid for scientific research (A), (B), and (C) from the Japan Society for the Promotion of Science.

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