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Beyond the Orbital Shape Correlation of Molecular Tunnel Ionization: Impact of Permanent Polarizability and Higher Parabolic Channels on the Orientation Dependence

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Abstract

Molecular tunnel ionization sets the stage for the subsequent attosecond processes. Therefore, a comprehensive understanding of its dependence on various molecular properties, such as binding energy, wave function shape, dipole moment, and polarizability, is crucial for tailoring attosecond science concepts for scientific and technological applications. While the first three properties have been relatively well understood, the effects of polarizability have not been explored to the same extent in studies of molecular tunnel ionization. To address this gap, in this work we reveal the peak-shifting effect of permanent polarizability in tunnel ionization rates as the ionizing field varies. By analyzing a specially defined rate gradient, we determine the characteristic directions of the shift from the sign of the local slope of the gradient curve. Furthermore, we show how ionization into higher parabolic channels can transform minima of orientation-dependent rates into maxima. These findings demonstrate how the common assumption that the orientation dependence of tunneling rates resembles orbital shape can break down. We benchmark the method employed, the weak-field asymptotic theory (WFAT), and demonstrate good agreement with *ab initio* results, underscoring the efficiency and accuracy of WFAT in simulating strong-field ionization at low-to-moderate field strengths.

Keywords: molecular tunnel ionization; strong-field processes; attosecond science

1. Introduction

The progress in attosecond science and technology is directly linked to the development of strong-field lasers—a class of lasers capable of generating electric fields comparable in strength to typical atomic electric fields [1–4]. Such intense electric fields can significantly alter an atom’s electronic configuration and eventually ionize some electrons [5–7]. For long laser wavelengths ($\lambda > 800$ nm), ionization occurs through tunneling, enabling us to “start the clock” to observe ultrafast electron dynamics, a fundamental concept in many attosecond imaging and spectroscopic techniques [8–19]. Once the clock starts, in order to reconstruct the dynamics up until the electron recombines, one needs to have the information on the properties of the ionized electron’s wave function [20–22]. Therefore, a thorough understanding of the dependence of molecular tunnel ionization on the properties of the ionized orbital, such as its shape, binding energy, dipole moment, and polarizability, will allow us to fully exploit tunnel ionization for attosecond science applications.

The impacts of the first three of the aforementioned properties of the ionized orbital on the field and orientation dependence of tunnel ionization rates have been relatively well studied. For instance, binding energy determines the overall magnitude of ionization



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rates [23–27]; orbital shape influences the orientation dependence of tunneling rates [28–30]; and permanent dipole moment affects the relative magnitude of rates between parallel and antiparallel orientations [31–36]. In this work, we focus on the impact of permanent polarizability in molecular tunnel ionization.

Several works have explored the dependence of tunnel ionization on permanent polarizability. For example, Refs. [37,38] demonstrate that the effects of the electrons remaining in the ion are encoded in the system's polarizability and Ref. [39] shows that polarizability can enhance dissociative ionization. In these and the other studies [31,33,34,36,40–42], the general approach is to introduce polarizability as a correction to the ionization potential. Despite these earlier works, to our knowledge, a study explicitly showing how polarizability governs the field and orientation dependence of tunnel ionization has not been conducted. In this work, we will elucidate this relationship in terms of a rate gradient defined as the changes in the orientation dependence of the rate as the field varies.

The specific definition of rate gradient used here enables us to show that polarizability contributes to the shifts of rate maxima as the field varies and to correlate the shift direction with the sign of a local slope of the gradient. Notably, we observe that polarizability primarily influences the tunneling rate by simultaneously shifting the peaks toward both parallel and antiparallel orientations. Beyond polarizability, we also demonstrate the distinct peak-shifting effects of the dipole moment and orbital distortion. Here, orbital distortion refers to field-induced modifications in the shape of the ionized orbital. We choose three families of halogenated molecules—haloacetylenes, dihaloacetylenes, and halomethanes—as platforms to illustrate these peak-shifting effects of dipole moment, polarizability, and orbital distortion.

Our tunnel ionization simulations are conducted using a recent implementation [43,44] of the weak-field asymptotic theory (WFAT), in the integral representation within the NWChem package [45,46]. This implementation supports the integral representations of both one-electron (OE-) and many-electron (ME-) WFAT in explicit [47] and partial-wave frameworks [43,48–51] and has been validated against early WFAT results [52–54], real-time time-dependent density functional theory [43], and time-dependent configuration interaction (TDCI) in bromomethane [55]. In addition to the rate gradient analysis mentioned above, we will also further benchmark our WFAT implementation against TDCI in other halomethanes and haloacetylenes when discussing the minima-to-maxima transforming effect of higher parabolic channels. This effect is relatively common at high field strengths [30,55–57] but often overlooked in molecular tunnel ionization studies [43].

In summary, this paper explores how peaks in tunnel ionization rates shift as the ionizing field varies and how they may emerge from minima as this field becomes stronger, providing insights into situations in which the orbital shape correlation in tunnel ionization no longer holds. We anticipate that our study will be valuable for future strong-field and ultrafast dynamics methods that are sensitive to the choice of orientations that maximize tunneling probabilities and the properties of the electron emitted at these orientations.

The following sections are organized as follows: Section 2 provides an overview of static field ionization, the WFAT, and the derivation of rate gradients. In Section 3, we present our analysis of rate gradients in our target molecules and compare our results with TDCI simulations regarding the effects of higher parabolic channels. The conclusion is presented in Section 4.

2. Theoretical Approach

The rate of ionization of an electron from a molecule is quantum mechanically modeled as an outward flux of one electron traveling at a distance far away (asymptotic distance) from the parent molecular ion. There are several approaches to quantify this asymptotic flux.

In time-dependent settings, such as those involving interaction with laser fields, a common approach is to record the amount of electron flux passing through a predefined absorbing potential wall placed at an asymptotic distance [55,58–62]. In another approach [63–68], the absorption effect is realized by scaling the asymptotic region by a complex factor.

When the field is static, time-independent methods are used; they include the Ammosov–Delone–Krainov (ADK) method [25], its molecular extension—MO-ADK [26,69], complex-variable-based methods [70–72], field-dressed Siegert states (SSs) [73–75], and the WFAT in both tail [35,52,76] and integral representations [43,47,51]. Since strong-field ionization studies are commonly carried out with long-wavelength lasers (longer than 800 nm) and intensities in the order of 10^{13} – 10^{15} W/cm² and we are not concerned with energy dependence, we can approximate the ionization as an adiabatic process and use static (time-independent) ionization theories [77,78].

In the following sections, a summary of ionization theory due to a static field will be given, followed by an overview of the WFAT in the integral representation, derivation of rate gradients, and explanation of higher parabolic channel effects.

2.1. Ionization Due to Static Electric Fields

We consider a molecule at an arbitrary orientation in an electric field directed in the positive z axis. In the event when electron correlation effects in ionization can be neglected, such as when the ionization comes from a weakly correlated valence orbital, we can approximate the original many-electron system as a single-active-electron system. Consequently, the Schrödinger equation in some space-fixed coordinate system, here referred to as the *laboratory frame* (LF), reads

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + Fz\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1)$$

where $V(\mathbf{r})$ is an effective potential describing the net effect of nuclear attraction and electron screening and that reduces to its multipole contributions as $r \rightarrow \infty$ [47,52]. A number of methods exist to numerically solve Equation (1), one of which is based on the Siegert state formulation [73–75], where an outgoing-wave boundary condition is supplied to Equation (1). The WFAT employed in this work constitutes a weak-field approximation to a field-dressed SS; therefore, we shall outline its basic ideas in the present section. The orientation between the molecule and the ionizing field is encoded in the orientation of $V(\mathbf{r})$ and $\psi(\mathbf{r})$ relative to the z axis. Since the ionizing field is uniform over the space, the orientation is characterized by only two rotations and the associated rotation angles, denoted by β and γ . Figure 1 illustrates these rotations for CH₃Br. Briefly, the first rotation rotates the molecule along with a molecule-fixed frame, called the *molecular frame* (MF) (that is, the molecule and the MF are rotated simultaneously) around the LF's y axis. The second rotation rotates the molecule and the MF around z_{MF} . The LF and MF coincide with each other at $\beta = \gamma = 0$, and regardless of β and γ , z_{MF} lies in the xz plane (see Figure 1b).

We are interested in the form of field-dressed SS in the asymptotic (i.e. ionization) region, which, for the field direction specified above, coincides with $z \rightarrow -\infty$. In parabolic coordinates, which allows for a separable solution (to be shown below) [35], this corresponds to $\eta \rightarrow \infty$. In the asymptotic region, we expand the wave function as

$$\psi(\mathbf{r})|_{\eta \rightarrow \infty} = \eta^{-1/2} \sum_{\nu} p_{\nu}(\eta) \Phi_{\nu}(\xi, \varphi), \quad (2)$$

where (η, ξ, φ) are parabolic coordinates, $\nu \equiv (n_{\xi}, m)$ denotes a pair of parabolic quantum numbers [74,75], $\Phi_{\nu}(\xi, \varphi)$ is called parabolic channel function [43,51], and $p_{\nu}(\eta)$ encodes the properties of the ionization rate, as will be shown below. Upon substituting Equation (2)

into the asymptotic form of Equation (1), projecting the resulting equation into a particular Φ_ν , and neglecting infinitely small terms, one obtains a second-order differential equation in η [73–75]. $p_\nu(\eta)$ is the outgoing-wave solution of this equation and can be shown to be directly related to the asymptotic form of the Airy function [51]. An important property of so-obtained $p_\nu(\eta)$ is that it can be factored out into a ν -dependent prefactor and some function of η , that is, $p_\nu(\eta) = f_\nu p(\eta)$ [73–75], which, upon substitution into Equation (2), yields an expression that is separable into η -only and (ξ, φ) -only functions. We note that this separation of Equation (2) is enabled by the use of parabolic coordinates.

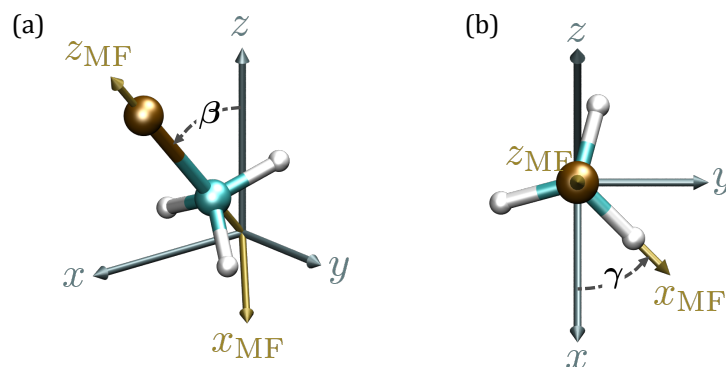


Figure 1. A CH₃Br molecule oriented at (β, γ) in the LF. (a) β is a rotation angle around y . (b) γ is a rotation angle around z_{MF} . Here, the MF consists of molecule-bound coordinate axes and is chosen so that the C–Br bond lies along z_{MF} and one of the BrCH planes coincides with the $x_{MF}z_{MF}$ plane. This MF configuration is used for our halomethanes targets.

Starting from the continuity equation for the part of the field-dressed SS in the asymptotic region, it can be shown that the amount of electron in the inner region changes at a rate of $\Gamma \approx \sum_\nu |f_\nu|^2$ [73]. Since this change is directly associated with a flux of electron leaving the inner region, Γ is the sought total ionization rate [73] and thus, the main objective is to find the expression for the f_ν 's.

2.2. The Weak-Field Asymptotic Theory in the Integral Representation

For arbitrary values of F , f_ν must be computed numerically [73–75]. However, the fields in the lower end of the strong-field regime can still be treated perturbatively within the static field framework, which leads to an analytical expression for the rate, facilitating a transparent view of the various quantities the rate depends on [35,52,79]. The WFAT defines a weak-field approximation to the field-dressed SS, which results in perturbative analytical formulas. In the following, we will present an overview of the OE-WFAT in the integral representation since many-electron effects are not very significant in most of our simulations.

To solve for f_ν through the integral representation of OE-WFAT, one rewrites Equation (1) into its equivalent integral form—the Lippmann–Schwinger equation,

$$\psi(\mathbf{r}) = - \int d^3\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \left(V(\mathbf{r}') + \frac{Z}{r'} \right) \psi(\mathbf{r}'), \quad (3)$$

where Z is the total charge of the ion and $G(\mathbf{r}, \mathbf{r}')$ is a Green's function that satisfies

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} + Fz - E \right) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

Equations (3) and (4) assume the ion to have zero total dipole moment, which can always be realized in the present work since the ions of our target molecules have a net charge of +1. Solving for $G(\mathbf{r}, \mathbf{r}')$ in Equation (4), putting it into Equation (3), and substituting all field-

dependent quantities with their respective perturbation expansion forms (e.g., the orbital and energy would be expanded as $\psi = \psi^{(0)} + F\psi^{(1)} + O(F^2)$ and $E = E^{(0)} + FE^{(1)} + O(F^2)$, respectively), one arrives at an integral expression for $\psi(\mathbf{r})$ valid for weak static fields. Comparing this with Equation (2) gives the sought weak-field integral expression for f_v [47,51], which, up to first order in F (taking $\ln(F)$ as a “constant”), reads

$$f_v \approx f_v^{(\text{as})} + f_v^{(\text{as})} F \left[\frac{A_v}{2} \ln \frac{F}{4\kappa^2} + \frac{1}{2} \left(\tilde{B}_v + 2o_v + \frac{2h_v}{g_v} - i\pi A_v \right) \right], \quad (5)$$

where $\kappa = \sqrt{2|E^{(0)}|}$ and

$$f_v^{(\text{as})} = \sqrt{\frac{\kappa}{2}} \left(\frac{4\kappa^2}{F} \right)^{\beta_v^{(0)}/\kappa} g_v \exp \left[\frac{i\pi}{4} + \frac{i\pi\beta_v^{(0)}}{\kappa} - \kappa\mu_z - \frac{\kappa^3}{3F} \right]. \quad (6)$$

The expressions for $\beta_v^{(0)}$, A_v , $\tilde{B}_v$, and o_v can be found in Ref. [47], while μ_z is the z component of the dipole vector of the unperturbed ionized orbital, $\psi^{(0)}$, in the LF,

$$\mu_z = -\langle \psi^{(0)} | \mathbf{r}_{\text{MF}} | \psi^{(0)} \rangle \cdot \mathbf{P}, \quad (7)$$

where $\mathbf{P} = (-\sin\beta\cos\gamma, \sin\beta\sin\gamma, \cos\beta)^T$ contains transformation coefficients that bring coordinates in the MF to the z coordinate in the LF and the subscript “MF” denotes coordinates in the MF. g_v and h_v contain the structure information of $\psi^{(0)}$ and its first-order distortion, $\psi^{(1)}$, respectively, that are important in determining the orientation dependence of f_v , and thus, the total ionization rate. The computations of g_v and h_v often make up a large fraction of the WFAT procedure since they depend on (β, γ) and involve expensive numerical integrations over the 3D space. Highly efficient methods to get around this by using a partial-wave expansion are formulated in Refs. [48,49] for g_v and more recently in Ref. [43] for h_v . The expressions of g_v and h_v in the partial-wave and the more expensive explicit frameworks can be found in Appendix A.

The use of perturbation expansions above induces similar field-based expansion for Γ_v . The lowest (or leading-order) term of this expansion, $\Gamma_v^{(0)}$, results from retaining up to only the first term in the right-hand side of Equation (5),

$$\Gamma_v^{(0)} = |f_v^{(\text{as})}|^2 = W_v(F) |G_v|^2, \quad (8)$$

where $G_v = e^{-\kappa\mu_z} g_v$ is called *structure factor* and depends on the field-free orbital shape $\psi^{(0)}$, and

$$W_v(F) = \frac{\kappa}{2} \left(\frac{4\kappa^2}{F} \right)^{2\beta_v^{(0)}/\kappa} \exp \left(-\frac{2\kappa^3}{3F} \right) \quad (9)$$

is called *field factor*. We see that the leading-order tunneling rate features a permanent dipole component μ_z as an argument of an exponential prefactor of G_v . For linear molecules affixed to the z axis of the MF, $\mu_z = -\langle \psi^{(0)} | z_{\text{MF}} | \psi^{(0)} \rangle \cos\beta$; thus, in linear molecules (and more generally also in long molecules), permanent dipole moments mainly affect the relative size of the lobes between parallel and antiparallel orientations [35].

In the leading order, we see that permanent polarizability is absent in the tunneling rate. Indeed, it first appears in the first-order correction to the rate formula. To include this correction, one takes the squared magnitude of the entire terms in Equation (5) and discards terms that depend on the second power of F or higher,

$$\Gamma_v^{(1)} = W_v(F) \left(|G_v|^2 \left(1 + A_v F \ln \frac{F}{4\kappa^2} + \tilde{B}_v F + 2Fo_v \right) + 2F \text{Re}[G_v^* H_v] \right), \quad (10)$$

where $H_v = e^{-\mu_z} h_v$. Since h_v depends on $\psi^{(1)}$ [43], H_v embodies the correction to the tunneling rate due to orbital distortion. It is important to mention that orbital distortion can also be incorporated into molecular tunnel ionization as the time dependence of an adiabatic ground state driven by the field in a strong-field approximation framework [80].

Polarizability enters Equation (10) through $\tilde{B}_v$ as α_{zz} —the polarizability component for the perturbation and response in the z direction of the LF [43,47]. Other than that, $\tilde{B}_v$ contains one term quadratic in μ_z , and, along with A_v and o_v , also contain terms that are linear in μ_z [43,47]. α_{zz} is explicitly given by

$$\alpha_{zz} = \mathbf{P}^T \cdot \boldsymbol{\alpha}_{\text{MF}} \cdot \mathbf{P}, \quad (11)$$

where $\boldsymbol{\alpha}_{\text{MF}}$ is the polarizability tensor in the MF and is a 3×3 symmetric matrix whose elements are given by

$$\alpha_{\text{MF},ss'} = -2 \sum_{i; \psi_i^{(0)} \notin \mathcal{D}[\psi^{(0)}]} \frac{\langle \psi^{(0)} | q_s | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} | q_{s'} | \psi^{(0)} \rangle}{E^{(0)} - E_i^{(0)}}, \quad (12)$$

where $q_s \in [x_{\text{MF}}, y_{\text{MF}}, z_{\text{MF}}]$, $\psi_i^{(0)}$ and $E_i^{(0)}$ are the eigenstates and eigenvalues of Equation (1) when $F = 0$, and the sum runs over all of these eigenstates except for a few states within $\mathcal{D}[\psi^{(0)}]$ —the degenerate subspace of the ionized orbital. In particular, for linear molecules, $\boldsymbol{\alpha}_{\text{MF}}$ is diagonal, which gives $\alpha_{zz} = (\alpha_{\text{MF},xx} \cos^2 \gamma + \alpha_{\text{MF},yy} \sin^2 \gamma) \sin^2 \beta + \alpha_{\text{MF},zz} \cos^2 \beta$.

Equation (10) suggests that the roles of permanent dipole, permanent polarizability, and orbital distortion in the first-order correction to the tunneling rate are more complicated than those of permanent dipole in the zeroth order. In Section 3, with the help of rate gradients introduced next, we will elucidate how exactly these quantities affect tunneling rates. We note here that permanent dipole, permanent polarizability, and orbital distortion may also have some effects in the higher-order correction terms beyond the first one. However, as has been shown in Ref. [81] for hydrogen, these higher-order corrections are significant only for field strengths approaching the over-the-barrier field [54,81].

2.3. Rate Gradients

In the zeroth-order, the WFAT tunneling rate formula (Equation (8)) is separable into field-only and orientation-only factors. Thus, as the field increases, only the overall magnitude increases, while the orientation dependence remains the same. When the first-order correction is taken into account, the rate formula has a factor in which the field and orientation dependences are coupled, namely, the terms in the parentheses in Equation (10), which makes the shape of the rate curve field-dependent. To study these field-induced changes in the shape of tunneling rate curves, we introduce a rate gradient $M(\beta, \gamma, F)$ defined to be the first partial derivative of the orientation-dependent part of the first-order corrected rate formula, $\Gamma_v^{(1)}$, with respect to F ,

$$M(\beta, \gamma, F) = \frac{\partial}{\partial F} \frac{\Gamma_v^{(1)}(\beta, \gamma, F)}{W_v(F)} = M_{\text{fr}}(\beta, \gamma, F) + M_{\text{in}}(\beta, \gamma), \quad (13)$$

where

$$M_{\text{fr}}(\beta, \gamma, F) = |G_v|^2 \left[A_v \left(\ln \frac{F}{4\mu^2} + 1 \right) + \tilde{B}_v + 2o_v \right], \quad (14)$$

$$M_{\text{in}}(\beta, \gamma) = 2 \text{Re}[G_v^* H_v]. \quad (15)$$

In the last part of Equation (13), we decompose the gradient into the field-free and field-induced parts. The field-free part, Equation (14), depends on the static properties of the orbital, such as binding energy, permanent dipole moment, permanent polarizability, and parabolic quantum numbers. The field-induced part, Equation (15), contains correction to the tunneling rate due to orbital distortion, which is induced by the field. We can further carry out the following decomposition of M_{fr} ,

$$M_{\text{fr}}(\beta, \gamma, F) = M_{\mu}(\beta, \gamma, F) + M_{\alpha}(\beta, \gamma) + (\beta, \gamma)\text{-independent terms}, \quad (16)$$

where we have extracted all terms that depend on μ_z into M_{μ} and those that depend on α_{zz} into M_{α} , leaving only the terms that are independent of β and γ . By substituting A_v , $\tilde{B}_v$, and o_v with their respective expressions given in Ref. [43], one obtains

$$M_{\mu}(\beta, \gamma, F) = |G_v|^2 \mu_z \left[\left(\frac{2\beta_v^{(0)}}{\varkappa^3} - \frac{2b_2^v}{\varkappa} \right) \left(\ln \frac{F}{4\varkappa^2} + 1 \right) - \frac{\mu_z}{\varkappa} + \frac{1}{\varkappa^2} + \frac{4\beta_v^{(0)}}{\varkappa^3} + 2o_2^v \right], \quad (17)$$

$$M_{\alpha}(\beta, \gamma) = -|G_v|^2 \varkappa \alpha_{zz}, \quad (18)$$

where b_2^v and o_2^v can be found in Ref. [43]. The separation of the dipole and polarizability contributions from the total field-free contribution will help us identify the dominant character of the peak shifts in tunneling rate curves, as will be shown in Section 3.

2.4. Degenerate Ionized Orbitals and Normalization of Gradients

When the ionized orbitals are degenerate, the observed average tunneling rate comprises a comparable amount of electrons ionized from each degenerate orbital. The total theoretical rate can therefore be approximated as the sum of the rates from individual degenerate orbitals. Likewise, we define the gradients of the rate from a set of degenerate orbitals as the sum of the gradients of each degenerate orbital in the set. At the same time, we see that the gradients defined in Equations (14), (15), (17) and (18) depend on G_v or its squared magnitude, which can vary quickly both in shape and magnitude between different molecules. Therefore, we shall normalize the previous definitions of gradient by the structure factor $|G_v|^2$ summed over the degenerate orbitals. Taking into account the above considerations for $M(\beta, \gamma, F)$ gives

$$\overline{M}(\beta, \gamma, F) = \frac{\sum_i M_i(\beta, \gamma, F)}{\sum_i |G_{iv}|^2}, \quad (19)$$

where M_i and $|G_{iv}|^2$ are the gradient (Equation (13)) and structure factors, respectively, of the i -th ionized orbital in the degenerate subspace. The sums in Equation (19) run over degenerate ionized orbitals and should be omitted for non-degenerate orbitals.

We can define the total, structure-factor-normalized versions of the field-free, field-induced, dipole, and polarizability contributions to the rate gradient in an analogous manner as $\overline{M}_{\text{fr}}$, $\overline{M}_{\text{in}}$, $\overline{M}_{\mu}$, and $\overline{M}_{\alpha}$, respectively, where the individual gradients in the numerator are evaluated using the corresponding single-orbital formula. For example, the total, structure-factor-normalized field-free contribution to the gradient is given by

$$\overline{M}_{\text{fr}}(\beta, \gamma, F) = \frac{\sum_i M_{i,\text{fr}}(\beta, \gamma, F)}{\sum_i |G_{iv}|^2}, \quad (20)$$

where $M_{i,\text{fr}}(\beta, \gamma, F)$ is calculated through Equation (14) using the i -th ionized orbital and its properties. In the remainder of this paper, we will refer to the above defined structure-factor-normalized gradient as simply ‘gradient’. As will be evident in Section 3, the normalization by the total structure factor introduced above also makes it possible to unambiguously

identify a feature of the normalized gradient curve that corresponds to a shift of the peak in the rate curve as the field varies.

2.5. Higher Parabolic Channels

In carrying out the summation over the partial rates $\Gamma_\nu = |f_\nu|^2$ to obtain the total ionization rate Γ_{tot} (Section 2.1), one has to ensure that all partial rates with similar magnitudes (in other words, they share a common power of F ; see Equations (8) and (10)) are included. This means that, if $\nu = (0, 0)$ is the dominant channel, which is true in many cases and in most regions of the (β, γ) plane, and is treated with the first-order correction, then the leading-order terms of the $\nu = (0, \pm 1)$ channels must also be included, that is,

$$\Gamma_{\text{tot}} \approx \Gamma_{00}^{(1)} + \Gamma_{0,+1}^{(0)} + \Gamma_{0,-1}^{(0)}. \quad (21)$$

Since we are less concerned with the absolute values, we will normalize the rates with $W_{00}(F)$, the field factor of the dominant channel, for all simulations below. We denote the $W_{00}(F)$ -normalized rates with an overbar, such as $\bar{\Gamma}_{\text{tot}}$. Finally, we sum over the rates from individual degenerate orbitals in the case of degeneracy [48].

3. Results and Discussion

In this section, we will present our simulation results and analyses on a series of haloacetylenes, dihaloacetylenes, and halomethanes, where for the halogen (X) we choose F, Cl, and Br. In Section 3.1, simulation setups and some pertinent parameters are given. In Section 3.2, shifting peaks in ionization rates are analyzed in terms of rate gradients. Section 3.3 discusses the contributions from higher parabolic channels and some benchmarks against tunneling data obtained through ab initio procedures.

3.1. Simulation Setup

We calculated ionization rates and gradients in the following using the implementation of the OE-WFAT(1) in the integral representation available in our development branch of NWChem [44] for all cases except for the benchmark of haloacetylenes, for which we also employ ME-WFAT(0). Since for weak-to-moderate field strengths, tunnel ionization from the HOMO dominates the ionization, we use Hartree–Fock (HF) HOMOs for the ionized orbitals. These HF calculations were performed in the pc-3 basis set [82] for haloacetylenes and dihaloacetylenes and cc-pVTZ [83–85] for halomethanes. While we do not perform basis set convergence tests, this choice of basis sets is sufficient to capture the change of the orientation-dependent behavior of the rates as the field varies and to avoid erroneously large WFAT integrals (Equations (A21) and (A22)), which typically occur when diffuse Gaussian functions are used. For all molecules below, we optimized their geometries using the density functional theory with the B3LYP functional [86–88] and the def2-SVP basis set [89]. The difference in the choice of basis and method to obtain optimized geometries from those used for the orbitals is not critical since tunneling rates only weakly depend on molecular geometry. The orbital binding energies of the ionized orbitals for each molecule are shown in Table 1.

The exact formulation of WFAT is origin-independent; nevertheless, in numerical implementations, one still needs to define the origin. Here, we use the optimal origin, chosen so that the total dipole vector of the Koopman cation is zero [43,48,49]. In this origin, the MF electronic dipole moments of the ionized orbitals are shown in Table 1. The nonzero components of the MF polarizability tensor of the ionized orbitals, calculated through Equations (11) and (12), are origin-independent and also shown in Table 1. For linear molecules such as haloacetylenes and dihaloacetylenes, the polarizability ten-

sors are diagonal, while for halomethanes, for reasons described below, the only nonzero off-diagonal elements are $\alpha_{\text{MF},xz}$ and $\alpha_{\text{MF},zx}$.

Table 1. Orbital binding energies ($E^{(0)}$), and nonzero dipole moment ($\mu_{\text{MF},z} = -\langle \psi^{(0)} | z_{\text{MF}} | \psi^{(0)} \rangle$) and polarizability (α_{MF}) components in the MF of one of the degenerate HOMOs (the ionized orbitals) of each target molecule studied in the present work. All quantities are in atomic units.

Molecule	$E^{(0)}$	$\mu_{\text{MF},z}$	$\alpha_{\text{MF},xx}$	$\alpha_{\text{MF},yy}$	$\alpha_{\text{MF},zz}$	$\alpha_{\text{MF},xz}$
HCCF	−0.41612	−0.35269	1.5858	1.3860	2.5282	0.0
HCCCl	−0.39435	−0.23608	1.4465	1.0757	−29.522	0.0
HCCBr	−0.38516	−0.18941	1.8071	1.0157	−65.376	0.0
FCCF	−0.42456	0.0	1.3870	1.1861	−1.7568	0.0
ClCCCl	−0.38306	0.0	1.3306	0.54588	−69.029	0.0
BrCCBr	−0.37049	0.0	1.8471	0.55598	−160.09	0.0
CH ₃ F	−0.52422	−0.77752	0.57666	−3.4319	−20.184	−2.9563
CH ₃ Cl	−0.43469	−0.84592	0.96295	−1.2599	−13.670	−2.0776
CH ₃ Br	−0.40138	−0.85153	1.7600	−0.69140	−5.8093	−1.0688

In the MF, we align haloacetylenes and dihaloacetylenes so that their molecular axes are aligned along the z axis and the halogen X points in the positive direction. As for halomethanes, we align them so that the $\text{C}-X$ bond is along the z_{MF} axis with the X end pointing in the positive direction, and one of the three XCH planes coincides with the $x_{\text{MF}}z_{\text{MF}}$ plane. In this geometry, $\alpha_{\text{MF},xy}$ vanishes because the orbitals are chosen to be either even or odd with respect to a reflection around the xz plane and the $\langle \psi^{(0)} | x | \psi_i^{(0)} \rangle$ s vanish when the $\langle \psi_i^{(0)} | y | \psi^{(0)} \rangle$ s do not (see Equation (12)). $\alpha_{\text{MF},yz}$ also vanishes for a similar reason.

We run our WFAT simulations within the partial-wave framework, in which g_ν and h_ν are expanded into partial-wave components (see Equations (A11) and (A20)) up to a maximum angular momentum (L_{max}) of 15, except for CH_3F , for which we use the explicit framework. In order to take advantage of the efficiency of the partial-wave framework in the presence of degeneracies, the optimal origin for the correct zeroth-order orbitals must depend weakly on the orientation [43], which is not satisfied in CH_3F . Appendix B gives a more detailed explanation as well as a representative convergence analysis.

We choose the ranges of field strengths for our WFAT results so that they are not too low to observe appreciable first-order effects but also not too high to prevent the rates from becoming strongly negative (unphysical negative rates are possible when G_ν and H_ν are close to zero (see Equation (10)).

3.2. Analysis of Rate Gradients

We will first analyze the role of permanent dipole moment, polarizability, and orbital distortion in the field-and-orientation-dependent behavior of Γ_{00} —the rate of the dominant channel—in the first-order correction.

The first-order corrected, $W_{00}(F)$ -normalized total rate to the dominant $\nu = (0,0)$ channel, $\bar{\Gamma}_{00}^{(1)}$, from the degenerate HOMOs of the three target haloacetylenes for several field strengths are shown in Figure 2b,f,j. For linear molecules oriented in the manner shown in the first column of Figure 2, $\bar{\Gamma}_{00}^{(1)}$ is independent of γ . The zeros of the rates at parallel and antiparallel orientations reflect the nodal plane of the (doubly degenerate) π -type HOMOs of haloacetylenes. The change in the relative heights of the peaks as the field increases is caused by the coupled field-orientation dependence of the first-order correction. We would like to point out that the decreasing magnitude of the rates as the field increases is due to the normalization by the field factor, while the true, unnormalized rates increase with field strength as they should.

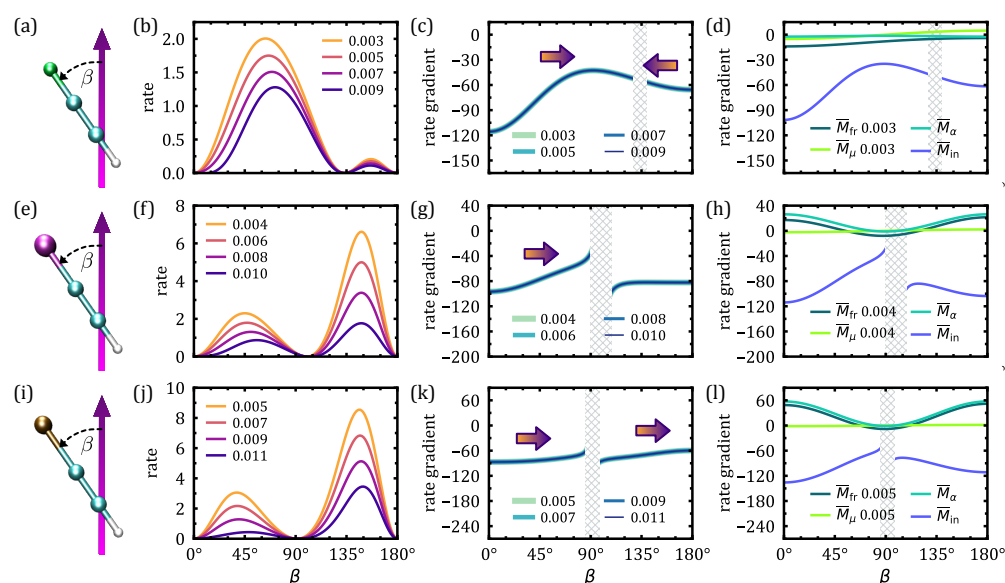


Figure 2. Analysis of the permanent dipole moment, permanent polarizability, and orbital distortion effects in the ionization rates from haloacetylenes. Panels (a–c) show the definition of β , $\bar{\Gamma}_{00}^{(1)}(\beta)$, and $\bar{M}(\beta)$, respectively, for several field strengths of the HOMOs of HCCF. Panel (d) shows the field-free, dipole, polarizability, and orbital distortion contributions to the gradient $\bar{M}(\beta)$ in panel (c). The arrows in panel (c) indicate the direction in which the peak at the corresponding location in panel (b) shifts as the field increases. Panels (e–l) display analogous analyses for HCCl and HCCBr, respectively. The hatched vertical regions mask the region of β where $\bar{M}(\beta)$ and $\bar{M}_{in}(\beta)$ become very sensitive to the accuracy of numerical integrations. In particular, they often diverge within these regions, and thus, are irrelevant for the present analysis.

Upon a closer inspection, the low- and high- β peaks in Figure 2b shift toward $\beta = 90^\circ$ as the field increases. These peak shifts are captured in the slope of the total gradients, shown in Figure 2c, in the same location as the shifting peak in the rate curve. The peak shifts toward the side where the gradient is less negative. Furthermore, Figure 2c shows that the gradients are nearly independent of the field within the simulated field range.

The total gradients in Figure 2c are decomposed into the field-free ($\bar{M}_{fr}$) and field-induced (or orbital distortion) ($\bar{M}_{in}$) contributions in Figure 2d. The dipole ($\bar{M}_{\mu}$) and polarizability ($\bar{M}_{\alpha}$) contributions to $\bar{M}_{fr}$ are also plotted in Figure 2d. We note again that $\bar{M}_{fr}$ and $\bar{M}_{\mu}$ depend on the field while $\bar{M}_{in}$ and $\bar{M}_{\alpha}$ are independent of it. However, since we have seen that the field-dependence of the gradient is negligible, we only show $\bar{M}_{fr}$ and $\bar{M}_{\mu}$ for one of the field values. By comparing Figure 2c,d, we clearly see that the field-induced effects dominate the gradient in HCCF. In HCCl (Figure 2f–h), only the low- β peak exhibits a shift, which moves toward perpendicular orientation. Figure 2h reveals that this shift is caused by orbital distortion effects and that the absence of the shift in the high- β peak is caused by a counteraction between the field-free and orbital distortion effects. In HCCBr (Figure 2j–l), both the low- and high- β peaks shift toward the same direction, but these shifts are small because of the counteraction between the field-free and orbital distortion effects. From Figure 2d,h,l, we can also see that the field-free contribution to the gradient in haloacetylenes is dominated by polarizability effects, which is increasingly stronger from F to Br. This is supported by the increasing $\alpha_{MF,zz}$ in Table 1 as one goes down the rows within the haloacetylenes part, which is consistent with common understanding that polarizability increases with the size of the molecule.

Applying the above gradient analysis on dihaloacetylenes provides a more transparent view of the contribution of permanent polarizability as these molecules have no permanent dipole moments. The second and third columns of Figure 3 reveal that, in dihaloacetylenes,

the peaks shift toward parallel orientations, with an increasing amount of shift from F to Br. Analysis of the various contributions to the gradients in Figure 3h,i further reveals that, in ClCCCl and BrCCBr, these shifts are dominated by the polarizability contributions after having been reduced by orbital distortions, while in FCCF, the shifts predominantly come from orbital distortions as the other contributions are negligible.

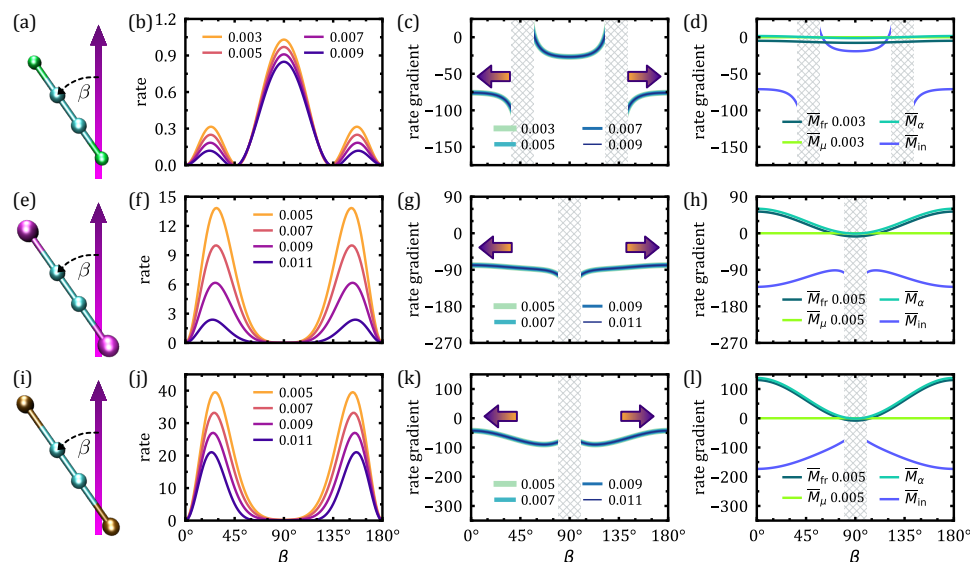


Figure 3. Analysis of the permanent dipole moment, permanent polarizability, and orbital distortion effects in the ionization rates from dihaloacetylenes. Panels (a–c) show the definition of β , $\bar{\Gamma}_{00}^{(1)}(\beta)$, and $\bar{M}(\beta)$, respectively, for several field strengths of the HOMOs of FCCF. Panel (d) shows the field-free, dipole, polarizability, and orbital distortion contributions to the gradient $\bar{M}(\beta)$ in panel (c). Panels (e–l) display analogous analyses for ClCCCl and BrCCBr, respectively. See Figure 2 for the explanation of the arrows and hatched regions.

We note that the polarizability and orbital distortion contributions to the gradient in the case of Cl and Br substitutions in both haloacetylenes and dihaloacetylenes have a positive and negative curvatures, respectively, with a similar magnitude, which then lead to the observed counteraction effects. The sign of the curvature of the polarizability contribution is determined by the sign of α_{zz} (see Equation (18)). However, the sign of the curvature of the orbital distortion contribution is more complicated to determine, and might be correlated with that of the polarizability contribution since similar terms as those in the right-hand side of Equation (12) appear in the first-order correction to the orbital.

Next, we investigate the field dependence of the rates from halomethanes and their gradients. Halomethanes present distinct chemical situations compared to haloacetylenes and dihaloacetylenes. First, their trend of $\alpha_{MF,zz}$ as one goes from F to Br is the opposite to and overall smaller than that in haloacetylenes and dihaloacetylenes (see the $\alpha_{MF,zz}$ column in Table 1). Second, Table 1 also shows that their dipole moments are generally larger than the two preceding families of halogenated molecules. Figure 4 shows the rates and gradients from the three halomethanes studied in the present work as the molecules are rotated around the LF y axis, during which one of the XCH planes remains coincident with the LF xz plane (the plane of the paper; see Figure 4a,e,i). Such orientations correspond to $\gamma = 0^\circ$. The HOMOs of halomethanes are also π -type doubly degenerate orbitals [50,55] with their nodal planes represented by the zeros of the rates at $\beta = 0^\circ$ and $\beta = 180^\circ$ in Figure 4. Due to the symmetry of the molecules, the rates and gradients in Figure 4 are repeated at $\gamma = 120^\circ$ and $\gamma = 240^\circ$.

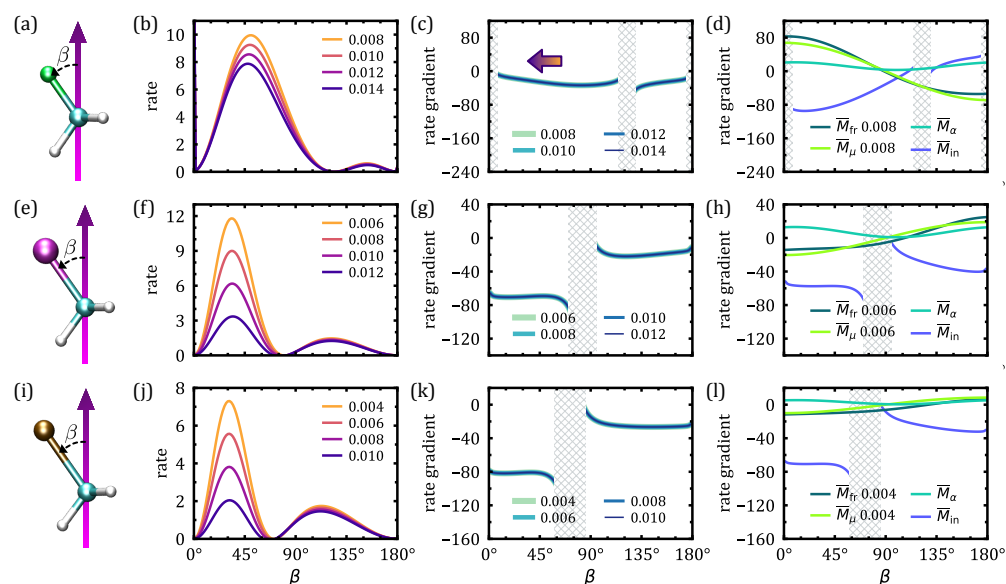


Figure 4. Analysis of the permanent dipole moment, permanent polarizability, and orbital distortion effects in the ionization rates from halomethanes at $\gamma = 0^\circ$. Panels (a–c) show the definition of β , $\bar{\Gamma}_{00}^{(1)}(\beta)$, and $\bar{M}(\beta)$, respectively, for several field strengths of the HOMOs of CH_3F . Panel (d) shows the field-free, dipole, polarizability, and orbital distortion contributions to the gradient $\bar{M}(\beta)$ in panel (c). Panels (e–l) display analogous analyses for CH_3Cl and CH_3Br , respectively. Panels (a,e,i) show how the molecules rotate when γ is maintained at 0° . See Figure 2 for the explanation of the arrows and hatched regions.

Analysis of gradient components in the fourth column of Figure 4 shows that, in halomethanes, $\bar{M}_\mu$ dominates the field-free contribution to the gradient, as opposed to the dominating $\bar{M}_\alpha$ in haloacetylenes and dihaloacetylenes. These permanent dipole contributions are counteracted by orbital distortion contributions (see the fourth columns of Figure 4), leading to the small shift in CH_3F and lack thereof in CH_3Cl and CH_3Br . The slope direction of $\bar{M}_\mu$ in CH_3F is seen to be the opposite to that in the other two halomethanes, although the signs of their $\mu_{\text{MF},z}$ are the same (see Table 1). This is, however, not a discrepancy, since there are multiple factors alongside the dipole moment itself that contribute to $\bar{M}_\mu$ (see Equation (17)).

We note that, however, another set of simulations on halomethanes performed using the pc-3 basis results in more peak shifts in the rates than the present results. Despite this inconsistent presence of peak shifts in different basis sets for halomethanes, we emphasize that the peak-shifting effects of the dipole, polarizability, and orbital distortion revealed in this work are physical phenomena independent of the choice of numerical parameters.

The present study of the gradients of molecular tunneling rates elucidates a hierarchical dependence of the correction orders to the rate on the field-free properties of the ionized orbital. In the leading-order correction, orbital binding energy and dipole moment are the only field-free parameters affecting tunneling rate. The energy determines the overall rate magnitude (see Equations (8) and (9)), while dipole moment affects the relative magnitude of the rate at parallel and antiparallel orientations [35]. In the first-order correction, polarizability tensor enters the rate formula. Along with the already present dipole moment and energy, polarizability causes the peaks in the rate to shift in a direction determined by its sign. Since this is the lowest order in which the polarizability appears, peak-shifting is the most prominent effect it has on tunneling rates. Therefore, by including the second-order correction to the tunneling rate, one could study how the rate is modified and what the roles of hyperpolarizabilities are in these modifications. For each of the above correction orders, the field-free orbital shape and its corrections also contribute to the type of modifications introduced in that correction order.

3.3. Contributions of Higher Parabolic Channels

In the previous section, we have seen and analyzed how permanent dipole, permanent polarizability, and orbital distortion affect the evolution of peak positions in the tunnel ionization rates to the dominant parabolic channel as the field varies. However, the total rate can also receive sizable contributions from the next-to-dominant channels, and for the molecules studied in the present work, these are the $\nu = (0, \pm 1)$ channels. The total rates are then calculated through Equation (21).

We compare the total rates with and without the contributions from the $\nu = (0, \pm 1)$ channels in HCCF, HCCCl, and HCCBr in Figures 5a, 5b and 5c (plotted in polar graphs), respectively. The similarity between the curves on the left and right halves of each polar graph for all simulated field strengths show that higher parabolic channels are negligible in haloacetylenes. Prior strong-field ionization studies on haloacetylenes can be found in Ref. [56], in which the TDCI is employed to propagate the wave function. Comparing our WFAT results with those in Ref. [56] (see Figures 2–4 therein), a good agreement is achieved in the case of HCCF, while for HCCCl and HCCBr, our WFAT calculations produce strongly disproportionate ratios between the low- and high- β lobes compared to the TDCI results even if the first-order correction is included. Nevertheless, our results exhibit a larger increase of the rates with increasing field strength near $\beta = 180^\circ$ compared to that near $\beta = 0^\circ$, which is attributable to the contributions from higher parabolic channels. This behavior agrees with TDCI results in Ref. [56] (see Figures 3d and 4d therein).

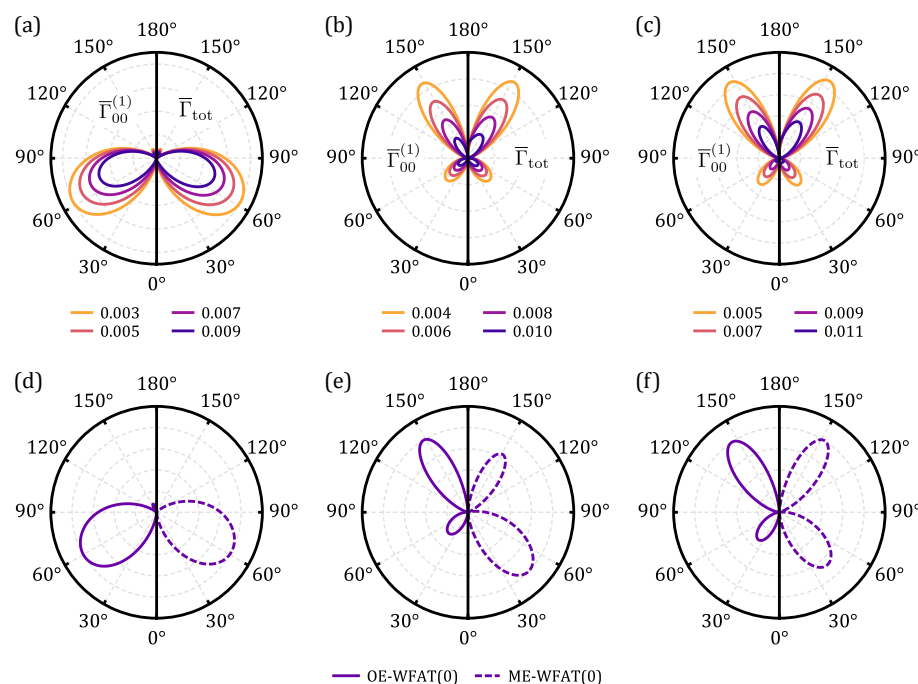


Figure 5. Ionization rates as a function of β in our target haloacetylenes. Panels (a–c) compare $\bar{\Gamma}_{00}^{(1)}$ (no $\nu = (0, \pm 1)$ contributions, left half) and $\bar{\Gamma}_{\text{tot}}$ (right half) for HCCF, HCCCl, and HCCBr, respectively. Panels (d–f) compare $\bar{\Gamma}_{00}^{(0)}$ calculated by OE-WFAT(0) (left half) and ME-WFAT(0) (right half) for HCCF, HCCCl, and HCCBr, respectively. These $\bar{\Gamma}_{00}^{(0)}$ curves are normalized so that their maximum is unity.

To investigate the source of the discrepancy between our OE-WFAT results and TDCI, we perform ME-WFAT(0) calculations of $\bar{\Gamma}_{00}^{(0)} = \sum_i |G_{iv}|^2$ for our target haloacetylenes and compare them with the OE-WFAT(0) results in Figure 5d–f. The two methods are in good agreement for HCCF (Figure 5d), but exhibit markedly different orientation dependence for the other two haloacetylenes (Figure 5e,f). In particular, the low- and high- β lobes have comparable magnitudes in the ME-WFAT(0) results, which are closer to the TDCI

counterparts. In performing our ME-WFAT(0) simulations, we use HF determinants for both the neutral and cation wave functions. Thus, this finding suggests that orbital relaxation effects play a significant role in the tunnel ionization from haloacetylenes [50,51]. Further improvement may be made by including first-order corrections to the above ME-WFAT(0) results, which is a subject of future study.

The total rates from the HOMOS of our dihaloacetylenes targets are shown in Figure 6. In this case, similar to haloacetylenes, the contributions of higher parabolic channels in the case of F and Br substitutions remain diminutive compared to the dominant channel. However, this contribution is enhanced when the substitute is Cl, as can be seen from the disappearing minima in the rate at parallel orientations for $F = 0.011$ in Figure 6b.

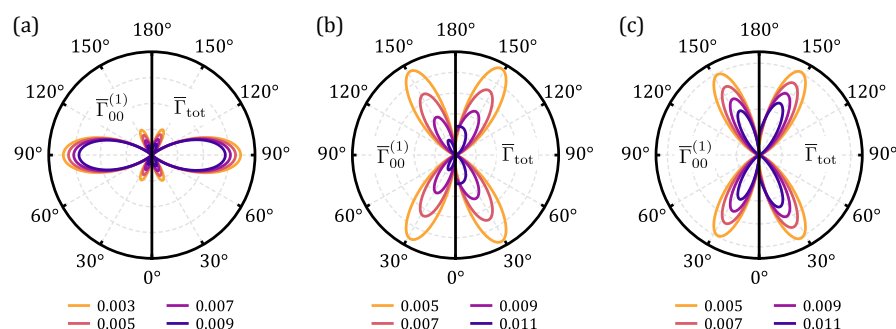


Figure 6. Ionization rates as a function of β in our target dihaloacetylenes. Panels (a–c) compare $\bar{\Gamma}_{00}^{(1)}$ (left half) and $\bar{\Gamma}_{\text{tot}}$ (right half) for FCCF, ClCCl, and BrCCBr, respectively.

The total rates as a function of β at $\gamma = 0$ from the HOMOs of our target halomethanes are shown in Figure 7a–c, which display negligible contributions from higher parabolic channel in CH_3F but significant ones in CH_3Cl and CH_3Br . In the latter two cases, the minima at parallel orientation transform into maxima at high field strengths. Since the rates from halomethanes also change with γ , it is illuminating to also inspect how higher parabolic channel effects manifest in the γ -dependence of the rates. Figure 7d–f show the rates from CH_3F , CH_3Cl , and CH_3Br , respectively, at two different values of β , which roughly correspond to the maxima of the two lobes in $\beta < 90^\circ$ and $\beta > 90^\circ$ in Figure 7a–c. Both rate slices at the low- β and high- β lobes exhibit a threefold rotational symmetry, inverted from each other at low field strengths. As the field increases, the symmetry of the rates at the low- β lobe in CH_3Cl and CH_3Br gradually transforms to that of the high- β lobe. Due to the negligible contribution of higher parabolic channels in CH_3F , no symmetry changes are observed in this molecule.

As we have seen, contributions from higher parabolic channels can transform minima associated to a nodal plane in the ionized orbital into maxima, destroying the correlation between orbital shape and the orientation-dependence of the tunnel ionization rate from that orbital. The parabolic channel function $\Phi_{0,\pm 1}(\xi, \varphi)$ has a π -type dependence on φ [35,47,74,75], which aligns perfectly with the π -type HOMOs when $\beta = 0^\circ$ and $\beta = 180^\circ$, leading to maxima in $\Gamma_{0,\pm 1}$ at these orientations. On the other hand, the leading channel's $\Phi_{00}(\xi, \varphi)$ has a σ -type dependence, which leads to zeros along the nodal planes of π -type orbitals. Since $\Gamma_{0,\pm 1}$ increases faster with F than Γ_{00} (consider the corresponding field factors; Equation (9)), at some point as F increases, the maxima of $\Gamma_{0,\pm 1}$ begin to emerge in the total rate at the orientations where $\Gamma_{00} = 0$.

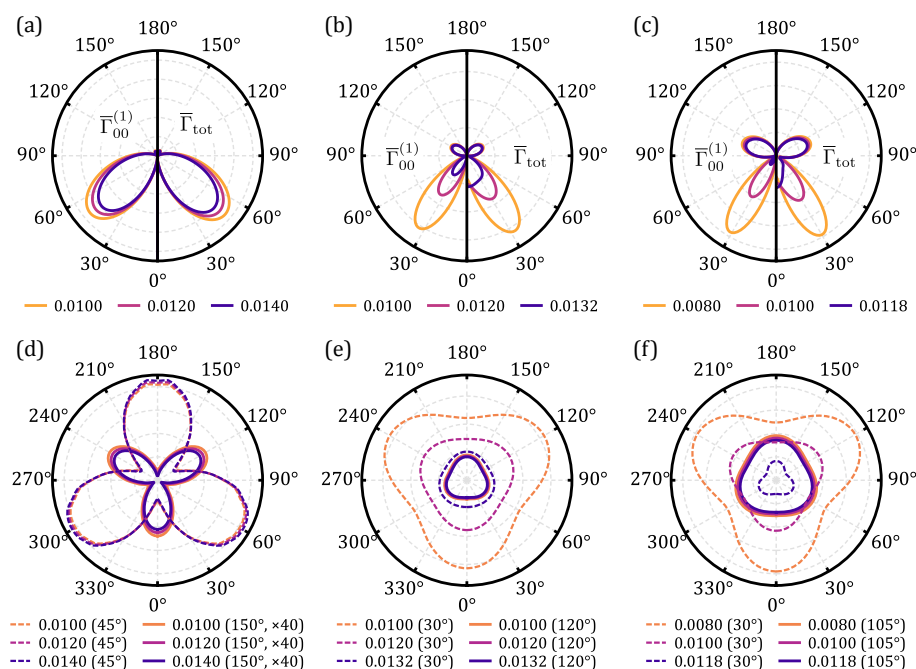


Figure 7. Ionization rates as a function of β and γ in our target halomethanes. Panels (a–c) compare $\bar{\Gamma}_{00}^{(1)}$ (left half) and $\bar{\Gamma}_{\text{tot}}$ (right half) at $\gamma = 0^\circ$ for CH_3F , CH_3Cl , and CH_3Br , respectively. Panels (d–f) show the γ -dependent total ionization rates $\bar{\Gamma}_{\text{tot}}$ from CH_3F , CH_3Cl , and CH_3Br , respectively, at the indicated values of β for several field strengths. Note that the rates at $\beta = 150^\circ$ in panel (d) (solid lines) have been multiplied by 40 to enhance visibility.

The field-driven minima-to-maxima transformation in the orientation dependence of molecular tunnel ionization rates has been observed in experiments and simulations on halomethanes [55–57]. We compare the total rates calculated by the WFAT to the results reported in Ref. [55] in Figure 8, from which good agreement in the overall behavior of the progression is evident. The different ranges of field strengths used in our WFAT calculations from those in Ref. [55] reflect the different quantum chemistry methods being employed between the two works and the different ways by which ionized electron probability are computed (asymptotic coefficients vs. absorbing potential). Orientation-dependent ionization in halomethanes has also been investigated in Ref. [61] using symmetric lasers (namely, those having roughly the same number of peaks and valleys with similar magnitudes in a single pulse), which, however, prevents a direct comparison with the present results.

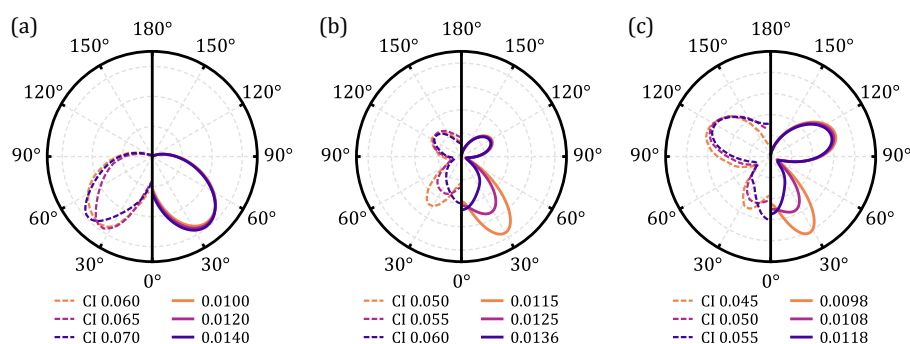


Figure 8. Ionization rates as a function of β in our target halomethanes. Panels (a–c) compare $\bar{\Gamma}_{\text{tot}}$ obtained by TDCI extracted from Ref. [55] (left half) and WFAT (right half) at $\gamma = 90^\circ$ for CH_3F , CH_3Cl , and CH_3Br , respectively. The TDCI data in panels (b,c) are normalized so that the maximum of the high- β lobe coincides with that of the corresponding WFAT data. For the TDCI data in panel (a), the low- β lobe is used as the reference.

4. Conclusions

The dependence of tunnel ionization from a molecule on its spatial orientation and the ionizing field strength is influenced by the properties of the ionized orbital. In particular, the orientation dependence of the tunneling rate usually resembles the orbital shape. In this study, we explored how this relationship may be broken at high field strengths.

First, we investigated how permanent polarizability, along with permanent dipole moment and orbital distortion, is responsible for shifts in the position of the peaks in orientation-dependent ionization rates as the ionizing field varies. Utilizing the weak-field asymptotic theory (WFAT), we initially defined a rate gradient as the first derivative of the total ionization rate, summed over degenerate ionized orbitals and normalized by the total structure factor. Subsequently, we broke down this rate gradient into contributions from the permanent dipole, permanent polarizability, and orbital distortion.

The rate gradients constructed above enabled us to identify the underlying cause of the shifting peaks in the ionization rates of some molecules as the field strength increases. It maps the shift onto a slope in the gradient at around the same orientation as the shifting peak in the rate curve, with the sign of the slope being directly related to the shift direction. Applying the rate gradient analysis on several haloacetylenes, dihaloacetylenes, and halomethanes, we reveal that the main role of permanent polarizability is to shift the peaks in tunnel ionization rates toward or away from the perpendicular orientation as a function of the field strength. Orbital distortion also has a peak-shifting effect, which tends to counteract the shifts caused by the polarizability.

Second, we also showed that the contributions from higher parabolic channels can lead to the appearance of a maximum at the orientation where a minimum was observed at low field strengths, reproducing an earlier work on halomethanes where TDCI was employed [55]. Our results on haloacetylenes only partially reproduced earlier TDCI results [56] and we found that orbital relaxation is most likely the missing parameter, highlighting cases where ME-WFAT might be necessary. Therefore, the present work demonstrated that the WFAT is a promising efficient alternative to calculate molecular tunnel ionization rates with qualitatively accurate field and orientation dependence.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request. The development branch of NWChem containing the WFAT implementation used to obtain simulation data for this work is accessible in [44].

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

WFAT	Weak-field asymptotic theory
SS	Siegert state
TDCI	Time-dependent configuration interaction
HF	Hartree–Fock
ADK	Ammosov–Delone–Krainov
MO-ADK	Molecular Ammosov–Delone–Krainov
HOMO	Highest occupied molecular orbital

Appendix A. The Partial-Wave Formulation of the WFAT

In this section, we will summarize the key steps in the derivation of the partial-wave formulations of OE-WFAT(0) and OE-WFAT(1). We refer the readers to Ref. [43] for the more detailed steps. We begin by stating the *explicit* but numerically expensive forms of the asymptotic coefficients g_ν and h_ν in the integral representation, which are

$$g_\nu = \int d\mathbf{r}^3 \Omega_\nu^{(0)}(\hat{R}^{-1}\mathbf{r}) \left(V(\mathbf{r}) + \frac{Z}{r} \right) \psi^{(0)}(\mathbf{r}), \quad (\text{A1})$$

$$h_\nu = \int d\mathbf{r}^3 \left(\Omega_\nu^{(0)}(\hat{R}^{-1}\mathbf{r}) \psi^{(1)}(\mathbf{r}) + \Omega_\nu^{(1)}(\hat{R}^{-1}\mathbf{r}) \psi^{(0)}(\mathbf{r}) \right) \left(V(\mathbf{r}) + \frac{Z}{r} \right), \quad (\text{A2})$$

where $\hat{R} \equiv \hat{R}(\beta, \gamma)$ is a 3D rotation matrix that transforms a coordinate in the LF to a coordinate in the MF ($\mathbf{P}$ is the third column of $\hat{R}$), and $\Omega_\nu^{(0)}(\mathbf{r})$ and $\Omega_\nu^{(1)}(\mathbf{r})$ are the solutions of the following differential equations [43,48,49],

$$\left(\frac{\nabla^2}{2} + \frac{Z}{r} + E^{(0)} \right) \Omega_\nu^{(0)}(\mathbf{r}) = 0 \quad (\text{A3})$$

$$\left(\frac{\nabla^2}{2} + \frac{Z}{r} + E^{(0)} \right) \Omega_\nu^{(1)}(\mathbf{r}) = (z + \mu_z) \Omega_\nu^{(0)}(\mathbf{r}). \quad (\text{A4})$$

μ_z in Equation (A4) is given by Equation (7). The expressions of $\Omega_\nu^{(0)}(\mathbf{r})$ and $\Omega_\nu^{(1)}(\mathbf{r})$ in the explicit framework can be found in Ref. [43]. Therefore, the orientation angles (β, γ) enter Equations (A1) and (A2) through $\hat{R}$. Due to this dependence, the integrals in Equations (A1) and (A2), which can only be solved numerically, have to be computed for every orientation angle of interest. We note that Equation (A3) is a hydrogen-like Schrödinger equation but without the usual boundary condition that requires its solutions to vanish at infinities. Because of this, $\Omega_\nu^{(0)}$ and $\Omega_\nu^{(1)}$ generally diverge in the asymptotic region and their partial-wave expansion coefficients (introduced below) cannot be determined using the usual overlap integral formula in quantum mechanics.

To overcome the computational cost of the explicit formulation, the partial-wave formulation of WFAT was introduced. In this formulation, $\Omega_\nu^{(0)}(\mathbf{r})$ and $\Omega_\nu^{(1)}(\mathbf{r})$ are expanded into spherical harmonics (partial waves),

$$\Omega_\nu^{(0)}(\mathbf{r}) = \sum_{l=|m|}^{\infty} R_l^\nu(r) Y_{lm}(\theta, \varphi), \quad (\text{A5})$$

$$\Omega_\nu^{(1)}(\mathbf{r}) = \sum_{l=|m|}^{\infty} Q_l^\nu(r) Y_{lm}(\theta, \varphi). \quad (\text{A6})$$

To obtain $R_l^\nu(r)$, one substitutes Equation (A5) into Equation (A4) and projects the resulting equation onto a particular $Y_{lm}(\theta, \varphi)$, resulting in an equation to be solved for $R_l^\nu(r)$,

$$\left(\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - l(l+1) + 2Zr + 2E^{(0)}r^2 \right) R_l^\nu(r) = 0. \quad (\text{A7})$$

The solution of Equation (A7) can be written as

$$R_l^\nu(r) = \omega_l^\nu(\varkappa r)^l e^{-\varkappa r} M(l+1-Z/\varkappa, 2l+2, 2\varkappa r), \quad (\text{A8})$$

where $M(a, b, z)$ is the confluent hypergeometric function of the first kind and ω_l^ν is an expansion coefficient that must be determined so that Equation (A5) is satisfied. It can be calculated as

$$\omega_l^v = \lim_{r \rightarrow 0} \left[(g_l^v(r))^{-1} \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta Y_{lm}^*(\theta, \varphi) \Omega_v^{(0)}(\mathbf{r}) \right], \quad (\text{A9})$$

where $g_l^v(r) = (\kappa r)^l e^{-\kappa r} M(l+1-Z/\kappa, 2l+2, 2\kappa r)$. After using the series representations of the involved special functions, an integral identity involving associated Legendre functions, and Vandermonde's identity, Equation (A9) gives

$$\begin{aligned} \omega_l^v &= (-1)^{l+(|m|-m)/2+1} 2^{l+3/2} \kappa \beta_v^{(0)/\kappa} \sqrt{(2l+1)(l+m)!(l-m)! (|m|+n_\xi)! n_\xi!} \\ &\times \frac{l!}{(2l+1)!} \sum_{k=0}^{\min(n_\xi, l-|m|)} \frac{\Gamma(l+v-k)}{k!(l-k)! (|m|+k)! (l-|m|-k)! (n_\xi-k)!}, \end{aligned} \quad (\text{A10})$$

where $\Gamma(z)$ is the gamma function, $v = 1 + n_\xi - Z/\kappa$, and $\beta_v^{(0)}$ can be found in Ref. [47].

The partial-wave expression of g_v follows from substituting Equation (A5) into Equation (A1), namely,

$$g_v(\beta, \gamma) = \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l d_{mm'}^l(\beta) e^{-im'\gamma} I_{lm'}^v, \quad (\text{A11})$$

where $d_{mm'}^l(\beta)$ is the Wigner function [90] and

$$I_{lm'}^v = \int d\mathbf{r}^3 R_v^l(r) Y_{lm'}^*(\theta, \varphi) \left(V(\mathbf{r}) + \frac{Z}{r} \right) \psi^{(0)}(\mathbf{r}). \quad (\text{A12})$$

The efficiency of Equation (A11) lies in the absence of orientation angles in the integrals $I_{lm'}^v$. This enables us to calculate $I_{lm'}^v$ for all of its indices and use them to compute g_v through Equation (A11), in which the orientation angles appear as arguments of quantities that are fast to calculate.

The derivation of $Q_l^v(r)$ proceeds in an analogous manner; in particular, it is the solution of the following equation,

$$\begin{aligned} \left(\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - l(l+1) + 2Zr + 2E^{(0)}r^2 \right) Q_l^v(r) &= 2r^2 \left(k_{l|m|} r R_{l-1}^v(r) \right. \\ &\left. + k_{l+1,|m|} r R_{l+1}^v(r) + \mu_z R_l^v(r) \right), \end{aligned} \quad (\text{A13})$$

where $k_{l|m|} = \sqrt{(l^2 - m^2)(4l^2 - 1)^{-1}}$. The steps toward the solution of Equation (A13) are outlined in Ref. [43]; here, we only present the final expression of $Q_l^v(r)$, which is given by

$$Q_l^v(r) = Q_1^{vl}(r) + \mu_z Q_2^{vl}(r), \quad (\text{A14})$$

where

$$\begin{aligned} Q_1^{vl}(r) &= d_1^{vl} g_l^v(r) + \frac{2^{2l+2} \kappa \Gamma(l+1-Z/\kappa)}{(2l+1)!} \int_0^r dr' r'^2 \left(k_{l|m|} r' R_{l-1}^v(r') + k_{l+1,|m|} r' R_{l+1}^v(r') \right) \\ &\times (g_l^v(r) h_l^v(r') - g_l^v(r') h_l^v(r)), \end{aligned} \quad (\text{A15})$$

$$Q_2^{vl}(r) = d_2^{vl} g_l^v(r) + \frac{2^{2l+2} \kappa \Gamma(l+1-Z/\kappa)}{(2l+1)!} \int_0^r dr' r'^2 R_l^v(r') (g_l^v(r) h_l^v(r') - g_l^v(r') h_l^v(r)), \quad (\text{A16})$$

$h_1^v(r) = (\kappa r)^l e^{-\kappa r} U(l+1-Z/\kappa, 2l+2, 2\kappa r)$, and $U(a, b, z)$ is the confluent hypergeometric function of the second kind [91]. The coefficients d_r^{vl} for $r = 1, 2$ and $\omega_{l'}^v$ for $l' = l, l \pm 1$ ensure that Equation (A6) is satisfied. The former of these is given by

$$\begin{aligned} d_r^{vl} = & (-1)^{l+(m-|m|)/2+1} \sqrt{(2l+1)(l+m)!(l-m)!n_\xi!} \frac{2^{l+3/2}l!}{(2l+1)!} \kappa \beta_v^{(0)/\kappa-2} \\ & \times \left[\sum_{i=n_\xi-2; i \neq n_\xi}^{n_\xi+2} \sqrt{\frac{(i+|m|)!i!}{n_\xi!}} \sum_{k=0}^{\min(i, l-|m|)} \frac{C_r^{im} \kappa^2 \Gamma(l+v-k)}{k!(l-k)!(|m|+k)!(l-|m|-k)!(i-k)!} \right. \\ & + \frac{\sqrt{(n_\xi+|m|)!}}{\Gamma(v+|m|)} \left\{ \frac{(-1)^{|m|+1}}{\Gamma(v)} \left(e_r^1 H_1^{vl} + e_r^2 H_2^{vl} + e_r^3 H_3^{vl} \right) - \Gamma(1-v) \right. \\ & \left. \left. \times \left(e_r^1 \tilde{H}_1^{vl} + e_r^2 \tilde{H}_2^{vl} + e_r^3 \tilde{H}_3^{vl} \right) \right\} \right], \end{aligned} \quad (\text{A17})$$

where

$$\begin{aligned} H_p^{vl} = & \sum_{(S_1+j'=l-2|m|-p)} (-1)^i \frac{\Gamma(v+|m|+j)\Gamma(v+|m|+k)\Gamma(v+|m|+k')}{(|m|+j)!(|m|+j')!(|m|+k)!(|m|+k')!i!j!k!k'!(n_\xi-j')!} \\ & \times \left(\frac{(k-k')(\mathcal{Y}(v+|m|+k) - \mathcal{Y}(1+k) - \mathcal{Y}(1+k+|m|))}{(l-|m|-k-j')(l-|m|-k'-j')} \right. \\ & \left. + \frac{1}{(l-|m|-k'-j')^2} \right), \end{aligned} \quad (\text{A18})$$

$$\begin{aligned} \tilde{H}_p^{vl} = & \sum_{(S_2+j'=l-2|m|-p)} (-1)^i \frac{\Gamma(v+|m|+j)\Gamma(v+|m|+k')(k-1)!(k+k')}{(|m|+j)!(|m|+j')!(|m|-k)!(|m|+k')!i!j!j'k'!} \\ & \times \frac{1}{\Gamma(1-v-|m|+k)(n_\xi-j')!(l-|m|+k-j')(l-|m|-k'-j')}, \end{aligned} \quad (\text{A19})$$

$\mathcal{Y}(a) = \Gamma'(a)/\Gamma(a)$, $e_r^1 = b_r^v \kappa$, $e_r^2 = -\delta_{r2}/2$, $e_r^3 = \delta_{r1}/(4\kappa)$, and $\delta_{rr'}$ is the Kronecker delta function. The summation notation in Equation (A18) denotes multiple sums over i, j, k, k' , and j' with each of these indices running from 0 to ∞ , such that the requirement $S_1 + j' = l - 2|m| - p$ is satisfied. This results in a finite number of terms [43]. Likewise, in Equation (A19), the five indices runs from 0 to ∞ except for k ($k \in [1, |m|]$) and j' ($j' \in [0, n_\xi]$) and the requirement to be satisfied by the summed terms is $S_2 + j' = l - 2|m| - p$.

Substituting Equations (A5) and (A6) into Equation (A2), one obtains the partial-wave form of h_v ,

$$h_v(\beta, \gamma) = \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l \left(K_1^{vlm'} + \mu_z K_2^{vlm'} + \sum_{s=1}^3 P_s I_s^{vlm'} \right) d_{mm'}^l(\beta) e^{-im'\gamma}, \quad (\text{A20})$$

where

$$J_s^{vlm'} = \int d\mathbf{r}^3 R_v^l(r) Y_{lm'}^*(\theta, \varphi) \left(V(\mathbf{r}) + \frac{Z}{r} \right) \sum_{i; \psi_i^{(0)} \notin \mathcal{D}[\psi^{(0)}]} \psi_i^{(0)}(\mathbf{r}) \frac{\langle \psi_i^{(0)} | q_s | \psi^{(0)} \rangle}{E^{(0)} - E_i^{(0)}}, \quad (\text{A21})$$

$$K_r^{vlm'} = \int d\mathbf{r}^3 Q_r^{vl}(r) Y_{lm'}^*(\theta, \varphi) \left(V(\mathbf{r}) + \frac{Z}{r} \right) \psi^{(0)}(\mathbf{r}), \quad (\text{A22})$$

and P_s is the s -th element of $\mathbf{P}$. As in the case of g_ν , the partial-wave form of h_ν in Equation (A20) is more efficient to compute than the explicit form of Equation (A2) because the expensive integrals the former depends on—Equations (A21) and (A22)—are independent of orientation angles. They can therefore be stored in memory or on disk for the calculations of Equation (A20) at arbitrary orientation angles.

We would like to emphasize that the main difference between the explicit and partial-wave formulations of the WFAT lies in the formula to calculate g_ν and h_ν —the explicit formulation employs Equations (A1) and (A2), whose partial-wave counterparts are given by Equations (A11) and (A20), respectively.

Appendix B. Convergence Analysis of the Partial-Wave Formulation

Theoretical tunneling rates calculated by the WFAT are independent of the coordinate origin chosen to evaluate the integrals of Equations (A1) and (A2), or their partial-wave counterparts, Equations (A12), (A21) and (A22). However, the use of numerical orbitals, such as those obtained from quantum chemistry programs, having an incorrect asymptotic behavior, introduces a weak dependence on the choice of origin. This has a consequence on the partial-wave formulation when the field-free ionized orbitals are degenerate. In this case, at every orientation angle of interest, the field-free ionized orbitals must be chosen so that they diagonalize the LF z position operator, $z = \mathbf{r}_{\text{MF}} \cdot \mathbf{P}$, and the optimal origin, $\mathbf{r}_c$, calculated as $\mathbf{r}_c = Z^{-1}(\mathbf{d}_T - \boldsymbol{\mu}_{\text{MF}})$ [43] becomes orientation-dependent through $\boldsymbol{\mu}_{\text{MF}}$, the dipole moment of the z -diagonalizing ionized orbitals. The orientation dependence of the optimal origin then induces an orientation dependence in the aforementioned integrals needed in the partial-wave formulation, which unfortunately cancels the advantage of this formulation over the explicit one, as explained in Appendix A.

There are two situations in which the optimal origin need not be recomputed at every orientation angle even if the orbitals are degenerate; these are when the orbitals exactly diagonalize the operator z already, such as the orbitals of linear molecules, or when they approximately diagonalize this operator— CH_3Cl and CH_3Br are examples of such situations. Below, we demonstrate the effect of omitting of the orientation dependence of the optimal origin in CH_3Cl , whose HOMOs approximately diagonalize z , through a convergence analysis of the maximum angular momentum for the partial-wave expansion.

Figure A1a–c display slices of the structure factors of one of the degenerate HOMOs of CH_3Cl (one that is even with respect to a reflection around the $x_{\text{MF}}z_{\text{MF}}$ plane) for several values of L_{max} . Figure A1b,c show two new quantities, $|J_\nu|^2$ and $|K_\nu|^2$, which separate the contributions of the field-induced distortions on the orbital, $\psi^{(1)}$, from the distortions in the parabolic channel function, $\Omega_\nu^{(1)}$, recall Equation (A2). They are given by

$$J_\nu(\beta, \gamma) = e^{-\kappa\mu_z} \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l \sum_{s=1}^3 P_s J_s^{\nu l m'} d_{mm'}^l(\beta) e^{-im'\gamma}, \quad (\text{A23})$$

$$K_\nu(\beta, \gamma) = e^{-\kappa\mu_z} \sum_{l=|m|}^{\infty} \sum_{m'=-l}^l \left(K_1^{\nu l m'} + \mu_z K_2^{\nu l m'} \right) d_{mm'}^l(\beta) e^{-im'\gamma}. \quad (\text{A24})$$

We note that $H_\nu = J_\nu + K_\nu$. This separation helps show the different convergence rate of $R_\nu^l(r)$ and $Q_\nu^l(r)$. From the lower graphs of Figure A1b,c, we can see that $R_\nu^l(r)$ converges $\Omega_\nu^{(0)}(\mathbf{r})$ faster than $Q_\nu^l(r)$ does $\Omega_\nu^{(1)}(\mathbf{r})$, which is an expected behavior. At $L_{\text{max}} = 8$, G_ν , J_ν , and K_ν can be considered to be converged; despite this, the explicit results (dashed line) are not perfectly reproduced (see the lower graphs in Figure A1a–c). Also note that the structure factors at $L_{\text{max}} = 8$ deviate slightly from having an exact threefold rotational symmetry, as exhibited by the explicit result.

To show that the above mismatch between the converged partial-wave results and the corresponding explicit results stems from the omission of orientation dependence in the optimal origin, we calculate $|G_v|^2$, $|J_v|^2$, and $|K_v|^2$ at $\beta = 30^\circ$ for the HOMO-1 of CH_3Cl , which is non-degenerate (thus, no diagonalizations are necessary) and show them in Figure A1d–f. In this case, the converged partial-wave results ($L_{\max} = 8$) exhibit an exact threefold rotational symmetry and perfectly reproduce the explicit results. Among our halomethanes targets, only CH_3F cannot be treated with the partial-wave formulation.

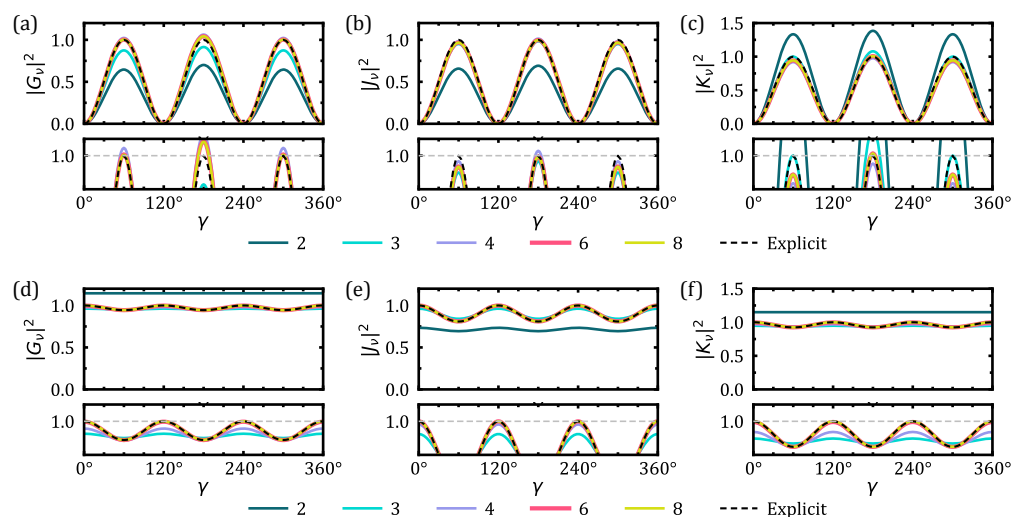


Figure A1. Analysis of convergence in terms of the maximum angular momentum for the partial-wave expansion. Panels (a–c) show $|G_v(\beta = 30^\circ, \gamma)|^2$, $|J_v(\beta = 30^\circ, \gamma)|^2$, and $|K_v(\beta = 120^\circ, \gamma)|^2$ for one of the HOMOs of CH_3Cl for several $L_{\max}$'s (2, 3, 4, 6, and 8) as well as using their explicit formulas. The curves are normalized so that the explicit results have a maximum of unity. The lower graphs show the same structure factors but in the range $[0.9, 1.05]$ of the vertical axes. A dashed horizontal line at 1 is also shown to guide the eye to determine the accuracy of the threefold rotational symmetry of the curves. Panels (d–f) show analogous data for the HOMO-1 of CH_3Cl , where the slices are taken at $\beta = 30^\circ$ for all three structure factors.

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