Origin and implication of ellipticity in high-order harmonic generation from aligned molecules

S. Ramakrishna, Paul A. J. Sherratt, Anthony D. Dutoi, and Tamar Seideman*
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA
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We address theoretically and numerically the possibility of observing ellipticity in high-order harmonic generation (HHG) from aligned molecules driven by linearly polarized fields—a subject of controversy in the recent literature with significant implications. To that end we develop a numerical method for solution of the electronic dynamics and extend a recently developed theory of HHG from aligned molecules. Our numerical results are in good agreement with recent experimental data. The theory explains analytically several observations of polarization experiments. We note the conditions under which ellipticity can be observed and the information content of elliptically polarized harmonics regarding the molecular system.

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High-order harmonic generation (HHG) from nonadiabatically aligned molecules [1] has been the topic of rapidly growing experimental [2] and theoretical [3] interest since the 2004 illustration [4] that harmonic signals from aligned molecules can provide information regarding the electronic structure of the underlying molecule. This effort led to new insights regarding the interaction of molecules with intense fields, along with impressive progress of the experimental and numerical technologies to quantitatively describe these interactions. Nonetheless, several fascinating questions at the qualitative level remain open.

The essential physics underlying HHG is understood in terms of a three-step model [5], wherein tunnel ionization is followed by acceleration of the freed electron by the strong field and, upon reversal of the field direction, recombinaton of the revisiting electron with its parent core with a consequent emission of harmonics of the incident frequency. Nonadiabatic alignment [6] is a coherent process, wherein the interaction of a moderately intense pulse with the (permanent, induced, or transition) dipole moment of the molecule sequentially populates a broad rotational wave packet. Provided that the pulse turn-off is short with respect to the system time scales, the phase relations among the rotational components guarantee that the wave packet will align after the pulse [7], and will subsequently exhibit a coherent revival pattern. In the case of isolated linear or symmetric top molecules, the initial alignment is periodically reconstructed at multiples of the rotational period [8].

To date, the vast majority of studies of HHG from aligned molecules have focused on the case of linearly polarized harmonics. In general, the case of common polarization direction of the alignment and ionization fields has been addressed, where the observed harmonics are linearly polarized along the field’s polarization axis. Recent experiments [9–11], however, pointed to the interest in elliptically polarized harmonics for a variety of applications. In other subdisciplines of optics and physics, birefringence phenomena are broadly utilized (see, e.g., [12] for lists of applications and references). The emission of elliptically polarized light from a linear molecule driven by a linearly polarized field is also a problem of significant fundamental interest, because it probes phase properties of the electronic subsystem while introducing new questions in angular momentum theory, as illustrated below. As of yet, however, this possibility is both controversial and remote from being understood. In particular, the experiments of [9,10] found no ellipticity in the emission of either N₂, O₂, or CO₂ at any angle between the ionizing and the alignment fields but argued that in principle emission of elliptically polarized harmonics is possible. Reference [11] reported strongly elliptical polarization in HHG from N₂ over a range of angles between the alignment and ionization fields’ polarization vectors, in contradiction with [9,10]. Reference [13] argued that in order for ellipticity to be observed it is necessary that the molecule be prepared in a state that carries an electric ring current, in contradiction to both the reasoning of [9,10] and the observations of [11]. Measurements of the angle of rotation of emitted, linearly polarized, light with respect to the ionization field polarization, reported in [14], were found in variance with the results of [9]. Several other observations reported in Refs. [9–11] remain to be understood and generalized. These include marked deviations from both extensively applied (and so far successful) models of HHG from molecules: the two-center interference model [15] and the strong field approximation (an extension of Lewenstein’s theory [16] to the molecular case).

To resolve the controversy, understand these and other observations, and develop general insight into when HHG driven by a linearly polarized field would exhibit elliptical polarization, one requires a theory that takes angular momentum into proper account. In addition, one requires a reliable numerical method to compute the underlying electronic dynamics. One goal of the present work is to develop such a theory as well as a numerical method and apply them to the experimentally relevant observables. A second goal is to explore the new information provided by ellipticity in HHG from aligned molecules.

Our theory is based on generalization of the formalism of [17], to the case where neither the harmonic detection direction (n) nor the alignment (pump) polarization vector ($\epsilon_{pu}$) is restricted to the ionization (probe) field polarization vector ($\epsilon_{pu}$). Since the previous literature has used all three x, y, and z axes to denote the ionization field polarization axis, we follow here the standard convention of defining the space-fixed z axis as the quantization axis, here the ionization field polarization vector, $\hat{z} = \epsilon_{pu}$, and take the alignment field polarization vector and the observation direction to lie in the...
Explicitly, for light emission as a partial wave series of electronic dipole expressing the time-dependent driven dipole that is responsible between the probe polarization and the observation direction, \( \eta \) of the emitted light is nonzero, \( \Delta \Phi^\ell = \Phi^\ell_{\eta=\vartheta_0}(\tau) - \Phi^\ell_{\eta=\vartheta_0+\pi/2}(\tau) \neq 0 \). For \( \Delta \Phi^\ell = 0 \), the signal is linearly polarized and the origin of ellipticity, and the contradictory results of recent experiments, are the conditions under which the emitted harmonics have a nonvanishing \( \eta \) component and those under which the phase difference between the \( \zeta \) and \( \eta \) components of the emitted light is nonzero, \( \Delta \Phi^\ell = \Phi^\ell_{\eta=\vartheta_0}(\tau) - \Phi^\ell_{\eta=\vartheta_0+\pi/2}(\tau) \neq 0 \).

Of particular interest for understanding the plausibility and origin of ellipticity, and the contradictory results of recent experiments, are the conditions under which the emitted harmonics have a nonvanishing \( \eta \) component and those under which the phase difference between the \( \zeta \) and \( \eta \) components of the emitted light is nonzero, \( \Delta \Phi^\ell = \Phi^\ell_{\eta=\vartheta_0}(\tau) - \Phi^\ell_{\eta=\vartheta_0+\pi/2}(\tau) \neq 0 \). For \( \Delta \Phi^\ell = 0 \), the signal is linearly polarized but rotated with respect to the ionization polarization vector, \( \hat{\eta} - \hat{\xi}_\text{pr} \). For \( \Delta \Phi^\ell \neq 0 \) the emitted harmonic is elliptically polarized.

Several key aspects of HHG from aligned molecules emerge directly from Eqs. (1)–(3), and, importantly, are independent of the molecule and of the accuracy of the calculation of the electronic dipole moments. First, for parallel orientation of the alignment and ionization fields (\( \hat{\xi}_\text{pr} \parallel \hat{\xi}_\text{pr} \)) and likewise for the mutually perpendicular (\( \hat{\xi}_\text{pr} \perp \hat{\xi}_\text{pr} \)) and isotropic (\( \hat{\xi}_\text{pr} = 0 \)) cases, harmonics can only be observed in the direction parallel to the ionization field polarization vector. This result follows from the selection rules implicit in the \( \rho^\ell(\tau) \) in Eq. (3). The matrix element of \( \hat{\Phi}_{\ell_{\parallel \cup}} \cdot \hat{y} \) in this equation, which gives rise to a \( \angle \) component of the harmonics, depends explicitly on the azimuthal angle \( \phi \), unlike the matrix element of \( \hat{\Phi}_{\ell_{\parallel \cup}} \cdot \hat{z} \) (which gives rise to a \( \angle \) component of the harmonics). Consequently, the former component can be nonzero only if \( \rho_{\ell_{\parallel \cup}M'}(\tau) \int_{0}^{2\pi} \exp[i(M - M')\phi] \sin \phi \, d\phi \neq 0 \). That is, only for \( |M - M'| = 1 \) in the absence of an aligning pulse, rotational coherences are absent and hence \( \rho_{\ell_{\parallel \cup}M'} \neq 0 \) only for \( M = M' \). When the pump pulse is parallel to the \( \angle \) axis \( \hat{\xi}_\text{pr} \parallel \hat{\xi}_\text{pr} \), the interaction Hamiltonian with the pump pulse is solely a function of polar angle \( \phi \), which ensures that \( \rho_{\ell_{\parallel \cup}M'} = 0 \) for \( M 
eq M' \). In the mutually perpendicular case, \( \hat{\xi}_\text{pr} \perp \hat{\xi}_\text{pr} \), the interaction with the alignment pulse is a function of \( \sin^2 \phi \) and only generates coherences that satisfy \( |M - M'| = 2 \). Hence, the condition \( |M - M'| = 1 \) is violated in these three geometries but is satisfied for other orientations of the pump field polarization with respect to that of the probe field. These results explain analytically the observations of the several recent polarization experiments [9–11,14,18], and generalize the measured data to an arbitrary molecule. From a physical perspective, these results are readily understood: in all three geometries, \( \hat{\xi}_\text{pr} \parallel \hat{\xi}_\text{pr} \), \( \hat{\xi}_\text{pr} \perp \hat{\xi}_\text{pr} \), and \( \hat{\xi}_\text{pr} = 0 \), the cylindrical symmetry of space is conserved, and hence emission cannot be observed in a direction that breaks this symmetry. The symmetry of the problem, as reflected in angular momentum selection rules analogous to the above, implies also that the component of the harmonics field perpendicular to the plane spanned by the pump and probe electric field vectors (here the \( \angle \) component) vanishes.

As a result of the above selection rules, the ratio of the intensities of the emitted harmonics in the \( \angle \) and \( \angle \) directions

\[
\mathbf{a}^\ell(\Omega, \tau) \cdot \hat{\eta} = \sum_{l',k',k} M^\ell_{l',l,k',k}(\tau) F_{\parallel}(l', l, k, \hat{\xi}_\text{pr}) \\
+ M^\ell_{l',l,k',k}(\tau) F_{\perp}(l', l, k, \hat{\xi}_\text{pr}), \quad (1)
\]

where \( \Omega \) is the frequency of the emitted harmonic, \( \hat{\eta} \) denotes the delay between the pump (alignment) and probe (ionization) pulses, \( l \) is the electronic angular momentum, and \( k \) is its projection onto the molecular axis. The \( M^\ell_{l',l,k',k}(\tau) \) contain the response of the rotational subsystem to the absorption pulse, \( \hat{\xi}_\text{pr}(\tau) \), and evolve on the rotational time scale. The \( F_{\parallel}(l', l, k, \hat{\xi}_\text{pr}) \) and \( F_{\perp}(l', l, k, \hat{\xi}_\text{pr}) \) contain the response of the electronic subsystem to the ionization pulse, \( \hat{\xi}_\text{pr}(t) = \hat{\xi}_\text{pr}(t) \hat{\xi}_\text{pr}(t) \), with their Fourier transforms,

\[
F_{\parallel}(l', l, k, \hat{\xi}_\text{pr}) = \frac{2}{\pi} \int_{l'-l}^{l} \sum_{|v_{\xi}|} |v_{\xi}|^{2} \int d k g |\mu_{l}(|\xi|)\Phi_{l}(k)|^2 \\
\times \int_{0}^{\infty} d t \rho_{\xi}(t) \hat{\xi}(t)|\Phi_{l}(\xi)| |\mu_{l}(|\xi|)| e^{-iS_{l}(t)}, \quad (2)
\]

evolving on the electronic time-scale. In Eq. (2), \( |v_{\xi}| \) and \( |v_{\xi}| \) are the neutral and ionic states vibrational indices, \( |v_{\xi}| \) and \( |v_{\xi}| \) are the corresponding eigenstates with eigenvalues \( E_{v_{\xi}} \) and \( E_{v_{\xi}} \), \( l \) is the absolute value of the continuum electron momentum, \( |g| \) and \( |\Phi_{l}(k)| \) denote the bound and continuum electronic states, respectively, \( |\mu_{l}| \) denotes the component of the dipole operator parallel (perpendicular) to the molecular axis, \( \rho_{\xi}(t) \) is the electronic component of the initial state density matrix, and \( S_{l} = \int_{0}^{\infty} d t \rho_{\xi}(t) \hat{\xi}(t) \cdot |\Phi_{l}(\xi)| |\mu_{l}(|\xi|)| e^{-iS_{l}(t)} \).

Thus, \( F_{\parallel}(l', l, k, \hat{\xi}_\text{pr}) \) describes ionization into an electron partial wave \( l \) followed by propagation subject to the strong field, during which the electron angular momentum \( l \) is not conserved, and, finally, a recombination of partial wave \( l \). These elements are independent of the geometry of the experiment and the discussion of their content in [17], in the context of \( \zeta = \eta = 0 \) studies, holds also in the general \( \zeta \neq 0 \), \( \eta \neq 0 \) case at hand (symmetry implies \( k' = k \) in the \( \zeta = \eta = 0 \) case). The new physics is contained in the rotational factors, \( M^\ell_{l',l,k',k}(\tau) \) which we generalize as

\[
M^\ell_{l',l,k',k}(\tau) = \langle Y_{l}' \hat{R}_{\parallel} | (\hat{\Phi}_{l_{\parallel \cup}} \cdot \hat{\eta})(\hat{\Phi}_{l_{\parallel \cup}} \cdot \hat{\xi}_\text{pr}) Y_{l} \hat{R}_{\parallel} \rangle \langle \hat{r}_{\parallel} | Y_{l}' \hat{R}_{\parallel} | (\hat{\Phi}_{l_{\parallel \cup}} \cdot \hat{\eta})(\hat{\Phi}_{l_{\parallel \cup}} \cdot \hat{\xi}_\text{pr}) Y_{l} \hat{R}_{\parallel} \rangle. \quad (3)
\]

In Eq. (3), \( Y_{l}(\hat{R}) \) are spherical harmonics with \( \hat{R} = [\hat{\theta}, \hat{\phi}] \), \( \hat{\theta} \) being the polar and \( \hat{\phi} \) the azimuthal Euler parameters, \( \rho^\ell(\hat{R}) \) is the rotational density operator, which contains the dependence of the signal on the alignment dynamics and the pump-probe time delay \( \tau \), and \( \hat{\Phi}_{l_{\parallel \cup}} \) is a unit vector parallel (perpendicular) to the molecular dipole vector, \( \hat{\Phi}_{l_{\parallel \cup}} = \hat{\Phi}_{l_{\parallel \cup}} \hat{\eta} + \hat{\Phi}_{l_{\parallel \cup}} \hat{\xi}_\text{pr} \). For \( \eta = \zeta = 0 \), the \( M^\ell_{l',l,k',k}(\tau) \) reduce to the rotational expectation value defined in [17]b, and likewise the harmonic amplitudes of Eq. (1).
has a broad peak about \( \pi/4 \) for a wide range of harmonic orders. This result, illustrated for the 23rd harmonic of \( N_2 \) in Fig. 1, is in nice agreement with, and explains the results of [11,18]. As expected from the above discussion, Fig. 1 shows that the intensities ratio depends sensitively on the molecular alignment and hence on the time delay.

A related observable of experimental and fundamental interest that can be analytically understood is the angle between which the peak of the harmonic emission is rotated with respect to the probe polarization vector. Recent experiments [9–11,14] on \( N_2 \) at a time delay that yields maximum alignment, found the rotation angle (denoted \( \rho \) in [9,10]) to be roughly 10°–20° and vary at most weakly with the harmonic order over a wide range. Both results can be understood by noting that for \( N_2 \) the partial waves series of rotational expectation values is dominated by the first term, \( \langle \cos^8 \theta \rangle F_1(1,1,0,0,\Omega) \). Consequently, the rotation angle roughly follows the rotational expectation value of the dominant term and is only weakly dependent on the electronic dipole elements (and hence the harmonic order), taking, in the single partial wave limit, the explicit form, \( \arctan[(\cos^8 \theta)/(\sin \phi \sin \theta \cos^3 \theta)] \). We found the rotation angle to be strongly dependent on the time delay \( \tau \) within certain time windows. This explains the finding of [14] that was reported as a discrepancy with the results of [9]. Our results agree with both measurements but note the sensitivity of the rotational angle to the difference in composition of the rotational wave packets in the two experiments, which, in turn, results from different experimental conditions and time delay.

Proceeding to address the possibility, origin, and implications of nonzero ellipticity, we first express the phase difference \( \Delta \phi^E \) as

\[
\Delta \phi^E = \arctan \left[ \frac{\sum_{\langle j \rangle} (F^j \{ |F^j|} - F^R \{ |F^j|}) M^0_{\langle j \rangle} M^2_{\langle j \rangle}^{\pi/2} \right]
\]

\[
\sum_{\langle j \rangle} (F^j \{ |F^j|} + F^R \{ |F^j|}) M^0_{\langle j \rangle} M^2_{\langle j \rangle}^{\pi/2}
\]

\[
= \arg \left\{ \sum_{\langle j \rangle} F((j), \Omega) F^*(|j\rangle, \Omega) M^0_{\langle j \rangle} M^2_{\langle j \rangle}^{\pi/2} \right\}, \quad (4)
\]

where \( \{j\} \) denotes collectively the set of indices \([l, l', k_l, k_{l'}, p], p = \parallel, \perp, F^R_{\langle j \rangle} \) is the real (imaginary) part of \( F((j), \Omega) \), and \( M^0_{\langle j \rangle} = \langle \theta(\tau) \rangle M^0_{\langle j \rangle} \rangle \). We remark that Eq. (4) is general, independent of the molecule and of approximations introduced in the calculation of the \( F((j), \Omega) = F_{\langle l \parallel \rangle}(l, l', k_l, k_{l'}, \Omega) \).

The result (4) neatly separates the rotational from the vibrational-electronic dynamics and usefully illustrates the conditions under which ellipticity may be observed. Several instructive limits are readily observed. First, in the limit of perfect alignment of the molecular axis with the alignment field polarization vector, assuming that the dipole is confined to either parallel or perpendicular to the molecular axis [i.e., either \( F_{\parallel}(l, l', k_l, k_{l'}, \Omega) = 0 \) or \( F_{\perp}(l, l', k_l, k_{l'}, \Omega) = 0 \) for all \([l, l', k_l, k_{l'}] \)], \( \Delta \phi^E \) vanishes identically, irrespective of the electronic dynamics and the nature of the molecule and regardless of the angle \( \xi \) between the alignment and ionization polarization vectors. A second limit of relevance is the case where the partial wave expansion reduces effectively to a single \( l, k_l \) component. Here \( \Delta \phi^E = 0 \) [see Eq. (4)] and the ellipticity once again vanishes. Of particular importance is the limit where the phases of the different contributing \( F_{\parallel}(l, l', k_l, k_{l'}, \Omega) \) dipole elements are equal. In this case, \( F_{\parallel}(l, l', k_l, k_{l'}, \Omega) = F_{\perp}(l, l', k_l, k_{l'}, \Omega) \) consists of the phase developed by the electronic wave during its journey in the strong field and the phases associated with the scattering of the electron from the ionic core in the ionization and recombination processes. The former is the same for the \( z \) and \( y \) components of the emitted field, but the latter is not. We therefore expect systems where the potential scattering phase is essentially independent of the electronic angular momentum \( l \) to generate at most very small ellipticity. Likewise, a numerical method that neglects the molecular potential (as is the extensively applied extended strong field approximation) is not expected to exhibit ellipticity. To date, the vast majority of calculations of HHG from aligned molecule were restricted to the strong field approximation.

Here, we develop two different approaches to compute the electronic dipole elements numerically. In both cases the electronic dynamics are computed by propagating the time-dependent Schrödinger equation in 2D, and the dependence of the dipole elements on the third coordinate (the azimuthal angle describing rotation about the ionizing field axis) is accounted for using the extended strong field approximation. The two methods differ in their approach of describing the molecular potential. One approach implements a novel inversion procedure to determine the potential from a calculation of the ground state electronic wave function. Since the ground state function can be computed to high accuracy, this approach yields reliable results that go well beyond the soft-core approximation. The second approach applies a soft-core potential. It is used here to test the sensitivity of the computed ellipticity to small modifications in the potential. Both methods predict a nonzero phase and hence significant ellipticity for a certain range of harmonic orders. Both methods predict an increase of the phase with harmonic order in the 19–29 harmonic range, in nice agreement with the experimental results of [11]. The magnitude of the phase computed by...
pulse polarization vector vs the harmonic order at $\zeta$ of harmonics emission parallel and perpendicular to the ionizing diamonds are the present calculations. the emitted harmonics have components both parallel and of the degree of ellipticity regarding the electronic dynam- above analysis illustrates the potential information content their strict validity range. Perhaps still more importantly, the valuable guidelines in the search for ellipticity also outside and is explained below.

The previous literature on the problem of HHG from aligned molecules has emphasized the information content of the signal regarding the bound electronic state of the molecule [4,15,19–22]. It is thus pleasing to note the information content of harmonic signals regarding the scattering wave function, in particular regarding its all-important phase. This phase contains most of the information about the molecular potential [23] and the electron scattering dynamics, and is silent in conventional experiments.

Summarizing, we extended the theory of [17] to the general $\zeta \neq 0, \eta \neq 0$ case and developed a numerical approach to compute the underlying electronic dynamics. We applied the methods to address the questions raised by recent polarization experiments. The theory explains analytically several recently published observations. It also determines the conditions required for observation of elliptically polarized harmonics and notes the information content of polarization measurements regarding the ionization continuum. Our numerical method predicts nonvanishing ellipticity over a substantial range of harmonic orders in N$_2$. The dependence on the harmonic order is in gratifying agreement with the experiments of [11].

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[23] This general statement is explicit in the WKB limit, where the scattering wave function is approximated as $\psi(x) \approx C_1 p^{-1/2} \exp\left[\frac{i}{p} \int p(x) dx\right] + C_2 p^{-1/2} \exp\left[-\frac{i}{p} \int p(x) dx\right]$, $p = \sqrt{2m(E - V)}$. 

FIG. 2. (Color online) Phase difference between the components of harmonics emission parallel and perpendicular to the ionizing pulse polarization vector vs the harmonic order at $\zeta = 40^\circ$. The black circles show the experimental results of Ref. [11]. The (blue) diamonds are the present calculations.