A theory of intense-field dynamic alignment and high harmonic generation from coherently rotating molecules and interpretation of intense-field ultrafast pump-probe experiments

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A theory of ultra-fast pump-probe experiments proposed by us earlier [F.H.M. Faisal et al., Phys. Rev. Lett. 98, 143001 (2007) and F.H.M. Faisal and A. Abdurrouf, Phys. Rev. Lett. 100, 123005 (2008)] is developed here fully and applied to investigate the phenomena of dynamic alignment and high harmonic generation (HHG) from coherently rotating linear molecules. The theory provides essentially analytical results for the signals that allow us to investigate the simultaneous dependence of the HHG signals on the two externally available control parameters, namely, the relative angle between the polarizations, and the delay-time between the two pulses. It is applied to investigate the characteristics of high harmonic emission from nitrogen and oxygen molecules that have been observed experimentally in a number of laboratories. The results obtained both in the time-domain and in the frequency-domain are compared with the observed characteristics as well as directly with the data and are found to agree remarkably well. In addition we have predicted the existence of a “magic” polarization angle at which all modulations of the harmonic emission from nitrogen molecule changes to a steady emission at the harmonic frequency. Among other things we have also shown a correlation between the existence of the “magic” or critical polarization angles and the symmetry of the active molecular orbitals, that is deemed to be useful in connection with the “inverse problem” of molecular imaging from the HHG data.

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I. INTRODUCTION

In recent years there has been much interest and progress in understanding the interaction of atoms and molecules with intense laser fields (e.g. reviews [1, 2]). Among the phenomena observed, the high-order harmonic generation (HHG) is of particular interest, no less because of its potential applications as a source of coherent ultraviolet light and/or for generation of ultrashort attosecond laser pulses. In contrast to atoms, molecules have extra degrees of freedom such as vibration, rotation, and motion of the molecular frame, and have additional symmetry properties, that give rise to richer physical phenomena when they interact with intense laser pulses. Among them is the phenomenon of alignment of linear molecules by strong and long laser pulses which has been investigated in the past [3, 4, 5, 6]. Much interest has recently been generated by the observation of recurrent dynamic alignments of linear molecules like N₂ and O₂ [7, 8], interacting with intense ultrashort laser pulses. They are monitored, for example, by non-destructive high harmonic generation signals from intense-field pump-probe experiments with delayed pairs of intense ultrashort pulses [9, 11, 12, 13]. The dynamic HHG signals have been used also to “reconstruct” the molecular orbitals [14], [11, 12, 13], to investigate proton motions [15] and molecular dynamics [16].

In this paper we derive fully a recently proposed [19, 20] quantum theory of intense-field dynamic alignment and high harmonic generation from linear molecules and apply it to analyze the observed dynamical HHG signals for N₂ and O₂ molecules. Theoretical expressions for the signals are given analytically as a simultaneous function of the two external operational parameters – the delay time, t_d, and the relative polarization angle, α, between the pump and the probe pulse [9, 10, 11, 12, 13].

Before proceeding further, we briefly discuss the main experimental characteristics of dynamic alignment and the HHG signals as observed for N₂ and O₂. We recall at the outset that the quantum measure of dynamical alignment of a rotating molecule is the quantum expectation value (with respect to the rotational wave-packet states induced by the pump pulse) of the “alignment operator” \( \cos^2 \theta \), that is averaged over the Boltzmann distribution of the initially occupied rotational states: \( A(t_d) \equiv \langle \langle \cos^2 \theta \rangle \rangle (t_d) \), where \( \theta \) is the angle between the molecular axis and the probe polarization direction; the double angular brackets stand for the expectation value with respect to the rotational wave-packets (inner brackets) and the statistical average with respect to the Boltzmann distribution (outer brackets) of the initially occupied rotational states. It was observed experimentally that the dynamic (or delay-time dependent) HHG signal for N₂ mimicked the “alignment measure” \( A(t_d) \). It exhibited the phenomenon of rotational revivals [3, 6, 21] including the “full-revival” with a period \( T_r = \frac{\pi B}{2} \), where \( B \) is the rotational constant [22], as well as a \( \frac{\pi}{2} \)-revival, and a \( \frac{\pi}{4} \)-revival. They are consistent with the time dependence of \( A(t_d) \) defined

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above, since the operator \( \cos^2 \theta \) can couple the rotational states with \( \Delta J = \pm 2 \) (Raman allowed transitions) among the rotational states of the induced wavepackets, and thus can give rise to fractional revival periods associated with the corresponding beat frequencies. In the case of \( \text{O}_2 \), unexpectedly, an additional \( \frac{1}{7} \)-revival appeared in the HHG signal \([11, 12, 13]\). The latter is impossible for the alignment measure \( A(t_d) \) to account for, since it can not couple the rotational states with \( \Delta J = \pm 4 \), that could give rise to a beat period \( \frac{1}{7}T_r \). Thus, to fit their data of \( \text{O}_2 \), Itatani et al. \([11]\) proposed, empirically, to consider the expectation value of the operator \( B(t_d) = \langle \sin^2 2\theta \rangle(t_d) \). Subsequently, some of the early theoretical models of the HHG signal (e.g. \([23, 24, 25]\)) gave a similar result for \( \text{O}_2 \) and thus appeared to justify the empirical fit. Such a model also suggests that the maximum HHG signal for \( \text{N}_2 \) can occur when the field polarization and the molecular axis were parallel, whereas the maximum signal of \( \text{O}_2 \) would occur when they are “diagonal” (i.e. make an angle \( \theta = 45^\circ \)). Unlike the time dependent signals themselves, their Fourier transform \( (F.T.) \), with sharply defined individual spectral lines and series, provide an alternative (and rather more precise) means of studying the dynamic alignment phenomenon. More recent experimental observations of the dynamic HHG signals for \( \text{N}_2 \) and \( \text{O}_2 \) and their \( F.T. \) have revealed surprising characteristics that can not be fully understood in terms of the earlier considerations. Thus:

(a) Kanai et al. \([12]\) found that their experimental HHG signals for \( \text{N}_2 \) and \( \text{O}_2 \) could not be well fitted, respectively, by the expectation values of the operators \( \cos^2 \theta \) and \( \sin^2 2\theta \), alone. They considered empirically additional operators involving higher powers of \( \cos^2 \theta \), or Legendre polynomials, to fit their data.

(b) Miyazaki et al. \([13]\) measured the dynamical HHG signals of \( \text{N}_2 \) and \( \text{O}_2 \) and Fourier transformed their signals and found not only spectral series containing strong Raman allowed but also weak Raman forbidden and anomalous lines, for both \( \text{N}_2 \) and \( \text{O}_2 \).

(c) Itatani et al. \([14]\) observed that the HHG signal from dynamically aligned \( \text{N}_2 \) was enhanced when the pump polarization was taken parallel to the probe polarization, and were suppressed when the polarizations were taken to be perpendicular.

(d) Kanai et al. \([12]\) and Miyazaki et al. \([13, 26]\) measured the HHG signal for the diatomic \( \text{N}_2 \), \( \text{O}_2 \), and the triatomic \( \text{CO}_2 \), for different relative angles \( \alpha \) between the pump and probe polarizations, and observed that the HHG signal modulations are not only smaller in the perpendicular case, compared to the parallel case, but also are of opposite phase in the two geometries.

(e) Kanai et al. \([12]\) proposed a planar emission model of HHG which produced an opposite phase relation, as observed, but it did not yield the unequal modulation amplitudes, observed in the two geometries.

(f) The present theory predicted (cf. \([20]\) and below) a “magic” polarization angle, \( \alpha_c \approx 55^\circ \), at which the harmonic emission from coherently rotating molecules with \( \sigma_g \) orbital symmetry (e.g. \( \text{N}_2 \)) becomes equal for all delay times \( t_d \). Most recent observations by Yoshii et al. \([27, 55]\) appear to confirm the same.

In this paper we present an \emph{ab initio} development of the above mentioned theory \([19, 20]\) that is shown to provide a unified theoretical account of all the phenomena noted above and other related characteristics of dynamic alignments and the HHG signals from the aligning molecules, as well as their Fourier spectra, that have been observed experimentally. To this end, below we begin with a short schematic description of a typical intense-field pump-probe experiment on dynamic alignments and the molecular HHG signals as a function of (a) the time delay, \( t_d \), and (b) the relative polarization angle, \( \alpha \), between the pump and the probe pulse. In Sec. II, III and IV, we systematically derive the S-matrix theory of molecular alignment and dynamic HHG signal from an ensemble of freely rotating linear molecule, discuss the connection between the “one” - and the “many”-molecule signals, and the relation between the quantum amplitude for the emission of the HHG photons and the expectation value of the dipole transition moment. In Sec. V, we apply the theory to \( \text{N}_2 \) and \( \text{O}_2 \) molecules and obtain analytic expressions for the “HHG operators” and the HHG signals for an arbitrary, \( \alpha \), and delay times, \( t_d \). In Sec. VI, we use the theoretical expressions to explicitly calculate the HHG signals for specific experimental parameters, for the linear molecules \( \text{N}_2 \) and \( \text{O}_2 \), both in the time domain and in the frequency domain, and discuss the results with reference to the corresponding experimental observations. In addition, we investigate in section VII a number of related problems of general interest including the influence of the probe pulse on the dynamic alignment, the effect of the initial temperature on the HHG signal, and the mean energy of the molecule after interaction with the pump pulse. We also discuss two other definitions used earlier for the HHG signal, as well as investigate the case of “adiabatic alignment” of a linear molecule, within the present theory, in the limit of long pulse durations. We end with a concluding summary in Sec. VIII.

In Fig. 1 we show a schematic of a typical intense-field pump-probe experiment. A laser beam is first split into two parts, \( L_1 \) and \( L_2 \), by a beam splitter \( (BS) \) with a desired ratio of the beam intensities. The probe-pulse \( L_2 \) is delayed by passing through a delay line system \( (D) \), by a finite amount \( t_d \), with respect to the pump-pulse \( L_1 \) and both are sent through a beam mixer \( (BM) \) to the target gas molecules from a gas jet. The high harmonic signal produced by the probe pulse is recorded by the detector system for each selected values of \( t_d \). In addition, a polarizer \( P \) can be inserted to rotate the angle of polarization of the probe pulse with respect to the polarization direction of the pump pulse at any desired angle \( \alpha \). The pulses are generally assumed to be effectively non-overlapping \( (t_d \neq 0) \) and that they are shorter than the period of the rotational degrees of freedom of interest.
Note that both \( t_d \) and \( \alpha \) provide controllable parameters on the high harmonic emission process from the outside.

![Figure 1: A scheme of a typical pump-probe experiment. See text for further explanation.](image)

**II. A QUANTUM THEORY OF INTENSE-FIELD PUMP-PROBE EXPERIMENTS AND MOLECULAR HIGH HARMONIC GENERATION SIGNALS**

**A. Total Hamiltonian and Equations of Motions of the Dynamical System**

Within the adiabatic Born-Oppenheimer approximation of the target molecule, the total Hamiltonian of the system can be written \[ H_{tot}(t) = H_N + V_{N-L_1}(t) + H_e + V_{e-L_2}(t-t_d) \] (1) where \( H_N \) is the nuclear Hamiltonian, \( V_{N-L_1}(t) \) is the interaction due to the pump pulse with the nuclear motion at time \( t \), \( H_e \) is the electronic Hamiltonian, and \( V_{e-L_2}(t-t_d) \) is the interaction of the probe pulse with the active electron at a delay \( t_d \). We describe the two laser pulses (in the long-wavelength dipole-approximation) of the laser fields, \( F(\phi_j(t)) \equiv f(t) \cos(\phi_j(t)) \) and the corresponding the vector potentials by \( A(\phi_j(t)) = -\frac{e_0}{c}f(t) \sin(\phi_j(t)) \), where \( f(t) \) is the slowly varying envelope of the electric field (compared to the period of the high harmonics, or the electron motion). The phase \( \phi_j(t) \) of the field at the position of the active electron of the molecule is given by \( \phi_j(t) = (\omega t - k_\omega X_j) \), where the C.M. of the molecule is assumed to be located at a position “\( X_j \)”; \( \omega \) and \( k_\omega \) are the laser of frequency and the wavenumber, respectively. For the sake of simplicity of writing, we may suppress the notation the full \( X_j \) and \( t \) dependence of the phase factor \( \phi_j(t) \) unless otherwise needed explicitly, e.g., while summing coherently the “many-molecule” emission amplitudes from different locations \( \{X_j\} \) to obtain the total amplitude associated with the signal macroscopically coherent signal. It will be found that the coherent signal appears significantly for the “elastic” scattering (the final state of the molecule is the same as the initial state) with respect to the target molecule, and (for an ideal gas medium) along the forward direction of the incident field (cf. §4, and references cited in that section).

Thus, we may write the laser-molecule interaction Hamiltonians appearing above as given by

\[
V_{N-L_1}(t) = -\mu \cdot F_1(t) - \frac{1}{2} F_1(\phi_j(t)) : \alpha : F_1(\phi_j(t)) \tag{2}
\]

where \( \mu \) is the permanent dipole moment (if non-zero) and \( \alpha \) with Cartesian components \( \alpha_{ij} \); \( (i, i') = (1, 2, 3) \) is the polarizability tensor of the molecule (always non-zero); and

\[
V_{e-L_2}(\phi_j(t-t_d)) = -\hat{d}_e \cdot \vec{F}(\phi_j(t-t_d)) \tag{3}
\]

where \( \hat{d}_e \) stands for the electronic dipole operator.

**B. Total Wavefunction in Intense-field S-Matrix Theory**

We first consider a systematic solution of the time-dependent Schrödinger equation of the system

\[
i \frac{\partial}{\partial t} \psi(t) = H_{tot}(t) \psi(t) \tag{4}
\]

using the general technique of intense-field many-body S-matrix theory (IMST) [2]. In this approach the total wavefunction of the system satisfying a given initial (final) condition can be written as a series expansion in such a way that the dominant virtual states, when present, can appear already in the leading terms of the series. To this end we introduce three partitions of the same total Hamiltonian, referring to the initial, “\( i \)”, the final, “\( f \)”, and the (deemed to be relevant) intermediate virtual state, “\( 0 \)”, interactions plus the corresponding “reference” Hamiltonians:

\[
H_{tot}(t) = H_i + V_i(t) = H_f + V_f(t) = H_0(t) + V_0(t). \tag{5}
\]

It is also useful to define the reference Green’s functions associated with the reference Hamiltonians, \( H_s(t); s \equiv i, f, 0 \) :

\[
\left( i \frac{\partial}{\partial t} - H_s(t) \right) G_s(t, t') = \delta(t-t'). \tag{6}
\]

In general, the Green functions can be obtained from the complete set of the fundamental solutions, \( \left| \psi_j^{(s)}(t) \right> \) of the Schrödinger equations governed by the reference Hamiltonians \( H_s(t); s \equiv i, f, 0 \):

\[
G_s(t, t') = -i \theta(t-t') \sum_{aj} \left| \psi_j^{(s)}(t) \right> \left< \psi_j^{(s)}(t') \right| \tag{7}
\]
The validity of the solutions Eq. (6) can be readily established by operating on the left hand side of Eq. (7) with \(i \frac{\partial}{\partial t} - H_0(t)\), using Eq. (6) and the completeness of the fundamental solutions, \(\sum_j \langle \psi_j^{(s)}(t) | \psi_j^{(s)}(t) \rangle = 1\) and the relation \(\frac{d}{dt} \theta(t - t') = \delta(t - t')\), to obtain a delta function integration on the right hand side, followed by the obvious simplification. Thus, we can express the total wavefunction of the interacting system, evolving from an arbitrary initial state, \(|\chi_i(t)\rangle\), as a series:

\[
|\Psi(t)\rangle = \sum_{j=0}^{\infty} |\Psi_i^{(j)}(t)\rangle
\]

with

\[
|\Psi_i^{(0)}(t)\rangle = |\chi_i(t)\rangle
\]

\[
|\Psi_i^{(1)}(t)\rangle = \int_{t_i}^{t_f} dt_1 G_{ij}^{0}(t, t_1) V_j(t_1) |\chi_i(t_1)\rangle
\]

\[
|\Psi_i^{(2)}(t)\rangle = \int_{t_i}^{t_f} \int_{t_i}^{t_f} dt_2 dt_1 G_{ij}^{0}(t, t_2) V_j(t_2) G_0(t_2, t_1) \\
\times V_i(t_1) |\chi_i(t_1)\rangle
\]

\[
|\Psi_i^{(n)}(t)\rangle = \int_{t_i}^{t_f} \cdots \int_{t_i}^{t_f} \int_{t_i}^{t_f} dt_n \cdots dt_2 dt_1 G_{ij}^{0}(t, t_n) \\
\times V_j(t_n) \cdots G_0(t_3, t_2) V_j(t_2) G_0(t_2, t_1) \\
\times V_i(t_1) |\chi_i(t_1)\rangle.
\]

III. MANY-MOLECULE VS. ONE-MOLECULE SIGNALS

A. Transition Amplitudes for High Harmonic Generation

Emission of a harmonic photon of frequency \(\Omega = n \omega\) and wavenumber \(K_\Omega\), from its vacuum state \(|0_\Omega\rangle\) (zero occupation number in Fock-space), into a singly occupied number space of the vacuum and the emitted photon (cf. e.g. [2, §4.5]). Nevertheless, exactly the same result for the single photon HHG emission amplitude can also be obtained using the ordinary quantum mechanics, simply by taking the quantum electrodynamical normalized interaction \(V^\ast(t)\) for the spontaneous emission of a photon of frequency \(\Omega\) and wavevector \(K_\Omega\) (cf. [28, 29, Lecture 2]):

\[
V^\ast(t) = N_\Omega e^{i\phi_f(t)} \epsilon_\Omega \cdot \hat{d}_e
\]

In the above, \(N_\Omega \equiv \sqrt{\frac{2\pi \hbar \Omega}{L^3}}\), \(L^3\) is the quantization volume, \(\epsilon_\Omega\) is the polarization vector of the emitted photon, and \(\hat{d}_e\) is the usual electronic transition dipole operator; the phase \(\Phi_f(t) = (\Omega t - k_\star \cdot X_j)\). As usual in the present dipole approximation, we have neglected the retardation factor, \(e^{-iK_\Omega \cdot r} \approx 1\); we may note explicitly that the exact position of the electron with respect to an arbitrary coordinate origin is given by \(X_j + \mathbf{r}\), where as before \(X_j\) is the C.M. of the \(j\)th molecule and \(\mathbf{r}\) is the position of the electron with respect to the C.M. of the molecule.

The HHG amplitude for the emission of a harmonic frequency \(\Omega\) from the \(j\)th molecule is given by (cf. [2 §4]) by the sum of two “Feynman-like” diagrams, (a) and (b), shown in Fig. 2. The diagram (a) corresponds to the so-called “direct” amplitude (associated with the retarded Green’s function), whereas the diagram (b) corresponds with the “time-reversed” amplitude (associated with the advanced Green’s function). The amplitude for the harmonic emission process can be written down analytically from diagram (a) by reading in the forward (upward) direction of time: First, the molecule is prepared by the “pump” laser pulse in the state \(i \equiv |\Phi_i(t)\rangle\). Next, the molecule interacts with the probe laser field (short horizontal line with a cross), then it propagates through \(G_0 = G_0^{(+)}\) (vertical line). Next it interacts with the vacuum-field by \(V^\ast\) (horizontal line ending in \(\Omega\)), and emits the harmonic photon of frequency \(\Omega\), and finally returns to the same state \(i \equiv |\Phi_i(t)\rangle\) as before. A similar interpretation holds for the time reversed diagram (b) except that here the system evolves backward in time thorough \(G_0 = G_0^{(-)}\). The quantum amplitude \(A_j(\Omega)\), for the emission of the HHG photon of frequency \(\Omega\), and wavenumber \(K_\Omega\), from the molecule located at

Figure 2: Quantum amplitude for coherent emission of a high harmonic photon of frequency \(\Omega\) is the sum of a direct (a) and a time-reversed (b) diagram.
Mathematically, we have

\[\text{diag.}(a) = -i \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \langle \phi_i(t) | V^*(t) \rangle \times G_0^{(+)}(t, t') V_{e-L_2}(t' - t_d) | \chi_i(t') \rangle \]

and,

\[\text{diag.}(b) = -i \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \langle \phi_i(t') | V_{e-L_2}(t' - t_d) \rangle \times G_0^{(-)}(t', t) V^*(t) | \chi_i(t) \rangle \]

B. A Relation between HHG Amplitude and F.T. of Dipole Expectation Value

1. Recasting the quantum HHG amplitude

Before proceeding further, we consider the relation between the quantum HHG amplitude, Eq. (14), and the expectation value of the electric dipole operator, \( \hat{d}_e \), that is popularly used for calculations of HHG signals. To this end we first rewrite the quantum amplitude Eq. (15) by introducing the first order wavefunction \( \Psi^{(1)} \) (cf. Eq. (10)) that arises from the initial state \( | \chi_i(t) \rangle \) due to the interaction with the probe pulse:

\[\left| \Psi^{(1)}(t) \right\rangle = \int_{-\infty}^{\infty} dt' G_0^{(+)}(t, t') \times V_{e-L_2}(t' - t_d) | \chi_i(t') \rangle \]

We may first rewrite Eq. (15) as:

\[\text{diag.}(a) = -i \int_{-\infty}^{\infty} dt \left\langle \chi_i(t) | V^*(t) \right| \Psi^{(1)}(t) \rangle \]

\[= -i \int_{-\infty}^{\infty} dt e^{i(\Omega t - \mathbf{K}_0 \cdot \mathbf{X}_i)} \times \left\langle \chi_i(t) \right| N_\Omega \epsilon_\Omega \cdot \hat{d}_e \left| \Psi^{(1)}(t) \right\rangle \]

where we have used the explicit form of the interaction \( V^*(t) \). Next we rewrite Eq. (15) using a standard relation satisfied by the advanced and the retarded Green functions (e.g. 20):

\[G_0^{(-)}(t', t) = \left[ G_0^{(+)}(t, t') \right]^* \]

We also note that the laser-molecule interaction is real (Hermitian), i.e.

\[V_{e-L_2}(t) = [V_{e-L_2}(t)]^* \]

Thus, the integral over \( dt' \) in Eq. (10) can be rewritten as,

\[\text{diag.}(b) = -i \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \langle \chi_i(t') | V_{e-L_2}(t' - t_d) \rangle \times G_0^{(-)}(t', t) V^*(t) | \chi_i(t) \rangle \]

\[= -i \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \times \left[ G_0^{(+)}(t, t') V_{e-L_2}(t' - t_d) \left| \chi_i(t') \right\rangle \right]^* \times V^*(t) | \chi_i(t) \rangle \]

\[= -i \int_{-\infty}^{\infty} dt \right\langle \Psi^{(1)}(t) \left| V^*(t) \right| \chi_i(t) \rangle \]

\[= \int_{-\infty}^{\infty} dt e^{i(\Omega t - \mathbf{K}_0 \cdot \mathbf{X}_i)} \times \left\langle \left. \Psi^{(1)}(t) \right| N_\Omega \epsilon_\Omega \cdot \hat{d}_e \right| \chi_i(t) \rangle \]

Hence, adding Eqs. (15) and (21), we get the quantum HHG amplitude in the suggestive form:

\[A_j(\Omega) = -i N_\Omega \epsilon_\Omega \cdot \int_{-\infty}^{\infty} dt e^{i(\Omega t - \mathbf{K}_0 \cdot \mathbf{X}_j)} \times \left\{ \left\langle \chi_i(t) \right| \hat{d}_e \left| \Psi^{(1)}(t) \rangle + \left\langle \Psi^{(1)}(t) \right| \hat{d}_e \left| \chi_i(t) \rangle \right\} \right. \]

\[= -i N_\Omega \epsilon_\Omega \cdot \int_{-\infty}^{\infty} dt e^{i(\Omega t - \mathbf{K}_0 \cdot \mathbf{X}_j)} \times \left\{ \left\langle \chi_i(t) \right| \hat{d}_e \left| \Psi^{(1)}(t) \rangle + \left\langle \Psi^{(1)}(t) \right| \hat{d}_e \left| \chi_i(t) \rangle \right\} \right. \]

where “c.c.” stands for the complex conjugate.

2. Dipole expectation value

The expectation value of the dipole operator, \( \hat{D}_{i,i}(t) \), of the transition dipole operator can be calculated within the lowest order KFR approximation \([30,31,32]\) of the wavefunction of the system as follows:

\[\hat{D}_{i,i}(t) = \left\langle \Psi(t) \left| \hat{d}_e \right| \Psi(t) \right\rangle \]

\[= \left\langle \chi_i(t) \right| \hat{d}_e \left| \chi_i(t) \right\rangle \]

\[+ \left\{ \left\langle \chi_i(t) \right| \hat{d}_e \left| \Psi^{(1)}(t) \rangle + \left\langle \Psi^{(1)}(t) \right| \hat{d}_e \left| \chi_i(t) \rangle \right\} + \cdots \right. \]

Note that the zeroth order term in the first line above vanishes for centrosymmetric systems; we have also neglected the quadratic powers of the first order KFR-correction (and the higher order terms).

Combining Eq. (23) with Eq. (22), the quantum HHG amplitude can be expressed in the form

\[A_j(\Omega) = -ie^{-iK_0 \cdot X_j} N_\Omega \epsilon_\Omega \cdot \int_{-\infty}^{\infty} dt e^{i\Omega t} \hat{D}_{i,i}(t) \]
Thus, the quantum HHG amplitude is clearly proportional to the Fourier transform (F.T.) of the expectation value of the transition dipole operator, Eq. (23). We may recall that the proportionality constant $N_\Omega$ above is of quantum electrodynamical origin and can not be derived from the classical electrodynamics alone [32].

In practice, the F.T. of interest can be conveniently obtained by Fast Fourier transform (or FFT) numerically [34]. Alternatively, for “slowly varying” pulse envelopes (compared to the high harmonic frequency) one may express the F.T. of $D_{i,i}(t)$ as a Fourier series [35]:

$$D_{i,i}(t) = \sum_n e^{-in(\omega t - k_\omega \cdot X_j)} \tilde{D}(n\omega)$$  \hspace{1cm} (25)

where $\tilde{D}(n\omega)$ is the F.T. evaluated at the $n$th harmonic frequency $\Omega = n\omega$. Thus, in terms of the F.T. components, the HHG amplitude $A_j(\Omega)$ becomes,

$$A_j(\Omega) = \sum_n -2\pi i \delta(\Omega - n\omega)e^{-i(K_\Omega - nk_\omega) \cdot X_j} \times N_\Omega \epsilon_\Omega \cdot \tilde{D}_{i,i}(n\omega)$$  \hspace{1cm} (26)

where we have carried out the time integration over $dt$, in terms of the Dirac delta-function.

C. Coherent Sum of HHG Amplitudes: Many-molecule vs. One-molecule Signal

It is interesting also to consider the total amplitude $A_{tot}(\Omega)$ of HHG emission from all the molecules interacting with the (probe laser) field. This is given by the coherent sum of the individual amplitudes emitted by the molecules at the positions $X_j$ for all $j = 1, 2, 3, \ldots N$, where $N$ is the number of molecules in the interaction volume, or

$$A_{tot}(\Omega) = \sum_{j=1}^{N} A_j(\Omega)$$

$$= \sum_n \left\{ \sum_{j=1}^{N} e^{-i(K_\Omega - nk_\omega) \cdot X_j} \right\}_1 \times \left\{-2\pi i \sum_n \delta(\Omega - n\omega)T_{i,i}(\Omega) \right\}_2$$  \hspace{1cm} (27)

where we may identify the basic HHG transition matrix element for the emission of the $n$th harmonic per molecule as,

$$T_{i,i}(\Omega) = N_\Omega \epsilon_\Omega \cdot \tilde{D}_{i,i}(\Omega)$$  \hspace{1cm} (28)

It can be seen from Eq. (27) that the $n$th harmonic emission amplitude in fact factorizes into two parts, the first factor corresponds to the sum of the macroscopic space dependent phases associated with the random positions $X_j$ of the C.M.s of the molecules in the interaction volume, and the second factor corresponds to the fundamental “one molecule” emission amplitude, independent of the position of the C.M.s of the molecules. The macroscopic phase factor is explicitly given by

$$\left\{ \ldots \right\}_1 = \left\{ \sum_{j=1}^{N} e^{-i(K_\Omega - nk_\omega) \cdot X_j} \right\}_1$$  \hspace{1cm} (29)

For a large number of molecules in the interaction volume, $N \gg 1$, the phase factor oscillates greatly and thus tends to average out to zero, except when the condition,

$$(K_\Omega - nk_\omega) = 0$$  \hspace{1cm} (30)

is fulfilled; in that case it yields the phase sum $\left\{ \ldots \right\}_1 = N$. It is readily understood that the condition (30) corresponds exactly to the momentum conservation between the final momentum of the emitted harmonic photon, $hK_\Omega$, and the sum of the momenta of $n$ laser photons, $n\hbar k_\omega$. This is the phase-matching condition in the forward direction [37].

The probability of emission of the harmonics is given as usual by the absolute square of the total amplitude Eq. (27). Under the phase-matching condition the latter is therefore coherently amplified by a (generally large) factor of $N^2$. This is also the origin of the quadratic pressure dependence of the high harmonic signals, as well as their unusual strengths, that had been found in the very first experimental observations (e.g. [38, 39]).

The second factor $\left\{ \ldots \right\}_2$ gives the fundamental “one-molecule” quantum emission amplitude. We also note that if the absolute probability of the harmonic emission is needed then the proportionality factor $N_\Omega = \sqrt{2\pi n\omega L}$ becomes essential, and that for a given polarization direction of the emitted photon, $\epsilon_\Omega$, the projection of the dipole expectation value must be taken in that direction.

D. Continuous Medium and the Phase-matching Function

If one assumes that the gas molecules are distributed effectively continuously with a distribution function $N\rho(R)d^3R$, where $\rho(R)$ is the so-called “density function per molecule”, then one may replace the sum over $j$ in Eq. (29) by the integration over the interaction volume. Clearly, in this case the square of the macroscopic phase factor, $|\left\{ \ldots \right\}_1|^2$, takes the form

$$|\left\{ \ldots \right\}_1|^2 = N^2 \mathcal{F}(K_\Omega - nk_\omega)$$  \hspace{1cm} (31)

where,

$$\mathcal{F}(K_\Omega - nk_\omega) = \left| \int d^3X \rho(X) e^{i(K_\Omega - nk_\omega) \cdot X} \right|^2$$  \hspace{1cm} (32)

which is the so-called phase-matching function. It peaks for its argument near zero (near the forward direction), but falls off rapidly away from it.
E. Coherent Elastic vs. Incoherent Inelastic Transitions

Eqs. (30) and (27) show, respectively, that both the phase matching condition (momentum conservation) and the frequency matching condition (energy conservation) in the process ought to be fulfilled simultaneously in order that the macroscopic signal to be coherently amplified in space and time. As already noted earlier, the former condition leads to the directional coherence (forward propagation) of the HHG emission, while the latter implies the elastic nature of the accompanying molecular transitions for which the final (“recombination”) state of the molecular system is the same as the initial state, with \( E_i = E_f \). In contrast, for an inelastic transition, \( i \to f \), when \( E_i \neq E_f \), there would be in general only “hyper-Raman” emissions, with frequencies \( \Omega_{if} = (n'\omega - |E_i - E_f|) \), that are generally incommensurate with the incident laser frequency or its multiple, or the HHG frequency, \( \Omega = n\omega \). Thus the non-vanishing relative phase difference \( \Delta \phi = (|E_i - E_f| - n\omega) t \) would fail to stimulate the hyper-Raman transitions by the incident field, unlike the stimulated spontaneous nature of the associated HHG. Also the non-vanishing momentum difference between hyper-Raman radiation and the multiple of the laser photons \( K_{\Omega i f} - nk_\omega \neq 0 \) makes the former macroscopically and directionally incoherent.

Finally, we note that the probability of the electronically inelastic processes associated with the transitions into the continuum (e.g. ionization) or between continua (e.g. inverse Bremsstrahlung) that are commensurate with the emission of the \( n \)th harmonic at the “one-molecule” level, will be incoherent spatially, and therefore would enhance only proportional to the total number of molecules, \( N \), in the interaction volume. This is in stark contrast to the coherent amplification of the HHG emission at the \( n \)th harmonic, that is proportional to \( N^2 \).

F. Differential Rate of Coherent High Harmonic Generation

To derive the explicit expression for the probability of HHG per unit time i.e. the rate of generation of coherent high harmonics, we take the absolute square of the total HHG amplitude Eq. (27) and divide by the long observation time \( T \), use a useful representation of the square of the delta-function (2, p. R12),

\[
\delta^2(\Omega - n\omega) = \lim_{T \to \infty} \frac{T}{2\pi} \delta(\Omega - n\omega),
\]

and sum over the emitted photon modes (with \( \sum_{K} \equiv L^3 \int dK_\Omega \int dK_\Omega K_{\Omega i f}^2 \)) and get:

\[
W(\Omega) = \lim_{T \to \infty} \sum_K \frac{|A_{tot}(\Omega)|^2}{T} = N^2 \sum_n \int dK_\Omega \mathcal{F}(K_\Omega - nk_\omega) \times \int dW(n\omega)
\]

where,

\[
dW(n\omega) = 2\pi\delta(\Omega - n\omega)L^3 \times \left| N_{i\Omega} \epsilon_{i\Omega} \cdot \hat{D}_{i,i}(n\omega) \right|^2 K_{\Omega i f}^2 dK_\Omega
\]

is the differential rate of HHG per molecule. Noting that the main contribution arises from the phase matching condition along the forward direction, we may carry out the mode-integrations to get:

\[
W(n\omega) = 2\pi \left| T_{i,i}^{(n)} \right|^2 \frac{(n\omega)^2}{e^3}
\]

where we have used, \( K_{\Omega i f} = \Omega_{\Omega i f} K_{\Omega} \), and the fundamental transition matrix element for the emission of the \( n \)th harmonic, \( T_{i,i}^{(n)} \), is given in terms of the F.T. of the dipole expectation value \( \hat{D}_{i,i}(n\omega) \) by:

\[
T_{i,i}^{(n)} = \sqrt{2\pi(n\omega)\epsilon_{i\Omega} \cdot \hat{D}_{i,i}(n\omega)}
\]

for, \( L^3 |N_{i\Omega}|^2 = 2\pi(n\omega) \).

IV. EVALUATION OF “ONE MOLECULE” HHG AMPLITUDE

Clearly the dynamical properties of the HHG signal are given by the rate of HHG emission per molecule, Eq. (30), while the total signal is the same to within a proportionality constant given by the square of the number of molecules in the interaction volume, \( N^2 \), and the phase-matching constant \( \int dK_\Omega \mathcal{F}(K_\Omega - nk_\omega) \) that peaks in the forward direction. We therefore proceed to evaluate the dynamical signal per molecule (in a relative scale) as follows: (i) solve the Schrödinger equation for the nuclear and the electronic motions of the interacting laser-molecule system, (ii) construct a complete set of orthonormal reference states, \( |i\rangle \equiv |\chi_i(t)\rangle \), of the molecule, created by the pump pulse, (iii) determine their statistical weights according to the one-to-one correspondence with the thermally occupied rotational eigenstates of the ensemble, (iv) calculate the “one molecule” probability amplitude for HHG for each member of the ensemble of linearly independent reference states \( |i\rangle \), using Eq. (30), and finally, (v) obtain the (scaled) signal “per molecule”
by thermally averaging the **probabilities** of HHG emission from each member of the ensemble of the reference states, using the distribution of their statistical weights.

In the Born-Oppenheimer approximation and non-overlapping pump and probe pulse condition, we may consider the evolution of the wavefunctions of the nuclear and the electronic parts separately and combine them together to obtain the wavefunction of the interacting system to evaluate the transition matrix elements of interest.

### A. Pump Pulse Interaction and Rotational Wavepackets as Reference States

The nuclear rotational motion under the action of the pump pulse is determined by the Schrödinger equation governed by the partial Hamiltonian

\[
H_N(t) + V_{N-L}(t),
\]

i.e.

\[
i \frac{\partial}{\partial t} \Phi_{JM}(t) = (H_N + V_{N-L}(t)) \Phi_{JM}(t). \tag{39}
\]

We first construct the fundamental set of linearly independent solutions of Eq. (39), each evolving independently from each of the occupied rotational eigenstates \{\{J_0M_0 \}\}. We expand it on the basis of the eigenstates \{\{JM \}\}, as

\[
\Phi_{J_0M_0}(t) = \sum_{JM} C_{JM}^{(J_0M_0)}(t) |JM\rangle e^{-iE_{JM}t} \tag{40}
\]

The coefficients \(C_{JM}^{(J_0M_0)}(t)\) satisfy the system of coupled linear differential equations

\[
\frac{\partial}{\partial t} C^{(J_0M_0)}_{JM}(t) = \sum_{J'M'} \langle JM | V_{N-L}(t) | J'M' \rangle C_{J'M'}^{(J_0M_0)}(t) \tag{41}
\]

This set of equations can be easily obtained (e.g. [41]) by projecting on a given eigenstate from the left. In practice we obtain the set of the fundamental solutions \{\Phi_{J_0M_0} \} by numerical integration using the well-known Runge-Kutta method [34], starting with the following independent initial conditions:

\[
C_{JM}^{(J_0M_0)}(t_i) = \delta_{J,J_0} \delta_{M,M_0} \tag{42}
\]

We may note explicitly here that (a) each independent wavepacket-state \(\Phi_{J_0M_0}(t)\) evolves in **one-to-one** correspondence with the initially occupied rotational eigenstate \(\{J_0M_0 \}\). Taken together they form a complete set of orthonormal rotational wavepacket-states (linear superposition of rotational eigenstates):

\[
\sum_{J_0M_0} |\Phi_{J_0M_0}(t)\rangle \langle \Phi_{J_0M_0}(t)| = 1 \tag{43}
\]

In general a gas jet of molecules in a pump-probe experiment at a finite temperature \(T\), is not in a pure quantum state but rather is in a state of thermal mixture of of the rotational eigenstates, \{\{JM \}\}. We therefore introduce the quantum statistical mechanical device of a hypothetical ensemble of mutually independent and identical reference molecules, each of which occupies the electronic ground state and the rotational eigenstates \{\{J_0M_0 \}\}, the latter with statistical weights \(\rho(J_0M_0)\), given by the Boltzmann distribution:

\[
\rho(e, J_0M_0) = (1) e^{-E_{J_0M_0}/kT}, \tag{44}
\]

where

\[
Z_P = \sum_{J_0} (2J_0 + 1) e^{-E_{J_0}/kT} \tag{45}
\]

is the rotational partition function; \(E_{J_0M_0} = J_0(J_0 + 1) hB_c\), for all \(M_0\); \(B\) stands for the rotational constant. We shall assume for the present purpose that the pump pulse is not too strong so that the change in the occupation probability of the ground electronic state after the pump pulse interaction is negligible and hence the ground electronic state at a time \(t\) before the interaction with the probe pulse evolves simply to \(|\phi_e(0)\rangle = e^{-iE_e t} |\phi_e(0)\rangle\), where \(E_e\) is the ground state energy. (We may assume that electronically only the ground electronic state \(|\phi_e(0)\rangle\) is occupied initially). Thus, the linearly independent reference states of the molecule, after the interaction of the pump pulse and immediately before the interaction with the probe pulse, can be written as the direct product of the nuclear rotational wavepacket states and the electronic ground state:

\[
|\chi_i(t)\rangle \equiv |\Phi_{J_0M_0}(t)\rangle |\phi_e(t)\rangle \quad i \equiv (e, J_0M_0). \tag{46}
\]

The reference density matrix describing the molecular ensemble prepared by the pump pulse takes the form:

\[
\rho_{mol}(e, J_0M_0) = \sum_i |\chi_i(t)\rangle \langle \chi_i(t) | = |\phi_e(t)\rangle |\Phi_{J_0M_0}(t)\rangle \rho(J_0M_0) \times |\Phi_{J_0M_0}(t)\rangle \langle \phi_e(t) | \tag{47}
\]

where, \(i \equiv (e, J_0M_0)\). The above ensemble of molecular states describes the effective “initial” condition of the system after the pump pulse, when the probe pulse arrives at the molecular at \(X_j\). To avoid any possible confusion regarding the presence of the “mixed-state” of the ensemble, and the “rotational coherence”, we may already point out explicitly that while the ensemble is characterized by the statistical occurrence of the orthonormal reference states \{\{\chi_{i=xJ_0M_0}(t)\}\}, each one of these states carries the information of the rotational coherence induced by the pump pulse, as coded in the individual rotational wavepackets \{\{\Phi_{J_0M_0}(t)\}\}. Thus, when the thermal average of the HHG emission signal must be taken with respect to the **probability** of emission from
B. Interaction with Probe-Pulse and Evolution of the Electronic State

To proceed further, we next consider the evolution of the electronic state, governed by the partial Hamiltonian

\[ H_e + V_{e-L_2} (t - t_d) . \]  

(48)

It is obtained conveniently from the knowledge of the electronic Green’s function \( G_e(t, t') \) [20], associated with the above Hamiltonian and defined by the inhomogeneous equation:

\[
\left\{ i \frac{\partial}{\partial t} - (H_e + V_{e-L_2} (t - t_d)) \right\} G_e(t, t') = \delta(t - t') \mathbf{1} .
\]

(49)

A solution of the above equation can be written as (in the strong-field KFR-approximation):

\[
G_e(t, t') = -i\theta(t - t') \sum_{j,p} |\phi_j^{(+)}\rangle \langle p(t-t_d) | e^{-iE_j^{+}t} \times \langle p(t'-t_d)| \langle \phi_j^{(+)} | \\
\times e^{\frac{1}{2} \int_{t'-t_d}^{t} \rho^2(u) \, du} | \langle p(t'-t_d)| e^{iE_j^{+}t'} \langle \phi_j^{(+)} | \\
\times \langle p(t'-t_d)| \langle \phi_j^{(+)} | .
\]

(50)

where \( j \) runs over all the ionic electronic states \(|\phi_j^{(+)}\rangle\), with eigenvalues \( E_j^{+} \), of the molecular ion and \( p \) is the free momentum of the electron; \( p(t) \) stands for the instantaneous momentum in the presence of the field, defined as \( p(t) = (p + A(t)) \). The validity of Eq. (50) (within the Born-Oppenheimer and KFR approximation) can be verified by substituting it in Eq. (49) and using the completeness relation

\[
\sum_p \langle r| \phi_p(t) \rangle \langle \phi_p(t)| r \rangle = 1
\]

(51)

of the of Volkov wavefunctions defined by:

\[
\langle r| \phi_p(t) \rangle = e^{ip(t)\cdot r - \frac{1}{2} \int (p^2(u) \, du)}
\]

(52)

as well as the completeness relation of the ionic states

\[
\sum_j |\phi_j^{(+)}\rangle \langle \phi_j^{(+)} | = 1
\]

(53)

We should note that the ionic states are generally much more tightly bound than the active electron in the highest occupied molecular orbital (HOMO). Thus in deriving \( G_e \) above, we have further neglected the change in the ionic states due the interaction with the probe pulse, which we may refer to as “bare-ion” approximation.

Finally, using Eqs. (49) and (50) we obtain the total Green’s function \( G_0(t, t') \) of the interacting system:

\[
G_0(t, t') = -i\theta(t - t') \sum_{jpJM} |\phi_j^{(+)}\rangle \langle \phi_p(t-t_d) | \\
\times \langle \Phi_{JM}(t)| e^{-iE_j^{+}(t-t')} \langle \Phi_{JM}(t') | \\
\times \langle \phi_p(t'-t_d)| \langle \phi_j^{(+)} | .
\]

(54)

The above Green’s function of the system [54] therefore holds under (a) the adiabatic Born-Oppenheimer, (b) the strong-field KFR and (c) the “bare-ion” approximations.

C. The Total Wavefunction in Strong-Field Molecular KFR-approximation

Combining the Eqs. (17) and (46), we obtain the total intense-field molecular wavefunction at the lowest order strong field KFR-approximation:

\[
|\Psi_i(t)\rangle = |\chi_i(t)\rangle + \int_{-\infty}^{\infty} dt' \times G_0(t, t') V_{e-L_2}(t'-t_d) |\chi_i(t')\rangle
\]

(55)

where,

\[
|\chi_i(t)\rangle = |\phi_e(t)\rangle |\Phi_{JM_0}(t)\rangle
\]

(56)

is a member of the ensemble of reference states of interest.

D. Evaluation of the Dipole Expectation Value

In the above we have obtained the necessary ingredients for evaluating the expectation of the dipole operator Eq. (23) explicitly. Substituting Eqs. (53) and (55) in Eq. (23), we get:

\[
D_{i,i}(t) = \langle \chi_i(t)| \hat{d}_e | \Psi_i^{(1)}(t) \rangle + c.c. \]

(57)

of the of Volkov wavefunctions defined by:

\[
\langle r| \phi_p(t) \rangle = e^{ip(t)\cdot r - \frac{1}{2} \int (p^2(u) \, du)}
\]

as well as the completeness relation of the ionic states

\[
\sum_j |\phi_j^{(+)}\rangle \langle \phi_j^{(+)} | = 1
\]

We should note that the ionic states are generally much more tightly bound than the active electron in the highest occupied molecular orbital (HOMO). Thus in deriving \( G_e \) above, we have further neglected the change in the ionic states due the interaction with the probe pulse, which we may refer to as “bare-ion” approximation.
is $\Phi_{J_0 M_0} (t + t_d) = e^{-iH_N t} \Phi_{J_0 M_0} (t_d)$, and similarly, at $(t' + t_d), \Phi_{J_0 M_0} (t' + t_d) = e^{-iH_N t} \Phi_{J_0 M_0} (t_d)$, (iii) the time dependence of the unperturbed initial electronic state at $\phi_c (t + t_d) = |\phi_c e^{-iE_c (t + t_d)}$ and similarly for the ionic state, $\phi^{(+)}_c (t + t_d) = |\phi^{(+)}_c e^{-iE^{(+)}_c (t - t_d)}$.

We shall now proceed to derive an explicit expression of the HHG transition operator $T_{\text{HHG}} (t)$, for an arbitrary relative angle $\alpha$ between the linear polarization directions of the pump and the probe pulse. To this end, we first consider the most common experimental geometry in which the pump and probe polarizations are chosen to be parallel.

1. HHG operator: Parallel polarization $\alpha = 0$

We recall that for a linearly polarized probe pulse $F_2 (t) = \epsilon_0 \mathbf{F} (t) \cos \omega t$, the corresponding vector potential is

$$A(t) = -\epsilon_0 \left( \frac{e F(t)}{\omega} \right) \sin \omega t$$

It is convenient in this case to take the space fixed polarization (z-axis) along the common direction of the polarizations $\mathbf{e}_1 \parallel \mathbf{e}_2 \parallel \hat{z}$. To evaluate the triply-integral over the intermediate momenta $p$ in Eq. (61) we employ the stationary phase method [42], with the stationary values

$$p_{st} (t, t') = \frac{1}{t - t'} \int_{t'}^{t} A(t'') dt'$$

for which the derivative of the action $S(t, t')$ with respect to $t' = t - \tau$ is equal to zero. The corresponding stationary value of the action is

$$S_{st} (t, t') = \int_{t'}^{t} \left[ \frac{1}{2} \left( p_{st} (t, t'') - \frac{1}{c} A(t'') \right)^2 + E_0 \right] dt''$$

where, $p (t) = p_{st} (t, t') - \frac{1}{c} A(t)$ and $p (t') = p_{st} (t, t') - \frac{1}{c} A(t')$. Thus, projecting the resulting value of $D_e (t)$ onto the polarization direction $\epsilon_0$ of the emitted harmonic we get,

$$D_e (t) = \frac{i}{c} \int_{0}^{t} dt' \left( \frac{\pi}{\epsilon + i(t - t')/2} \right)^{3/2}$$

We may note that the first matrix element in this expression (reading from the right to the left) corresponds to the “ionization” transition at time $t'$, $d_{\text{ion}} (t') \equiv \left< \phi^{(-)}_c | \mathbf{F} (t') \cdot \mathbf{r} | \phi^{(0)}_e \right>$, whereas the last matrix element corresponds to a “recombination” transition of the electron back to the same initial state at a time $t$, $d_{\text{rec}} (t) \equiv \left< \phi^{(-)}_c | \epsilon_0 \mathbf{r} \cdot \mathbf{F} | \phi^{(0)}_e \right>$.
weak depletion due to ionization could be accounted for without difficulty by introducing in the above expression the exponential decay factor: $e^{-\gamma(t+t')}$, where $\gamma$ is the total ionization rate.

2. The “ionization” and “recombination” matrix elements

To evaluate the matrix elements of “ionization” and “recombination” in Eq. (69), we assume that the wavefunction of the active electron may be given by the highest occupied molecular orbital or HOMO. This can be written either in the multi-center LCAO-MO form, or, by transforming it into an equivalent single-center-MO (by appropriate transformations, e.g. [43, 44]). It is useful also to note that in the latter form, it often suffices for problems of interaction of molecules with long-wavelength laser fields, and in conjunction with the "length gauge", to retain only the asymptotic limit of the orbitals at distances away from the molecular center.

In general, let the unperturbed MO of the active electron of a linear molecule, in the Born-Oppenheimer approximation, be given in the body fixed frame by the single-center expansion:

$$\phi^{(0)}(r) = \sum_l C^{(m)}_l R_l(r) Y_{lm}(\hat{r}) \tag{67}$$

where $C^{(m)}_l$ are the expansion coefficients (at a given internuclear separation $R$), $R_l(r)$ are the radial waves of angular momentum $l$, $Y_{lm}(\hat{r})$ are the spherical harmonics, and $m$ is the projection of the angular momentum of the active electron along the molecular axis, that is conserved and hence also characterizes the MO.

Next, we transform the molecular orbitals Eq. (67) from the body fixed frame to the space fixed frame by using the Wigner transformation $D$, 

$$\phi^{(0)}_e(r) = D \phi^{(0)}(r) = \sum_l C^{(m)}_l R_l(r) \times \sum_\mu D^{(l)}_{\mu m}(\phi, \theta, \chi)c_{\mu m}(r') \tag{68}$$

Above $D^{(l)}_{\mu m}(\phi, \theta, \chi) = e^{-i\mu\phi}d^{(l)}_{\mu m}(\theta)e^{-i\mu\chi}$ is the Wigner rotation matrix where $(\phi, \theta, \chi)$ are the Euler’s angles which define the orientation of the molecular axis to the space fixed coordinate frame [15]. The middle term of the Wigner matrix, $d^{(l)}_{\mu m}(\theta)$, have been tabulated e.g. in reference [15, 16]. The matrix element of the dipole along the direction of the probe pulse, appearing in Eq. (69), then reads:

$$d_{\text{ion}}(t') = F(t') \sum_l C^{(m)}_l \sum_\mu D^{(l)}_{\mu m}(\phi, \theta, \chi) \langle e^{ip_{\nu}\cdot r} | \epsilon_{\omega, r} | R_l(r) Y_{lm}(\hat{r}) \rangle \tag{69}$$

Further, we expand $e^{ip_{\nu}\cdot r}$ in spherical harmonics,

$$e^{ip_{\nu}\cdot r} = \frac{2\pi}{\sqrt{p_{\nu}^2}} \sum_{l'm'} (i)^{l'} J_{l'+1/2}(p_{\nu}r) \times Y_{lm'}(\vec{p}_{\nu}) Y_{lm'}(\vec{r}) \tag{70}$$

and note that in this system of axes we have,

$$\epsilon_{\omega, r} = r \sqrt{\frac{4\pi}{3}} Y_{10}(\hat{r}) \tag{71}$$

Note also that the instantaneous momentum $p_{\nu}$ can be either parallel or anti-parallel with respect to the direction of the field so that $\theta_{pi} = 0, \pi$ and $\phi_{pi} = 0$. Therefore, the spherical harmonics with the argument $\vec{p}_{\nu}$ can be simplified to $Y_{lm'}(\vec{p}_{\nu}) = (\sigma)^{l'} \sqrt{\frac{2l'+1}{4\pi}} \delta_{lm',0}$, with $\sigma = 1$ for $\theta_{pi} = 0$ and $\sigma = -1$ for $\theta_{pi} = \pi$. Substituting Eqs. (70) and (71) in Eq. (69) we obtain (with $t' = l$),

$$d_{\text{ion}}(t') = F(t') \sum_l C^{(m)}_l \sum_\mu D^{(l)}_{\mu m}(\phi, \theta, \chi) \beta_{\text{ion}}(l, m; t') \tag{72}$$

$$\beta_{\text{ion}}(l, m; t') = \frac{(2\pi)^{3/2}}{\sqrt{p_{\nu}}} \sum_l (i\sigma)^{l'} \sqrt{2l' + 1} \times \langle l_0 | 10 | l \mu \rangle I_{l, \nu}(t') \tag{73}$$

where, we have defined the radial integrals ($m$ fixed) by

$$I_{l, \nu}(t') = \int_0^\infty J_{l+\nu}(p_{\nu}r) R_{l_\nu}(r) r^{-1/2} r^2 dr \tag{74}$$

Using the Slater orbitals representation of the single center radial functions, $R_{l\nu}(r) = r^{\nu-1}e^{-ar}$, the radial integrals ($I$’s) appearing in $d_{\text{ion}}$(Eq. (72)) can be evaluated explicitly by using the formula [17]

$$\int_0^\infty e^{-ar}J_{l}(bx) x^{\mu-1} dx = \frac{\left(\frac{a}{b}\right)^\nu \Gamma(\nu + \mu)}{\sqrt{\alpha^2 + \beta^2}^\nu \Gamma(\nu + 1)} \times F\left(\frac{\nu + \mu}{2}, \frac{1 - \mu + \nu}{2}, \nu + 1; \frac{\beta^2}{\alpha^2 + \beta^2}\right) \tag{75}$$

where $F(a, b; c; x)$ is a hypergeometric function. Note that since the argument $x \equiv \frac{\beta^2}{\alpha^2 + \beta^2} < 1$ the hypergeometric function is guaranteed to converge for all values of $a$, $b$, and $c$. For ionization step, the radial integration
reads
\[
I_{i, l, 1}(t') = \frac{\frac{n_p}{2} l+3/2}{\sqrt{(l_B^2 + p_c^2) (l+Z_c/pB+4)}}
\times \frac{1}{2} \left( l + \frac{5}{2} \frac{p_c^2}{p_B^2 + p_c^2} \right),
\]
\[
I_{i, l, -1}(t') = \frac{\frac{n_p}{2} l+1/2}{\sqrt{(l_B^2 + p_c^2) (l+Z_c/pB+2)}}
\times \frac{1}{2} \left( l + \frac{1}{2} \frac{p_c^2}{p_B^2 + p_c^2} \right). \tag{76}
\]

Exactly the same expressions hold for the radial integrals appearing in the recombination dipole \( d_{\text{rec}}(l_r, m; t) \) except that \( l_i \) is changed to \( l_r \), and \( t' \) to \( t \), in Eq. (76), throughout.

The Clebsch-Gordan coefficient in Eq. (73) implies that only the \( \mu = 0 \) term and \( l = l_i \pm 1 \) terms survive in the sums and we get for the ionization dipole,
\[
d_{\text{ion}}(t') = F(t') \sum_{l_i} \beta_{\text{ion}}(l_i, m; t') \tag{77}
\]
with
\[
\beta_{\text{ion}}(l_i, m; t') = \frac{2\pi}{\sqrt{2p_i}} \sqrt{2l_i + 1}
\times \left( (i\sigma)^{l_i+1} (l_i + 1) I_{l_i,l_i+1}(t') + (i\sigma)^{l_i-1} l_i I_{l_i,l_i-1}(t') \right) \tag{78}
\]

In the above we have introduced the angular momentum notation \( l_i \) for the initial bound state in the “ionization” matrix element and \( l_r \) in the “recombination” matrix element.

We may assume that the emitted harmonic is observed with its polarization along the same direction as the probe pulse polarization. (There is no difficulty, except lengthier algebra, to obtain the expression for the polarization direction orthogonal to it, but the former would give the dominant contribution under phase matching condition. Following an analogous calculation as above we get the “recombination” matrix element as:
\[
d_{\text{rec}}(t) = \sum_{l_r} \beta_{\text{rec}}(l_r, m; t') \tag{79}
\]
with
\[
\beta_{\text{rec}}(l_r, m; t) = \frac{2\pi}{\sqrt{2p_r}} \sqrt{2l_r + 1}
\times \left( (i\sigma)^{l_r+1} (l_r + 1) I_{l_r,l_r+1}(t) + (i\sigma)^{l_r-1} l_r I_{l_r,l_r-1}(t) \right) \tag{80}
\]

Substituting Eqs. (77-78) and (79-80) in Eq. (66), we obtain
\[
D_{t}(t) = i \sum_{l_i,t} d_{\text{ion}}^*(\theta) d_{\text{ion}}^t(\theta) \times \left[ C_{l_r}^{(m)*} C_{l_r}^{(m)} M_{t}(t) + c.c. \right] \tag{81}
\]
where we have used the relation
\[
D_{\text{ion}}(\phi, \theta, \chi) D_{\text{ion}}^*(\phi, \theta, \chi) = d_{\text{ion}}^*(\theta) d_{\text{ion}}(\theta) \tag{82}
\]
and defined the radial integral,
\[
M_{t}(t) = i \int_{-\infty}^{t_d+t} dt' \left( \frac{\pi}{(\epsilon + i(t-t')(2/\pi))} \right)^{3/2} \times \beta_{\text{rec}}(l_r, m; t') e^{-iS_{\text{ion}}(t,t')} \times F(t') \beta_{\text{ion}}(l_i, m; t') \tag{83}
\]
Next, by integrating over \( t' \), taking the Fourier transform with respect to \( t \), we obtain (cf. Eq. (28)), the HHG operator \( T_{t}^{(n)}(\theta, \phi; 0) \) for the \( \text{nth} \) harmonic generation:
\[
T_{t}^{(n)}(\theta, \phi; 0) = \sqrt{2\pi(n\omega) D_{t}(n\omega)} \times \sqrt{2\pi(n\omega)} \sum_{l_i,l_r} \bar{a}_{l_{zz}}(l_{zz}, l_{zz}; m) \tag{84}
\]
where, \( \bar{a}_{l_{zz}}(l_{zz}, l_{zz}; m) \) is given by the \( n \)th Fourier coefficient of \( D_{t}(t) \):
\[
\bar{a}_{l_{zz}}(l_{zz}, l_{zz}; m) = F.T. \left[ C_{l_r}^{(m)*} C_{l_r}^{(m)} M_{r}(t) + c.c. \right] (n\omega) \tag{85}
\]
Next, by substituting Eq. (84) in Eq. (62), we obtain the rotational matrix elements,
\[
\left\{ \Phi_{J_0,M_0}(t_d) \right| d_{\text{rec}}^*(\theta) d_{\text{ion}}^t(\theta) \left| \Phi_{J_0,M_0}(t_d) \right\} \tag{86}
\]
which can be evaluated directly by using the tabulated values of the \( d_{\text{ion}}^t(\theta) \) given by elementary trigonometric functions (see, Tab. I). Alternatively, we may first combine the product
\[
d_{\text{ion}}(\theta) d_{\text{ion}}^t(\theta) = \sqrt{\frac{4\pi}{2l_r + 1}} (-1)^m Y_{l_r, m}(\theta, \phi) \sqrt{\frac{4\pi}{2l_i + 1}} Y_{l_i, m}(\theta, \phi) \tag{87}
\]
and we obtain
\[
T_{t}^{(n)}(\theta, \phi; 0) = \sum_{l_{i, l_{r}, L}} \bar{a}_{l_{zz}}(l_{zz}, l_{zz}, m) P_L(\cos \theta) \tag{88}
\]
where,
\[
\tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) = \sqrt{2\pi(n\omega)}\alpha^{(n)}_{zz}(l_r, l_i; l_m) \\
\times (-1)^m (l_r, l_i, -m, m|l_m, 0) \\
\times (l_r, l_i, 0, 0|l_m, 0). \tag{89}
\]

Thus, the expectation value of the transition operator with respect to the rotational wavepacket can be obtained more elegantly in terms of the Legendre polynomials moments:
\[
\langle P_L \rangle_{J_0M_0}(t_d) \equiv \langle \Phi_{J_0M_0}(t_d) | P_L(\theta) | \Phi_{J_0M_0}(t_d) \rangle \tag{90}
\]

Finally, by substituting the above relations (Eq. (55)) in Eq. (62), and taking the statistical average over the ensemble of the emission probabilities from the ensemble of rotational wavepackets, we obtain the HHG signal (i.e. the rate per unit time of generation of the nth harmonic per molecule) in the special case of parallel polarizations (cf. [19]):
\[
S^{(n)}(t_d; 0) = 2\pi \sum_{J_0M_0} \rho(J_0) \sum_{L_jL_i} \tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) \times \langle P_L \rangle_{J_0M_0}(t_d) \frac{2(n\omega)^2}{c^3} \tag{91}
\]

\[
T^{(n)}(\theta', \phi'; \alpha) = \sqrt{2\pi(n\omega)} \sum_{l_r,l_i,L_m} \tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) \times \langle P_L(\theta') | \tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) \rangle \tag{92}
\]

where, \( \alpha \) is the operational laboratory angle. It should be noted that, in general, if the molecular orbital coefficients were assumed to be complex,
\[
C^{(m)}_l \equiv \left| C^{(m)}_l \right| e^{i\phi_l}, \tag{93}
\]

then we should rewrite the dynamic parameters \( \tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) \) (Eq. (55)) as:
\[
\tilde{a}^{(n)}_{zz}(l_r, l_i; l_m) = F.T. \left[ C^{(m)}_l * C^{(m)}_l \right] M_e(t) + c.c. \]
\[
= 2 \left| C^{(m)}_l \right|^2 \left[ \cos \phi_{l_r,l_i} \tilde{u}^{(n)}_{l_r,l_i,m} \right. \]
\[
- \sin \phi_{l_r,l_i} \tilde{v}^{(n)}_{l_r,l_i,m} \right) \tag{94}
\]

where,
\[
\phi_{l_r,l_i} \equiv \left( \phi_{l_r} - \phi_{l_i} \right). \tag{95}
\]

Thus, finally, we can express the general transition matrix element for the nth order harmonic as an expansion in Legendre polynomials in \( \cos \alpha \), and the corresponding Legendre moments of the time-dependent axis distribution of the molecule:

\[
M_e(t) \text{ is given by Eq. (55), and we have defined,}
\]
\[
\tilde{u}^{(n)}_{l_r,l_i,m} = F.T. \left[ \left| M_e(t) \right| \left| e^{i\phi_{l} \phi_{l'}} \right| \right] (n\omega) \tag{96}
\]
\[
\tilde{v}^{(n)}_{l_r,l_i,m} = F.T. \left[ \left| M_e(t) \right| \left| e^{i\phi_{l} \phi_{l'}} \right| \right] (n\omega) \tag{97}
\]
where, we have taken the expectation value of the 
harmonic signal from a linear molecule, for any value of 
Eq. (91) (cf. [19]).

This follows from the observation that the magnetic 
quantum numbers of all the rotational eigenstates in the 
special case of parallel polarizations, $\phi_i, l_r = (0, \pi)$ and therefore the quantity in the square brackets in 
Eq. (101) simplifies to $[...] = \left[ \cos (\phi_i, l_r) u^{(n)}_{i, l_r, l_r, m} \right]$ only.

G. A General Formula for the HHG Signal

Thus, finally, we substitute Eq. (101) in Eq. (91) and 
obtain the desired general expression (cf. 24) for the $n$th harmonic signal from a linear molecule, for any value of $t_d$ and $\alpha$:

$$T^{(n)} (t_d, \alpha) = \langle \Phi_{j_0, M_0} (t_d) |T^{(n)}(\theta, \phi; \alpha) \Phi_{j_0, M_0} (t_d) \rangle \equiv \sum_{L, l_r, l_i} \sqrt{2 \pi (\pi \omega)} \left[ \cos (\phi_i, l_r) u^{(n)}_{i, l_r, l_r, m} \right]$$

$$- \sin (\phi_i, l_r) u^{(n)}_{i, l_r, l_r, m} \left[ 2 |C_{l_i}^{(m)}| |C_{l_i}^{(m)}| \right]$$

$$\times (-1)^m \langle l_r, l_i, -m, m; L, 0 \rangle$$

$$\times \langle l_i, l_i, 0, 0; L, 0 \rangle$$

$$\times \langle P_L \rangle_{j_0, M_0} (t_d) P_L (\cos \alpha) \delta_{M, 0} \rangle$$

This simplifies to $[...] = \left[ \cos (\phi_i, l_r) u^{(n)}_{i, l_r, l_r, m} \right]$ only.

Table I: Explicit form of $d_{2m}^n (\theta)$ required for evaluating Eq. (93) [43, 46]

| $l$ | $N_2 \ (m = 0)$ | $O_2 \ (m = 1)$ |
|-----|-----------------|-----------------|
| 0   | 1               | -               |
| 2   | $\frac{1}{2} (3 \cos^2 \theta - 1)$ | $\sqrt{\frac{2}{\pi}} \sin \theta \cos \theta$ (3 - $\cos^2 \theta$) |

V. APPLICATIONS TO DIATOMIC MOLECULES $N_2$ AND $O_2$

A. Parallel Geometry, $\alpha = 0$: Elementary Expression of $T^{(n)} (\theta, \alpha = 0)$ for $N_2$

$N_2$ has $\sigma_g$ symmetry, and we approximate its MO by the asymptotic approximation from single center molecule (Eq. (67)) with $m = 0$ and $l = 0, 2, 4$ [48, 49] whose angular coefficient are given in Table II. The radial part of electronic wave function is given by

$$R_t (r) = r^{\eta-1} e^{-p \theta r}$$

with $\eta = Z_c / p_B$: $Z_c$ is the core charge and $p_B = \sqrt{2|E_B|}$ with $E_B$ is binding energy.

Evaluating Eq. (93) for $m = 0$ and $l_i, l_r = 0, 2, 4$ give us the HHG operator for $N_2$

$$T_e^{(n)} (\theta) = \sqrt{2 \pi (\pi \omega)} \sum_{l_i, l_r = 0, 2, 4} d_{2m}^n (\theta) \tilde{u}^{(n)}_{l_r, l_i} (l_r, l_i; 0) d_{00} (\theta)$$

Using the expressions for the reduced rotation matrices from Tab. II and simplifying, we may rewrite the operator as a sum of powers of $\cos^2 \theta$ only,

$$T_e^{(n)} (\theta) = \sqrt{2 \pi (\pi \omega)} \left[ b_0^{(n)} + b_1^{(n)} \cos^2 \theta + b_2^{(n)} \cos^4 \theta + b_3^{(n)} \cos^6 \theta + b_4^{(n)} \cos^8 \theta \right]$$

(106)
where the coefficients \( b^{(n)}_j \)’s reads,

\[
\begin{align*}
 b^{(n)}_0 &= \tilde{a}^{(n)}_{zz}(0, 0; 0) - \frac{1}{2}\tilde{a}^{(n)}_{zz}(2, 2; 0) + \frac{3}{8}\tilde{a}^{(n)}_{zz}(4, 4; 0) \\
 &\quad - \frac{1}{2}\left(\tilde{a}^{(n)}_{zz}(0, 2; 0) + \tilde{a}^{(n)}_{zz}(2, 0; 0)\right) \\
 &\quad + \frac{3}{8}\left(\tilde{a}^{(n)}_{zz}(0, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 0; 0)\right) \\
 &\quad - \frac{3}{16}\left(\tilde{a}^{(n)}_{zz}(2, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 2; 0)\right) \\
 b^{(n)}_1 &= -\frac{3}{2}\tilde{a}^{(n)}_{zz}(2, 2; 0) \\
 &\quad + \frac{3}{2}\left(\tilde{a}^{(n)}_{zz}(0, 2; 0) + \tilde{a}^{(n)}_{zz}(2, 0; 0)\right) \\
 &\quad - \frac{15}{4}\left(\tilde{a}^{(n)}_{zz}(0, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 0; 0)\right) \\
 &\quad - \frac{21}{16}\left(\tilde{a}^{(n)}_{zz}(2, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 2; 0)\right) \\
 b^{(n)}_2 &= \frac{35}{8}\left(\tilde{a}^{(n)}_{zz}(0, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 0; 0)\right) \\
 &\quad - \frac{125}{16}\left(\tilde{a}^{(n)}_{zz}(2, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 2; 0)\right) \\
 b^{(n)}_3 &= \frac{105}{16}\left(\tilde{a}^{(n)}_{zz}(2, 4; 0) + \tilde{a}^{(n)}_{zz}(4, 2; 0)\right) \\
 b^{(n)}_4 &= \frac{1225}{16}\tilde{a}^{(n)}_{zz}(4, 4; 0)
\end{align*}
\]

Thus, by using Eq. (92), the nth harmonic signal for \( \text{N}_2 \) becomes,

\[
S^{(n)}(t_d) = C \sum_{j=0}^{3} \sum_{j'=0}^{3} \epsilon^{(n)}_{jj'} \left\langle \cos^{2j} \theta \cos^{2j'} \theta \right\rangle (t_d)
\]

\[
= C \left\{ \epsilon^{(n)}_{00} + \epsilon^{(n)}_{01} \left\langle \cos^{2} \theta \right\rangle (t_d) + \epsilon^{(n)}_{11} \left\langle \cos^{2} \theta \right\rangle (t_d) + \epsilon^{(n)}_{02} \left\langle \cos^{4} \right\rangle (t_d) + \epsilon^{(n)}_{12} \left\langle \cos^{4} \right\rangle (t_d) + \epsilon^{(n)}_{22} \left\langle \cos^{4} \right\rangle (t_d) \right\}
\]

where \( C = \sqrt{2 \pi \alpha \omega^2} \), \( \alpha = \frac{2 \pi}{\lambda} \), and \( \lambda = (2 \pi)^2 \). The coefficients \( \epsilon^{(n)}_{jj'} \) are related to \( b^{(n)}_j \) as follows

\[
\epsilon^{(n)}_{jj'} = \left\{ \begin{array}{ll}
\frac{|b^{(n)}_j|^2}{2Re(b^{(n)}_j b^{(n)*}_j)} & \text{for } j = j' \\
0 & \text{for } j \neq j'
\end{array} \right.
\]

The leading two terms of the signal for \( \text{N}_2 \), Eq. (108), consist of a constant term proportional to \( \epsilon^{(n)}_{00} \) that arises from the leading angular momentum term \( l = 0 \) of the active molecular orbital of \( \text{N}_2 \), and a term proportional to the second moment \( \left\langle \cos^{2} \theta \right\rangle (t_d) \) that corresponds to the usual “degree of alignment” \( A(t_d) \). We may note in passing that the above result does not support a recent model calculation [52] that emphasizes that the leading contribution for HHG signal from \( \text{N}_2 \) arises from the fourth moment \( \left\langle \cos^{4} \theta \right\rangle \); that would require, for example, dropping the basic contribution of the \( l = 0 \) term i.e.

Table II: The molecular properties used in this work. \( I_p \) is adiabatic ionization potential, \( B \) is rotational constant of molecule, \( \alpha_\parallel \) and \( \alpha_\perp \) are parallel and perpendicular polarizability, and \( C^{(m)}_l \)’s are angular coefficient of the electronic wave function.

| \( \text{N}_2 \) | \( \sigma_g, m = 0 \) | \( \pi_g, m = 1 \) | \( \text{O}_2 \) | \( \text{Ref.} \) |
|----------------|----------------|----------------|----------------|--------|
| \( I_p \) (eV) | 15.58 | 12.03 | [48] |
| \( B \) (cm\(^{-1}\)) | 2.0 | 1.4377 | [51] |
| \( \alpha_\parallel \) (Å\(^3\)) | 2.38 | 2.35 | [52] |
| \( \alpha_\perp \) (Å\(^3\)) | 1.45 | 1.21 | [52] |
| \( C^{(2n)}_0 \) | 2.02 | - | [48] |
| \( C^{(2n)}_2 \) | 0.78 | 0.62 | [48] |
| \( C^{(4n)}_4 \) | 0.04 | 0.03 | [48] |

\( b^{(n)}_0 \) in Eq. (106) – for the HHG operator for \( \text{N}_2 \) – that of course would not be justifiable due to the \( \sigma \) symmetry of its active orbital.

B. Parallel Geometry, \( \alpha = 0 \): Elementary Expression of \( T^{(n)}_e(\theta; \alpha = 0) \) for \( \text{O}_2 \)

\( \text{O}_2 \) has \( \pi_g \) symmetry, and thus we approximate its MO by the asymptotic approximation with \( m = 1 \) and \( l = 2, 4 \), whose angular coefficient are given in table III. The HHG operator (Eq. 84) for \( \text{O}_2 \) reads

\[
T^{(n)}_e(\theta) = \sqrt{2 \pi (n \omega)} \left\{ \begin{array}{l}
\sum_{l_i, l_f=2,4} d^{(n)}_{01}(\theta) \tilde{a}^{(n)}_{zz}(l_i, l_f ; 1) d^{(n)}_{01}(\theta)
\end{array} \right.
\]

By using the expressions for the reduced rotation matrices from Tab. III and simplifying, we may rewrite the operator as a sum of powers of \( \sin^2 \theta \cos 2n \theta \) only,

\[
T^{(n)}_e(\theta) = \sqrt{2 \pi (n \omega)} \left[ b^{(n)}_1 \sin^2 \theta \cos^2 \theta + b^{(n)}_2 \sin^2 \theta \cos^2 \theta + b^{(n)}_3 \sin^2 \theta \cos^6 \theta \right]
\]

where \( b^{(n)}_j \) coefficients are given by

\[
\begin{align*}
 b^{(n)}_1 &= \frac{3}{2} \tilde{a}^{(n)}_{zz}(2, 2; 1) + \frac{45}{16} \tilde{a}^{(n)}_{zz}(4, 4; 1) \\
 &\quad + \frac{3}{4} \sqrt{\frac{15}{2}} \left( \tilde{a}^{(n)}_{zz}(2, 4; 1) + \tilde{a}^{(n)}_{zz}(4, 2; 1) \right) \\
 b^{(n)}_2 &= -\frac{105}{8} \tilde{a}^{(n)}_{zz}(4, 4; 1) \\
 &\quad + \frac{7}{4} \sqrt{\frac{15}{2}} \left( \tilde{a}^{(n)}_{zz}(2, 4; 1) + \tilde{a}^{(n)}_{zz}(4, 2; 1) \right) \\
 b^{(n)}_3 &= \frac{245}{16} \tilde{a}^{(n)}_{zz}(4, 4; 1)
\end{align*}
\]
Finally, substituting operator expression (Eq. 111) in Eq. (62) we obtain the \( n \)th signal of \( O_2 \) reads

\[
S^{(n)}(t_d) = C \sum_{j=1}^{3} \sum_{j' \geq j} c_{j,j'}^{(n)} \left\langle \sin^2 \theta \cos 2\theta' \right| \left\langle \sin^2 \theta \cos 2\theta' \right\rangle (t_d)
\]

\[
= C \left\{ c_{11}^{(n)} \left\langle \sin^2 \theta \cos 2\theta' \right\rangle^2 (t_d)
+ c_{12}^{(n)} \left\langle \sin^2 \theta' \cos 2\theta' \left\rangle \sin^2 \theta' \cos 4\theta' \right\rangle (t_d)
+ \cdots + c_{33}^{(n)} \left\langle \sin^2 \theta \cos 6\theta' \right\rangle^2 (t_d) \right\}
\]

(113)

Above, coefficients \( c_{j,j'}^{(n)} \) are related to \( b_{j,j'}^{(n)} \) coefficients of Eq. (112) through Eq. (119).

We note that, unlike in the case of \( N_2 \) considered above, now there is no constant leading term in the signal for \( O_2 \), Eq. (113). This is a consequence of the \( \pi - symmetry \) of the active orbital for \( O_2 \), which does not permit the lowest \( l = 0 \) angular momentum component for its active orbital.

### C. Arbitrary Relative Polarization Angle \( \alpha \): HHG Signal

We now consider the signals for \( N_2 \) and \( O_2 \) in the general case in which the probe and the pump polarizations make an arbitrary angle \( \alpha \) between them, as shown in Fig. 8. Unlike alignment angle \( \theta \), the pump-probe angle \( \alpha \) can be controlled in the laboratory and may provide a possible control of HHG of molecule. To obtain the signals in terms of elementary trigonometric functions in this more general case, we refer to Fig. 3. The direction of the molecular axis is now denoted by \( (\theta', \phi') \). The same expression for the signal as in the parallel case now holds in terms of the primed angles. The HHG signal (Eq. 118) for \( N_2 \) and Eq. (113) for \( O_2 \) for arbitrary angle \( \alpha \) now can be written as:

\[
S^{(n)}(t_d; \alpha) = C \left\{ c_{00}^{(n)} + c_{11}^{(n)} \left\langle \cos^2 \theta' \right\rangle (t_d)
+ c_{22}^{(n)} \left\langle \cos^2 \theta' \right\rangle^2 (t_d)
+ \cdots + c_{44}^{(n)} \left\langle \cos^8 \theta' \right\rangle^2 (t_d) \right\}
\]

(114)

for \( N_2 \) and

\[
S^{(n)}(t_d; \alpha) = C \left\{ c_{11}^{(n)} \left\langle \sin^2 \theta' \cos^2 \theta' \right\rangle^2 (t_d)
+ c_{12}^{(n)} \left\langle \sin^2 \theta' \cos^2 \theta' \right\rangle \langle \sin^2 \theta' \cos^4 \theta' \rangle (t_d)
+ \cdots + c_{33}^{(n)} \left\langle \sin^2 \theta' \cos^6 \theta' \right\rangle^2 (t_d) \right\}
\]

(115)

for \( O_2 \). Above, \( \left\langle f(\theta') \right\rangle (t_d) = \sum_{j_0,j_0'} \rho(j_0) \Phi_{j_0} \left( t_d, \theta \right) |f(\theta')\rangle \Phi_{j_0'} (t_d, \theta) \rangle \) is an expectation value of function \( f(\theta') \) given in probe frame but evaluated with respect to the rotational wave packet obtained in the pump frame. Before evaluating the above integral, it is convenient, therefore, to transform the HHG operators in the variables \( (\theta', \phi') \) in the angles \( (\theta, \phi) \) of the pump-frame (i.e. with the \( z \) along the pump polarization). This can be done by the simple transformations, given by Eq. (102), where \( \phi \) is the angle between plane of molecular axis - pump pulse and plane of pump - probe pulses. The elementary expression for the expectation value of the alignment operator \( A(t_d; \alpha) = \langle \cos^2 \theta' \rangle \) in the case of non-zero angle \( \alpha \) reads:

\[
A(t_d; \alpha) = \langle \cos^2 \theta' \rangle
= \left( \cos^2 \alpha - \frac{1}{2} \sin^2 \theta \right) \langle \cos^2 \theta' \rangle + \frac{1}{2} \sin^2 \alpha
+ \frac{1}{4} \sin^2 \alpha \left( \langle \sin^2 \theta \epsilon^{2i\phi} \rangle + c.c. \right)
+ \frac{1}{2} \sin 2\alpha \left( \langle \sin \theta \cos \theta e^{i\phi} \rangle + c.c. \right)
\]

(116)

where \( \langle \sin \theta \cos \theta \epsilon^{\pm i\phi} \rangle \) couples the \( J' \) states with \( \Delta J = 0, \pm 2 \) and \( \Delta M = \pm 1 \) whereas \( \langle \sin^2 \theta \epsilon^{\pm 2i\phi} \rangle \) couples the \( J' \) states with \( \Delta J = 0, \pm 2 \) and \( \Delta M = \pm 2 \). We note that for the linearly polarized pump pulse of the present interest, the interaction Hamiltonian is proportional to \( \cos^2 \theta \), which is independent of \( M \) in the space fixed pump-frame. Thus the \( M \)-quantum number of the rotational wave packet remains constant, or \( M = M_0 \), throughout the evolution. Hence, the expectation values of \( \langle \sin \theta \cos \theta \epsilon^{\pm i\phi} \rangle \) and \( \langle \sin^2 \theta \epsilon^{\pm 2i\phi} \rangle \) vanish and we get,

\[
\langle \cos^2 \theta' \rangle = \frac{1}{2} \left( 3 \cos^2 \alpha - 1 \right) \langle \cos^2 \theta' \rangle + \frac{1}{2} \sin^2 \alpha
\]

(117)

In a similar way, we obtain the expectation value for higher order

\[
\langle \cos^4 \theta' \rangle = \frac{1}{8} \left( 35 \cos^4 \alpha - 30 \cos^2 \alpha + 3 \right) \langle \cos^4 \theta' \rangle
+ \frac{3}{8} \left( -10 \cos^4 \alpha + 12 \cos^2 \alpha - 2 \right) \langle \cos^2 \theta' \rangle
+ \frac{3}{8} \sin^4 \alpha
\]

(118)

We note in passing that for \( \alpha = 0 \), \( \langle \cos^2 \theta' \rangle \) in Eq. (117) and \( \langle \cos^4 \theta' \rangle \) in Eq. (118) reduce to \( \langle \cos^2 \theta' \rangle \) and \( \langle \cos^4 \theta' \rangle \), respectively.

Thermal averaging Eq. (117) gives us the “degree of alignment” or the alignment-moment:

\[
A(t_d, \alpha) = \frac{1}{2} \left( 3 \cos^2 \alpha - 1 \right) \langle \langle \cos^2 \theta' \rangle \rangle (t_d) + \frac{1}{2} \sin^2 \alpha
\]

(119)

which also appears in the second leading term of the signal for \( N_2 \), for arbitrary angle \( \alpha \) (see, Eq. (114)). Squaring and taking the thermal average of Eq. (117) gives us \( \langle \langle \cos^2 \theta' \rangle \rangle \), which is the third term of HHG signal of \( N_2 \). The thermal average of Eq. (118) gives us \( \langle \langle \cos^4 \theta' \rangle \rangle \).
which appears in the fourth term of HHG signal of N$_2$. 
The difference of Eq. (117) and Eq. (118) gives us

$$\langle \sin^2 \theta \cos^2 \theta \rangle = \frac{1}{8} (-35 \cos^4 \alpha + 30 \cos^2 \alpha - 3) \langle \cos^4 \theta \rangle$$

$$+ \frac{1}{8} (30 \cos^4 \alpha - 24 \cos^2 \alpha + 2) \langle \cos^2 \theta \rangle$$

$$+ \frac{1}{8} (-3 \sin^4 \alpha + 4 \sin^2 \alpha)$$

Squaring and then thermally averaging Eq. (120) yields the leading term of HHG signal of O$_2$, given by Eq. (119). In a similar way, we can explicitly exhibit the \(\alpha\)-dependence of the higher order terms in the signal for O$_2$, Eq. (115), as well.

VI. RESULTS AND DISCUSSIONS

A. Signals in the Time Domain

We now apply the theory to analyze the observed HHG signals from the diatomic molecules, N$_2$ and O$_2$. In typical recent experiments (e.g. [11, 12, 13, 55]) an ensemble of N$_2$ or O$_2$ molecules is first set into free rotation by a femtosecond pump pulse. The HHG signals were detected by monitoring the emission due to a second more intense femtosecond probe pulse, that was delayed with respect to the first by successively increasing the time intervals, \(t_d\), in the picosecond domain, between them.

In the experiments for N$_2$, for example by Miyazaki et al. [13, 55], a peak pump-intensity \(I_1 = 0.8 \times 10^{14} \text{ W/cm}^2\), a peak probe-intensity \(I_2 = 1.7 \times 10^{14} \text{ W/cm}^2\) were used; the central wavelength \(\lambda = 800 \text{ nm}\) and the pulse duration \(\tau = 40 \text{ fs}\) were kept the same for both the pulses. For the experiment with O$_2$, the harmonic signal was measured in a similar fashion for \(I_1 = 0.5 \times 10^{14} \text{ W/cm}^2\) and \(I_2 = 1.2 \times 10^{14} \text{ W/cm}^2\); the other parameters were kept the same as in the case of N$_2$. For the purpose of a direct comparison, our calculations were performed for the same parameter values as in these experiments [13, 55]. In Fig. 4 and Fig. 5 we compare the calculated HHG signals as a function of \(t_d\) for N$_2$ and O$_2$, with the experimental data obtained for the 19th order harmonic. The effective ensemble temperature was taken to be \(T = 200 \text{ K}\), that was estimated from the matching of the peak position of the spectral distribution with that of the Boltzmann distribution as suggested first in [19]. It can be seen from Fig. 4 that the experimental data for N$_2$ show the “revival” phenomenon with a full revival period \(T_{\text{rev}} = 8.4 \text{ ps}\) (which is consistent with the rotational constant of N$_2$ (cf. Tab. III)) as well as a \(\frac{1}{2}\) and a \(\frac{1}{4}\) fractional-revival. The observed signal for O$_2$ shows, in addition to the full revival (period for O$_2$ is \(T_{\text{rev}} = 11.6 \text{ ps}\)) and two fractional revivals similar to the two seen for N$_2$, an additional \(\frac{1}{2}\) revival. The calculated signals can be seen to follow the same sequence of the full and the three fractional revivals as seen in the experimental signal. We note that these observations for N$_2$ and O$_2$ are also consistent with the data of Itatani et al. [11] and Kanai et al. [12].

To understand the similarities and the differences between the signals for N$_2$ and O$_2$, we use the analytical results of the present theory below. The properties of the HHG signal of N$_2$ are governed by Eq. (108). The first term gives a constant background. The second term \(\langle \langle \cos^2 \theta \rangle (t_d) \rangle\) is the dominant dynamic term and makes the signal to mimic the “degree of alignment” \(A(t_d) \equiv \langle \langle \cos^2 \theta \rangle \rangle (t_d)\). The third term \(\langle \langle \cos^2 \theta \rangle^2 \rangle (t_d)\) give unequal maxima and minima i.e. the difference between the maximum signal and the average signal is greater than the the difference between the average signal and the minimum signal. Furthermore we point out that at a lower initial temperature, the valley of \(\langle \langle \cos^2 \theta \rangle^2 \rangle (t_d)\) that occurs, for higher temperatures, at the \(\frac{1}{4}T_{\text{rev}}\) revival, can split into two valleys, due to
this term, and thus the third term can strongly affect
the HHG spectrum, as can be seen in the experiment
by Itatani, et al [11, 14]. Another earlier puzzle
regarding its dynamic signal observed was the failure of
the alignment measure $A(t_d)$ to account for the dynamic HHG signal for O$_2$, observed by
Itatani et al. [11]. In fact, Itatani et al. found that
their data behaved more closely to the expectation value
$B(t_d) = \langle \langle \sin^2 2\theta \rangle \rangle (t_d)$. From Eq. (114) it can be seen
that the leading term of the signal for O$_2$ is given
by $\langle \langle \sin^2 \theta \cos^2 \theta \rangle \rangle (t_d) = \frac{1}{10} \langle \langle \sin^2 2\theta \rangle \rangle (t_d)$, which is
directly proportional to the observed signal. Moreover,
the present theory also predicts that there ought to be
modifications to this result due to the higher order terms
in Eq. (113). In contrast to N$_2$ there is no significant
difference between minima and maxima for O$_2$, since all
terms in Eq. (73) have similar minima and maxima. The
present theory also predicts that there ought to be modifi-
cations to this result due to the higher order terms in
Eq. (113). In contrast to N$_2$, however, there should not
be a significant asymmetry between the size of the
maxima and minima for O$_2$, since the terms in Eq. (73)
have similar maxima and minima. The can be, however,
quantitative contributions from the higher order terms
predicted by the theory. In fact, as mentioned earlier,
Kanai et al. [12] found empirically that their experimental
HHG signals for N$_2$ and O$_2$ demanded heuristic intro-
troduction of operators involving higher orders of $\cos^2 \theta$
functions, or Legendre polynomials, as the dynamic sig-
nal could not be well expressed in term of $\langle \langle \cos^2 \theta \rangle \rangle (t_d)$
only for N$_2$, or $\langle \langle \sin^2 2\theta \rangle \rangle (t_d)$ only for O$_2$. In fact, the
present theory provides an ab initio derivation of the de-
sired general expansion of the HHG signal in terms of the
moments of the Legendre polynomials Eq. (113) and/or
of the powers of $\cos^2 \theta$, e.g. Eqs. (114) and (115).

A related characteristic of interest first observed by
Miyazaki et al. (e.g. [52]) is the appearance of extra se-
ries and lines in the Fourier spectrum of the dynamic
HHG signal for both N$_2$ and O$_2$, that are Raman for-
bidden. These extra lines can not be attributed to $A(t_d) = \langle \langle \cos^2 \theta \rangle \rangle (t_d)$, for N$_2$, or to $B(t_d) = \langle \langle \sin^2 2\theta \rangle \rangle (t_d)$ for
O$_2$. It will be seen below that the F.T. of the higher or-
ders terms of Eq. (115) for N$_2$ and of Eq. (113) for O$_2$,
given by the present theory can consistently account for
their appearance.

Comparing the expressions for the signals for N$_2$ and
O$_2$ and directly calculating the $C^{(n)}_{lj}$ coefficients in
the respective signals it is found that the signal for N$_2$ is much
stronger than that for O$_2$, as also observed experimentally.

We may briefly discuss here the dependency of the
HHG signals on the initial temperature, an example of
which is shown in Fig. 6. It can be seen from the figure
that the lower initial temperature gives a greater am-
pitude of revival. This may be understood as follows. A
lower initial temperature gives a lower value of the max-
imum of the statistically occupied $J_0$ levels and hence
also a lower value of the maximum initial value of $M_0$, than
at a higher temperature. As a result of interaction
with the linearly polarized pump pulse (quantization
axis along the polarization axis) at a given intensity, each
wavepacket that evolves from a given initial $|J_0, M_0\rangle$ state,
can couple to the higher levels $J' > \text{max}(J_0)$, but can
not raise the initial maximum value of $M_0$. Therefore,
for a given intensity, the ratio of $J'$ to $M_0$ is higher for
a lower temperature, and as a consequence the degree of
alignment $A(t_d) = \langle \langle \cos^2 \theta \rangle \rangle$ tends to be also higher, implying
that the molecule becomes more strongly aligned
during a revival.

B. Rotational Revivals: Periods and Phases

If a linear molecule has a permanent dipole moment
(e.g. hetero-nuclear diatomics), then the interaction
Hamiltonian of the (pump) laser with the molecular
frame depends on the first power of $\cos \theta$, where $\theta$ is
the angle of rotation of the molecular axis with respect to
the laser polarization axis. In contrast, the interaction
with the polarization of the molecule (e.g. for homo-
or hetero-nuclear diatomics) depends on $\cos^2 \theta$. Thus in
general the interaction may contain the operators $\cos^n \theta$
with $n = 1$ and/or 2. Then in either case, the rotational
wavepackets created by the later can be written in the
form:

$$
\Phi_{J_0, M_0}(t) = \sum_{j=0,1,2,3...} C_{J_0+nj,M_0}(t) \times e^{-i E_{J_0+nj} t} |J_0 + nj, M_0\rangle
$$ (121)

This can be obtained, for example, from a consider-
ation of the perturbative solution of Eq. (59) in suc-
cessive power of the interaction Hamiltonian, and noting

![Figure 6: The dependency of HHG signal on the harmonic order and on the initial temperature of the gas. Solid and dashed lines are for the 19th and the 21th order, respectively.](image-url)
that the rotational eigenstates couple either by $P_2(\cos \theta)$ (in the absence of a permanent dipole moment) with a minimum (non-zero) $n = 2$ or by $P_1(\cos \theta)$ and $P_2(\cos \theta)$ (in the presence of a permanent dipole moment) with a minimum $n = 1$. It can be readily understood from the well known properties of the vector addition coefficients that appear in the integration over the product of three spherical harmonics (cf. para below) that the expectation value of the $N$th cosine-moment with respect to a rotational wavepacket at a time $t = t_d$, takes the form:

$$
\langle \cos^N \theta \rangle_{J_0,M_0}(t_d) = \langle \Phi_{J_0,M_0}(t_d) | \cos^N \theta | \Phi_{J_0,M_0}(t_d) \rangle = \\
\sum_{s} \sum_{p} C_{J_0+n_j+p,M_0}(t_d) C_{J_0+n_j,M_0}(t_d) \times a_s \langle Y_{J_0+n_j+p,M_0} | Y_{s,0} | Y_{J_0+n_j,M_0} \rangle \times \exp \left(-\frac{i}{\hbar} (E_{J_0+n_j+p} - E_{J_0+n_j}) t_d \right)
$$

(122)

where, the integers $s$ and $p$ have the same parity (even or odd) as the parity of $N$. This follows from the fact that $\cos^N \theta$ can be expressed as a linear combination: $\cos^N \theta = \sum_a a_s P_a(\cos \theta)$, for all $s$ up to $N$, and since the matrix elements $\langle Y_{J_0+n_j',M_0} | Y_{s,0} | Y_{J_0+n_j,M_0} \rangle = 0$, unless, $J_0 + n_j' = J_0 + n_j + (p-s) \geq 0$, and $J_0 + n_j + (p-s) + J_0 + n_j + s = \text{even}$. Thus, the phase of each individual term of Eq. (122), for any given value of the integers $J_0, n, N, j$, is given by

$$
\Delta \phi_{n,N}^{J_0}(t_d) = \frac{1}{\hbar} (E_{J_0+n_j+p} - E_{J_0+n_j}) t_d \times 2\pi Bct \pm \frac{2pJ_0 \pm 2npj + p^2 \pm p}{2}.
$$

(123)

where, we have used $E_{J,M} \equiv E(J+1)Bc$; $B$ is the rotational constant, $T_{rev} \equiv \frac{1}{2\pi Bc}$ is the rotational period, and $h = 2\pi \hbar$. We note first that the quantity in the last parentheses above is an integer, independent of the value of $j$ and $J_0$. We note that the maximum value of $s$ or $p$ above is $N$. The phase difference (Eq. 123) therefore equals to an even or odd multiple of $\pi$, or odd multiple of $\frac{\pi}{2}$, depending on the parity of the groups of rotational states. Therefore, the shortest time period for which the phases of all terms or all terms within a parity group become equal in Eq. (123), and hence coherently enhance the signal, is clearly

$$
T_{\min} = \frac{1}{nN} T_r.
$$

(124)

For times between the successive coherent enhancements or “revivals”, the individual phases in Eq. (123) disperse away from one another and the revival peaks tend to be washed out by destructive interference, and the HHG signal reduces to the average or the background level.

We may summarize the above result as a “revival theorem”: If the laser-molecule interaction Hamiltonian is characterized by the lowest power $n$ of $\cos^n \theta$, with $n = 1$ or 2, $\theta$ is the rotation angle, and if the highest discernible (numerically significant) moment in the expression of the signal is $\langle \Phi_{J_0,M_0}(t) | \cos^n \theta | \Phi_{J_0,M_0}(t) \rangle$, $N \geq 1$, then the experimental signal would exhibit as many as $n \times N$ revivals within a full period $T_r = \frac{1}{2\pi Bc}$, $B$ is the rotational constant. Inversely, by counting the number of fractional revivals in the observed HHG signal, one may determine the highest order, $N$, and hence also the significant “cosine moments” (up to the order $N$) that would be necessary to fit the observed signal. We may note that the above theorem covers the well-known cases of fractional revivals discussed earlier [57, 57, 58, 59] as special cases.

For homonuclear diatomic molecules with no permanent dipole moment, the lowest order pump pulse interaction is due to the polarizability tensor with $n = 2$. Thus for the standard alignment moment, $A(t_d) \equiv \langle \cos^2 \theta(t_d) \rangle$ with $N = 2$, we get the lowest fractional period $T_{\frac{1}{2}} = \frac{1}{2} T_r$, and the subsequent two fractional revivals $T_{\frac{1}{4}}$, $T_{\frac{1}{8}}$ (defined analogously) and the full revival at $T_r$, with in a period. Thus the presence of the highest significant fourth cosine-moment with $N = 4$ would show the lowest $\frac{1}{nN} = \frac{1}{4}$ revival, plus the subsequent six fractional revivals at $\left(\frac{1}{4}, \frac{3}{8}, \frac{3}{8}, \frac{5}{8}, \frac{5}{8}, \frac{7}{8} \right) T_r$, within a

Figure 7: Revival structure of the moment $\langle \cos^2 \theta(t_d) \rangle$, for the case of O2, on the beat frequency: for all $\Delta J$ retained (panel a), with $\Delta J = 0$ only (panel b), with $\Delta J = \pm 2$ only (panel c), and with $\Delta J = \pm 4$ only (panel d). It is clear that the transition with $\Delta J = \pm 4$ has the lowest fractional revival at $\frac{1}{4} T_r$, and has the shortest period.
full period $T_r$. An example containing the effect of the fourth cosine-moment is $B(t_d) = \langle \sin^2 2\theta \rangle (t_d)$, which is illustrated in Fig. [7]. For a heteromolecular diatomic molecule with a permanent dipole moment, the lowest order interaction Hamiltonian is characterized by the first power of $\cos \theta$ i.e. $n = 1$. Thus the alignment measure, a cosine moment with $N = 2$, will show $n \times N = 2$ revivals within the full period. Higher order revivals may occur since Eq. (124) in principle holds for any combination $(N, n)$. We may recall, however, that for large $N$, the expectation value might be too weak for the lowest fractional revivals to be measured with sufficient resolution in practice. This circumstance is illustrated in Fig. [8] which shows the high order fractional revivals for $N = 6$ and $N = 8$ cosine-moments, $\langle \cos^6 \theta \rangle (t_d)$ and $\langle \cos^8 \theta \rangle (t_d)$, along with their magnifications.

C. Phase Relations of Fractional Revivals

Can one predict the relative phases of the fractional revivals? We may answer this question positively. From the phase difference (Eq. (123)), one finds:

$$\Delta \phi_{2,2}^{J_0} (T_{rev}) - \Delta \phi_{2,2}^{J_0} (T_{rev}/2) = 4\pi$$

$$\Delta \phi_{2,2}^{J_0} (T_{rev}/2) - \Delta \phi_{2,2}^{J_0} (T_{rev}/4) = 2\pi$$

$$\Delta \phi_{2,2}^{J_0} (T_{rev}/4) - \Delta \phi_{2,2}^{J_0} (T_{rev}/2) = \pi$$

Eq. (125) predicts that at $1/T_r$ the phase for $J_{even}$ is an exact mirror image of the phase for $J_{odd}$, as in fact is the case in Fig. [9] calculated for $N_2$. From the above, we may further predict that:

(a) for $O_2$, which possess $J_{odd}$ levels only, will show a “peak” at $T_r/4$,

(b) CO$_2$, which possesses $J_{even}$ levels only, will show a “valley” at $T_r/4$, and

(c) $N_2$, which possesses both the majority $J_{even}$ levels and the and the minority $J_{odd}$ levels in the ratio 2 : 1 (due to the nuclear statistics of the molecule [22]), will show the the revival at $T_r/4$ that would be a “valley” like the one for the $J_{even}$ levels only, but with only half its normal “depth’, due to the counter contribution from the minority $J_{odd}$ levels.

We note that one may also predict the nuclear statistics of such molecules by comparing the revival shape at $T_{rev}/2$ and $T_{rev}/4$. Let us first define a modulation amplitude at half-revival to be equal to the difference between peak and the base (or average) signal: $(A_{1/2} = S_{1/2}^{top} - S_{1/2}^{av})$. Similarly, a modulation amplitude at quarter-revival is equal to the difference between the top and the base (average) signal: $(A_{1/4} = S_{1/4}^{top} - S_{1/4}^{av})$. The amplitude at half-revival is a sum of even and odd $J$ contributions, and therefore $A_{1/2}$ is always positive. In contrast, the amplitude at the quarter-revival arises from their difference, and therefore $A_{1/4}$ can be positive (if it makes a “top” alignment) or negative (if it makes an “anti-top” alignment). Therefore, the existence of a “top” signal at the quarter-revival is a sign that even $J$ levels are dominant. Similarly the presence of an “anti-top” signal at the quarter-revival signal is a sign of dominant odd $J$ levels. From this observation, one can deduce the nuclear statistics from the ratio between the effective
A (finite) number of even and the odd $J$ levels ($J_{\text{even}}$ and $J_{\text{odd}}$, respectively) excited:

$$\frac{J_{\text{even}}}{J_{\text{odd}}} = \frac{A_{1/2} - A_{1/4}}{A_{1/2} + A_{1/4}}$$

(126)

Thus, for example, the dynamic signal of $O_2$ shows $A_{1/2} = A_{1/4}$ indicating the absence of the even $J$ levels. In contrast, $A_{1/2} = -A_{1/4}$ for CO$_2$, indicating the absence odd $J$ levels. For $N_2$, we have $A_{1/4} = -\frac{1}{3}A_{1/2}$, and hence we have $J_{\text{even}} : J_{\text{odd}} = 2 : 1$. This property might be used for detecting the existence of isotopes of a molecular sample, as has been suggested recently [60].

D. Beat Frequencies

From Eq. (127), it is seen that the phase difference associated with $\langle \cos^2 \theta \rangle$ is $(B/h)(4J+6)$. For $B$ in cm$^{-1}$, the phase difference reads

$$\Delta \phi (J \rightarrow J \pm 2) = 2\pi Bc(4J + 6)$$

(127)

with $c$ in cm/second. According to Eq. (127), one can make a Fourier transform of $\langle \cos^2 \theta \rangle$ using $Bc$ as basis frequency and find a series of peaks at $(4J + 6)$. Fig. 10 shows the Fourier transform of $\langle \cos^2 \theta \rangle$ of $N_2$, $O_2$, and CO$_2$. The spectrum of O$_2$ has peak series at (10, 18, 26, ...) $Bc = (4J_{\text{odd}} + 6)Bc$, showing that O$_2$ has odd $J$ levels only. In contrast, the peak series of CO$_2$ are located at (6, 14, 22, 30, ...) $Bc = (4J_{\text{even}} + 6)$, showing that CO$_2$ has even $J$ levels only. For N$_2$, we obtain a series (6, 14, 22, 30, ...) $Bc = (4J_{\text{even}} + 6)$ that is twice as strong as the series (10, 18, 26, ...) $Bc = (4J_{\text{odd}} + 6)Bc$. It implies that both even and odd $J$ levels are present for N$_2$, in the ratio $J_{\text{even}} : J_{\text{odd}} = 2 : 1$. These conclusions are consistent with the analysis based on the dynamic signals.

For $\langle \sin^2 2\theta \rangle$, there are two kinds of difference beat frequency. The first one is related to the transitions with $\Delta J = \pm 2$ and is expressed by Eq. (127). The second one is related to the transitions with $\Delta J = \pm 4$ and can be expressed as

$$\Delta \phi (J \rightarrow J \pm 4) = 2\pi Bc(8J + 20)$$

As a result, in addition to the series of lines $(4J + t)$ the Fourier transform of $\langle \sin^2 2\theta \rangle$ also has another series of lines at $(8J + 20)$, with $\Delta J = 4$. Fig. 11 shows the calculated Fourier transform of $\langle \sin^2 2\theta \rangle$ of O$_2$. It is seen from Fig. 11 that the first series $\langle \sin^2 2\theta \rangle$ reaches its maximum at $J_{\text{max}} = 11$, while the second one $(\Delta J = \pm 4)$ at $J_{\text{max}} = 13$. This difference comes from the fact that the $\Delta J = 4$ transition requires $J_{\text{max}} = 12$, an intermediate transition. As a result, a $\Delta J = 4$ transition can occur one step after the $\Delta J = 2$ transition; for O$_2$ with only $J_{\text{odd}}$ levels present, this implies a shift in $J$ by 2, from $J_{\text{max}} = 11$ to $J_{\text{max}} = 13$, as seen above. From Fig. 11 one also finds that the intensity of the second transition is smaller than that of the first one. This arises

![Figure 10: Fourier transform of the alignment moment $A(t_d) \equiv \langle \cos^2 \theta \rangle(t_d)$, plotted using $Bc$ as the basis frequency (lower scale). Following the $(4J + 6)$-rule for the line positions from $\langle \cos^2 \theta \rangle$, the peak frequencies are seen to occur for odd $J$ only, for the case of O$_2$, even $J$ only for the case of CO$_2$, and for both even and odd $J$, for the case of N$_2$. The corresponding $J$ values are shown in upper scale.](image)

![Figure 11: Fourier transform of $\langle \sin^2 2\theta \rangle$ of O$_2$ : all lines (panel a), line from transitions with $\Delta J = \pm 2$ only (panel b), and lines from transition with $\Delta J = \pm 4$ only (panel c); pulse of intensity $0.5 \times 10^{14}$ W/cm$^2$, FWHM = 40 fs, initial temperature 300 K.](image)
from the circumstance that the allowed matrix element of the second transition with the greater separation in \( J \) is weaker than the one with the lesser separation.

E. Signals in the Frequency Domain

To further compare with experimental data, we Fourier transform the calculated dynamic signals to get their spectra in the frequency domain. They may then be compared with the F.T. of the experimental data. The results for the 19th harmonic signal for \( N_2 \) is compared with the experimental data in Fig. 12a. It can be seen that the experimental spectrum (panel a) exhibits two prominent series I: \((6, 14, 22, 30, 38, \ldots) Bc\) and II: \((10, 18, 26, 34, 42, \ldots) Bc\), which are also present in the theoretical spectrum (panel b). They can be easily understood to arise from the F.T. of the \( \langle \cos^2 \theta \rangle \) term in Eq. 108 which vanishes unless \( \Delta J = 0, \pm 2; \) this produces a sequence of lines \((E_{J+2} - E_J)/2\pi = (4J + 6) Bc\), and gives the series I and II, for the even and the odd \( J \) levels, respectively. The relative prominence of the series I over the series II, from both experiment and theory, seen in the two panels in Fig. 12a could be understood as the 2 : 1 ratio of the \( J \) even over \( J \) odd levels, a well-known consequence of the nuclear spin statistics of \( N_2 \) (e.g. 8, 22). The weakly resolved series III: \((20, 28, 36, 44, \ldots) Bc\) and series IV: \((4, 8, 12, 16, \ldots) Bc\) in Fig. 12a are the unexpected series that could not be produced by the F.T. of the leading term \( \langle \cos^2 \theta \rangle \) term. We note that the series III and IV, although weak, are certainly also present in the theoretical spectrum in Fig. 12b. To interpret their origin, we consider the two higher order terms involving \( \langle \cos^4 \theta \rangle \) in the signal for \( N_2 \), Eq. 108. Because of the presence of the square of the second moment, the expected beat frequency from \( \langle \cos^2 \theta \rangle \) not only includes the frequencies \((4J + 6) Bc\) but also their sum and difference frequencies, as indicated below:

\[
(a + b \cos \omega_1 t)(a' + b' \cos \omega_1' t) = \cos \omega_1 t + ab' \cos \omega_1 t + b' \cos \omega_1 t \cos \omega_1' t + b' \cos \omega_1 t + a \cos \omega_1' t \cos \omega_1 t + \frac{b'}{2} \cos (\omega_1 + \omega_1') t + \frac{b'}{2} \cos (\omega_1 - \omega_1') t
\]

(129)

Above, the term \( a \) arises from transition with \( \Delta J = 0 \) and \( \omega_0 = 0 \). The frequency \( \omega_1 \) arises from transition with \( \Delta J = \pm 2 \). The sum frequency \((\omega_1 + \omega_1')\) yields \((E_{J+2} - E_J)/2\pi = (4J + 12) Bc\) series whereas the difference \((\omega_1 - \omega_1')\) produces \((E_{J+2} - E_J)/2\pi = (4J - 12) Bc\). For integer \( J \) and \( J' \) they yield the series IV: \((4, 8, 12, 16, \ldots) Bc\). The next term \( \langle \cos^4 \theta \rangle \) vanishes unless \( \Delta J = 0, \pm 2, \) and \( \pm 4 \) produces not only \((E_{J+2} - E_J)/2\pi = (4J + 6) Bc\) series lines but also \((E_{J+4} - E_J)/2\pi = (8J + 20) Bc\).
Table III: List of all the predicted series arising from the moments \( \langle \cos^2 \theta \rangle \), \( \langle \cos^2 \theta \rangle^2 \), and \( \langle \cos^4 \theta \rangle \) that are present in the expression for the signal for N\(_2\) (for which both odd and even \( J \)’s are allowed).

| No. | Group freq. | Weighting factor | Formula | Peak series (in Bc) | Expt. series |
|-----|-------------|------------------|---------|---------------------|-------------|
| \( \langle \cos^2 \theta \rangle \) | | | | | |
| 1 | - | \( a \) | - | 0 | - |
| 2 | \( \omega_1 \) | \( b \) | \( 4J + 6 \) | 10, 18, 26, ... for odd \( J \) | II |
| | | | | 6, 14, 22, ... for even \( J \) | I |
| \( \langle \cos^2 \theta \rangle^2 \) | | | | | |
| 3 | - | \( aa' \) | - | 0 | - |
| 4 | \( \omega_1 \) and \( \omega'_1 \) | \( a'b \) and \( ab' \) | \( 4J + 6 \) | 10, 18, 26, ... for odd \( J \) | II |
| | | | | 6, 14, 22, ... for even \( J \) | I |
| 5 | \( \omega_1 + \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 4(J + J') + 12 \) | 20, 28, 36, ... | III |
| 6 | \( \omega_1 - \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 4(J - J') > 0 \) | 4, 8, 12, ... | IV |
| \( \langle \cos^4 \theta \rangle \) | | | | | |
| 7 | - | \( a \) | - | 0 | - |
| 8 | \( \omega_1 \) | \( b \) | \( 4J + 6 \) | 10, 18, 26, ... for odd \( J \) | II |
| | | | | 6, 14, 22, ... for even \( J \) | I |
| 9 | \( \omega_2 \) | \( c \) | \( 8J + 20 \) | 28, 44, 60, ... | III |

Table IV: All possible frequency arising from \( \langle \sin^2 \cos^2 \theta \rangle^2 \) for O\(_2\) whose only odd \( J \)’s are allowed. The weak frequencies are noticed with (*).

| No. | Group freq. | Weighting factor | Formula | Peak series (in Bc) | Expt. series |
|-----|-------------|------------------|---------|---------------------|-------------|
| 1 | - | \( aa' \) | - | 0 | - |
| 2 | \( \omega_1 \) and \( \omega'_1 \) | \( a'b \) and \( ab' \) | \( 4J + 6 \) | 10, 18, 26, ... | II |
| 3 | \( \omega_2 \) and \( \omega'_2 \) | \( ac \) and \( ac' \) | \( 8J + 20 \) | 28, 44, 60, ... | III |
| 4 | \( \omega_1 + \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 4(J + J') + 12 \) | 20, 28, 36, ... | III |
| 5 | \( \omega_1 - \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 8(J - J') > 0 \) | 8, 16, 24, ... | V |
| 6 | \( \omega_2 + \omega'_2 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 8(J + J') + 40 \) | 56, 72, 88, ... | I* |
| 7 | \( \omega_2 - \omega'_2 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 8(J - J') > 0 \) | 16, 32, 48, ... | V* |
| 8 | \( \omega_1 + \omega'_2 \) and \( \omega_2 + \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) and \( \frac{\omega_{bb'}}{\omega} \) | \( 4(J + 2J') + 26 \) | 38, 46, 54, ... | VI* |
| 9 | \( \omega_1 - \omega'_2 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 4(J - 2J') - 14 > 0 \) | 6, 14, 22, ... | VI* |
| 10 | \( \omega_2 - \omega'_1 \) | \( \frac{\omega_{bb'}}{\omega} \) | \( 4(-J + 2J') + 14 > 0 \) | 2, 10, 18, ... | II* |

gives series III \((20, 28, 36, 44, ...)\)Bc. All the possible series arising from these three leading terms and their grouping according to those observed experimentally are shown in table III. Note that series III is identical, and overlap, with the series IV: \((4, 8, 12, 16, 32, ...)\)Bc and adds to its strength. Moreover, the remaining lines at \((4, 8, 12, 16, 24, 32, ...)\)Bc found in the experimental spectrum in Fig. 12(a) as well as in the theoretical spectrum in Fig. 12(b), confirm the existence of the series IV which is distinct from the series III. The existence of series III and IV is a prove of the fact that the dynamic signal of N\(_2\) can not be described in term of \( \langle \cos^2 \theta \rangle \) only.

In Fig. 13 we compare the experimental spectrum (panel a) for O\(_2\) with the theoretical spectrum (panel b) calculated from Eq. 113. Both the experimental and the theoretical spectra in Fig. 13 show the Raman-allowed series II: \((10, 18, 26, 34, 42, ...)\)Bc, but not the series I: \((6, 14, 22, 30, 38, ...)\)Bc, seen for N\(_2\). The anomalous series III: \((20, 28, 36, 44, ...)\)Bc, discussed in the case of N\(_2\) above, however, appears for O\(_2\) as well. Finally, another anomalous sequence V: \((8, 16, 24, ...)\)Bc can be seen to be present in the data for O\(_2\) in Fig. 13, that, we point out, can not be generated by F.T. of \( \langle \sin^2 \theta \rangle \) term. To interpret the origin of the observed series in O\(_2\) we first consider the leading term given by Eq. 110, \( \langle \sin^2 \theta \cos^2 \theta \rangle \). The matrix element \( \langle \sin^2 \theta \cos^2 \theta \rangle \) vanishes unless \( \Delta J = 0, \pm 2, \pm 4 \) corresponds to frequency \( \omega_0, \omega_1, \omega_2 \). Thus, there will be the various sum and difference frequencies that arise from the presence of the squared moment, as follows:
\[(a + b \cos \omega_1 t + c \cos \omega_2 t) (a' + b' \cos \omega_1' t + c' \cos \omega_2' t) =
\begin{align*}
&= aa' + ab' \cos \omega_1' t + a'b \cos \omega_1 t
+ ac' \cos \omega_2' t + a'c \cos \omega_2 t
+ \frac{bb'}{2} \cos (\omega_1 + \omega_1') t
+ \frac{bb}{2} \cos (\omega_1 - \omega_1') t
+ \frac{cc'}{2} \cos (\omega_2 + \omega_2') t
+ \frac{cc}{2} \cos (\omega_2 - \omega_2') t
+ \frac{bc'}{2} \cos (\omega_1 + \omega_2') t
+ \frac{bc}{2} \cos (\omega_1 - \omega_2') t
+ \frac{b'c}{2} \cos (\omega_2 + \omega_1') t
+ \frac{b'c}{2} \cos (\omega_2 - \omega_1') t
\end{align*}
\]

with \(a > b > c\). As discussed before, the frequency \(\omega_2\) generates the lines \((4J + 6)\) that for odd \(J\) give the series II: \((10, 18, 26, \ldots) Bc\). The series I: \((6, 14, 22, \ldots) Bc\) that would exist for even \(J\) is absent from the \(O_2\) spectrum. This is easily understood as due to the nuclear spin of \(O\) atoms, which is 0, that strictly forbids any even \(J\) rotational levels for \(O_2\) (as dictated by the overall symmetry of the total wavefunction for \(O_2\)). For odd \(J\), the frequency \(\omega_2\) produces the lines \((8J + 20) Bc = (28, 44, 60, \ldots) Bc\), whereas the sum frequency \((\omega_1 + \omega_1')\) produces the lines \((4J + J') + 12) Bc = (20, 28, 36, \ldots) Bc\); taken together they generate the series III: \((20, 28, 36, 44, \ldots) Bc\). Similarly, the difference frequency \(\omega_1 - \omega_2\) gives rise to the series V: \((8, 16, 24, \ldots) Bc\) as shown in table II. All the above predicted series are observed in the Fourier spectrum for \(O_2\). It is also shown in table IV that frequency \(\omega_1 + \omega_2'\) and \(\omega_2 + \omega_1'\), produces the weak (strength of order order “bc” ) series VI: \((4J + 2J') + 26) Bc = (38, 46, 54, \ldots) Bc\). Despite its weakness the existence of this series too is evidenced by the presence of the line at 38 \(Bc\). It is worth noting that the series V and VI can not be generated from the moment \(\langle \sin^2 2\theta \rangle\) alone. The remaining higher order terms in Eq. (13) contribute, generally very weakly, either to the lines in series above or to some additional lines that can be seen in Fig. (13b), but hardly resolved in Fig. (13a). Finally, we may point out that the heights of the few lowest frequency lines in the experimental data in Fig. (13a) for \(O_2\) are believed to be due to the fluctuation of the laser outputs in the experiment (see, foot-note [20] of 13).

We may point out that during the test calculations, the relative strengths of the lines in a calculated spectrum were found to depend sensitively (cf. Fig. 11) on the assumed molecular temperature, which is rather difficult to determine experimentally. This sensitivity, on the other hand, provides a way to estimate the temperature of the molecular ensemble of interest in the experiment, by requiring that the rotational line for the maximum height of the Fourier spectrum of the dynamic signal to match with the peak of the Boltzmann distribution of the initially occupied rotational levels, and adjusting the latter to find the matching temperature.

Fig. 14 shows a calculated spectrum for initial temperature 75 K whose peaks are shifted from one of 200 K (Figs. 12 and 13). We also point out that our adiabatic theory produces series III in for \(N_2\) and series V and VI for \(O_2\). These terms arise from the cross-term, and hence can not be produced from frozen nuclei approximation. Thus, the spectrum in frequency domain gives more succinct and clearer information of the HHG signal and therefore power full to test the model 13.

F. Interplay of Polarization Geometry \(\alpha\) and Delay Time \(t_d\)

So far we have limited our applications to the HHG signal for parallel geometry of the pump and probe polarizations. We now consider the more general case when probe polarization is rotated by a given angle \(\alpha\). Fig. 16 (upper panel) shows our computational results of the HHG signals as a function of \(t_d\), at three different fixed angle \(\alpha\), i.e. \(\alpha = 0^\circ, 45^\circ,\) and \(90^\circ\), for \(N_2\). We note that the signal for \(\alpha = 90^\circ\) changes its phase by \(\pi\) with respect to the signal for \(\alpha = 0^\circ\), a phenomenon that is also observed recently 12, 27, 55. In contrast, the signal for \(\alpha = 45^\circ\) is seen to remain rather flat with change of \(\alpha\).

To see qualitatively the \(\alpha\) dependence of HHG signal of \(N_2\), we consider the leading term of Eq. (111) which
Figure 15: Calculated 19th harmonic dynamic signal for N\textsubscript{2} (upper panel) and O\textsubscript{2} (lower panel) for various pump-probe polarization angles, i.e. \( \alpha = 0^\circ \), \( \alpha = 45^\circ \), and \( \alpha = 90^\circ \). The laser parameters are similar with one in Figs. 4 and 5 for N\textsubscript{2} and O\textsubscript{2}, respectively. The initial temperature is 200 K.

is given by

\[
S^{(n)}(t_d; \alpha) = c_0^{(n)} + c_1^{(n)} \left[ \frac{1}{2} \sin^2 \alpha + \frac{1}{2} (3 \cos^2 \alpha - 1) \right]
\]

\[
\times \langle \langle \cos^2 \theta \rangle \rangle (t_d) + \ldots
\]

\text{(131)}

Thus, for the parallel polarizations we have, \( S^{(n)}(t_d; 0^\circ) \approx c_0^{(n)} + c_1^{(n)} \langle \langle \cos^2 \theta \rangle \rangle (t_d) \) and for the perpendicular polarizations, \( S^{(n)}(t_d; 90^\circ) \approx c_0^{(n)} + c_1^{(n)} \left( 1 - \langle \langle \cos^2 \theta \rangle \rangle (t_d) \right) \) which are clearly of opposite phase as a function of \( t_d \). These above expressions also show that the modulation depth for \( \alpha = 90^\circ \) is smaller than one for \( \alpha = 0^\circ \), that can not be obtained by planar model [12]. Eq. \text{(131)} also implies that the extrema of the signal would occur for \( \sin \alpha \cos \alpha = 0 \), or the maximum at \( \alpha = 0^\circ \) and the minimum for \( \alpha = 90^\circ \), as seen in Fig. 15 (upper) and confirmed experimentally [12, 20, 55]. Eq. \text{(131)} also implies that at a critical angle \( \alpha_c \) given by \( (3 \cos^2 \alpha_c - 1) = 0 \), or \( \alpha_c \approx 55^\circ \), the

signal essentially remains constant and independent of the delay \( t_d \) between the pulses. This geometry therefore can be used to generate a steady state HHG signal from N\textsubscript{2}, with femtosecond pulses.

The magic angle in fact is a generic signature for the \( \sigma_g \) symmetry of the active molecular orbitals.

For O\textsubscript{2}, the leading term of HHG signal (Eq. \text{(115)}) reads

\[
S^{(n)}(t_d; \alpha) = \frac{c_1^{(n)}}{64} \langle \langle \left( (-35 \cos^4 \alpha + 30 \cos^2 \alpha - 3) \cos^4 \theta \right) \rangle (t_d)
\]

\[
+ (30 \cos^4 \alpha - 24 \cos^2 \alpha + 2) \langle \cos^2 \theta \rangle
\]

\[
+ (-3 \sin^4 \alpha + 4 \sin^2 \alpha) \rangle^2 \rangle + \ldots
\]

\text{(132)}

Thus, for the parallel polarizations we have, \( S^{(n)}(t_d; 0^\circ) \approx c_1^{(n)} \langle \langle \left( -\cos^4 \theta + \cos^2 \theta \right) \rangle \rangle \) for the perpendicular polarizations, \( S(t_d; 90^\circ) \approx \frac{c_1^{(n)}}{64} \langle \langle \left( -3 \cos^4 \theta + 2 \cos^2 \theta + 1 \right) \rangle \rangle \). It was clear that the sign of \( \langle \cos^4 \theta \rangle \) does not change and hence the phase of eighth revival also remains constant, as shown in Fig. 16 (lower panel) and confirmed experimentally [12, 27, 55]. These above expressions also can be expressed as

\[
S(t_d; 90^\circ) \approx \frac{c_1^{(n)}}{64} \left( \frac{3}{8} \langle \langle \sin^2 \theta \cos^2 \theta \rangle \rangle - \frac{1}{8} \langle \langle \cos^2 \theta \rangle \rangle + \frac{1}{8} \langle \langle \cos^2 \theta \rangle \rangle^2 \right)
\]

shows that the modulation depth for \( \alpha = 90^\circ \) is smaller than one for \( \alpha = 0^\circ \), that can not be obtained by planar
vival probe pulses. In Fig. 16 we show the results for \( N \) relative polarization direction between pump and model \([12]\).

The initial temperature is 200 K. The laser parameters are similar to that in 4 and 5 for \( N \) relative angle \( \alpha \) (lower panel) as simultaneous function of delay time \( t \) \( \alpha \) critical value of \( \alpha \approx 55^\circ \). For the case of \( O_2 \) \( \alpha \approx 55^\circ \), and increase again but in opposite phase above the critical angle. The results for \( \theta = 90^\circ - 180^\circ \) are exactly mirror image of the results for \( \theta = 0^\circ - 90^\circ \).

Before concluding this section it is also worthwhile to point out that the \( \alpha \)-dependence of the HHG signals for the more complex tri-atomic molecule \( \text{CO}_2 \) and the organic molecule acetylene, \( HC \equiv CH \), because of their active \( \pi \) orbital symmetry, are predicted from the general structure of the HHG signal given by Eq. (103) (even with out detailed calculations) to exhibit a “cross-over” neighborhood near \( \alpha \approx 55^\circ \); this is indeed the case, as has been recently observed experimentally \([63]\).

Clearly, the presence of the “magic” angle and the cross-over neighborhood provide a signature of the symmetry of the active molecular orbital, which can be useful in the context of the “inverse” problem of molecular imaging \([63]\) from the HHG data as suggested first in \([20]\). Finally, the agreement between the present results and experimental data provides a clear possibility to control the HHG signals by varying both the time- delay and the relative pump-probe polarization angle, simultaneously.

**VII. SOME PROBLEMS OF GENERAL INTEREST RELATED TO PUMP-PROBE SIGNALS FOR HHG**

Before concluding this paper we report on the results of our investigations of a number of pump-probe experiment related problems of interest in the present context.

**A. Effect of Probe Pulse on the Alignment**

In pump-probe experiments it is generally assumed that the dynamical alignment of the molecular axis is governed by the ultrashort pump pulse, while the ultrashort probe pulse that leads to the HHG signal does not affect the alignment. To check the validity or otherwise of this assumption, we directly compare here the dynamic alignment moment, \( A(t_d; \alpha = 0) \) calculated as usual as...
Figure 18: Shift of the alignment signal vs. delay time: \( \langle \cos^2 \theta \rangle \) for \( \text{N}_2 \) (upper panel), and \( \langle \sin^2 2\theta \rangle \) for \( \text{O}_2 \) (lower panel) at 300 K; \( I_{\text{pump}} = 0.8 \times 10^{14} \text{W/cm}^2 \) and \( I_{\text{probe}} = 1.7 \times 10^{14} \text{W/cm}^2 \) with FWHM 40 fs. See, text for further explanation.

In the latter case, the total field consists of the superposition of the two pulses with a displacement \( \Delta t \) in time between them:

\[
F(t) = F_1 \cos(\omega_1 t) + F_2 \cos(\omega_2 (t - \Delta t))
\]

\[
= \varepsilon_{10} \sqrt{g_1(t)} \cos(\omega_1 t) + \varepsilon_{20} \sqrt{g_2(t - \Delta t)} \cos(\omega_2 (t - \Delta t))
\]

and

\[
\langle \varepsilon^2 (t) \rangle = \frac{1}{2} \varepsilon_{10}^2 g_1(t) + \frac{1}{2} \varepsilon_{20}^2 g_2(t - \Delta t) + 2\varepsilon_{10}\varepsilon_{20} g_1(t) g_2(t - \Delta t) \times \langle \cos(\omega_1 t) (\cos(\omega_2 (t - \Delta t))) \rangle
\]

In the above the indices 1 and 2 stand for pump and probe pulse, respectively. Suppose the data are recorded after the probe pulse dies out, then the observing time is \( t = \Delta t + \tau \), where \( \tau \) is the duration of the probe pulse. Eq. (133) then reads

\[
\langle \varepsilon^2 (\Delta t + \tau) \rangle = \frac{1}{2} \varepsilon_{10}^2 g_1(\Delta t + \tau) + \frac{1}{2} \varepsilon_{20}^2 g_1(\tau) + 2\varepsilon_{10}\varepsilon_{20} g_1(\Delta t + \tau) g_2(\tau) \times \langle \cos(\omega_1 (\Delta t + \tau)) (\cos(\omega_2 \tau)) \rangle
\]

showing its dependence on the delay between the two pulses \( \Delta t \) and the length of interaction of the probe pulse \( \tau \). In Fig. 18 we plot the alignment moment \( \langle \cos^2 \theta \rangle (\Delta t + \tau) \) and \( \langle \sin^2 2\theta \rangle (\Delta t + \tau) \) for \( \text{O}_2 \), plotted as a function of delay between two pulses \( \Delta t \), for a fixed \( \tau = 40 \text{ fs} \), as shown by the solid curve. The results are compared with that obtained from for the pump pulse alone (dashed curve), recorded at the same time. The comparison clearly shows that the probe pulse changes the dynamic alignment \( \langle \cos^2 \theta \rangle (t_d) \) in that the signal is shifted upward by the presence of the probe pulse as may be expected from the enhanced intensity of the field when both the pulses overlap significantly (before it dies out). Thus, except perhaps when the two pulses overlap (or are separated only negligibly) this do not change the general characteristics of the dynamical signals. Therefore, within the above mentioned exception, one may neglect the effect of the probe pulse on the dynamical signals.

B. Effect of Initial Temperature

We assume that the rotational eigenstates \( |J_0, M_0\rangle \) of the molecule are occupied thermally before the interaction with the pump pulse. Unlike an upward transitions \( (J_0, M_0) \rightarrow (J'_0, M_0) \) to the states with an arbitrarily high \( J'_0 \), the downward transition toward \( J'_0 \geq M_0 \) can be restricted. As a result, a wavepacket state created by the pump pulse would consist of eigenstates with higher occupation of \( J'_0 \geq M_0 \), implying that the vector of rotational angular momentum would tend to lie in a plane perpendicular to the pump polarization direction. Since the rotational angular momentum itself is perpendicular to the internuclear axis of a linear molecule, the above condition, \( J'_0 \geq M_0 \), means also that the molecular axis would tend to align in the direction of the laser polarization. This is the physical reason why the alignment angle of the molecular axis with respect to the polarization direction after the laser interaction is generally smaller after the interaction than before it, i.e. the degree of alignment increases on interaction with the pump pulse. Since at a lower initial temperature, the lower \( M_0 \) states are relatively more occupied initially, the “degree of alignment” \( A \equiv \langle \cos^2 \theta \rangle \) would tend to be higher, allowing the molecules to be more readily aligned at a lower initial temperature.

C. Mean Energy of the Molecule after the Pump Pulse

It is interesting also to examine the way the mean energy of the molecule changes with increasing intensity of the pump pulse. Fig. 20 shows the calculated mean energy \( \langle E \rangle_{kB,T} (t) \) at a time \( t \), before and after the arrival of the peak of the pump pulse (of length \( t_p \)). As expected, the figure shows that increasing the peak pulse intensity, increases the mean energy of the molecule or, the “effective temperature” \( T_{eff} \equiv (E)_{kB,T} (t > t_p) / k_B \), where \( k_B \) is the Boltzmann constant. However, it should be remembered that after the pulse interaction, the molecular system is not a state of thermal equilibrium, rather it is in a state of dynamical equilibrium (or steady state) that can not be characterized thermodynamically.
at three values of the delay time \( t \), with the laser pulse, for different initial temperatures. The vertical dashed lines indicate the extent of the pulse duration; \( I = 0.5 \times 10^{14} \text{ W/cm}^2 \) and FWHM=40 fs. See, text for further explanation.

To estimate an effective “temperature” of the rotational wavepacket states \( |\Phi_{J_0M_0}(t)\rangle \), in the steady state regime, i.e. for \( t_{\text{pump}} \leq t \leq t_{\text{probe}} \), we note (a) that the rotational wavepacket states \( |\Phi_{J_0M_0}(t)\rangle \) form a linearly independent set of states like the set of rotational eigenstates \( |J_0M_0\rangle \) from which they evolve, (b) that the individual rotational wavepacket states evolve in one-to-one correspondence with the initially occupied rotational eigenstates \( |J_0M_0\rangle \), (c) that the mean energy of each of the rotational wavepacket states reach a steady state, also one-to-one of energy from \( \langle E \rangle_{J_0M_0}(t > t_{\text{pump}}) = E_{J_0M_0} + \langle E \rangle_{J_0M_0}(t \geq t_{\text{pump}}) \). If further the above change in the mean energy \( \langle E \rangle_{J_0M_0}(t > t_{\text{pump}}) - \langle E \rangle_{J_0M_0}(t \geq t_{\text{pump}}) \) is independent of the initial states chosen (indices \( \{J_0M_0\} \)) then one might use it to define an effective “temperature” change, \( \Delta T_{\text{eff}} \), given by

\[
\Delta T_{\text{eff}} = \frac{\langle E \rangle (t \geq t_{\text{pump}})}{k_B} \tag{136}
\]

We may note in Fig. 20 that the change in the mean energy in the steady state regime is indeed essentially independent of the states of the system chosen. Thus, the effective “temperature” of the system, at the end of the interaction with the pump pulse, becomes

\[
T_{\text{eff}} = T_0 + \Delta T_{\text{eff}} \tag{137}
\]

Note that \( T_{\text{eff}} \), is in general greater than the initial gas (jet) temperature, \( T_0 \), and it tends to increase with the increase of the pump intensity. Later on we shall describe a method of determining this “effective temperature” of the system from a theoretical analysis of the experimental HHG data.

### D. Some Non-equivalent Definitions of the HHG Signal

In this sub-section we briefly discuss two alternative definitions of HHG signals that have been employed earlier and compare them with the definition of the HHG signal of the present theory, and with experimental data. The present theory defines the quantum transition amplitudes for the linearly independent reference states \( |\chi_i(t)\rangle, i \equiv \{e,J_0M_0\} \), (consisting of the product of the ground electronic and the coherent rotational wavepacket states) to obtain the independent harmonic emission probabilities, and in accordance with the quantum statistical theory averages the latter to define the HHG signal (cf. e.g. Eq. (62):

\[
S^{(\nu)}(t_d) = C \sum_{J_0M_0} \rho(J_0) \left| \langle \Phi_{J_0M_0}(t_d,\theta) | T_{\text{c}}^{(\nu)}(\theta) | \Phi_{J_0M_0}(t_d,\theta) \rangle \right|^2 \tag{138}
\]

It is worth noting that the quantum amplitude calculation in the present theory corresponds to the “adiabatic
Theoretical Fourier spectrum of the dynamic 19th harmonic signal for O$_2$: pump intensity $I = 0.5 \times 10^{14}$ W/cm$^2$, probe intensity $I = 1.2 \times 10^{14}$ W/cm$^2$, duration 40 fs, wavelength 800 nm, and temperature 200 K. The calculations are done using the present theory, Eq. (138), (left-lower panel), model A Eq. (139), (right-upper panel), and model B, Eq. (140), (right-lower panel). For comparison, the experimental spectrum (left-upper panel) is also shown.
In the case of model B, on the other hand, the series for the adiabatic case, in which we choose a long (300 ps) sequence $V$, is rather weakly developed. The ratio of the peaks of the series III to series II is satisfactory, that from model A is similar, except that the theory and the experimental data is seen to be very satisfactory, that from model A is similar, except that the parameters are the same as in Fig. 13. The similarity of the calculated spectrum from the present theory and the experimental data is seen to be very satisfactory, that from model A is similar, except that the ratio of the peaks of the series III to series II is generally too small compared to the experimental data, and series V $(8, 16, 24, \ldots)$ $B_c$ is rather weakly developed. In the case of model B, on the other hand, the series V $(8, 16, 24, \ldots)$ $B_c$ is simply missing. It may be noted that the present comparison also illustrates the ability of the experimental data at the level of the (discrete) Fourier spectrum, to better distinguish between the various theoretical models than may be possible at the level of the time-domain signal.

E. Adiabatic Alignment

Finally, we apply the present dynamic theory also to the adiabatic case, in which we choose a long (300 ps) pump pulse and a short (70 fs) probe pulse, as in an adiabatic alignment experiment used earlier. The results of our calculations for $N_2$, using Eqs. for both $\alpha = 0^\circ$ (solid curve), and $\alpha = 90^\circ$ (dash-dot curve), are shown in Fig. 22. For the sake of comparison we also show the intensity profile (dashed curve) of the pump pulse (right scale). As can be seen immediately from the figure, in the parallel case, the HHG signal closely follows the evolution of the long pump pulse itself (which might be expected for an adiabatic process) and the maximum of the signal occurs at the maximum of pulse, for $\alpha = 0^\circ$. On the other hand, a minimum is predicted for the signal at the maximum intensity, in the perpendicular case, for $\alpha = 90^\circ$. These characteristics of the adiabatic signals for $N_2$ are consistent with the experimental observations made some time ago.

VIII. CONCLUSIONS

To conclude, we have presented an ab initio intense-field S-matrix theory of dynamic alignment of linear molecules and the characteristic HHG signals from them as detected in intense-field femtosecond pump-probe experiments. Useful analytical expressions for the molecular alignment and the HHG signal as a function of both the delay-time, $t_d$, and the relative polarization angle, $\alpha$, between the pump and probe pulse, are derived. Thus, we give the general HHG signal Eq. (103), the signal for $N_2$ (generically, active $\sigma$ orbital symmetry) Eq. (114), or its leading term Eq. (131), as well as the signal for $O_2$ (generically, active $\pi$ orbital symmetry) Eq. (115), or its leading term, Eq. (132). They are used to make detailed analysis of the molecular alignment and the observed experimental data for the HHG signals from coherently rotating $N_2$ and $O_2$ molecules, both in the time-domain and in the frequency domain. The results show a remarkable agreement between the theory and the experimental observations. Additional predictions about the existence of critical relative polarization angles, $\alpha_c$, and their relation to the symmetry of the active orbitals and the form of the dynamic signals are made. At a “magic” angle, $\alpha_c \approx 55^\circ$, the dynamic HHG signals for all delay times $t_d$, are predicted to approach each other closely for a linear molecule with a $\sigma$ orbital symmetry, or exhibit a “crossing neighborhood”, for the $\pi$ orbital symmetry; it is also predicted to produce a steady emission of high harmonic radiation at the magic angle from $N_2$. Moreover, we have investigated a number of theoretical questions and experimental effects of general interest in connection with the interpretation of the pump-probe HHG signals. Finally, we have shown that the case of “adiabatic-alignment”, and the resulting HHG signal, can be analyzed and understood equally well within the present dynamical theory, using simply a long duration of the pump pulse.
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