Effects of orientation and alignment in high-harmonic generation and above threshold ionization

C. B. Madsen, A. S. Mouritzen, T. K. Kjeldsen, and L. B. Madsen
Lundbeck Foundation Theoretical Center for Quantum System Research,
Department of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark.
(Dated: August 15, 2018)

When molecules interact with intense light sources of femtosecond or shorter duration the rotational degrees of freedom are frozen during the response to the strong nonperturbative interaction. We show how the frozen degrees of freedom affect the measurable signals in high-harmonic generation and above threshold ionization. High-harmonic generation exhibits optical coherence in the signal from different orientations of the molecule. For ionization, the contributions from different orientations are added incoherently. The effects are demonstrated for realistic alignment and orientation schemes.

PACS numbers: 42.65.Ky, 33.80.Rv

Currently, intense few-cycle pulses of femtosecond duration are produced in several laser laboratories worldwide. It is of fundamental interest to investigate how such pulses interact with quantum systems. Gas phase atoms and molecules are ideal test systems for these studies. As this research field is maturing, interesting applications are evolving: tomographic reconstruction [1], laser-induced electron diffraction [2] and molecular clocks [3, 4, 5, 6] being examples under current study.

Molecules are particularly well-suited for such studies since they inherently carry the time scales that match those of the new laser sources: nuclei move on the femtosecond timescale, electrons on the attosecond timescale. Hence, the new ultrashort sources are perfect for looking inside molecules and for gaining insight into nuclear and electronic dynamics. Conversely, if the dynamics of the system under study is well-understood, information about the characteristics of the few-cycle pulse can be obtained. For instance, in atoms, where an accurate description of the electrons can be obtained, the carrier-envelope phase difference may be extracted in this way [7, 8, 9]. For molecules, the extra nuclear degrees of freedom may be used to control the process of interest. As an example, the ability to orient molecules [10] with respect to an external axis may be used to enhance the high-harmonic yield [11, 12]. Solving the dynamics of the molecule in the strong field is, however, much more difficult than the atom due to the extra degrees of freedom. In fact, not even the simplest case of H$_2^+$ interacting with strong IR fields has been solved in full 6-dimensional time dependent calculations. Fortunately, the interesting prospect of ever shorter pulse durations introduces a simplification in the description: the timescales of rotation and vibration are often much longer than the actual applied pulses themselves, and therefore some of these degrees of freedom may be treated as frozen during the interaction with the field. In the present work, we describe how frozen degrees of freedom affect the outcome of an experiment in a non-trivial manner. We show that the influence of the dynamics and the formulation of the theory of measurement depend very much on the process considered: we obtain completely different behavior for above threshold ionization (ATI) and high-harmonic generation (HHG) with respect to the coherence in the signal from rotational degrees of freedom. The discussion is exemplified using realistic alignment and orientation schemes.

We consider HHG and ATI in molecules interacting with an ultrashort strong laser pulse. In these experiments, there are many molecules in the laser focus, but the phase space density is low and we can use the single-particle density operator $\hat{\rho}(t_0)$ for calculations. At time $t = t_0$ prior to any probe or pump pulse, the molecule is in a time-independent thermal state at temperature $T$. By definition, $\hat{\rho}(t_0) = \exp(-\hat{H}/k_B T)/Z$, with partition function $Z = \text{Tr}[\exp(-\hat{H}/k_B T)]$, $\hat{H}$ the field-free molecular Hamiltonian and $k_B$ Boltzmann’s constant. The initial state is resolved on energy eigenstates $|\alpha\rangle$ with energy $E_\alpha$. We concentrate on diatomics where, prior to the applied pulses, only the electric and vibrational ground states are populated. Consequently, the energy eigenstate is characterized by the angular momentum quantum number, $J$, and its projection on a space fixed axis, $M$, i.e., $\alpha = (J, M)$. The discussion is straightforwardly generalized to more complicated cases and the conclusions remain unaffected. There is no decay on the timescales we are considering so propagation is described by a unitary operator $\hat{U}(t)$: $\hat{U}(t)|\alpha\rangle = |\Psi_\alpha(t)\rangle$; $\dot{\hat{\rho}}(t) = \hat{U}(t)\hat{\rho}(t_0)\hat{U}(t)\dagger(t) = \sum_\alpha P_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|$, with the Boltzmann weight $P_\alpha = \exp(-E_\alpha/k_B T)/Z$. The evolution due to $\hat{U}(t)$ can contain both alignment pulses and a subsequent ultrashort probe pulse producing ATI and HHG.

We separate out the relatively slow rotational movement of the nuclei to obtain $\Psi_{JM}(r, R, \Omega, t) \approx \psi(r, R, t; \Omega) \phi_{JM}(\Omega, t)$, with $R$ the internuclear distance and $\Omega = (\theta, \phi)$ the spherical polar solid angle composed of the usual polar and azimuthal angles. The variables
that enter only parametrically in the wave function are put after the semicolon. If we consider the response to a femtosecond probe pulse, the rotational degrees of freedom can be considered frozen during the probe pulse centered at $t_p$, i.e., the full wave function is approximated by
\[
\Psi_{JM}(r_e, R, \Omega, t) \approx \psi(r_e, R, t; \Omega, t_p) \phi_{JM}(\Omega, t_p). \tag{1}
\]
In the case of a prealigning or orienting pump pulse between $t_0$ and $t_p$, $\phi_{JM}(\Omega, t_p)$ is the rotational wave packet evolving from $Y_{JM}(\Omega)$ at time $t_0$. If no pump pulse is used then $\phi_{JM}(\Omega, t_p) = Y_{JM}(\Omega)$.

Treating HHG first, the complex amplitude for the emission of harmonics polarized along the unit vector $e$ with frequency $\omega$, is obtained from the Fourier transform of the dipole acceleration
\[
A_e(\omega) = e \cdot \int dt \, e^{-i\omega t} \frac{d^2}{dt^2} \langle \hat{d}(t) \rangle,
\tag{2}
\]
with $\langle \hat{d}(t) \rangle = \text{Tr} \left[ \hat{\rho}(t) \hat{d} \right] = \sum_\alpha P_\alpha \langle \Psi_\alpha(t) | \hat{d} | \Psi_\alpha(t) \rangle$ the expectation value of the dipole operator $\hat{d}$ of the molecule. The corresponding power density reads \[15\]:
\[
S_e(\omega) \propto |A_e(\omega)|^2.
\tag{3}
\]

We note that one can observe interferences in the intensity $S(\omega)$ from incoherent members of the ensemble, i.e., members belonging to different $\alpha$. This effect of intensity interferences stemming from adding electric fields is known as “polarization beats” to distinguish it from coherent quantum waves \[10\]:

We insert the wave function \[11\] into the expression for $\langle \hat{d}(t) \rangle$ and obtain
\[
\langle \hat{d}(t) \rangle = \int d\Omega \, G(\Omega, t_p) \langle \hat{d} \rangle^{e,\text{vib}}(t; t_p, \Omega), \tag{4}
\]
with the vibronic dipole $\langle \hat{d} \rangle^{e,\text{vib}}(t; t_p, \Omega) = \langle \psi(t; t_p, \Omega) | \hat{d}_e | \psi(t; t_p, \Omega) \rangle$ and
\[
G(\Omega, t_p) = \sum_{JM} P_J |\phi_{JM}(\Omega, t_p)|^2, \tag{5}
\]
the angular distribution at time $t_p$. The corresponding spectrum is obtained from \[21\] - \[33\]
\[
S(\omega, t_p) \propto \int d\Omega \, G(\Omega, t_p) A_{e,\text{vib}}^{\omega}(\omega, \Omega, t_p)^2, \tag{6}
\]
with $A_{e,\text{vib}}^{\omega}(\omega, \Omega, t_p)$ the complex amplitude for generation of high-harmonics at frequency $\omega$ and polarization $e$ from the electronic dipole $\langle \hat{d} \rangle^{e,\text{vib}}(t; t_p, \Omega)$ in a molecule fixed at $\Omega$. If no alignment pulses are used, $G(\Omega, t_p)$ is isotropic. This follows from $G(\Omega, t_p) = \sum_J P_J |\phi_{JM}(\Omega, t_p)|^2$.

\[
\sum_J P_J \sum_M |Y_{JM}(\Omega)|^2 = \sum_J P_J (2J + 1)/(4\pi) \text{ which is independent of angles. In this case, the spectrum arises from the coherent summation of amplitude contributions from different orientations, $A_{e,\text{vib}}^{\omega}(\omega, \Omega, t_p)$, independent on the temperature of the sample. In general, the signals always contain optical coherences, except in the trivial case $G(\Omega, t_p) = \delta(\Omega - \Omega')$. Apart from being physically well-justified and displaying the effects of the frozen molecular degrees of freedom, the relevance of \[10\] is that the numerical propagation during the ultrashort pulse is immensely more manageable when the dimensionality is reduced. For molecules with vibrational frequencies much smaller than the inverse duration of the applied laser pulse, the vibrational coordinates can also be treated as fixed, and one can separate out the vibrational part of the vibronic wave function in \[10\] as well.

For CO with frozen rotations, Fig. 1 shows the results of simulations of the emitted high-harmonics of the same polarization as the linearly polarized driving 800 nm probe field with peak intensity $2 \times 10^{14}$ W/cm$^2$. The model used to calculate the harmonic signal resembles the Lewenstein model. Further details are given in \[15\]. Panel (a) shows three cases corresponding to (i) uniform orientational distribution, (ii) perfect parallel orientation, i.e., the permanent molecular dipoles (each pointing from the O to the less electronegative C) are all directed along the polarization vector of the probe pulse and (iii) perfect perpendicular orientation. The panel clearly shows that the HHG signals depend critically on the direction of the orientation. We first discuss cases (ii) and (iii) and return to the unaligned case in the end of this section. There is no dependence of the azimuthal angle in any of the cases, and so we only consider the polar part of the solid angle. The occurrence and absence

![Harmonic signal (arb. units)](image-url)

**FIG. 1:** (Color online) Harmonic generation from CO. The signal is polarized along the linearly polarized driving laser of wave length 800 nm and intensity $2 \times 10^{14}$ W/cm$^2$. (a) HHG yield for (i) an isotropic, unaligned ensemble, (ii) perfect orientation along the driving laser polarization (||) and (iii) perfect orientation perpendicular to the driving laser polarization ($\perp$). (b) HHG yield from CO after field-free orientation by a half cycle pump pulse. The delay of the probe pulse with respect to the orienting pulse is denoted by $t_p$. 

\[
S(\omega, t_p) \propto \int d\Omega \, G(\Omega, t_p) A_{e,\text{vib}}^{\omega}(\omega, \Omega, t_p)^2, \tag{6}
\]
of even harmonics in the signal in (ii) and (iii), respectively, may be understood by recalling that emission of harmonic of order N comprises N+1 dipole transitions (N absorptions of a laser photon, and the emission of one high-harmonic photon). In case (ii), only the component $\parallel$ of the dipole operator parallel to the internuclear axis is present and this component has a $\Delta \Lambda = 0$ selection rule, with $\Lambda$ the absolute value of the projection of the electronic orbital angular momentum on the internuclear axis. Initially the molecule is in its $\Sigma$ ground state and because of $\Delta \Lambda = 0$ it stays in the manifold of $\Sigma$ states. The $\Sigma$ state, from which the final recombination step occurs, is hence accessible by the absorption of both an even or odd number of photons and, consequently, both even or odd harmonics are produced. Turning to case (iii), only the component $\perp$ of the dipole operator perpendicular to the internuclear axis is present and this component has a $\Delta \Lambda = \pm 1$ selection rule. Consequently, only odd harmonics are observed since the $\Pi$ state, from which the recombination occurs, can only be reached by the absorption of an odd number of photons. In the unaligned case (i), the situation is analyzed by considering the transition operator $\hat{O}_N = \prod_{i=1}^{N+1} (\cos \theta_i + \hat{\perp}_i \sin \theta_i)$ corresponding to emission of a harmonic of order N for a molecule with the permanent dipole oriented at an angle $\theta$ with respect to the polarization vector of the probe laser field. In the limits of parallel ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$) orientation we retrieve the results discussed above. In general the operator $\hat{O}_N$ contains even and odd powers of cosines and sines. In the unaligned case $G(180^\circ - \theta, t_p) = G(\theta, t_p)$, and we see from Eq. (6) that only combinations of the cosines and sines yielding an even function on [0, $\pi$] will survive, i.e., the terms containing an even number of the $\parallel_i$ operator. From the selection rules it is, however, clear that the total number of $\Lambda$ changing transition must be an even number and thus the total number of dipole transitions is even, explaining why only odd harmonics are emitted in the unaligned case.

In order to simulate a more realistic orientational distribution, we present in (b) the prediction of the harmonic signal from an ensemble of partially oriented CO molecules. To obtain orientation, a half cycle pulse (HCP) with amplitude 870 kV/cm and a duration of 0.5 ps (FWHM) is followed 4.14 ps later by a linearly polarized laser pulse of 0.5 ps duration and a peak intensity of $5 \times 10^{12}$ W/cm$^2$. In order to model the orientation we solve the time-dependent Schrödinger equation for the rotational degrees of freedom subject to the rotational constant $B = 57.9$ GHz, dipole moment $\mu = 0.112$ D, and polarizability volume components $\alpha_\perp = 1.925$ Å$^3$ and $\alpha_\parallel = 1.420$ Å$^3$ [19]. The initial rotational temperature is 5 K. The probe field which generates high-harmonics is as in panel (a). We plot the harmonic signal at two different delays with respect to the peak of the HCP. The time delay $t_p = 5$ ps is chosen to illustrate the case with an almost symmetric orientational distribution: $G(180^\circ - \theta, 5 \text{ ps}) \approx G(\theta, 5 \text{ ps})$, and in this case the even harmonics are suppressed as expected from arguments similar to the ones used in the discussion of the unaligned case in panel (a). At longer delays the molecules have time to orient obtaining a maximum after 8.1 ps with $\langle \cos \theta \rangle = -0.11$. At this time delay the CO dipoles tend to be pointing opposite to the polarization vector of the HCP, and this asymmetric distribution allows for even and odd harmonics of comparable strength.

We now turn to a discussion of ATI. The fundamental quantity is the probability $W(k)$ for measuring the momentum $k$ of the outgoing electron. The associated measurement projection operator is $\hat{P}_k = |\psi_k^\perp\rangle \langle \psi_k^\perp| \otimes \hat{I}_R$ which projects on an electron scattering state $|\psi_k^\perp\rangle$ with asymptotic momentum $k$ and leaves the nuclei unaffected ($\hat{I}_R$). Accordingly, $W(k) = \langle \hat{\rho}(t) \hat{P}_k \rangle = \text{Tr} [\hat{\rho}(t) \hat{P}_k]$ where $\hat{\rho}(t)$ is the density matrix of the system. We evaluate the trace in the position-eigenstate basis and obtain $W(k) = \int dr_e \int dR |r_e, R, \hat{\rho}(t) \hat{P}_k| r_e, R|^2 = \sum_{\rho} \int dR \int dr_e |\psi^\perp_k(r_e, R)|^2 |\psi_{\rho, r_e, R, t}|^2$. Introducing the wave functions (11), we obtain:

$$W(k, t_p) = \int d\Omega G(\Omega, t_p) \int dRR^2 |A(k; R, t_p)|^2,$$

with $G(\Omega, t_p)$ defined in (5) and the complex amplitude $A(k; R, t_p) = \int dr_e |\psi^\perp_k(r_e)| \psi(r_e, R, t; \Omega, t_p)$ describing the transition for frozen rotations at time $t_p$. The time $t$ may be any time after the ionizing pulse. In contrast to the HHG signal (6) which is optically coherent in nuclear motion, the ATI signal is emitted along the polarization axis of the probe laser and thus the total number of dipole transitions is even, explaining why only odd harmonics are emitted in the unaligned case.
FIG. 2: (Color online) Angular differential ionization rates. We use an 800 nm probe laser polarized along the z axis for N$_2$ (a)-(c) at $2 \times 10^{14}$W/cm$^2$ and O$_2$ (d)-(f) at $1.2 \times 10^{14}$W/cm$^2$. (a) N$_2$ isotropic, unaligned ensemble. (b) N$_2$ maximally aligned along the z axis. (c) N$_2$ maximally aligned along the z axis. (d) O$_2$ isotropic, unaligned ensemble. (e) O$_2$ maximally aligned along the z axis. (f) O$_2$ maximally aligned along the x axis. The numbers adjacent to the z axis indicate the scale with respect to the randomly aligned case s (a) and (d). The plots present an experimentally realizable demonstration of the effects of alignment on ATI.

In conclusion, we have developed the theory of how to deal with frozen nuclear degrees of freedom in HHG and ATI. The frozen coordinates affect the motion in a non-trivial way and coherence issues depend on the degree of orientation. Physically, the phase coherence in HHG with respect to different orientations may be understood by the superposition principle for the electric field generated by an ensemble of oscillators with different orientations. The incoherence in the ATI signal follows from the fact that we in principle, by looking at the nuclear motion after the pulse, may infer the orientation of the molecule at the instant of ionization. The present work form the theoretical basis for future work on molecules interacting with strong few-cycle pulses.

This work is supported by the Danish Research Agency (Grant. No. 2117-05-0081).

[1] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, Nature (London) 432, 867 (2004).
[2] H. Niikura, F. Légaré, R. Hasbani, A. D. Bandrauk, M. Y. Ivanov, D. M. Villeneuve, and P. B. Corkum, Nature (London) 417, 917 (2002).
[3] H. Niikura, F. Légaré, R. Hasbani, M. Y. Ivanov, D. M. Villeneuve, and P. B. Corkum, Nature (London) 421, 826 (2003).
[4] A. S. Alnaser, X. M. Tong, T. Osipov, S. Voss, C. M. Maharajan, P. Ranitovic, B. Ulrich, B. Shan, Z. Chang, C. D. Lin, et al., Phys. Rev. Lett. 93, 183202 (2004).
[5] A. S. Alnaser, T. Osipov, E. P. Benis, A. Wech, B. Shan, C. L. Cocke, X. M. Tong, and C. D. Lin, Phys. Rev. Lett. 91, 163002 (2003).
[6] S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirila, M. Lein, J. W. G. Tisch, and J. P. Marangos, Science 312, 424 (2006).
[7] G. G. Paulus, F. Lindner, H. Walthier, A. Baltuška, E. Goulielmakis, M. Lezius, and F. Krausz, Phys. Rev. Lett. 91, 253004 (2003).
[8] C. A. Haworth, L. E. Chipperfield, J. S. Robinson, P. L. Knight, J. P. Marangos, and J. W. G. Tisch, Nature Physics 3, 52 (2007).
[9] C. P. J. Martiny and L. B. Madsen, Phys. Rev. Lett. 97, 093001 (2006).
[10] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. 75, 543 (2003).
[11] N. Hay, R. Velotta, M. Lein, R. de Nalda, E. Heesel, M. Castillejo, and J. P. Marangos, Phys. Rev. A 65, 053805 (2002).
[12] J. Itatani, D. Zeidler, J. Levesque, M. Spanner, D. M. Villeneuve, and P. B. Corkum, Phys. Rev. Lett. 94, 123902 (2005).
[13] T. Kanai, S. Minemoto, and H. Sakai, Nature (London) 435, 470 (2005).
[14] M. Lein, R. de Nalda, E. Heesel, N. Hay, E. Springate, R. Velotta, M. Castillejo, P. L. Knight, and J. P. Marangos, J. Mod. Opt. 52, 465 (2005).
[15] B. Sundaram and P. W. Milonni, Phys. Rev. A 41, 6571 (1990).
[16] K. Burnett, V. C. Reed, J. Cooper, and P. L. Knight, Phys. Rev. A 45, 3347 (1992).
[17] J. Faeder, I. Pinkas, G. Knopp, Y. Prior, and D. J. Tanner, J. Chem. Phys. 115, 8440 (2001).
[18] C. B. Madsen and L. B. Madsen, Phys. Rev. A 74, 023403 (2006).
[19] Y. Y. Liao, Y. N. Chen, and D. S. Chuu, Phys. Rev. B 70, 233410 (2004).
[20] T. K. Kjeldsen and L. B. Madsen, J. Phys. B 37, 2033 (2004).
[21] J. Ortigoso, M. Rodríguez, M. Gupta, and B. Friedrich, J. Chem. Phys. 110, 3870 (1999).
[22] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A 74, 023407 (2006).