Efficient Simulation of High Harmonic Generation Using Gaussian Basis Functions

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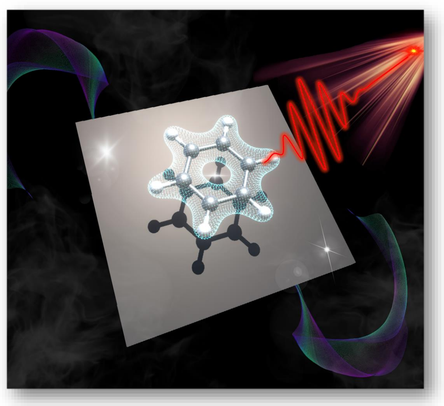
SCAN ME

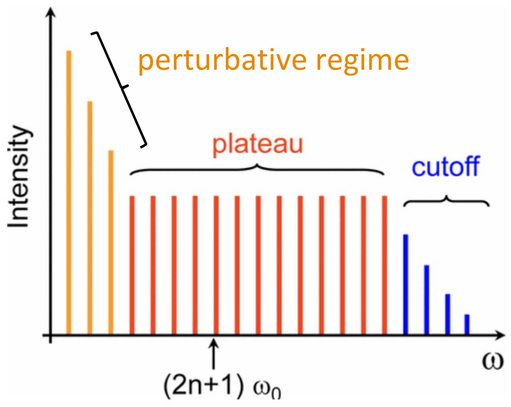
HIGH HARMONIC GENERATION

High harmonic generation (HHG) is a fascinating nonlinear phenomenon that occurs when atoms, molecules, or solids are exposed to intense laser pulses. This interaction triggers the emission of light at frequencies that are exact multiples of the laser's frequency[1].



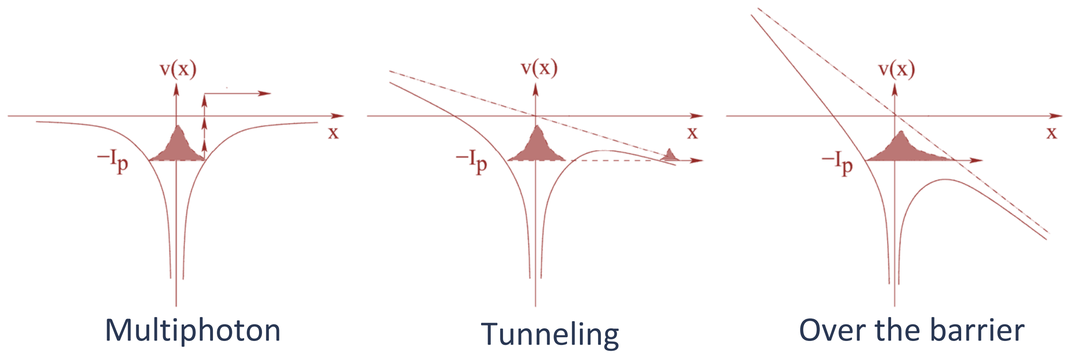
Artistic illustration of a molecule interacting with a laser pulse

Resulting HHG spectrum



Schematic representation of a typical HHG spectrum based on Corkum's three-step model

To better understand the HHG spectra, we need to look at the different modes of ionization that can occur:



Schematic representation of different ionization modes, depending on laser intensity

SIMULATING HHG

Real-time time-dependent density functional theory (RT-TDDFT) is a widely used computational method for studying HHG.

RT-TDDFT involves solving the single-particle time-dependent Kohn-Sham equations

$$i\frac{\partial \psi_{\mathrm{m}}(\mathbf{r},t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_{\mathrm{eff}}^{\mathrm{KS}}[\rho](\mathbf{r},t)\right]\psi_{\mathrm{m}}(\mathbf{r},t)$$

In particular, grid-based RT-TDDFT has been successfully employed in explaining the essential features of HHG spectra and is taken as numerical reference for such simulations.

In this work, we extend the RT-TDDFT implementation[2] in the TURBOMOLE[3] program package to simulate HHG. The implementation utilizes localized Gaussian type orbitals (GTO) as basis functions.

Cartesian GTO $\chi = Nx^i y^j z^k e^{-\alpha\left(x^2+y^2+z^2\right)}$

The following are the pros and cons of our implementation as compared against the typical grid-based RT-TDDFT implementation

Pros

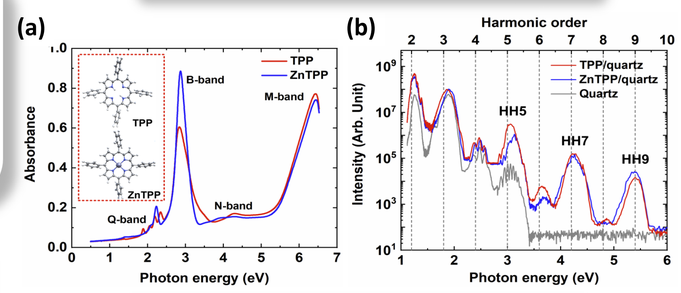
- Up to 10x faster
- Feasible to use various XC functionals (LDA, GGA, mGGA)
- Can handle large molecules
- Environmental effects via DFT-based embedding[4]

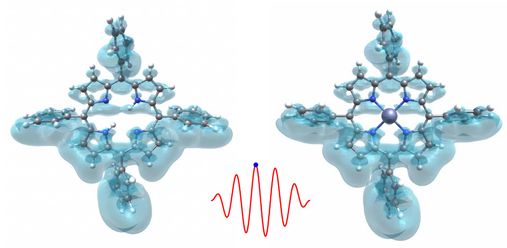
Cons

- Requires ghost atoms with diffuse functions to describe Rydberg and continuum states.
- Suited for low to moderately high intensities (I <10^{15} W/cm^2)

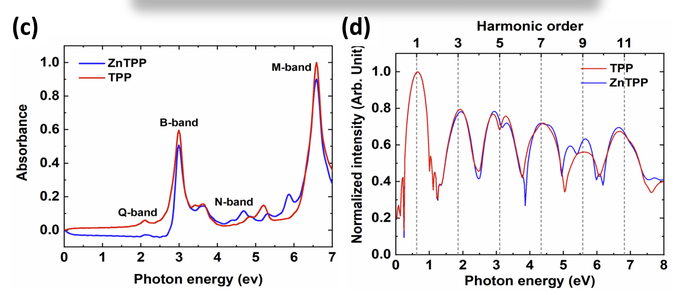
RESULTS

1 Using GTO-based RT-TDDFT for HHG simulations, we provided theoretical support to experiments on tetraphenylporphyrins (TPP) successfully[5].

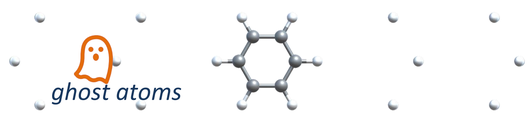




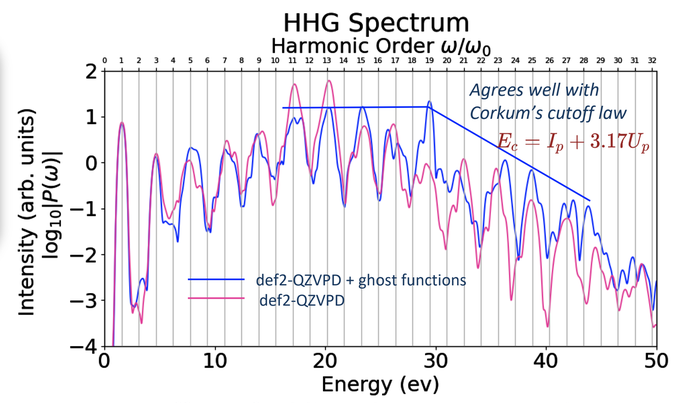
Snapshots of the time-dependent differential electron density of TPP and ZnTPP.[5]



2 Employing ghost atoms, with diffuse GTOs , allows for a better description of higher harmonics under intense laser pulses (I~10^{14} W/cm^2).



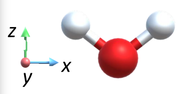
Benzene molecule

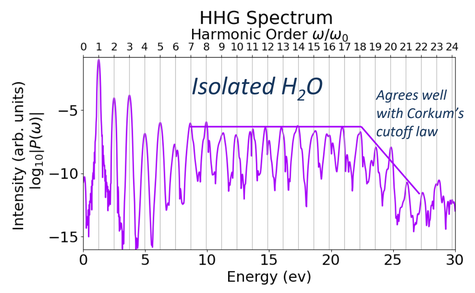


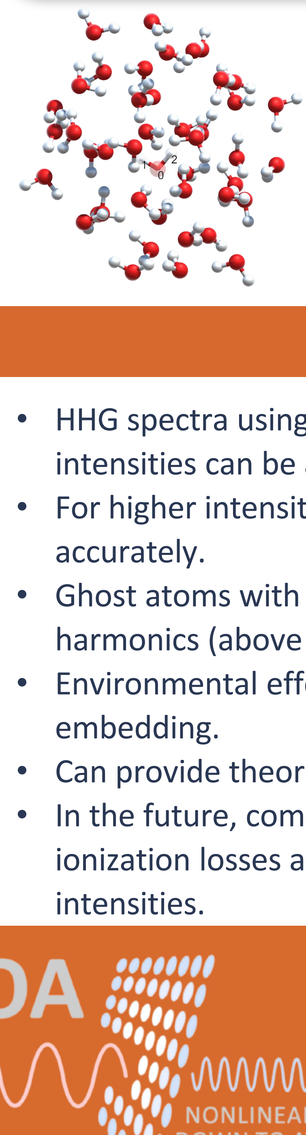
Effect of adding ghost atoms on the HHG spectrum of Benzene

3 Harmonic cutoff of the H_2O molecule is found to decrease in the presence of other water molecules, whose effect is included via DFT-based embedding.

Agrees well with ref 7.

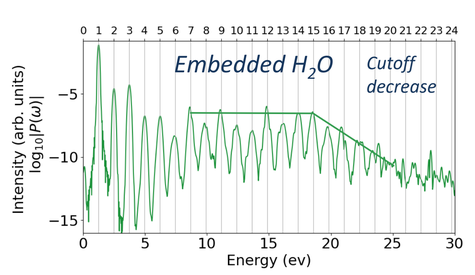






H_2O molecule embedded in a cluster of 43 water molecules (envrionment).

- *Embedded H_2O treated via metaGGA.*
- *Environment H_2O treated via GGA.*



CONCLUSION & OUTLOOK

- HHG spectra using low (~10^{12} W/cm^2) to moderate (~10^{13} W/cm^2) laser intensities can be accurately simulated with localized Gaussian basis-sets.
- For higher intensities (~10^{14} W/cm^2), lower harmonics can be simulated accurately.
- Ghost atoms with diffuse basis functions can be used for simulating higher harmonics (above I_p) for high laser intensities.
- Environmental effects can be successfully accounted for by employing DFT-based embedding.
- Can provide theoretical support for experimental results
- In the future, complex absorbing potentials can be implemented to handle ionization losses and accurately simulate HHG spectra at even stronger laser intensities.

References:

1. P. Corkum, *Phys. Rev. Lett.* **71**, 1994–1997 (1993).
2. C. Müller, M. Sharma, M. Sierka, *J. Comput. Chem.* **41**, 2573 (2020).
3. TURBOMOLE , a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com. (development version)
4. M. Sharma, M. Sierka, *J. Chem. Theory Comput.* **18** (11), 6892-6904 (2022).
5. W. Li, A. Saleh, M. Sharma, C. Hünecke, M. Sierka, M. Neuhaus, et al., *Adv. Opt. Mat.*, 2203070 (2023).
6. M. De Santis, L. Belpassi, C. Jacob, A. Gomes, F. Tarantelli, L. Visscher, and L. Storchi, *J. Chem. Theory Comput.* **16** (9), 5695–5711 (2020).

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