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# Supplemental Data for Characterizing Particle-Like Charge-Migration Dynamics with High-Order Harmonic Sideband Spectroscopy

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# Supplemental data for Characterizing particle-like charge-migration dynamics with high-order harmonic sideband spectroscopy

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This documentation describes the time-dependent density-functional theory (TDDFT) data, and Python scripts, we use to make the figures published in "Characterizing particle-like charge-migration dynamics with high-order harmonic sideband spectroscopy" [Hamer 2022]. All the supplemental data were obtained with the Octopus package [Andrade 2012, Andrade 2015], version 8.4.

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# 1 Octopus-package license



# 2 Supplemental data types

Overall, we provide 4 types of supplemental-data files, with the naming conventions:

- `acceleration_*`: time-dependent dipole acceleration signal used to compute harmonic spectra.
- `laser_*`: the corresponding laser field.
- `KSdens_*`: Kohn-Sham-orbital-resolved transverse-integrated electron density as a function of position along the molecular backbone
- `*.cube`: three-dimensional volumetric data used to store wavefunctions or densities.

## 2.1 Dipole acceleration files (`acceleration_*`)

In each dipole acceleration file, the first column indicates the iteration number (the number of time steps that have been performed up to that point in the simulation), the second column indicates the time (in atomic units), and columns 3-to-5 indicate the dipole acceleration in the x, y, and z directions, respectively. For further information on how the data is used to calculate the high-harmonic sideband spectrum, see [Hamer 2022].

## 2.2 Laser files (`laser_*`)

In each laser file, the first column corresponds to the iteration number and the second column to the time (in atomic units). After that, each successive group of 3 columns corresponds to a component of the driving laser field (x, y, and z components, respectively), starting with the mid-infrared and then the odd harmonics 9-through-17 that make up the attosecond pulse train ionization seed [Hamer 2021].

## 2.3 Kohn-Sham density files (`KSdens_*`)

For a molecule aligned along the z axis, each file corresponds to the transverse-integrated density, at a given time $t$ defined as

$$\rho_k(z,t) = \int_{box} dx\, dy\, |\psi_k(x,y,z,t)|^2,$$

where $\psi_k$ is the $k^{th}$ Kohn-Sham orbital. In each density file, the first column corresponds to the position $z$ along the axis parallel to the molecular backbone, in atomic units; and the second column corresponds to the orbital density.

We sample the density with a time step of 0.25 a.u., such that the absolute time is recovered as $t = 0.05n$, with the iteration number $n$ indicated in the file name.

### 2.4 Volumetric Data Files (`*.cube`)

This is a standard Gaussian CUBE file – more information can be found at https://octopus-code.org/wiki/Manual:Visualization.

## 3 Supplemental data content

The supplemental data are sorted into 7 archive (zip) files – see below for further details:

- *Angle-Dependent Calculations*: contains the results of the harmonic-generation simulations with varying the molecular-alignment angle; used to produce Fig. 6 in the text.
- *Charge Migration Dynamics*: contains the time-dependent density of the Kohn-Sham orbital in which an electron is removed to induce charge migration, used in Figs. 1(b) and 5(b) in the main text.
- *CM Initial Condition*: contains the initial three-dimensional data for the Kohn-Sham orbital in which an electron is removed to start the CM, used in Fig. 1(a) of the main text.
- *Control (no CM, 1800 nm) Calculation*: contains the results of the high-harmonic-generation (HHG) simulation in neutral bromobutadiyne, with a driving laser wavelength of 1800 nm, used in Fig. 1(c) of the main text.
- *Delay-Dependent Calculations*: contains the results of the HHG simulations with varying the sub-cycle delay between the initiation of the charge migration and the driving laser field, used in Fig. 5(a) of the main text.
- *Python Scripts:* contains the scripts used to generate the figures seen in the paper. Discussed in Section 4.
- *Wavelength-Dependent Calculations*: contains the results of the HHG simulations with varying driving-laser wavelength, used in Figs. 1(c), 2-4, and 7 in the text.

### 3.1 Angle-Dependent Calculations archive

This archive contains 17 dipole acceleration files and 17 laser files, each labeled by the molecular-orientation angle theta ($\theta$) in the file names. $\theta = 0$ corresponds to perpendicular orientation, in which the laser field is polarized along the x-axis and the molecular backbone is parallel to the $z$-axis. These angles range from -90 degrees to +90 degrees.

### 3.2 Charge Migration Dynamics archive

This archive contains many files, labeled by their iteration index $n$, each containing the time-dependent density, as a function of position, at the corresponding time $t = 0.05n$ (in atomic units). The density is sampled with a time step of 0.25 atomic units.

### 3.3 CM Initial Condition archive

This archive contains one file: the three-dimensional Kohn-Sham orbital density corresponding to the initial condition for charge migration, in the CUBE file format. The molecular geometry used for our harmonic-generation simulations is also embedded within the header of this file.

### 3.4 Control (no CM, 1800 nm) Calculation archive

This archive contains two files: (1) the total dipole acceleration and (2) the laser field for HHG simulation at 1800 nm and without charge migration (in the neutral molecule).

### 3.5 Delay-Dependent Calculations archive

This archive has 8 dipole acceleration files and 8 laser files, labeled by their sub-cycle delay. In each of the file names, the decimal point has been removed, such that the suffix `_delay=3125` corresponds to $\Delta = 0.3125$ optical cycles.

### 3.6 Wavelength-Dependent Calculations archive

This archive has 14 dipole acceleration files and 14 laser files, labeled by their wavelength lambda, in nanometers.

## 4 Python scripts

The 'Python Scripts/' directory contains the Python scripts we used to produce the figures in the paper. There are 8 scripts in total:

- fig1b,5b.py
- fig1c.py
- fig2,3.py
- fig4.py
- fig5a.py
- fig6.py
- fig7.py
- utils.py

The first 7 scripts produce the figures and subfigures of the paper, with self-explanatory names; the last script, utils.py, contains methods that are used throughout all of the scripts. If the scripts do not work on first execution, make sure that your integrated development environment (IDE) can locate utils.py. We have validated all the scripts on the Spyder IDE with Python 3.7.9.

## 5 Acknowledgments

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