Time-Dependent Density Functional Theory Simulations of Coulomb Explosion

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HUNGARIAN GOVERNMENT
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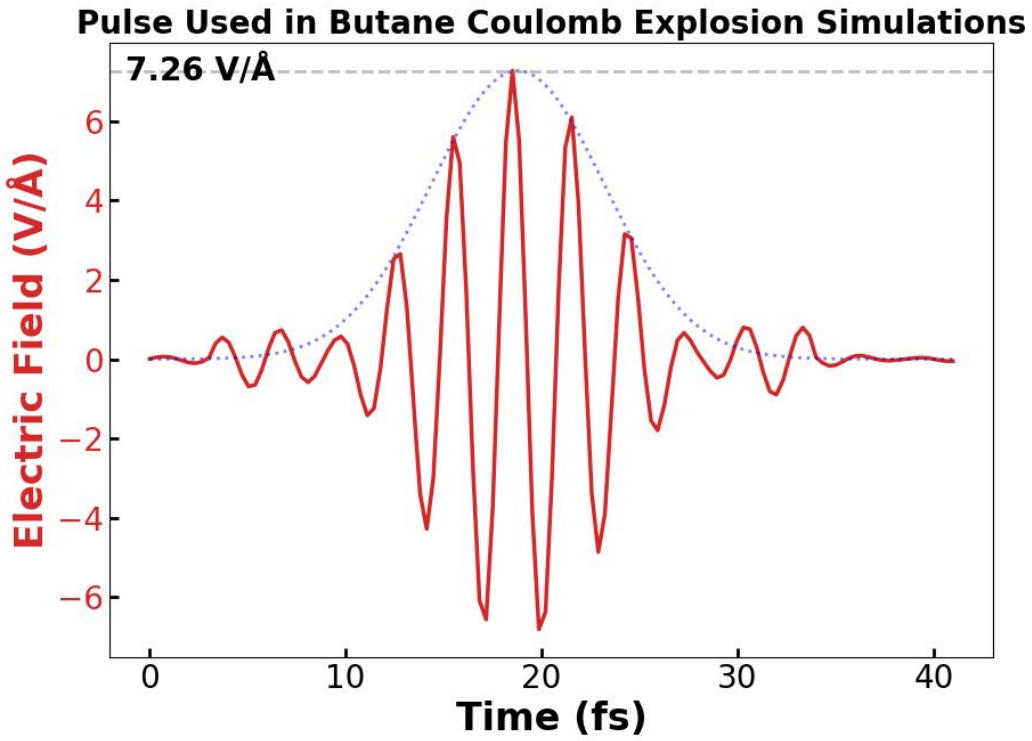
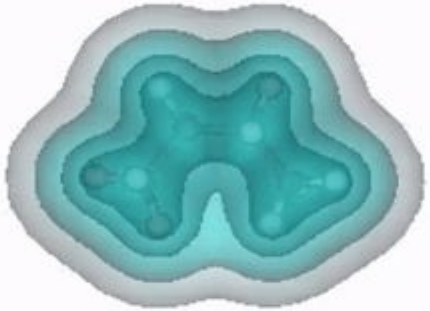
Introduction

Introduction

Coulomb Explosion:

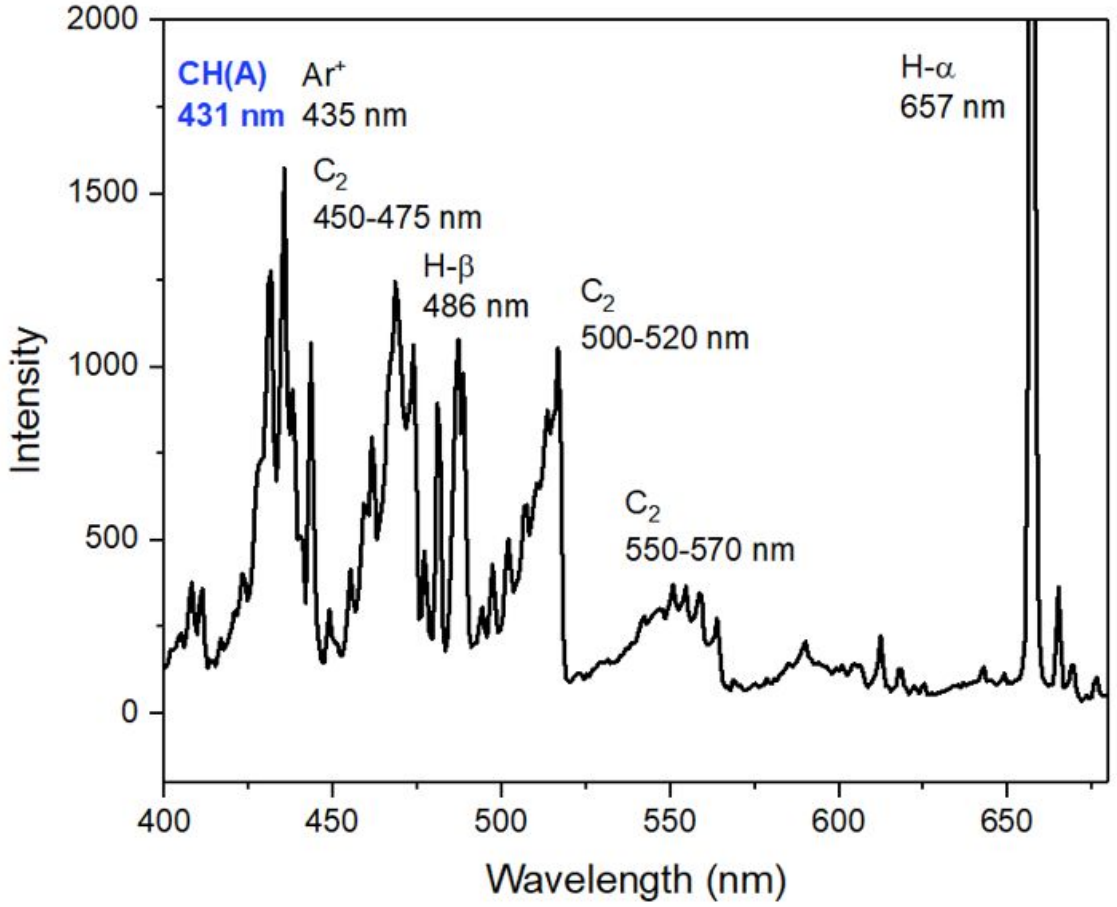
- Rapid ionization due to very strong laser pulse
- Coulomb force causes ions to repel

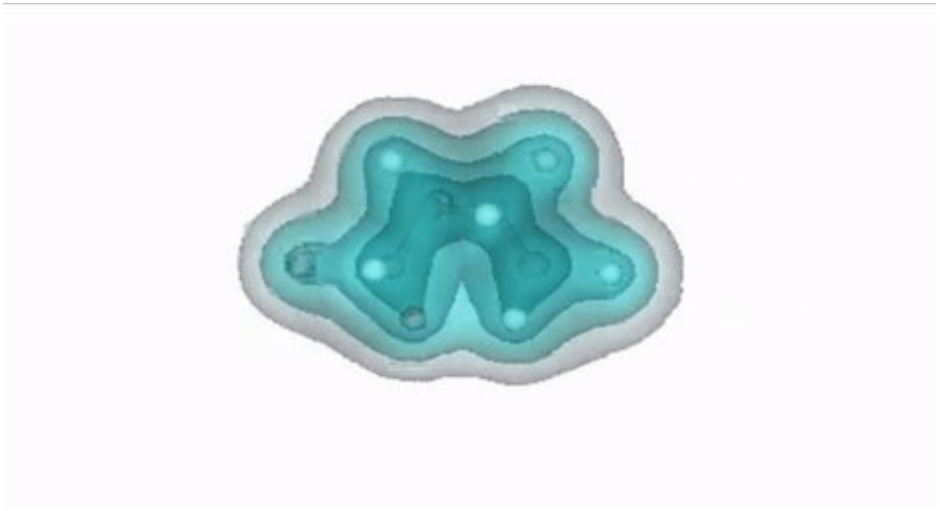




Introduction

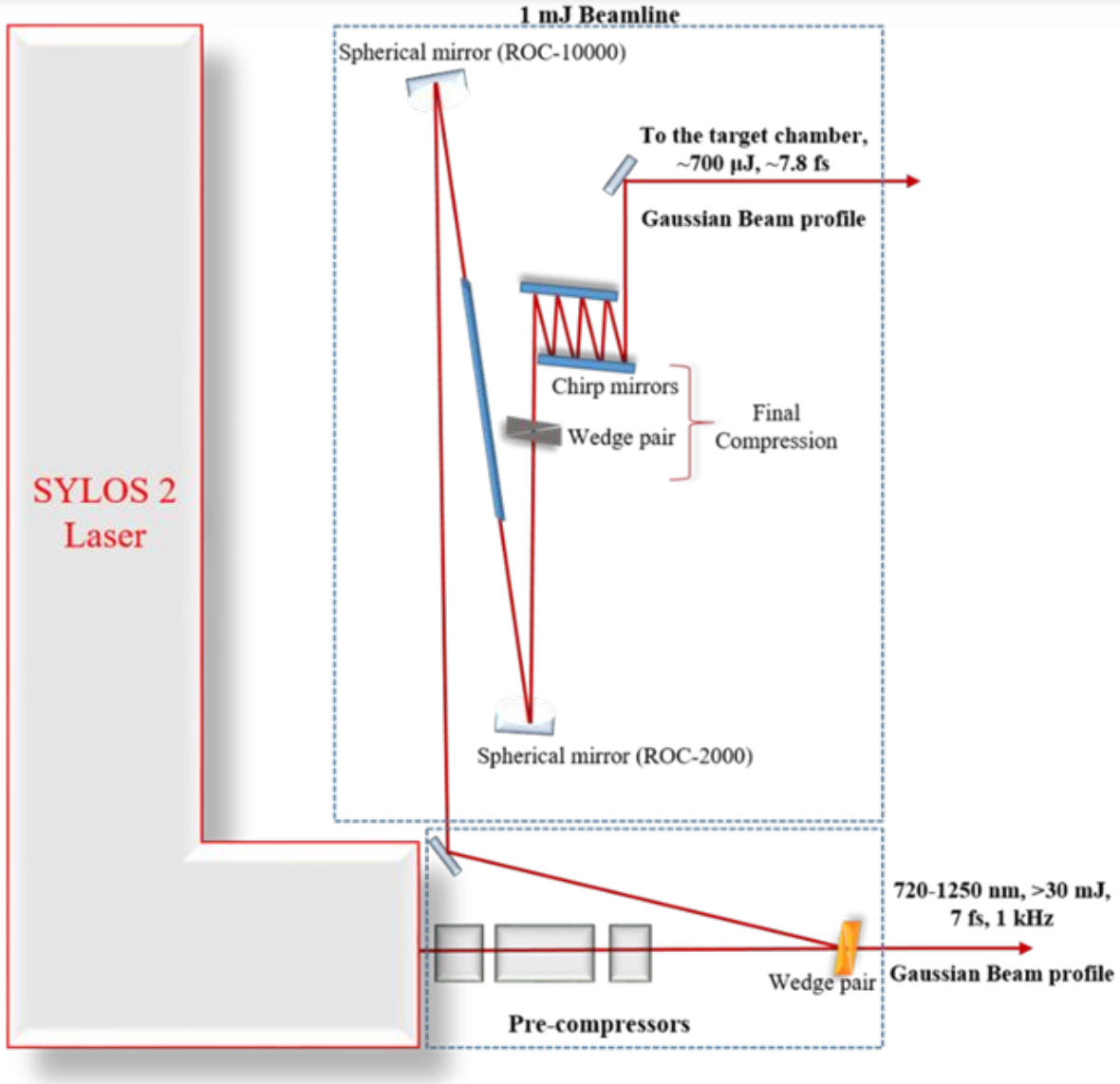
CE can lead to the formation of other molecules. CH(A) neutral radicals



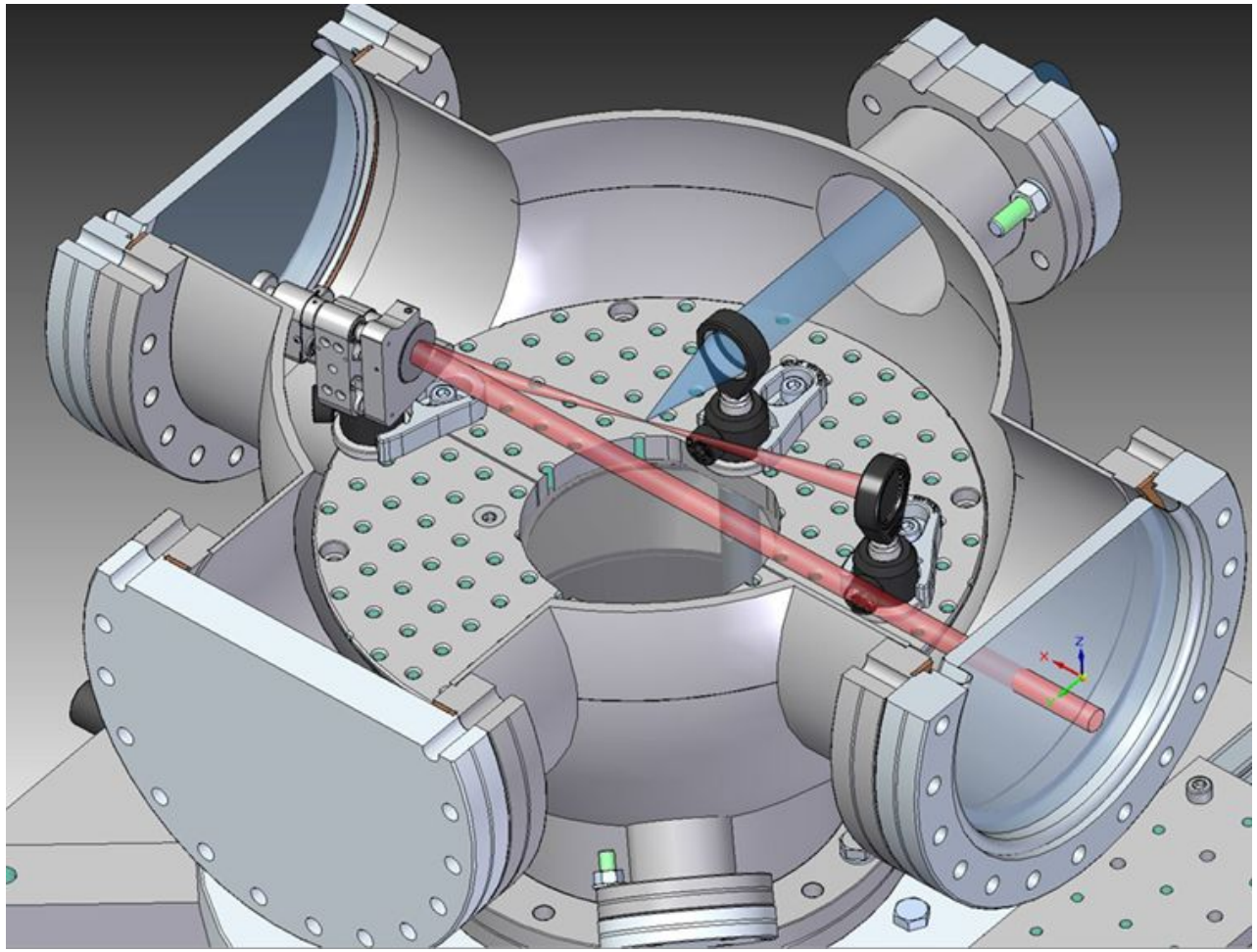


Overview emission spectrum measured from the brightest butane-argon plasma with the CH(A), C_2 emission bands and H atomic lines b, High resolution emission spectra from argon-butane plasma measured at 50 and 250 ns time points (1 cm^{-1} spectral resolution)

Introduction - The Experiment



Schematic view of the SYLOS 2A laser system and 1 mJ beam line for the photodissociation experiments



The reaction chamber used in the photodissociation experiments (red beam represents the SYLOS beam and the blue one the collected fluorescent light)

Motivation

- **Show neutral species can be produced from Coulomb explosion**
  - CH neutral radicals - important in many different chemical processes
    - Chemical processes in space, hydrocarbon flames, and plasma-enhanced chemical vapor deposition

- **TDDFT**: Match the experimental data with **theoretical predictions**

- **Contribute to deeper understanding of:**
  - Radical formation in intense laser fields
  - Various chemical processes in different environments
  - Coulomb Explosion and the production of neutral fragments

Computational Details

Computational Details

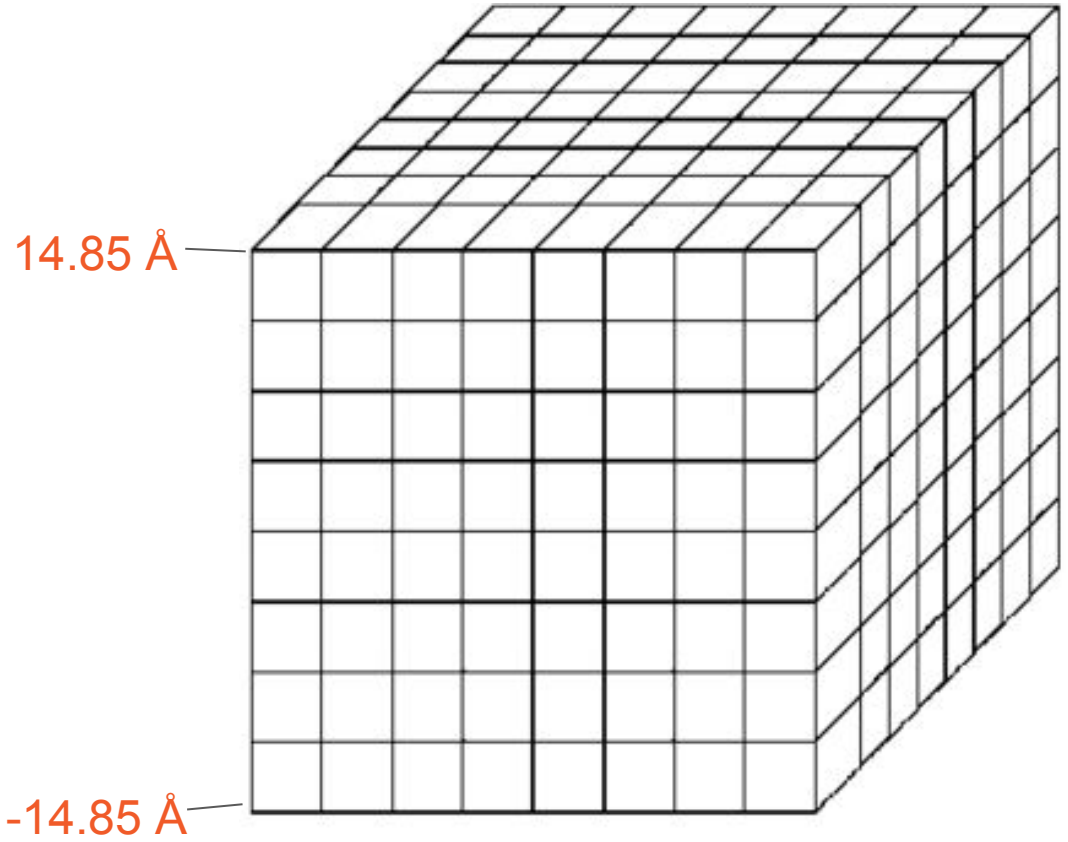
Summary of the Process:

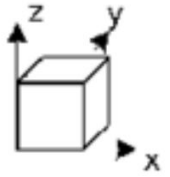
- **Density Functional Theory** (DFT) calculation performed to calculate the **ground state**
  - **Real-space grid used**. Core electrons represented with norm-conserving Troullier-Martin pseudopotentials

- The time–dependent orbitals are propagated using a **fourth-order Taylor expansion of the time-evolution operator**
- Motions of the ions in the simulation are treated **classically** with electron-ion force modeled via Ehrenfest theorem
- A **complex absorbing potential (CAP)** is implemented to prevent reflections of the wave function at the boundary

Overview

Overview
Real-space Grid used in DFT





29.7 × 29.7 × 29.7 Å^3 Grid

Grid Details and Overview

- Grid is from -14.85 to 14.85 Å on each axis (x,y,z)
- Size is 29.7 × 29.7 × 29.7 Å^3
- There are 100 lattice points on every axis
- Grid of 100 × 100 × 100 = **1,000,000 points**
- Every observable quantity and calculation in the simulation is made from the grid points
- Wave function, matrix operators, electron density
- Distance between each point is **0.3** Å

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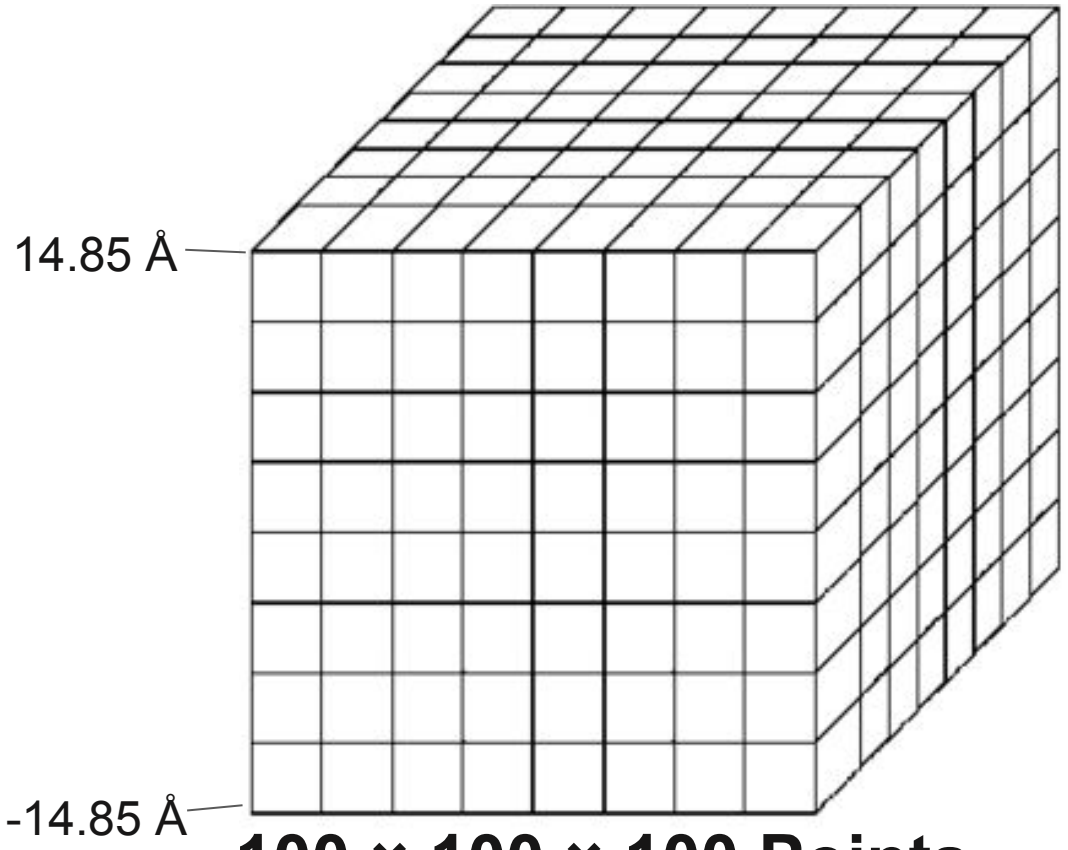

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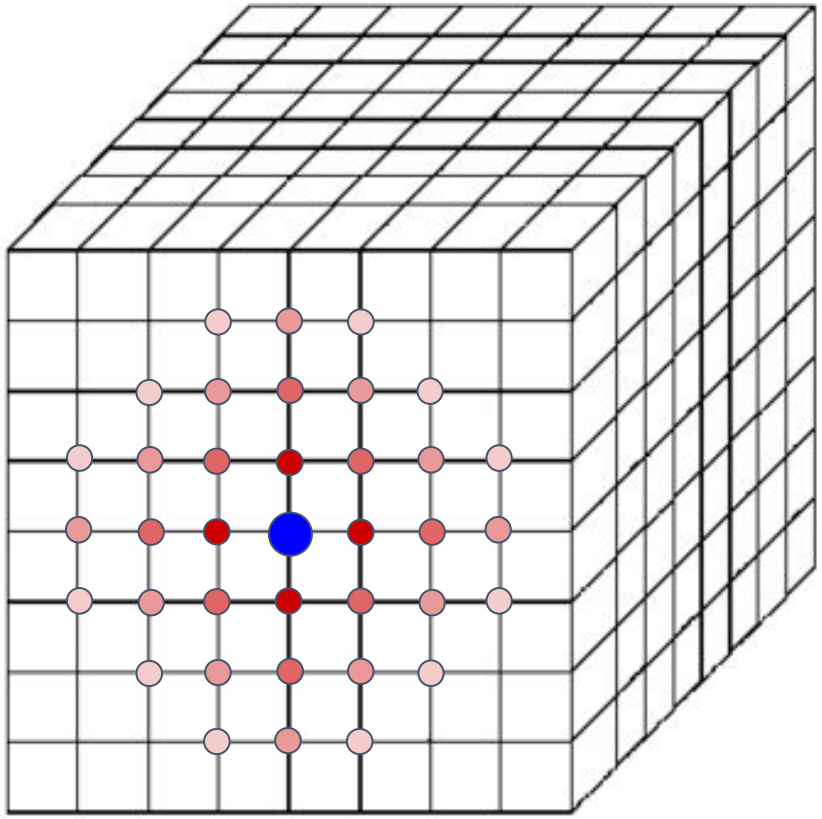
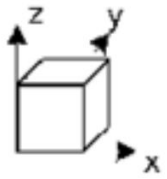


- Hydrogen

- Electron Density Point



Example: Using the Grid to calculate number of electrons around a molecule

- Radial “density integration”
- To find the number of electrons **N**, we need to sum up all of the valence electron density points around a molecule.

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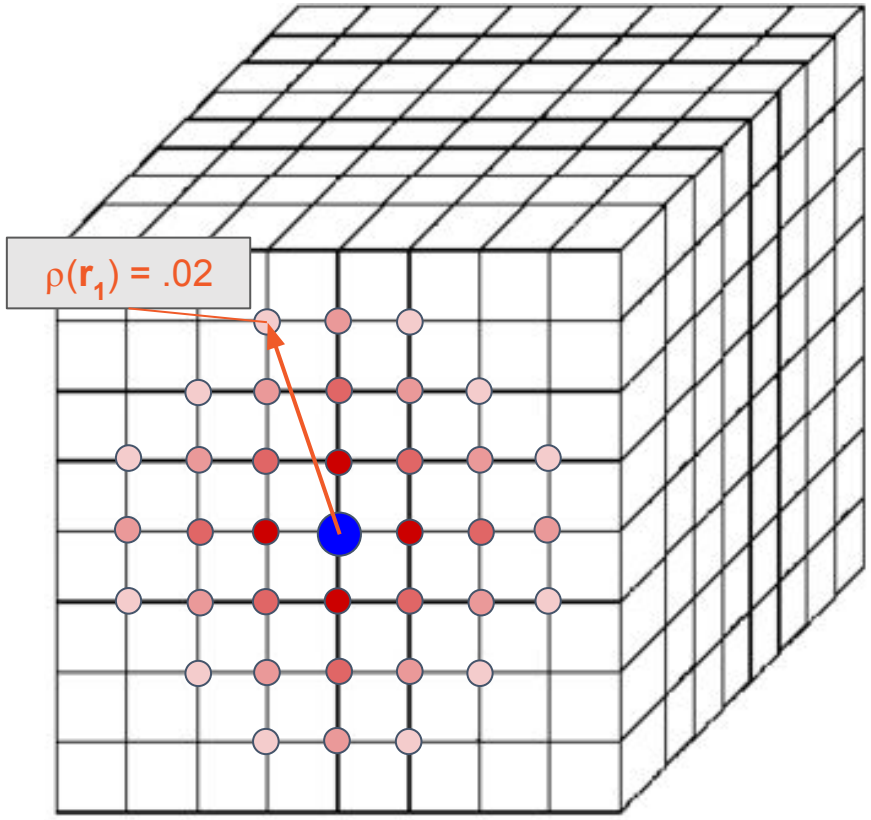

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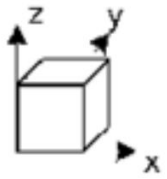

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N = .02 +

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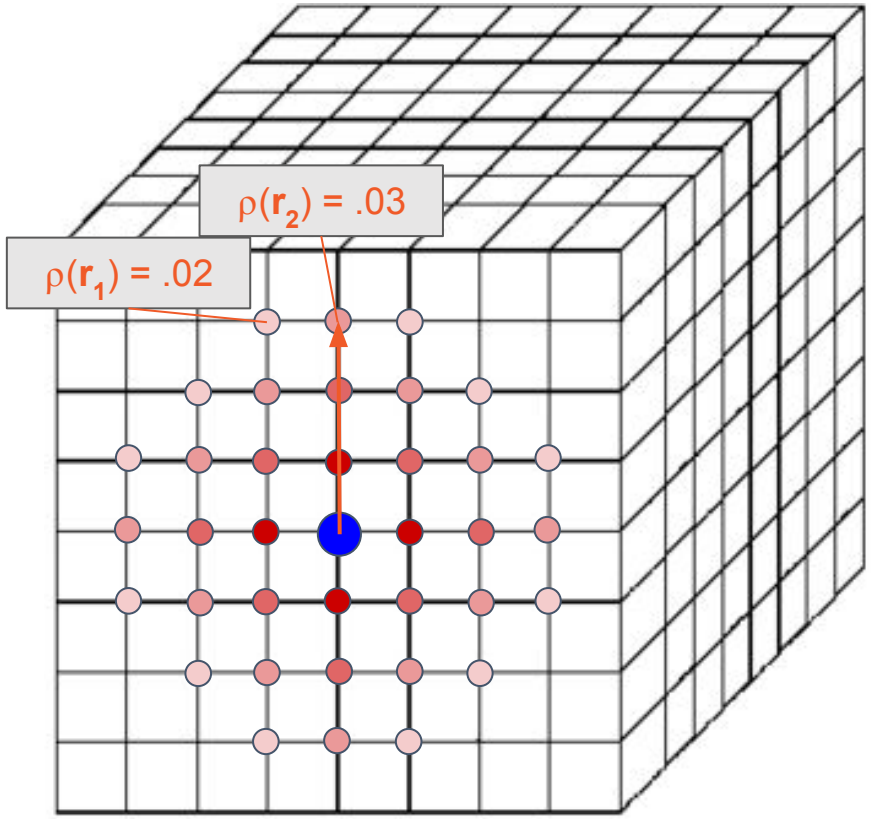

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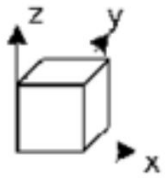

<u>Example:</u> Using the Grid to calculate number of electrons around a molecule

- Radial “density integration”
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$N = .02 + .03$

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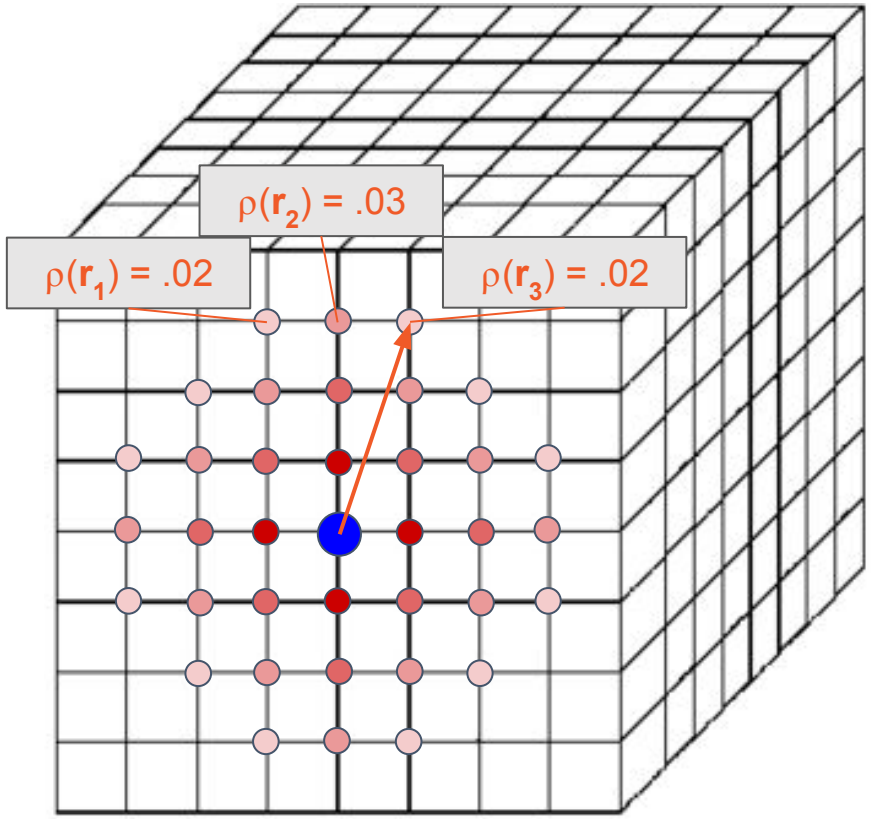
Real-space Grid: Example



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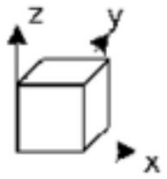

Example: Using the Grid to calculate number of electrons around a molecule

- Radial “density integration”
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$N = .02 + .03 + .02$

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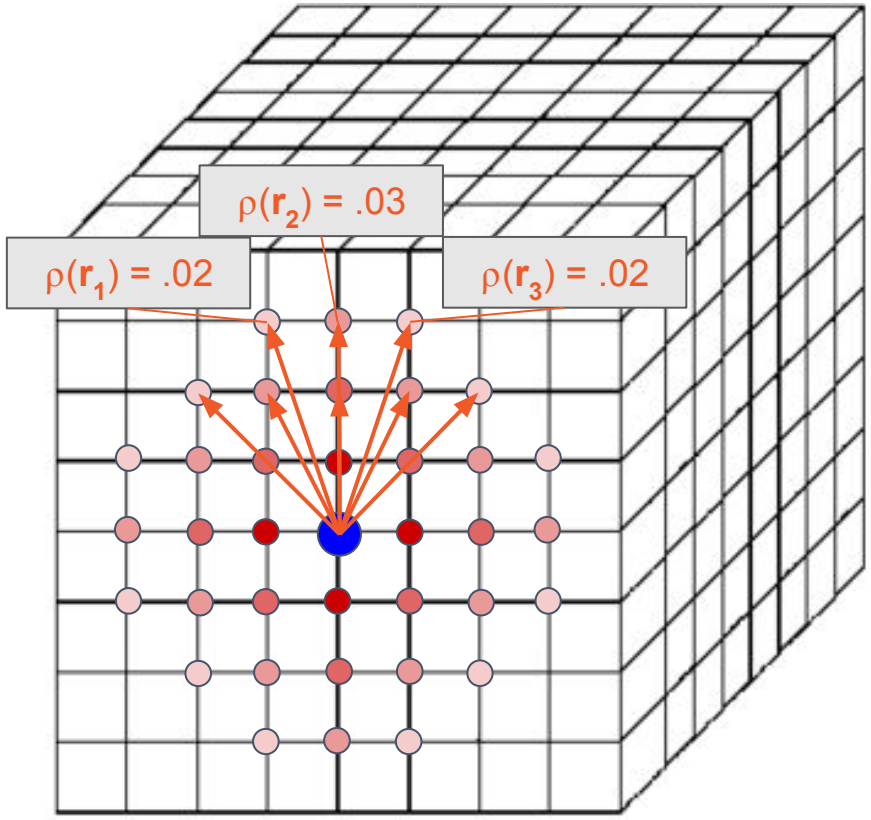
Real-space Grid: Example



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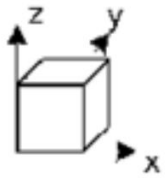

Example: Using the Grid to calculate number of electrons around a molecule

- Radial "density integration"
- To find the number of electrons **N**, we need to sum up all of the valence electron density points around a molecule.

N = .02 + .03 + .02 + … = .70

The charge is 1 - .70 = **0.30^{+}**

(30% probability of being positively charged)

Time-independent calculations

Formalism
DFT Calculation - Kohn Sham

DFT calculation

- Construct Hamiltonian and solve the Kohn-Sham (KS) Equation to find the KS orbitals $\psi_i(\mathbf{r})$

$$H_{\mathrm{KS}}\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r}), \qquad H_{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 + V^{\mathrm{KS}}[n(\mathbf{r})]$$

- Solving for the Kohn-Sham orbitals can give us the electron density $n(\mathbf{r})$ as follows:

$$n(\mathbf{r}) = f_k \sum_{i=1}^{N_{\mathrm{occupied}}} |\Psi_i(\mathbf{r})|^2$$

- where f_k is the occupation number of each orbital.
- f_k may take on the values 1 and 2 ($f_k = 2$ is permitted via spin degeneracy)

- The Kohn-Sham potential depends on the density, and yet that is what we are solving for

- **Goal**: solve this equation self-consistently with evolving values for $n(\mathbf{r})$.

Formalism
Kinetic Energy

$$H_{\mathrm{KS}}\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r})$$

$$H_{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 + V^{\mathrm{KS}}[n(\mathbf{r})]$$

Kinetic energy operator

$$-\frac{\hbar^2}{2m}\nabla^2$$

- The Laplacian ∇^2 is approximated using second derivative, 9-point central finite difference

Table 2.2 Higher-order finite difference coefficients for the second derivative

k	C_i^k	$C_{i\pm1}^k$	$C_{i\pm2}^k$	$C_{i\pm3}^k$	$C_{i\pm4}^k$	$C_{i\pm5}^k$	$C_{i\pm6}^k$
1	-2	1					
2	$-\frac{5}{2}$	$\frac{4}{3}$	$-\frac{1}{12}$				
3	$-\frac{49}{18}$	$\frac{3}{2}$	$-\frac{3}{20}$	$\frac{1}{90}$			
4	$-\frac{205}{72}$	$\frac{8}{5}$	$-\frac{1}{5}$	$\frac{8}{315}$	$-\frac{1}{560}$		
5	$-\frac{5269}{1800}$	$\frac{5}{3}$	$-\frac{5}{21}$	$\frac{5}{126}$	$-\frac{5}{1008}$	$\frac{1}{3150}$	
6	$-\frac{5369}{1800}$	$\frac{12}{7}$	$-\frac{15}{56}$	$\frac{10}{189}$	$-\frac{1}{112}$	$\frac{2}{1925}$	$-\frac{1}{16\,632}$

Look at 9 points:

Current point,
4 to the left,
4 to the right,

to approximate the Laplacian
h = 0.3 Å

$$\phi''(x) = -\frac{1}{560}[\phi(x+4h)+\phi(x-4h)]+\frac{8}{315}[\phi(x+3h)+\phi(x-3h)]-\frac{1}{5}[\phi(x+2h)+\phi(x-2h)]+\frac{8}{5}[\phi(x+h)+\phi(x-h)]-\frac{205}{72}\phi(x)$$

Formalism
Ion potential

$$H_{\mathrm{KS}}\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r})$$

$$H_{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 + V^{\mathrm{KS}}[n(\mathbf{r})]$$

Kohn-Sham potential

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{ion}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})$$

- $\mathbf{V_{ion}}$ - The potential experienced on valence electrons from the ionic core
- Divide the electrons of the atoms into **core electrons** and **valence electrons**
  - Core electron wavefunctions remain essentially unchanged when in different chemical environments
  - Don’t solve for core electrons→ represent as: **Troullier Martins Pseudopotentials** for the interactions with the valence electrons

$$\hat{V}^{\mathrm{PP}}_{\mathrm{ion}}(r) = V^{\mathrm{PP}}_{\mathrm{ion,local}}(r) + \sum_l V_{\mathrm{nonlocal},l}(r)\hat{P}_l \ ,$$

where $V^{\mathrm{PP}}_{\mathrm{ion,local}}(r)$ is the local potential and,

$$V_{\mathrm{nonlocal},l}(r) = V^{\mathrm{PP}}_{\mathrm{ion},l}(r) - V^{\mathrm{PP}}_{\mathrm{ion,local}}(r)$$

```
[u.st199789@aces-login1 data]$ ls
ag_pp.dat  au_pp.dat  b_pp.dat   cl_pp.dat  cs_pp.dat  f_pp.dat   he_pp.dat  k_pp.dat   mg_pp.dat  Ng_6       n_pp.dat   pd_pp.dat  rb_pp.dat  s_pp.dat   v_pp.dat
al_pp.dat  be_pp.dat  br_pp.dat  c_pp.dat   cu_pp.dat  ge_pp.dat  h_pp.dat   li_pp.dat  na_pp.dat  ni_pp.dat  o_pp.dat   p_pp.dat   si_pp.dat  ti_pp.dat  w_pp.dat
```

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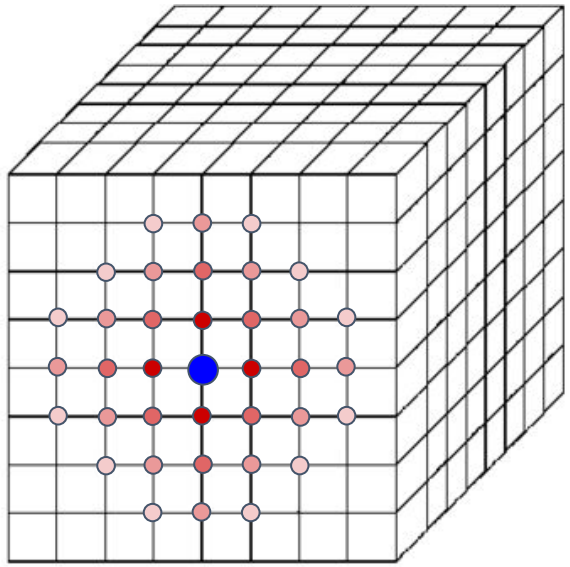
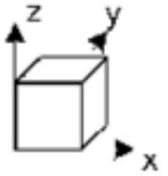
- $\mathbf{V_{Hartree}}$ - The electron-electron coulomb interaction

$$V_{\mathrm{H}}(\mathbf{r}) = \int_{\Omega} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- The sum of **all** the densities n(**r**') at each point **r**





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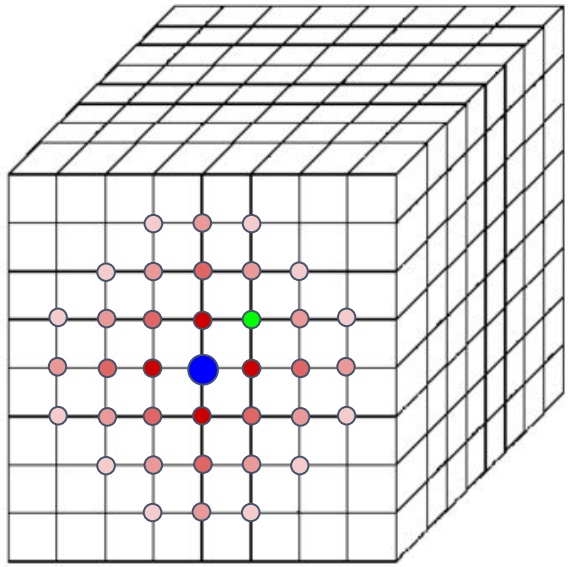

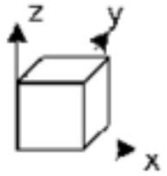

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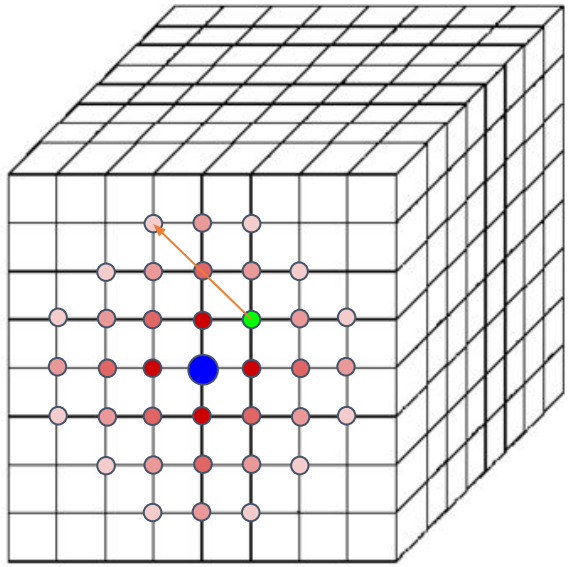

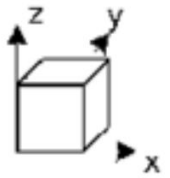

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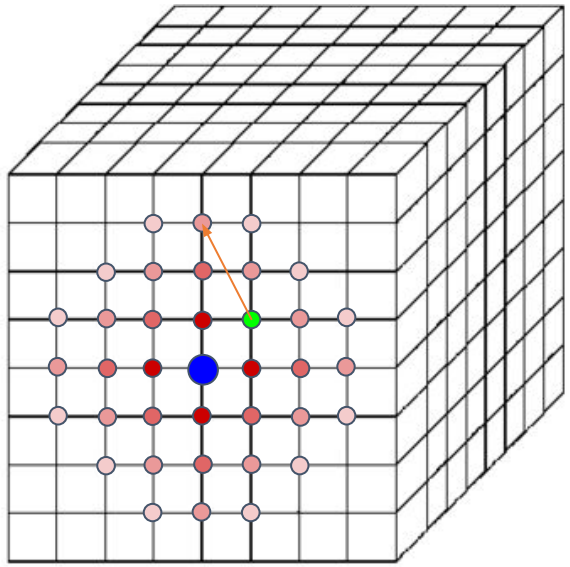

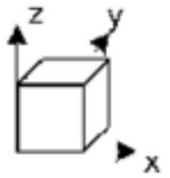

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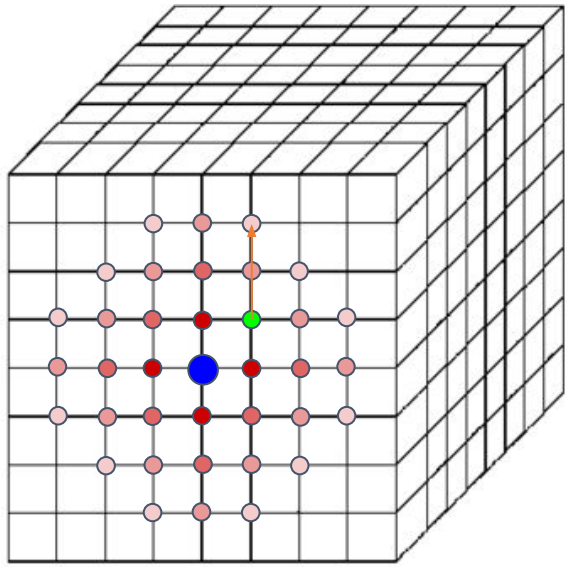

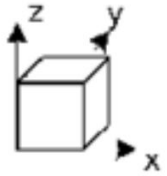

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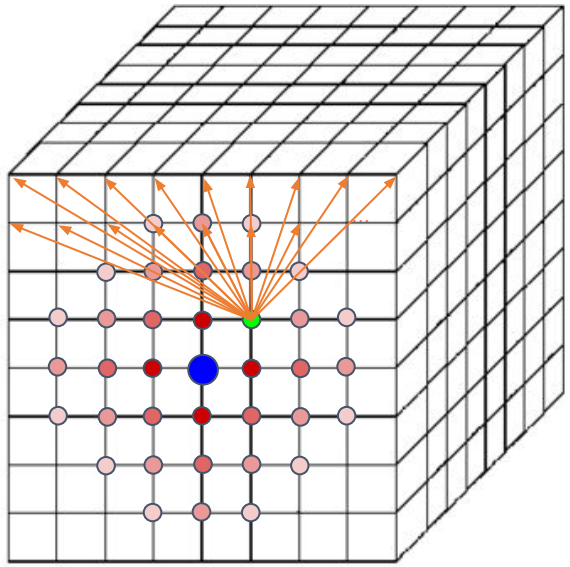


The Calculation

- For every single of the 1,000,000 grid points, must sum the resulting effect from 1,000,000 other points
- The work:
  - $1{,}000{,}000^2 = (10^6)^2 = \mathbf{10^{12}}$ calculations performed

Formalism
Exchange Correlation

$$H_{KS}\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r})$$

$$H_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + V^{KS}[n(\mathbf{r})]$$

Kohn-Sham potential

$$V_{KS}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$$

- $\mathbf{V_{xc}}$ - The Exchange and Correlation Potentials – Quantum mechanical electron-electron effects

$$V^{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta[n(\mathbf{r})]}$$

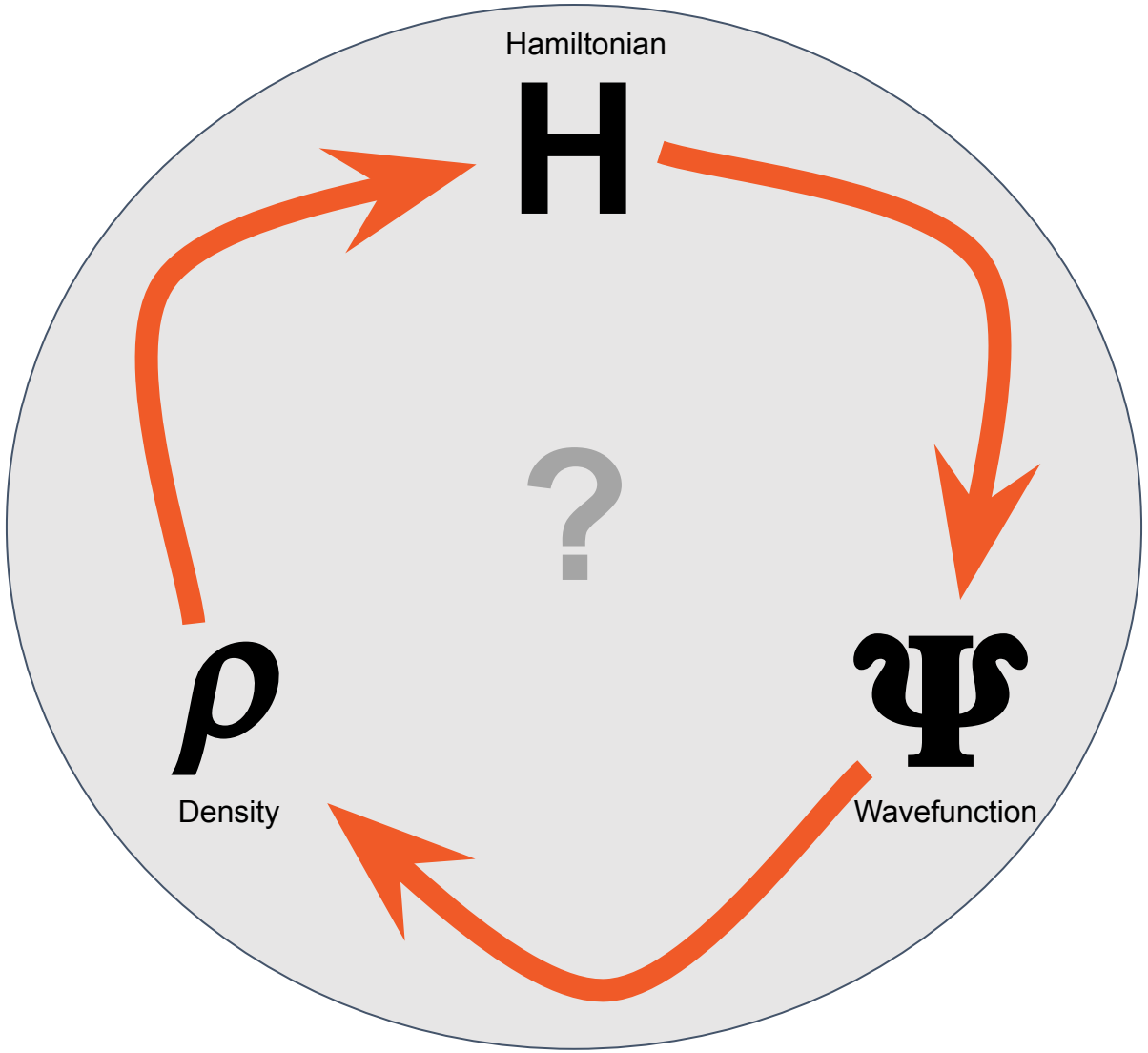
- **Exchange**: Energy change that occurs when electrons exchange positions in a system of indistinguishable particles. Comes from Pauli Exclusion principle
- **Correlation**: Includes many-body effects and dynamic correlations beyond the mean-field approximation (Hartree) such as instantaneous positions and momenta of electrons.

Local Density Approximation: $E_{xc}^{LDA} = \int d\mathbf{r}\,\epsilon[n(\mathbf{r})]n(\mathbf{r}),$

where $\epsilon[n(\mathbf{r})]$ is the exchange-correlation energy per unit volume of a homogeneous electron gas of density $n(\mathbf{r})$.

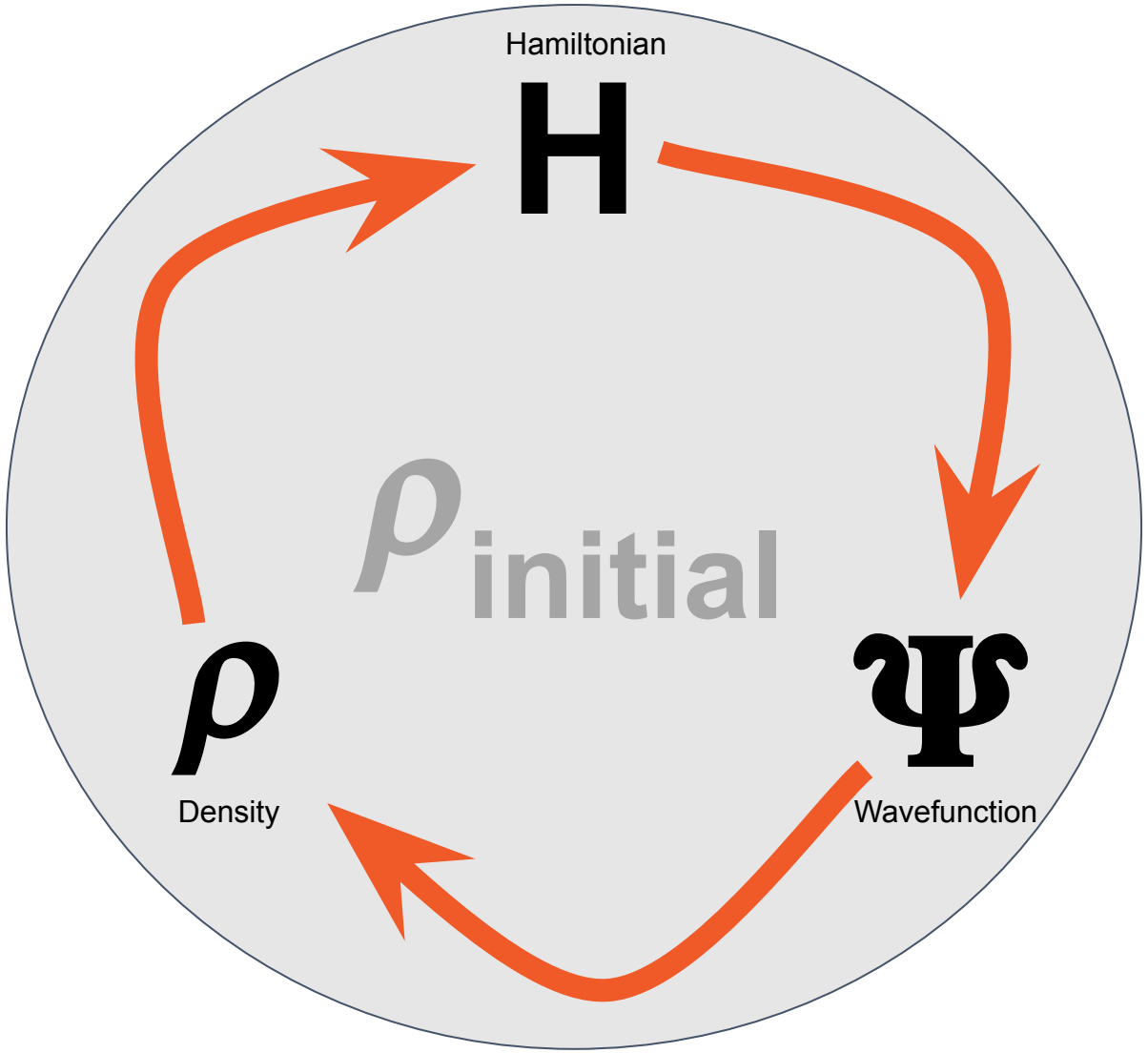
Resulting LDA potential: $V_{xc}(\mathbf{r}) = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r})\frac{d\epsilon_{xc}}{dn}|_{n=n(\mathbf{r})}$

Formalism
Functionals and Self-Consistency



- The Hamiltonian **H** is a function of the density ρ
- Need ρ to get **H**
- Need **H** to get Ψ
- Need Ψ to get ρ
- *How do we break this loop?*

Formalism
Functionals and Self-Consistency



- The Hamiltonian **H** is a function of the density ρ .
- Need ρ to get **H**
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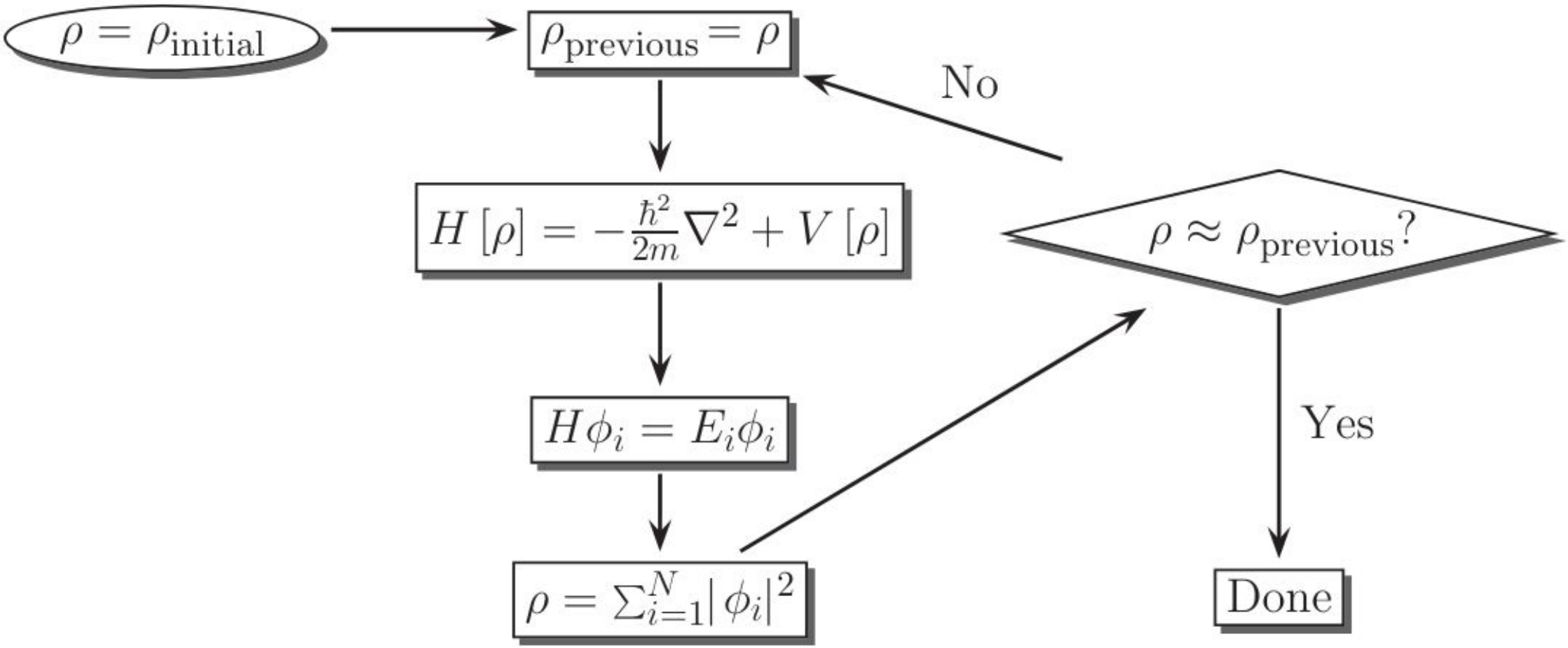
- *How do we break this loop?*
- **Initial Guess for** ρ

Formalism
DFT Flow Chart



Time-dependent calculations

Formalism
External Potential

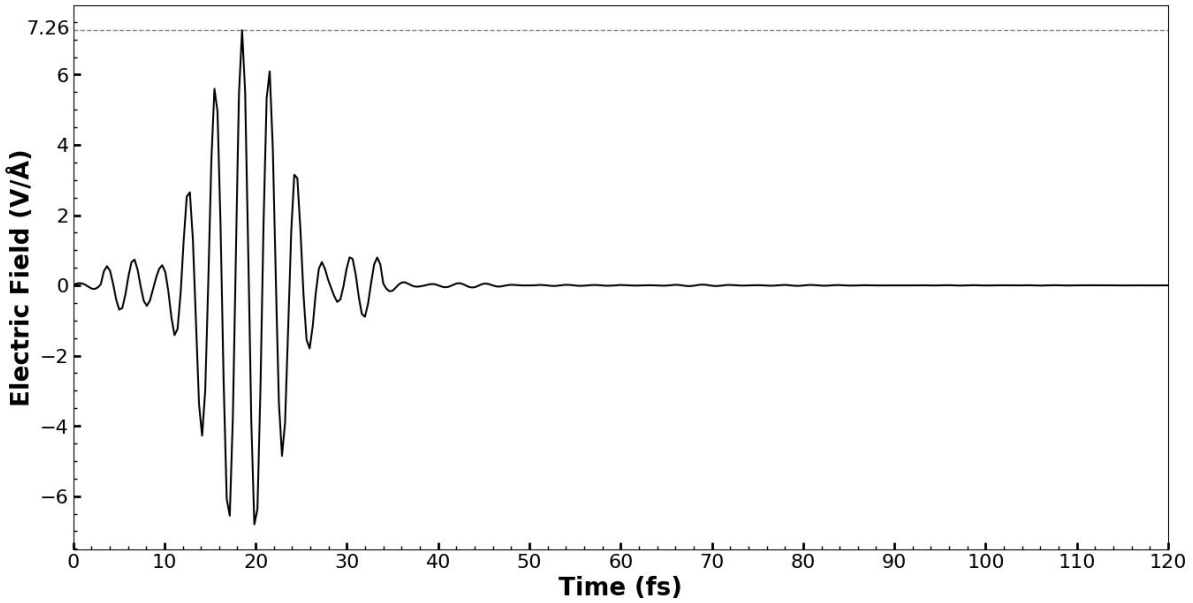
$$H_{\mathrm{KS}}\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r})$$

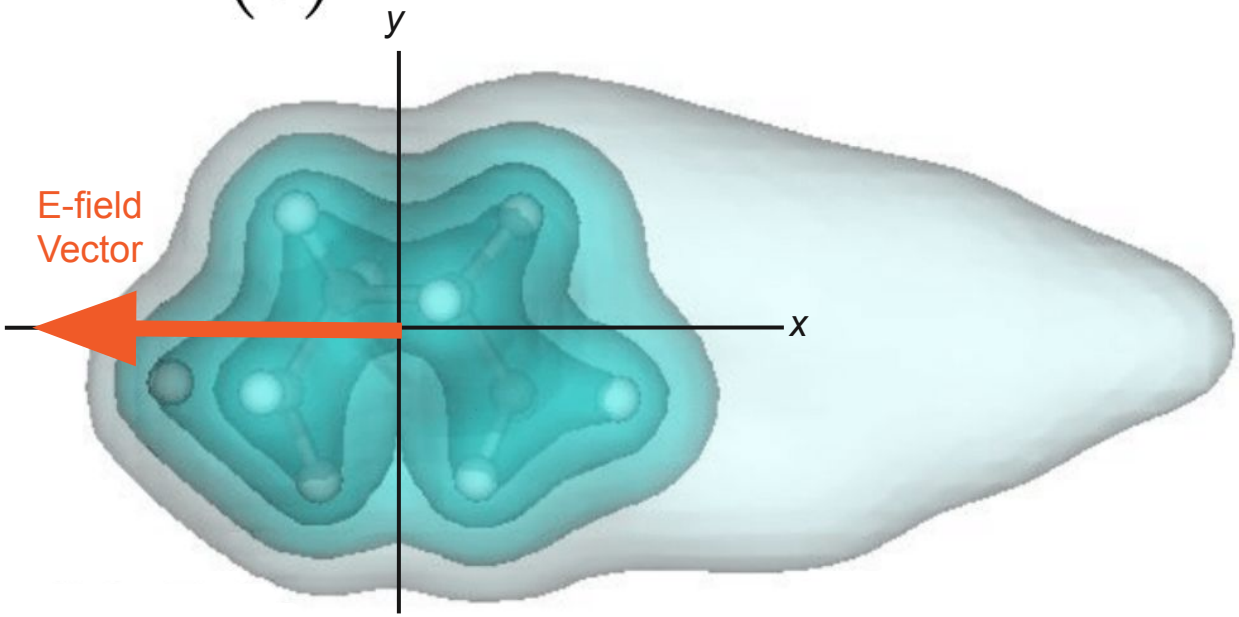
$$H_{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 + V^{\mathrm{KS}}[n(\mathbf{r})]$$

Laser / Electric field potential

- Described using the dipole approximation
- Our laser is polarized in the x-direction–**The E-field strictly exists in the x-axis**

$$V_{\mathrm{laser}} = \mathbf{r} \cdot \mathbf{E}(t)$$





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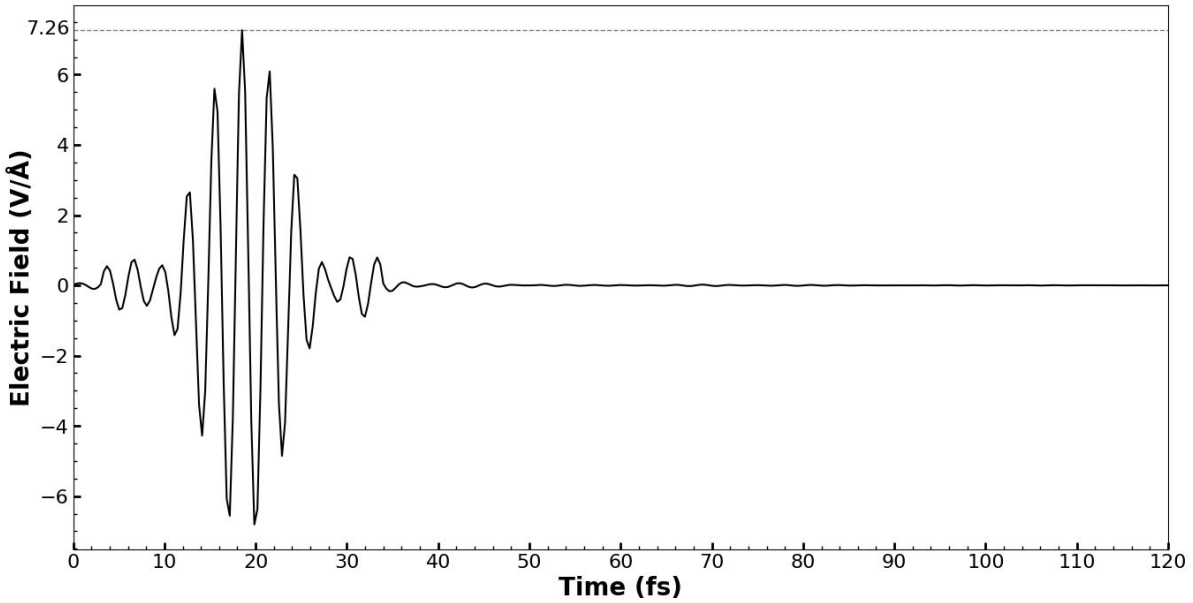
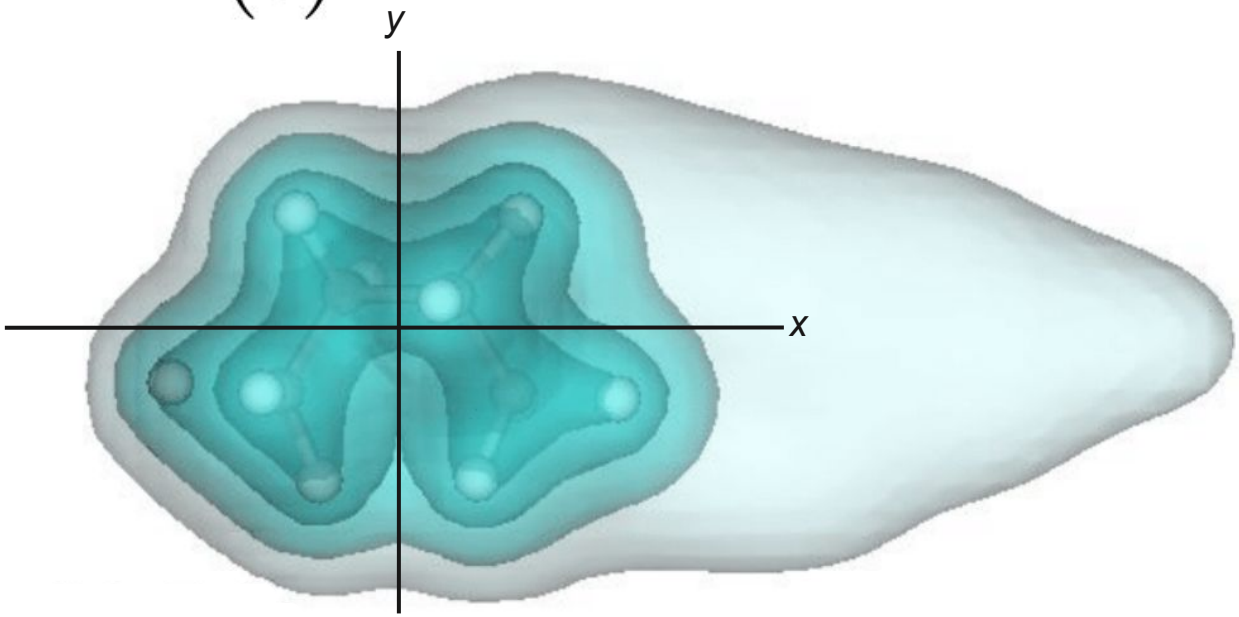
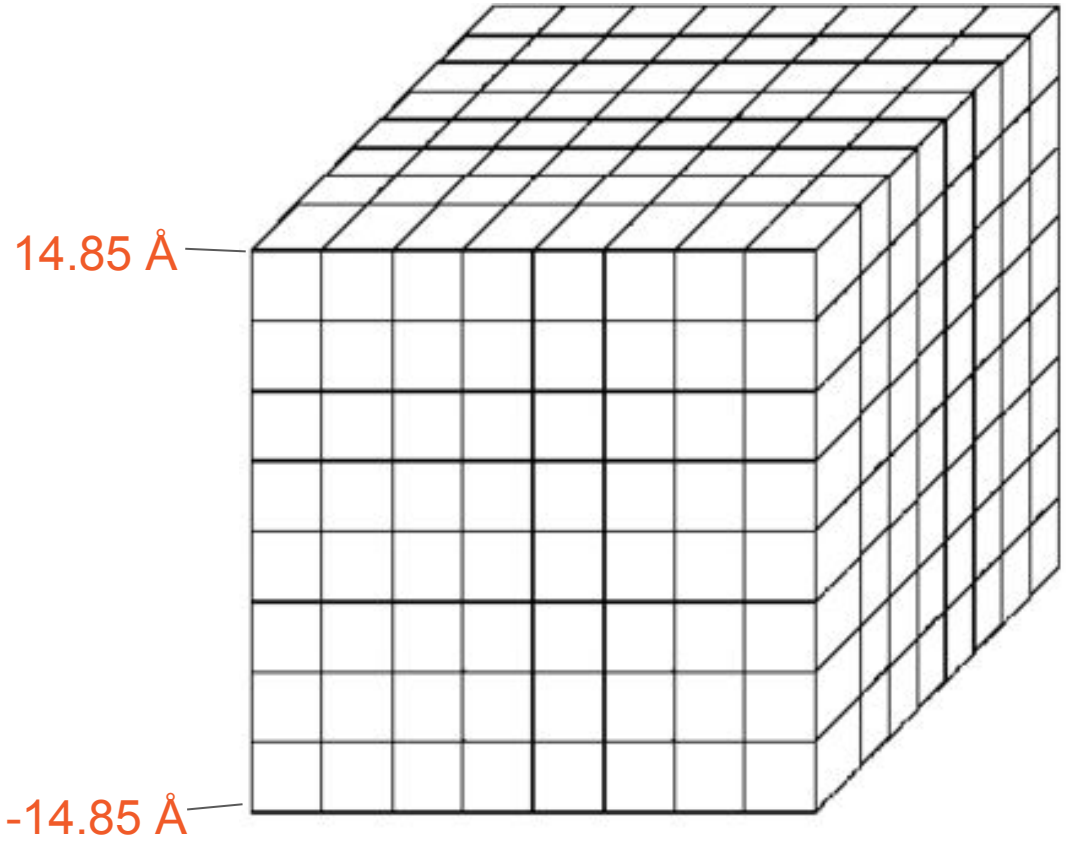
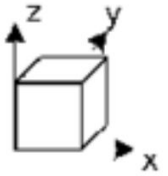




Overview
Real-space Grid used in TDDFT





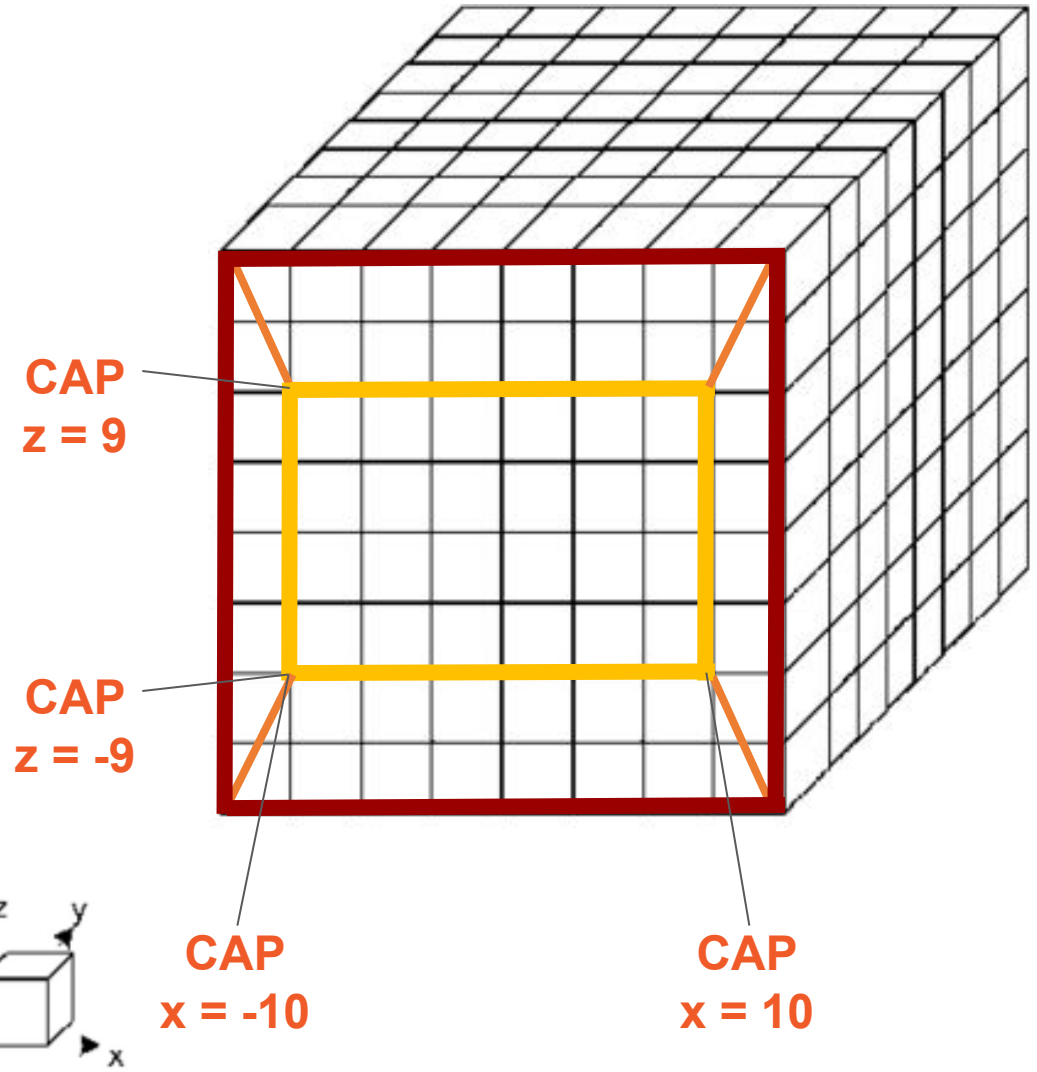
29.7 × 29.7 × 29.7 Å^3 Grid

Grid Details and Overview

- **Same grid as in DFT calculation**, since the ground state density is used in the TDDFT calculation.

- Grid is from -14.85 to 14.85 Å on each axis (x,y,z)
- Size is 29.7 × 29.7 × 29.7 Å^3
- There are 100 lattice points on every axis
- Grid of 100 × 100 × 100 = **1,000,000 points**
- Distance between each point is **0.3** Å

Overview
Complex Absorbing Potential (CAP)



Complex Absorbing Potential (CAP)

- CAP used to prevent unphysical reflections of the wavefunction
- Implemented as an **imaginary potential** added to the Hamiltonian near the bounds of the simulation
  - *Smooth exponential function to gradually damp wave functions*
- CAP is set at:
  - -10 to 10 Å on the x-axis
  - -9 to 9 Å on the y and z-axis
- **Without the CAP:** Ejected electrons could reflect off the boundary of the grid into the computational domain
  - Like ripples of water reflecting off of walls
- With no CAP, the boundaries of the grid are treated as boundary conditions with effectively infinite potential → **reflections**

Formalism
Complex Absorbing Potential (CAP)

Complex Absorbing Potential

- **CAP** is a potential that is added to the Hamiltonian. CAP by **Manolopoulos**

$$-iw(x) = -i\frac{\hbar^2}{2m}\left(\frac{2\pi}{\Delta x}\right)^2 f(y)$$

- $\mathbf{x_1}$ is the start and $\mathbf{x_2}$ is the end of the absorbing region,
- $\Delta\mathbf{x} = \mathbf{x_2} - \mathbf{x_1}$
- **m** is the electron's mass

$$f(y) = \frac{4}{c^2}\left(\frac{1}{(1+y)^2} + \frac{1}{(1-y)^2} - 2\right), \quad y = \frac{(x - x_1)}{\Delta x}$$

- **c** is a numerical constant = (2.62)
- Smooth continuous function: **Minimizes transmission and reflection**, maximizes absorption

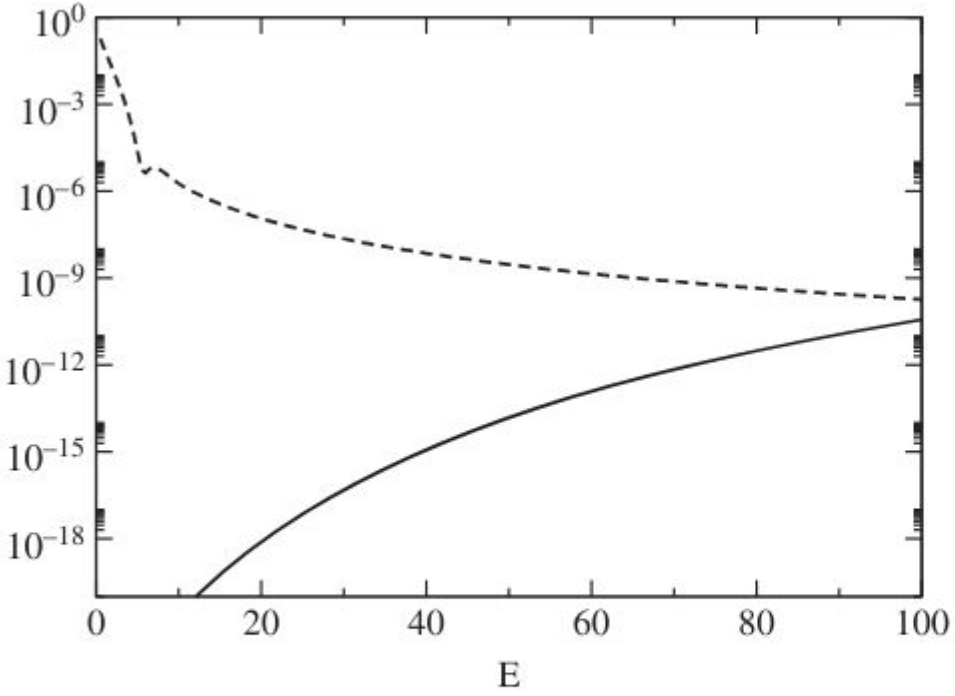
Formalism
Additional info: Other CAPs

Power function CAP

$$W(x) = -\mathrm{i}\eta(x - x_K)^n, \qquad x_K < x < x_k + L$$

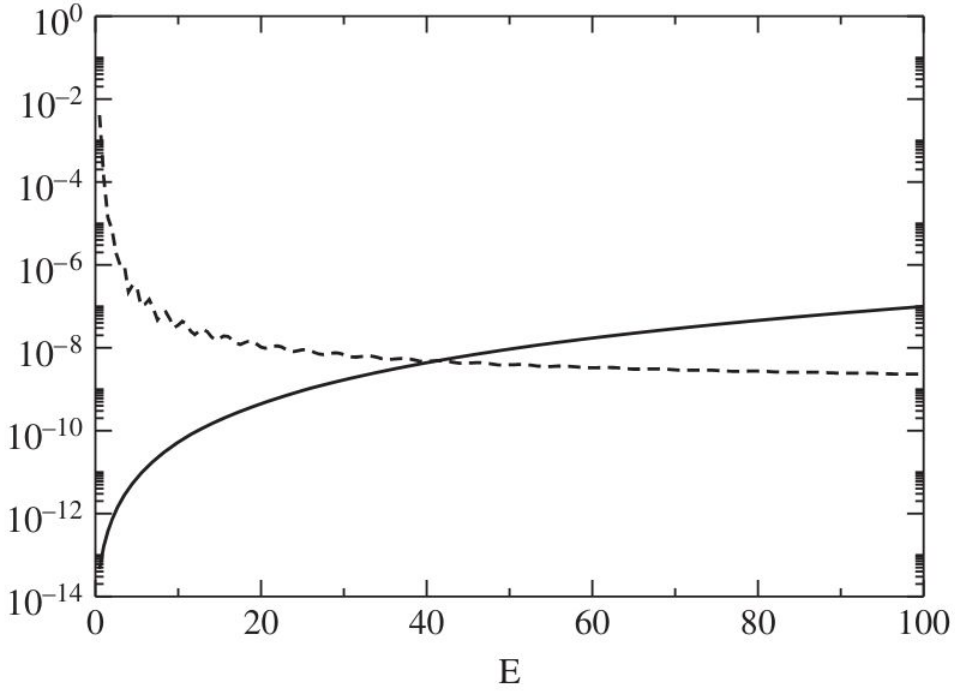
where x_K $(K = \mathrm{L}, \mathrm{R})$ is the starting point of the complex potential

L is the range of the complex potential



Manolopoulos CAP

$$-iw(x) = -i\frac{\hbar^2}{2m}\left(\frac{2\pi}{\Delta x}\right)^2 f(y)$$



- - - Dashed line:
Reflection Probability

—— Solid line:
Transmission Probability

*For our simulations: The Manolopoulos CAP best **minimizes reflection** and transmission*

Formalism
Time Evolution Operator

Time Evolution Operator

$$\psi(t + \Delta t) = U(t + \Delta t, t)\psi(t)$$

- We use the time evolution operator to propagate the wave function throughout time

$$U(t + \Delta t, t) = \mathrm{e}^{-\mathrm{i}H_{\mathrm{KS}}(t)\Delta t/\hbar}$$

- We have to approximate the exponential operator to use this approach. **4th Order Taylor Expansion**

$$\mathrm{e}^{-\mathrm{i}H_{\mathrm{KS}}\Delta t/\hbar} \approx \sum_{n=0}^{N} \frac{(-\mathrm{i}\Delta t/\hbar)^n H_{\mathrm{KS}}^n}{n!}$$

- In our simulations, **Δt = .001 fs** (1×10^{-18} s) = **1 as**
- Our simulations last 120 fs. So, in a simulation we have **120000 iterations of time propagation.**

Formalism
Time Evolution Operator

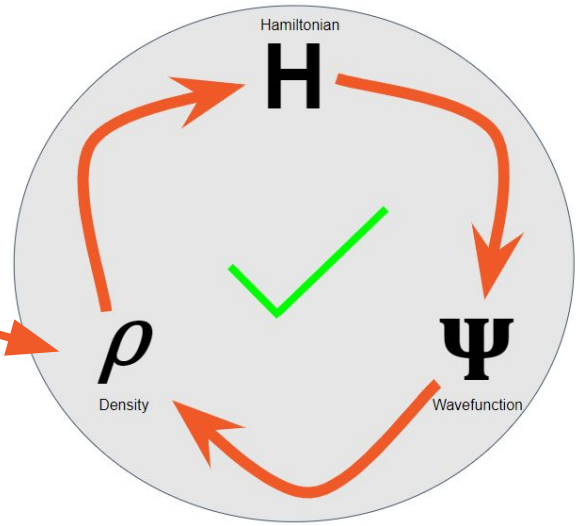
Time Evolution Operator

$$U(t+\Delta t,t)=\mathrm{e}^{-\mathrm{i}H\Delta t/\hbar}\approx\sum_{n=0}^{N}\left(\frac{(-\mathrm{i}\Delta t/\hbar)^n H^n}{n!}\right)$$

- Where the Hamiltonian is the **H(t)** → the Kohn-Sham Hamiltonian + V_{ext}

$$H(t)=-\frac{\hbar^2}{2m}\nabla^2+V_{\mathrm{ion}}(\mathbf{r},t)+V_H[\rho](\mathbf{r},t)+V_{\mathrm{xc}}[\rho](\mathbf{r},t)+V_{\mathrm{laser}}(\mathbf{r},t)$$

Density already known
DFT calculation



Formalism
Ion movement - Classical

Ion movement

- Movement of the ions treated classically. **Newton's second law: F=ma**

$$M_i \frac{d^2\mathbf{R}_i}{dt^2} = Z_i \mathbf{E}_{\text{laser}}(t) + \sum_{j \neq i}^{N_{\text{ions}}} \frac{Z_i Z_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \nabla_{\mathbf{R}_i} \int V_{\text{ion}}(\mathbf{r}, \mathbf{R}_i) \rho(\mathbf{r}, t) d\mathbf{r}$$

Newton's Law

Coulomb's Law
- Ion → Laser
- Ion → Ion

Ehrenfest Theorem
- Quantum forces on the ions due to the electrons

- $\mathbf{M_i}$ is the mass and $\mathbf{Z_i}$ is the charge of the $\boldsymbol{i^{th}}$ ion. $\mathbf{N_{ions}}$ is the total number of ions

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Ion movement - Classical

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Computational Details

Summary of the Process:

- **Density Functional Theory** (DFT) calculation performed to calculate the **ground state**
  - **Real-space grid used**. Core electrons represented with norm-conserving Troullier-Martin pseudopotentials

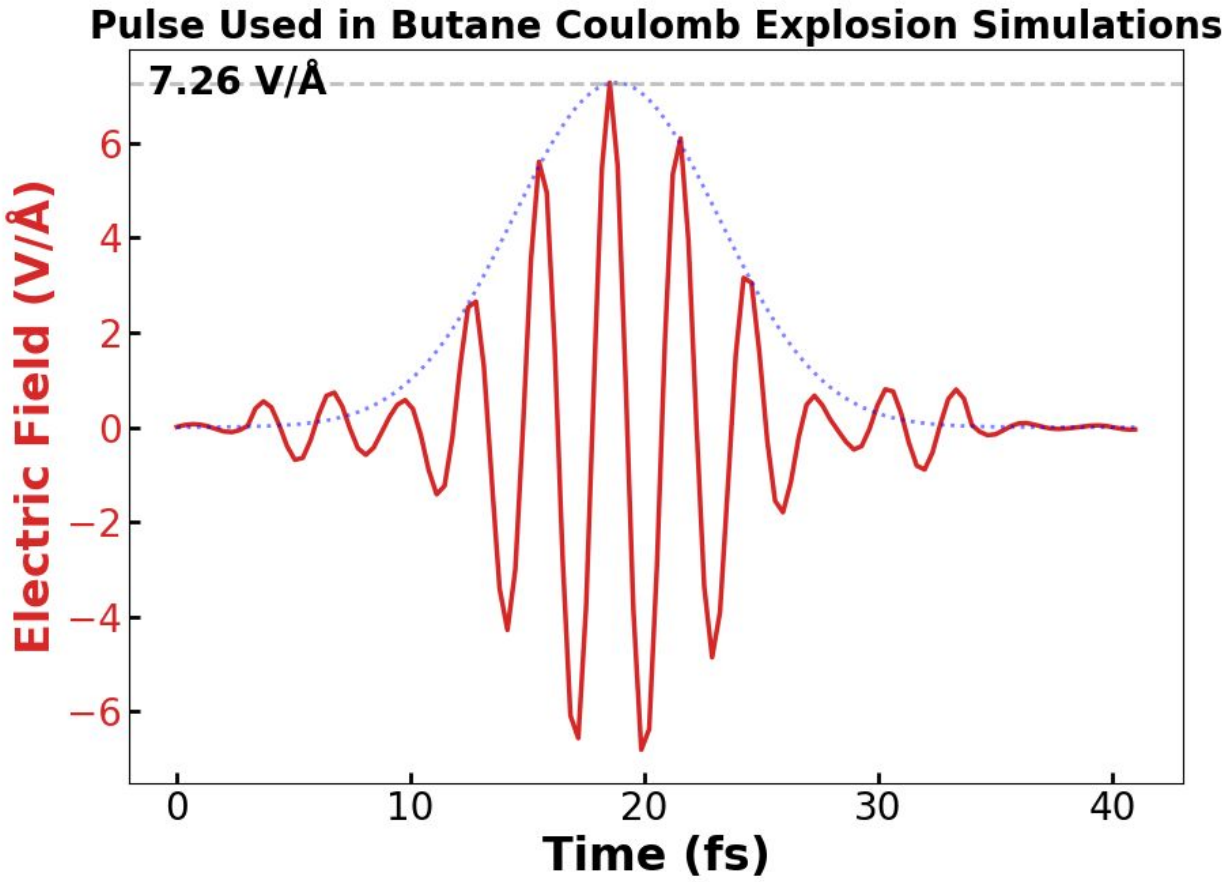
- The time–dependent orbitals are propagated using a **fourth-order Taylor expansion of the time-evolution operator**
- Motions of the ions in the simulation are treated **classically** with electron-ion force modeled via Ehrenfest theorem
- A **complex absorbing potential (CAP)** is implemented to prevent reflections of the wave function at the boundary

Results & Discussion

Coulomb Explosion of Butane (C_4H_{10})

Parameters

- Butane C_4H_{10} Gauche conformation
- Atoms set with random velocities according to *Boltzmann Distribution* at 300 K
- **Laser**:
  - *Intensity*: **7×10^{14} W/cm^2**
  - *Peak E-field Strength*: **7.26 V/Å**
  - *GDD*: **0 fs^2**
  - *Duration*: **7.8 fs (FWHM)**
  - *Polarization*: **x-direction**
  - *Wavelength*: **890 nm**
  - *Original GDD=0 pulse used in the experiment, but scaled by a factor of 3/16*



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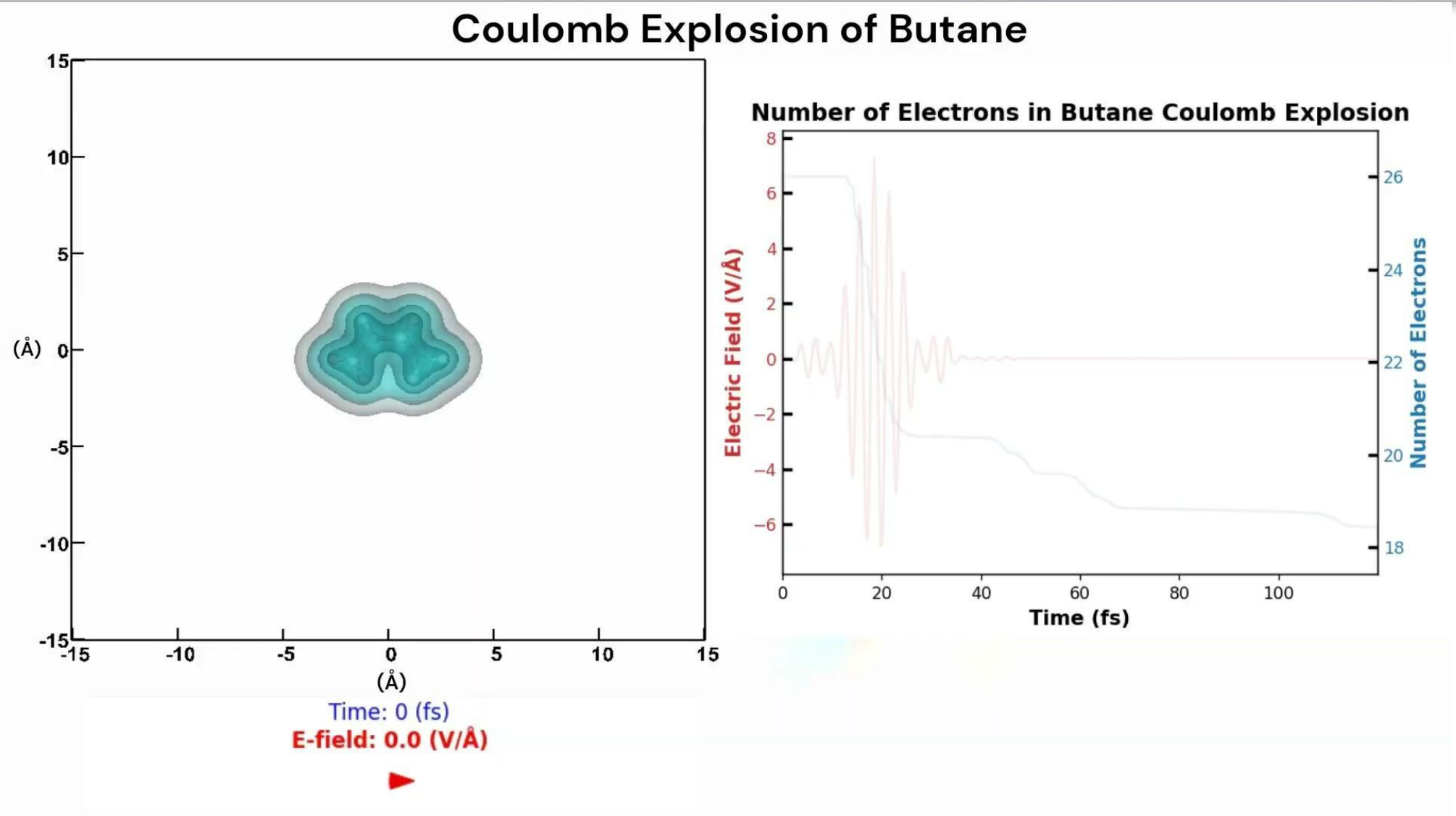
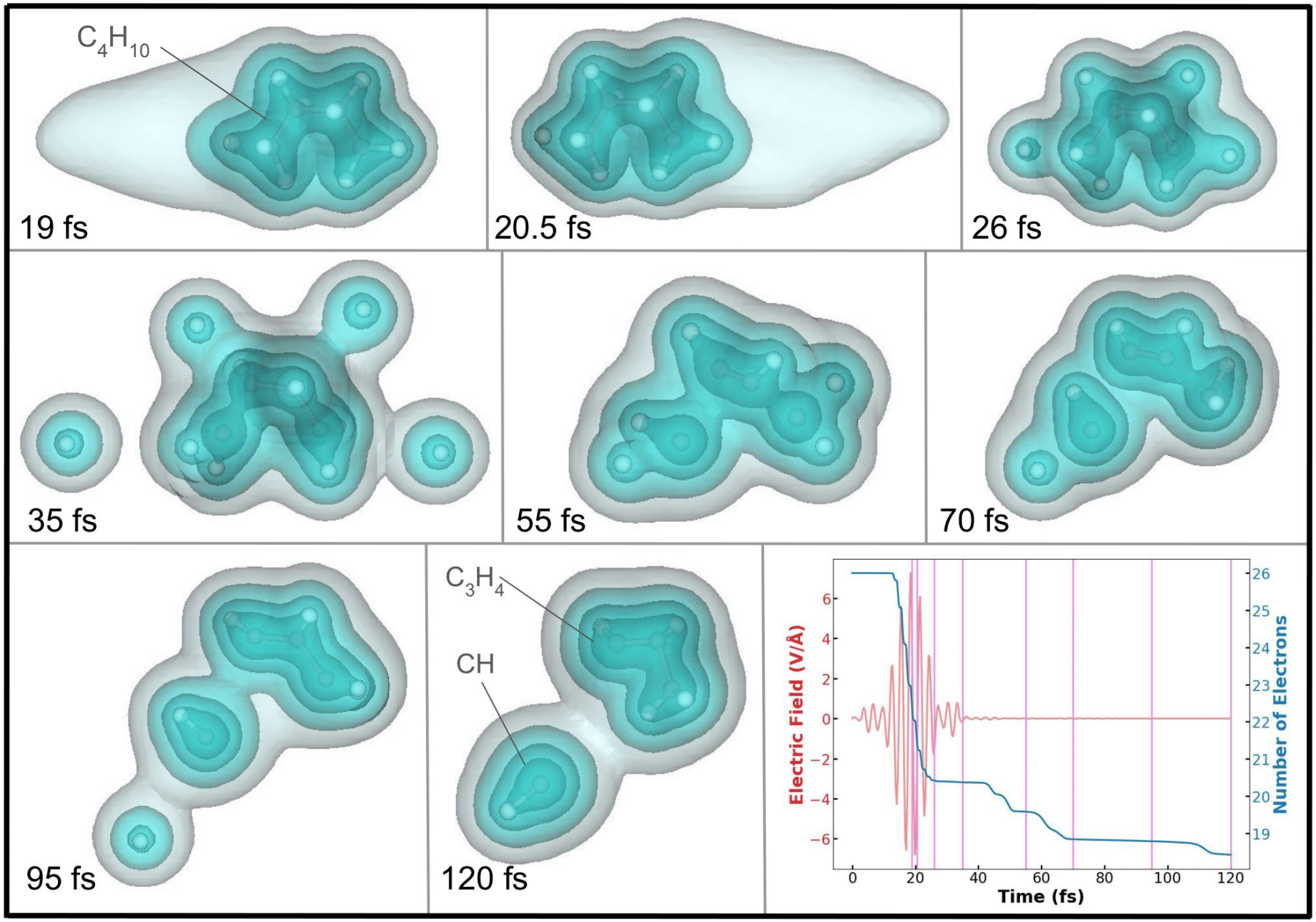
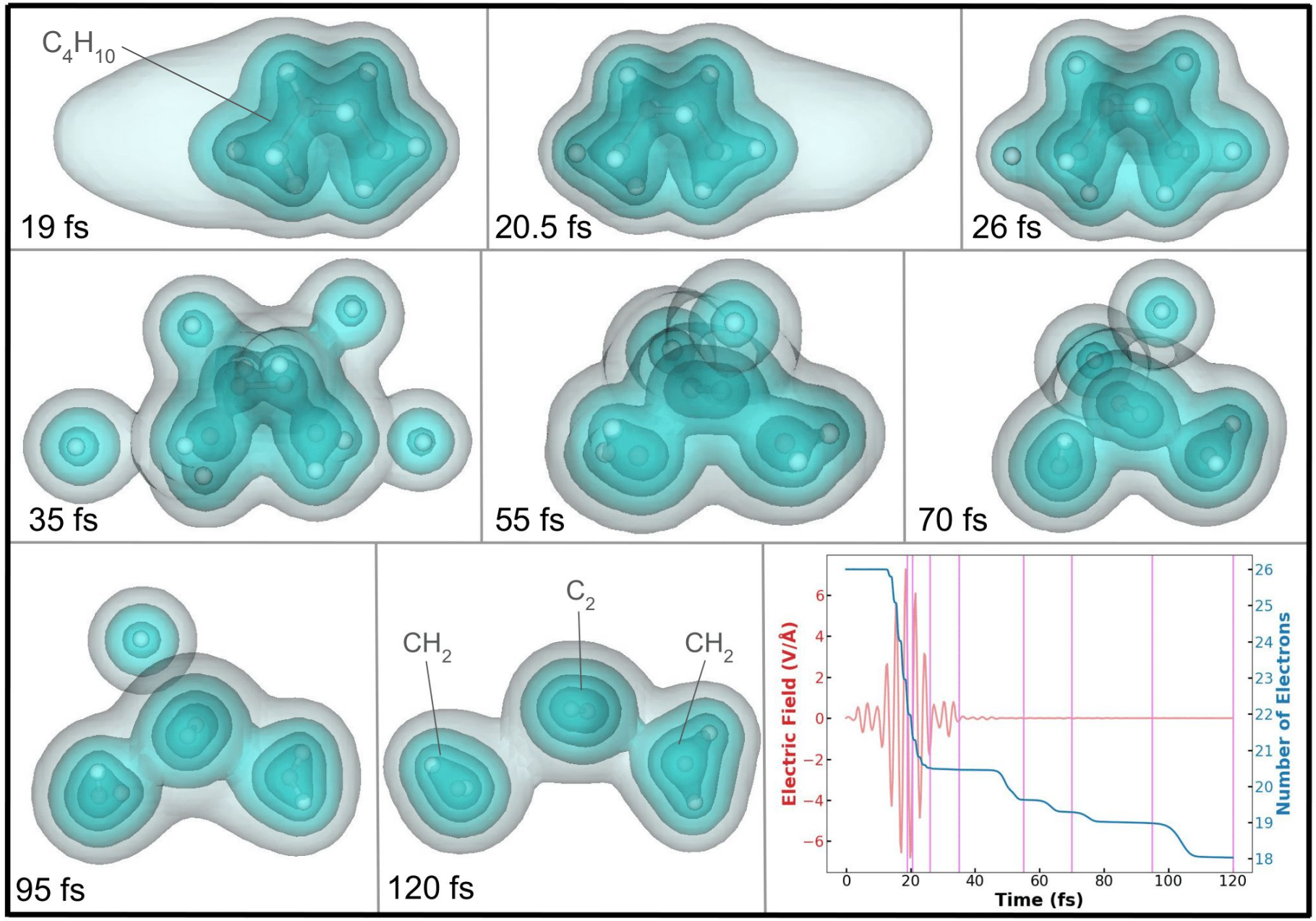


$$C_4H_{10} \rightarrow C_3H_4^{1.9+} + CH^{0.7+} + 3H^{0.7+} + 2H^{0.5+} + 5.8e^-$$



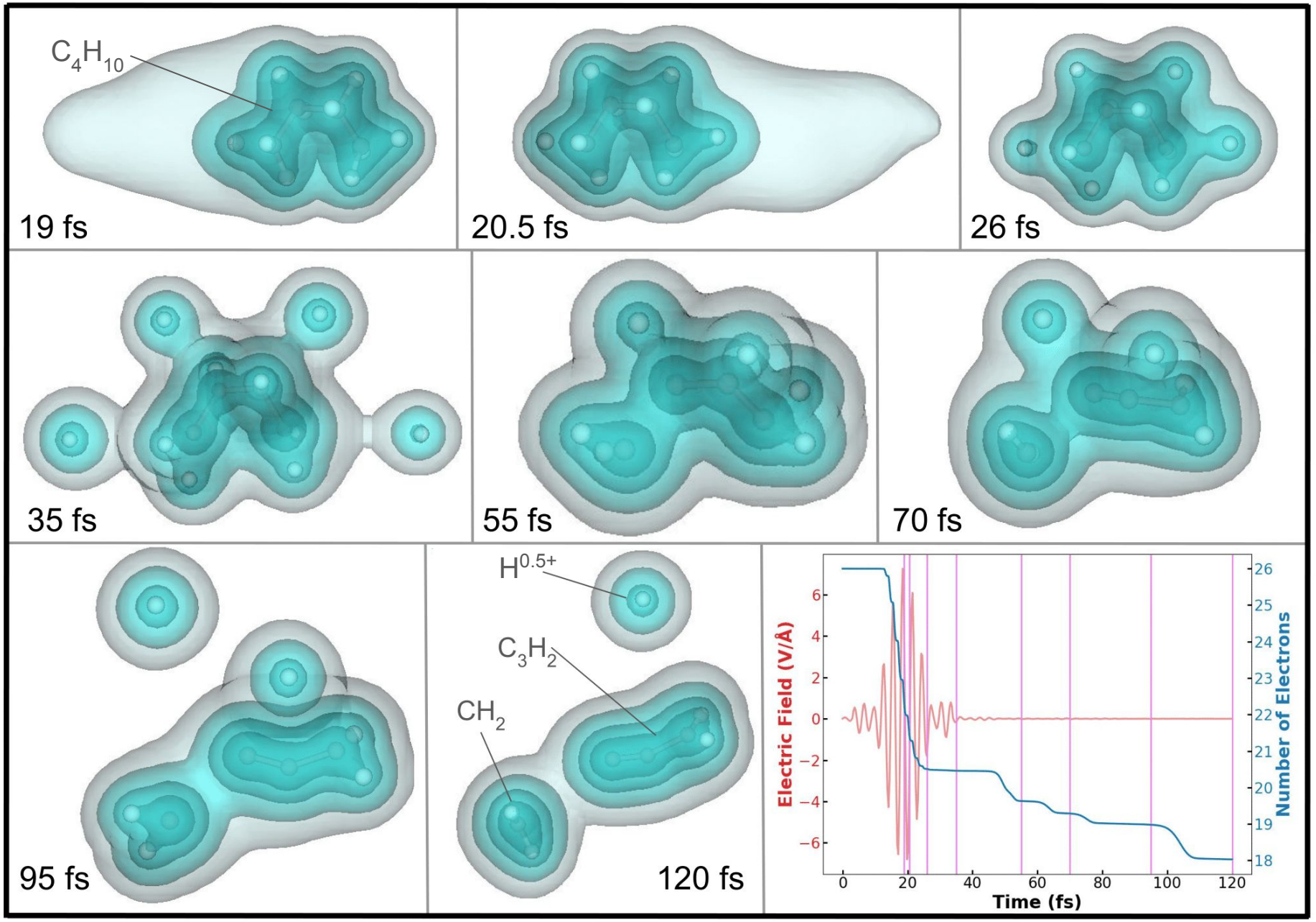
$$C_4H_{10} \rightarrow C_2^{0.5+} + CH_2^{0.8+} + CH_2^{0.7+} + 3H^{0.7+} + H^{0.6+} + 2H^{0.5+} + 5.7e^-$$

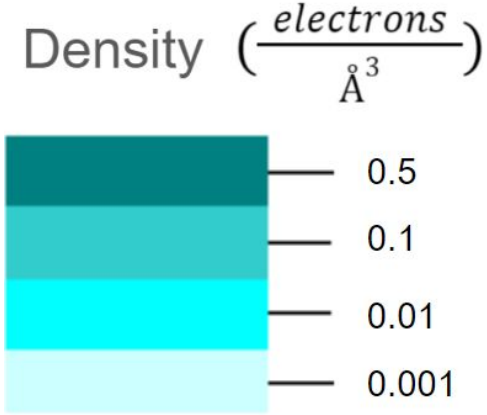


Density $(\frac{electrons}{Å^3})$

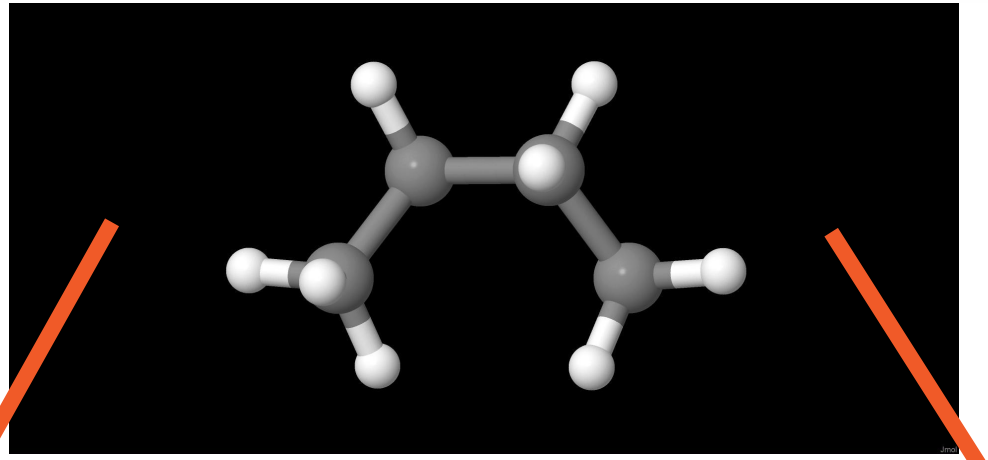
0.5
0.1
0.01
0.001

$$C_4H_{10} \rightarrow C_3H_2^{1.4+} + CH_2^{1+} + H^{0.8+} + H^{0.7+} + H^{0.6+} + 2H^{0.5+} + H^{0.4+} + 5.8e^-$$



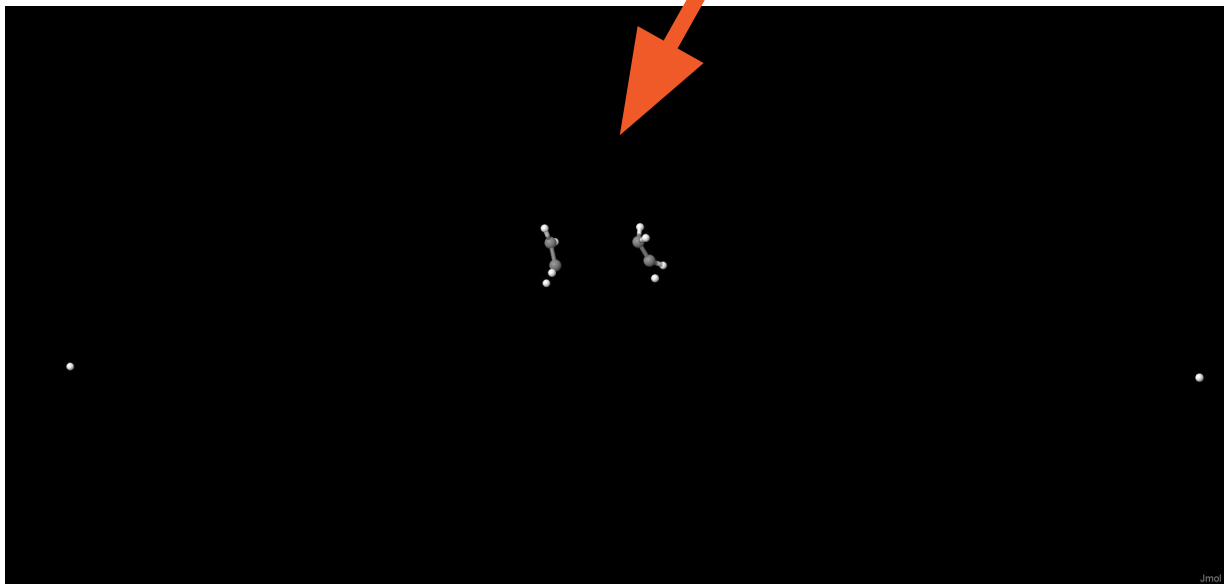


Why reduce the experimental maximum laser intensity (2×10^{16} W/cm^2) by a factor of $(15/80)^2$ to an intensity of 7×10^{14} W/cm^2?



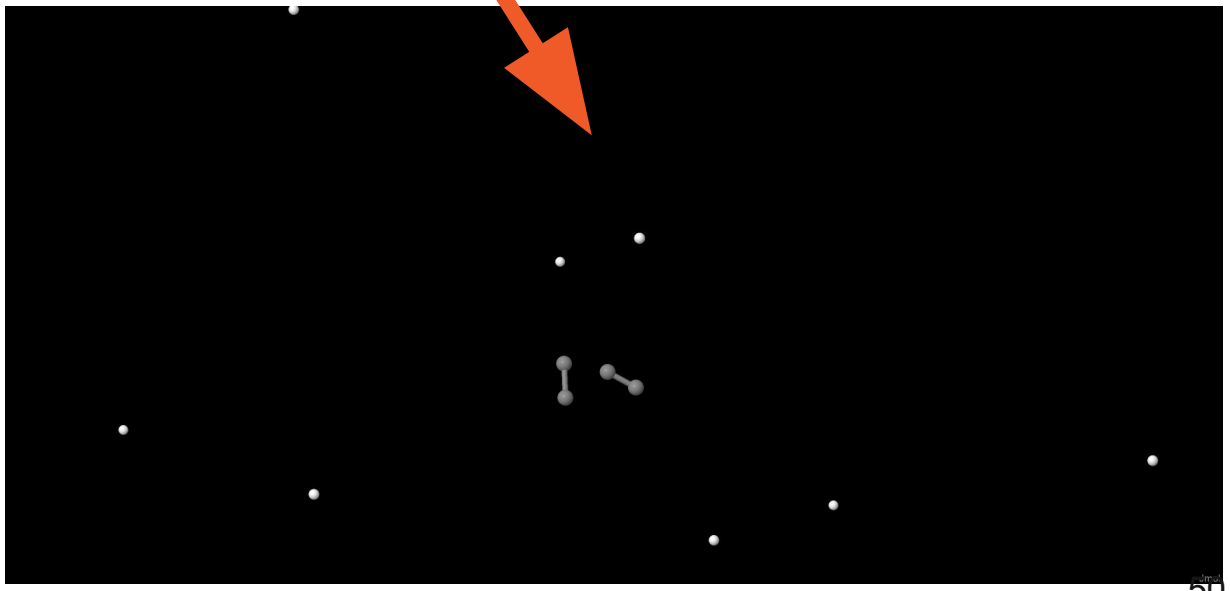
Reduced by factor of $(14/80)^2$

Intensity: $6.125 * 10^{14}$

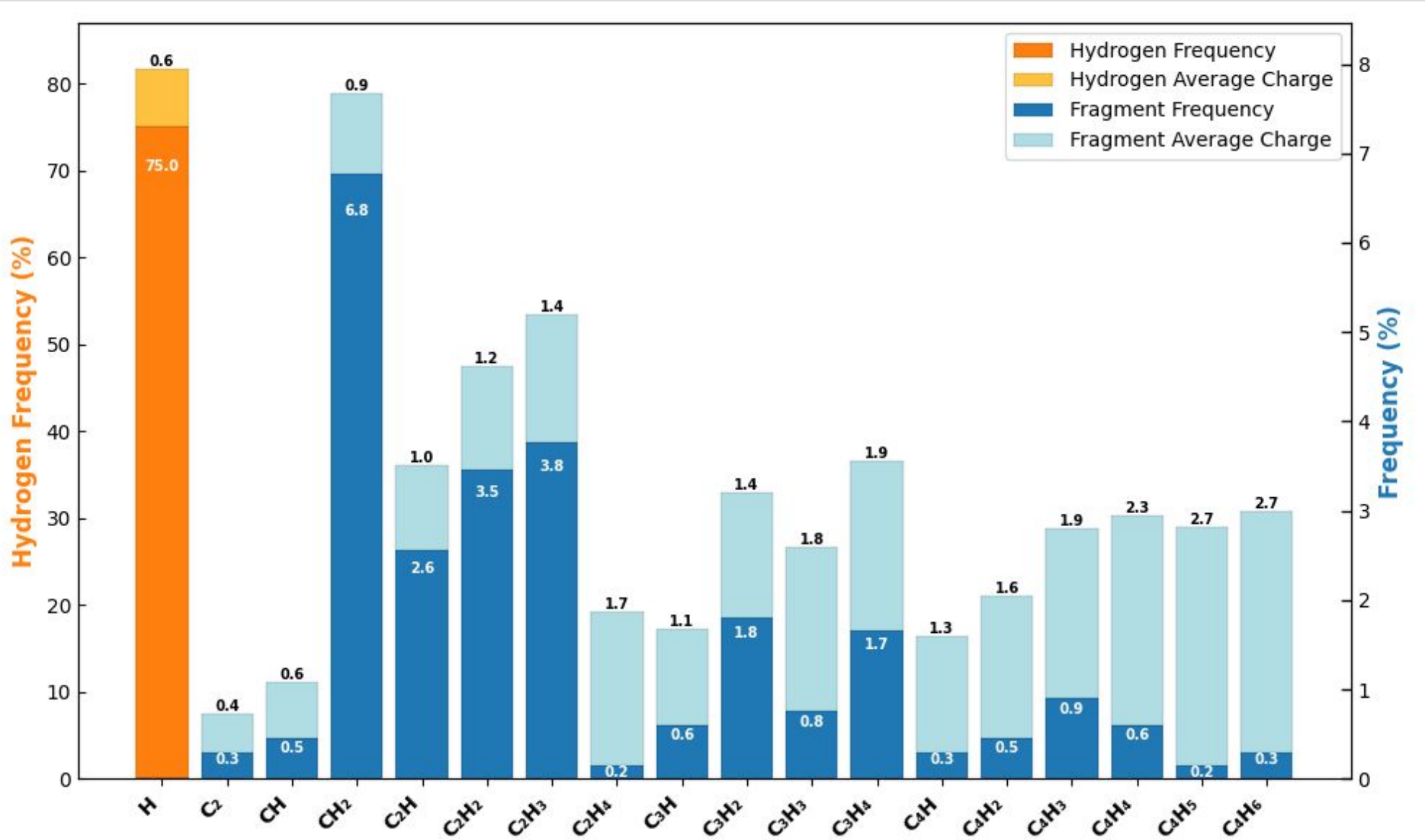


Reduced by factor of $(16/80)^2$

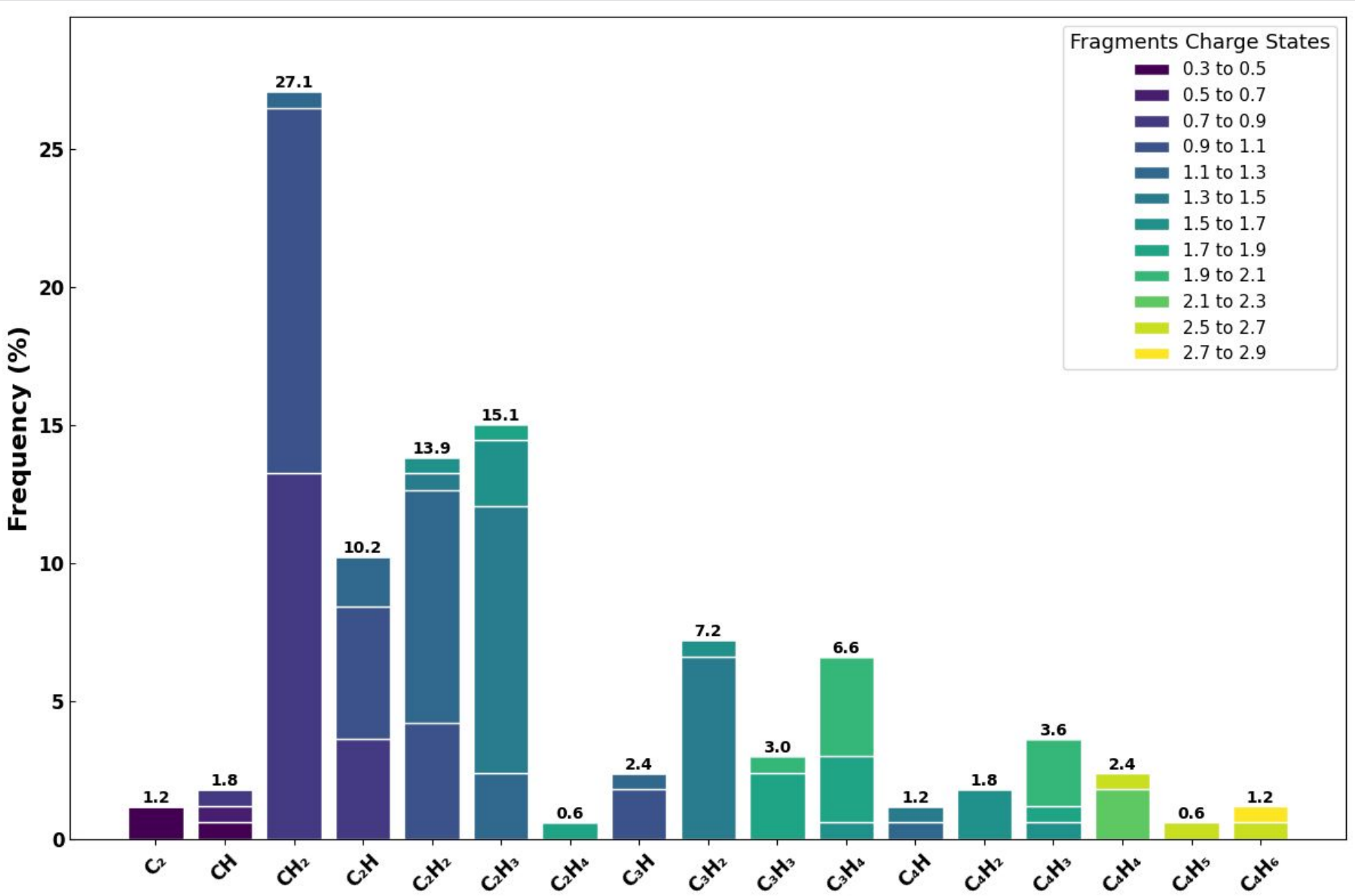
Intensity: $8 * 10^{14}$



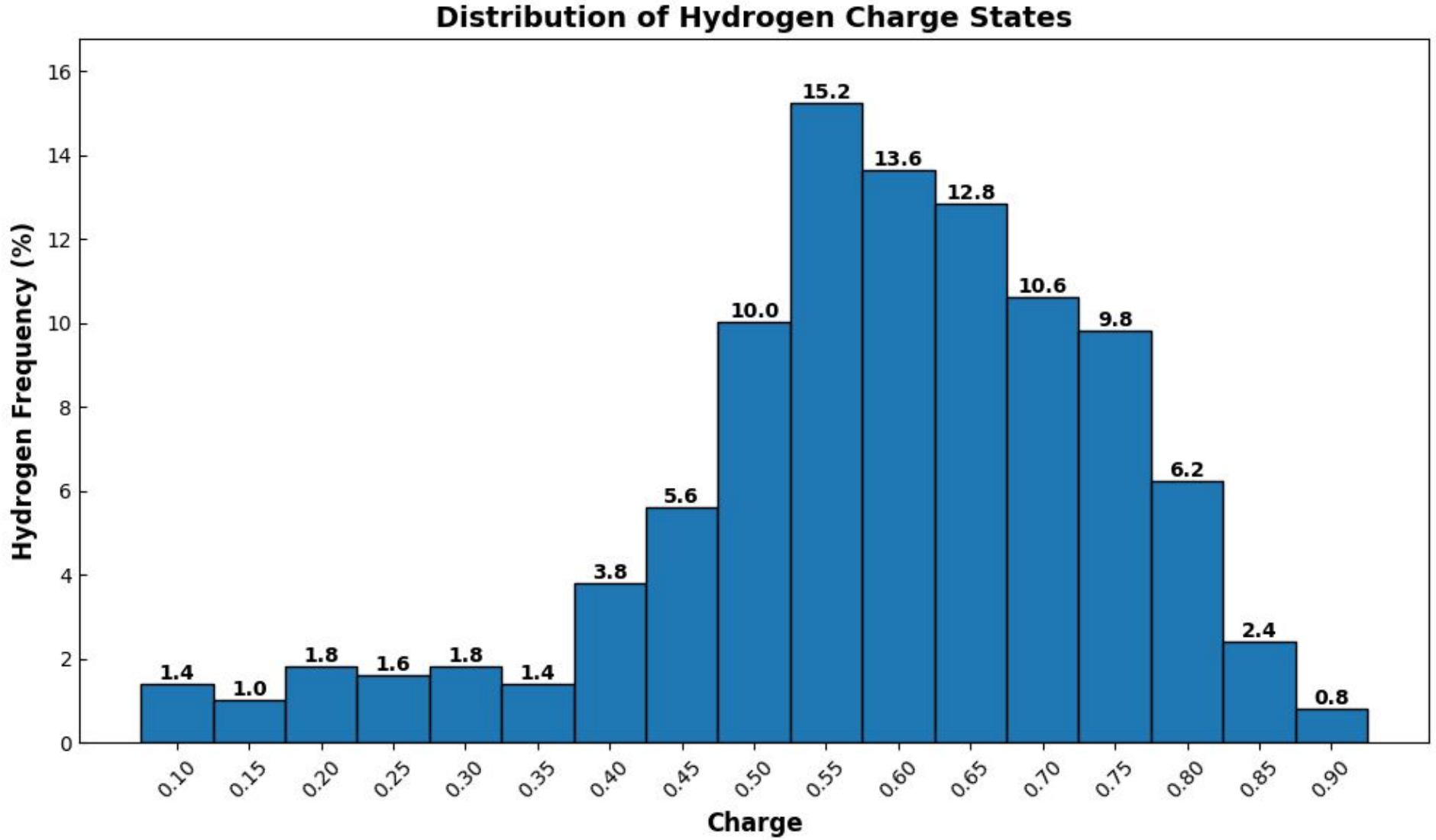
Distribution of Fragments from 88 Butane Coulomb Explosions (Fig. 1)



Distribution of Fragments from 88 Butane Coulomb Explosions (Fig. 2)



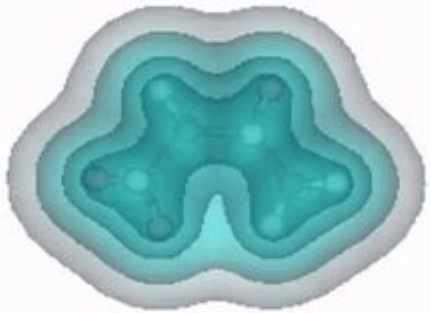
Distribution of Charge States from Ejected Hydrogen



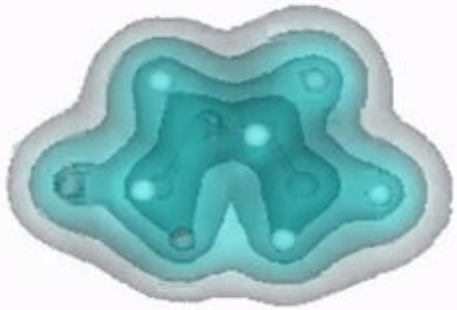
Conclusion

Conclusion

TDDFT can be used to accurately predict Coulomb explosion products.



Neutral fragments can be formed from coulomb explosion



Future work

Currently doing:

- C_4H_{10} with GDD = - 40 fs^2 pulse
- Methane, ethane, propane with GDD = 0 pulse
- Using supercomputer for the computations
  - ACES (Accelerating Computing for Emerging Sciences)
  - Texas A&M University
- Proton / hydrogen collisions with C_4H_{10} (Other student)

To do:

- Changing direction of laser on molecules
- Other conformations of Butane
- *You tell me!*

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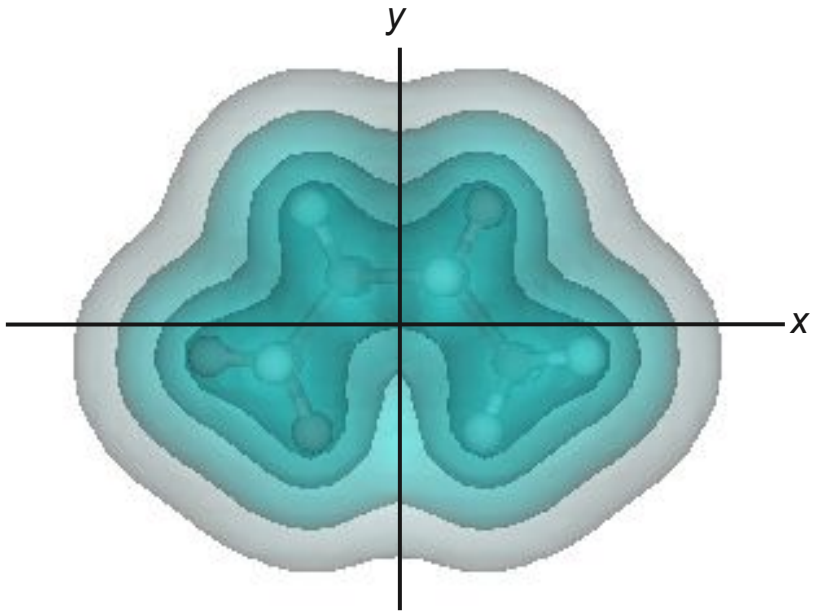

THANK YOU FOR YOUR ATTENTION!

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