

# Molecular Structure and Quantum Dynamics without the Born-Oppenheimer Approximation

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Workshop on Quantum Theory: Foundations and Extensions of Density-Functional Theory, OsloMet, December 2– 6, 2024

# WATOC 2025 – Registration is Open!

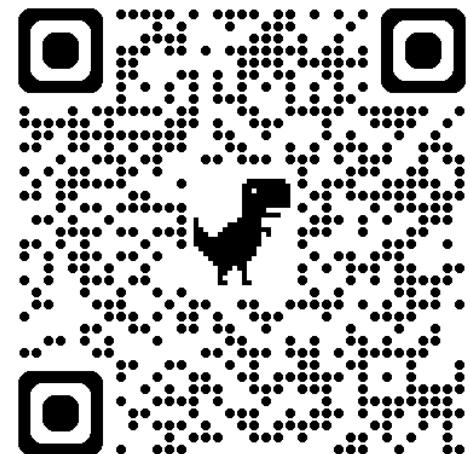


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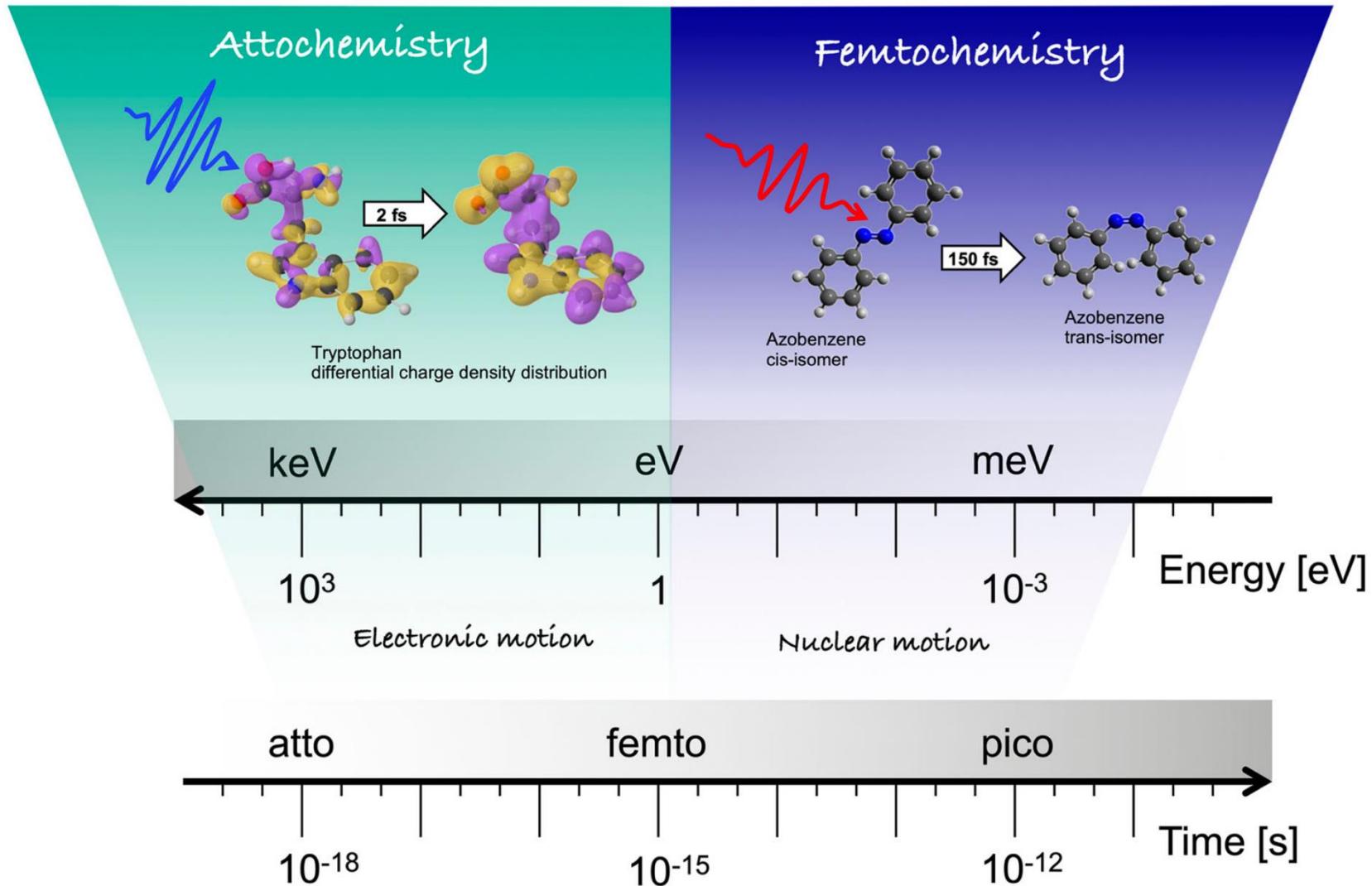
# OSLO 2025

[ WATOC 2025: June 22–27, Oslo, Norway ]

- Lectures: 12 Plenary, 150 Invited, 150 Contributed
- 3 Poster sessions
- Young WATOC on June 21, 2025



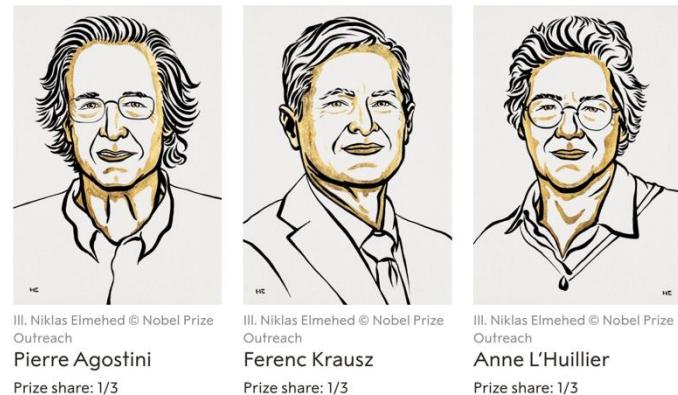
# Ultrafast Processes: Molecular Time and Energy Scales



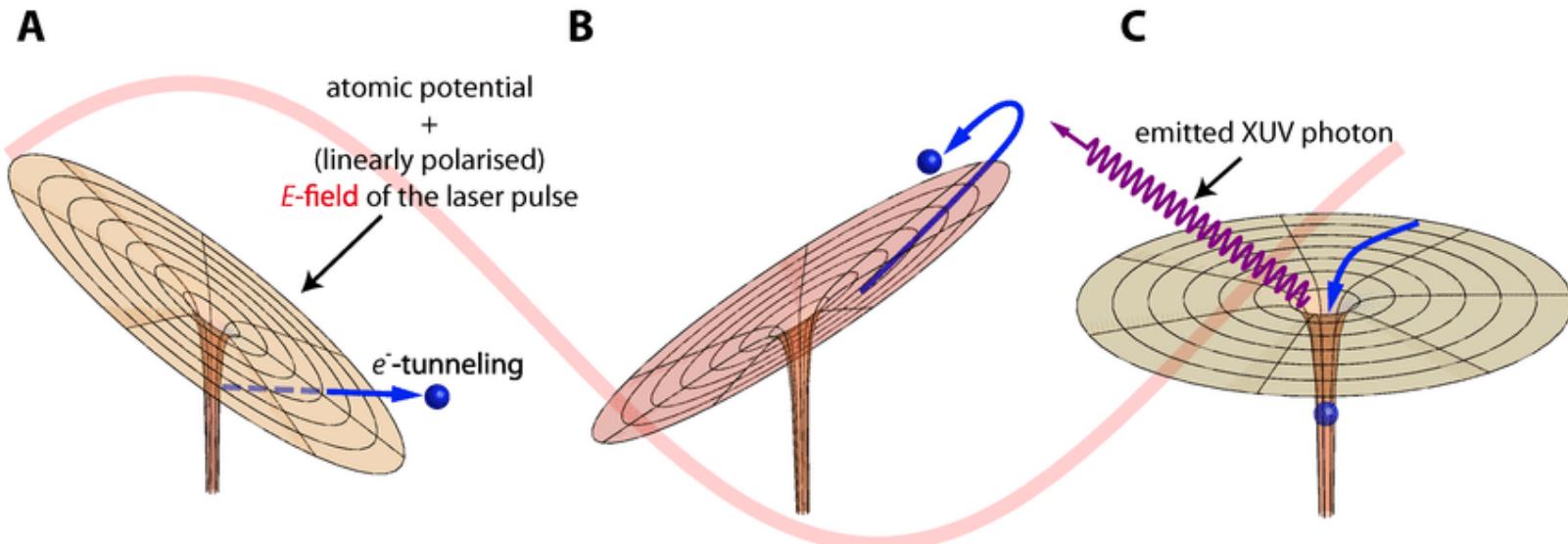
Calegari and Martín, Commun. Chem. **6**, 184 (2023)

# Attosecond Laser Pulses & High Harmonic Spectroscopy

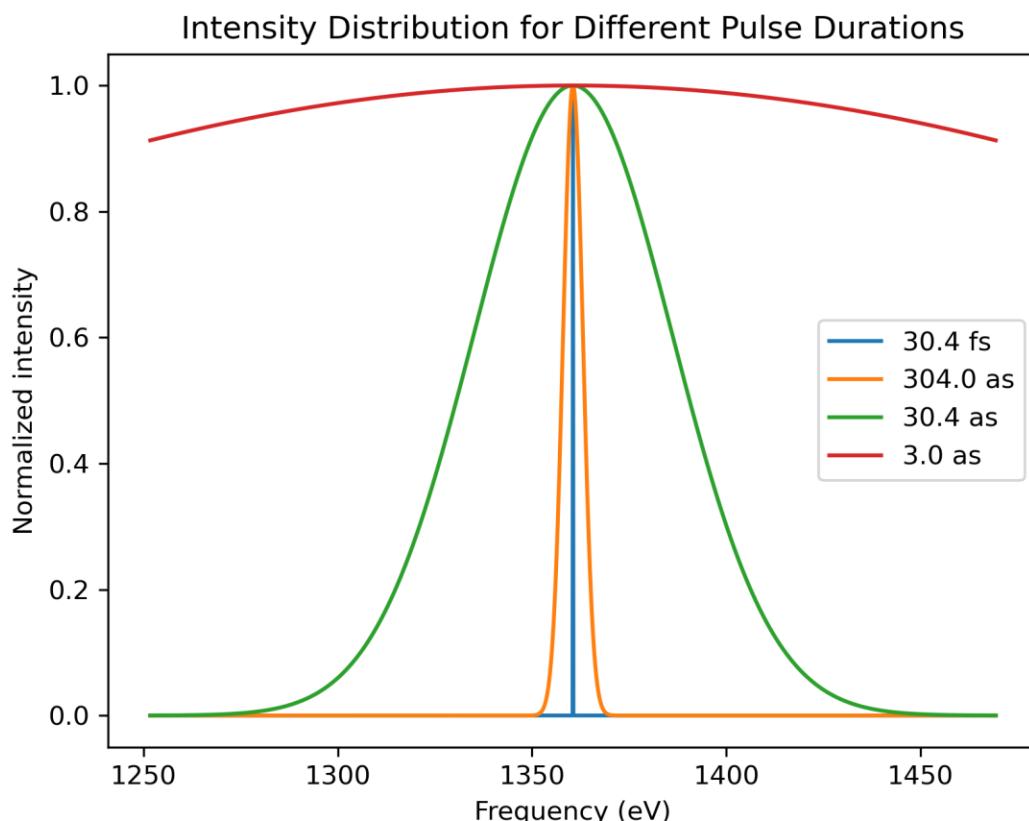
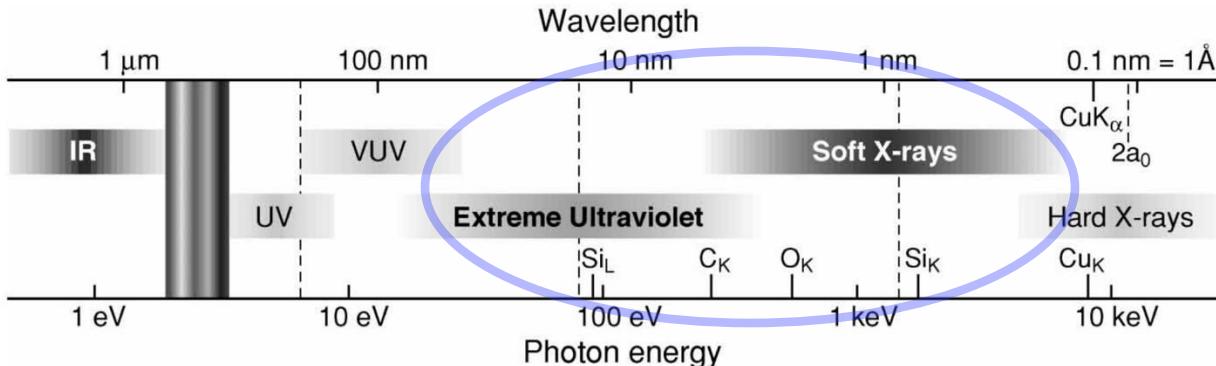
- Key process: high harmonic generation (HHG)
- NIR driving laser (typically 800 nm)
- Competing processes
  - Ionization
  - Light induced electron diffraction (LIED)
  - Recombination (HHG)



The Nobel Prize in Physics 2023 was awarded to Pierre Agostini, Ferenc Krausz and Anne L'Huillier "for experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter"



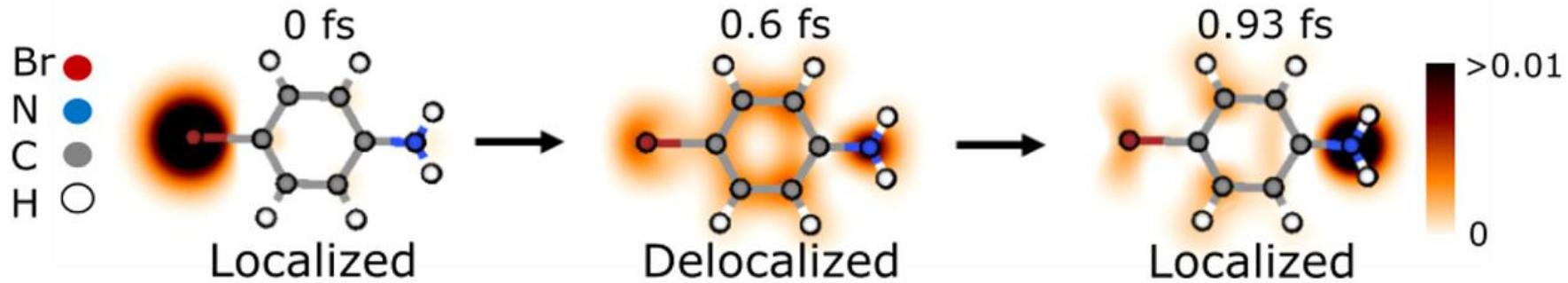
# Short in Time – Broad in Frequency



$$50 \text{ Hartree} = 1361 \text{ eV}$$

- Peak intensities up to  $10^{21} \text{ W/cm}^2$
- Peak electric-field strength:  $86\,802 \text{ V/nm}$  (168 a.u.)
- Peak magnetic-field strength:  $290\,000 \text{ T}$  (1.23 a.u.)
- Nonperturbative!
- Many electronic states populated
- Ionization processes
- Non-dipole effects, relativity

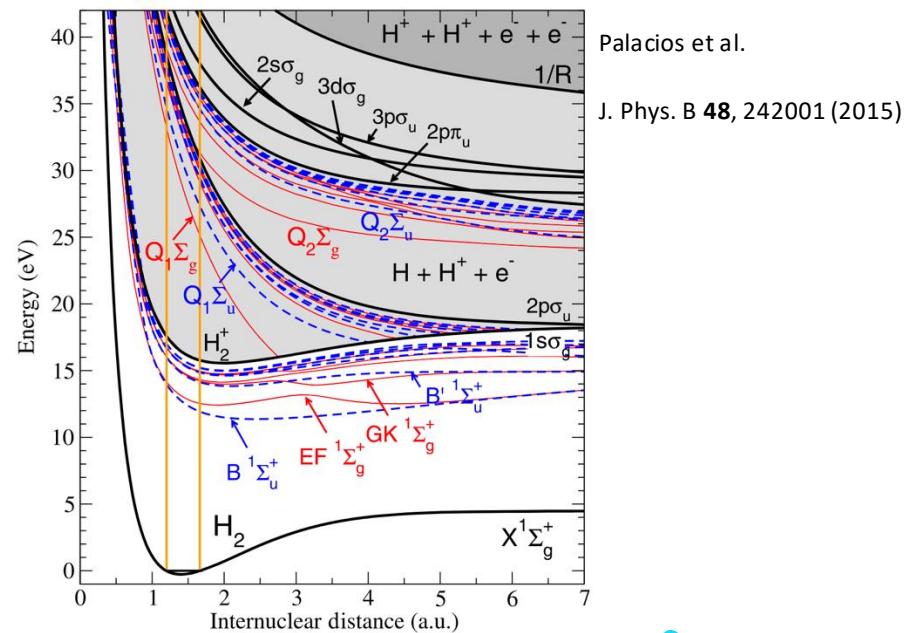
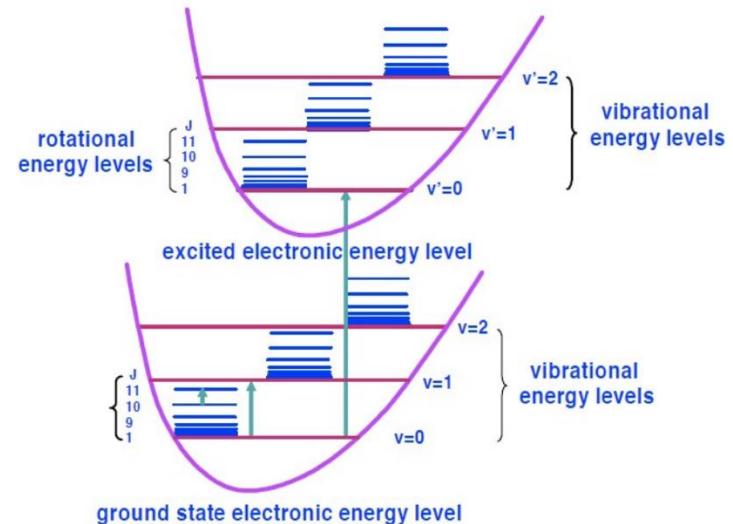
## Example: Charge Migration Following Attosecond Core Ionization



- Predicted by Cederbaum and Zobeley [CPL **307**, 205-210 (1999)]
- Main driving force: electron correlation
  - Charge transfer driving force: nuclear motion
- Simulation challenge: Initial state?
  - < 100% ionization probability: motion on N and N-1 PESs simultaneously
  - Several N-1 states likely involved
  - Born-Oppenheimer?

# Adiabatic Born-Oppenheimer Approximation Breaks Down

- Initial response by electrons, but
  - Several electronic states populated
  - Ionization processes *must* be accounted for
- Nuclear response within a few fs ( $\sim 10$  fs)
  - Mainly due to changes in electronic energy
  - Adiabatic BO approximation breaks down  
Movement «on several PESs» simultaneously
- How to proceed?
  - Ehrenfest dynamics (average force field)?
  - Born-Huang / Feshbach close-coupling?
  - Exact factorization?



# Start from Scratch

- Molecular TDSE

$$i\partial_t \Phi(\mathbf{R}, t) = \mathcal{H}(t)\Phi(\mathbf{R}, t)$$

$$\Phi(\mathbf{R}, t = 0) = \Phi_0(\mathbf{R})$$

- Molecular minimal-coupling Hamiltonian in the lab frame

$$\mathcal{H}(t) = \sum_{i=1}^N \frac{(\mathbf{P}_i - Q_i \mathbf{A}(\mathbf{R}_i, t))^2}{2M_i} + \sum_{i < j}^N \frac{Q_i Q_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

- Laser field in Coulomb gauge (zero scalar potential)

$$\mathbf{E}(\mathbf{r}, t) = -\partial_t \mathbf{A}(\mathbf{r}, t) \quad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t)$$

- Notes

- BO approximation undefined, except perhaps for initial state (if stationary)
- Center-of-mass motion not trivially separable for non-uniform fields
  - coupling of CoM with field
  - becomes separable in electric-dipole approximation for neutral systems
  - inseparable for static, uniform magnetic fields



# Electric-Dipole Approximation for Neutral Systems

- Molecular **internal** TDSE

$$i\partial_t \Psi(\mathbf{r}, t) = H(t)\Psi(\mathbf{r}, t)$$

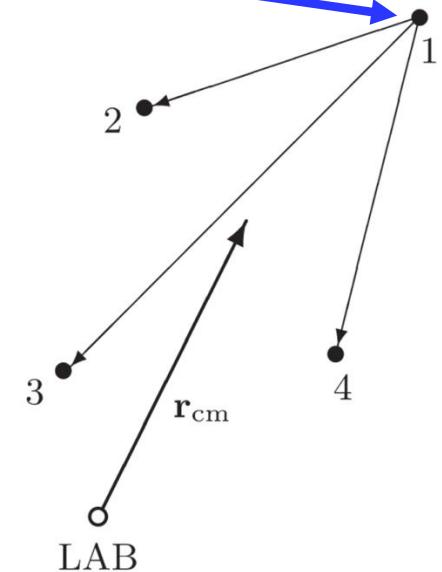
$$\Psi(\mathbf{r}, 0) = \Psi_0(\mathbf{r})$$

- Internal** Hamiltonian with origin at chosen **reference particle**

$$H(t) = H_0 + V(t)$$

$$H_0 = \sum_{i=1}^n \left[ \frac{p_i^2}{2m_i} + \frac{q_0 q_i}{r_i} \right] + \sum_{i < j}^n \left[ \frac{q_i q_j}{r_{ij}} + \frac{\mathbf{p}_i \cdot \mathbf{p}_j}{m_0} \right]$$

$$V(t) = - \sum_{i=1}^n q_i \mathbf{r}_i \cdot \mathbf{E}(t)$$



- CoM unaffected by electric field (neutral systems only)
- Atom-like**: interacting (pseudo-)particles moving in the central potential of the reference particle

# ECG Approach for Stationary States

- Molecular internal TISE

$$H_0 \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

- Ansatz

$$\Psi(\mathbf{r}) = \hat{\mathcal{P}} \sum_{\mu=1}^N \phi_{\mu}(\mathbf{r}) c_{\mu}$$

- ECG *many-body* basis functions (other forms possible)

$$\phi_{\mu}(\mathbf{r}) = \exp [-(\mathbf{r} - \mathbf{q}_{\mu})^T \mathbf{C}_{\mu} (\mathbf{r} - \mathbf{q}_{\mu})]$$

- Variational parameters

$$\begin{array}{llll} N & \mathbf{C}_{\mu} = \mathbf{A}_{\mu} + i \mathbf{B}_{\mu} & \mathbf{q}_{\mu} & c_{\mu} \\ \mathbf{A}_{\mu}, \mathbf{B}_{\mu} \in \mathbb{R}^{3n \times 3n} & & \mathbf{q}_{\mu} \in \mathbb{R}^{3n} & \end{array}$$

- **Key idea:** optimize basis to span just the part of Hilbert space needed  
(Reiher, Matyus, Varga, Adamowicz,...)
- Highly accurate for few-body systems (f.ex. H<sub>3</sub>, LiH)

# Generalization to Time-Dependent Non-Stationary States

- Molecular internal TDSE

$$\mathrm{i}\partial_t\Psi(\boldsymbol{r},t) = H(t)\Psi(\boldsymbol{r},t) \quad \Psi(\boldsymbol{r},0) = \Psi_0(\boldsymbol{r})$$

- Ansatz

$$\Psi(\boldsymbol{r},t) = \hat{\mathcal{P}} \sum_{\mu=1}^{N(t)} \phi_\mu(\boldsymbol{r},t) c_\mu(t)$$

- ECG *wave packets*: an overcomplete set

$$\phi_\mu(\boldsymbol{r},t) = \exp \left[ -(\boldsymbol{r} - \boldsymbol{q}_\mu(t))^T \boldsymbol{C}_\mu(t) (\boldsymbol{r} - \boldsymbol{q}_\mu(t)) + \mathrm{i} \boldsymbol{p}_\mu^T (\boldsymbol{r} - \boldsymbol{q}_\mu(t)) \right]$$

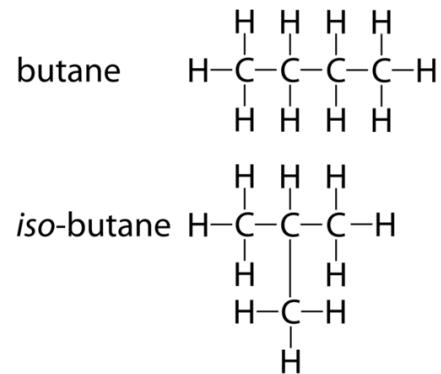
- Time-dependent variational parameters same as above, plus

$$\boldsymbol{p}_\mu(t) \in \mathbb{R}^{3n}$$

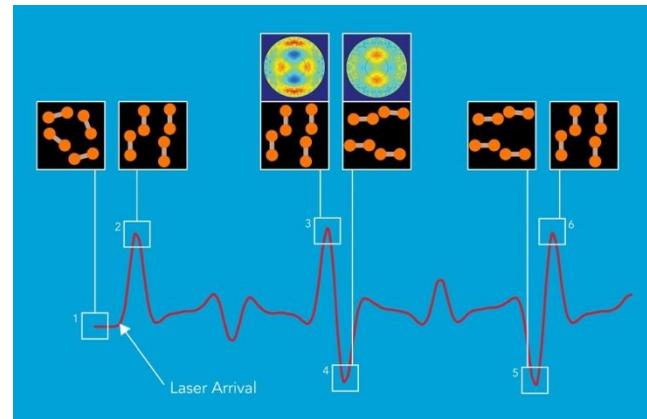
- **Key idea**: optimize basis to span just the part of Hilbert space needed  
(Single-particle gaussian wave packets used in vibrational dynamics  
since the 1970s – Heller, Burghardt, Vanicek...)

# Challenges

- Molecular structure?
  - Same Hamiltonian for multiple isomers
  - Which molecule depends on chosen initial state
  - Is classical structure actually defined?



- Impulsive laser-induced alignment routinely used in attosecond experiments
  - How to study spectroscopic processes of aligned molecules without a definite structure?



SLAC National Accelerator Lab

- Can we solve the time-dependent optimization problem with completely free ECG wave packets? Are ionization and dissociation/fragmentation processes included? → **Simon Schrader's talk**

# Can ECG Wave Packets Capture Violent Quantum Dynamics?

- Wozniak, Adamowicz, Pedersen, Kvaal  
*Gaussians for Electronic and Rovibrational Quantum Dynamics*  
J. Phys. Chem. A **128**, 3659– 3671 (2024)
- Fit to accurate grid solutions for 2D systems exposed to extreme laser pulses
- Grid solver: split-step Fourier

# Proof of Principle: Fitting to Grid Solutions

- Wozniak, Adamowicz, Pedersen, Kvaal

*Gaussians for Electronic and Rovibrational Quantum Dynamics*

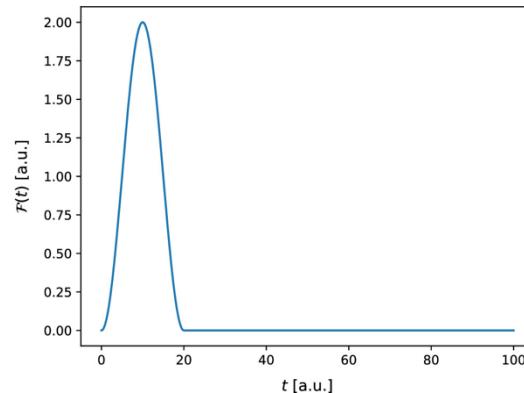
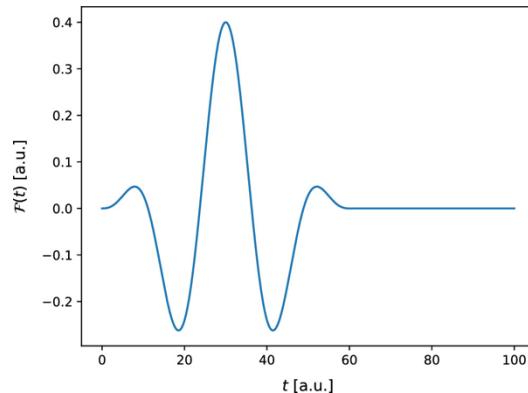
J. Phys. Chem. A **128**, 3659– 3671 (2024)

- Hamiltonian for 2D laser-driven dynamics:

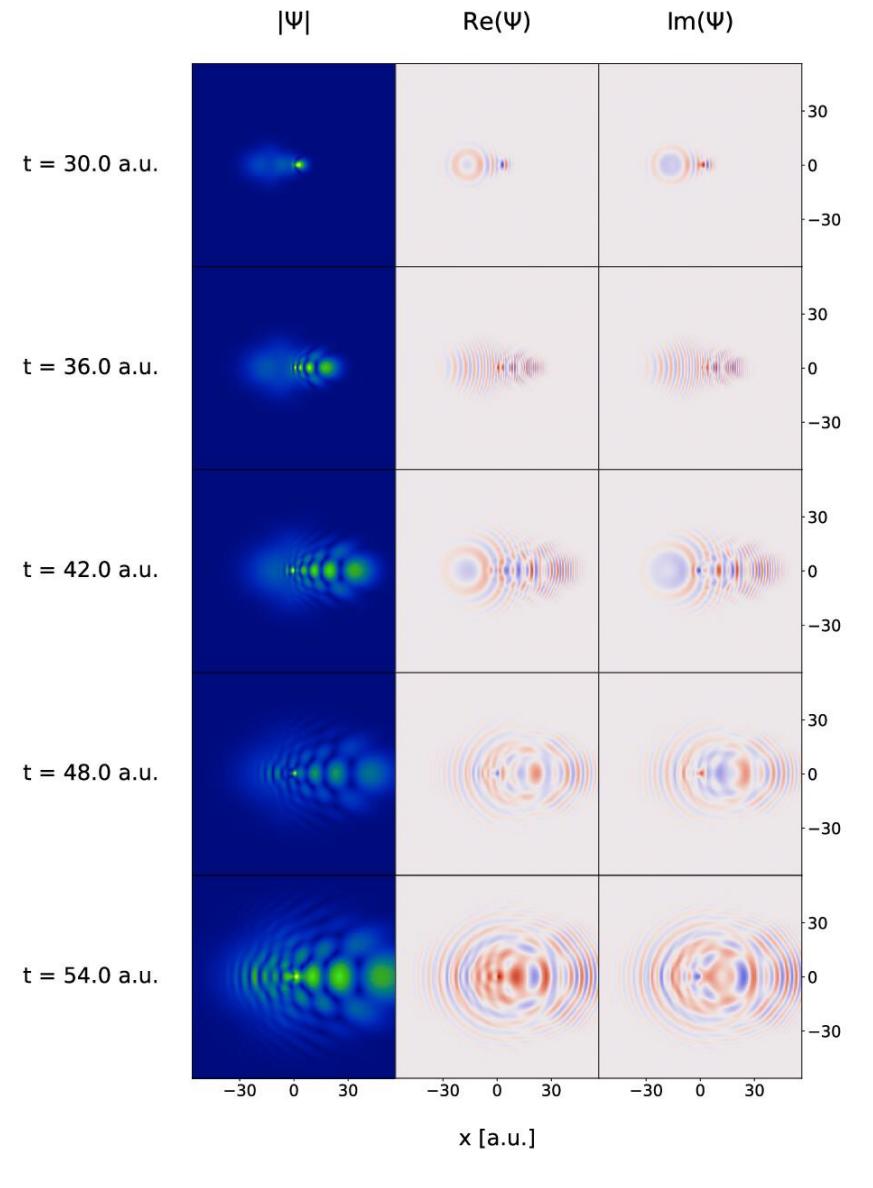
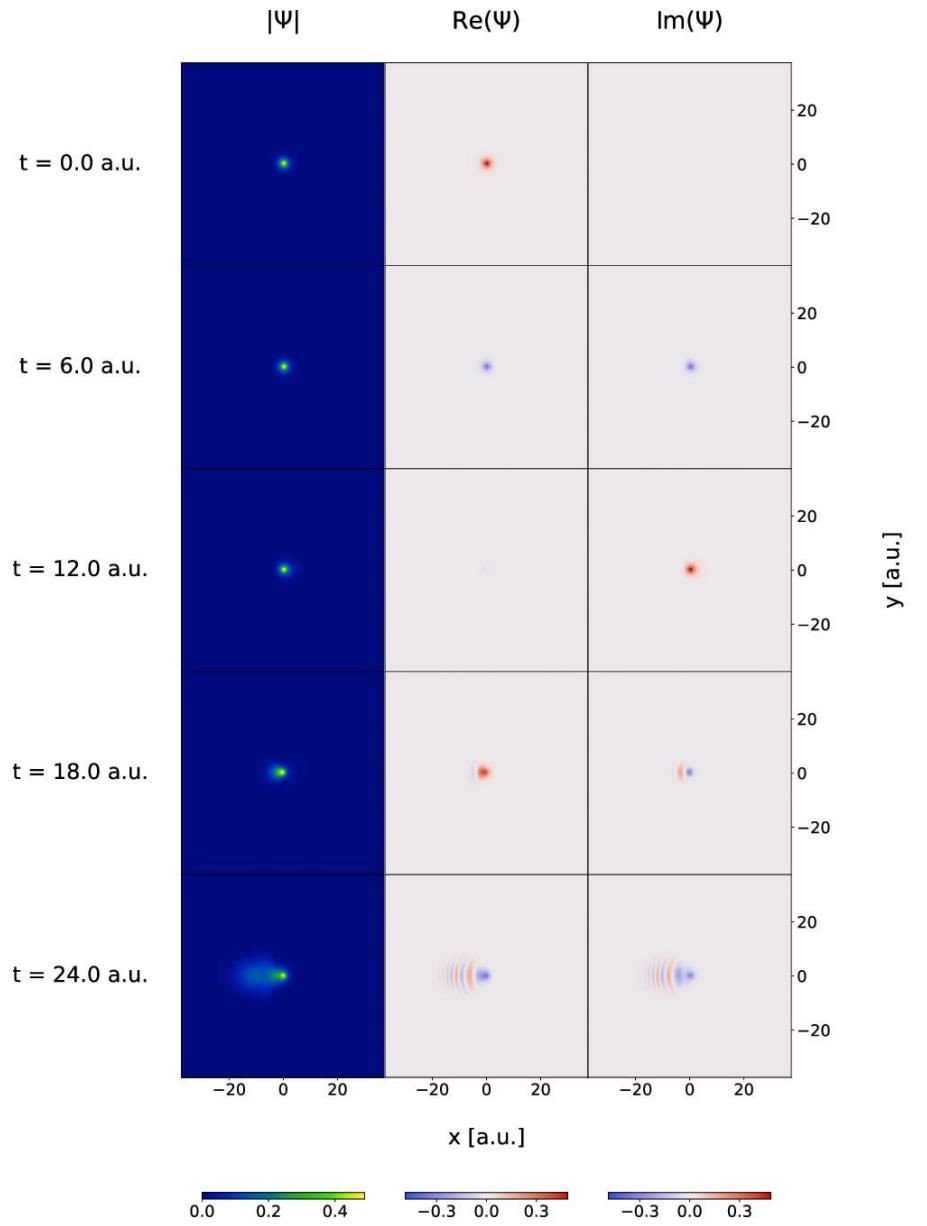
$$\hat{H}(t) = -\frac{1}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y) + qxE(t)$$

$$V(x, y) = \begin{cases} -\frac{1}{\sqrt{x^2+y^2+\frac{1}{2}}} & \sim \text{hydrogen} \\ D_e \left[ 1 - \exp \left( -\alpha \left( \sqrt{x^2 + y^2} - r_e \right) \right) \right]^2 & \text{Morse} \end{cases}$$

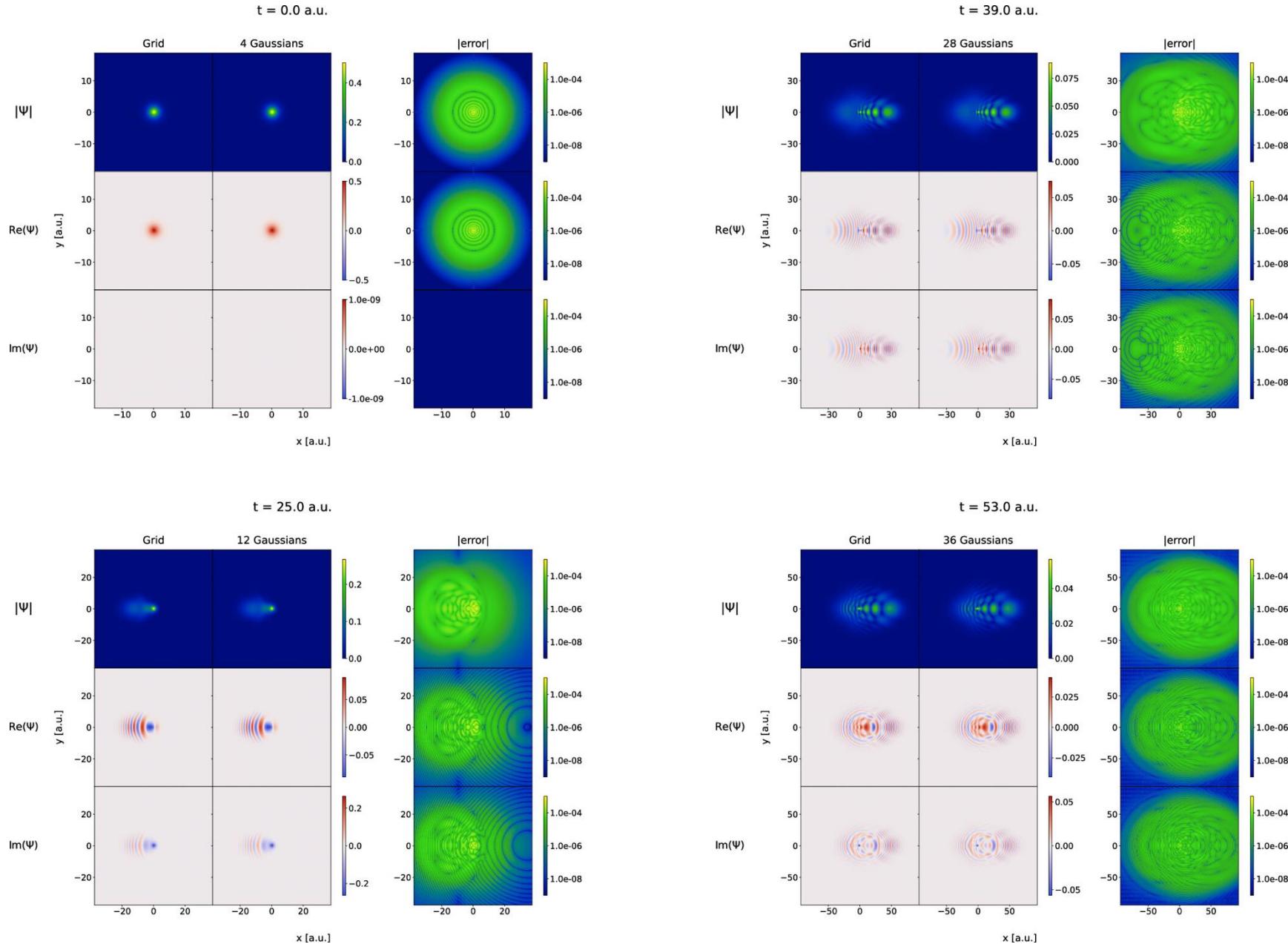
- Laser fields E(t):



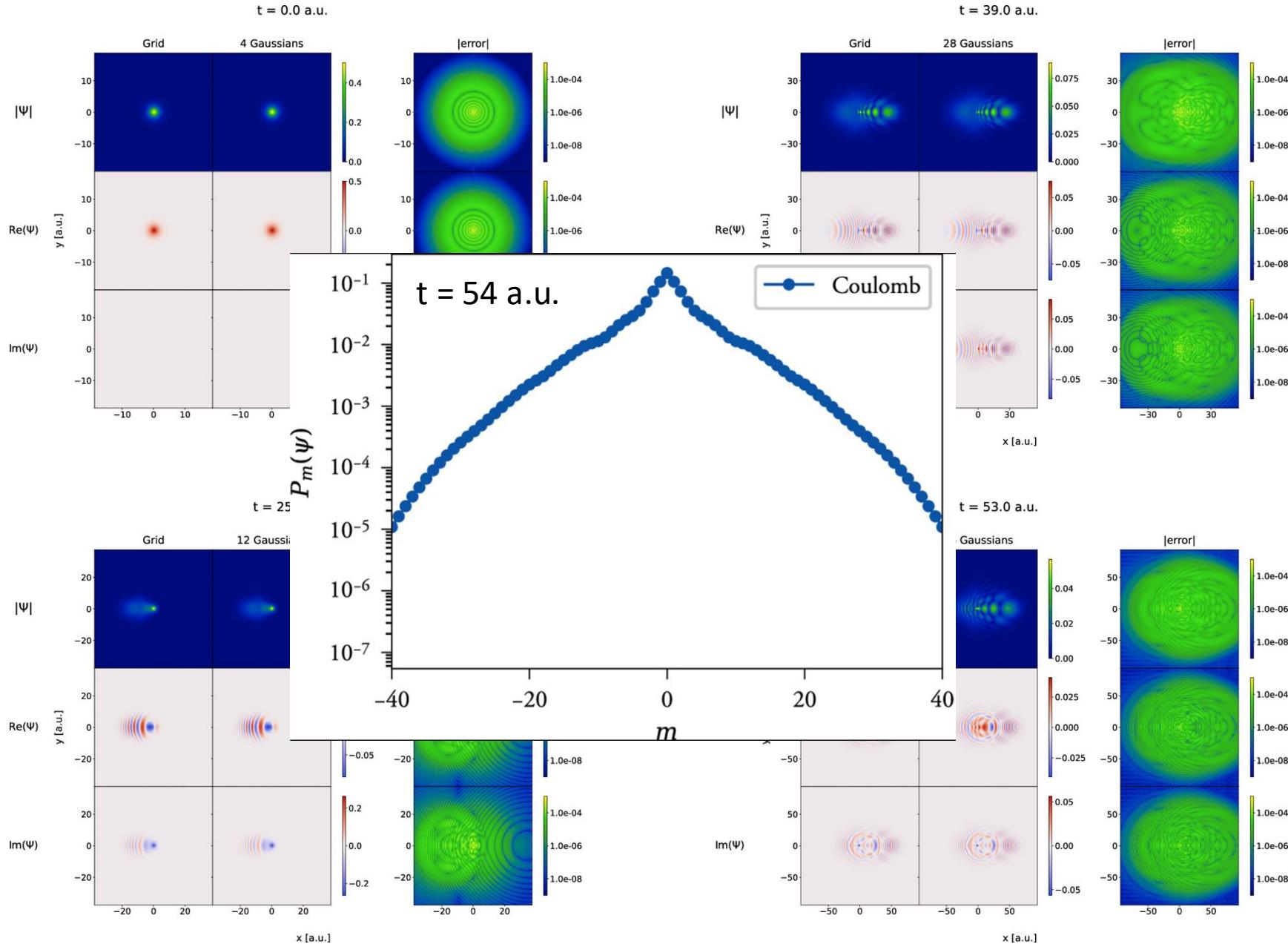
# Grid Results for 2D Hydrogen



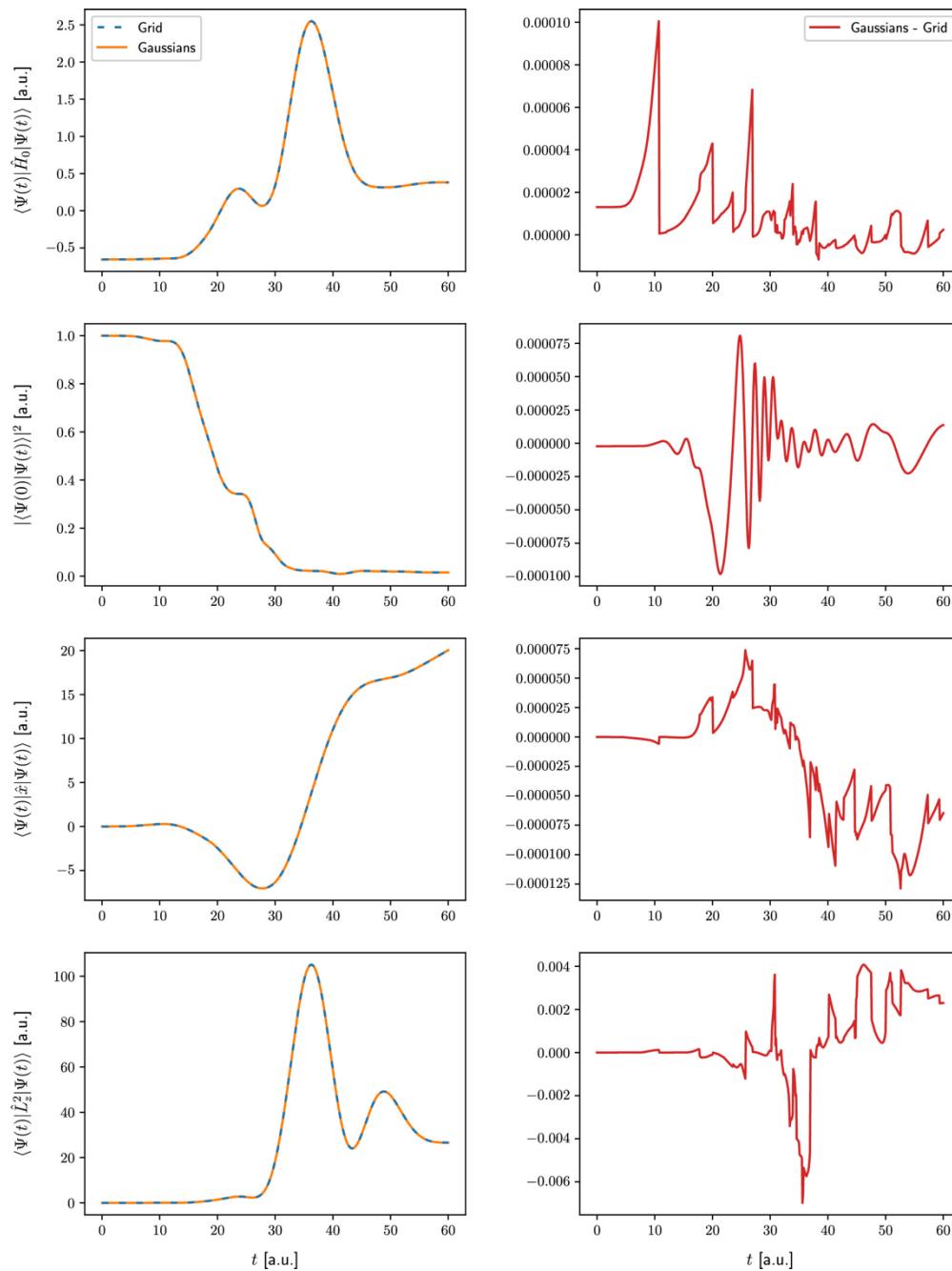
# Fitting Errors for 2D Hydrogen



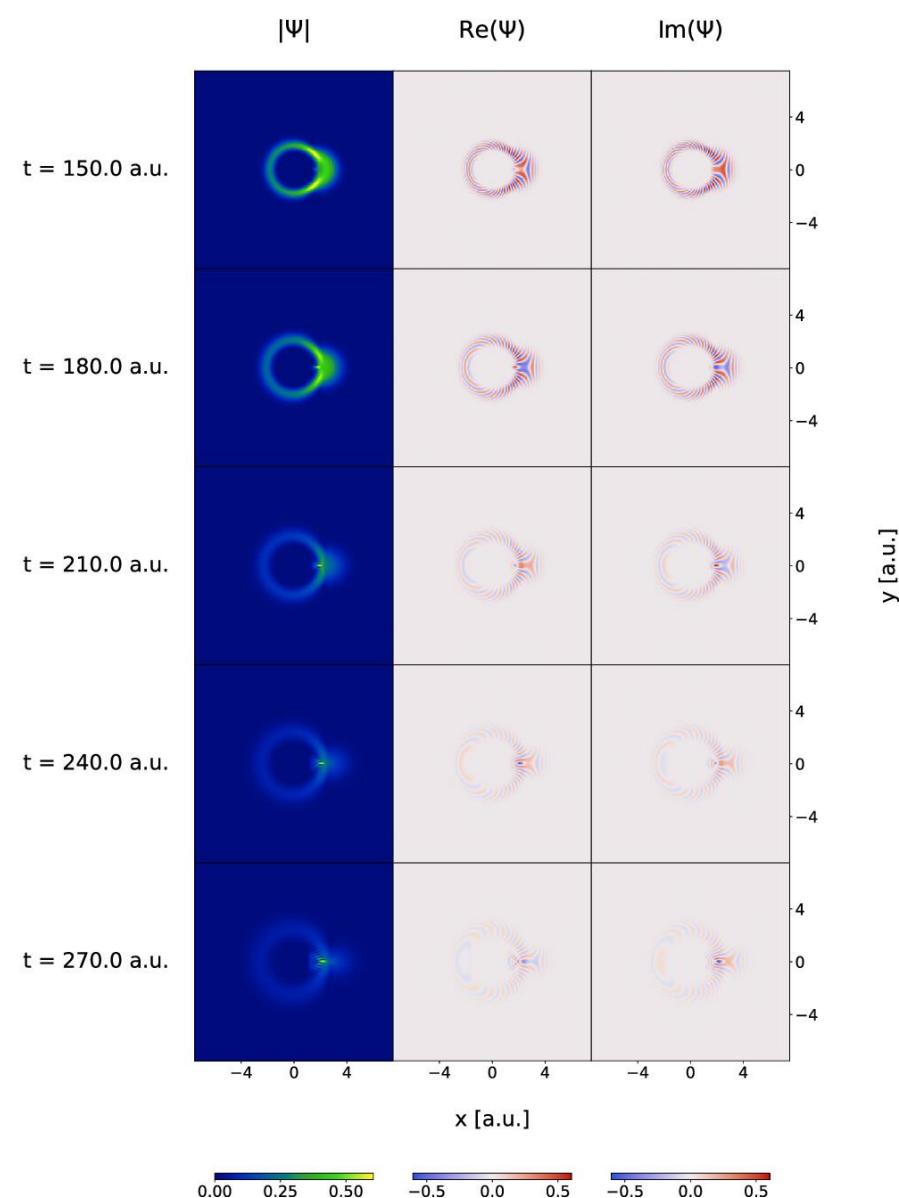
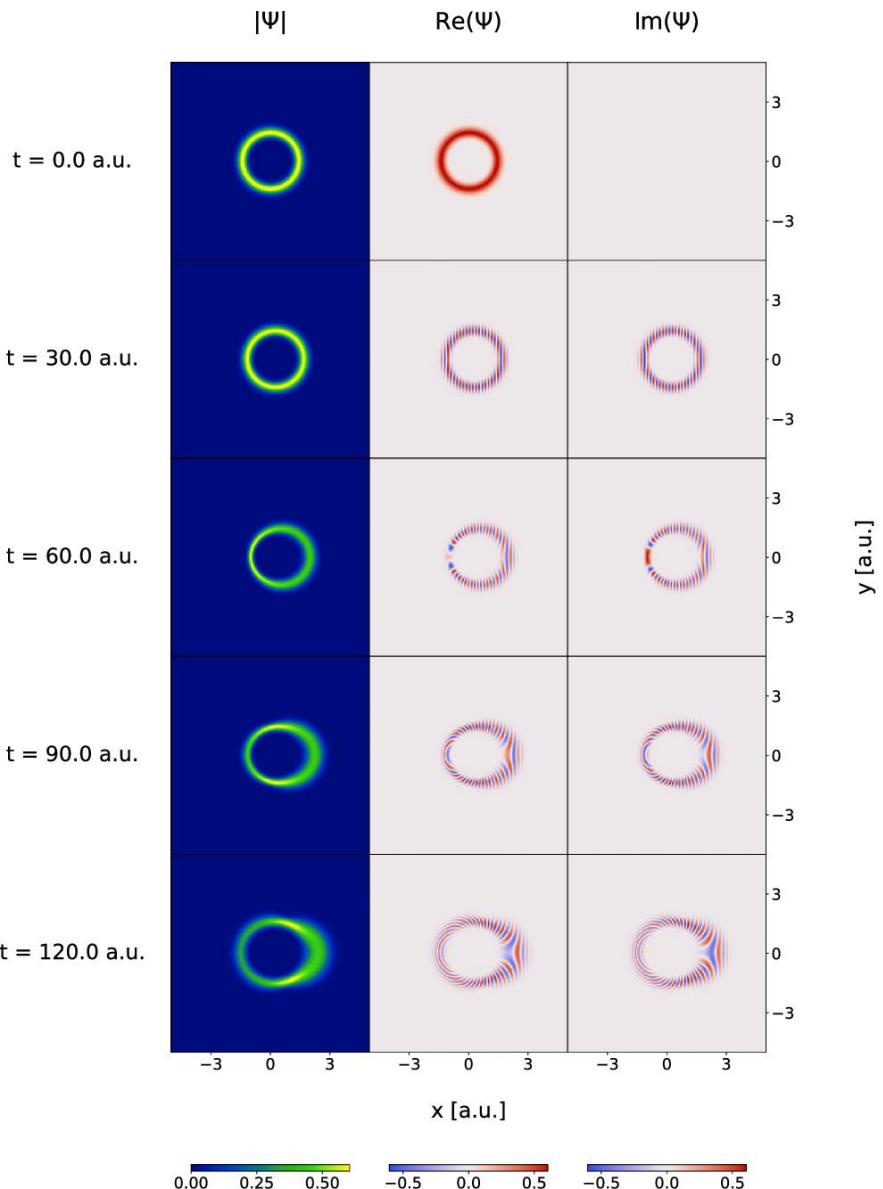
Fitting Errors for 2D Hydrogen – Angular Momentum Components



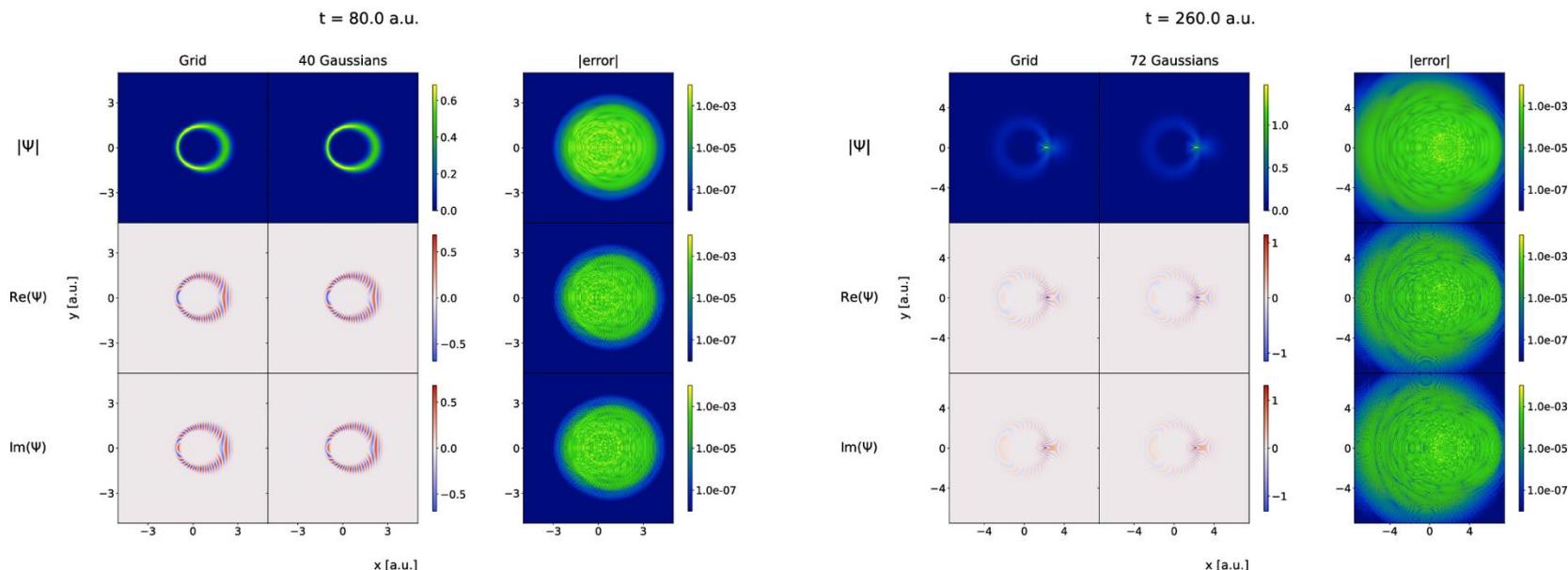
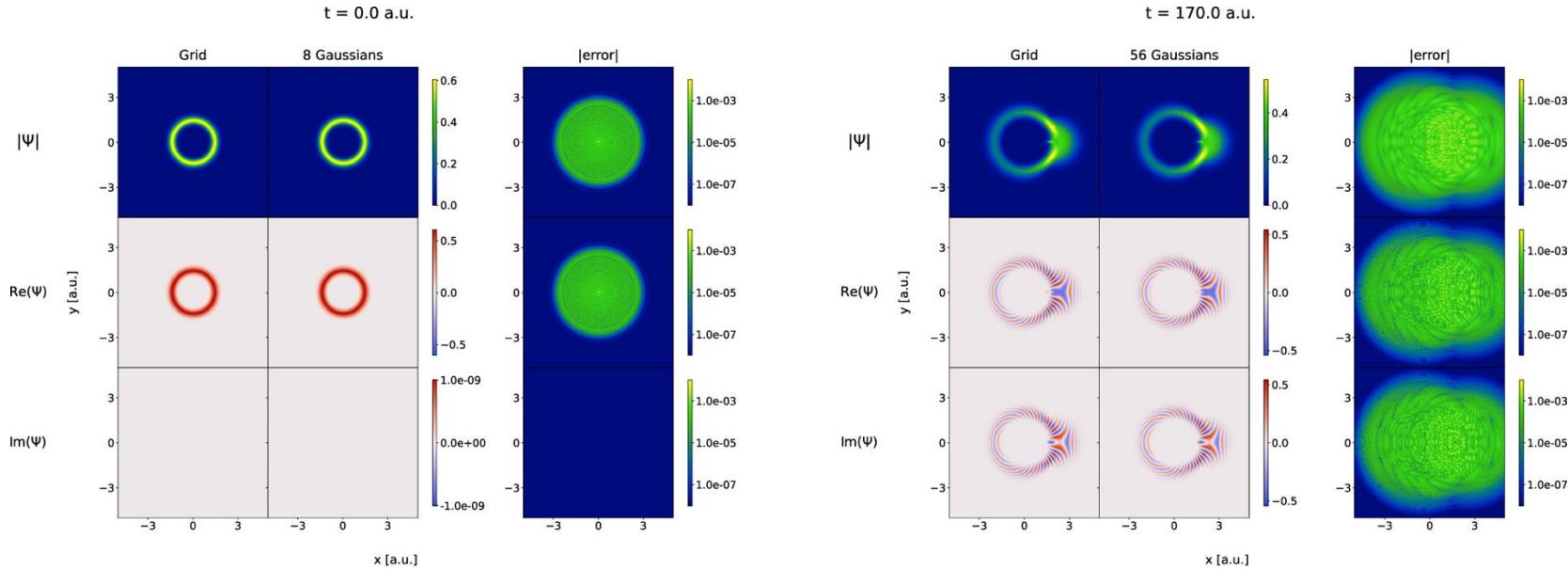
# Fitting Errors for 2D Hydrogen - Properties



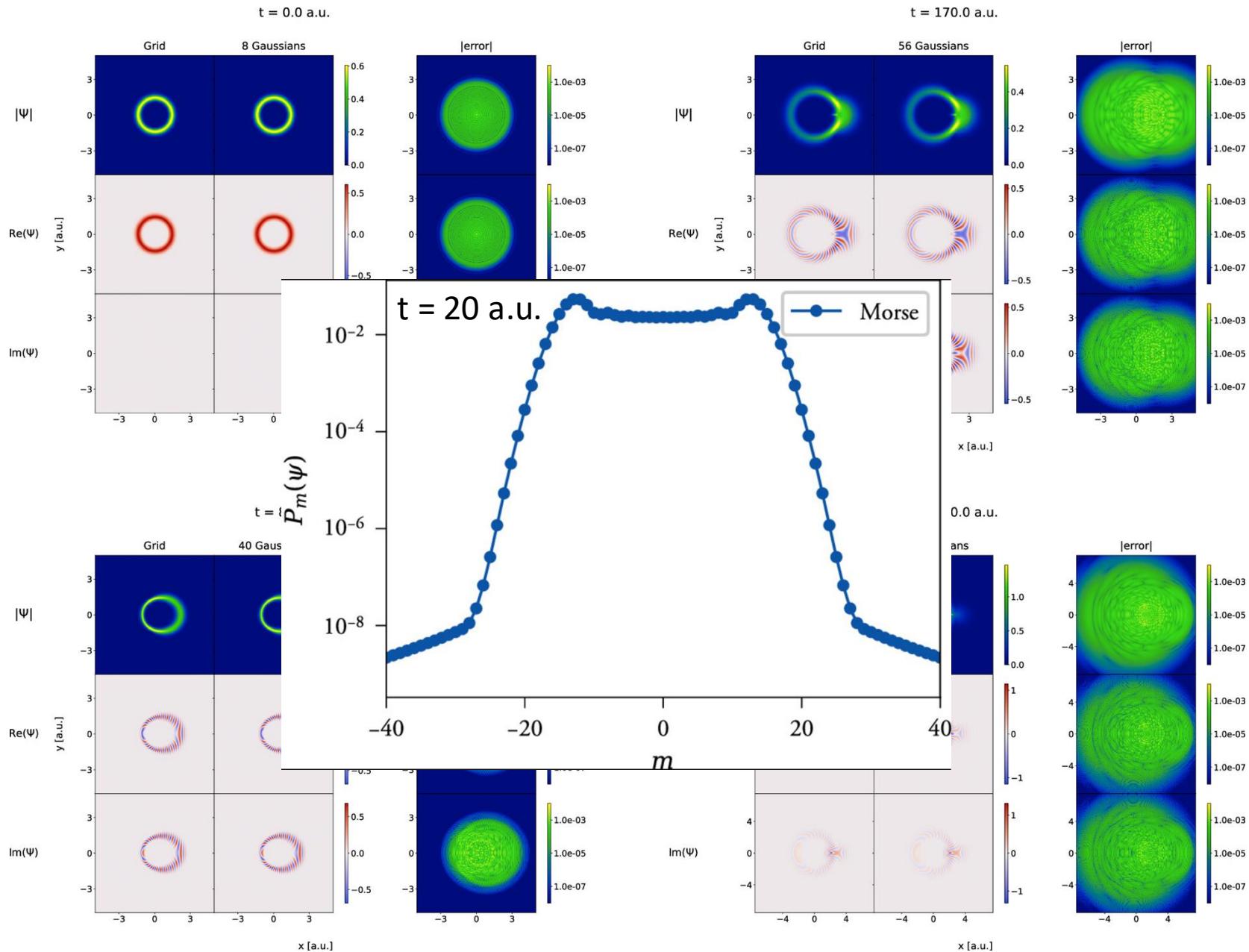
# Grid Results for 2D Morse Potential



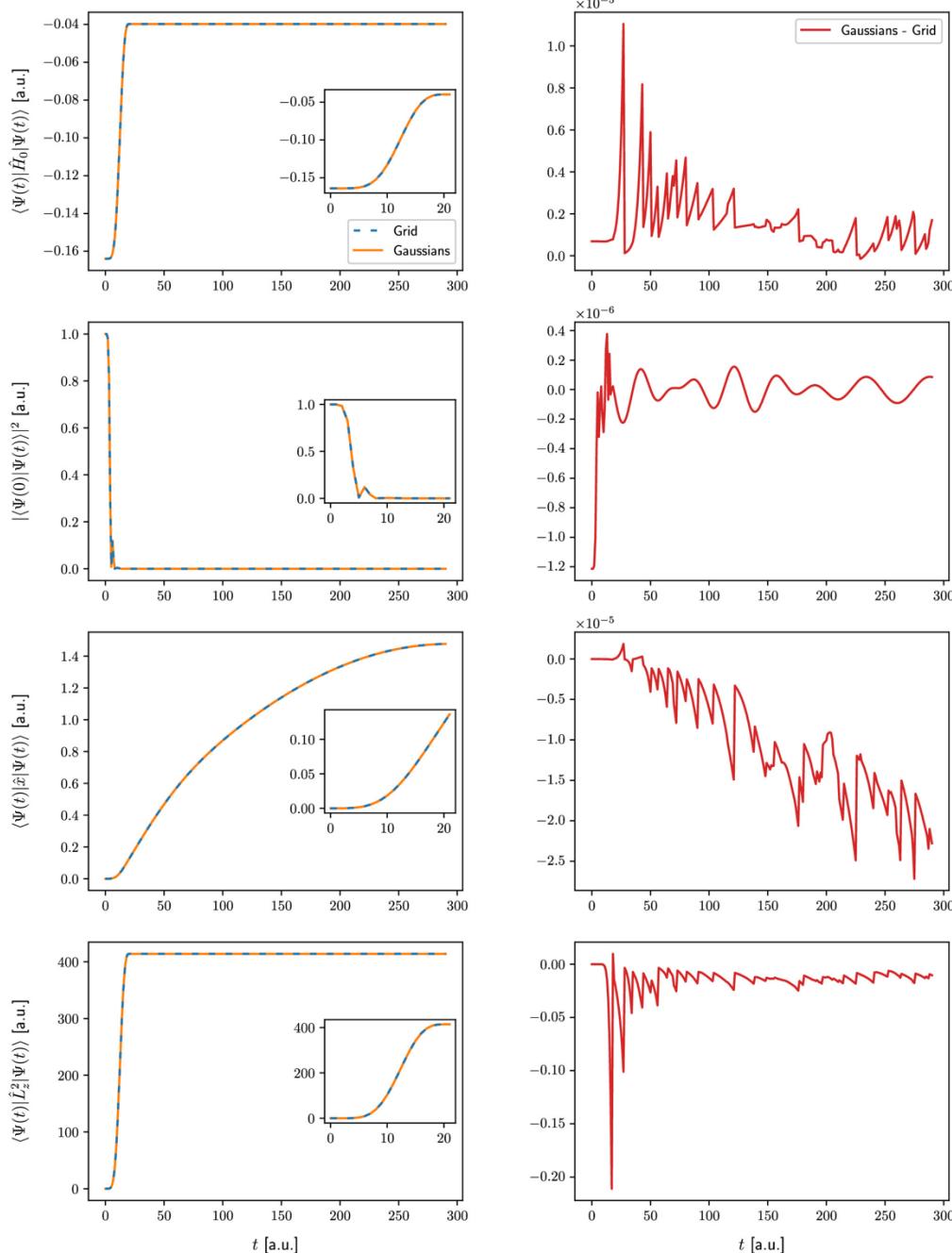
# Fitting Errors for 2D Morse Potential



## Fitting Errors for 2D Morse Potential – Angular Momentum Components



# Fitting Errors for 2D Morse Potential - Properties

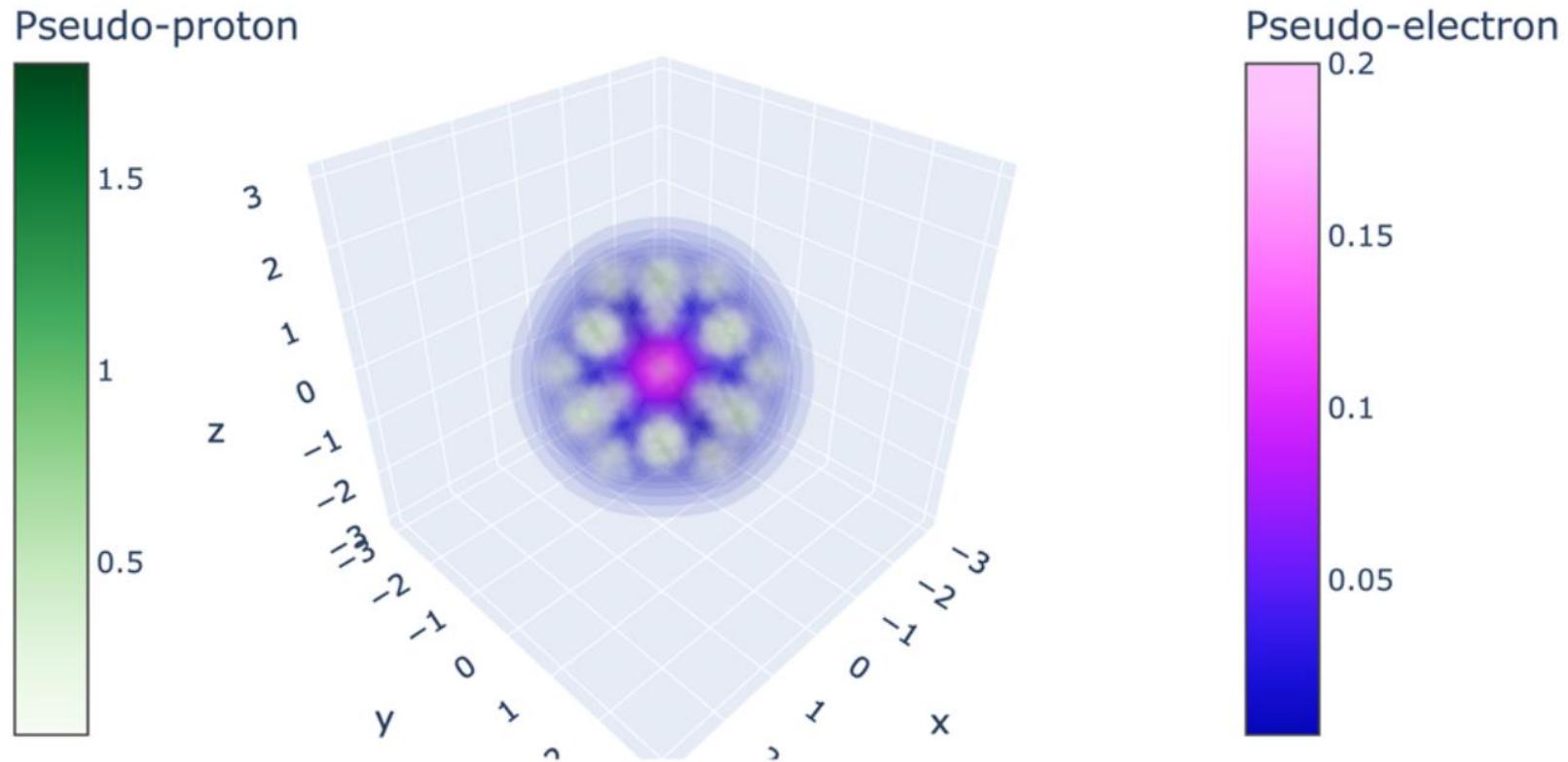


## Interpretation in «chemical» terms

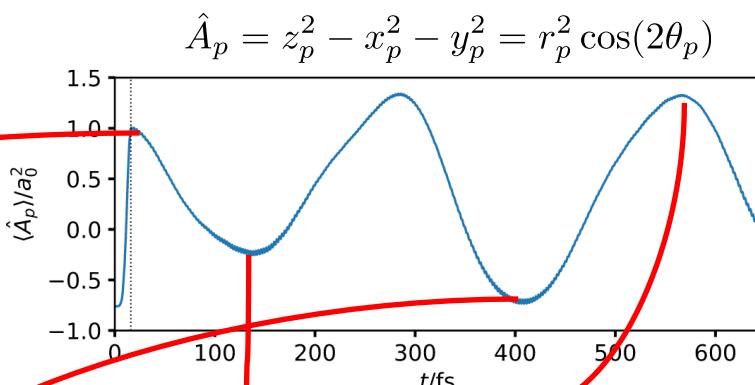
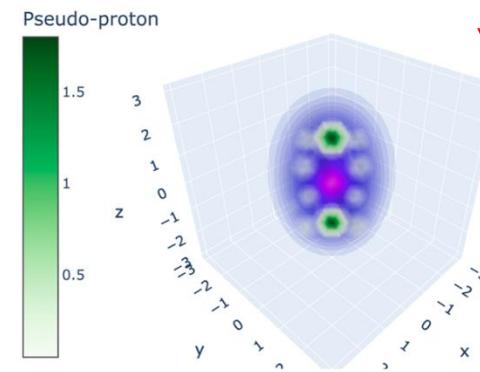
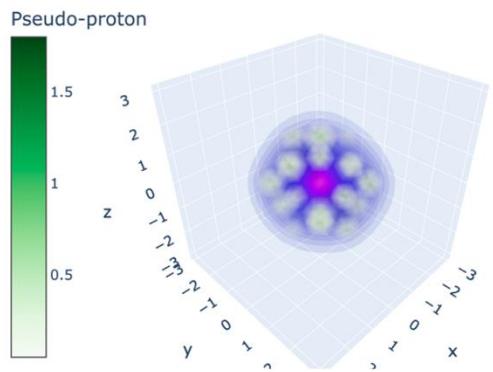
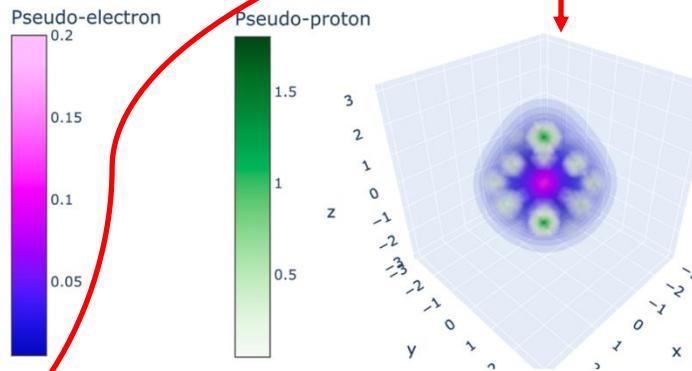
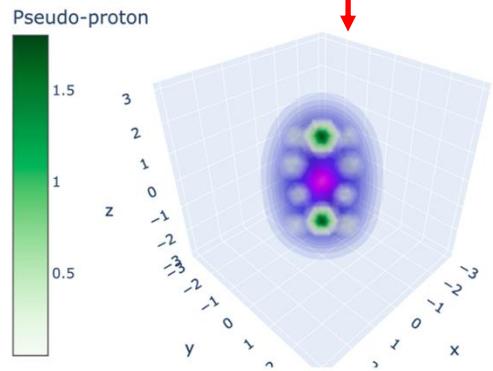
- ECG wave packets appear to efficiently represent the wave function, even for dynamics induced by rather extreme fields!
- But, can the results of non-BO simulations be easily interpreted/visualized in «chemical» terms (structural changes etc.)?

# Laser-Induced Alignment without BO

- HD molecule, internal frame with origin at the deuteron
- ECG basis optimized at various static, uniform electric-field strengths up to dissociation; distributed in space to approximate spherical symmetry
- Initial state: the ground state; impulsive laser pulse



# Laser-Induced Alignment without BO



## Interpretation in «chemical» terms

- ECG wave packets appear to efficiently represent the wave function, even for dynamics induced by rather extreme fields!
- Alignment appears to emerge in qualitative agreement with standard experimental techniques!
- Can we extract structure from the non-BO wave function?

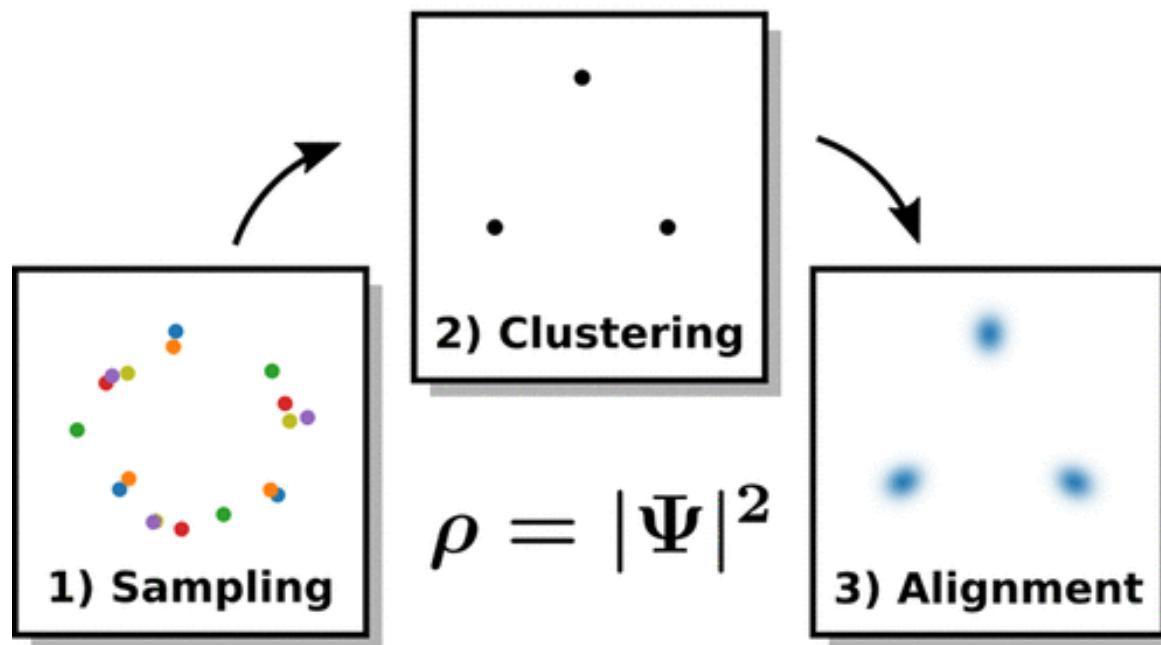
# Quantum Definition of Molecular Structure

- Old idea:

(Claverie & Diner, Isr. J. Chem. **19**, 54-81 (1980); Tostes, Theor. Chim. Acta **59**, 229-235 (1981))

*Molecular structure is a manifestation of strong statistical correlation between the positions of the nuclei in the joint probability distribution*

## Molecular structure of $D_3^+$



# Quantum Definition of Molecular Structure

BO:



non-BO:



Isovalues:    0.03            0.05            0.1            0.15            0.2

## Concluding remarks

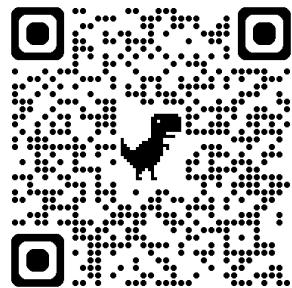
- Quantum dynamics without BO is possible
  - ECG wave packets capture low- and high-angular-momentum continua quite efficiently
  - Impulsive alignment can be simulated when required by experimental conditions
  - Visualization using statistical definition of structure
- Propagation of linear combinations of ECG wave packets
  - Possible by rephrasing propagation as an optimization problem
  - Simon Schrader's talk

# Postdoc opportunities at UiO

## DSTrain

DSTrain is a 5-year postdoctoral programme that will award **36 postdoctoral fellowship positions of 36 months each** in two calls over the programme period within the overarching frame of data science. The programme will train researchers and innovators with disciplinary, interdisciplinary and transferable skills and a foundation in data science methods enabling them to become Europe's digital leaders across disciplines and sectors.

<https://www.uio.no/dscience/english/dstrain/>



## Research Themes



Data-driven synthetic chemistry and catalyst design



Machine learning in theoretical and computational chemistry

Astrophysics



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Geosciences



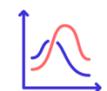
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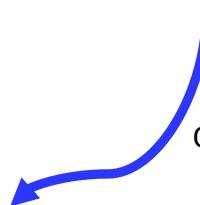
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Technology Systems



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## Quantum dynamics positions at Hylleraas



Official announcement: **January 6, 2025**

Application deadline: **April 6, 2025**

# Acknowledgments

## Collaborators:



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The Research  
Council of Norway

