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Time evolution as optimization: Solving the time-dependent Schrödinger equation with Gaussians

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Motivation

- Goal: Solve the time-dependent Schrödinger equation and find $\Psi(t)$
- Initial state: $\Psi(0)$
- Time dependent Hamiltonian $H(t)$
- Example: Molecule in strong laser field

$$H(t) = H_{el.} + V(t)$$

$$V(t) = E_0 f(t) \sin(\omega t) \sum_{i=1}^{N_e} \hat{z}_i$$

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- Fixed Gaussian basis sets not suitable for those dynamics
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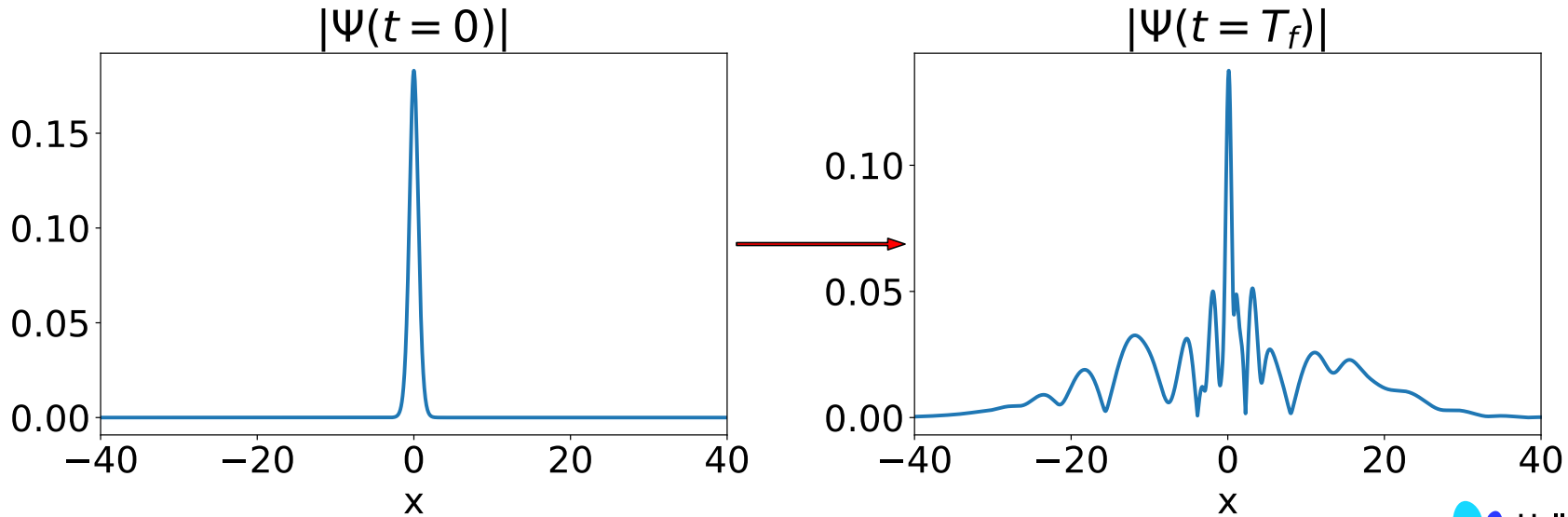

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Gaussians for complicated wave functions

- $\Psi(t = T_f)$ is represented using hundreds of complex numbers on the grid.
- How many Gaussians of the form $g_m = c_m \exp\left(-a_m(x - \mu_m)^2\right)$ are needed?

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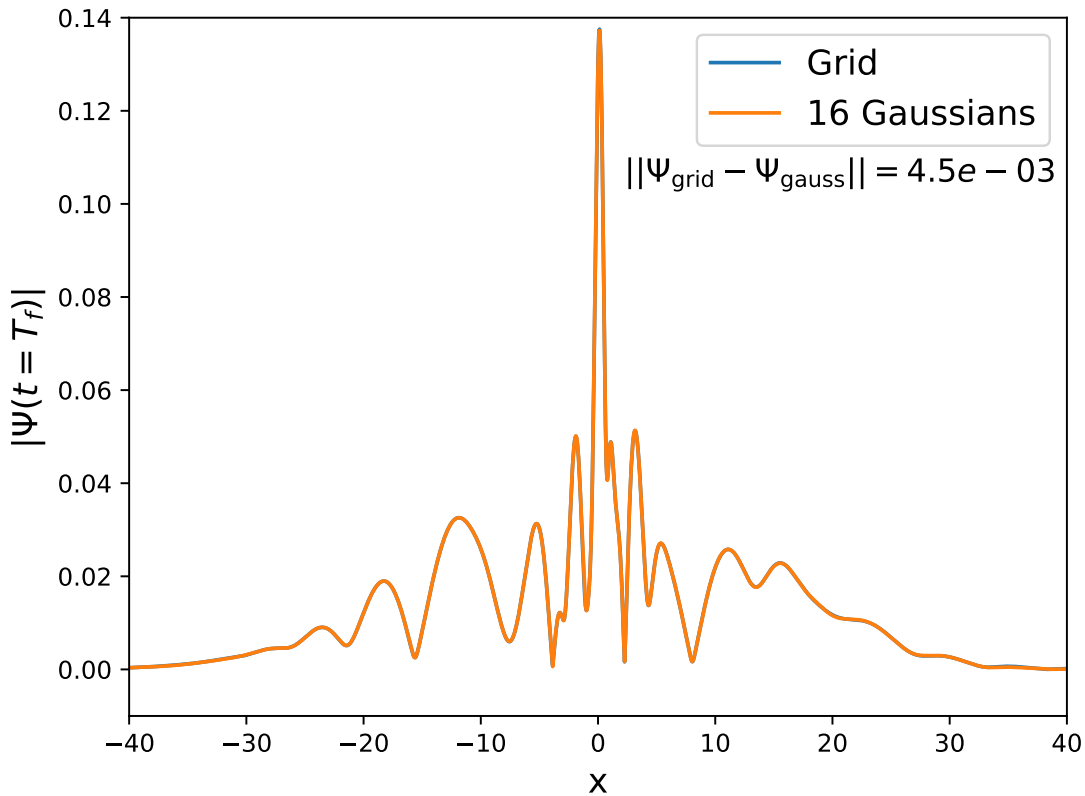

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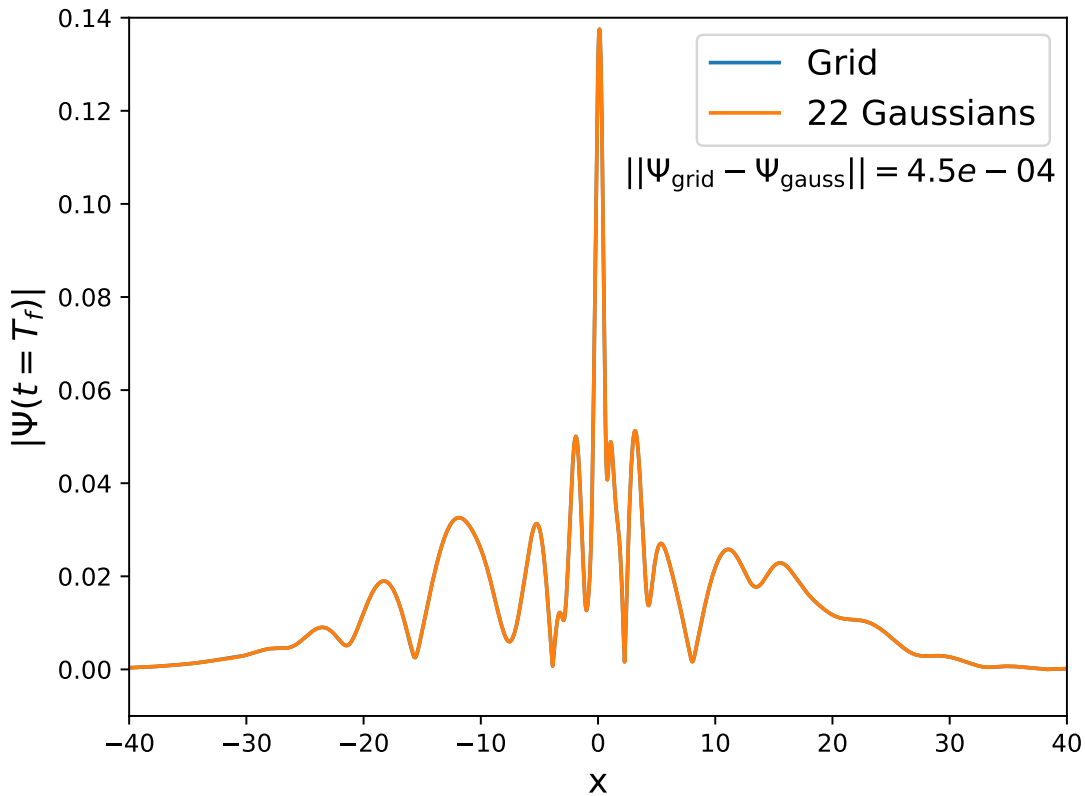

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Explicitly correlated Gaussians

Explicitly Correlated Gaussians (ECGs):

- General shape

$$g_m(\boldsymbol{r}) = g(\boldsymbol{r}; \boldsymbol{\alpha}_m) = g(\boldsymbol{r}; \boldsymbol{A}_m, \boldsymbol{\mu}_m) = \exp\left(-(\boldsymbol{r} - \boldsymbol{\mu}_m)^T \boldsymbol{A}_m (\boldsymbol{r} - \boldsymbol{\mu}_m)\right) \tag{1}$$

- Wave function written as a linear combination of different ECGs placed at different centers
- Analytical evaluation of $O_{mn} = \langle g_m | \hat{O} | g_n \rangle$ possible for many $\hat{O}$
- Efficient parameterization of of highly accurate states[1] as well as time-dependent wave functions in strong fields[2]

[1] J. Mitroy et al. **"Theory and application of explicitly correlated Gaussians".** In: *Rev. Mod. Phys.* 85 (2 May 2013). DOI: 10.1103/RevModPhys.85.693.

[2] A. P. Woźniak et al. **"Gaussians for Electronic and Rovibrational Quantum Dynamics".** In: *J. Phys. Chem. A* 128.18 (2024), pp. 3659–3671. DOI: 10.1021/acs.jpca.4c00364.

Time evolution of ECGs

- We want to approximately solve the time-dependent Schrödinger equation (TDSE)

$$i\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) \approx \hat{H}(t)\Psi(\boldsymbol{r},t) \tag{2}$$

- Aim: Write the approximate solution of the TDSE as a linear combination of ECGs

$$\Psi(\boldsymbol{r},t) = \Psi(\boldsymbol{r};\boldsymbol{\alpha}(t),\boldsymbol{c}(t)) = \sum_{m=1}^{M} c_m(t)g(\boldsymbol{r};\boldsymbol{\alpha}_m(t)) \tag{3}$$

Time-dependent variational principle?

- Obvious approach: A time dependent variational principle (e.g. McLachlan)[3]

$$\frac{\partial}{\partial t}\Psi(t) = \arg\min_{\chi} \left\| \hat{H}(t)\Psi(t) - i\chi \right\|^2 \tag{4}$$

  $\rightarrow$ Find coupled ODE for all parameters

- With ECGs, this is very hard to solve (singular matrix needs to be inverted).

[3] A. D. McLachlan. **"A variational solution of the time-dependent Schrodinger equation".** In: *Mol. Phys.* 8 (1964), pp. 39–44. DOI: 10.1080/00268976400100041.

Rothe's method

- Apply the Crank-Nicolson scheme to the time-dependent SE

$$\Psi(t_{i+1}) = (\hat{A}_i)^{-1}\hat{A}_i^\dagger \Psi(t_i) + O((\Delta t)^3) \tag{5}$$

with

$$\hat{A}_i = \left[\hat{I} + i\frac{\Delta t}{2}\hat{H}\left(t_i + \frac{\Delta t}{2}\right)\right] \tag{6}$$

- Variational reformulation:

$$\Psi(t_{i+1}) = \arg\min_{\chi} \left\| \hat{A}_i \chi - \hat{A}_i^\dagger \Psi(t_i) \right\|^2. \tag{7}$$

Compared to eq. (4), we now solve for the *wave function* at the next time step, not the time derivative. This is Rothe's method.[4]

[4] S. Kvaal et al. ***No need for a grid: Adaptive fully-flexible gaussians for the time-dependent Schrödinger equation.*** 2023. arXiv: 2207.00271.

Rothe's method (2)

- Starting from the variational formulation

$$\Psi(t_{i+1}) = \arg\min_{\chi} \left\| \hat{A}_i \chi - \hat{A}_i^{\dagger} \Psi(t_i) \right\|^2 \tag{8}$$

the basis is introduced. This leads to an **optimization problem**

$$\begin{aligned} \boldsymbol{\alpha}^{i+1}, \boldsymbol{c}^{i+1} &= \arg\min_{\boldsymbol{\alpha}, \boldsymbol{c}} \mathrm{r}_{i+1}(\boldsymbol{\alpha}, \boldsymbol{c}) \\ \Psi(t_{i+1}) &= \sum_{m=1}^{M(t)} c_m^{i+1} g(\boldsymbol{\alpha}_m^{i+1}) \end{aligned} \tag{9}$$

where we introduced the Rothe error

$$\mathrm{r}_{i+1}(\boldsymbol{\alpha}, \boldsymbol{c}) = \left\| \sum_{m=1}^{M(t)} c_m(\boldsymbol{\alpha}) A_i g(\boldsymbol{\alpha}_m) - A_i^{\dagger} \Psi(t_i) \right\|^2$$

Rothe's method (3)

- Optimization of $r_{i+1}(\boldsymbol{\alpha}, \boldsymbol{c})$ carried out with Quasi-Newton methods
- The cumulative Rothe error is an upper bound for the time evolution error

$$\left\| \Psi(T_f) - \Psi^{\text{exact}}(T_f) \right\| \leq \sum_{i=1}^{N_T} \sqrt{r_i}, \tag{10}$$

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Advantages to TDVP

- Dynamic parameterization of wave functions
- Error control
- Overcome issues with singular matrices

Disadvantages

- Optimization problem is hard
- Expensive matrix elements

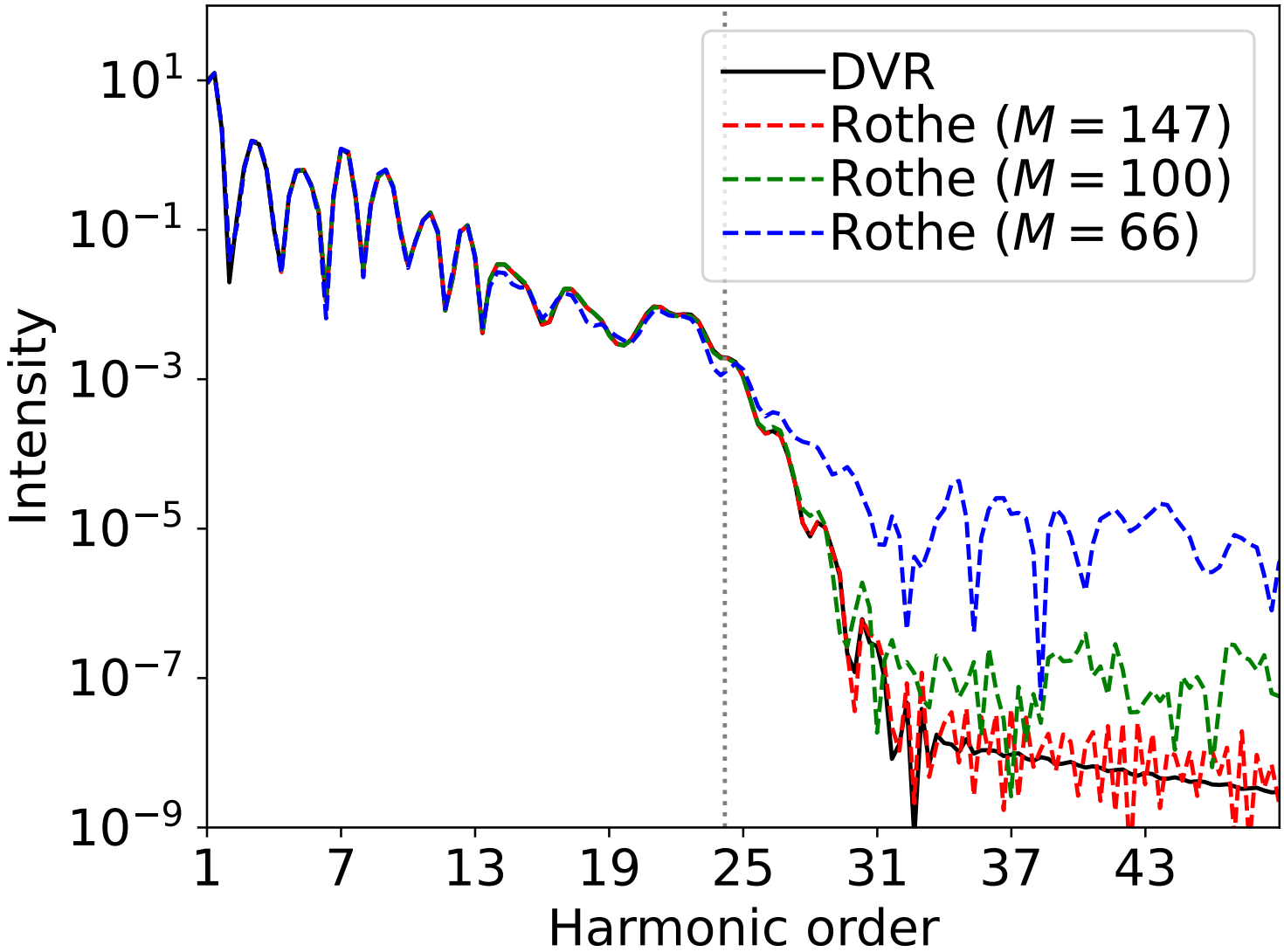
The Hydrogen atom in a strong laser field[5]

- We consider the Hydrogen atom in a strong laser field
  $\Rightarrow$ delocalized, oscillatory wave function
- Quantity of interest: **HHG spectrum** - Fourier transform of the dipole moment $\mu(t)$.
- Basis functions: Isotropic Gaussians with complex width and shift
- Hamiltonian:

$$\hat{H}(t) = -\frac{1}{2}\nabla^2 - \frac{\mathrm{erf}(\mu r)}{r} + E_0 f(t)\sin(0.057t)z \tag{11}$$

[5] S.E. Schrader et al. **"Time evolution as an optimization problem: The hydrogen atom in strong laser fields in a basis of time-dependent Gaussian wave packets".** In: *J. Chem. Phys.* 161.4 (July 2024), p. 044105.

HHG spectrum in strong field, $E_0 = 0.06$ a.u.



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The Henon-Heiles potential[6]

- (dimensionless) Henon-Heiles Hamiltonian

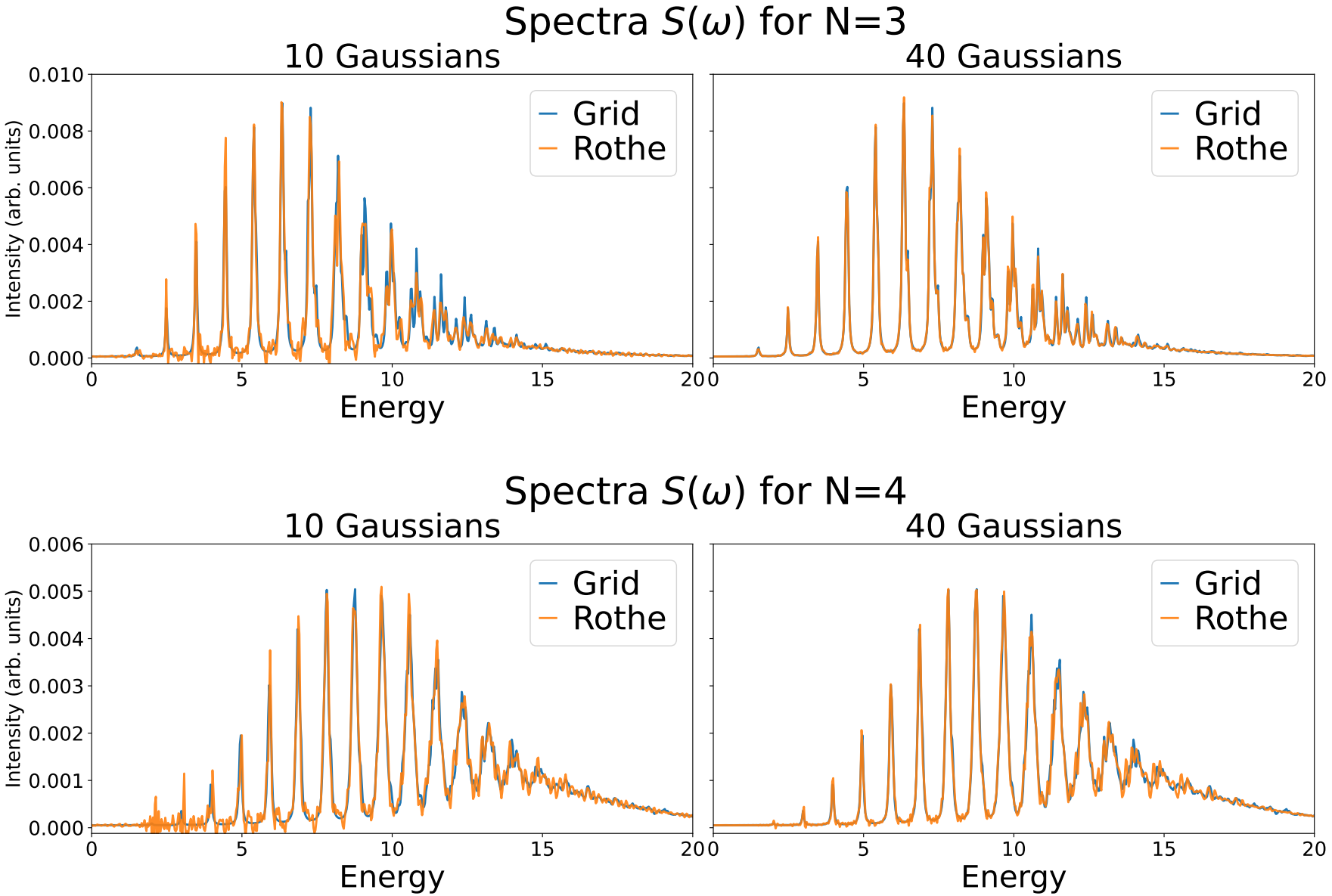
$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2}{\partial r_i^2} + \frac{1}{2}\sum_{i=1}^{N} r_i^2 + 1/\sqrt{80}\sum_{i=1}^{N-1}\left(r_i^2 r_{i+1} - \frac{1}{3}r_{i+1}^3\right) \tag{12}$$

- ECGs used as basis functions
- $\Psi(0)$ is an uncorrelated Gaussian with standard width, with $\boldsymbol{\mu} = [2, \ldots, 2]^T$
- Quantity of interest is the **spectrum** - the Fourier transform of the autocorrelation function:

$$S(\omega) \propto \mathrm{Re}\int_0^\infty e^{i\omega t}\,\langle \Psi^*(t/2) \mid \Psi(t/2)\rangle\, dt \tag{13}$$

[6] S.E. Schrader, T.B. Pedersen, and S. Kvaal. ***Multidimensional quantum dynamics with explicitly correlated Gaussian wave packets using Rothe's method.*** 2024. arXiv: 2411.05459 [physics.chem-ph]. URL: https://arxiv.org/abs/2411.05459.

Henon-Heiles results



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Time-dependent Hartree-Fock: Rothe's method for orbital equations

The time dependent Hartree–Fock equations read for each orbital $j = 1, \ldots, N$

$$\dot{\phi}_j = -i\hat{F}(\Phi, t)\phi_j \tag{14}$$

Defining the operator

$$\tilde{A}_i(\Phi, \Delta t) = \hat{I} + \mathrm{i}\frac{\Delta t}{2}\hat{F}\left(\Phi, t_i + \frac{\Delta t}{2}\right), \tag{15}$$

the Crank-Nicolson scheme gives:

$$\phi_j(t_i + \Delta t) = (\tilde{A}_i)^{-1}\tilde{A}_i^{\dagger}\phi_j(t_i) \qquad \Rightarrow \qquad \left\|\tilde{A}_i\phi_j(t_i + \Delta t) - \tilde{A}_i^{\dagger}\phi_j(t_i)\right\|^2 = 0. \tag{16}$$

This holds true for all orbitals, so

$$\sum_{j=1}^{N}\left\|\tilde{A}_i\phi_j(t_i + \Delta t) - \tilde{A}_i^{\dagger}\phi_j(t_i)\right\|^2 = 0. \tag{17}$$

This can be formulated as an optimization problem:

$$\Phi(t_i + \Delta t) = \arg\min_{\Omega}\sum_{j=1}^{N}\left\|\tilde{A}_i\omega_j - \tilde{A}_i^{\dagger}\phi_j(t_i)\right\|^2 \tag{18}$$

$\Rightarrow$ Rothe's method applicable to sets of orbital equations!

Application to 1D test system: LiH and $(LiH)_2$ in strong laser field

- Hamiltonian: Electronic Hamiltonian with soft-coulomb interaction, in a laser field
- Quantity of interest: **HHG spectrum**
- Basis functions: Fully flexible 1D Gaussians

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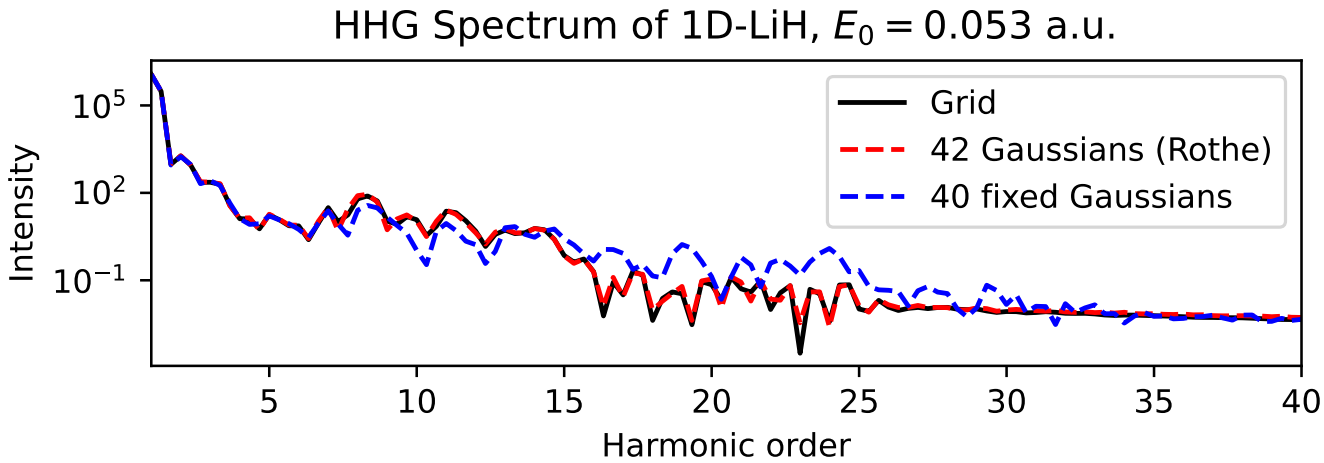

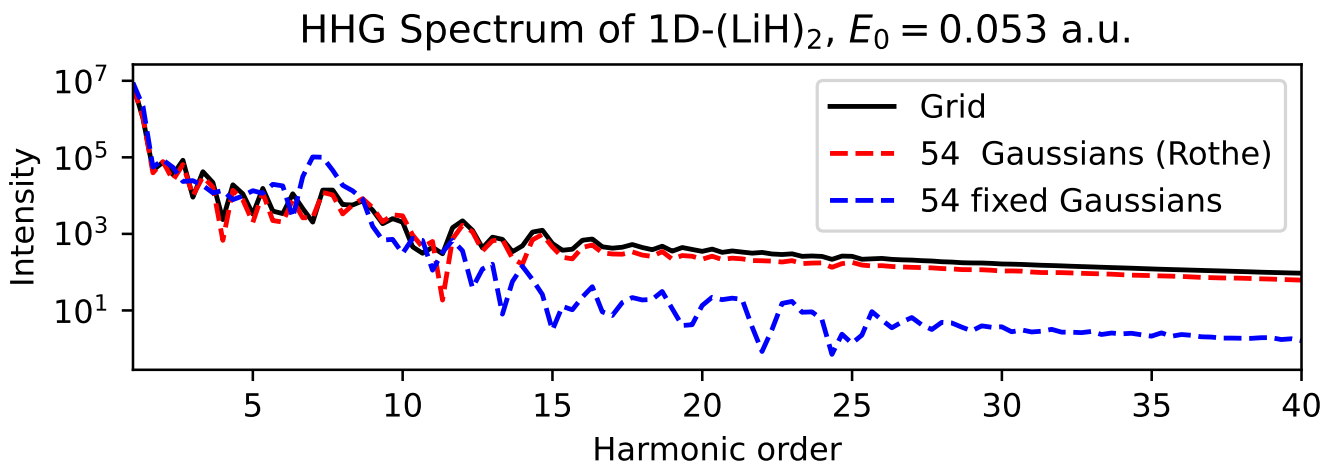

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Summary

- Quantum dynamics can be extremely demanding to model
- ECGs are a good basis for high-accuracy calculation of (time-dependent) systems.
- Rothe's method makes it possible to propagate ECGs with high accuracy, with both unbounded and time-dependent Hamiltonians.

Outlook

- Future systems to model
  - Time evolution of molecules and atoms with and without BO approximation
- Future implementation aspects
  - Improved optimization: Acceleration and momentum methods, machine learning?
  - Techniques that don't require $\hat{H}^2$
  - Rothe's method for correlated methods: TDCI, TDCC, TDDFT...

Acknowledgments

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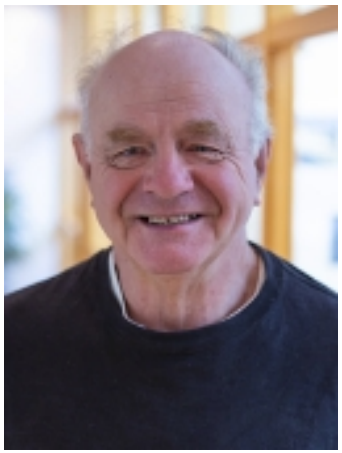
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