Time-dependent configuration interaction for high-harmonic generation

GDR CORREL meeting

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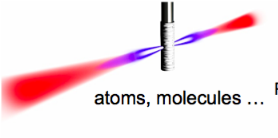
Outline

HHG: overview

HHG is a nonlinear optical process

Laser source:
ω_L= 800 nm
10^{14}-10^{15} W/cm^2
linear polarization

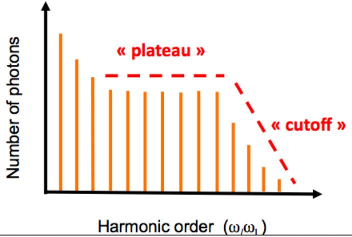


- **Energy: *XUV/Soft-X rays***
- **Temporal resolution: *attosecond pulses***

P. M. Paul et al. Nature **414**, 509 (2001)

Harmonic spectrum

LASER output

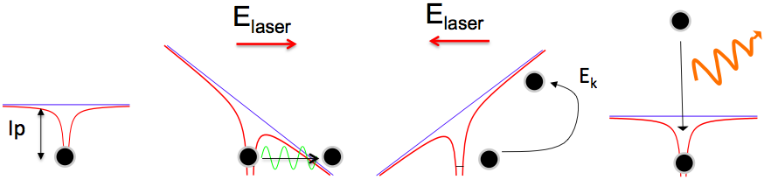


McPherson et al.
JOSA B **4**, 595 (1987)

ω_H=(2n+1) ω_L

HHG: overview

P. B. Corkum, Phys. Rev. Lett. 71, 1994 (1993)
M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum
Phys. Rev. A 49, 2117 (1994)



Electron in fundamental state

1 Tunnel ionization

2 Acceleration in the electric LASER field

3 Recombination to fundamental state

Hamiltonian and HHG

- Electron dynamics in real time

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

- $|\Psi(t_0)\rangle = |\Psi_0\rangle$
- Length gauge (LG) for the field interaction

$$\hat{H} = \hat{H}_0 - \hat{\mu}F(t)$$

- $\hat{H}_0 = -\frac{\nabla^2}{2} - \frac{1}{r} \rightarrow$ field-free Hamiltonian (for hydrogen)
- $-\hat{\mu}F(t) \rightarrow$ coupling between the dipole μ and the external laser field $F(t)$
- Time-evolution of $\hat{\beta} = \hat{\mu}, \hat{v}, \hat{a}$

$$\beta(t) = \langle\Psi(t)|\hat{\beta}|\Psi(t)\rangle$$

- HHG spectrum as Fourier transform of $\beta(t)$

$$P(\omega)_\beta = \left|\frac{1}{t_f - t_i}\int_{t_i}^{t_f} e^{-i\omega t}\beta(t)dt\right|^2$$

Time-dependent configuration interaction

- Field-free $\hat{H}_0$ treated at CIS level
- Configuration interaction expansion with only singly excited configurations

$$
\begin{aligned}
\hat{H}_0|\chi^{CIS}\rangle &= E^{CIS}|\chi^{CIS}\rangle \\
|\chi_n^{CIS}\rangle &= \sum_{ia} C_{i,n}^a |\chi_i^a\rangle \\
|\chi_i^a\rangle &= \hat{a}_a^\dagger \hat{a}_i |\chi_0\rangle
\end{aligned}
$$

- $|\Psi(t)\rangle$ expanded in the field-free CIS eigenstates

$$|\Psi(t)\rangle = \sum_s \tilde{R}_s(t)|\chi_s^{CIS}\rangle$$

- CIS eigenstates in Gaussian basis
- Coefficients $\tilde{R}_s(t)$ by solving the TDSE

Time-dependent configuration interaction

- Explicitly

$$
\begin{aligned}
i\frac{\partial}{\partial t}\sum_s \tilde{R}_s(t)|\chi_s^{CIS}\rangle &= \hat{H}\sum_s \tilde{R}_s(t)|\chi_s^{CIS}\rangle \\
i\frac{\partial}{\partial t}\tilde{R}_r(t) &= \sum_s \left[E_s^{CIS}\delta_{rs} - \langle\chi_r^{CIS}|\hat{\mu}|\chi_s^{CIS}\rangle F(t)\right]\tilde{R}_s(t) \\
\tilde{\mathbf{R}}(t_i+\Delta t) &= \mathbf{U}^\dagger \exp\left[i\mu_d F(t)\Delta t\right]\mathbf{U}\exp\left[-i\mathbf{E}^{CIS}\Delta t\right]\tilde{\mathbf{R}}(t_i)
\end{aligned}
$$

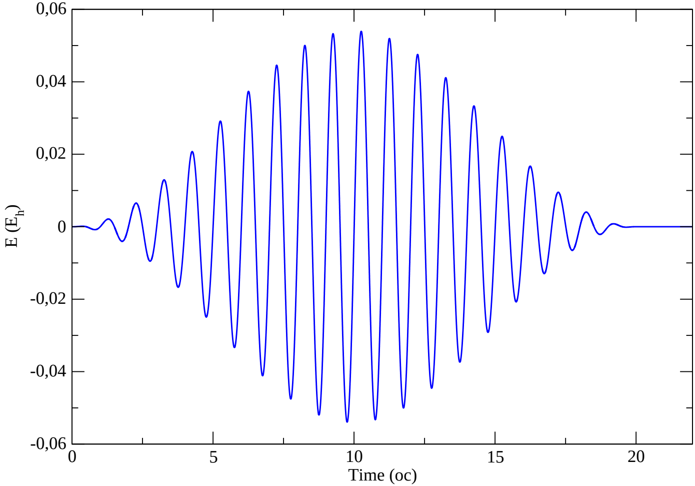
- Time discretization and splitting operator
- $\exp\left[i\mu_d F(t)\Delta t\right]$: diagonal representation of the dipole
- **U** unitary transformation matrix, from energy-diagonal to dipole-diagonal
- $\beta(t)^{CIS} = \sum_{rs}\tilde{R}_r^*(t)\tilde{R}_s(t)\langle\chi_r^{CIS}|\hat{\beta}|\chi_s^{CIS}\rangle$

Modeling the laser field

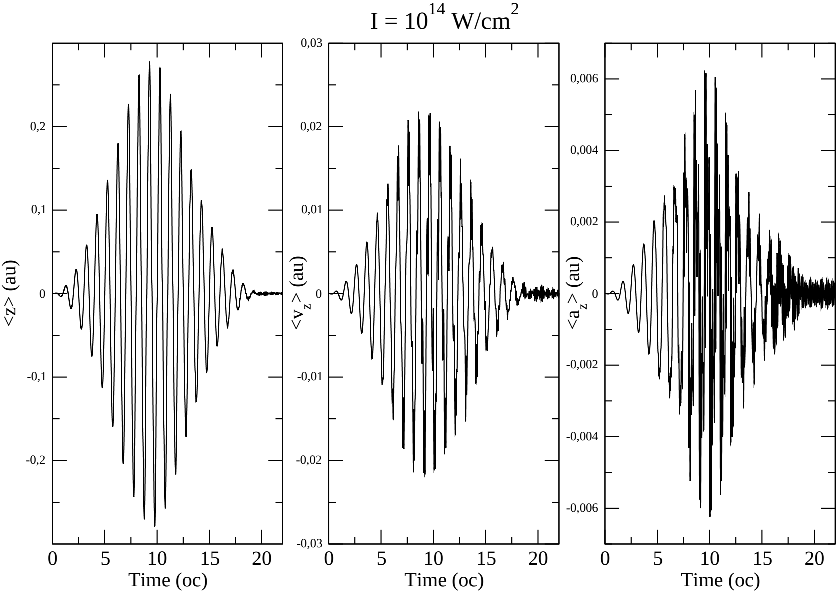
- $\mathbf{F}(t) = \mathbf{n} f(t) \sin(\omega_0 t + \phi)$
- Linear polarization (z axis)

$$f(t) = \begin{cases} f_0 \cos^2(\frac{\pi}{2\sigma}(\sigma - t)) & \text{if} |t - \sigma| \leq \sigma \\ 0 & \text{otherwise} \end{cases}$$

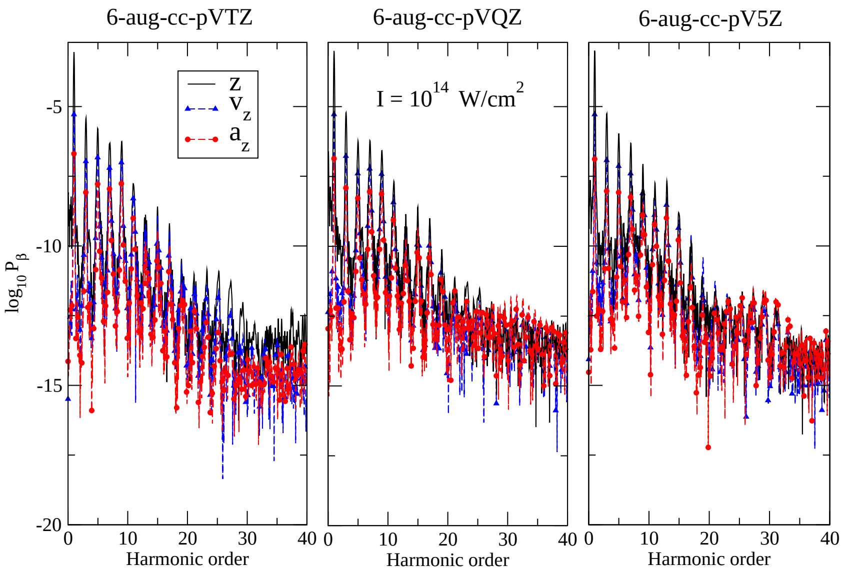
- I (f_0^2)= 5×10^{13}, 10^{14} and 2×10^{14} W/cm^2
- ω_0= 1.55 eV ($\lambda_0 = 800$ nm)
- σ = 20 oc, 1 oc = $\frac{2\pi}{\omega_0}$



Dipole, velocity and acceleration



HHG spectra

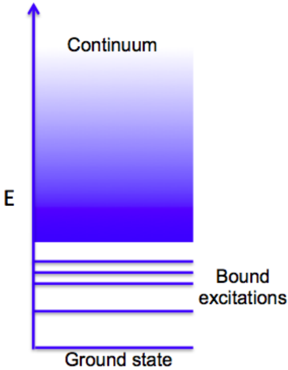


EC, B. Mussard, J. Toulouse and E. Luppi, *in prep.*

L^2 discretization of the continuum

- Goal: reliable representation of (discrete) field-free continuum states from CIS
- Continuum states necessary for modeling HHG

- Asymptotic behaviour from the free-electron Schrödinger equation
- For $\mathbf{r} \to \infty$ $\Psi_{k,l,m}(\mathbf{r}) \sim j_l(kr) Y_{lm}(\theta, \phi)$ $(k = \sqrt{2E})$
- Spherical waves $j_l \propto \frac{\sin[kr]}{r}$ $\quad (\frac{\cos[kr]}{r})$
- L^2 wave functions cannot satisfy asymptotic conditions for the continuum
- How Ψ L^2 representation can contain continuum information?



W. P. Reinhardt, *Comp. Phys. Comm.*, **17**, 1 (1979)

L^2 discretization of the continuum

- Eigenfunctions of a L^2 discretized $\tilde{\hat{H}} \rightarrow$ quadrature representation of $\hat{H}$

$$\hat{H} = \sum_i |\psi_i\rangle E_i \langle\psi_i| + \int_0^\infty dE |\psi(E)\rangle E \langle\psi(E)|$$

$$\tilde{\hat{H}} = \sum_{\tilde{E}_i<0} |\chi_i\rangle \tilde{E}_i \langle\chi_i| + \sum_{\tilde{E}_j>0} |\chi_j\rangle \tilde{E}_j \langle\chi_j|$$

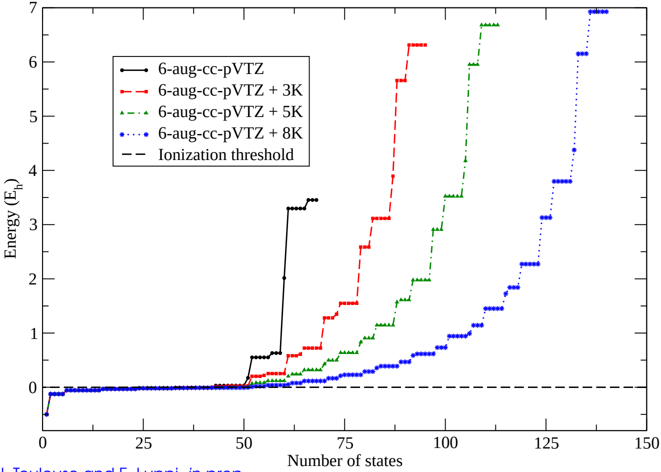
- Arguments to build up “good” basis sets
  1. Increasing the number of “discrete” states with $\tilde{E}_j > 0$
  2. Improving the state density
- Optimal Gaussian functions for the continuum
- Several techniques: fitting Slater (max overlap), fitting Bessel...

W. P. Reinhardt, *Comp. Phys. Comm.*, **17**, 1 (1979)

K. Kaufmann, W. Baumeister and M. Jungen *J. Phys. B: Mol. Opt. Phys.*, **22**, 2223 (1989)

Eigenspectrum

	6-aug-cc-pVTZ	+3K	+5K	+8K
Total	68	95	113	140
Bound	42	42	46	51
Continuum	26	53	67	89
Max energy	3.454	6.313	6.681	6.927



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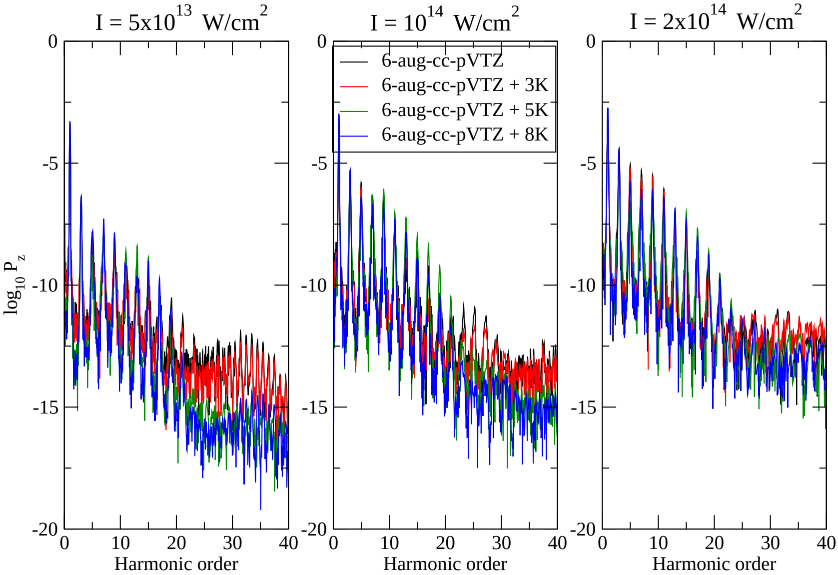
HHG spectra ($\hat{\mu}$ form)



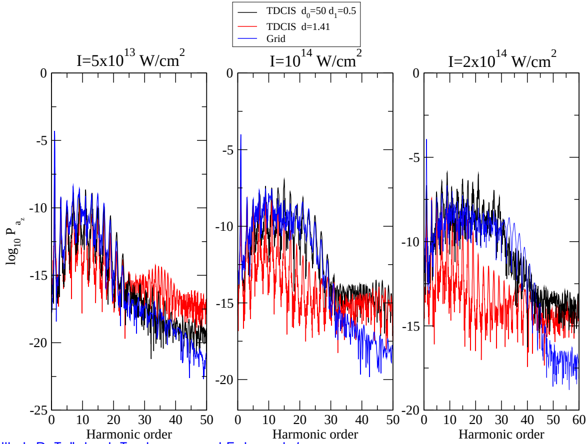
EC, B. Mussard, J. Toulouse and E. Luppi, *in prep.*

HHG spectra ($\hat{a}$ form)

- Escape velocity $v = \frac{d}{\tau}$, d characteristic escape length (au)
- $\tau = \frac{d}{\sqrt{2\epsilon_a}}$

$$\Gamma_n = \begin{cases} 0 & \text{if} \quad E_n^{CIS} < 0, \\ \sum_{ia} |C_{i,n}^a|^2 \sqrt{2\epsilon_a}/d & \text{if} \quad E_n^{CIS} > 0 \quad \text{and} \quad \epsilon_a > 0 \end{cases}$$

- Double-d heuristic model: d_0 if $E_n^{CIS} < I_p^{eff}$, $I_p^{eff} = 3.17 U_p$ ($U_p = \frac{I}{(2\omega_0)^2}$) (6-aug-cc-pVTZ + 8K)



EC, M. Labeye, J. Caillat, R. Taïeb, J. Toulouse and E. Luppi, *in prep.*

Conclusions

- Gaussian-based time-dependent configuration interaction approach able to describe HHG for the hydrogen atom
- Good agreement with grid calculations (different laser parameters)
- Improving the L^2 representation of the continuum $\rightarrow$ extending energy and radial interval for L^2 continuum wavefunctions
- Estimation of the lifetimes beyond the heuristic model
- Molecules (H_2, N_2...)

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- Jeremie Caillat (LCPMR, UPMC)
- Marie Labeye (LCPMR, UPMC)

Appendix: HHG spectrum for the H atom

Ionization issue: heuristic model

- Energy-dependent lifetime τ to account for above-threshold ionization losses
- Ionization rate $\Gamma \rightarrow$ replacing each CIS energy by a complex energy

$$\begin{aligned} E_n^{CIS} &\rightarrow E_n^{CIS} - \frac{i}{2}\Gamma_n \\ \tau_n &= 1/\Gamma_n \end{aligned}$$

- $-\frac{i}{2}\Gamma_n$ as an absorbing potential for state n
- Depopulation with lifetime $\tau_n = 1/\Gamma_n$
- Excited state CIS wavefunction

$$|\chi_n^{CIS}\rangle = \sum_{ia} C_{i,n}^a |\chi_i^a\rangle$$

- Heuristic model $\rightarrow$ similar to the complex absorbing potential approach
- Single-active electron with classical kinetic energy $\epsilon_a = \frac{1}{2}v^2$ ($\epsilon_a > 0$)
- Escape velocity $v = \frac{d}{\tau}$
- d characteristic escape length which the electron can travel during the time interval τ
- $\tau = \frac{d}{\sqrt{2\epsilon_a}}$

$$\Gamma_n = \begin{cases} 0 & \text{if } E_n^{CIS} < 0, \\ \sum_{ia} |C_{i,n}^a|^2 \sqrt{2\epsilon_a}/d & \text{if } E_n^{CIS} > 0 \text{ and } \epsilon_a > 0 \end{cases}$$

S. Klinkusch, P. Saalfrank and T. Klamroth, *J. Chem. Phys.*, **131**, 114304 (2009)

Keldysh model

$\lambda_0 = 800$ nm	5×10^{13} W/cm^2	10^{14} W/cm^2	2×10^{14} W/cm^2
$\gamma = \sqrt{\frac{I_p}{2U_p}}$	1.51	1.06	0.76
U_p (E_h)	0.11	0.22	0.44
N_{cut}	~ 15	~ 21	~ 33

Dipole, velocity and acceleration

- Three forms of HHG spectrum: $P_\mu(\omega)$, $P_v(\omega)$ and $P_a(\omega)$
- If $\langle \mu(t_f) \rangle \sim \langle \mathbf{v}(t_f) \rangle \sim 0$

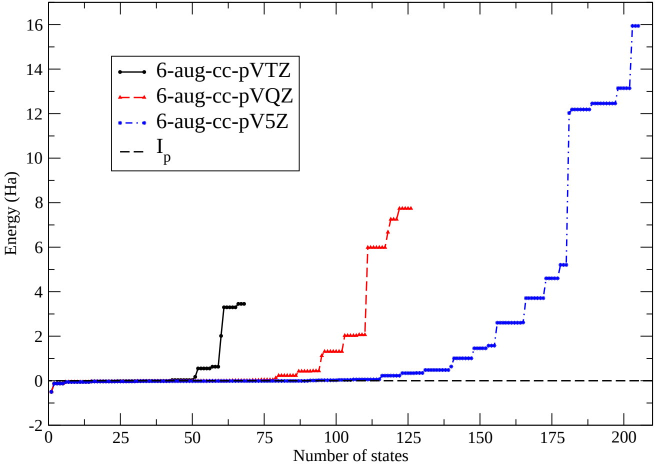
$$P_a(\omega) = \omega^2 P_v(\omega) = \omega^4 P_\mu(\omega)$$

$$\begin{aligned}
\langle \mu(t) \rangle &= \sum_{k,s} R_k^*(t) R_s(t) \langle \psi_k | \hat{\mu} | \psi_s \rangle \\
\langle \mathbf{v}(t) \rangle &= \sum_{k,s} R_k^*(t) R_s(t) \langle \psi_k | \hat{\mathbf{v}} | \psi_s \rangle \\
\langle \mathbf{a}(t) \rangle &= \sum_{k,s} R_k^*(t) R_s(t) \langle \psi_k | \hat{\mathbf{a}} | \psi_s \rangle
\end{aligned}$$

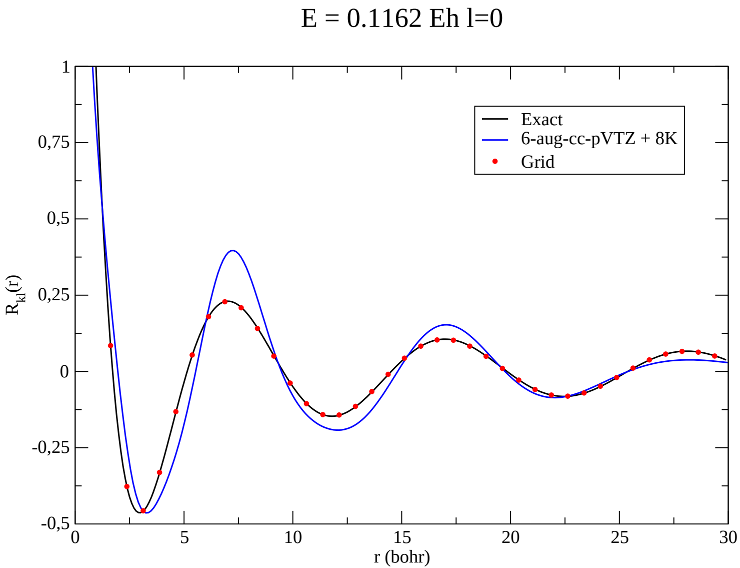
$$\begin{aligned}
\langle \hat{\mu} \rangle &= \langle \hat{\mathbf{r}} \rangle \\
\langle \hat{\mathbf{v}} \rangle &= \frac{d \langle \hat{\mu} \rangle}{dt} = \langle \hat{\mathbf{p}} \rangle = \langle -i \nabla \rangle \\
\langle \hat{\mathbf{a}} \rangle &= \frac{d \langle \hat{v} \rangle}{dt} = \langle -\nabla V - F(t) \rangle
\end{aligned}$$

Electronic states

	6-aug-cc-pVTZ	6-aug-cc-pVQZ	6-aug-cc-pV5Z
Total	68	126	205
Bound	42	63	90
Continuum	26	63	115
Max energy	3.454	7.738	15.941



Continuum radial wave function



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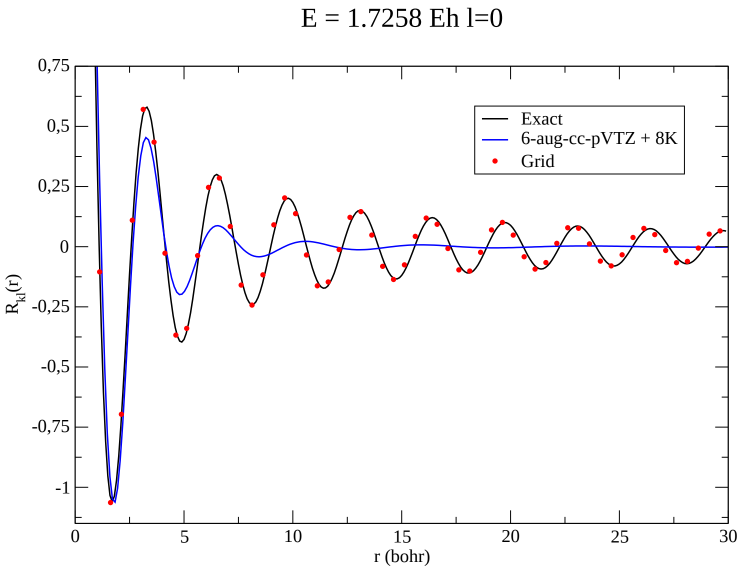
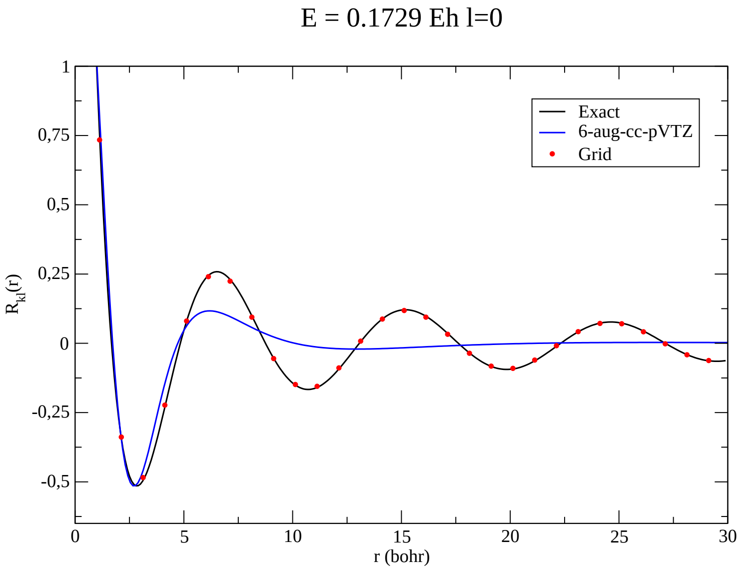
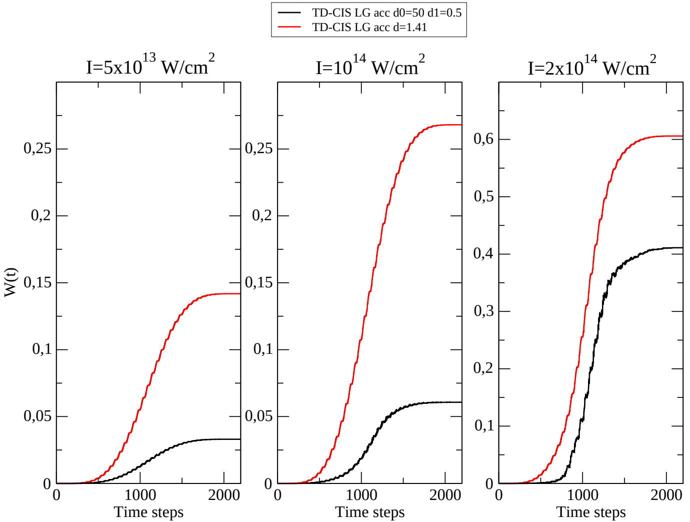


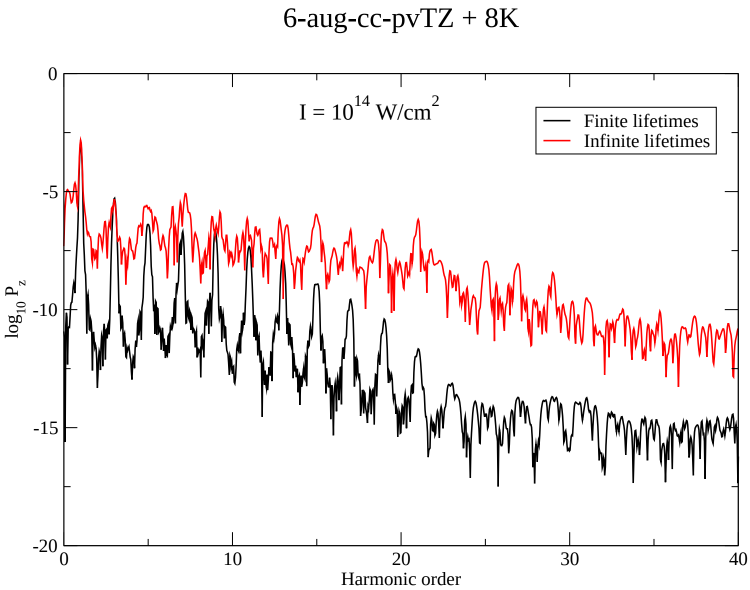
Continuum radial wave function



- Modified heuristic model: two values for d (d_0 and d_1)



Finite lifetimes on HHG spectrum



Appendix: L^2 representation of the continuum

L^2 discretization of the continuum

- Completeness of eigenfunctions ψ_i of $\hat{H}$

$$\hat{H} = \sum_i |\psi_i\rangle E_i \langle\psi_i| + \int_0^\infty dE |\psi(E)\rangle E \langle\psi(E)|$$

- $|\psi_i\rangle$ bound state (L^2) eigenfunctions

$$\begin{aligned} \hat{H}|\psi_i\rangle &= E_i|\psi_i\rangle \\ \langle\psi_i|\psi_j\rangle &= \delta_{ij} \end{aligned}$$

- $|\psi(E)\rangle$ continuum eigenfunctions

$$\begin{aligned} \hat{H}|\psi(E)\rangle &= E|\psi(E)\rangle \\ \langle\psi(E)|\psi(E^{'})\rangle &= \delta(E - E^{'}) \end{aligned}$$

W. P. Reinhardt, *Comp. Phys. Comm.*, **17**, 1 (1979)

L^2 discretization of the continuum

- Matrix representation $\tilde{\hat{H}}$ in finite basis of L^2 functions

$$\begin{aligned} \tilde{\hat{H}}|\chi_i\rangle &= \tilde{E}_i|\chi_i\rangle \\ \langle\chi_i|\chi_j\rangle &= \delta_{ij} \end{aligned}$$

- Discretized spectral resolution

$$\tilde{\hat{H}} = \sum_{\tilde{E}_i<0} |\chi_i\rangle\tilde{E}_i\langle\chi_i| + \sum_{\tilde{E}_j>0} |\chi_j\rangle\tilde{E}_j\langle|\chi_j|$$

- Discrete continuum eigenfunctions as a numerical quadrature

$$\sum_{\tilde{E}_j>0} |\chi_j\rangle\tilde{E}_j\langle\chi_j| \sim \int_0^\infty dE|\psi(E)\rangle E\langle\psi(E)|$$

- For a generic $L^2|\phi\rangle$

$$\begin{aligned} \langle\phi|\hat{H}|\phi\rangle &= \langle\phi|\sum_i |\psi_i\rangle E_i\langle\psi_i|\phi\rangle + \langle\phi|\int_0^\infty dE|\psi(E)\rangle E\langle\psi(E)|\phi\rangle \\ \langle\phi|\int_0^\infty dE|\psi(E)\rangle E\langle\psi(E)|\phi\rangle &\sim \langle\phi|\sum_{\tilde{E}_j>0} |\chi_j\rangle\tilde{E}_j\langle\chi_j|\phi\rangle \quad \text{(from diagonalization)} \\ \langle\phi|\int_0^\infty dE|\psi(E)\rangle E\langle\psi(E)|\phi\rangle &\sim \langle\phi|\sum_j \omega_j|\psi(E_j)\rangle E_j\langle\psi(E_j)|\phi\rangle \quad \text{(from quadrature)} \end{aligned}$$

W. P. Reinhardt, *Comp. Phys. Comm.*, **17**, 1 (1979)

Quadrature for $\hat{\mu}$

- Positive energy eigenvalues of $\tilde{\hat{H}}$ as quadrature abscissas
- Difference in normalization between $|\chi_j\rangle$ and $|\psi(\tilde{E}_j)\rangle$ given by the weight ω_j

$$|\chi_j\rangle \sim (\omega_j)^{1/2}|\psi(\tilde{E}_j)\rangle \quad \text{(over a limited region of coordinate space)}$$

- From completeness $\hat{I} = \sum_j |\psi_j\rangle\langle\psi_j| + \int_0^\infty dE|\psi(E)\rangle\langle\psi(E)|$

$$\begin{aligned}
|\Psi(t)\rangle &= \sum_j R_j(t)|\psi_j\rangle + \int_0^\infty dE \quad R(E,t)|\psi(E)\rangle \\
\langle\Psi(t)|\hat{\mu}|\Psi(t)\rangle &= \sum_{ij} R_i^*(t)R_j(t)\langle\psi_i|\hat{\mu}|\psi_j\rangle \\
&+ \int_0^\infty dEdE' \quad R^*(E',t)R(E,t)\langle\psi(E')|\hat{\mu}|\psi(E)\rangle \\
&+ \sum_j R_j^*(t)\int_0^\infty dE \quad R(E,t)\langle\psi_j|\hat{\mu}|\psi(E)\rangle \\
&+ \sum_j R_j(t)\int_0^\infty dE \quad R^*(E,t)\langle\psi(E)|\hat{\mu}|\psi_j\rangle
\end{aligned}$$

- Discrete representation (recovering CIS equations)

$$\begin{aligned}
|\Psi(t)\rangle &= \sum_j \tilde{R}_j(t)|\chi_j\rangle \\
\langle\Psi(t)|\hat{\mu}|\Psi(t)\rangle &= \sum_{ij} \tilde{R}_i^*(t)\tilde{R}_j(t)\langle\chi_i|\hat{\mu}|\chi_j\rangle
\end{aligned}$$

Gaussian functions for the continuum

$$R_{nl}(r) = (2\zeta)^{3/2}\left(\frac{(n-l-1)!}{[(n+l+1)!]^3}\right)^{1/2}(2\zeta r)^l L_{n+l+1}^{2l+2}(2\zeta r)\exp(-\zeta r)$$

- L_{n+l+1}^{2l+2} associated Laguerre polynomial of degree $n-l-1$
- Approximating *one* Slater (n) by *one* Gaussian (exponent α)

$$\begin{aligned}\chi_{lm}(\alpha,\mathbf{r}) &= N_{\alpha l}r^l\exp(-\alpha r^2)Y_{lm}(\Omega_{\mathbf{r}})\\ \chi_{nlm}(\zeta,\mathbf{r}) &= N_{\zeta n}r^{n-1}\exp(-\zeta r)Y_{lm}(\Omega_{\mathbf{r}})\end{aligned}$$

- Maximization of the overlap S_{nl} between Slater and Gaussian

$$S_{nl}(\alpha) = N_{\zeta n}N_{\alpha l}\int_0^\infty r^{\nu-1}\exp(-\zeta r)\exp(-\alpha r^2)dr$$

- Defining $x = \zeta/2\sqrt{\alpha}$ the maximum overlap is

$$2(n+l+2)(n+l+3)i^{(n+l+3)}\mathrm{erfc}(x_M) - (l+\frac{3}{2})i^{(n+l+1)}\mathrm{erfc}(x_M) = 0$$

- x_M linear function of n for each l

$$x_M(n,l) \sim a_l n + b_l$$

- a_l and b_l tabulated

$$\alpha_{n,l} = \left(\frac{\zeta}{2x_M(n,l)}\right)^2 \sim \left(\frac{\zeta}{2(a_l n + b_l)}\right)^2$$

- $\zeta = 1$ for the scattering electron

$$\alpha_{n,l} \sim \frac{1}{4(a_l n + b_l)^2}$$

K. Kaufmann, W. Baumeister and M. Jungen *J. Phys. B: Mol. Opt. Phys.*, **22**, 2223 (1989)

Appendix: time evolution

Time-evolution operator

- Schrödinger picture: "natural" time-dependence for operators and wavefunctions
- The time-evolution operator $\hat{U}$ defined as

$$|\Psi(t)\rangle \equiv \hat{U}(t, t_0)|\Psi(t_0)\rangle$$

-

$$i\frac{\partial}{\partial t}\hat{U}(t, t_0)|\Psi(t_0)\rangle = \hat{H}\hat{U}(t, t_0)|\Psi(t_0)\rangle$$

- True for any initial function

$$i\frac{\partial}{\partial t}\hat{U}(t, t_0) = \hat{H}\hat{U}(t, t_0)$$

- $\hat{U}(t_0, t_0) = 1$
- $\hat{U}(t, t_0)$ is unitary, time-reversible and short-time propagation holds

Time-evolution operator

- Proof:

$$\begin{aligned} |\Psi(t)\rangle &= \hat{U}(t,t')|\Psi(t')\rangle \\ &= \hat{U}(t,t')\hat{U}(t',t_0)|\Psi(t_0)\rangle \\ \rightarrow \hat{U}(t,t_0) &= \hat{U}(t,t')\hat{U}(t',t_0) \end{aligned}$$

- For $t = t_0$

$$\begin{aligned} 1 &= \hat{U}(t_0,t')\hat{U}(t',t_0) \\ \rightarrow \hat{U}(t,t_0)^{-1} &= \hat{U}(t_0,t) \end{aligned}$$

- Operator equation and its adjoint

$$\begin{aligned} \frac{\partial \hat{U}}{\partial t} &= -i\hat{H}\hat{U} \\ \frac{\partial \hat{U}^\dagger}{\partial t} &= i\hat{U}^\dagger\hat{H} \quad [(\hat{H}\hat{U})^\dagger = \hat{U}^\dagger\hat{H}^\dagger = \hat{U}^\dagger\hat{H}] \end{aligned}$$

Time-evolution operator

$$\begin{aligned}\frac{\partial}{\partial t}\left[\hat{U}^\dagger\hat{U}\right] &= \frac{\partial\hat{U}^\dagger}{\partial t}\hat{U} + \hat{U}^\dagger\frac{\partial\hat{U}}{\partial t} \\ &= i\hat{U}^\dagger\hat{H}\hat{U} - i\hat{U}^\dagger\hat{H}\hat{U} = 0 \\ \rightarrow \hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) &= \text{constant}\end{aligned}$$

- Since $\hat{U}(t_0,t_0) = 1 \rightarrow \hat{U}^\dagger(t_0,t_0) = 1$

$$\begin{aligned}\rightarrow \hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) &= 1 \\ \hat{U}^\dagger(t,t_0) &= \hat{U}^{-1}(t,t_0)\end{aligned}$$

- For time-independent $\hat{H}$ the solution of the TDSE is

$$\hat{U}(t,t_0) = \exp\left[-i\hat{H}(t-t_0)\right]$$

- For time-dependent $\hat{H}$ the solution of the TDSE is

$$\hat{U}(t,t_0) = T\exp\left[-i\int_{t_0}^{t} d\tau\hat{H}(\tau)\right]$$

Time-evolution operator

- Differential operator TDSE

$$i\frac{\partial}{\partial t}\hat{U}(t,t_0) = \hat{H}(t)\hat{U}(t,t_0)$$

- Integral operator TDSE

$$\hat{U}(t,t_0) = 1 - i\int_{t_0}^{t}\hat{H}(t_1)\hat{U}(t_1,t_0)dt_1 \quad (\hat{U}(t_0,t_0) = 1)$$

- The integral equation solved by substitutions

$$\begin{aligned}
\hat{U}_0(t,t_0) &= 1 \\
\hat{U}_1(t,t_0) &= 1 - i\int_{t_0}^{t}\hat{H}(t_1)dt_1 \\
\hat{U}_2(t,t_0) &= 1 - i\int_{t_0}^{t}\hat{H}(t_1)\hat{U}_1(t_1,t_0)dt_1 \\
&= 1 - i\int_{t_0}^{t}\hat{H}(t_1)dt_1 + (-i)^2\int_{t_0}^{t}\hat{H}(t_1)\int_{t_0}^{t_1}\hat{H}(t_2)dt_2dt_1 \\
&\ldots
\end{aligned}$$

Time-evolution operator

$$\hat{U}_N(t,t_0) = 1 + \sum_{k=1}^{N} U^{(k)}(t,t_0)$$

- with

$$U^{(k)}(t,t_0) = (-i)^k \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 ... \int_{t_0}^{t_{k-1}} dt_k \hat{H}(t_1)...\hat{H}(t_k)$$

- By construction $t_0 \leq t_k \leq t_{k-1} \leq ... \leq t_1 \leq t$
- Assuming convergence

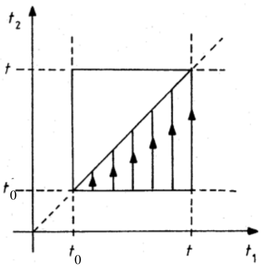
$$\hat{U}(t,t_0) = \lim_{N\to\infty} \hat{U}_N(t,t_0) = 1 + \sum_{k=1}^{\infty} U^{(k)}(t,t_0)$$

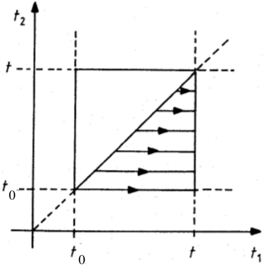
- Perturbation expansion of $\hat{U}(t,t_0)$ in terms of $\hat{H}(t)$

Time-evolution operator

$$\hat{U}^{(2)}(t, t_0) = (-i)^2 \int_{t_0}^{t} \hat{H}(t_1) \int_{t_0}^{t_1} \hat{H}(t_2) dt_2 dt_1$$

- Simplification by removing one integration variable
- Square integration instead of triangular integration
- In general $\hat{H}(t_1)\hat{H}(t_2) \neq \hat{H}(t_2)\hat{H}(t_1)$





$$\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} \hat{H}(t_1)\hat{H}(t_2) dt_2$$
$$= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} \hat{H}(t_1)\hat{H}(t_2) dt_2 + \frac{1}{2}\int_{t_0}^{t} dt_2 \int_{t_2}^{t} \hat{H}(t_1)\hat{H}(t_2) dt_1$$

E. K. U. Gross, E. Runge and O. Heinonen, *Many-particle Theory*, Adam Hilger Ed. (1991)

Time-evolution operator

- By renaming integral variables

$$\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} \hat{H}(t_1)\hat{H}(t_2)dt_2$$
$$= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} \hat{H}(t_1)\hat{H}(t_2)dt_2 + \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_1}^{t} \hat{H}(t_2)\hat{H}(t_1)dt_2$$

- Time-ordered product

$$T[\hat{A}(t_1)\hat{B}(t_2)] \equiv \begin{cases} \hat{A}(t_1)\hat{B}(t_2) & \text{if} \quad t_1 > t_2 \\ \hat{B}(t_2)\hat{A}(t_1) & \text{if} \quad t_2 > t_1 \end{cases}$$

- $$\hat{U}^{(2)}(t,t_0) = \frac{(-i)^2}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 T[\hat{H}(t_1)\hat{H}(t_2)]$$

- T not defined for $t_1 = t_2 \rightarrow [\hat{H}(t_1), \hat{H}(t_2)] = 0$

Time-evolution operator

- Time-ordered product of k operators

$$\hat{U}^{(k)}(t,t_0) = \frac{(-i)^k}{k!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 ... \int_{t_0}^{t} dt_k T[\hat{H}(t_1)\hat{H}(t_2)...\hat{H}(t_k)]$$

- Time-evolution operator

$$\begin{aligned}
\hat{U}(t,t_0) &= \sum_{k=0}^{\infty}\frac{(-i)^k}{k!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 ... \int_{t_0}^{t} dt_k T[\hat{H}(t_1)\hat{H}(t_2)...\hat{H}(t_k)] \\
&= T\sum_{k=0}^{\infty}\frac{(-i)^k}{k!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 ... \int_{t_0}^{t} dt_k \hat{H}(t_1)\hat{H}(t_2)...\hat{H}(t_k) \\
&= T\sum_{k=0}^{\infty}\frac{(-i)^k}{k!}\left(\int_{t_0}^{t} d\tau \hat{H}(\tau)\right)^k \\
&= T\exp\left[-i\int_{t_0}^{t} d\tau \hat{H}(\tau)\right]
\end{aligned}$$

Properties of $\hat{U}$: summary

$$\begin{aligned}\hat{U}(t,t_0) &= T\exp\left[-i\int_{t_0}^{t} d\tau \hat{H}(\tau)\right] \\ &= \exp\left[-i\int_{t_0}^{t} d\tau \hat{H}(\tau)\right] \quad \text{if} \quad [\hat{H}(t_1),\hat{H}(t_2)] = 0 \\ &= \exp\left[-i\hat{H}(t-t_0)\right] \quad \text{if} \quad \hat{H} \neq \hat{H}(t)\end{aligned}$$

- $\hat{U}(t,t_0)$ is unitary: $\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) = 1$
- $\hat{U}$ has time-reversal symmetry: $\hat{U}(t,t_0) = \hat{U}^{-1}(t_0,t)$
- $\hat{U}(t,t_0) = \hat{U}(t,t_1)\hat{U}(t_1,t_0)$

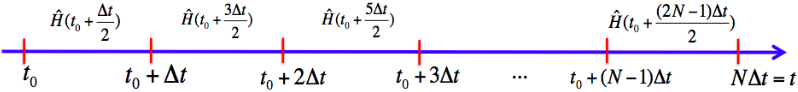
$$\hat{U}(t,t_0) = \prod_{i=0}^{N-1} \hat{U}(t_i+\Delta t, t_i) \quad (t_{i+1} = t_i + \Delta t, t = t_0 + N\Delta t)$$

- Short-time propagation

$$|\Psi(t_i+\Delta t)\rangle = T\exp\left[-i\int_{t_i}^{t_i+\Delta t} d\tau \hat{H}(\tau)\right]|\Psi(t_i)\rangle$$

Time discretization

- Short-time propagation is exact
- But solving the integral is impractical



$$
\begin{aligned}
\hat{U}(t_0 + N\Delta t, t_0) &= \prod_{i=0}^{N-1} T\exp\left[-i\int_{t_i}^{t_i+\Delta t} d\tau \hat{H}(\tau)\right] \\
&\sim \prod_{i=0}^{N-1} F\left[-i\hat{H}(t_0 + f(i)\Delta t)\Delta t\right]
\end{aligned}
$$

Time discretization

- Why discretizing $[t_0, t]$?
  - time dependence of $\hat{H}$ is alleviated
  - Smaller values for the exp argument (increases linearly with Δt)
- $\Delta t \leq \Delta t_{max} \sim 1/\omega_{max}$ (ω_{max} maximum frequency)
- ω_{max} of $\hat{H}$ determined by the kinetic term

$$\omega_{max} = \frac{G_{max}^2}{2} = \frac{2\pi^2}{h^2}$$

- $G_{max} \rightarrow$ maximum reciprocal lattice vector in pw expansion
- $h \rightarrow$ mesh radial spacing in real-space discretization of $\hat{H}$
- Criterion for Gaussian basis?

A. Castro, M. A. L. Marques and A. Rubio, *J. Chem. Phys.*, **121**, 3425 (2004)

Time discretization

- Algorithm stable, accurate and efficient
- Stable:
- $\forall \Delta t < \Delta t_{\text{max}}$ $\hat{U}$ fulfills "contractivity", $||\hat{U}(t + \Delta t, t)|| \leq 1$
- If $\hat{U}$ is unitary is also contractive
- A non-contractive scheme can yield larger errors at each time step
- Accurate:
- "Best" method to minimize the error
- Efficiency:
- Larger Δt

A. Castro, M. A. L. Marques and A. Rubio, *J. Chem. Phys.*, **121**, 3425 (2004)

Approximating $\hat{U}$

- Finding an approximate $|\Psi(t_i + \Delta t)\rangle$ from $|\Psi(t_i)\rangle$ and $\hat{H}(\tau)$ $(t_i \leq \tau \leq t_i + \Delta t)$
- Crank-Nicolson

$$\hat{U}_{\text{CN}}(t_i + \Delta t, t_i) \equiv \frac{1 - \frac{i}{2}\Delta t \hat{H}(t_i + \Delta t/2)}{1 + \frac{i}{2}\Delta t \hat{H}(t_i + \Delta t/2)}$$

- Linear system (implicit midpoint method)

$$\begin{aligned} \hat{L}|\Psi(t_i + \Delta t)\rangle &= |b\rangle \\ \hat{L} &= 1 + \frac{i}{2}\Delta t \hat{H}(t_i + \Delta t/2) \\ |b\rangle &= \left[1 - \frac{i}{2}\Delta t \hat{H}(t_i + \Delta t/2)\right] |\Psi(t_i)\rangle \end{aligned}$$

- $\| |\Psi(t_i + \Delta t)\rangle - |\Psi_{\text{CN}}(t_i + \Delta t)\rangle \| \propto \Delta t^2$
- Dependence on the third time derivative of $|\Psi\rangle$ (high oscillatory)
- Accurate only with small Δt
- Unitary and time-reversal symmetry

Approximating $\hat{U}$

- Exponential midpoint rule

$$\hat{U}_{\mathrm{EM}}(t_i + \Delta t, t_i) \equiv \exp\left[-i\Delta t \hat{H}(t_i + \Delta t/2)\right]$$

- Exponential calculated exactly
- Calculated at midpoint $t_i + \Delta t/2$
- $\| |\Psi(t_i + \Delta t)\rangle - |\Psi_{\mathrm{EM}}(t_i + \Delta t)\rangle \| \propto \Delta t^2$
- Independent of time derivatives of $|\Psi\rangle$
- Unitary and time-reversible
- Improved over Crank-Nicolson
- Larger Δt can be taken for the same accuracy

Approximating $\hat{U}$

- Splitting operator (SO)
- $\exp\left[\hat{A}+\hat{B}\right] = \exp\left[\hat{A}\right]\exp\left[\hat{B}\right]$ only if $\left[\hat{A},\hat{B}\right] = 0$
- $\hat{H} = \hat{H}_0 - \hat{\mu}F(t)$, $\bar{t}_i = t_i + \Delta t/2$

$$\exp\left[-i\left(\hat{H}_0 - \hat{\mu}F(\bar{t}_i)\right)\Delta t\right] = \exp\left[-i\hat{H}_0\Delta t\right]\exp\left[i\hat{\mu}F(\bar{t}_i)\Delta t\right] + \mathcal{O}(\Delta t^2)$$

- or

$$\exp\left[i\hat{\mu}F(\bar{t}_i)/2 * \Delta t\right]\exp\left[-i\hat{H}_0\Delta t\right]\exp\left[i\hat{\mu}F(\bar{t}_i)/2 * \Delta t\right] + \mathcal{O}(\Delta t^3)$$

- Unitary and stable, $||\nabla^2\Psi||$ in the error
- Convenient for diagonal representation of each $\exp\left[\hat{A}\right]$
- Error(EM) and error(SO)