Eleonora Luppi

Laboratoire de Chimie Théorique, Sorbonne Université

Molecular High-Harmonic Generation from Quantum Chemistry :

Toward Predictive Spectroscopy

High Harmonic Generation (HHG)

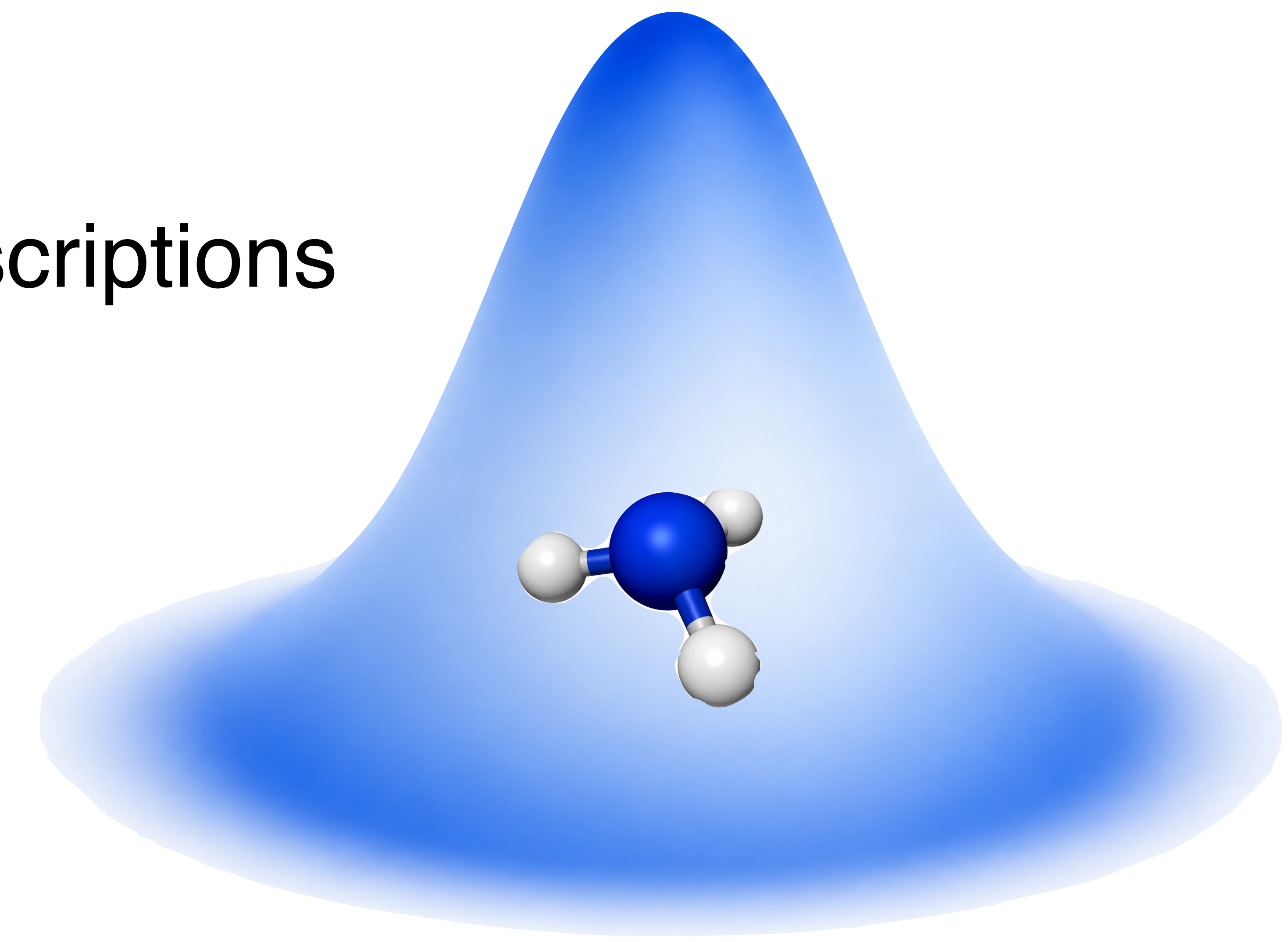
- Source of attosecond pulses (2023 Nobel Prize in Physics)
- Ultrafast electronic dynamics (Attochemistry)

Ab initio Quantum Chemistry (QC) and localised Gaussian orbitals

Accurate electron correlation → Accurate molecular properties

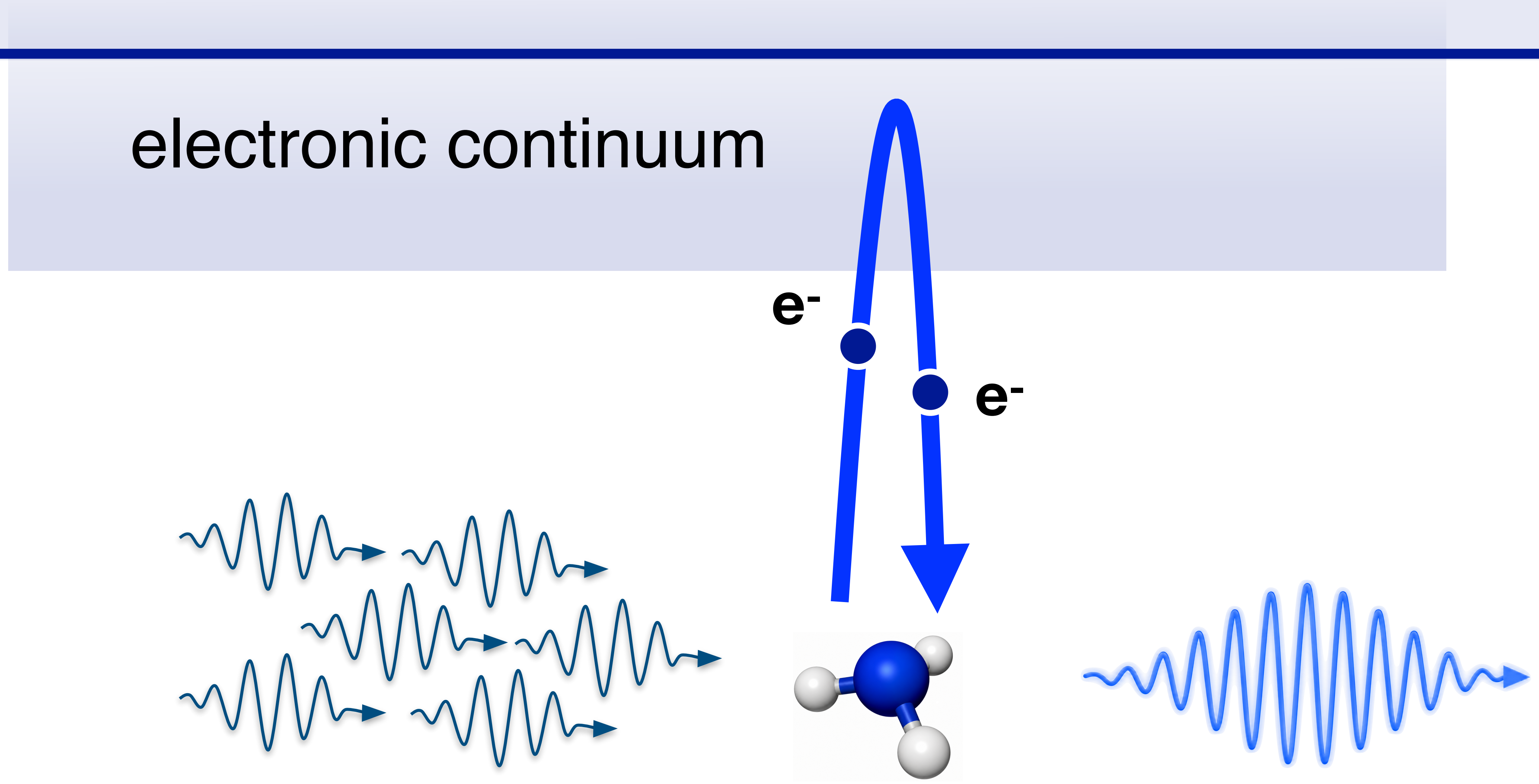
energy, vibrations, reactivity, excitations …

Localized Gaussian orbital descriptions



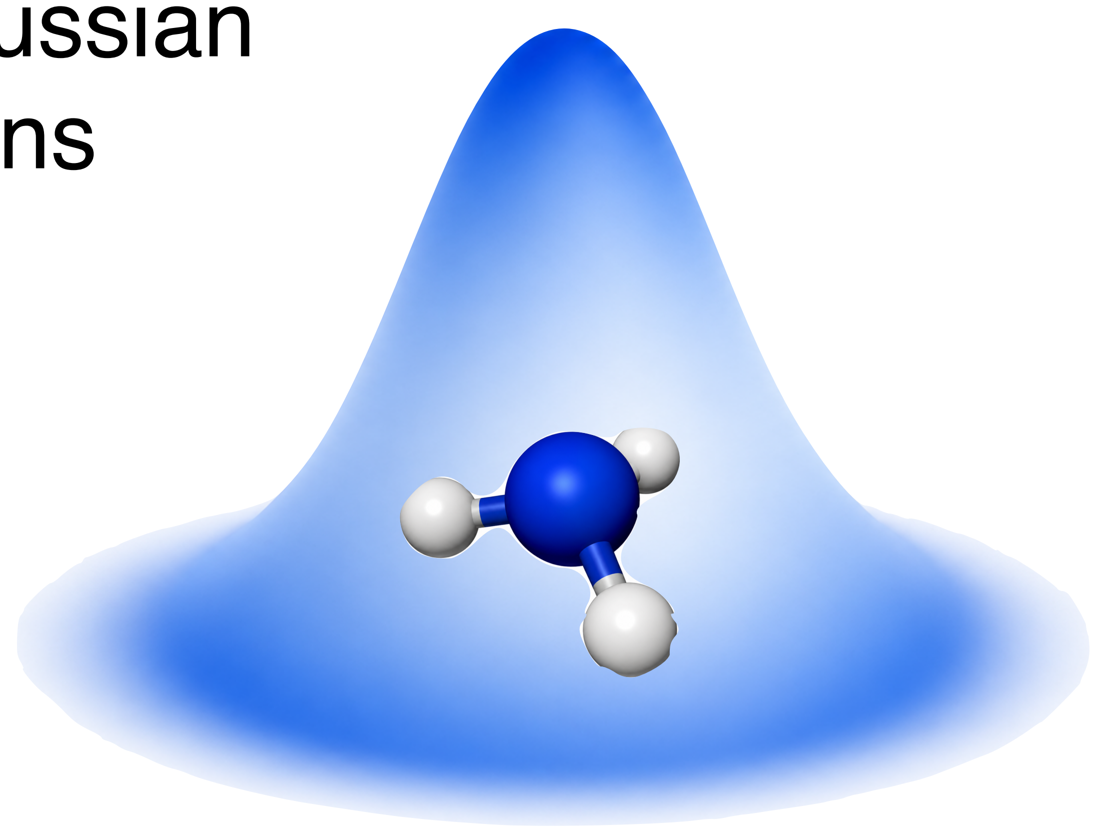
What about electron dynamics in strong field ?

HHG and QC



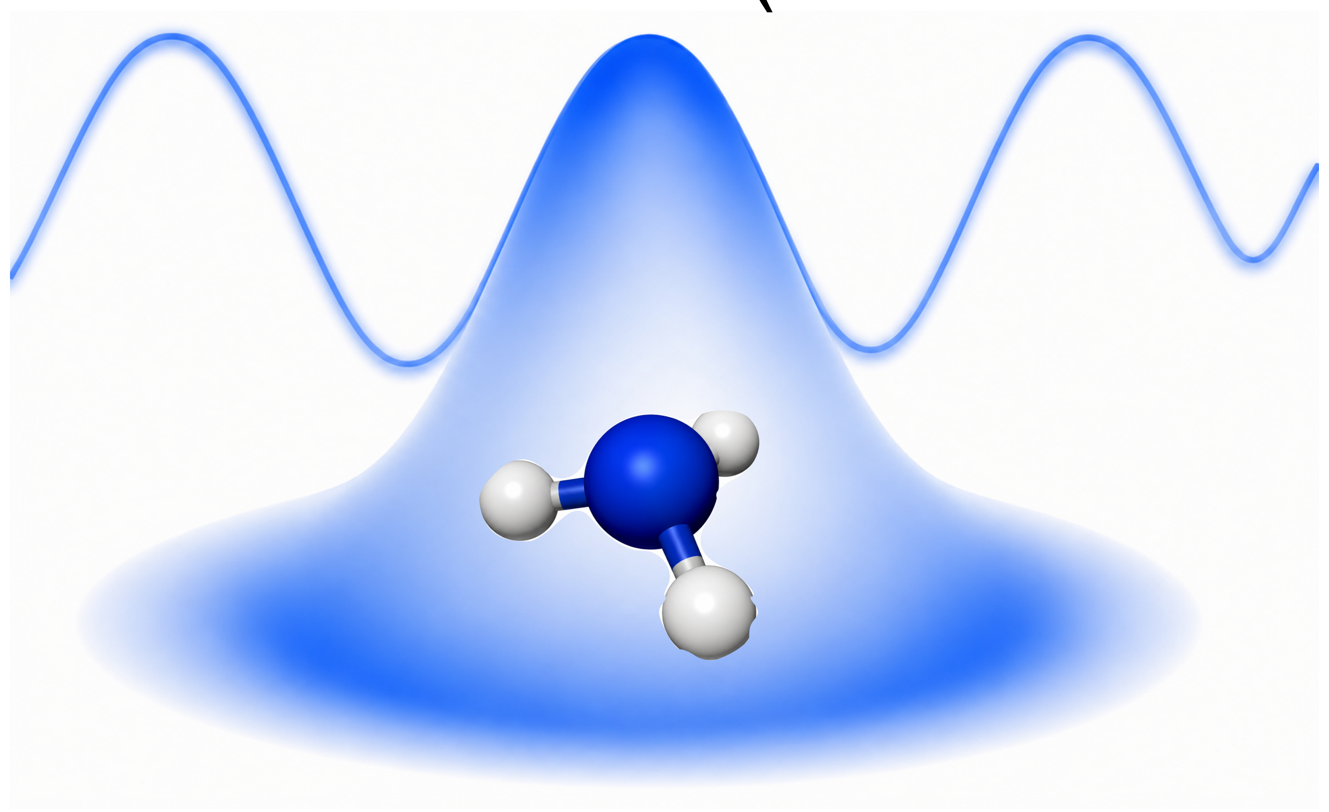
QC

Localized Gaussian descriptions



HHG

Delocalised description (electronic continuum)



Main developments :

- Modeling electronic continuum
- Ionisation
- Interference effects

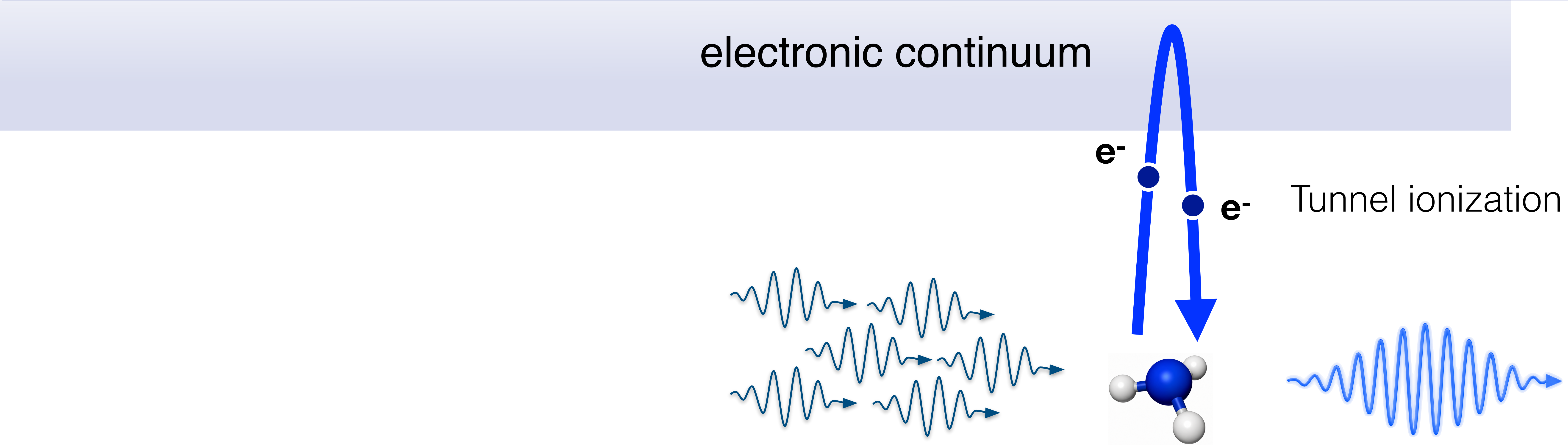
Light

J. Chem. Phys. 163, 024135 (2025)
PCCP 27, 12801–12811 (2025).
J. Chem. Phys. 161, 204111 (2024)
JCTC 14, 5846–5858 (2018)

Outline

- Quantum Chemistry in real time : TD-CIS and TD-CSID
- Optimal-Gaussian for continuum
- Ionisation
- Dynamical Symmetry and TD-MO decomposition for HHG

HHG and QC



Tunnel ionization → acceleration → recombination

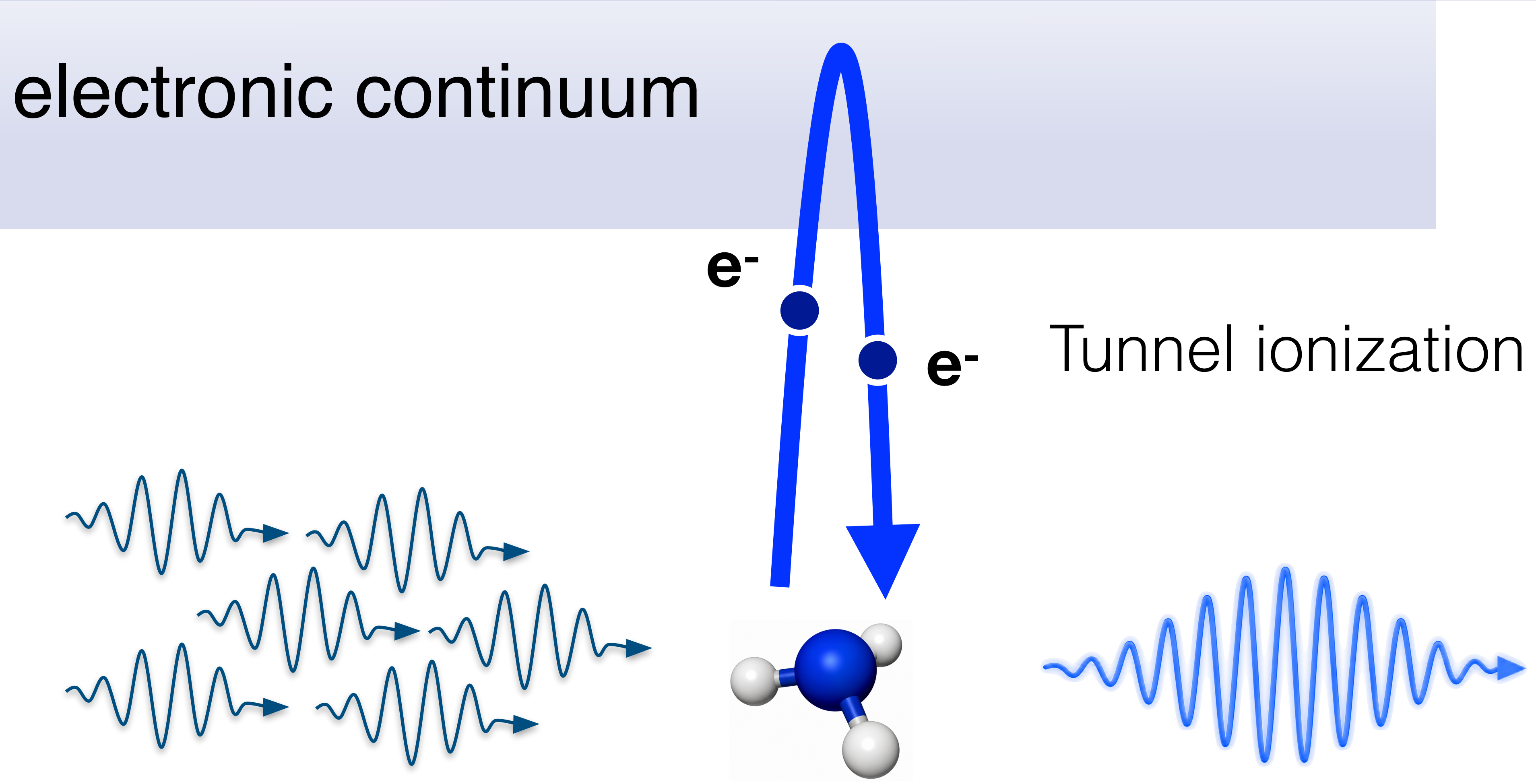
3SM

Corkum PRL (1993)
Kulander et al. SILAP III Workshop (1993)
Lewenstein et al. PRA (1994)

Real-time electron dynamics in the laser field

$$i \frac{\partial}{\partial t} | \Psi(t) \rangle = \left(\hat{H}_0 - \hat{\mu} \cdot \mathbf{E}(t) \right) | \Psi(t) \rangle$$

HHG and Quantum Chemistry



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Real-time electron dynamics in the laser field

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = \left(\hat{H}_0 - \hat{\mu} \cdot \mathbf{E}(t) \right) |\Psi(t)\rangle$$

Correlated many-electron expansion

$$|\Psi(t)\rangle = \sum_n c_n(t) \, |\Psi_n^{\mathrm{CISD}}\rangle$$

Beyond single-active-electron models

E. Coccia, E. Luppi, Theor. Chem. Acc. 135, 43 (2016).
E. Luppi, M. Head-Gordon, J. Chem. Phys. 139, 074121 (2013).

Quantum chemistry

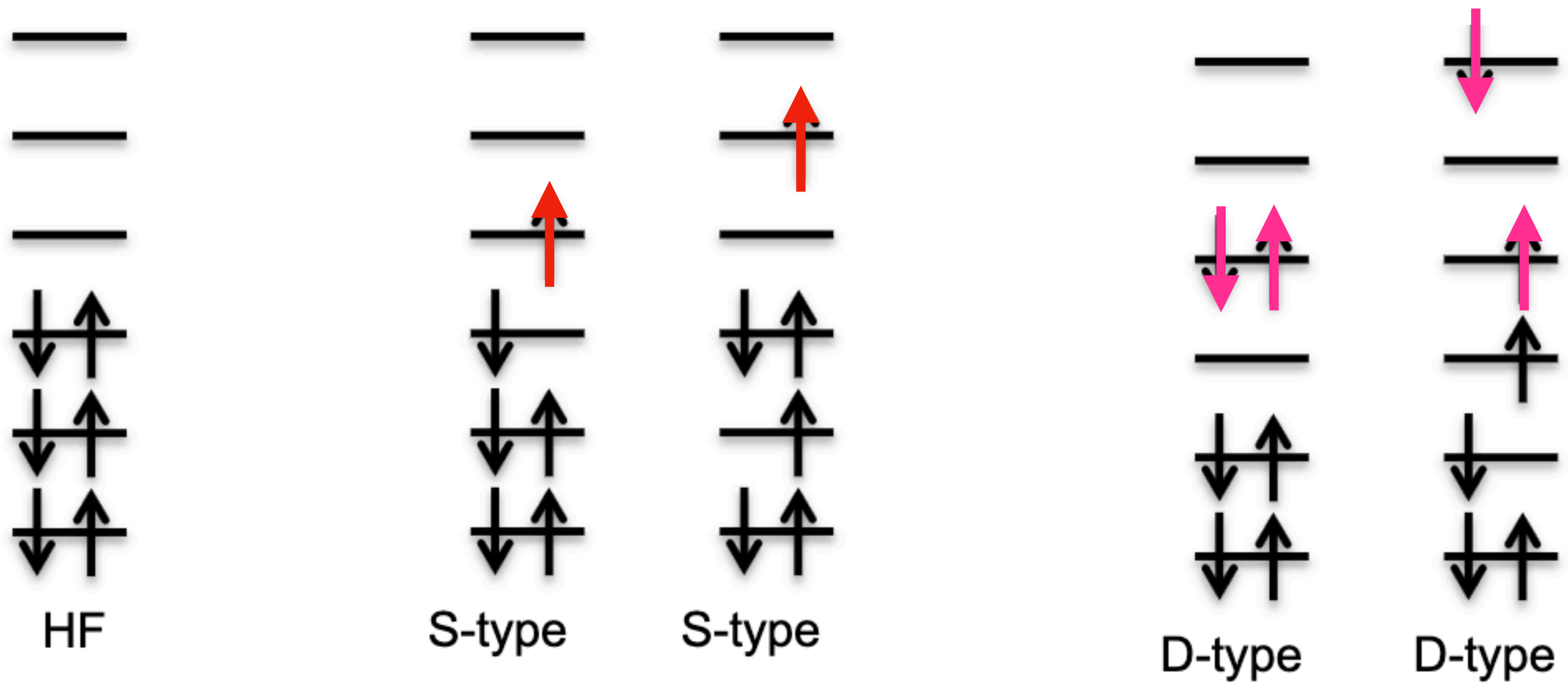
Correlated electron dynamics beyond the single-active-electron approximation

$$|\Psi_n^{\mathrm{CISD}}\rangle = c_0|\Phi_0\rangle + \sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} c_i^a |\Phi_i^a\rangle + \sum_{i<j}^{\mathrm{occ}}\sum_{a<b}^{\mathrm{virt}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle$$

Single excitation correlations

Double excitation correlations

Single and double excitations account for electron correlation effects

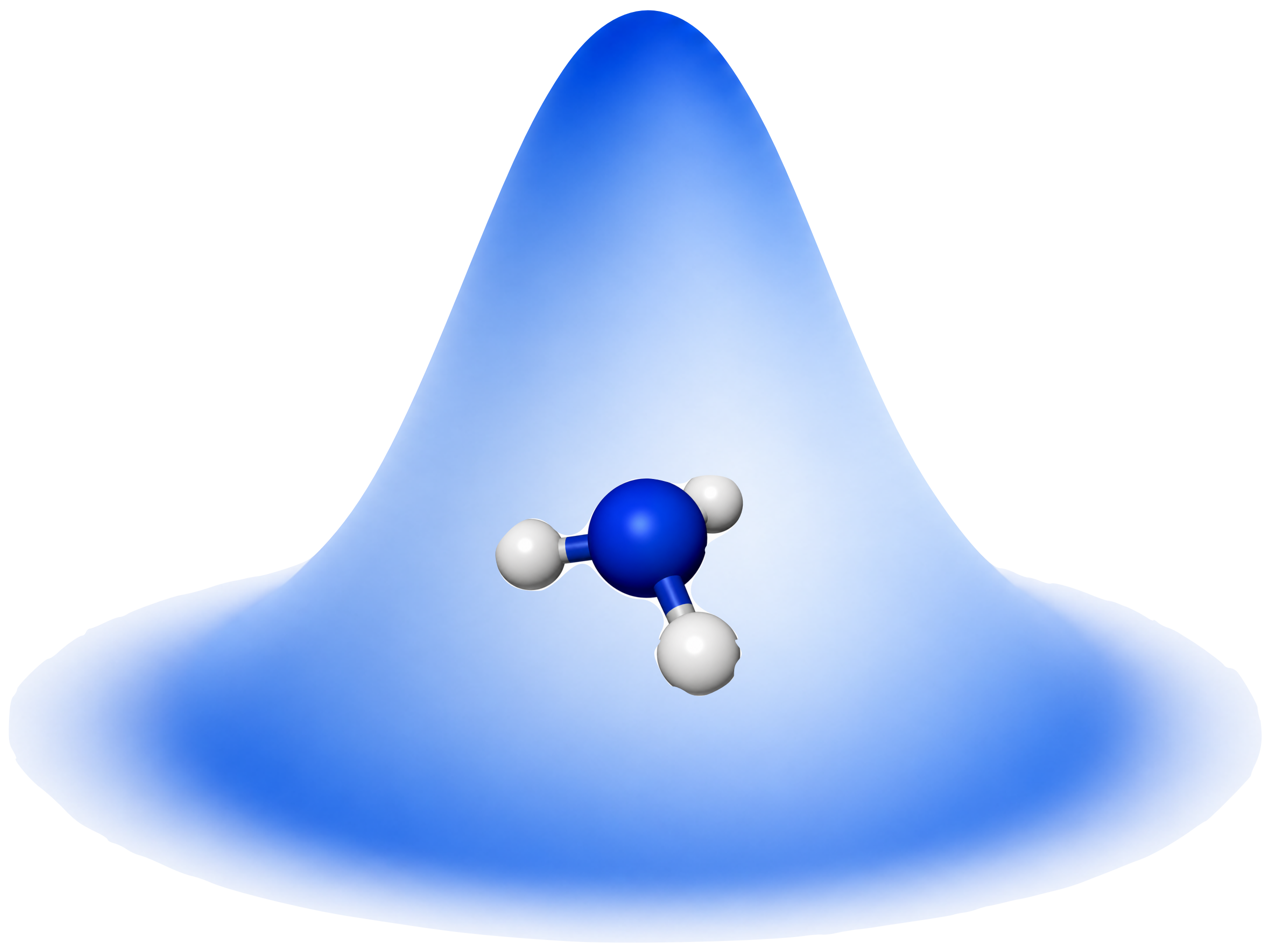


A. Szabo, N. S. Ostlund, Modern Quantum Chemistry, Dover (1996)

Quantum chemistry

$$|\Psi_n^{\text{CISD}}\rangle = c_0|\Phi_0\rangle + \sum_i^{\text{occ}}\sum_a^{\text{virt}} c_i^a|\Phi_i^a\rangle + \sum_{i<j}^{\text{occ}}\sum_{a<b}^{\text{virt}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle$$

Representation in Localized Gaussian descriptions



Gaussian basis set

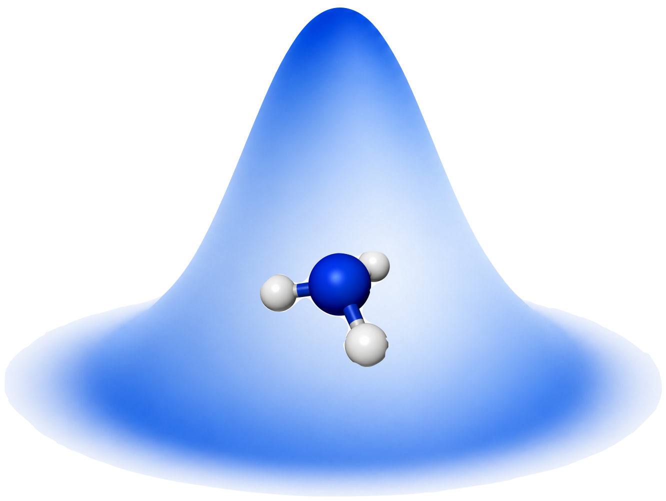
d-aug-cc-pV5Z

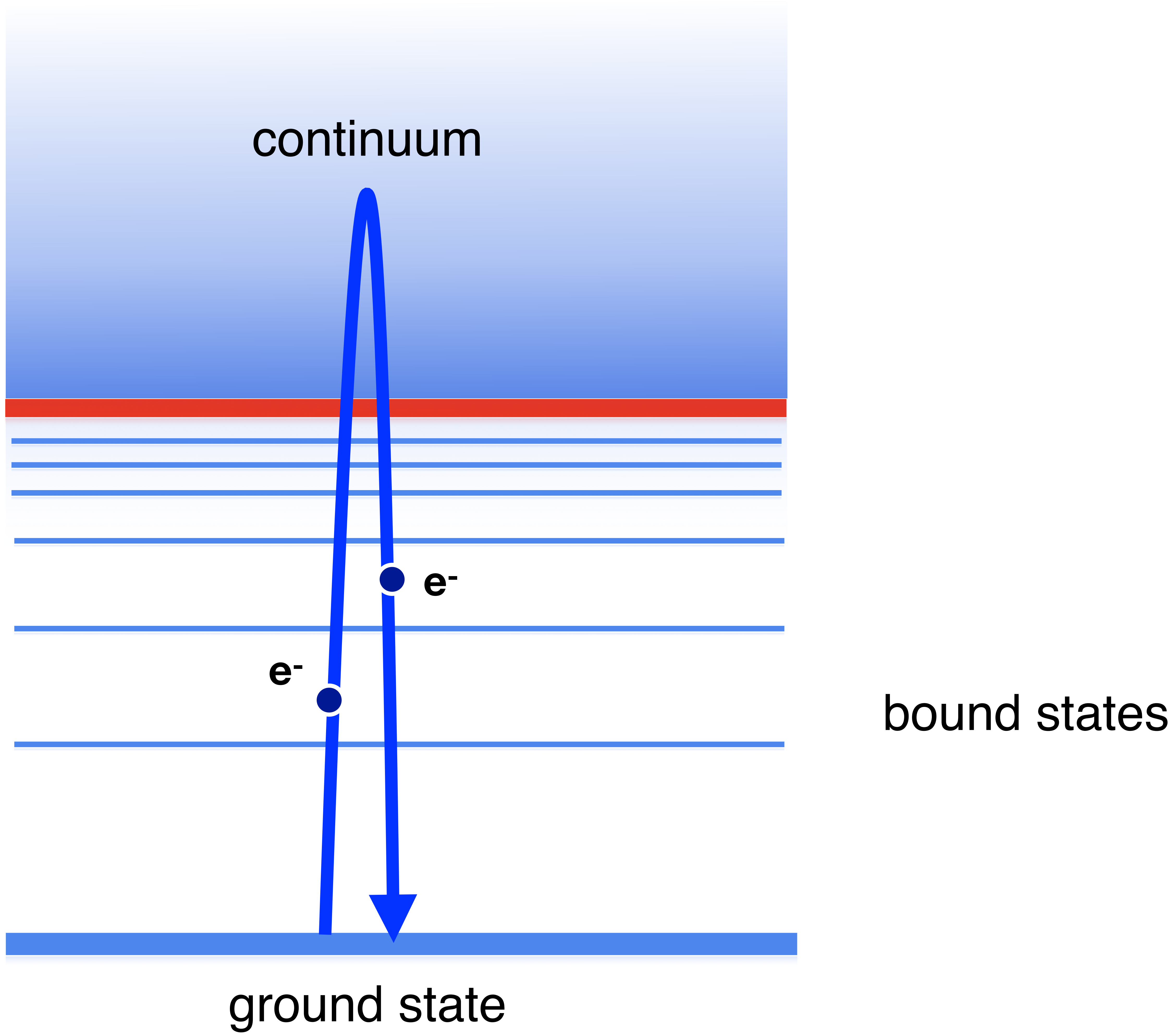
diffuse functions

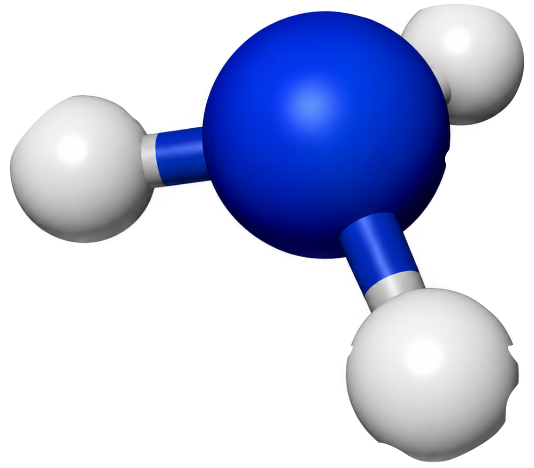
angular momentum

Quantum Chemistry : Ground-Bound-Continuum

Standard Gaussian basis set

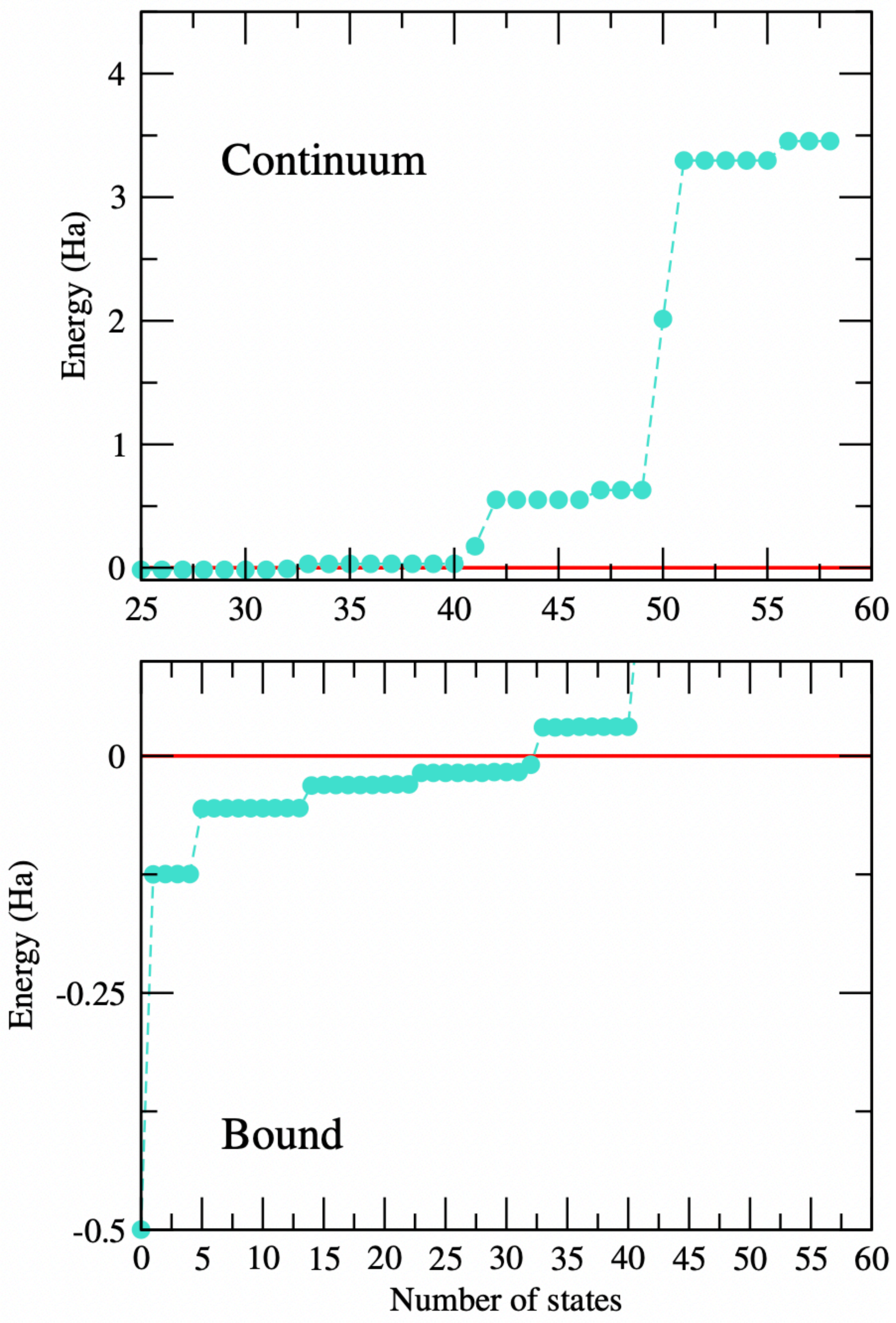






F. White, C. J. Heide, P. Saalfrank, M. Head-Gordon, E. Luppi, *Mol. Phys.* 114, 947–956 (2016)

Standard Gaussian basis sets : the example of the H atom

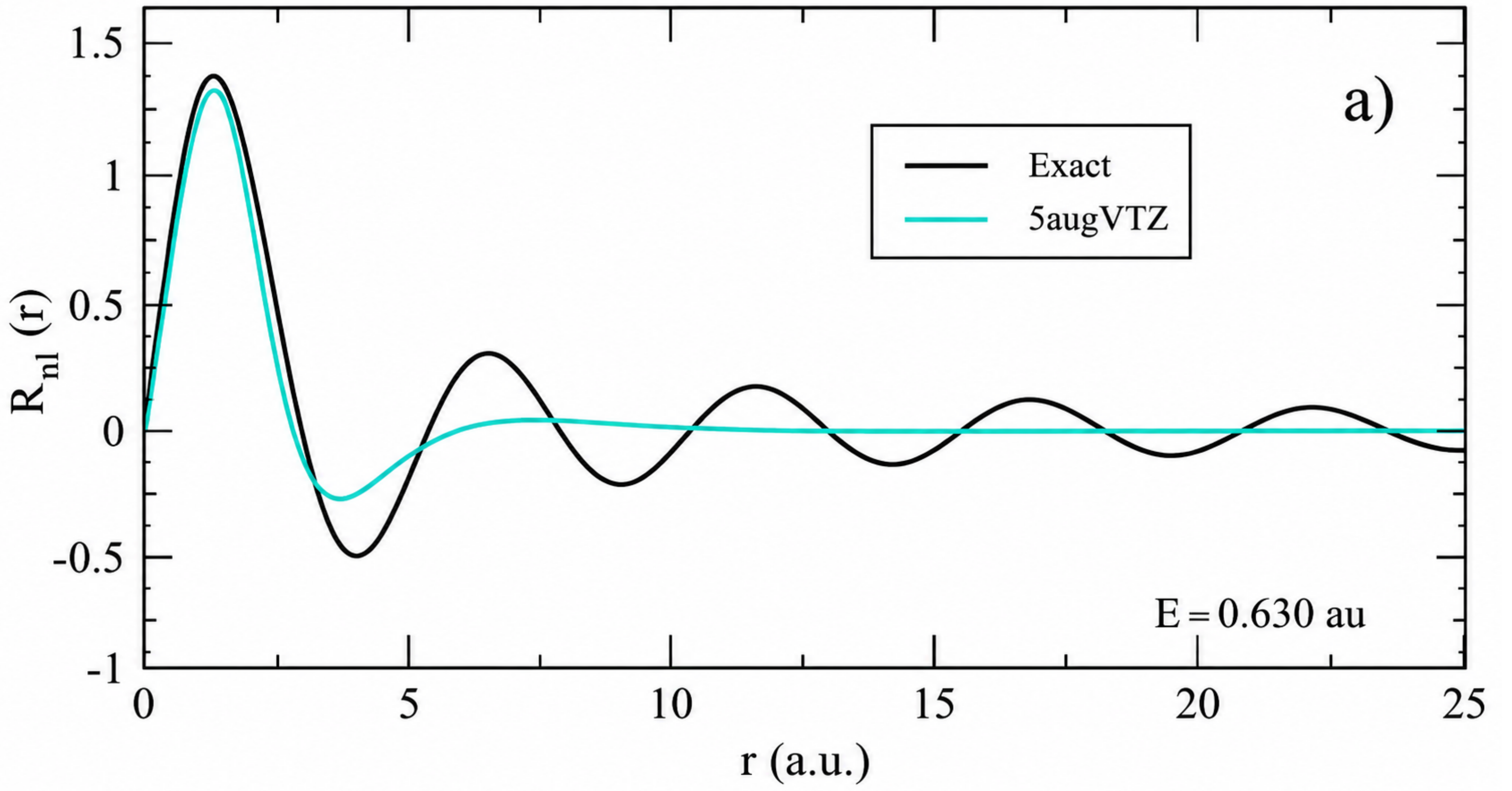


Dunning's Gaussian Basis Set

5-aug-cc-pVTZ

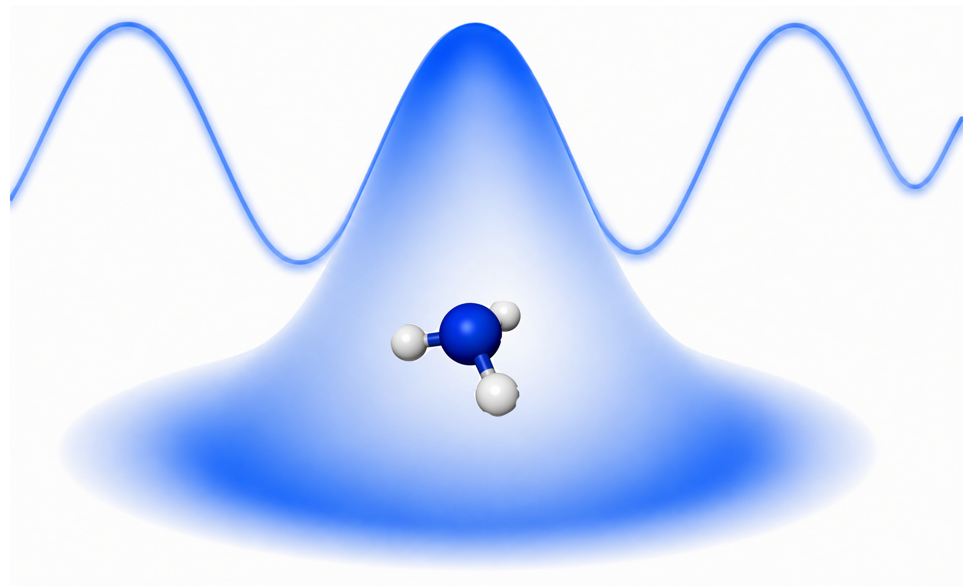
5 sets of diffuse functions
for each angular momentum

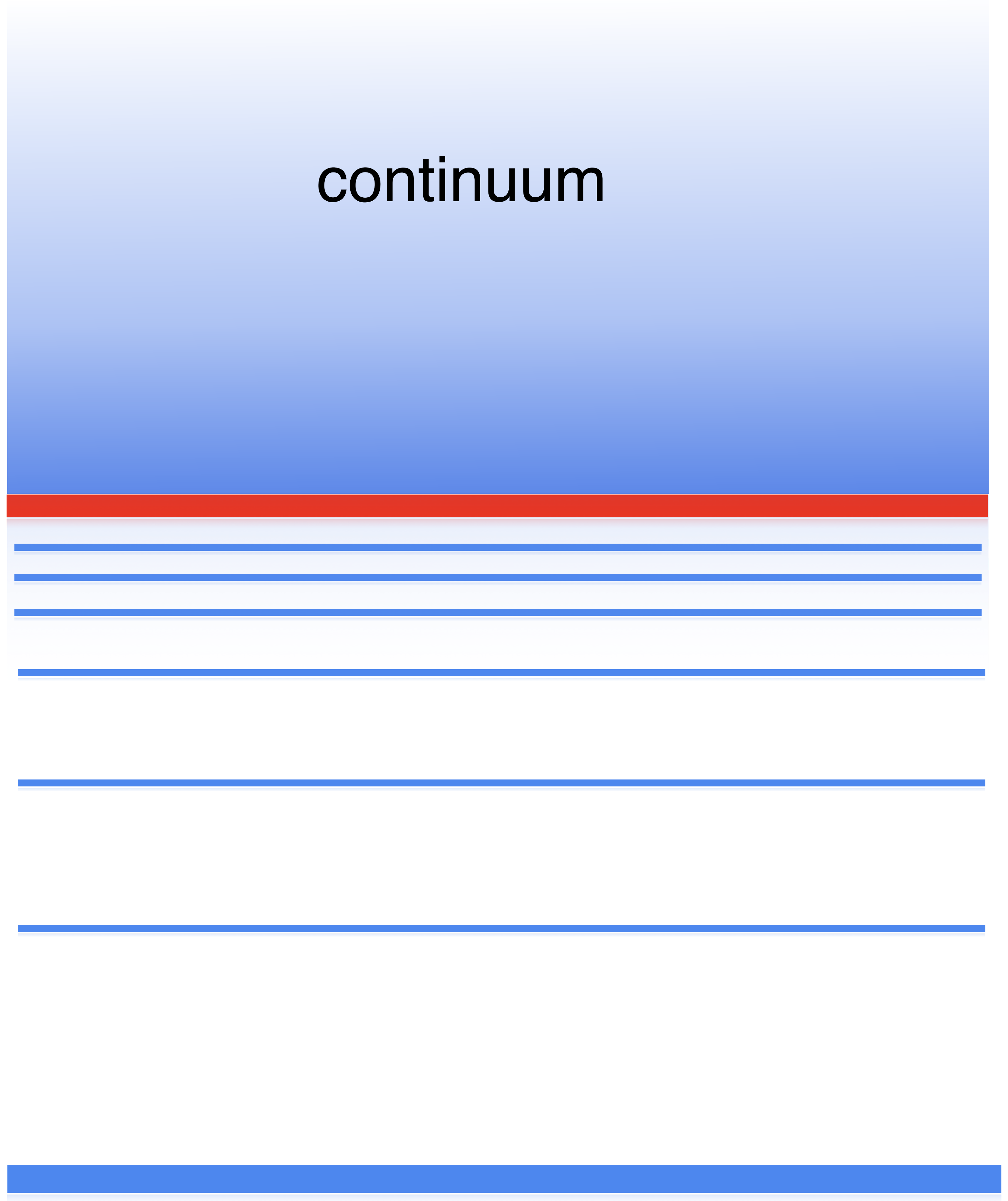
angular momentum: s,p,d



Quantum Chemistry : Ground-Bound-Continuum

Standard Gaussian basis set + Optimised Gaussian for the continuum





bound states

ground state

Kaufmann (K) functions:

Kaufmann, Baumeister and Jungen, JPB: At. Mol. Opt. Phys. (1989)

Bessel (B) functions:

Nestmann and Peyerimhoff, JPB: At. Mol. Opt. Phys. (1989);
Faure, Gorfinkiel, Morgan and Tennyson, CPC (2002)

Active Range Optimized (ARO) functions:

Wozniak, Lesiuk, Przybytek et al., JCP (2021)

Time-Dependent Gaussian Basis Sets

Schrader, Kristiansen, Pedersen, Kvaal, J. Chem. Theory Comput. (2025)

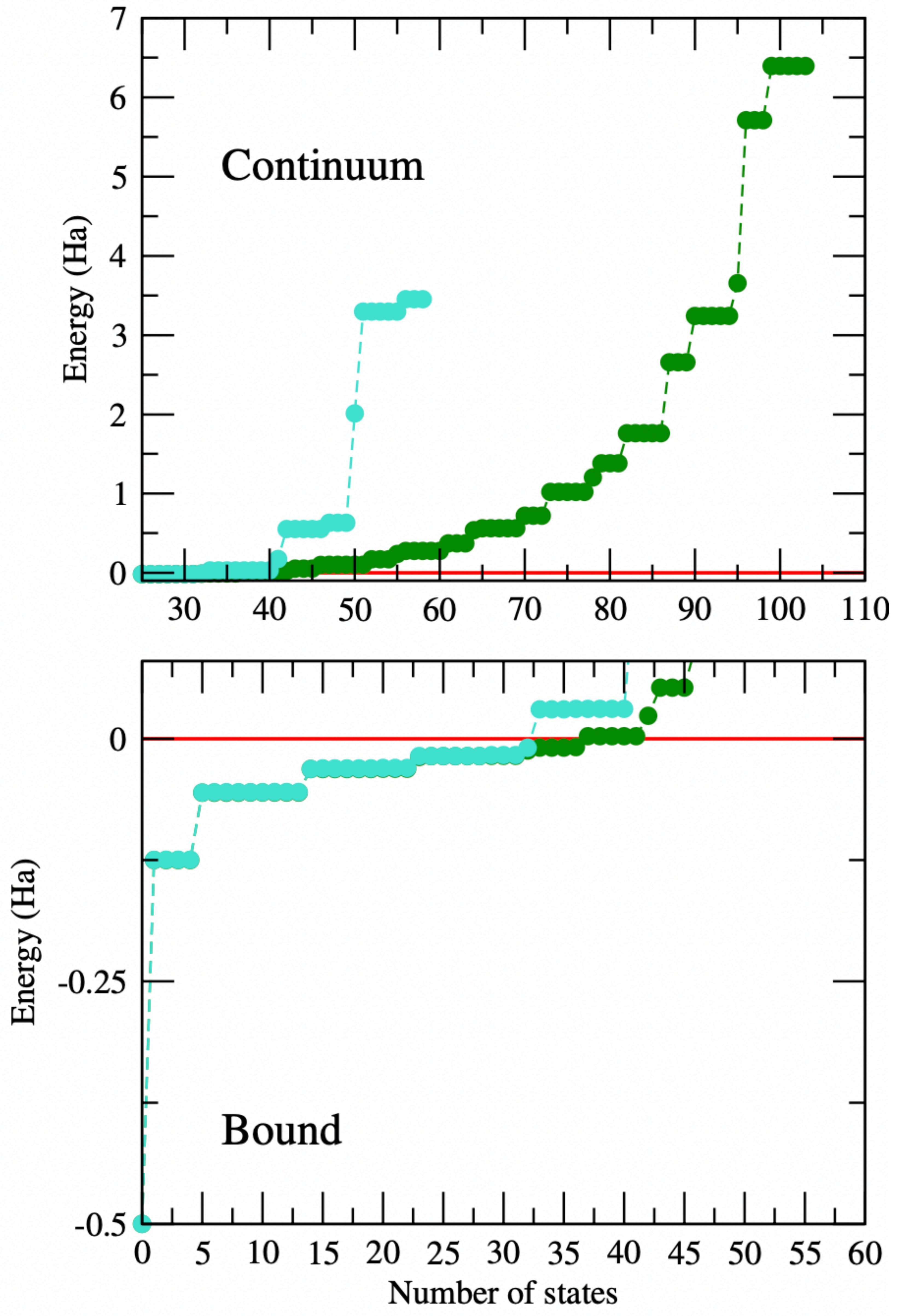
Photoionization spectra in Gaussian basis sets

I. Duchemin and A. Levitt, J. Chem. Phys. (2023)

C. Morassut, E. Coccia, E. Luppi, J. Chem. Phys. 159, 124112 (2023)

Morassut, Ravindran, Ciavardini, Luppi, De Ninno and Coccia JCPA (2024)

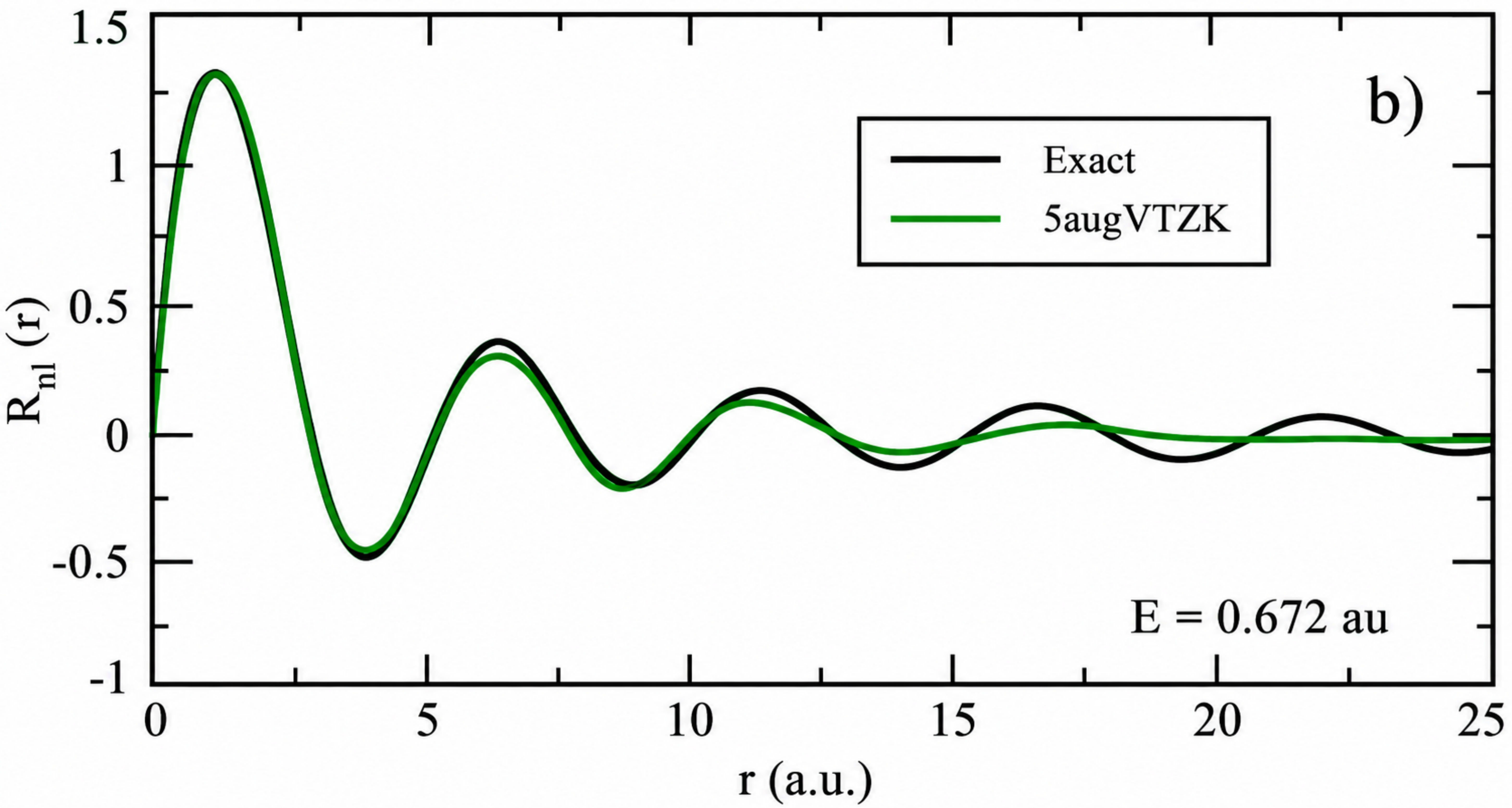
Optimised-Continuum Gaussian basis sets : the example of the H atom



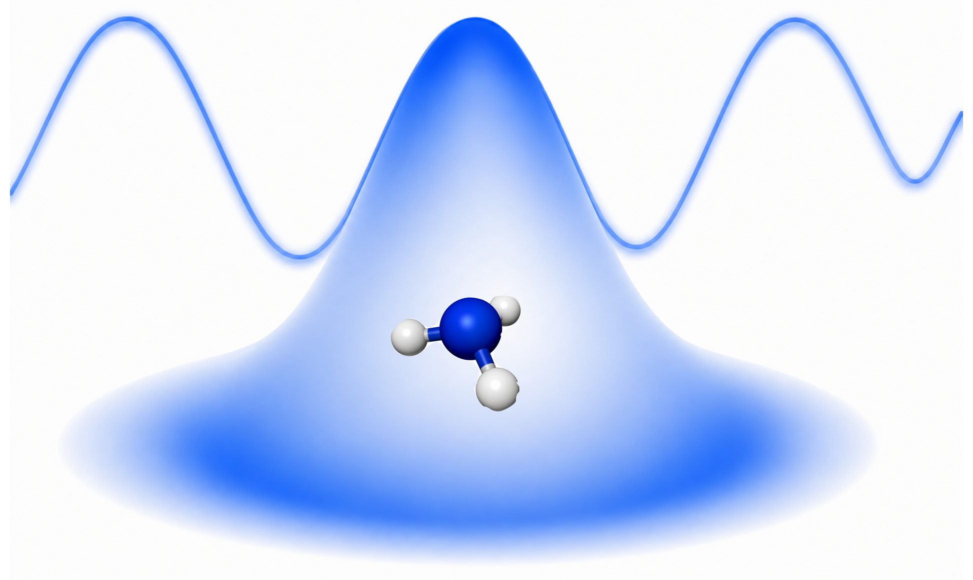
Dunning and Continuum-Optimised's Gaussian Basis Set

5-aug-cc-pVTZ+876K

8GTOs **s**,7GTOs **p**,6GTOs **d** + 8K **s**, 7K **p**, 6K **d**

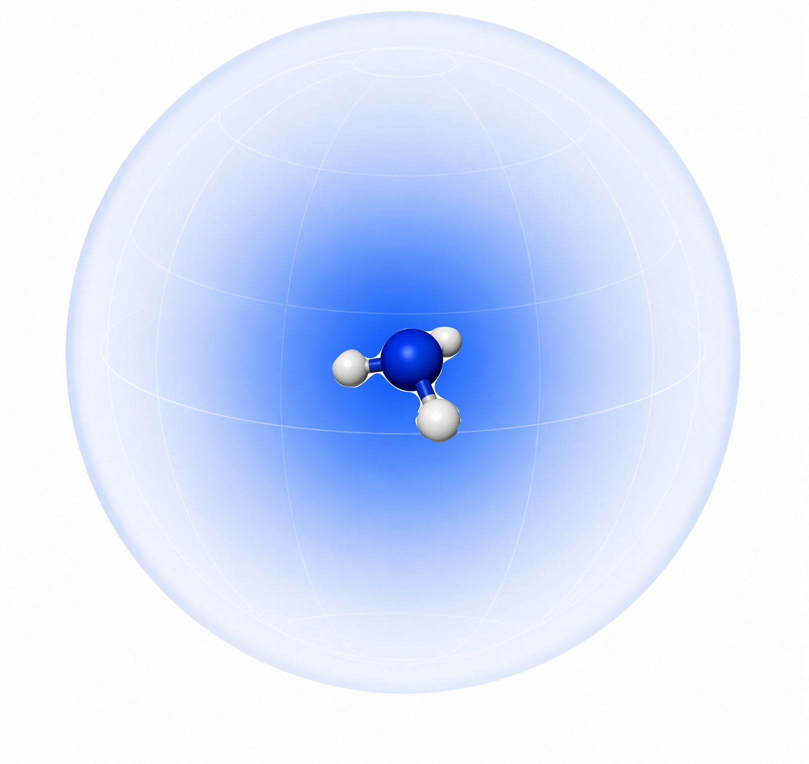


HHG : Optimised-Continuum Gaussian versus Grid and B-splines



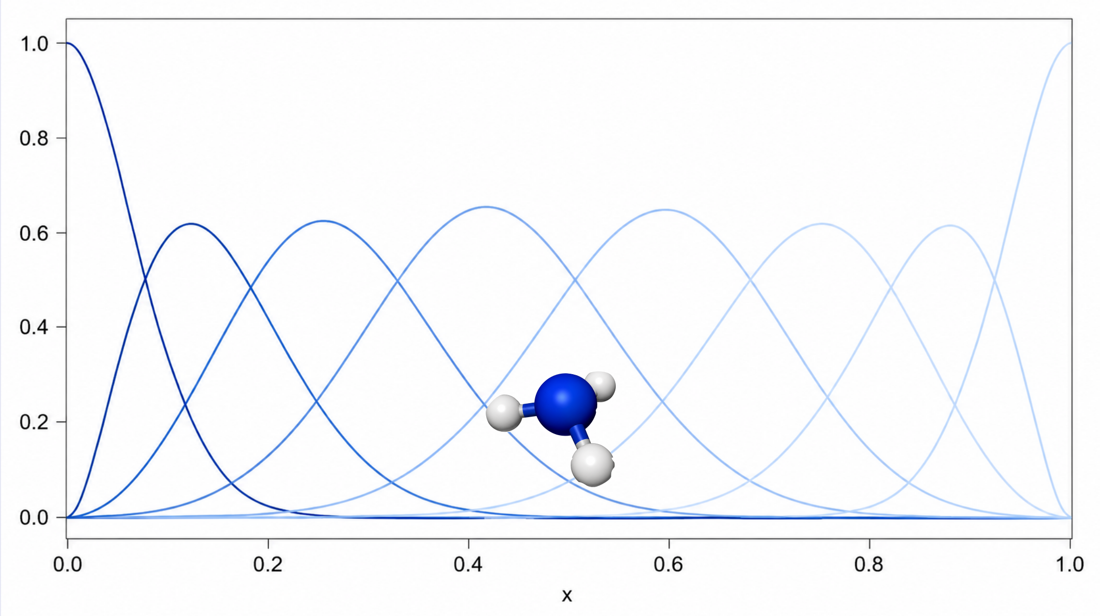
Grid

Kulander et al. PRA (1989)
Chu et al. PRA (2012)
Guliemakis et al. Nature (2010)
Phuong Mai Dinh et al. EPJB (2018)
many others …



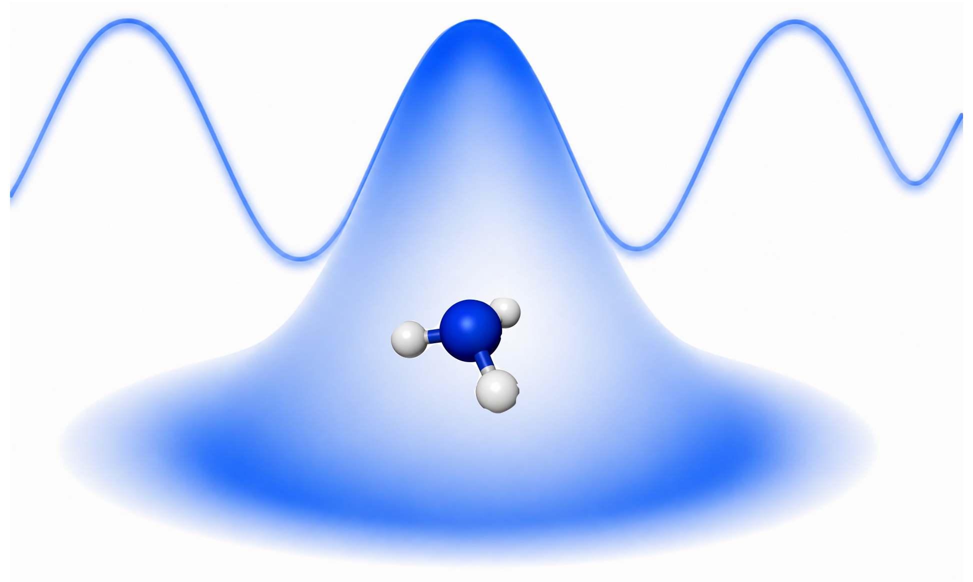
B-splines

Stener et al. JCP (2001)
Bachau et al. RPP (2001)
Stener et al. TCA (2007)
Fetic et al. PRE (2017)

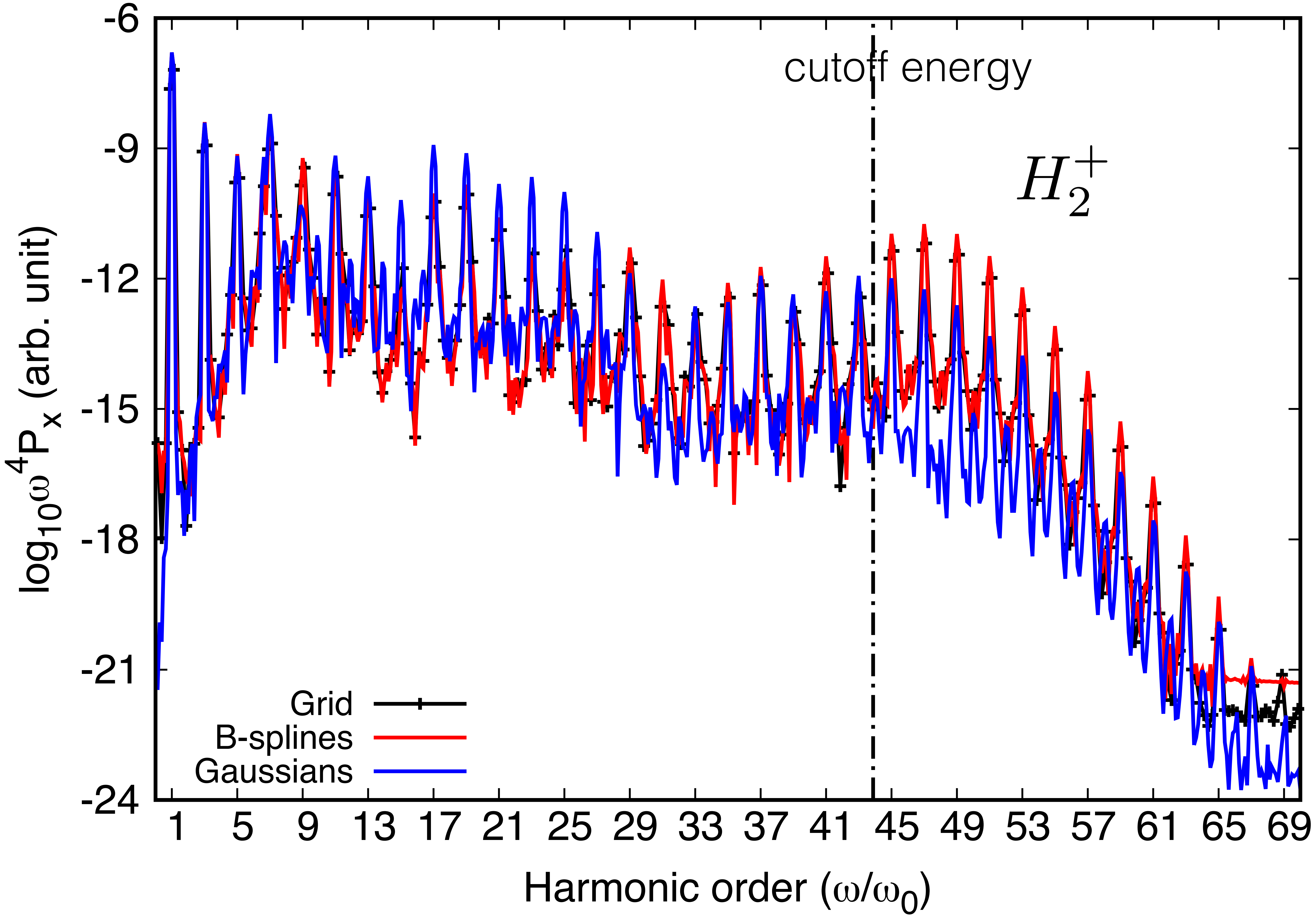


Grid and B-splines basis sets have demonstrated to be **very accurate** to describe continuum in atoms and molecules

HHG : Optimised-Continuum Gaussian versus Grid and B-splines



$$I = 2 \times 10^{14}\ W/cm^2$$



Labeye, Zapata, Coccia, Veniard, Toulouse Caillat, Taıeb, Toulouse, Taieb, Luppi, JCTC (2018)

Grid

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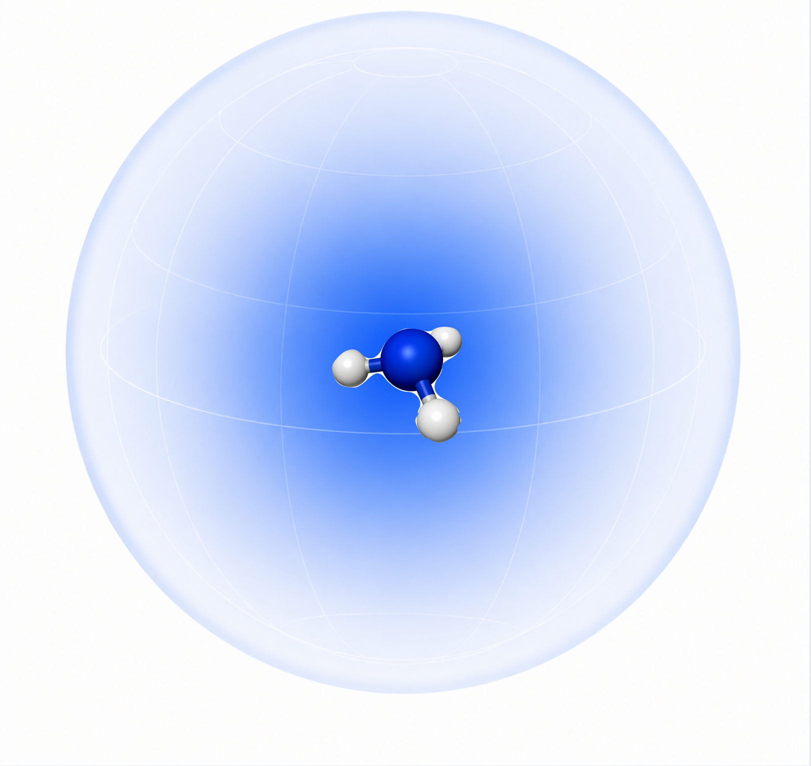

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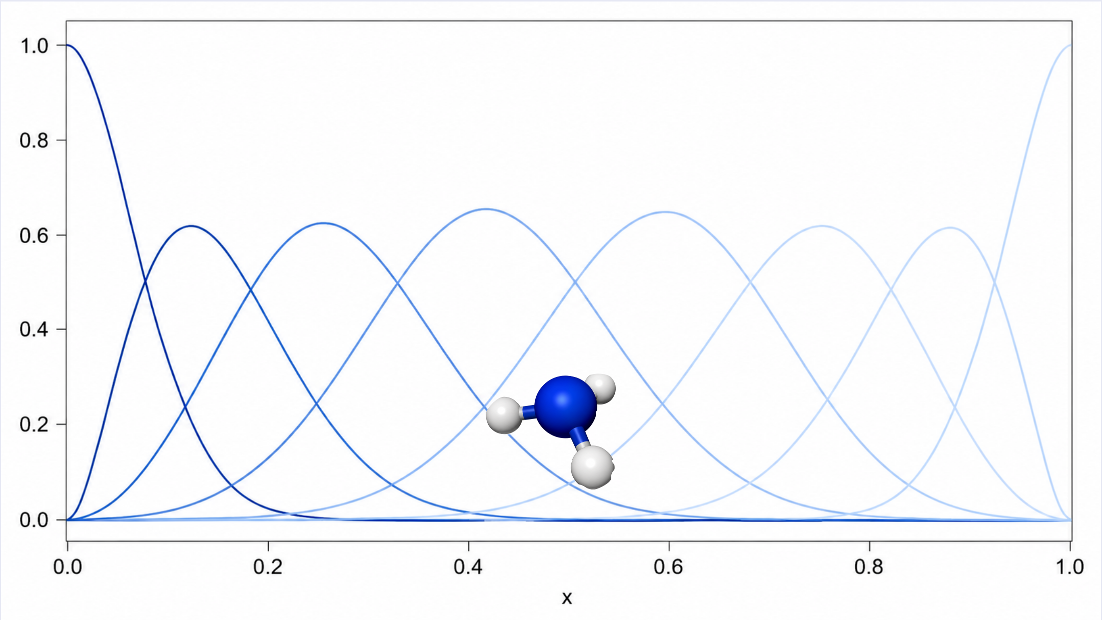
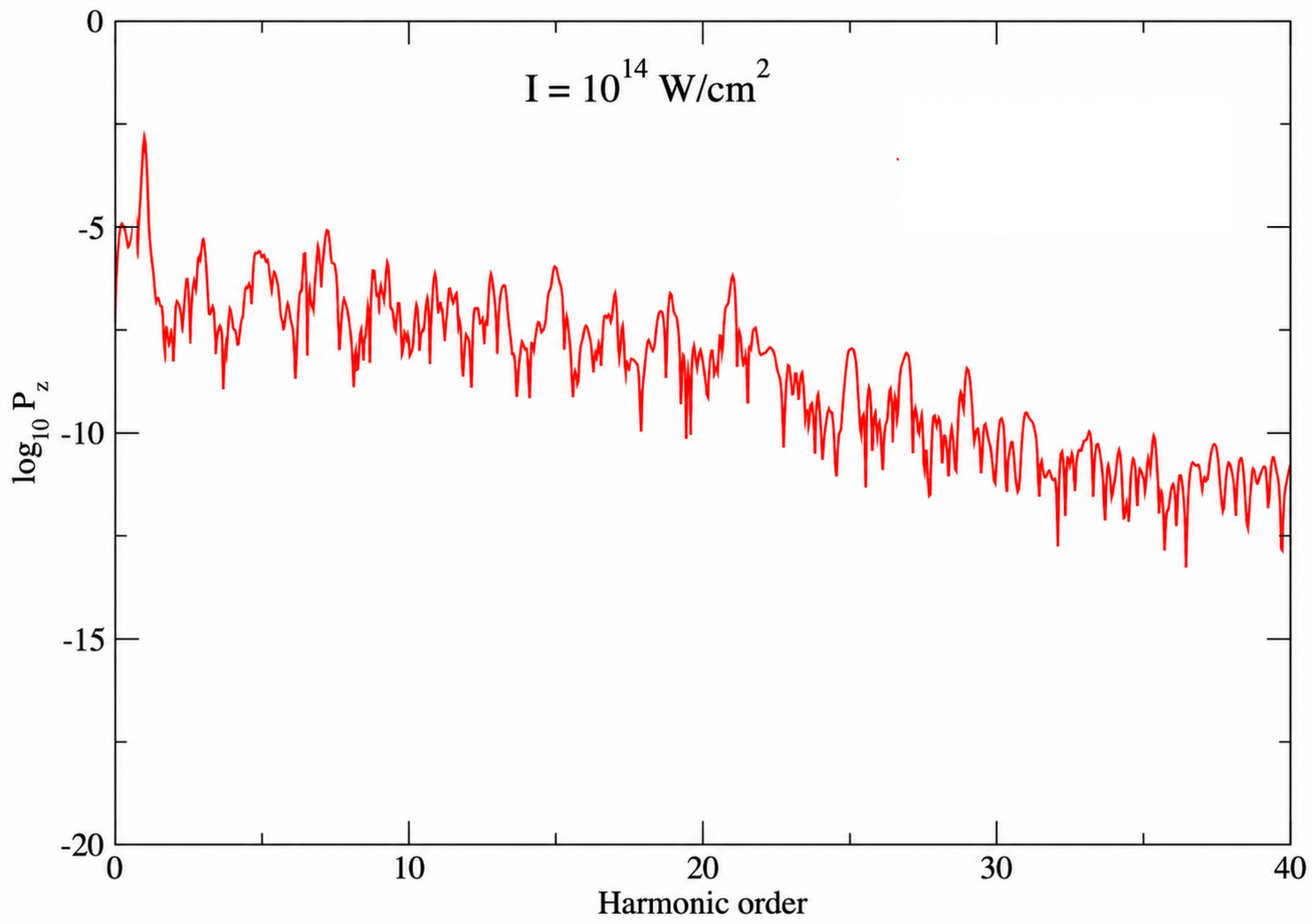


Grid and B-splines basis sets have demonstrated to be **very accurate** to describe continuum in atoms and molecules

The problem of ionisation

Electron dynamics driven by the laser field

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = \left(\hat{H}_0 - \hat{\mu} \cdot \mathbf{E}(t)\right) |\Psi(t)\rangle$$



Quantum chemistry in strong fields

Electron dynamics driven by the laser field

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\hat{H}_0 - \hat{\mu}\cdot\mathbf{E}(t)\right)|\Psi(t)\rangle$$

Open-system description of continuum losses

$$\hat{H}_0 \to \hat{H}_0 - \frac{i}{2}\hat{\Gamma}$$

Complex energies encode ionization rates

$$E_k \to E_k - \frac{i}{2}\Gamma_k$$

Ionization rates Γ_k

Electronic depletion and continuum dynamics

$$\psi_k(t) \propto e^{-iE_k t}\, e^{-\Gamma_k t/2}$$

The problem of ionisation for HHG : Lifetimes models

Ionization rates Γ_k

1. Heuristic lifetimes model (1 parameters)

Ecis-SdHLM

S. Klinkusch , P. Saalfrank, T. Klamrot JCP 131, 114304 (2009)

2. Double **Heuristic** lifetimes model (2 parameters)

Ecis-DdHLM

Coccia, Mussard, Labeye, Caillat, Taıeb, Toulouse, Luppi,
IJQC 116, 1120 (2016)

3. Double **Heuristic** lifetimes model (2 parameters)

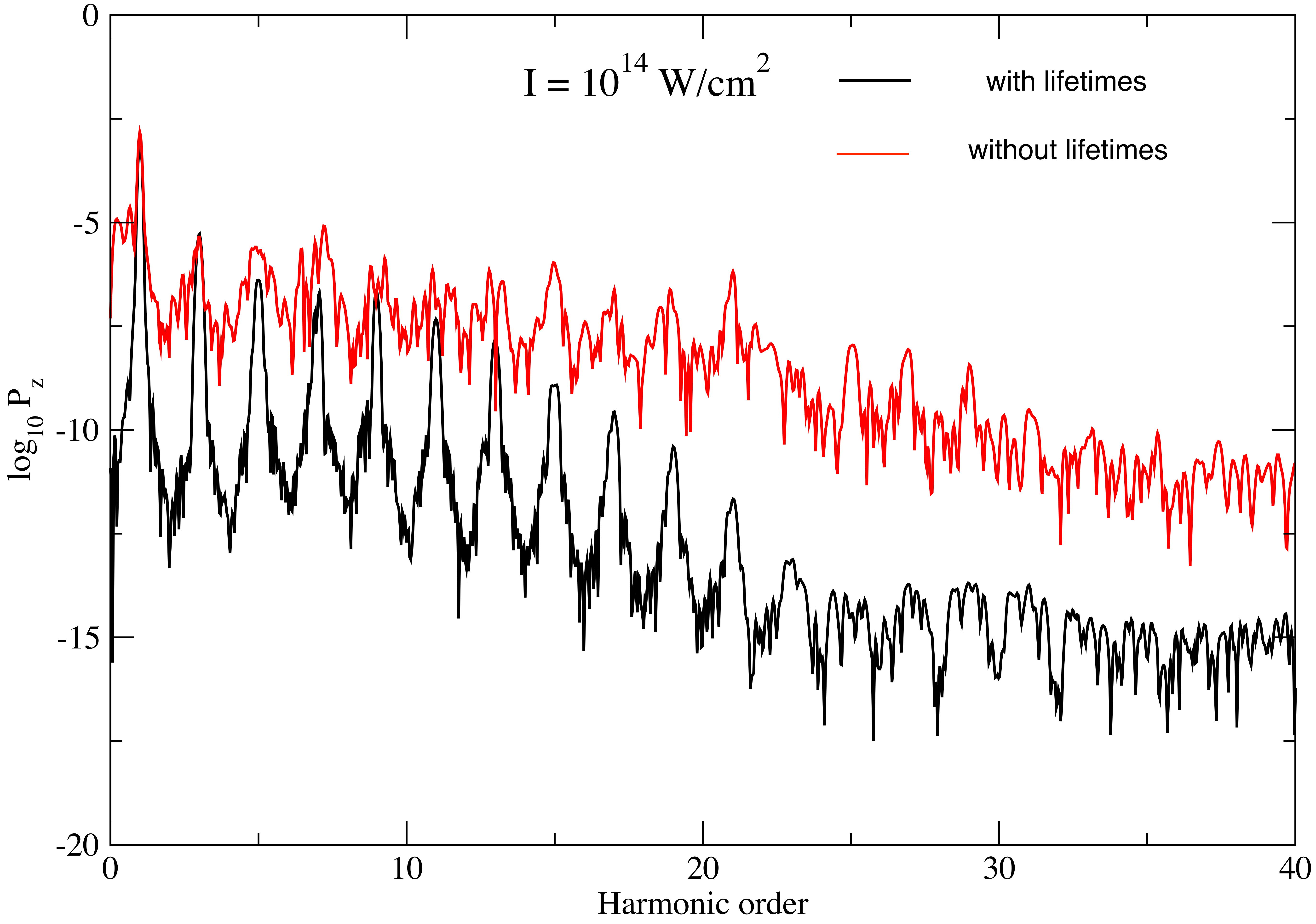
Emo-DdHLM

A.P. Woźniak, M. Przybytek, M. Lewenstein, R. Moszyiżsk
JCP 156, 174016 (2022)

4. Ab initio lifetimes model **AbILM**

E. Coccia, R. Assaraf, E. Luppi, J.Toulouse, JCP 147, 01410 (2017)

The problem of ionisation for HHG : Lifetimes models



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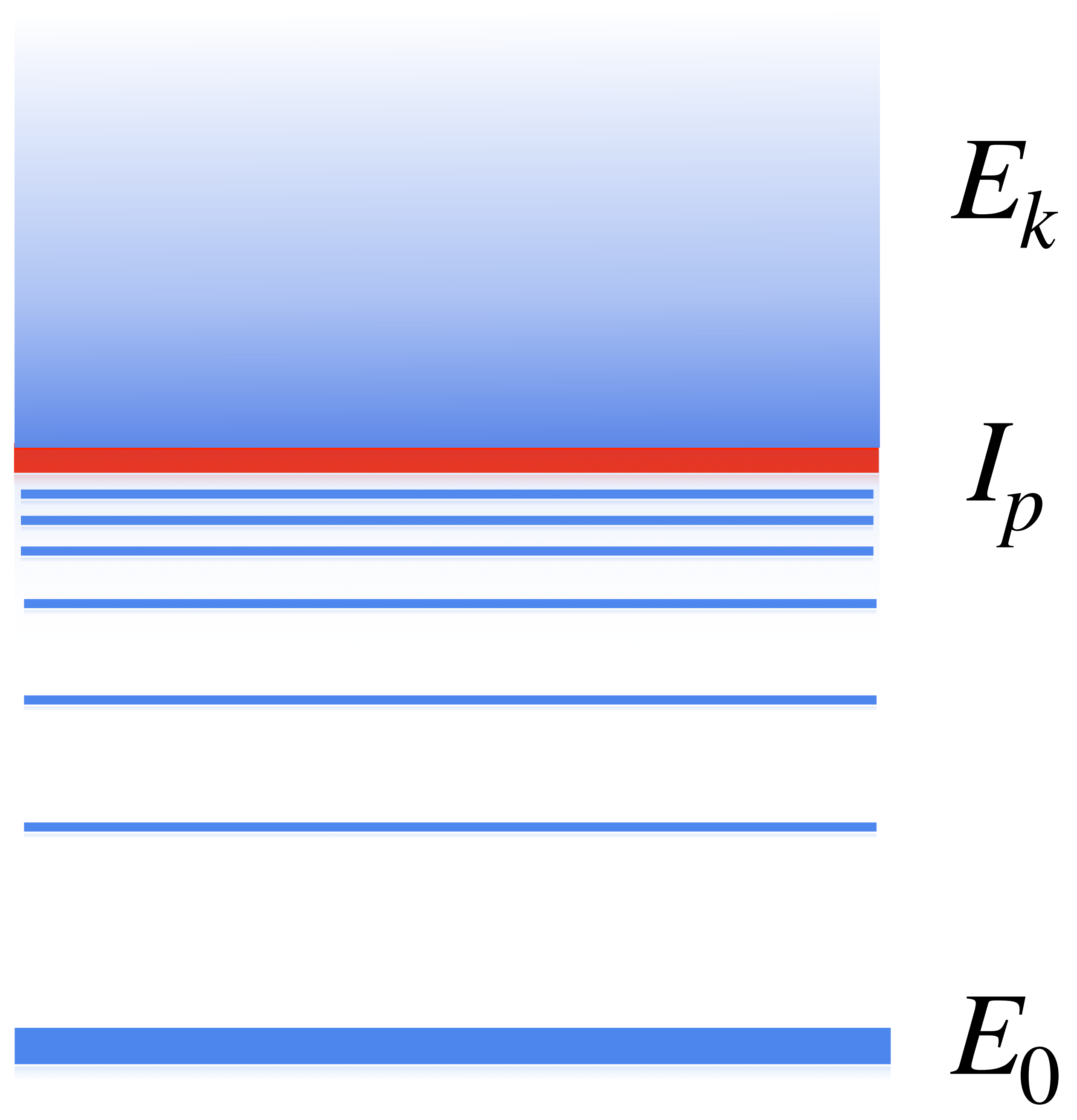
The problem of ionisation for HHG : Lifetimes models

$$E_k \to E_k - \frac{i}{2}\Gamma_k$$



The problem of ionisation for HHG : Lifetimes models

$$E_k \rightarrow E_k - \frac{i}{2}\Gamma_k$$

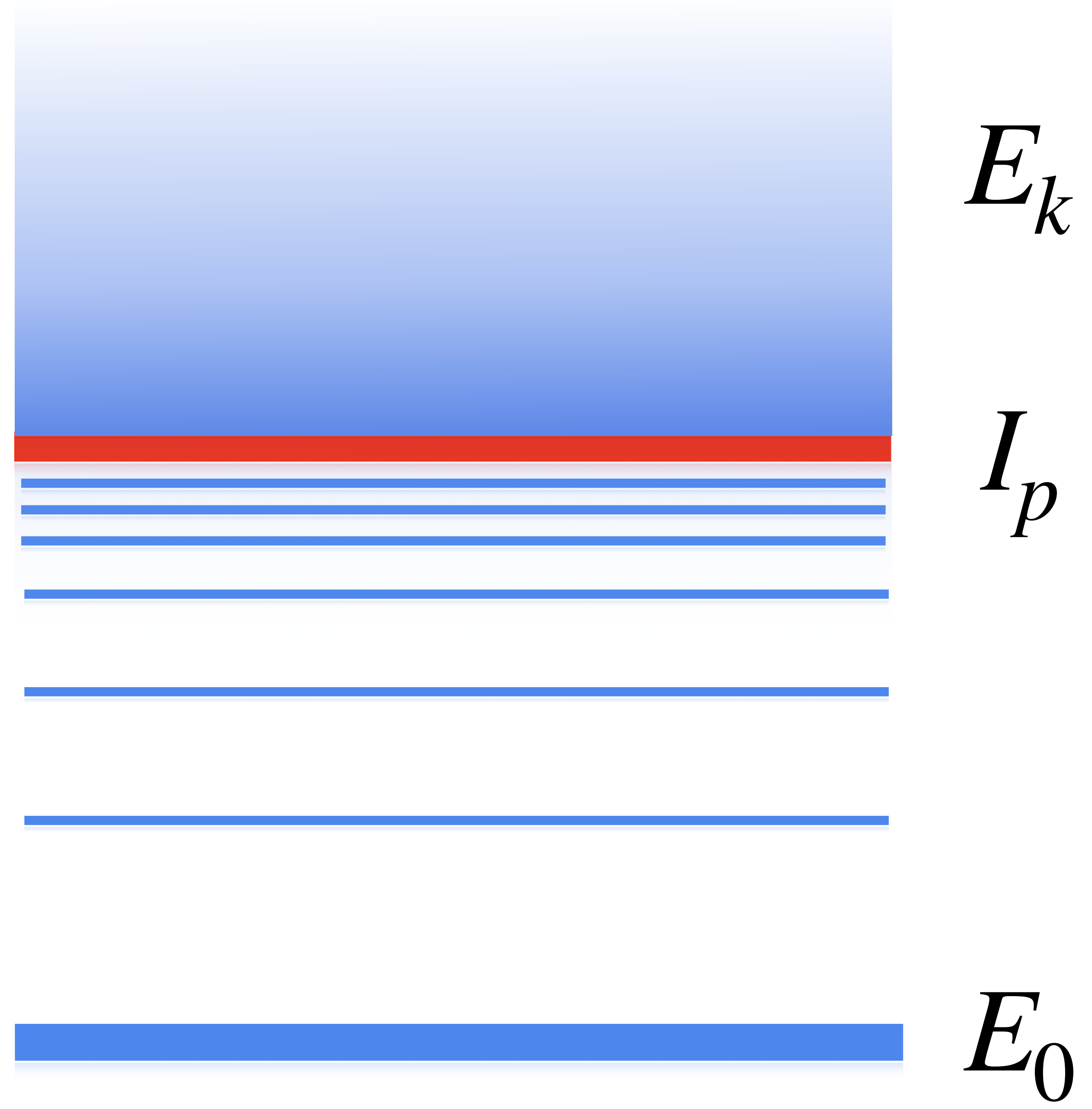
$$\Gamma_k = \begin{cases} 0 & \text{if} \quad E_k - E_0 < I_\mathrm{p} \\ \sum_i^{\mathrm{occ}} \sum_a^{\mathrm{vir}} |r_{i,k}^a|^2 \, \gamma_a^k + \sum_{i,j}^{\mathrm{occ}} \sum_{a,b}^{\mathrm{vir}} |r_{ij,k}^{ab}|^2 \, (\gamma_a^k + \gamma_b^k) & \text{if} \quad E_k - E_0 \geq I_\mathrm{p} \end{cases}$$

Single excitation correlations — **Single and Double excitation correlation**

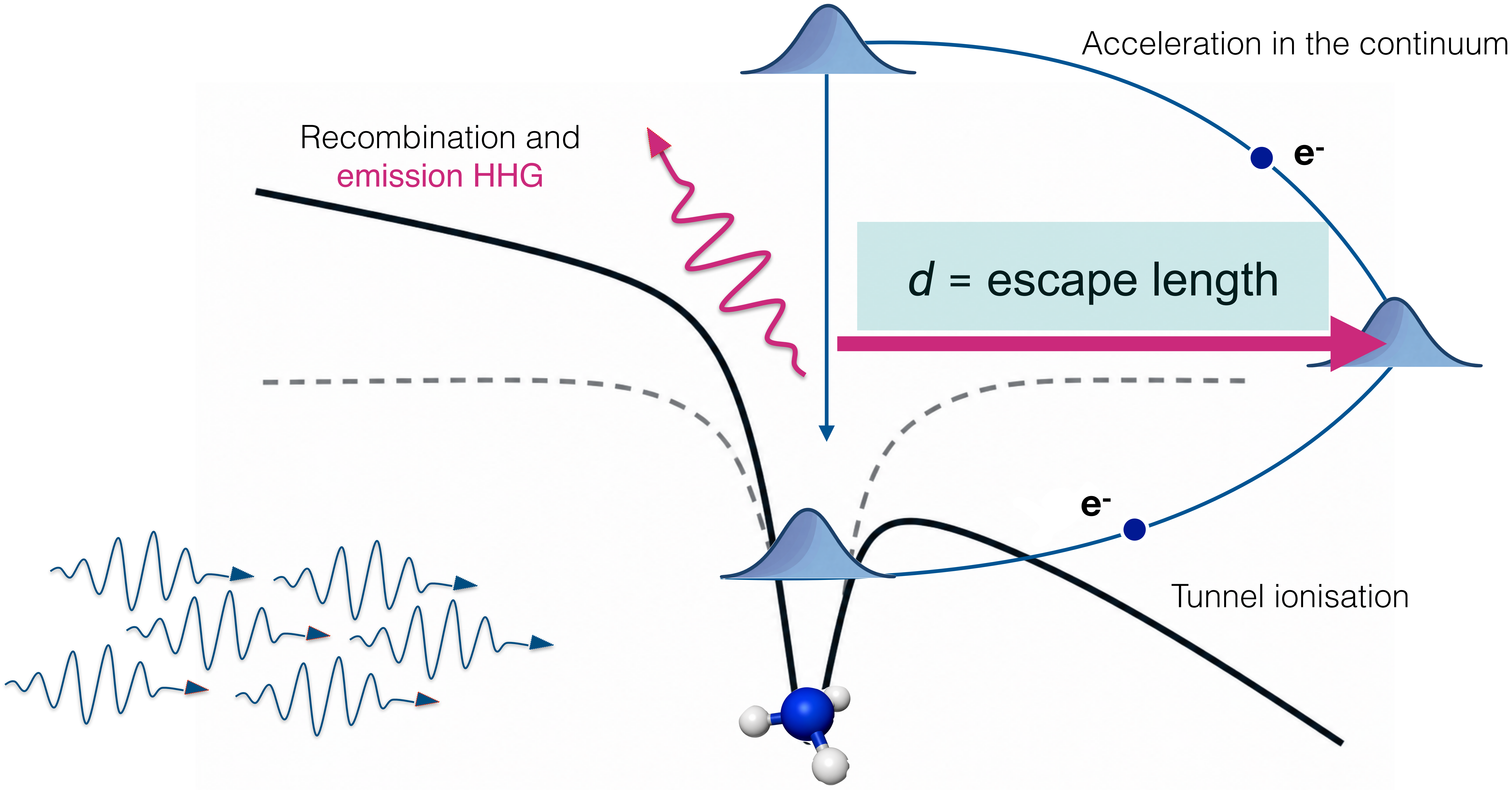
γ_a^k

Heuristic lifetimes model

Ab Initio lifetimes model



Heuristic lifetimes models and 3SM for HHG



$$\gamma_i^a \propto \frac{1}{d}$$

S. Klinkusch , P. Saalfrank, T. Klamrot JCP 131, 114304 (2009)

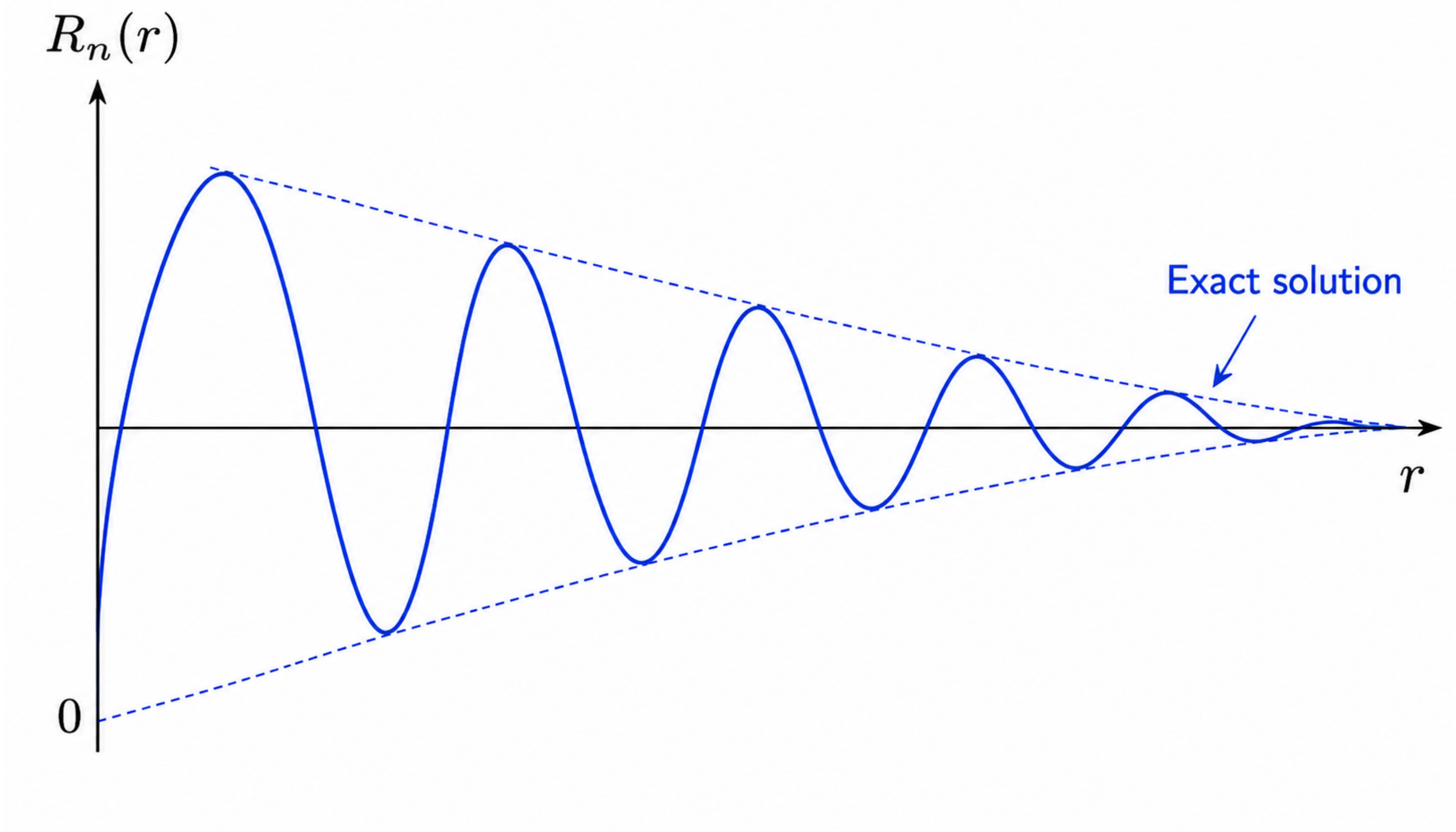
Coccia, Mussard, Labeye, Caillat, Taıeb, Toulouse, Luppi,
IJQC 116, 1120 (2016)

A.P. Woźniak, M. Przybytek, M. Lewenstein, R. Moszyiżsk
JCP 156, 174016 (2022)

Ab Initio lifetimes model

Solving the radial equation for H atom without boundary conditions :

$$-\frac{1}{2}\left(R''(r)+\frac{2}{r}R'(r)-\frac{\ell(\ell+1)}{r^2}R(r)\right)-\frac{Z}{r}R(r)=E\ R(r)$$

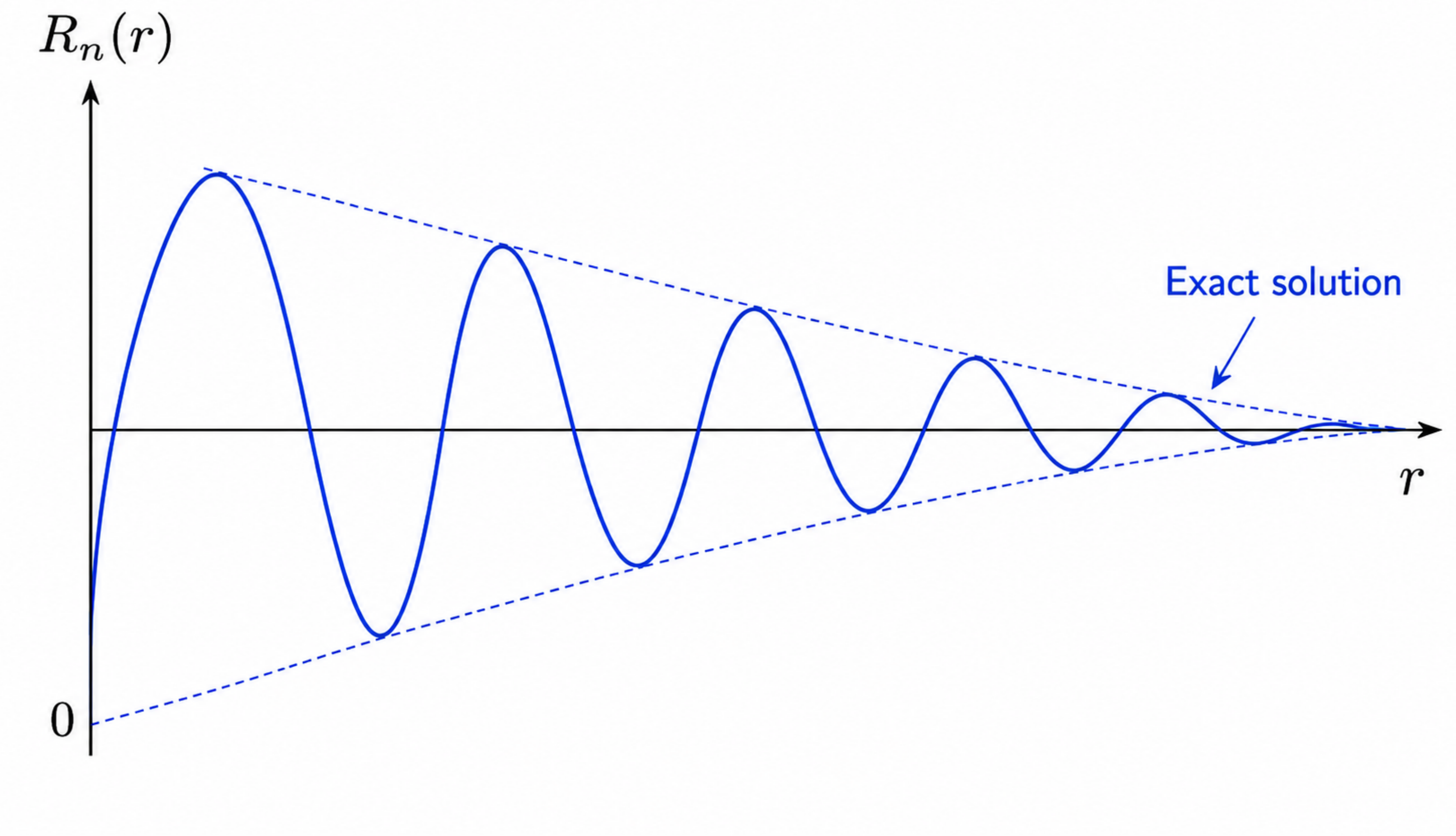


$$E_n=\varepsilon_n-\frac{i}{2}\gamma_n \qquad R_n(r)\sim\frac{e^{-k_n r}}{r}$$

Ab Initio lifetimes model

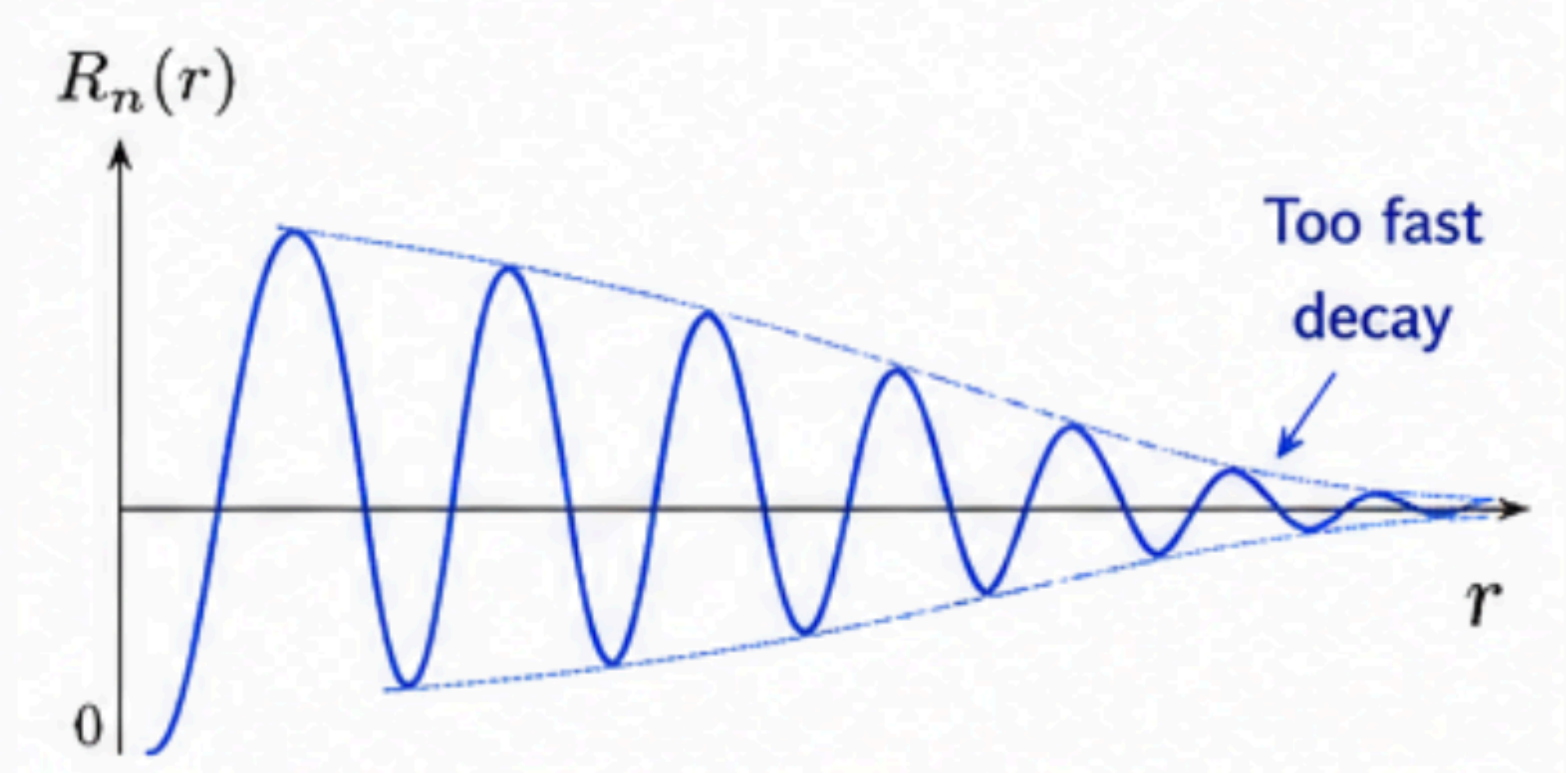
Solving the radial equation for H atom without boundary conditions :

$$-\frac{1}{2}\left(R''(r) + \frac{2}{r}R'(r) - \frac{\ell(\ell+1)}{r^2}R(r)\right) - \frac{Z}{r}R(r) = E\ R(r)$$



$$E_n = \varepsilon_n - \frac{i}{2}\gamma_n \qquad R_n(r) \sim \frac{e^{-k_n r}}{r}$$

Solving the equation in Quantum Chemistry with Gaussian basis set (artificial localisation):



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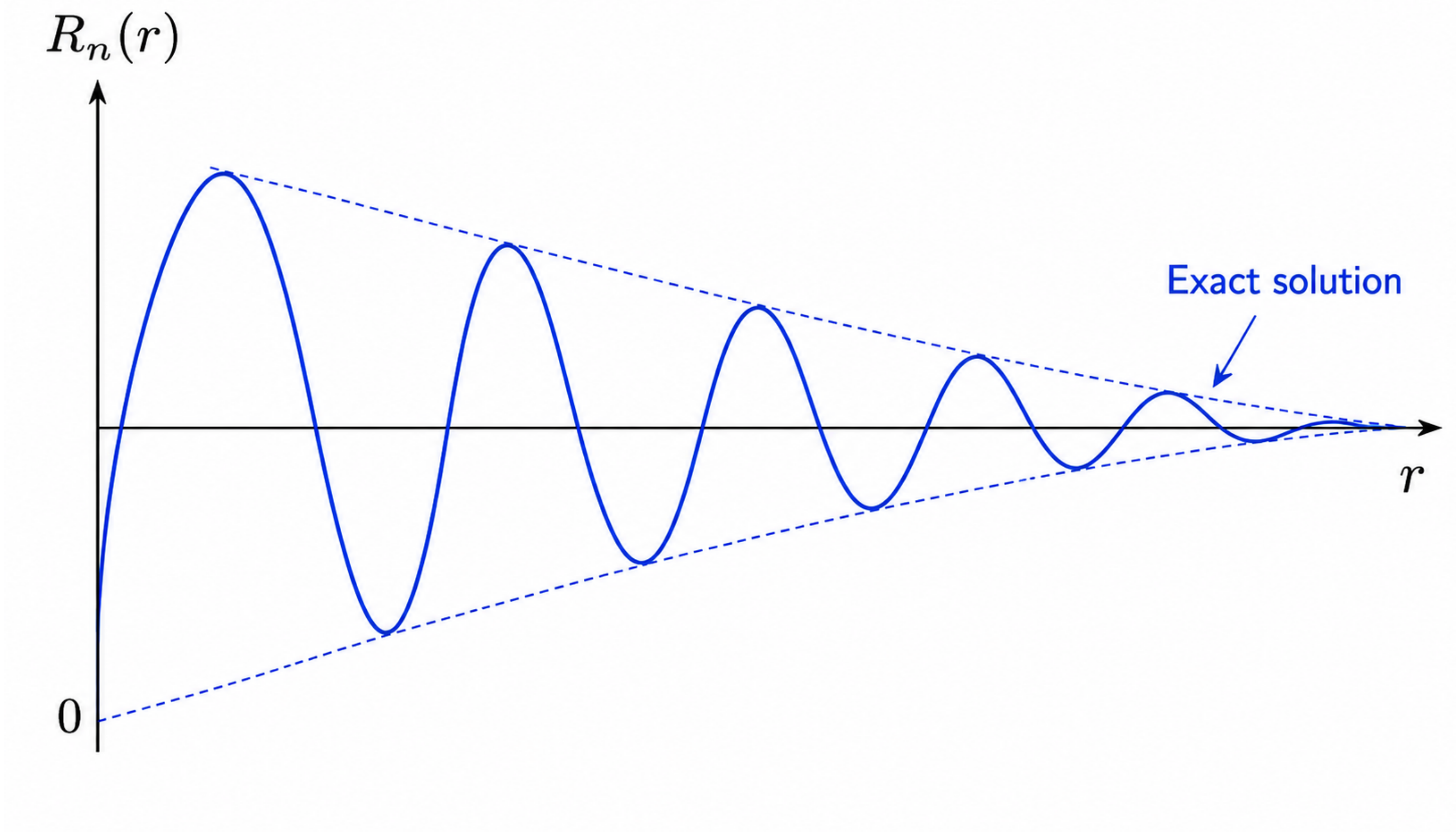

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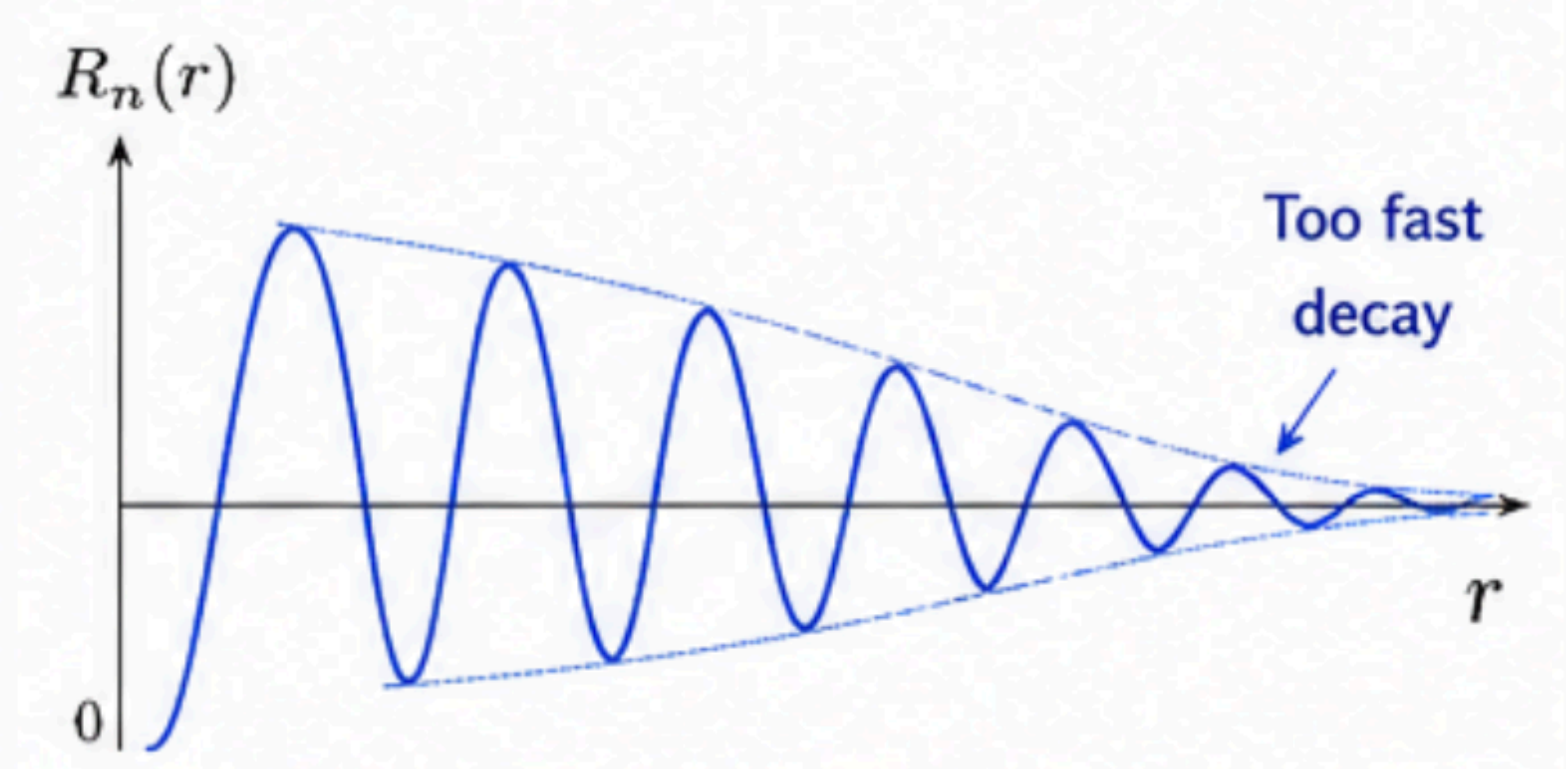

? **?**

$$E_n=\varepsilon_n-\frac{i}{2}\gamma_n \qquad R_n(r)\sim\frac{e^{-B_n r}}{r}$$

Ab Initio lifetimes model

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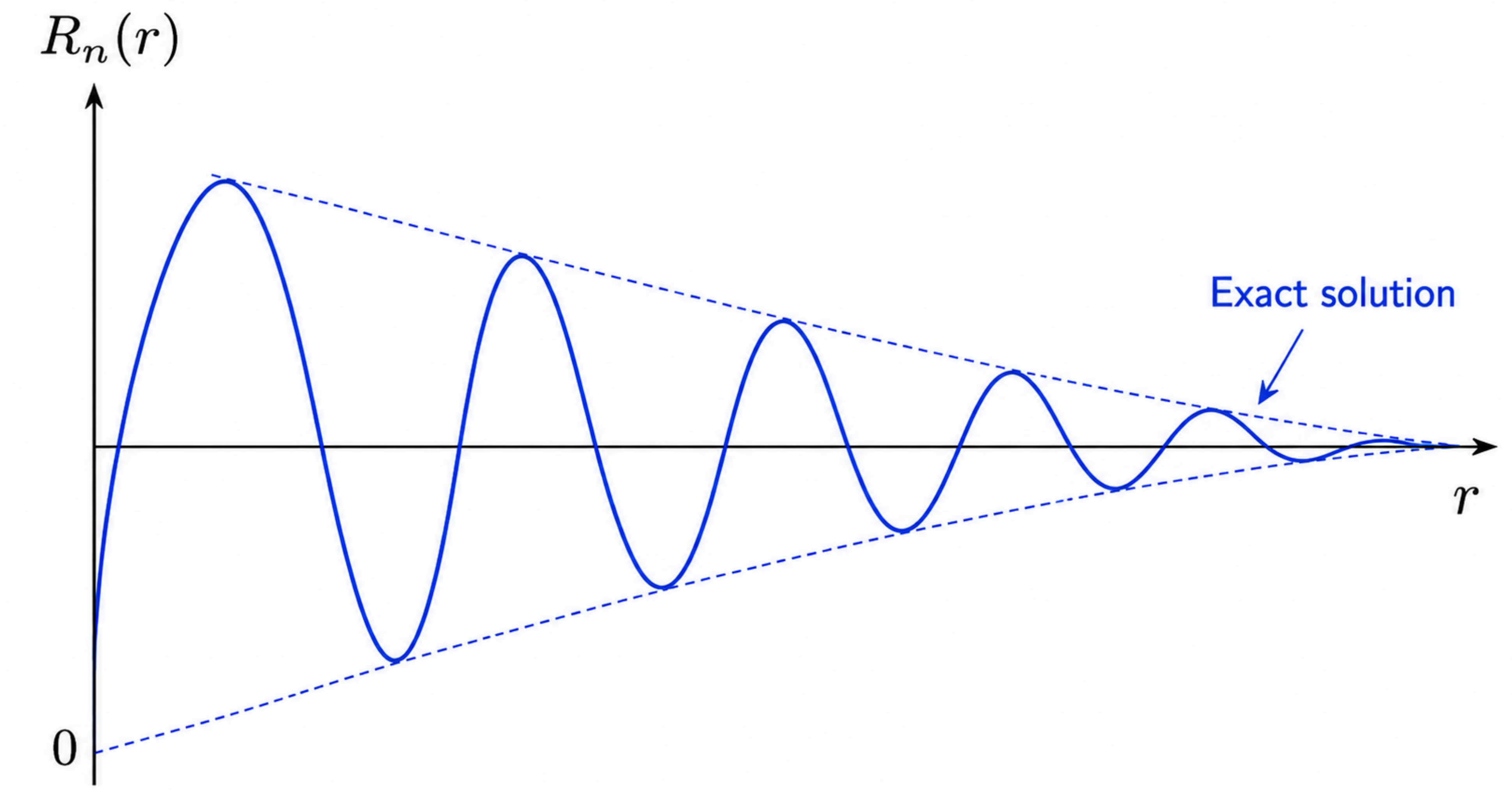

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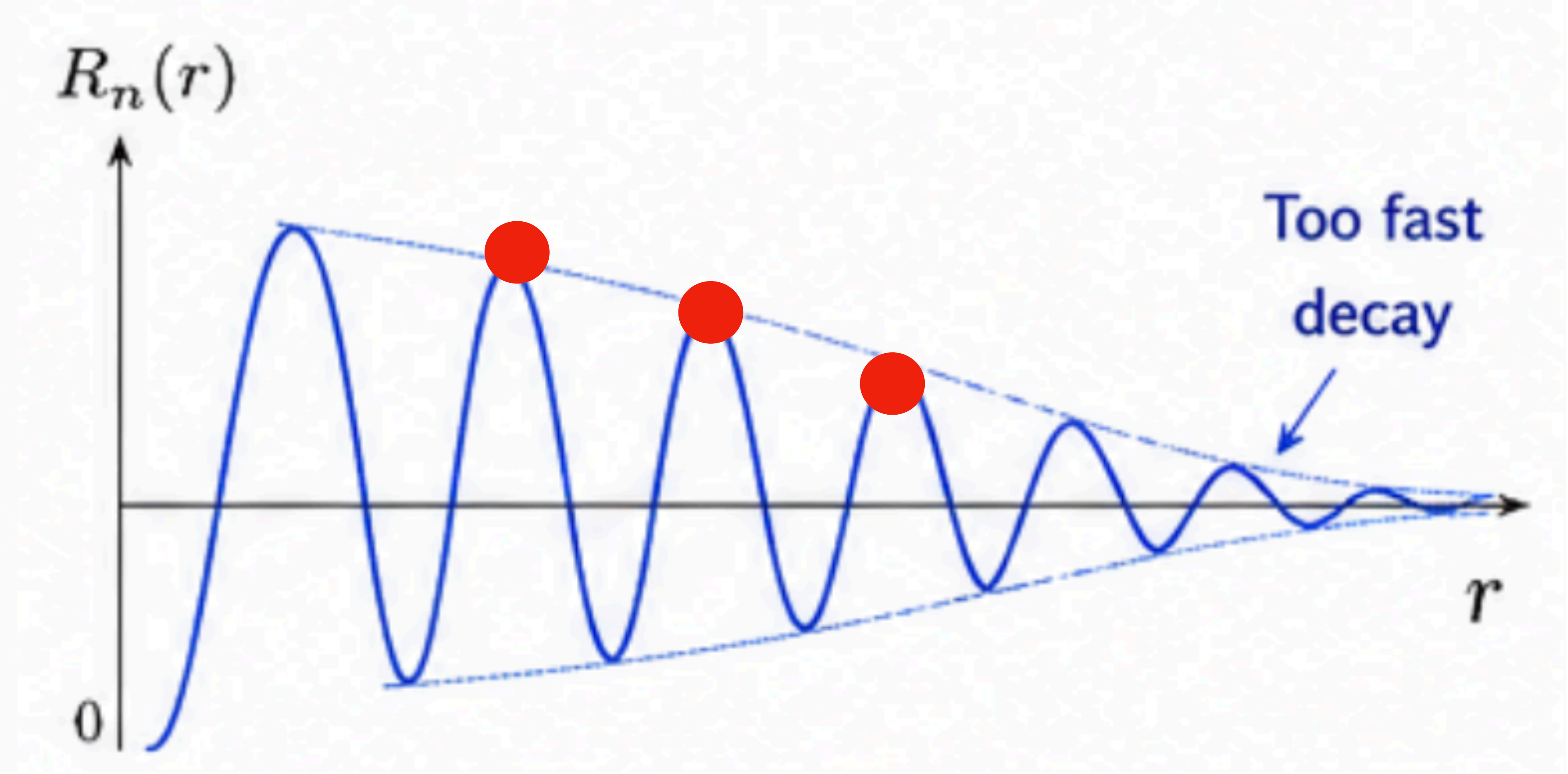
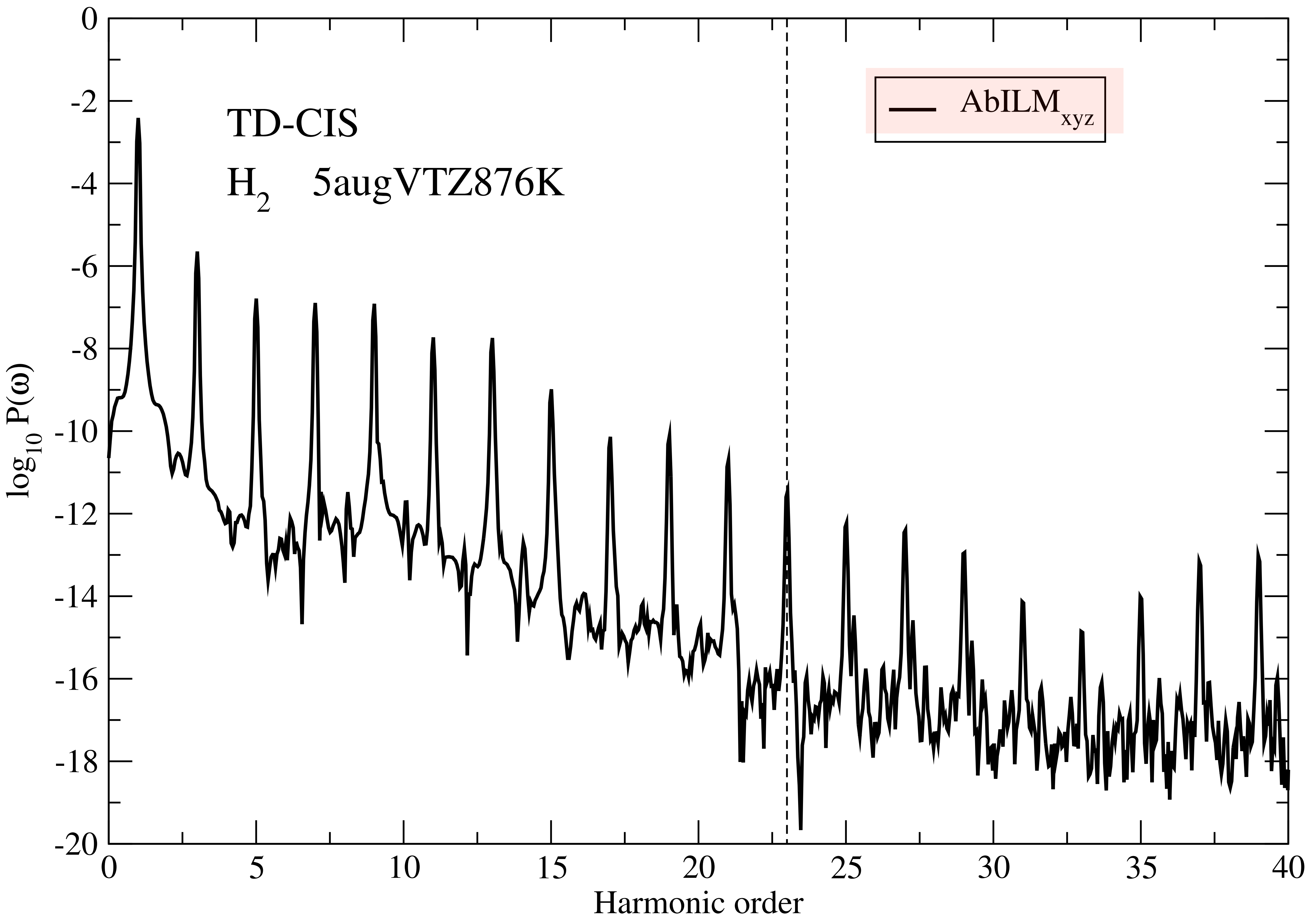


● fitting

$$E_n = \varepsilon_n - \frac{i}{2}\gamma_n \ \text{?} \qquad R_n(r) \sim \frac{e^{-B_n r}}{r} \rightarrow \gamma_n = 2B_n\sqrt{2\varepsilon_n + B_n^2}$$

Lifetimes model for continuum

Single excitation correlations

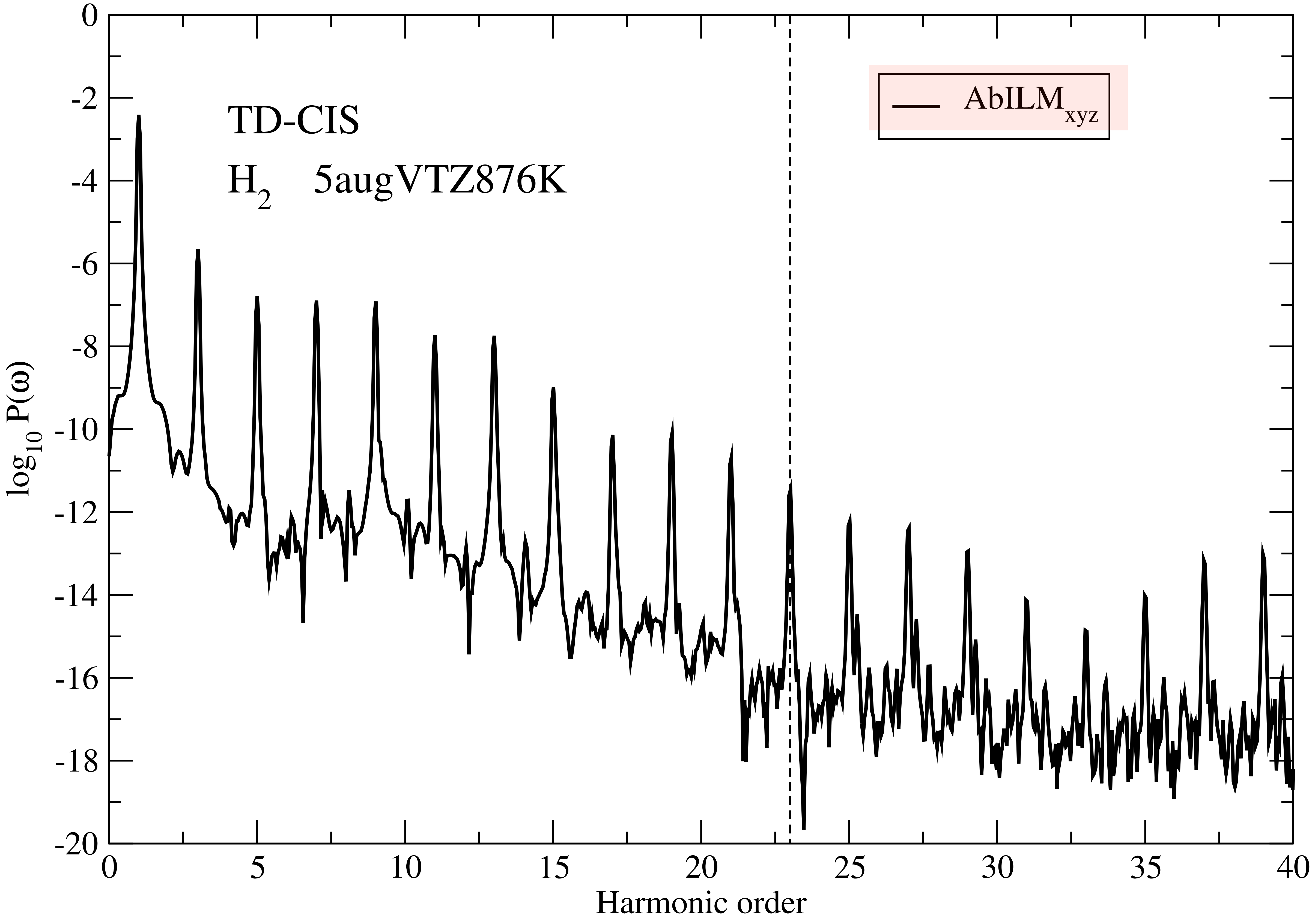


Ab Initio lifetimes model versus electron correlation

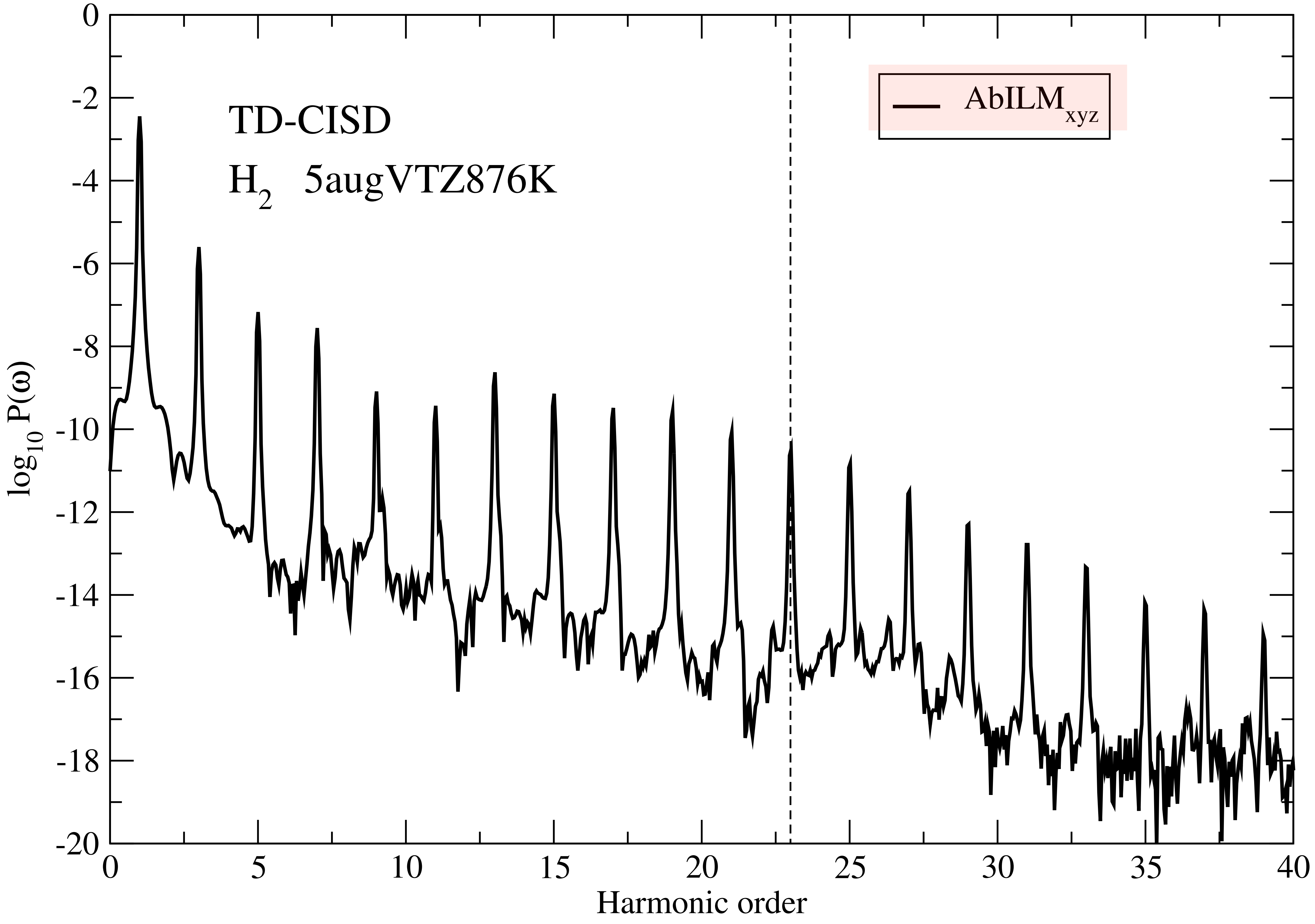
P. A. Albrecht, C. Morassut, E. Coccia, T. Klamroth, P. Saalfrank, E. Luppi, J. Chem. Phys. 163, 024111 (2025).

Lifetimes model for continuum

Single excitation correlations



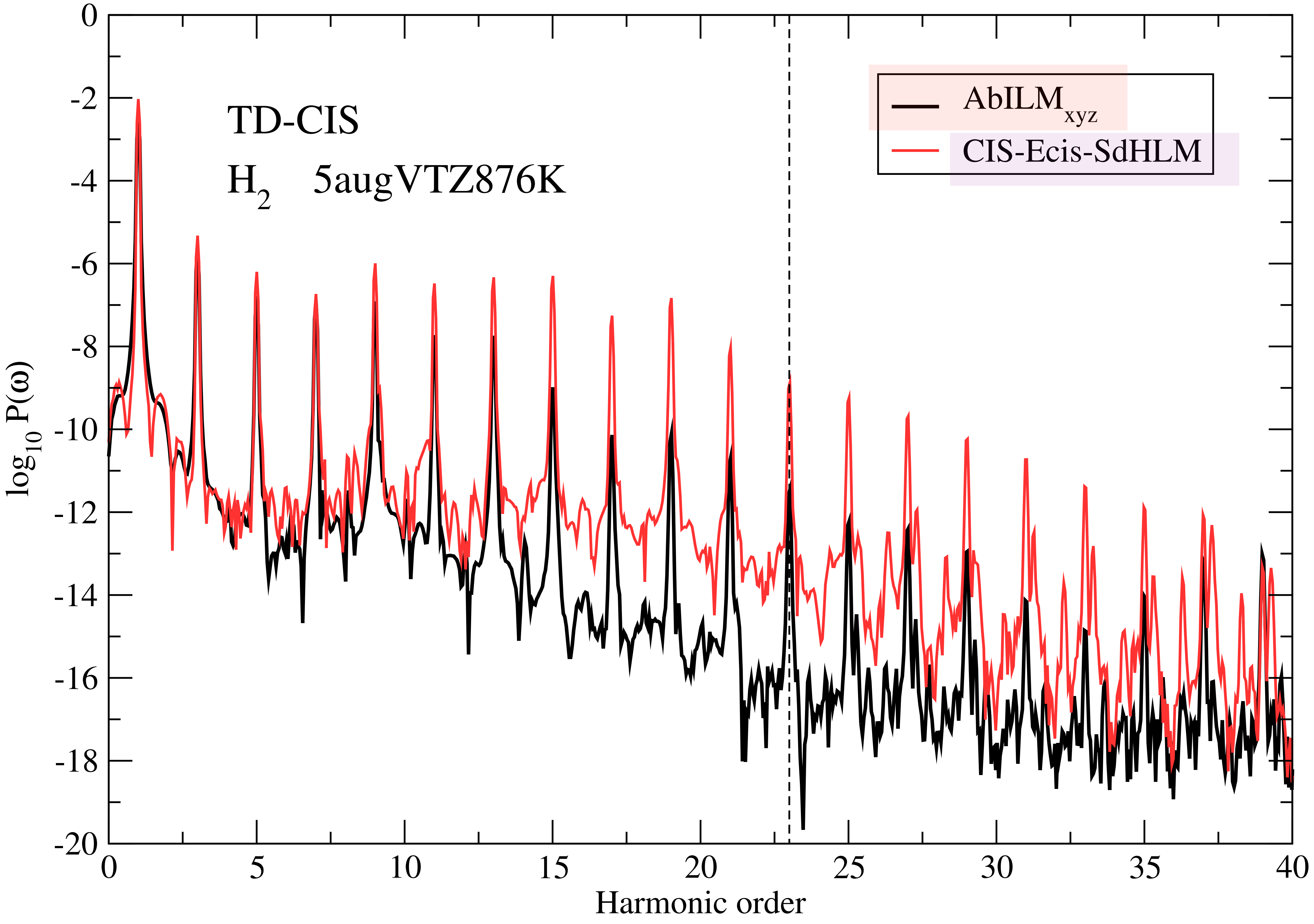
Single and Double excitation correlations



Ab Initio lifetimes model versus electron correlation

Lifetimes model for continuum

Single excitation correlations

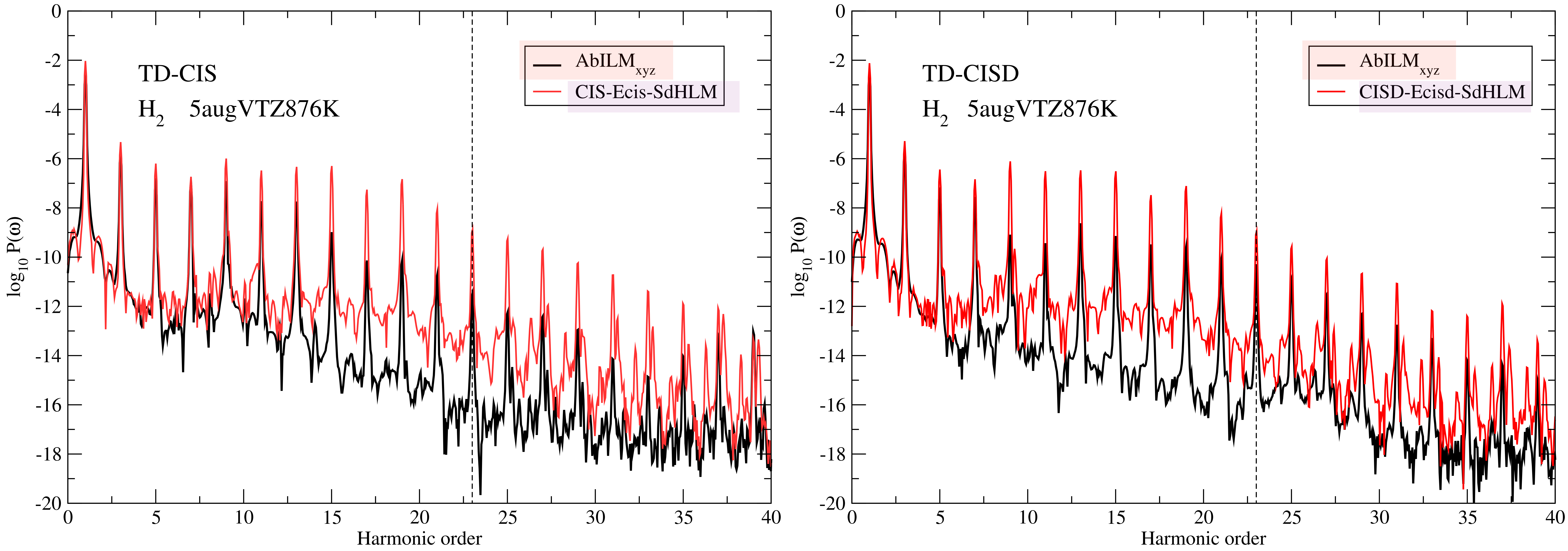


Ab Initio versus Heuristic lifetimes models

Lifetimes model for continuum

Single excitation correlations

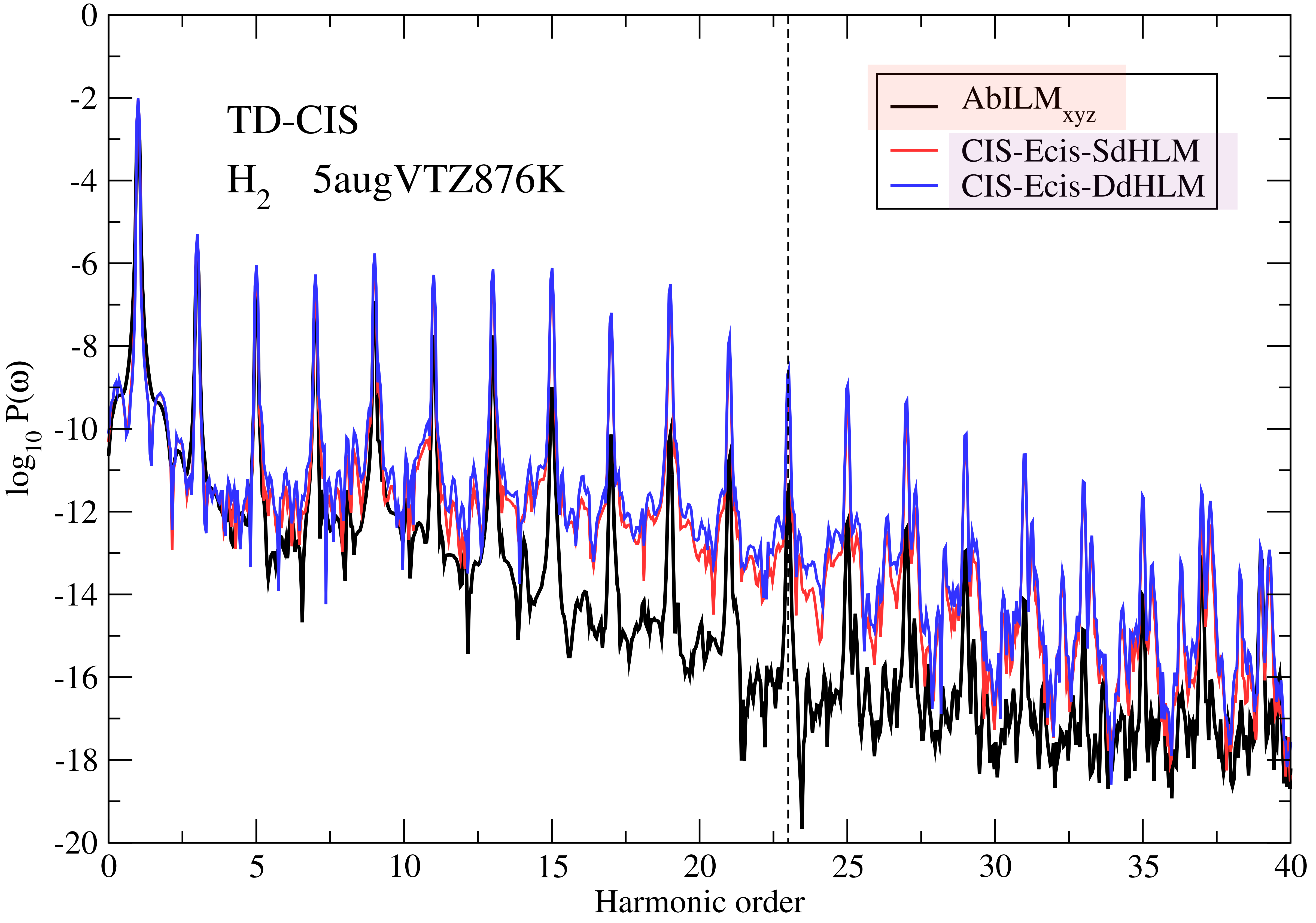
Single and Double excitation correlations



Ab Initio versus Heuristic lifetimes models

Lifetimes model for continuum

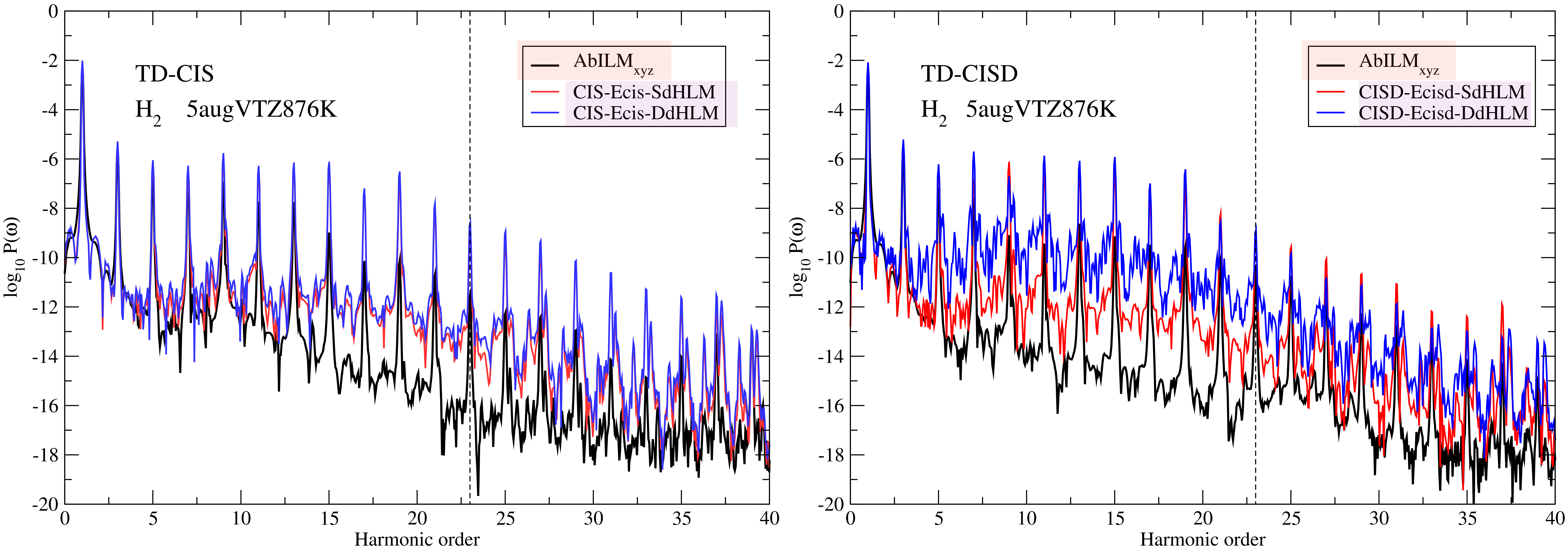
Single excitation correlations



Ab Initio versus Heuristic lifetimes models

Lifetimes model for continuum

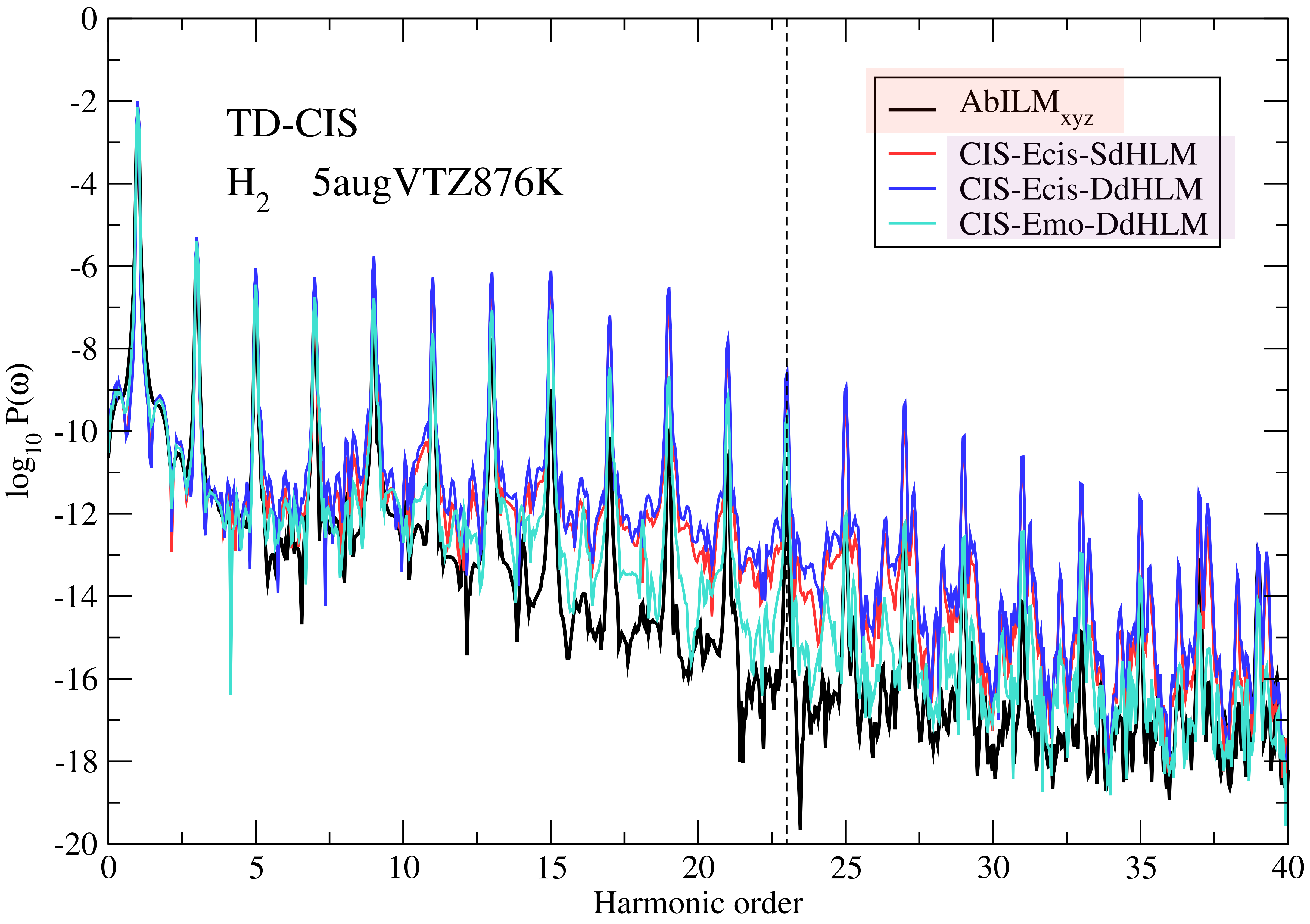
Single excitation correlations | Single and Double excitation correlations



Ab Initio versus Heuristic lifetimes models

Lifetimes model for continuum

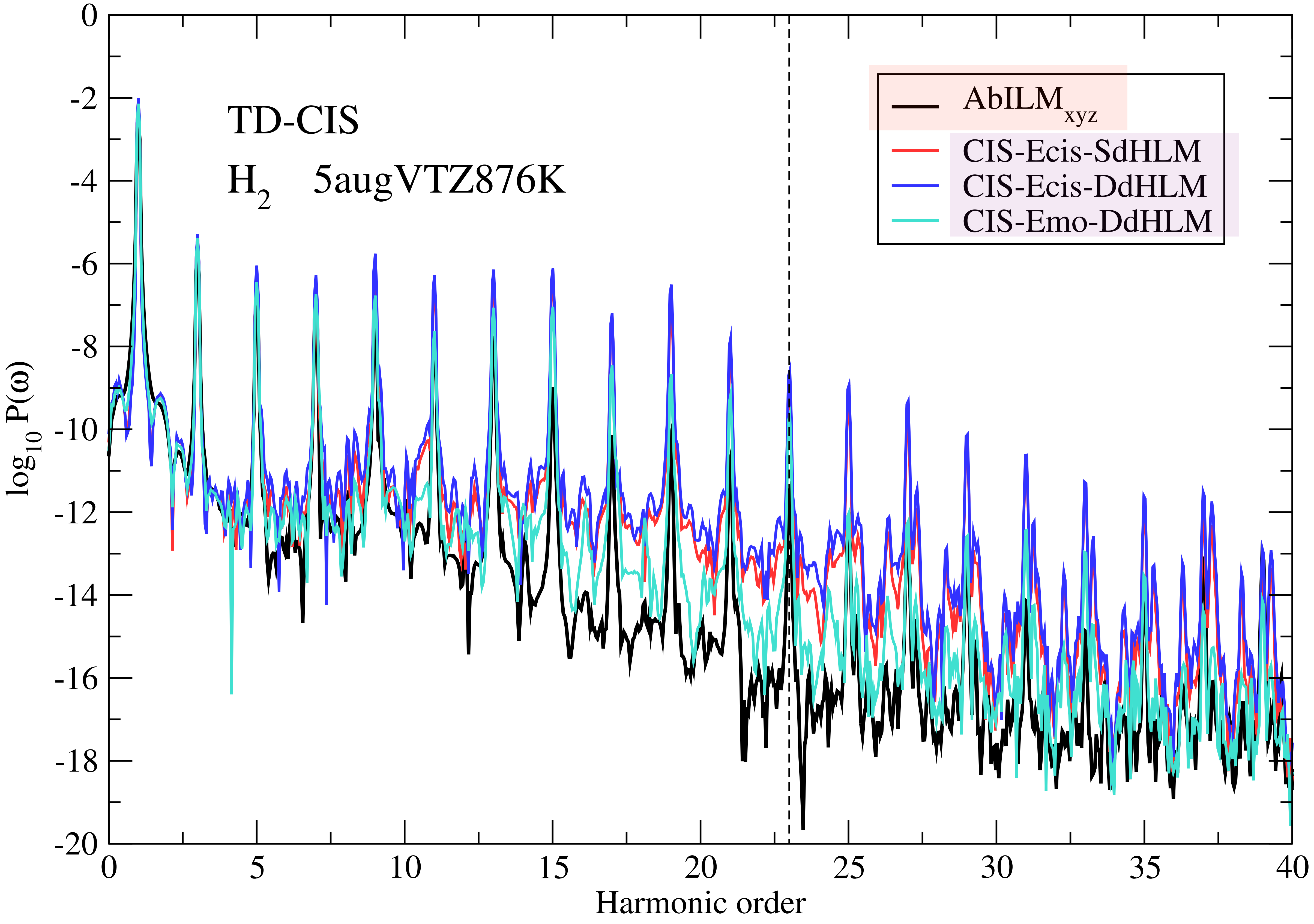
Single excitation correlations



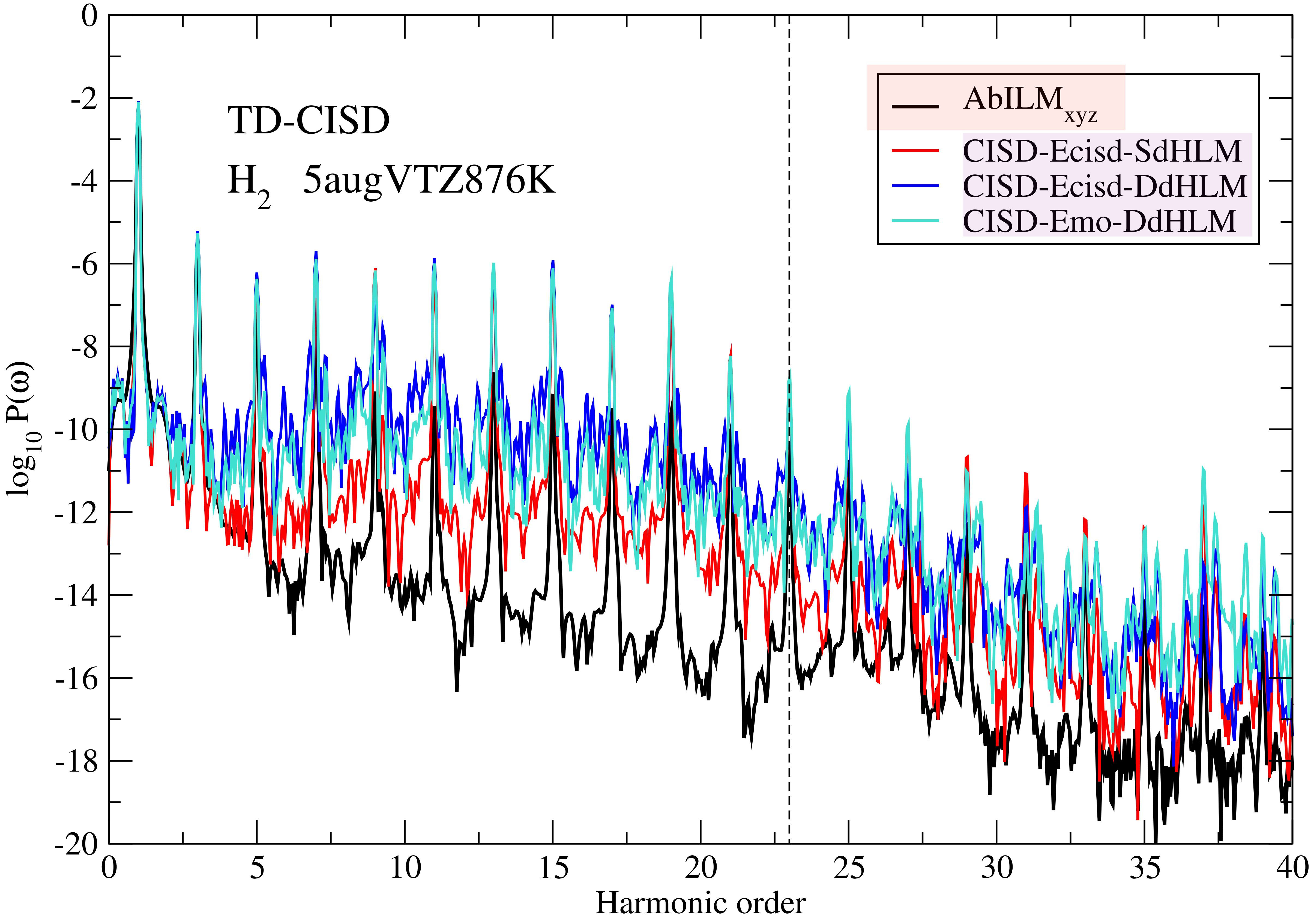
Ab Initio versus Heuristic lifetimes models

Lifetimes model for continuum

Single excitation correlations



Single and Double excitation correlations

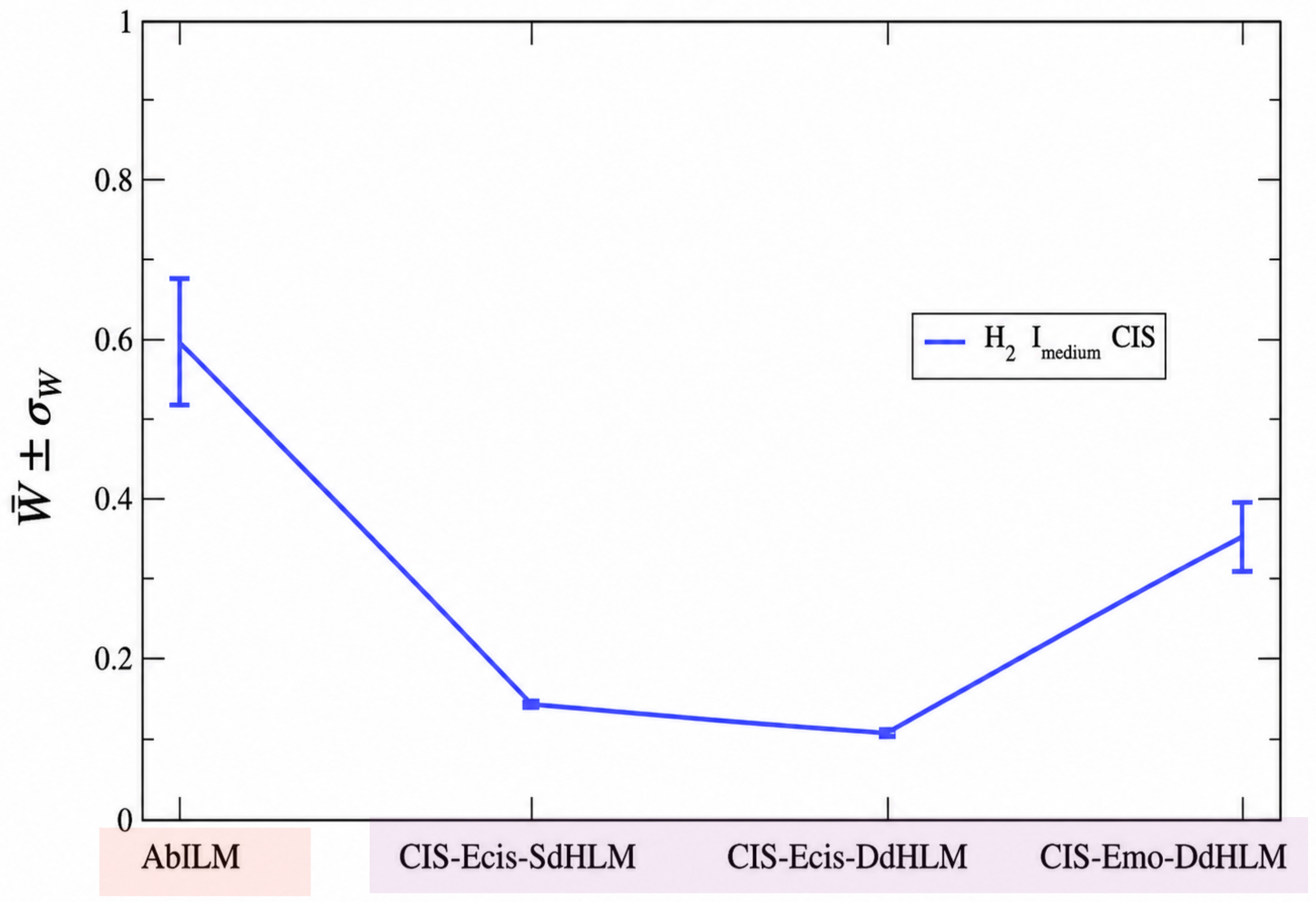


Ab Initio versus Heuristic lifetimes models

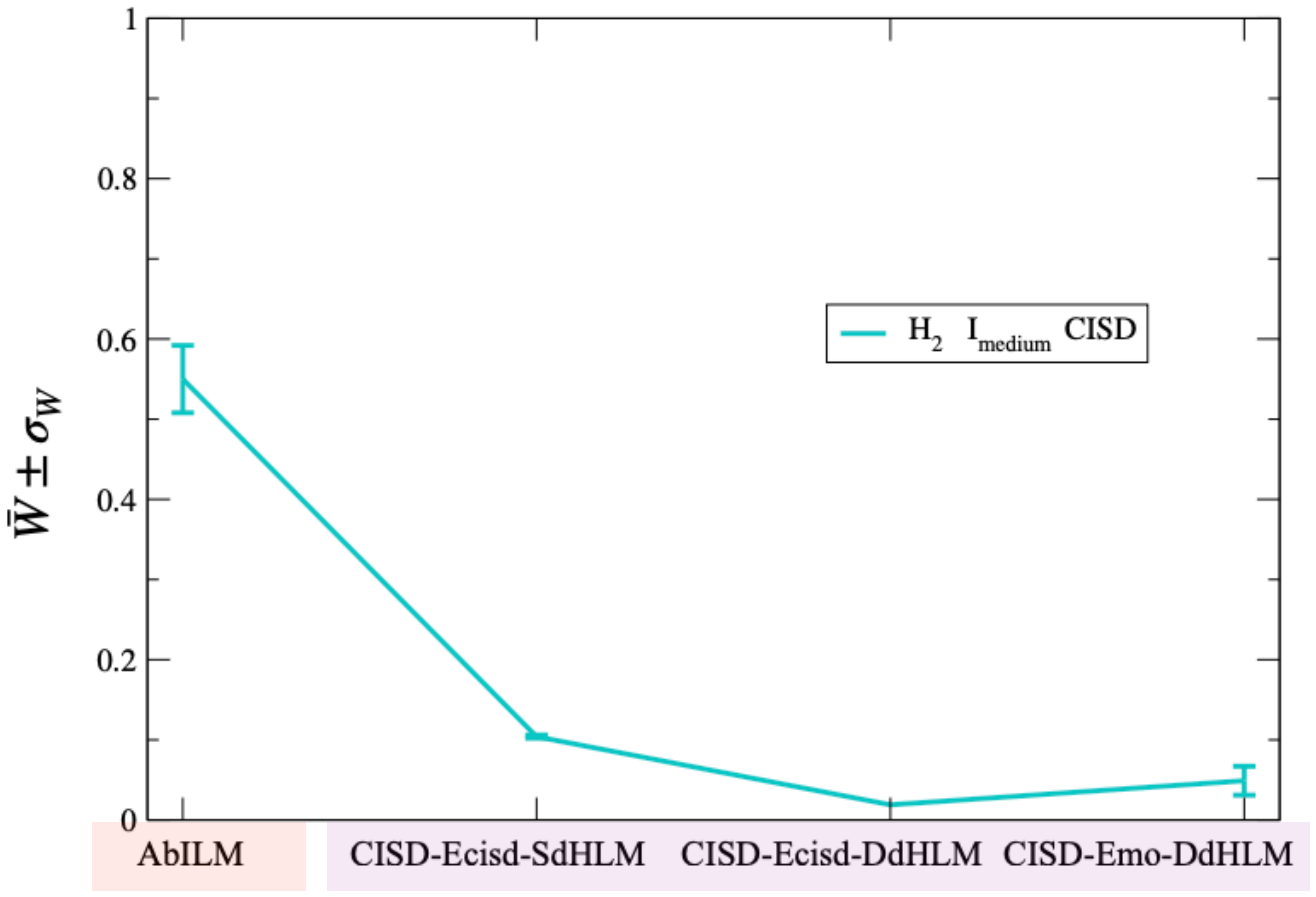
Lifetimes model for continuum

Ground-state depletion at the end of the laser

Single excitation correlations



Single and Double excitation correlations



Ionisation depends on the lifetimes model

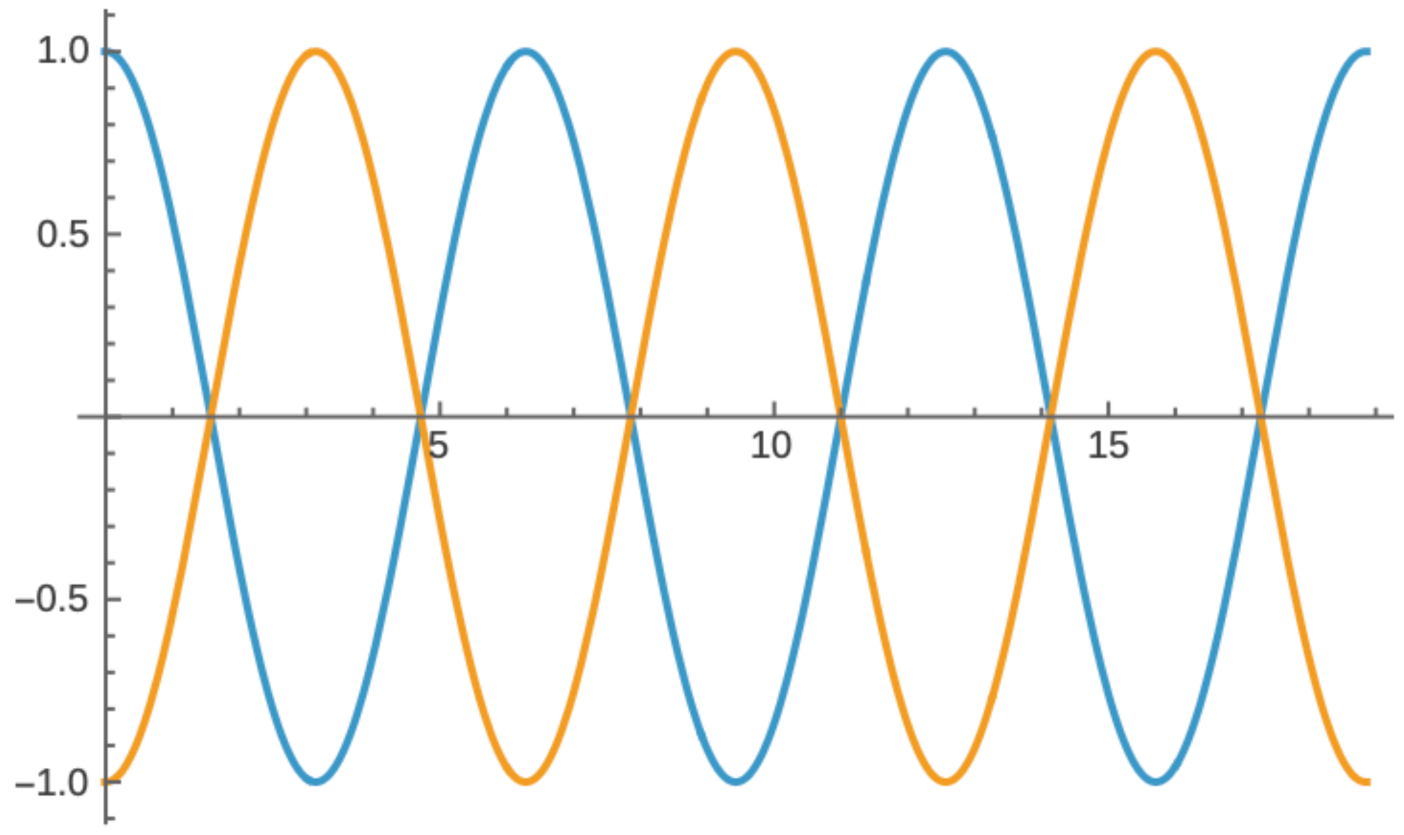
Control HHG through Dynamical Symmetry

A dynamical symmetry operator combines: a spatial operation + a temporal translation

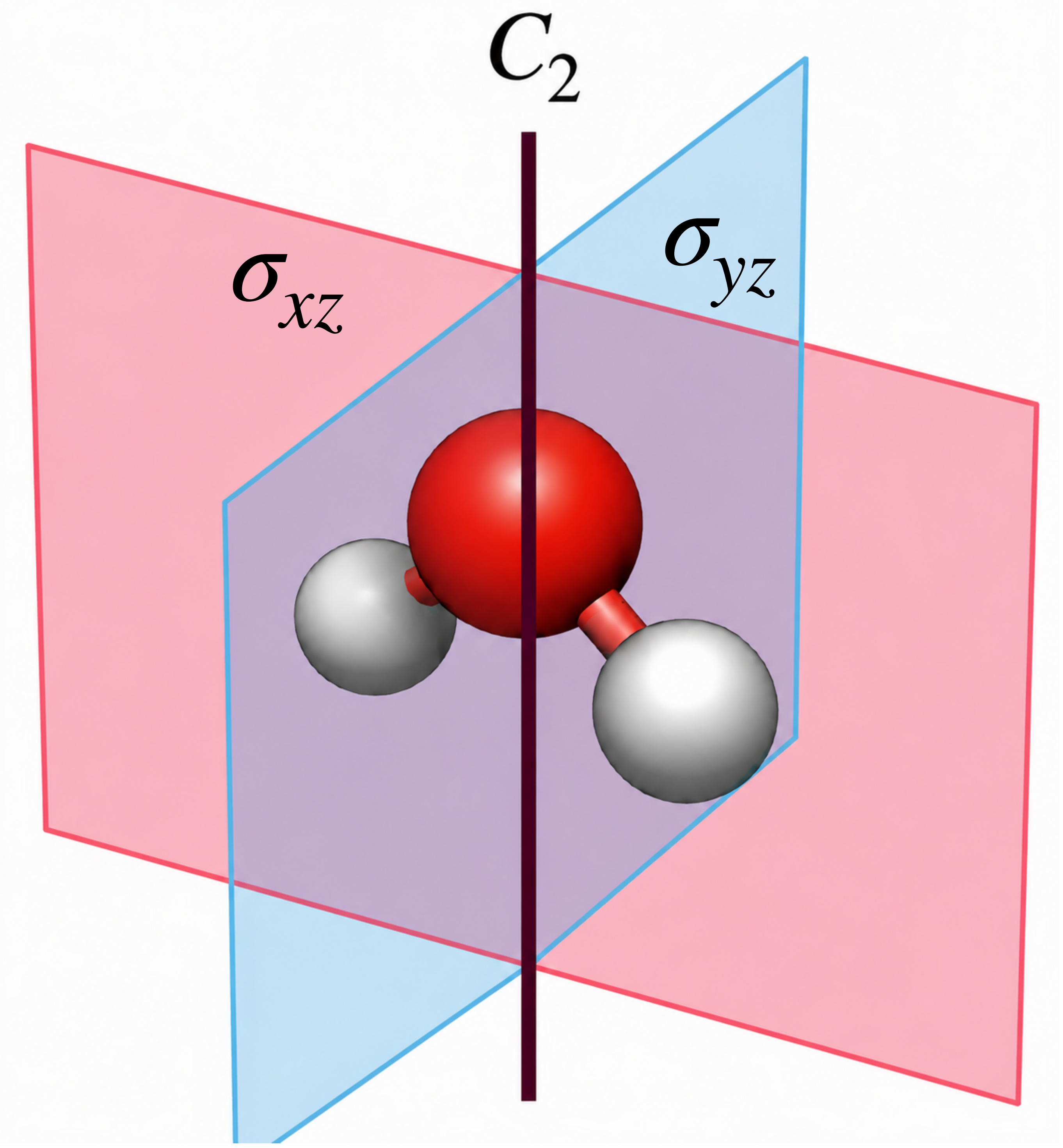
linear polarization

$$E(t) = -E(t+T/2) = -\tau_{T/2}E(t)$$

```
Plot[{Cos[t], Cos[ t+2 Pi / 2]}, {t, 0, 6 Pi}]
```



$$\hat{\sigma}_{yz} H_0 \hat{\sigma}_{yz}^{-1} = H_0$$



$$\hat{Z}_{yz} = \hat{\sigma}_{yz} \cdot \tau_{T/2}$$

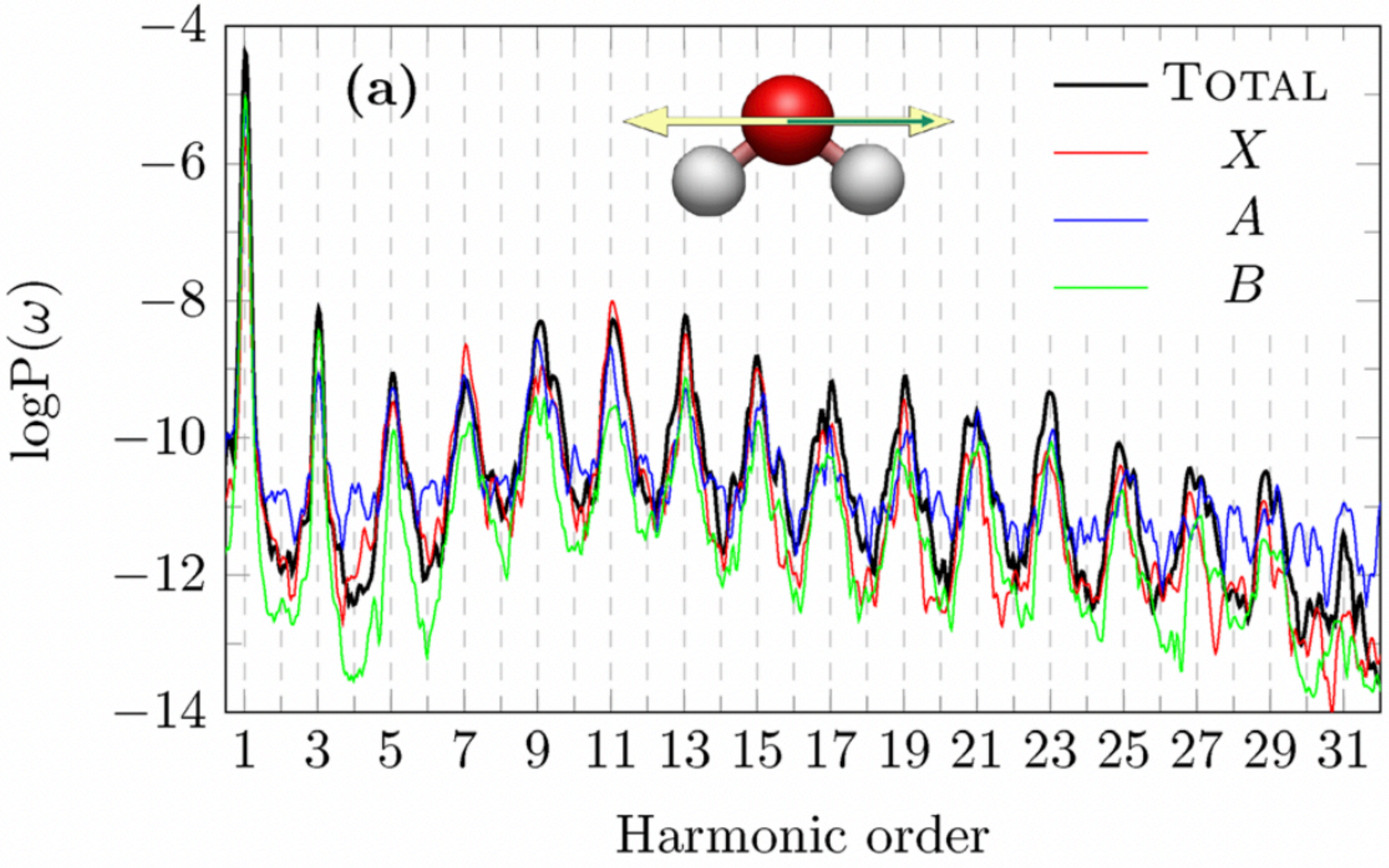
$$\hat{Z}_{yz} H(t) \hat{Z}_{yz}^{-1} = H(t)$$

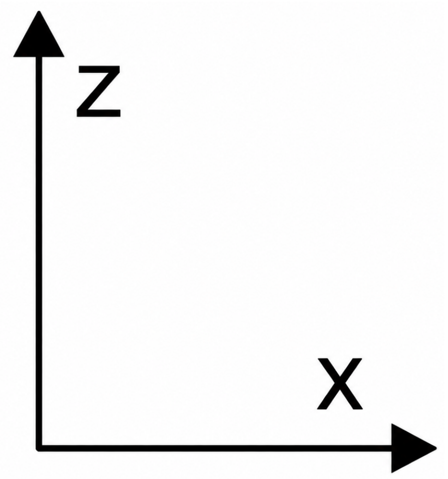
Control HHG through Dynamical Symmetry

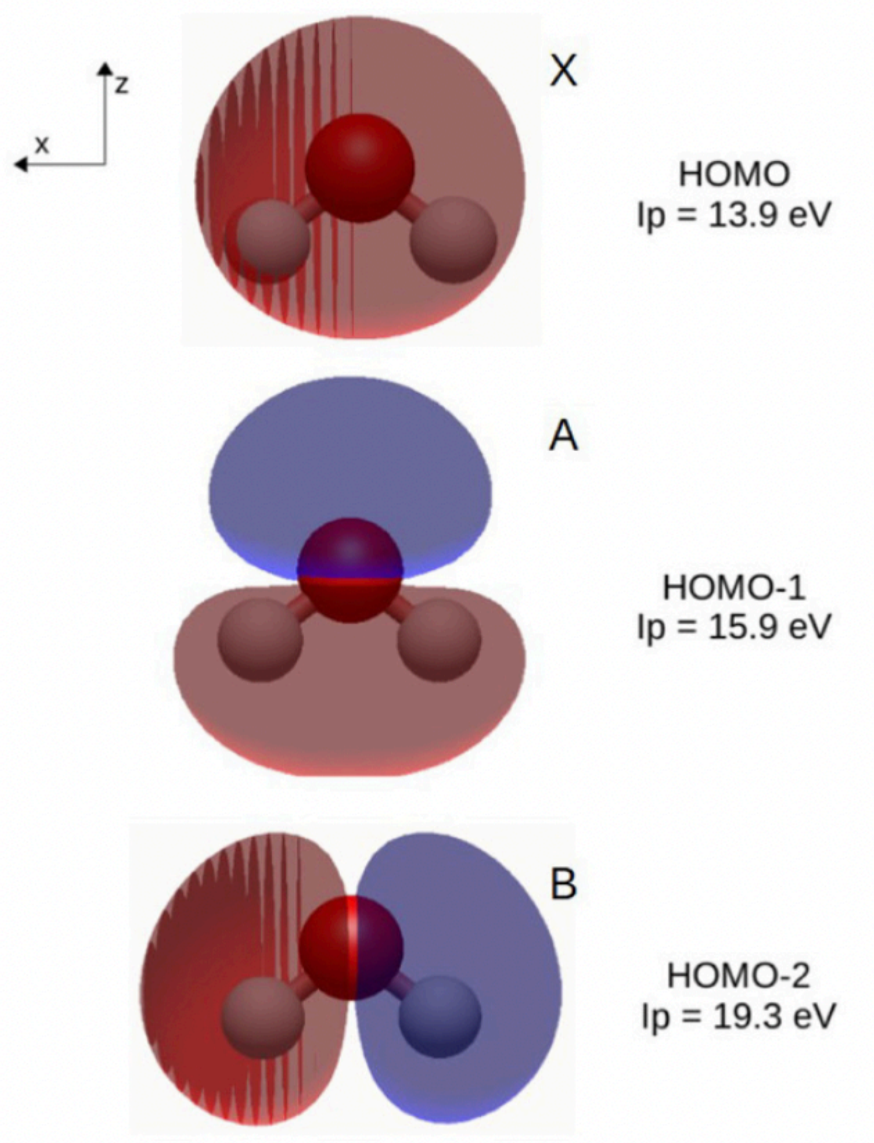
H_2O

$$\mu_x(t + T/2) = -\mu_x(t)$$

odd harmonics







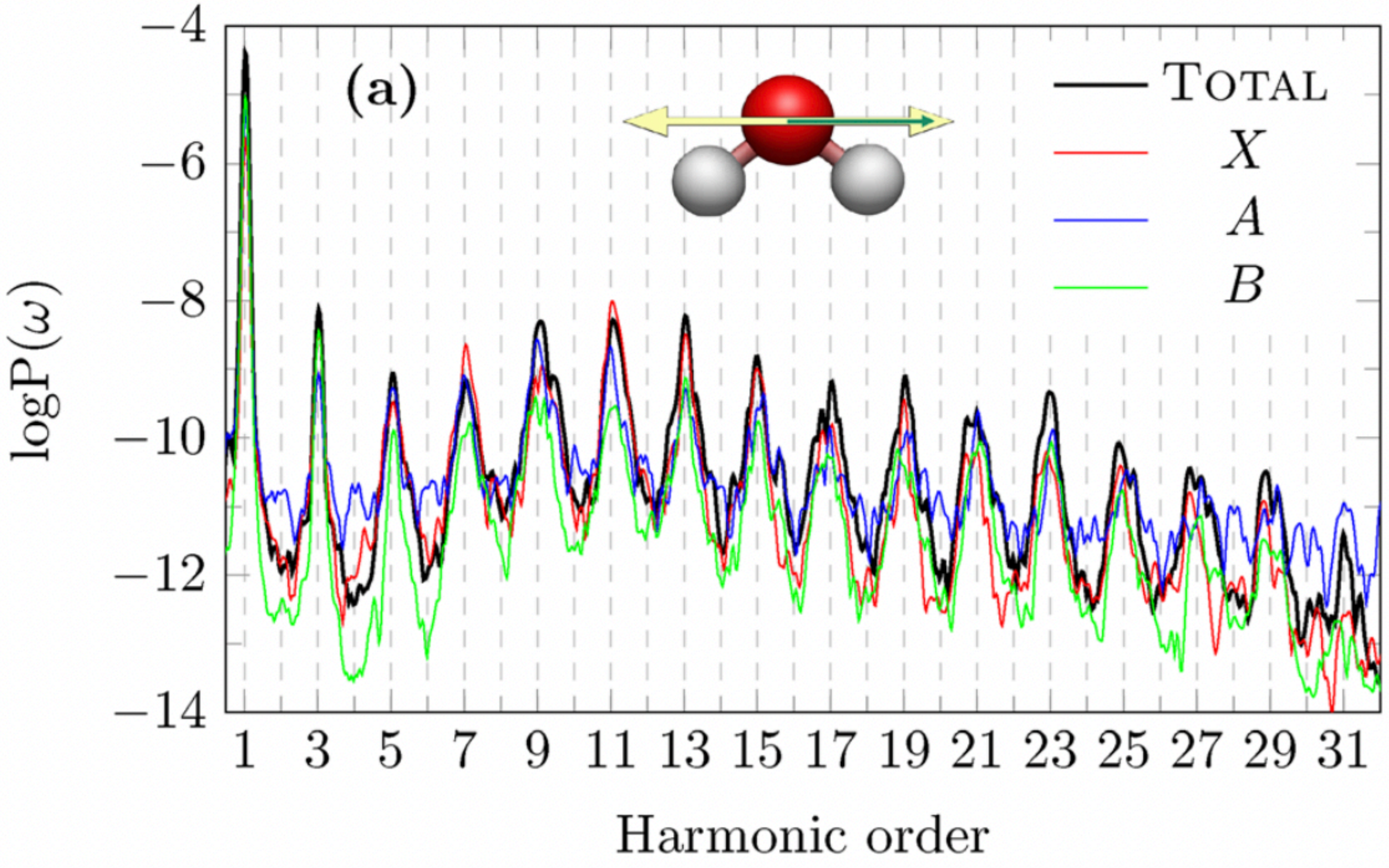
M. Marchetta, E. Luppi, E. Coccia, Phys. Chem. Chem. Phys. 27, 12801 (2025).

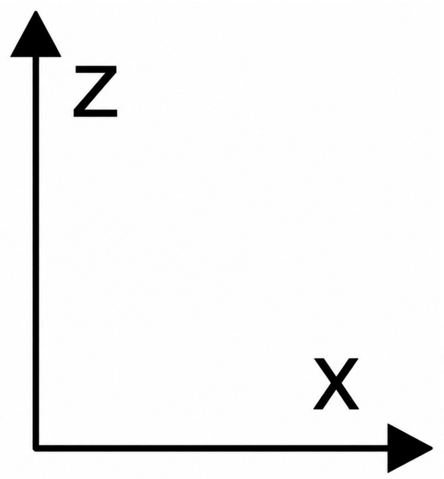
M. Marchetta, C. Morassut, J. Toulouse, E. Coccia, E. Luppi, J. Chem. Phys. 161, 204111 (2024).

Control HHG through Dynamical Symmetry H_2O

$$\mu_x(t + T/2) = -\mu_x(t)$$

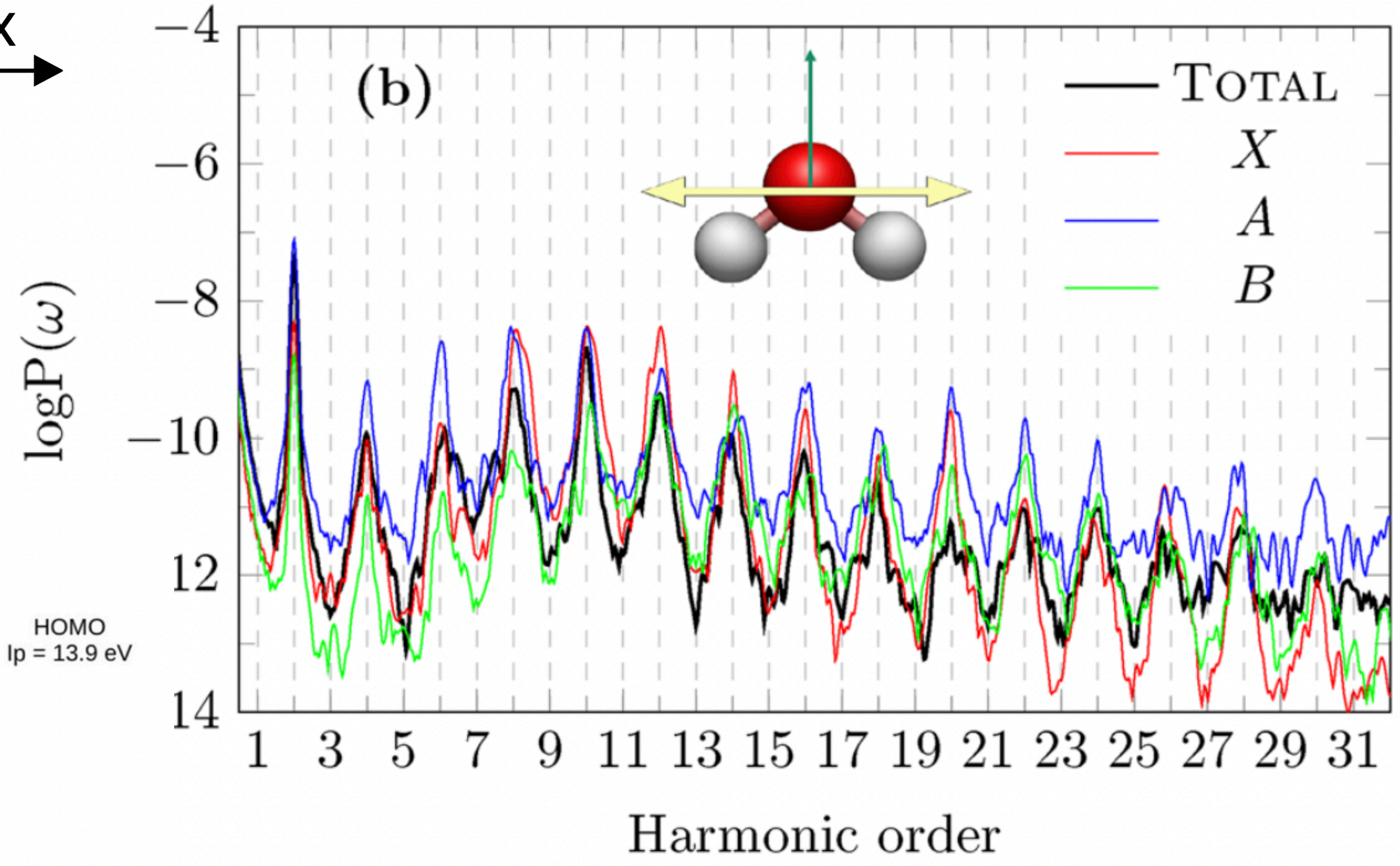
odd harmonics

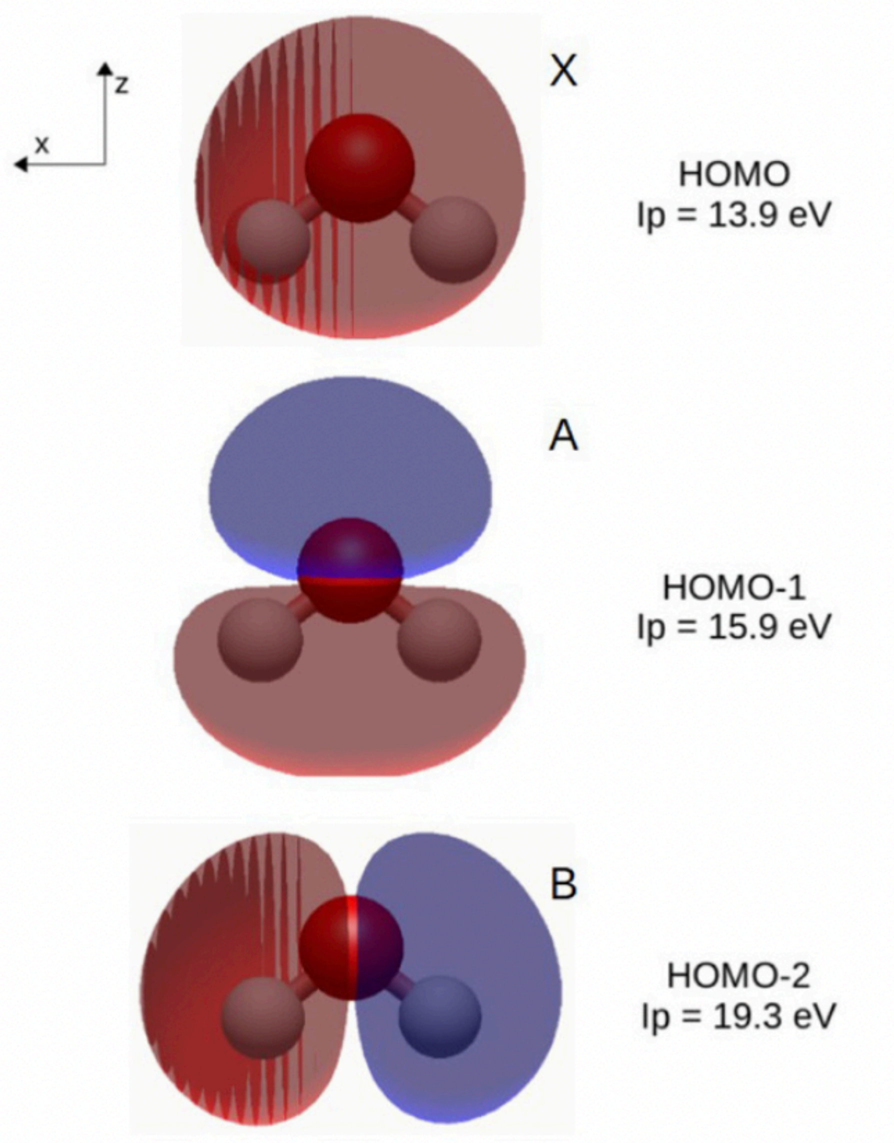




$$\mu_z(t + T/2) = +\mu_z(t)$$

even harmonics





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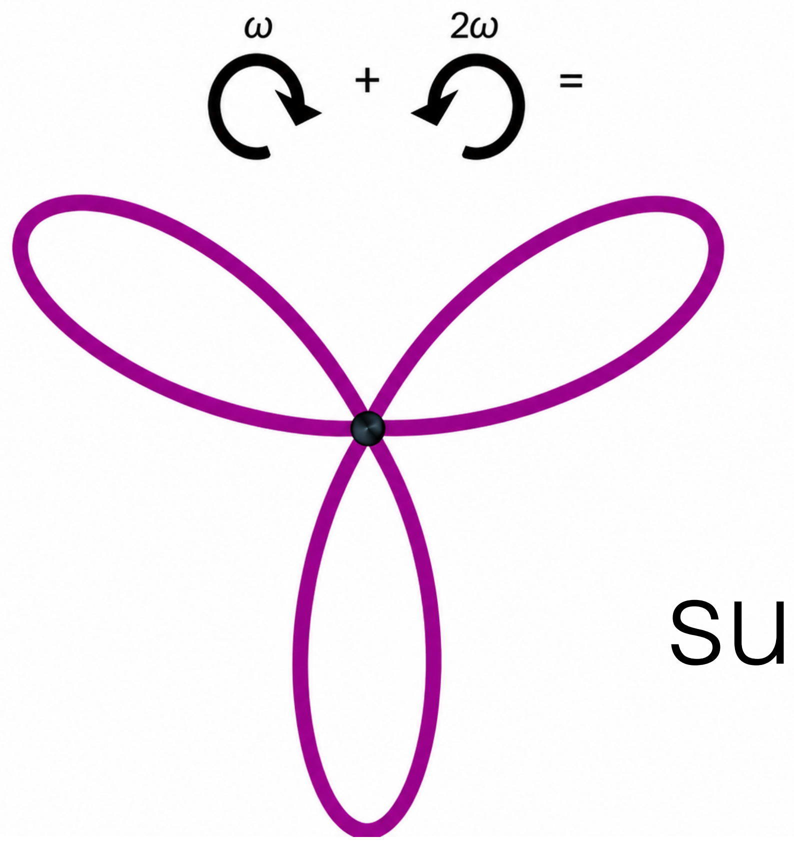
Control HHG through Dynamical Symmetry

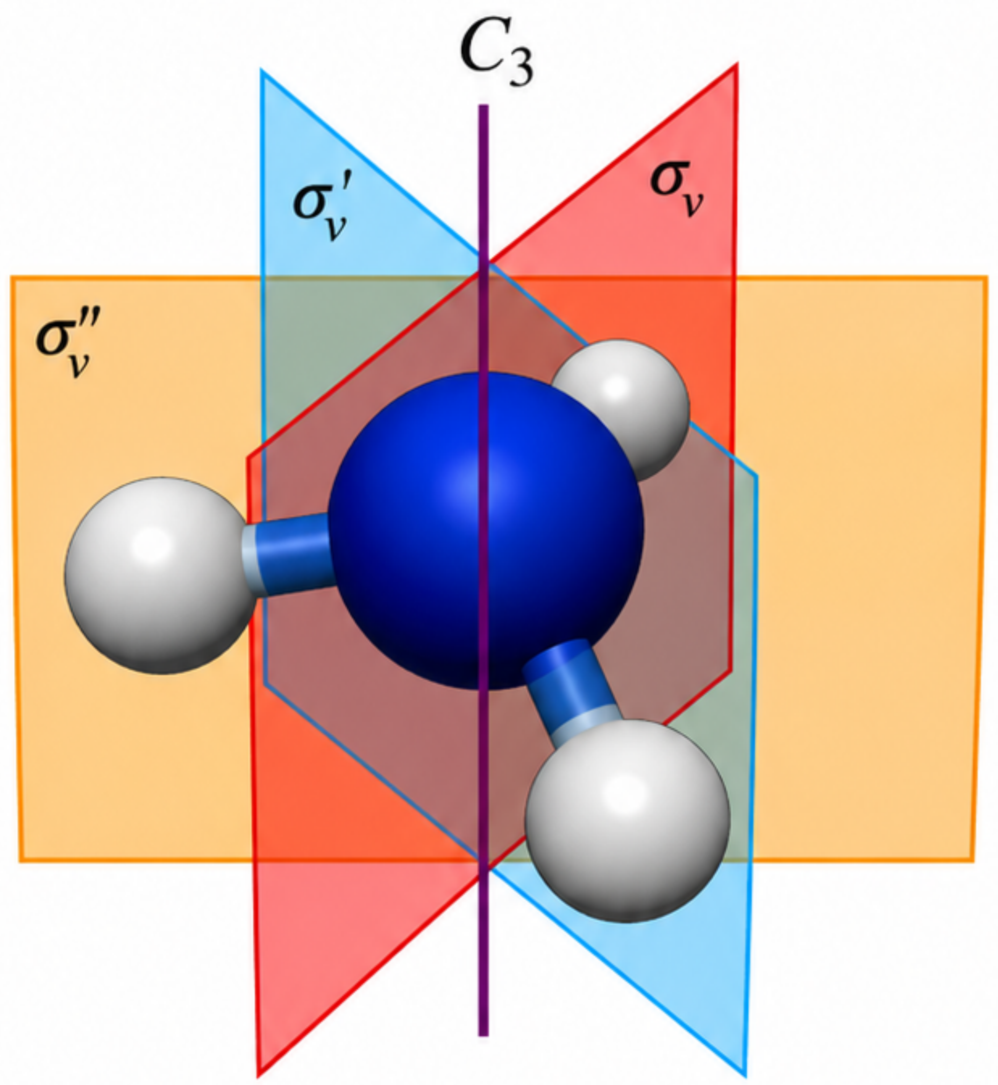
Counter-rotating bicircular laser field ω–2ω



Symmetry $\hat{C}_3$

Selection rules:

suppression of harmonics that are multiples of three



$$\mathbf{E}(t + T/3) = \hat{C}_3\mathbf{E}(t)$$

$$\hat{C}_3 H_0 \hat{C}_3^{-1} = H_0$$

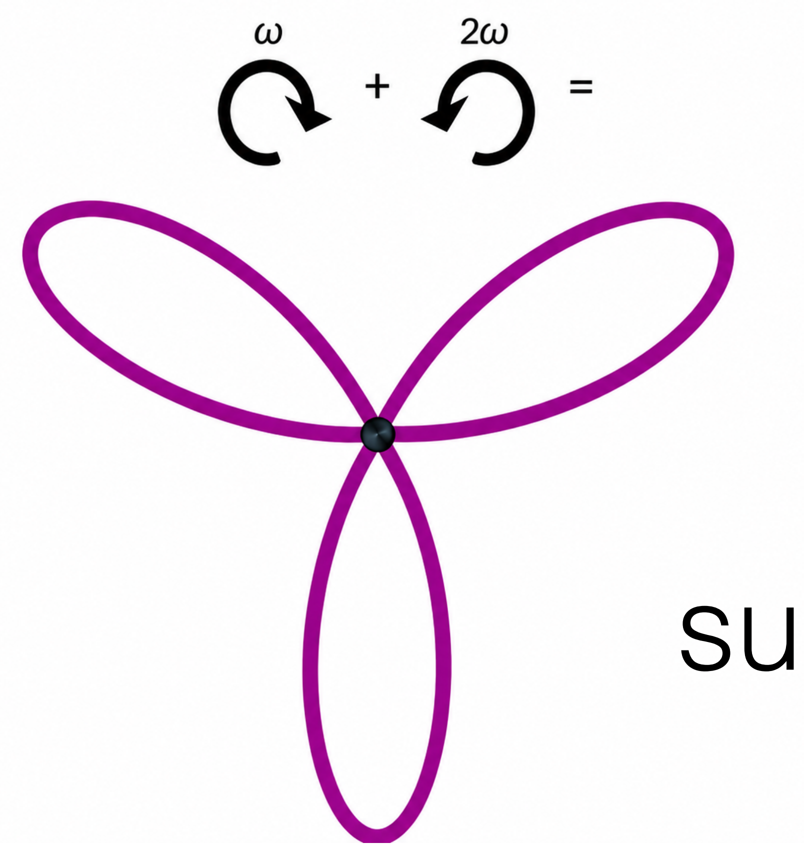
Light

Experimental collaboration
C. Vozzi and D. Faccialà

In preparation

Control HHG through Dynamical Symmetry

Counter-rotating bicircular laser field ω–2ω



Symmetry $\hat{C}_3$

Selection rules:

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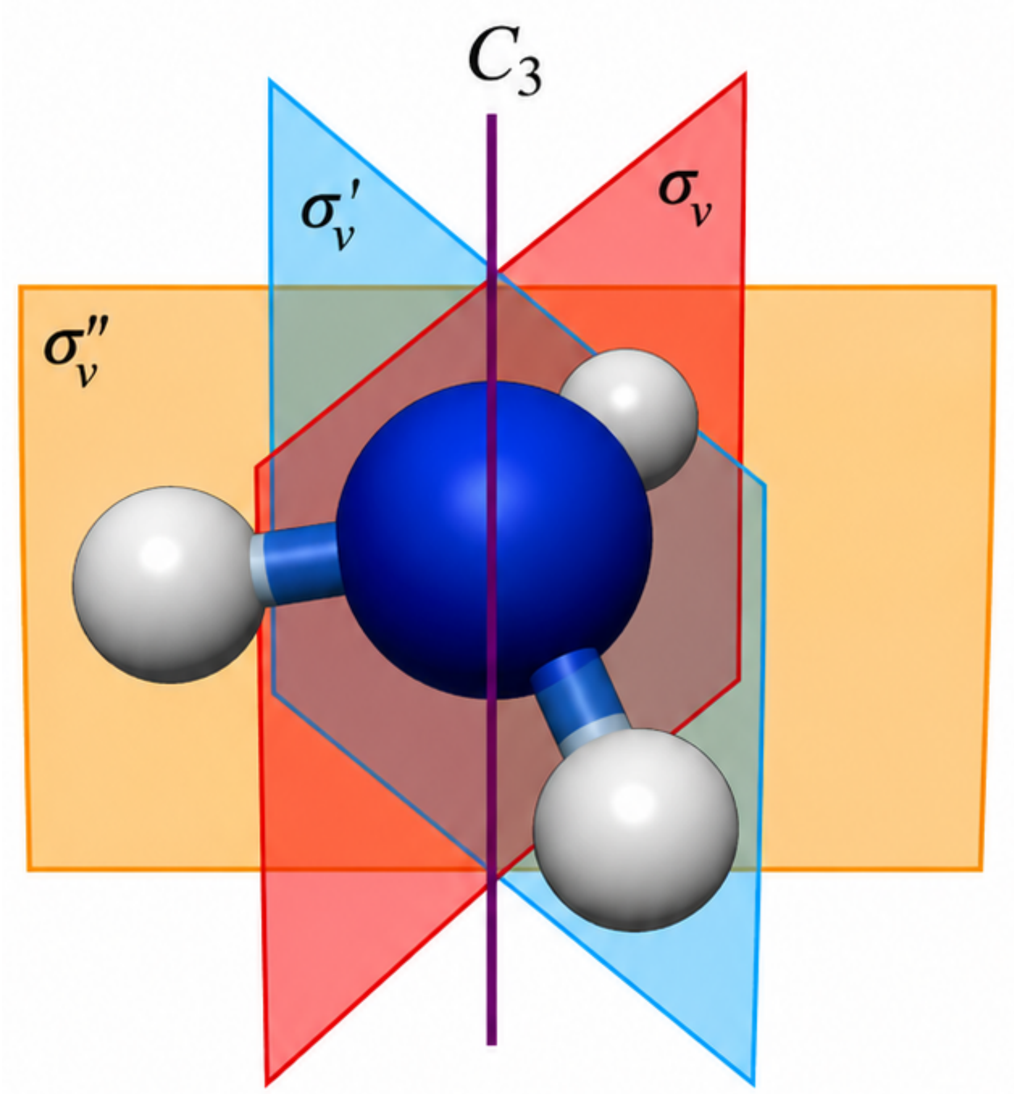
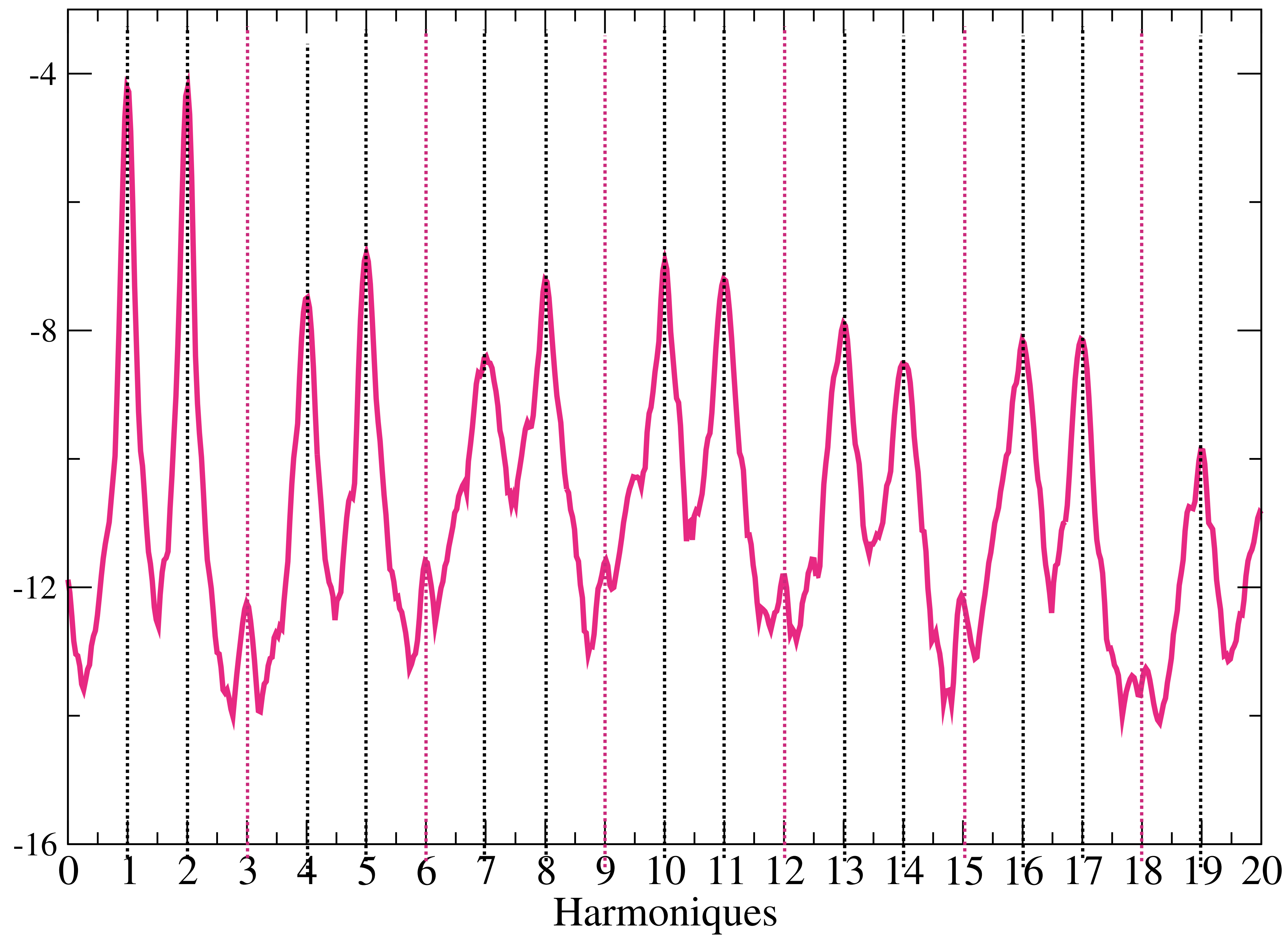


$$\mathbf{E}(t + T/3) = \hat{C}_3\mathbf{E}(t)$$

$$\hat{C}_3 H_0 \hat{C}_3^{-1} = H_0$$

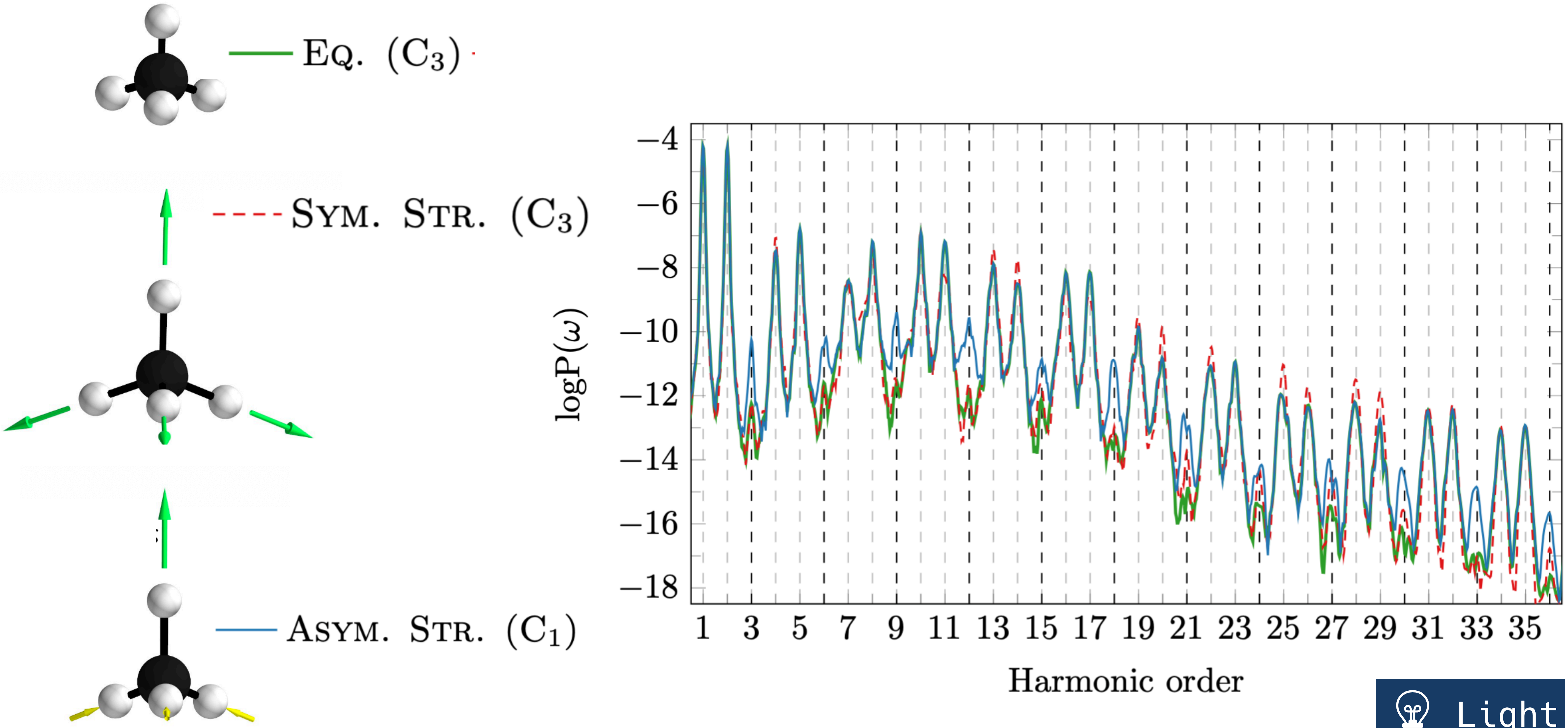


Light

Experimental collaboration
C. Vozzi and D. Faccialà

In preparation

HHG through Dynamical Symmetry : the effect of nuclear motion



Light

Thanks :)

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