Gaussian continuum basis functions for calculating high-harmonic generation spectra

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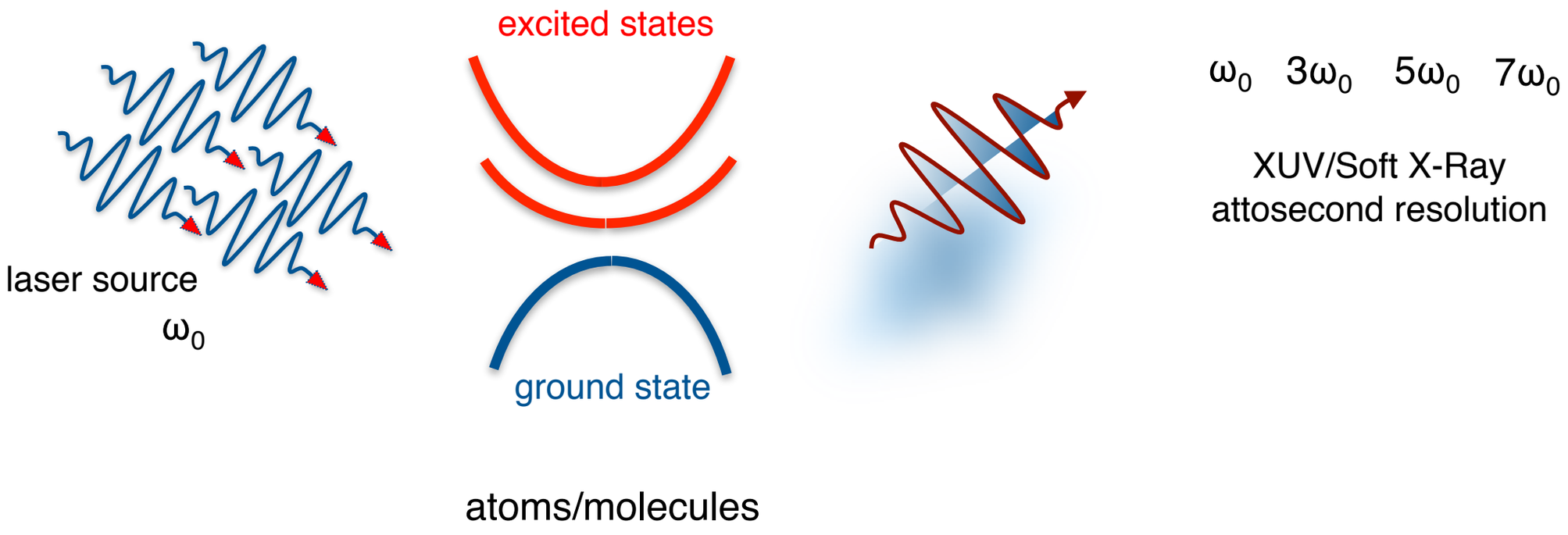
Quantum chemistry and high-harmonic generation

Quantum chemistry theoretical methods *(Configuration interaction, Coupled clusters, …)* are very efficient to calculate molecular properties :

1. total energy, vibrational frequencies, reactivity

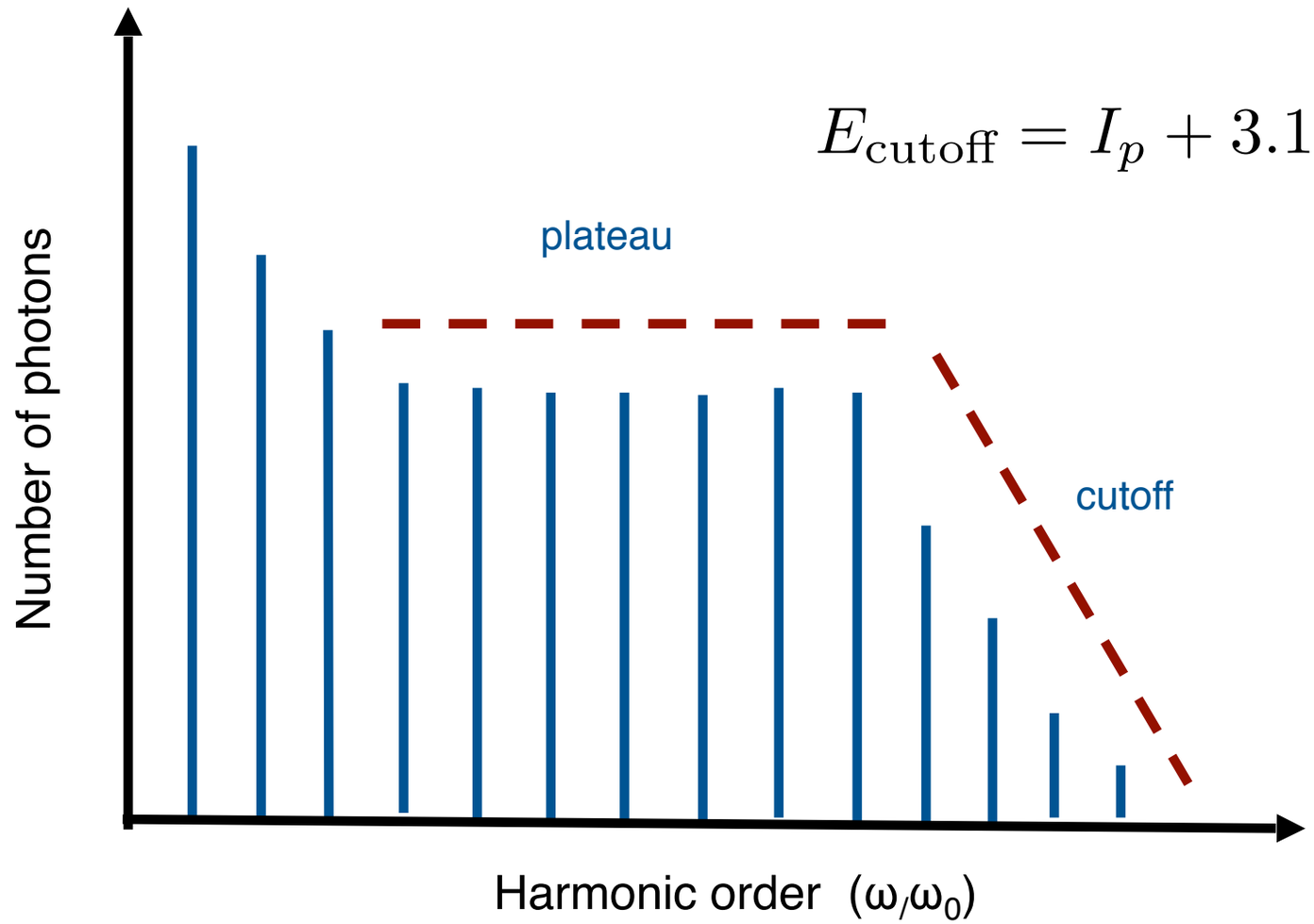
2. linear response excitations (weak field)

3. what about electron dynamics in strong field and in particular high-harmonic generation ?



Quantum chemistry and high-harmonic generation

Is it possible to describe HHG spectra with quantum chemistry approaches ?



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

HHG spectrum contains the structural and dynamical information of the molecules

Extending quantum chemistry to the time domain

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

$$\hat{H}(t) = \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

field-free hamiltonian $\hat{H}_0$

laser-field interaction (lenght gauge) $\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$

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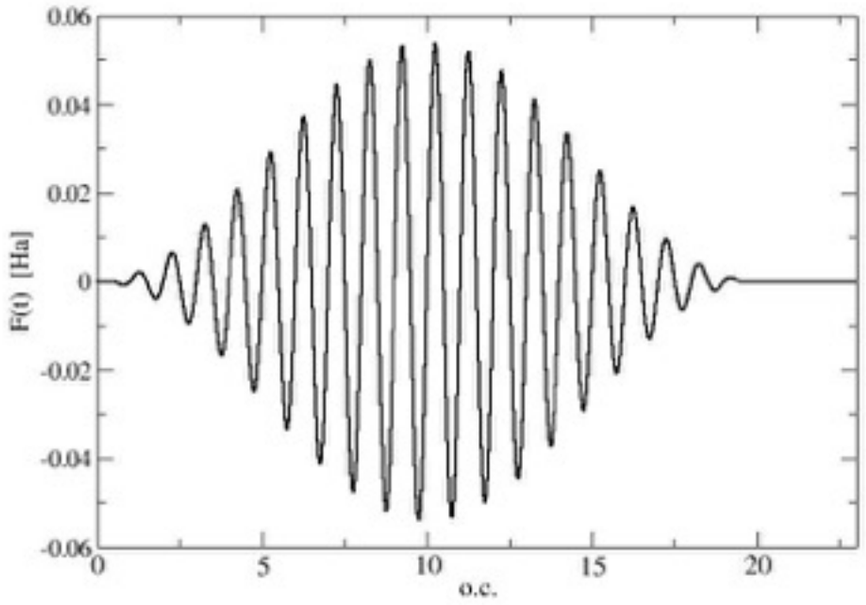
$$\mathbf{E}(t) = \hat{\mathbf{n}} f(t) sin(\omega_0 t + \phi)$$

$$f(t) \approx cos^2(\Omega t)$$

ω_0 = 1.55 eV



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field-free hamiltonian $\hat{H}_0$ ⇢ ϵ_k^{CI} ψ_k^{CI}

$$|\Psi(t)\rangle = \sum_{k=0} c_k(t)|\psi_k\rangle$$

Configuration Interaction

laser-field interaction (lenght gauge) $\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$

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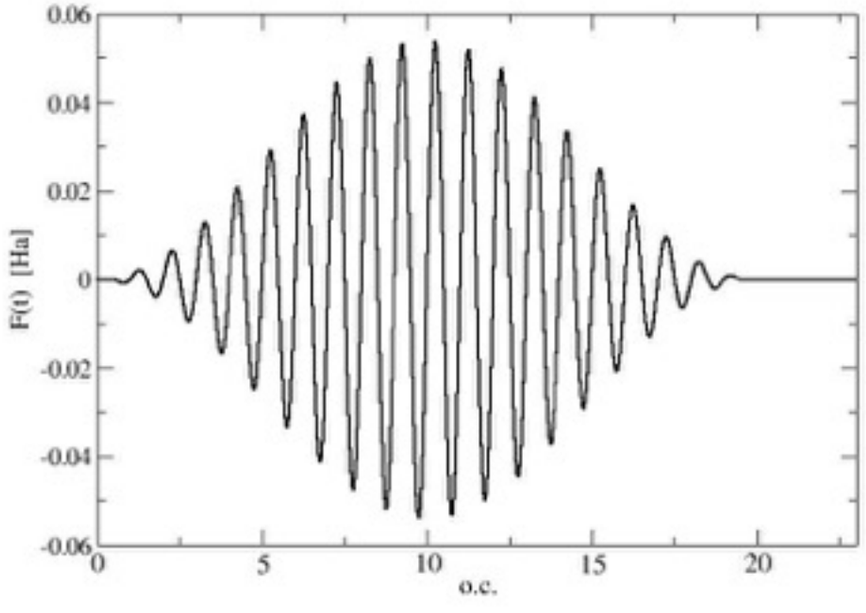

Time Dependent Configuration Interaction (TDCI)

$$i\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = \sum_s (E_s^{\mathrm{CI}}\delta_{ks} - \mu_{ks}E(t))c_s(t)$$

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$$P_\mu(\omega) = \left|\frac{1}{t_f - t_i}\int_{t_i}^{t_f} e^{-i\omega t}\boldsymbol{\mu}(t)dt\right|^2 = \left|\frac{1}{t_f - t_i}\sum_{s,k}\int_{t_i}^{t_f} e^{-i\omega t}c_s^*(t)c_k(t)\boldsymbol{\mu}_{ks}^{CI}dt\right|^2$$

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* time-dependent velocity $\boldsymbol{v}(t)$ and acceleration $\boldsymbol{a}(t)$

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

TDCI and ionisation

$$i\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = \sum_s (E_s^{\mathrm{CI}}\delta_{ks} - \mu_{ks}E(t))c_s(t)$$

We replace every state energy by a complex energy!

$$E_k^{\mathrm{CI}} \rightarrow E_k^{\mathrm{CI}} + \Gamma_k$$

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- Heuristic lifetimes model S. Klinkusch e al. JCP 131, 114304 (2009) $\Gamma_i \propto \frac{1}{d}$

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- Ab-initio lifetimes model Coccia, Luppi, Assaraf, Toulouse work in progress

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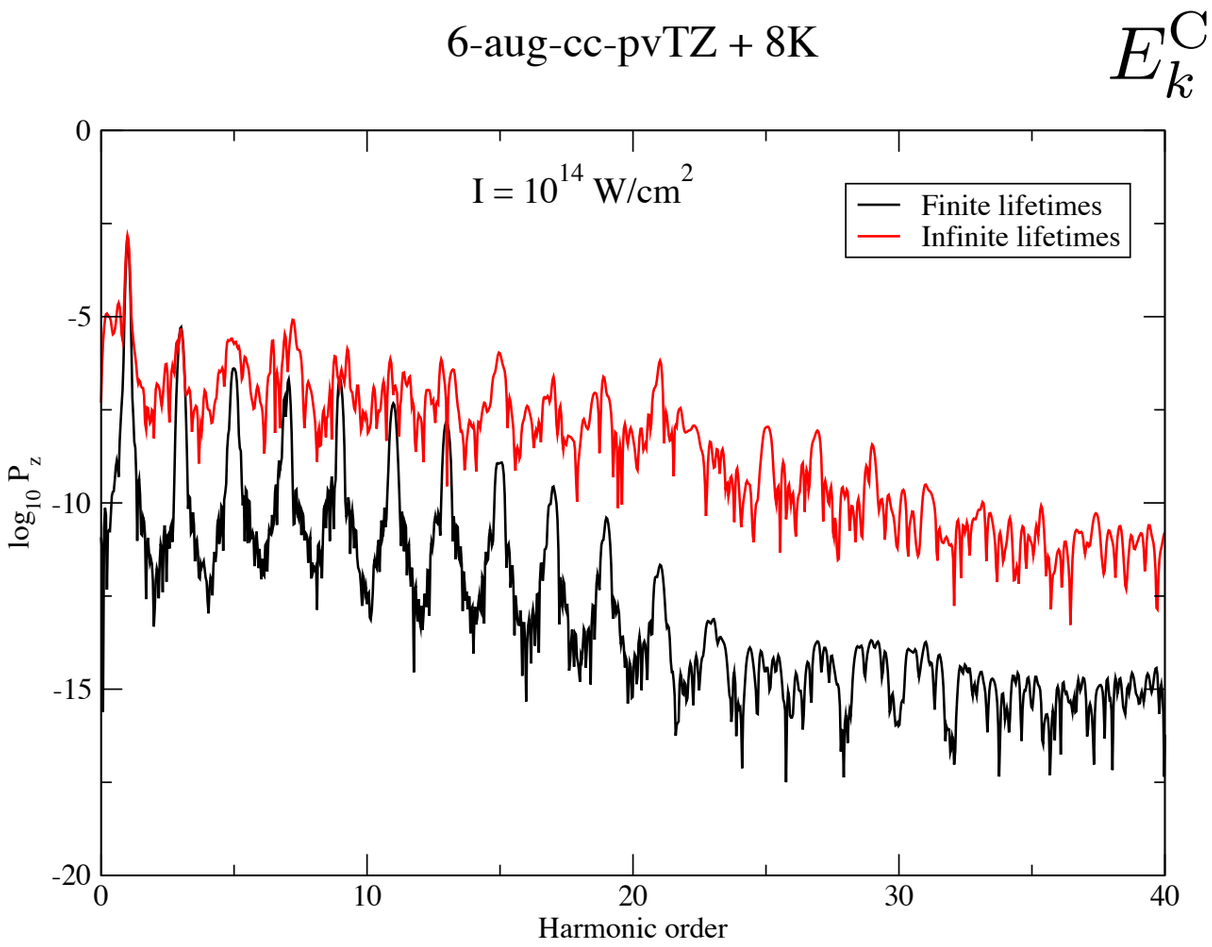


- Heuristic lifetimes model

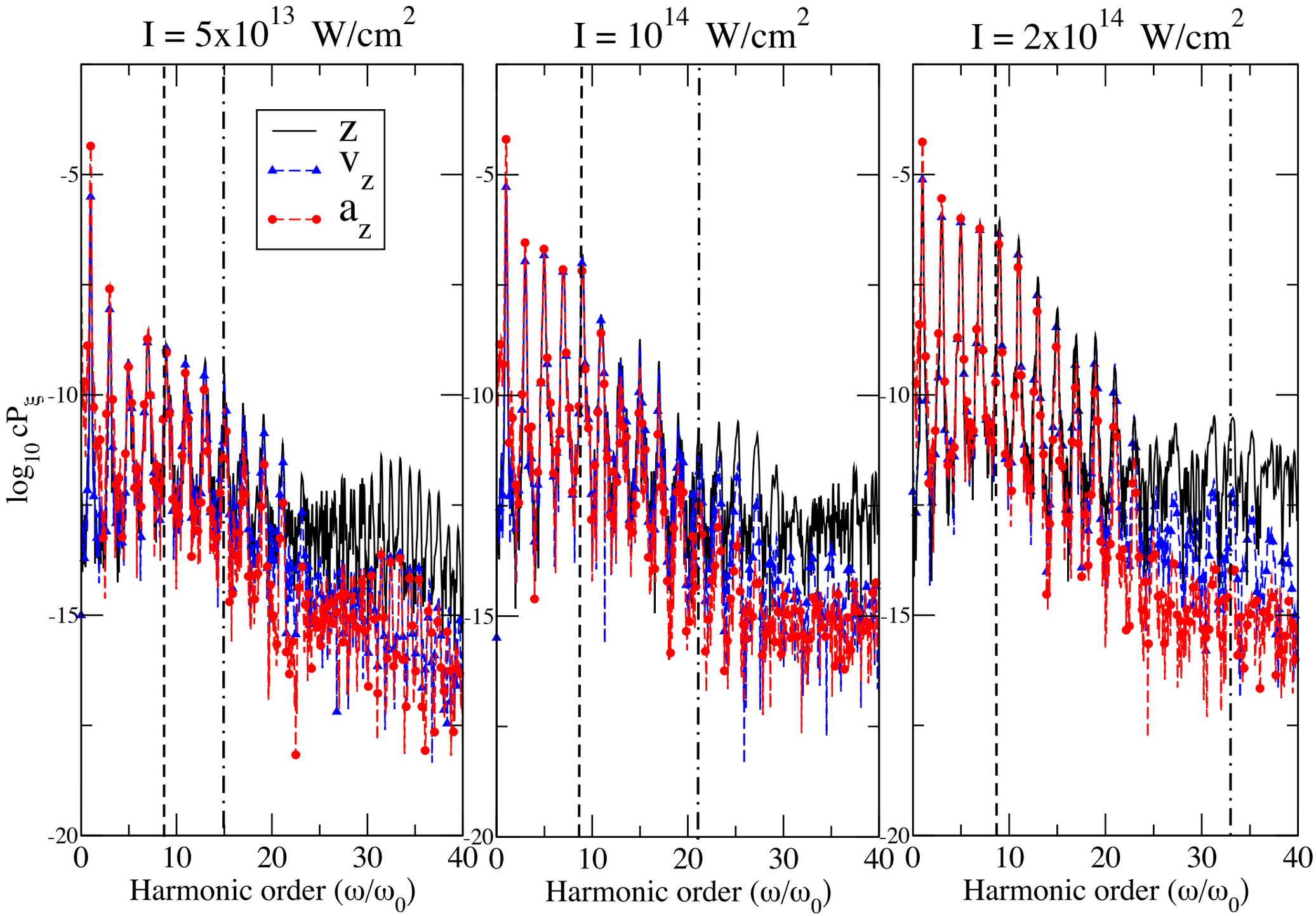
  S. Klinkusch e al. JCP 131, 114304 (2009)

HHG and TDCI for H atom

6-aug-cc-PVTZ

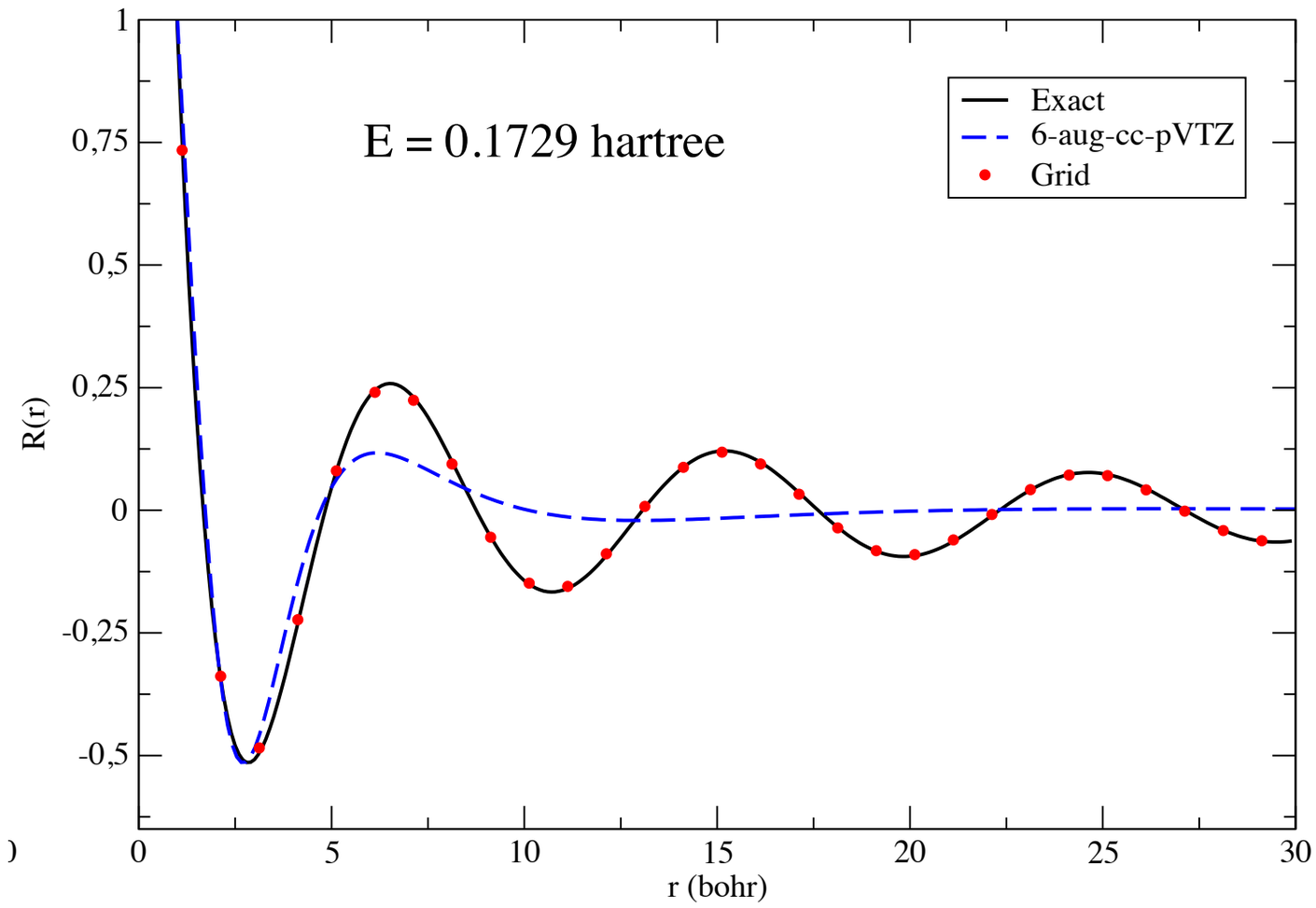
Vertical dashed $\rightarrow I_p/\omega_0$ (I_p ionization potential)

Vertical dot-dashed $\rightarrow E_{cut}/\omega_0 = (I_p + 3.17U_p)/\omega_0$ ($U_p \propto I/\omega_0^2$)



What about using Gaussian basis sets in TDCI ?

How 6-aug-cc-PVTZ describe the continuum states ?



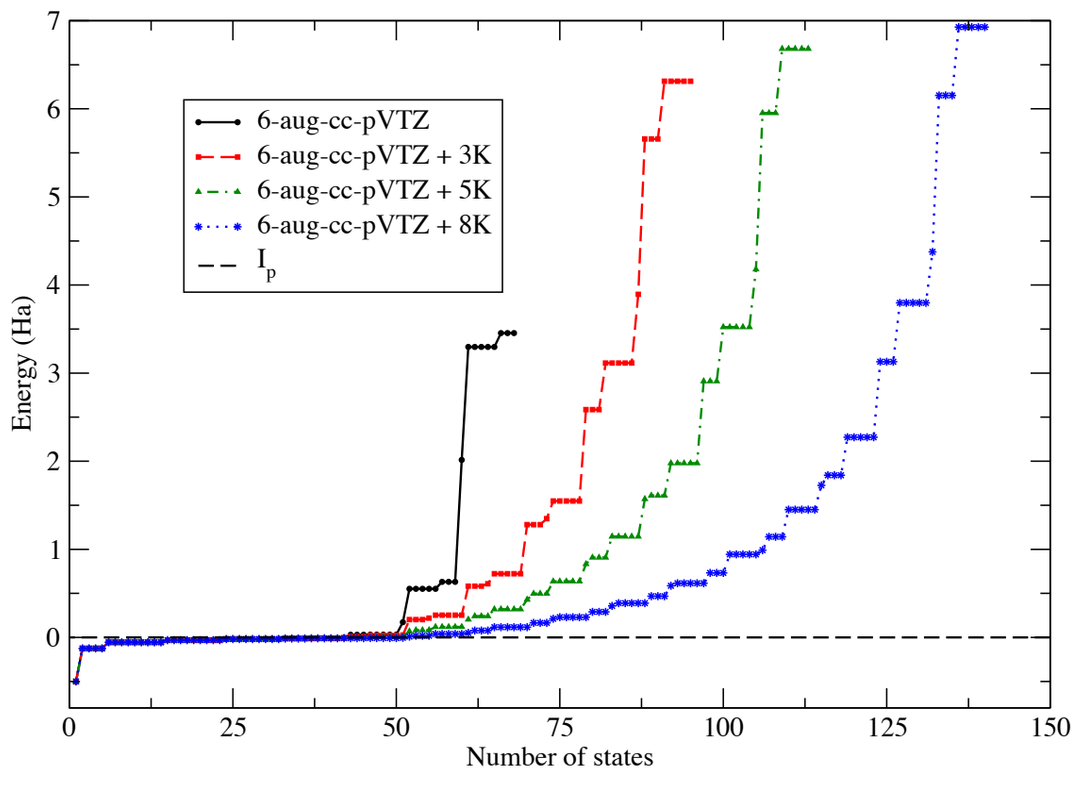
Asymptotic behaviour ($r \rightarrow \infty$) from the free-electron Schrodinger equation

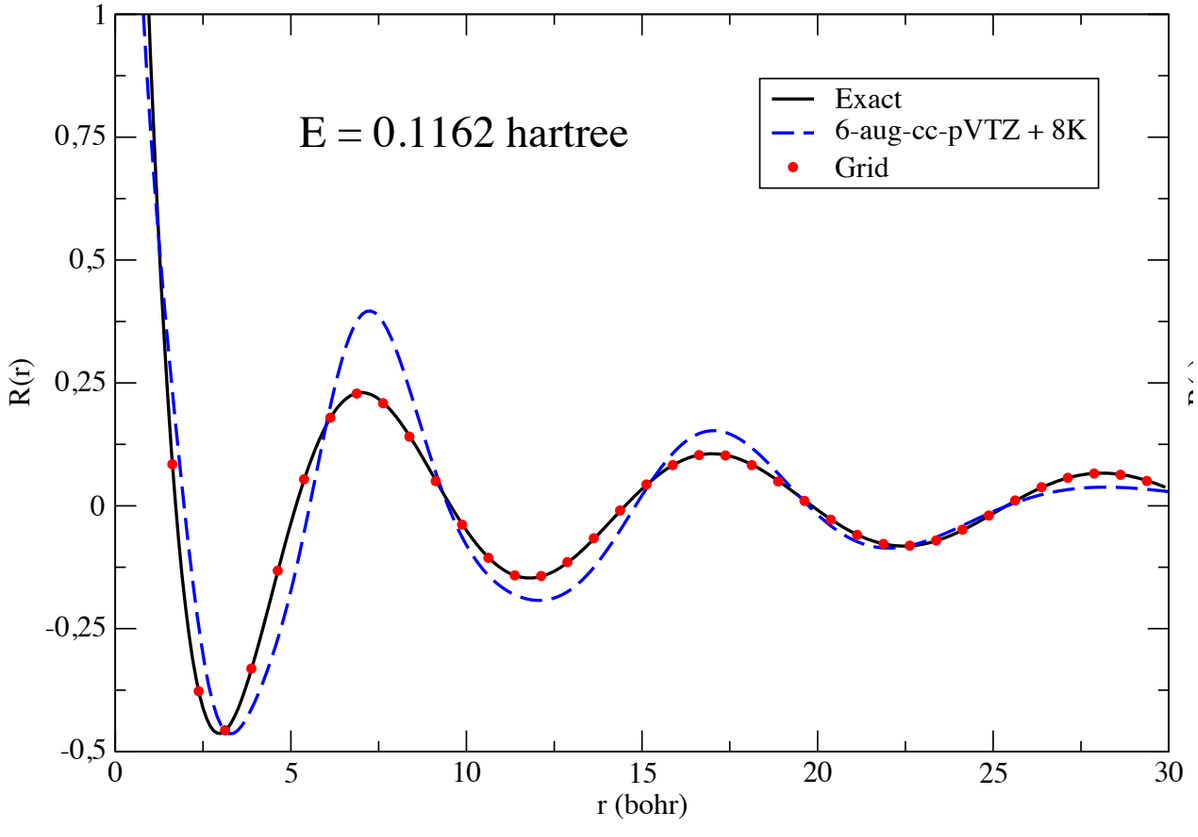
What about using Gaussian basis sets in TDCI ?

Universal Gaussian basis set of Kaufman et al. J. Phys. B (1989)

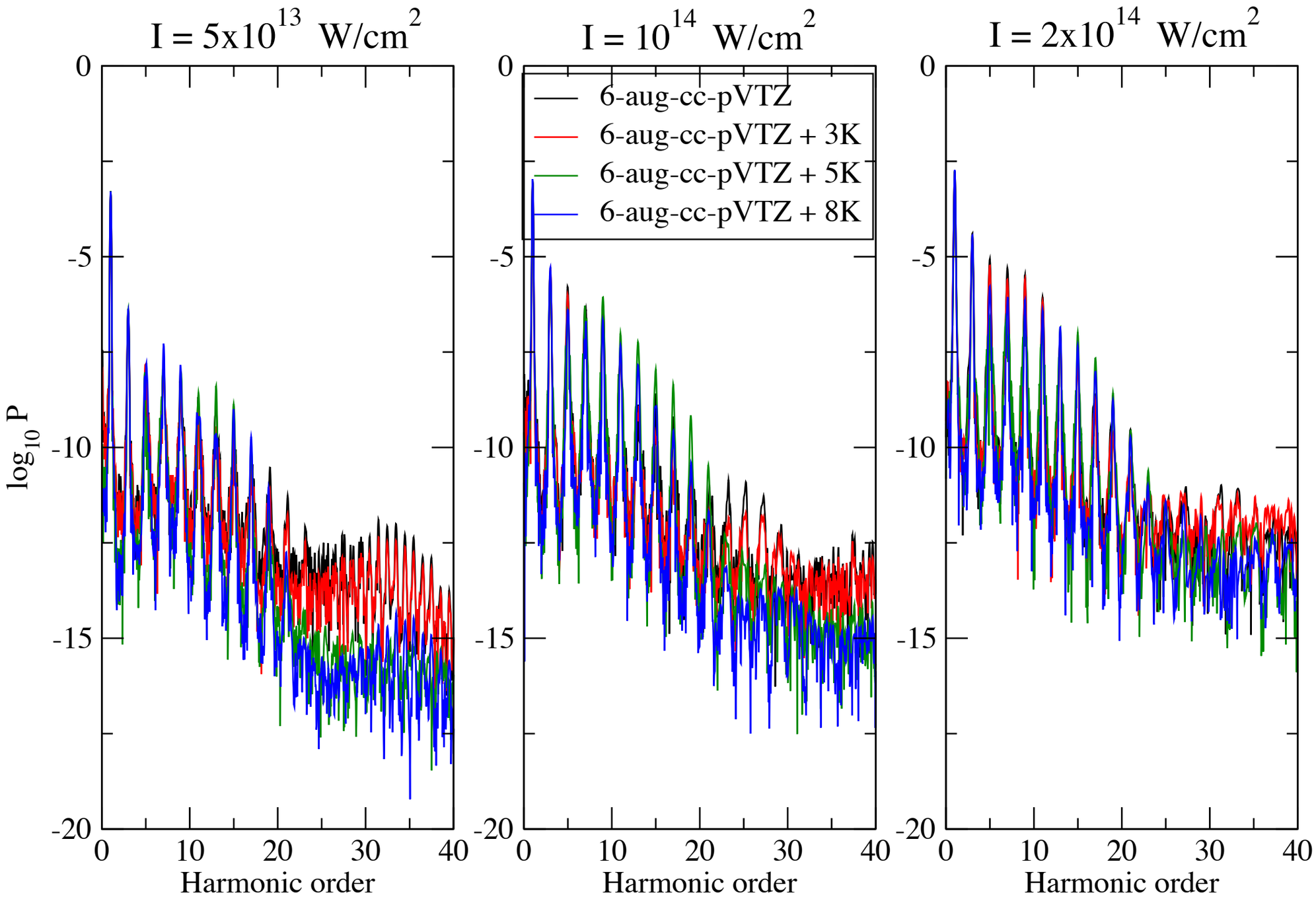
Generating sequences of exponents spanning low-energy continuum solutions

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

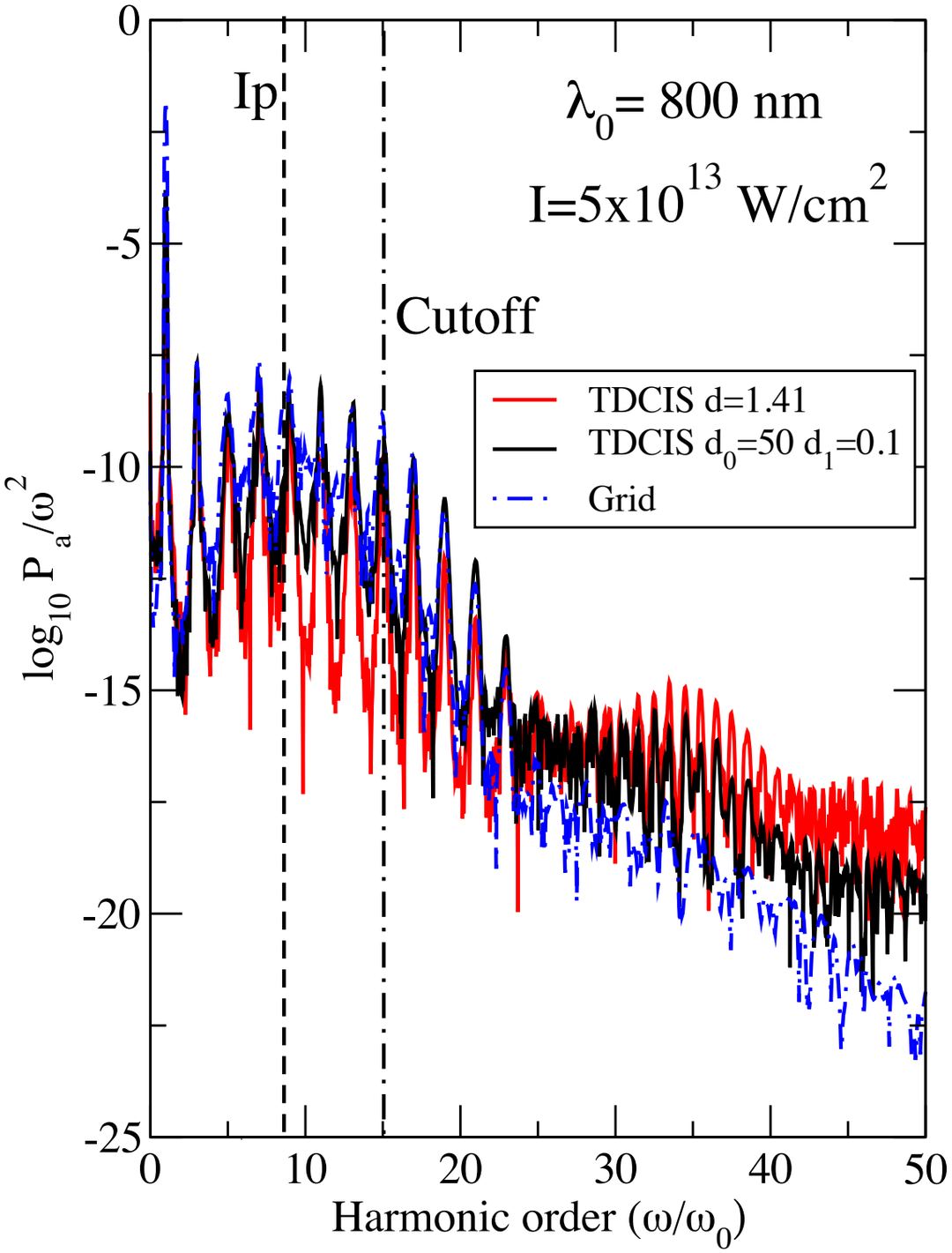




HHG and TDCI for H atom : optimal continuum Gaussian



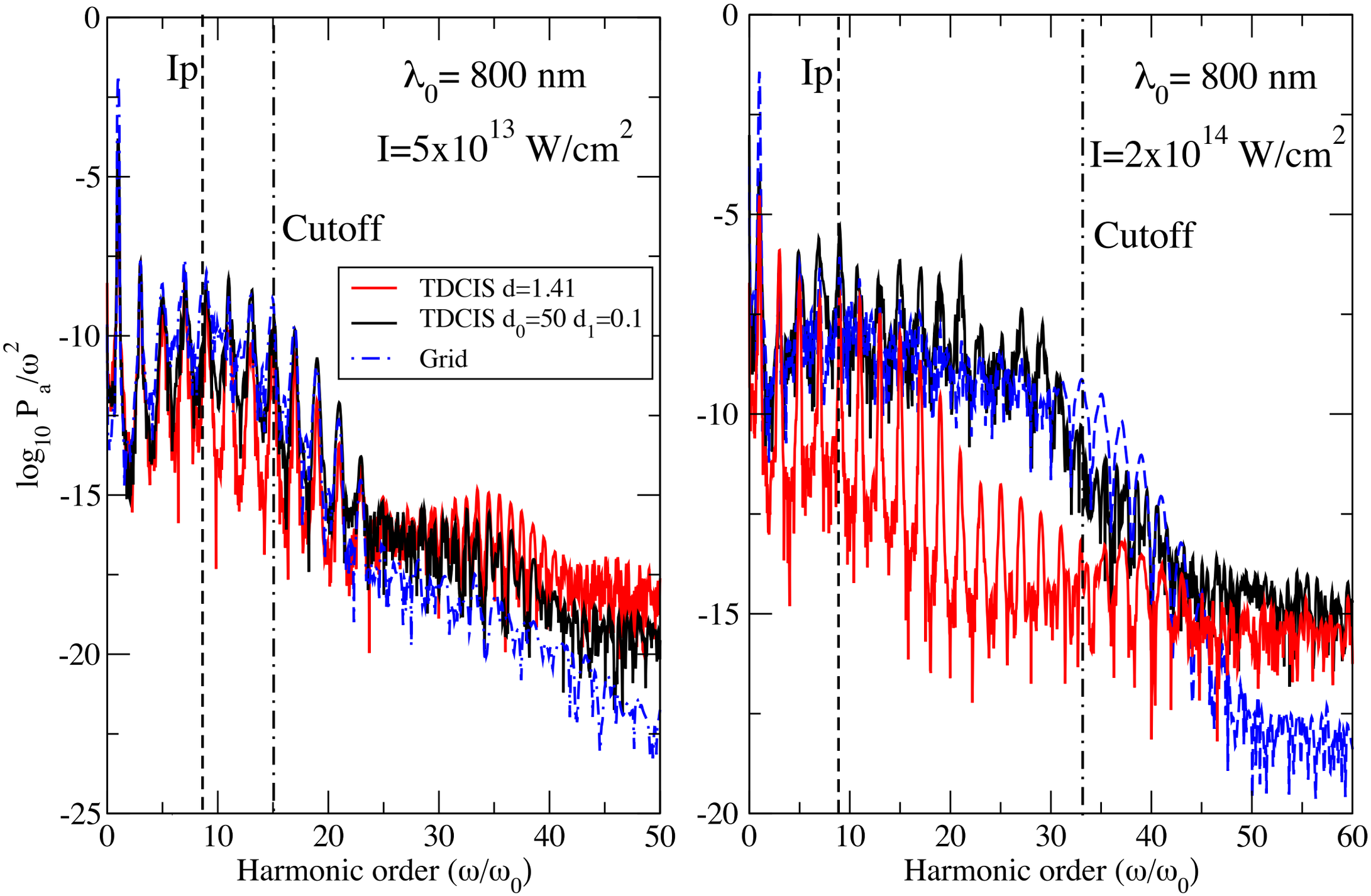
HHG : gaussian *vs* grid



6-aug-cc-pVTZ+8K

Coccia *et al.* Int. J. Quantum Chem (2015)

HHG : gaussian *vs* grid



6-aug-cc-pVTZ+8K

Coccia *et al.* Int. J. Quantum Chem (2015)

Conclusion

TDCI with Gaussian basis seems
to be a promising method to describe the electron dynamics in HHG

This afternoon Felipe Zapata will present what happens when we describe HHG in small molecular systems.

Thanks :)

Dr. Emanuele COCCIA
Dr. Julien TOULOUSE
Dr. Bastien Mussard
Felipe Zapata
Laboratoire de Chimie Théorique France

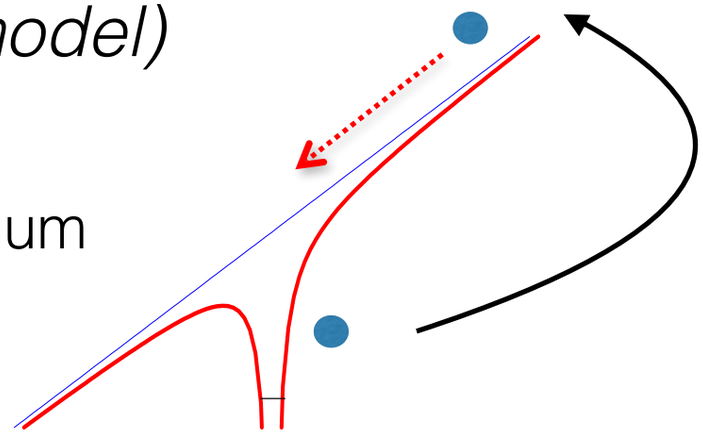
Dr. Jérémie CAILLAT
Dr. Richard TAÏEB
Marie Labaye
Laboratoire de Chimie Physique Matière et Rayonnement

Dr. Valerie VENIARD
Ecole Polytechnique France

TD-CI in Gaussian basis set

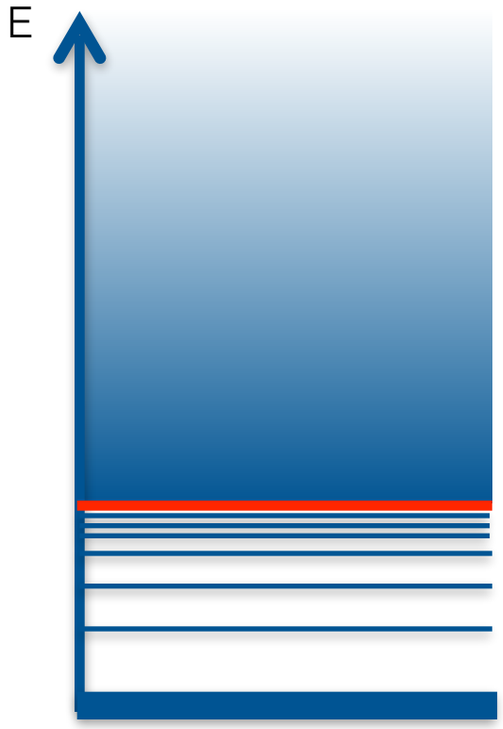
The method has to be studied, analysed and improved keeping in mind the physics beyond HHG (*3 step model)*

2. How good gaussian basis for continuum



continuum

exact

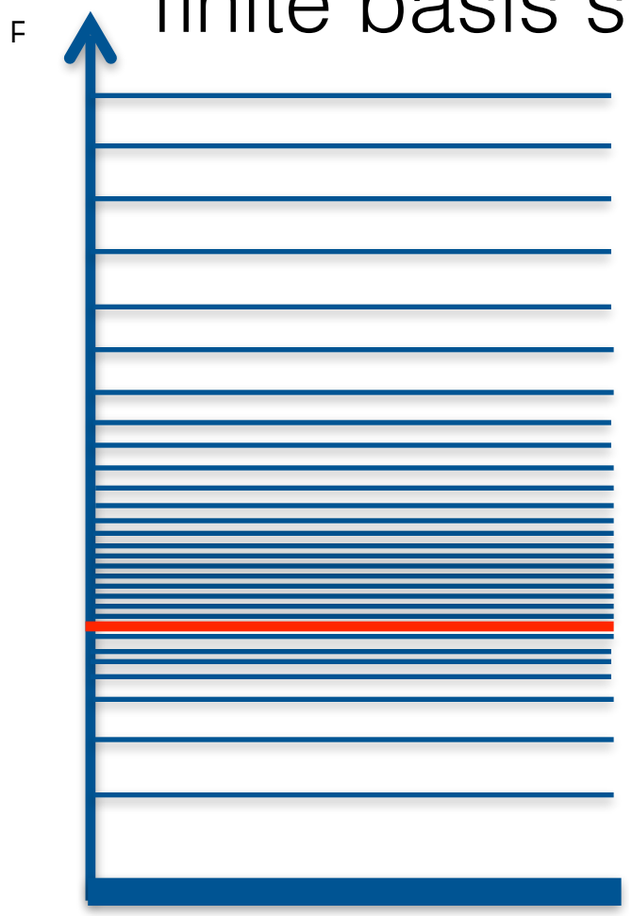


Ip

bound

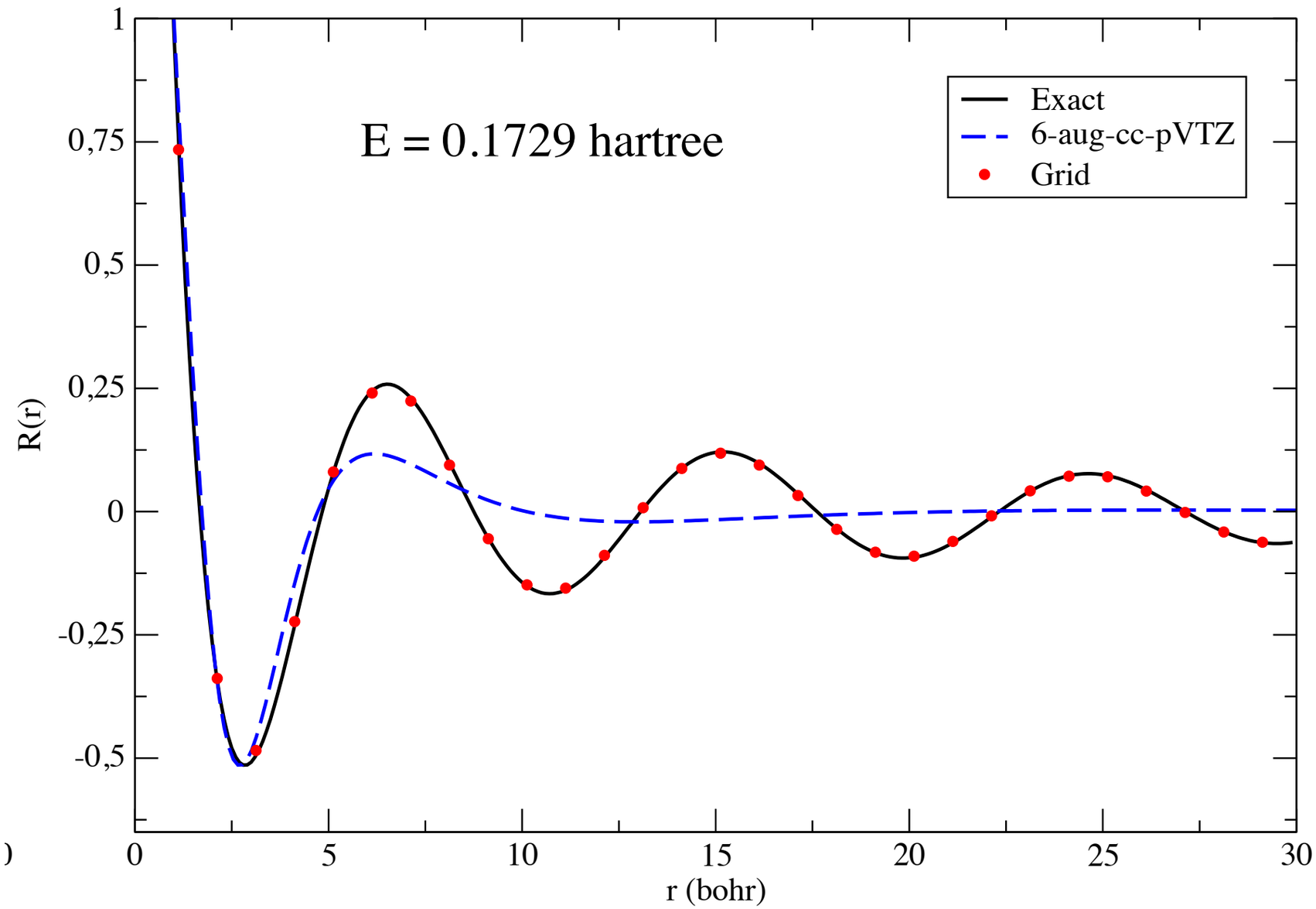
ground

finite basis set

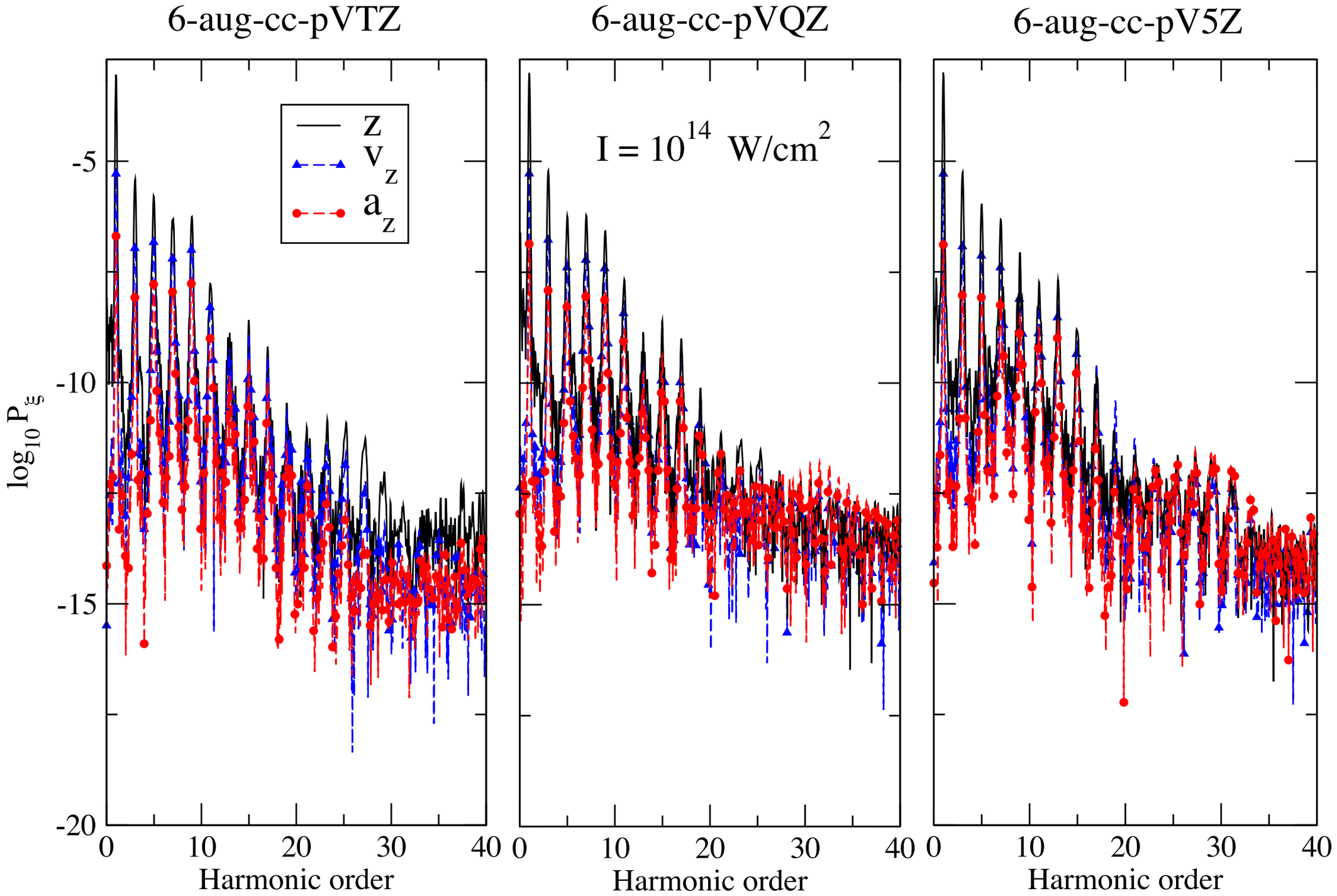


Continuum

TD-CI in Gaussian basis set

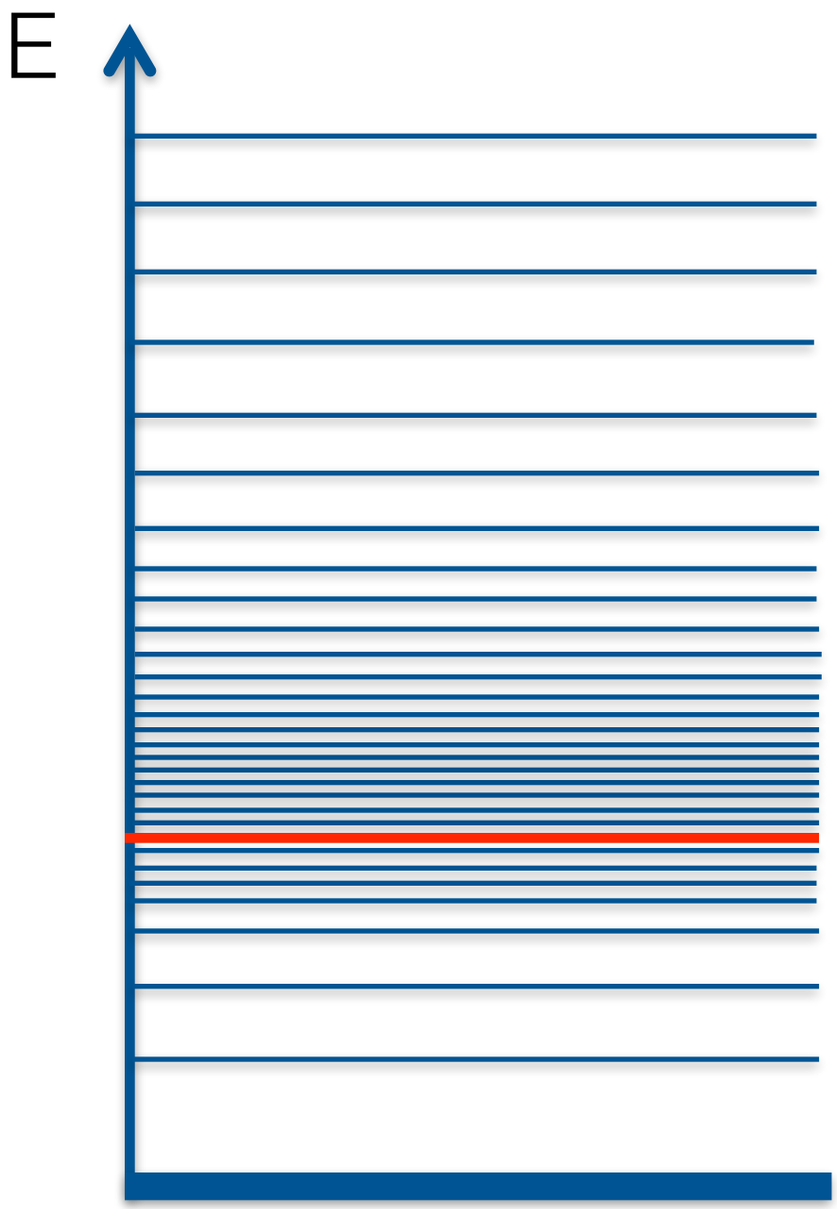


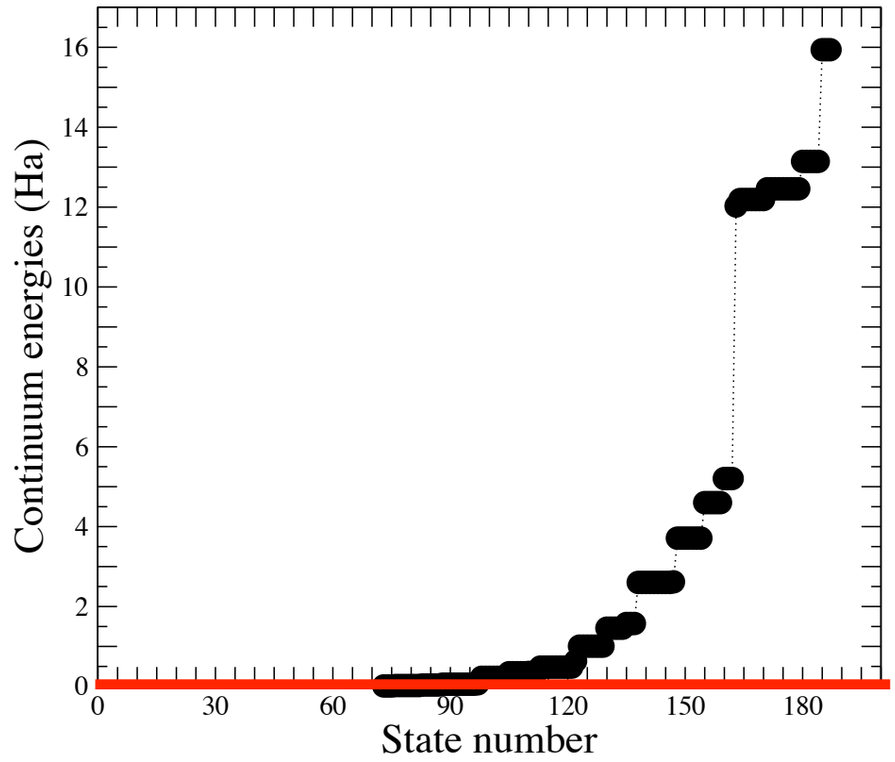
Asymptotic behaviour ($r \rightarrow \infty$) from the free-electron Schrodinger equation

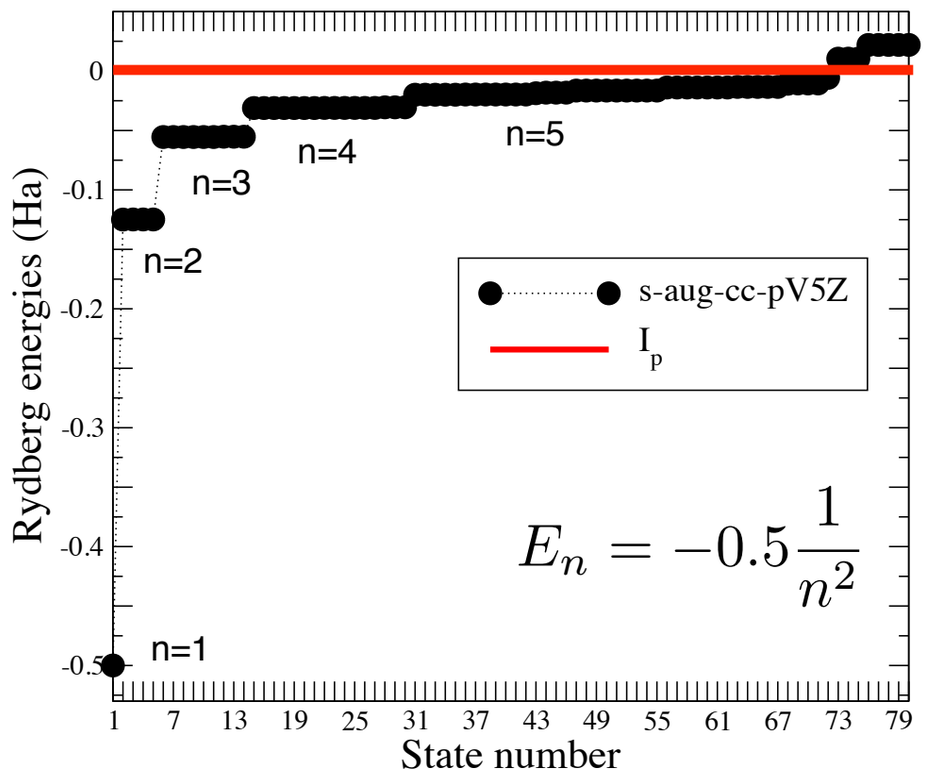

6-aug-cc-pVTZ
6-aug-cc-pVQZ
6-aug-cc-pV5Z
z
v_z
a_z
I = 10^14 W/cm^2
log10 P_ξ
-5
-10
-15
-20
0
10
20
30
40
Harmonic order

Continuum

TD-CI in Gaussian basis set







1.

Ionisation: the heuristic lifetime model

S. Klinkusch, P. Saalfrank, and T. Klamroth

Laser-induced electron dynamics including photoionization:
A heuristicmodel within time-dependent configuration interaction theory

J. Chem. Phys. 131, 114304 (2009)

e^- →

ε_r virtual energies

v escape velocity

d escape lenght

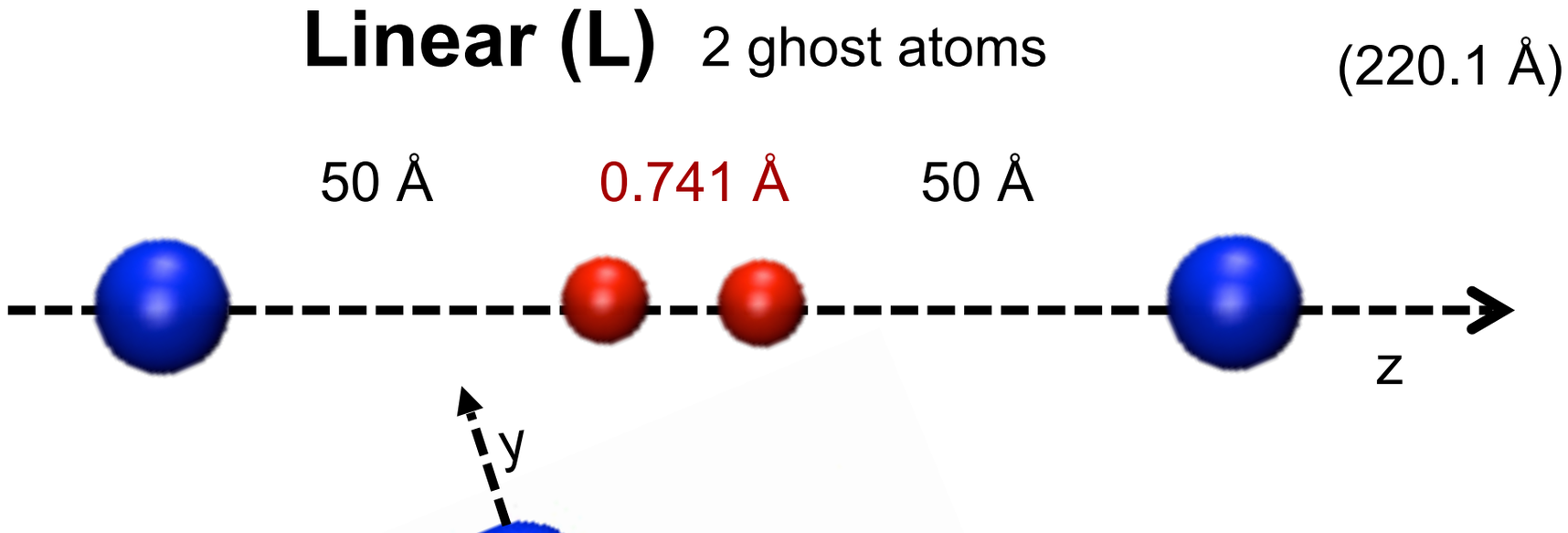
τ lifetimes

$$\varepsilon_r = \frac{1}{2} v^2 \qquad v = \sqrt{2\varepsilon_r} = \frac{d}{\tau} \qquad \tau = \frac{1}{\Gamma}$$

$$\Gamma_i = \begin{cases} 0 & E_i^{CIS} < I_p \\ \sum_{a,r} \left| C_{a,i}^r \right|^2 \frac{\sqrt{2\varepsilon_r}}{d} & E_i^{CIS} > I_p \end{cases}$$

3. The role of additional basis function centers

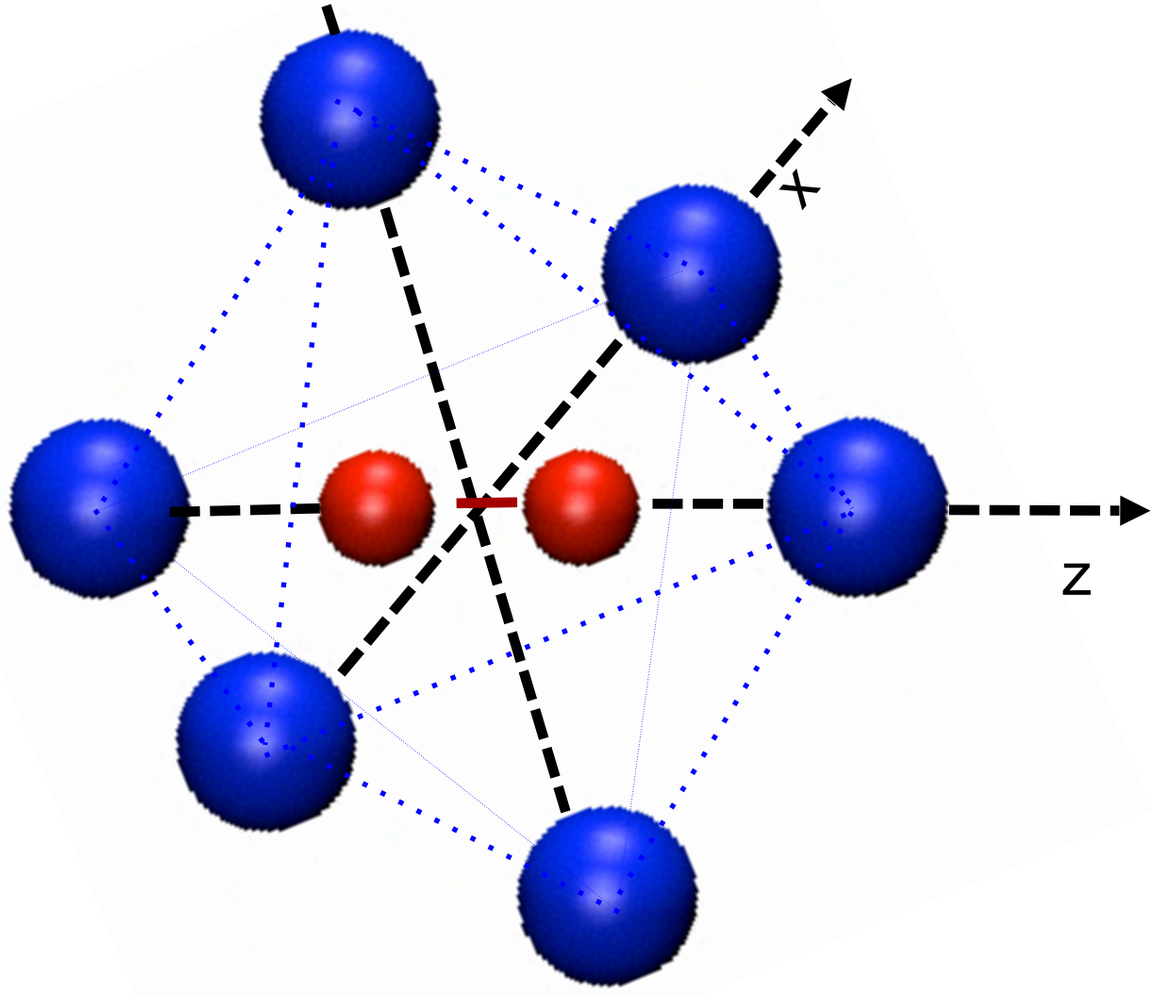
5-aug-cc-pVTZ (110.1 Å)



Octhaedral (O)

6 ghost atoms

distance from the origin
50.3705 Å



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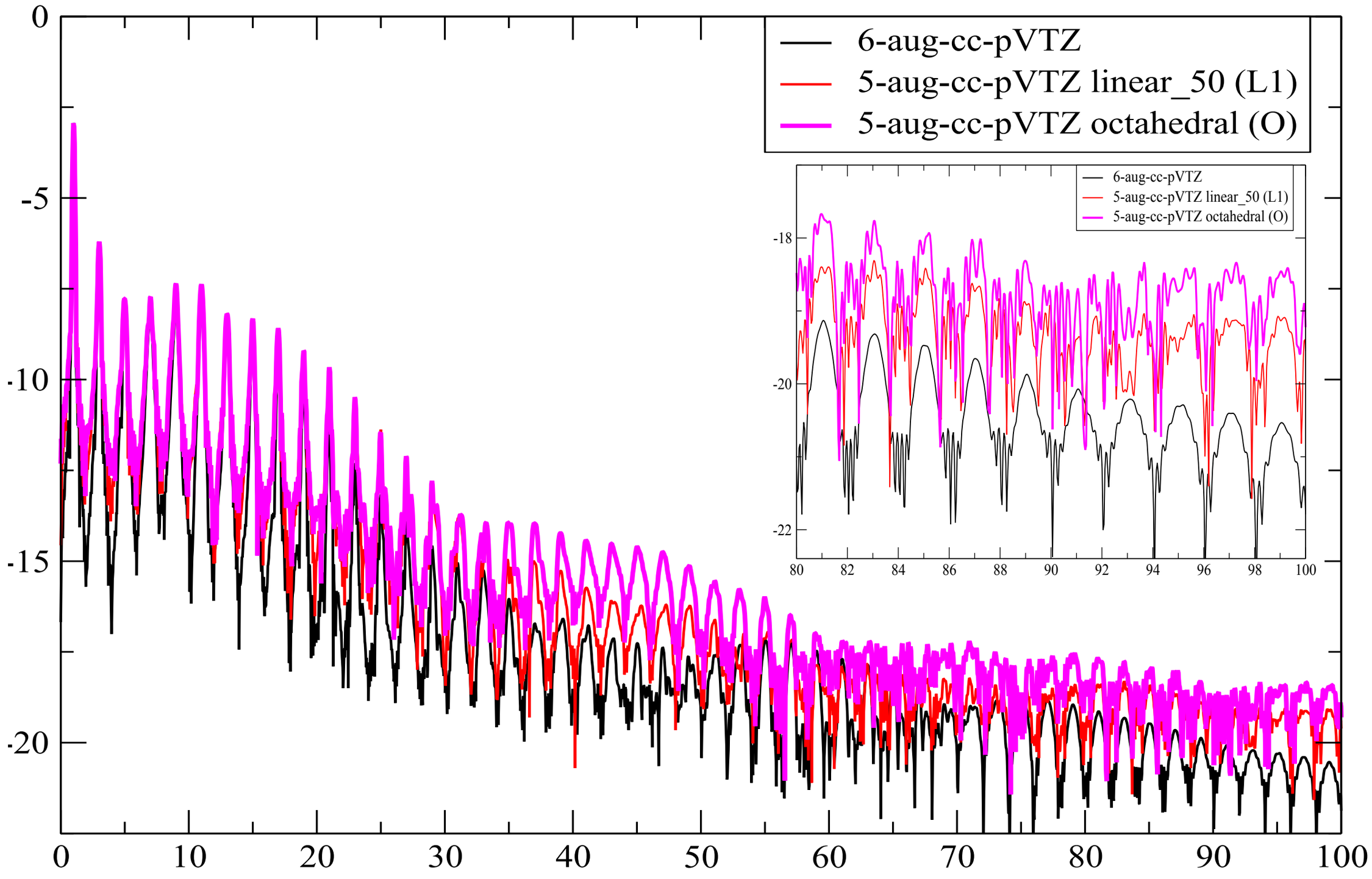
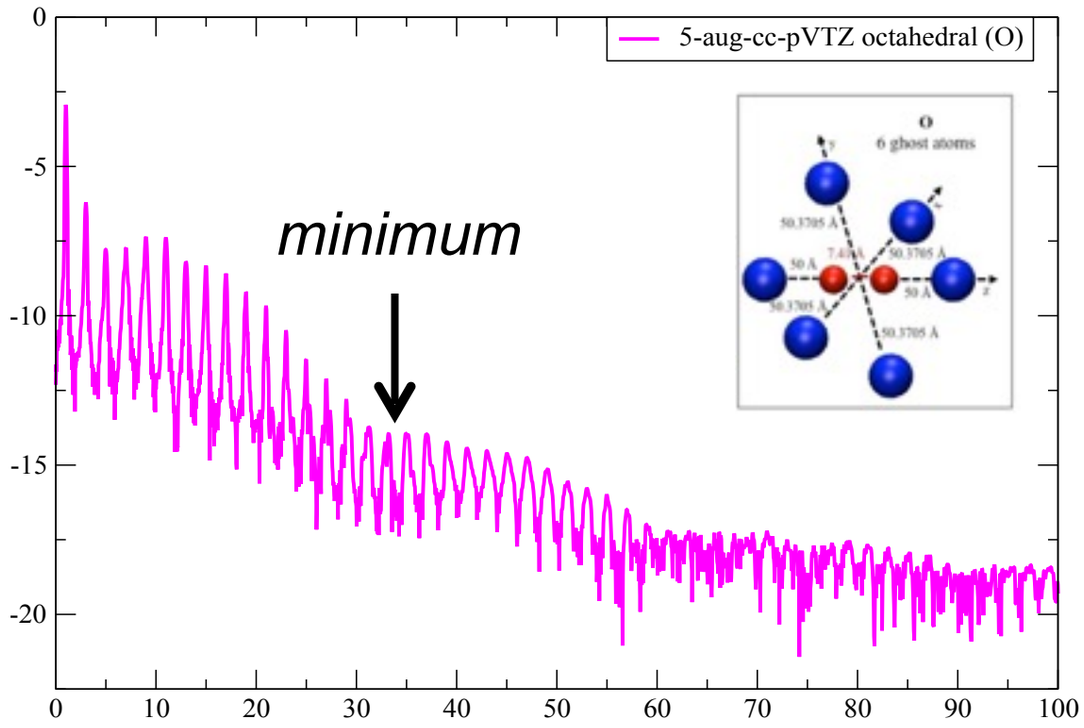
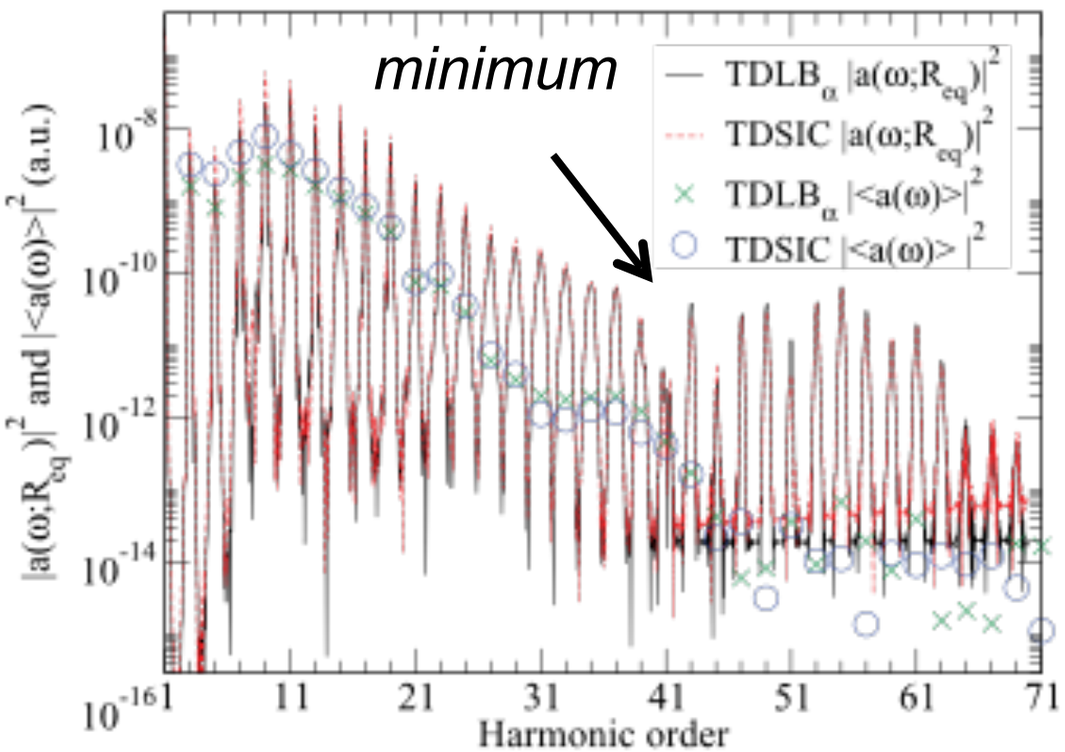


3. One center vs Two centers recombination

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



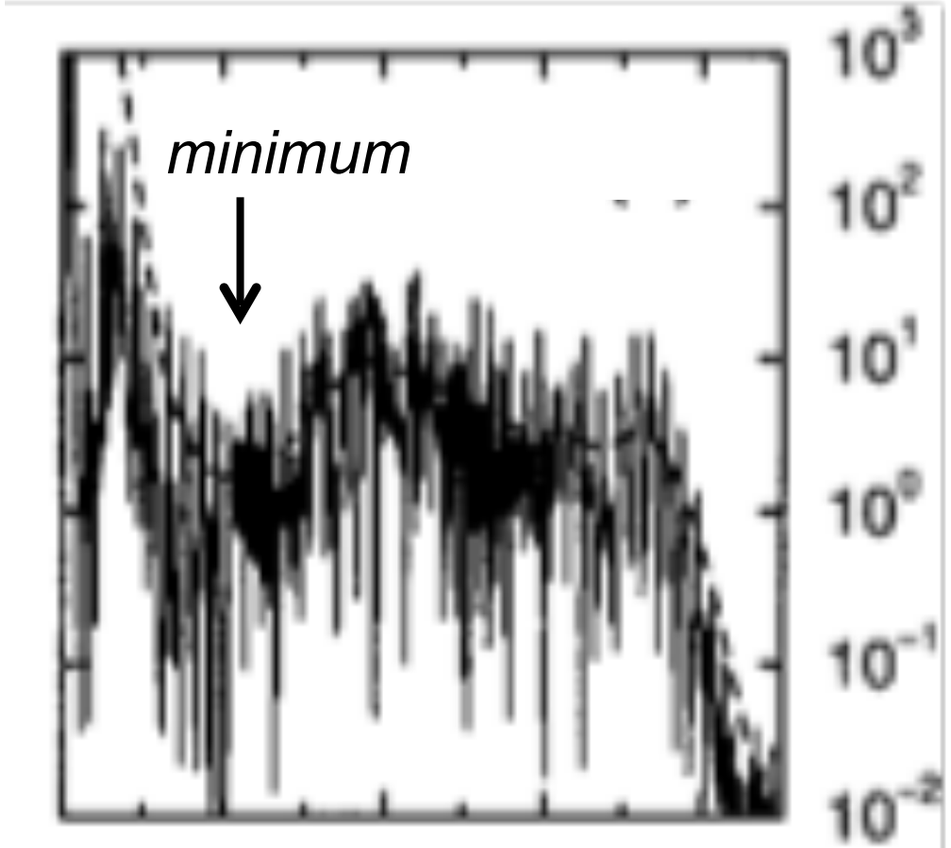
TDDFT (grid) $I = 2 \times 10^{14}$ W/cm^2



X. Chu and G. C. Groenenboom PRA **85**, 053402 (2012)

Model Hamiltonian (grid)

$I = 5 \times 10^{14}$ W/cm^2



M. Lein et al. PRA **66**, 023805 (2012)

State of the art:
HHG and basis representation

Grid

- Theoretical model (single-active electron)

Bandrauk et al. PRA (2009)
Gordon et al. PRL (2006)
Taieb et al. PRA (2003)
Ruiz et al. PRA (2006)

- Time-dependent density-functional theory TD-DFT

Telnov et al. PRA (2013)
Chu et Groenenboom PRA (2012)

- Wavefunction methods:

TD configuration-interaction single/double (TD-CIS/D)
TD restricted-active-space self-consistent-field (TD-RASSCF)

Greenman et al. PRA (2010)
Miyagi and Madsen PRA (2014)

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B-splines

- Algebraic diagrammatic construction (ADC)

Ruberti et al. JCP (2014)

Sturmian

- Floquet theory

Dorr et al. JOSA B (1990)
Mese, Potvliege, JPB: At. Mol. Opt. Phys. (2006)

Bessel

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Milosevic and Piraux, PRA (1996)

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Gaussian

- Wavefunction methods:

TD configuration-interaction single/double (TD-CIS/D)
TD equation of motion coupled-cluster single/double (TD-EOM-CCSD)
TD Hartree-Fock (TD-HF)

Krause et al. JCP (2007)
E. Luppi et al. JCP (2013)
E. Luppi et al. Mol. Phys. (2012)
Ding et al. JCP (2011)

- Time-dependent density-functional theory TD-DFT

HHG with TD-CI(S) with Gaussian basis set

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

$$\hat{H}(t) = \hat{H}_0 - \hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

Configuration Interaction $\quad \hat{H}_0 \longrightarrow \quad E_k^{\mathrm{CI}} \quad \psi_k^{\mathrm{CI}}$

$$|\Psi(t)\rangle = \sum_k c_k(t)|\psi_k^{\mathrm{CI}}\rangle$$

HHG with TD-CI(S) with Gaussian basis set

$$i\frac{dc_k(t)}{dt} = \sum_s (E_k^{\mathrm{CI}}\delta_{ks} - \boldsymbol{\mu}_{ks}\cdot\boldsymbol{E}(t))c_s(t)$$

$$\boldsymbol{\mu}(t) = \sum_{ks} c_k^*(t)c_s(t)\boldsymbol{\mu}_{ks}^{\mathrm{CI}}$$

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

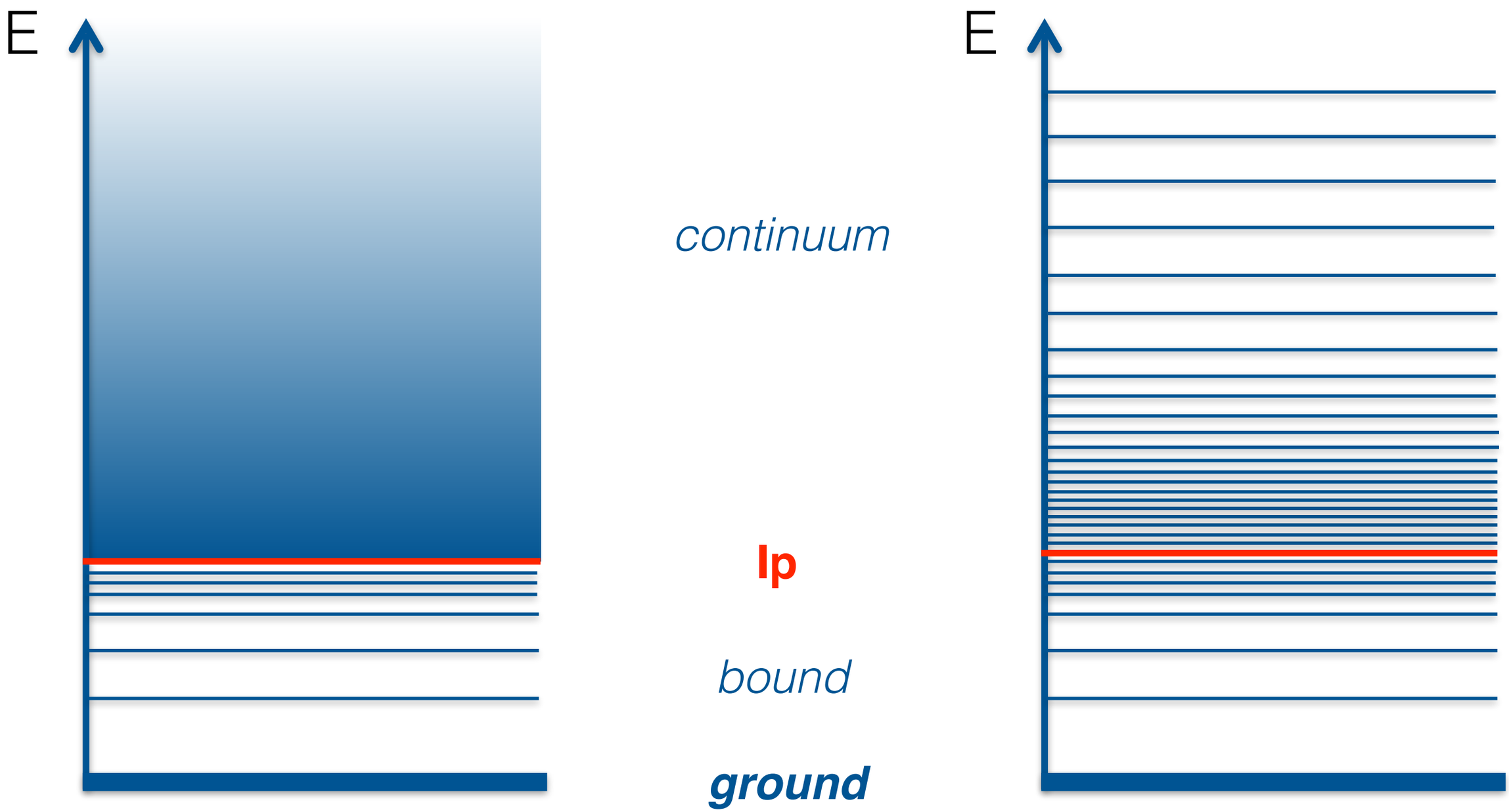
velocity $v(t)$ and acceleration $a(t)$ $\quad P_a(\omega) \approx \omega^2 P_\nu(\omega) \approx \omega^{(4)} P_\mu(\omega)$

HHG with TD-CI(S) with Gaussian basis set

the problem of using a finite basis set

exact

finite basis set



HHG with TD-CI(S) with Gaussian basis set:

ionisation losses

we replace every state energy by a complex energy

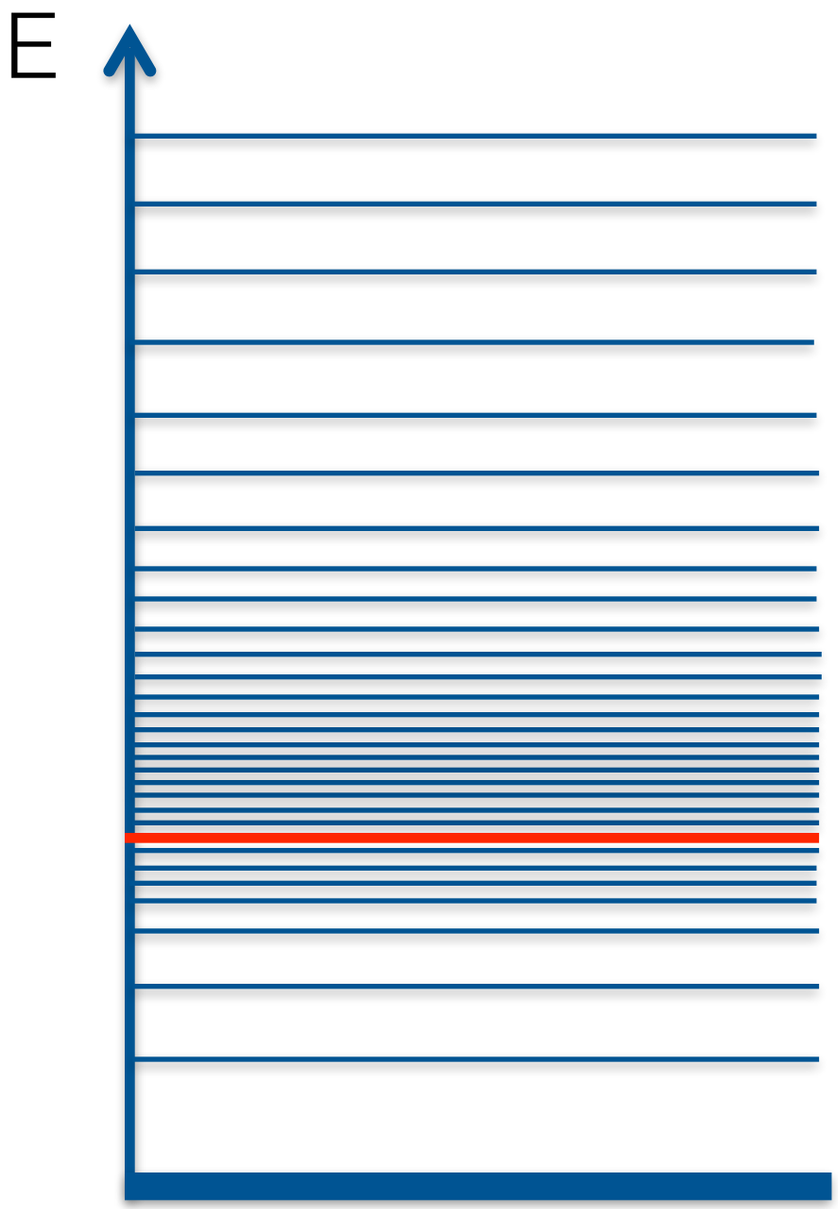
$$E_k^{\mathrm{CI}} \rightarrow E_k^{\mathrm{CI}} + \Gamma_k$$

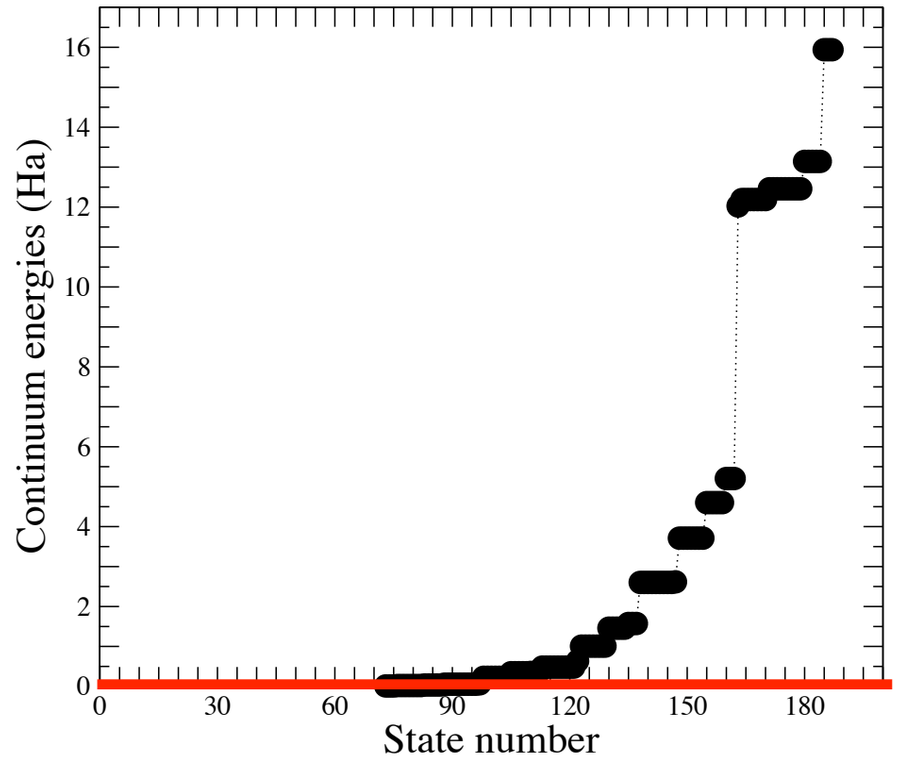
ionization rate of CI state *k*

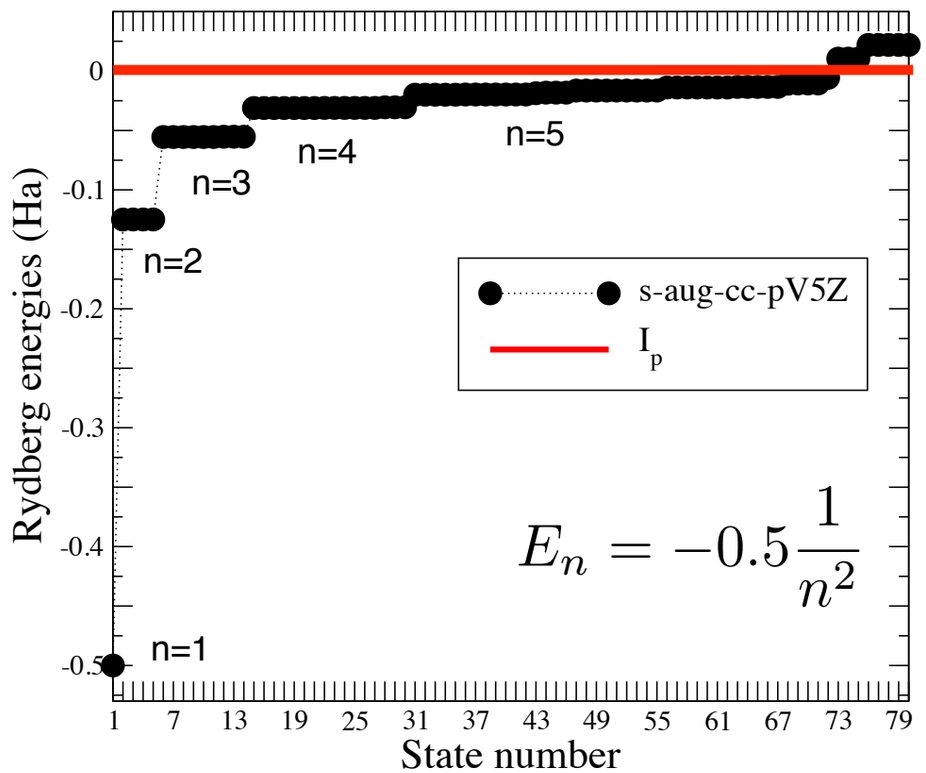
S. Klinkusch e al. JCP 131, 114304 (2009)

The role of bound and continuum states:

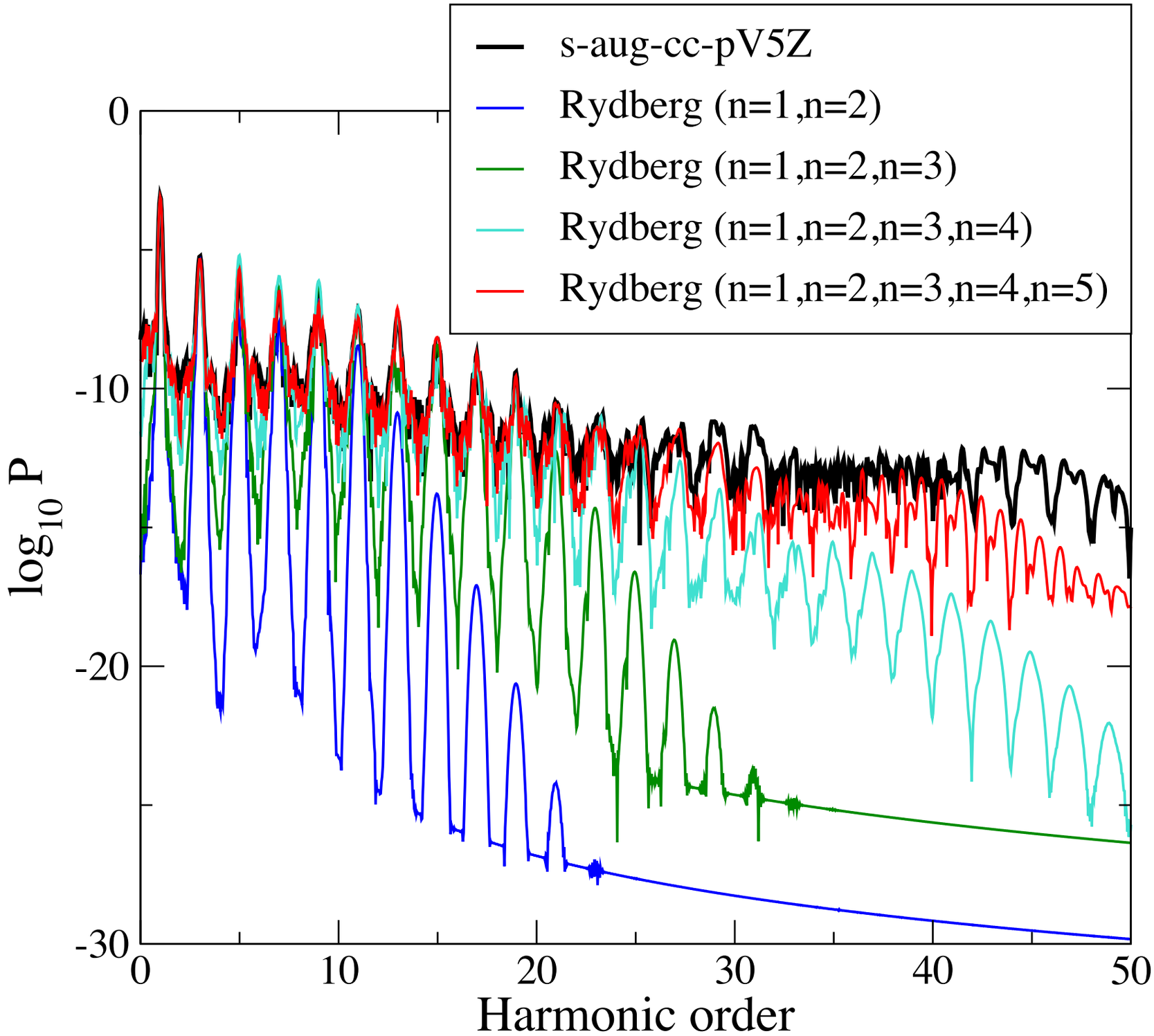
Gaussian basis set





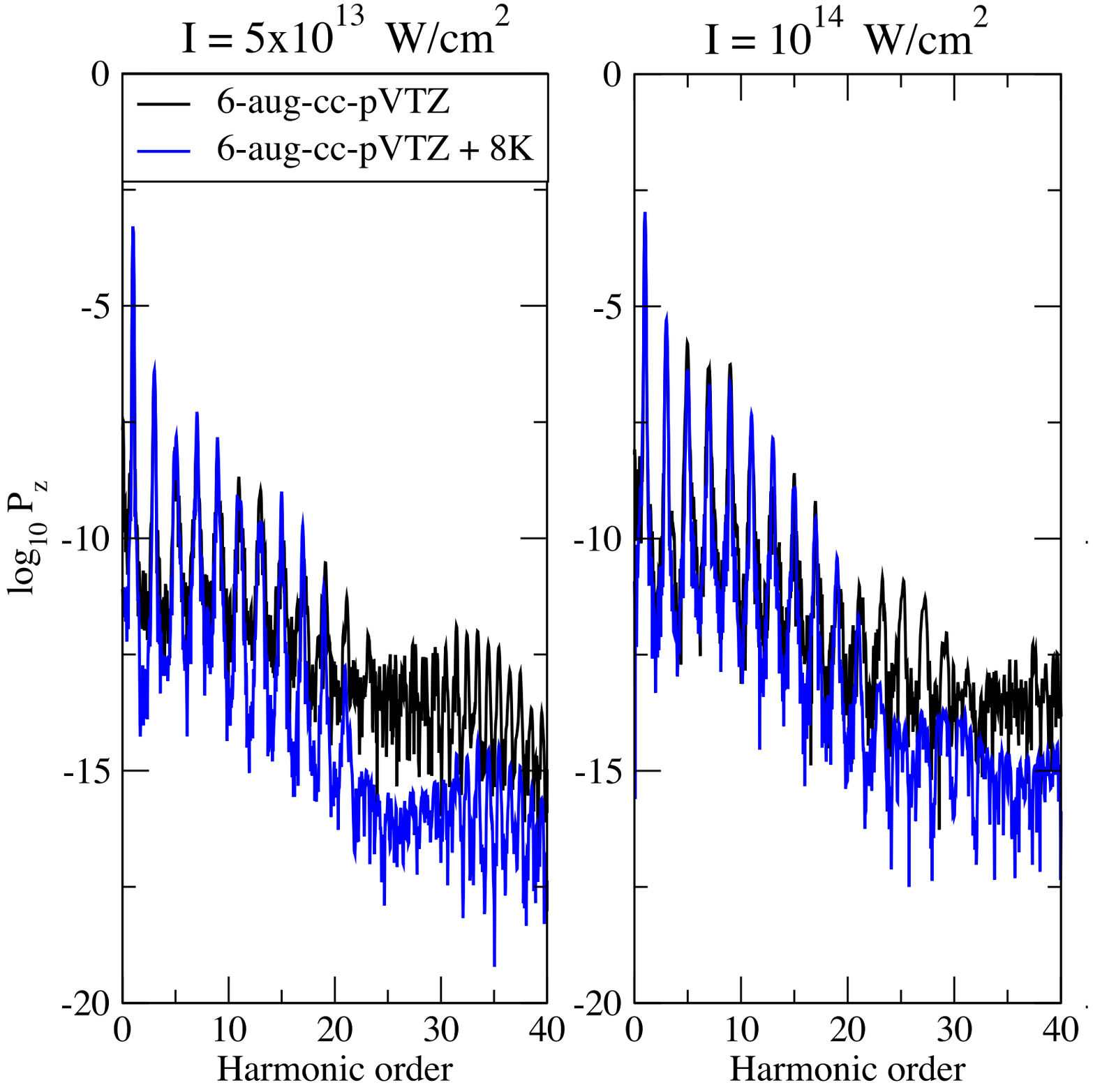


The role of bound Rydberg



The role of continuum states:

Gaussian exponents spanning low-energy continuum



HHG: gaussian vs grid representation

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