New theoretical approaches to study single- and multi-photon ionisation in atoms and molecules :

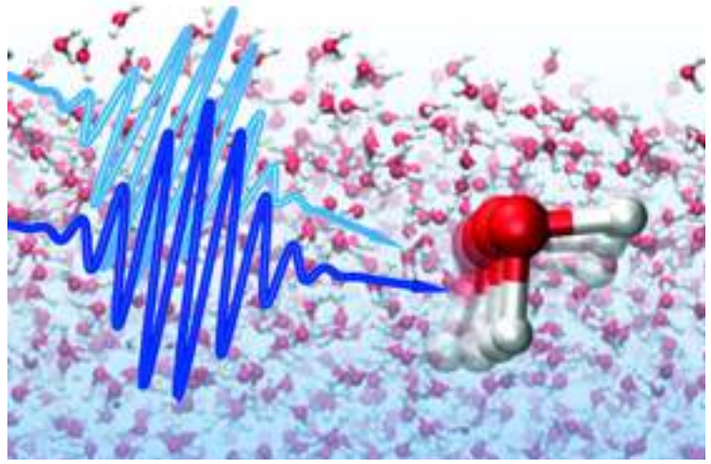
challenging the continuum

Eleonora LUPPI

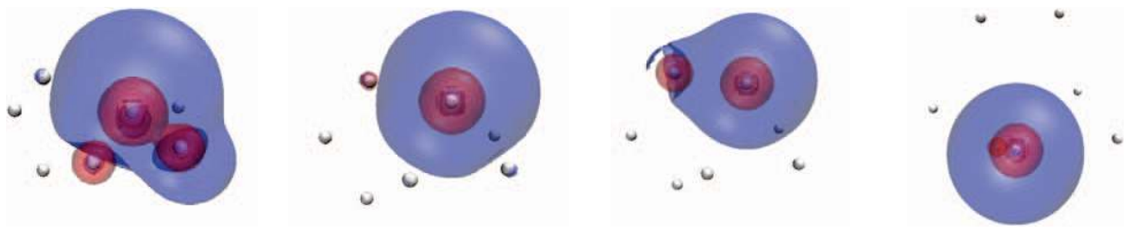
Laboratoire de Chimie Théorique
Sorbonne Université - CNRS, Jussieu Paris, France

Time Scale

ps = 10^{-12} s

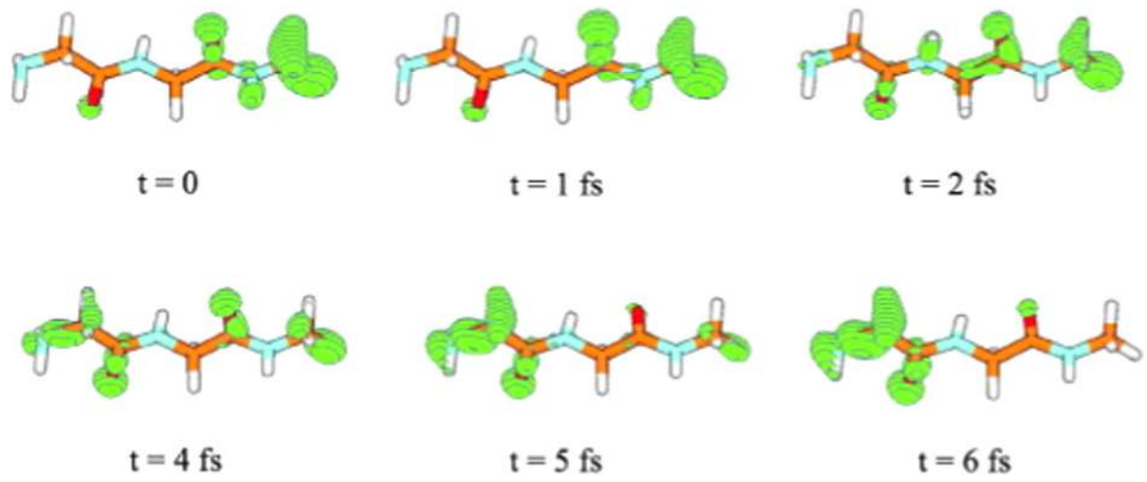


Nat. Comm. (2015)



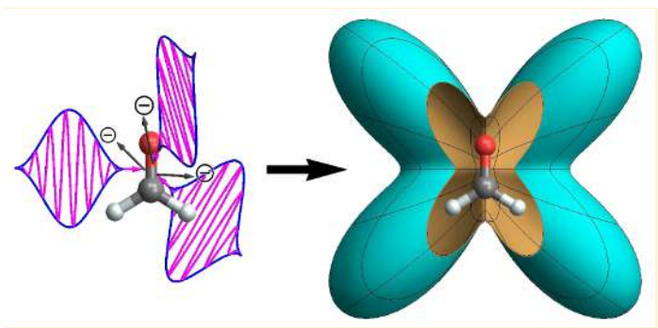
J. Chem. Phys. (2014)

fs = 10^{-15} s



J. Phys. B: At. Mol. Opt. Phys. (2016)

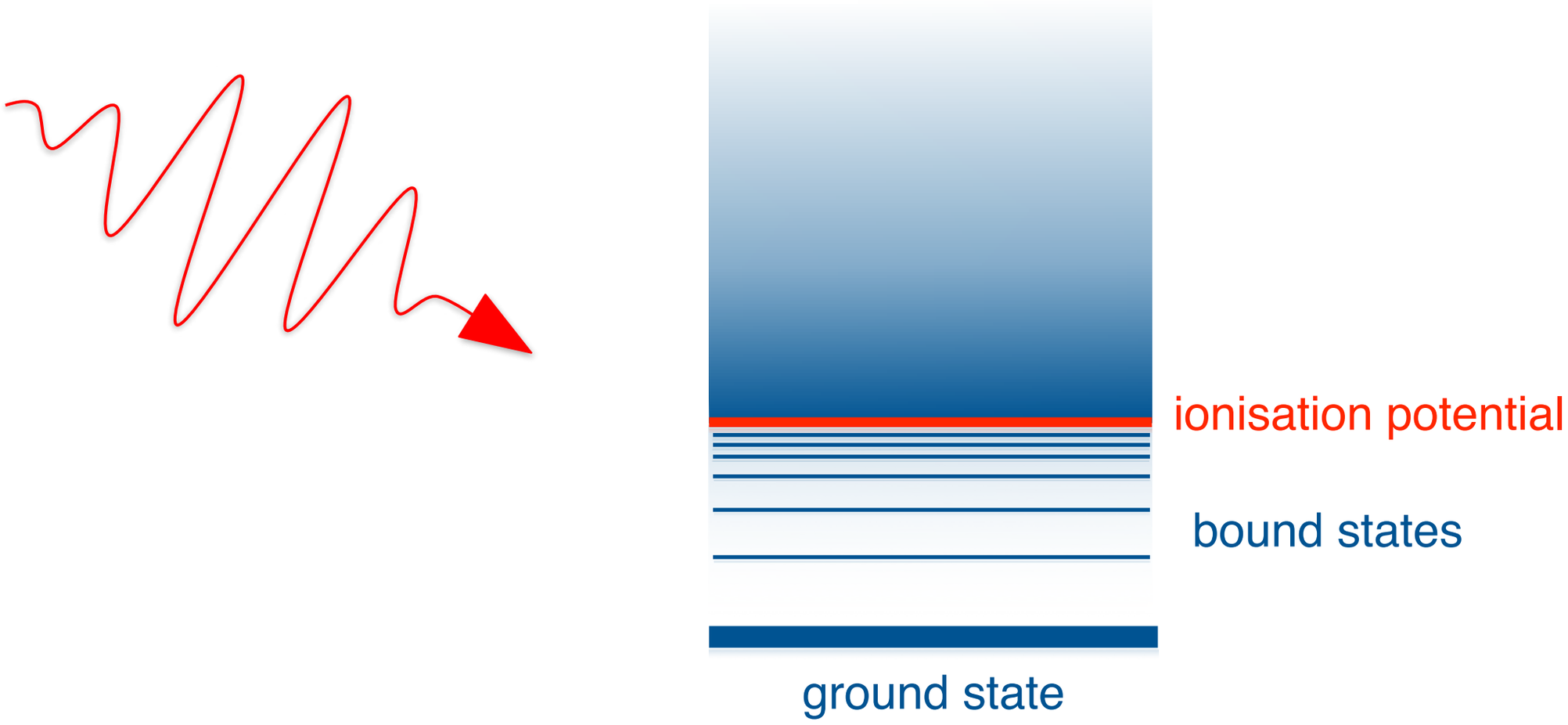
as = 10^{-18} s



J. Phys. Chem. Lett. (2015)

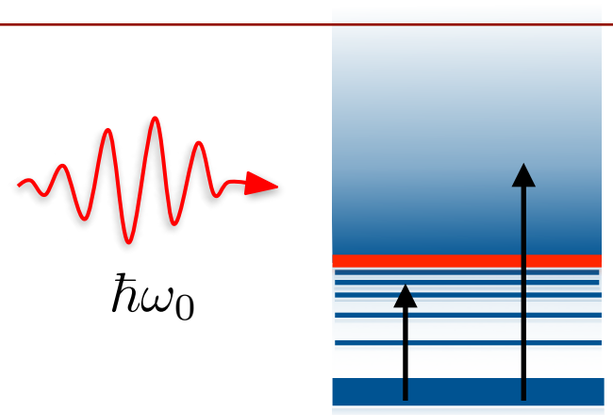
Attosecond science and new theory

continuum is a challenge for theory



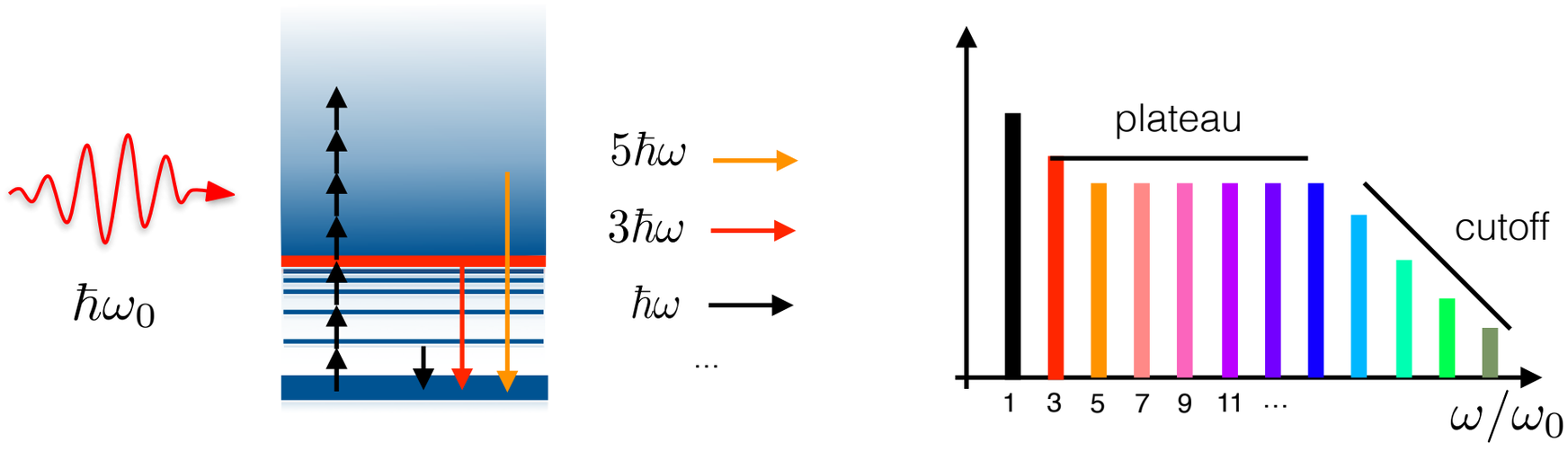
- Investigating linear-response range-separated density-functional theory with B-splines for continuum

  applied to photoexcitation/photoionization



- Gaussian basis sets optimised for continuum

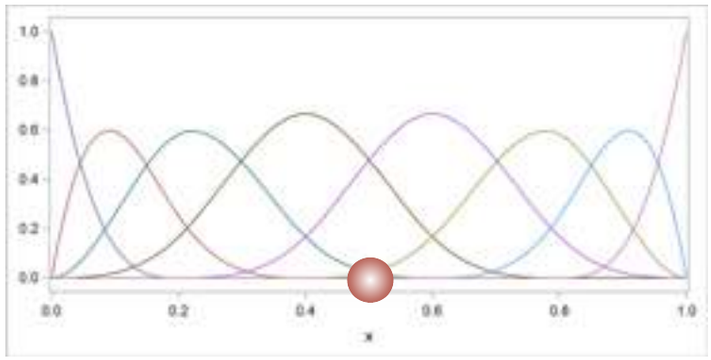
  applied to High-Harmonic Generation spectroscopy



- New ab-initio lifetimes model for continuum

  applied to High-Harmonic Generation spectroscopy

B-splines and range-separated DFT



- B-splines basis set is a piecewise polynomial functions
- **B-splines** basis set is **powerful** to describe **continuum** for atoms and molecules
- New algorithms needs to be developed to fully exploits their potentials

Stener et al. JCP (2001), Bachau et al. RPP (2001), Fetic et al. PRE (2017) …

Range-separated hybrid (RSH)

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}^{\mathrm{sr}}(\mathbf{x})\right)\varphi_p(\mathbf{x}) + \int v_{\mathrm{x}}^{\mathrm{lr,HF}}(\mathbf{x},\mathbf{x}')\varphi_p(\mathbf{x}')\mathrm{d}\mathbf{x}' = \epsilon_p\varphi_p(\mathbf{x})$$

LDA limit (→ 0)
HF limit (→ infinity)

Range-separated exact exchange hybrid (RSH-EXX)

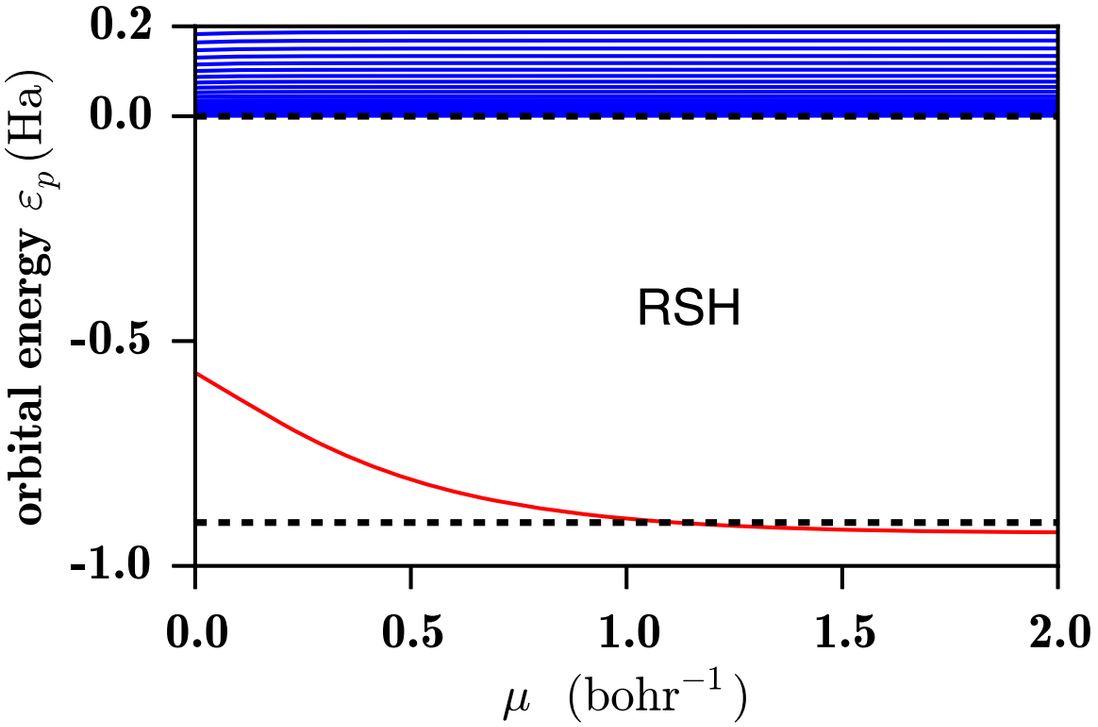
$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}^{\mathrm{sr}}(\mathbf{x}) + v_{\mathrm{x}}^{\mathrm{lr,EXX}}(\mathbf{x})\right)\varphi_p(\mathbf{x}) = \epsilon_p\varphi_p(\mathbf{x})$$

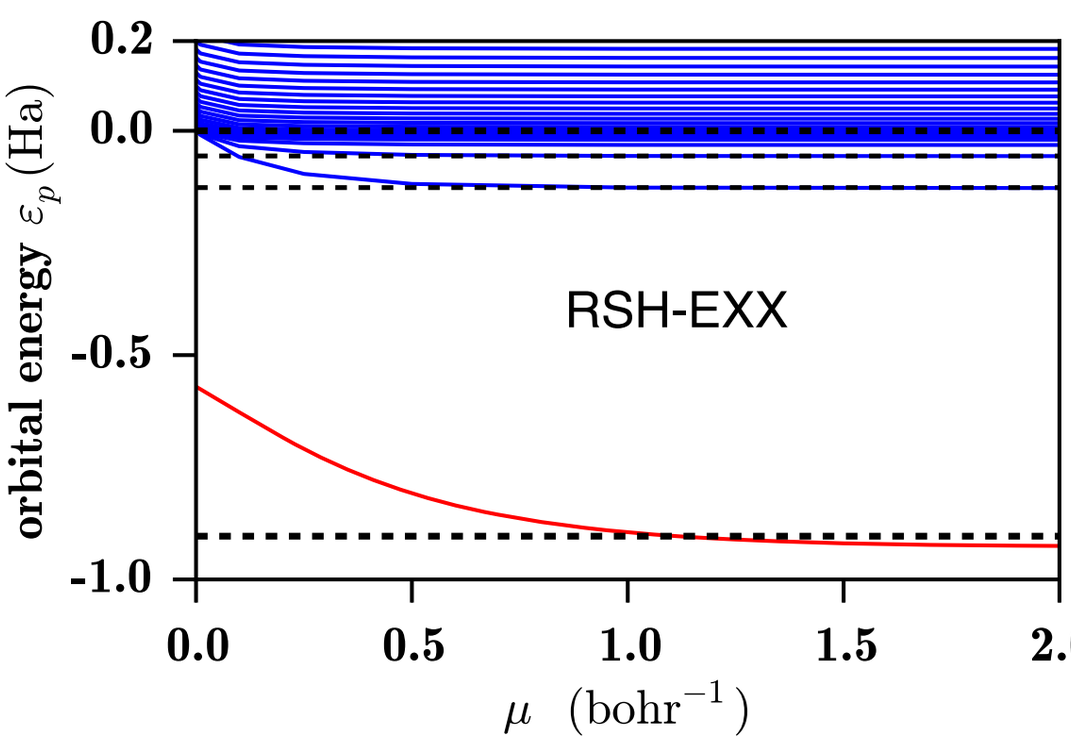
LDA limit (→ 0)
EXX limit (→ infinity)

Extension to the linear response (Casida's equations)

Zapata, Luppi, Toulouse JCP (2019)

B-splines and (linear response) range-separated DFT : He atom



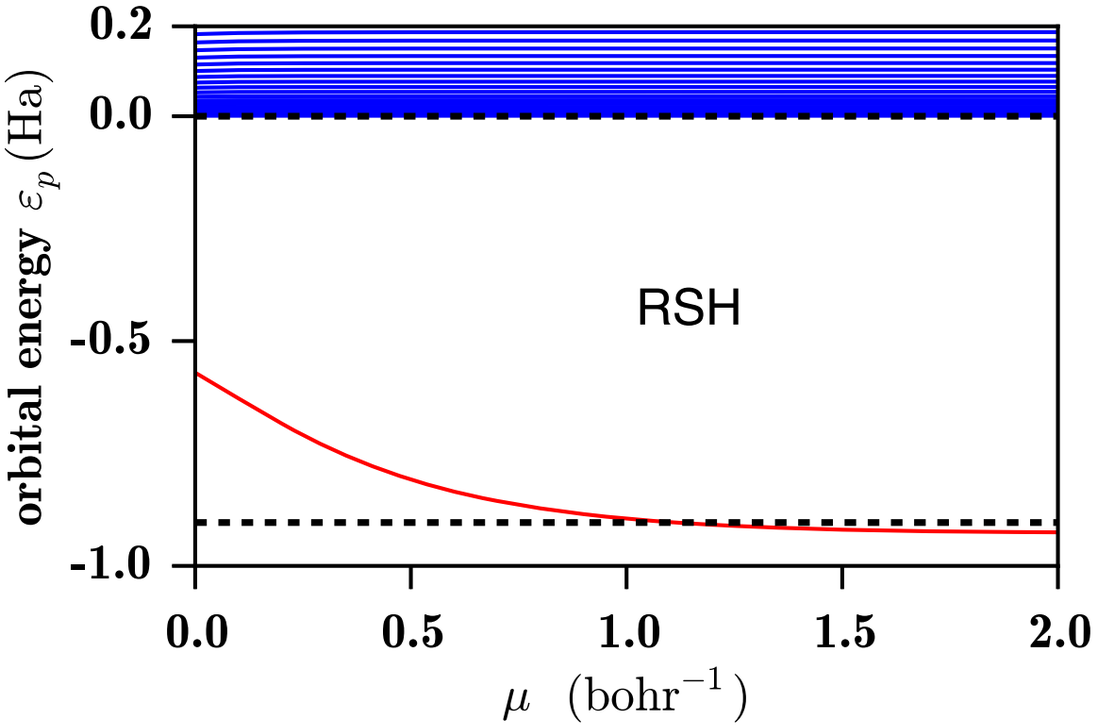


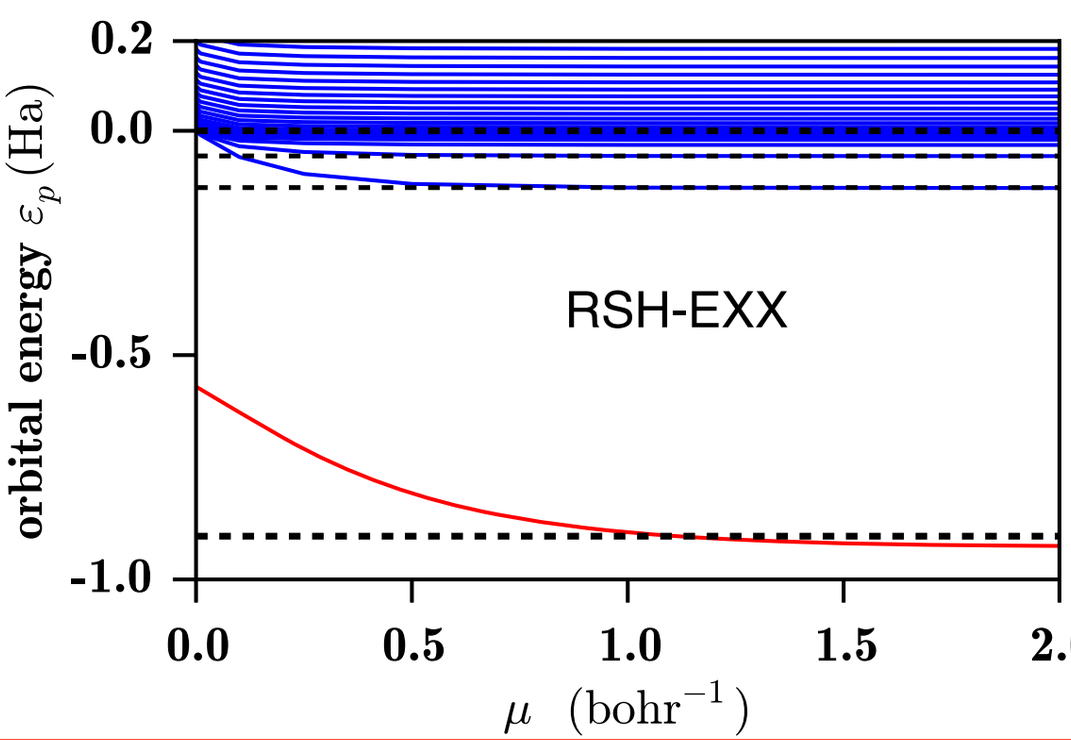
red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy
- ionisation limit

B-splines and (linear response) range-separated DFT : He atom





red :
-1s ground state
blue :
-p excited states
black :
- opposite of the exact ionisation energy
- ionisation limit

$\mu = 0$

1s energy is too high : LDA self-interaction error

$\mu = \infty$

1s energy converges

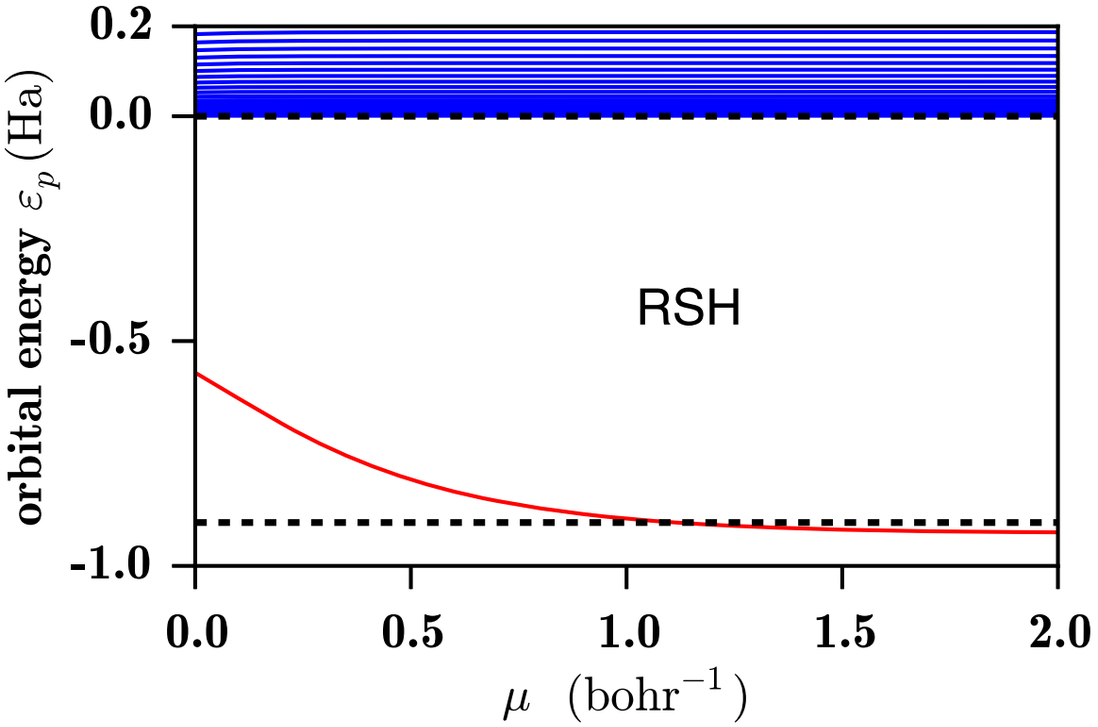
HF ⋮ EXX

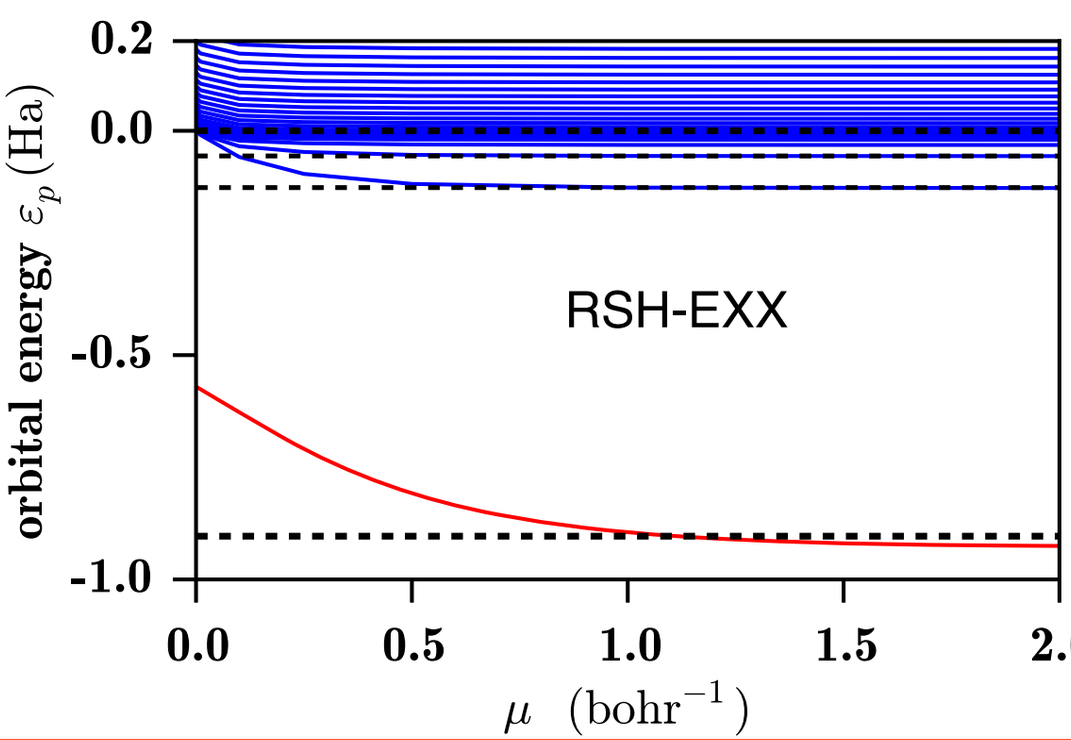
not equal to the opposite of the exact ionisation energy (missing correlation effects)

$\mu = 1.115$

*optimally tuned range-separated hybrids

B-splines and (linear response) range-separated DFT : He atom





red :
-1s ground state
blue :
-p excited states
black :
- opposite of the exact ionisation energy
- ionisation limit

$\mu = 0$

1s energy is too high : LDA self-interaction error

$\mu = \infty$

1s energy converges

HF | EXX

not equal to the opposite of the exact ionisation energy (missing correlation effects)

$\mu = 1.115$

*optimally tuned range-separated hybrids

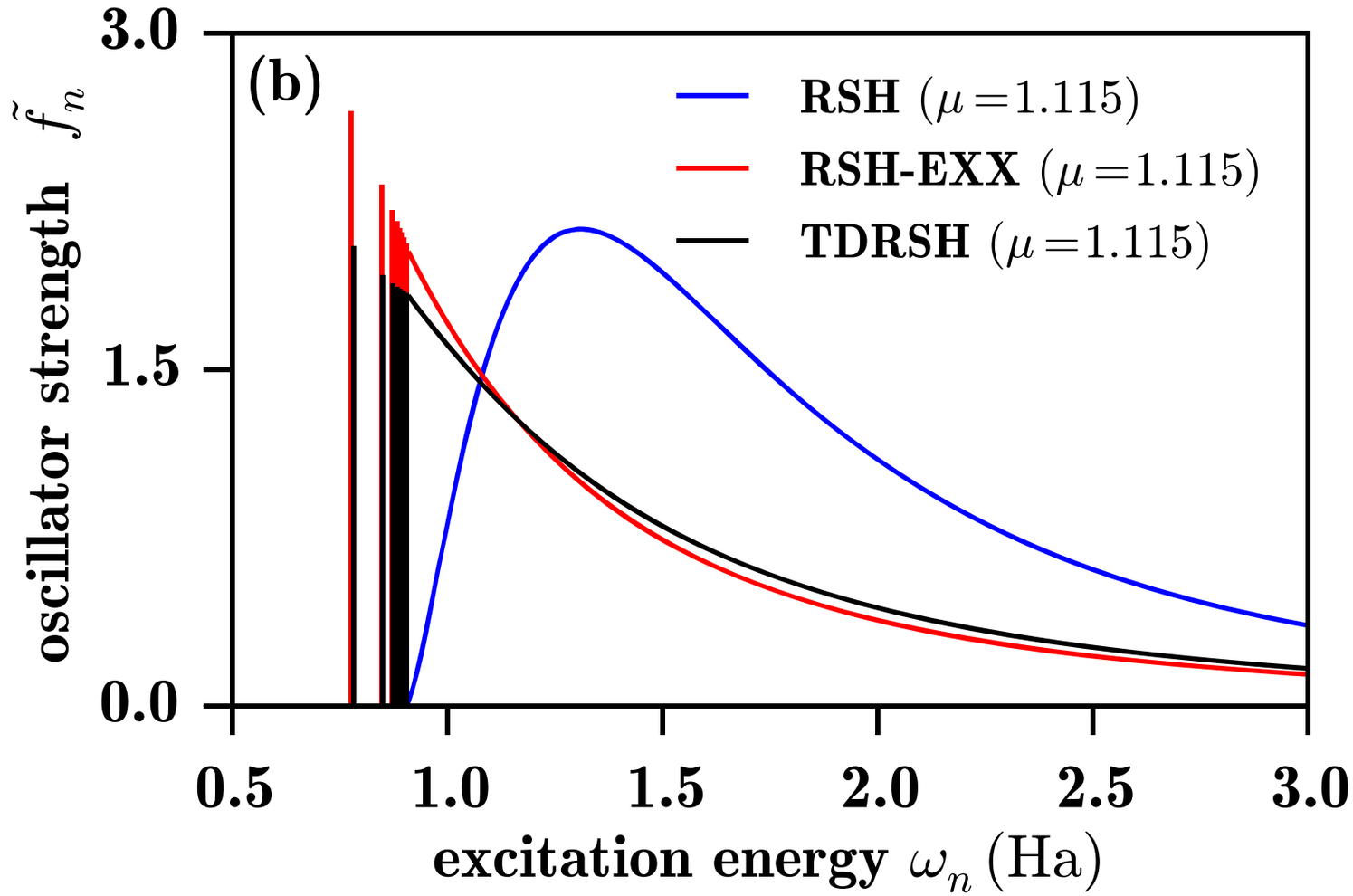
$\mu > 0$

p orbitals (and all unoccupied orbitals)

unbound | bound
(Rydberg from continuum)

Photoexcitation and Photoionisation spectra

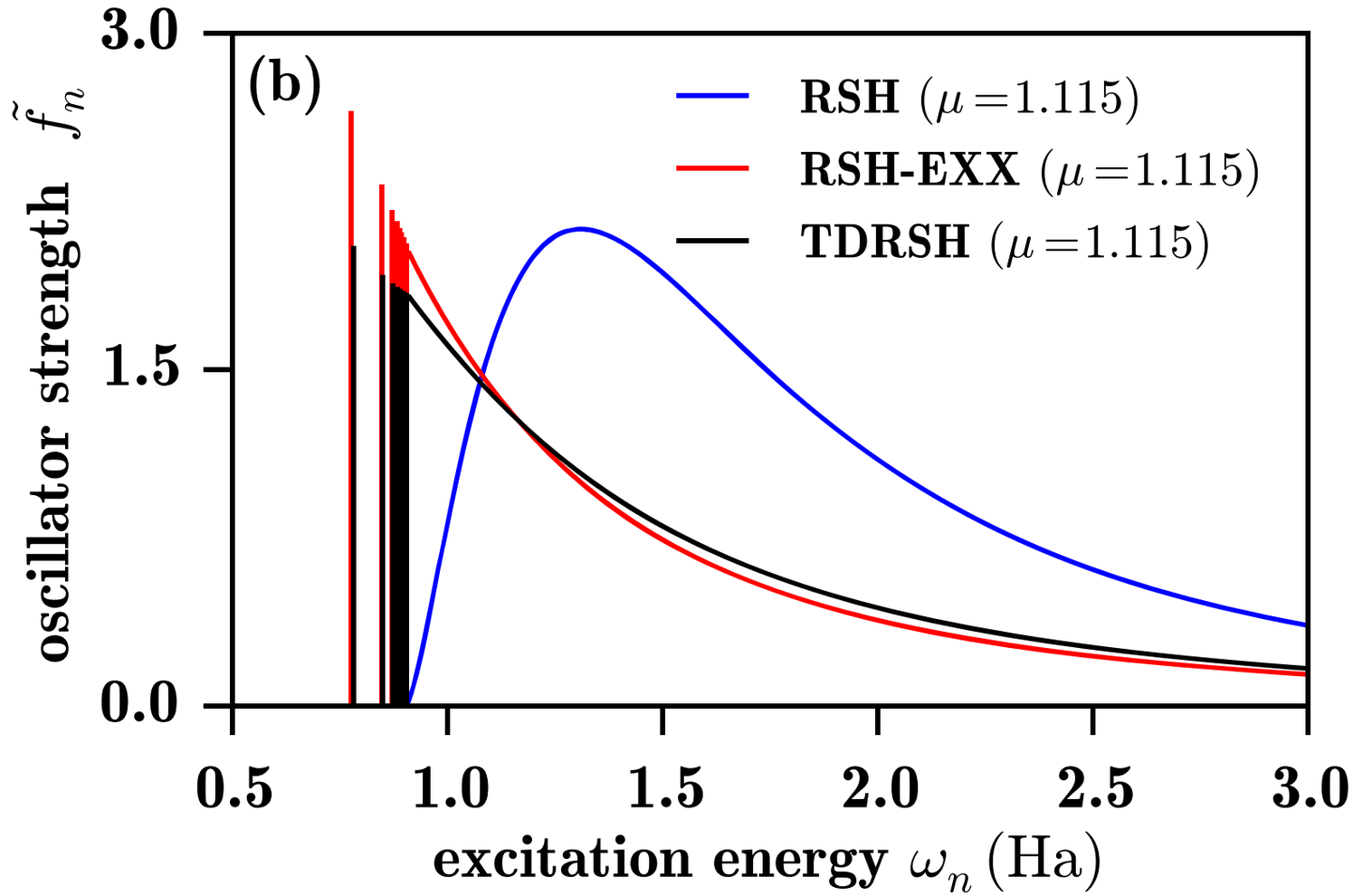
Lyman series (1s → np)



RSH : no discrete photoexcitations (photodetachment H^-)

Photoexcitation and Photoionisation spectra

Lyman series (1s → np)



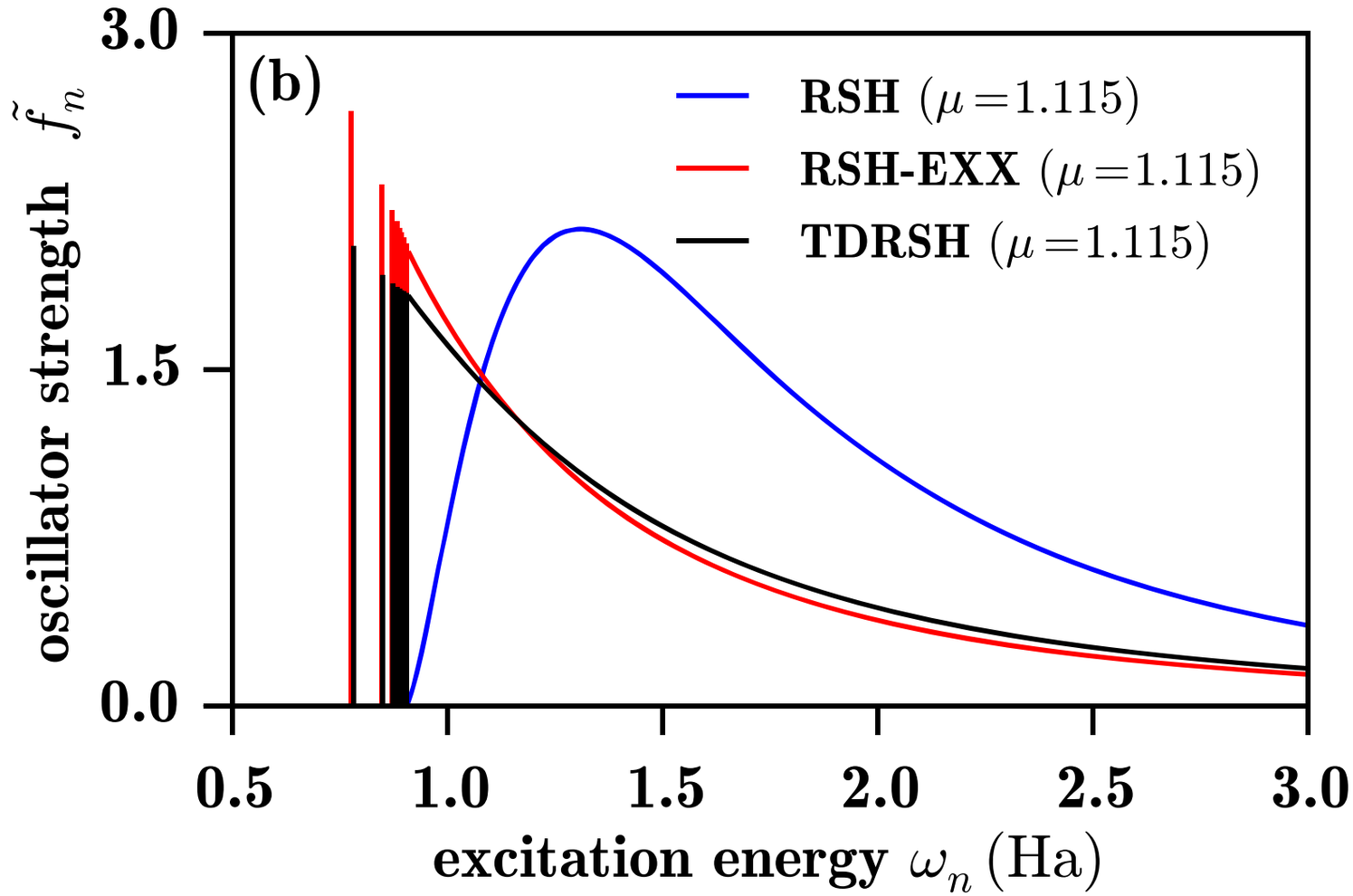
RSH : no discrete photoexcitations (photodetachment H^-)

RSH-EXX : reasonable photoexcitation/photoionization spectrum

* Only EXX local potential supports Rydberg states

Photoexcitation and Photoionisation spectra

Lyman series (1s → np)



RSH : no discrete photoexcitations (photodetachment H^-)

RSH-EXX : reasonable photoexcitation/photoionization spectrum

* Only EXX local potential supports Rydberg states

TDRSH : ~ RSH-EXX

* Most accurate (from comparison with exact) : TDRSH > RSH-EXX

Perspectives

- correlation effects

- calculating photoexcitation/photoionization spectra of larger atoms an molecule (screening effects are important)

- resonances

- applications to strong field

Gaussian basis set optimised for continuum

applied to High-Harmonic Generation spectroscopy

Kaufman et al. J. Phys. B (1989)

Faure et al. Comp. Phys. Comm. (2002)

Gaussian exponents “optimised” to describe scattering properties

M Labeye, F Zapata et al. JCTC (2018)

Coccia *et al.* Int. J. Quantum Chem (2016)

Gaussian basis set optimised for continuum

applied to High-Harmonic Generation spectroscopy

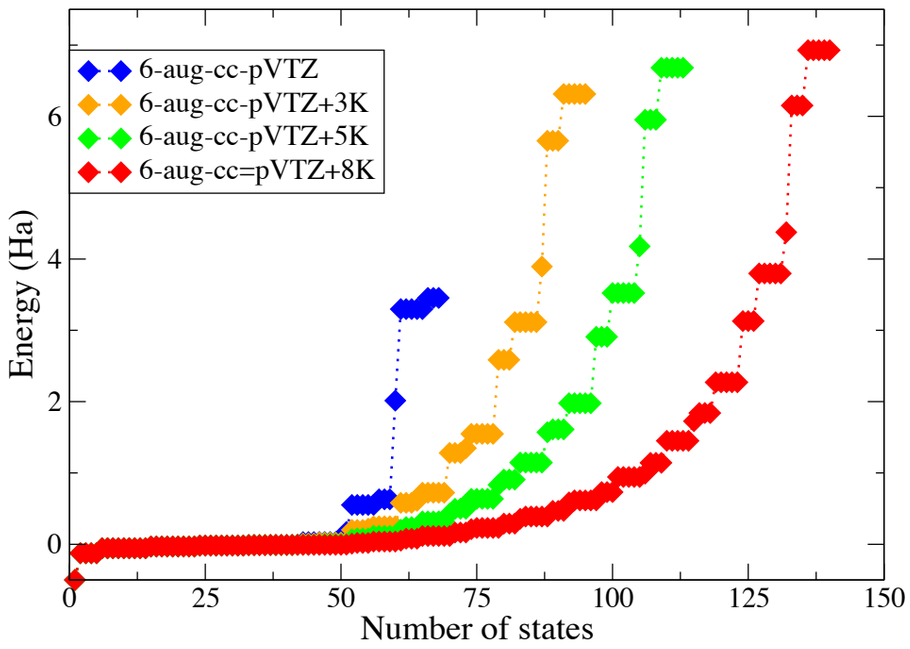
Kaufman et al. J. Phys. B (1989)

Faure et al. Comp. Phys. Comm. (2002)

Gaussian exponents “optimised” to describe scattering properties

increase

continuum energy density



M Labeye, F Zapata et al. JCTC (2018)

Coccia *et al.* Int. J. Quantum Chem (2016)

Gaussian basis set optimised for continuum

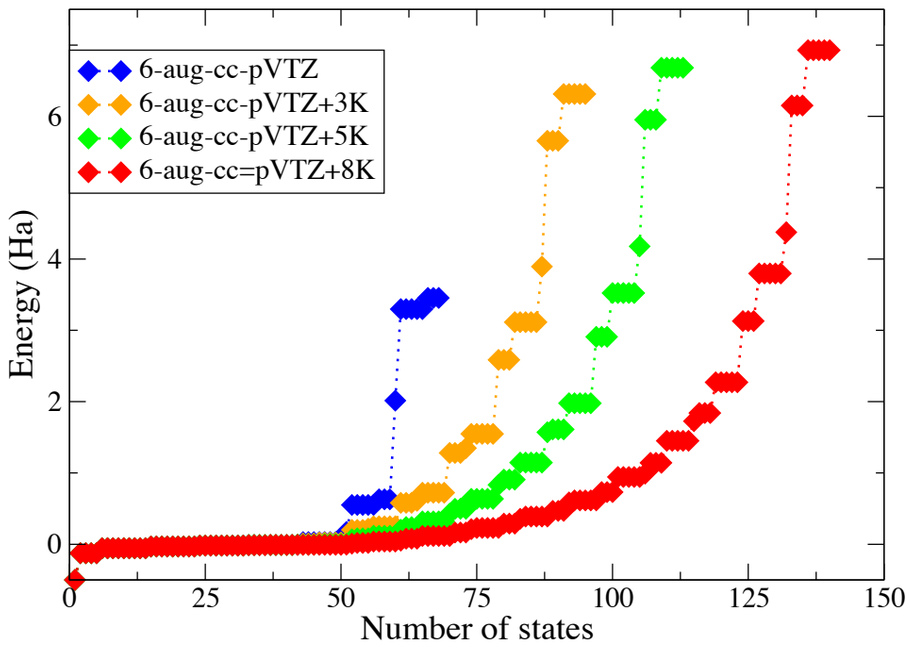
applied to High-Harmonic Generation spectroscopy

Kaufman et al. J. Phys. B (1989)

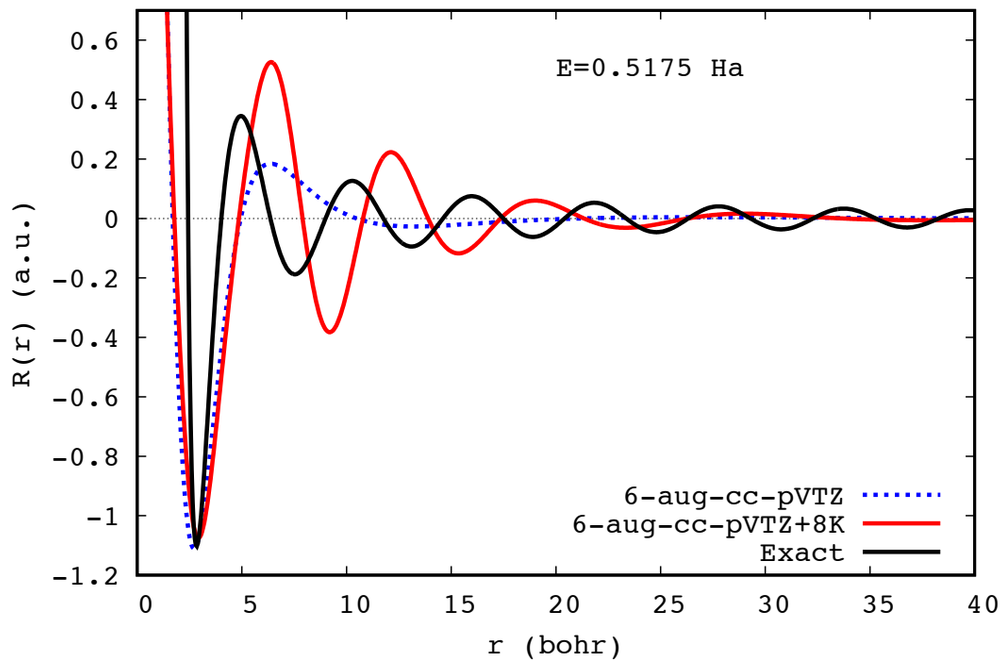
Faure et al. Comp. Phys. Comm. (2002)

Gaussian exponents “optimised” to describe scattering properties

increase
continuum energy density



reproduce
continuum wafefunction oscillations



M Labeye, F Zapata et al. JCTC (2018)

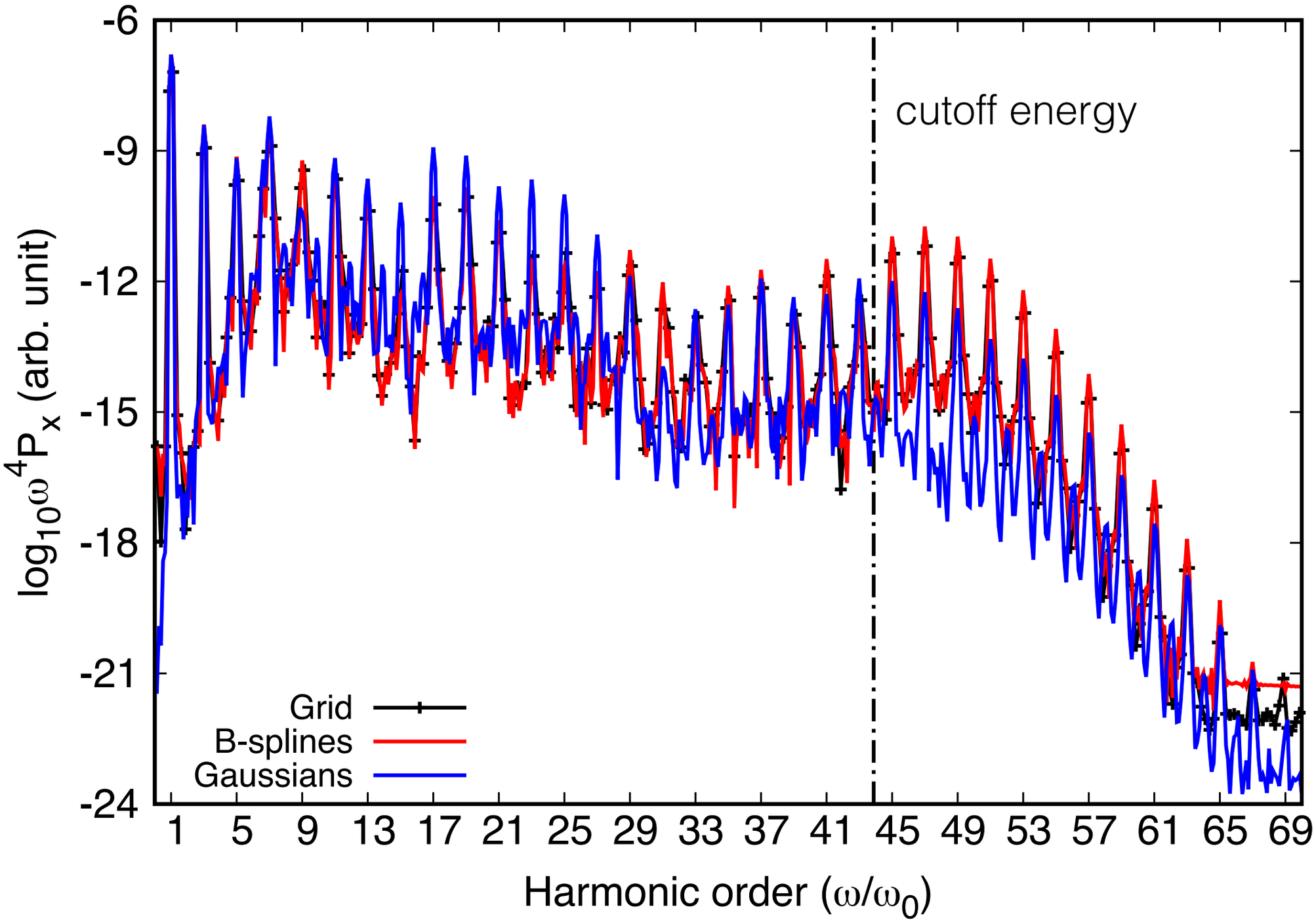
Coccia *et al.* Int. J. Quantum Chem (2016)

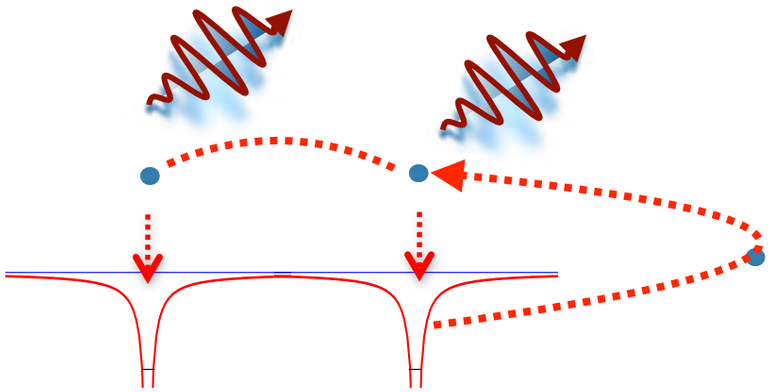
HHG

H_2^+

Gaussians compared to Grid and B-splines (exact references)

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



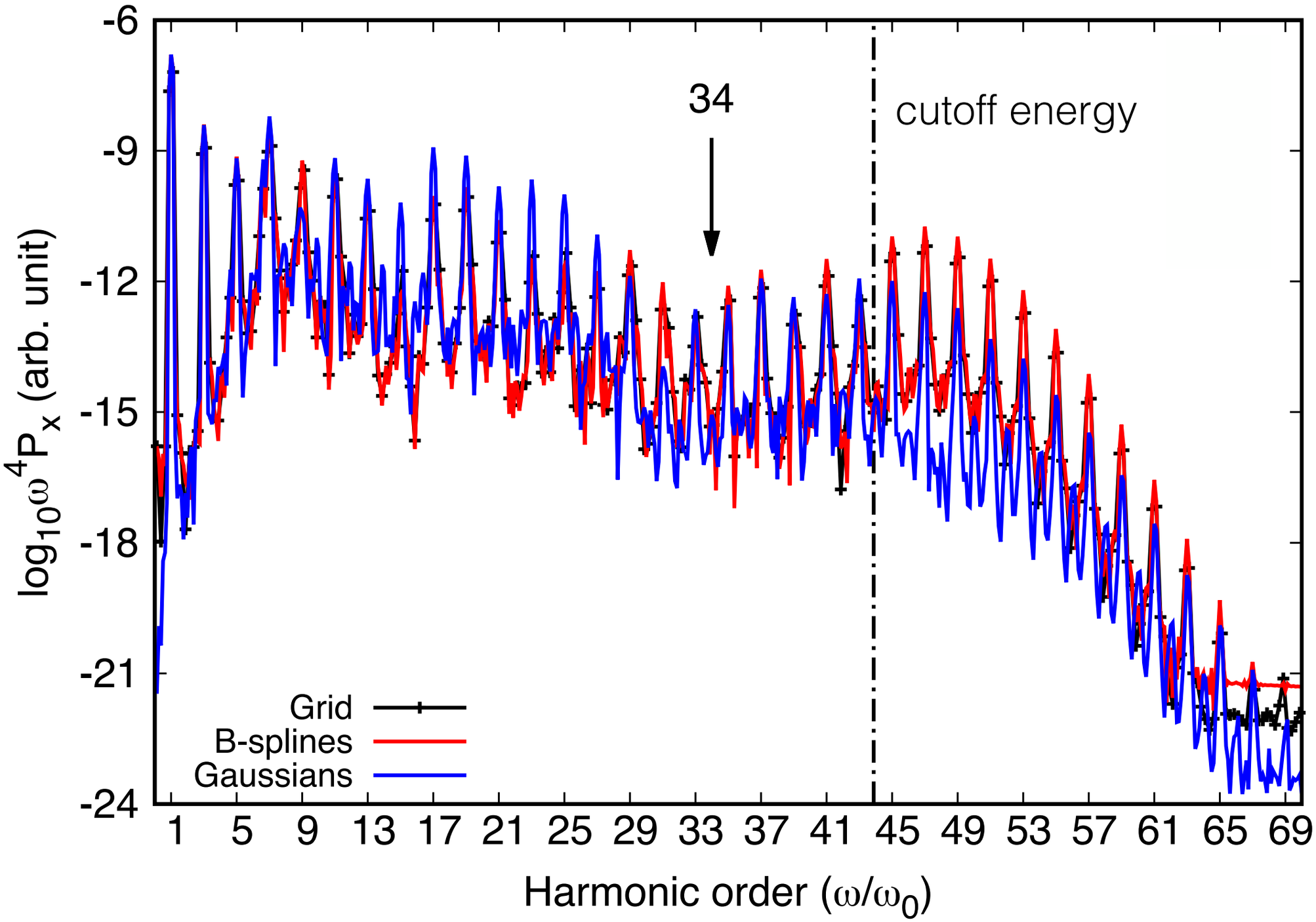


Minimum : two center interference

Lein et al. PRA (2002)

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

H_2^+

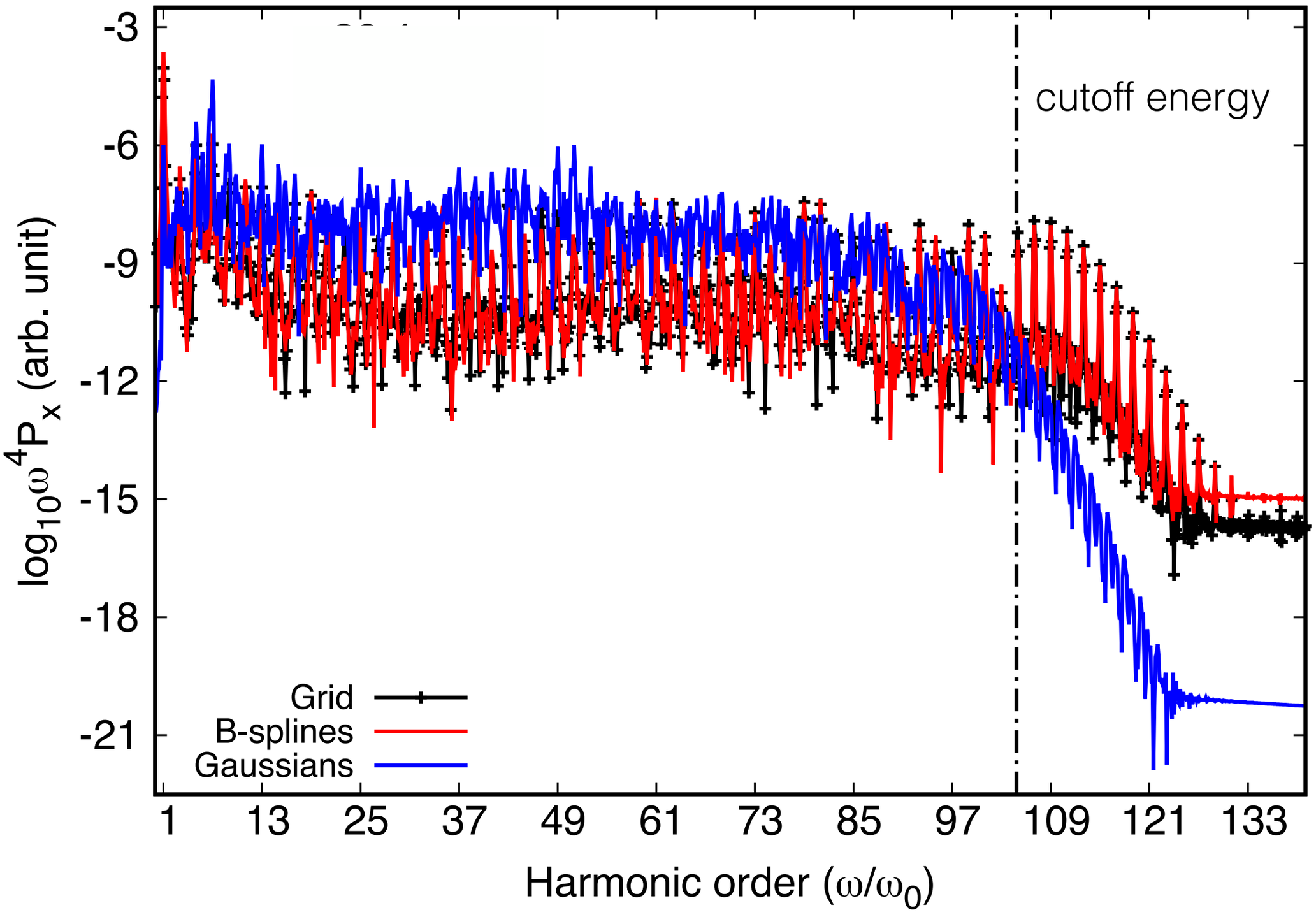


HHG

Gaussians compared to Grid and B-splines (exact references)

H_2^+

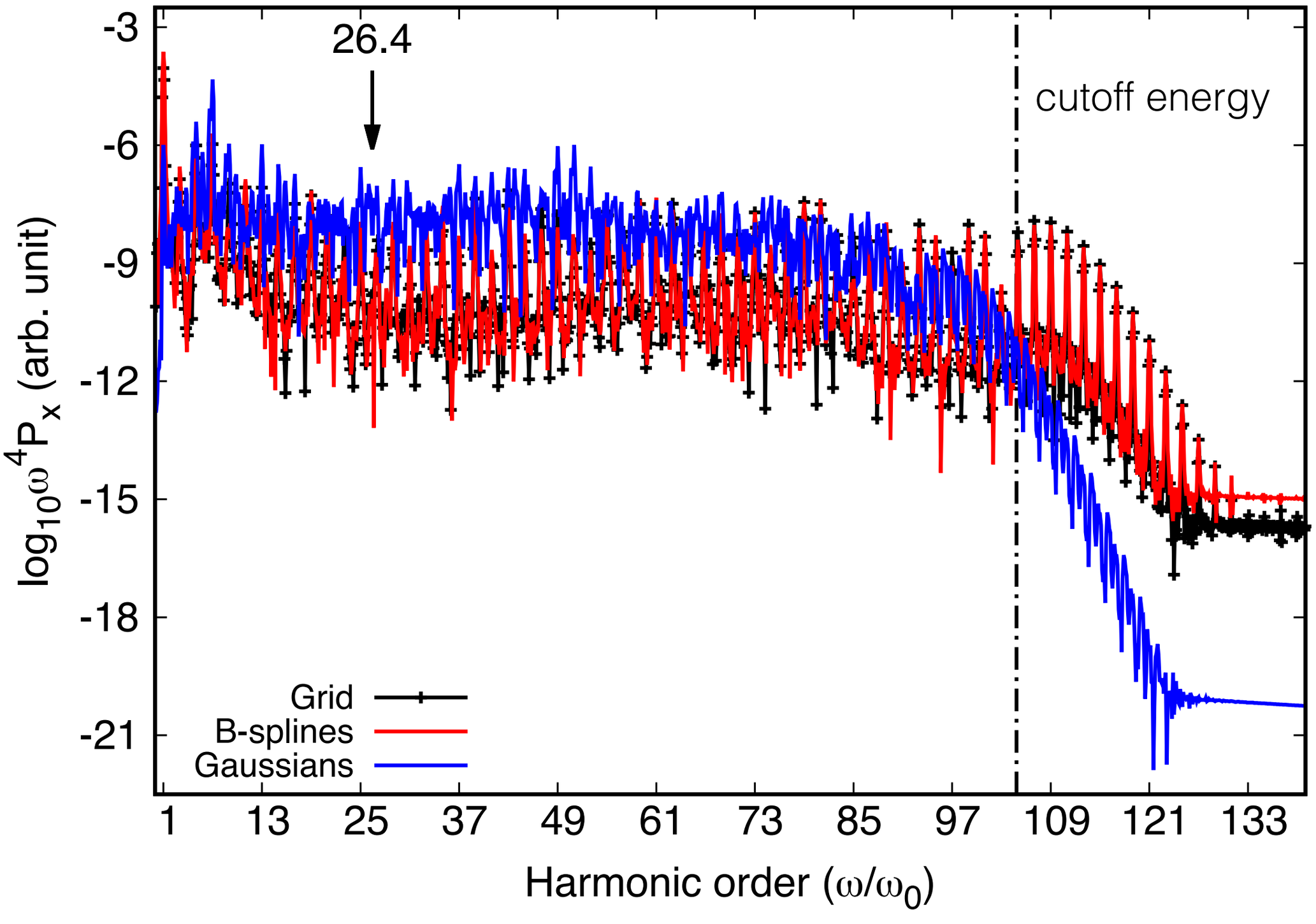
$I = 7 \times 10^{14}\, W/cm^2$



Minimum : two center interference

H_2^+

$I = 7 \times 10^{14}\, W/cm^2$



Perspectives

- study of electron correlation in strong field for molecules

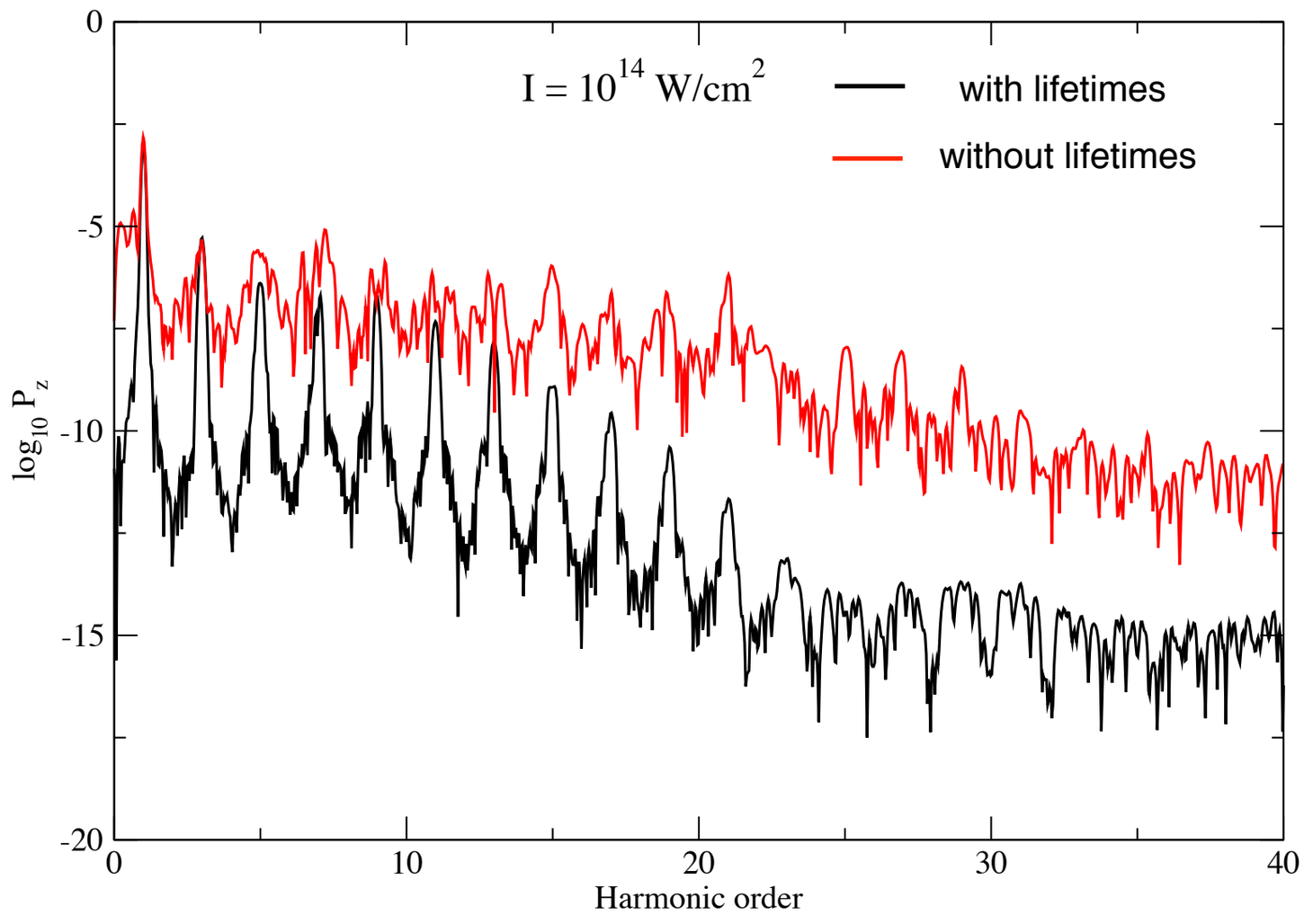
- simulation of two color field (pump/probe experiments) to study multiorbitals and inter-channel coupling in HHG

New ab-initio lifetimes model for continuum

applied to Gaussian and High-Harmonic Generation spectroscopy

Finite basis set generates an incomplete and discrete set of continuum states :
artificial reflection

- CAP, complex scaling, absorber, Heuristic lifetimes …



1. Heuristic lifetimes model (1 parameters)

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

2. Double Heuristic lifetimes model (2 parameters)

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

New ab-initio lifetimes model for continuum

applied to Gaussian and High-Harmonic Generation spectroscopy

1. Solving the radial equation for H atom without boundary conditions :

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

Discrete bound states : $E=\epsilon$ real $\epsilon<0$

Continuum scattering states : $E=\epsilon$ real $\epsilon>0$

Decaying states with a finite lifetimes : $E=\epsilon-\frac{i}{2}\gamma$ complex $\epsilon>0$ $\gamma>0$

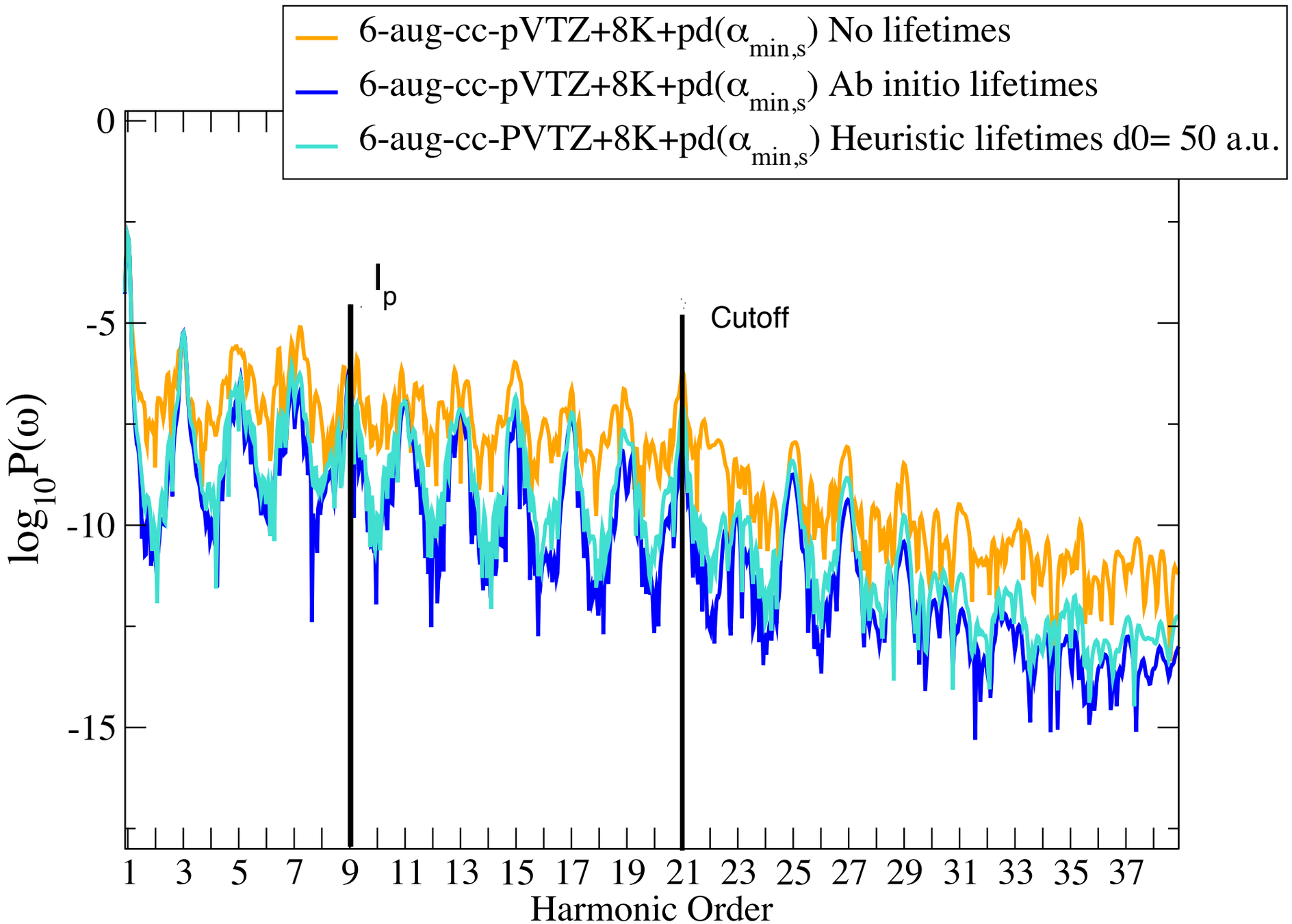
$\tau=1/\gamma$

2. $|R(r)|\longrightarrow$ calculated with (incomplete) Gaussian basis set corresponds to the solution of complex energy and the asymptotic decay gives γ

Coccia et al. JCP (2016)

Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



Perspectives

- extension to molecules

Thanks :)

Dr. Julien TOULOUSE
Dr. Roland ASSARAF
Dr. Felipe ZAPATA
Laboratoire de Chimie Théorique France

Dr. Emanuele COCCIA
Universitá di Trieste Italia

Dr. Valerie VENIARD
Ecole Polytechnique France

Lifetimes

Ab initio lifetimes model :

Hydrogen-like atom with complex energy

The radial equation with **complex energy** E

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

has the general solution **without imposing any boundary conditions**

$$R(r) \quad = \quad c_1 R_1(r) + c_2 R_2(r)$$

$$R_1(r) = L\left(\nu, 2\ell+1, 2\sqrt{-2E}\ r\right) r^\ell e^{-\sqrt{-2E}\ r}$$

$$R_2(r) = U\left(-\nu, 2\ell+2, 2\sqrt{-2E}\ r\right) r^\ell e^{-\sqrt{-2E}\ r}$$

$$\nu = Z/\sqrt{-2E} - \ell - 1$$

L is the generalised Laguerre function

U is the Tricorni confluent hypergeometric function

Different type of states

If $E = \varepsilon$ is real with $\varepsilon < 0$:

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$ *except for* $\varepsilon = -Z^2/(2n^2)$ where $n \in \mathbb{N}^*$. In the latter case, $R_1(r) \propto R_2(r)$ which is finite and normalizable

$\Longrightarrow$ **discrete bound states**

If $E = \varepsilon$ is real with $\varepsilon > 0$:

$|R_1(r)| \underset{r\to\infty}{\sim} 1/r$ and $R_2(r)$ diverges for $r \to 0$. We choose $R(r) = c_1 R_1(r)$ which is finite but not normalizable

$\Longrightarrow$ **continuum scattering states**

If $E = \varepsilon - i\gamma/2$ is complex with $\varepsilon > 0$ and $\gamma > 0$:

The survival probability decays in time as $|\psi(\mathbf{r}, t)|^2 \propto e^{-\gamma t}$

$\Longrightarrow$ **decaying states with a finite lifetime** $\tau = 1/\gamma$

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$

$\Longrightarrow$ on the space of such diverging functions, the Hamiltonian is not a self-adjoint operator which is why E can be complex

Ab initio lifetime correction to one-electron scattering states for incomplete basis sets

*one-electron hydrogen-like atom

For each state *p*, the radial function is expanded on *M* basis functions $\{\chi_\mu(r)\}$

$$R_p(r) = \sum_{\mu=1}^{M} c_{\mu,p}\, \chi_\mu(r)$$

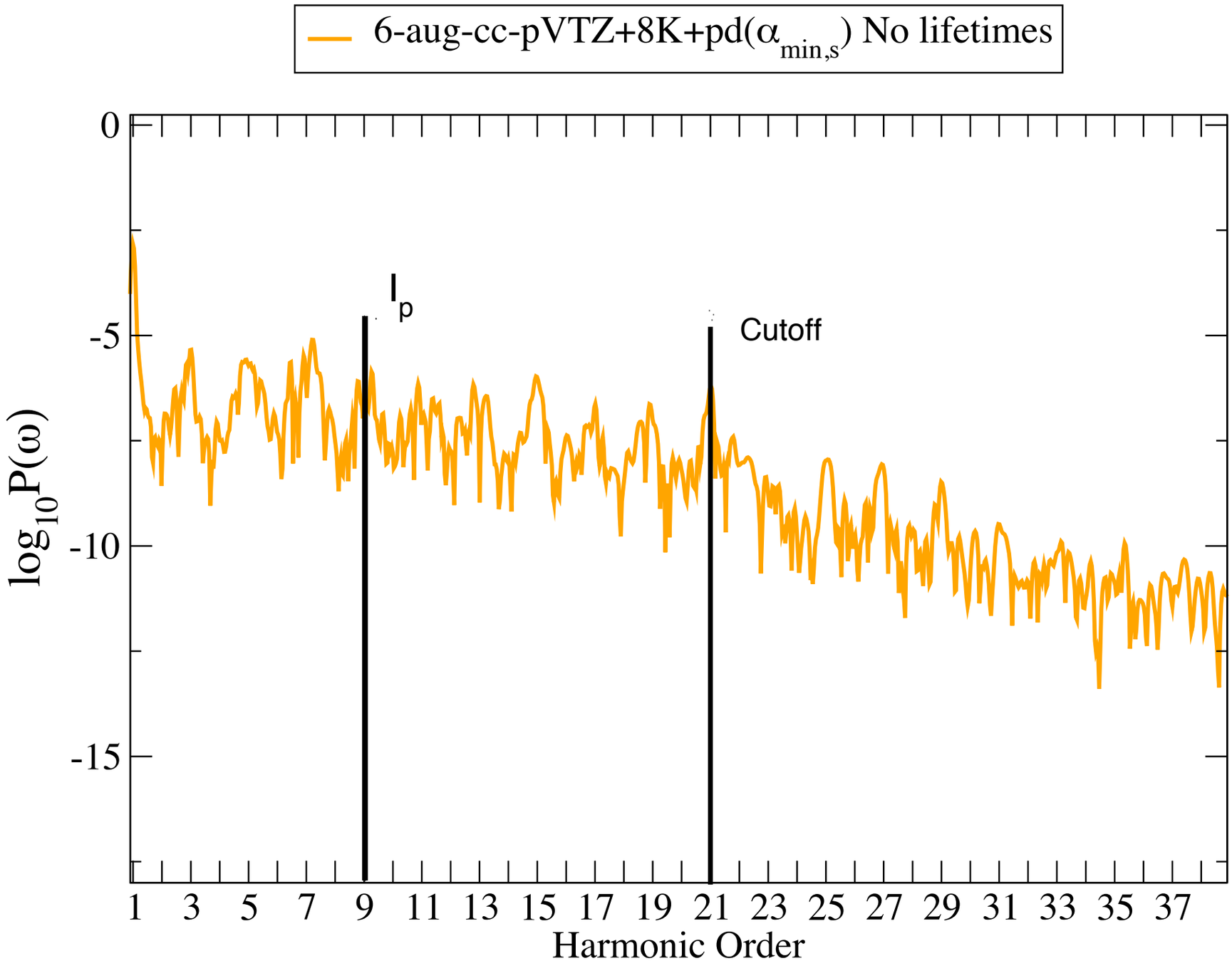
$c_{\mu,p}$ are the calculated orbital coefficients

The key idea: **In a radial window, the radial part $R_p(r)$ of an approximate scattering state p calculated with the incomplete Gaussian basis set is a better approximation to a state $R_2(r)$ with complex energy than to an scattering state $R_1(r)$ with real energy**

$E = \varepsilon - i\gamma/2$ is complex with $\varepsilon > 0$ and $\gamma > 0$:

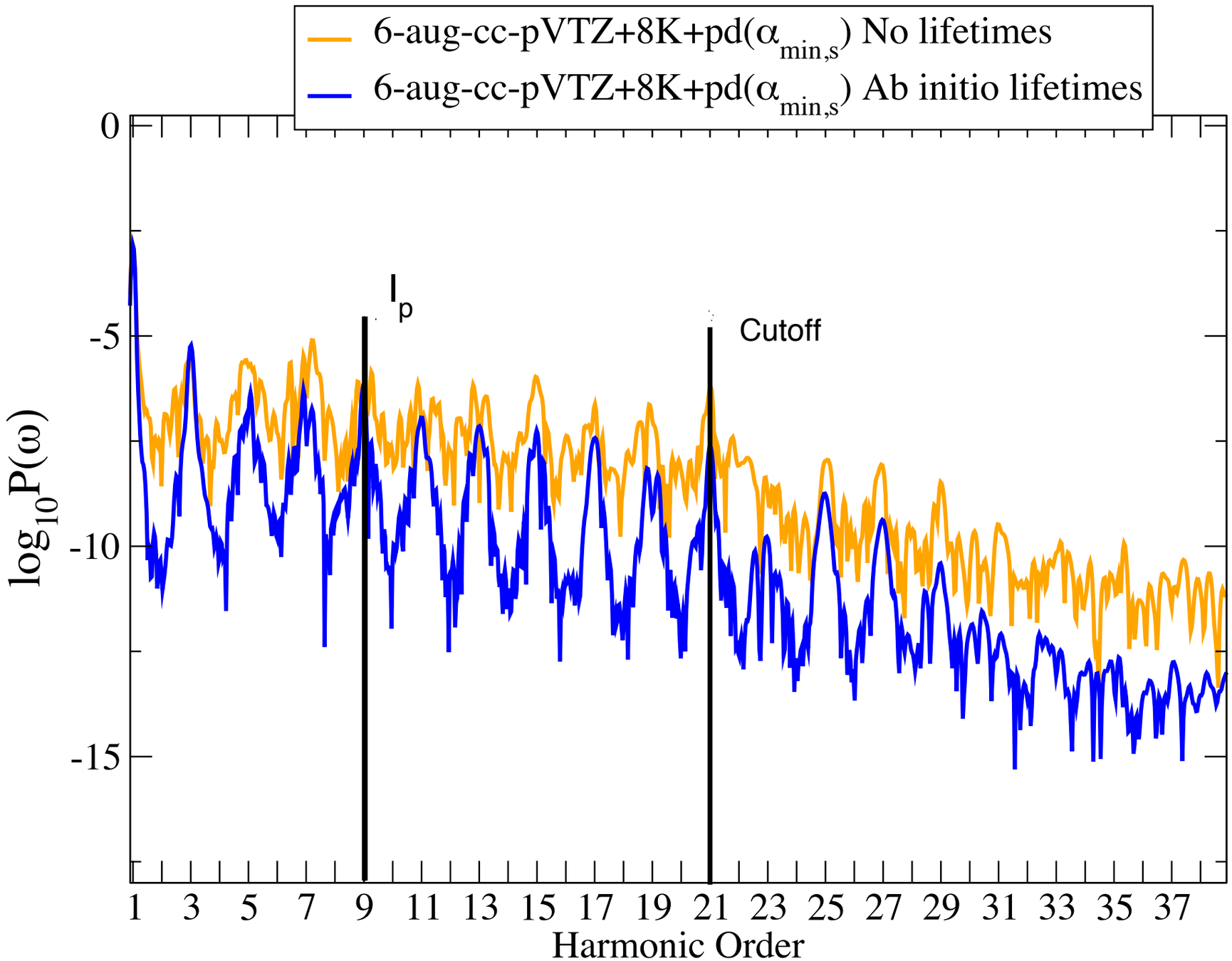
Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



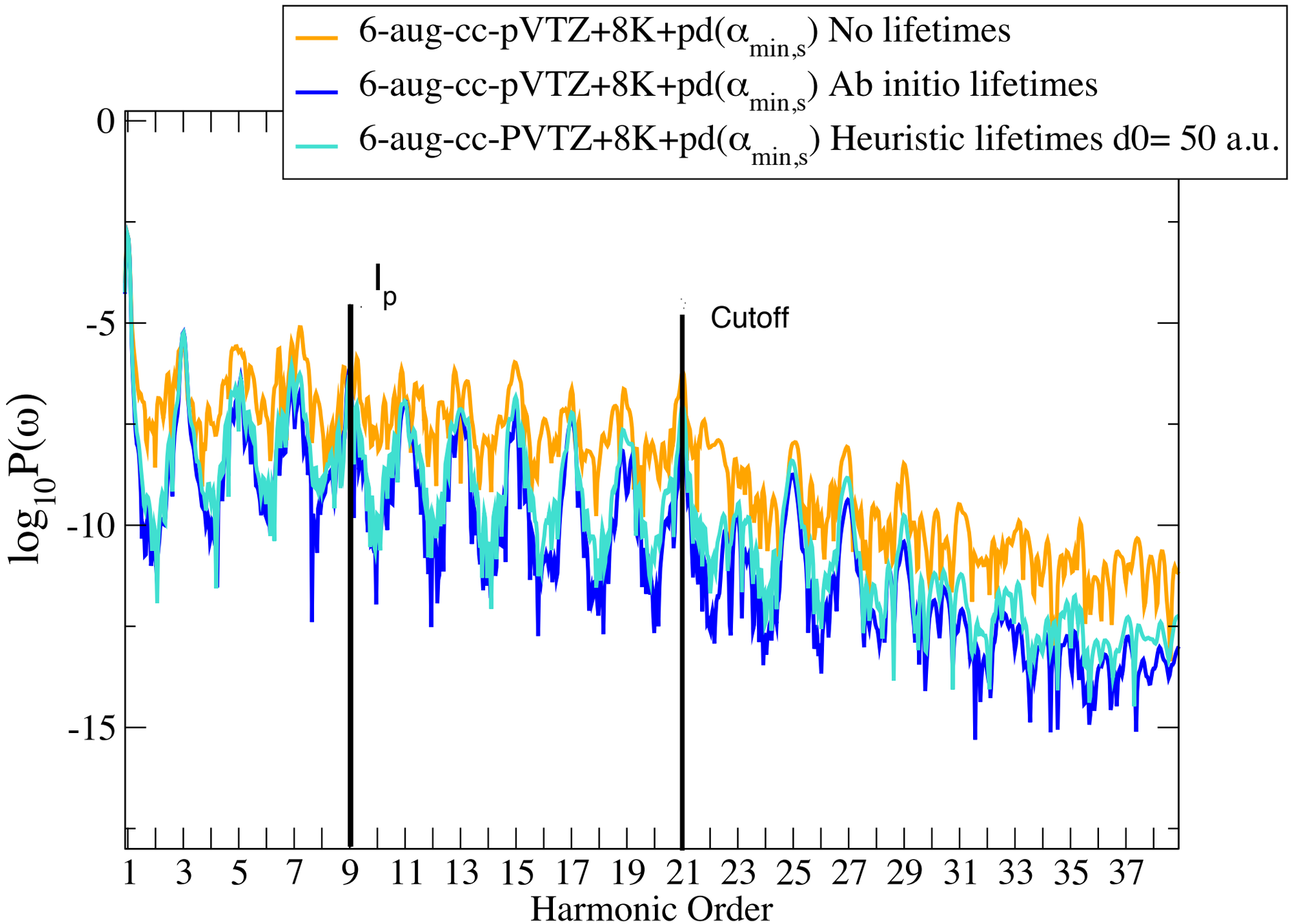
Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



Calculated inverse lifetimes for the H atom

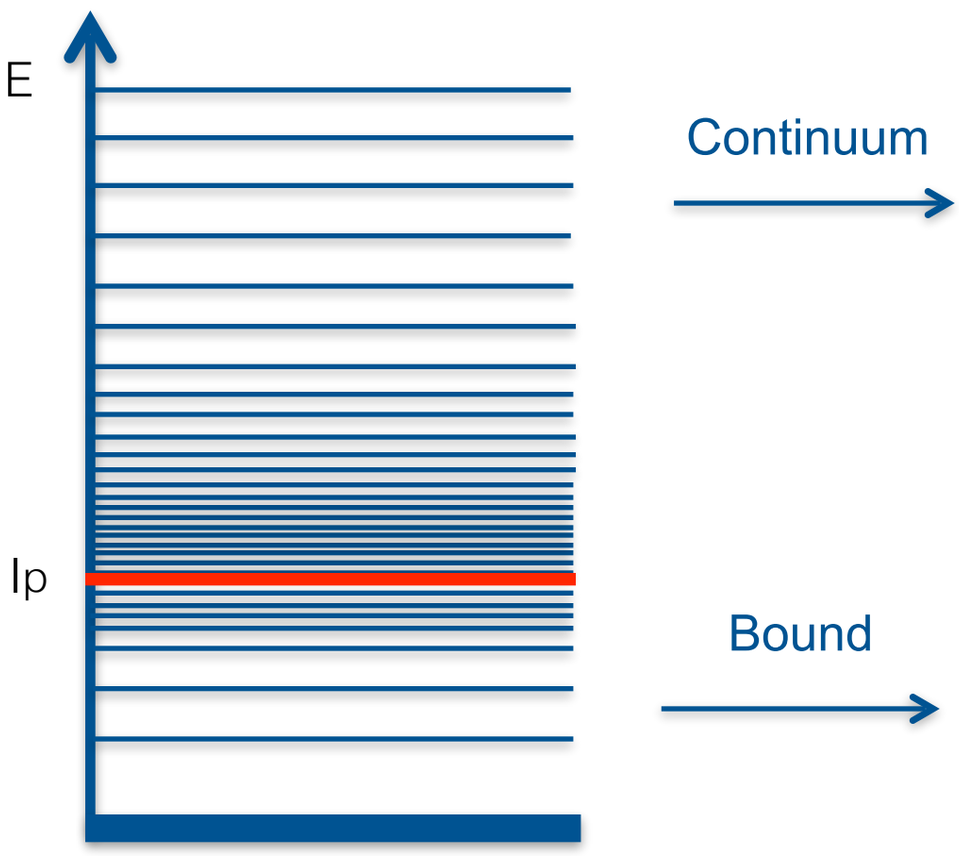
For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:

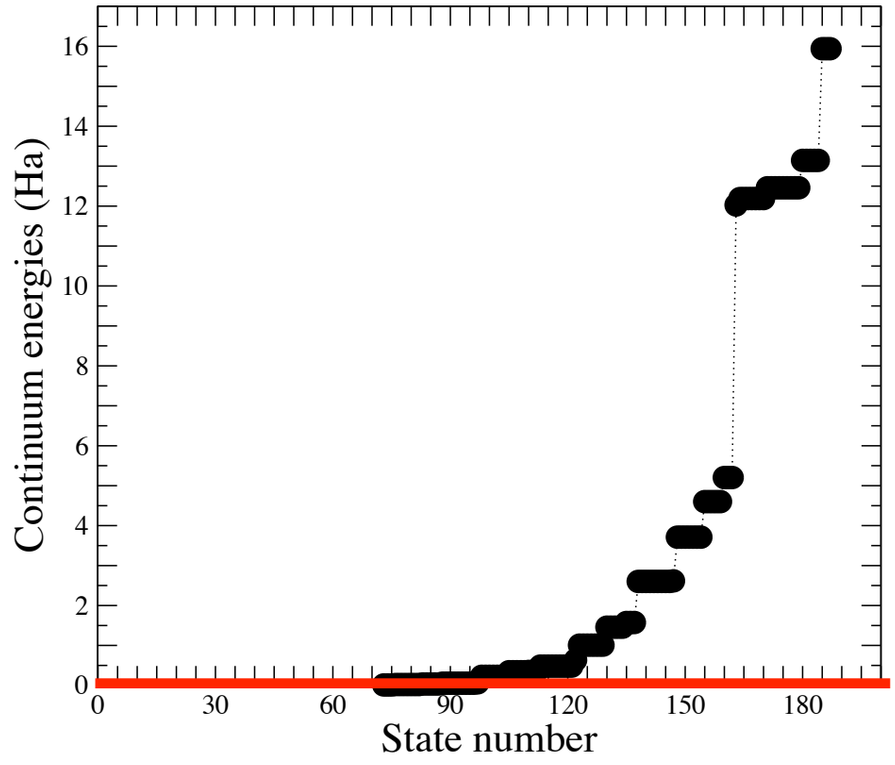


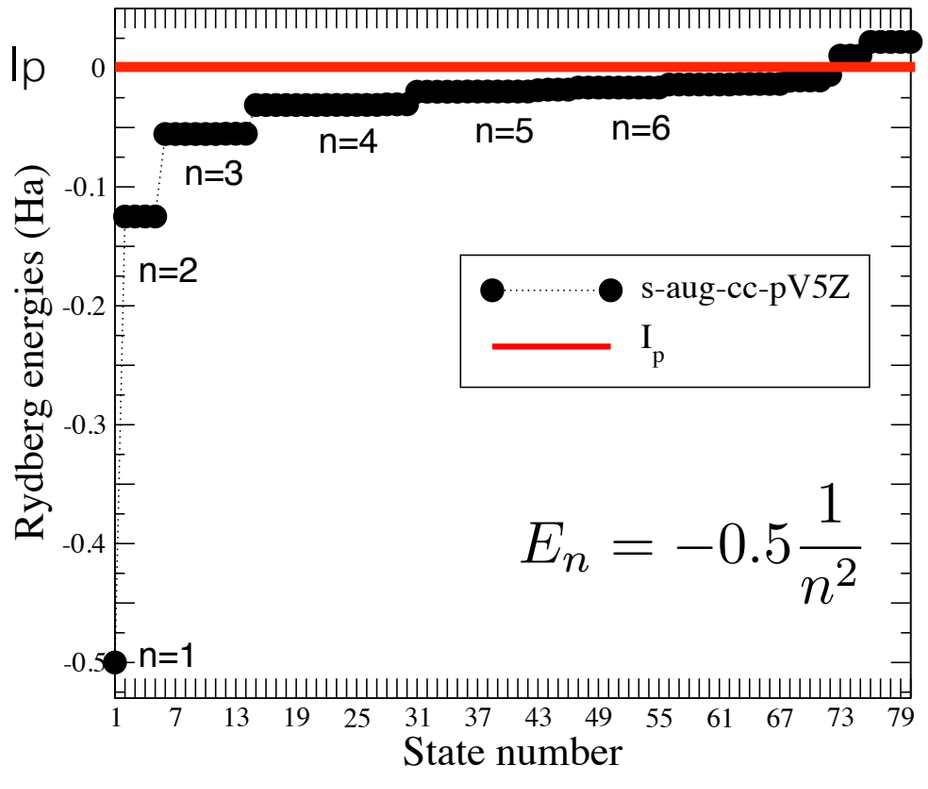
trovare un modo di spiegare in due parole …

Gaussian basis functions : bound (Rydberg) and continuum
H atom

s-aug-cc-pV5Z





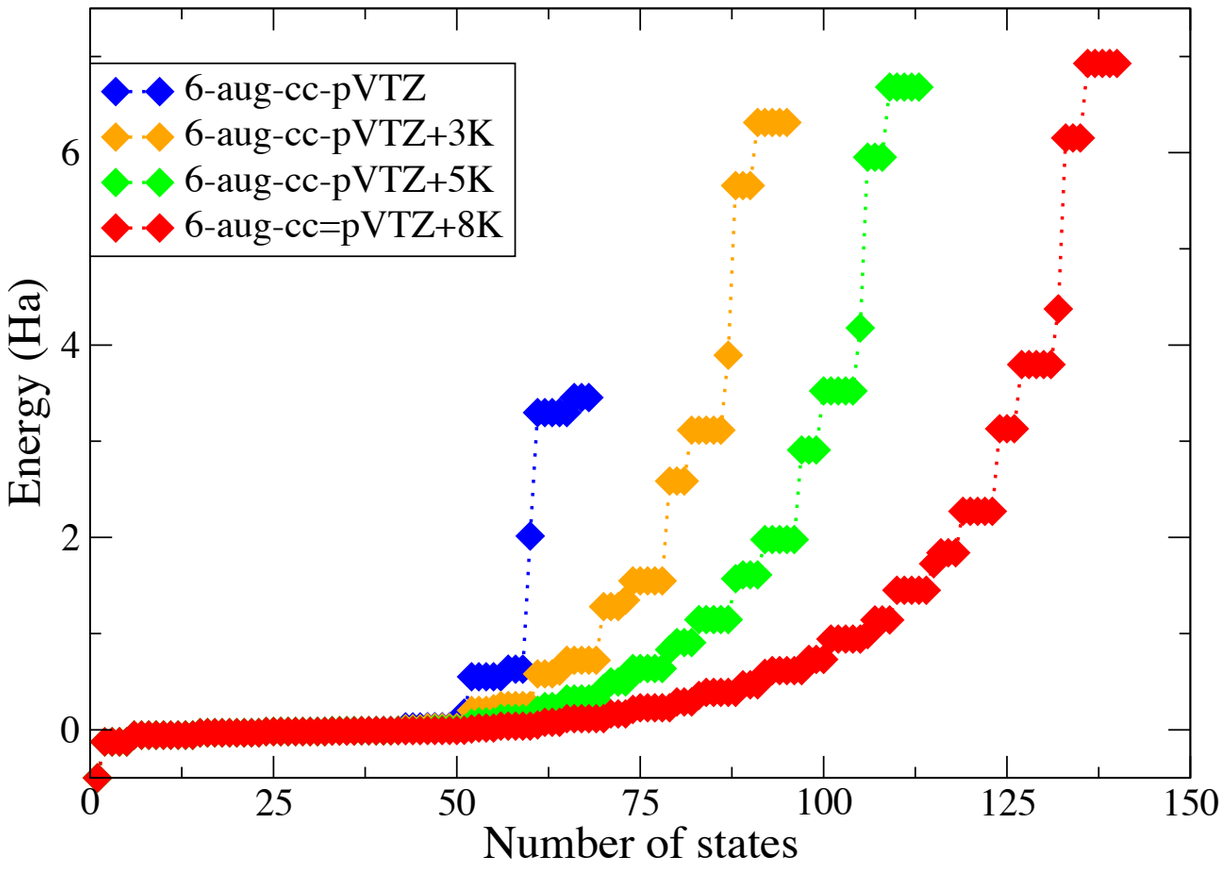


Luppi and Head-Gordon JCP 2013

Exponents optimised for scattering states

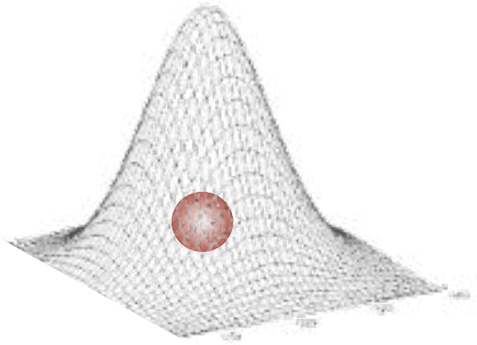
Generating sequences of exponents spanning low-energy continuum solutions

Kaufman et al. J. Phys. B (1989)

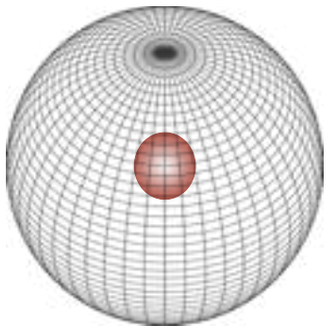


	6-aug-cc-pVTZ	+3K	+5K	+ 8K
Total	68	95	113	140
Bound	42	42	46	51
Continuum	26	53	67	89

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

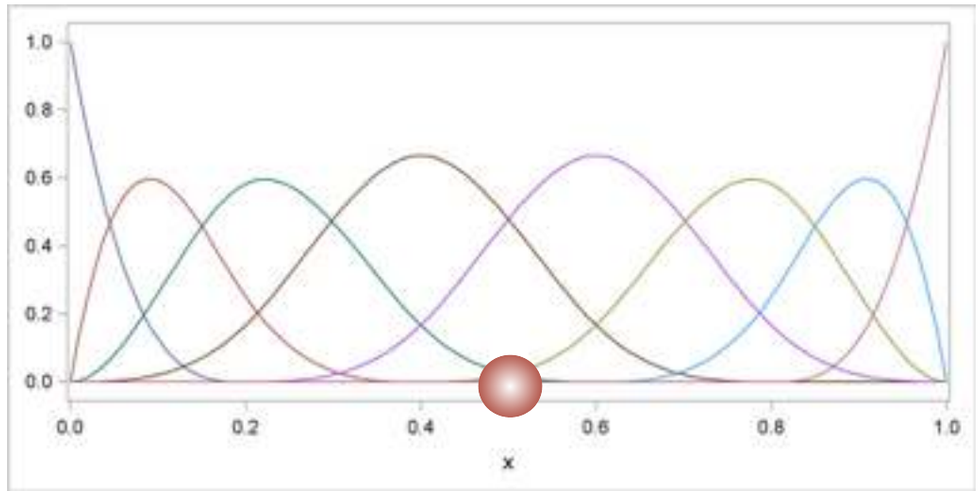


Optimised Gaussian basis sets versus



Grid

B-splines



- Theoretical model (single-active electron)

  Kulander et al. PRA (1989)

  Bandrauk et al. PRA (2009)

  Taieb et al. PRA

  Ruiz et al. PRA (2006)

  Gordon et al. PRL (2006)

- Time-dependent density-functional theory TD-DFT

  Telnov et al. PRA (2013)

  Vincendon et al. Comp. Mat. Science (2017)

- 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)

- Theoretical model

  Martin, Journal of Physics B: Atomic, Molecular and Optical Physics 32 (16), R197

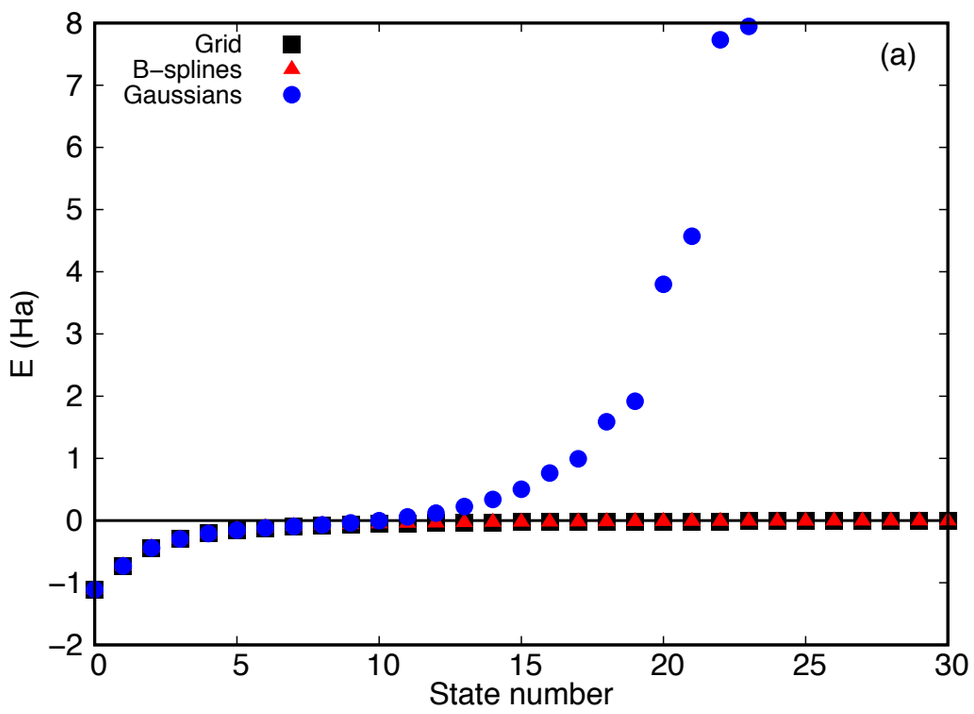
  Bachau et al. Reports on Progress in Physics 64 (12), 1815 (2001)

- Algebraic diagrammatic construction (ADC)

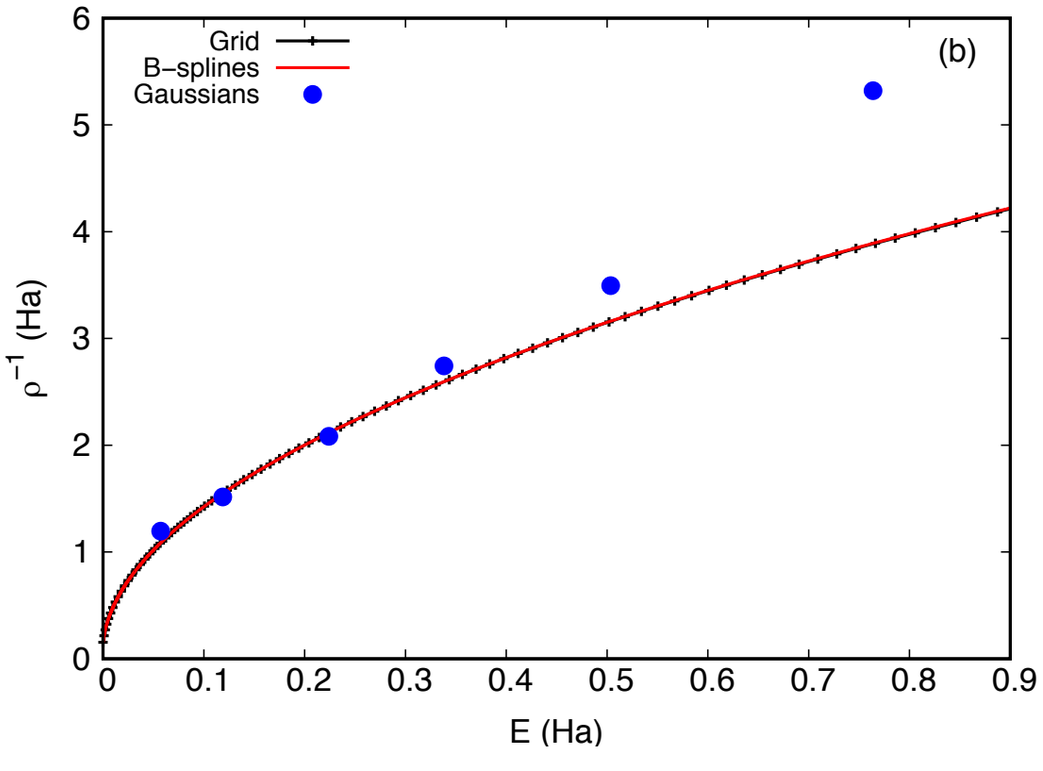
  Ruberti et al. JCP (2014)

Optimised Gaussians Grid B-splines H_2^+

Eigenvalues up to the 30th eigenstate

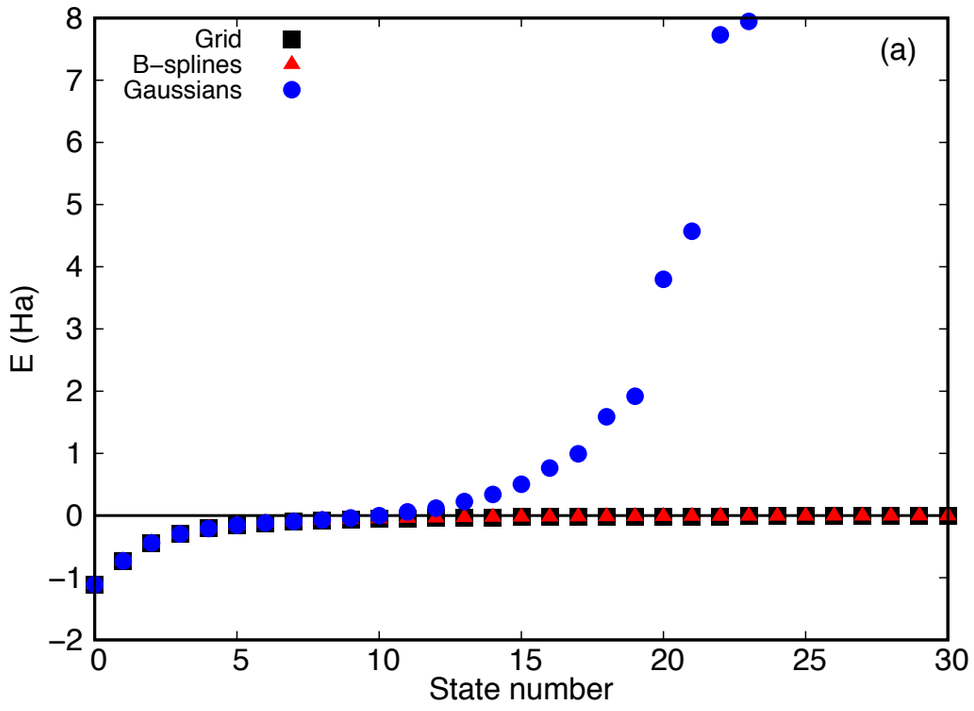


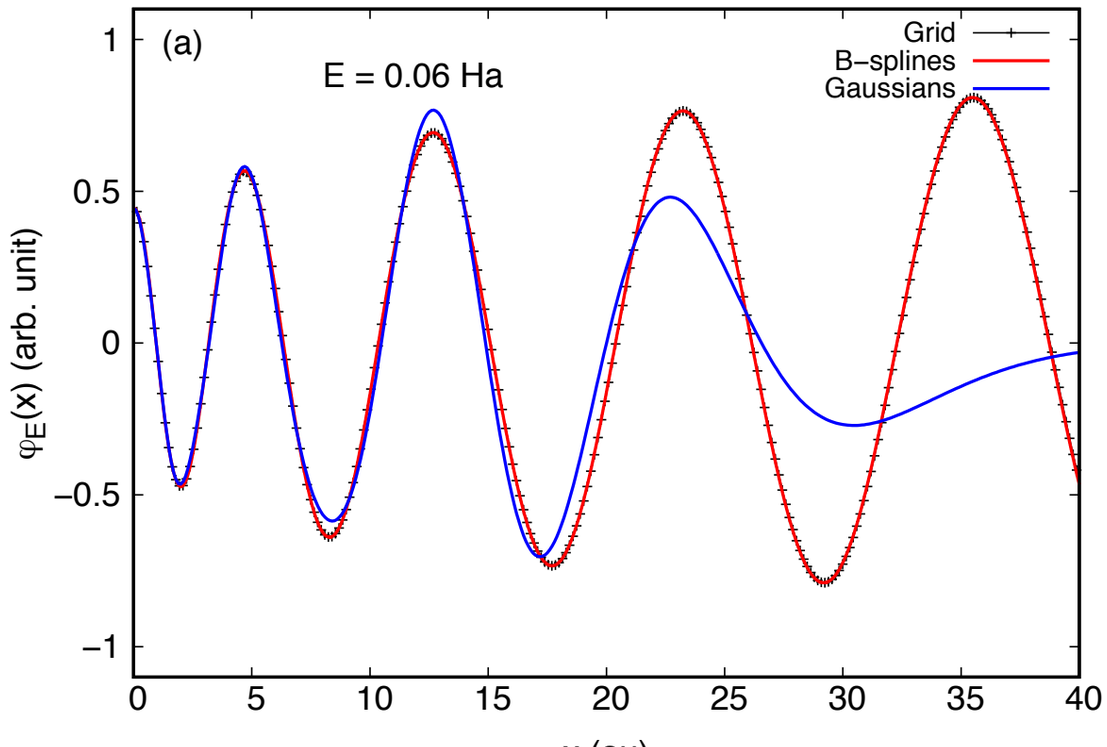
Inverse of the density of continuum states



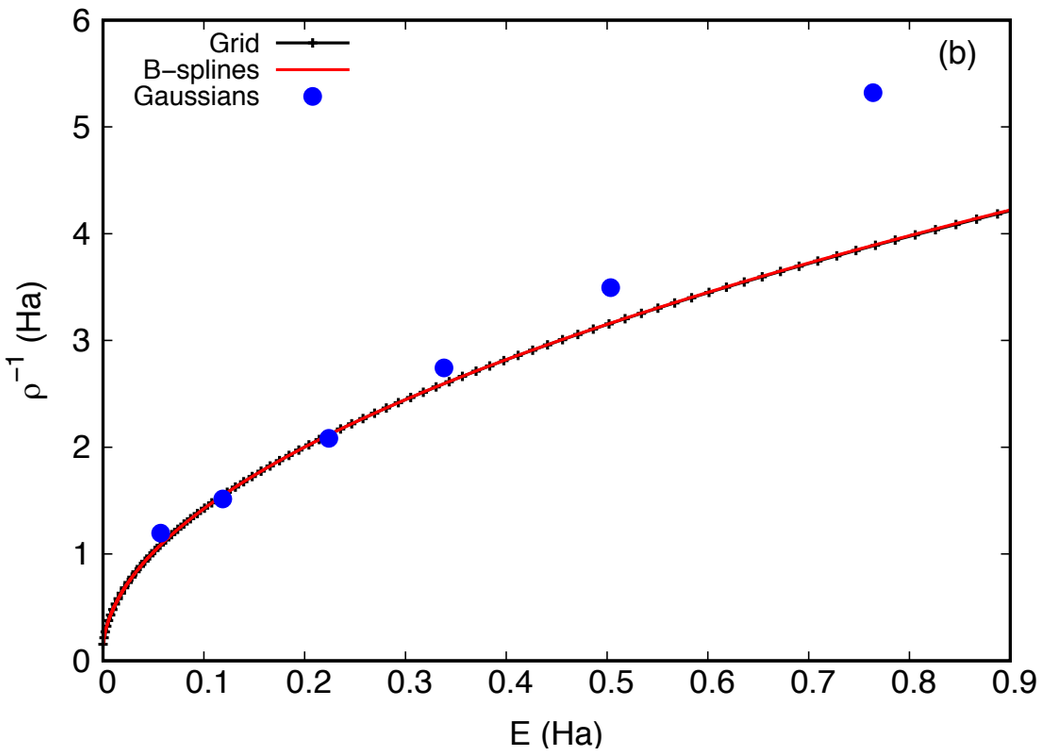
Optimised Gaussians Grid B-splines H_2^+

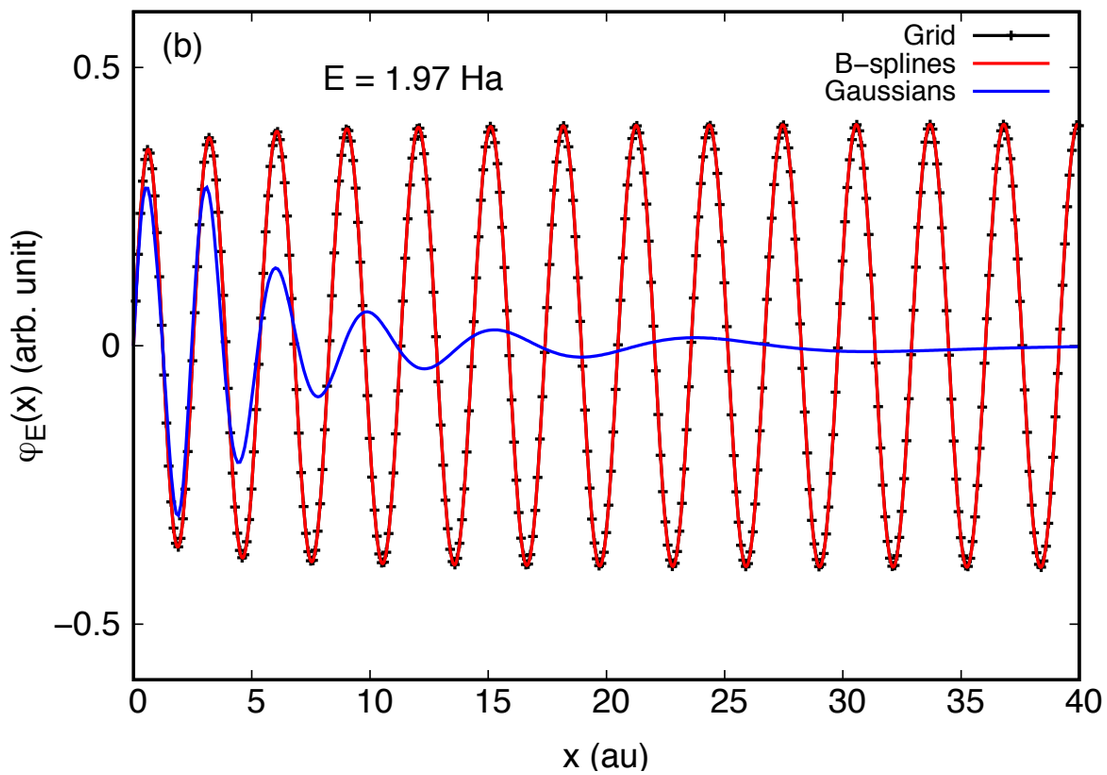
Eigenvalues up to the 30th eigenstate





Inverse of the density of continuum states





The problem of ionisation : the lifetimes

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

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

Incomplete Gaussian basis set produce artificial reflections

The problem of ionisation : the lifetimes

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

Incomplete Gaussian basis set → produce artificial reflections

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

We replace every state energy by a complex energy !

inverse lifetimes

* Propagation on a grid: CAP, complex-scaling, wavefunction absorber

Lifetimes

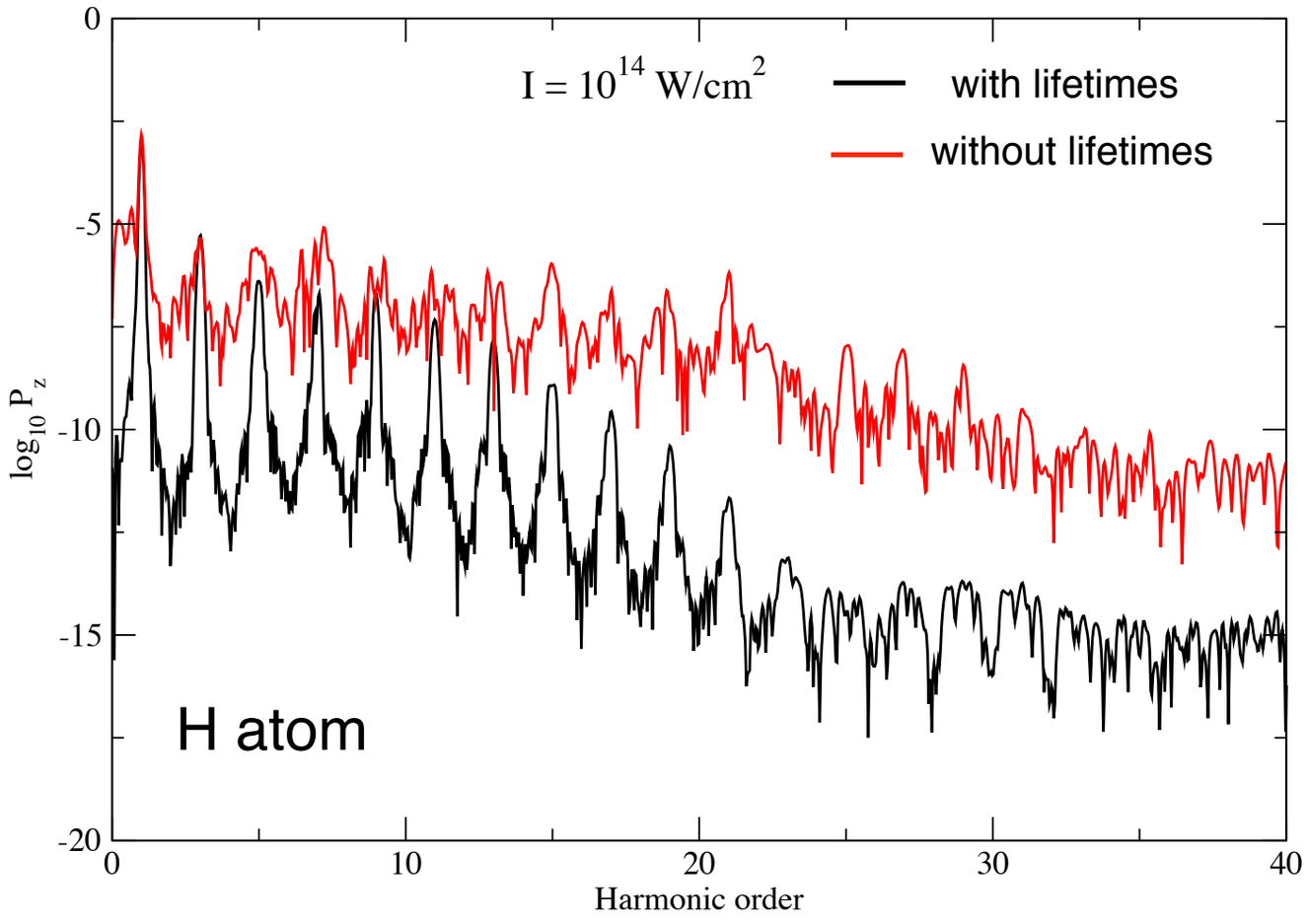
$$i\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = \sum_s (E_s^{\mathrm{CI}}\delta_{ks} - \mu_{ks}E(t))c_s(t)$$

Incomplete Gaussian basis set → produce artificial reflections

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

We replace every state energy by a complex energy !

inverse lifetimes



* Propagation on a grid: CAP, complex-scaling, wavefunction absorber

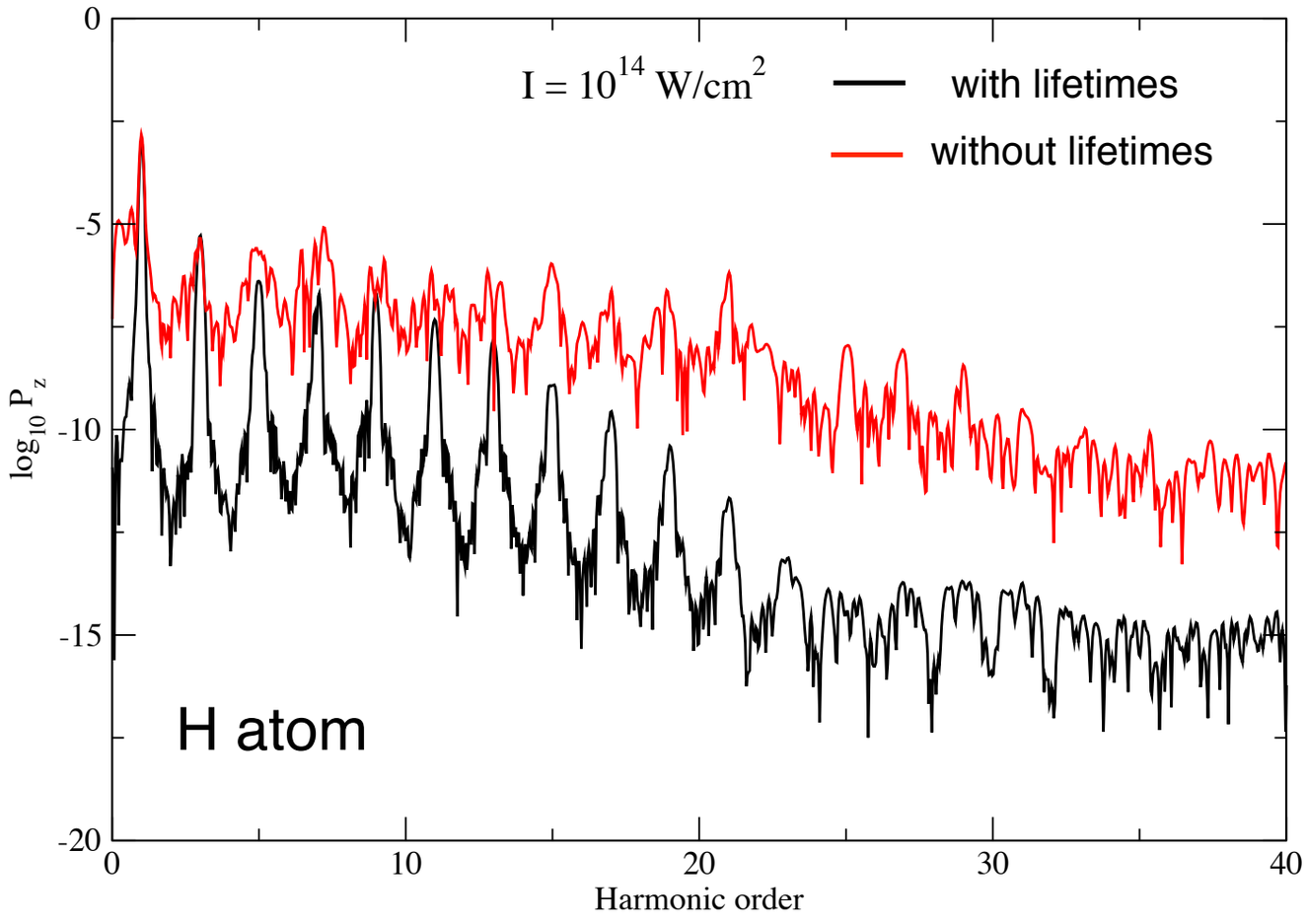
Lifetimes

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

Incomplete Gaussian basis set | produce artificial reflections

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

We replace every state | energy by a complex energy !



inverse lifetimes

1. Heuristic lifetimes model

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

2. Double Heuristic lifetimes model

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

3. Ab initio lifetimes model

Coccia, Assaraf, Luppi, Toulouse
JCP 147, 014106 (2016)

* Propagation on a grid: CAP, complex-scaling, wavefunction absorber

Lifetimes

Coccia et al. JCP 147, 014106 (2016)

Ab initio lifetimes model :

Hydrogen-like atom with complex energy

The radial equation with **complex energy** E

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

has the general solution **without imposing any boundary conditions**

Lifetimes

Ab initio lifetimes model :

Hydrogen-like atom with complex energy

The radial equation with **complex energy** E

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

has the general solution **without imposing any boundary conditions**

$$R(r) \quad = \quad c_1 R_1(r) + c_2 R_2(r)$$

Lifetimes

Ab initio lifetimes model :

Hydrogen-like atom with complex energy

The radial equation with **complex energy** E

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

has the general solution **without imposing any boundary conditions**

$$R(r) \quad = \quad c_1 R_1(r) + c_2 R_2(r)$$

$$R_1(r) = L\left(\nu, 2\ell+1, 2\sqrt{-2E}\ r\right) r^{\ell} e^{-\sqrt{-2E}\ r}$$

$$\nu = Z/\sqrt{-2E} - \ell - 1$$

L is the generalised Laguerre function

Lifetimes

Ab initio lifetimes model :

Hydrogen-like atom with complex energy

The radial equation with **complex energy** E

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

has the general solution **without imposing any boundary conditions**

$$R(r) \quad = \quad c_1 R_1(r) + c_2 R_2(r)$$

$$R_1(r) = L\left(\nu, 2\ell+1, 2\sqrt{-2E}\ r\right) r^\ell e^{-\sqrt{-2E}\ r}$$

$$R_2(r) = U\left(-\nu, 2\ell+2, 2\sqrt{-2E}\ r\right) r^\ell e^{-\sqrt{-2E}\ r}$$

$$\nu = Z/\sqrt{-2E} - \ell - 1$$

L is the generalised Laguerre function

U is the Tricorni confluent hypergeometric function

Different type of states

If $E = \varepsilon$ is real with $\varepsilon < 0$:

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$ *except for* $\varepsilon = -Z^2/(2n^2)$ where $n \in \mathbb{N}^*$. In the latter case, $R_1(r) \propto R_2(r)$ which is finite and normalizable

$\Longrightarrow$ **discrete bound states**

Different type of states

If $E = \varepsilon$ is real with $\varepsilon < 0$:

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$ *except for* $\varepsilon = -Z^2/(2n^2)$ where $n \in \mathbb{N}^*$. In the latter case, $R_1(r) \propto R_2(r)$ which is finite and normalizable

$\Longrightarrow$ **discrete bound states**

If $E = \varepsilon$ is real with $\varepsilon > 0$:

$|R_1(r)| \underset{r\to\infty}{\sim} 1/r$ and $R_2(r)$ diverges for $r \to 0$. We choose $R(r) = c_1 R_1(r)$ which is finite but not normalizable

$\Longrightarrow$ **continuum scattering states**

Different type of states

If $E = \varepsilon$ is real with $\varepsilon < 0$:

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$ *except for* $\varepsilon = -Z^2/(2n^2)$ where $n \in \mathbb{N}^*$. In the latter case, $R_1(r) \propto R_2(r)$ which is finite and normalizable

$\Longrightarrow$ **discrete bound states**

If $E = \varepsilon$ is real with $\varepsilon > 0$:

$|R_1(r)| \underset{r\to\infty}{\sim} 1/r$ and $R_2(r)$ diverges for $r \to 0$. We choose $R(r) = c_1 R_1(r)$ which is finite but not normalizable

$\Longrightarrow$ **continuum scattering states**

If $E = \varepsilon - i\gamma/2$ is complex with $\varepsilon > 0$ and $\gamma > 0$:

The survival probability decays in time as $|\psi(\mathbf{r}, t)|^2 \propto e^{-\gamma t}$

$\Longrightarrow$ **decaying states with a finite lifetime** $\tau = 1/\gamma$

$R_1(r)$ diverges at $r \to \infty$ and $R_2(r)$ diverges for $r \to 0$

$\Longrightarrow$ on the space of such diverging functions, the Hamiltonian is not a self-adjoint operator which is why E can be complex

Ab initio lifetime correction to one-electron scattering states for incomplete basis sets

*one-electron hydrogen-like atom

For each state *p*, the radial function is expanded on *M* basis functions $\{\chi_\mu(r)\}$

$$R_p(r) = \sum_{\mu=1}^{M} c_{\mu,p}\, \chi_\mu(r)$$

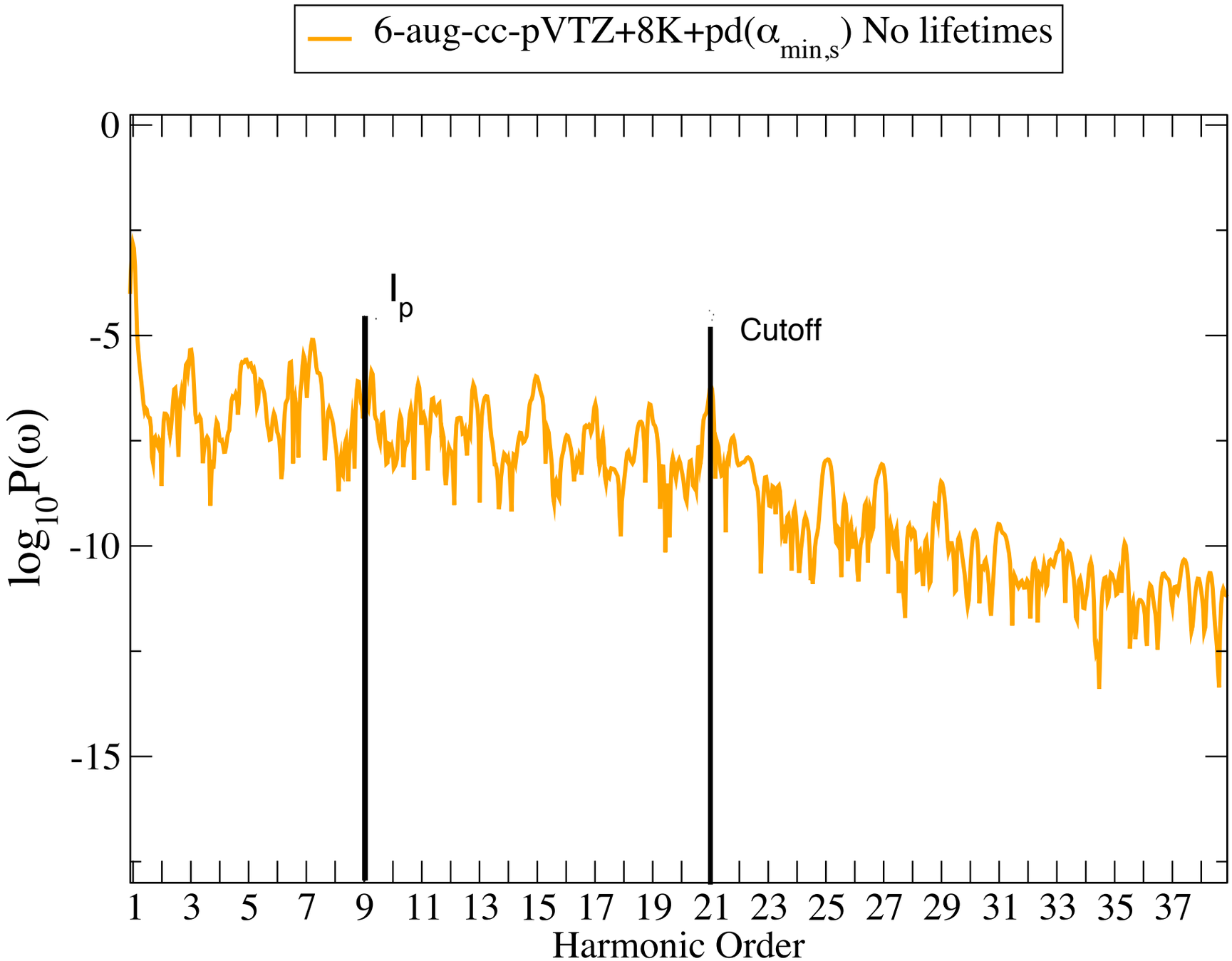
$c_{\mu,p}$ are the calculated orbital coefficients

The key idea: **In a radial window, the radial part $R_p(r)$ of an approximate scattering state p calculated with the incomplete Gaussian basis set is a better approximation to a state $R_2(r)$ with complex energy than to an scattering state $R_1(r)$ with real energy**

$E = \varepsilon - i\gamma/2$ is complex with $\varepsilon > 0$ and $\gamma > 0$:

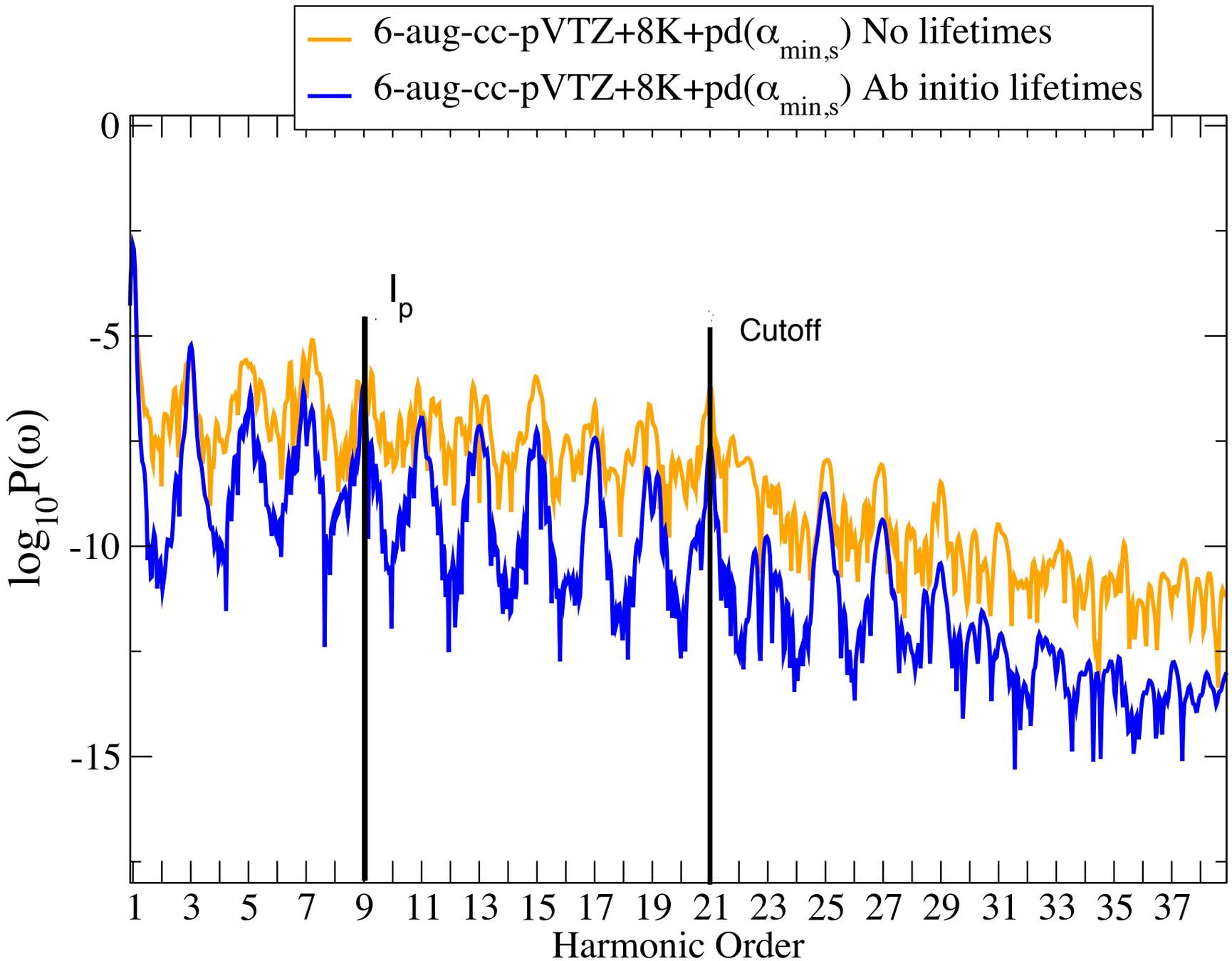
Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



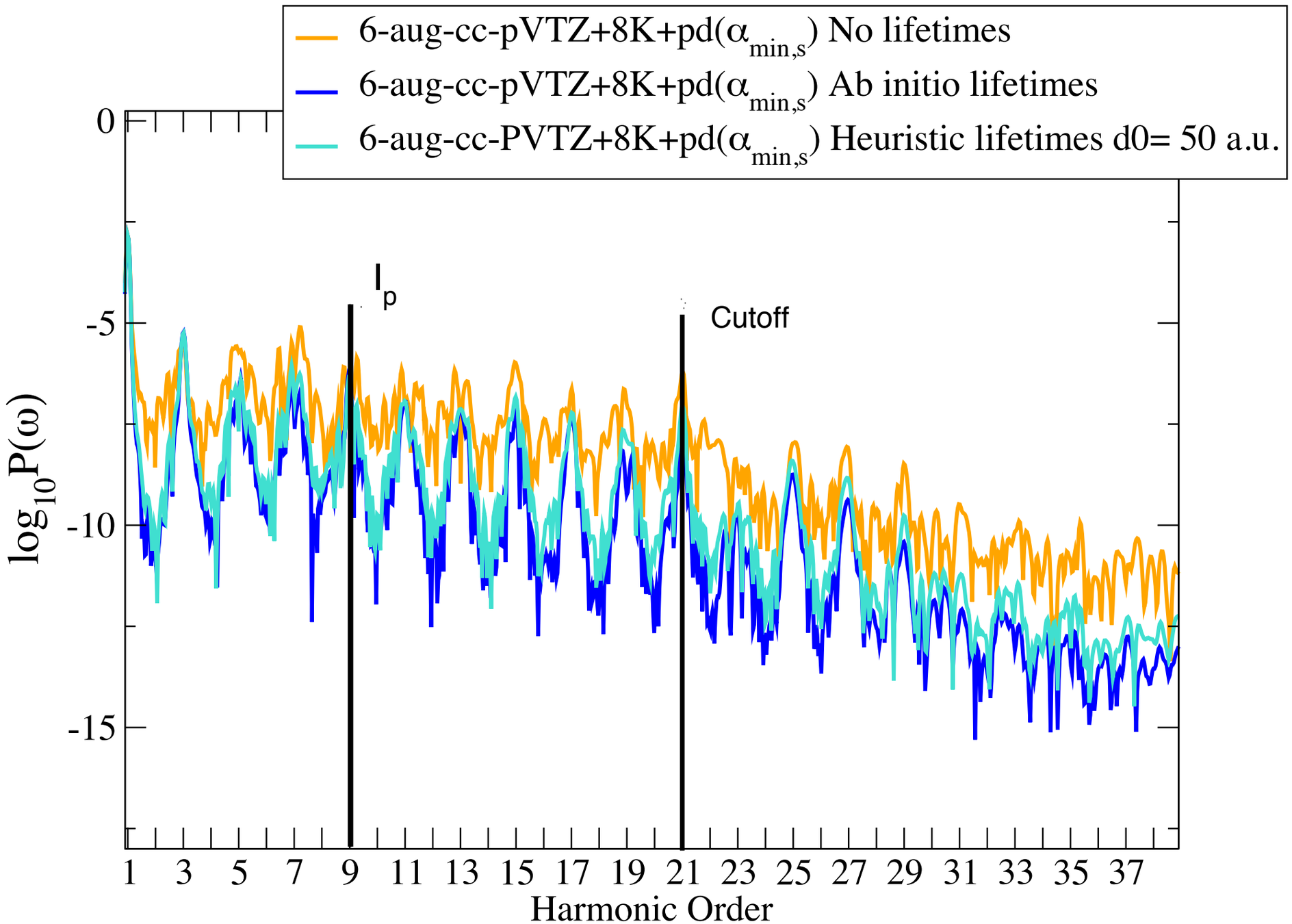
Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



Calculated inverse lifetimes for the H atom

For a laser of wavelength $\lambda_0 = 800$ nm and intensity $I = 10^{14}$ W/cm^2, and 6-aug-cc-pVTZ+8K+pd($\alpha_{\mathrm{min,s}}$) basis set:



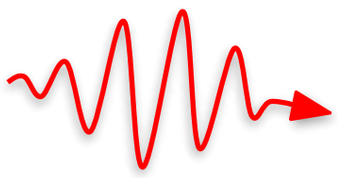
High-Harmonic Generation

laser source

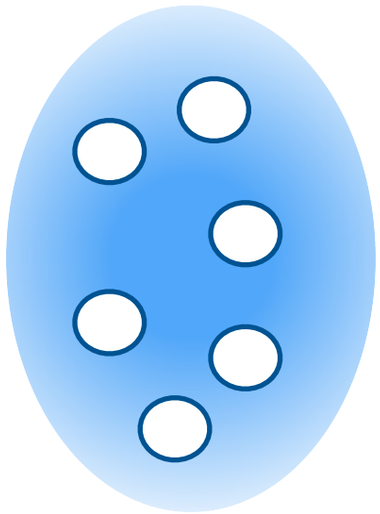
ω_0 = 800 nm

I = 10^{13}-10^{15} W/cm^2

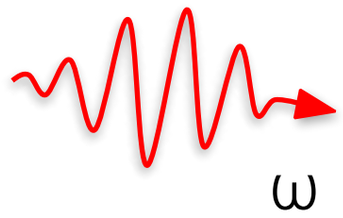
linear polarisation



ω



Gas of atoms/molecules



ω

3ω

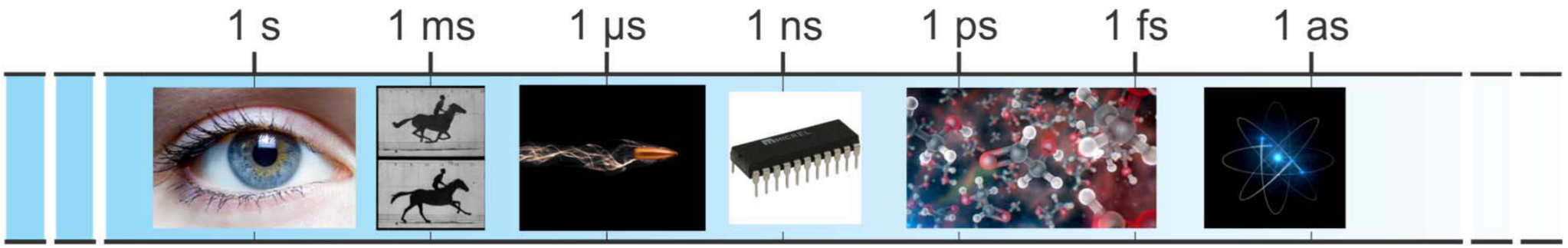
5ω

...

odd harmonics:
inversion symmetry

XUV and soft X-ray
with
attosecond
temporal resolution

- Attosecond science studies electron dynamics at its natural timescale



Cireasa et al. : *Probing molecular chirality on a sub-femtosecond timescale* Nat. Phys. 2015

Ossiander et al. : *Attosecond correlation dynamics* Nat. Phys. 2016

E. Goulielmakis et al. : *Real-time observation of valence electron motion* Nat. Phys. 2010

and many many other :) !

Theory for optical spectroscopy

Two families of methods to describe these process :

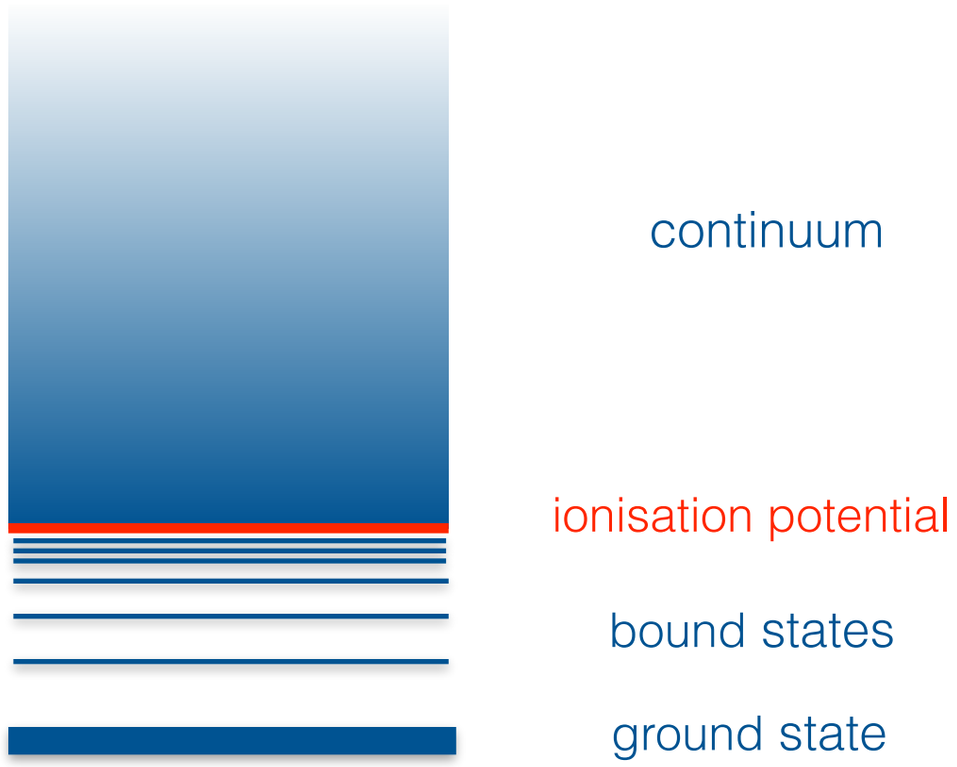
- **time-dependent wave function methods**

- **time-dependent density-functional theory (TDDFT)**

developments have been focused on the accurate description of
electron correlation

Theory for optical spectroscopy

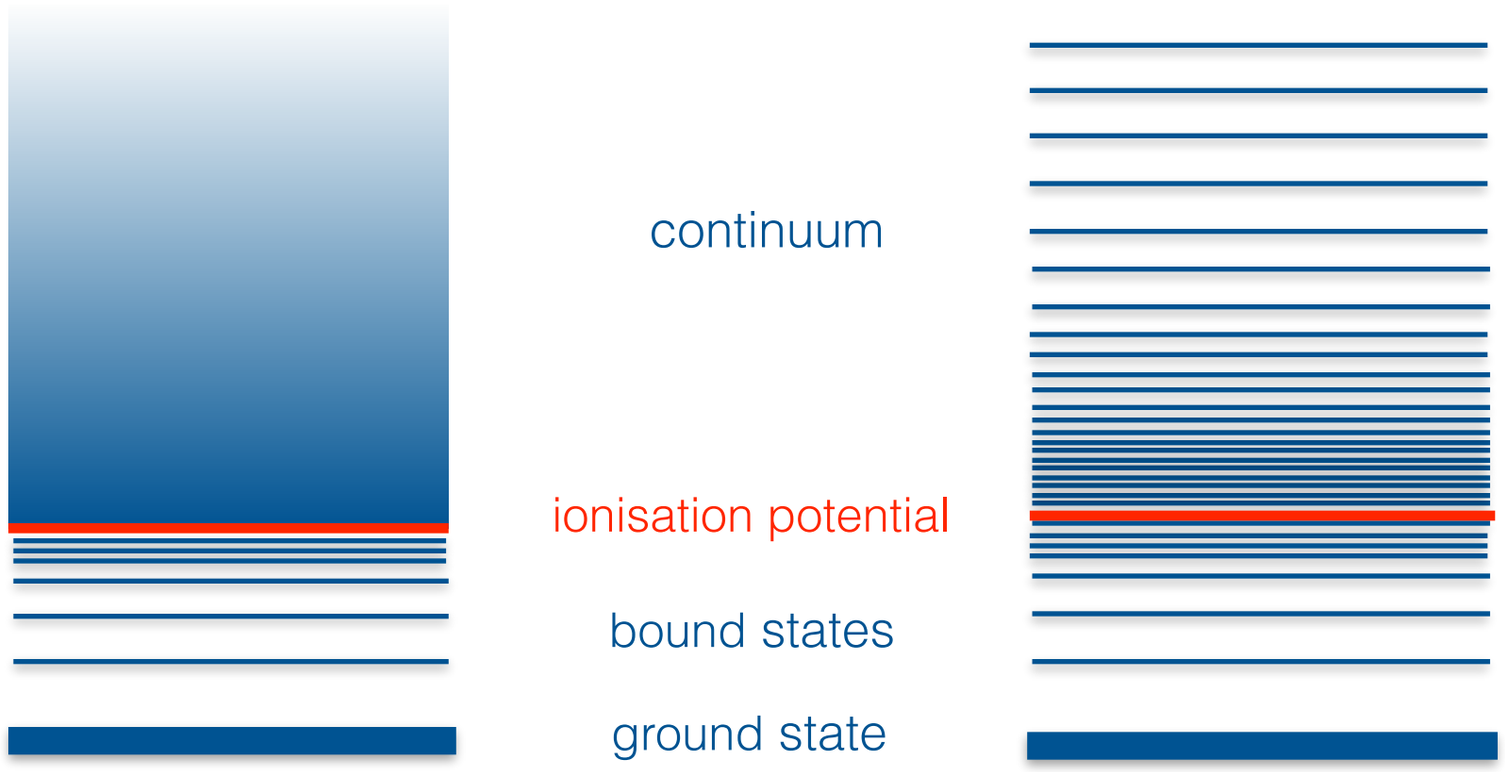
However, before correlation
another important aspect needs to be carefully addressed:
the continuum



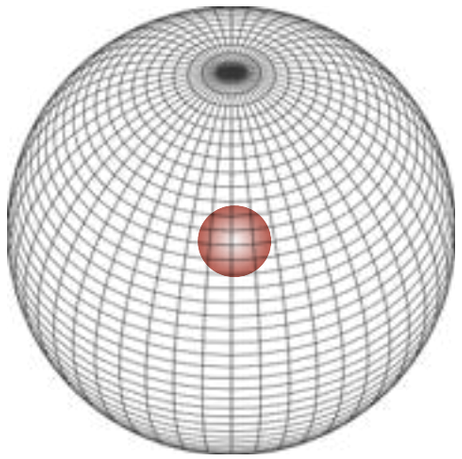
Theory for optical spectroscopy

However, before correlation
another important aspect needs to be carefully addressed:
the continuum

The choice of the one-electron basis for representing the time-dependent wave function :
Gaussians, Grid, B-splines …



Numerical grid



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

Computational cost can be very high and strategies involving multi-level parallelization schemes are developed

Kulander et al. PRA (1989)

De Giovannini et al. PRA (2012)

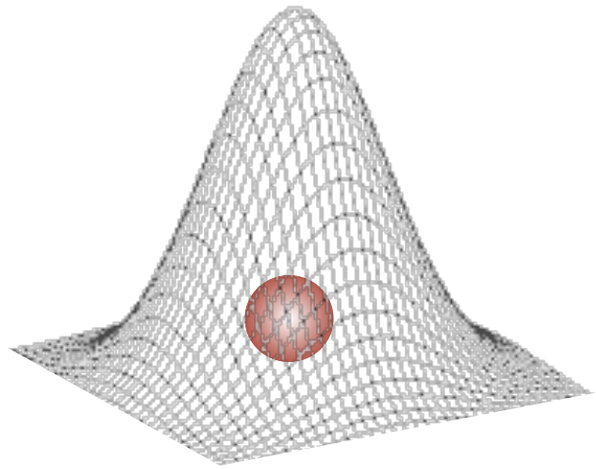
Chu et al. PRA (2012)

Guliemakis et al. Nature (2010)

Phuong Mai Dinh et al. EPJB (2018)

many others …

Gaussian basis sets



Gaussians describe **poorly** the continuum

Different strategies to **improve Gaussians** for the continuum exists !

Luppi and Head-Gordon JCP (2018)

White et al. MP (2016)

Labeye, Zapata et al. JCTC (2018)

Thanks :)

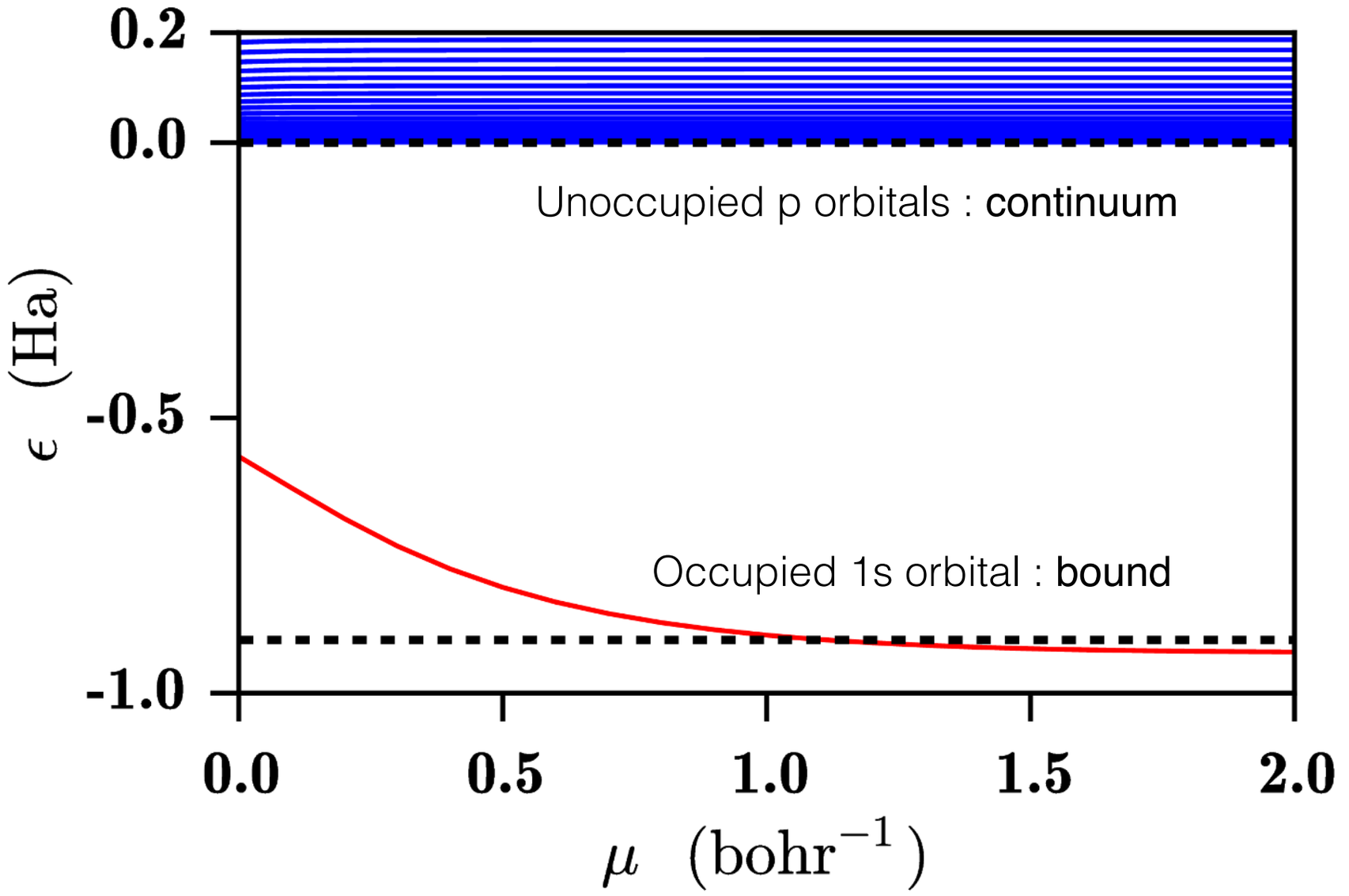
Dr. Emanuele COCCIA
Dr. Julien TOULOUSE
Dr. Bastien Mussard
Dr. Roland Assaraf
Felipe Zapata
Laboratoire de Chimie Théorique France

Dr. Jérémie CAILLAT
Dr. Richard TAIEB
Dr. Marie Labeye
Laboratoire de Chimie Physique Matière et Rayonnement

Dr. Valerie VENIARD
Ecole Polytechnique France

Prof. Martin Head-Gordon
Alec White
University of Berkeley California USA

RSH orbital energies : He atom

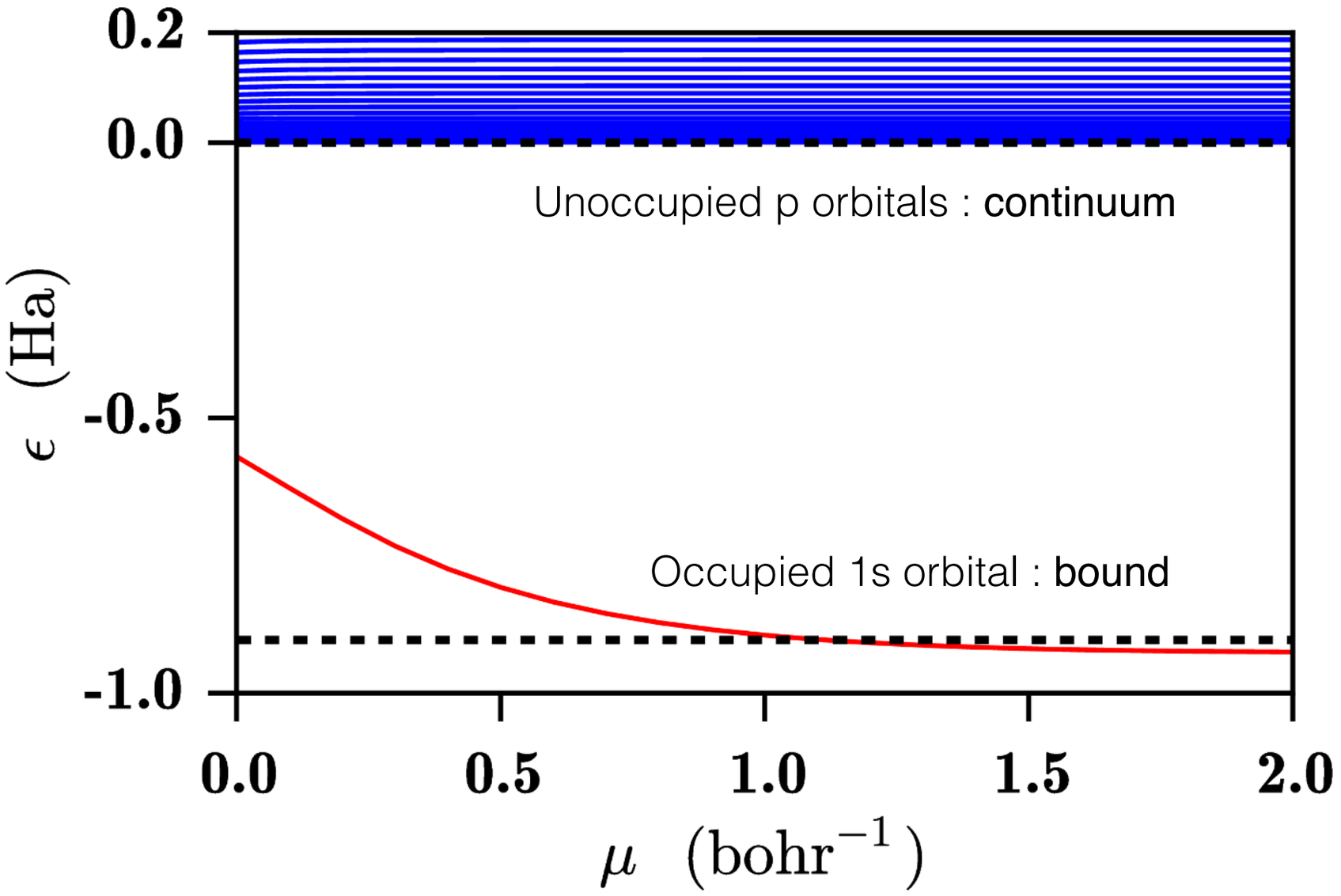


red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

RSH orbital energies : He atom



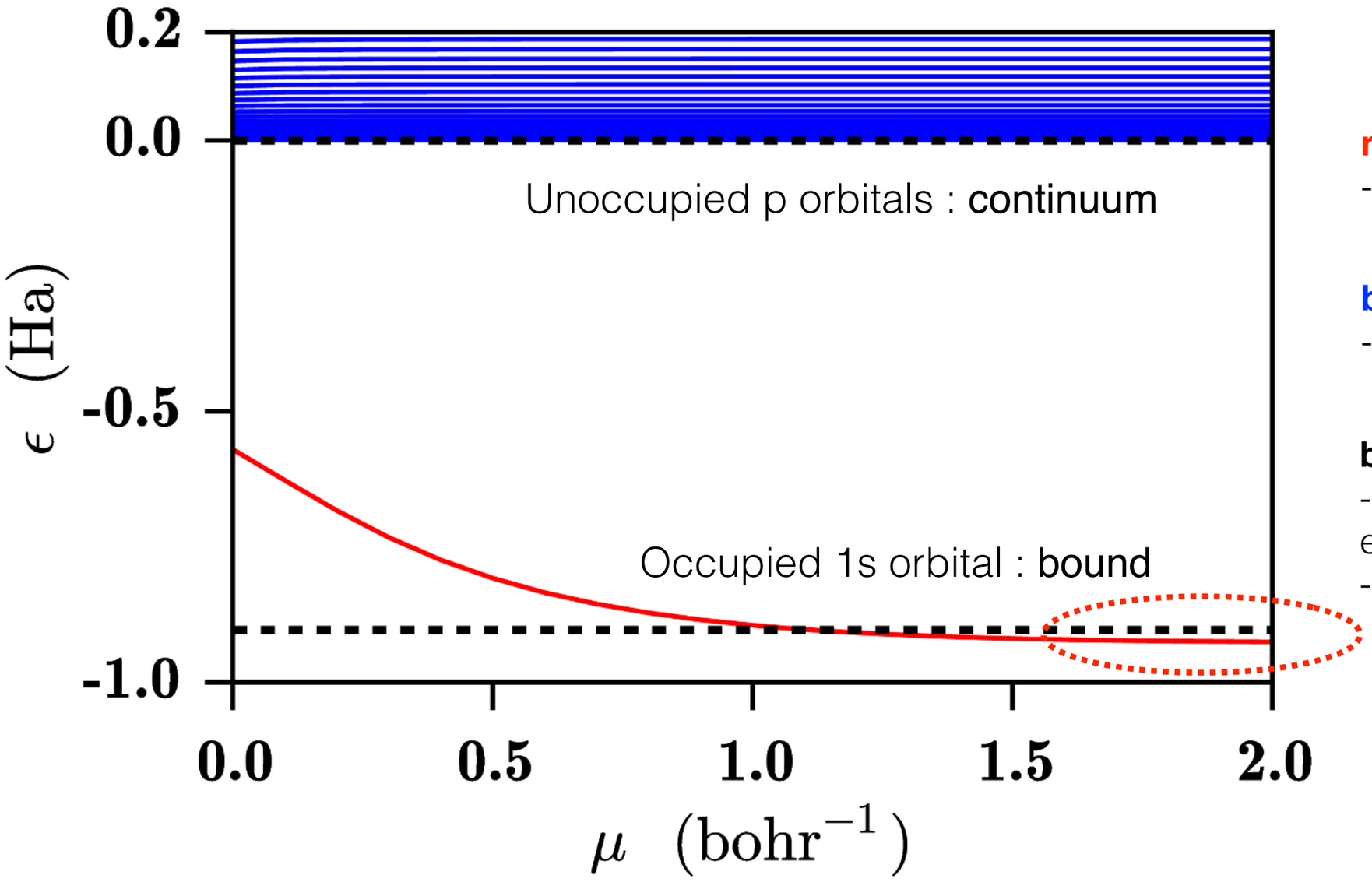
red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

$\mu = 0$ 1s energy is too high : LDA self-interaction error

RSH orbital energies : He atom



red :
-1s ground state

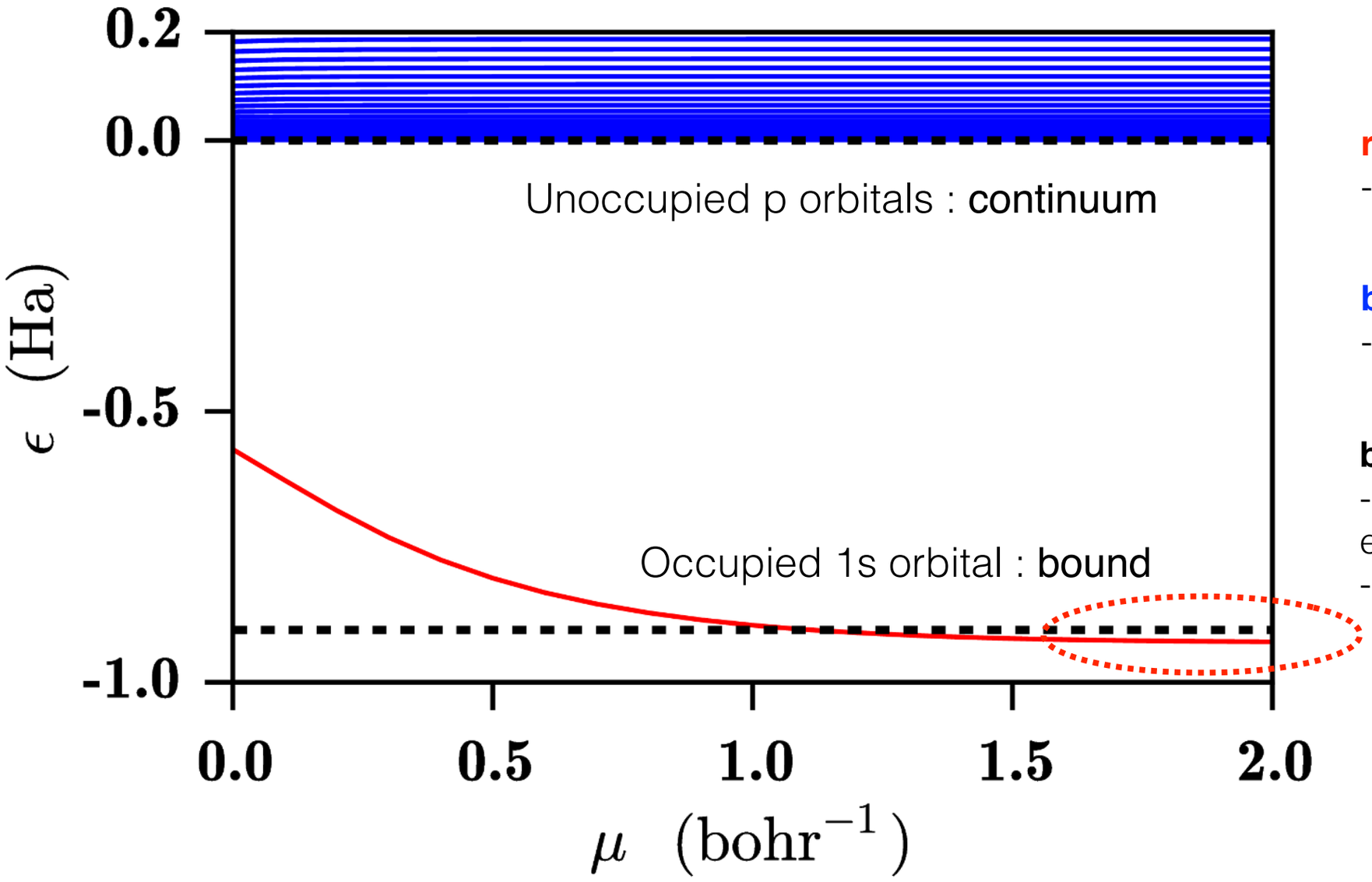
blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

$\mu = 0$ 1s orbital energy is too high : LDA self-interaction error

$\mu = \infty$ 1s orbital energy converges to HF : not equal to the opposite of the exact ionisation energy but too low due to missing correlation effects

RSH orbital energies : He atom



red :
-1s ground state

blue :
-p excited states

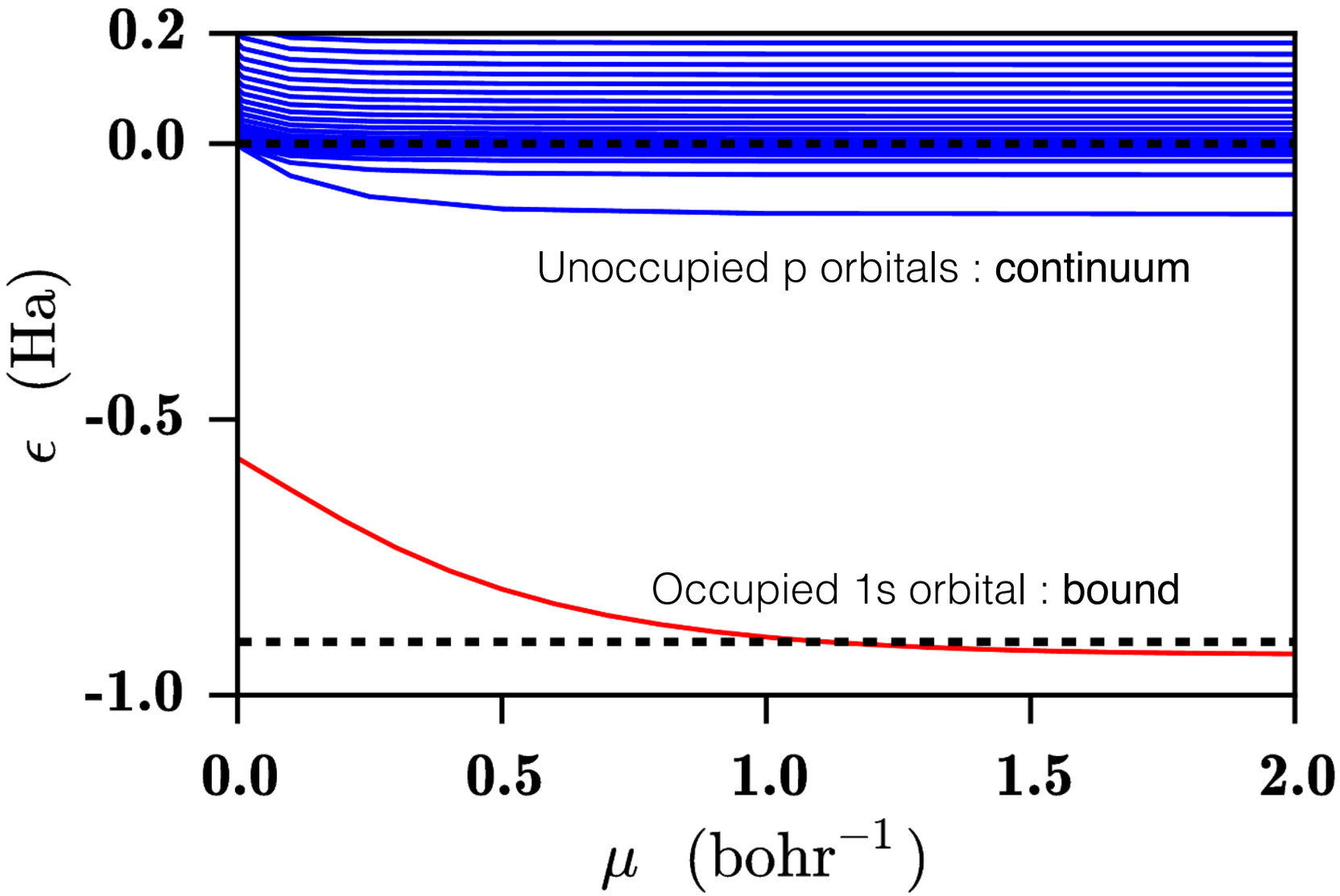
black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

$\mu = 0$ 1s orbital energy is too high : LDA self-interaction error

$\mu = \infty$ 1s orbital energy converges to HF : not equal to the opposite of the exact ionisation energy but too low due to missing correlation effects

p orbitals (and all the other unoccupied orbitals) are unbound : insensible to μ

RSH-EXX orbital energies : He atom

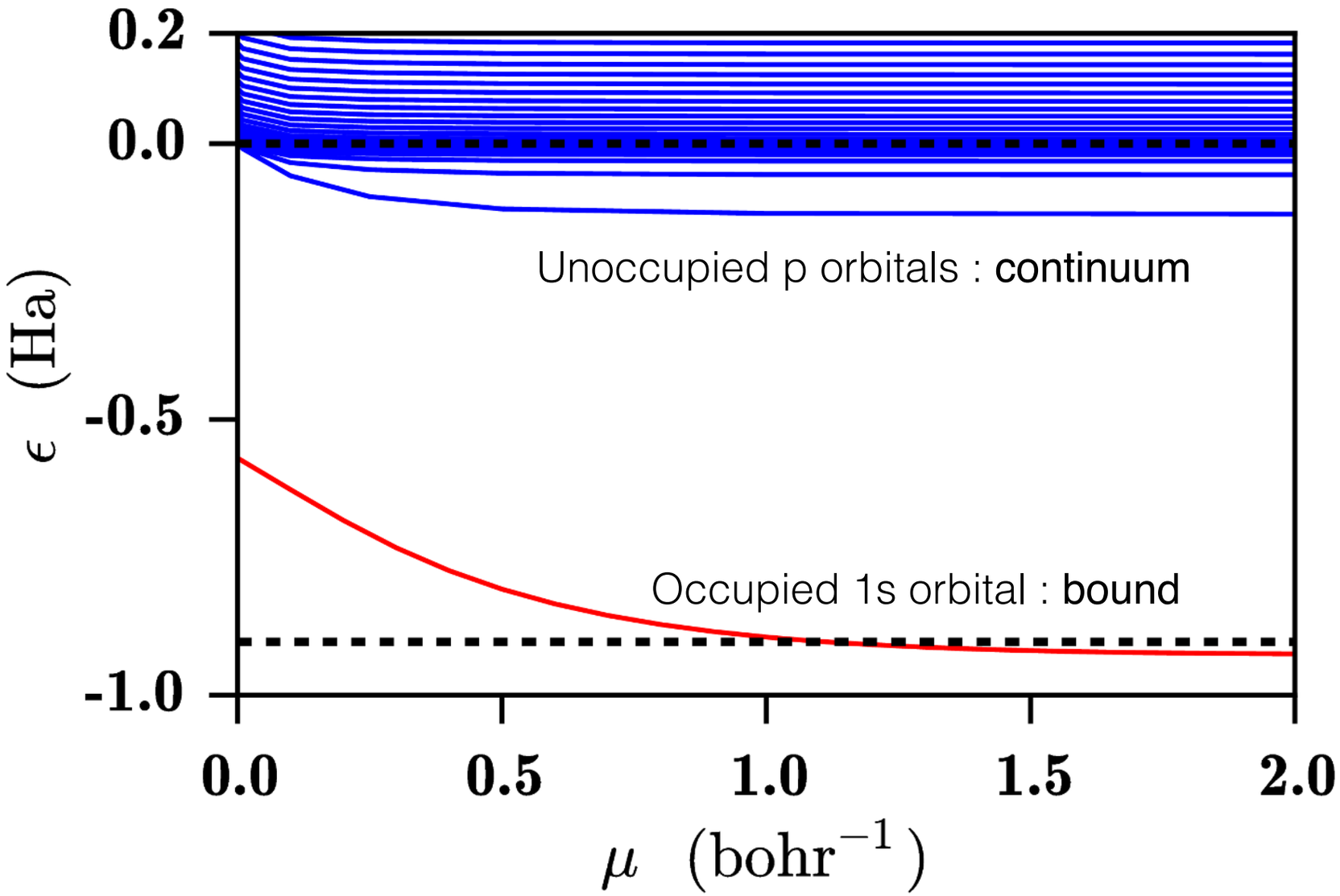


red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

RSH-EXX orbital energies : He atom



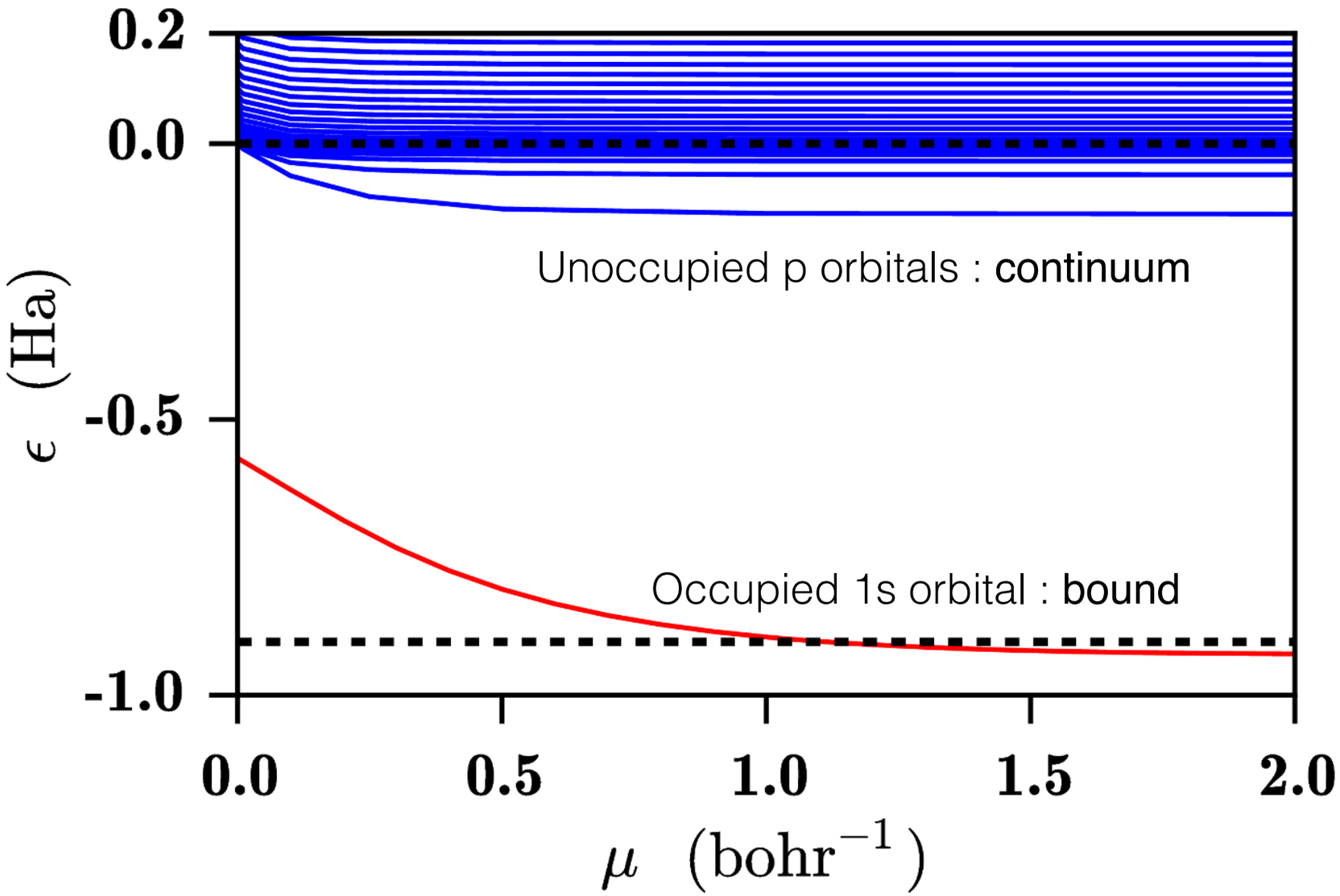
red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

1s RSH-EXX orbital energy is identical to the 1s RSH orbital energy

RSH-EXX orbital energies : He atom



red :
-1s ground state

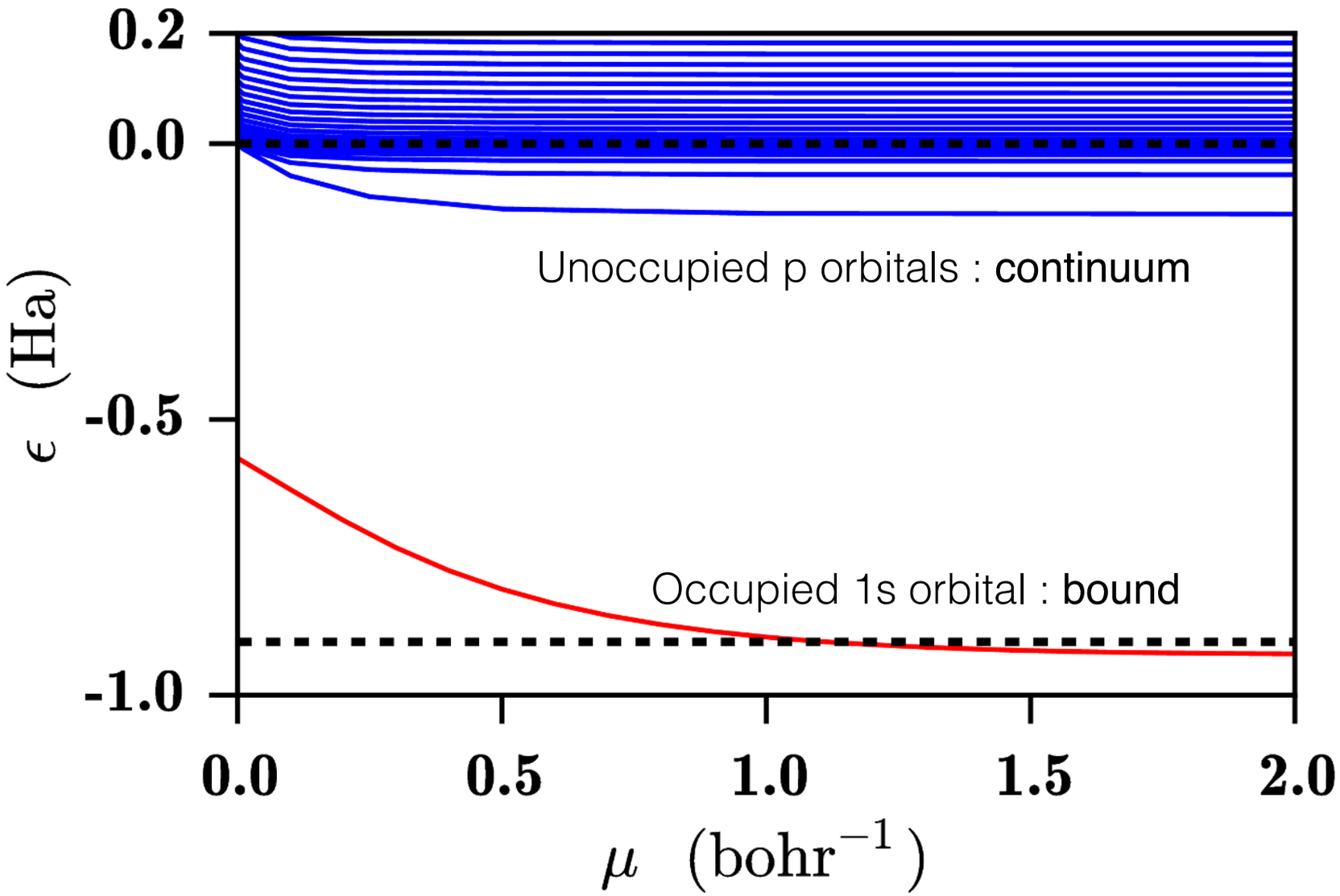
blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

1s RSH-EXX orbital energy is identical to the 1s RSH orbital energy

$\mu > 0$ bound Rydberg states from continuum (differently affected by self-interaction error)

RSH-EXX orbital energies : He atom



red :
-1s ground state

blue :
-p excited states

black :
- opposite of the exact ionisation energy (Umrigar (Springer 1998))
- ionisation limit

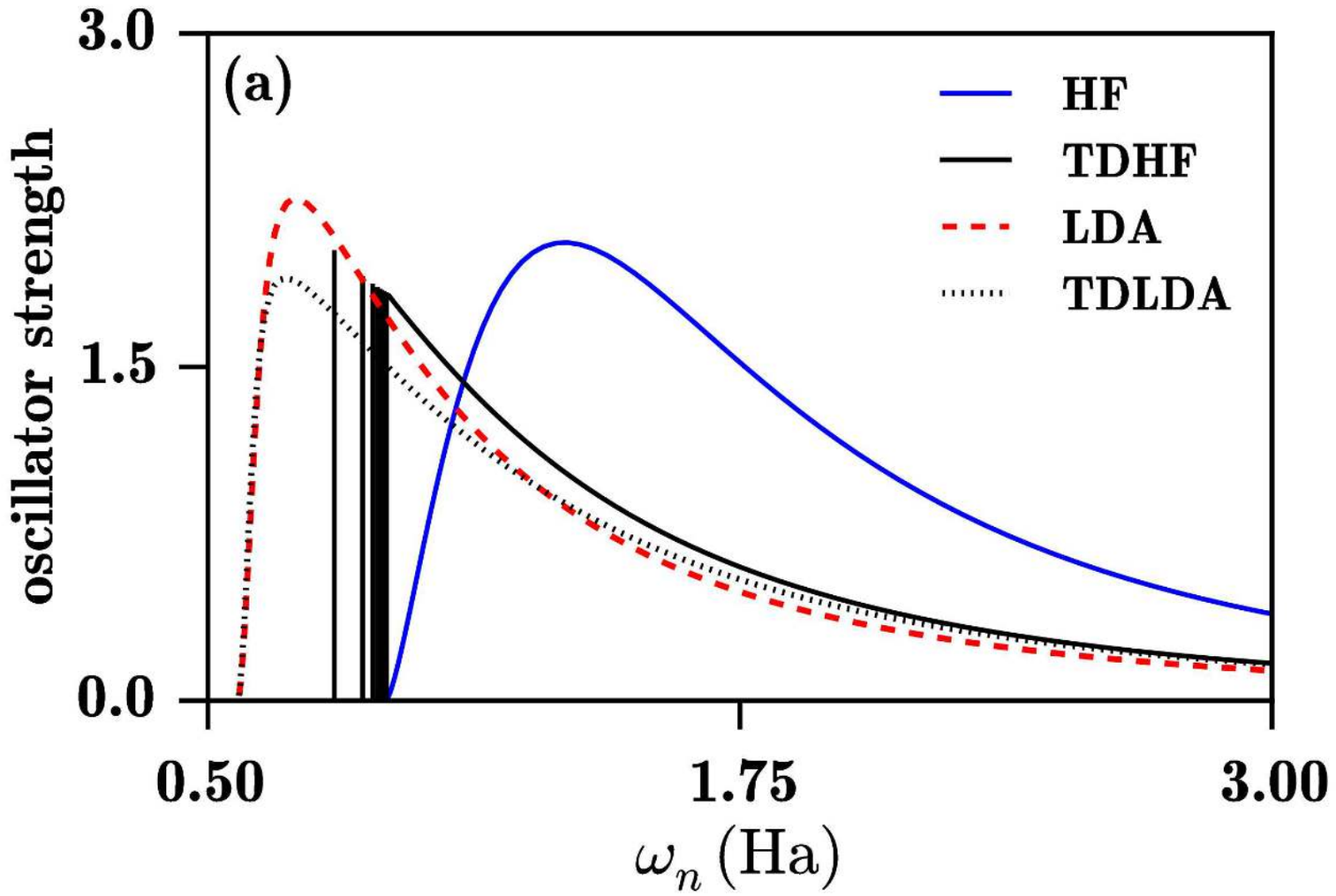
1s RSH-EXX orbital energy is identical to the 1s RSH orbital energy

$\mu > 0$ bound Rydberg states from continuum (differently affected by self-interaction error)

$\mu = \infty$ bound Rydberg states converging to KS-EXX energies ~ KS exact (Umrigar (Springer 1998))

no effect of correlation

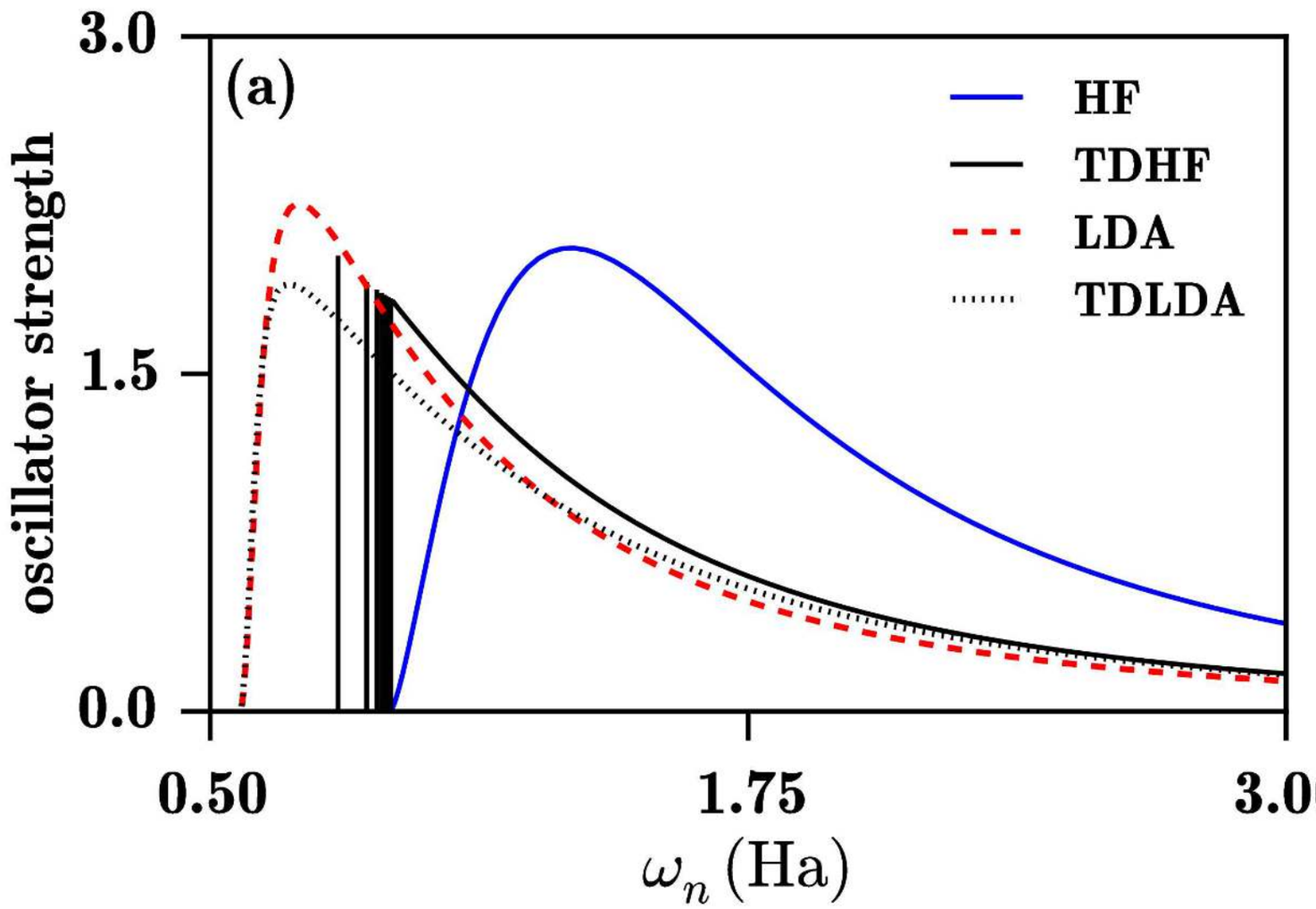
Photoexcitation and photoionization spectra : He atom



Lyman series (1s → np)

TDHF : - reasonable photoexcitation/photoionization spectrum

Photoexcitation and photoionization spectra : He atom

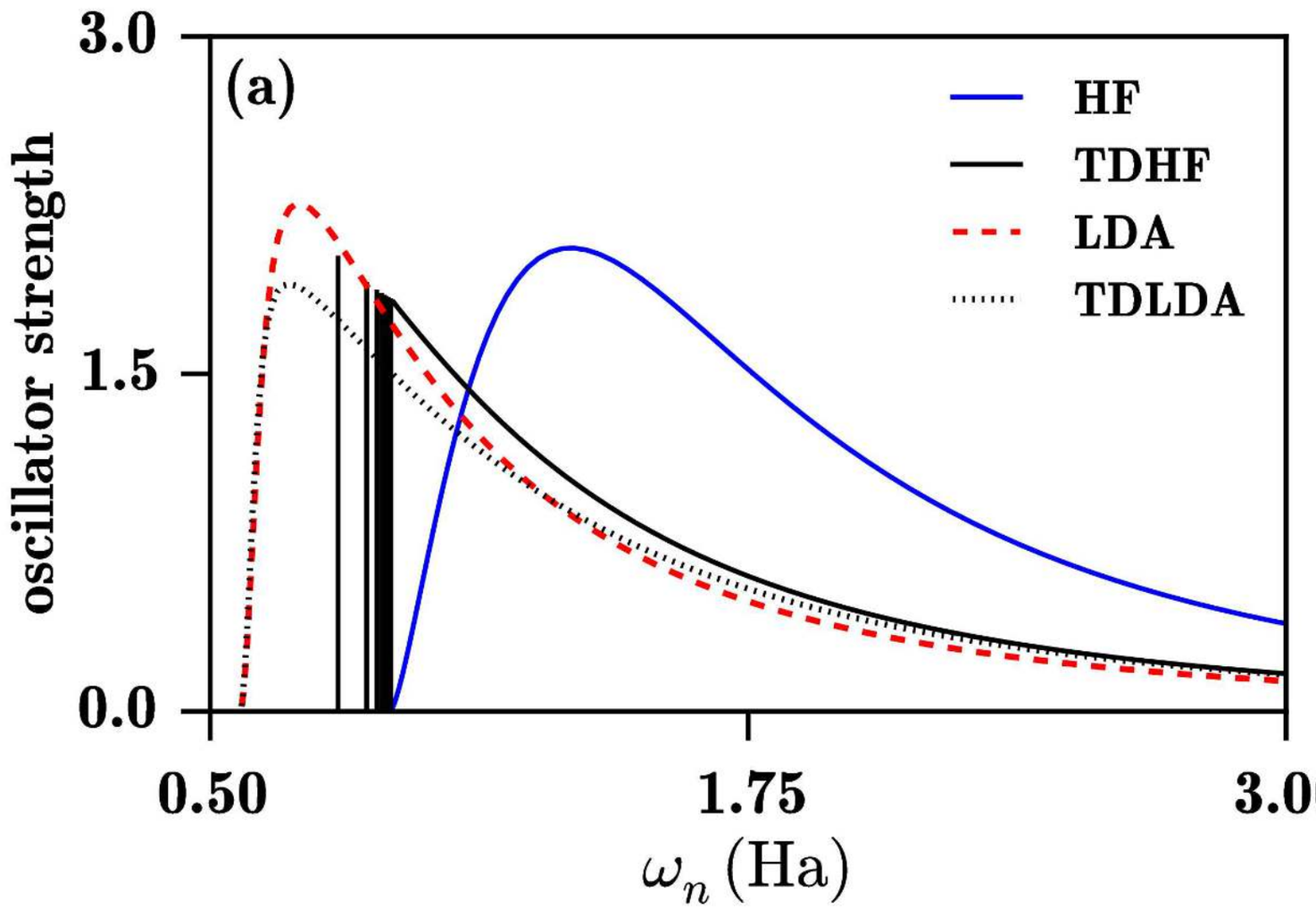


Lyman series (1s → np)

TDHF : - reasonable photoexcitation/photoionization spectrum

LDA : - no discrete photoexcitation energies
- ionization threshold too low (the self-interaction error)
- continuum oscillator strengths : good approximations to exact discrete oscillator strengths
- asymptotically exact in the high energy limit

Photoexcitation and photoionization spectra : He atom



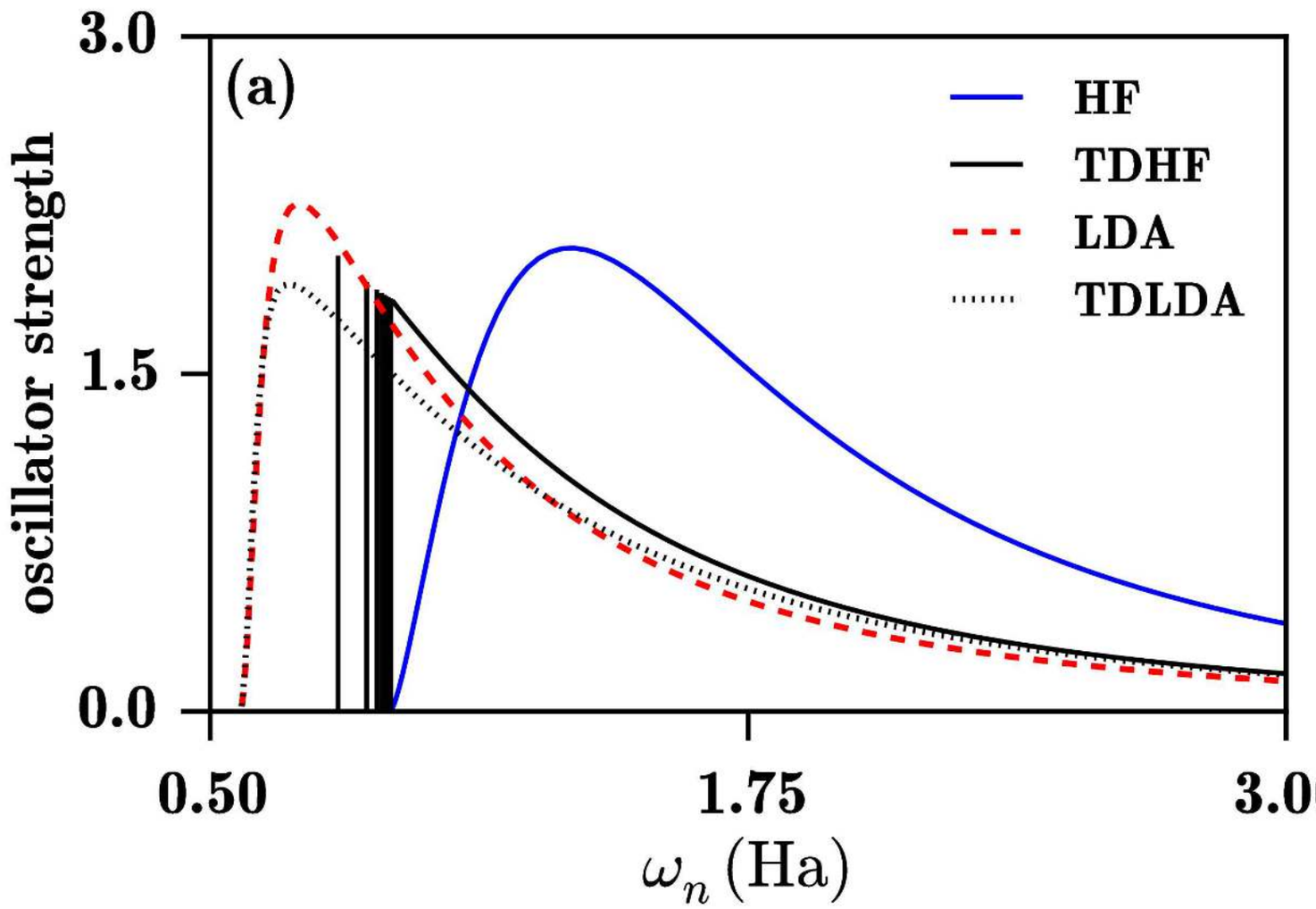
Lyman series (1s → np)

TDHF : - reasonable photoexcitation/photoionization spectrum

LDA : - no discrete photoexcitation energies
- ionization threshold too low (the self-interaction error)
- continuum oscillator strengths : good approximations to exact discrete oscillator strengths
- asymptotically exact in the high energy limit

TDLDA : ~ **LDA**

Photoexcitation and photoionization spectra : He atom



Lyman series (1s → np)

TDHF : - reasonable photoexcitation/photoionization spectrum

LDA : - no discrete photoexcitation energies
- ionization threshold too low (the self-interaction error)
- continuum oscillator strengths : good approximations to exact discrete oscillator strengths
- asymptotically exact in the high energy limit

TDLDA : ~ **LDA**

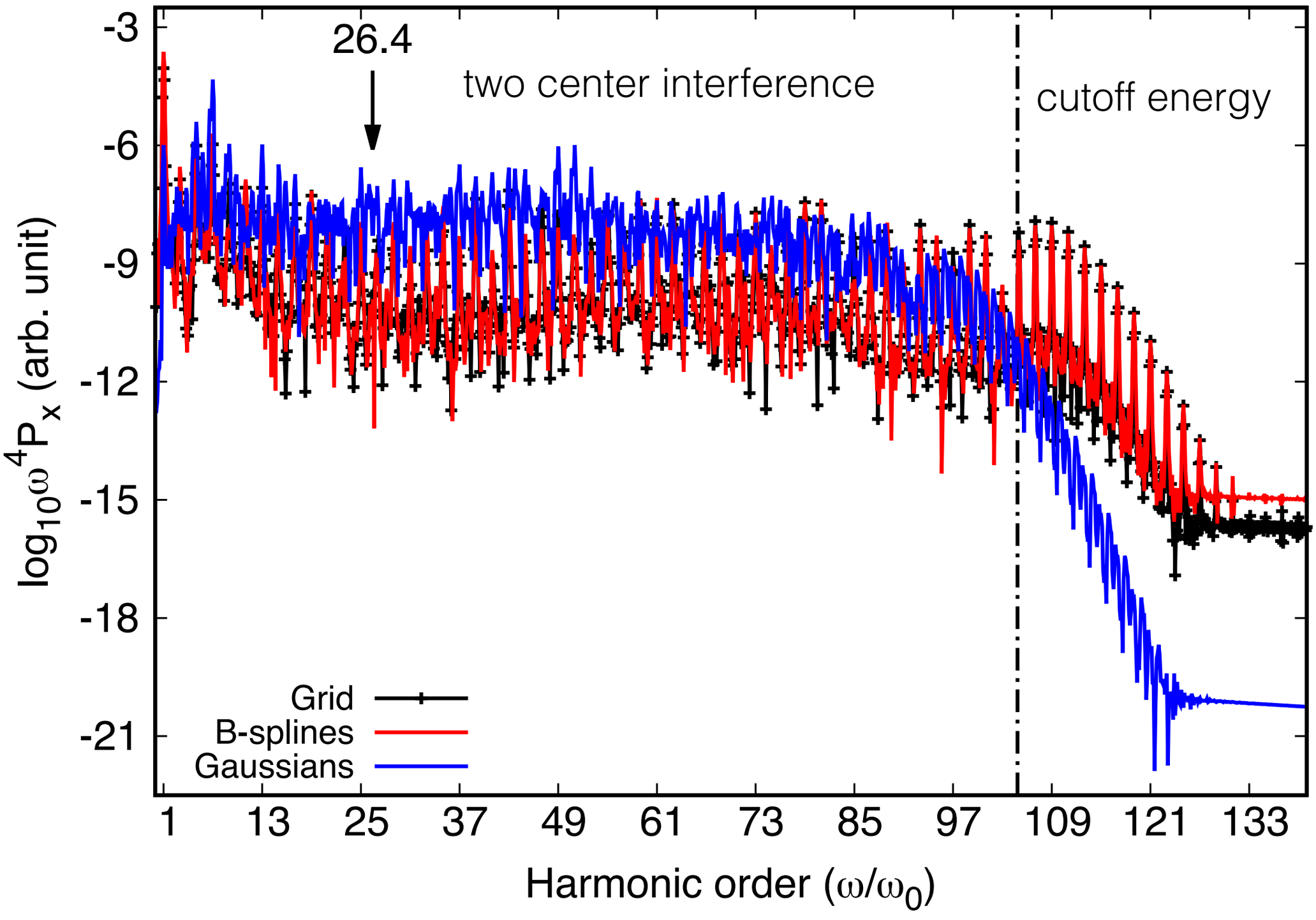
HF : - no discrete photoexcitation
- photodetachment spectrum of the H^- anion

HHG

Gaussians Grid B-splines

H_2^+

$I = 7 \times 10^{14}\, W/cm^2$



Real-time propagation

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

$$\mathbf{E}(t) = E_0\mathbf{n}_z \sin(\omega_0 t + \phi) f(t)$$

amplitude polarisation cos^2 enveloppe

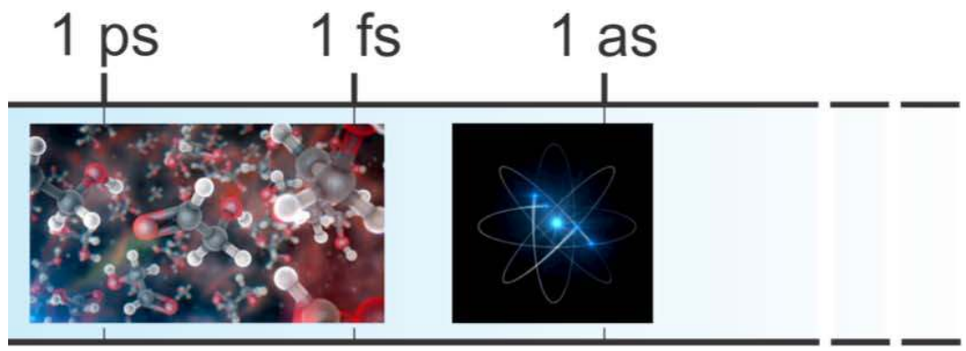
HHG

$$P_{\mu_x}(\omega) = \left| \int_0^\tau \langle\Psi(t)|\mu_x|\Psi(t)\rangle W(t) e^{-i\omega t} dt \right|^2$$

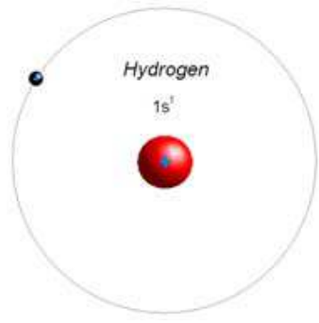
Labeye, Zapata et al. JCTC (2018)

Attosecond Science

ımics at its natural timescale



- Hydrogen:
  - Orbital period of e^- in ground state of Bohr atom: ~150 as



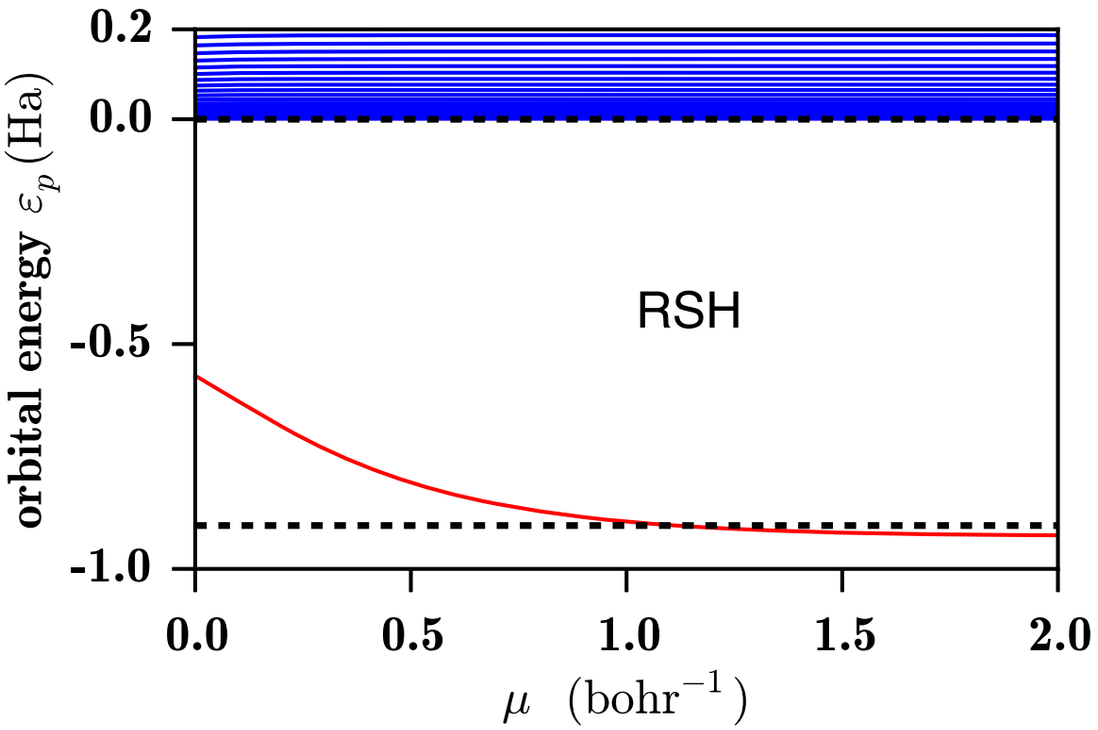
1 femtosecond = 1 fs = 10^{-15} s

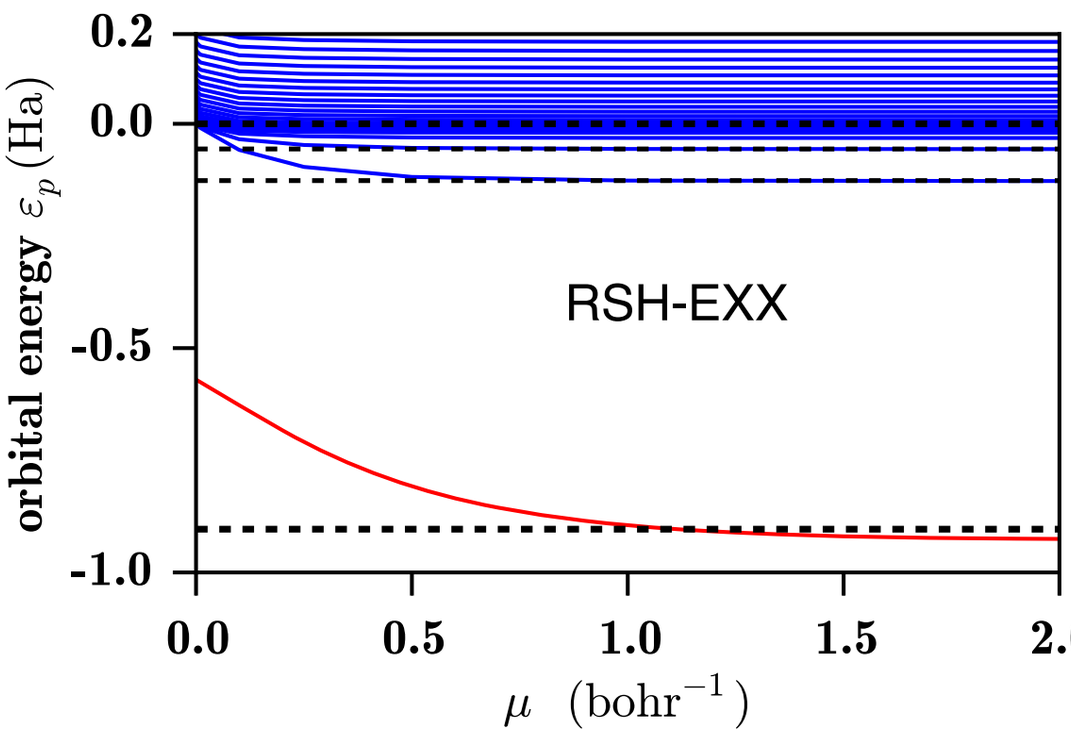
- Hydrogen molecule:
  - Vibrational period: ~8 fs

1 attosecond = 1 as = 10^{-18} s

- Attosecond dynamics are the dynamics of the electrons
  - Fastest charge transfer
  - Fastest energy transfer

B-splines and (linear response) range-separated DFT





red :
-1s ground state
blue :
-p excited states
black :
- opposite of the exact ionisation energy
- ionisation limit

$$\mu = 0$$

1s energy is too high : LDA self-interaction error

$$\mu = \infty$$

1s energy converges to HF :
not equal to the opposite of the exact ionisation energy
(missing correlation effects)

bound Rydberg states converging to KS-EXX energies ~ KS exact (Umrigar (1998))

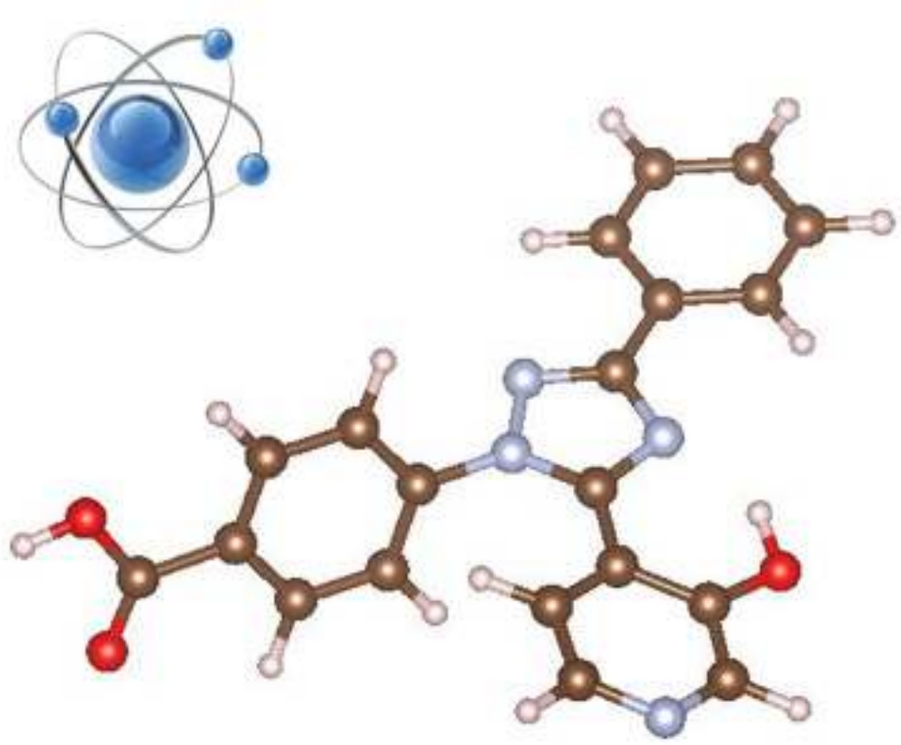
$$\mu > 0$$

p orbitals (and all unoccupied orbitals) are unbound

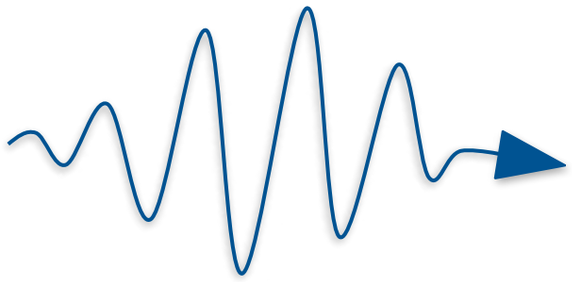
bound Rydberg states from continuum
(differently affected by self-interaction error)

Optical spectroscopy of atoms and molecules

(weak/strong)
electric field



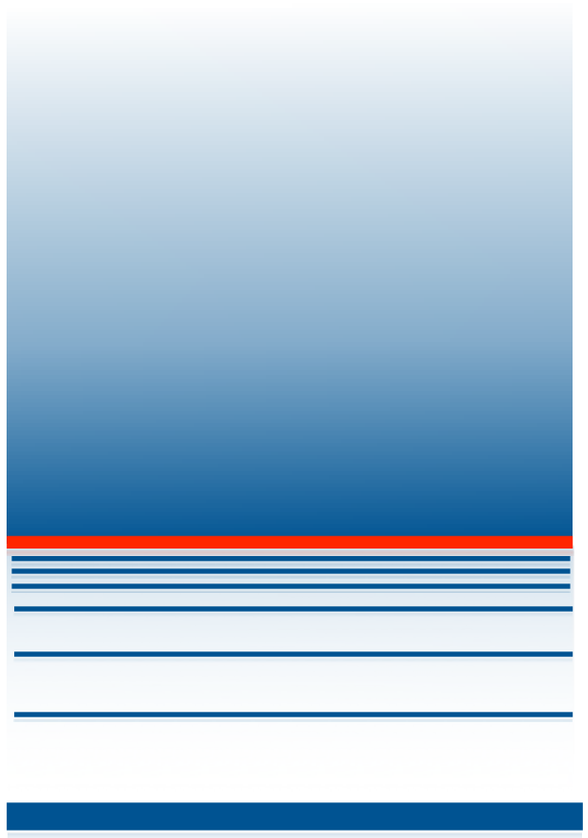
optical response



Many interesting optical phenomena are observed in weak and strong field :

absorption
single-photon ionisation
second-harmonic generation
high-harmonic generation
above-threshold ionisation
…

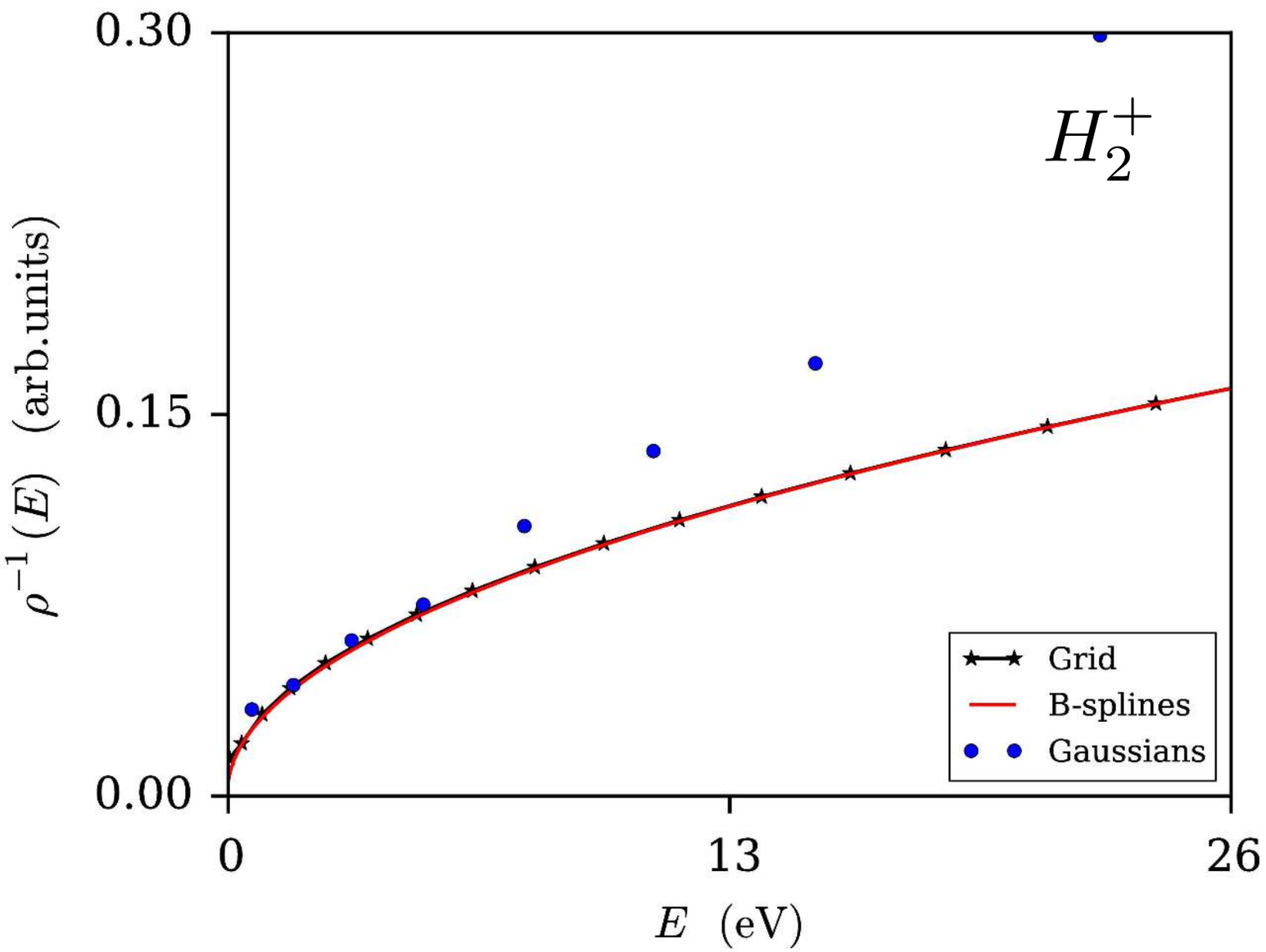
The description of the continuum scattering states can be much improved



ground state

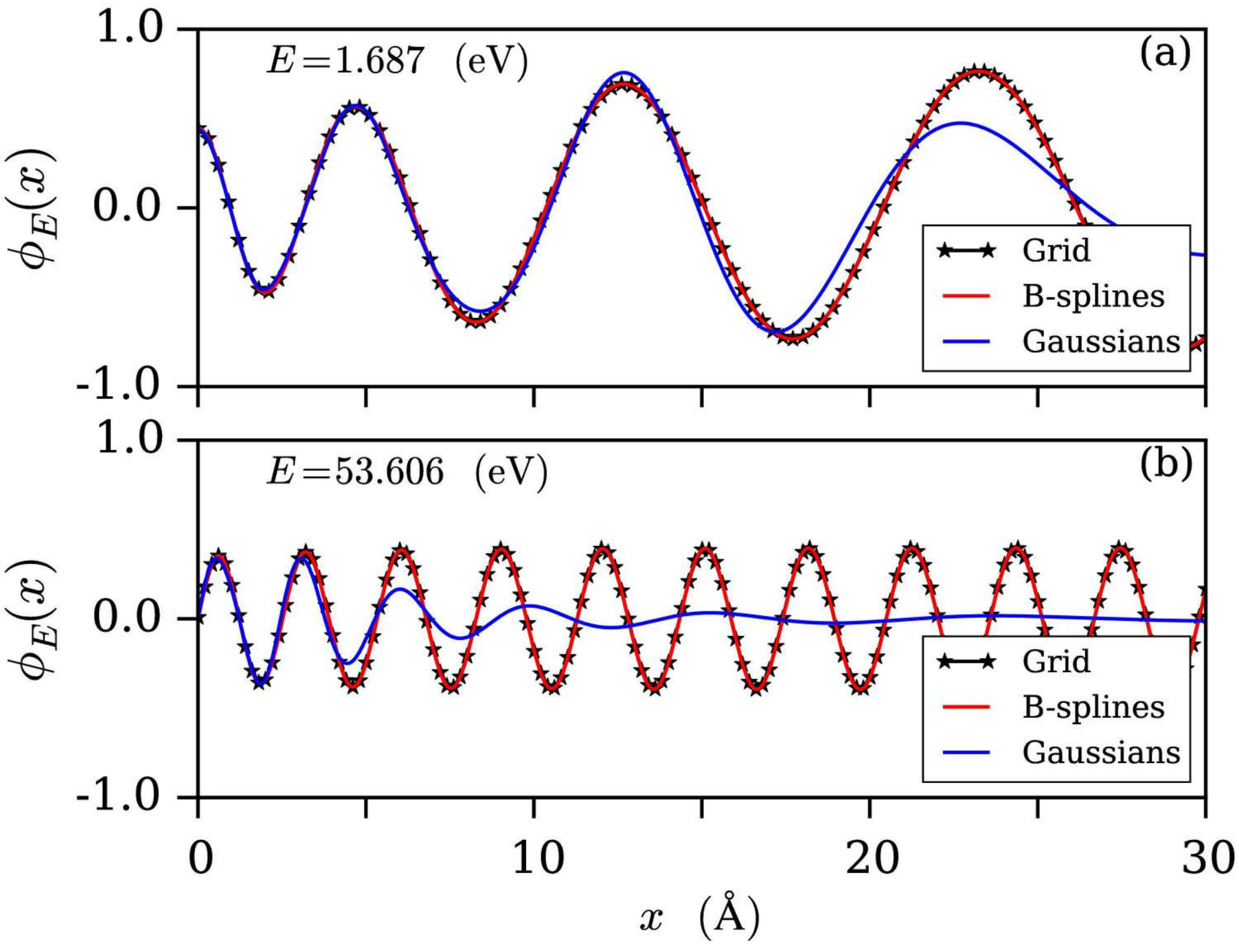
Performance of optimal Gaussian vs Grid and B-splines

Inverse of the density of the continuum states (from the spectrum field free Hamiltonian)



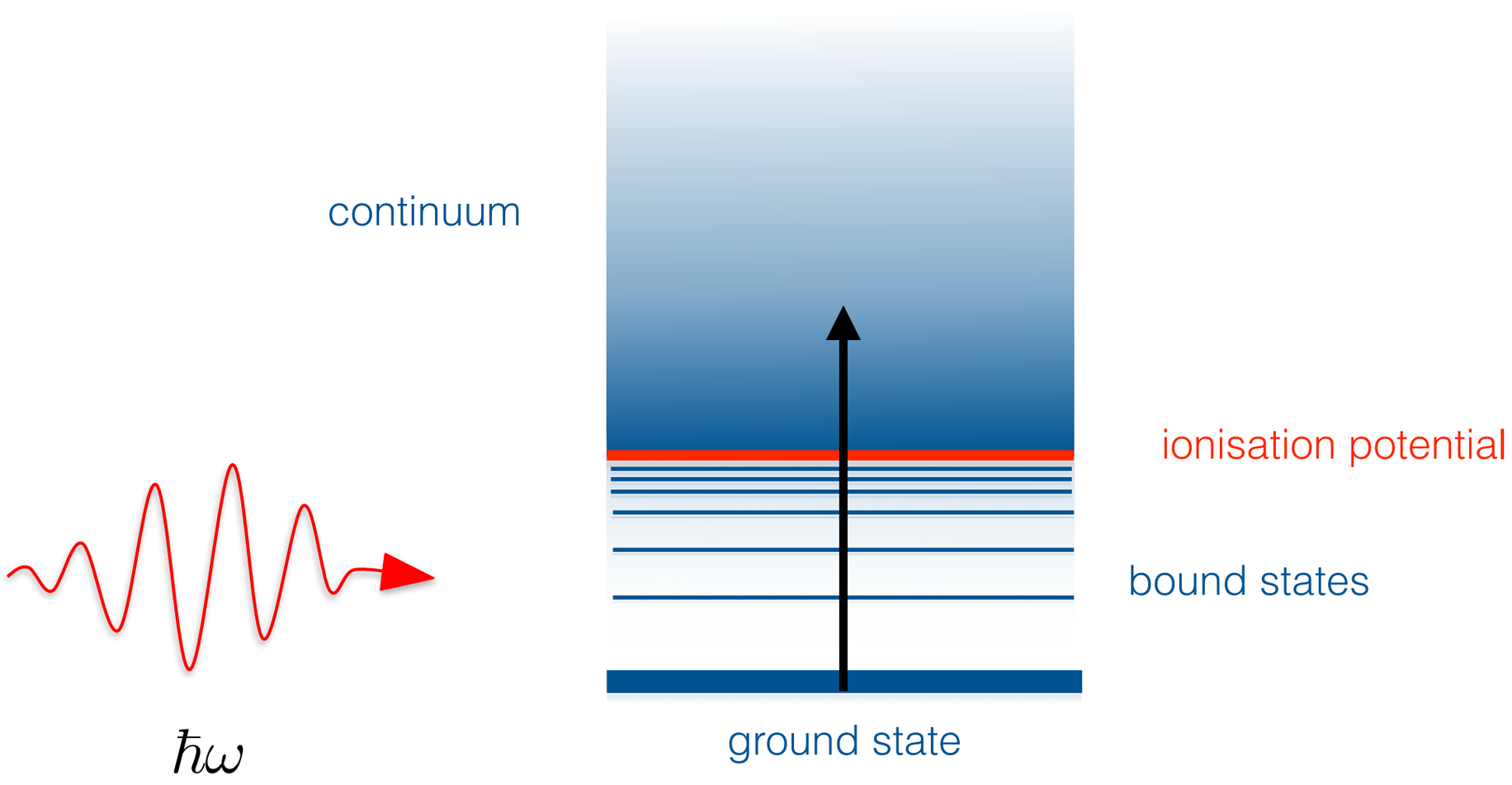
Performance of optimal Gaussian vs Grid and B-splines

Continuum wavefunction (from the spectrum field free Hamiltonian)



New development in B-splines of linear-response range-separated density-functional theory

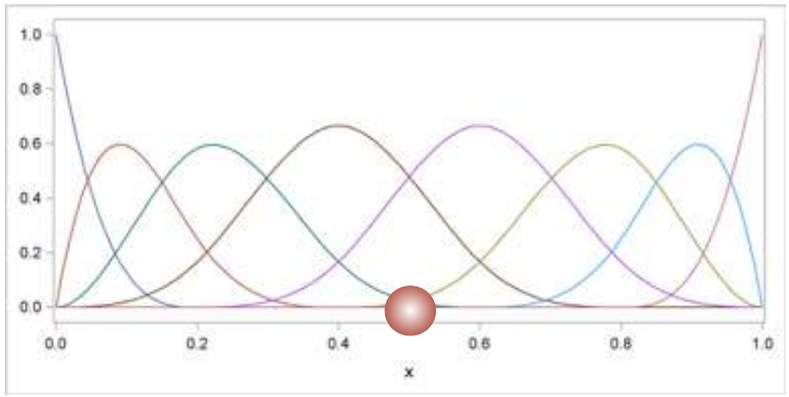
applied to single-photon ionisation



* measure of the photoelectrons

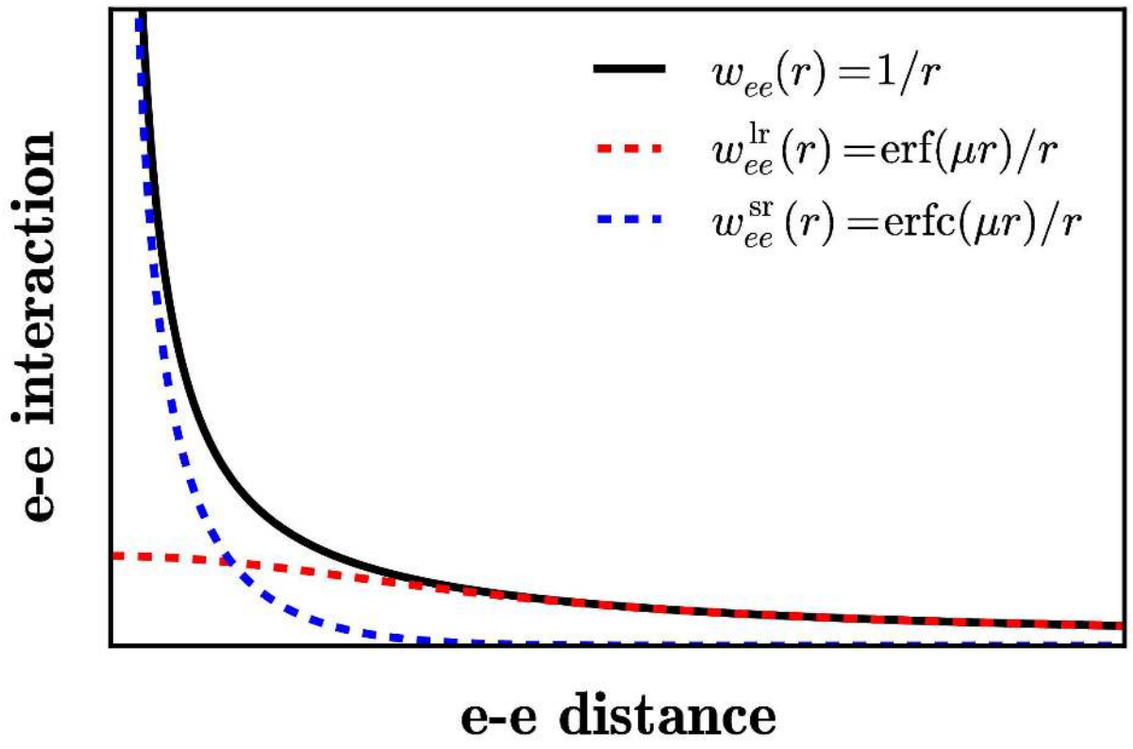
* measure of the ionised atoms/molecules

B-splines and range-separated DFT



- B-splines basis set is a piecewise polynomial functions
- B-splines basis set is powerful to describe continuum for atoms and molecules
- New algorithms needs to be developed to fully exploits their potentials

Stener et al. JCP (2001), Bachau et al. RPP (2001), Fetic et al. PRE (2017) …

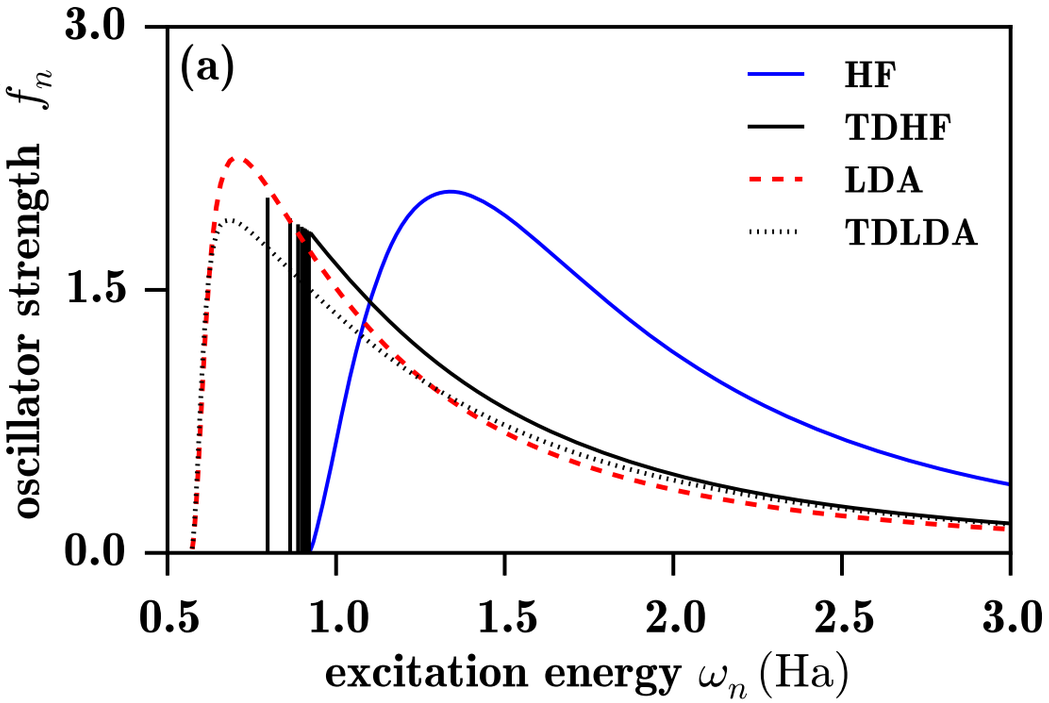


- Range-separated DFT is based on the splitting of the Coulomb electron-electron interaction
- Combination of a long-range wave-function approach with a complementary short-range DF approximation

Toulouse et al. JCP 2013, XXX

Photoexcitation and Photoionisation spectra

Lyman series (1s → np)

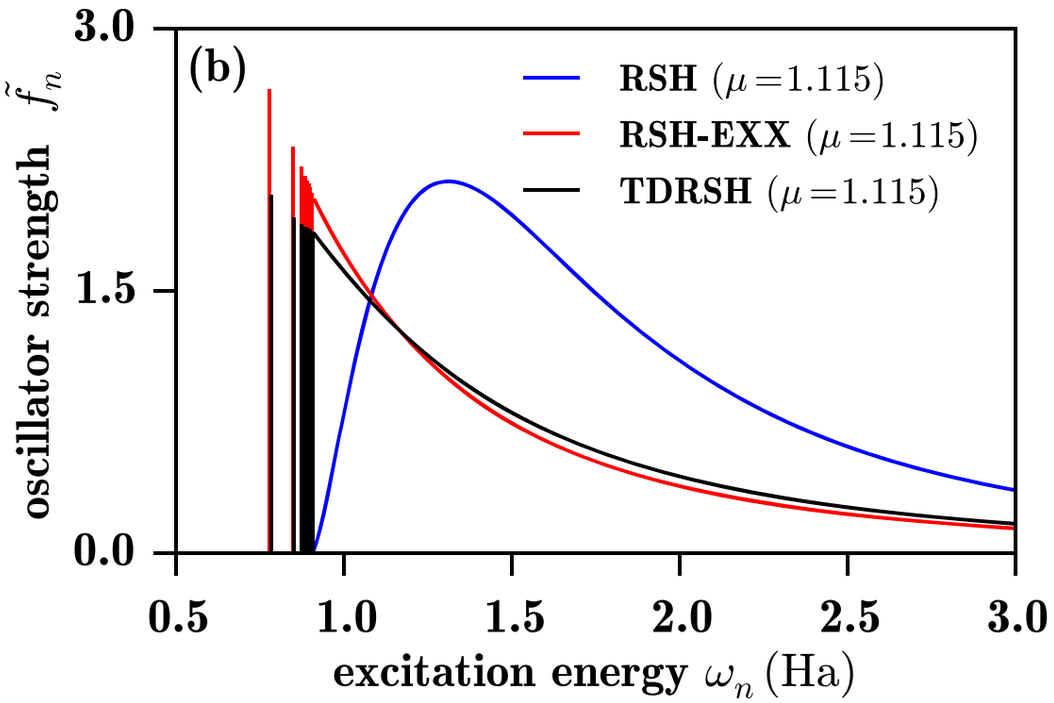


HF : no discrete photoexcitations (photodetachment H^-)

TDHF : reasonable photoexcitation/photoionization spectrum

LDA : no discrete photoexcitations
ionization too low (the self-interaction error)
continuum oscillator strengths : good approximations to exact discrete oscillator strengths
asymptotically exact in the high energy limit

TDLDA : ~ **LDA**



RSH : no discrete photoexcitations (photodetachment H^-)

RSH-EXX : reasonable photoexcitation/photoionization spectrum

* Only EXX local potential supports Rydberg states

TDRSH : ~ RSH-EXX

* Most accurate (from comparison with exact) : TDRSH > RSH-EXX