Tackling two aspects of basis-set incompleteness: Short-range correlation and continuum states

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The roots of basis-set incompleteness evil

- The space of one-electron states $\mathfrak{H} = L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\}, \mathbb{C})$ and the space of N-electron states $\mathcal{H} = \bigwedge^N \mathfrak{H}$ are **infinite-dimensional** Hilbert spaces.

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  - The Coulomb nuclei-electron potential is non-confining, leading to a continuous spectrum with "continuum states" (not belonging to the Hilbert space)

    $\Longrightarrow$ **Slow or impossible basis convergence of many properties depending on the continuum states**

Outline

1. Basis-set correction based on DFT for short-range correlation

2. TDDFT with Robin boundary conditions for continuum states

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with T. Anderson, R. Assaraf, A. Ferté, **E. Giner**, J. Li, P.-F. Loos,
B. Pradines, A. Savin, A. Scemama, D. Traore, C. Umrigar, Y. Yao

2. TDDFT with Robin boundary conditions for continuum states

Slow basis convergence of wave-function theory

- The **full-configuration interaction (FCI)** ground-state energy in a basis $\mathcal{B}$ is

$$E_{\mathrm{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Psi \rangle$$

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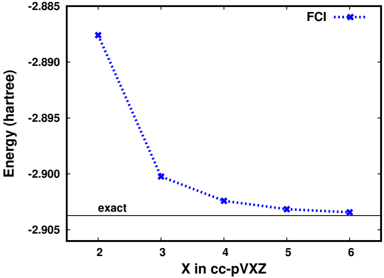
- Example of the He atom with the **series of basis sets** $\mathcal{B} =$ "cc-pVXZ":



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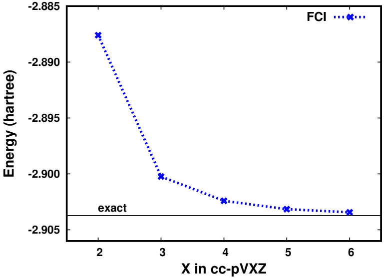

- Two main strategies to deal with short-range basis-set incompleteness error:
  - Extrapolation to the CBS limit: $E_{\text{FCI}}^{X} = E_{\text{FCI}}^{\text{CBS}} + c\, X^{-3}$
  - Explicitly correlated F12 methods (use a two-electron basis depending explicitly on the interelectronic distance)

Wave-function theory with DFT basis correction (1/2)

- In **standard DFT** (complete basis set), the **exact ground-state energy** is expressed as

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where $\mathcal{D}^{\text{CBS}} = \{\rho \mid \exists \Psi \in \mathcal{W}^{\text{CBS}} \text{ s.t. } \rho_\Psi = \rho\}$ is the set of N-representable densities, and $F[\rho]$ is the **Levy-Lieb universal density functional**

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- For an **incomplete basis set** $\mathcal{B}$, we can define an approximation to the ground-state energy by **restriction to densities representable in** $\mathcal{B}$

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- The restriction on densities representable in $\mathcal{B}$ is **much weaker** that the restriction on wave functions representable in $\mathcal{B}$, so we expect

$$E_{\text{FCI}}^{\mathcal{B}} \gg E_0^{\mathcal{B}} \gtrsim E_0$$

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018

Wave-function theory with DFT basis correction (2/2)

- We then **decompose the universal density functional** $F[\rho]$ as

$$F[\rho] = \min_{\substack{\Psi \in \mathcal{W}^{\mathcal{B}} \\ \Psi \to \rho}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle + \bar{E}^{\mathcal{B}}[\rho]$$

where $\bar{E}^{\mathcal{B}}[n]$ is a **complementary density functional correcting for the basis-set restriction on the wave function**.

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- We will consider a **non-self-consistent approximation** using the FCI wave function:

$$E_{\text{FCI+DFT}}^{\mathcal{B}} = \langle \Psi_{\text{FCI}}^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi_{\text{FCI}}^{\mathcal{B}} \rangle + \bar{E}^{\mathcal{B}}[\rho_{\Psi_{\text{FCI}}^{\mathcal{B}}}]$$

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- We can also add the DFT basis correction to any **approximate wave-function theory (WFT) method**:

$$E_{\text{WFT+DFT}}^{\mathcal{B}} = E_{\text{WFT}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[\rho_{\Psi_{\text{WFT}}^{\mathcal{B}}}]$$

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018

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Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018
Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

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with a local range-separation parameter $\mu^{\mathcal{B}}(\mathbf{r})$.

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- We can then recycle a **short-range PBE density functional** developed for this modified electron-electron interaction to build an approximate basis-correction functional

$$\bar{E}^{\mathcal{B}}_{\text{PBE}}[\rho] = \int e_{\text{c}}^{\text{srPBE}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \mu^{\mathcal{B}}(\mathbf{r}))\, d\mathbf{r}$$

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018
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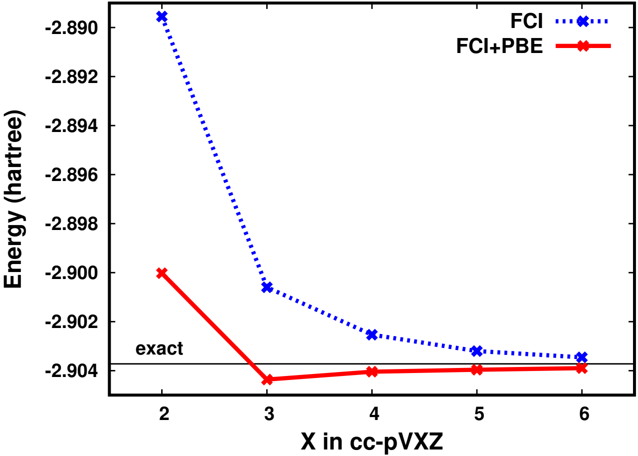
- **This approximate basis-correction functional contains the physics of the electron-electron cusp, automatically adapts to each basis set $\mathcal{B}$, and correctly vanishes in the CBS limit**

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018
Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

Convergence of the total energy with respect to the basis set

Example of the He atom with the **series of basis sets** $\mathcal{B} =$ "cc-pVXZ":



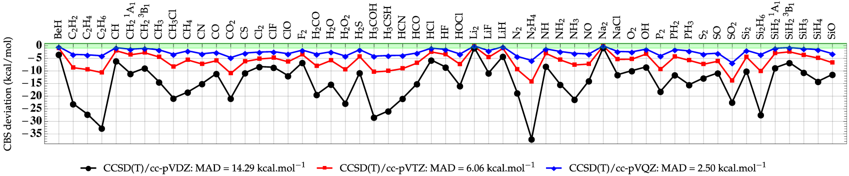
$\Longrightarrow$ **Much faster basis-set convergence without altering the CBS limit**

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018
Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

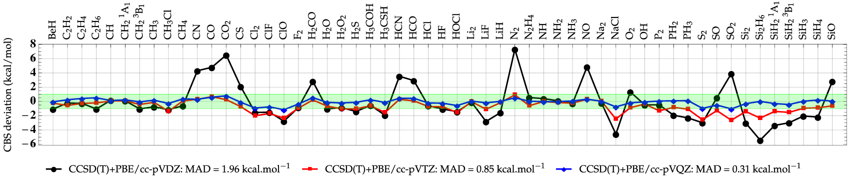
Tests on atomization energies

Basis-set convergence of **55 atomization energies** (G2 set) with cc-pV*X*Z basis sets:

CCSD(T):



CCSD(T)+PBE:



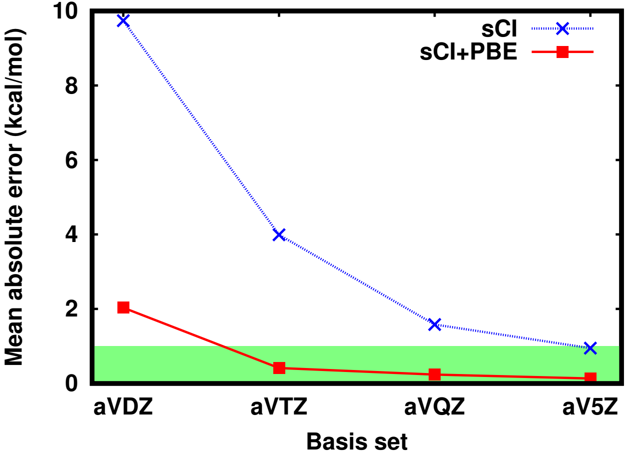
Mean absolute deviation with respect to CBS limit (in kcal/mol):

	VDZ	VTZ	VQZ
CCSD(T)	14.29	6.06	2.50
CCSD(T)+PBE	1.96	0.85	0.31

Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

Tests on dissociation energies of transition metal monoxides

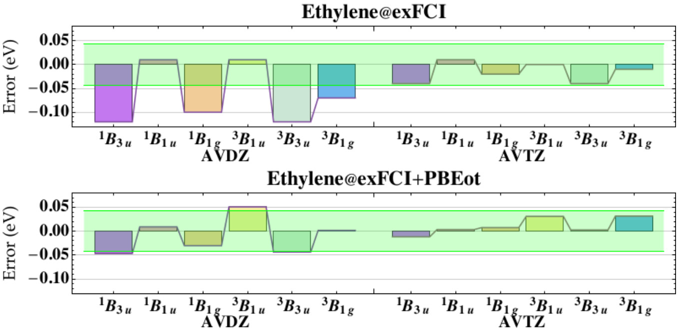
Dissociation energies of transition metal monoxides (ScO, TiO, VO, CrO, MnO, FeO, CuO) with selected CI calculations with aug-cc-pVXZ basis sets and pseudopotentials:



Yao, Giner, Anderson, Toulouse, Umrigar, JCP, 2021

Tests on excitation energies

Valence and Rydberg excitation energies of ethylene calculated by difference of total energies with aug-cc-pVXZ (AVXZ) basis sets (using a variant of the PBE basis correction functional depending on the on-top pair density):



$\Longrightarrow$ **FCI+PBEot reaches near "chemical accuracy" with AVDZ basis set**

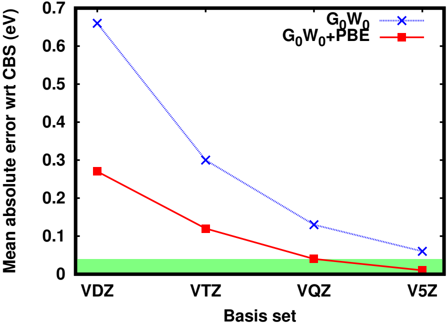
Giner, Scemama, Toulouse, Loos, JCP, 2019

Extension of the basis correction to many-body Green-function theory

- **Extension to many-body Green-function theory for GW calculations:**

$$E_0^{\mathcal{B}} = \underset{G^{\mathcal{B}}}{\text{stat}} \left\{ \Omega^{\mathcal{B}}[G^{\mathcal{B}}] + \bar{E}^{\mathcal{B}}[n_{G^{\mathcal{B}}}] \right\} \Longrightarrow (G^{\mathcal{B}})^{-1} = (G_0^{\mathcal{B}})^{-1} - \Sigma_{\text{Hxc}}^{\mathcal{B}}[G^{\mathcal{B}}] - V^{\mathcal{B}}[n_{G^{\mathcal{B}}}]$$

- Example of the **calculation of the IP of 20 molecules** by the G_0W_0 method:



$\Longrightarrow$ **The basis correction also accelerates the convergence of G_0W_0**

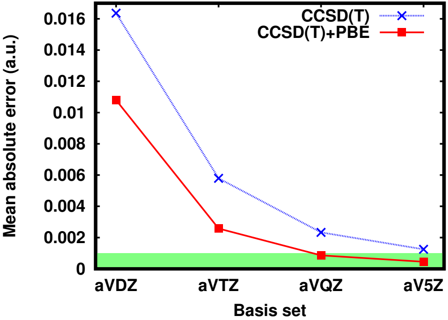
Loos, Pradines, Scemama, Giner, Toulouse, JCTC, 2020

Dipole moments

- Calculation of the **dipole moment** by response to an electric field $\mathcal{E}$:

$$E_0^{\mathcal{B}}(\mathcal{E}) = E_{\mathrm{WFT}}^{\mathcal{B}}(\mathcal{E}) + \bar{E}^{\mathcal{B}}[\rho_{\Psi_{\mathrm{WFT}}^{\mathcal{B}}(\mathcal{E})}] \implies d_0^{\mathcal{B}} = -\left.\frac{\mathrm{d}E_0^{\mathcal{B}}(\mathcal{E})}{\mathrm{d}\mathcal{E}}\right|_{\mathcal{E}=0}$$

- Example of calculations on a set of 14 molecules with aug-cc-pVXZ basis sets:



$\implies$ **The basis correction also accelerates the convergence of dipole moments**

Giner, Traore, Pradines, Toulouse, JCP, 2021
Traore, Toulouse, Giner, JCP, 2022

Conclusions on the DFT basis-set correction

- **Summary:**
  - DFT basis-set correction which automatically adapts to each basis set
  - based on pre-existing short-range correlation functional
  - accelerates basis convergence of energies and properties

- **Outlook:**
  - Construction of a more rigorous basis-correction functional
  - Extension to linear-response theory
  - Extension to density fitting for larger systems

- Implemented in **QUANTUM PACKAGE** and **MOLPRO**

Outline

1. Basis-set correction based on DFT for short-range correlation

2. TDDFT with Robin boundary conditions for continuum states

with E. Cancès, A. Levitt, **E. Luppi**, K. Schwinn, F. Zapata

Photoionization spectra from TDDFT/TDHF: The naive way

- We would like to calculate the **photoabsorption cross section**

  $$\sigma(\omega) = \lim_{\eta \to 0^+} \frac{4\pi\omega}{c} \mathrm{Im}[\alpha(\omega + \mathrm{i}\eta)]$$

  where $\alpha(\omega)$ is the dynamic dipole polarizability. For $\omega \geq \mathrm{IP}$, we have **photoionization**.

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- In a **finite basis set**, the linear-response (adiabatic) TDDFT/TDHF equations are

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}$$

  with $A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \langle aj|\hat{f}_{\mathrm{Hxc}}|ib\rangle$ and $B_{ia,jb} = \langle ab|\hat{f}_{\mathrm{Hxc}}|ij\rangle$.

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- We obtain **excitation energies** ω_n and associated **oscillator strengths** f_n. The photoabsorption cross section is then

  $$\sigma(\omega) = \frac{2\pi^2}{c} \sum_n f_n \, \delta(\omega - \omega_n)$$

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$$\sigma(\omega) = \frac{2\pi^2}{c} \sum_n f_n \, \delta(\omega - \omega_n)$$

- For $\omega \geq \mathrm{IP}$, the **photoionization cross section** at $\omega = \omega_n$ may be approximated as

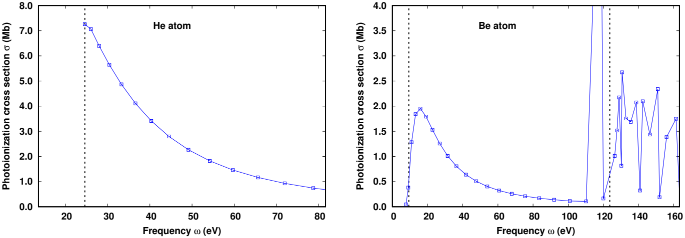
$$\sigma(\omega_n) \approx \frac{2\pi^2}{c} f_n \, \rho_{\mathrm{DOS}}(\omega_n)$$

  where $\rho_{\mathrm{DOS}}(\omega_n) \approx 2/(\omega_{n+1} - \omega_{n-1})$ is an estimate of the density of states at $\omega = \omega_n$.

Photoionization spectra of He and Be

- We use a **B-spline basis set**, i.e. localized piecewise polynomial functions in a spherical box Ω, with Dirichlet (zero) boundary conditions.

- TDHF photoionization spectra of the He and Be atoms:



$\Longrightarrow$ **Reasonable spectra for He but it does not work for core ionization in Be**

Zapata, Luppi, Toulouse, JCP, 2019

Sternheimer formulation of linear-response TDDFT/TDHF

- Let us look at a **basis-independent** formulation of linear-response TDDFT/TDHF.

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$$\mathrm{i}\frac{\partial}{\partial t}\psi_i(t) = \hat{h}[\gamma(t)]\psi_i(t) + \hat{v}(t)\psi_i(t)$$

where $\hat{h}[\gamma(t)]$ is the KS/HF Hamiltonian depending on the density matrix $\gamma(t)$ and $\hat{v}(t) = -\hat{d}\mathcal{E}\left(e^{-\mathrm{i}\omega t} + e^{+\mathrm{i}\omega t}\right)$ is the electric-dipole interaction.

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- At **first order in the electric field**, the perturbed occupied orbitals (in the interaction picture) are

$$\psi_i^{(1)}(t) = \psi_i^{(+)}(\omega)e^{-\mathrm{i}\omega t} + \psi_i^{(-)}(\omega)e^{+\mathrm{i}\omega t}$$

  where the Fourier modes $\psi_i^{(\pm)}(\omega)$ satisfy the **TDDFT/TDHF Sternheimer equations**

$$\left(\pm\omega + \varepsilon_i - \hat{h}[\gamma^{(0)}]\right)\psi_i^{(\pm)}(\omega) = \left(\hat{v}_{\mathrm{Hxc}}^{(\pm)}(\omega) - \hat{d}\right)\psi_i^{(0)}$$

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- The **dynamic dipole polarizability** is then obtained as

$$\alpha(\omega) = \sum_{i=1}^{N}\langle\psi_i^{(0)}|\hat{d}|\psi_i^{(+)}(\omega)\rangle + \langle\psi_i^{(-)}(\omega)|\hat{d}|\psi_i^{(0)}\rangle$$

Tackling the continuum with Robin boundary conditions

- For $\omega \geq -\varepsilon_i$, the first-order perturbed occupied orbital $\psi_i^{(+)}(\omega)$ is a "**continuum wave function**" (i.e., not belonging to the Hilbert space).

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- For spherical symmetry, this leads to **local Robin boundary conditions** for $\psi_i^{(+)}(\omega)$

$$\forall \mathbf{r} \in \partial\Omega, \; \frac{\mathbf{n}(\mathbf{r})\cdot\boldsymbol{\nabla}\psi_i^{(+)}(\mathbf{r},\omega)}{\psi_i^{(+)}(\mathbf{r},\omega)} = \frac{\mathbf{n}(\mathbf{r})\cdot\boldsymbol{\nabla}\bar{\psi}_i^{(+)}(\mathbf{r},\omega)}{\bar{\psi}_i^{(+)}(\mathbf{r},\omega)}$$

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- For non-spherical symmetry, it is extended to **nonlocal Robin boundary conditions**

$$\forall \mathbf{r} \in \partial\Omega, \ \mathbf{n}(\mathbf{r})\cdot\boldsymbol{\nabla}\psi_i^{(+)}(\mathbf{r},\omega) = \int_{\partial\Omega} \bar{K}_i(\mathbf{r},\mathbf{r}';\omega)\psi_i^{(+)}(\mathbf{r}',\omega)\mathrm{d}\mathbf{r}'$$

  where the kernel $\bar{K}_i(\mathbf{r},\mathbf{r}';\omega)$ contains information about $\bar{\psi}_i^{(+)}(\omega)$.

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  where the kernel $\bar{K}_i(\mathbf{r},\mathbf{r}';\omega)$ contains information about $\bar{\psi}_i^{(+)}(\omega)$.

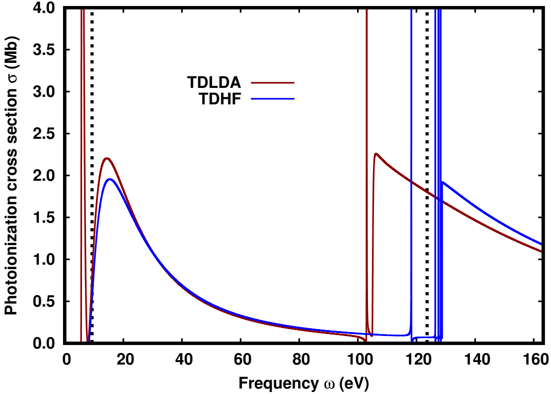
- Using now a basis set in the box, it amounts to using the **kinetic integrals**

$$t_{i,\mu,\nu}(\omega) = \frac{1}{2} \int_{\Omega} \nabla \chi_\mu^*(\mathbf{r}) \cdot \nabla \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r} - \frac{1}{2} \int_{\partial\Omega^2} \chi_\mu^*(\mathbf{r}) \bar{K}_i(\mathbf{r},\mathbf{r}';\omega) \chi_\nu(\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

Photoionization spectra of Be

- We use a **B-spline basis set**, i.e. localized piecewise polynomial functions in a spherical box Ω, **with Robin boundary conditions**.

- TDHF and TDLDA photoionization spectra of the Be atom:



$\Longrightarrow$ **We can now easily converge the spectra for all frequencies**

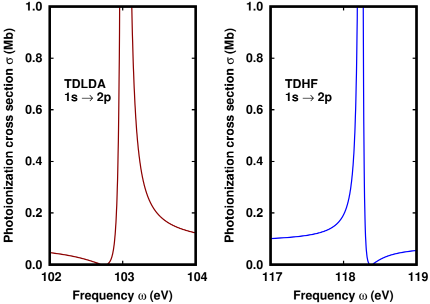
Schwinn, Zapata, Levitt, Cancès, Luppi, Toulouse, JCP, 2022

Core resonances in the Be atom

- The 1s → np core excitations are embedded in the continuum of the valence excitations from the 2s $\Longrightarrow$ they are **resonances**, i.e. **quasi-bound states with finite lifetimes**.

Core resonances in the Be atom

- The 1s → *n*p core excitations are embedded in the continuum of the valence excitations from the 2s $\Longrightarrow$ they are **resonances**, i.e. **quasi-bound states with finite lifetimes**.
- Example of the 1s → 2p core resonance (resonance energy E_R and inverse lifetime Γ):



	E_R (eV)	Γ (meV)
TDLDA	103.0	2.3
TDHF	118.3	0.2
TDLRSH	114.8	0.1
Reference	115.5	37

$\Longrightarrow$ **Good resonance energy with TDLRSH but much too small inverse lifetime**

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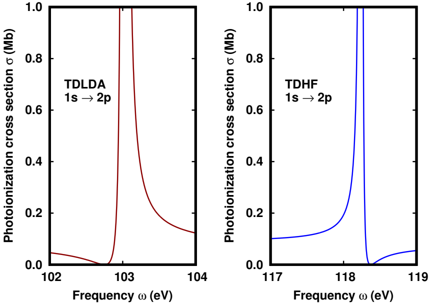

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- The resonance decays via the **Auger process**

$$1s2s^2 2p \rightarrow 1s^2 2p + e$$

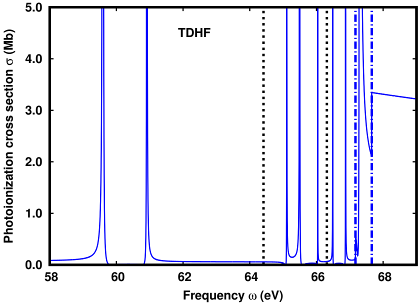
The configuration $1s^2 2p$ is a double excitation with respect to the ground state $1s^2 2s^2$ and thus cannot be described by adiabatic TDDFT/TDHF.

Core resonances in the Li atom

- In Li, due to spin, each 1s → np resonance split in two resonances.

Core resonances in the Li atom

- In Li, due to spin, each $1s \to np$ resonance split in two resonances.
- Example of the $1s_\uparrow \to 2p_\uparrow$ and $1s_\downarrow \to 2p_\downarrow$ core resonance:



$1s_\uparrow \to 2p_\uparrow$

	E_R (eV)	Γ (meV)
TDLDA	49.7	0.3
TDHF	59.6	5.6
TDLRSH	58.8	5.4
Reference	58.9	3.3

$1s_\downarrow \to 2p_\downarrow$

	E_R (eV)	Γ (meV)
TDLDA	50.3	0.1
TDHF	60.9	0.2
TDLRSH	60.4	0.3
Reference	60.4	9.6

$\Longrightarrow$ **Again, good resonance energies with TDLRSH but unreliable inverse lifetimes**

Core resonances in the Li atom

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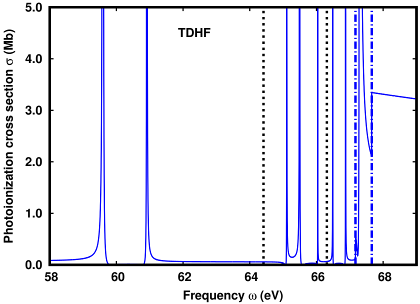

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$1s_\downarrow \rightarrow 2p_\downarrow$

	E_R (eV)	Γ (meV)
TDLDA	50.3	0.1
TDHF	60.9	0.2
TDLRSH	60.4	0.3
Reference	60.4	9.6

⟹ **Again, good resonance energies with TDLRSH but unreliable inverse lifetimes**

- Note that now the resonances decay via the **Auger process**

$$1s2s2p \rightarrow 1s^2 + e$$

which does not invove any double excitation with respect to the ground state $1s^2 2s$.

Toulouse, Schwinn, Zapata, Levitt, Cancès, Luppi, JCP, 2022

Conclusions on TDDFT with Robin boundary conditions

- **Summary:**
  - TDDFT/TDHF with special boundary conditions for describing continuum states
  - It allows calculations of photoionization spectra of atoms, including core resonances
  - TDLRSH gives good resonance energies but unreliable lifetimes
- **Outlook:**
  - Extension to Gaussian basis sets
  - Extension to molecules
  - Extension to time propagation for nonlinear optical properties

`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_nantes_23.pdf`