Two strategies for continuum excited states: Robin boundary conditions and semiclassical approximations

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Outline

1. Difficulties with continuum states

2. Robin boundary conditions

3. Semiclassical approximations

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1. Difficulties with continuum states
2. Robin boundary conditions
3. Semiclassical approximations

The problem with “continuum states”

- The Coulomb nuclei-electron potential is non-confining, which leads to a **continuous energy spectrum** with **“continuum states”**.

- Mathematically, **the continuum states are not truly energy eigenstates** since they do not belong to the L^2 Hilbert space.
- In principle, **pointwise/distribution convergence to continuum states** can be obtained with L^2 basis functions.
- In practice, **convergence to continuum states** (or to properties crucially depending on continuum states) **can be very slow or impossible with straightforward basis expansions**.

Reinhardt, Comp. Phys. Comm., 1979

Photoionization cross section

- The **photoabsorption cross section** is

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

where $\alpha(\omega)$ is the dynamic dipole polarizability.

- For $\omega \geq$ IP, this is the **photoionization cross section**, which crucially depends on continuum states.

- If $\hat{H}$ were diagonalizable in a complete eigenfunction basis $\{\Psi_n\}_{n \in \mathbb{N}}$, the cross section could be written as

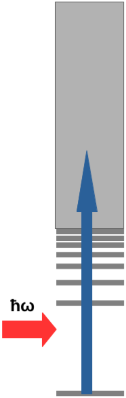
$$\sigma(\omega) = \frac{4\pi^2\omega}{c} \sum_{n=0}^{\infty} |\langle \Psi_0 | \hat{d} | \Psi_n \rangle|^2 \; \delta(\omega - (E_n - E_0))$$

where $\hat{d}$ is the dipole-moment operator (along the direction of the electric field).

- Formally, it can be expressed as an expectation value

$$\sigma(\omega) = \frac{4\pi^2\omega}{c} \langle \Psi_0 | \hat{d} \; \delta(\omega + E_0 - \hat{H}) \; \hat{d} | \Psi_0 \rangle$$

where $\delta(\omega + E_0 - \hat{H})$ is the spectral-density operator.



Photoionization from linear-response TDDFT/TDHF: The naive way

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

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

$$\sigma(\omega) = \frac{2\pi^2}{c} \sum_{n=1}^{M} f_n \, \delta(\omega - \omega_n)$$

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

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

  where $\rho_{\text{DOS}}(\omega_n)$ is a finite-difference estimate of the **density of states** at $\omega = \omega_n$

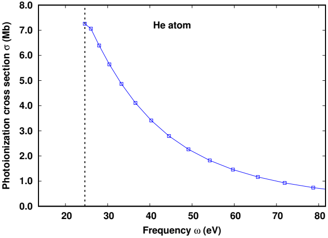
$$\rho_{\text{DOS}}(\omega_n) = \frac{\text{d}n}{\text{d}\omega_n} \approx \frac{2}{\omega_{n+1} - \omega_{n-1}}$$

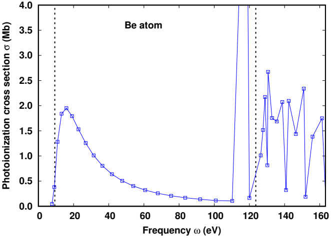
Macías, Martín, Riera, Yánez, Int. J. Quantum Chem., 1988
Yang, van Faassen, Burke, J. Chem. Phys., 2009
Zapata, Luppi, Toulouse, J. Chem. Phys., 2019

Photoionization cross sections 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 cross sections of the He and Be atoms:





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

Zapata, Luppi, Toulouse, J. Chem. Phys., 2019

So, how to deal with continuum states?

Some approaches for calculating cross sections involving continuum states:

- Various techniques involving the **complex-frequency plane**
  E.g., analytical continuation of $\alpha(\omega)$:
  Tenorio, Coriani, Rocha, Nascimento, Prog. Theor. Chem. Phys., 2021

- Imposing **boundary conditions adapted to continuum states**
  E.g., in TDDFT:
  Stener, Decleva, Lisini, J. Phys. B, 1995

$\Longrightarrow$ **Here, I will talk about using Robin boundary conditions**

- **Semiclassical approximations**
  E.g., in nuclear physics:
  Schuck, Hasse, Jaenicke, Grégoire, Rémaud, Sébille, Suraud, Prog. Part. Nucl. Phys., 1989

$\Longrightarrow$ **Here, I will talk about semiclassical approximations for photoionization**

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1. Difficulties with continuum states

2. Robin boundary conditions

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

3. Semiclassical approximations

Sternheimer formulation of linear-response TDDFT/TDHF

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

- In (adiabatic) TDDFT/TDHF, the **occupied orbitals evolve in time** according to

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

  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.

- 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**

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

- 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).

- **Key idea: Expand $\psi_i^{(+)}(\omega)$ in a basis set only in a box Ω and use an analytical asymptotic approximation $\bar{\psi}_i^{(+)}(\omega)$ to it outside the box. Match the two functions on the box surface $\partial\Omega$ by equating the normal logarithmic derivatives.**

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

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

  where $\bar{\psi}_i^{(+)}(\mathbf{r},\omega)$ are chosen as hydrogen-like continuum wave functions.

- 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 $\bar{\psi}_i^{(+)}(\omega)$.

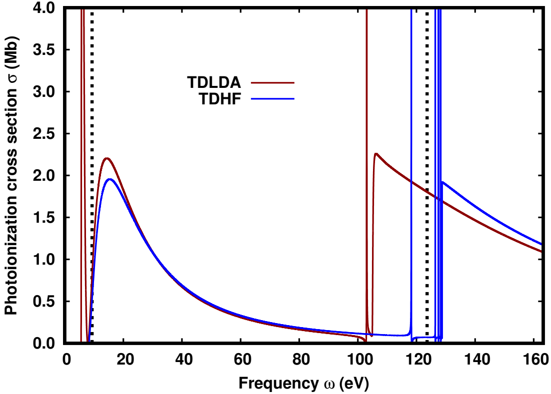
- Using now a basis set in the box, it amounts to using the **kinetic integrals**

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

Photoionization cross section of Be

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

- TDLDA and TDHF photoionization cross sections of the Be atom:



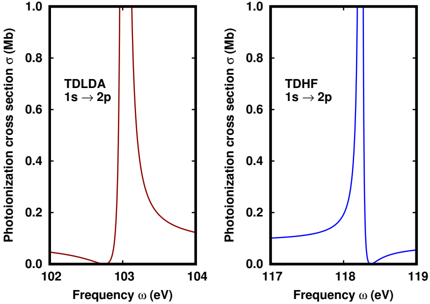
$\Longrightarrow$ **We can now easily converge the spectra for all frequencies**

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

Core resonances in the Be atom

- The 1s → *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**

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

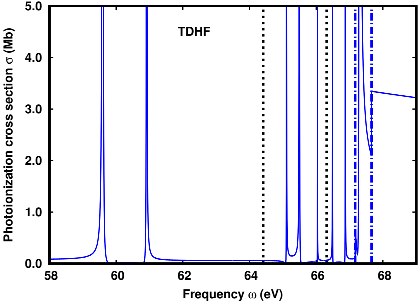
$$1s2s^2 2p \rightarrow 1s^2 2p + e$$

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.

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

Core resonances in the Li atom

- In Li, due to spin, each 1s → *n*p 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**

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

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

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 Robin boundary conditions

- **Summary:**
  - TDDFT/TDHF with special boundary conditions for describing continuum states
  - It allows for calculations of photoionization spectra of atoms, including core resonances
  - TDLRSH gives good resonance energies but unreliable lifetimes

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

- **Outlook:**
  - Extension to double excitations
  - Extension to molecules
  - Extension to time propagation for nonlinear optical properties

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started with P. Schuck

Photoionization cross section in the velocity gauge

- We start from the **photoionization cross section in the velocity gauge**

$$\sigma(\omega) = \frac{4\pi^2}{c\omega}\langle\Psi_0|\hat{P}\;\delta(\omega + E_0 - \hat{H})\;\hat{P}|\Psi_0\rangle$$

  where $\hat{P}$ is the total momentum operator (along the direction of the field).

- We introduce the operators

$$\hat{A} = \delta(\omega + E_0 - \hat{H}) \qquad \text{and} \qquad \hat{B} = \hat{P}\;\hat{A}\;\hat{P}$$

  and the ground-state density matrix

$$\hat{\rho}_0 = |\Psi_0\rangle\langle\Psi_0|$$

- We arrive at the following expression for the **photoionization cross section**

$$\sigma(\omega) = \frac{4\pi^2}{c\omega}\mathrm{Tr}[\hat{B}\;\hat{\rho}_0] = \frac{4\pi^2}{c\omega}\int_{\mathbb{R}^{6N}} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' B(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r}',\mathbf{r})$$

  where $B(\mathbf{r},\mathbf{r}') = \langle\mathbf{r}|\hat{B}|\mathbf{r}'\rangle$ and $\rho_0(\mathbf{r}',\mathbf{r}) = \langle\mathbf{r}'|\hat{\rho}_0|\mathbf{r}\rangle$.

Wigner representation of the photoionization cross section

- Let us introduce the **Wigner transform** of an operator $\hat{C}$

$$[\hat{C}]_{\mathrm{W}}(\mathbf{q},\mathbf{p}) \equiv C_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = \int_{\mathbb{R}^{3N}} \mathrm{d}\mathbf{s}\; e^{-i\mathbf{p}\cdot\mathbf{s}} \langle \underbrace{\mathbf{q}+\mathbf{s}/2}_{=\mathbf{r}} | \hat{C} | \underbrace{\mathbf{q}-\mathbf{s}/2}_{=\mathbf{r}'} \rangle$$

  where $\mathbf{q} = (\mathbf{r}+\mathbf{r}')/2 \in \mathbb{R}^{3N}$ is the average position vector, $\mathbf{s} = \mathbf{r}-\mathbf{r}' \in \mathbb{R}^{3N}$ is the relative position vector, $\mathbf{p} \in \mathbb{R}^{3N}$ is the conjugate momentum vector of $\mathbf{s}$.

  Ring, Schuck, The Nuclear Many-Body Problem, Springer, 2004

  Case, Am. J. Phys., 2008

- The **Wigner transformation preserves the trace** of a product of operators, so we have

$$\sigma(\omega) = \frac{4\pi^2}{c\omega} \int_{\mathbb{R}^{6N}} \frac{\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}}{(2\pi)^{3N}}\; B_{\mathrm{W}}(\mathbf{q},\mathbf{p}) \rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$$

- We have put the photoionization cross section in the form of a **phase-space integral**.

- So far, everything is exact. We will assume that we know the Wigner function of the ground state $\rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$, and we will now use a **semiclassical expansion approximation** for $B_{\mathrm{W}}(\mathbf{q},\mathbf{p})$.

Semiclassical expansion

- The **Wigner transform of a product of operators** is given by the Groenewold/Moyal/star-product formula:

$$[\hat{C}\hat{D}]_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = C_{\mathrm{W}}(\mathbf{q},\mathbf{p})e^{(i\hbar/2)\overleftrightarrow{\Lambda}}D_{\mathrm{W}}(\mathbf{q},\mathbf{p})$$

  where $\overleftrightarrow{\Lambda} = \overleftarrow{\nabla}_{\mathbf{q}} \cdot \overrightarrow{\nabla}_{\mathbf{p}} - \overleftarrow{\nabla}_{\mathbf{p}} \cdot \overrightarrow{\nabla}_{\mathbf{q}}$ is the Poisson bracket differential operator.

- Using this formula, we find the Wigner transform of $\hat{B} = \hat{P}\hat{A}\hat{P}$

$$B_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = \frac{1}{3}\mathbf{P}^2 A_{\mathrm{W}}(\mathbf{q},\mathbf{p}) + \frac{\hbar^2}{12}\mathbf{D}^2 A_{\mathrm{W}}(\mathbf{q},\mathbf{p})$$

  where $\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$ and $\mathbf{D} = \sum_{i=1}^{N} \nabla_{\mathbf{q}_i}$.

- We also find the semiclassical expansion of the Wigner transform of $\hat{A} = \delta(\omega + E_0 - \hat{H})$

$$A_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = A_{\mathrm{W}}^{(0)}(\mathbf{q},\mathbf{p}) + \hbar^2 A_{\mathrm{W}}^{(2)}(\mathbf{q},\mathbf{p}) + O(\hbar^4)$$

  where $A_{\mathrm{W}}^{(0)}(\mathbf{q},\mathbf{p}) = \delta(\omega + E_0 - H(\mathbf{q},\mathbf{p}))$ and $H(\mathbf{q},\mathbf{p}) = \frac{\mathbf{p}^2}{2} + V(\mathbf{q})$

$$\begin{aligned} A_{\mathrm{W}}^{(2)}(\mathbf{q},\mathbf{p}) =& \frac{1}{8}\Big[-\nabla_{\mathbf{q}}^2 V(\mathbf{q})\, \delta''(\omega + E_0 - H(\mathbf{q},\mathbf{p})) \\ & + \frac{1}{3}\Big((\nabla_{\mathbf{q}} V(\mathbf{q}))^2 + (\mathbf{p}\cdot\nabla_{\mathbf{q}})^2 V(\mathbf{q}) \Big)\, \delta'''(\omega + E_0 - H(\mathbf{q},\mathbf{p})) \Big] \end{aligned}$$

Semiclassical expansion of the photoionization cross section

- We obtain the **semiclassical expansion of the photoionization cross section** (for $\hbar = 1$):

$$\sigma(\omega) = \sigma^{(0)}(\omega) + \sigma^{(2)}(\omega) + \cdots$$

- The zeroth-order term is

$$\sigma^{(0)}(\omega) = \frac{4\pi^2}{3c\omega} \int_{\mathbb{R}^{6N}} \frac{\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}}{(2\pi)^{3N}}\ \mathbf{P}^2 A_{\mathrm{W}}^{(0)}(\mathbf{q},\mathbf{p}) \rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$$

- The second-order term is

$$\sigma^{(2)}(\omega) = \frac{4\pi^2}{3c\omega} \int_{\mathbb{R}^{6N}} \frac{\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}}{(2\pi)^{3N}}\ \left[\mathbf{P}^2 A_{\mathrm{W}}^{(2)}(\mathbf{q},\mathbf{p}) + \frac{1}{4}\mathbf{D}^2 A_{\mathrm{W}}^{(0)}(\mathbf{q},\mathbf{p})\right] \rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$$

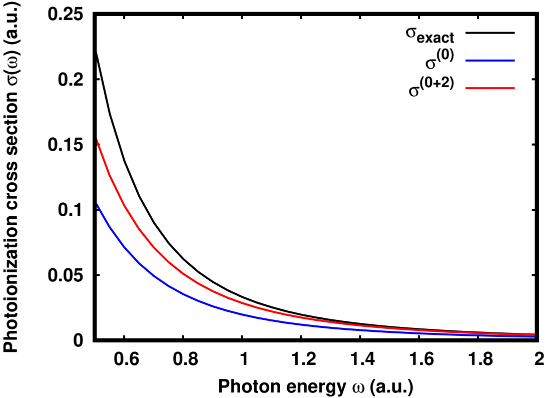
- We have arrived at an approximation to the photoionization cross section that only requires to know the ground-state Wigner function $\rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$ but does not require the calculation of the continuum states.

- Note that it is not a full expansion in powers of $\hbar$ since we do not expand $\rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$.

Toulouse, EPJA, 2023

Photoionization cross section of the hydrogen atom

Calculation of $\sigma^{(0)}(\omega)$ and $\sigma^{(2)}(\omega)$ by numerical integration:



$\Longrightarrow$ **As expected, the semiclassical expansion correctly captures the high-energy part of the spectrum**

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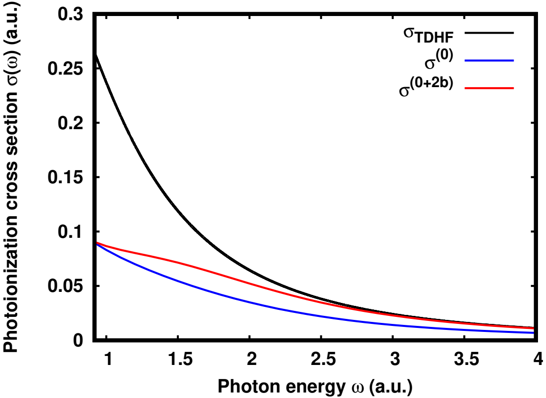
Photoionization cross section of the helium atom

Calculation of $\sigma^{(0)}(\omega)$ and an approximation to $\sigma^{(2)}(\omega)$ by numerical integration:



$\Longrightarrow$ **Again, the semiclassical expansion correctly captures the high-energy part of the spectrum**

Toulouse, EPJA, 2023

Conclusions on semiclassical approximations

- **Summary:**
  - We derived semiclassical approximations for photoionization cross sections
  - Tests on atoms confirm that they correctly captures the high-energy part of the spectrum

Toulouse, EPJA, 2023

- **Outlook:**
  - Extension to linear-response TDHF/TDDFT
  - Extension to many-body calculations with Monte Carlo integration
  - Extension to other properties such as second-order correlation energy
  - Development of hybrid methods: basis set for low-energy part + semiclassical approximations for high-energy part

`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_toulouse_24.pdf`