An attempt at semiclassical methods for electronic-structure theory

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QMBC conference in memory of Peter Schuck

IJCLab, Orsay, France

March 2023

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Interactions with Peter Schuck

- I first met Peter Schuck in 2010 when we organized a **multidisciplinary workshop on RPA** in Paris, together with János Ángyán, John Dobson, and Gustavo Scuseria.

  `https://wiki.lct.jussieu.fr/workshop/index.php/Multidisciplinary_Workshop_on_RPA`

- In 2017, Maria Hellgren, Eleonora Luppi, Nathalie Pillet, Peter Schuck, and I organized another **multidisciplinary workshop on RPA** in Paris.

  `https://wiki.lct.jussieu.fr/workshop/index.php/RPA_workshop_2017`

- In 2019, Valerio Olevano, Peter Schuck, and I published a paper on the **Bethe-Salpeter equation with only one frequency**.

  V. Olevano, J. Toulouse, P. Schuck, *A formally exact one-frequency-only Bethe-Salpeter-like equation. Similarities and differences between GW+BSE and self-consistent RPA*, Journal of Chemical Physics **150**, 084112 (2019)

- After a visit in Grenoble in 2019, Peter Schuck and I started to collaborate on **semiclassical methods for electronic-structure theory**.

Outline

1. Semiclassical approximations for photoionization cross sections

2. Results on the H and He atoms

Outline

Photoionization cross section

- We consider a N-**particle Hamiltonian**:

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\mathbf{p}}_i^2}{2} + \hat{V}$$

with eigenstates $\{|\Psi_n\rangle\}_{n\in\mathbb{N}}$ and eigenvalues $\{E_n\}_{n\in\mathbb{N}}$.

- The eigenstates above the ionization threshold, $E_n \geq E_{\text{thres}}$, are **"continuum states"** assumed to be discretized for simplicity (e.g., by putting the system in a box).

- The **photoionization cross section**, corresponding to transitions from the ground state $|\Psi_0\rangle$ to continuum states $|\Psi_n\rangle$, in the velocity gauge is, for $\omega \geq E_{\text{thres}} - E_0$,

$$\sigma(\omega) = \frac{4\pi^2}{3c\omega} \sum_{\mu\in\{x,y,z\}} \sum_{n=0}^{\infty} |\langle\Psi_0|\hat{P}_\mu|\Psi_n\rangle|^2 \, \delta(\omega - (E_n - E_0))$$

where $\hat{P}_\mu = \sum_{i=1}^{N} \hat{p}_{i,\mu}$.

- **A straightforward calculation is difficult since it involves a sum over all continuum states!**

Photoionization cross section without explicit continuum states

- We can get rid of the explicit sum over the continuum states

$$\begin{aligned}\sigma(\omega) &= \frac{4\pi^2}{3c\omega} \sum_{\mu\in\{x,y,z\}} \sum_{n=0}^{\infty} \langle\Psi_0|\hat{P}_\mu|\Psi_n\rangle\langle\Psi_n|\delta(\omega + E_0 - \hat{H})\hat{P}_\mu|\Psi_0\rangle \\ &= \frac{4\pi^2}{3c\omega} \sum_{\mu\in\{x,y,z\}} \langle\Psi_0|\hat{P}_\mu\delta(\omega + E_0 - \hat{H})\hat{P}_\mu|\Psi_0\rangle\end{aligned}$$

- We introduce the operators

$$\hat{A} = \delta(\omega + E_0 - \hat{H}) \quad \text{and} \quad \hat{B} = \sum_{\mu\in\{x,y,z\}} \hat{P}_\mu \hat{A}\,\hat{P}_\mu$$

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**

$$\sigma(\omega) = \frac{4\pi^2}{3c\omega}\mathrm{Tr}[\hat{B}\,\hat{\rho}_0] = \frac{4\pi^2}{3c\omega}\int_{\mathbb{R}^{6N}} d\mathbf{r}d\mathbf{r}' B(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r}',\mathbf{r})$$

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 $\hat{C}$

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

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 $\mathbf{s}$.

Hillery, O'Connell, Scully, Wigner, Phys. Rep., 1984

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

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

- 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 $B_{\mathrm{W}}(\mathbf{q},\mathbf{p})$.

- 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 $\hat{B} = \sum_{\mu \in \{x,y,z\}} \hat{P}_\mu \hat{A} \hat{P}_\mu$

$$B_{\mathrm{W}}(\mathbf{q},\mathbf{p}) = \mathbf{P}^2 A_{\mathrm{W}}(\mathbf{q},\mathbf{p}) + \frac{\hbar^2}{4} \mathbf{D}^2 A_{\mathrm{W}}(\mathbf{q},\mathbf{p})$$

  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 $H(\mathbf{q},\mathbf{p}) = \frac{\mathbf{p}^2}{2} + V(\mathbf{q})$

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

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 $\rho_{0,\mathrm{W}}(\mathbf{q},\mathbf{p})$.

Outline

Hydrogen atom

- We consider the **hydrogen atom**, i.e. $N = 1$ electron and the Coulomb potential

$$V(\mathbf{q}) = -1/q$$

- Surprisingly, the Wigner function of the ground state is not known in a closed form, but it can be expressed as the integral

$$\rho_{0,\mathrm{W}}(q, p, \mathbf{q}\cdot\mathbf{p}) = \int_0^1 \mathrm{d}u \; f(q, p, \mathbf{q}\cdot\mathbf{p}, u)$$

where

$$f(q, p, \mathbf{q}\cdot\mathbf{p}, u) = \frac{16 e^{2i\mathbf{q}\cdot\mathbf{p}(2u-1) - 2qg(p,u)} (1-u)u \left(3 + 6qg(p,u) + 4q^2 g(p,u)^2\right)}{g(p,u)^5}$$

with $g(p, u) = \sqrt{1 + 4p^2(1-u)u}$.

Praxmeyer, Mostowski, Wódkiewicz, J. Phys. A, 2006

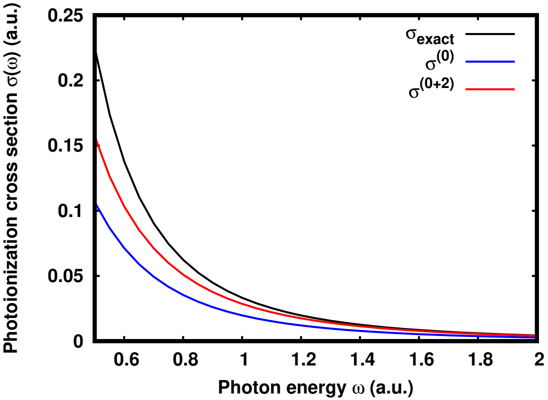
- We obtain the **zeroth-order photoionization cross section** as

$$\sigma^{(0)}(\omega) = \frac{4\pi}{3c\omega} \int_0^1 \mathrm{d}u \int_0^\infty \mathrm{d}q \; q^2 (2(\omega + E_0 + 1/q))^{3/2} \; \tilde{f}\left(q, \sqrt{2(\omega + E_0 + 1/q)}, u\right)$$

where $\tilde{f}(q, p, u) = \int_{-1}^{1} \mathrm{d}x \; f(q, p, qpx, u)$ is the spherical average of f.

- $\sigma^{(2)}(\omega)$ has a similar expression but with derivatives of $\tilde{f}$ with respect to p.

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**

Helium atom

- We consider the **helium atom**, i.e. $N = 2$ electrons and the total potential

$$V(\mathbf{q}_1, \mathbf{q}_2) = -2/q_1 - 2/q_2 + 1/||\mathbf{q}_1 - \mathbf{q}_2||$$

- We consider the **Hartree-Fock ground-state wave function**

$$\Phi(\mathbf{q}_1, \mathbf{q}_2) = \phi(\mathbf{q}_1)\phi(\mathbf{q}_2)$$

The corresponding **Wigner function** can be factorized as

$$\rho_{\mathrm{HF,W}}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) = \rho_{\phi,\mathrm{W}}(q_1, p_1, \mathbf{q}_1 \cdot \mathbf{p}_1)\rho_{\phi,\mathrm{W}}(q_2, p_2, \mathbf{q}_2 \cdot \mathbf{p}_2)$$

where $\rho_{\phi,\mathrm{W}}(q, p, \mathbf{q} \cdot \mathbf{p})$ is the Wigner function associated with the orbital ϕ.

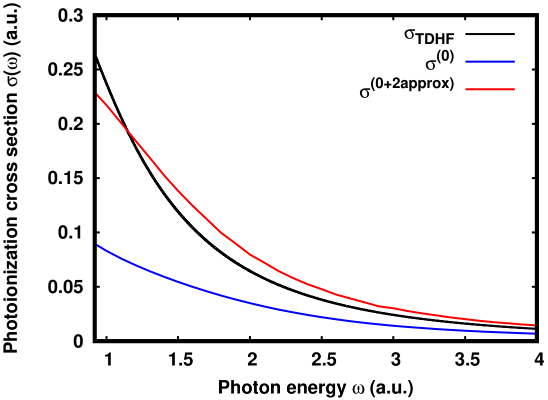
- As usual in quantum chemistry, we expand the orbital ϕ in **Gaussian basis functions**. The Wigner function $\rho_{\phi,\mathrm{W}}(q, p, \mathbf{q} \cdot \mathbf{p})$ can then be calculated analytically.

Dahl, Springborg, Mol. Phys., 1982

- Finally, $\sigma^{(0)}(\omega)$ and $\sigma^{(2)}(\omega)$ can be expressed as integrals over 4 variables.

Photoionization spectrum 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**

Conclusions

- **Summary:**
  - We derived semiclassical approximations for photoionization cross sections
  - Tests on atoms confirm that they correctly captures the high-energy part of the spectrum
- **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_orsay_23.pdf`