Single and double ionization potentials of molecular systems with the *GW* approximation

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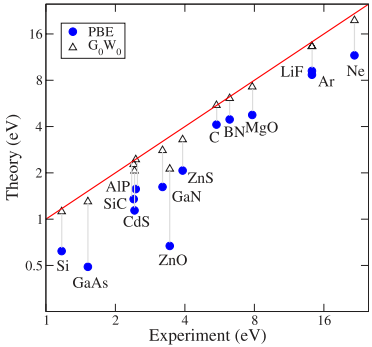
Context

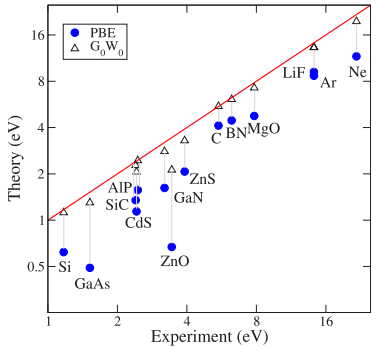
Band gaps of solids



Adapted from Shishkin and Kresse Phys. Rev. B 75 235102 (2007)

Context

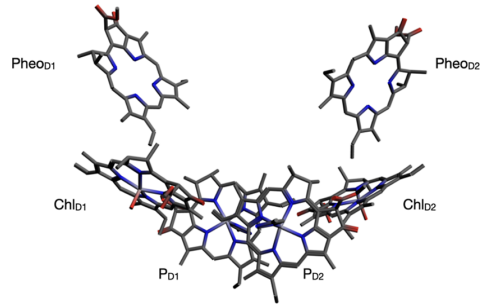
Band gaps of solids



Adapted from Shishkin and Kresse Phys. Rev. B 75 235102 (2007)

Recent example

Photosystem II reaction center (~2000 electrons/~11000 basis functions)



Extracted from Förster and Visscher J. Chem. Theory Comput. 18 6779 (2022)

Context

Wave function formalism

- Wave function exponentially large $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$
- Energy functional $E = \langle \Psi | \hat{H} | \Psi \rangle$

Density functional theory

- One-body density $\rho(\mathbf{x}_1)$
- Exact energy functional unknown $E[\rho]$

Context

Wave function formalism

- Wave function exponentially large $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$
- Energy functional $E = \langle \Psi | \hat{H} | \Psi \rangle$

Many-body perturbation theory

- One-body Green's function $G(\mathbf{x}_1, \mathbf{x}_{1'}; t_1 - t_{1'})$
- Galitskii-Migdal functional $E[G]$

Density functional theory

- One-body density $\rho(\mathbf{x}_1)$
- Exact energy functional unknown $E[\rho]$

Definitions

One-body density

$$\rho(\mathbf{x}_1) = N \int \mathrm{d}(\mathbf{x}_2 \dots \mathbf{x}_N)\, \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) = \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_1) | \Psi_0 \rangle \, .$$

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One-body reduced density matrix

$$\gamma(\mathbf{x}_1, \mathbf{x}_{1'}) = N \int \mathrm{d}(\mathbf{x}_2 \dots \mathbf{x}_N)\, \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi_0(\mathbf{x}_{1'}, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) = \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_{1'}) | \Psi_0 \rangle \, .$$

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One-body Green's function

$$G(\mathbf{x}_1, \mathbf{x}_{1'}; t_1 - t_{1'}) = (-\mathrm{i}) \, \langle \Psi_0 | \hat{T} \left[\hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}_{1'} t_{1'}) \right] | \Psi_0 \rangle \, .$$

Links between reduced quantities

One-body density

$$\rho(\mathbf{x}_1) = -\mathrm{i} \lim_{\mathbf{x}_{1'} \to \mathbf{x}_1} \lim_{t_{1'} \to t_1^+} G(\mathbf{x}_1 \mathbf{x}_{1'}; t_1 - t_{1'}).$$

One-body reduced density matrix

$$\gamma(\mathbf{x}_1, \mathbf{x}_{1'}) = -\mathrm{i} \lim_{t_{1'} \to t_1^+} G(\mathbf{x}_1 \mathbf{x}_{1'}; t_1 - t_{1'}).$$

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Time-dependence

One-body Green's function

$$G(\mathbf{x}_1, \mathbf{x}_{1'}; t_1 - t_{1'}) = (-\mathrm{i}) \langle \Psi_0 | \hat{T} \left[\hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}_{1'} t_{1'}) \right] | \Psi_0 \rangle .$$

Time ordering

$$G(\mathbf{x}_1, \mathbf{x}_{1'}; t_1 - t_{1'}) = \begin{cases} -\mathrm{i} \langle \Psi_0 | \hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}_{1'} t_{1'}) | \Psi_0 \rangle & \text{if } t_1 > t_{1'}. \\ +\mathrm{i} \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}_{1'} t_{1'}) \hat{\psi}(\mathbf{x}_1 t_1) | \Psi_0 \rangle & \text{if } t_1 < t_{1'}. \end{cases}$$

- Upper term measures the propagation of an electron
- Lower term measures the propagation of a hole

Link to photoemission spectroscopy

Frequency representation

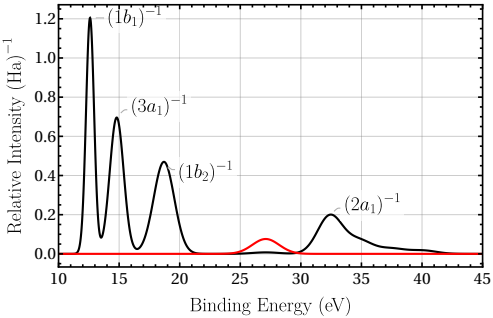
$$G(\mathbf{x}_1, \mathbf{x}_{1'}; \omega) = \sum_S \frac{\mathcal{I}_S(\mathbf{x}_1)\mathcal{I}_S^*(\mathbf{x}_{1'})}{\omega - (E_0^N - E_S^{N-1}) - \mathrm{i}\eta} + \sum_S \frac{\mathcal{A}_S(\mathbf{x}_1)\mathcal{A}_S^*(\mathbf{x}_{1'})}{\omega - (E_S^{N+1} - E_0^N) + \mathrm{i}\eta}$$

S-th ionization potentials

S-th electron affinities

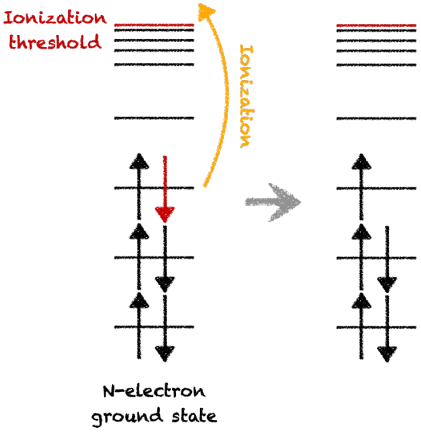
Spectral function

$$A(\omega) = \frac{1}{\pi} \int \mathrm{d}(\mathbf{x}_1 \mathbf{x}_{1'}) \, |\mathrm{Im}\, G(\mathbf{x}_1, \mathbf{x}_{1'}; \omega)|$$

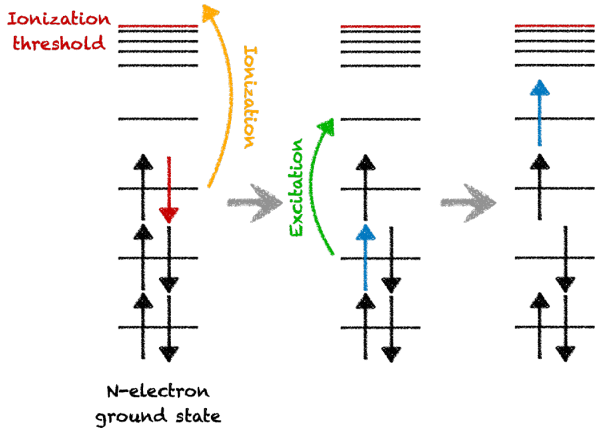


Satellites

Single ionization



Satellite excitations



Self-energy and *GW* approximation

Quasi-particle equation

$$\Big[\boldsymbol{F} + \boldsymbol{\Sigma}_c\left(\omega = \epsilon_p\right) \Big] \psi_p(\mathbf{x}) = \epsilon_p \, \psi_p(\mathbf{x}),$$

Fock matrix — **Self-energy** — **Poles of the Green's function**

Self-energy and *GW* approximation

Quasi-particle equation

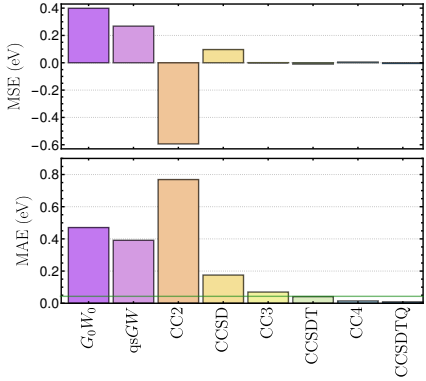
$$\Big[\boldsymbol{F} + \boldsymbol{\Sigma}_c \left(\omega = \epsilon_p\right) \Big] \psi_p(\mathbf{x}) = \epsilon_p \, \psi_p(\mathbf{x}),$$

Fock matrix — **Self-energy** — **Poles of the Green's function**

GW **approximation**

Self-energy that accounts for the correlation due to the screening of the Coulomb interaction

Errors w.r.t. FCI for 58 IP of 23 small molecules in the aug-cc-pVTZ basis set

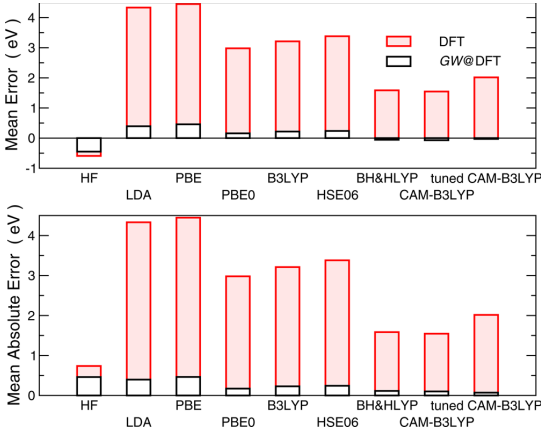


Marie and Loos J. Chem. Theory Comput. 20 4751 (2024)

Computational cost:

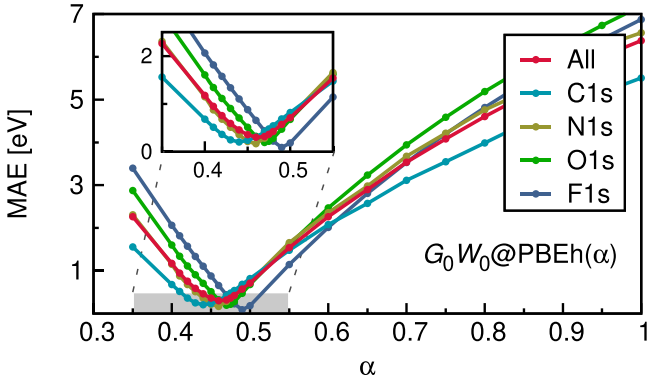
- G_0W_0 $\mathcal{O}(N^4)$
- CC2 $\mathcal{O}(N^5)$
- CCSD $\mathcal{O}(N^6)$

Errors w.r.t. △CCSD(T) for 34 IP of 34 small molecules in the cc-pVQZ basis set



Extracted from Bruneval and Marques J. Chem. Theory Comput. 9 324 (2013)

Errors w.r.t. experiments for 65 core IP of 32 small to medium-sized molecules in the complete basis set limit



Extracted from Golze *el al.* J. Phys. Chem. Lett. 11 1840 (2020)

Total energy

Galitskii-Migdal functional

$$E^{\mathrm{GM}} = -\frac{\mathrm{i}}{2}\int \mathrm{d}\mathbf{x}_1 \lim_{t_{1'}\to t_1^+}\left[\mathrm{i}\frac{\partial}{\partial t_1} + h(\mathbf{x}_1)\right] G(\mathbf{x}_1,\mathbf{x}_1;t_1 - t_{1'})$$

Open problem

Find good approximation of G for correlation energy

Double ionizations potentials

Open question

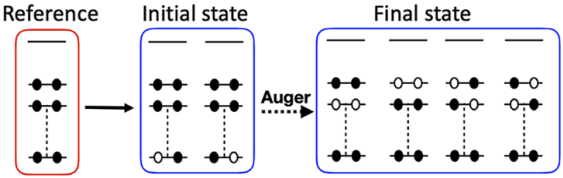
How to compute double ionization potentials?

Double ionizations potentials

Open question

How to compute double ionization potentials?

Auger-Meitner effect



Extracted from Jayadev *et al.* J. Chem. Phys. 158 064109 (2023)

Two-body Green's function

Definition

$$G_2(t_1 - t_{1'}, t_2 - t_{2'}, t_1 - t_2) = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}(1) \; \hat{\psi}(2) \hat{\psi}^\dagger(2') \hat{\psi}^\dagger(1') \right] \middle| \Psi_0^N \right\rangle$$

where $1 = (\mathbf{x}_1, t_1)$

One-body Green's function

$$G(t_1 - t_{1'}) = (-\mathrm{i}) \left\langle \Psi_0 \middle| \hat{T}\left[\hat{\psi}(1) \hat{\psi}^\dagger(1') \right] \middle| \Psi_0 \right\rangle .$$

Particle-particle channel

Electron-electron/hole-hole pair propagation

If $t_1 = t_2, t_{1'} = t_{2'}$, the time-dependence becomes $G_2(t_1 - t_{1'})$ and G_2 describes the propagation of two electrons or two holes.

Particle-particle channel

Electron-electron/hole-hole pair propagation

If $t_1 = t_2, t_{1'} = t_{2'}$, the time-dependence becomes $G_2(t_1 - t_{1'})$ and G_2 describes the propagation of two electrons or two holes.

Spectral representation

$$K(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_{1'}\mathbf{x}_{2'};\omega) = \sum_\nu \frac{L_\nu^{N+2}(\mathbf{x}_1\mathbf{x}_2)R_\nu^{N+2}(\mathbf{x}'_1\mathbf{x}'_2)}{\omega - (E_\nu^{N+2} - E_0^N) + \mathrm{i}\eta} - \sum_\nu \frac{L_\nu^{N-2}(\mathbf{x}'_1\mathbf{x}'_2)R_\nu^{N-2}(\mathbf{x}_1\mathbf{x}_2)}{\omega - (E_0^N - E_\nu^{N-2}) - \mathrm{i}\eta}$$

Double electron affinities **Double ionization potentials**

Electron-hole channel

Electron-hole pair propagation

If $t_1 = t_{1'}, t_2 = t_{2'}$, the time-dependence becomes $G_2(t_1 - t_2)$ and G_2 describes the propagation of an electron-hole pair.

Electron-hole channel

Electron-hole pair propagation

If $t_1 = t_{1'}, t_2 = t_{2'}$, the time-dependence becomes $G_2(t_1 - t_2)$ and G_2 describes the propagation of an electron-hole pair.

Spectral representation

$$L(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_{1'}\mathbf{x}_{2'};\omega) = \sum_{\nu>0} \frac{L^N_\nu(\mathbf{x}_2\mathbf{x}_{2'})R^N_\nu(\mathbf{x}_1\mathbf{x}_{1'})}{\omega - (E^N_\nu - E^N_0) + \mathrm{i}\eta} - \sum_{\nu>0} \frac{L^N_\nu(\mathbf{x}_2\mathbf{x}_{2'})R^N_\nu(\mathbf{x}_1\mathbf{x}_{1'})}{\omega - (E^N_0 - E^N_\nu) - \mathrm{i}\eta}$$

N-th Excitation energies

Electron-hole channel

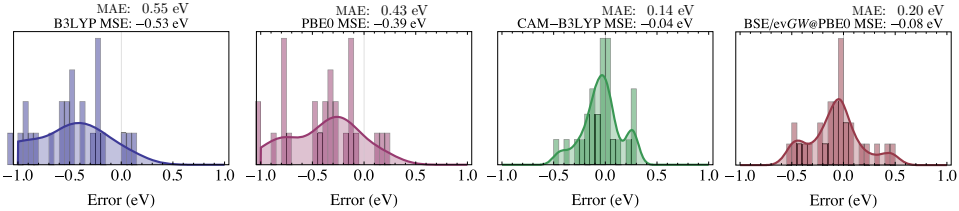
Eigenvalue problem

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + \Xi^{\text{eh}}_{ia,jb}$$
$$B_{ia,bj} = \Xi^{\text{eh}}_{ia,bj}$$

This is the same eigenvalue problem as in TD-DFT but with a different kernel!

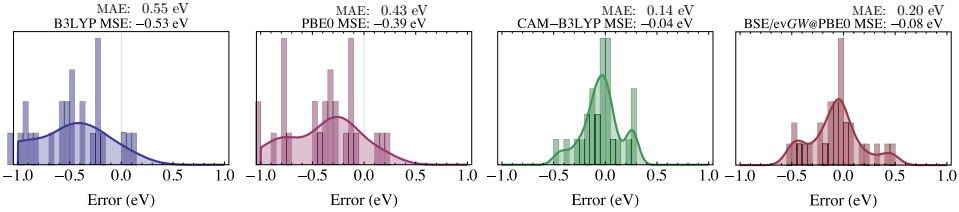
Errors w.r.t. CCSDT for 30 charge-transfer excitation of 17 medium molecules in the cc-pVTZ basis set



Extracted from Loos *el al.* J. Chem. Theory Comput. 17 3666 (2021)

Charge transfer and TDDFT

Errors w.r.t. CCSDT for 30 charge-transfer excitation of 17 medium molecules in the cc-pVTZ basis set



Extracted from Loos *el al.* J. Chem. Theory Comput. 17 3666 (2021)

Analytical gradients for *GW* and BSE are finally available!

J. Tölle J. Phys. Chem. Lett. 16 3672 (2025)

Particle-particle channel

Eigenvalue problem

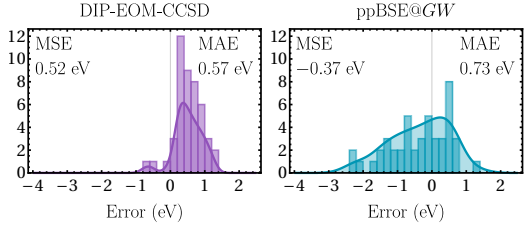
$$\begin{pmatrix} \boldsymbol{C} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{D} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

$$\begin{aligned} C_{ab,cd} &= (\epsilon_a + \epsilon_b)\delta_{ac}\delta_{bd} + \Xi^{\text{pp}}_{ab,cd} \\ B_{ab,ij} &= \Xi^{\text{pp}}_{ab,ij} \\ D_{ij,kl} &= -(\epsilon_i + \epsilon_j)\delta_{ik}\delta_{jl} + \Xi^{\text{pp}}_{ij,kl} \end{aligned}$$

More details in Marie *et al.* J. Chem. Phys. 162, 134105 (2025)

Valence double ionization potentials

Error distribution (w.r.t. FCI) for 46 DIP of 23 small molecules in the aug-cc-pVTZ basis set



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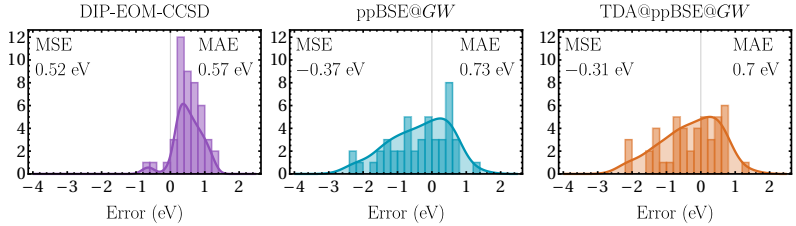

Tamm-Dancoff approximation

$$\begin{pmatrix} \boldsymbol{C} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{D} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \quad \rightarrow \quad \begin{aligned} \boldsymbol{CX} &= \omega \boldsymbol{X} \\ \boldsymbol{DY} &= -\omega \boldsymbol{Y} \end{aligned}$$

Conclusion

Conclusions

- Green's functions provide a natural framework to describe excited states and spectroscopy
- ppBSE brings quantitative improvements for double ionization
- Toward a *GW* description of Auger spectroscopy

Acknowledgements

- Pierre-François Loos (PhD advisor)
- Pina Romaniello
- Xavier Blase

Questions?