Bethe-Salpeter equation for the particle-particle propagator

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December 13, 2024

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

Two-body Green's function

Definition

$1 = (\mathbf{r}_1, \sigma_1, t_1)$

$$G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \left| \hat{T}[\ \hat{\psi}(1)\ \ \hat{\psi}(2)\ \ \hat{\psi}^\dagger(2')\ \ \hat{\psi}^\dagger(1')\ ] \right| \Psi_0^N \right\rangle$$

***N*-electron ground-state**

Field operators

Time ordering

- **Electron-hole pair propagation**

$$t_2, t_{2'} > t_1, t_{1'} \qquad G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}(2)\hat{\psi}^\dagger(2')\right] \hat{T}\left[\hat{\psi}(1)\hat{\psi}^\dagger(1')\right] \middle| \Psi_0^N \right\rangle$$

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$$t_2, t_{2'} > t_1, t_{1'} \qquad G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}(2)\hat{\psi}^\dagger(2')\right] \hat{T}\left[\hat{\psi}(1)\hat{\psi}^\dagger(1')\right] \middle| \Psi_0^N \right\rangle$$

- **Electron-electron pair propagation**

$$t_1, t_2 > t_{1'}, t_{2'} \qquad G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}(1)\hat{\psi}(2)\right] \hat{T}\left[\hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2')\right] \middle| \Psi_0^N \right\rangle$$

- **Hole-hole pair propagation**

$$t_{1'}, t_{2'} > t_1, t_2 \qquad G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2')\right] \hat{T}\left[\hat{\psi}(1)\hat{\psi}(2)\right] \middle| \Psi_0^N \right\rangle$$

Electron-hole channel

Electron-hole propagator

$$L(12;1'2') = -G_2(12;1'2') + G(11')G(22')$$

Lehman representation

$x_{1'} = (\mathbf{r}_{1'}, \sigma_{1'})$

$$L(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_{1'}\mathbf{x}_{2'};\omega) = \sum_{\nu>0} \frac{L_\nu^N(\mathbf{x}_2\mathbf{x}_{2'})R_\nu^N(\mathbf{x}_1\mathbf{x}_{1'})}{\omega - (E_\nu^N - E_0^N) + \mathrm{i}\eta} - \sum_{\nu>0} \frac{L_\nu^N(\mathbf{x}_2\mathbf{x}_{2'})R_\nu^N(\mathbf{x}_1\mathbf{x}_{1'})}{\omega - (E_0^N - E_\nu^N) - \mathrm{i}\eta}$$

N**-th Excitation energies**

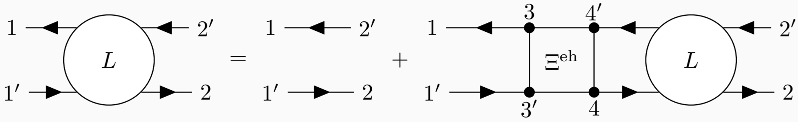
Electron-hole channel

Electron-hole Bethe-Salpeter equation

$$L(12;1'2') = L_0(12;1'2') + \int \mathrm{d}(3456)\, L_0(14;1'3)\, \Xi^{\mathrm{eh}}(36;45)\, L(52;62')$$

Independent particle propagator — **eh kernel**

where $L_0(12;1'2') = G(12')G(21')$ $\quad\quad \Xi^{\mathrm{eh}}(12;34) = \left.\dfrac{\delta\Sigma(13)}{\delta G(42)}\right|_{U=0}$



Electron-hole channel

Eigenvalue problem

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

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

$$B_{ia,bj} = \Xi^{\text{eh}}_{ia,bj}$$

Electron-hole channel

Eigenvalue problem

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

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

$$B_{ia,bj} = \Xi^{\text{eh}}_{ia,bj}$$

Kernels

$$\Xi^{\text{eh,RPA}}_{ia,jb} = \langle ib|aj\rangle \qquad \Xi^{\text{eh},GW}_{ia,jb} = \langle ib|aj\rangle - W_{ibja}(\omega = 0)$$

- Second-order kernel
- T-matrix kernel
- ...

Usual linear response

Schwinger relation

$$-G_2(12;1'2') + G(11')G(22') = \left.\frac{\delta G(11';[U])}{\delta\, U^{\text{eh}}(2'2)}\right|_{U=0} = L(12;1'2')$$

External potential

External potential

$$\hat{\mathcal{U}}(t_1) = \int \mathrm{d}(\mathbf{x}_1\mathbf{x}_{1'}t_1')\, \hat{\psi}^\dagger(\mathbf{x}_1) U^{\text{eh}}(11') \hat{\psi}(\mathbf{x}_{1'})$$

Pairing field linear response

Another external potential ...

$$\hat{\mathcal{U}}(t_1) = \frac{1}{2}\left(\int \mathrm{d}(\mathbf{x}_1\mathbf{x}_{1'}t_1')\,\hat{\psi}(\mathbf{x}_1)U^{\mathrm{hh}}(11')\hat{\psi}(\mathbf{x}_{1'}) + \int \mathrm{d}(\mathbf{x}_1\mathrm{d}\mathbf{x}_{1'}t_1')\;\hat{\psi}^\dagger(\mathbf{x}_{1'})\;U^{\mathrm{ee}}(11')\;\hat{\psi}^\dagger(\mathbf{x}_{1'})\right)$$

Non-number conserving

Pairing field linear response

Another external potential ...

$$\hat{\mathcal{U}}(t_1) = \frac{1}{2}\left(\int \mathrm{d}(\mathbf{x}_1\mathbf{x}_{1'}t_1')\,\hat{\psi}(\mathbf{x}_1)U^{\mathrm{hh}}(11')\hat{\psi}(\mathbf{x}_{1'}) + \int \mathrm{d}(\mathbf{x}_1\mathrm{d}\mathbf{x}_{1'}t_1')\;\hat{\psi}^{\dagger}(\mathbf{x}_{1'})\;U^{\mathrm{ee}}(11')\;\hat{\psi}^{\dagger}(\mathbf{x}_{1'})\right)$$

Non-number conserving

...leading to an alternative Schwinger relation

$$\frac{1}{2}\left(-G_2(12;1'2';[U]) + G^{\mathrm{hh}}(12;[U])G^{\mathrm{ee}}(2'1';[U])\right)\Bigg|_{U=0} = \frac{\delta G^{\mathrm{ee}}(1'2';[U])}{\delta U^{\mathrm{hh}}(12)}\Bigg|_{U=0} = K(12;1'2')$$

Description of a non-number conserving Hamiltonian

Anomalous propagators

$$G^{\mathrm{hh}}(11';[U]) = (-\mathrm{i})\,\langle\Psi_0|\hat{T}\left[\hat{\psi}(1)\hat{\psi}(1')\right]|\Psi_0\rangle \quad G^{\mathrm{ee}}(11';[U]) = (-\mathrm{i})\,\langle\Psi_0|\hat{T}\left[\hat{\psi}^\dagger(1)\hat{\psi}^\dagger(1')\right]|\Psi_0\rangle$$

Nambu formalism and the Gorkov propagator

$$\boldsymbol{G}(11') = (-i)\,\langle\Psi_0|\hat{T}\left[\begin{pmatrix}\hat{\psi}(1)\hat{\psi}^\dagger(1') & \hat{\psi}(1)\hat{\psi}(1') \\ \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(1') & \hat{\psi}^\dagger(1)\hat{\psi}(1')\end{pmatrix}\right]|\Psi_0\rangle = \begin{pmatrix}G^{\mathrm{he}}(11') & G^{\mathrm{hh}}(11') \\ G^{\mathrm{ee}}(11') & G^{\mathrm{eh}}(11')\end{pmatrix}.$$

Gorkov-Dyson equation

$$\boldsymbol{G}^{-1}(11') = \boldsymbol{G}_0^{-1}(11') - \begin{pmatrix}\Sigma^{\mathrm{he}}(11') & \Sigma^{\mathrm{hh}}(11') + U^{\mathrm{ee}}(11') \\ \Sigma^{\mathrm{ee}}(11') + U^{\mathrm{hh}}(11') & \Sigma^{\mathrm{eh}}(11')\end{pmatrix}$$

Particle-particle channel

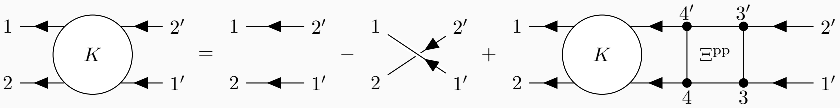
Particle-particle Bethe-Salpeter equation

$$K(12;1'2') = K_0(12;1'2') - \int d(3456)\, K(12;56)\, \Xi^{pp}(56;34)\, K_0(34;1'2')$$

Independent particle propagator

pp kernel

where $K_0(12;1'2') = \frac{1}{2}[G(21')G(12') - G(11')G(22')]$ $\quad \Xi^{pp}(56;34) = \left.\frac{\delta\Sigma^{ee}(34)}{\delta G^{ee}(56)}\right|_{U=0}$



Particle-particle channel

Lehman 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**

Particle-particle channel

Eigenvalue problem

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

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

Particle-particle channel

Eigenvalue problem

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

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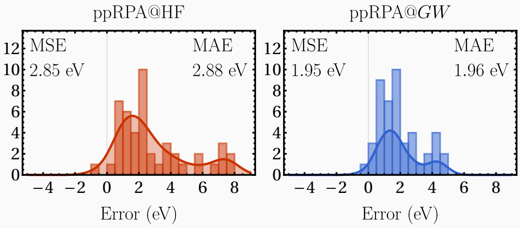
Kernels

$$\Xi^{\text{pp,RPA}}_{ij,kl} = \langle ij||kl\rangle \qquad \Xi^{\text{pp},GW}_{ij,kl} = W_{ijkl}(\omega = 0) - W_{ijlk}(\omega = 0)$$

- Second-order kernel
- T-matrix kernel
- ...

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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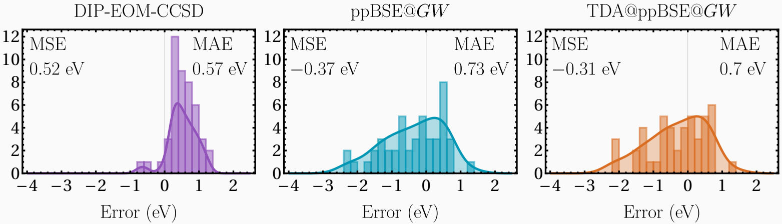

Valence double ionization potentials

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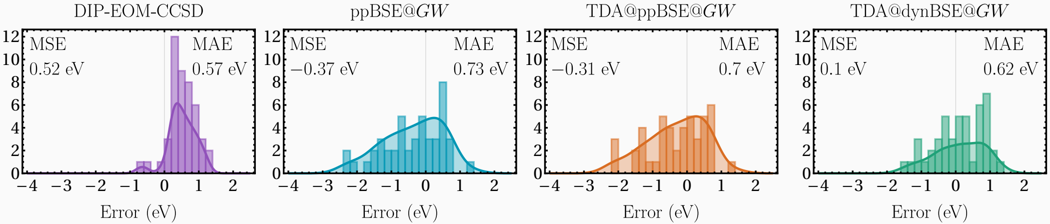
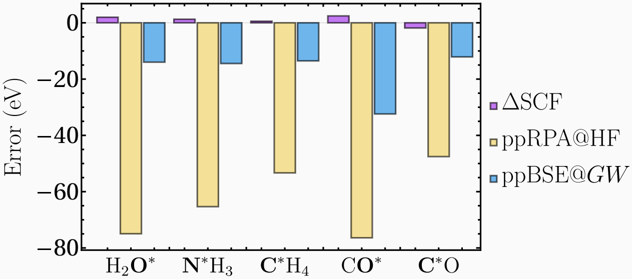


Sangalli *et al.* J. Chem. Phys. 158 (2011) 034115

Core double ionization potentials

Error with respect to CVS-FCI in the aug-cc-pCVTZ basis set



Conclusion and open questions

Conclusions

- Simple expression for the kernel of the particle-particle channel
- ppBSE brings quantitative improvements for double ionization
- More details in arXiv:2411.13167

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- ppBSE brings quantitative improvements for double ionization
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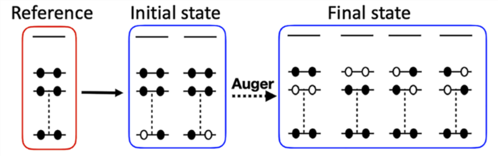
Open questions/problems

- Correlation energy through adiabatic connection
- Auger spectrum at the *GW* level



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

Questions?

Particle-particle Bethe-Salpeter equation

Derivation

$$K(12;1'2') = \left.\frac{\delta G^{\text{ee}}(1'2')}{\delta U^{\text{hh}}(12)}\right|_{U=0} \tag{1}$$

$$= G(31')\left.\frac{\delta (G^{-1})^{\text{ee}}(33')}{\delta U^{\text{hh}}(12)}\right|_{U=0} G(3'2') \tag{2}$$

$$= -G(31')\left.\frac{\delta U^{\text{hh}}(33')}{\delta U^{\text{hh}}(12)}\right|_{U=0} G(3'2') - G(31')\left.\frac{\delta \Sigma^{\text{ee}}(33')}{\delta U^{\text{hh}}(12)}\right|_{U=0} G(3'2') \tag{3}$$

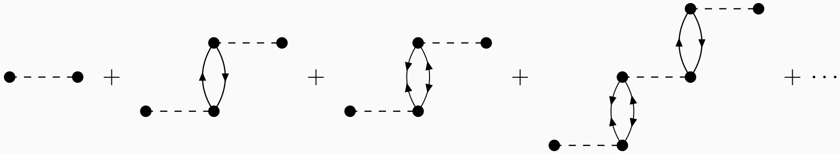
$$= K_0(12;1'2') - \left.\frac{\delta G^{\text{ee}}(44')}{\delta U^{\text{hh}}(12)}\right|_{U=0}\left.\frac{\delta \Sigma^{\text{ee}}(33')}{\delta G^{\text{ee}}(44')}\right|_{U=0} G(3'2')G(31') \tag{4}$$

Gorkov *GW*

Self-energy

$$\boldsymbol{\Sigma}(11') = \mathrm{i} \int \mathrm{d}(33') \begin{pmatrix} W(13';31')G^{\mathrm{he}}(33') & -W(13';31')G^{\mathrm{hh}}(33') \\ -W(31';13')G^{\mathrm{ee}}(33') & W(31';13')G^{\mathrm{eh}}(33') \end{pmatrix}$$

Screened interaction



GW kernel

eh *GW* kernel

$$\Xi^{\text{eh},GW}(12;1'2') = \mathrm{i}\,\frac{\delta\Sigma(11')}{\delta G(2'2)}\bigg|_{U=0} = -\,\frac{\delta\left[G(33')W(11';33')\right]}{\delta G(2'2)}\bigg|_{U=0}$$

$$= -W(11';2'2) - G(33')\,\frac{\delta W(11';33')}{\delta G(2'2)}\bigg|_{U=0}$$

pp *GW* kernel

$$\mathrm{i}\Xi^{\text{ee},GW}(11';22') = \mathrm{i}\,\frac{\delta\Sigma^{\text{ee}}(22')}{\delta G^{\text{ee}}(11')}\bigg|_{U=0} = \frac{\delta\left[G^{\text{ee}}(33')W(33';22')\right]}{\delta G^{\text{ee}}(11')}\bigg|_{U=0} = \frac{1}{2}\left[W(11';22') - W(11;2'2)\right]$$

Valence double ionization potentials

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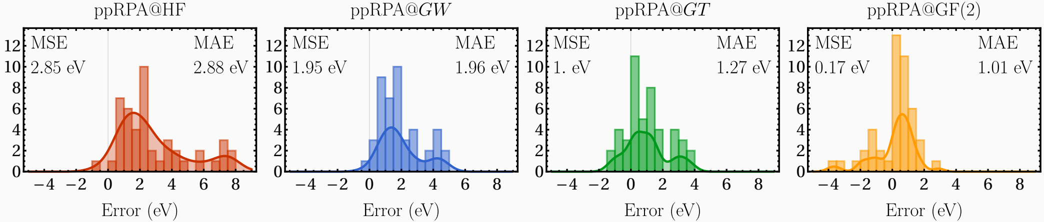

Alternative kernels

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