Anomalous propagators and the particle-particle correlation channel of many-body perturbation theory

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Definitions, Hedin's equations and usual approximations

One-body Green's function

Definition

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

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

Field operators

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

Charged excitations

Definition

$$G(11') = (-\mathrm{i}) \left\langle \Psi_0^N \middle| \hat{T} \left[\hat{\psi}(1) \hat{\psi}^\dagger(1') \right] \middle| \Psi_0^N \right\rangle$$

Lehmann representation

$x_1 = (\mathbf{r}_1, \sigma_1)$

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

S-th ionization potentials

S-th electron affinities

How to compute G?

The Dyson equation

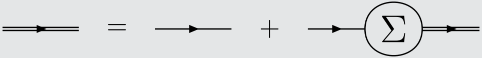
$$G(11') = G_0(11') + \int \mathrm{d}(22')\, G_0(12)\, \Sigma(22')\, G(2'1')$$

Self-energy

How to compute G?

The Dyson equation

$$G(11') = G_0(11') + \int \mathrm{d}(22')\, G_0(12)\Sigma(22')G(2'1')$$



How to compute G?

The Dyson equation

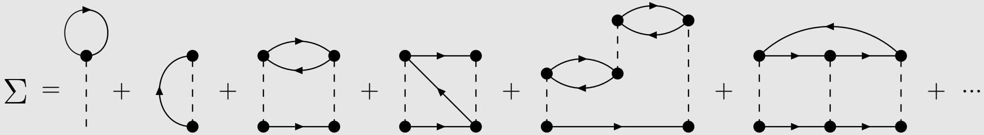
$$G(11') = G_0(11') + \int \mathrm{d}(22')\, G_0(12)\Sigma(22')G_0(2'1') + \int \mathrm{d}(22'33')\, G_0(12)\Sigma(22')G_0(2'3)\Sigma(33')G_0(3'1') + \dots$$

How to compute G?

The Dyson equation

$$G(11') = G_0(11') + \int \mathrm{d}(22')\, G_0(12)\Sigma(22')G(2'1')$$

An exact expression for the self-energy



Another exact formalism

Self-consistent set of equations

$$G(11') = G_0(11') + G_0(12)\Sigma(22')G(2'1')$$

$$\Sigma(11') = \Sigma_{\mathrm{H}}(11') + \mathrm{i}\int \mathrm{d}(22'33')\; V(12;2'3)G(2'3')\Gamma(3'3;1'2)$$

$$\Gamma(12;1'2') = \delta(12')\delta(1'2) + \int \mathrm{d}(33'44')\,\frac{\delta\Sigma(11')}{\delta G(33')}G(34)G(4'3')\Gamma(42;4'2')$$

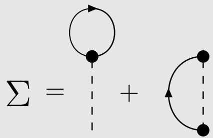
A few iterations

Initial condition

$$\Sigma^{(0)}(11') = 0 \qquad \Rightarrow \qquad \frac{\delta\Sigma^{(0)}(11')}{\delta G(33')} = 0$$

First iteration

$$\Gamma^{(1)}(12;1'2') = \delta(12')\delta(1'2') \qquad \Sigma^{(1)}(11') = \Sigma_{\mathsf{H}}(11') + \mathrm{i}\int \mathrm{d}(22')\ V(12;2'1')G(2'2)$$



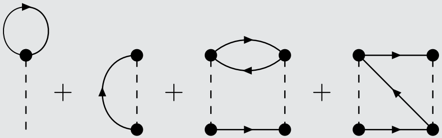
A few iterations

Second iteration

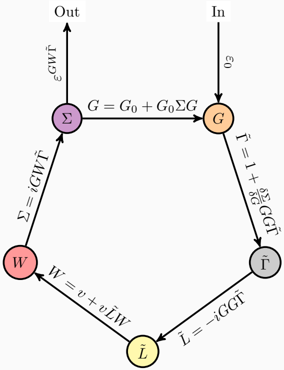
$$\frac{\delta\Sigma^{(1)}(11')}{\delta G(33')} = V(13';31') - V(13';1'3) = \bar{V}(13';31')$$

$$\Gamma^{(2)}(12;1'2') = \delta(12')\delta(1'2) + \int \mathrm{d}(33'44')\, \frac{\delta\Sigma^{(1)}(11')}{\delta G(33')} G(34)G(4'3')\Gamma^{(1)}(42;4'2')$$

$$\Sigma^{(2)}(11') = \Sigma_{\mathsf{Hx}}(11') + \mathrm{i}\int \mathrm{d}(22'33'44')\;\; V(12;2'3)G(2'3')\bar{V}(3'4';41')G(42)G(34)$$

$\Sigma =$ 

Hedin's Pentagon



Hedin, Phys Rev 139 (1965) A796

The wonderful equations of Hedin

$$G(11') = G_0(11') + \int G_0(12)\Sigma(22')G(2'1')\,\mathrm{d}(34)$$

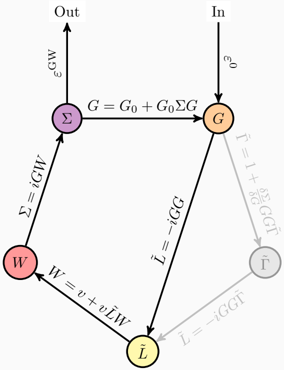
$$\underbrace{\tilde{\Gamma}(12;1'2')}_{\text{vertex}} = \delta(12')\delta(1'2) + \int \frac{\delta\Sigma_{\text{xc}}(11')}{\delta G(33')} G(34)G(4'3')\tilde{\Gamma}(42;4'2')$$

$$\underbrace{\tilde{L}(12;1'2')}_{\text{polarizability}} = -\mathrm{i}\int G(13)G(3'1')\tilde{\Gamma}(32;3'2')\,\mathrm{d}(33')$$

$$\underbrace{W(12;1'2')}_{\text{screening}} = V(12;1'2') + \int W(14;1'4')\tilde{L}(3'4';34)V(23;2'3')$$

$$\underbrace{\Sigma_{\text{xc}}(12)}_{\text{self-energy}} = \mathrm{i}\int G(33')W(12';32)\tilde{\Gamma}(3'2;1'2')\,\mathrm{d}(22'33')$$

Hedin's Square



Hedin, Phys Rev 139 (1965) A796

The *GW* approximation

$$G(11') = G_0(11') + \int G_0(12)\Sigma(22')G(2'1')\,\mathrm{d}(34)$$

$$\underbrace{\tilde{\Gamma}(12;1'2')}_{\text{vertex}} = \delta(12')\delta(1'2)$$

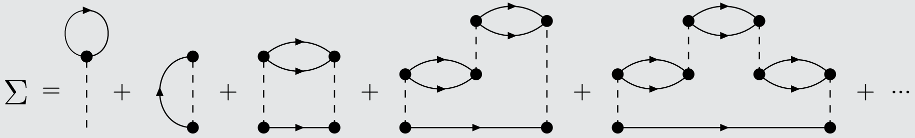
$$\underbrace{\tilde{L}(12;1'2')}_{\text{polarizability}} = -\mathrm{i}G(12')G(21')$$

$$\underbrace{W(12;1'2')}_{\text{screening}} = V(12;1'2') + \int W(14;1'4')\tilde{L}(3'4';34)V(23;2'3')$$

$$\underbrace{\Sigma_{\text{xc}}(12)}_{\text{self-energy}} = \mathrm{i}\int G(32')W(12';31')\,\mathrm{d}(2'3)$$

Diagrammatic content of the *GW* approximation

The *GW* resummation



Diagrammatic content of the GW approximation

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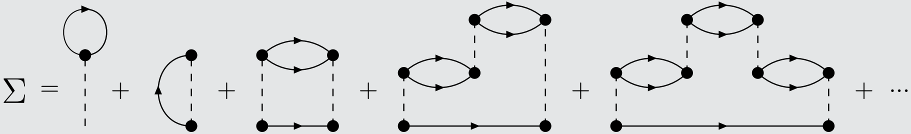
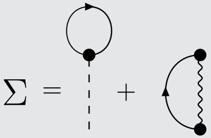
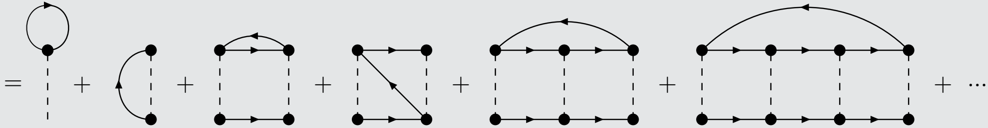




Some other resummation-based self-energies

Particle-particle *T*-matrix

$\Sigma =$ 

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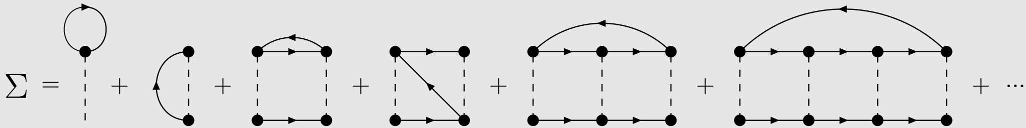
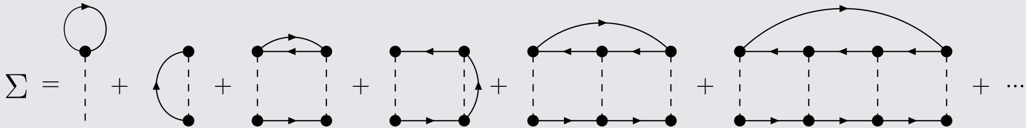


Electron-hole T-matrix



Romaniello, Bechstedt and Reining, Phys. Rev. B 85 (2012) 155131

Some other resummation-based self-energies

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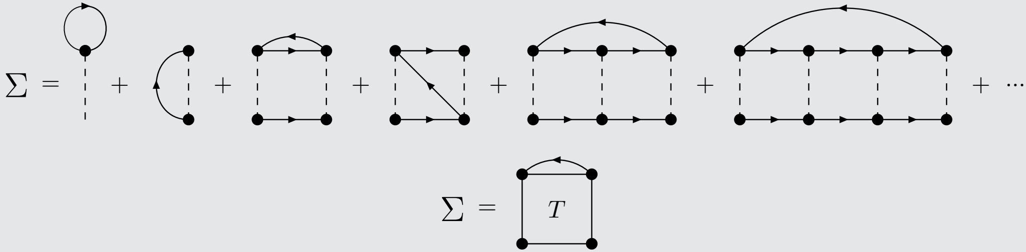
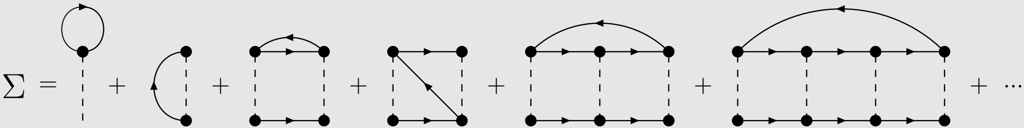
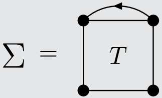


What's missing with respect to the *GW* self-energy?

Some other resummation-based self-energies

Particle-particle T-matrix



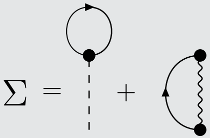


What's missing with respect to the GW self-energy?

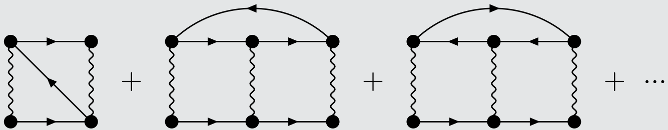
A systematic way to go beyond!

Vertex corrections to the GW self-energy

Zeroth iteration



First iteration



Mejuto-Zaera and Vlček, Phys. Rev. B 106 (2022) 165129

An alternative closed set of equations for G

Key step of the derivation

Self-energy and equation of motion

$$\Sigma(11') = -\mathrm{i} \int \mathrm{d}(33'44')\, V(13;4'3')\; G_2(4'3';43)\; G^{-1}(41')$$

Two-body Green's function

Key step of the derivation

Self-energy and equation of motion

$$\Sigma(11') = -\mathrm{i} \int \mathrm{d}(33'44')\, V(13;4'3')\, G_2(4'3';43)\, G^{-1}(41')$$

Two-body Green's function

The Schwinger relation

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

External potential

Key step of the derivation

Self-energy and equation of motion

$$\Sigma(11') = -\mathrm{i} \int \mathrm{d}(33'44')\, V(13;4'3')\; G_2(4'3';43)\; G^{-1}(41')$$

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

External potential

The external potential

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

Alternative Schwinger

Another external potential ...

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

Alternative Schwinger

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

...leading to an alternative Schwinger relation

Anomalous propagator

$$G_2(12;1'2') = -2\,\frac{\delta\, G^{\mathrm{ee}}(1'2')}{\delta U^{\mathrm{hh}}(12)}\bigg|_{U=0}$$

Description of a non-number conserving Hamiltonian

Anomalous propagators

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

Description of a non-number conserving Hamiltonian

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Nambu formalism and the Gorkov propagator

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

Description of a non-number conserving Hamiltonian

Anomalous propagators

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

Nambu formalism and the Gorkov propagator

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

Strategy

Derive a closed set of equations for the Gorkov propagator and then take the number-conserving limit.

The particle-particle Hedin's equations

A new set of equations

$$G(12) = G_0(12) + \int G_0(13)\Sigma(34)G(42)\,\mathrm{d}(34)$$

$$\tilde{\Gamma}(12;1'2') = \frac{1}{2}\left(\delta(1'2)\delta(2'1) - \delta(1'1)\delta(2'2)\right) - \left.\frac{\delta\Sigma_{\mathrm{c}}^{\mathrm{ee}}(1'2')}{\delta G^{\mathrm{ee}}(33')}\right|_{U=0} G(43)G(4'3')\tilde{\Gamma}(12;44')$$

$$\tilde{K}(12;1'2') = \mathrm{i}G(31')G(3'2')\tilde{\Gamma}(12;33')$$

$$T(12;1'2') = -\bar{V}(12;1'2') - T(12;33')\tilde{K}(33';44')\bar{V}(44';1'2')$$

$$\Sigma(11') = \mathrm{i}G(2'2)T(12;33')\tilde{\Gamma}(33';2'1')$$

The particle-particle vertex

The T-matrix as a first approximation

$$
\begin{aligned}
G(12) &= G_0(12) + \int G_0(13)\Sigma(34)G(42)\,\mathrm{d}(34) \\
\tilde{\Gamma}(12;1'2') &= \frac{1}{2}\left(\delta(1'2)\delta(2'1) - \delta(1'1)\delta(2'2)\right) \\
\tilde{K}(12;1'2') &= \frac{\mathrm{i}}{2}\left(G(12')G(21') - G(22')G(11')\right) \\
T(12;1'2') &= -\bar{V}(12;1'2') - T(12;33')\tilde{K}(33';44')\bar{V}(44';1'2') \\
\Sigma(11') &= \mathrm{i}G(2'2)T(12;1'2')
\end{aligned}
$$

The particle-particle vertex

The T-matrix as a first approximation

$$G(12) = G_0(12) + \int G_0(13)\Sigma(34)G(42)\,\mathrm{d}(34)$$

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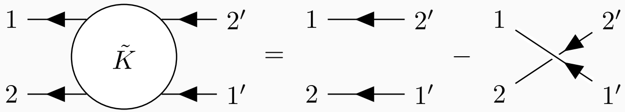
$$\tilde{K}(12;1'2') = \frac{\mathrm{i}}{2}\left(G(12')G(21') - G(22')G(11')\right)$$

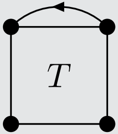
$$T(12;1'2') = -\bar{V}(12;1'2') - T(12;33')\tilde{K}(33';44')\bar{V}(44';1'2')$$

$$\Sigma(11') = \mathrm{i}G(2'2)T(12;1'2')$$



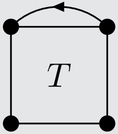
Vertex corrections to the *GT* self-energy

Zeroth iteration

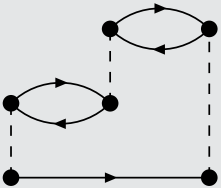
$$\Sigma =$$ 

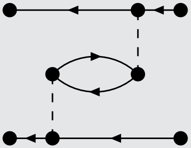
Vertex corrections to the GT self-energy

Zeroth iteration

$\Sigma =$ 

Second iteration: outer and inner corrections



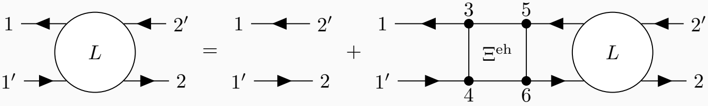


The particle-particle Bethe-Salpeter equation

Two-body Bethe-Salpeter equations

The electron-hole Bethe-Salpeter equation

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



Two-body Bethe-Salpeter equations

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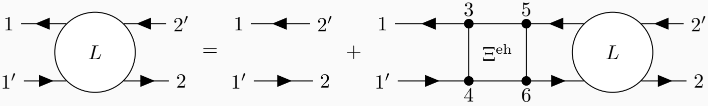
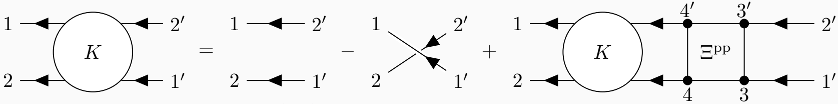


The particle-particle Bethe-Salpeter equation

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



What's the difference?

The two kernels

$$\Xi^{\text{eh}}(12;34) = \left.\frac{\delta\Sigma^{\text{eh}}(13)}{\delta G^{\text{eh}}(42)}\right|_{U=0}$$

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$$\Xi^{\mathsf{eh}}(12;34) = \left.\frac{\delta\Sigma^{\mathsf{eh}}(13)}{\delta G^{\mathsf{eh}}(42)}\right|_{U=0}$$

$$\int \mathrm{d}(3'44')\, G(24)\Xi^{\mathsf{pp}}(34;3'4')K(3'4';1'2') = \int \mathrm{d}(3'44')\, G(41')\Xi^{\mathsf{eh}}(34';43')L(3'2;4'2')$$

Csanak, Taylor and Yaris, Adv. Atom. Mol. Phys. 7 (1971) 287-361

What's the difference?

The two kernels

$$\Xi^{\text{eh}}(12;34) = \left.\frac{\delta\Sigma^{\text{eh}}(13)}{\delta G^{\text{eh}}(42)}\right|_{U=0}$$

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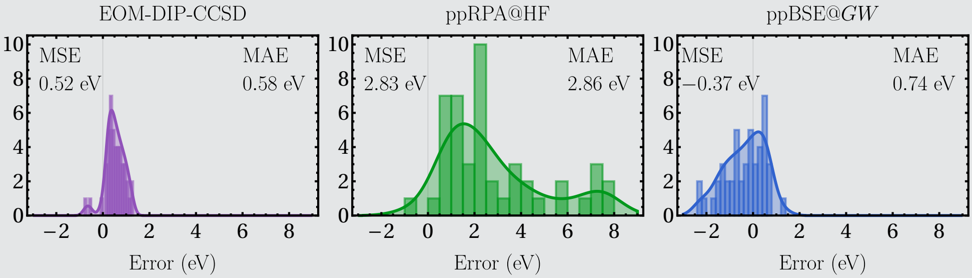
Csanak, Taylor and Yaris, Adv. Atom. Mol. Phys. 7 (1971) 287-361

A new expression for the particle-particle kernel

$$\Xi^{\text{pp}}(12;34) = \left.\frac{\delta\Sigma^{\text{ee}}(34)}{\delta G^{\text{ee}}(12)}\right|_{U=0}$$

Valence double ionization potentials

Error distribution for 46 DIP of 23 small molecules



Conclusion and perspectives

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- A set of equations has been derived for the one-body propagator
- The pp T-matrix self-energy has no second-order term and the third order term might be really expensive
- Can we couple W and T thanks to the Nambu formalism?

Conclusion and perspectives

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- A set of equations has been derived for the one-body propagator
- The pp T-matrix self-energy has no second-order term and the third order term might be really expensive
- Can we couple W and T thanks to the Nambu formalism?

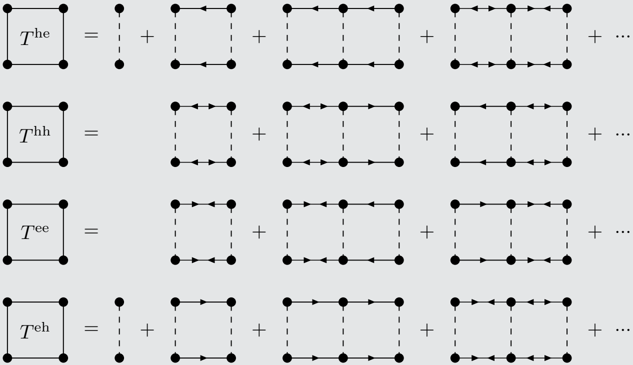
Anomalous propagators are also useful for two-body equations

- Simple expression for the kernel of the particle-particle channel!
- Accuracy of the particle-particle Bethe-Salpeter for double ionization?
- “Spin-flip-like” strategy for neutral excited states?

Questions?

Gorkov-Hedin equations: effective interaction

Generalized T-matrix



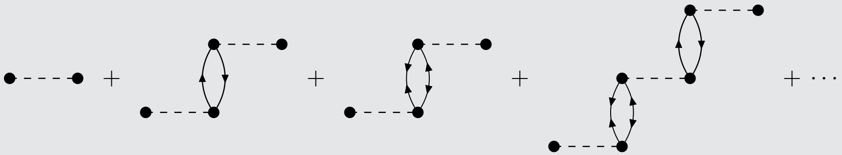
Bozek, Phys Rev C 65 (2002) 034327

Gorkov *GW*

Self-energy

$$\boldsymbol{\Sigma}(11') = \mathrm{i} \int \mathrm{d}(33') \begin{pmatrix} W(13';31')G^{\mathrm{he}}(33') & -W(13';31')G^{\mathrm{hh}}(33') \\ -W(31';13')G^{\mathrm{ee}}(33') & W(31';13')G^{\mathrm{eh}}(33') \end{pmatrix} \quad (1)$$

Screened interaction



Lehman representations

Electron-hole propagator

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

Particle-particle interaction

$$K(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_{1'}\mathbf{x}_{2'};\omega) = \sum_{\nu} \frac{L_\nu^{N+2}(\mathbf{x}_1\mathbf{x}_2)R_\nu^{N+2}(\mathbf{x}_1'\mathbf{x}_2')}{\omega - (E_\nu^{N+2} - E_0^N - \mathrm{i}\eta)} - \sum_{\nu} \frac{L_\nu^{N-2}(\mathbf{x}_1'\mathbf{x}_2')R_\nu^{N-2}(\mathbf{x}_1\mathbf{x}_2)}{\omega - (E_0^N - E_\nu^{N-2} + \mathrm{i}\eta)} \tag{3}$$

Particle-hole and particle-particle RPA eigenvalue problem

phRPA

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}, \tag{4}$$

$$\begin{aligned} A^{\text{RPA}}_{ia,bj} &= (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + \langle ib|aj \rangle \\ B^{\text{RPA}}_{ia,bj} &= \langle ij|ab \rangle \end{aligned} \tag{5}$$

ppRPA

$$\begin{pmatrix} \boldsymbol{C} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{D} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}, \tag{6}$$

$$\begin{aligned} C^{\text{RPA}}_{ab,cd} &= (\epsilon_a + \epsilon_b)\delta_{ac}\delta_{bd} + \langle ab||cd \rangle \\ B^{\text{RPA}}_{ab,ij} &= \langle ab||ij \rangle \\ D^{\text{RPA}}_{ij,kl} &= -(\epsilon_i + \epsilon_j)\delta_{ik}\delta_{jl} + \langle ij||kl \rangle \end{aligned} \tag{7}$$