Particle-particle Bethe-Salpeter equation and Parquet theory

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The two-body Green's function

$$G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}[\overbrace{\hat{\psi}(1)}^{1=(\mathbf{x}_1,t_1)} \hat{\psi}(2) \hat{\psi}^\dagger(2') \hat{\psi}^\dagger(1')] \middle| \underbrace{\Psi_0^N}_{\text{Ground-state wave function}} \right\rangle$$

- If $t_2 = t_{2'}, t_1 = t_{1'}$, G_2 describes the propagation of an electron-hole pair
- If $t_1 = t_2, t_{1'} = t_{2'}$, G_2 describes the propagation of an electron-electron pair or a hole-hole pair

Spectral representations

- Electron-hole propagator

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

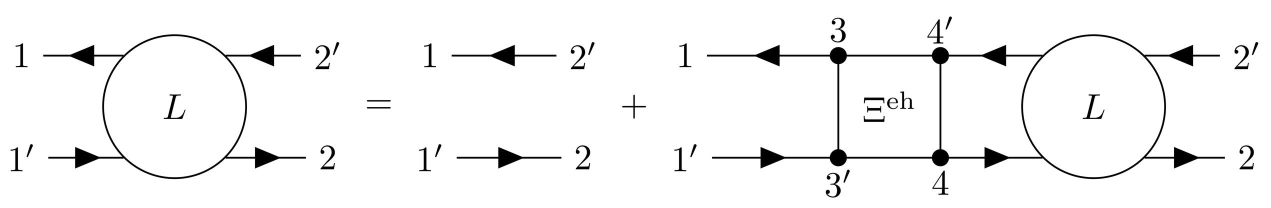
- Particle-particle propagator

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

Electron-hole Bethe-Salpeter equation

The electron-hole propagator can be expressed as

$$L(12;1'2') = G(12')G(21') + G(13)G(3'1')\Xi^{\text{eh}}(34;3'4')L(4'2;42')$$



G. Strinati Riv. Nuovo Cimento 11, 186 (1988).

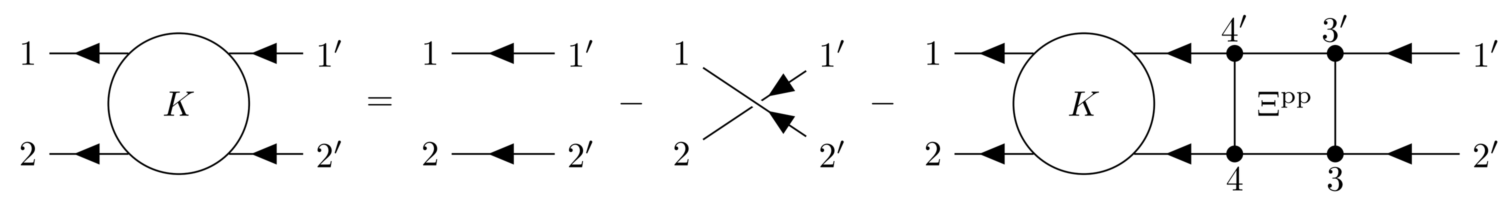
This equation can be solved by diagonalizing the following matrix

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \qquad \begin{aligned} A_{ia,jb} &= (\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + \Xi^{\text{eh}}_{ia,jb}(\omega = 0) \\ B_{ia,bj} &= \Xi^{\text{eh}}_{ia,bj}(\omega = 0) \end{aligned}$$

Particle-particle Bethe-Salpeter equation

The particle-particle propagator can be expressed as

$$K(12;1'2') = \frac{1}{2}\left[G(11')G(22') - G(21')G(12')\right] - K(12;44')\Xi^{\text{pp}}(44';33')G(31')G(3'2')$$

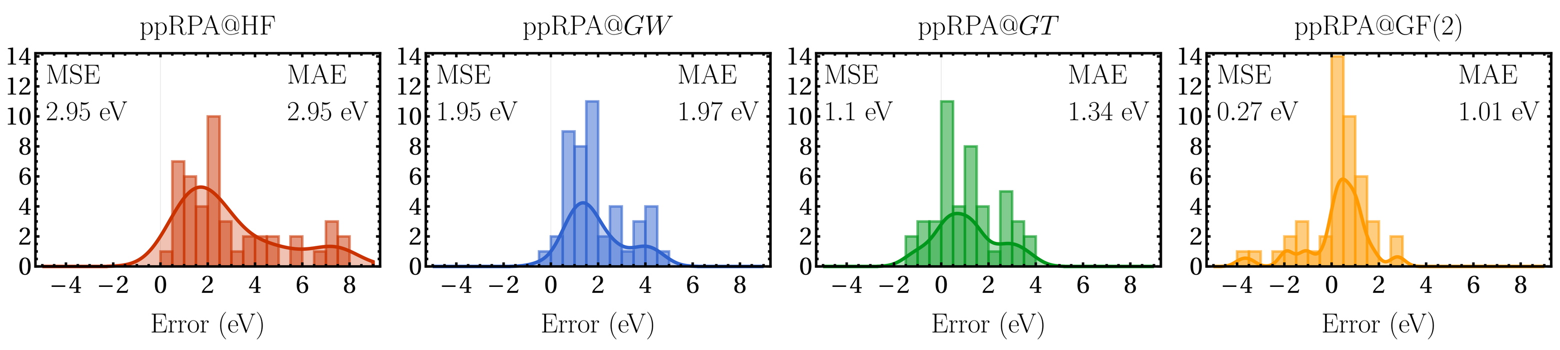


Marie, Romaniello, Blase and Loos J. Chem. Phys. 162, 134105 (2025).

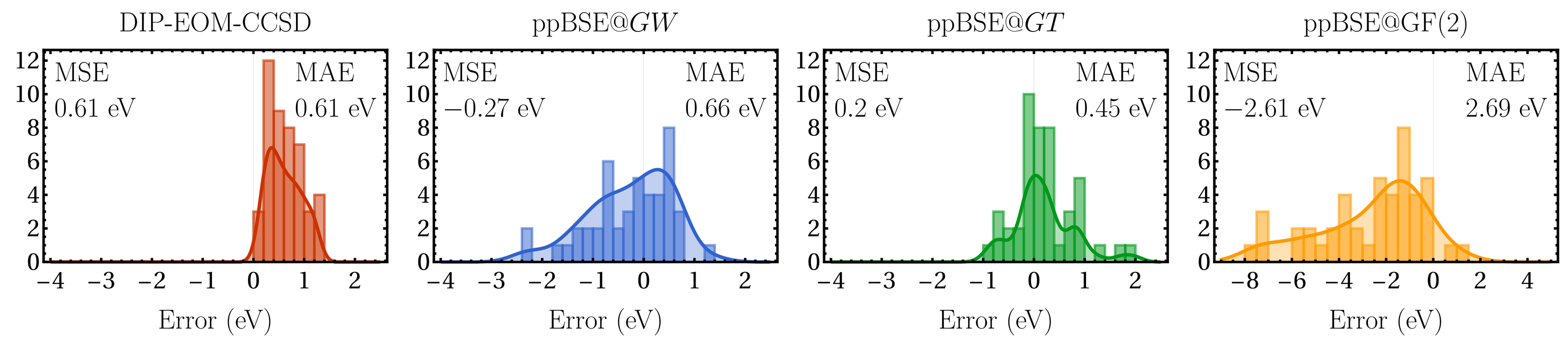
This equation can be solved by diagonalizing the following matrix

$$\begin{pmatrix} \boldsymbol{C} & \boldsymbol{B} \\ \boldsymbol{B}^\dagger & \boldsymbol{D} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \qquad \begin{aligned} C_{ab,cd} &= (\epsilon_a + \epsilon_b)\delta_{ac}\delta_{bd} + \Xi^{\text{pp}}_{ab,cd}(\omega = 0) \\ B_{ab,ij} &= \Xi^{\text{pp}}_{ab,ij}(\omega = 0) \\ D_{ij,kl} &= -(\epsilon_i + \epsilon_j)\delta_{ik}\delta_{jl} + \Xi^{\text{pp}}_{ij,kl}(\omega = 0) \end{aligned}$$

Influence of one-body energies on DIP

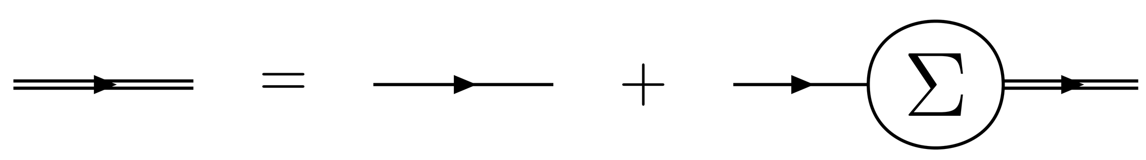


Influence of the kernel on DIP

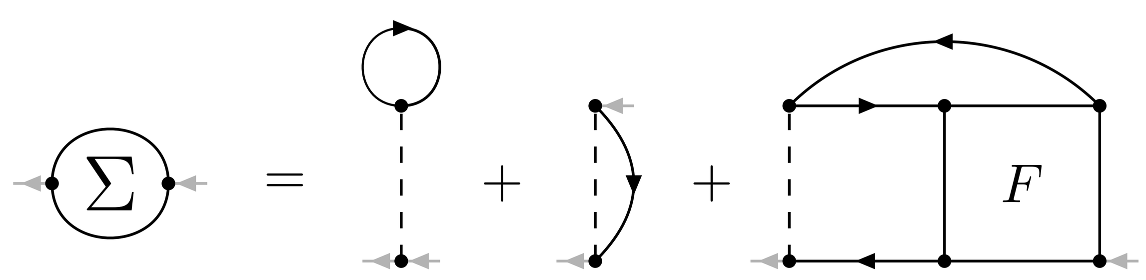


Self-energy

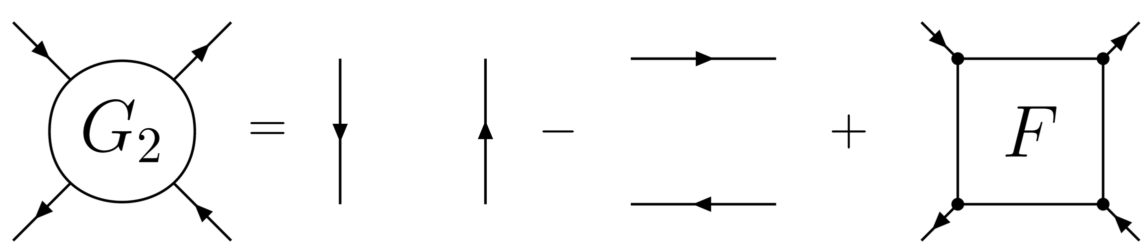
The one-body Green's function is computed through the Dyson equation



where the self-energy can be written as

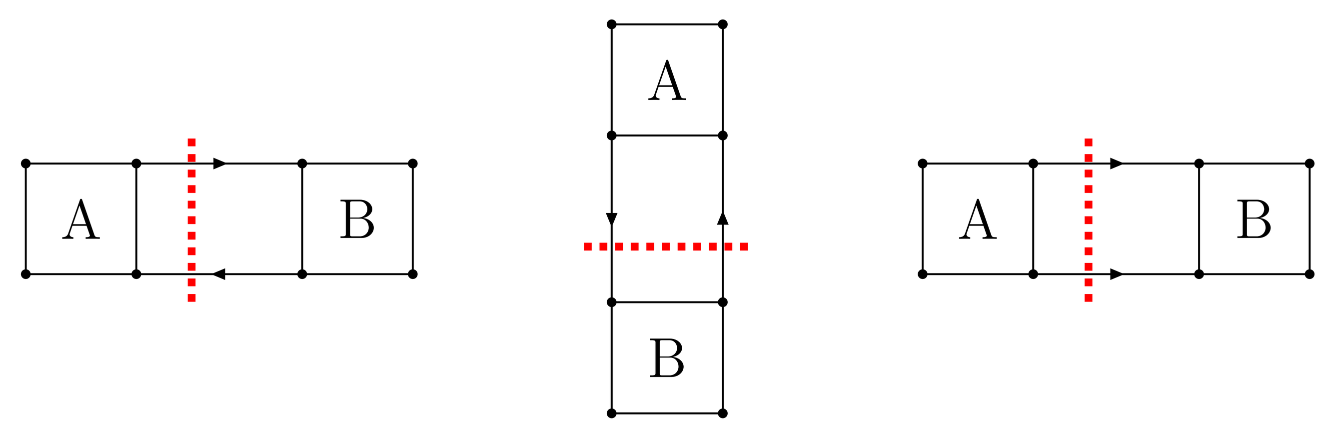


in terms of the two-body vertex defined as



Two-particle reducibility

There are three different ways for a two-particle diagram to be reducible



so the two-body vertex can be separated as

$$F(12;34) = \Lambda(12;34) + \Phi^{\text{eh}}(12;34) + \Phi^{\overline{\text{eh}}}(12;34) + \Phi^{\text{pp}}(12;34)$$

in terms of the irreducible vertex Λ and the reducible ones that can be expressed as

$$\Phi^{\text{eh}}(12;34) = \Gamma^{\text{eh}}(13';31')L(1'2';3'4')\Gamma^{\text{eh}}(4'2;2'4) = -\Phi^{\overline{\text{eh}}}(12;43)$$

$$\Phi^{\text{pp}}(12;34) = -\frac{1}{2}\Gamma^{\text{pp}}(12;1'2')K(1'2';3'4')\Gamma^{\text{pp}}(3'4';34)$$

where $\Gamma^{\text{eh/pp}}(12;34) = \Lambda(12;34) + \Phi^{\overline{\text{eh}}}(12;34) + \Phi^{\text{pp/eh}}(12;34)$

The Parquet approximation

- Λ needs to be approximated: its lowest-order term is the antisymmetric Coulomb interaction
- This leads to a self-energy exact up to fourth order
- Parquet equations couples the electron-hole and particle-particle Bethe-Salpeter equations with the one-body Dyson equation

Parquet in practice

- At the first iteration the ionization potentials are greatly underestimated.
- These IPs are then renormalized through self-consistency.
- **How to reach convergence for the solution of this non-linear set of equations?**

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