DOUBLE EXCITATIONS IN FINITE SYSTEMS

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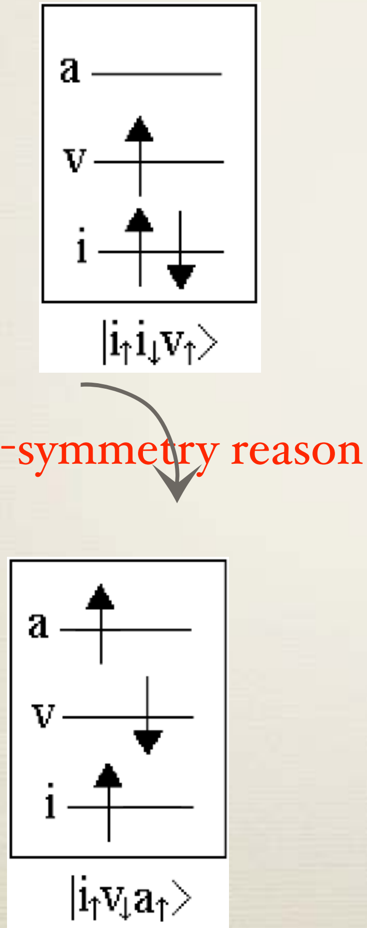
Outline

- Excitation energies in TDDFT: double excitations...problematic
- Double excitations using BSE
- Application to simple models
- From BSE back to TDDFT
- Conclusions

Double excitations

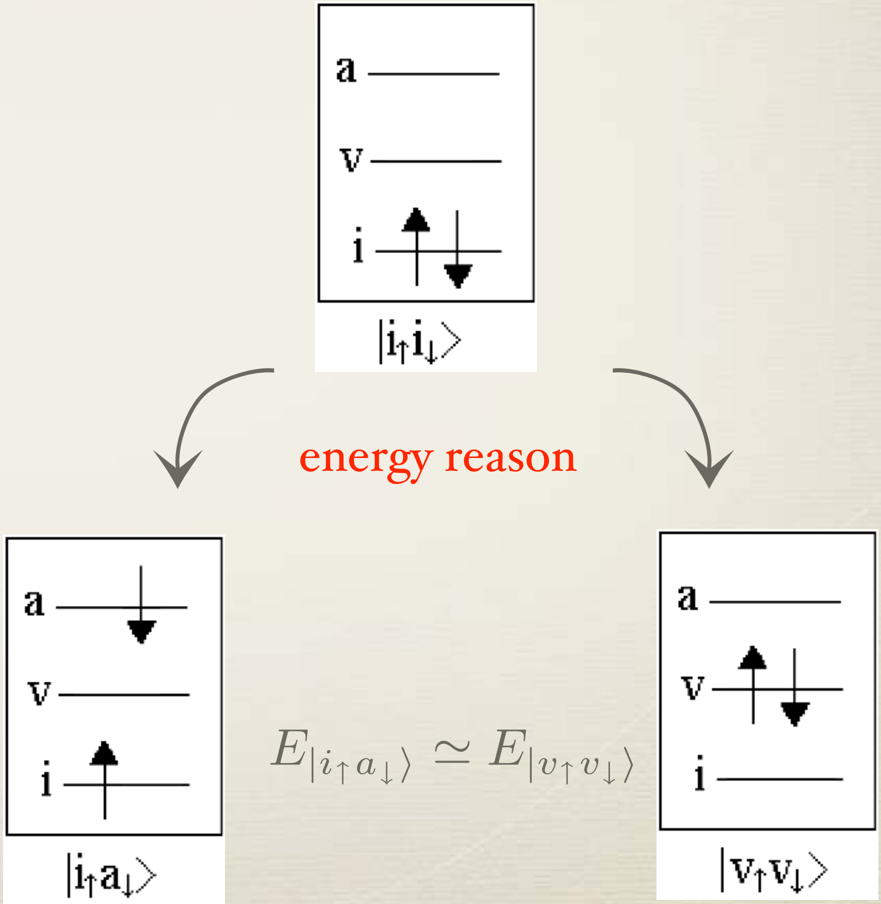
- Electron excitations in one-electron picture

- open-shell



spin-symmetry reason

- closed-shell



energy reason

$E_{|i_\uparrow a_\downarrow\rangle} \simeq E_{|v_\uparrow v_\downarrow\rangle}$

M. E. Casida *et al.*, Lect. Notes Phys., 706, 243-257 (2006), R. J. Cave *et al.*, Chem. Phys. Lett., 389, 39 (2004)

Excitation energies in TDDFT

- Dyson-like response equation

$$\chi(x_1,x_2,\omega) = \chi_s(x_1,x_2,\omega)+\chi_s(x_1,x_3,\omega)\left[\frac{1}{|x_3-x_4|}+f_{xc}(x_3,x_4,\omega)\right]\chi(x_4,x_2,\omega)$$

projection in transition space

- Casida's equations

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}$$

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ab}\delta_{ij}(\epsilon_{a\sigma}-\epsilon_{i\tau}) + K_{ia\sigma,jb\tau}$$

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}$$

$$K_{ia\sigma,jb\tau} = \int\int \psi^*_{i\sigma}(\mathbf{r})\psi_{a\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}+f^{\sigma\tau}_{xc}(\mathbf{r},\mathbf{r}',\omega)\right]\psi^*_{b\tau}(\mathbf{r}')\psi_{j\tau}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Excitation energies in TDDFT

- Dyson-like response equation

$$\chi(x_1,x_2,\omega) = \chi_s(x_1,x_2,\omega)+\chi_s(x_1,x_3,\omega)\left[\frac{1}{|x_3-x_4|}+f_{xc}(x_3,x_4,\omega)\right]\chi(x_4,x_2,\omega)$$

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ALDA

- only singly-excited configurations
- n. eigenvalues=n. single-excitations

Reduced space → ω-dependence

- $m \times m$ eigenvalue problem $\longrightarrow$ lower-dimensional one

$$\begin{pmatrix} S & C_1 \\ C_2 & D \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \omega \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} \xrightarrow{e_2 = (\omega - D)^{-1} C_2 e_1} [S + \underbrace{C_1 (\omega - D)^{-1} C_2}_{K(\omega)}] e_1 = \omega e_1$$

- Many-body hamiltonian ⟶ "one-particle" hamiltonian

- Multiple-excitation space ⟶ single-excitation space
  (D in double excitation space, S in single-excitation space (Casida's within ALDA))

- Four-point BSE ⟶ two-point TDDFT ($f_{xc}(\omega)$ even if the BSE kernel can be static)

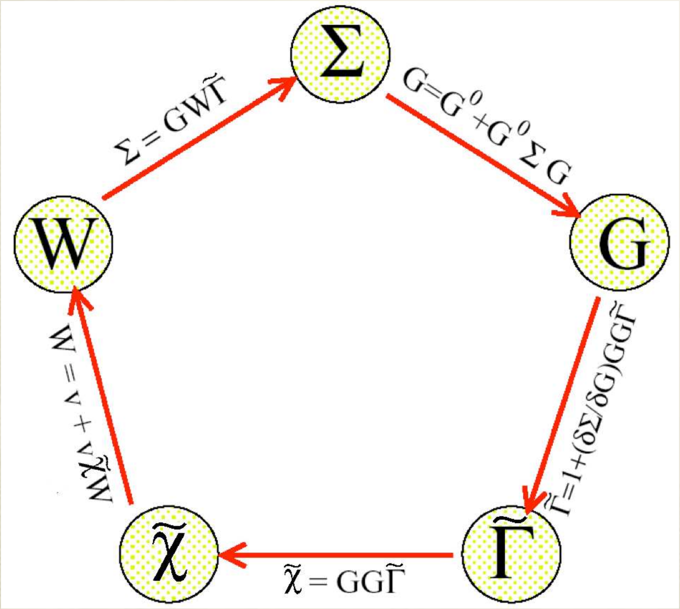
Bethe-Salpeter equation

$$L(1,2,1',2') = L_0(1,2,1',2') + L_0(1,4,1',3)\Xi(3,5,4,6)L(6,2,5,2')$$

$$L_0(1,2,1',2') = -iG(1,2')G(2,1')$$

$$\Xi(3,5,4,6) = \delta(3,4)\delta(5,6)v(3,6) + i\frac{\delta\Sigma(3,4)}{\delta G(6,5)}$$

$$\chi(1,2) = L(1,2,1,2)$$



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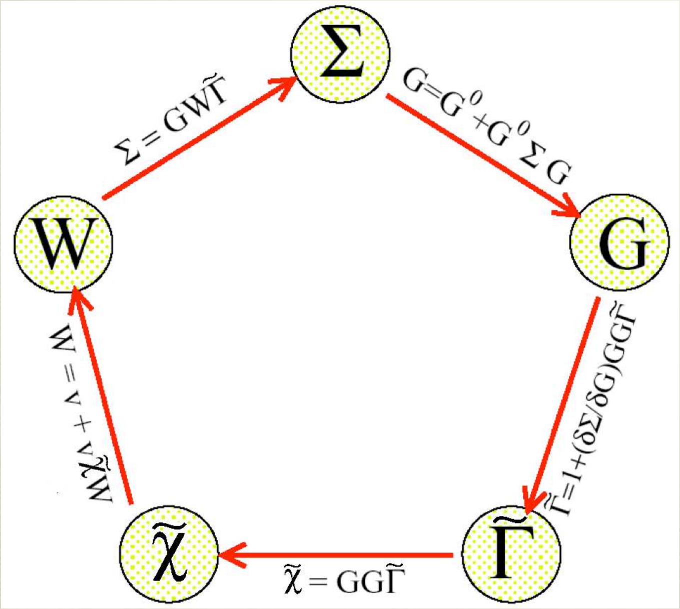


approximations

$$\Sigma = GW$$

$$\frac{\delta\Sigma}{\delta G} = W + G\frac{\delta W}{\delta G} \simeq W$$

$$W(t-t') \simeq W\delta(t-t')$$

Bethe-Salpeter equation

- Two-particle propagator

$$L(1,2,1',2') = -G(1,2,1',2') + G(1,1')G(2,2')$$

- 1-particle GF $G(1,2) = -i\langle N|T[\psi(1)\psi^\dagger(2)]|N\rangle$
- 2-particle GF $G(1,2,1',2') = (-i)^2\langle N|T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]|N\rangle$

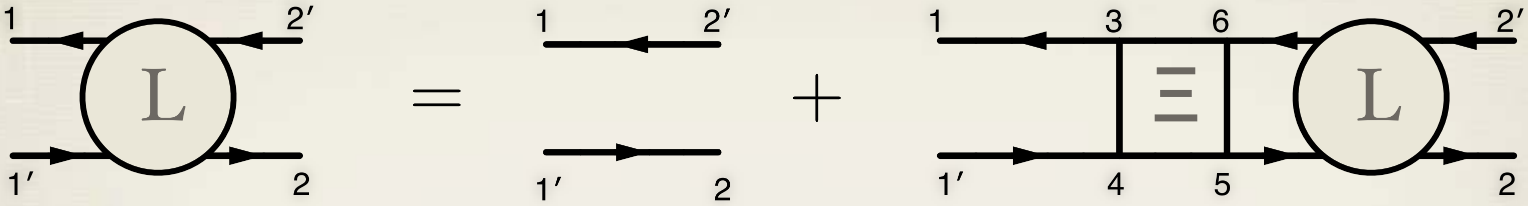
$$\Big\downarrow \begin{array}{l}\text{pp}\\ \text{hh}\\ \text{ph}\end{array}$$

$$G(\tau = [(t_1 + t_{1'})/2 - (t_2 + t_{2'})/2], \tau_1 = t_1 - t_{1'}, \tau_2 = t_2 - t_{2'})$$

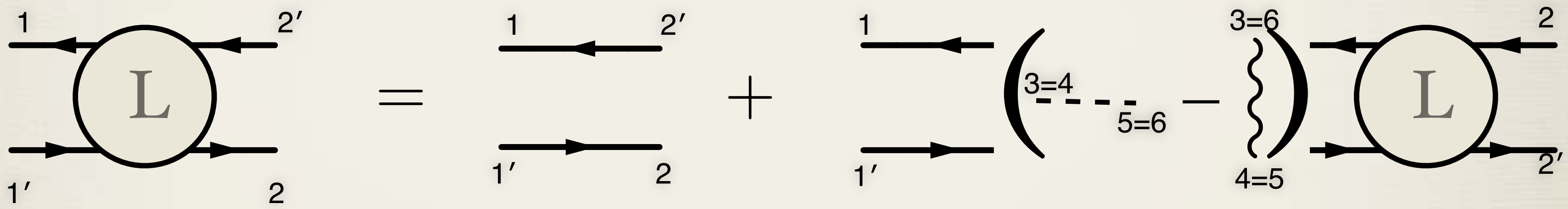
G. Csanak, H. S. Taylor, and R. Yaris, Adv. At. Mol. Phys., 7, 289, (1971)

Bethe-Salpeter equation

- BSE

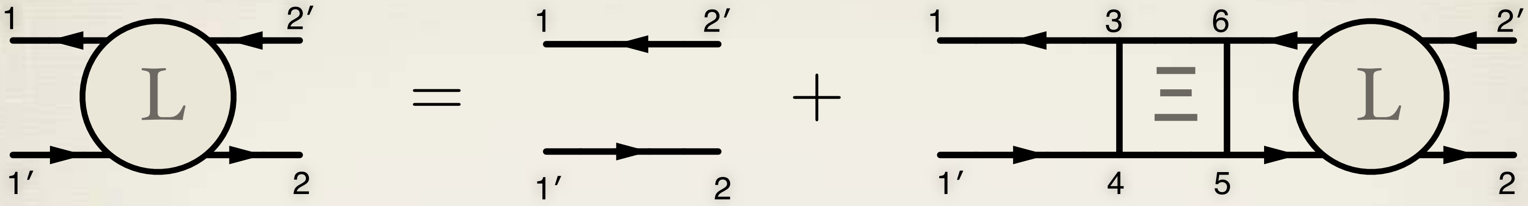


- BSE with $\Xi = v - W$



Bethe-Salpeter equation

- BSE



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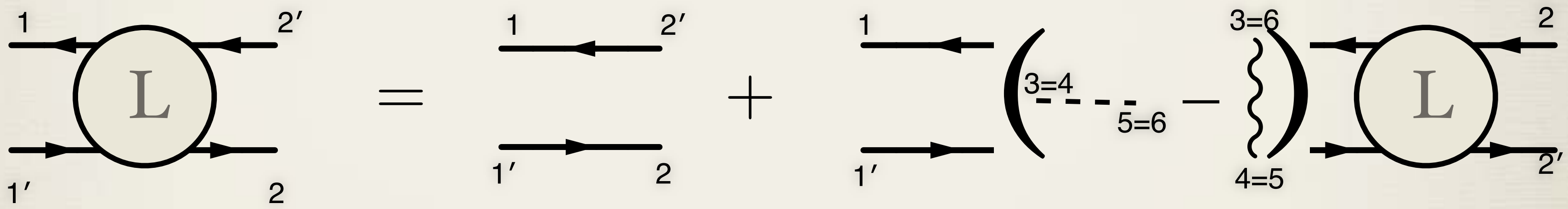
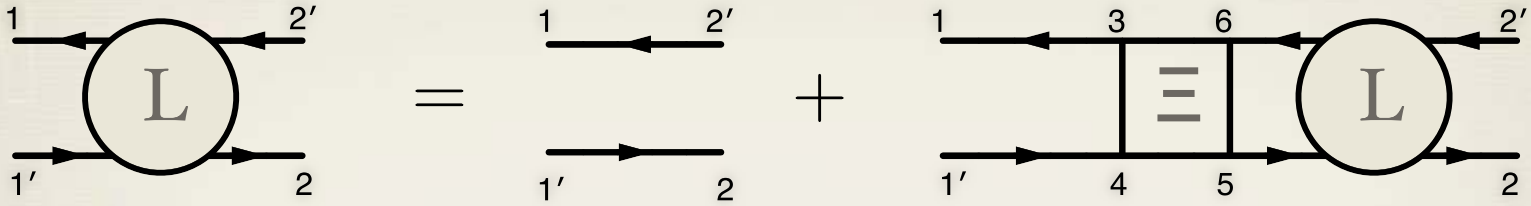


Bethe-Salpeter equation

- BSE



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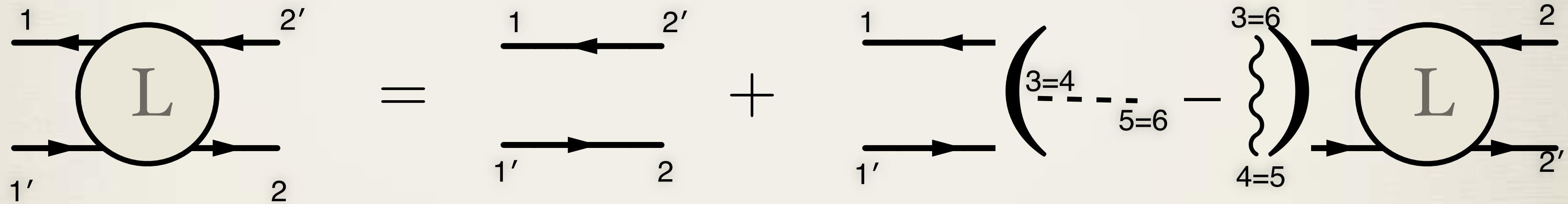
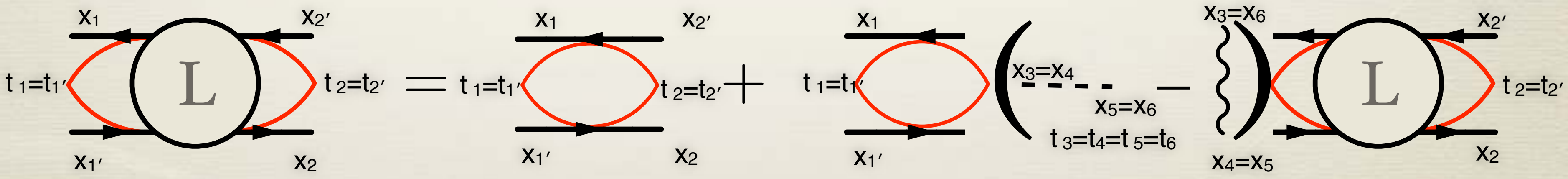


- BSE with $W\delta(t-t')$



$$L(t_1 - t_2) \rightarrow L(\omega)$$

Bethe-Salpeter equation

- BSE in frequency space

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') - iG(\omega'+\omega/2)G(\omega'-\omega/2)\times$$

$$\left[v\int\frac{d\tilde{\omega}}{2\pi}L(\omega,\tilde{\omega},\omega'') - \int\frac{d\tilde{\omega}}{2\pi}W(\omega'-\tilde{\omega})L(\omega,\tilde{\omega},\omega'')\right]$$

Bethe-Salpeter equation

- BSE in frequency space

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') - iG(\omega'+\omega/2)G(\omega'-\omega/2)\times \left[v\int \frac{d\tilde{\omega}}{2\pi}L(\omega,\tilde{\omega},\omega'') - \int \frac{d\tilde{\omega}}{2\pi}W(\omega'-\tilde{\omega})L(\omega,\tilde{\omega},\omega'')\right]$$

- Independent quasiparticle response function

$$L_0(\omega,\omega',\omega'') = -2\pi\, i\delta(\omega'-\omega'')G(\omega'+\omega/2)G(\omega''-\omega/2)$$

- One-particle Green's function

$$G(x_1,x_2,\omega) = \sum_n \frac{\phi_n(x_1)\phi_n^*(x_2)}{\omega - \epsilon_n + i\eta sign(\epsilon_n - \mu)}$$

Bethe-Salpeter equation

- BSE in frequency space

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$$G(x_1,x_2,\omega) = \sum_n \frac{\phi_n(x_1)\phi_n^*(x_2)}{\omega-\epsilon_n+i\eta sign(\epsilon_n-\mu)}$$

Self-energy dynamical effects neglected

Bethe-Salpeter equation

- BSE in frequency space

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') - iG(\omega'+\omega/2)G(\omega'-\omega/2)\times$$

$$\left[v\int\frac{d\tilde{\omega}}{2\pi}L(\omega,\tilde{\omega},\omega'') - \int\frac{d\tilde{\omega}}{2\pi}W(\omega'-\tilde{\omega})L(\omega,\tilde{\omega},\omega'')\right]$$

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$W(\omega) \simeq W(\omega = 0)$

$$\tilde{L}(\omega) = \tilde{L}_0(\omega) + \tilde{L}_0(\omega)K\tilde{L}(\omega)$$

Bethe-Salpeter equation

- BSE in frequency space

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') - iG(\omega'+\omega/2)G(\omega'-\omega/2)\times$$

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$W(\omega)\simeq W(\omega=0)$

$$\tilde{L}(\omega) = \tilde{L}_0(\omega) + \tilde{L}_0(\omega)K\tilde{L}(\omega)$$

- Two-particle Hamiltonian

$$\tilde{L}_{(n_{1'}n_1)(n_2n_{2'})} = \int dx_1dx_2dx_{1'}dx_{2'}\tilde{L}(x_1,x_2,x_{1'},x_{2'};\omega)\phi^*_{n_1}(x_1)\phi_{n_{1'}}(x_{1'})\phi_{n_{2'}}(x_{2'})\phi^*_{n_2}(x_2)$$

Bethe-Salpeter equation

- BSE in frequency space

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') - iG(\omega'+\omega/2)G(\omega'-\omega/2)\times$$

$$\left[v\int\frac{d\tilde{\omega}}{2\pi}L(\omega,\tilde{\omega},\omega'') - \int\frac{d\tilde{\omega}}{2\pi}W(\omega'-\tilde{\omega})L(\omega,\tilde{\omega},\omega'')\right]$$

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$$\tilde{L}_{(n_{1'}n_1)(n_2n_{2'})} = \int dx_1dx_2dx_{1'}dx_{2'}\tilde{L}(x_1,x_2,x_{1'},x_{2'};\omega)\phi^*_{n_1}(x_1)\phi_{n_{1'}}(x_{1'})\phi_{n_{2'}}(x_{2'})\phi^*_{n_2}(x_2)$$

$$\tilde{L}_{0(n_{1'}n_1)(n_2n_{2'})} = \frac{\delta_{n_{1'}n_2}\delta_{n_1n_{2'}}(f_{n_{1'}} - f_{n_1})}{\omega - (\epsilon_{n_1} - \epsilon_{n_{1'}}) + i\eta sign(\epsilon_{n_1} - \epsilon_{n_{1'}})}$$

$$\tilde{L}_{(n_{1'}n_1)(n_2n_{2'})} = \left[H^{2p} - I\omega\right]^{-1}_{(n_{1'}n_1)(n_2n_{2'})}(f_{n_2} - f_{n_{2'}})$$

$$H^{2p}_{(n_{1'}n_1)(n_2n_{2'})} = (\epsilon_{n_1} - \epsilon_{n_{1'}})\delta_{n_1,n_{2'}}\delta_{n_{1'},n_2} + (f_{n_{1'}} - f_{n_1})K_{(n_{1'}n_1)(n_{2'}n_2)}$$

S. Albretcht, Ph.D. thesis, Ecole Polytechnique, France (1999);F. Sottile, Ph.D. thesis, Ecole Polytechnique, France (2003)

Bethe-Salpeter equation

- Excitonic Hamiltonian

$$H^{2p,exc} = \begin{pmatrix} H^{2p,reso}_{(vc)(v'c')} & K^{coupling}_{(vc)(c'v')} \\ -[K^{coupling}_{(vc)(c'v')}]^* & -[H^{2p,reso}_{(vc)(v'c')}]^* \end{pmatrix}$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})} A_\lambda^{(n_2n_{2'})} = \omega_\lambda A_\lambda^{(n_{1'}n_1)}$$

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$$\tilde{L}(x_1, x_2, x_{1'}, x_{2'}, \omega) = \sum_{\lambda\lambda'} \left[\sum_{n_1 n_{1'}} \frac{A_\lambda^{(n_{1'}n_1)} \phi_{n_1}(x_1)\phi^*_{n_{1'}}(x_{1'})}{\omega_\lambda - \omega + i\eta sign(\epsilon_{n_{1'}} - \epsilon_{n_1})} \times \right.$$

$$\left. S^{-1}_{\lambda\lambda'} \sum_{n_2 n_{2'}} A_{\lambda'}^{*(n_2n_{2'})} \phi_{n_2}(x_2)\phi^*_{n_{2'}}(x_{2'})(f_{n_{2'}} - f_{n_2}) \right]$$

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$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})} A_\lambda^{(n_2n_{2'})} = \omega_\lambda A_\lambda^{(n_{1'}n_1)}$$

Static kernel

- only singly-excited configurations
- n. eigenvalues=n. single-excitations

$$\tilde{L}(x_1, x_2, x_{1'}, x_{2'}, \omega) = \sum_{\lambda\lambda'} \left[\sum_{n_1 n_{1'}} \frac{A_\lambda^{(n_{1'}n_1)} \phi_{n_1}(x_1) \phi^*_{n_{1'}}(x_{1'})}{\omega_\lambda - \omega + i\eta sign(\epsilon_{n_{1'}} - \epsilon_{n_1})} \times \right.$$

$$\left. S^{-1}_{\lambda\lambda'} \sum_{n_2 n_{2'}} A^{*(n_2n_{2'})}_{\lambda'} \phi_{n_2}(x_2) \phi^*_{n_{2'}}(x_{2'}) (f_{n_{2'}} - f_{n_2}) \right]$$

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Bethe-Salpeter equation

- Excitonic Hamiltonian: $W(\omega)$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A^{(n_2n_{2'})}_\lambda(\omega_\lambda)=\omega_\lambda A^{(n_{1'}n_1)}_\lambda(\omega_\lambda)$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)=(\epsilon_{n_1}-\epsilon_{n_{1'}})\delta_{n_{1'},n_2}\delta_{n_1n_{2'}}+(f_{n_{1'}}-f_{n_1})\left[v_{(n_{1'}n_1)(n_2n_{2'})}-\tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)\right]$$

G. Strinati, Rev. Nuovo Cimento 11, 1, (1988)

Bethe-Salpeter equation

- Excitonic Hamiltonian: $W(\omega)$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A_\lambda^{(n_2n_{2'})}(\omega_\lambda) = \omega_\lambda A_\lambda^{(n_{1'}n_1)}(\omega_\lambda)$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = (\epsilon_{n_1}-\epsilon_{n_{1'}})\delta_{n_{1'},n_2}\delta_{n_1n_{2'}}+(f_{n_{1'}}-f_{n_1})\left[v_{(n_{1'}n_1)(n_2n_{2'})} - \tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)\right]$$

  - ω-dependent screening

$$\tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = i\int\frac{d\omega}{2\pi}W_{(n_{1'}n_1)(n_2n_{2'})}(\omega)\left[\frac{1}{\omega_\lambda-\omega-(\epsilon_{n_{2'}}-\epsilon_{n_{1'}})+i\eta}+\frac{1}{\omega_\lambda+\omega-(\epsilon_{n_1}-\epsilon_{n_2})+i\eta}\right]$$

G. Strinati, Rev. Nuovo Cimento 11, 1, (1988)

Bethe-Salpeter equation

- Excitonic Hamiltonian: $W(\omega)$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A_\lambda^{(n_2n_{2'})}(\omega_\lambda) = \omega_\lambda A_\lambda^{(n_{1'}n_1)}(\omega_\lambda)$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = (\epsilon_{n_1}-\epsilon_{n_{1'}})\delta_{n_{1'},n_2}\delta_{n_1n_{2'}}+(f_{n_{1'}}-f_{n_1})\left[v_{(n_{1'}n_1)(n_2n_{2'})} - \tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)\right]$$

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$$\tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = i\int \frac{d\omega}{2\pi} W_{(n_{1'}n_1)(n_2n_{2'})}(\omega)\left[\frac{1}{\omega_\lambda-\omega-(\epsilon_{n_{2'}}-\epsilon_{n_{1'}})+i\eta}+\frac{1}{\omega_\lambda+\omega-(\epsilon_{n_1}-\epsilon_{n_2})+i\eta}\right]$$

$W = v + v\chi v$

$$W_{(n_{1'}n_1)(n_2n_{2'})}(\omega) = v_{(n_{2'}n_1)(n_2n_{1'})}+\sum_\lambda\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} v_{(n_{2'}n_1)(\tilde{v}\tilde{c})}\frac{A_\lambda^{(\tilde{v}\tilde{c}),static}A_\lambda^{*(\tilde{v}'\tilde{c}'),static}}{\omega-\omega_\lambda^{static}+i\eta}v_{(\tilde{v}'\tilde{c}')(n_2n_{1'})}$$

$$-\sum_\lambda\sum_{\tilde{c}\tilde{v},\tilde{c}'\tilde{v}'} v_{(n_{2'}n_1)(\tilde{c}\tilde{v})}\frac{A_\lambda^{(\tilde{c}\tilde{v}),static}A_\lambda^{*(\tilde{c}'\tilde{v}'),static}}{\omega+\omega_\lambda^{static}-i\eta}v_{(\tilde{c}'\tilde{v}')(n_2n_{1'})}$$

G. Strinati, Rev. Nuovo Cimento 11, 1, (1988)

Bethe-Salpeter equation

- Excitonic Hamiltonian: $W(\omega)$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A_\lambda^{(n_2n_{2'})}(\omega_\lambda)=\omega_\lambda A_\lambda^{(n_{1'}n_1)}(\omega_\lambda)$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)=(\epsilon_{n_1}-\epsilon_{n_{1'}})\delta_{n_{1'},n_2}\delta_{n_1n_{2'}}+(f_{n_{1'}}-f_{n_1})\left[v_{(n_{1'}n_1)(n_2n_{2'})}-\tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)\right]$$

  - ω-dependent screening

Bethe-Salpeter equation

- Excitonic Hamiltonian: $W(\omega)$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A^{(n_2n_{2'})}_\lambda(\omega_\lambda) = \omega_\lambda A^{(n_{1'}n_1)}_\lambda(\omega_\lambda)$$

$$H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = (\epsilon_{n_1}-\epsilon_{n_{1'}})\delta_{n_{1'},n_2}\delta_{n_1n_{2'}}+(f_{n_{1'}}-f_{n_1})\left[v_{(n_{1'}n_1)(n_2n_{2'})} - \tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)\right]$$

- ω-dependent screening

$$\tilde{W}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda) = v_{(n_{2'}n_1)(n_2n_{1'})}+\sum_{\lambda'}\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} v_{(n_{2'}n_1)(\tilde{v}\tilde{c})}\frac{A^{(\tilde{v}\tilde{c}),static}_{\lambda'}A^{*(\tilde{v}'\tilde{c}'),static}_{\lambda'}}{\omega_\lambda - \omega^{static}_{\lambda'} - (\epsilon_{n_{2'}} - \epsilon_{n_{1'}}) + i\eta}v_{(\tilde{v}'\tilde{c}')(n_2n_{1'})}$$

$$+\sum_{\lambda'}\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} v_{(n_{2'}n_1)(\tilde{v}\tilde{c})}\frac{A^{(\tilde{v}\tilde{c}),static}_{\lambda'}A^{*(\tilde{v}'\tilde{c}'),static}_{\lambda'}}{\omega_\lambda - \omega^{static}_{\lambda'} - (\epsilon_{n_{2'}} - \epsilon_{n_{1'}}) + i\eta}v_{(\tilde{v}'\tilde{c}')(n_2n_{1'})}$$

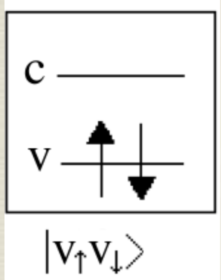
Strategy

1. Solve the $H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}A^{(n_2n_{2'})}_\lambda = \omega_\lambda A^{(n_{1'}n_1)}_\lambda$ with a static screening W^{static}
2. Build the polarizability $\chi(\omega)$ from the eigenvalues ω^{static}_λ and eigenvectors A^{static}_λ
3. Build the screening $W(\omega) = v + v\chi(\omega)v$
4. Solve the $H^{2p,exc}_{(n_{1'}n_1)(n_2n_{2'})}(\omega_\lambda)A^{(n_2n_{2'})}_\lambda(\omega_\lambda) = \omega_\lambda A^{(n_{1'}n_1)}_\lambda(\omega_\lambda)$ with this frequency-dependent screening

A simple model I.

- Two-electron system

Eigenvalue eq.

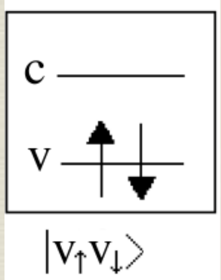


$$\left(\begin{array}{c|cc} & (v\uparrow c\uparrow) & (v\downarrow c\downarrow) \\ \hline (v\uparrow c\uparrow) & \Delta\epsilon_{vc} + v_{(vc)(vc)} - \tilde{W}_{(vc)(vc)}(\omega) & v_{(vc)(vc)} \\ (v\downarrow c\downarrow) & v_{(vc)(vc)} & \Delta\epsilon_{vc} + v_{(vc)(vc)} - \tilde{W}_{(vc)(vc)}(\omega) \end{array}\right) A = \omega A$$

A simple model I.

- Two-electron system

Eigenvalue eq.



$$\left(\begin{array}{c|cc} & (v\uparrow c\uparrow) & (v\downarrow c\downarrow) \\ \hline (v\uparrow c\uparrow) & \Delta\epsilon_{vc}+v_{(vc)(vc)}-\tilde{W}_{(vc)(vc)}(\omega) & v_{(vc)(vc)} \\ (v\downarrow c\downarrow) & v_{(vc)(vc)} & \Delta\epsilon_{vc}+v_{(vc)(vc)}-\tilde{W}_{(vc)(vc)}(\omega) \end{array}\right) A = \omega A$$

$W^{static}_{(vc)(vc)}$

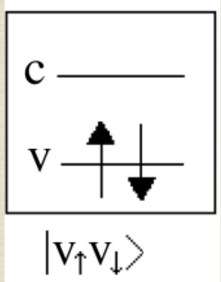
Singlet $$\omega_1^{static} = \Delta\epsilon_{vc} + 2v_{(vc)(vc)} - W^{static}_{(vc)(vc)},\ \ A_1^{static} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Triplet $$\omega_2^{static} = \Delta\epsilon_{vc} - W^{static}_{(vc)(vc)},\ \ A_2^{static} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

A simple model I.

- Two-electron system

Eigenvalue eq.



$$\left(\begin{array}{c|cc} & (v\uparrow c\uparrow) & (v\downarrow c\downarrow) \\ \hline (v\uparrow c\uparrow) & \Delta\epsilon_{vc}+v_{(vc)(vc)}-\tilde{W}_{(vc)(vc)}(\omega) & v_{(vc)(vc)} \\ (v\downarrow c\downarrow) & v_{(vc)(vc)} & \Delta\epsilon_{vc}+v_{(vc)(vc)}-\tilde{W}_{(vc)(vc)}(\omega) \end{array}\right) A = \omega A$$

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$$(\omega^{static} - 2v_{(vc)(vc)} + v_{(cc)(vv)})^2 >> 8\Re[v_{(cc)(vc)}v_{(vc)(vv)}] \;\Big\downarrow\; \tilde{W}_{(vc)(vc)}(\omega) = v_{(cc)(vv)} + 2\frac{\Re[v_{(cc)(vc)}v_{(vc)(cc)}]}{\omega - \omega_1^{static} - \Delta\epsilon_{vc}}$$

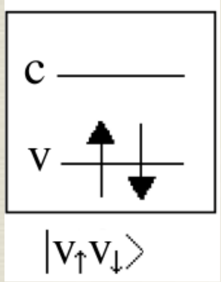
double-excitation

Singlets $$\omega_1 = \Delta\epsilon_{vc} + 2v_{(vc)(vc)} - v_{(cc)(vv)} \qquad \omega_3 = 2\Delta\epsilon_{vc} + 2v_{(vc)(vc)} - W^{static}_{(vc)(vc)}$$

A simple model I.

- Two-electron system

Eigenvalue eq.



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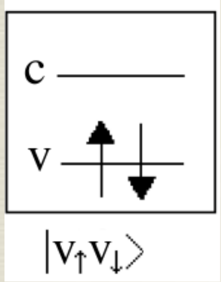
A simple model I.

- Two-electron system

Eigenvalue eq.



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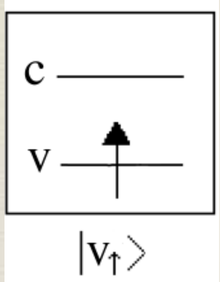
Triplets $$\omega_2 = \Delta\epsilon_{vc} - v_{(cc)(vv)} \qquad \omega_4 \cancel{=} 2\Delta\epsilon_{vc} + 2v_{(vc)(vc)} - W^{static}_{(vc)(vc)}$$

A simple model II.

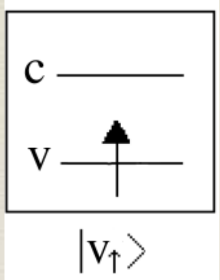
- One-electron system



$$\left[\Delta\epsilon_{vc} + v_{(vc)(vc)} - \tilde{W}_{(vc)(vc)}(\omega)\right] A = \omega A$$ Eigenvalue eq.

A simple model II.

- One-electron system



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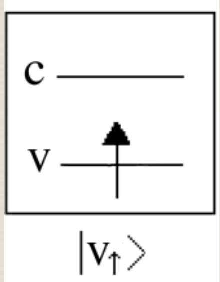
$$\Big\downarrow W^{static}_{(vc)(vc)}$$

$$\omega^{static} = \Delta\epsilon_{vc} + v_{(vc)(vc)} - W^{static}_{(vc)(vc)}, \quad A^{static} = 1$$

A simple model II.

- One-electron system



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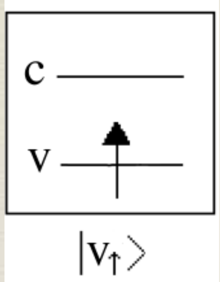
$$\omega_1 = \Delta\epsilon_{vc} + v_{(vc)(vc)} - v_{(cc)(vv)}$$

A simple model II.

- One-electron system



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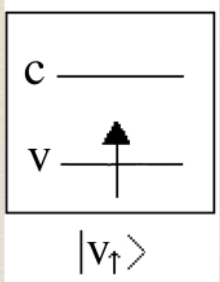
$$\omega_1 = \Delta\epsilon_{vc} + v_{(vc)(vc)} - v_{(cc)(vv)} \qquad \omega_2 = 2\Delta\epsilon_{vc} + v_{(vc)(vc)} - W^{static}_{(vc)(vc)}$$

A simple model II.

- One-electron system



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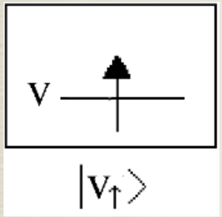
Self-screening

Where does the self-screening come from???

- Self-screening problem



$$[i\partial_{t_1} - h(1)]\,G(1,2) - \int d3\Sigma(1,3)G(3,2) = \delta(1,2) \quad h(1) = -\nabla^2/2 + U(1) + v_H(1)$$

W. Nelson et al., Phys. Rev. B 75, 032505 (2007)

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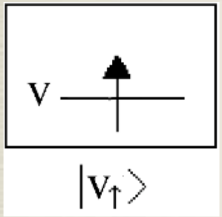

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$$\mathrm{HF} \rightarrow \Sigma(1,2) = iG(1,2)v(1^+,2) = -\sum_n^{occ} \phi_n(x_1)\phi_n^*(x_2)v(x_1,x_2)$$

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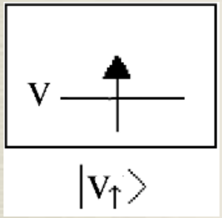

$$[i\partial_{t_1} - h(1)]\, G(1,2) - \int d3 \Sigma(1,3) G(3,2) = \delta(1,2) \quad h(1) = -\nabla^2/2 + U(1) + v_H(1)$$

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$$[i\partial_{t_1} + \nabla^2/2 - U(1)]\, G(1,2) - \int dx_3 v(x_1,x_3)\left[\phi(x_3)\phi^*(x_3) - \phi(x_3)\phi^*(x_3)\right] G(1,2) = \delta(1,2)$$

W. Nelson et al., Phys. Rev. B 75, 032505 (2007)

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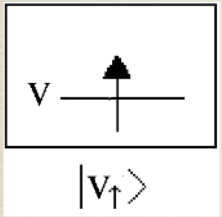

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W. Nelson et al., Phys. Rev. B 75, 032505 (2007)

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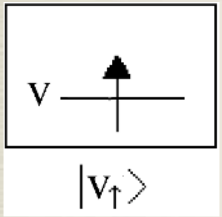

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GW → $\Sigma = i\,[Gv + G(W - v)]$

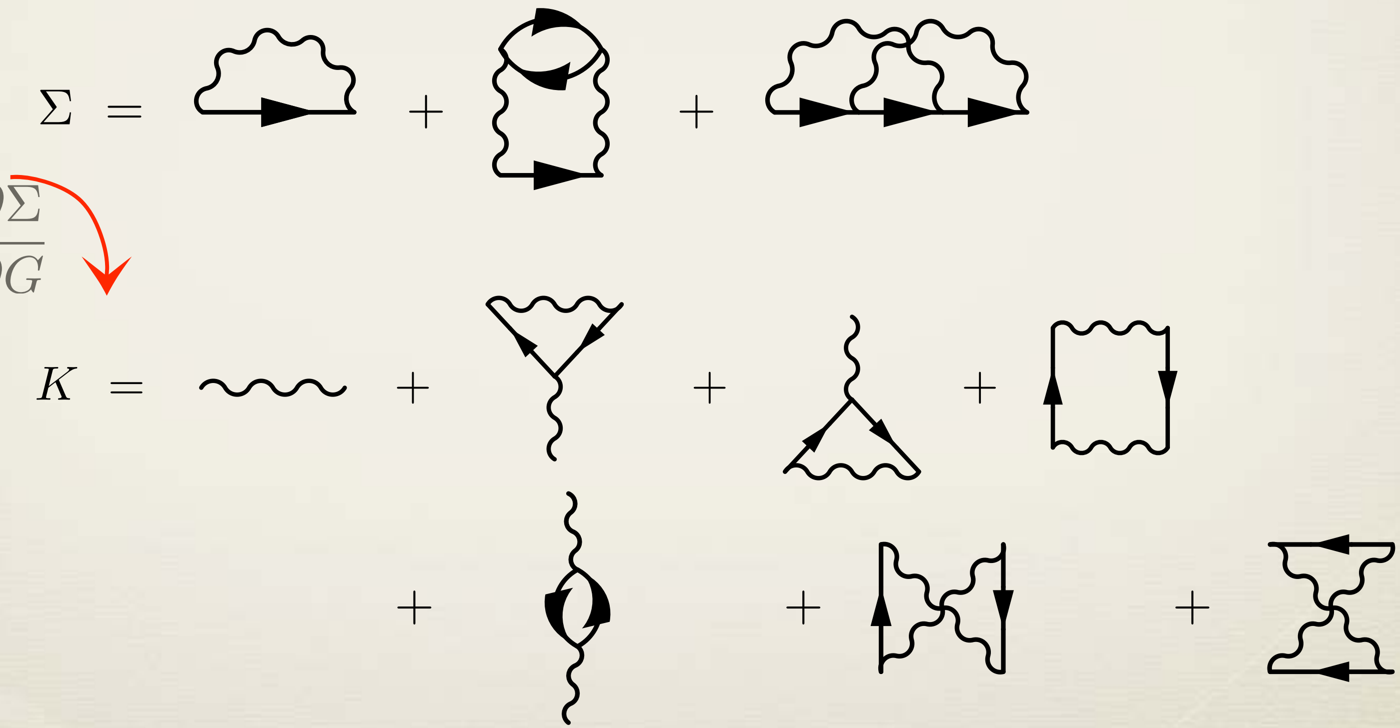
Self-screening

W. Nelson et al., Phys. Rev. B 75, 032505 (2007)

Where does the self-screening come from???

- Second order self-energy and kernel*

$$K = v + i\frac{\partial \Sigma}{\partial G}$$



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* See Davide Sangalli's poster: Hunting double excitations

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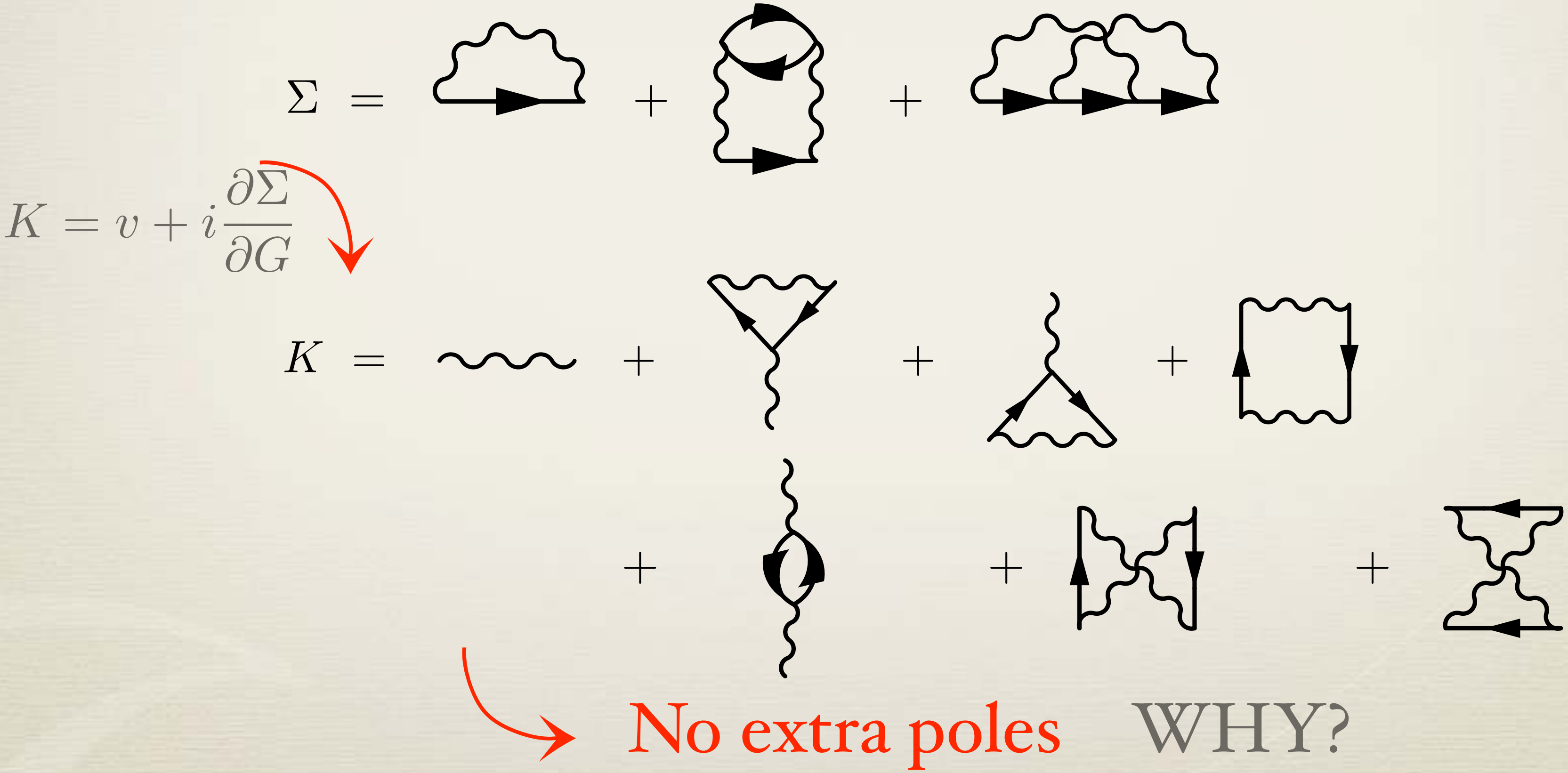
- Second order self-energy and kernel*



$$K = v + i\frac{\partial\Sigma}{\partial G}$$

No extra poles WHY?

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* See Davide Sangalli's poster: Hunting double excitations

Conclusions

- A frequency-dependent kernel can create extra poles in the response function
- $W(\omega)$ creates double excitations...
- ...and spurious solutions...
- Vertex corrections needed

From BSE back to TDDFT

- The frequency-dependent xc kernel

$$f_{xc}(1,2) = f_{xc}^{(1)}(1,2) + f_{xc}^{(2)}(1,2)$$

I. V. Tokatly, et al. Phys. Rev. B 65, 113107 (2002); F. Bruneval, at al. Phys. Rev. Lett. 94, 186402, (2005) ; M. Gatti, et al. Phys. Rev. Lett. 99, 057401, (2007)

From BSE back to TDDFT

- The frequency-dependent xc kernel

$$f_{xc}(1,2) = f_{xc}^{(1)}(1,2) + f_{xc}^{(2)}(1,2)$$

$$f_{xc}^{(1)}(1,2) = \chi_{KS}^{-1}(1,2) - \chi_0^{-1}(1,2)$$

$$f_{xc}^{(2)}(1,2) = -i\chi_0^{-1}(1,5)G(5,3)G(4,5)\frac{\delta\Sigma(3,4)}{\delta\rho(2)}$$

I. V. Tokatly, et al. Phys. Rev. B 65, 113107 (2002); F. Bruneval, at al. Phys. Rev. Lett. 94, 186402, (2005) ; M. Gatti, et al. Phys. Rev. Lett. 99, 057401, (2007)

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$$\delta\Sigma/\delta G = -W$$

$$f_{xc}^{(2)}(1,2) \simeq -\chi_0^{-1}(1,5)L_0(1,4,1,3)W(3,4)L_0(3,2,4,2)\chi_0^{-1}(6,2)$$

I. V. Tokatly, et al. Phys. Rev. B 65, 113107 (2002); F. Bruneval, at al. Phys. Rev. Lett. 94, 186402, (2005) ; M. Gatti, et al. Phys. Rev. Lett. 99, 057401, (2007)

From BSE back to TDDFT

- The frequency-dependent xc kernel

$$f_{xc}(\omega) = -\chi_0^{-1}(\omega)\Big[\int \frac{d\omega' d\omega''}{(2\pi)^2} L_0(\omega,\omega',\omega'') \int \frac{d\omega''' d\tilde{\omega}}{(2\pi)^2} W(\omega' - \tilde{\omega}) L_0(\omega,\tilde{\omega},\omega''')\Big]\chi_0^{-1}(\omega)$$

P. Romaniello et all. to be submitted

From BSE back to TDDFT

- The frequency-dependent xc kernel

$$f_{xc}(\omega) = -\chi_0^{-1}(\omega)\left[\int \frac{d\omega' d\omega''}{(2\pi)^2} L_0(\omega,\omega',\omega'') \int \frac{d\omega''' d\tilde{\omega}}{(2\pi)^2} W(\omega'-\tilde{\omega}) L_0(\omega,\tilde{\omega},\omega''')\right]\chi_0^{-1}(\omega)$$

$$\boxed{f_{xc}(\omega) = -\sum_{vc,v'c'} \chi_0^{-1}(\omega)\tilde{L}_0^{vc}(\omega)\tilde{W}_{v'c'}^{vc}(\omega)\tilde{L}_0^{v'c'}(\omega)\chi_0^{-1}(\omega)}$$

$$\tilde{W}_{v'c'}^{vc}(x_5,x_6,\omega) = v(x_5,x_6) + \sum_\lambda v(x_5,x_{1'})\left[\frac{\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} A_\lambda^{(\tilde{v}\tilde{c}),static}\phi_{\tilde{v}}^*(x_{1'})\phi_{\tilde{c}}(x_{1'})\phi_{\tilde{v}'}(x_{2'})\phi_{\tilde{c}'}^*(x_{2'})A_\lambda^{*(\tilde{v}'\tilde{c}'),static}}{\omega-\omega_\lambda^{static}-(\epsilon_{c'}-\epsilon_v)+i\eta}\right.$$

$$\left.+\frac{\sum_{\tilde{c}\tilde{v},\tilde{c}'\tilde{v}'} A_\lambda^{(\tilde{c}\tilde{v}),static}\phi_{\tilde{c}}^*(x_{1'})\phi_{\tilde{v}}(x_{1'})\phi_{\tilde{c}'}(x_{2'})\phi_{\tilde{v}'}^*(x_{2'})A_\lambda^{*(\tilde{c}'\tilde{v}'),static}}{\omega-\omega_\lambda^{static}-(\epsilon_c-\epsilon_{v'})+i\eta}\right]v(x_{2'},x_6)$$

P. Romaniello et all. to be submitted

From BSE back to TDDFT

- The frequency-dependent xc kernel
  - This work

$$f_{xc}(\omega) = A + \frac{B}{\omega - \omega^{static} - (\epsilon_c - \epsilon_v)}$$

  - N. Maitra et al.

$$f_{xc}(\omega) = \tilde{A} + \frac{\tilde{B}}{\omega - (H_{DD} - H_{00})}$$

P. Romaniello et all. to be submitted; N. Maitra et al. J. Chem. Phys. 120, 5932 (2004)