Excited states from many body perturbation theory

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Funded by the Austrian FWF

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Motivation

- Band gap error
  - Huge errors in band gaps
  - Electronic properties: Prediction of defect properties is difficult (or impossible)
  - Optical properties
- Errors in total energies
  - Van der Waals bonding
  - Covalent bonding
  - Strong correlation

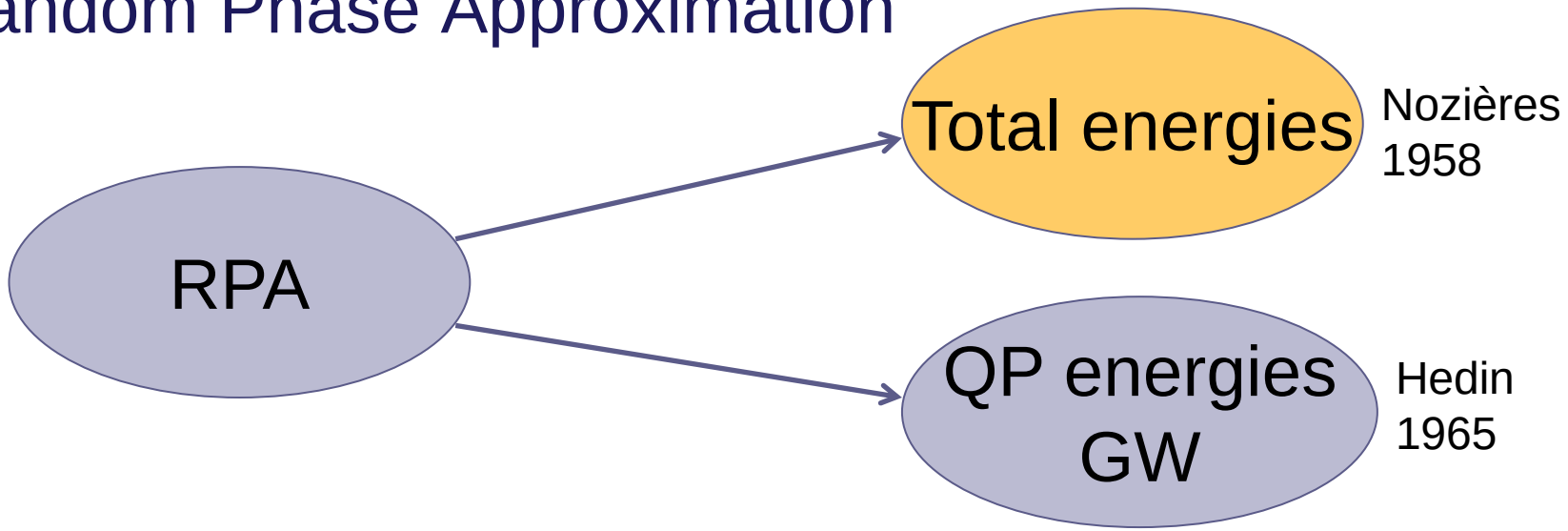
no $1/r^5$

Overview

- RPA and GW a first look
  - The QP equation, Green's functions
  - Feynman diagrams
  - The RPA approximation and what is missing
- GW for band gaps
  - Prototypical systems
  - The many flavours of GW
  - Beyond the RPA/ GW approximations and the importance of vertices

Overview: Theory

- Random Phase Approximation



RPA → screened exchange

Electronic structure methods and one-electron theories

- Density functional theory, hardly improved in last 10 years

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{Hartree}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r})\right)\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})$$

- Hartree Fock theory → hybrid functionals

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r})\right)\phi_n(\mathbf{r}) + \int V^{\text{x}}(\mathbf{r},\mathbf{r}')\phi_n(\mathbf{r}')d^3\mathbf{r}' = E_n\phi_n(\mathbf{r})$$

- One electron Green's functions: Nozières, Phys. Rev. **111**, 442; Hedin, Phys. Rev. **139**, A796

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r})\right)\phi_n(\mathbf{r}) + \int \Sigma^{\text{xc}}(\mathbf{r},\mathbf{r}',E_n)\phi_n(\mathbf{r}')d^3\mathbf{r}' = E_n\phi_n(\mathbf{r})$$

The single particle Green's function

- Green's function is the resolvent of the Hamiltonian

$$1 = (\omega - H)G \quad \Leftrightarrow \quad G^{-1} = (\omega - H)$$

- Spectral presentation (Lehmann presentation)

$$\omega\delta(\mathbf{r},\mathbf{r}') - H(\mathbf{r},\mathbf{r}') = \sum_{\text{all}} \phi_m^*(\mathbf{r})(\omega - \varepsilon_m)\phi_m(\mathbf{r}')$$

- Single part. Green's function of a Hamiltonian

$$G_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\text{all}} \frac{\phi_m^*(\mathbf{r})\phi_m(\mathbf{r}')}{\omega - \varepsilon_m + i\delta\,\text{sgn}[\varepsilon_m - \varepsilon_{\text{Fermi}}]}$$

The interacting Green´s function:

- "Frequency-dependent Hamiltonian"

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r})\right) + \Sigma^{\text{xc}}(\mathbf{r},\mathbf{r}',\omega) = H(\omega)$$

$$H_0 + \Sigma^{\text{xc}}(\omega) = H$$

- Convenient to use Green´s function

$$(H_0 - \omega) + \Sigma^{\text{xc}}(\omega) = (H - \omega) \quad \text{using} \quad G^{-1}(\omega) = (\omega - H)$$

$$-G_0^{-1}(\omega) + \Sigma^{\text{xc}}(\omega) = -G^{-1}(\omega)$$

$$G^{-1}(\omega) = G_0^{-1}(\omega) - \Sigma^{\text{xc}}(\omega) \quad \Leftrightarrow$$

$$G(\omega) = G_0(\omega) + G_0(\omega)\Sigma^{\text{xc}}(\omega)G(\omega)$$

Last equation introduced by Dyson (Dyson equation)

The Green's function: physical interpretation

- Green's function describes the propagation of an added electron or hole from position and time $(\mathbf{r}, t)$ to $(\mathbf{r}', t')$
- Green's function $$G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\text{all}} \frac{\phi_m^*(\mathbf{r}_1)\phi_m(\mathbf{r}_2)}{\omega - \varepsilon_m + i\delta\,\mathrm{sgn}[\varepsilon_m - \varepsilon_{Fermi}]}$$
- Fourier transformation to time
- Particle propagator $G(1,2) = G(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$ $t_2 > t_1$

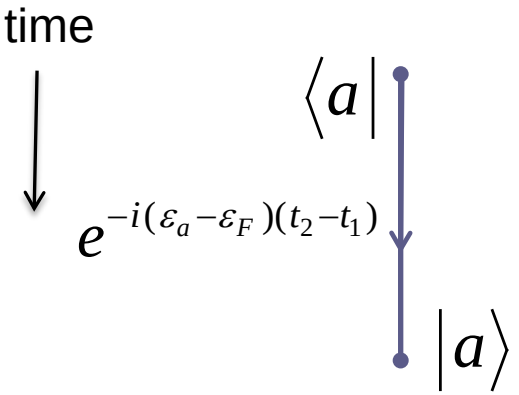
$$G_0(1,2) = \sum_{a \in \text{virt}} \phi_a^*(\mathbf{r}_1)\phi_a(\mathbf{r}_2) e^{-i(\varepsilon_a - \varepsilon_F)(t_2 - t_1)}$$

- Hole propagator $G(1,2)$ $t_2 < t_1$

$$G_0(1,2) = -\sum_{i \in \text{occ.}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2) e^{-i(\varepsilon_i - \varepsilon_F)(t_1 - t_2)}$$

Diagrams and single particle Green's function

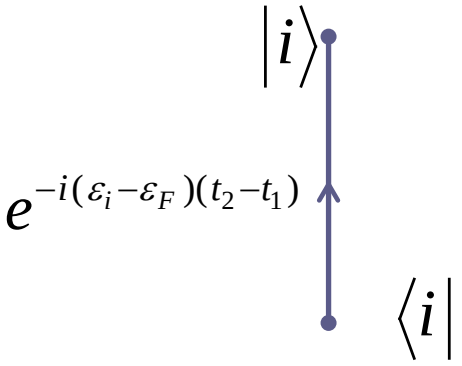
- Straight line = Green's function describing the propagation of an electron or hole from position and time $(\mathbf{r}_1, t_1)$ to $(\mathbf{r}_2, t_2)$
- Particle propagator $\mathrm{G}(1,2) = \mathrm{G}(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$ $\quad t_2 > t_1$



$$G_0(1,2) = \sum_{a \in \text{virt}} \phi_a^*(\mathbf{r}_1)\phi_a(\mathbf{r}_2)e^{-i(\varepsilon_a - \varepsilon_F)(t_2 - t_1)}$$

- Hole propagator $\quad \mathrm{G}(1,2) \quad t_2 < t_1$

QC: propagation by unperturbed H

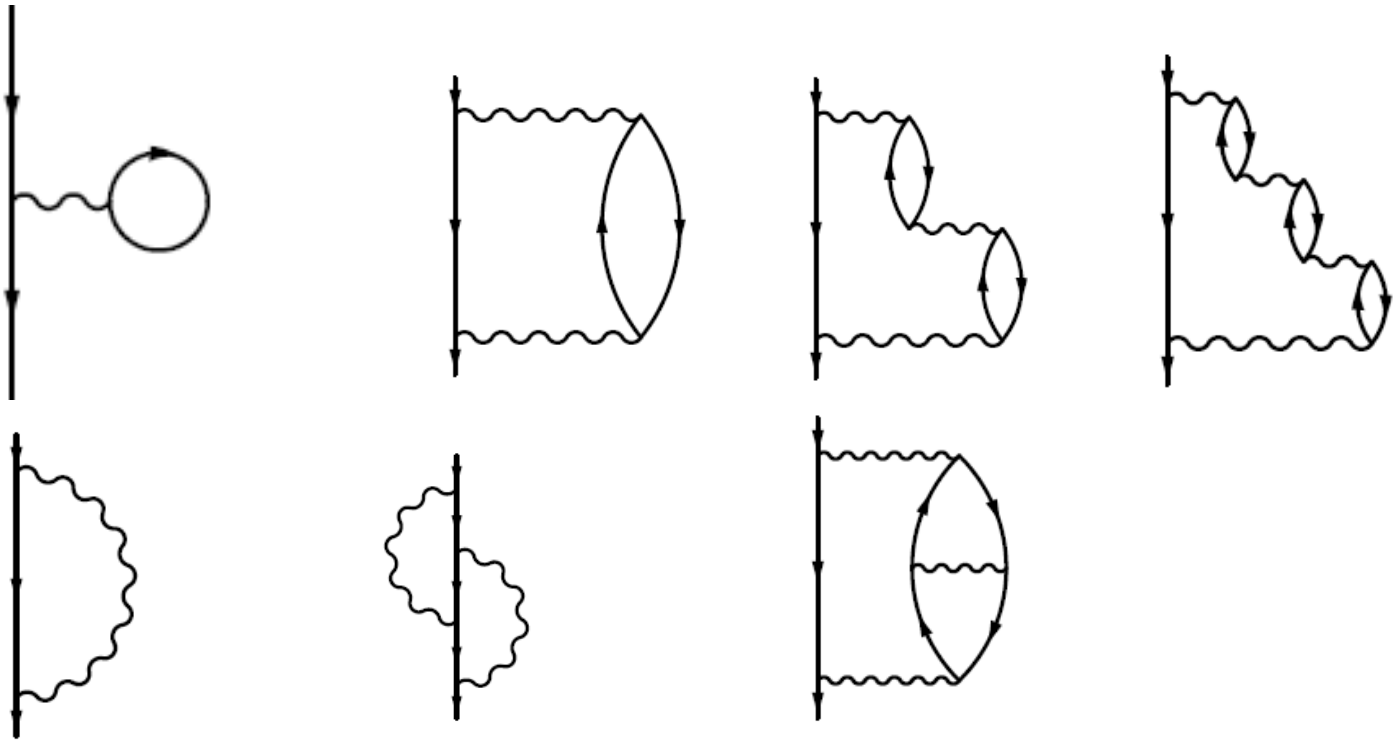


$$G_0(1,2) = -\sum_{i \in \text{occ.}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)e^{-i(\varepsilon_i - \varepsilon_F)(t_1 - t_2)}$$

Perturbation theory: Σ is a "function" of G

- All Feynman diagrams with one in-going and one out-going line yield the self-energy (properly amputed)
- $G(1,2) = \langle \Psi_0 | T\psi(1)\psi^+(2) | \Psi_0 \rangle$ and apply Wick theorem

  $\psi^+(2)$ create particle at $\mathbf{r}_2, t_2$; $\psi(1)$ annihilate particle at $\mathbf{r}_1, t_1$

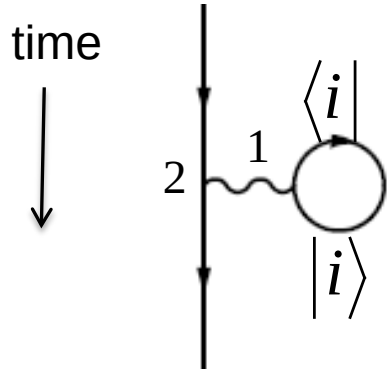


1st. order 2nd. order 3rd. order 4th. order

Example two simple diagrams

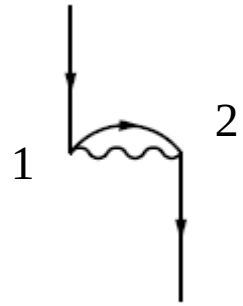
The two first order diagrams (single Coulomb line) yield just the Hartree and exchange energy
(recall, sign depends on number of closed Fermi-loops)

Hartree



$$G(1,1) = \sum_{i \in \text{occ.}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)e^{-i(\varepsilon_i-\varepsilon_F)(t_1-t_1)} = n(\mathbf{r}_1)$$

$$\int v(\mathbf{r}_2,\mathbf{r}_1)n(\mathbf{r}_1)d\mathbf{r}_1 = \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1$$



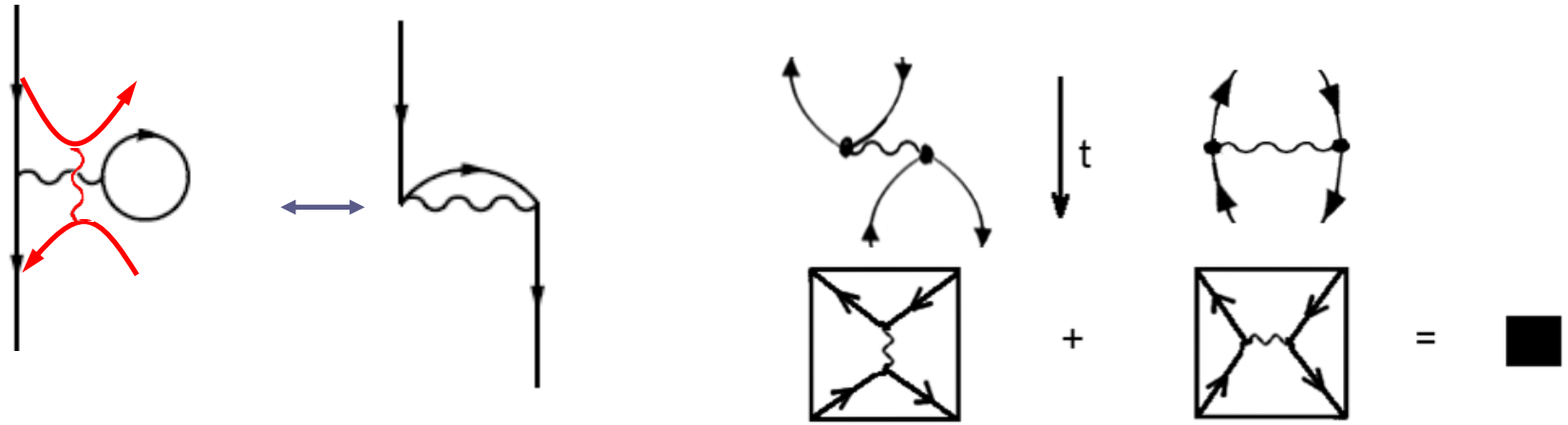
$$G(1,2) = \sum_{i \in \text{occ.}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)e^{-i(\varepsilon_i-\varepsilon_F)(t_1-t_1)} = \gamma(\mathbf{r}_1,\mathbf{r}_2)$$

$$-G(1,2)v(1,2) = -v(\mathbf{r}_1,\mathbf{r}_2)\gamma(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\gamma(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \quad t_1 = t_2$$

exchange

Anti-symmetry: "turning the Coulomb line"

A "good" subset requires that all Coulomb interactions are properly anti-symmetrized



Hartree

Exchange:
turn Coulomb line around and change sign
This is related to anti-symmetry of the electronic wavefunction
(adds one closed Fermionic loop)

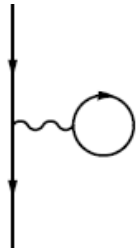
Hartree-Fock theory

- Lacks correlation and much too large band gaps
- But properly anti-symmetric
- Expectation value

$$\phi_i^* \left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}} + V^{\text{el}} + V^{x} \right) \phi_i$$

- Hartree or electrostatic interaction between electrons

$$\int\int d^3\mathbf{r} d^3\mathbf{r}' \sum_{i \in \text{occ}} \phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}') \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r})\phi_j^*(\mathbf{r})$$

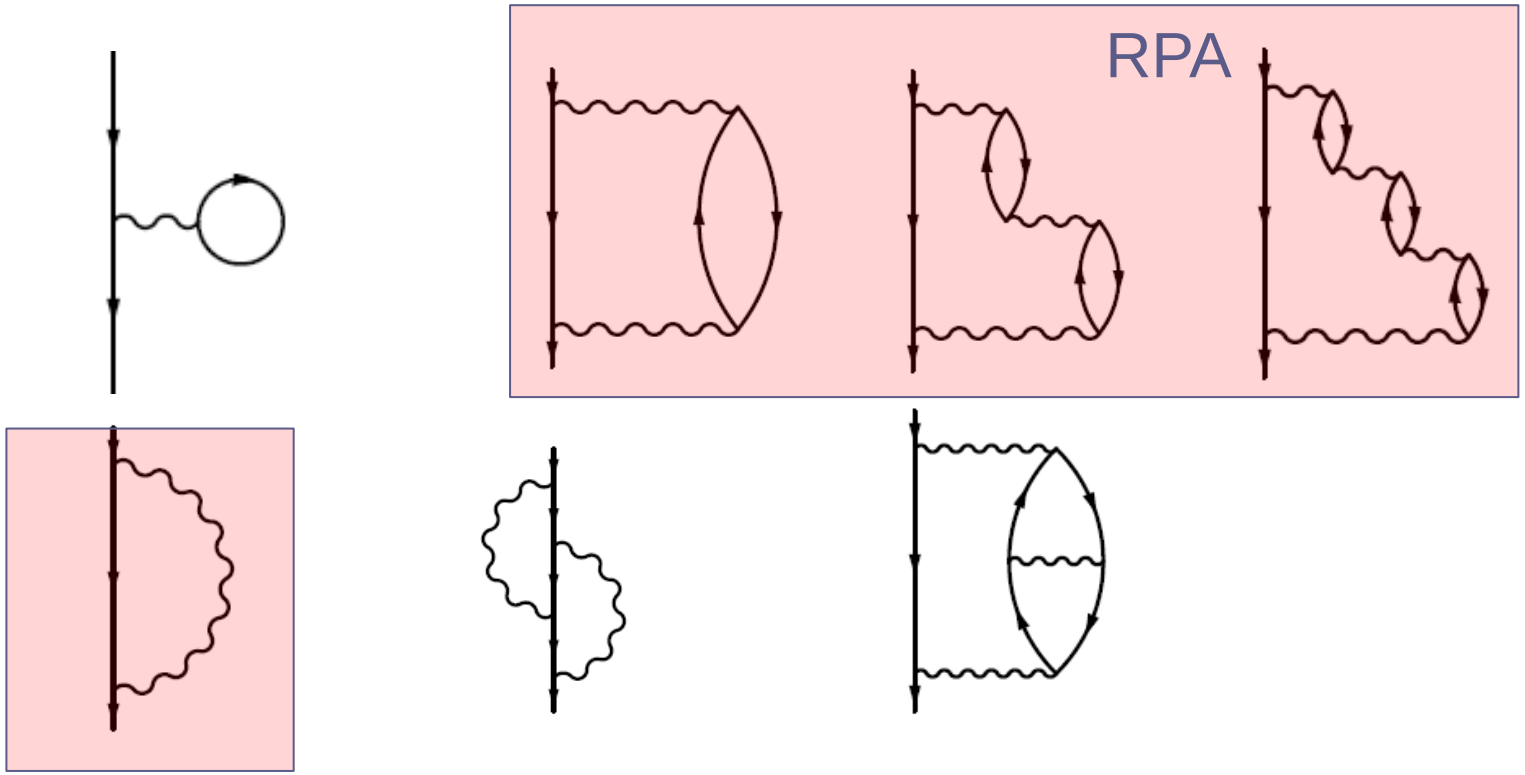


- Exchange interaction between electrons (anti-symmetry)

$$-\int\int d^3\mathbf{r} d^3\mathbf{r}' \sum_{i \in \text{occ}} \phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}') \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r})\phi_i^*(\mathbf{r})$$

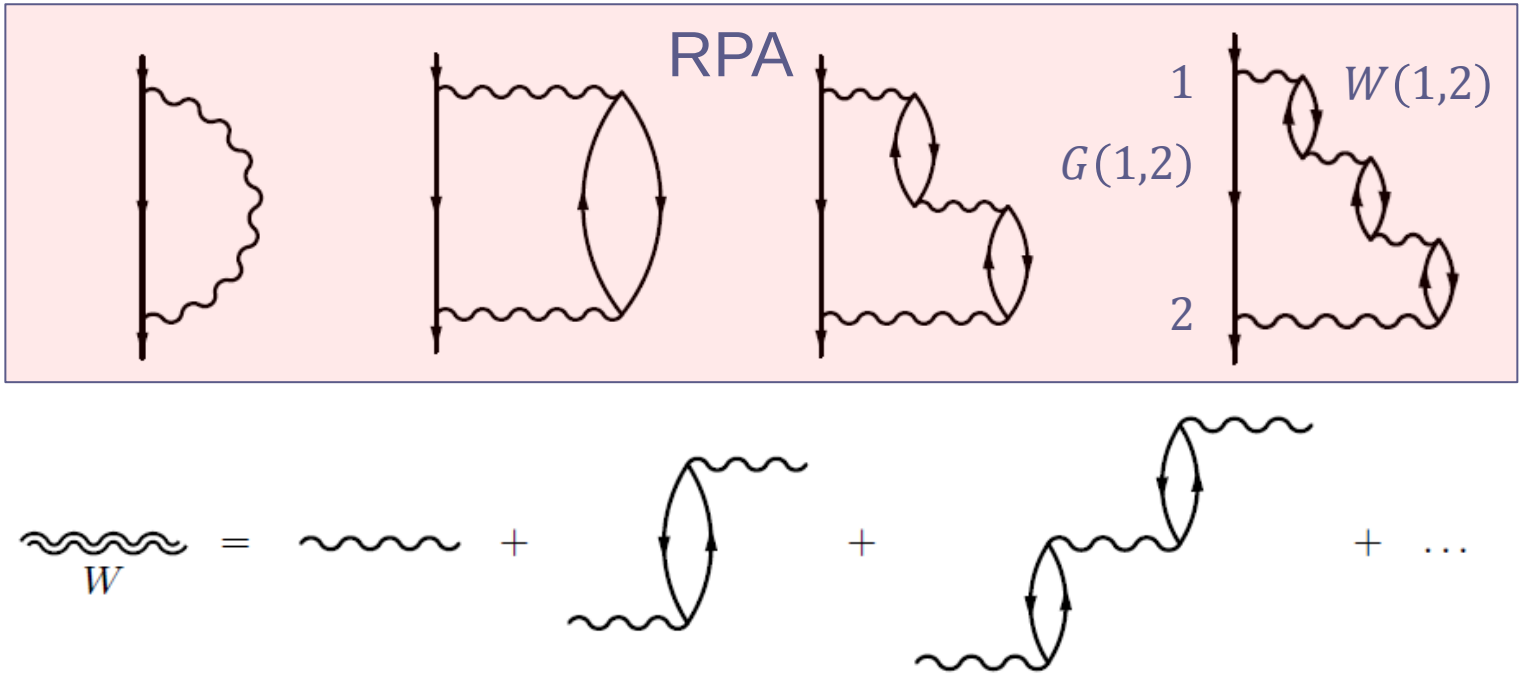
Perturbation theory: Σ is a function of G

RPA: some diagrams are simpler to calculate then others; let us sum those “simple” diagrams



Screened interaction W

To make the task easier, we introduce a screened Coulomb interaction W



Interaction W is time dependent, acts even at non equal times

$$\Sigma(1,2) = G(1,2)W(1,2)$$

Random phase approximation or GW

- Hartree-Fock: bare non-local Fock exchange

$$V^x(\mathbf{r},\mathbf{r}') = -\sum_{\text{occ}} \phi_m(\mathbf{r})\phi_m^*(\mathbf{r}') \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$$

G v

- GW: replaces bare 1/|**r-r'**| by screened Coulomb operator

$$\Sigma^{xc}(\mathbf{r},\mathbf{r}',\omega') = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega \sum_{\text{all}} \frac{\phi_m(\mathbf{r})\phi_m(\mathbf{r}')}{\omega'-\omega-\varepsilon_m+i\delta\,\text{sgn}[\varepsilon_m-\varepsilon_F]} \times$$

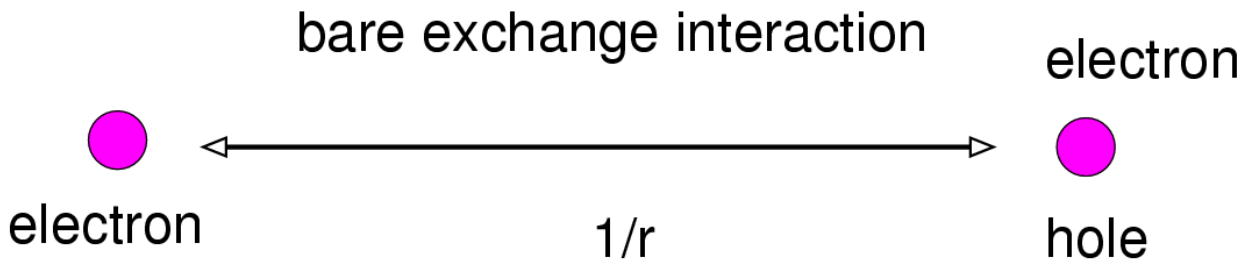
$G(\omega'-\omega)$

$$\times\; e^2\int d\mathbf{r}'' \frac{\hat{\varepsilon}^{-1}(\mathbf{r},\mathbf{r}'',\omega)}{|\mathbf{r}''-\mathbf{r}'|}$$

$W(\omega)$

Bare exchange in HF

The exchange interaction between two particles

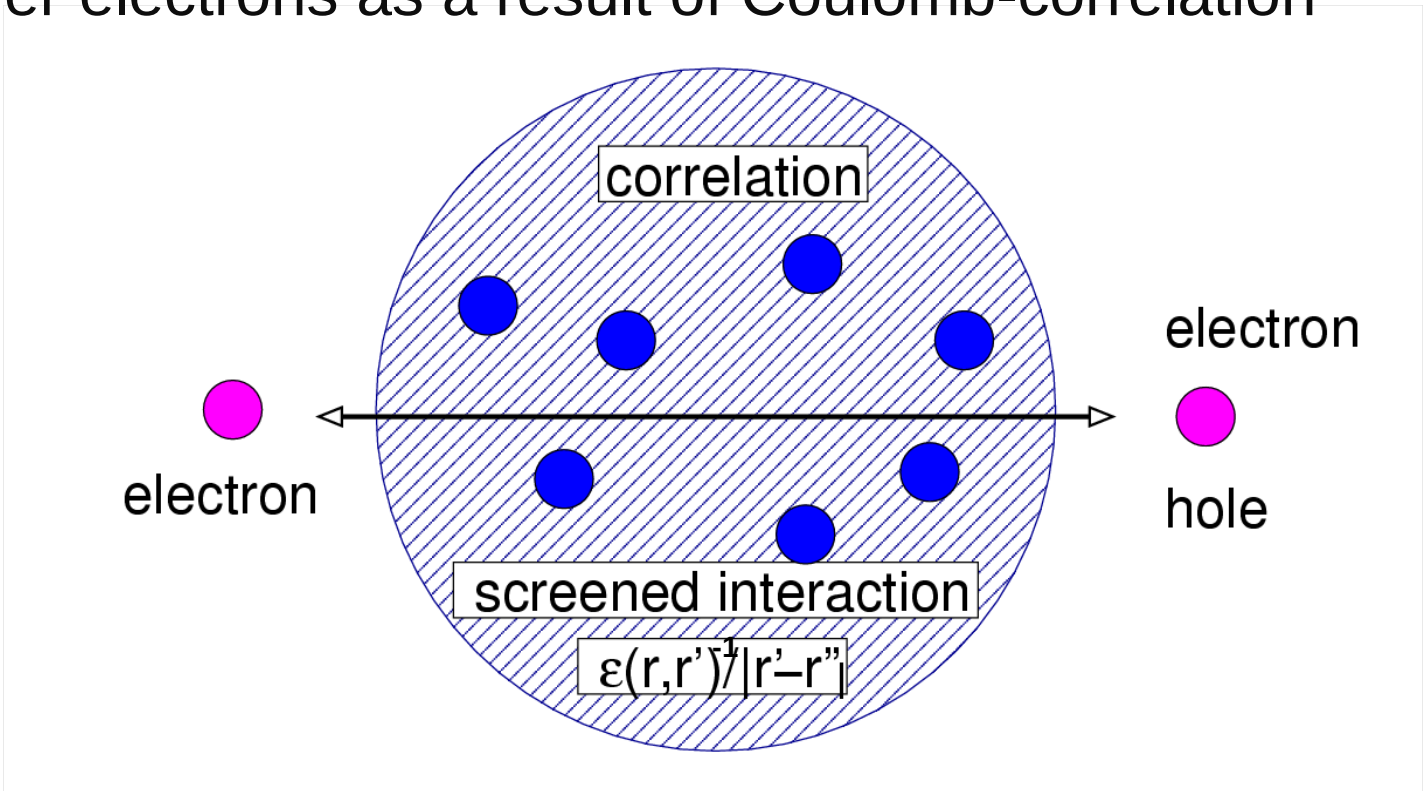


$$-\int\int d^3\mathbf{r}d^3\mathbf{r}' \sum_{n\in occ} \phi_m(\mathbf{r}')\phi_n^*(\mathbf{r}') \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_n(\mathbf{r})\phi_m^*(\mathbf{r})$$

GW: The correlation

Nozières, Phys. Rev. **111**, 442; L. Hedin, Phys. Rev. **139**, A796 (1965)

The electrons move in the exchange potential screened by all other electrons as a result of Coulomb-correlation



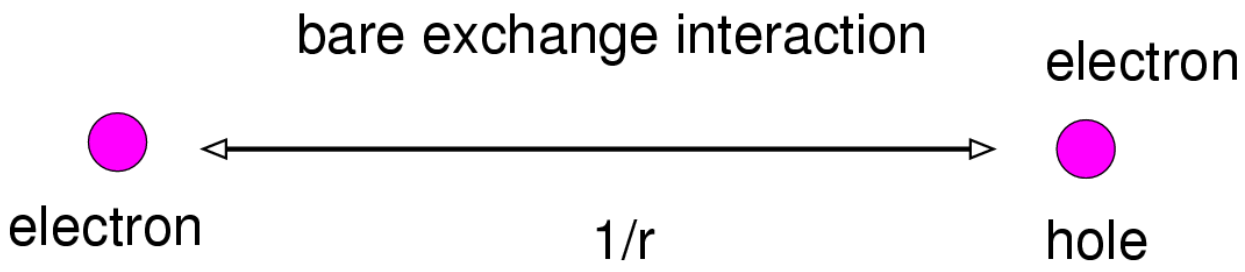
$$W = V + V\,\chi_0\,V + V\,\chi_0\,V\,\chi_0\,V + \dots$$

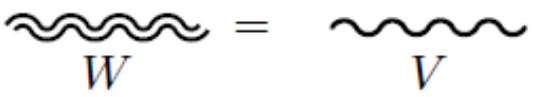
What does RPA do ?

Nozières, Phys. Rev. **111**, 442; L. Hedin, Phys. Rev. **139**, A796 (1965)

Coulomb correlation from “symmetric” part of wave function (over-correlates about 130 % of correct correlation energy)

$$v \Rightarrow W$$

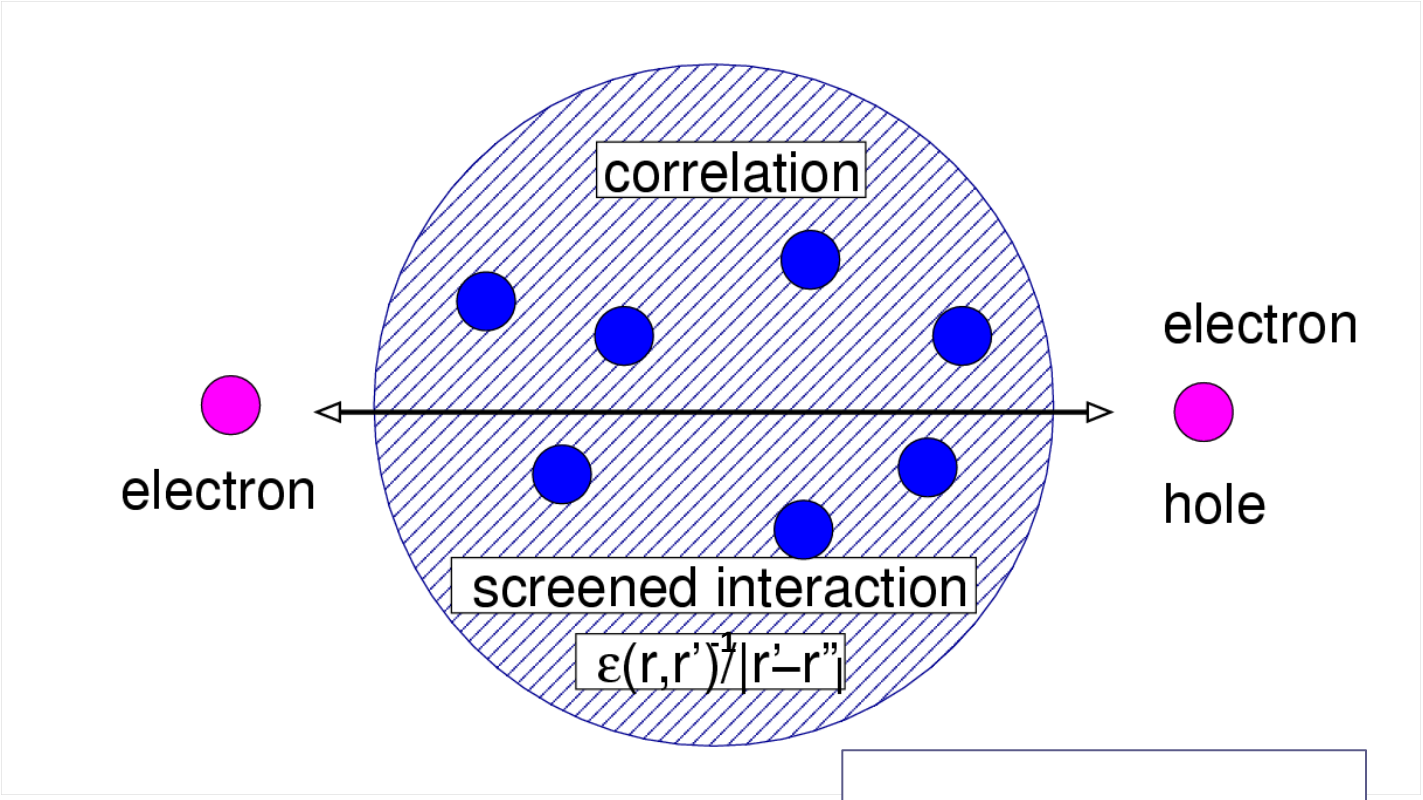


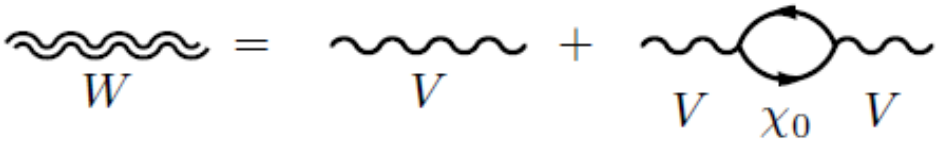


bare Coulomb interaction

Lets calculation the interaction: RPA

The interaction between two particles

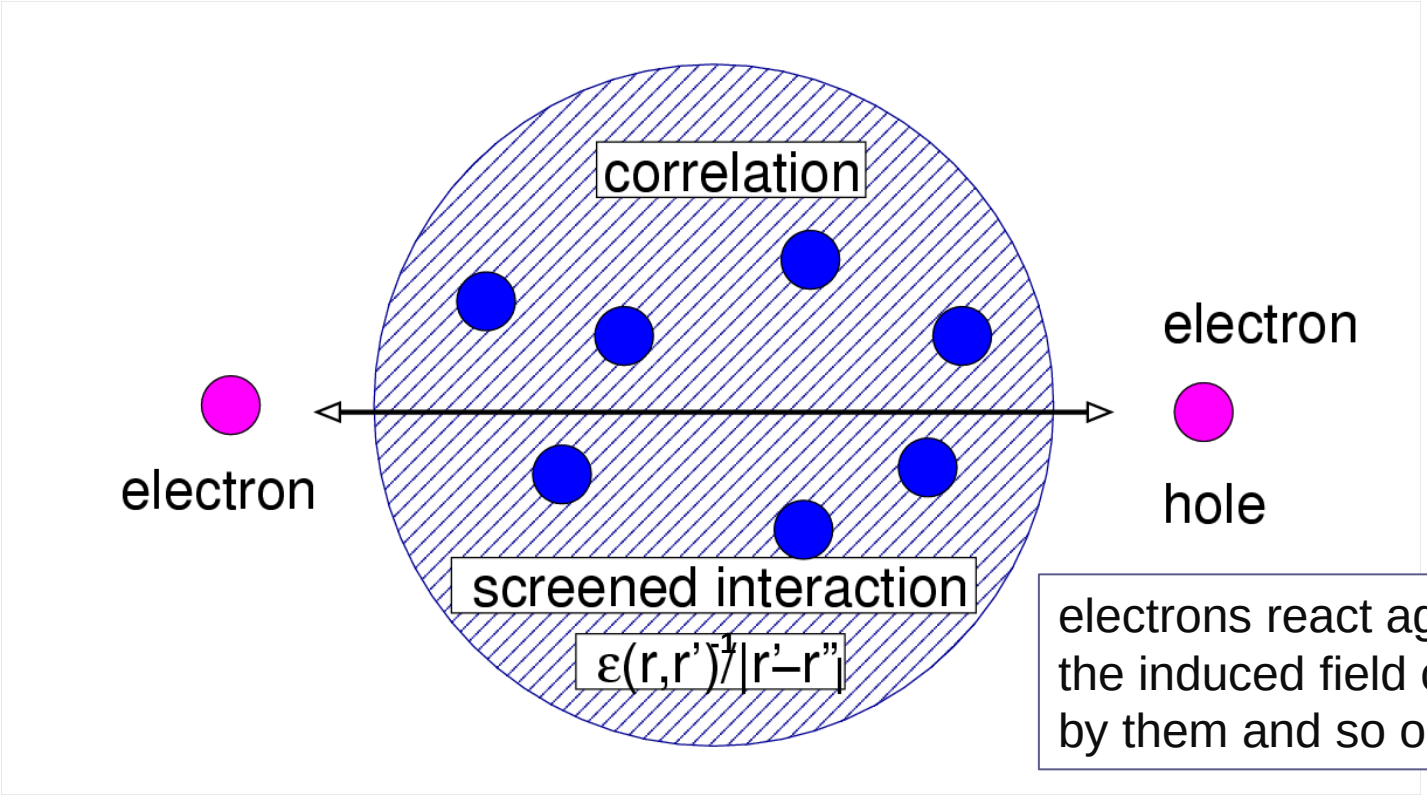




other electrons react to the created field of one particle

Lets calculation the interaction: RPA

The interaction between two particles



$W = V + V\,\chi_0\,V + V\,\chi_0\,V\,\chi_0\,V + \ldots$

Polarizability direct-RPA - dRPA

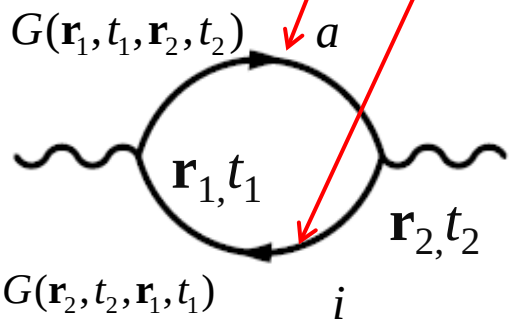
Independent particle polarizability

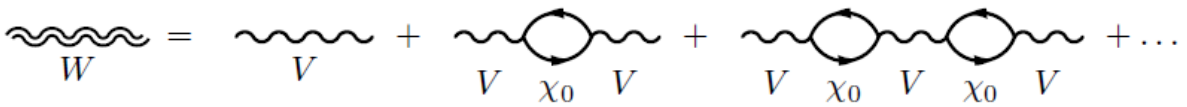
$$\chi_0(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) = -G(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2)G(\mathbf{r}_2,t_2,\mathbf{r}_1,t_1)$$

$$\chi_0(\mathbf{r}_1,\mathbf{r}_2,\omega) = \sum_{\substack{i\in\text{occ}\\ a\in\text{unocc}}} \frac{\langle\phi_a|\mathbf{r}_1|\phi_i\rangle\langle\phi_i|\mathbf{r}_2|\phi_a\rangle}{\varepsilon_i-\varepsilon_a-\omega} + \sum_{\substack{i\in\text{occ}\\ a\in\text{unocc}}} \frac{\langle\phi_i|\mathbf{r}_1|\phi_a\rangle\langle\phi_a|\mathbf{r}_2|\phi_i\rangle}{-\varepsilon_i+\varepsilon_a-\omega}$$

electron
(originally unocc.)

hole





$$W = v + v\chi v + v\chi v\chi v + v\chi v\chi v\chi v +$$

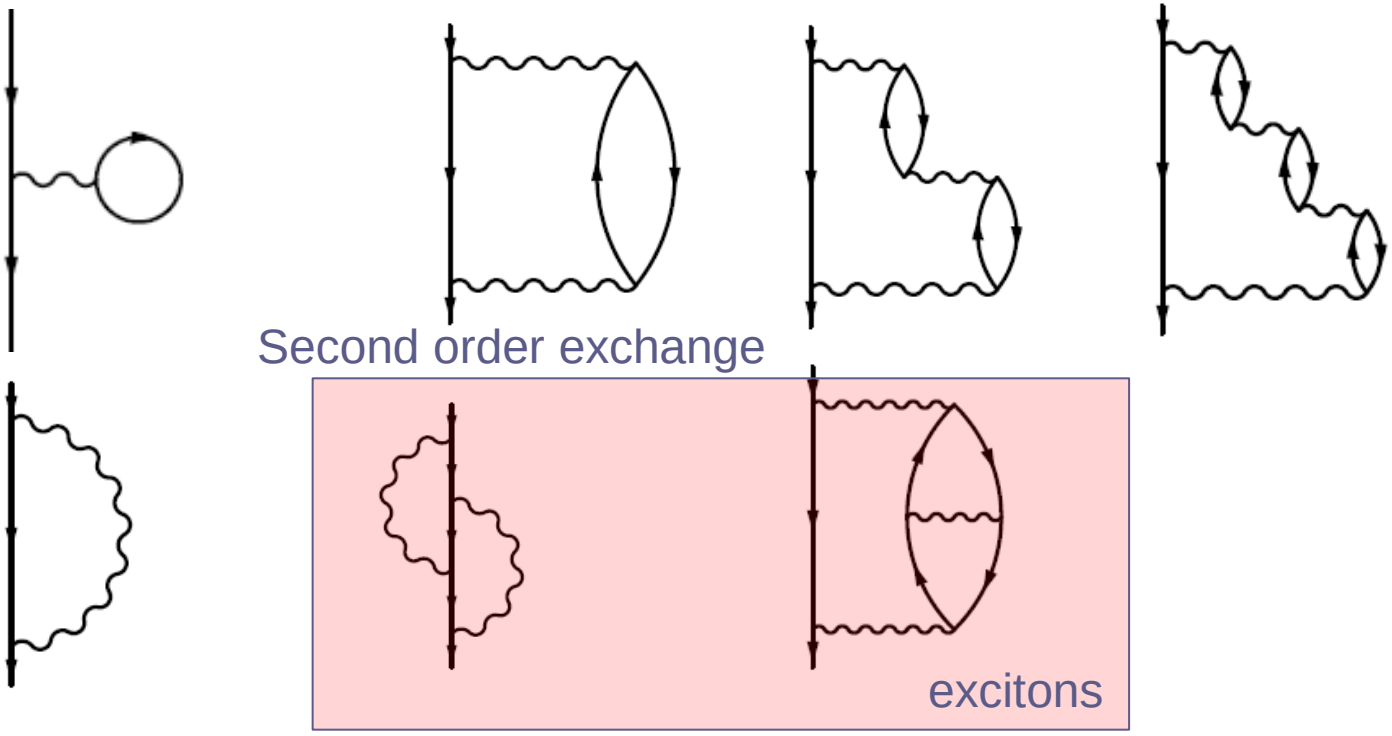
$$= v(1+\chi v)^{-1}$$ geometrical series

$$= v + v\chi W$$ Dyson equation

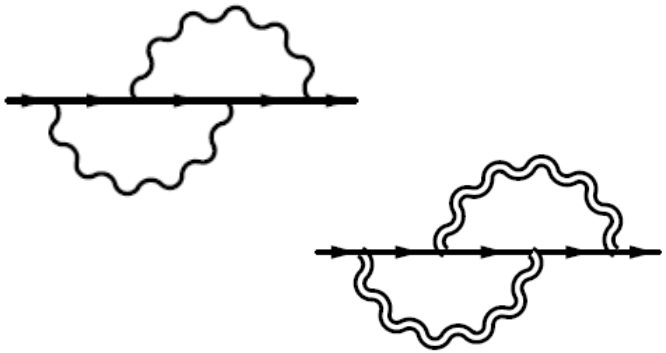
$$v^{-1} = W^{-1} + \chi$$

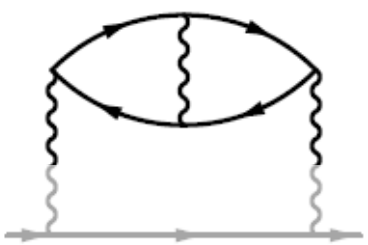
What did we neglect: a lot, that's the problem

We have even neglected one second order diagram, the "second order" exchange
In third order, excitonic effects and many more diagrams have been neglected



What did we neglect:





Second order exchange:

- In GW, vertex in self-energy
- No simple “physical” interpretation (as for exchange)
- Important to remove self-interaction

Particle-Hole ladder diagram:

- Electrostatic interaction between electrons and holes
- Vertex corrections in W
- Important to remove self-screening

Overview

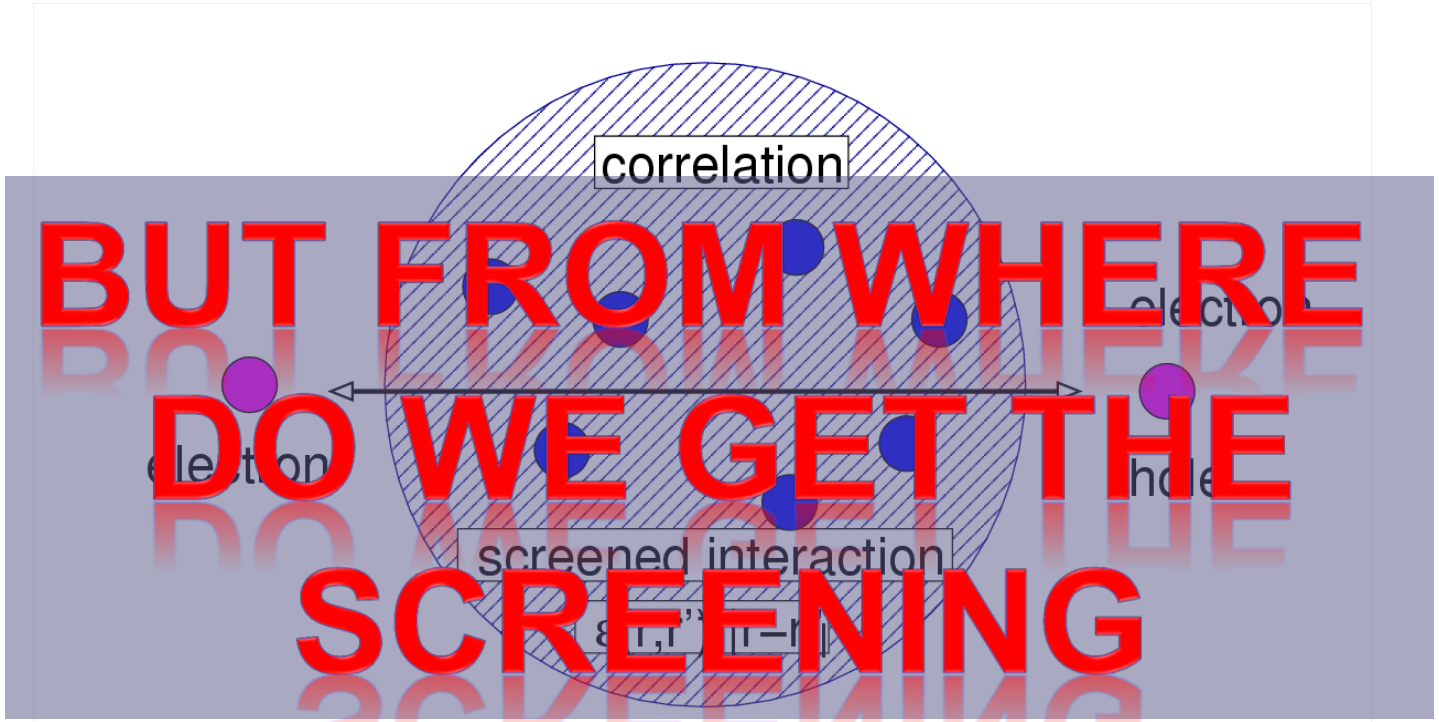
- RPA and GW a first look
  - The QP equation, Green's functions
  - Feynman diagrams
  - The RPA approximation and what is missing
- GW for band gaps
  - Prototypical systems
  - The many flavours of GW

The crux: screening properties

Nozières, Phys. Rev. **111**, 442; L. Hedin, Phys. Rev. **139**, A796 (1965)

Exchange interaction is screened by other electrons

Polarizability (screening) is the essential ingredient



BUT FROM WHERE DO WE GET THE SCREENING

$$W = V + V\,\chi_0\,V + V\,\chi_0\,V\,\chi_0\,V + \dots$$

G_0W_0 approximation

M. S. Hybertsen, S. G. Louie, Phys. Rev. B **34**, 5390 (1986)

- Calculate DFT orbitals

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{el}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r})\right)\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})$$

- Determine G_0, W_0 and $\Sigma = G_0W_0$ from DFT orbitals
- Determine first order change of one-electron energies

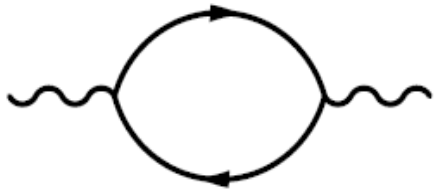
$$\left\langle \phi_n \middle| -\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}} + V^{\text{el}} + \sum(E_n) \middle| \phi_n \right\rangle = E_n$$

- Alternative formulation G_0W_0 : determine poles of

$$G(\omega) = G_0(\omega) + G_0(\omega)(\Sigma(\omega) - V^{xc})G_0(\omega)$$

G_0W_0: Polarizability and Greens function

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\substack{i\in\text{occ}\\ a\in\text{unocc}}} \frac{\langle\phi_i|\mathbf{r}|\phi_a\rangle\langle\phi_a|\mathbf{r}'|\phi_i\rangle}{\varepsilon_i-\varepsilon_a-\omega} + \ldots$$



$$W = v + v\chi v + v\chi v\chi v + v\chi v\chi v\chi v + \ldots = v\underbrace{(1+\chi v)^{-1}}_{\varepsilon^{-1}}$$

$$\Sigma^{xc}(\mathbf{r},\mathbf{r}',\omega') = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega \sum_{\text{all}} \frac{\phi_m(\mathbf{r})\phi_m(\mathbf{r}')}{\omega'-\omega-\varepsilon_m+i\delta\,\text{sgn}[\varepsilon_m-\varepsilon_F]} \times$$

$G(\omega'-\omega)$

$$\times\; e^2\int d\mathbf{r}''\frac{\hat{\varepsilon}^{-1}(\mathbf{r},\mathbf{r}'',\omega)}{|\mathbf{r}''-\mathbf{r}'|}$$

$W(\omega)$

GW_0 approximation

M. S. Hybertsen, S. G. Louie, Phys. Rev. B **34**, 5390 (1986)

- Calculate DFT orbitals

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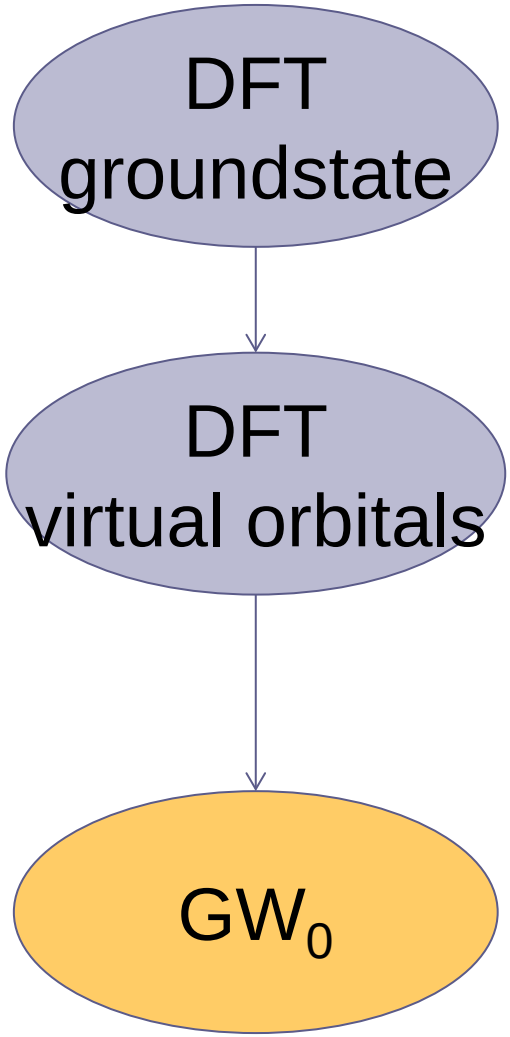
- Determine G_0, W_0 and $\Sigma = G_0W_0$ from DFT orbitals
- Determine first order change of one-electron energies

$$\left\langle \phi_n \middle| -\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}} + V^{\text{el}} + \sum(E_n) \middle| \phi_n \right\rangle = E_n$$

- Update G using new one electron energies and recalculate $\Sigma = GW_0$ and continue

G_0W_0 and GW_0 flow chart



ISMEAR = 0 ; SIGMA = 0.05
EDIFF = 1E-8

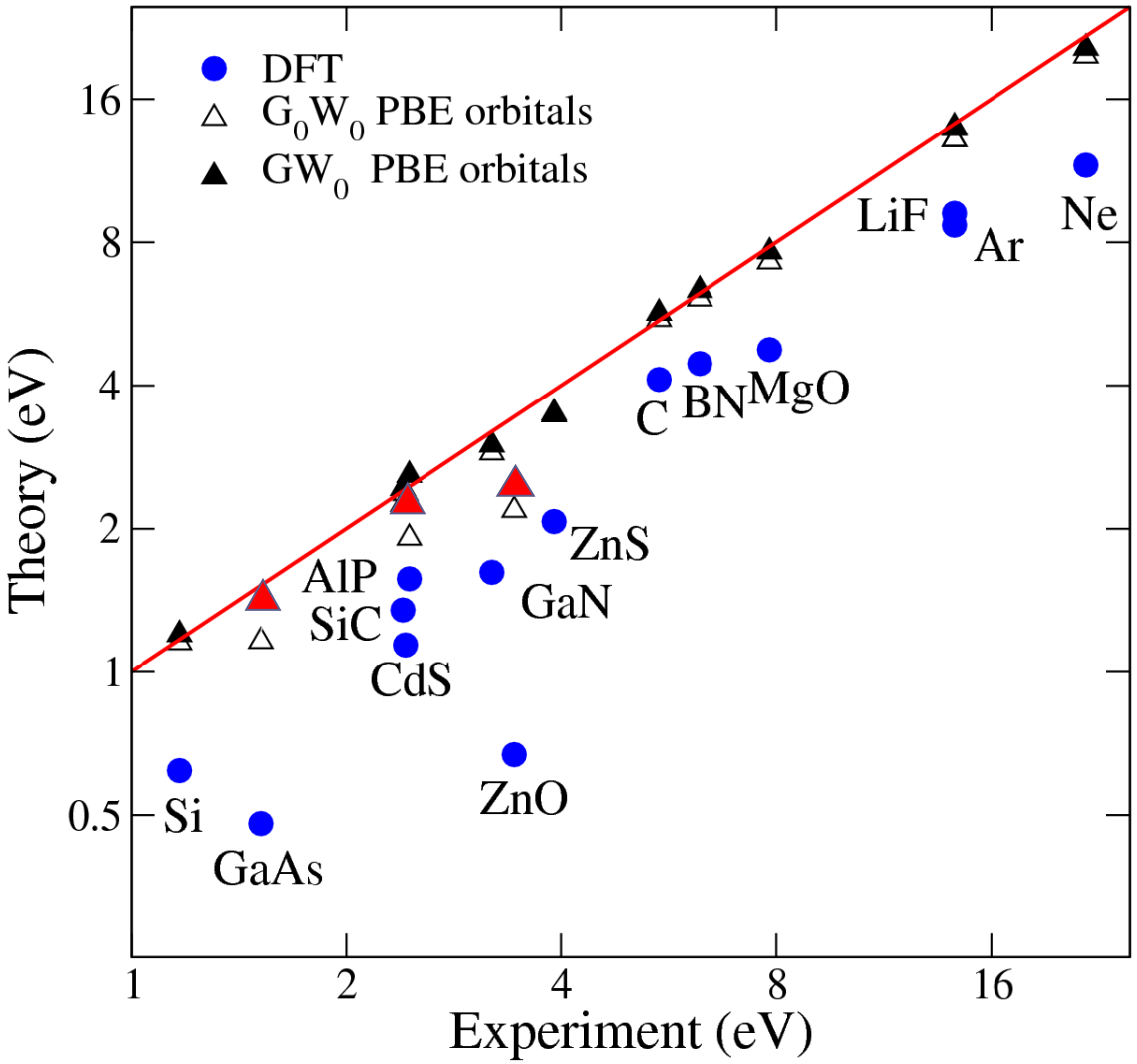
NBANDS = 50-200 per atom
ALGO = Exact
ISMEAR = 0 ; SIGMA = 0.05
LOPTICS = .TRUE.

NBANDS = 50-200 per atom
ALGO = GW0
ISMEAR = 0 ; SIGMA = 0.05
NELM=1 → G0W0
NELM=4-6 → converged GW0

The many test you could and should do

NBANDS	total number of bands
	set NBANDS to the total number of plane waves
NOMEGA	number of frequency points
	default: 50 is pretty good (maybe test 100-200) small gap systems might need more freq. points little performance penalty (requires more memory)
ENCUTGW	plane wave energy cutoff for response functions
	default: 2/3 ENCUT is pretty good
ENCUT	plane wave energy cutoff for orbitals

PBE orbitals and screening: GW_0 band gaps[1]



- Improvement over G_0W_0
  - G_0W_0: MARE 8.5 %
  - GW_0 : MARE 4.5 %

M. Shishkin, G. Kresse, PRB **75**, 235102 (2007).

M. Shishkin, M. Marsman, PRL **95**, 246403 (2007)

A. Grüneis, G. Kresse, PRL **112**, 096401 (2014)

Let us update the orbitals: sc-QPGW

Faleev, van Schilfgaarde, Kotani, Phys. Rev. Lett. **93**, 126406 (2004)

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{el}}(\mathbf{r})\right) + \Sigma(\mathbf{r},\mathbf{r}',\omega)$$

Construct a Hermitian (one-electron) approximation to $\Sigma(\omega)$ and diagonalize that approximate Hamiltonian

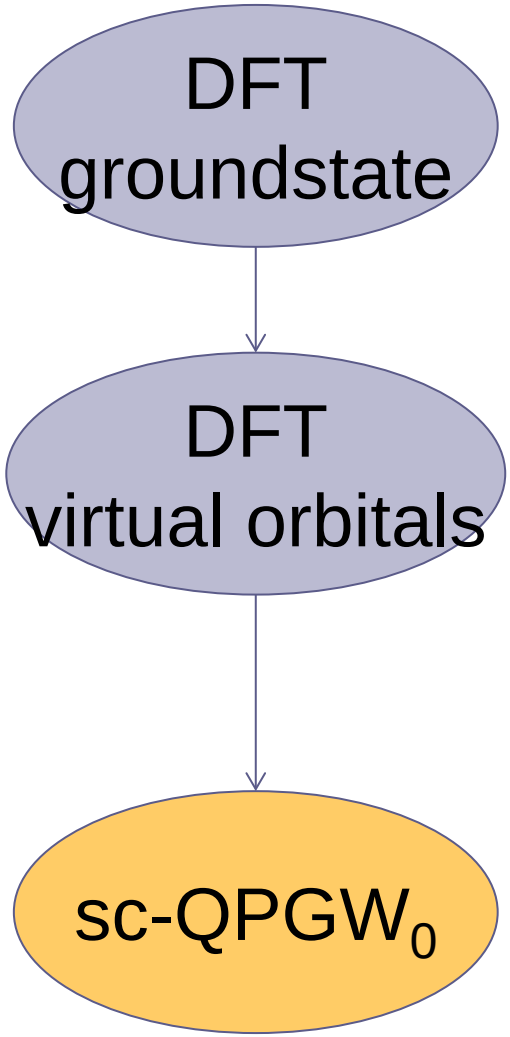
$$(T+V)\phi + \boldsymbol{\Sigma}(E)\phi = E\phi$$

$$(T+V)\phi + \left(\boldsymbol{\Sigma}(E_0)\phi + \frac{d\boldsymbol{\Sigma}(E_0)}{dE_0}(E-E_0)\,\phi\right) = E\phi$$

$$(T+V)\phi + \left(\boldsymbol{\Sigma}(E_0) - \frac{d\boldsymbol{\Sigma}(E_0)}{dE_0}E_0\right)\phi = E\left(1 - \frac{d\boldsymbol{\Sigma}(E_0)}{dE_0}\right)\phi$$

$$\Sigma^{\text{Herm}}\phi = E\mathbf{S}\phi \quad \Leftrightarrow \quad \mathbf{S}^{-1/2}\Sigma^{\text{Herm}}\mathbf{S}^{-1/2}\,\phi' = E\,\phi'$$

sc-QPGW_0 *flow chart*

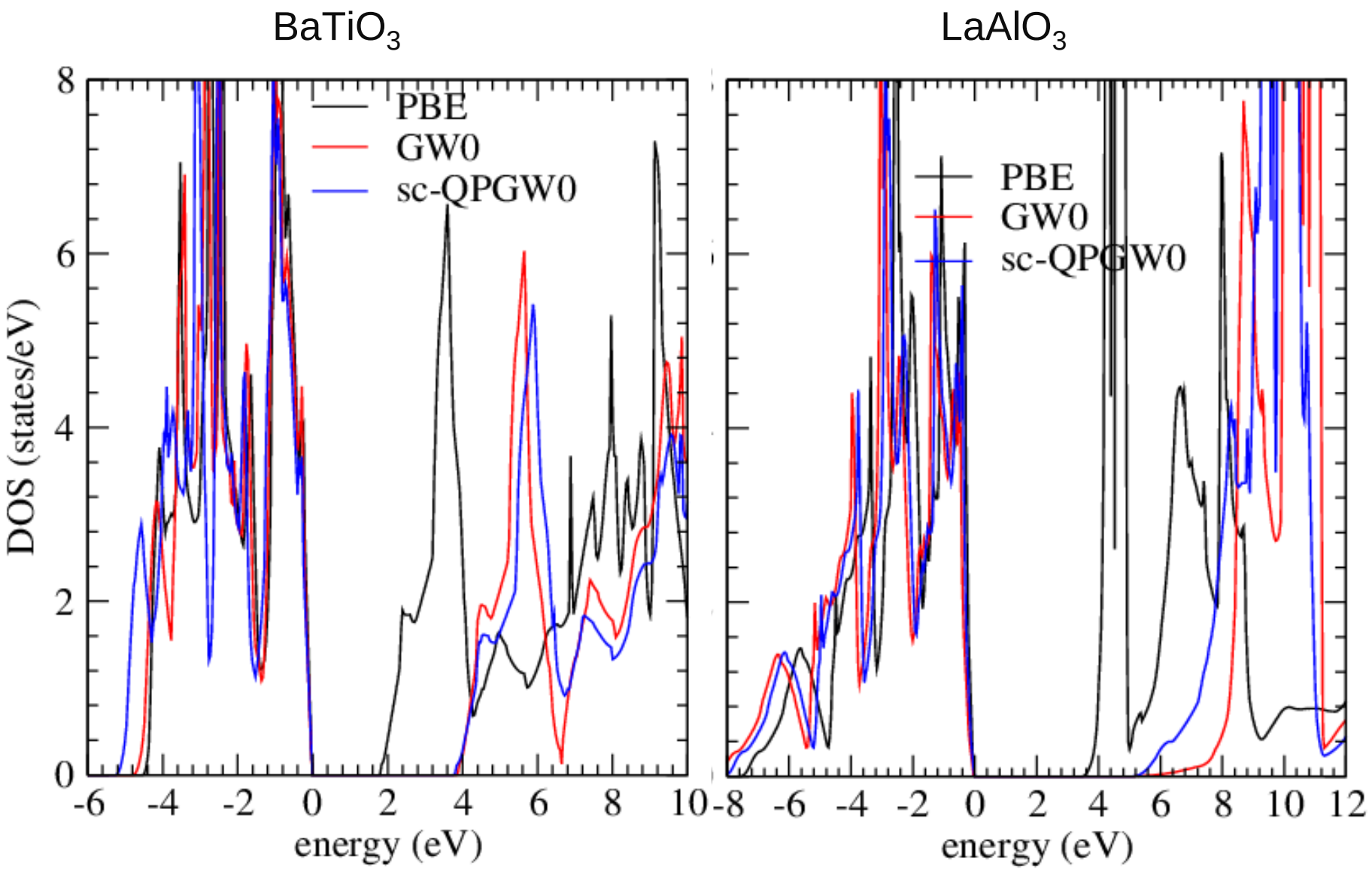


ISMEAR = 0 ; SIGMA = 0.05
EDIFF = 1E-8

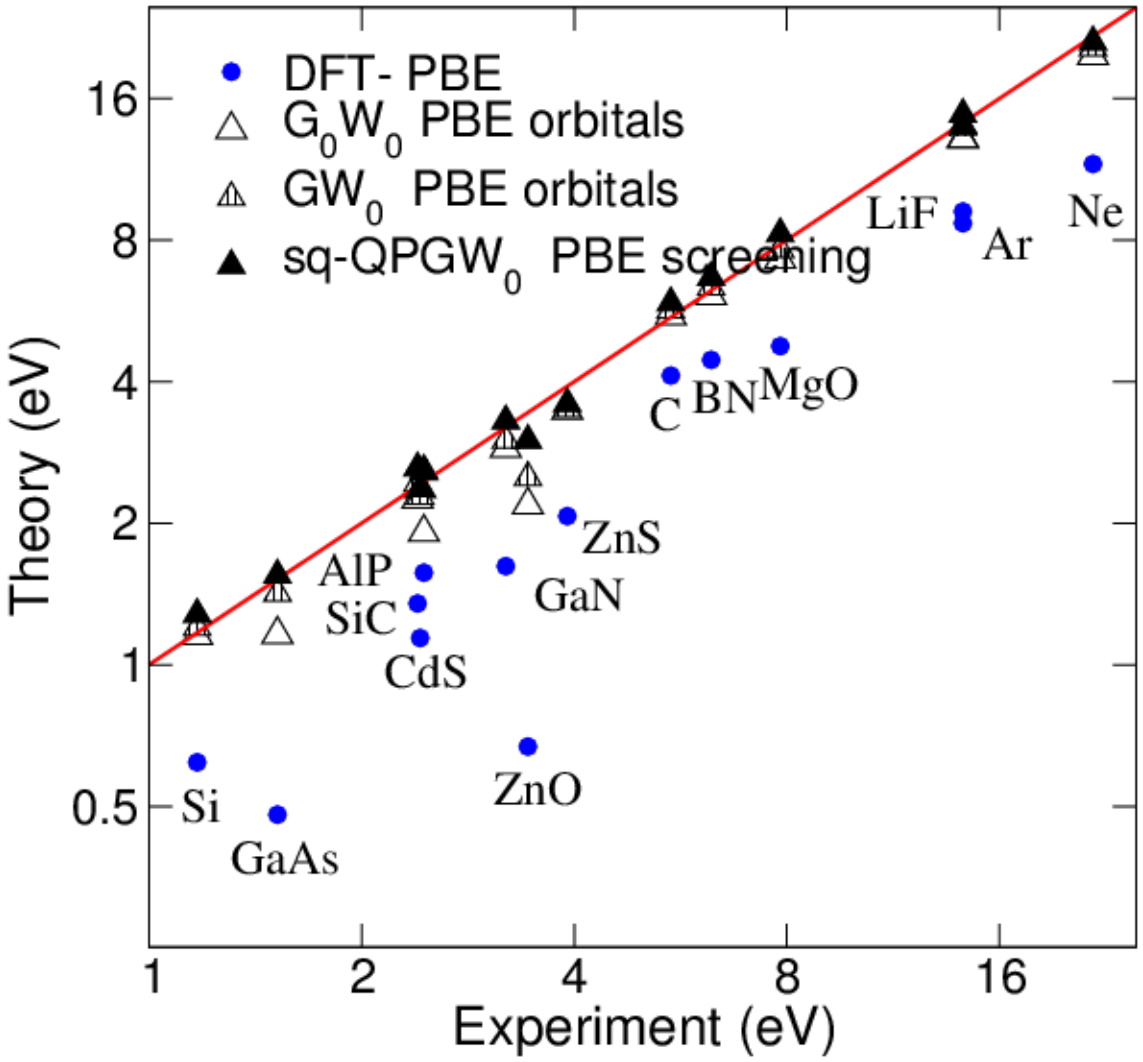
NBANDS = 50-200 per atom
ALGO = Exact
ISMEAR = 0 ; SIGMA = 0.05
LOPTICS = .TRUE.

NBANDS = 50-200 per atom
ALGO = QPGW0
ISMEAR = 0 ; SIGMA = 0.05
NELM=5-10 → converged QPGW0

When do you need sc-QPGW$_0$



PBE screening: sc-QPGW$_0$ band gaps[1]



- Little improvement over *GW$_0$*
- On average too large gaps

M. Shishkin, M. Marsman, PRL 95, 246403 (2007)

scQPGW : Updating G and W

M. S. Hybertsen, S. G. Louie, Phys. Rev. B **34**, 5390 (1986)

- Calculate DFT orbitals

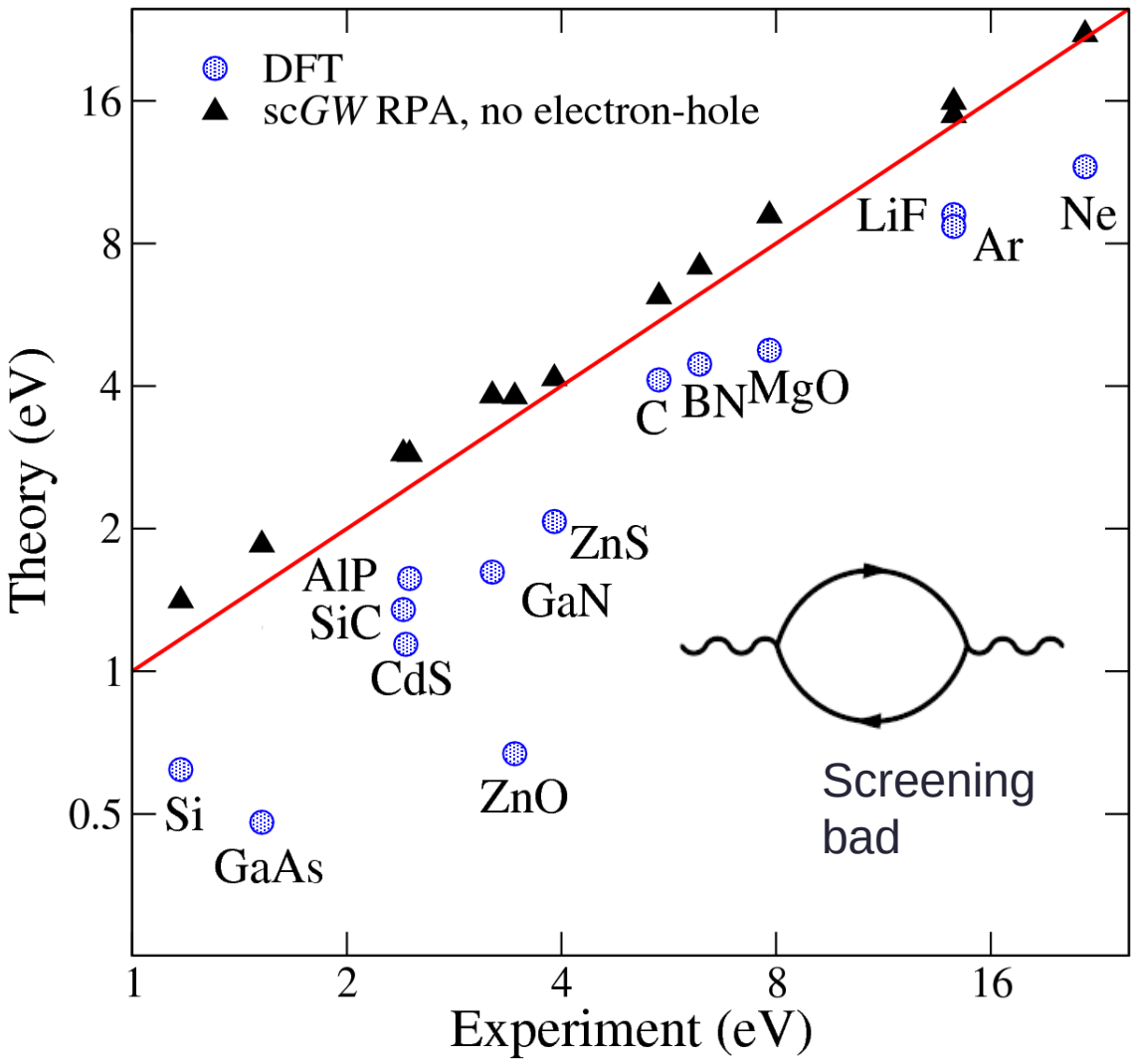
$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r})\right)\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})$$

- Determine G_0, W_0 and $\Sigma = G_0 W_0$ from DFT orbitals
- Determine change of orbitals and one-electron energies

$$(\mathbf{T}+\mathbf{V})\phi + \left(\boldsymbol{\Sigma}(E_0) - \frac{d\boldsymbol{\Sigma}(E_0)}{dE_0}E_0\right)\phi = E\left(1 - \frac{d\boldsymbol{\Sigma}(E_0)}{dE_0}\right)\phi$$

- Update G, W using new one electron energies and orbitals and recalculate $\Sigma = GW$ and continue

Selfconsistent scQPGW band gaps[1]



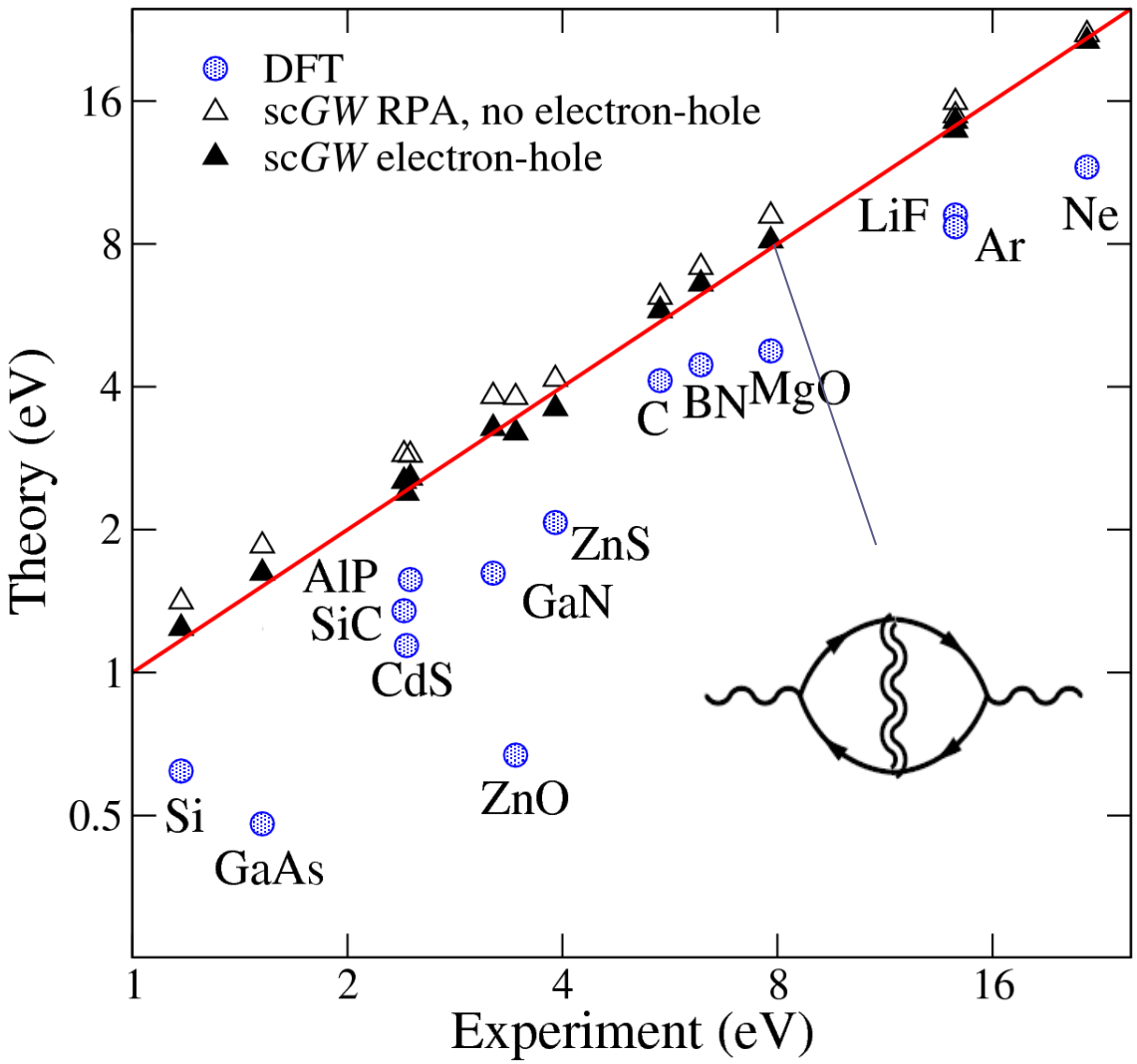
Update G and W

Schilfgaarde & Kotani
PRL 96, 226402 (2006)

- Well this is dis-appointing, isn't it ?
- worse than GW_0
- Static dielectric constants are now too small by 20 %

[1] M. Shishkin, M. Marsman, G. Kresse, PRL 95, 246403 (2007)

Self-consistent QPGW$^{TC\text{-}TC}$ band gaps[1]



e-h interaction: L. Reining
Nano-quanta kernel

- Excellent results across all materials
  - *MARE: 3.5 %*
- Further slight improvement over GW_0 (PBE)
- Too expensive for large scale applications but fundamentally important

[1] M. Shishkin, M. Marsman, G. Kresse, PRL 95, 246403 (2007)

Dielectric properties ε using scQPGW

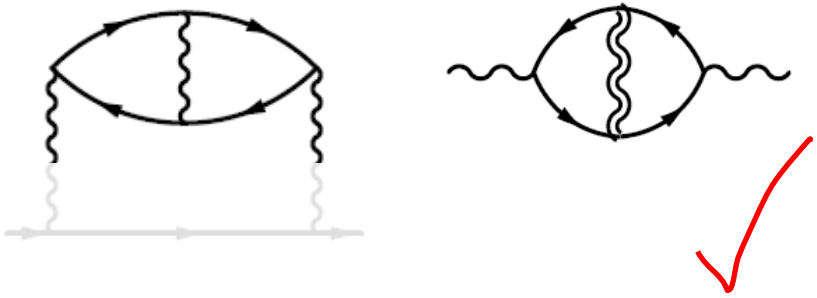
	sc*GW*$^{TC\text{-}TC}$	sc*GW*$^{TC\text{-}TC}$ TC-TC	EXP
GaAs	8.2	10.4	11.1
Si	9.2	11.4	11.9
SiC	5.22	6.48	6.52
C	5.00	5.58	5.70
ZnO	2.84	3.80	3.74
MgO	2.30	2.96	3.00

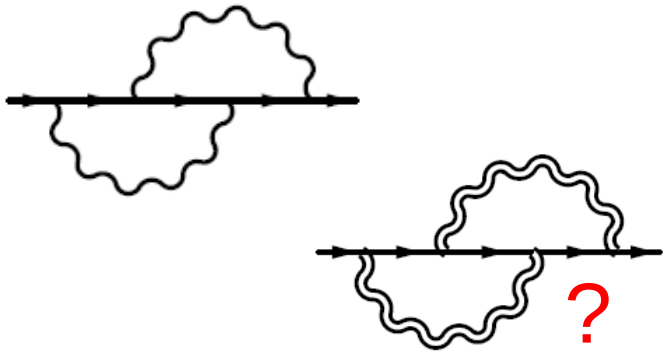
Vertex correction include e-h interaction

Scaling: N^5-N^6

- Selfconsistent GW (or any other method with good band gaps) yields reasonable screening properties only if
  - = particle-hole ladder diagrams in screening
  - e-h interactions in W are included = solution of BSE
  - = vertex corrections in W are included

What did we neglect:





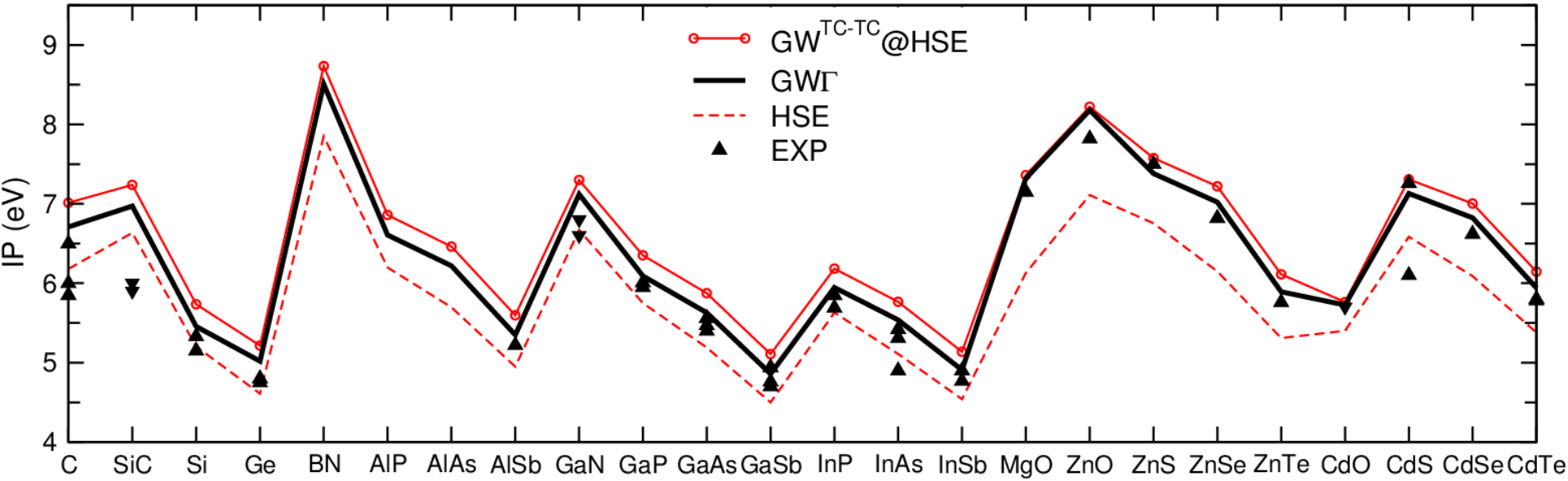
Particle-Hole ladder diagram:

- Electrostatic interaction between electrons and holes
- Vertex corrections in W
- Important to remove self-screening

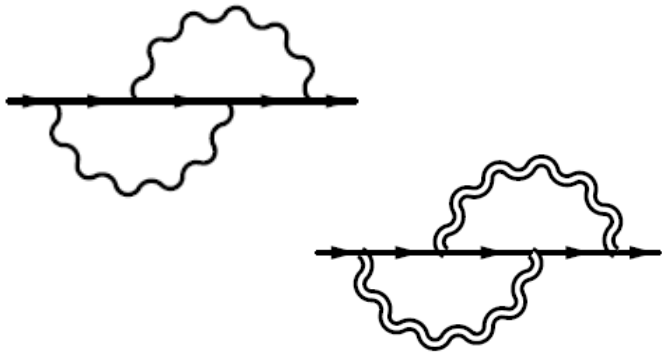
Second order exchange:

- Vertex in self-energy
- No simple “physical” interpretation (as for exchange)
- Important to remove selfinteraction

Vertex in the self-energy (and polarizability)

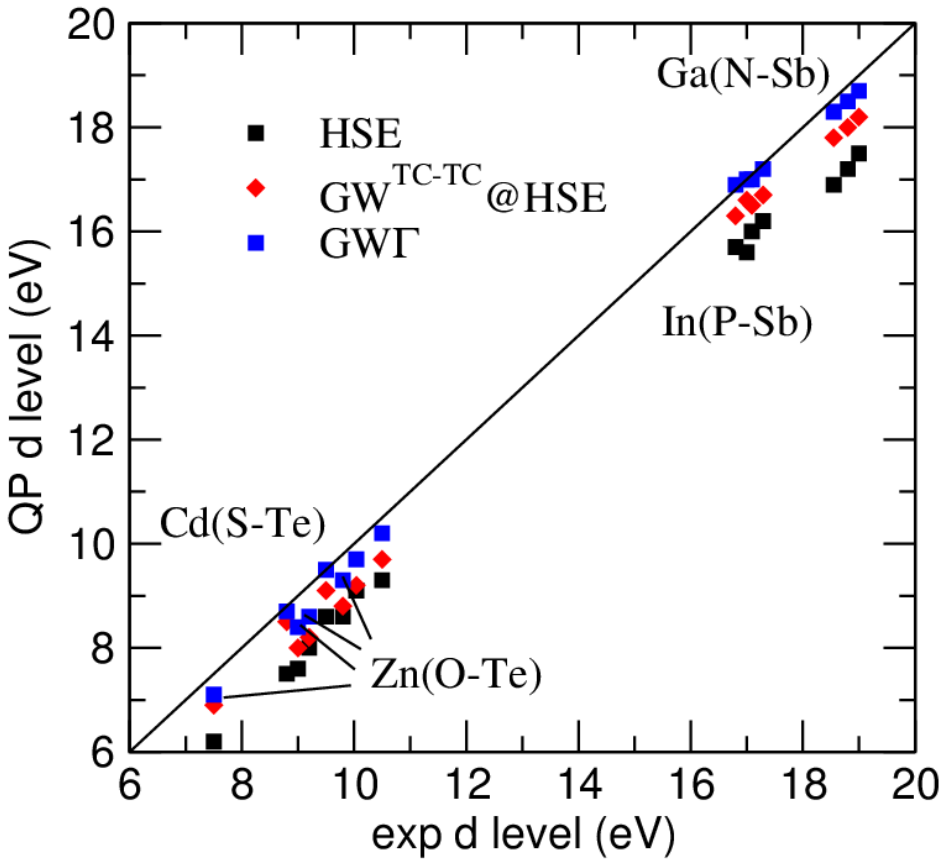


- Vertex in the self-energy raises valence and conduction states towards vacuum level



A. Grüneis, G. Kresse, Y. Hinuma, F. Oba, PRL. **112** 096401

Vertex in the self energy lowers d-levels



Vertex in the self energy lowers d-levels

d level then agree very well with experimental measurements

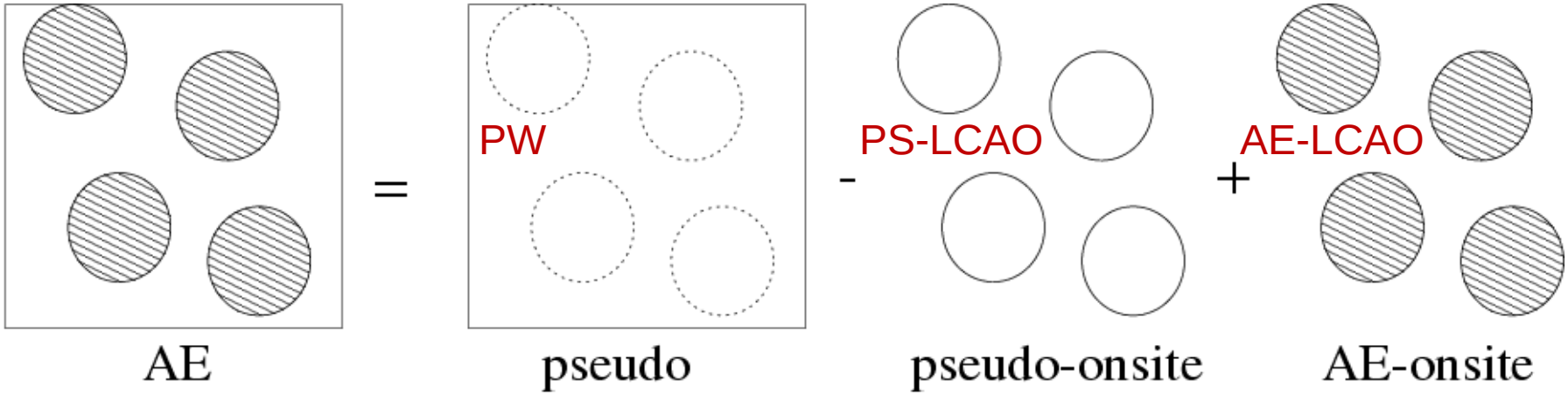
Typically binding energy increases by 0.5 eV, if the vertex in the selfenergy is included

A. Grüneis, G. Kresse, Y. Hinuma, F. Oba, PRL. **112** 096401

VASP: PAW methods

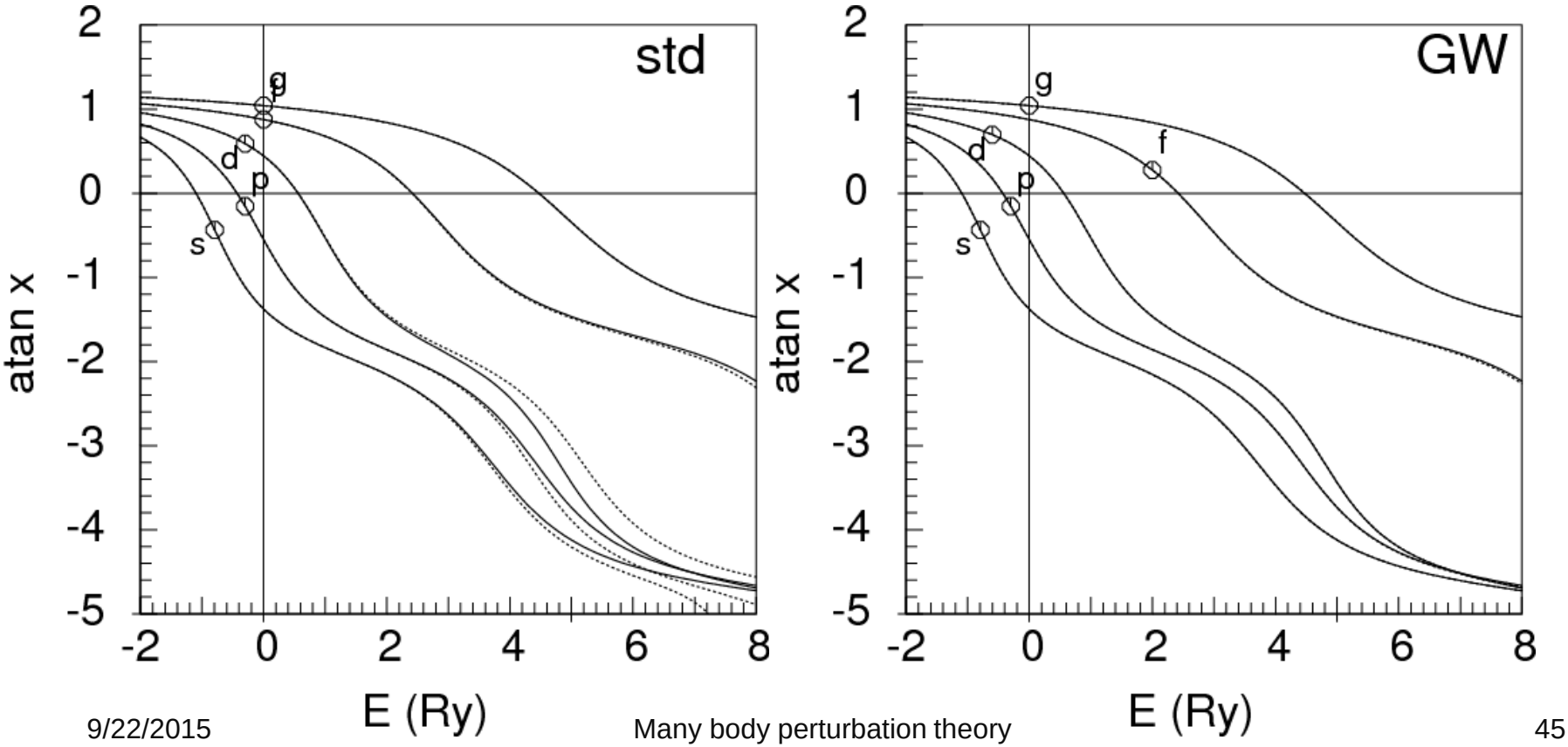
P. Blöchl, PRB 50, 17953 (1994), G. Kresse, et. al. PRB 59, 1758 (1998).

- PAW method: full potential (all-electron method)
- Core-valence interaction is described at same level as valence electrons, core states are frozen at DFT level
- Plane waves everywhere in space (pseudo)
- LCAO corrections in the spheres (one center terms)



The subtle issues: GW potentials

- PAW allows to describe scattering properties accurately at a selected number of reference energies
- Since GW is sensitive to high lying conduction bands an appropriate description of conduction bands is important
- Scattering properties for Si:



An important issue: the PAW technique

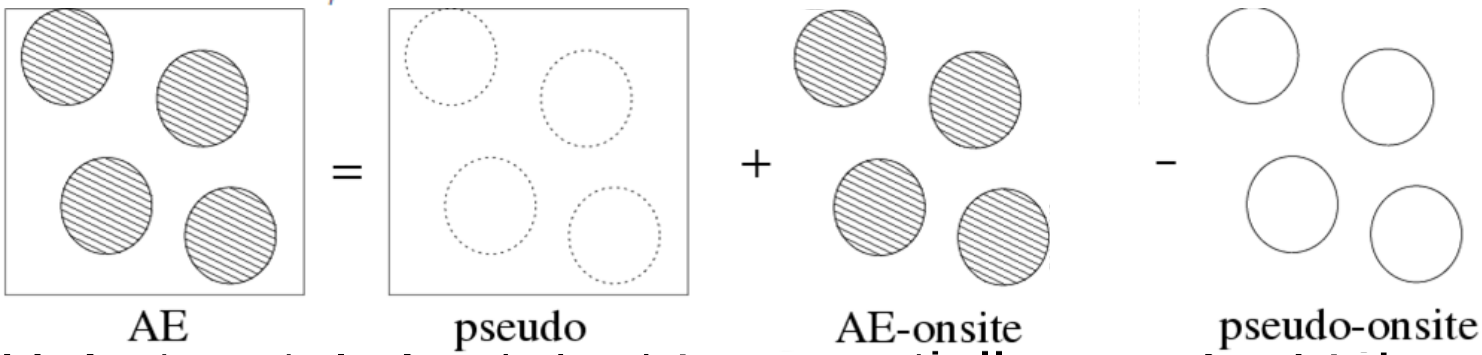
- Relation between AE and pseudo orbital

$$|i\rangle = |\tilde{i}\rangle + \underbrace{\sum_{\alpha}(|\alpha\rangle - |\tilde{\alpha}\rangle)\langle p_\alpha|\tilde{i}\rangle}_{|i^{\mathrm{aug}}\rangle}$$

$$\langle a|\mathbf{r}\rangle\langle\mathbf{r}|i\rangle = \langle\tilde{a}|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{i}\rangle + \langle a^{\mathrm{aug}}|\mathbf{r}\rangle\langle\mathbf{r}|i^{\mathrm{aug}}\rangle + \langle a^{\mathrm{aug}}|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{i}\rangle + \langle\tilde{a}|\mathbf{r}\rangle\langle\mathbf{r}|i^{\mathrm{aug}}\rangle$$

- Approximation:

$$\langle a|\mathbf{r}\rangle\langle\mathbf{r}|i\rangle \approx \langle\tilde{a}|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{i}\rangle + \sum_{\alpha\beta}\langle\tilde{a}|p_\alpha\rangle(\langle\alpha|\mathbf{r}\rangle\langle\mathbf{r}|\beta\rangle - \langle\tilde{\alpha}|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\beta}\rangle)\langle p_\beta|\tilde{i}\rangle$$



- Unfortunately for $\langle a|p_\alpha\rangle$ is essentially zero for high energies (30 Ry above vacuum level)

PAW problem

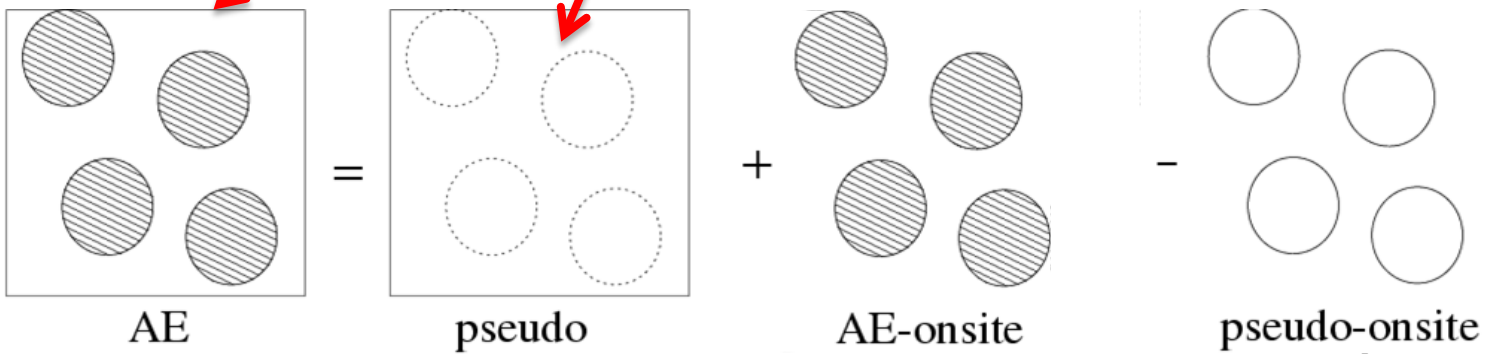
- Extremely simply final equation for the correlation energy from inter-electron cusp

$$E(\mathbf{G},\mathbf{G}') = -\frac{1}{2}|\rho(\mathbf{G}-\mathbf{G}')|^2 \frac{4\pi}{\mathbf{G}'^2}\frac{4\pi}{\mathbf{G}^2}\frac{2}{\mathbf{G}^2+\mathbf{G}'^2}$$

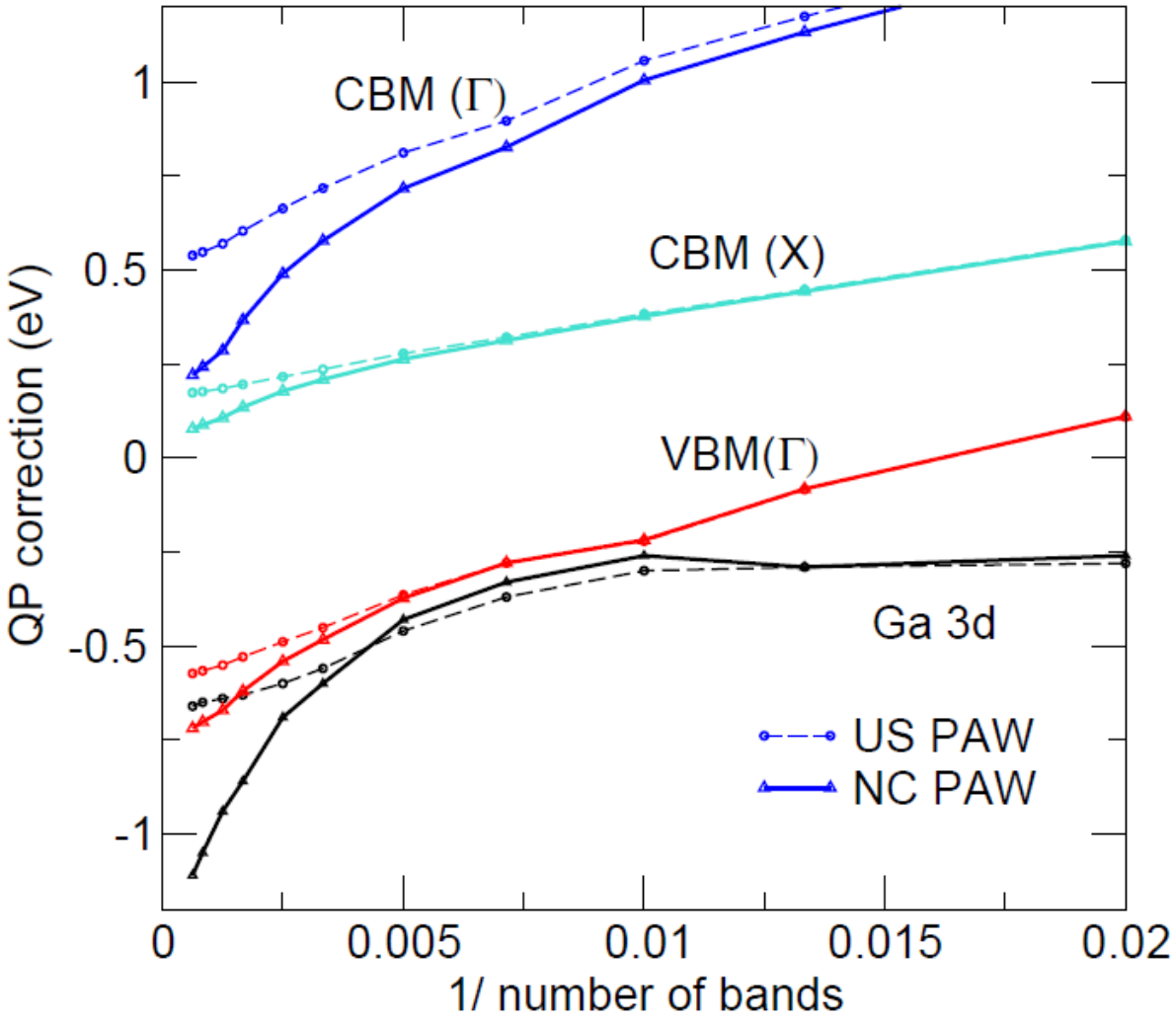
we want !

we get !

- Involves only groundstate density distribution but if one follows the derivation carefully, one realizes that in the PAW method, only the original non-normalized density is considered (completeness problem)



NC-PAW potentials versus standard PAW



- Standard PAW yields wrong QP energies for localized states
- Errors around 1 eV (huge by any means)
- FLAPW and LMTO methods suffers from related problems
- Explains why results between different codes are so different

Klimes, Kaltak, Kresse, PRB 90, 075125 (2014).

GW potentials, and non NC-GW potentials

- To be released GW potentials for VASP for all elements in the periodic table except f-elements
- Very accurate
  - Most are superior to all previous potentials even for groundstate calculations
  - Usually all semi-core states are treated as valence
  - In practice, there is usually very little difference between standard and GW potentials for groundstate calculations

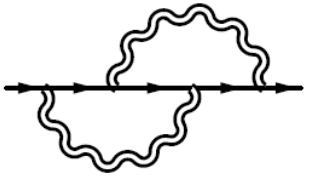
WIEN2k-VASP std POTCAR	0.76 meV/atom
WIEN2k-VASP(GW POTCAR)	0.42 meV/atom

Lejaeghere, Speybroeck, Oost and Cottenier, Critical Reviews in Solid State and Materials Sciences **39**, 1-24 (2014).

From a practitioners point of view

- GW is an approximate method
  - Vertex in W: Neglect of e-h interaction
  - Vertex in Σ: Not self-interaction free for localized electrons

In principle this is solvable, but very time consuming



- The best practical approaches right now

Use G_0W_0 or GW_0 or possibly sc-QPGW_0 on top of PBE, if PBE yields reasonable screening for host

Possibly try G_0W_0 on top of HSE, if PBE is not reasonable, slightly too large band gaps because RPA screening on top of HSE is not great

Strongly localized states might be wrong (too high) !

What to read

- Many-Body Approach to Electronic Excitations: Concepts and Applications (Springer Series in Solid-State Sciences)
  Friedhelm Bechstedt
- Quantum Theory of Many-Particle Systems
  (Dover Books on Physics),
  Alexander L. Fetter, John Dirk Walecka
- A Guide to Feynman Diagrams in the Many-Body Problem
  (Dover Books on Physics & Chemistry)
  Richard D. Mattuck