Many-Body Perturbation Theory
The *GW* approximation

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Overview

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  - Feynman diagrams
  - *GW* approximation
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  - Correlation: Imaginary-frequency formulation
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  - Zinc Oxide
  - Metallic Na
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  - Full band structure
  - Self-consistent QS*GW*
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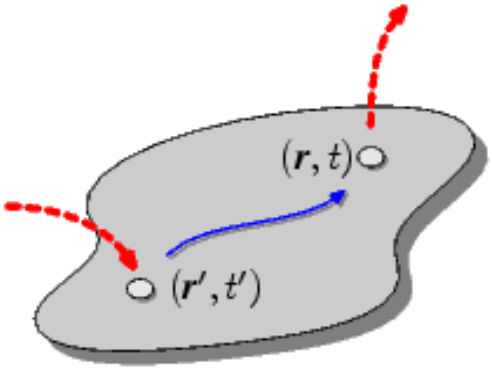

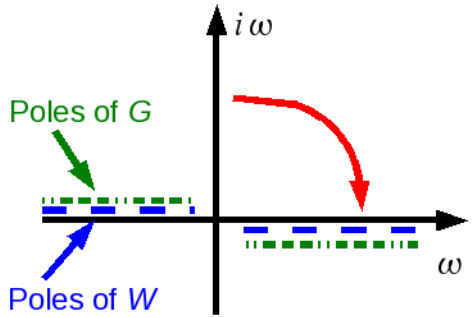

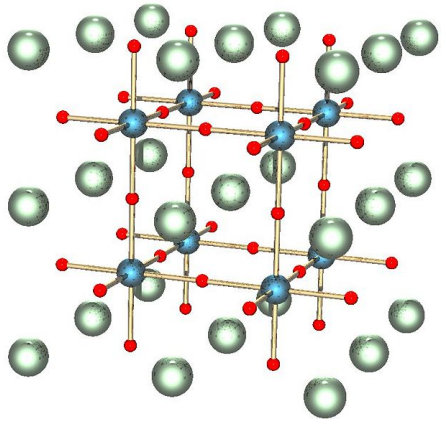

Density functional theory (DFT)

Kohn-Sham (KS) equations:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r})\right]\phi_{n\mathbf{k}}(\mathbf{r}) + v_{\mathrm{xc}}[\rho](\mathbf{r})\phi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\phi_{n\mathbf{k}}(\mathbf{r})$$

Exchange and correlation potential
Approximations: **LDA, GGA**

➔ real ρ(**r**) ➔ $E_0[\rho]$

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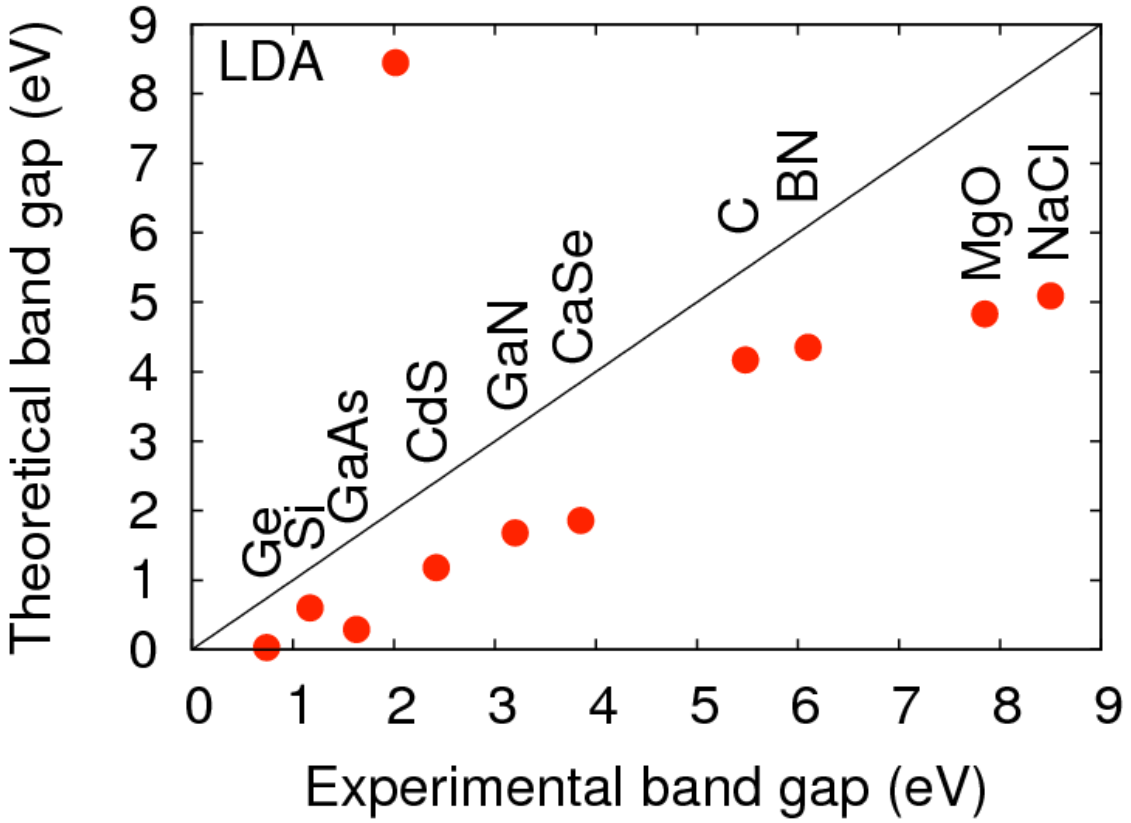

Density functional theory (DFT)

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Exchange and correlation potential

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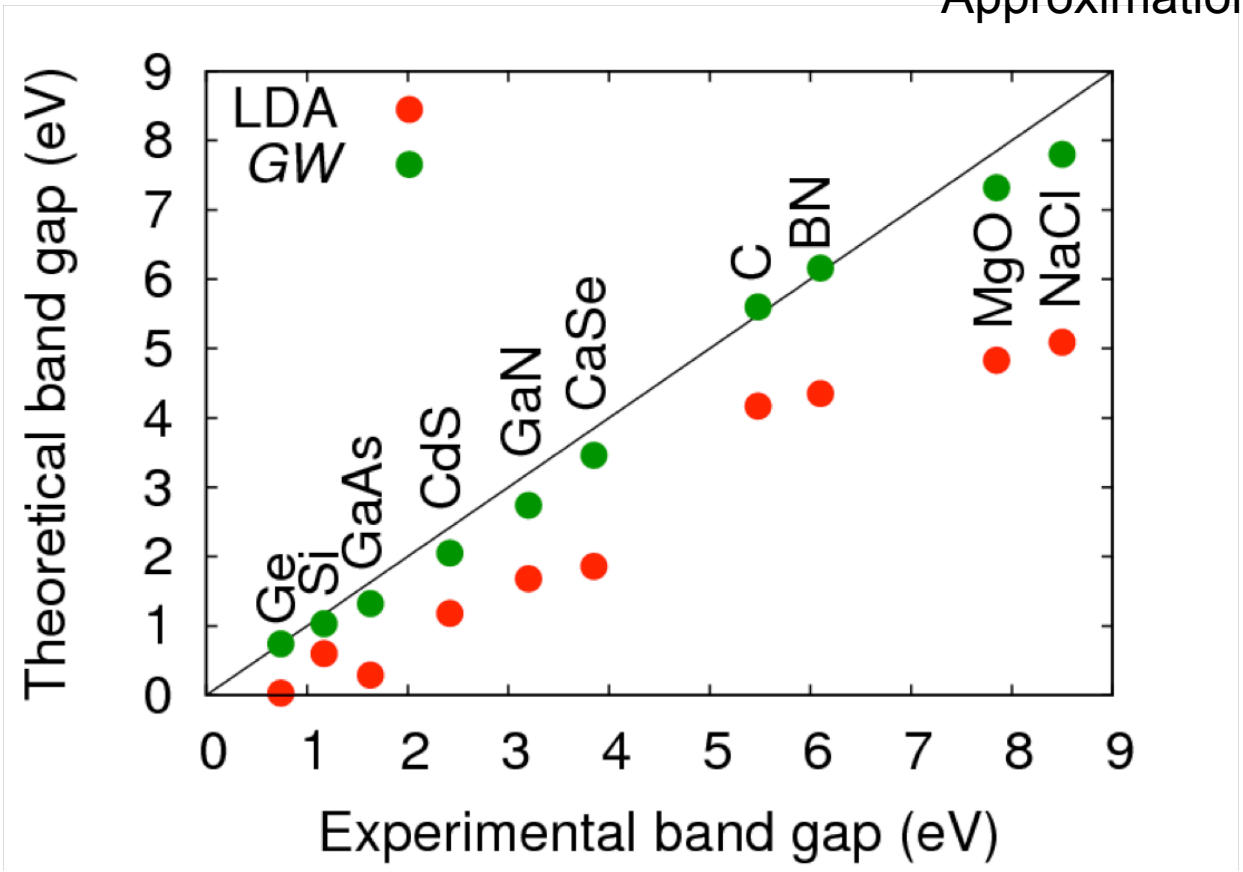

Density functional theory (DFT)

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Kohn-Sham (KS) equations:

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r})\right]\phi_{n\mathbf{k}}(\mathbf{r}) + \boxed{v_{\mathrm{xc}}[\rho](\mathbf{r})\phi_{n\mathbf{k}}(\mathbf{r})} = \epsilon_{n\mathbf{k}}\phi_{n\mathbf{k}}(\mathbf{r})$$

Exchange and correlation potential

Approximations: **LDA, GGA**

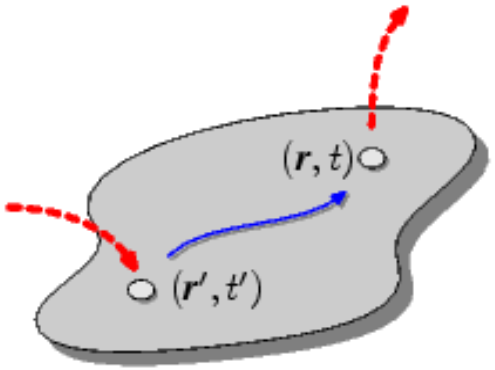
Many-body Schrödinger equation:

$$\left[-\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i} + \sum_i v_{\mathrm{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i,j}\frac{1}{\mathbf{r}_i - \mathbf{r}_j}\right]\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots) = E_n\Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots)$$

Theory
Green function

Central quantity is the single-particle Green function
(probability amplitude for the propagation of a particle)

$$G(\mathbf{r},\mathbf{r}';t-t') = -i\langle\Psi_0^N|\hat{T}[\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')]|\Psi_0^N\rangle$$



which contains poles at the excitation energies of the many-electron system (photoelectron spectroscopy),

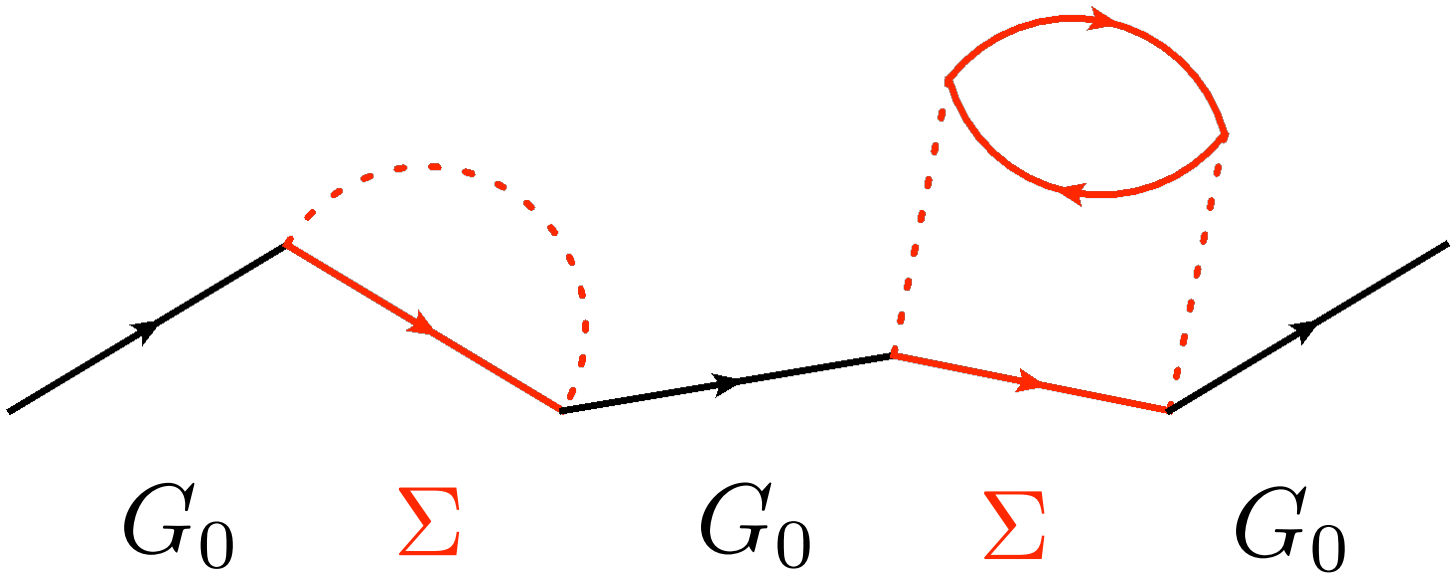
seen by Fourier transformation $t - t' \longrightarrow \omega$

$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\psi_n^{N+1}(\mathbf{r})\psi_n^{N+1*}(\mathbf{r}')}{\omega - E_n^{N+1} + i\eta} + \sum_n \frac{\psi_n^{N-1}(\mathbf{r})\psi_n^{N-1*}(\mathbf{r}')}{\omega - E_n^{N-1} - i\eta}$$

inverse direct

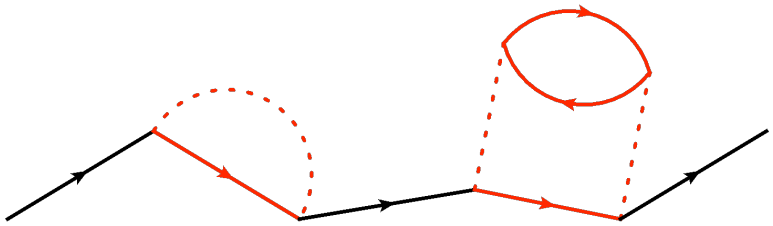
Excitation energy measured in photoemission spectroscopy

Theory
Feynman diagrams



Self-energy: sum over all scattering diagrams

Theory
Dyson equation



$$G = G_0 + G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0\Sigma G_0 + \ldots$$

Σ is the electronic self-energy (scattering potential).

The Dyson equation can be rewritten as the quasiparticle equation

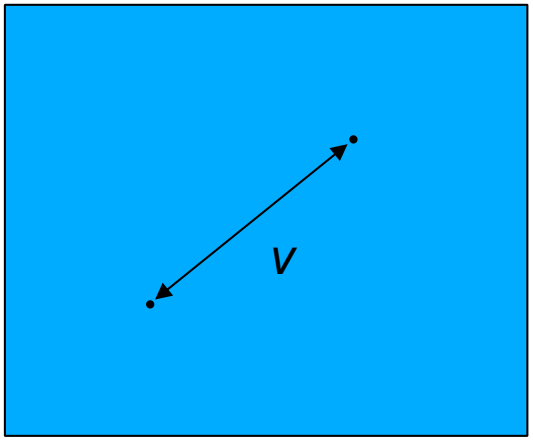
$$-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$

complex energy contains
- excitation energies (real part)
- excitation lifetimes (imaginary part)

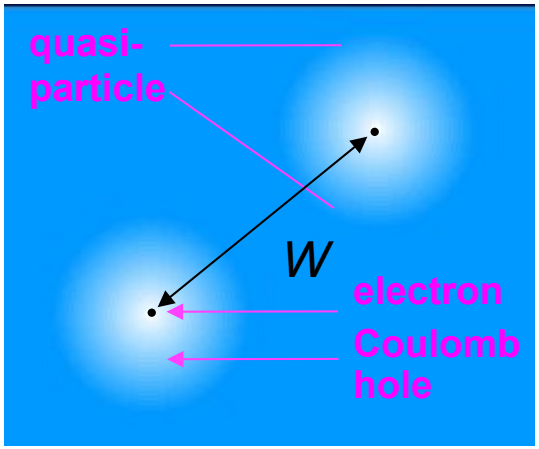
$$\hat{h}_0(\mathbf{r})\psi_n(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_n)\psi_n(\mathbf{r}')d^3r' = \epsilon_n\psi_n(\mathbf{r})$$

Theory
Self-energy

strong electron interaction *v*



weak quasiparticle interaction *W*



Expansion up to linear order

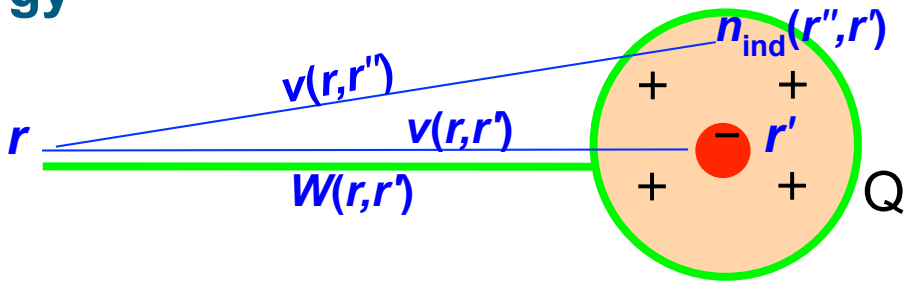
in Coulomb interaction v $\longrightarrow$ $\Sigma^{HF} = iG_0 v$ (Hartree-Fock)

in screened interaction W $\longrightarrow$ $\Sigma^{GW} = iG_0 W$ (*GW* approximation)

The *GW* approximation contains electron exchange and a large part of electron correlation.

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';\tau) = iG_0(\mathbf{r},\mathbf{r}';\tau)W(\mathbf{r},\mathbf{r}';\tau+\eta)$$

Theory
Self-energy

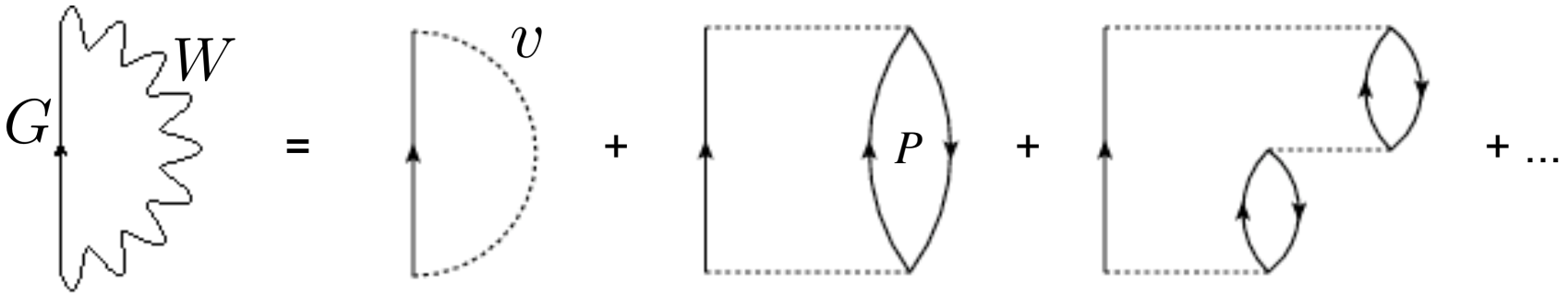


$$W(\mathbf{r},\mathbf{r}') = v(\mathbf{r},\mathbf{r}') + \int v(\mathbf{r},\mathbf{r}'')n_{\mathrm{ind}}(\mathbf{r}'',\mathbf{r}')\,d^3r''$$

Random-phase approximation

$$W = v + vPv + vPvPv + vPvPvPv + \ldots = v + vPW$$

$$\Sigma = iGW = iGv + iGvPv + iGvPvPv + \ldots$$



Theory
Hedin equations

Lars Hedin, 1965

$1 = (\mathbf{r}_1, \sigma_1, t_1),\ 2 = \ldots$

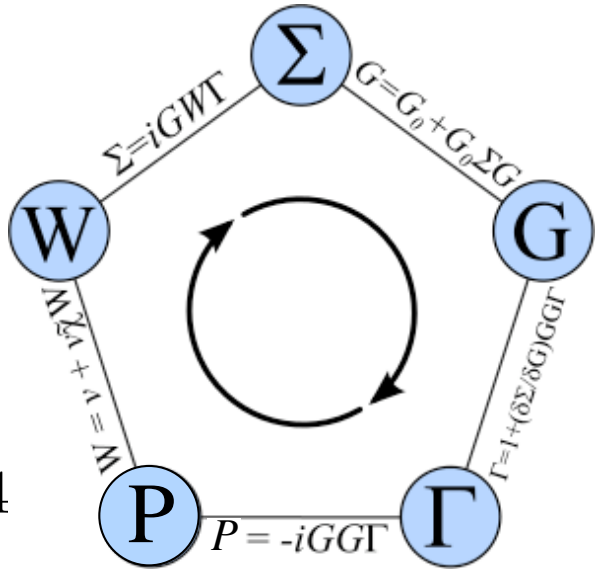
$$\Gamma(12;3) = \delta(12)\delta(13) - \iiint \frac{\delta\Sigma(12)}{\delta G(45)} G(56)\Gamma(67;3)G(74)\, d4\, d5\, d6\, d7$$

$$P(12) = -i \iint G(13)\Gamma(34;2)G(41)\, d3\, d4$$

$$W(12) = v(12) + \iint v(13)P(34)W(42)\, d3\, d4$$

$$\Sigma(12) = i \iint G(13)W(1^+4)\Gamma(32;4)\, d3\, d4$$

$$G(12) = G_0(12) + \iint G_0(13)\Sigma(34)G(42)\, d3\, d4$$



GW approximation corresponds to the 1st iteration starting from Σ=0:

$$\Gamma(12;3) = \delta(12)\delta(13)$$
$$P(12) = -iG(12)G(21)$$
$$\Sigma(12) = iG(12)W(1^+2)$$

Implementation

Dyson equation ➔ quasiparticle equations:

true excitation energies

GW: $\hat{h}_0(\mathbf{r})\psi^\sigma_{\mathbf{k}n}(\mathbf{r}) + \int \Sigma^{GW}_\sigma(\mathbf{r},\mathbf{r}';E^\sigma_{\mathbf{k}n})\psi^\sigma_{\mathbf{k}n}(\mathbf{r}')d^3r' = E^\sigma_{\mathbf{k}n}\psi^\sigma_{\mathbf{k}n}(\mathbf{r})$

DFT: $\hat{h}_0(\mathbf{r})\varphi^\sigma_{\mathbf{k}n}(\mathbf{r}) + v^{\mathrm{xc}}_\sigma(\mathbf{r})\varphi^\sigma_{\mathbf{k}n}(\mathbf{r}) = \epsilon^\sigma_{\mathbf{k}n}\varphi^\sigma_{\mathbf{k}n}(\mathbf{r})$

energies of a fictitious system

Similarity motivates the use of perturbation theory

$$E^\sigma_{\mathbf{k}n} = \epsilon^\sigma_{\mathbf{k}n} + \langle\varphi^\sigma_{\mathbf{k}n}|\Sigma^{GW}_\sigma(E^\sigma_{\mathbf{k}n}) - v^{\mathrm{xc}}_\sigma|\varphi^\sigma_{\mathbf{k}n}\rangle$$

direct solution

$$\boxed{\Sigma(E) = \Sigma(\epsilon) + \Sigma'(\epsilon)(E-\epsilon)}$$

$$E^\sigma_{\mathbf{k}n} = \epsilon^\sigma_{\mathbf{k}n} + Z^\sigma_{\mathbf{k}n}\langle\varphi^\sigma_{\mathbf{k}n}|\Sigma^{GW}_\sigma(\epsilon^\sigma_{\mathbf{k}n}) - v^{\mathrm{xc}}_\sigma|\varphi^\sigma_{\mathbf{k}n}\rangle$$

linearized solution

renormalization factor

$$Z^\sigma_{\mathbf{k}n} = \left(1 - \langle\varphi^\sigma_{\mathbf{k}n}|\Sigma'^{GW}_\sigma(\epsilon^\sigma_{\mathbf{k}n})|\varphi^\sigma_{\mathbf{k}n}\rangle\right)^{-1}$$

Implementation
Basis sets

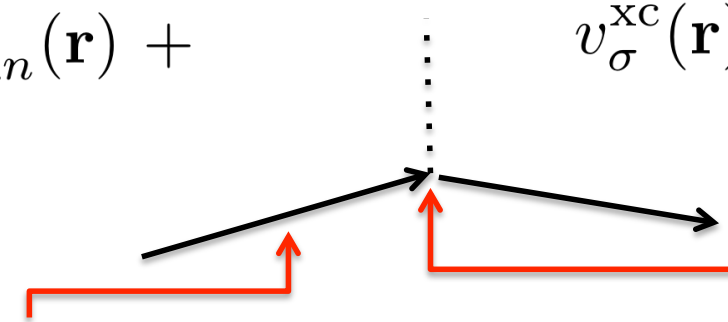
Dyson equation ➔ quasiparticle equations:

true excitation energies

GW: $\hat{h}_0(\mathbf{r})\psi^\sigma_{\mathbf{k}n}(\mathbf{r}) + \int \Sigma^{GW}_\sigma(\mathbf{r},\mathbf{r}';E^\sigma_{\mathbf{k}n})\psi^\sigma_{\mathbf{k}n}(\mathbf{r}')d^3r' = E^\sigma_{\mathbf{k}n}\psi^\sigma_{\mathbf{k}n}(\mathbf{r})$

DFT: $\hat{h}_0(\mathbf{r})\varphi^\sigma_{\mathbf{k}n}(\mathbf{r}) + v^{\mathrm{xc}}_\sigma(\mathbf{r})\varphi^\sigma_{\mathbf{k}n}(\mathbf{r}) = \epsilon^\sigma_{\mathbf{k}n}\varphi^\sigma_{\mathbf{k}n}(\mathbf{r})$

energies of a fictitious system



Basis set for wavefunctions

$$\varphi_{\mathbf{k}n}(\mathbf{r}) = \sum_\mu c^\mu_{\mathbf{k}n}\,\zeta_{\mathbf{k}\mu}(\mathbf{r})$$

Gaussians
Plane waves (Pseudopotential)
PAW
LMTO
FLAPW
...

Basis set for wavefunction products

$$\varphi^*_{\mathbf{k}n}(\mathbf{r})\varphi_{\mathbf{k}'n'}(\mathbf{r}) = \sum_\nu C^\nu_{\mathbf{k}\mathbf{k}'nn'}\,\xi_{\mathbf{k}\mathbf{k}'\nu}(\mathbf{r})$$

Auxiliary Gaussian set (density fitting)
Plane waves
Plane waves
Product basis
Mixed product basis

`spex.inp:` section “MBASIS”.

...

Implementation
FLAPW method

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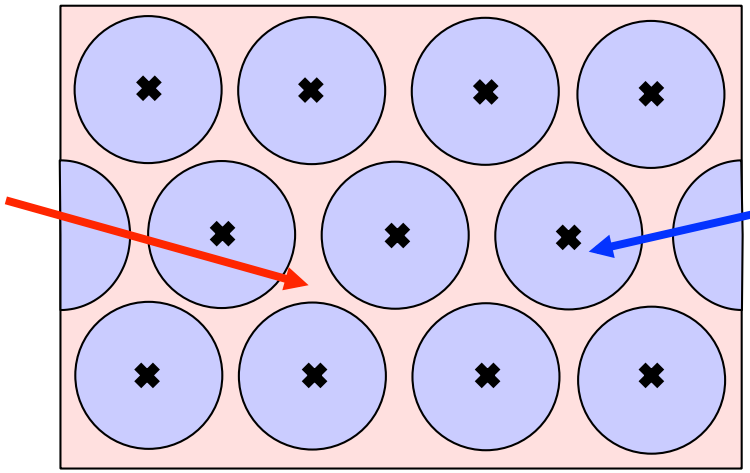
SPEX
www.flapw.de/spex

Interstitial region:

interstitial plane waves



Muffin-tin (MT) spheres:

numerical MT functions

$$u_{lp}(r)Y_{lm}(\hat{\mathbf{r}})$$

cutoff $l \le l_{\max}$

In our *GW* implementation we use the mixed product basis, generated from the products of (1) interstitial plane waves (cutoff $G'_{\max}$)

$$e^{\mathrm{i}(\mathbf{k}+\mathbf{G})\mathbf{r}}e^{\mathrm{i}(\mathbf{k}'+\mathbf{G}')\mathbf{r}} = e^{\mathrm{i}(\mathbf{k}+\mathbf{k}'+\underbrace{\mathbf{G}+\mathbf{G}'}\,)\mathbf{r}}$$

➔ $G'_{\max} = 2G_{\max}$

and (2) MT functions (cutoff $l'_{\max}$)

$$u_{lp}(r)u_{l'p'}(r)\underbrace{Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})}$$

up to $l+l'$ ➔ $l'_{\max} = 2l_{\max}$

T. Kotani and M. van Schilfgaarde,
Solid State Commun. 121, 461 (2002).

Implementation
Mixed product basis

$$G_{\max} = 3.6\,\text{bohr}^{-1}$$

exact $\quad G'_{\max} = 2G_{\max}$

converged $\quad G'_{\max} \sim 0.75\,G_{\max}$

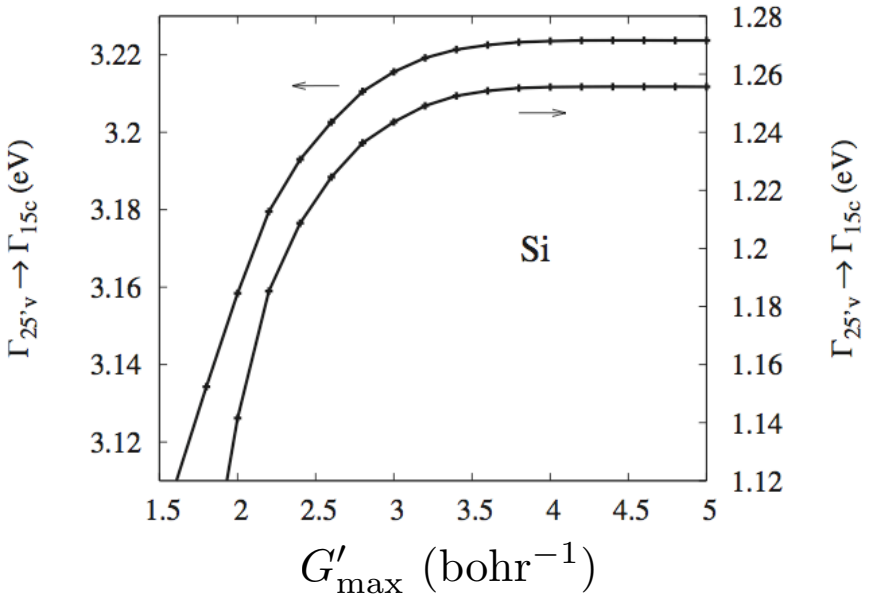
`spex.inp:` keyword “GCUT”.

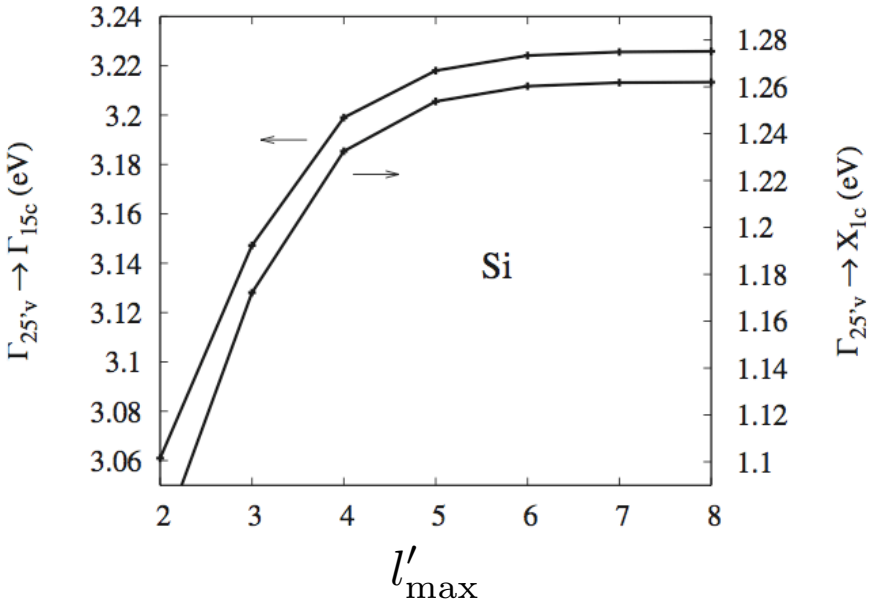
$$l_{\max} = 8$$

exact $\quad l'_{\max} = 2l_{\max}$

converged $\quad l'_{\max} \sim 0.63\,l_{\max}$

`spex.inp:` keyword “LCUT”.





Implementation
Exchange Self-energy

The self-energy can be decomposed into an exchange and a correlation term:

$$\Sigma^{GW}(\omega) = iG_0W = iG_0v + iG_0(W - v) = \Sigma^{\mathrm{x}} - \Sigma^{\mathrm{c}}(\omega)$$

The exchange contribution is given analytically by the Hartree-Fock expression

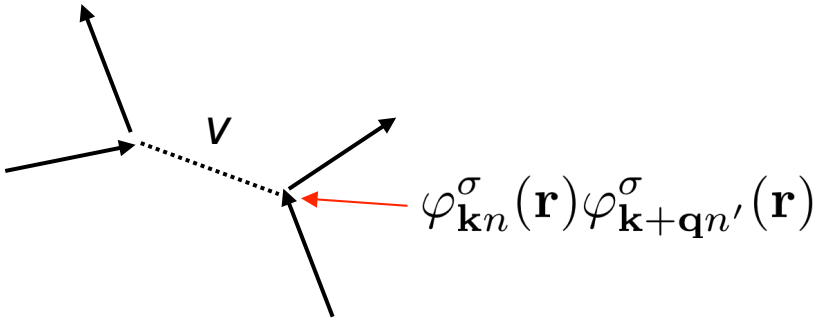
$$\Sigma^{\mathrm{x}}(\mathbf{r},\mathbf{r}';-\eta) = iG(\mathbf{r}t,\mathbf{r}'t+\eta)v(\mathbf{r},\mathbf{r}') = -\langle\Psi_0^N|\hat{\psi}^\dagger(\mathbf{r}'t+\eta)\hat{\psi}(\mathbf{r}t)|\Psi_0^N\rangle v(\mathbf{r},\mathbf{r}')$$

Density matrix

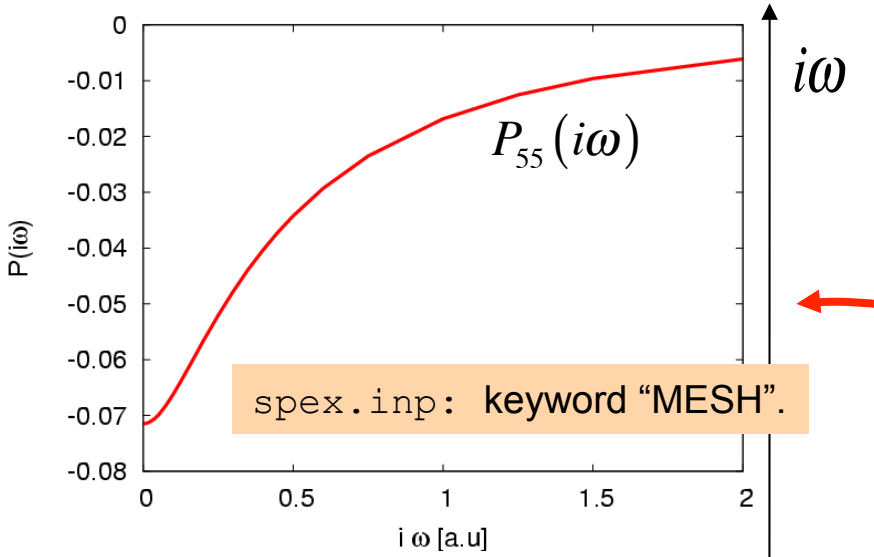
$$n(\mathbf{r},\mathbf{r}') = \sum_n^{\mathrm{occ.}} \varphi_n^*(\mathbf{r})\varphi_n(\mathbf{r}')$$

$$\langle\varphi_m|\Sigma^{\mathrm{x}}|\varphi_{m'}\rangle = -\sum_n^{\mathrm{occ.}} \iint \varphi_m^*(\mathbf{r})\varphi_n(\mathbf{r})v(\mathbf{r},\mathbf{r}')\varphi_n^*(\mathbf{r}')\varphi_{m'}(\mathbf{r}')\,d^3r\,d^3r'$$

$1 = \sum_I |M_I\rangle\langle M_I|$



Implementation
Imaginary-frequency formulation



`spex.inp:` keyword “MESH”.

The quantities (e.g. the polarization function *P*) are much smoother along the imaginary frequency axis than along the real axis.

`spex.inp:` keyword “HILBERT”.

`spex.inp:` keyword “NBAND”.

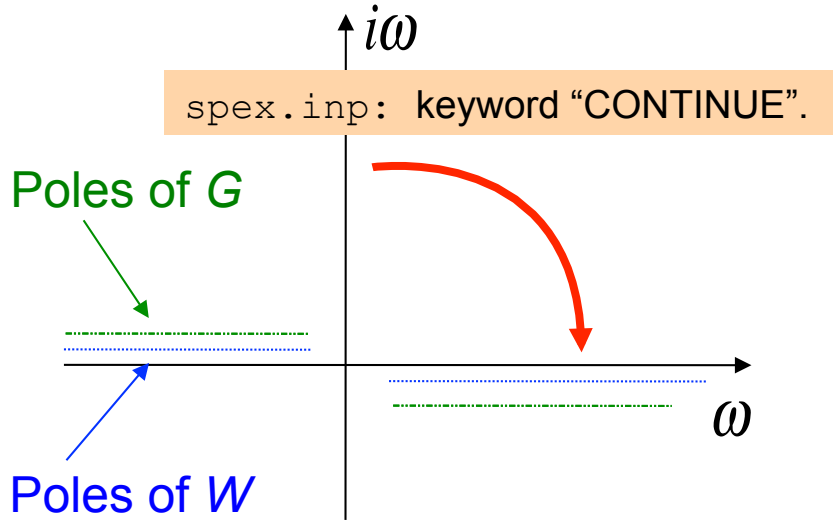
$$P_{IJ}(\mathbf{k},\omega) = \sum_{\sigma,\mathbf{q}} \sum_{n}^{occ} \sum_{n'}^{unocc} \dots \left(\frac{1}{\omega + \epsilon^{\sigma}_{\mathbf{q}n} - \epsilon^{\sigma}_{\mathbf{k}+\mathbf{q}n'} + i\eta} - \dots \right)$$

Implementation
Correlation Self-energy

$$\Sigma^c(i\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} G_0(\omega+\omega')W^c(\omega')d\omega'$$

Analytic Continuation

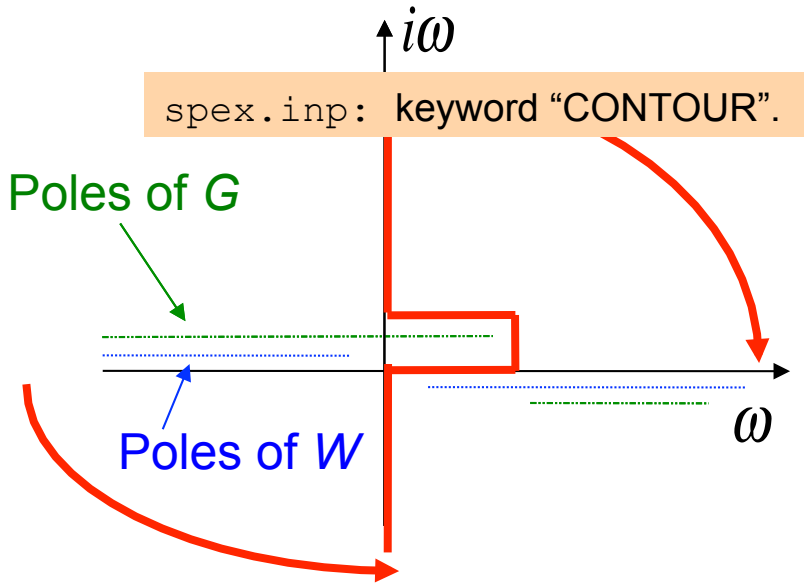
$$\Sigma^c(i\omega) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} G_0(i\omega+i\omega')W^c(i\omega')d\omega'$$



- Easy to implement
- Fast computation
- Analytic continuation critical

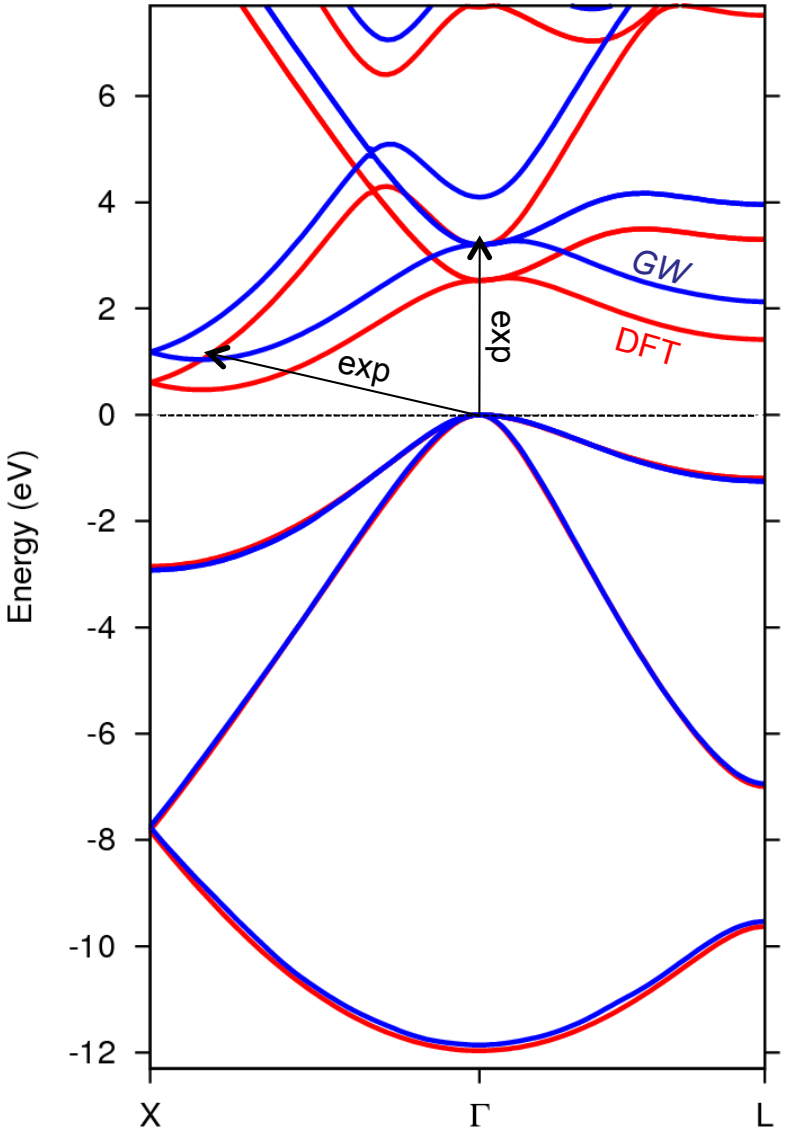
Contour integration

$$\Sigma^c(\omega) = \frac{i}{2\pi}\int G_0(\omega+\omega')W^c(\omega')d\omega'$$



- Accurate evaluation of Σ^c
- More parameters necessary
- Takes more time

Applications
Bulk Silicon

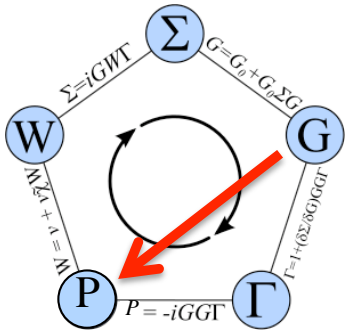


- Si was the first material to which *GW* was applied (Hybertsen, Louie 1985; Godby, Schlüter, Sham 1986).
- The one-shot *GW* calculation yields more accurate band gaps:

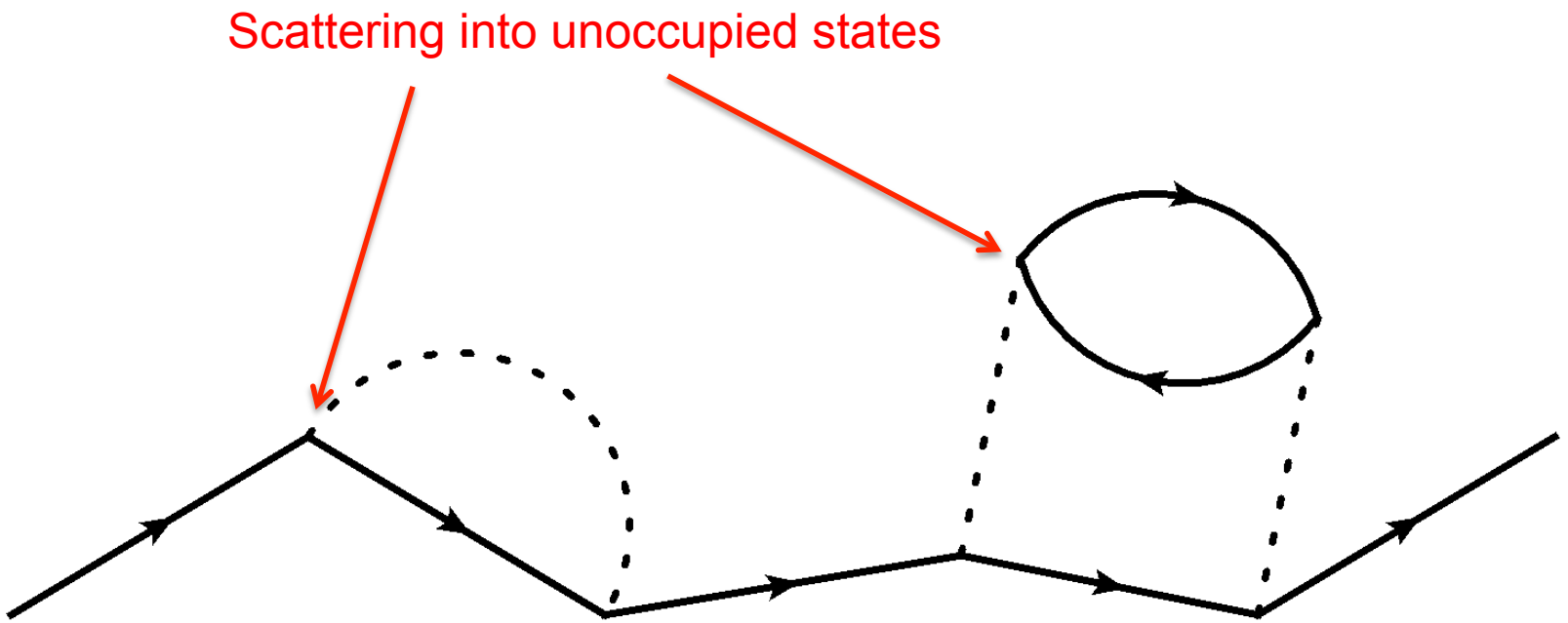
	DFT	*GW*	exp.
direct:	2.53	3.20	3.40 eV
indirect:	0.47	1.04	1.17 eV

- Quasiparticle self-consistent *GW* (QS*GW*) tends to overestimate the gaps:

	QS*GW*
direct:	3.60 eV
indirect:	1.34 eV



Applications
Band convergence



`spex.inp:` keyword “NBAND”.

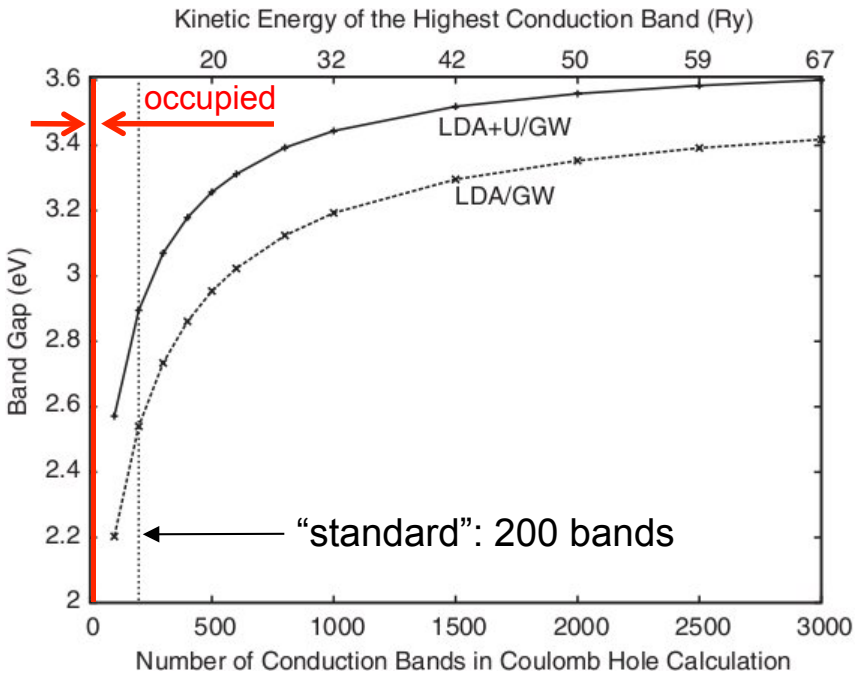
Applications
Zinc Oxide - band convergence

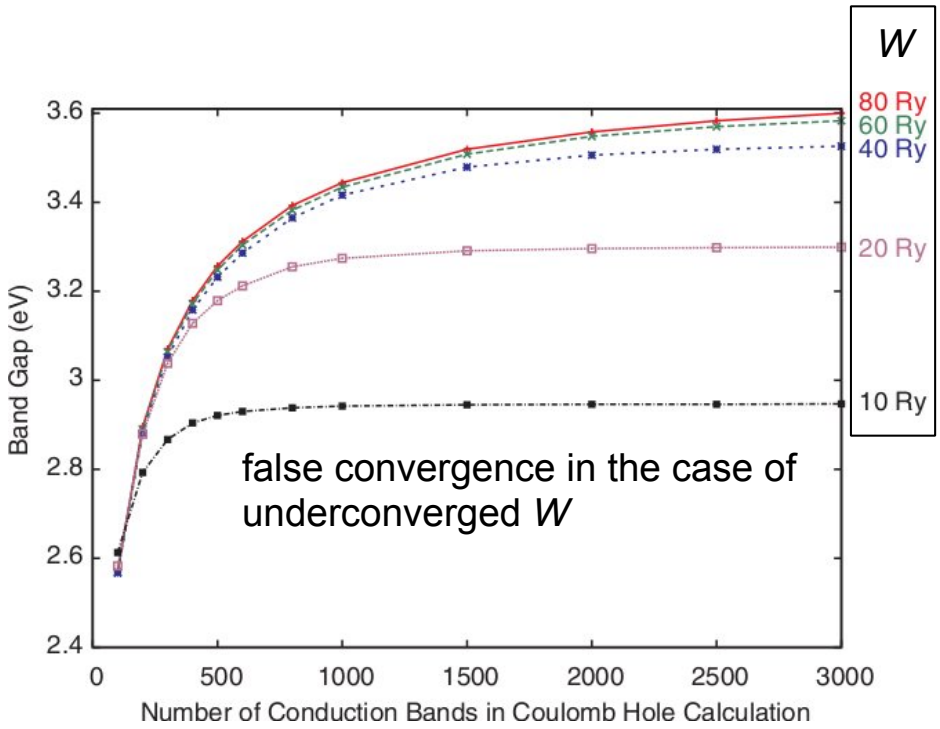
Large scatter of band-gap values from *one-shot GW* calculations (exp: 3.4 eV):

2.44 eV (FLAPW) [M. Usuda *et al.*, Phys. Rev. B **66**, 125101 (2002)]
2.12 eV (PAW) [M. Shishkin and G. Kresse, PRB **75**, 235102 (2007)
2.14 eV (PAW) [F. Fuchs *et al.*, Phys. Rev. B **76**, 115109 (2007)]
2.6 eV (PW-PP) [P. Gori *et al.*, Phys. Rev. B **81**, 125207 (2010)]

but then:

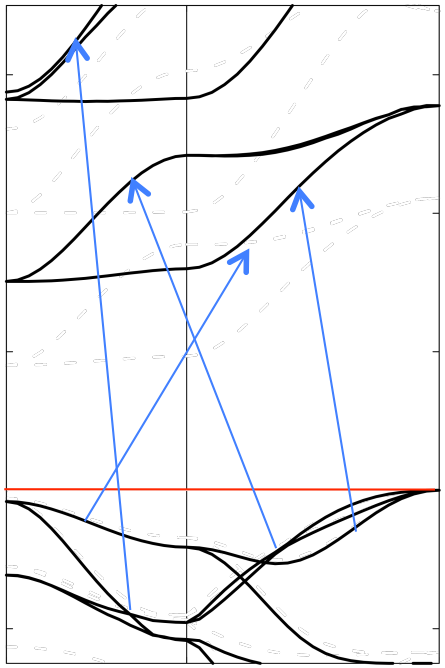
3.4 eV!! (PW-PP) [B.-C. Shih *et al.*, Phys. Rev. Lett. **105**, 146401 (2010)]





Applications
GW for metals

semiconductor

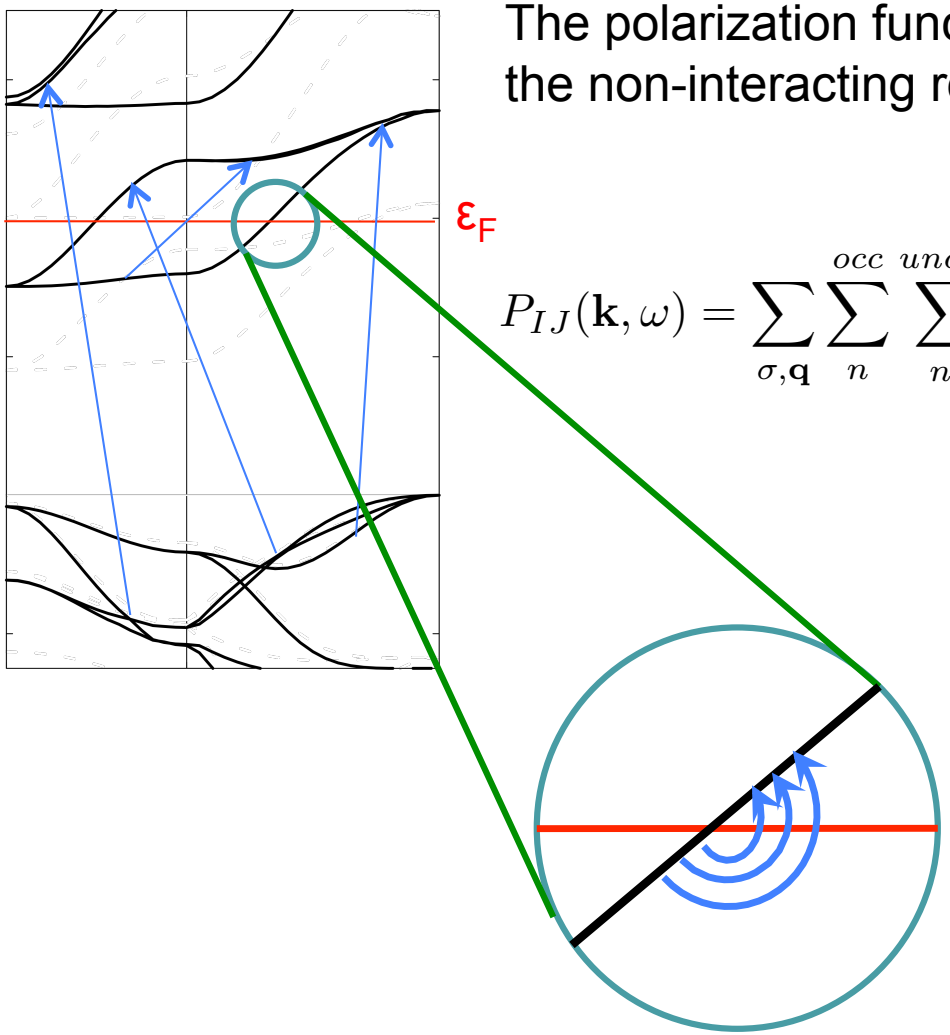


The polarization function is sum over virtual transitions in the non-interacting reference system.

$$P_{IJ}(\mathbf{k},\omega) = \sum_{\sigma,\mathbf{q}} \sum_{n}^{occ} \sum_{n'}^{unocc} \ldots \left(\frac{1}{\omega + \epsilon^{\sigma}_{\mathbf{q}n} - \epsilon^{\sigma}_{\mathbf{k}+\mathbf{q}n'} + i\eta} - \ldots \right)$$

Applications
GW for metals

metal



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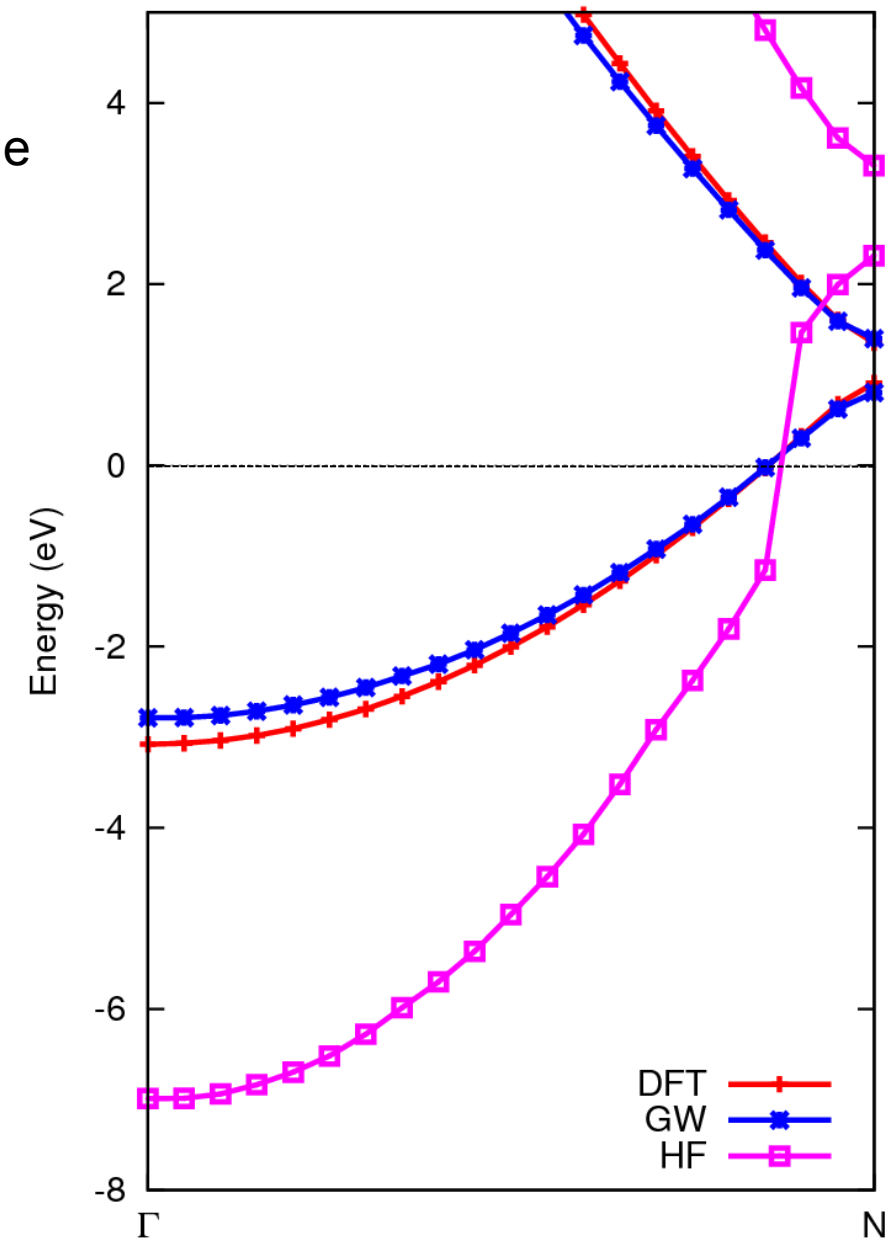
Virtual transitions of zero energy just across the Fermi surface produce the Drude term

$$P^{\mathrm{D}}_{\mathrm{head}}(\mathbf{k}, i\omega) \sim \frac{k^2}{4\pi} \frac{\omega^2_{\mathrm{pl}}}{\omega(\omega + i\eta)}$$

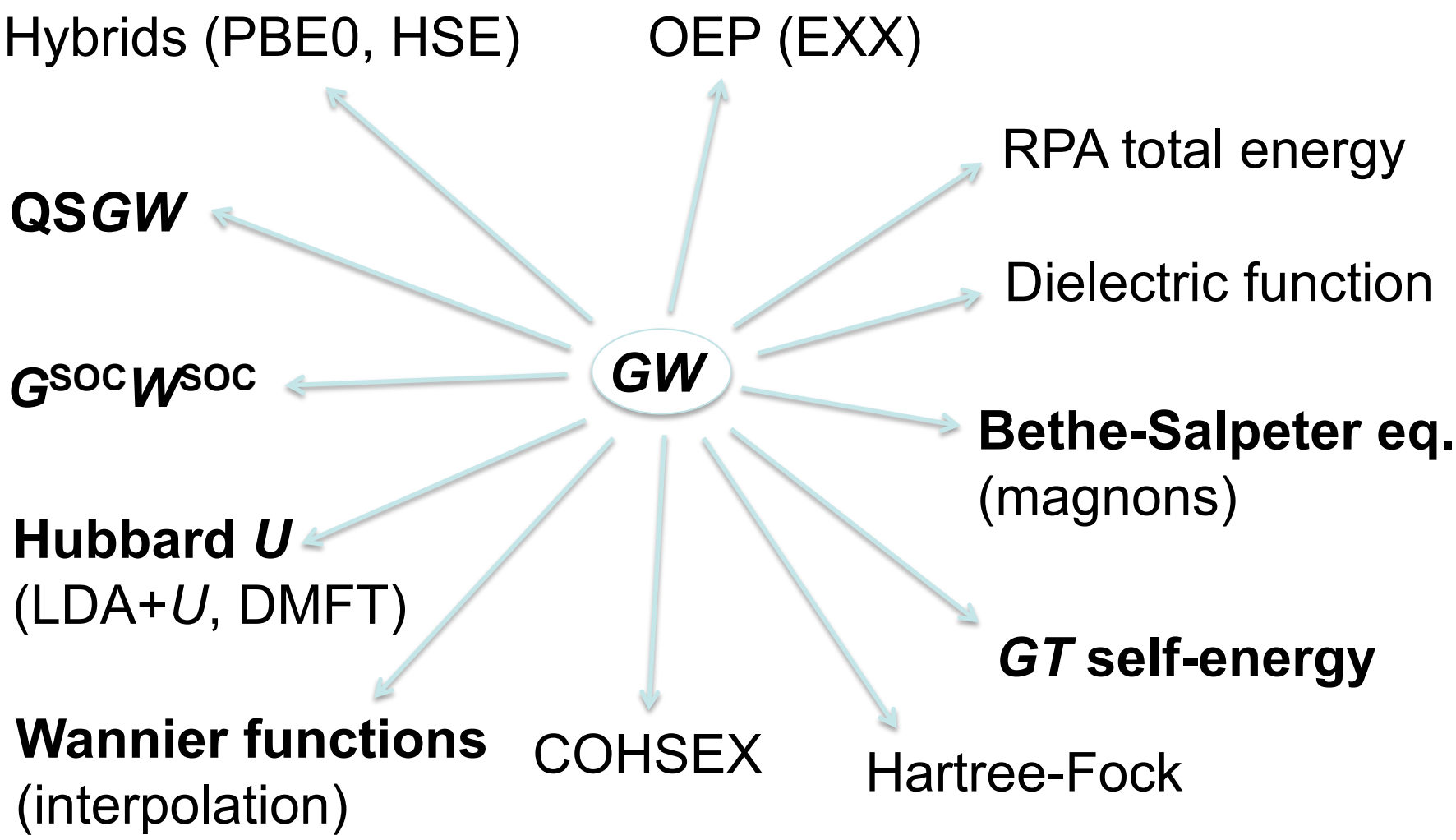
for $k \to 0$.

Applications
Sodium

- Vanishing of the density of states at the Fermi energy in HF is exactly compensated by the *GW* correlation self-energy.
- *GW* band width smaller than KS band width due to increased effective (quasiparticle) mass.



SPEX


Hybrids (PBE0, HSE)
OEP (EXX)
RPA total energy
QS*GW*
Dielectric function
$G^{soc}W^{soc}$
GW
Bethe-Salpeter eq.
(magnons)
Hubbard *U*
(LDA+*U*, DMFT)
***GT* self-energy**
Wannier functions
(interpolation)
COHSEX
Hartree-Fock

Summary

- Excitation energies and lifetimes of the (N+1) and (N-1)-electron system can be readily obtained from the one-particle Green function. These excitation energies form the band structure in solids.

- The Green function obeys an integral Dyson equation which may be rewritten as a quasiparticle equation with the self-energy as a scattering potential that takes into account all exchange and correlation effects beyond the Hartree potential.

- The *GW* approximation constitutes the expansion of the self-energy up to linear order in the screened interaction W.

- It is usually implemented as a perturbative correction on a DFT band structure. But a self-consistent solution (QS*GW*) is possible, too.