CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

Istituto Nanoscienze
S3 center, Modena, Italy

The GW method: From theory to practice

Andrea Ferretti

YaMBo©

23 Jan 2017
QE Adv tutorial

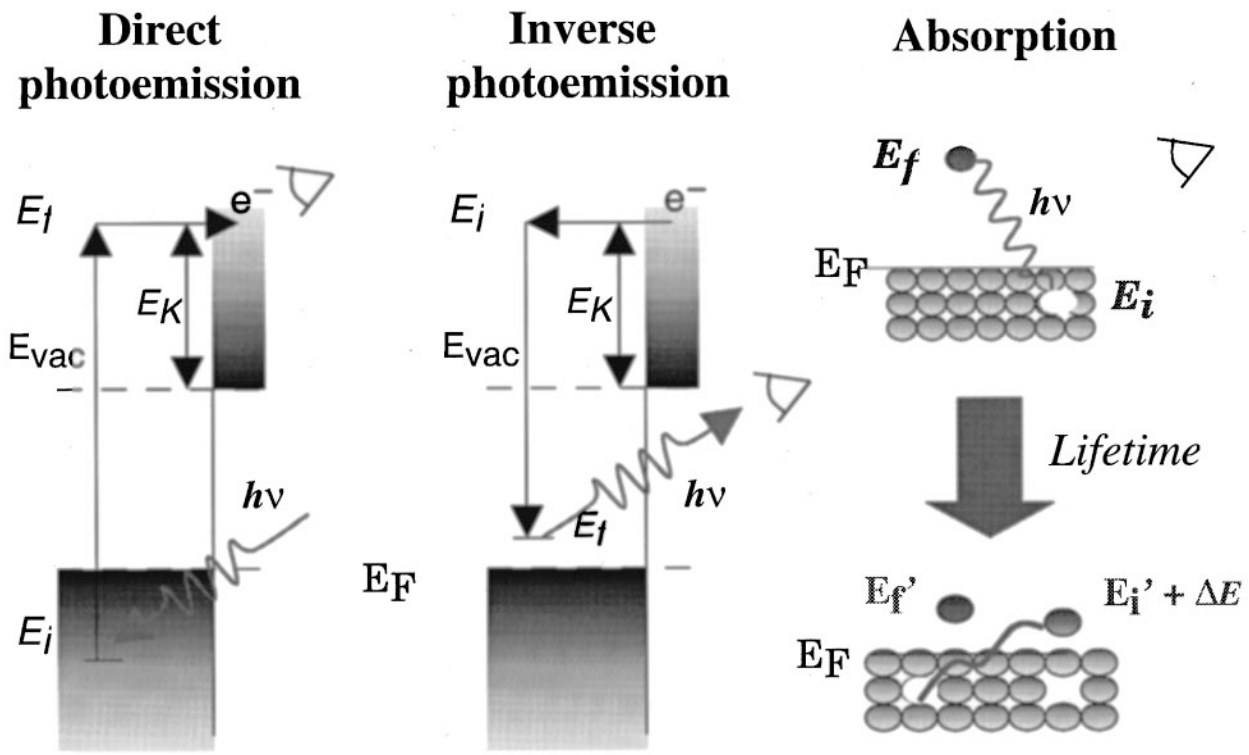
outline

- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

outline

- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

excitations



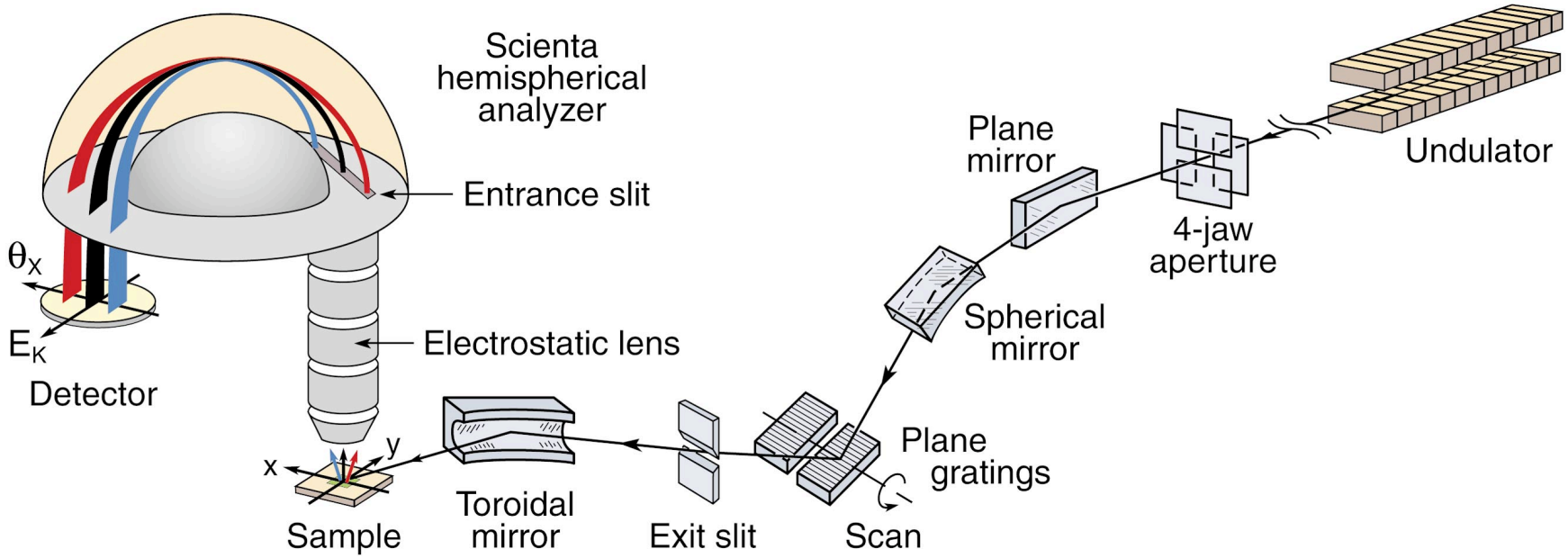
N-1 electrons

N+1 electrons

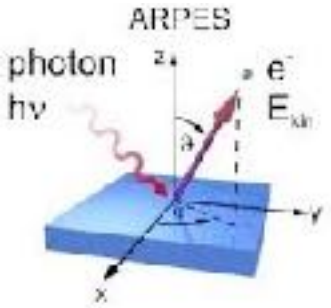
N electrons

the ARPES experiment

Damascelli, Hussain, Shen, Rev. Mod. Phys. **75**, 473 (2003)

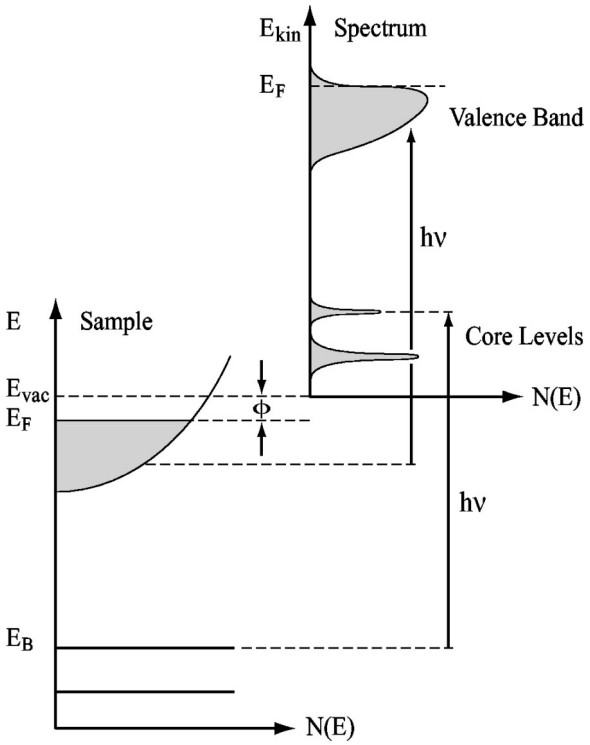


- **incident photons** (hw, angle, polarization)
- the method measures the **kinetic energy** (and the exit **angles**) of outcoming electrons
- allows to access **electronic (band) structures**



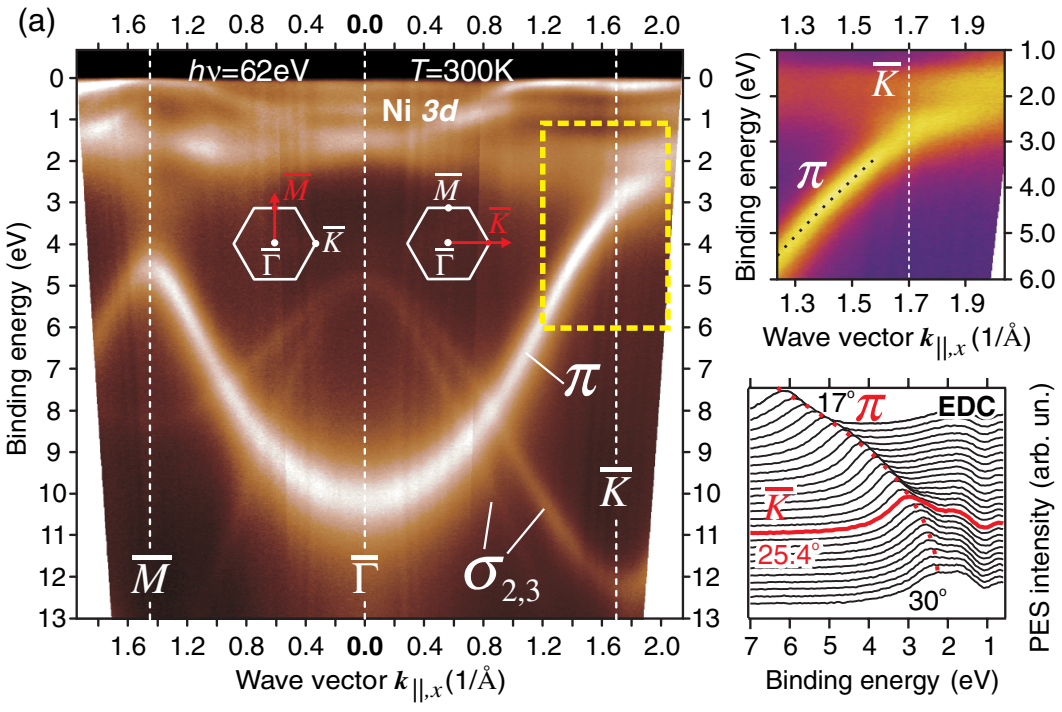
the ARPES experiment

model



Rev. Mod. Phys. **75**, 473 (2003)

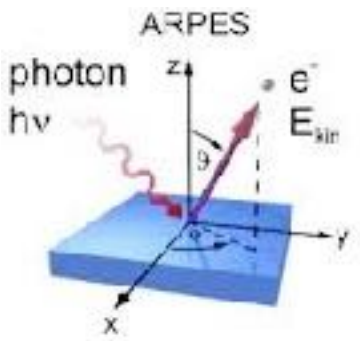
realistic system



Varykhalov et al, PRX **2**, 041017 (2012)

CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

theoretical treatment



see Hedin, Michiels, Inglesfield, PRB **58**, 15565 (1998)
Damascelli et al, RMP **75**, 473 (2003)

Photocurrent J by using the **Fermi golden rule:**

$$J_{\mathbf{k}}(\omega) = \sum_s |\langle \Psi_{\mathbf{k},s}|\Delta|\Psi_i\rangle|^2 \; \delta(\omega - \epsilon_{\mathbf{k}} + \epsilon_s)$$

$$\Delta = \mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}$$

Kinetic energy of the outcoming electron

$$\epsilon_{\mathbf{k}} = \mathbf{k}^2/2$$

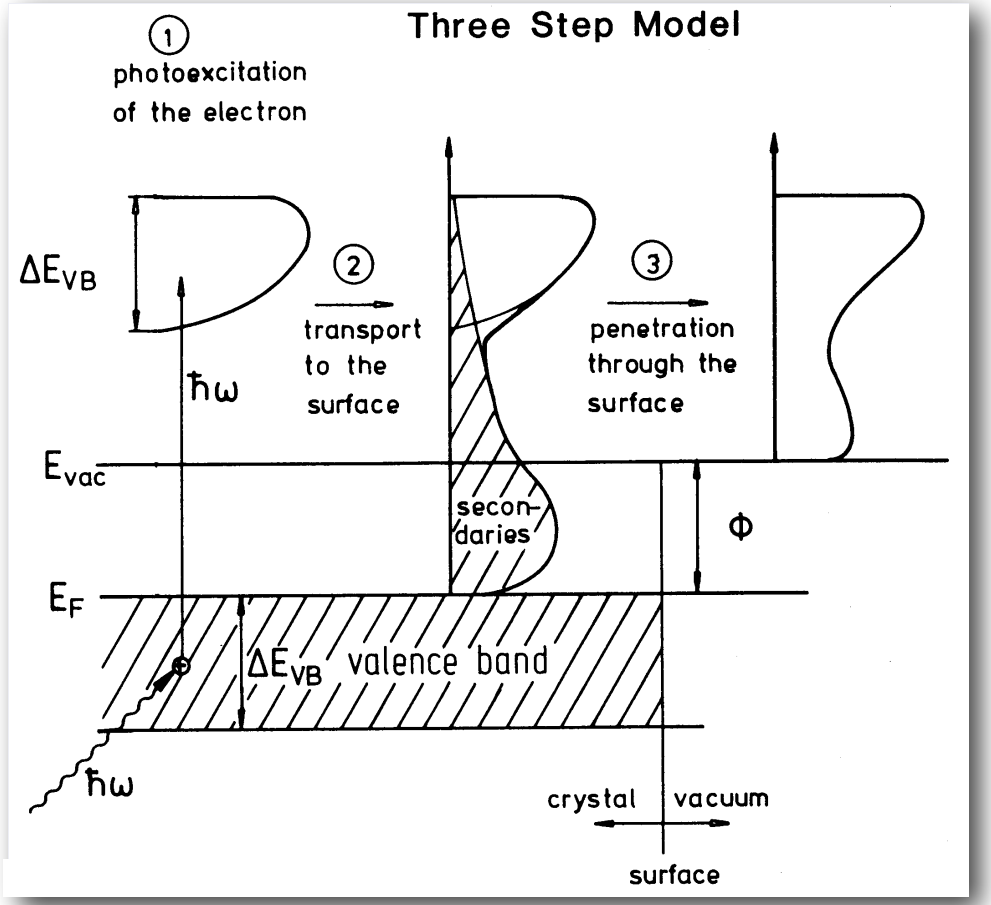
excitation left over

$$\epsilon_s = E(N,0) - E(N-1,s)$$

final state

$$|\Psi_{\mathbf{k},s}\rangle = \left[1 + \frac{1}{E - H - i\eta}(H - E)\right] c^\dagger_{\mathbf{k}}|N-1,s\rangle$$

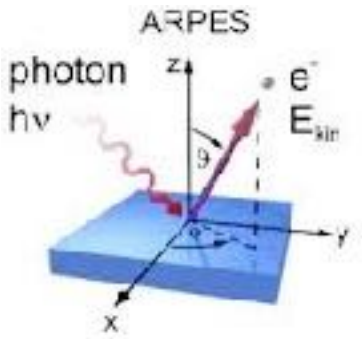
the 3 steps model



- (1) **photoexcitation intrinsic losses** are accounted for (satellite structures)
- (2) transport to the surface **extrinsic losses**
- (3) transmission through the surface

S. Hufner, Photoelectron Spectroscopy, Third Edition.
see also Slides from Matthias Kreier, Humboldt Uni (2007)

sudden approximation



see Hedin, Michiels, Inglesfield, PRB **58**, (1998)
Damascelli et al, RMP **75**, 473 (2003)

$$|\Psi_{\mathbf{k},s}\rangle = \left[1 + \frac{1}{E - H - i\eta}(H - E)\right] c^{\dagger}_{\mathbf{k}} |N-1, s\rangle$$

extrinsic losses neglected

spectral function

sudden approx

k fast enough

$$J_{\mathbf{k}}(\omega) = \sum_{ij} \Delta_{\mathbf{k}i}\, A_{ij}(\epsilon_{\mathbf{k}} - \omega)\, \Delta_{j\mathbf{k}}$$

$$A_{ij}(\omega) = \sum_{s}^{\varepsilon_s < \mu} \langle N|c_i^{\dagger}|N-1,s\rangle\langle N-1,s|c_j|N\rangle\delta(\omega - \varepsilon_s)$$

connecting to the GF's

Angle-resolved photoemission studies of the cuprate superconductors

Andrea Damascelli*

Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

Zahid Hussain

Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Zhi-Xun Shen

Department of Physics, Applied Physics and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305

(Published 17 April 2003)

In this context, angle-resolved photoemission spectroscopy (ARPES) plays a major role because it is the most direct method of studying the electronic structure of solids (see Sec. II). Its large impact on the development of many-body theories stems from the fact that this technique provides information on the single-particle Green's function, which can be calculated starting from a

the **Green's function** contains info about the **spectral function** → **ARPES**

outline

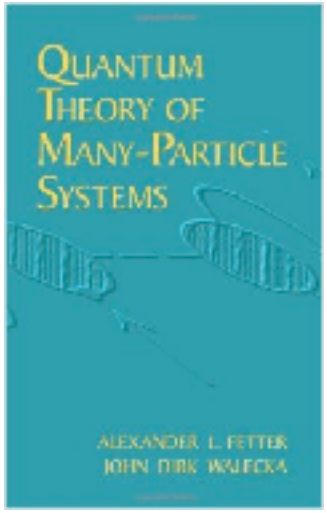
- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

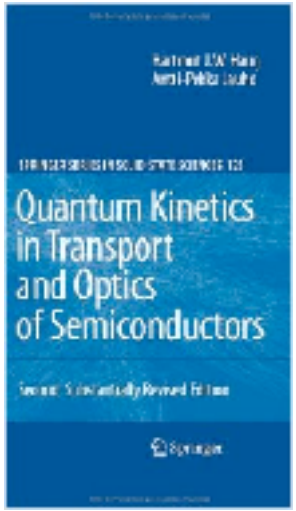
the Green's function

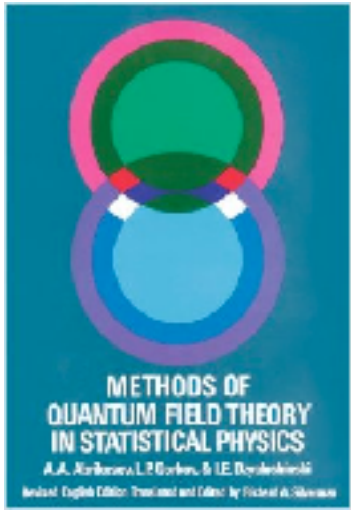
$$iG(\mathbf{x}_1, \mathbf{x}_2, t_1 - t_2) = \langle N | \, T\left[\psi(\mathbf{x}_1 t_1), \psi^\dagger(\mathbf{x}_2 t_2)\right] | \, N \rangle$$

$$= \theta(t_1 - t_2) \langle N | \psi(\mathbf{x}_1 t_1) \psi^\dagger(\mathbf{x}_2 t_2) | N \rangle$$

$$- \theta(t_2 - t_1) \langle N | \psi^\dagger(\mathbf{x}_2 t_2) \psi(\mathbf{x}_1 t_1) | N \rangle$$







the Green's function

$$iG(\mathbf{x}_1, \mathbf{x}_2, t_1 - t_2) = \langle N | \, T \left[\psi(\mathbf{x}_1 t_1), \psi^\dagger(\mathbf{x}_2 t_2) \right] | \, N \rangle$$

$$= \theta(t_1 - t_2) \langle N | \psi(\mathbf{x}_1 t_1) \psi^\dagger(\mathbf{x}_2 t_2) | N \rangle$$

$$- \theta(t_2 - t_1) \langle N | \psi^\dagger(\mathbf{x}_2 t_2) \psi(\mathbf{x}_1 t_1) | N \rangle$$

the Lehmann representation

- Using the **completeness** of the eigenvectors at **N+1 and N-1 electrons**

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{f_s(\mathbf{x})\, f_s^*(\mathbf{x}')}{\omega - \epsilon_s + i\eta_s}$$

as for non-interacting systems

- **charged excitations**

$$\epsilon_s = E_0^N - E_s^{N-1} \qquad \eta_s = -i0^+$$
$$\epsilon_s = E_s^{N+1} - E_0^N \qquad \eta_s = \quad i0^+$$

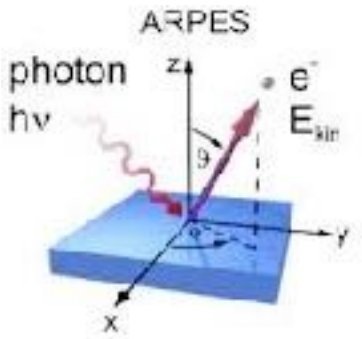
plays the role of the non-int **eigenvalues**

- **Dyson** orbitals

$$\epsilon_s < \mu \qquad f_s(\mathbf{x}) = \langle N-1, s|\, \hat{\psi}(\mathbf{x})\, |N, 0\rangle$$
$$\epsilon_s \geq \mu \qquad f_s(\mathbf{x}) = \langle N, 0|\, \hat{\psi}(\mathbf{x})\, |N+1, s\rangle$$

plays the role of the non-int **eigenvectors**

sudden approximation



see Hedin, Michiels, Inglesfield, PRB **58**, (1998)
Damascelli et al, RMP **75**, 473 (2003)

$$|\Psi_{\mathbf{k},s}\rangle = \left[1 + \frac{1}{E - H - i\eta}(H - E)\right] c^{\dagger}_{\mathbf{k}} |N-1, s\rangle$$

extrinsic losses neglected

spectral function

sudden approx

k fast enough

$$J_{\mathbf{k}}(\omega) = \sum_{ij} \Delta_{\mathbf{k}i}\, A_{ij}(\epsilon_{\mathbf{k}} - \omega)\, \Delta_{j\mathbf{k}}$$

$$A_{ij}(\omega) = \sum_{s}^{\varepsilon_s < \mu} \langle N|c_i^{\dagger}|N-1,s\rangle\langle N-1,s|c_j|N\rangle\delta(\omega - \varepsilon_s)$$

the Lehmann representation

- Using the **completeness** of the eigenvectors at **N+1 and N-1 electrons**

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{f_s(\mathbf{x})\, f_s^*(\mathbf{x}')}{\omega - \epsilon_s + i\eta_s}$$

- The **spectral function**

$$A(\mathbf{x},\mathbf{x}',\omega) = \frac{1}{2\pi i}\left[G(\omega) - G^\dagger(\omega)\right]_{\mathbf{x},\mathbf{x}'} \mathrm{sgn}(\mu - \omega)$$

$$G(\mathbf{x},\mathbf{x}',\omega) = \int \frac{A(\mathbf{x},\mathbf{x}',\omega')}{\omega - \omega' \pm i0^+} d\omega'$$

Kramers-Kronig transform

$$A(\mathbf{x},\mathbf{x}',\omega) = \sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}')\, \delta(\omega - \epsilon_s)$$

spectral info

the Lehmann representation

- Using the **completeness** of the eigenvectors at **N+1 and N-1 electrons**

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{f_s(\mathbf{x})\, f_s^*(\mathbf{x}')}{\omega - \epsilon_s + i\eta_s}$$

- The **spectral function**

$$A(\mathbf{x},\mathbf{x}',\omega) = \frac{1}{2\pi i}\left[G(\omega) - G^\dagger(\omega)\right]_{\mathbf{x},\mathbf{x}'} \mathrm{sgn}(\mu - \omega)$$

$$G(\mathbf{x},\mathbf{x}',\omega) = \int \frac{A(\mathbf{x},\mathbf{x}',\omega')}{\omega - \omega' \pm i0^+} d\omega'$$

Kramers-Kronig transform

$$\rho(\mathbf{x},\omega) = \sum_s |f_s(\mathbf{x})|^2\, \delta(\omega - \epsilon_s)$$

spectral info

the Lehmann representation

Assuming we knew the self-energy

$$G(\omega) = G_0(\omega) + G_0(\omega)\Sigma(\omega)G(\omega)$$

$$G(\omega) = \left[\omega - H_0 - \Sigma(\omega)\right]^{-1}$$

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{f_s(\mathbf{x})\, f_s^*(\mathbf{x}')}{\omega - \epsilon_s + i\eta_s}$$

Assuming discrete states:

$$\left[H_0 + \Sigma(\epsilon_s)\right]|f_s\rangle = \epsilon_s|f_s\rangle$$

- frequency (orbital) dependent potential
- see Onida, Reining, Rubio, Rev. Mod. Phys. **74**, 602 (2002)

the QP representation

the **Dyson** Equation

$$G(\omega) = \left[\omega - H_0 - \Sigma(\omega)\right]^{-1}$$

by direct **diagonalization**

$$\left[h_0 + \Sigma(\omega)\right]|\psi_{s\omega}\rangle = E_s(\omega)|\psi_{s\omega}\rangle$$

$$G(\omega) = \sum_s \frac{|\psi_{s\omega}\rangle\langle\psi^{s\omega}|}{\omega - E_s(\omega)}$$

- Sgm is **non-hermitian**
- diag leads to left and right (dual) eigenvectors
- $E_s(\omega)$ can be **complex**
- **relevant poles** can be selected according to the condition

see Onida et al, RMP **74**, 602 (2002)
Farid preprint cond-mat/0110481 (2001)
phyl mag B **82**, 1413 (2002)

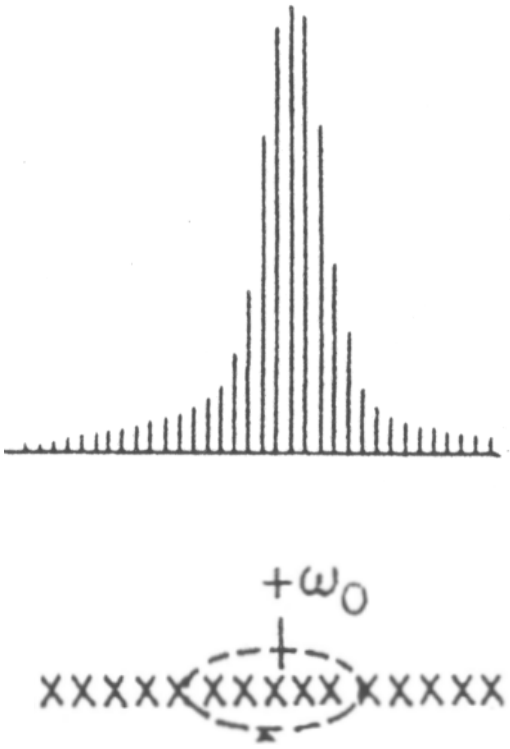
QP approximation

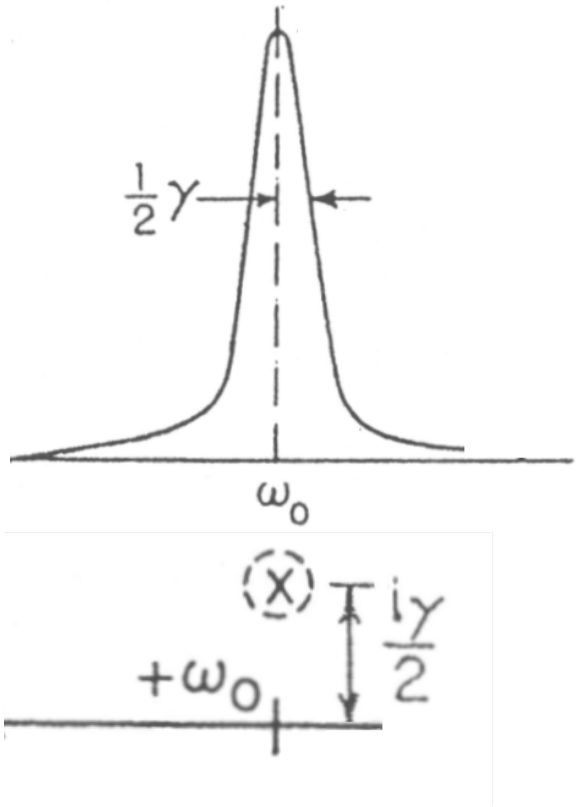
$$E_s(z_m^{\mathrm{QP}}) = z_m^{\mathrm{QP}}$$

Lehmann vs QP

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{f_s(\mathbf{x})\, f_s^*(\mathbf{x}')}{\omega - \epsilon_s + i\eta_s}$$

$$G(\mathbf{x},\mathbf{x}',\omega) = \sum_m \frac{\langle \mathbf{x}|\psi_m^{\mathrm{QP}}\rangle\langle\psi^{\mathrm{QP}m}|\mathbf{x}'\rangle}{\omega - z_m^{\mathrm{QP}}}$$



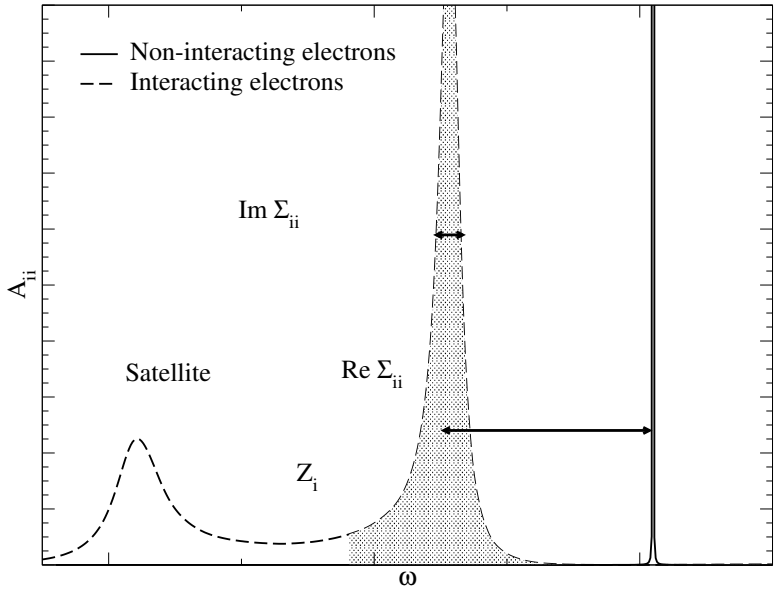


Farid preprint cond-mat/0110481 (2001)
phyl mag B **82**, 1413 (2002)

Figures adapted from M. Gatti PhD thesis

the spectral function

Figure from F. Bruneval PhD thesis



Let's **assume**:

Σ and G are **diagonal** on the basis of the **non-int Hamiltonian**

$$H_0|\phi_i\rangle = \epsilon_i|\phi_i\rangle$$

$$\Sigma_{ii}(\omega) = \langle\phi_i|\Sigma(\omega)|\phi_i\rangle$$

$$G_{ii}(\omega) = [\omega - \epsilon_i - \Sigma_{ii}(\omega)]^{-1}$$

Making a Taylor expansion of Σ(**ω**) around $E_i = \epsilon_i + \mathrm{Re}\Sigma_{ii}(E_i)$

$$\Sigma_{ii}(\omega) = \Sigma_{ii}(E_i) + \frac{\partial\Sigma_{ii}}{\partial\omega}(\omega - E_i)$$

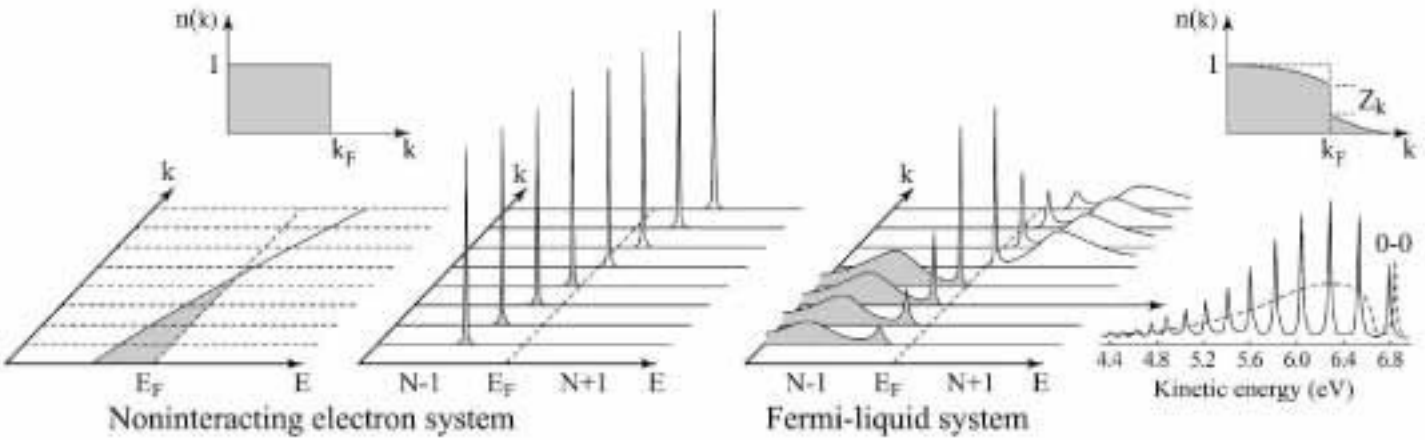
$$G_i(\omega) = \frac{Z_i}{\omega - E_i - i\Gamma_i}$$

renormalization factor

$$Z_i = (1 - \frac{\partial\Sigma_{ii}}{\partial\omega}_{|E_i})^{-1}$$

$$\Gamma_i = \mathrm{Im}\Sigma_{ii}(E_i)$$

the spectral function



Manybody features include

- **satellites**
- **lifetimes**
- **renormalization**

All the above features depend on the **dynamical** and **non-hermitian** nature of **Σ(ω)**

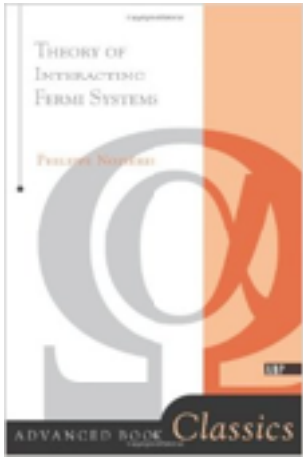


Figure from: Damascelli, Hussain, Shen, Rev. Mod. Phys. **75**, 473 (2003)

outline

- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

Hedin's equations

L. Hedin, Phys. Rev. **139**, A796 (1965)

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†
Argonne National Laboratory, Argonne, Illinois
(Received 8 October 1964; revised manuscript received 2 April 1965)

We write the Schrödinger representation of the Hamiltonian for the system to be considered as

$$H = H_0 + H_1 ,$$

$$H_0 = \int \psi^\dagger(\mathbf{x}) h(\mathbf{x}) \psi(\mathbf{x}) d\mathbf{x} + \frac{1}{2} \int \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') v(\mathbf{x},\mathbf{x}') \psi(\mathbf{x}') \psi(\mathbf{x}) d\mathbf{x} d\mathbf{x}' , \quad \text{(A1)}$$

$$H_1 = \int \rho(\mathbf{x}) w(\mathbf{x},t) d\mathbf{x} , \quad \rho(\mathbf{x}) = \psi^\dagger(\mathbf{x}) \psi(\mathbf{x}) ,$$

Hedin's equations

L. Hedin, Phys. Rev. **139**, A796 (1965)

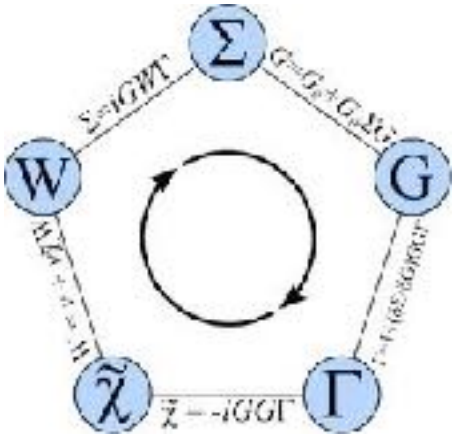
$$G(12) = G_0(12) + \int d34\, G_0(13)\Sigma(34)G(42)$$

$$W(12) = v(12) + \int d34\, v(13)P(34)W(42)$$

$$\Sigma(12) = i \int d34\, G(13)W(41)\Gamma(324)$$

$$P(12) = -i \int d34\, G(13)G(41)\Gamma(342)$$

$$\Gamma(123) = \delta(12)\delta(13) + \int d4567\, \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)$$



$$1 \equiv x_1 t_1$$

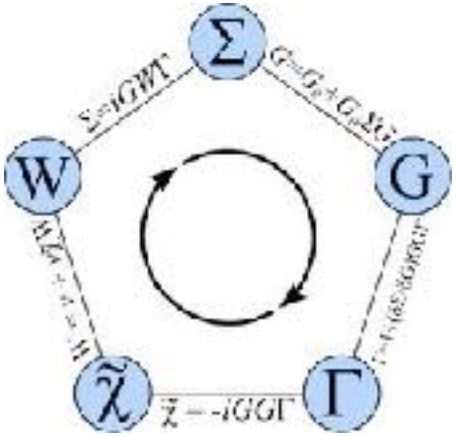
$$G_0 \longleftrightarrow H_0 = T + V_{\text{ext}} + V_H$$

Hedin's equations

L. Hedin, Phys. Rev. **139**, A796 (1965)

$$G(12) = G_0(12) + \int d34\, G_0(13)\Sigma(34)G(42)$$

$$W(12) = v(12) + \int d34\, v(13)P(34)W(42)$$

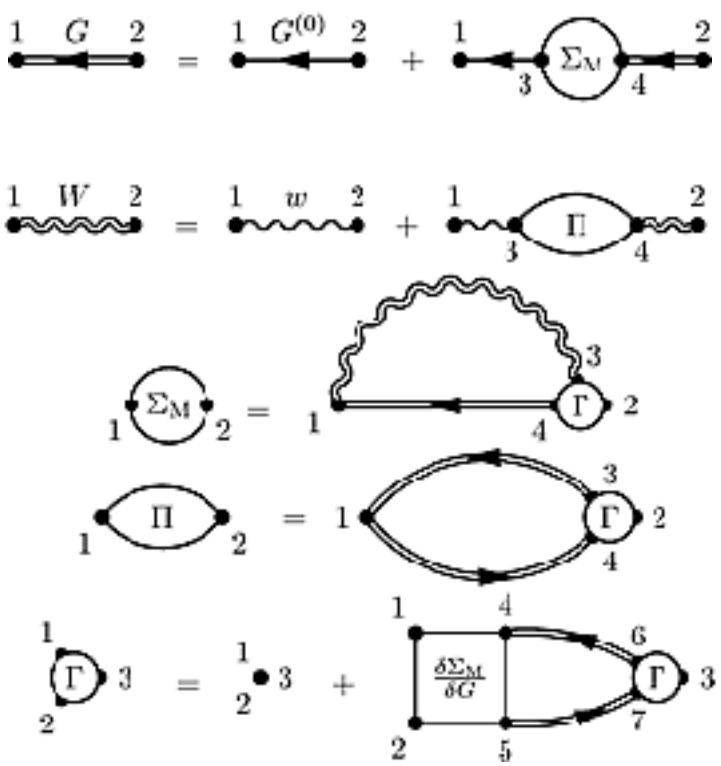


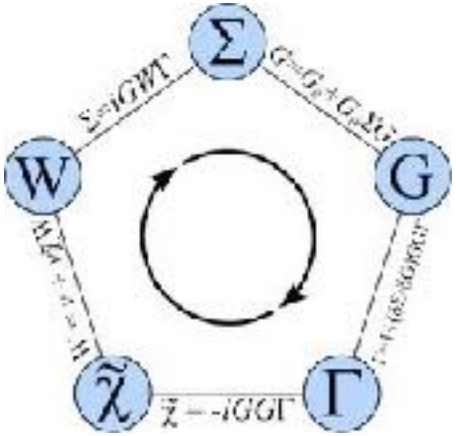
Dyson-like equations:

$$\begin{aligned} W &= v + vPv + vPvPv + vPvPvPv + \ldots \\ &= \sum_{n=0}^{\infty} (vP)^n v \qquad \text{formal solution} \\ &= [1 - vP]^{-1} v \qquad \text{summation using the} \\ &= \epsilon^{-1} v \qquad \textbf{geometric series} \end{aligned}$$

Hedin's equations

L. Hedin, Phys. Rev. **139**, A796 (1965)





Hedin's Eq to GW

L. Hedin, Phys. Rev. **139**, A796 (1965)

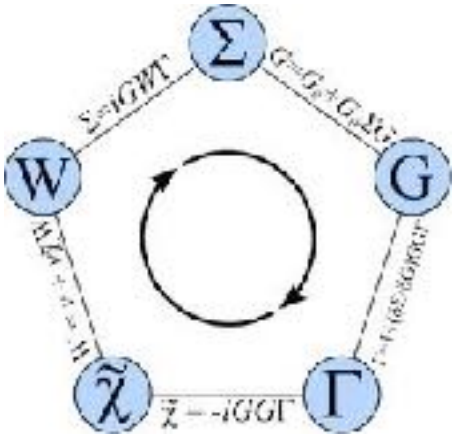
$$G(12) = G_0(12) + \int d34\, G_0(13)\Sigma(34)G(42)$$

$$W(12) = v(12) + \int d34\, v(13)P(34)W(42)$$

$$\Sigma(12) = i \int d34\, G(13)W(41)\Gamma(324)$$

$$P(12) = -i \int d34\, G(13)G(41)\Gamma(342)$$

$$\Gamma(123) = \delta(12)\delta(13) + \int d4567\, \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)$$



the GW approximation

L. Hedin, Phys. Rev. **139**, A796 (1965)

$$G(12) = G_0(12) + \int d34\, G_0(13)\Sigma(34)G(42)$$

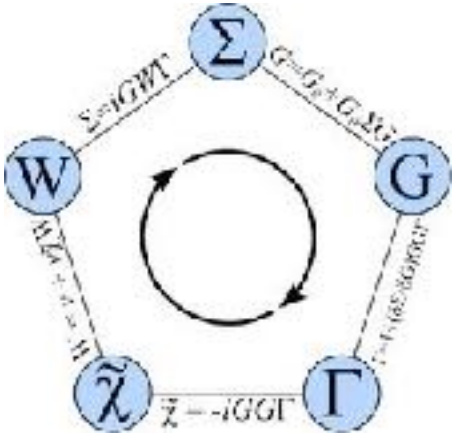
$$W(12) = v(12) + \int d34\, v(13)P(34)W(42)$$

$$\Sigma(12) = iG(12)W(21)$$

$$P(12) = -iG(12)G(21)$$

$$\Gamma(123) = \delta(12)\delta(13)$$

the GW approximation



RPA polarizability
(independent particles)

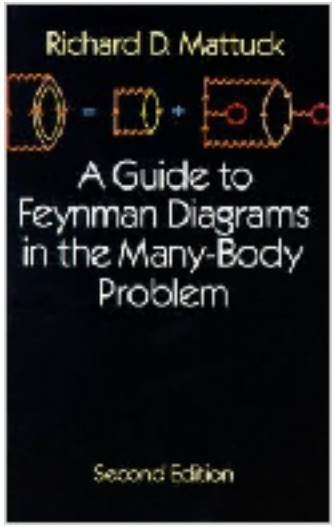
the GW approximation

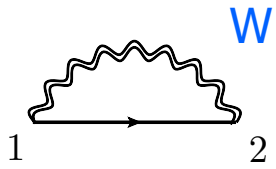
L. Hedin, Phys. Rev. **139**, A796 (1965)

$$\Sigma(12) = iG(12)W(21)$$

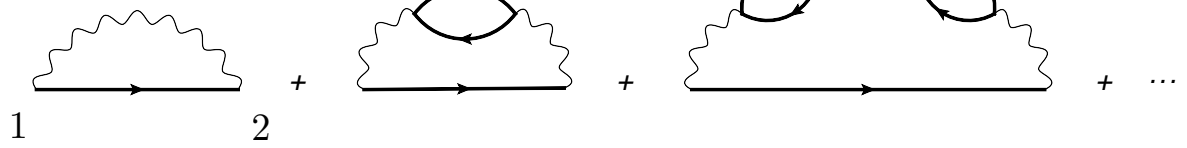
$$P(12) = -iG(12)G(21)$$

$$\Gamma(123) = \delta(12)\delta(13)$$



$\Sigma^{\mathrm{GW}}(12) =$ 

Indep particle bubble

$=$ 

RPA screening

the GW approximation

L. Hedin, Phys. Rev. **139**, A796 (1965)

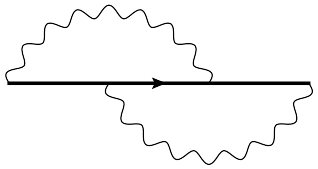
$$\Sigma(12) = iG(12)W(21)$$

$$P(12) = -iG(12)G(21)$$

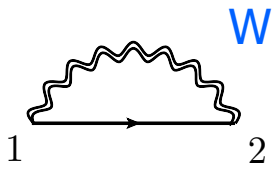
$$\Gamma(123) = \delta(12)\delta(13)$$

beware: GW is not the whole story

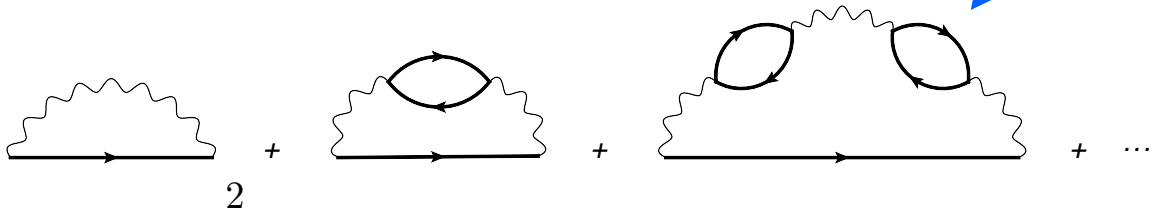
e.g. 2nd order exchange is not there



$\Sigma^{\mathrm{GW}}(12) =$



$=$

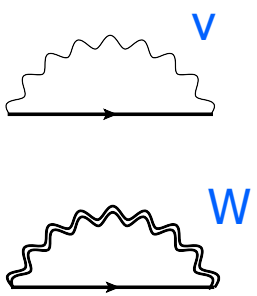


related approximations

Hartree-Fock

$$\Sigma^{\mathrm{HF}}(12) = iG(12)v(21)$$

$$\Sigma^{\mathrm{GW}}(12) = iG(12)W(21)$$



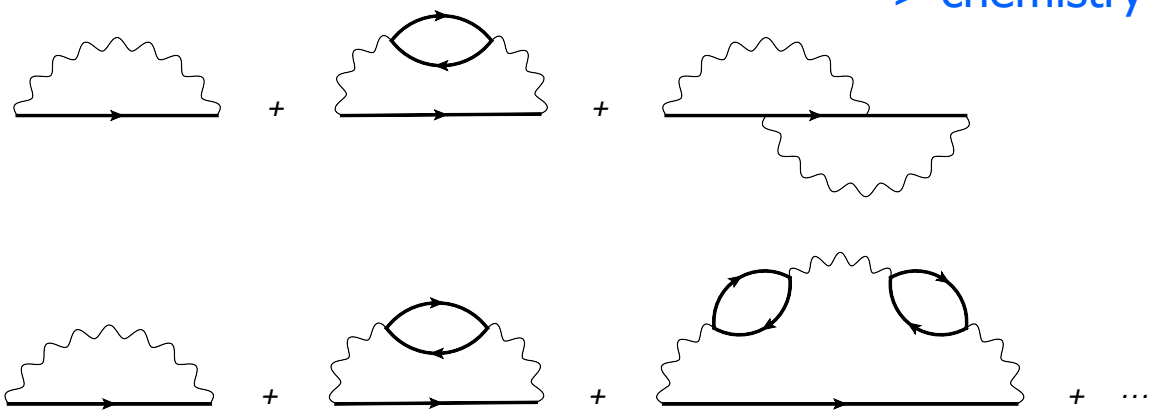
no screening

2nd Born approx (MP2)

-> chemistry

$$\Sigma^{\mathrm{2B}}(12) =$$

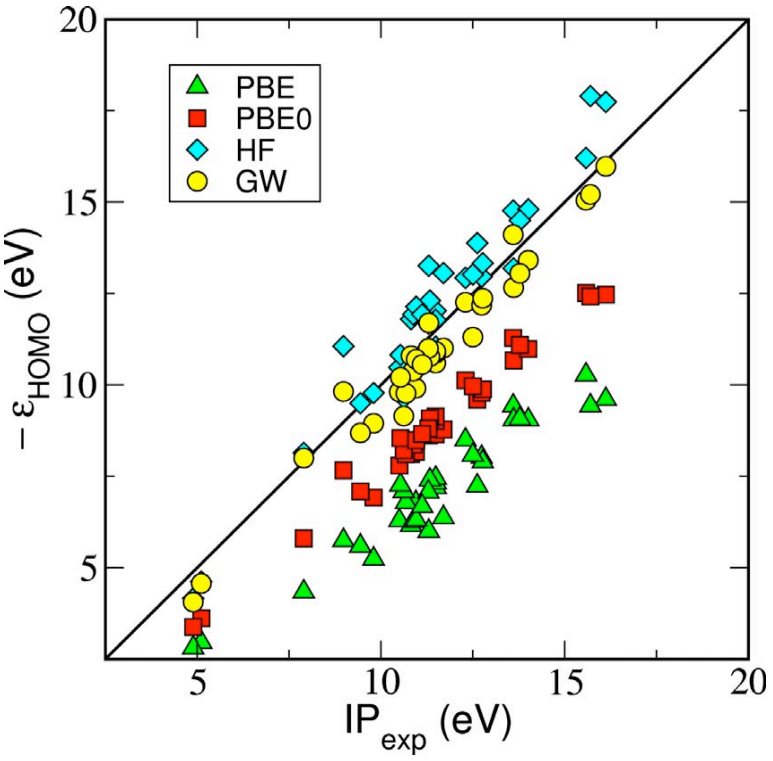
$$\Sigma^{\mathrm{GW}}(12) =$$



-> solids

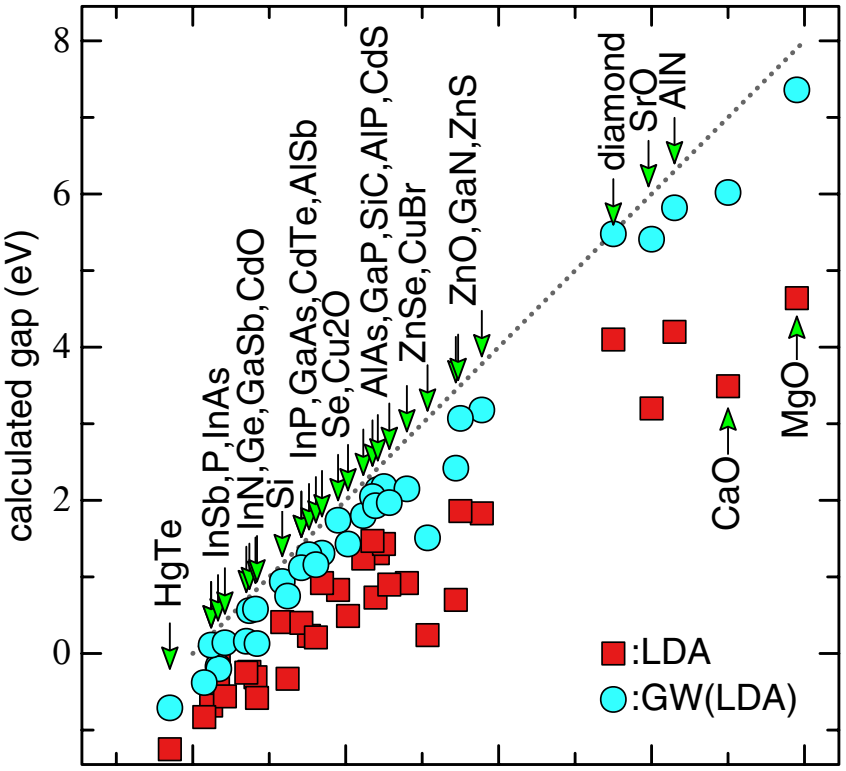
it works!

Molecules



C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen,
PRB **81**, 085103 (2010)

Solids



M. van Schilfgarde, T. Kotani, S. Faleev,
PRL **96**, 226402 (2006)

CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

but...

self-interaction in GW

PHYSICAL REVIEW A **75**, 032505 (2007)

Self-interaction in Green's-function theory of the hydrogen atom

W. Nelson,[1,*] P. Bokes,[2,3] Patrick Rinke,[3,4] and R. W. Godby[1,3,†]
[1]*Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom*
[2]*Department of Physics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 841 04 Bratislava, Slovak Republic*
[3]*European Theoretical Spectroscopy Facility (ETSF)*
[4]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
(Received 5 December 2006; published 14 March 2007)

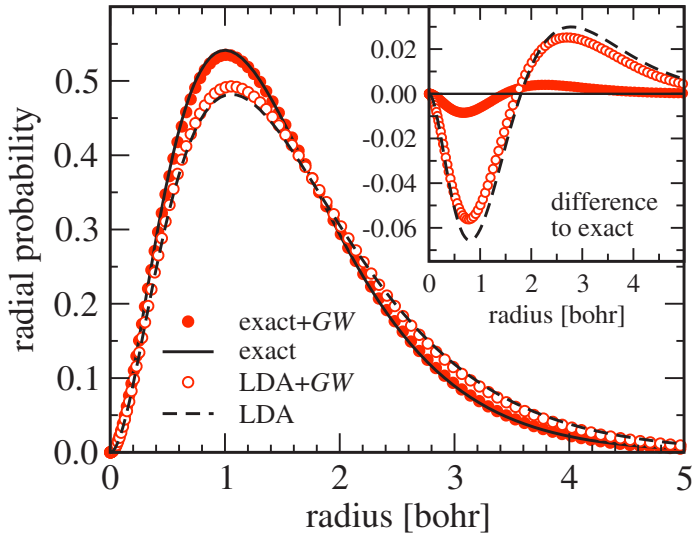
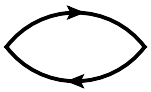


TABLE I. Quasiparticle energies (eV) for the 1*s* state of hydrogen (the ionization potential) obtained by diagonalizing the quasiparticle Hamiltonian (1). Two *GW* calculations are shown, starting from the LDA and from exact Kohn-Sham, respectively. For comparison, the Hartree-Fock (HF) and LDA eigenvalues are also shown.

Exact	HF	LDA	LDA+*GW*	Exact+*GW*
−13.61	−13.61	−6.36	−12.66	−13.40

because of the **RPA polarizability** (self-screening)

P = $-i$ 

CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

beyond the GW approx

THE JOURNAL OF CHEMICAL PHYSICS **131**, 154111 (2009)

The self-energy beyond *GW*: Local and nonlocal vertex corrections

P. Romaniello,[1,a)] S. Guyot,[2] and L. Reining[1]
[1]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS-CEA/DSM, F-91128 Palaiseau, France and European Theoretical Spectroscopy Facility (ETSF), F-91128 Palaiseau, France*
[2]*LiSSi, E. A. 3956, Université Paris 12, 94010 Créteil, France*

(Received 13 July 2009; accepted 27 September 2009; published online 20 October 2009)

Ionization Potentials of Solids: The Importance of Vertex Corrections

Andreas Grüneis,[1] Georg Kresse,[1,*] Yoyo Hinuma,[2] and Fumiyasu Oba[2,3,†]
[1]*Faculty of Physics and Center for Computational Materials Science, University of Vienna, Sensengasse 8/12, A-1090 Vienna, Austria*
[2]*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*
[3]*Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
(Received 12 September 2013; published 7 March 2014)

The ionization potential is a fundamental key quantity with great relevance to diverse material properties. We find that state of the art methods based on density functional theory and simple diagrammatic approaches as commonly taken in the *GW* approximation predict the ionization potentials of semiconductors and insulators unsatisfactorily. Good agreement between theory and experiment is obtained only when diagrams resulting from the antisymmetry of the many-electron wave function are taken into account via vertex corrections in the self-energy. The present approach describes both localized and delocalized states accurately, making it ideally suited for a wide class of materials and processes.

DOI: 10.1103/PhysRevLett.112.096401 PACS numbers: 71.10.-w, 31.15.A-

beyond the GW approx

PRL **107,** 166401 (2011) PHYSICAL REVIEW LETTERS week ending 14 OCTOBER 2011

Valence Electron Photoemission Spectrum of Semiconductors: *Ab Initio* Description of Multiple Satellites

Matteo Guzzo,[1,2,*] Giovanna Lani,[1,2] Francesco Sottile,[1,2] Pina Romaniello,[3,2] Matteo Gatti,[4,2] Joshua J. Kas,[5] John J. Rehr,[5,2] Mathieu G. Silly,[6] Fausto Sirotti,[6] and Lucia Reining[1,2,†]

- **beyond GW** by using a cumulant-expansion like self-energy
- models photoemission **including extrinsic losses**

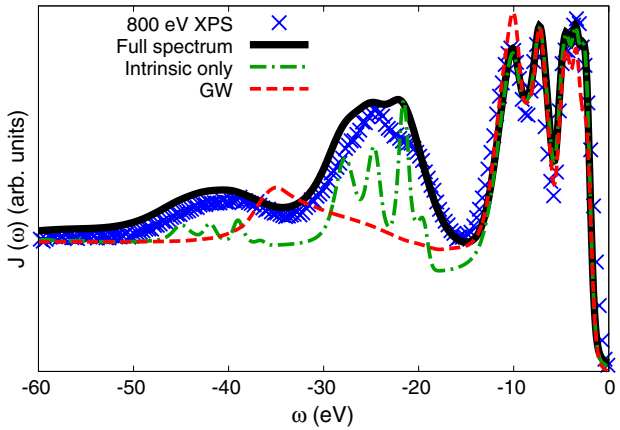


FIG. 1 (color online). Experimental XPS spectrum of Si at 800 eV photon energy (blue crosses), compared to the theoretical intrinsic $A(\omega)$ calculated from G_0W_0 (red dashed line), and from Eq. (4) (green dot-dashed line). On top of the latter the black solid line also includes extrinsic and interference effects. All spectra contain photoabsorption cross sections, a calculated secondary electron background and 0.4 eV Gaussian broadening to account for finite k-point sampling and experimental resolution. The Fermi energy is set to 0 eV.

CNRNANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

outline

- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

GW in practice

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

$$\Sigma^{GW}(\mathbf{r_1},\mathbf{r_2};\tau) = i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)W(\mathbf{r_1},\mathbf{r_2};\tau+\eta)$$

In Fourier space

$$\Sigma^{GW}(\mathbf{r}_1,\mathbf{r_2};\omega) = \frac{i\hbar}{2\pi}\int_{-\infty}^{\infty} G_0(\mathbf{r}_1,\mathbf{r_2};\omega+\omega')W(\mathbf{r}_1,\mathbf{r_2};\omega')e^{i\omega'\eta}d\omega'$$

$$W = v + vPW$$

$$P(\mathbf{r_1},\mathbf{r_2};\tau) = -i\hbar G_0(\mathbf{r_1},\mathbf{r_2};\tau)G_0(\mathbf{r_2},\mathbf{r_1};-\tau)$$

different implementations

Reciprocal Space & Frequency Domain:

M. Hybertsen and S. Louie, PRB **34**, 5390 (1986)

Real Space and Real Time:

H.N. Rojas, R. W. Godby and R. J. Needs, PRL **74**, 1827 (1995)

Mixed:

Liu, Kaltak, Klimes, Kresse, PRB **94**, 165109 (2016)

Use of localized basis set:

H. Huebener, M. A. Perez-Osorio, P. Ordejon, F. Giustino, Eur. Phys. J. B **85**, 321 (2012)
M. Rohlfing, P. Kruger, and J. Pollmann, PRB **52**, 1905 (1995)
X. Blase, C. Attaccalite, V. Olevano, PRB **83**, 115103 (2011)
F. Bruneval, et al, Comput. Phys. Commun. **208**, 149 (2016)

Use of Wannier Function:

P. Umari, G. Stenuit, S. Baroni, PRB **79**, 201104(R) (2009)

Avoiding sums over empty states:

P. Umari, G. Stenuit, S. Baroni, PRB **81**, 115104 (2010)
F. Giustino, M.L. Cohen, S.G. Louie, PRB **81**, 115105 (2010)
M. Govoni, et al, J. Chem. Theory Comput. **11**, 2680 (2015)

G_0W_0-PPA

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

HERE: G_0W_0 + Plasmon Pole Approx
(using PWs + pseudopotentials)

M. Hybertsen and S. Louie,
PRB **34**, 5390 (1986)

- GF build **on top of KS-DFT** electronic structure (no self-consistency)
- [**QP wfcs** assumed equal to KS-DFT ones] (a practical assumption)
- **Freq-dependency of W** approximated using PPA => leading to analytical free-integration

G_0W_0-PPA

G_0 is used to evaluate Sgm:

$$\Sigma(12) = iG_0(12)W_0(21)$$

G_0 = G @ KS-DFT

$$W_0 = [1 - vP_0]^{-1}v$$

$$\Sigma(x_1, x_2, \omega) = -\frac{1}{2\pi i}\int d\omega'\, e^{-i\omega'\eta}\, G(x_1, x_2, \omega - \omega')W(x_1, x_2, \omega')$$

$$G_0(x_1, x_2, \omega) = \sum_i \frac{\phi_i(x_1)\phi_i^*(x_2)}{\omega - \epsilon_i \pm i0^+}$$

$$P_0(x_1, x_2, \omega) = \sum_{cv}\left[\frac{\phi_v^*(x_1)\phi_c(x_1)\phi_c^*(x_2)\phi_v(x_2)}{\omega - \omega_{cv} + i0^+} - \frac{\phi_v^*(x_2)\phi_c(x_2)\phi_c^*(x_1)\phi_v(x_1)}{\omega + \omega_{cv} - i0^+}\right]$$

Plasmon pole approx

Consider the Lehmann representation (eps^-1 prop to W)

$$\tilde{\epsilon}^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \sum_I \left[\frac{R_I^{(+)}(\mathbf{q},\mathbf{G},\mathbf{G}')}{\omega - E_I^N + i\delta} - \frac{R_I^{(-)}(\mathbf{q},\mathbf{G},\mathbf{G}')}{\omega + E_I^N - i\delta} \right],$$

for each (q,G,G'), the **PPA** assumes that all the weight is given by a **single excitation**:

$$\tilde{\epsilon}^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) \approx \left[\frac{R_{\mathbf{G},\mathbf{G}'}(\mathbf{q})}{\omega - \tilde{\omega}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) + i\delta} - \frac{R_{\mathbf{G},\mathbf{G}'}(\mathbf{q})}{\omega + \tilde{\omega}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) - i\delta} \right].$$

- Allows for **analytical integral** over frequency
- Motivated on physical grounds (compare with loss function)
- **Several recipes** for the calculation of the parameters (Hybertsen-Louie, Godby-Needs, …)
- Often works, **but not always (**see eg Marini et al, PRL 2002)

G_0W_0-PPA

$$\hat{H}_0(\mathbf{r})f_s(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s)f_s(\mathbf{r}')d^3\mathbf{r}' = \epsilon_s f_s(\mathbf{r})$$

Once we know $\Sigma^{GW} = G^0W^0$

$f_i^{QP}(\mathbf{r}) \approx \phi_i^{KS}(\mathbf{r})$ frequently used approximations (not always valid)

Treat the Self-Energy term as a perturbation

$$\epsilon_i \approx \epsilon_i^{KS} + \langle \phi_i^{KS} | \Sigma(\epsilon_i) - V_{xc}) | \phi_i^{KS} \rangle$$

G_0W_0-PPA

$$\epsilon_i \approx \epsilon_i^{KS} + \langle \phi_i^{KS} | \Sigma(\epsilon_i) - V_{xc}) | \phi_i^{KS} \rangle$$

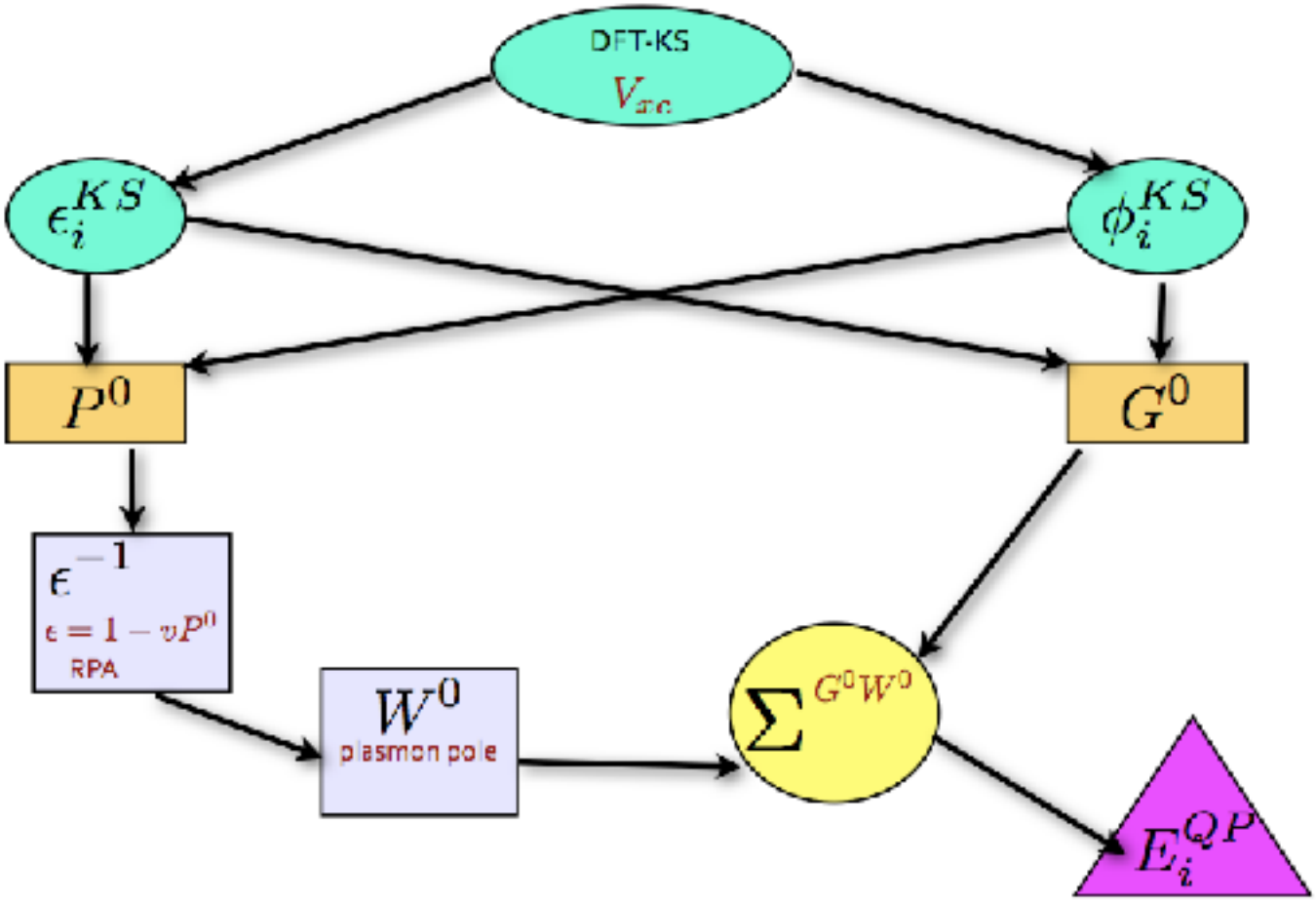
Non linear equation: linear expansion:

$$\Sigma(\mathbf{r_1}, \mathbf{r_2}; c_i) \approx \Sigma(\mathbf{r_1}, \mathbf{r_2}; c_i^{KS}) + (c_i - c_i^{KS}) \frac{\partial \Sigma(\mathbf{r_1}, \mathbf{r_2}; \omega)}{\partial \omega} \Big|_{\epsilon_i^{KS}}$$

$$\epsilon_i \approx \epsilon_i^{KS} + Z_i \langle \phi_i^{KS} | \Sigma(\epsilon_i^{KS}) - V_{xc}) | \phi_i^{KS} \rangle$$

$$Z_i = \left(1 - \left\langle \phi_i^{KS} \middle| \frac{\partial \Sigma(\mathbf{r_1}, \mathbf{r_2}; \omega)}{\partial \omega} |_{\epsilon_i^{KS}} \middle| \phi_i^{KS} \right\rangle\right)^{-1}$$

summary of G_0W_0



outline

- **ARPES** from a theory perspective
- Connection to the **Green's function theory**
- The **GW self-energy**
- Practical **implementation**
- GW on a daily basis

The GW self-energy

$$\langle n\mathbf{k}|\Sigma_x(\mathbf{r_1},\mathbf{r_2})|\mathbf{n'k'}\rangle = -\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{\mathbf{(2\pi)^3}}\sum_{\mathbf{G}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q,G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q,G})\mathbf{f_{n_1k_1}}$$

$$\rho_{nn1}(\mathbf{q+G}) = \langle n\mathbf{k}|e^{i(\mathbf{q+G})\cdot\mathbf{r}}|n1\mathbf{k_1}\rangle$$

$$\langle n\mathbf{k}|\Sigma_c(\mathbf{r_1},\mathbf{r_2};\omega)|\mathbf{n'k'}\rangle = \frac{\mathbf{1}}{\mathbf{2}}\sum_{\mathbf{n_1}}\int_{\mathbf{Bz}}\frac{\mathbf{d^3q}}{\mathbf{(2\pi)^3}}\Big\{\sum_{\mathbf{GG'}}\mathbf{v(q+G)}\rho_{\mathbf{n,n_1}}(\mathbf{q,G})\rho^*_{\mathbf{n'n_1}}(\mathbf{q,G'})\times$$

$$\times\int\frac{d\omega'}{2\pi}\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega')\Big[\frac{f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}-i\delta}+\frac{1-f_{n1(\mathbf{k-q})}}{\omega-\omega'-\epsilon^{LDA}_{n1(\mathbf{k-q})}+i\delta}\Big]\Big\}$$

Care is needed:

Integration over the Brillouin zone
Sum over states
Frequency integral (=> PPA)
wfc representation

yambo input file

Integration over Bz

k-points samplings

plane wave cutoffs

screening convergence

Plasmon-pole approximation validity

sum over unoccupied states

converge

converge

converge

```
#  __   __   _________   ___ __ __   _______   ______
# /_/\/_/\ /________/\ /__//_//_/\ /_______/\ /_____/\
# \ \ \ \ \\::: _  \ \\::\| \| \ \\::: _  \ \\::::_\ \ \
#  \:\_\ \ \\::(_)  \ \\:.      \ \\::(_)  \/_\:\ \ \ \
#   \::::_\/ \:: __  \ \\:.\-/\  \ \\::  _  \ \\:\ \ \ \
#     \::\ \  \:.\ \  \ \\. \  \  \ \\::(_)  \ \\:\_\ \ \
#      \__\/   \__\/\__\/ \__\/ \__\/ \_______\/ \_____\/
#
#                http://www.yambo-code.org
#
ppa                             # [R Xp] Plasmon Pole Approximation
gw0                             # [R GW] GoWo Quasiparticle energy levels
HF_and_locXC                    # [R XX] Hartree-Fock Self-energy and Vxc
em1d                            # [R Xd] Dynamical Inverse Dielectric Matrix
FFTGvecs= 19117         RL      # [FFT] Plane-waves
EXXRLvcs= 10019         RL      # [XX] Exchange RL components
Chimod= "Hartree"                       # [X] IP/Hartree/ALDA/LRC/BSfxc
% BndsRnXp
   1 |  50 |                    # [Xp] Polarization function bands
%
NGsBlkXp= 100            RL     # [Xp] Response block size
% LongDrXp
 1.000000 | 0.000000 | 0.000000 |        # [Xp] [cc] Electric Field
%
PPAPntXp= 27.21138      eV      # [Xp] PPA imaginary energy
% GbndRnge
  1 |  20|                      # [GW] G[W] bands range
%
GDamping=  0.10000      eV      # [GW] G[W] damping
dScStep=  0.10000       eV      # [GW] Energy step to evalute Z factors
DysSolver= "n"                  # [GW] Dyson Equation solver (`n`,`s`,`g`)
%QPkrange                       # [GW] QP generalized Kpoint/Band indices
  1| 16|  1| 50|
%
%QPerange                       # [GW] QP generalized Kpoint/Energy indices
  1| 16| 0.0|-1.0|
%
```

References

Original Papers

L. Hedin, Phys. Rev. **139**, A796 (1965)
L. Hedin and S. Lundquist, Sol. State Phys. **23** (1969)

Review Papers

F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998)
W.G. Aulbur et al, Sol State Phys. **54**, 1 (2000)

C. Friedrich and A. Schindlmayr, "Computational Nanoscience: Do it yourself!"
NIC Series, Vol **31**, 335 (2006)
https://juser.fz-juelich.de/record/51139/files/NIC-Band-31.pdf

Some details about the yambo code:

A. Marini, C. Hogan. M. Gruning, D. Varsano, Comp Phys. Comm **180**, 1392 (2009)

thanks