

# The GW Approximation

Manish Jain<sup>1</sup>

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Indian Institute of Science  
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July 8, 2014



# Ground-state properties

Properties that are intrinsic to a system with all its electrons in equilibrium.



- Density functional theory is the “standard model” for understanding **ground-state** properties.
- Total energy is a functional of the charge density.
- Kohn-Sham formulation: Map the interacting many-electron problem to non-interacting electrons moving in a self-consistent field.

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right) \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

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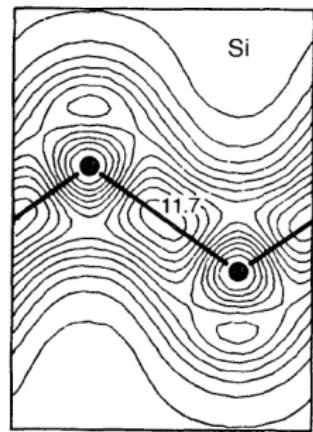
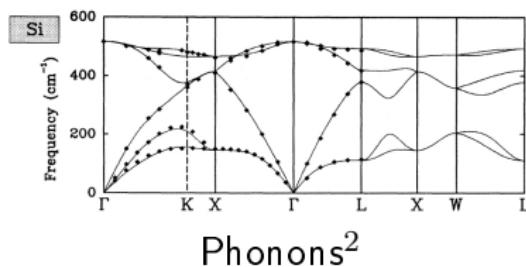
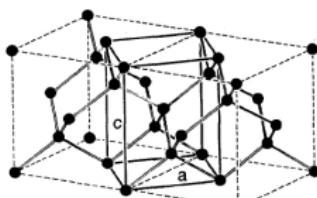
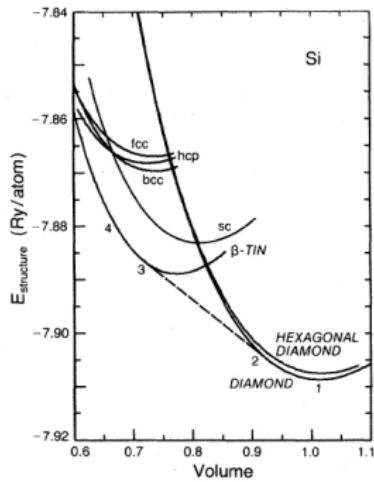
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Local density approximation  
Generalized gradient approximation

# Ground-state properties



<sup>1</sup>M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

<sup>2</sup>P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B, **43**, 7231 (1991).

## Excited-state properties

Spectroscopic properties that involve experiments creating an excited particle above the ground state.

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Light source

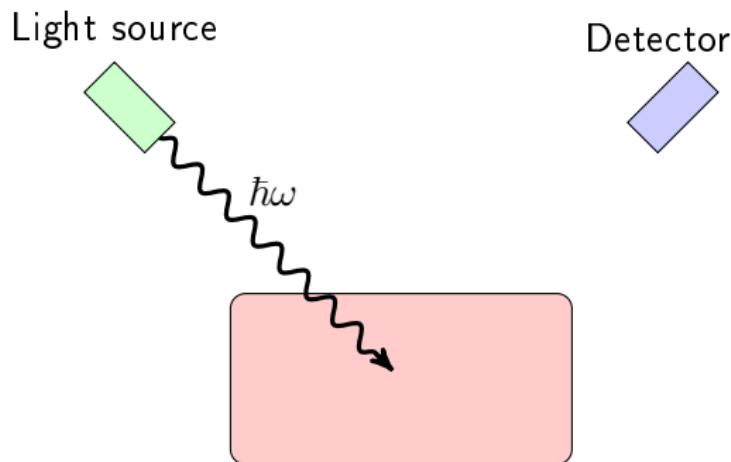


Detector



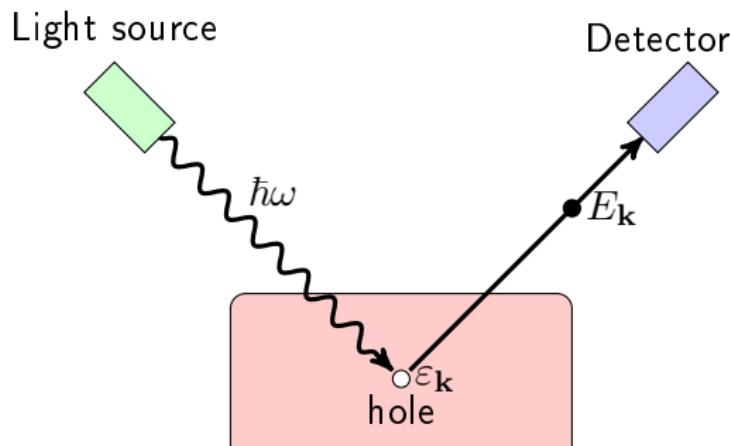
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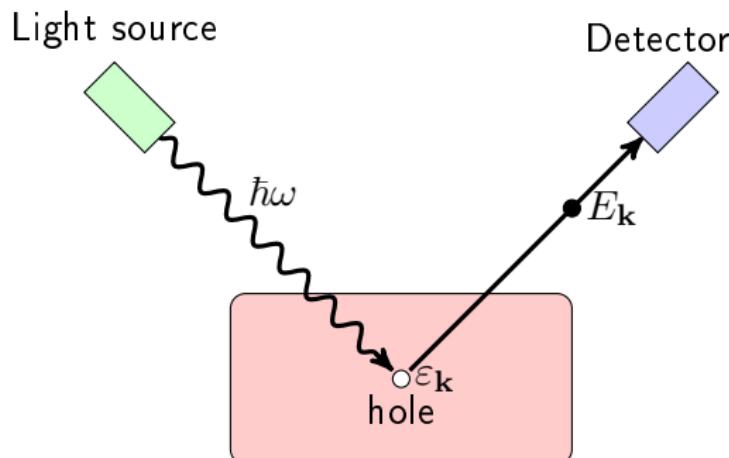
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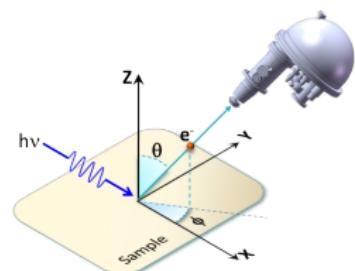
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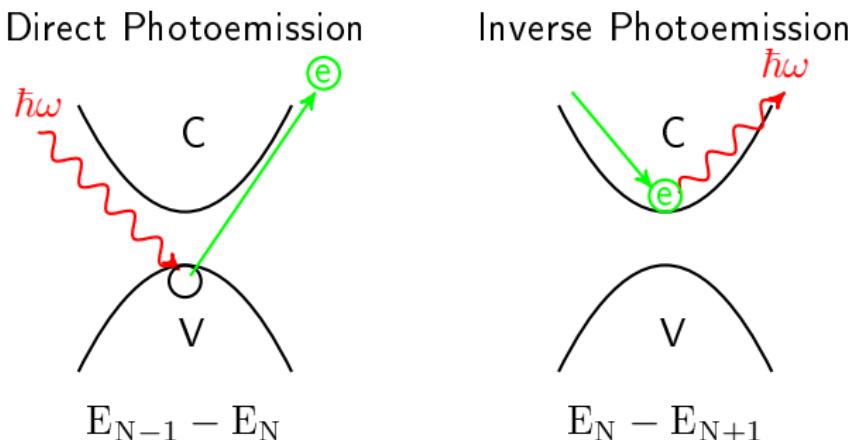


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<http://www.arpes.co.uk>

# Excited-state properties - Quasiparticle gap



- Quasiparticle band gap defined as

$$\begin{aligned}E_g &= \text{Ionization Energy} - \text{Electron Affinity} \\&= E_{N+1} + E_{N-1} - 2E_N\end{aligned}$$

- Different from Optical gap.

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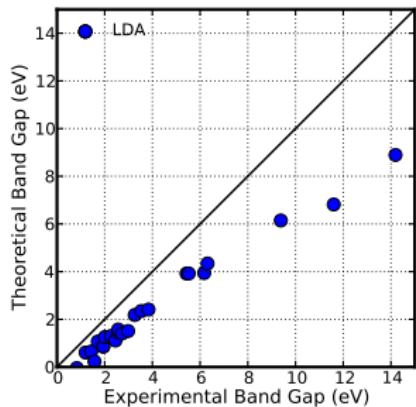
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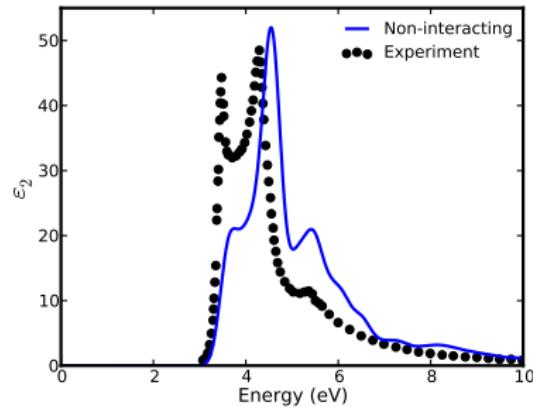
- Kohn-Sham DFT works well for the ground state.
- Kohn-Sham eigenvalues are Lagrange multipliers.
- Kohn-Sham eigenvalues – eigenvalues of a fictive system.
- Kohn-Sham energies cannot be interpreted as removal/addition energies (except the energy of the highest occupied molecular orbital in a finite system).

# Excited-state properties

Materials:  
InSb, InAs, Ge,  
GaSb, Si, InP,  
GaAs, CdS,  
AlSb, AlAs,  
CdSe, CdTe,  
BP, SiC, C<sub>60</sub>,  
GaP, AlP,  
ZnTe, ZnSe,  
c-GaN, w-GaN,  
InS, w-BN,  
c-BN,  
diamond,  
w-AlN, LiCl,  
Fluorite, LiF



Quasiparticle Gap<sup>1</sup>



Optical absorption<sup>2</sup>

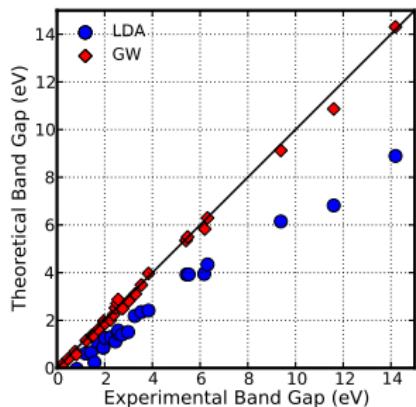
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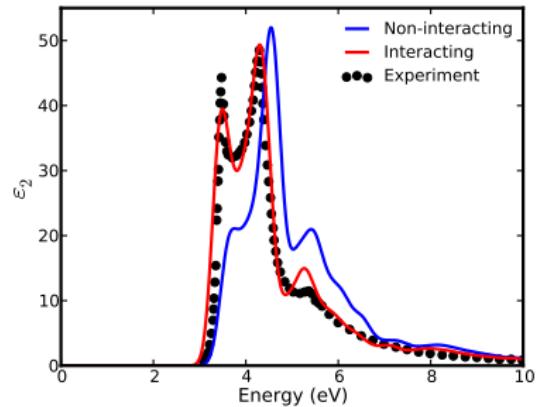
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PHYSICAL REVIEW

VOLUME 139, NUMBER 3A

2 AUGUST 1965

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

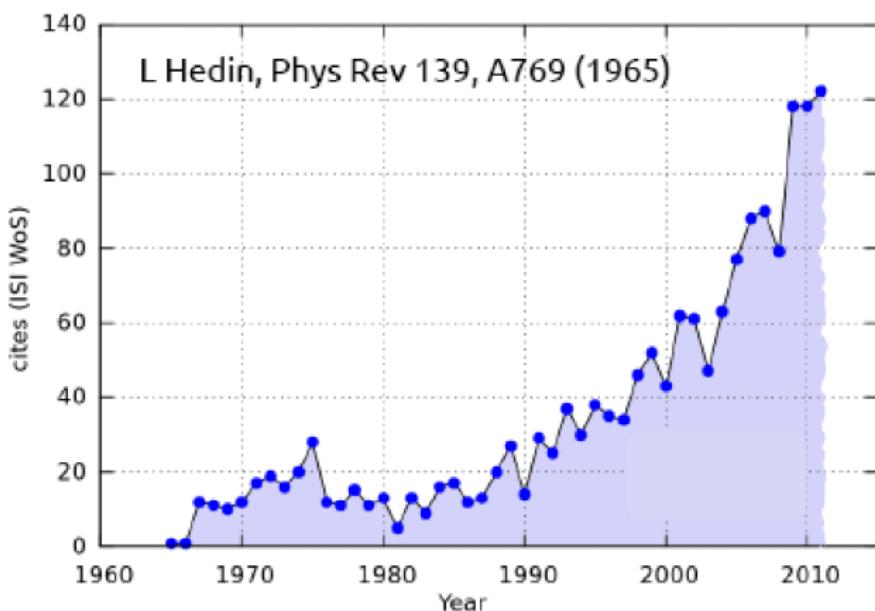
LARS HEDIN†

*Argonne National Laboratory, Argonne, Illinois*

(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies  $E(\mathbf{k})$  and quasiparticle interactions  $f(\mathbf{k}, \mathbf{k}')$ . The very first approximation gives a good value for the magnitude of  $E(\mathbf{k})$ . To estimate the derivative of  $E(\mathbf{k})$  we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for  $f$ . Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

# The GW approximation



From Feliciano Giustino's slides

## Greens function

$$G(\mathbf{r} t, \mathbf{r}' t') = -i \langle \Psi_N^0 | T[\hat{\psi}(\mathbf{r} t) \hat{\psi}^\dagger(\mathbf{r}' t')] | \Psi_N^0 \rangle$$

$|\Psi_N^0\rangle$  the exact N electron ground state:  $\hat{H}|\Psi_N^0\rangle = E_N^0|\Psi_N^0\rangle$

the field operator (Heisenberg picture):  $\hat{\psi}(\mathbf{r} t) = e^{i\hat{H}t}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t}$

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$$= \begin{cases} -i \langle \Psi_N^0 | \hat{\psi}(\mathbf{r} t) \hat{\psi}^\dagger(\mathbf{r}' t') | \Psi_N^0 \rangle & \text{when } t > t' \text{ (electron)} \\ i \langle \Psi_N^0 | \hat{\psi}^\dagger(\mathbf{r}' t') \hat{\psi}(\mathbf{r} t) | \Psi_N^0 \rangle & \text{when } t < t' \text{ (hole)} \end{cases}$$

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$$= -i \langle \Psi_N^0 | \hat{\psi}(\mathbf{r} t) \hat{\psi}^\dagger(\mathbf{r}' t') | \Psi_N^0 \rangle \theta(t - t')$$

$$+ i \langle \Psi_N^0 | \hat{\psi}^\dagger(\mathbf{r}' t') \hat{\psi}(\mathbf{r} t) | \Psi_N^0 \rangle \theta(t' - t)$$

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Insert the completeness relation:

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with quasiparticle amplitudes:

$$g_s(\mathbf{r}) = \langle \Psi_N^0 | \hat{\psi}(\mathbf{r}t) | \Psi_{N+1}^s \rangle$$

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Upon Fourier transforming:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_s \frac{g_s(\mathbf{r}) g_s^*(\mathbf{r}')}{\omega - (E_{N+1}^s - E_N^0) + i\eta} + \sum_s \frac{f_s(\mathbf{r}) f_s^*(\mathbf{r}')}{\omega + (E_{N-1}^s - E_N^0) - i\eta}$$

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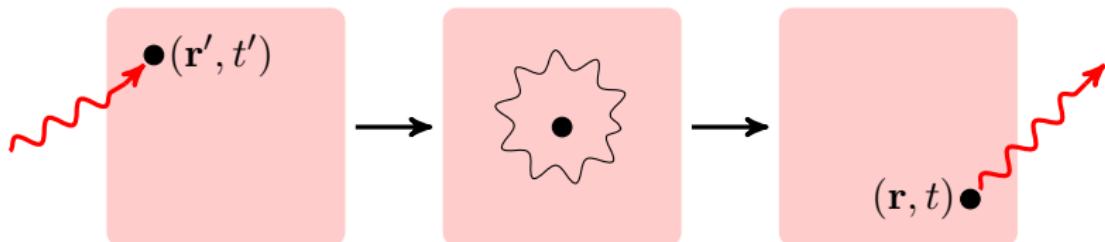
## Spectral function

$$\begin{aligned} A(\mathbf{r}, \mathbf{r}'; \omega) &= \frac{1}{\pi} |Im G(\mathbf{r}, \mathbf{r}'; \omega)| \\ &= \sum_s g_s(\mathbf{r}) g_s^*(\mathbf{r}') \delta(\omega - (E_{N+1}^s - E_N^0)) \\ &\quad + \sum_s f_s(\mathbf{r}) f_s^*(\mathbf{r}') \delta(\omega + (E_{N-1}^s - E_N^0)) \end{aligned}$$

# Physical interpretation of the Greens function

For  $t > t'$ ,  $\langle \Psi_N^0 | \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') | \Psi_N^0 \rangle$

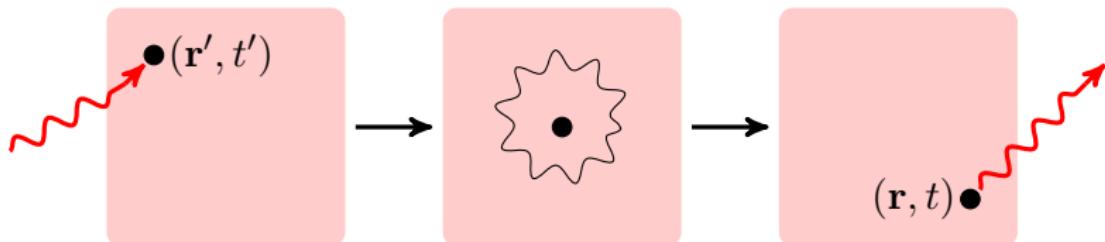
probability amplitude that electron created at  $(\mathbf{r}', t')$  will go to  $(\mathbf{r}, t)$



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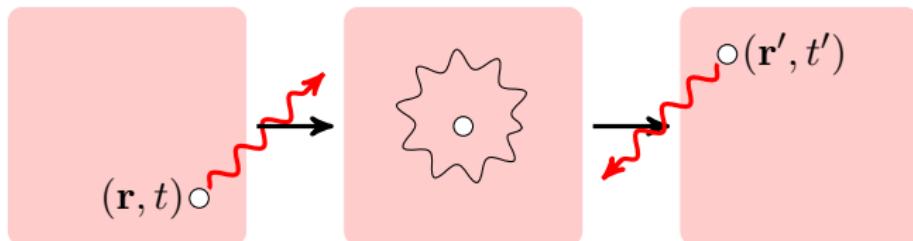
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probability amplitude that hole created at  $(\mathbf{r}, t)$  will go to  $(\mathbf{r}', t')$



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Quasiparticle equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) \right) \phi(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{\text{QP}}) \phi(\mathbf{r}') = E_{\text{QP}} \phi(\mathbf{r})$$

Kohn-Sham equation:

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J. Phys.: Condens. Matter **11** (1999) R489–R528. Printed in the UK

PII: S0953-8984(99)66997-1

## REVIEW ARTICLE

### On correlation effects in electron spectroscopies and the GW approximation

Lars Hedin

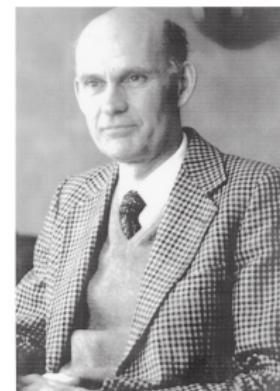
Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden

and

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received 28 June 1999

**Abstract.** The *GW* approximation (GWA) extends the well-known Hartree–Fock approximation (HFA) for the self-energy (exchange potential), by replacing the bare Coulomb potential  $v$  by the *dynamically screened potential*  $W$ , e.g.  $V_{ex} = iGv$  is replaced by  $\Sigma_{GW} = iGW$ . Here  $G$  is the one-electron Green's function. The GWA like the HFA is self-consistent, which allows for solutions beyond perturbation theory, like say spin-density waves. In a first approximation,  $iGW$  is a sum of a statically screened exchange potential plus a Coulomb hole (equal to the electrostatic energy associated with the charge pushed away around a given electron). The Coulomb hole part is larger in magnitude, but the two parts give comparable contributions to the dispersion of the quasi-particle energy. The GWA can be said to describe an *electronic polaron* (an electron surrounded by an electronic polarization cloud), which has great similarities to the ordinary polaron (an electron surrounded by a cloud of phonons). The dynamical screening adds new crucial features beyond the HFA. With the GWA not only bandstructures but also spectral functions can be calculated, as well as charge densities, momentum distributions, and total energies. We will discuss the ideas behind the GWA, and generalizations which are necessary to improve on the rather poor GWA satellite structures in the spectral functions. We will further extend the GWA approach to fully describe spectroscopies like photoemission, x-ray absorption, and electron scattering. Finally we will comment on the relation between the GWA and theories for strongly correlated electronic systems. In collecting the material for this review, a number of new results and perspectives became apparent, which have not been published elsewhere.



LARS HEDIN

1933–2002

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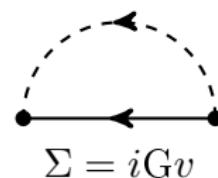
LARS HEDIN

1933-2002

# The GW approximation

## Hartree-Fock Approximation

$$\begin{aligned}\Sigma_x(\mathbf{r}, \mathbf{r}') &= iG(\mathbf{r}, \mathbf{r}'; t)v(\mathbf{r} - \mathbf{r}') \\ &= -\sum_j^{\text{occ}} \psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')v(\mathbf{r} - \mathbf{r}')\end{aligned}$$

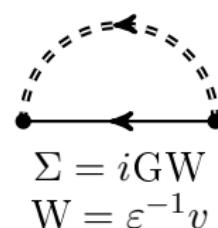


## GW Approximation

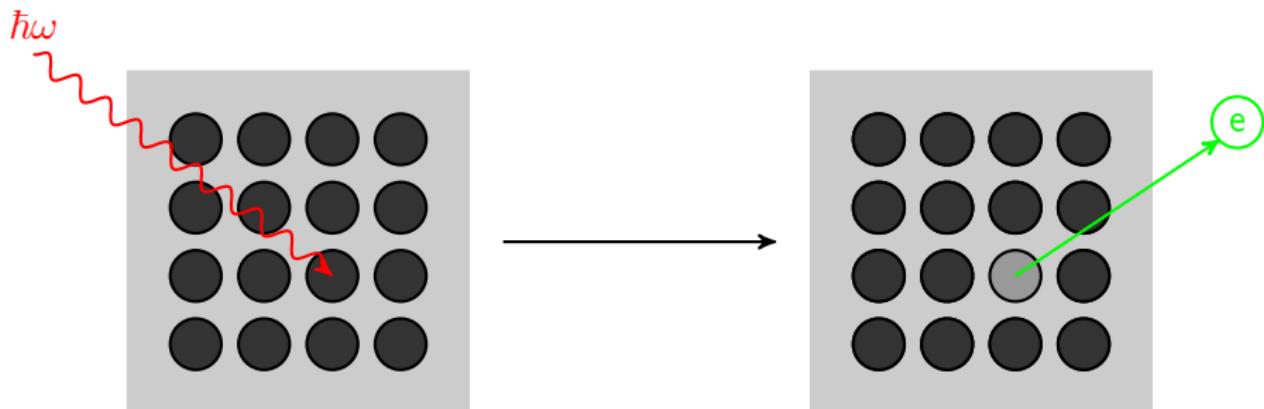
$$\Sigma_{\text{GW}}(\mathbf{r}, \mathbf{r}') = iG(\mathbf{r}, \mathbf{r}'; t)W(\mathbf{r}, \mathbf{r}', t)$$

W: screened Coulomb interation

Lars Hedin, Phys. Rev. 139, A796 (1965)



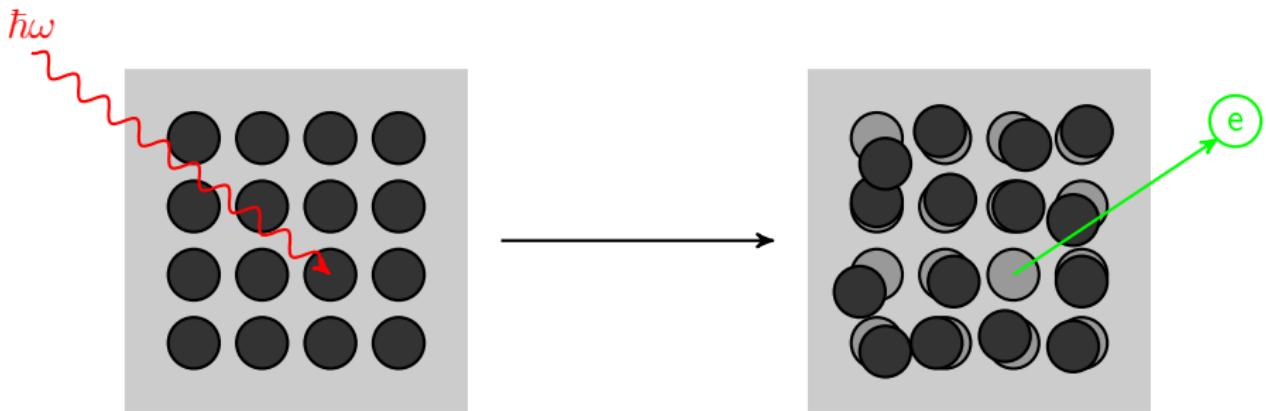
# Photoemission process within Hartree-Fock



Additional charge  $\rightarrow$  Independent particles.  
No relaxation of the system.  
Does not describe the physics in solids.

Adapted from slides by M. Gatti

# Photoemission process within GW



Additional charge  $\rightarrow$  polarization and screening.  
Polarization from non-interacting electron-hole pairs (RPA)  
Classical interaction between additional charge and induced charge.  
Describes the physics well.

Adapted from slides by M. Gatti

# Quasiparticles



real horse



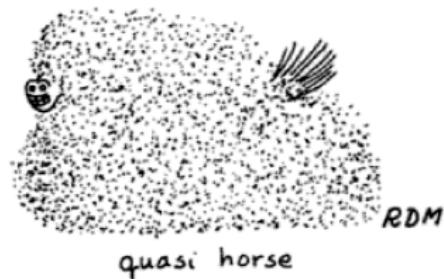
quasi horse

R. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem*, McGraw-Hill Book Company, New York (1976)

# Quasiparticles



real horse



quasi horse

Particle gets “dressed”!

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# Quasiparticles

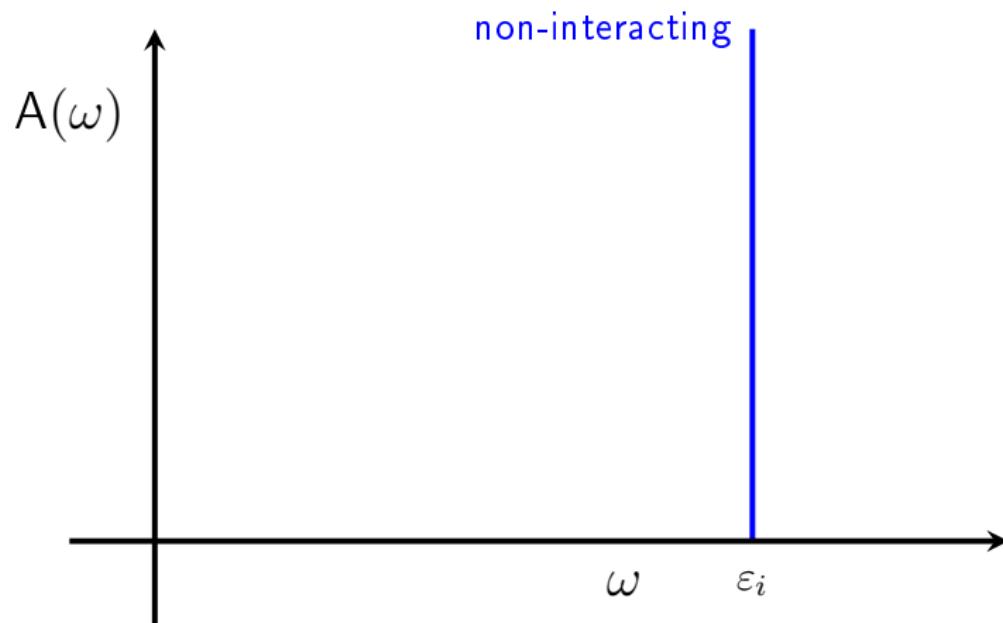


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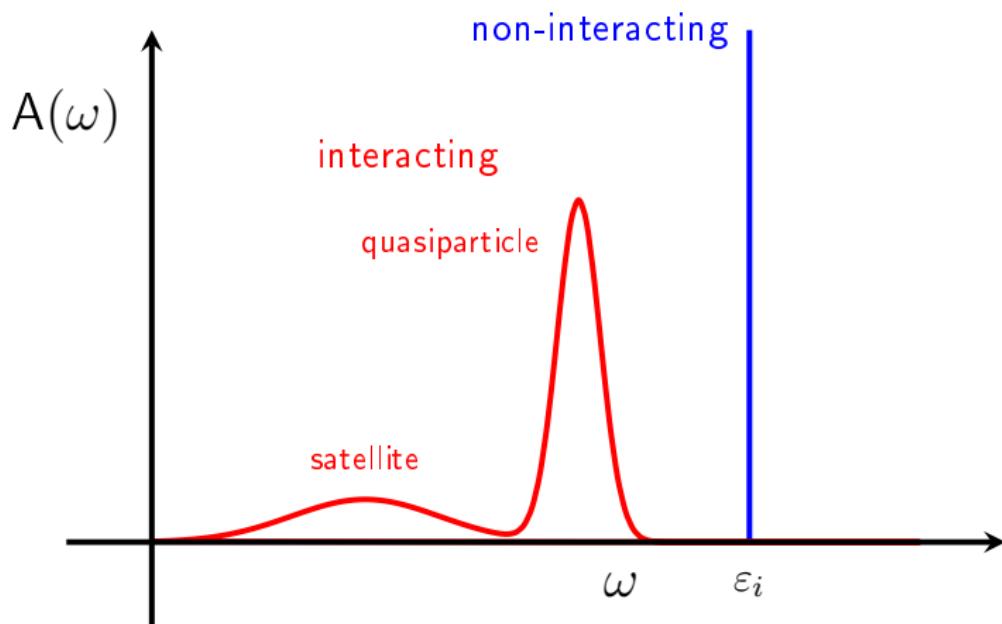
There is a polarization cloud around the particle which screens its interactions with the rest of the system.

R. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem*, McGraw-Hill Book Company, New York (1976)

# Spectral function



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## Green function in the interaction representation

The self-energy may be evaluated by using Wick's theorem or by Schwinger's functional derivative method.

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$$\hat{S} = T \exp [-i \int d^3 \phi(3) \hat{\rho}(3)] \quad 1 \equiv \mathbf{r}_1 t_1$$

$\Psi_0$  the exact ground state without perturbation:  $\hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$

the field operator (interaction picture) is independent of  $\phi$ :

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$$\frac{\delta \hat{S}}{\delta \phi(3)} = -i T[\hat{S} \hat{\rho}(3)]$$

Adapted from slides by F. Aryasetiawan

# Equation of motion

Equation of motion of the single particle Green function:

$$\left( i \frac{\partial}{\partial t_1} - h_0(\mathbf{r}_1) \right) G(1, 2) + i \int d3 v(1-3) G^{(2)}(1, 2, 3, 3^+) = \delta(1-2)$$

$$h_0 = -\frac{\nabla^2}{2} + V_{\text{ext}} \quad \text{independent-particle Hamiltonian}$$

$$v(1-3) = v(\mathbf{r}_1 - \mathbf{r}_3) \delta(t_1 - t_3)$$

$$G^{(2)}(1, 2, 3, 4) = \frac{\langle \Psi_0 | T[\hat{S}\hat{\psi}(1)\hat{\psi}(3)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(2)] | \Psi_0 \rangle}{\langle \Psi_0 | \hat{S} | \Psi_0 \rangle} \quad \text{two-particle Green Function}$$

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Unfortunately hierarchy of equations:

$$G(1, 2) \leftarrow G^{(2)}(1, 2, 3, 4)$$

$$G^{(2)}(1, 2, 3, 4) \leftarrow G^{(3)}(1, 2, 3, 4, 5, 6)$$

$$\vdots \qquad \vdots \qquad \vdots$$

Adapted from slides by F. Aryasetiawan

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Define the mass operator:

$$i \int d3 v(1-3) G^{(2)}(1, 2, 3, 3^+) \equiv - \int d3 M(1, 3) G(3, 2)$$
$$M = -iv G^{(2)} G^{-1}$$

Adapted from slides by F. Aryasetiawan

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$$\text{Self Energy: } \Sigma = M - V_{\text{Hartree}} = -ivG \frac{\delta G^{-1}}{\delta \phi}$$

Adapted from slides by F. Aryasetiawan

## Derivation of Hedin's equations

$$\Sigma(1, 2) = -i \int d3d4 v(1 - 3)G(1, 4) \frac{\delta G^{-1}(4, 2)}{\delta \phi(3)}$$

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$$\Sigma(1,2) = -i \int d3d4 W(1,3)G(1,4) \frac{\delta G^{-1}(4,2)}{\delta V(3)}$$

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$$\Sigma(1,2) = -i \int d3d4 W(1,3)G(1,4)\Gamma(4,2,3)$$

Vertex       $\Gamma(4,2,3) = - \frac{\delta G^{-1}(4,2)}{\delta V(3)}$

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$$\text{Vertex} \quad \Gamma(4,2,3) = -\frac{\delta G^{-1}(4,2)}{\delta V(3)}$$

$$\text{From equation of motion} \quad G^{-1} = i \frac{\partial}{\partial t} - h_0 - V_{\text{Hartree}} - \phi - \Sigma$$

$$\implies \Gamma = -\frac{\delta G^{-1}}{\delta V} = \left[ 1 + \frac{\delta \Sigma}{\delta V} \right]$$

# Derivation of Hedin's equations

$$\Gamma = 1 + \frac{\delta \Sigma}{\delta V} = 1 + \frac{\delta \Sigma}{\delta G} \frac{\delta G}{\delta V} = 1 - \frac{\delta \Sigma}{\delta G} G \frac{\delta G^{-1}}{\delta V} G = 1 + \frac{\delta \Sigma}{\delta G} G \Gamma G$$

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Polarization       $P = \frac{\delta\rho}{\delta V} = -i \frac{\delta G}{\delta V} = iG \frac{\delta G^{-1}}{\delta V} G = iG \Gamma G$

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Screened interaction  $W = \epsilon^{-1}v = \frac{\delta V}{\delta \phi}v = \left[1 + \frac{\delta V_{\text{Hartree}}}{\delta \phi}\right]v = \left[1 + v \frac{\delta \rho}{\delta \phi}\right]v$   
 $= \left[1 + v \frac{\delta \rho}{\delta V} \frac{\delta V}{\delta \phi}\right]v = \left[1 + v \frac{\delta \rho}{\delta V} \epsilon^{-1}\right]v = v + v P W$

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$$W = v + vP W$$

Adapted from slides by F. Aryasetiawan

## Hedin's equations

$$\Gamma(123) = \delta(12)\delta(13) + \int d(4567) \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(47)\Gamma(673)$$

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

$$P(12) = -i \int d(34) G(23)G(42)\Gamma(341)$$

$$W = v + v P W$$

$$\Sigma(12) = i \int d(34) G(14)W(1^+3)\Gamma(423)$$

# Hedin's equations

Start iteration

$$\Sigma = 0 \implies G = G_0 \quad (\text{Hartree Approximation})$$

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

$$P_0(12) = -iG_0(21)G_0(12)$$

$$\implies W_0 = v + vP_0W_0$$

$$\Sigma(12) = iG(12)W(1^+2)$$

- Can show that if you iterate then you will get the same diagrammatic expansion as with Wick's theorem.
- Wick's theorem diagrams are of the same order – while here they come in different orders together.

# Diagrammatic expansion in $W$

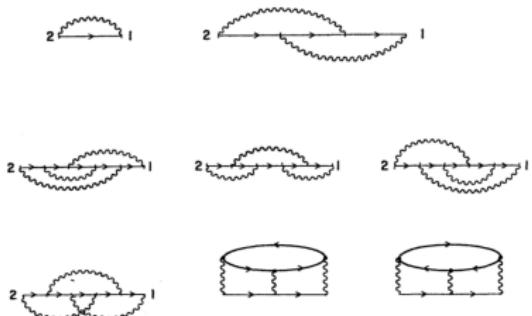


FIG. 1. Diagrams representing the expansion of  $M(1,2)$ . The one-particle Green's function  $G(1,2)$  is represented by an arrow from 2 to 1, and the screened potential  $W(1,2)$  by a wiggly line between 1 and 2.

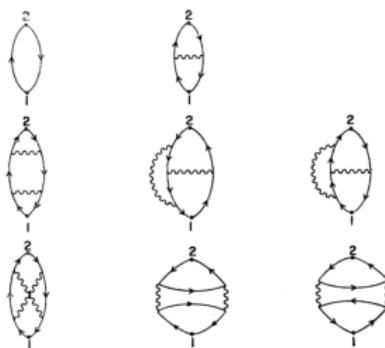


FIG. 2. Diagrams representing the expansion of  $P(1,2)$ .

Lars Hedin, Phys. Rev. 139, A796 (1965)

# Physical interpretation – Coulomb hole + screened exchange

$$\Sigma = \Sigma_{\text{SEX}} \quad + \Sigma_{\text{COH}}$$

screened exchange + Couloumb hole

$$\Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}', \omega) = - \sum_n^{\text{occ.}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \text{ReW}(\mathbf{r}, \mathbf{r}', \omega - \epsilon_n)$$

$$\Sigma_{\text{COH}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_n^{\text{all}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \int_0^\infty d\omega' \frac{\text{ImW}(\mathbf{r}, \mathbf{r}', \omega')}{\omega - \epsilon_n - \omega'}$$

$$\Sigma = \Sigma_{\text{SEX}} + \Sigma_{\text{COH}}$$

## Coulomb Hole (COH)

Interaction of electrons with excitations  
(electron-hole, plasmons) *i.e.* screening  
charge

## Screened Exchange (SEX)

Dynamically screened exchange  
(replacement  $v$  with  $W$ )

# Static limit – Coulomb hole + screened exchange

$$\Sigma = \Sigma_{\text{SEX}} + \Sigma_{\text{COH}}$$

$$\Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}') = - \sum_n^{\text{occ.}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}')$$

$$\Sigma_{\text{COH}}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} [W(\mathbf{r}, \mathbf{r}') - v(\mathbf{r}, \mathbf{r}')] \delta(\mathbf{r} - \mathbf{r}')$$

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Interaction of electrons with excitations  
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Dynamically screened exchange  
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# Actual implementation

Quasiparticle equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{\text{QP}}) \phi_i(\mathbf{r}') = E_{\text{QP}} \phi_i(\mathbf{r})$$

Kohn-Sham equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = E_{\text{DFT}} \psi_i(\mathbf{r})$$

# Actual implementation

Quasiparticle equation:

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Kohn-Sham equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = E_{\text{DFT}} \psi_i(\mathbf{r})$$

Assume  $\phi_i(\mathbf{r}) \approx \psi_i(\mathbf{r})$

# Actual implementation

Quasiparticle equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{\text{QP}}) \phi_i(\mathbf{r}') = E_{\text{QP}} \phi_i(\mathbf{r})$$

Kohn-Sham equation:

$$\left( -\frac{\nabla^2}{2} + V_{\text{ionic}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = E_{\text{DFT}} \psi_i(\mathbf{r})$$

Assume  $\phi_i(\mathbf{r}) \approx \psi_i(\mathbf{r})$

$$E_{\text{QP}} = E_{\text{DFT}} + \langle \psi_i(\mathbf{r}) | \Sigma - V_{\text{xc}} | \psi_i(\mathbf{r}) \rangle$$

# Actual implementation

Best G, Best W approach

$$(H_0^{\text{DFT}} + V_{\text{xc}}^{\text{DFT}})\psi^{\text{DFT}} = \epsilon^{\text{DFT}}\psi^{\text{DFT}}$$

# Actual implementation

Best G, Best W approach

$$(H_0^{\text{DFT}} + V_{\text{xc}}^{\text{DFT}})\psi^{\text{DFT}} = \epsilon^{\text{DFT}}\psi^{\text{DFT}}$$



$$\chi_0(12) = -iG_{\text{DFT}}(12)G_{\text{DFT}}(21)$$

# Actual implementation

Best G, Best W approach

$$(H_0^{\text{DFT}} + V_{\text{xc}}^{\text{DFT}})\psi^{\text{DFT}} = \epsilon^{\text{DFT}}\psi^{\text{DFT}}$$



$$\chi_0(12) = -iG_{\text{DFT}}(12)G_{\text{DFT}}(21)$$



$$\Sigma_{\text{GW}}(12) = iG_{\text{DFT}}(12)W_{\text{DFT}}(1^+2)$$

# Actual implementation

Best G, Best W approach

$$(H_0^{\text{DFT}} + V_{\text{xc}}^{\text{DFT}})\psi^{\text{DFT}} = \epsilon^{\text{DFT}}\psi^{\text{DFT}}$$



$$\chi_0(12) = -iG_{\text{DFT}}(12)G_{\text{DFT}}(21)$$

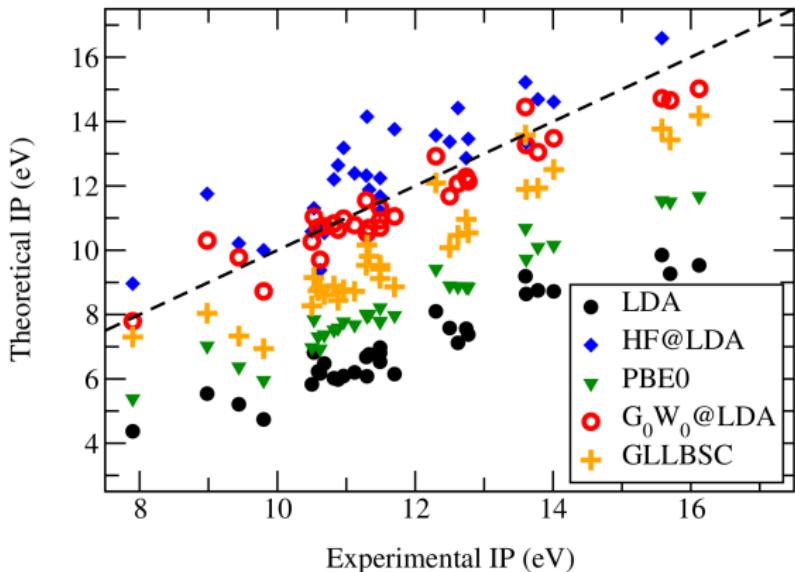


$$\Sigma_{\text{GW}}(12) = iG_{\text{DFT}}(12)W_{\text{DFT}}(1^+2)$$



$$\epsilon^{\text{QP}} = \epsilon^{\text{DFT}} + \langle\psi^{\text{DFT}}|\Sigma_{\text{GW}} - V_{\text{xc}}^{\text{DFT}}|\psi^{\text{DFT}}\rangle$$

# Excited-state properties – molecules

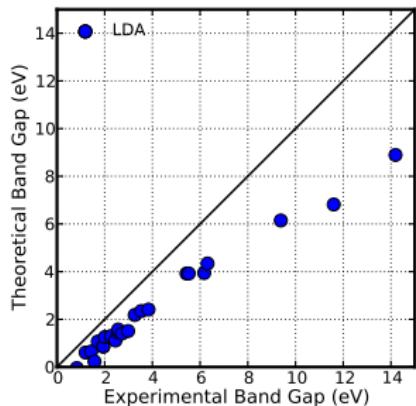


**Figure 5.3:** Calculated IPs for the 32 molecules listed in Table 5.1 plotted against the experimental values. The dashed line indicates equality.

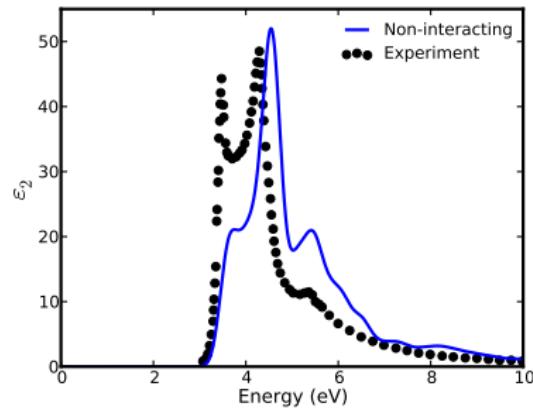
# Excited-state properties – solids

## Materials:

InSb, InAs, Ge,  
GaSb, Si, InP,  
GaAs, CdS,  
AlSb, AlAs,  
CdSe, CdTe,  
BP, SiC, C<sub>60</sub>,  
GaP, AlP,  
ZnTe, ZnSe,  
c-GaN, w-GaN,  
InS, w-BN,  
c-BN,  
diamond,  
w-AlN, LiCl,  
Fluorite, LiF



Quasiparticle Gap<sup>1</sup>



Optical absorption<sup>2</sup>

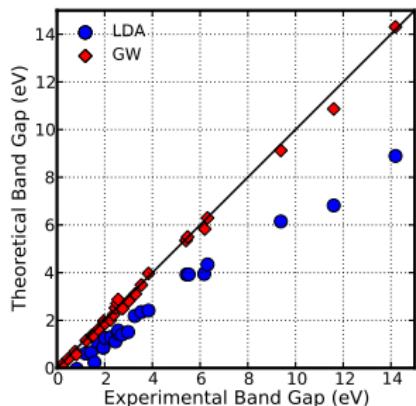
<sup>1</sup>S. G. Louie in Topics in Computational Materials Science, edited by C. Y. Fong (World Scientific, Singapore, 1997).

<sup>2</sup>J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Comput. Phys. Commun. **183**, 1269 (2012).

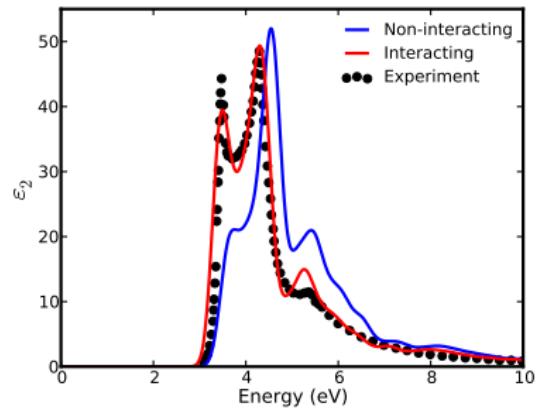
# Excited-state properties – solids

## Materials:

InSb, InAs, Ge,  
GaSb, Si, InP,  
GaAs, CdS,  
AlSb, AlAs,  
CdSe, CdTe,  
BP, SiC, C<sub>60</sub>,  
GaP, AlP,  
ZnTe, ZnSe,  
c-GaN, w-GaN,  
InS, w-BN,  
c-BN,  
diamond,  
w-AlN, LiCl,  
Fluorite, LiF



Quasiparticle Gap<sup>1</sup>



Optical absorption<sup>2</sup>

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# Excited-state properties – Code



BerkeleyGW

<http://www.berkeleygw.org>

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<sup>1</sup>J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Comput. Phys. Commun. **183**, 1269 (2012).

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