Quasiparticle Band Structures and the *GW* Approximation

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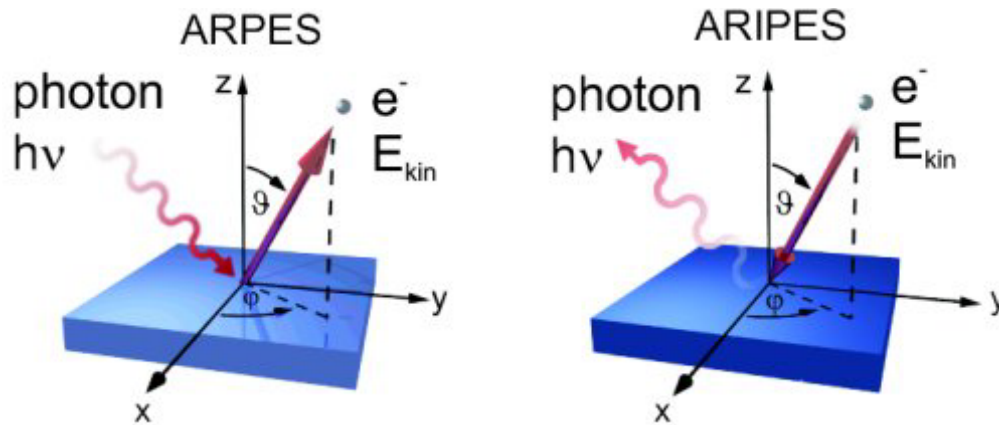
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Band-Structure Measurements

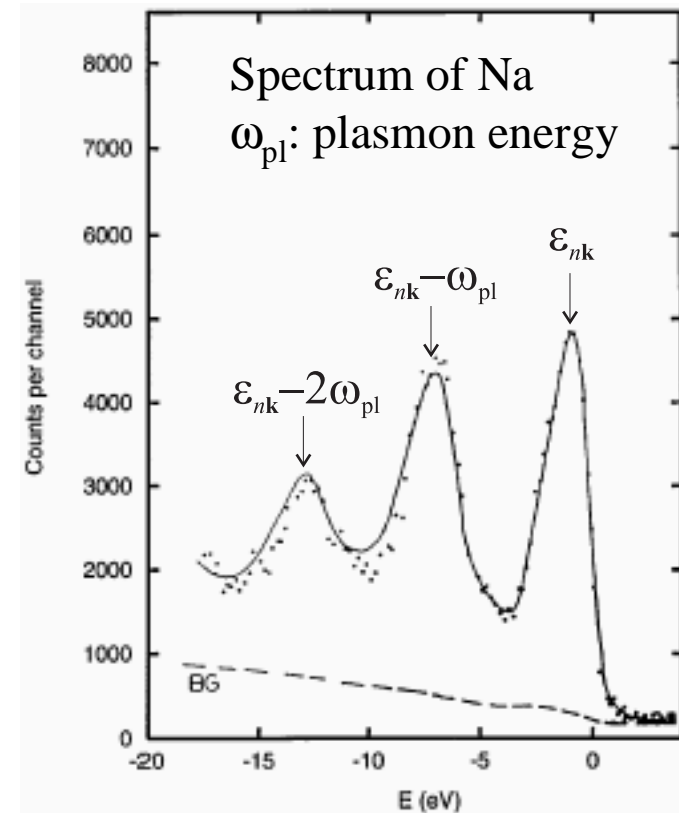Angle-Resolved (Inverse) Photoemission Spectroscopy

Measured binding energy (band structure):

$$\varepsilon_{n\mathbf{k}} = h\nu - E_{\text{kin}} = E^*(N-1) - E(N)$$

$E(N)$:   Ground state with N electrons

$E^*(N-1)$: Excited state with $N-1$ electrons

Spectrum of Na
ω_{pl}: plasmon energy

F. Aryasetiawan et al., Phys. Rev. Lett. **77**, 2268 (1996).

Definition of the Band Structure

The electronic band structure marks the complete set of electron-removal and electron-addition energies accessible from the ground state, i.e., total-energy differences between two systems with different particle numbers:

$$\varepsilon_{n\mathbf{k}} = E(N) - E(N-1, n\mathbf{k}) \qquad \text{for occupied valence states}$$
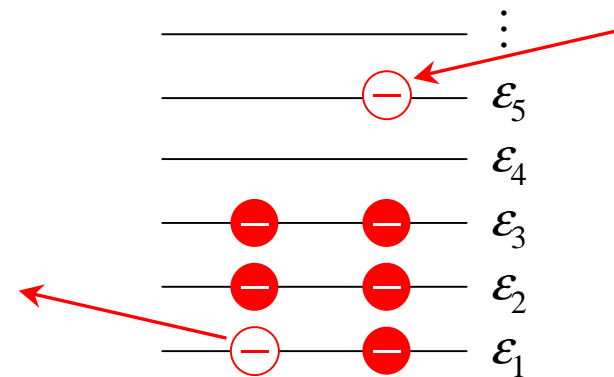$$\varepsilon_{n\mathbf{k}} = E(N+1, n\mathbf{k}) - E(N) \qquad \text{for unoccupied conduction states}$$

In order to obtain reliable numerical results, we need a way to calculate the band structure directly, not from total-energy differences, because $\varepsilon_{n\mathbf{k}} \ll E(N)$.

Example: Noninteracting electrons

$$\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$E(N) = \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r})\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right]\varphi_i(\mathbf{r})\,d^3r = \sum_{i=1}^{N} \varepsilon_i$$
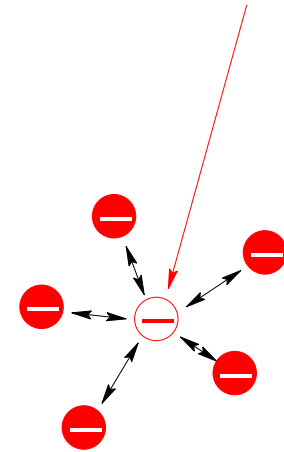
$$E(N) - E(N-1, j) = \sum_{i=1}^{N} \varepsilon_i - \sum_{\substack{i=1 \\ i \neq j}}^{N} \varepsilon_i = \varepsilon_j$$

Hartree-Fock Theory

$$\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})\right]\varphi_i(\mathbf{r})+\int\underbrace{\sum_{j=1}^{N}\frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r'}_{V_{\text{H}}^{(N)}(\mathbf{r})}\varphi_i(\mathbf{r})+\int\underbrace{-\sum_{j=1}^{N}\frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{V_{\text{F}}^{(N)}(\mathbf{r},\mathbf{r}')}\varphi_i(\mathbf{r}')d^3r'=\varepsilon_i\varphi_i(\mathbf{r})$$

$$E(N)=\sum_{i=1}^{N}\varepsilon_i-\frac{1}{2}\sum_{i=1}^{N}\int\varphi_i^*(\mathbf{r})V_{\text{H}}^{(N)}(\mathbf{r})\varphi_i(\mathbf{r})d^3r-\frac{1}{2}\sum_{i=1}^{N}\int\varphi_i^*(\mathbf{r})V_{\text{F}}^{(N)}(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')d^3r\,d^3r'\neq\sum_{i=1}^{N}\varepsilon_i$$

Koopmans' theorem:

$$E(N)=\underbrace{\sum_{\substack{i=1\\i\neq j}}^{N}\varepsilon_i-\frac{1}{2}\sum_{\substack{i=1\\i\neq j}}^{N}\int\varphi_i^*(\mathbf{r})V_{\text{H}}^{(N-1,j)}(\mathbf{r})\varphi_i(\mathbf{r})d^3r-\frac{1}{2}\sum_{\substack{i=1\\i\neq j}}^{N}\int\varphi_i^*(\mathbf{r})V_{\text{F}}^{(N-1,j)}(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')d^3r\,d^3r'}_{E(N-1,j)}+\varepsilon_j$$

Si	ε_{g}
HF	6.3
Expt.	1.17

S. Massidda et al., Phys. Rev. B **48**, 5058 (1993).

Koopmans' theorem allows us to identify the Hartree-Fock eigenvalues with the physical band structure (electron addition and removal energies), but the neglect of correlation grossly overestimates the fundamental band gap.

Density-Functional Theory

$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) + \underbrace{\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \varphi_i(\mathbf{r})}_{V_{\text{H}}^{(N)}(\mathbf{r})} + \underbrace{\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \varphi_i(\mathbf{r})}_{V_{\text{xc}}^{(N)}(\mathbf{r})} = \varepsilon_i \varphi_i(\mathbf{r}) \ , \ \ n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$
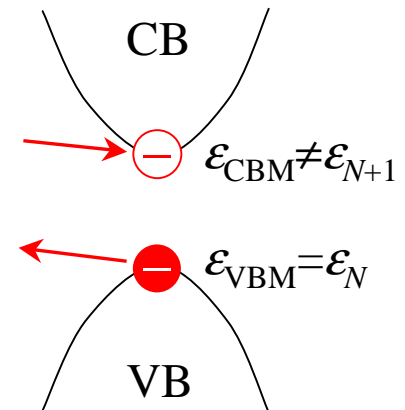
Harris functional: $E(N) = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int V_{\text{H}}^{(N)}(\mathbf{r}) n(\mathbf{r}) d^3 r - \int V_{\text{xc}}^{(N)}(\mathbf{r}) n(\mathbf{r}) d^3 r + E_{\text{xc}}[n]$

CB

$\varepsilon_{\text{CBM}} \neq \varepsilon_{N+1}$

$\varepsilon_{\text{VBM}} = \varepsilon_{N}$
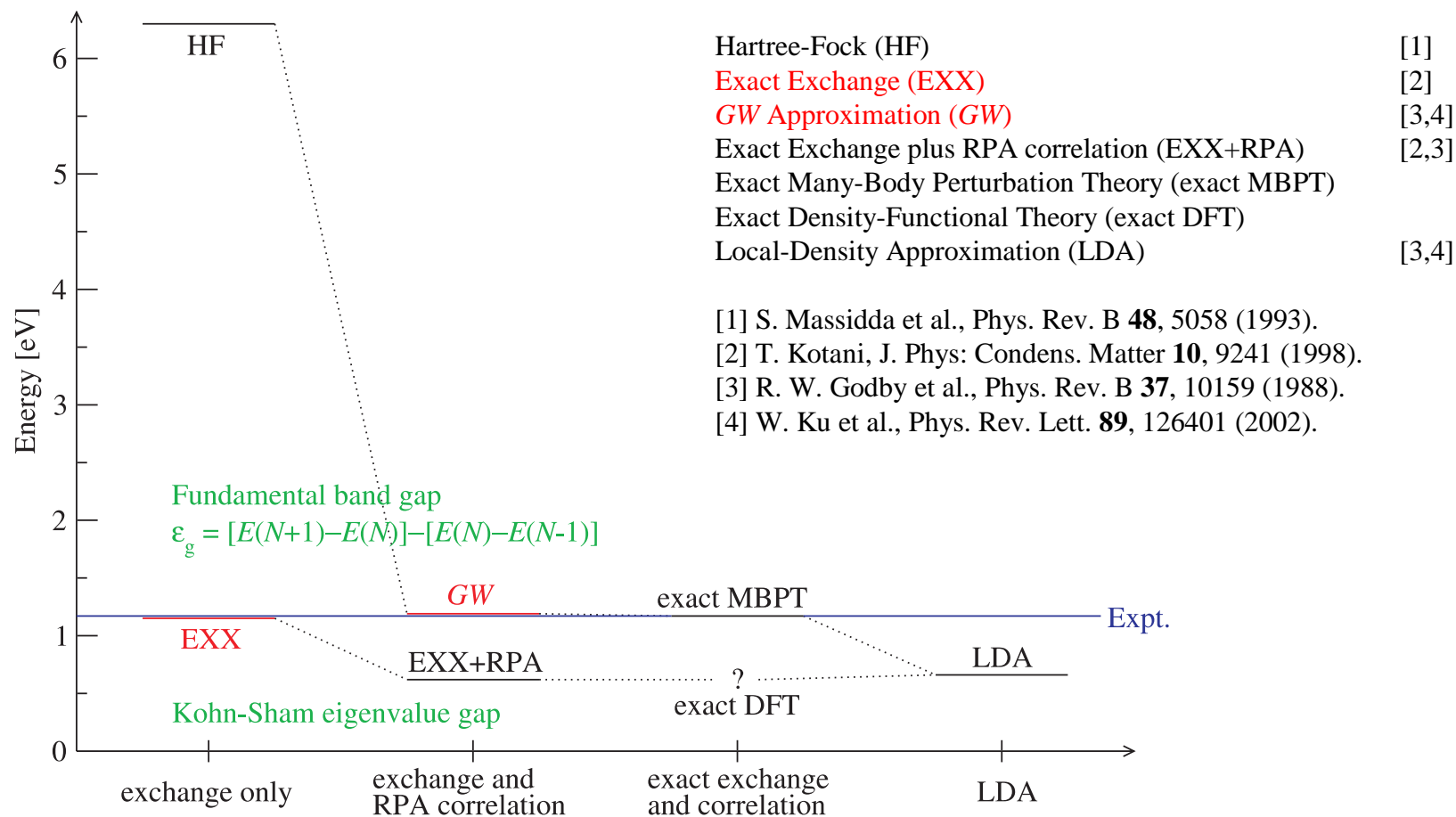
VB

In general:

$\varepsilon_j \neq E(N) - E(N-1, j)$

Janak's theorem:

$\varepsilon_N = \mu = \dfrac{dE(N)}{dN}$

In density-functional theory, there is no simple relationship between total-energy differences and Kohn-Sham eigenvalues. Hence the latter cannot be interpreted as excitation energies (except for the highest occupied state).

Calculated Band Gaps of Silicon
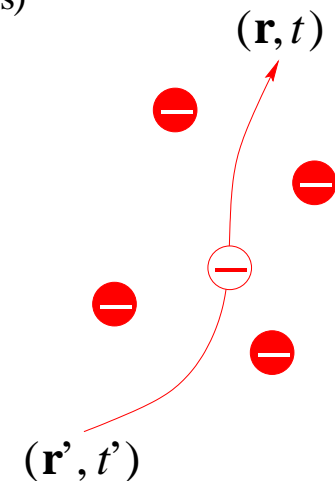
The Green-Function Approach

Noninteracting particles: $\left[i\dfrac{\partial}{\partial t}-h_0(\mathbf{r})\right]G_0(\mathbf{r},\mathbf{r}';t-t')=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$, $h_0(\mathbf{r})=-\dfrac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})$

$$G_0(\mathbf{r},\mathbf{r}';t-t')=\begin{cases}-i\displaystyle\sum_{n\mathbf{k}}^{\text{unocc}}\varphi_{n\mathbf{k}}(\mathbf{r},t)\varphi_{n\mathbf{k}}^*(\mathbf{r}',t')=-i\sum_{n\mathbf{k}}^{\text{unocc}}\varphi_{n\mathbf{k}}(\mathbf{r})\varphi_{n\mathbf{k}}^*(\mathbf{r}')e^{-i\varepsilon_{n\mathbf{k}}(t-t')} & \text{for } t>t' \text{ (electrons)}\\[2mm] i\displaystyle\sum_{n\mathbf{k}}^{\text{occ}}\varphi_{n\mathbf{k}}(\mathbf{r},t)\varphi_{n\mathbf{k}}^*(\mathbf{r}',t')=i\sum_{n\mathbf{k}}^{\text{occ}}\varphi_{n\mathbf{k}}(\mathbf{r})\varphi_{n\mathbf{k}}^*(\mathbf{r}')e^{-i\varepsilon_{n\mathbf{k}}(t-t')} & \text{for } t'>t \text{ (holes)}\end{cases}$$

Fourier analysis:

$$G_0(\mathbf{r},\mathbf{r}';\omega)=\int_{-\infty}^{\infty}G_0(\mathbf{r},\mathbf{r}';\tau)e^{i\omega\tau}d\tau=\lim_{\eta\to0}\sum_{n\mathbf{k}}\frac{\varphi_{n\mathbf{k}}(\mathbf{r})\varphi_{n\mathbf{k}}^*(\mathbf{r}')}{\omega-\varepsilon_{n\mathbf{k}}+\operatorname{sgn}(\varepsilon_{n\mathbf{k}}-\mu)i\eta}$$

$$A(\mathbf{r},\mathbf{r};\omega)=-\frac{\operatorname{sgn}(\varepsilon_{n\mathbf{k}}-\mu)}{\pi}\operatorname{Im}G_0(\mathbf{r},\mathbf{r};\omega)=\sum_{n\mathbf{k}}|\varphi_{n\mathbf{k}}(\mathbf{r})|^2\delta(\omega-\varepsilon_{n\mathbf{k}})$$
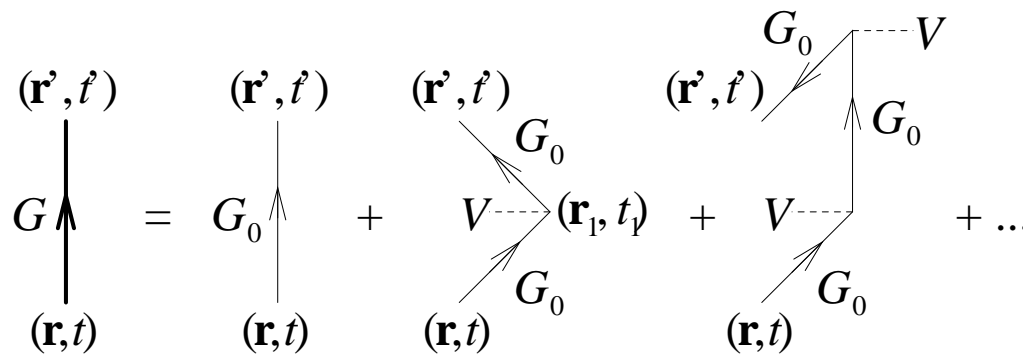
$(\mathbf{r},t)$

$(\mathbf{r}',t')$

The Green function is a propagator that takes the influence of the environment fully into account. The excitation energies correspond to the poles of G or, alternatively, to the peaks of the spectral function A on the frequency axis.

Dyson's Equation

$$\left[i\frac{\partial}{\partial t}-h_0(\mathbf{r})-V(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';t-t')=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \text{ with an additional potential } V(\mathbf{r})$$

Solution: $G(\mathbf{r},\mathbf{r}';t-t')=G_0(\mathbf{r},\mathbf{r}';t-t')+\int G_0(\mathbf{r},\mathbf{r}_1;t-t_1)V(\mathbf{r}_1)G(\mathbf{r}_1,\mathbf{r}';t_1-t')d^3r_1\,dt_1$

Feynman diagrams:

Richard P. Feynman
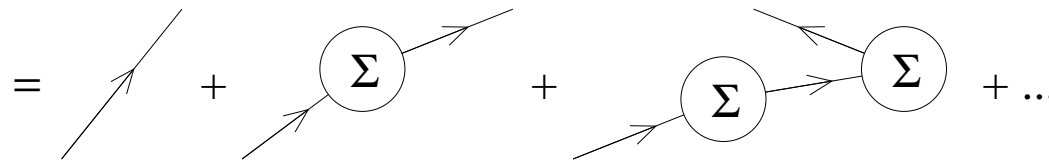Nobel Prize 1965

For practical applications, Dyson's equation
$$G(\omega)=G_0(\omega)+G_0(\omega)VG_0(\omega)+G_0(\omega)VG_0(\omega)VG_0(\omega)+\ldots=G_0(\omega)\sum_{\nu=0}^{\infty}\left[VG_0(\omega)\right]^{\nu}=\frac{G_0(\omega)}{1-VG_0(\omega)}$$
relates the Green function G to the known solution G_0 of a simpler problem.
It has a direct interpretation in terms of propagators and scattering events.

The Self-Energy: Quasiparticles

$$G(\mathbf{r},\mathbf{r}';\omega)=G_0(\mathbf{r},\mathbf{r}';\omega)+\int G_0(\mathbf{r},\mathbf{r}'';\omega)\Sigma(\mathbf{r}'',\mathbf{r}''';\omega)G(\mathbf{r}''',\mathbf{r}';\omega)d^3r''d^3r'''$$
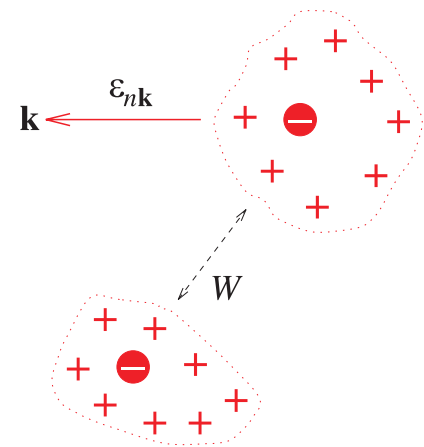

In interacting systems, electron-electron scattering can be rigorously described by the self-energy Σ, which is, in general, complex, nonlocal and energy-dependent.

$$\left[-\tfrac{1}{2}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})\right]\psi_s(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_s)\psi_s(\mathbf{r}')d^3r_1=\varepsilon_s\psi_s(\mathbf{r})$$

$$G(\mathbf{r},\mathbf{r}';\omega)=\lim_{\eta\to 0}\sum_s\frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\omega-\varepsilon_s+\text{sgn}(\varepsilon_s-\mu)i\eta}$$

$$\varepsilon_s=E(N)-E(N-1,s)\ \text{ for }\ \varepsilon_s<\mu\ \checkmark$$

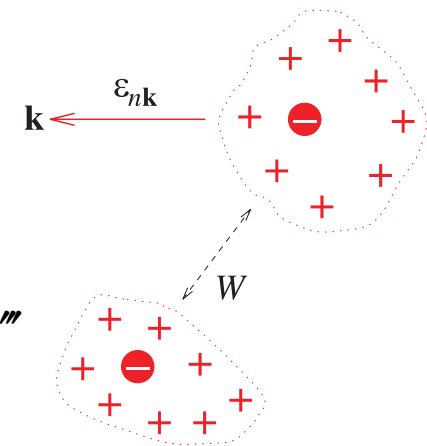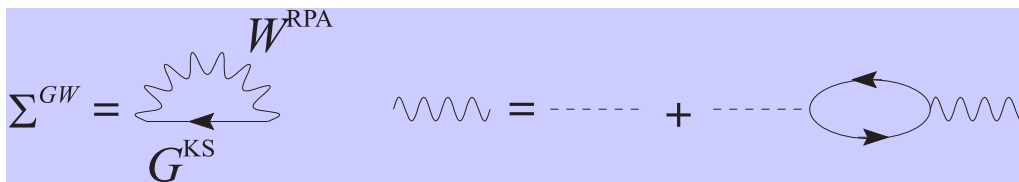$$\varepsilon_s=E(N+1,s)-E(N)\ \text{ for }\ \varepsilon_s>\mu\ \checkmark$$

The *GW* Approximation

GW: $\Sigma^{GW}(\mathbf{r},\mathbf{r}';t-t')=iG(\mathbf{r},\mathbf{r}';t-t')W(\mathbf{r},\mathbf{r}';t^{+}-t')$

HF : $\quad iG(\mathbf{r},\mathbf{r}';t-t')v(\mathbf{r}-\mathbf{r}')\delta(t^{+}-t')=-\sum_{j=1}^{N}\dfrac{\varphi_{j}(\mathbf{r})\varphi_{j}^{*}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}=V_{\mathrm{F}}(\mathbf{r},\mathbf{r}')$

The *GW* approximation for the self-energy is an extended Hartree-Fock method with a screened Coulomb interaction. Besides exact exchange, it describes dynamic screening in a system of itinerant electrons, which is the dominant correlation effect in many solids.

Historically, model screening functions were frequently employed.
Modern calculations use the random-phase approximation (RPA):

$W^{\mathrm{RPA}}(\mathbf{r},\mathbf{r}';\omega)=v(\mathbf{r}-\mathbf{r}')+\int v(\mathbf{r}-\mathbf{r}'')P(\mathbf{r}'',\mathbf{r}''';\omega)W^{\mathrm{RPA}}(\mathbf{r}''',\mathbf{r}';\omega)d^{3}r''d^{3}r'''$

$\quad P(\mathbf{r},\mathbf{r}';t-t')=-2iG(\mathbf{r},\mathbf{r}';t-t')G(\mathbf{r}',\mathbf{r};t'-t)$

Perturbative *GW* Treatment

Quasiparticle equation:

$$\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\varepsilon_{n\mathbf{k}})\,\psi_{n\mathbf{k}}(\mathbf{r}')d^3r_1 = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

$$\underbrace{\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]}_{h_{\text{KS}}(\mathbf{r})}\psi_{n\mathbf{k}}(\mathbf{r}) + \int \underbrace{\left[\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_{n\mathbf{k}}) - V_{\text{xc}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]}_{\Delta\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_{n\mathbf{k}})}\psi_{n\mathbf{k}}(\mathbf{r}')d^3r_1 = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

Kohn-Sham equation:

$$h_{\text{KS}}(\mathbf{r})\varphi^{\text{KS}}_{n\mathbf{k}}(\mathbf{r}) = \varepsilon^{\text{KS}}_{n\mathbf{k}}\varphi^{\text{KS}}_{n\mathbf{k}}(\mathbf{r}) \qquad \Rightarrow$$

First-order perturbation theory:

$$\varepsilon_{n\mathbf{k}} \approx \varepsilon^{\text{KS}}_{n\mathbf{k}} + \int \varphi^{\text{KS}}_{n\mathbf{k}}(\mathbf{r})^* \Delta\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_{n\mathbf{k}})\varphi^{\text{KS}}_{n\mathbf{k}}(\mathbf{r}')d^3r\,d^3r'$$

In practice, the *GW* self-energy correction is usually evaluated non-self-consistently within first-order perturbation theory. The calculated $\varepsilon_{n\mathbf{k}}$ are then actually proper density functionals!

$$\Sigma^{GW} = \overset{W^{\text{RPA}}}{\underset{G^{\text{KS}}}{\longleftarrow}}$$

The *GW* Space-Time Method

$$G_0(\mathbf{r},\mathbf{r}';i\tau) = -i\sum_{n\mathbf{k}}^{\text{occ}}\varphi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})\varphi_{n\mathbf{k}}^{\text{KS}*}(\mathbf{r}')e^{\varepsilon_{n\mathbf{k}}^{\text{KS}}\tau}\Theta(\tau) + i\sum_{n\mathbf{k}}^{\text{unocc}}\varphi_{n\mathbf{k}}^{\text{KS}}(\mathbf{r})\varphi_{n\mathbf{k}}^{\text{KS}*}(\mathbf{r}')e^{\varepsilon_{n\mathbf{k}}^{\text{KS}}\tau}\Theta(-\tau)$$

$$P(\mathbf{r},\mathbf{r}';i\tau) = -2iG_0(\mathbf{r},\mathbf{r}';i\tau)G_0(\mathbf{r}',\mathbf{r};-i\tau)$$

FFT

$$\varepsilon_{\mathbf{GG}'}(\mathbf{k},i\omega) = \delta_{\mathbf{GG}'} - P_{\mathbf{GG}'}(\mathbf{k},i\omega)v_{\mathbf{G}'}(\mathbf{k})$$

Matrix inversion

$$W_{\mathbf{GG}'}(\mathbf{k},i\omega) = v_{\mathbf{G}}(\mathbf{k})\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{k},i\omega)$$

FFT

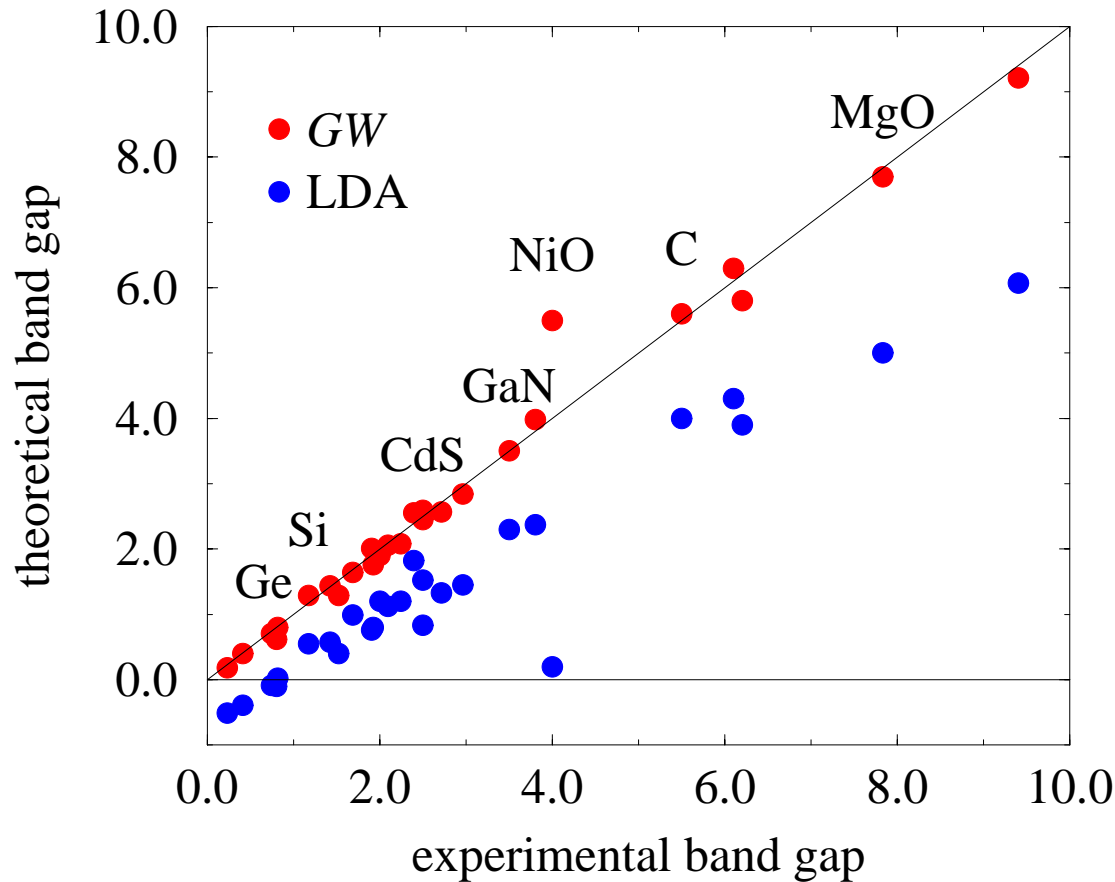$$\Sigma(\mathbf{r},\mathbf{r}';i\tau) = iG_0(\mathbf{r},\mathbf{r}';i\tau)W(\mathbf{r},\mathbf{r}';i\tau)$$

Analytic continuation to real energies

FFT

$$\varepsilon_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}}^{\text{KS}} + \left\langle\varphi_{n\mathbf{k}}^{\text{KS}}\middle|\Sigma(\mathbf{k},\varepsilon_{n\mathbf{k}})-V_{\text{xc}}\middle|\varphi_{n\mathbf{k}}^{\text{KS}}\right\rangle$$

M. M. Rieger, L. Steinbeck, I. D. White, H. N. Rojas and R. W. Godby, Comp. Phys. Commun. **117**, 211 (1999).
L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I. D. White and R. W. Godby, Comp. Phys. Commun. **125**, 105 (2000).

The Band Gap of Semiconductors

✓ The *GW* approximation yields very good excitation spectra for materials with weak or medium correlation including all typical semiconductors.

✗ Strongly correlated materials such as NiO, a Mott-Hubbard insulator, are less accurately described, because the *GW* self-energy misses important contributions.

The Band Width of Metals

Band width of alkali metals

	LDA	GW	Expt.
Li	3.45	2.84	3.0
Na	3.16	2.52	2.65
K	2.27	1.58	1.4

J. E. Northrup et al., Phys. Rev. B **39**, 8198 (1989).
M. P. Surh et al., Phys. Rev. B **38**, 5976 (1988).

Homogeneous electron gas

Exact DFT: $\dfrac{k_F^2}{2}$

Hartree-Fock: $\dfrac{k_F^2}{2} + \dfrac{k_F}{\pi} > \dfrac{k_F^2}{2}$

GW: $\dfrac{k_F^2}{2} + \left[\Sigma(k_F, \varepsilon_{k_F}) - \Sigma(0, \varepsilon_0) \right] < \dfrac{k_F^2}{2}$

✓ The *GW* approximation correctly describes the correlation-induced band narrowing, due to the heavier quasiparticle effective mass compared to the bare electron mass.
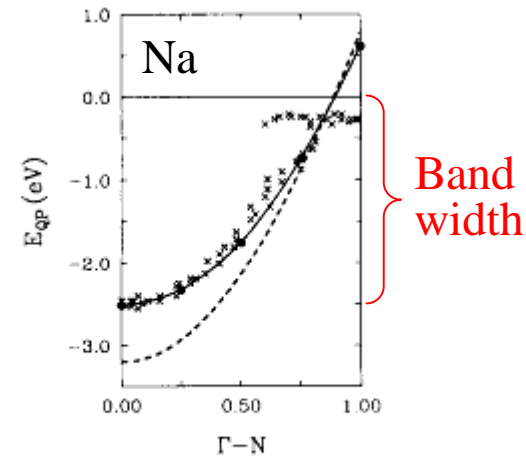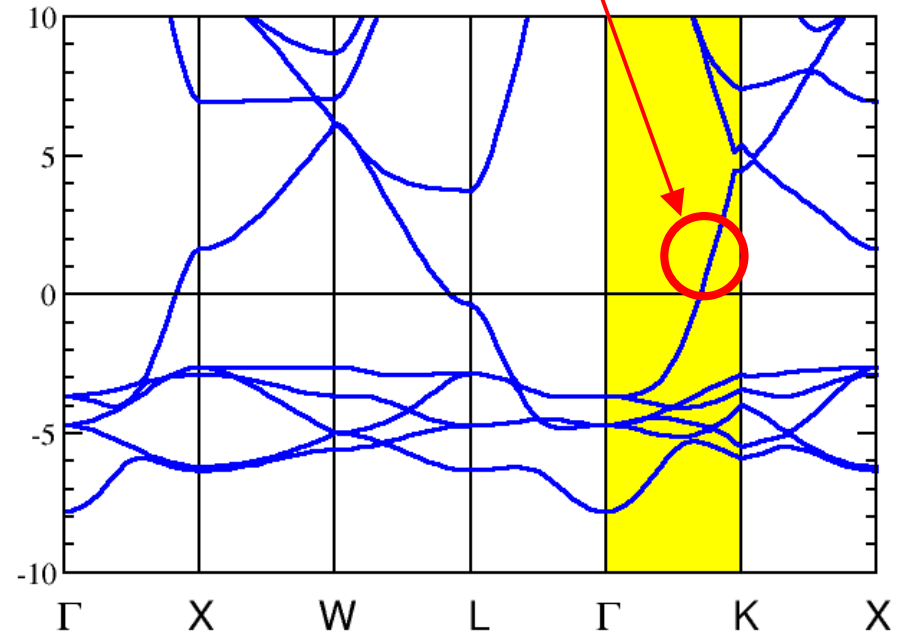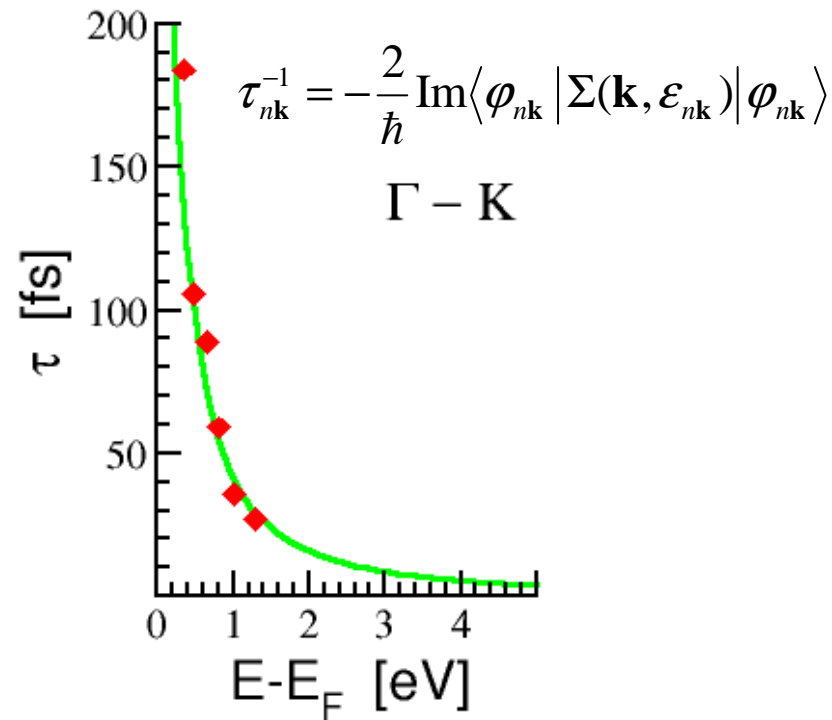

FIG. 1. Quasiparticle energies for Na: Experimental data from Ref. 3 (crosses), LDA eigenvalues (dashed line), and calculated quasiparticle energies (filled circles).

J. E. Northrup et al., Phys. Rev. Lett. **59**, 819 (1987).

Quasiparticle Lifetimes

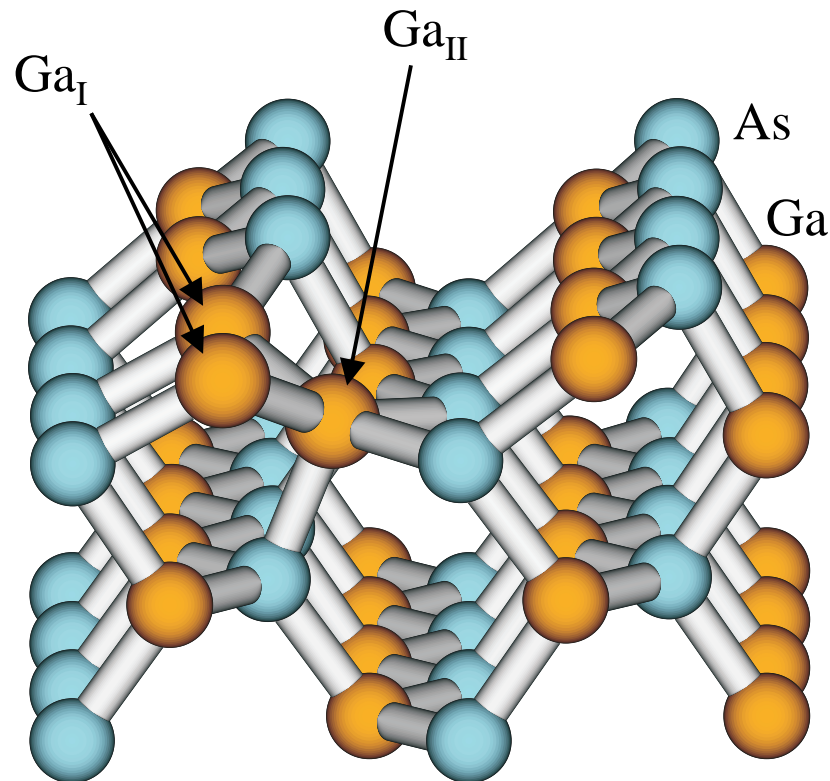Lifetime of excited electrons in the conduction bands of silver

$$\tau_{n\mathbf{k}}^{-1} = -\frac{2}{\hbar} \mathrm{Im}\langle \varphi_{n\mathbf{k}} | \Sigma(\mathbf{k}, \varepsilon_{n\mathbf{k}}) | \varphi_{n\mathbf{k}} \rangle$$

$$\Gamma - K$$

R. Keyling et al., Phys. Rev. B **61**, 1670 (2000).
♦ : Expt. (Time-Resolved Two-Photon Photoemission Spectroscopy)

Defects on Semiconductor Surfaces

As vacancy V_{As} on p-GaAs(110)

Ga$_{II}$

Ga$_{I}$

As

Ga

Equivalent: P vacancy V_P on p-InP(110)

As sublattice

Ga sublattice
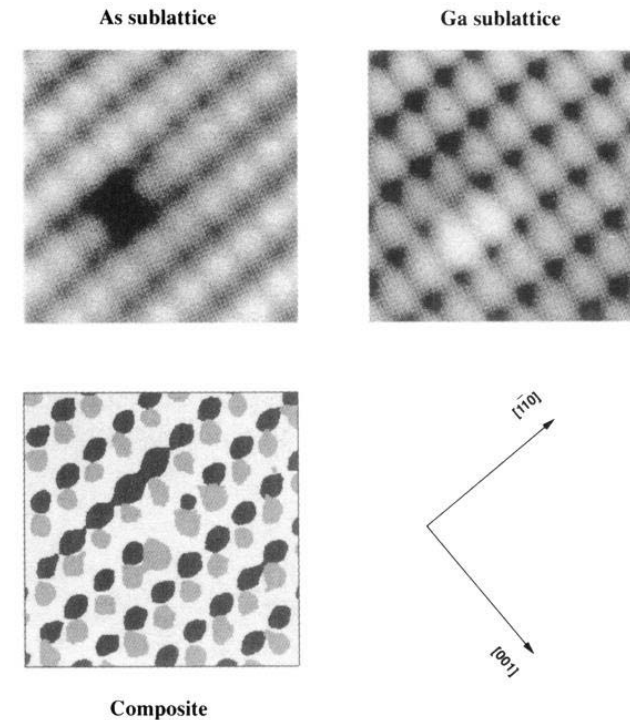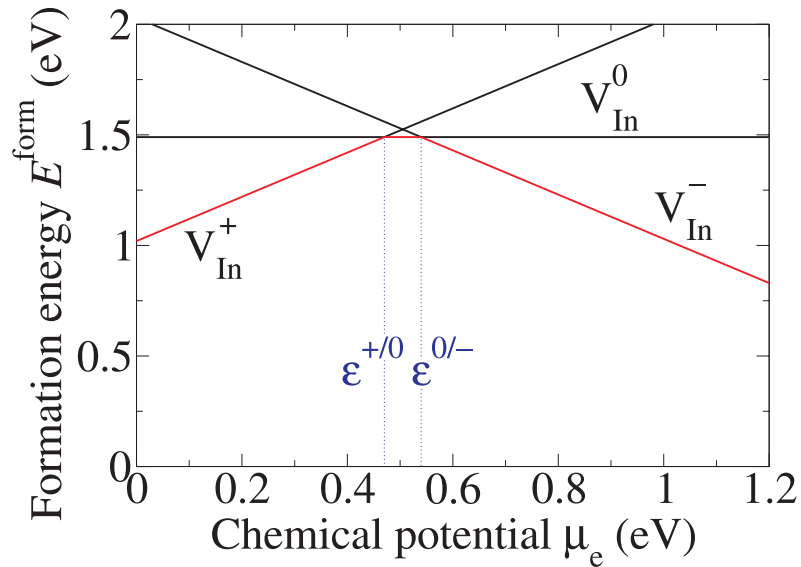
[$\bar{1}$10]

[001]

Composite

FIG. 1. Simultaneously acquired filled- and empty-state images of the missing As defect on degenerate p-GaAs(110). Defect composite shows the registry of the As (black) and Ga (gray) sublattices.

G. Lengel *et al.*, Phys. Rev. Lett. **72**, 836 (1994).

Charge Transition Levels

Defect formation energy:

$$E^{\text{form}}(q, \mu_e) = E_q^{\text{v}}(q) + \mu_{\text{In}} + q(\varepsilon_{\text{VBM}} + \mu_e) - E^{\text{slab}}$$

geometry   charge state

$$E^{\text{form}}(q, \varepsilon^{q/q'}) = E^{\text{form}}(q', \varepsilon^{q/q'})$$

InP(110)	$\varepsilon^{+/0}$ (eV)	$\varepsilon^{0/-}$ (eV)
LDA	0.47	0.54
Expt.	0.75±0.1	—

Experiment (STM and Photoelectron Spectroscopy):
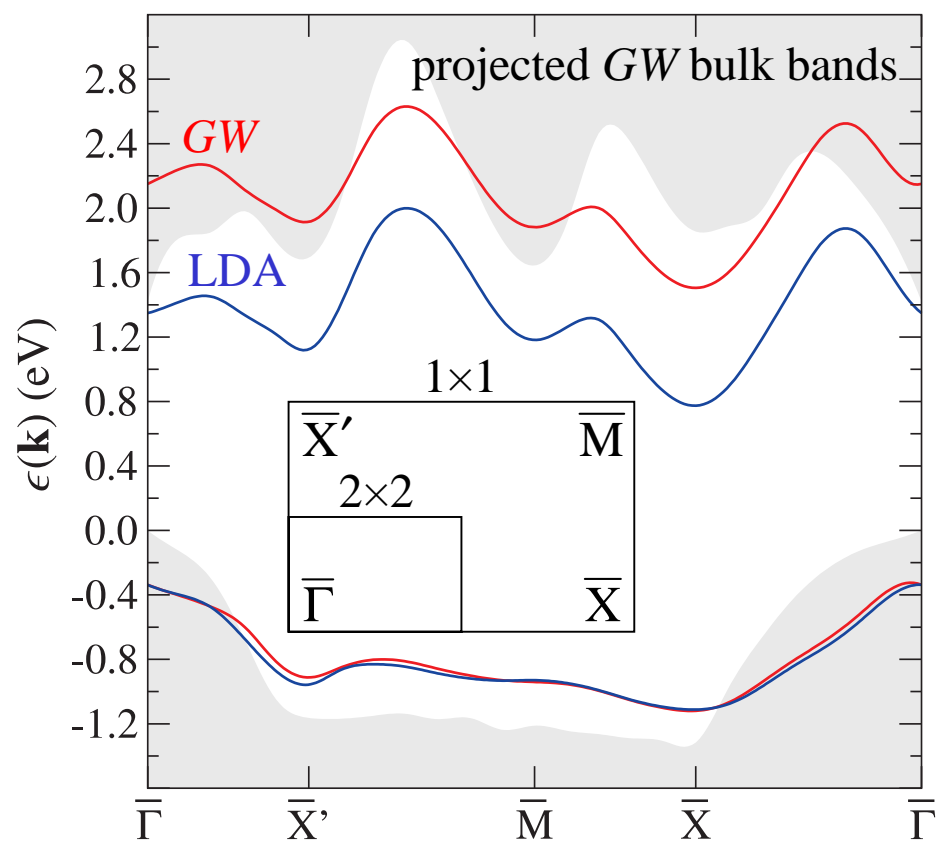Ph. Ebert *et al.*, Phys. Rev. Lett. **84**, 5816 (2000).

Separation of different energy contributions:

$$\varepsilon^{+/0} = \underbrace{E_0^{\text{v}}(+) - E_+^{\text{v}}(+)}_{\text{relaxation energy}} + \underbrace{E_0^{\text{v}}(0) - E_0^{\text{v}}(+) - \varepsilon_{\text{VBM}}}_{\text{electron affinity}}$$
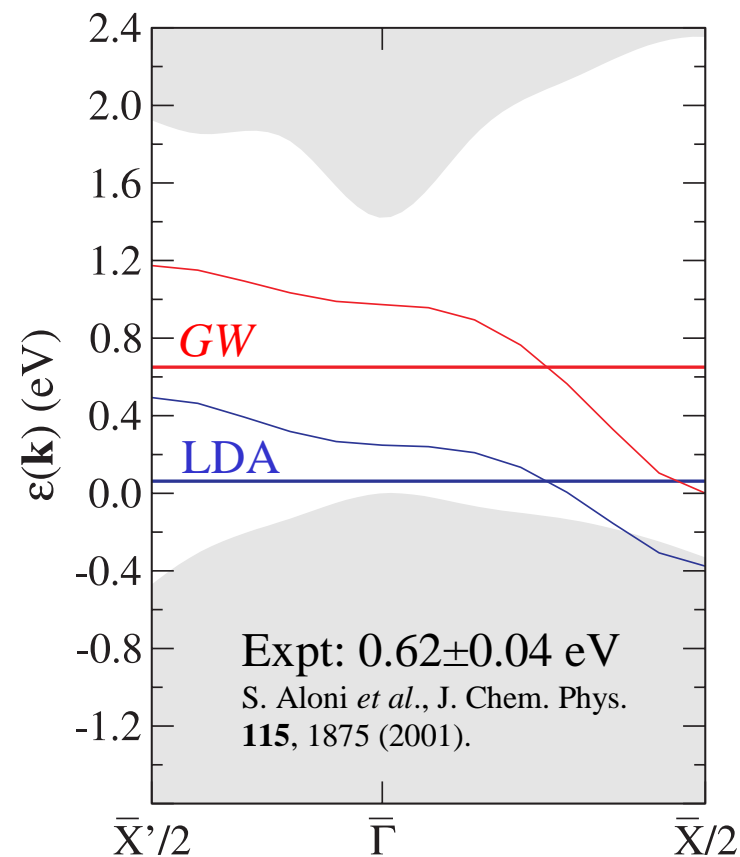
$$\varepsilon^{0/-} = \underbrace{E_-^{\text{v}}(-) - E_0^{\text{v}}(-)}_{\text{relaxation energy}} + \underbrace{E_0^{\text{v}}(-) - E_0^{\text{v}}(0) - \varepsilon_{\text{VBM}}}_{\text{ionization potential}}$$
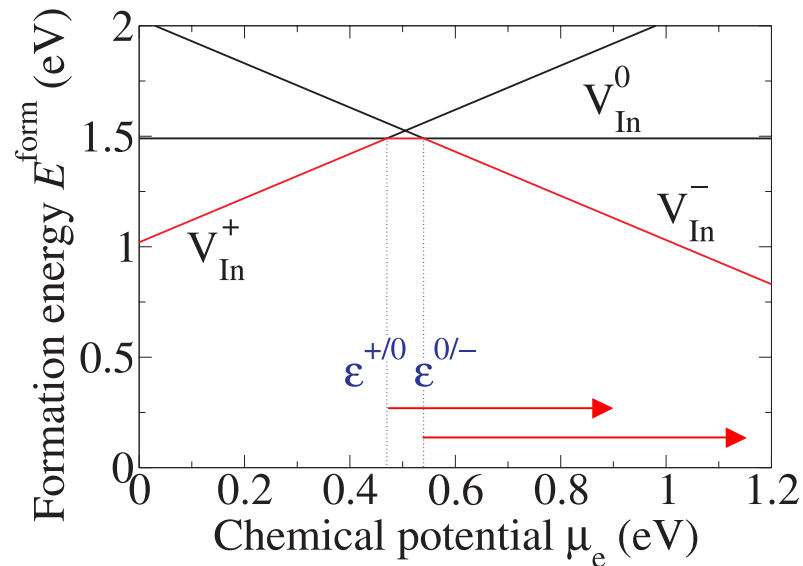
GaAs(110) Surface Band Structure

Improved Charge Transition Levels

InP(110)	$\varepsilon^{+/0}$ (eV)	$\varepsilon^{0/-}$ (eV)
LDA	0.47	0.54
GW	0.90	1.16
Expt.	0.75±0.1	—

GaAs(110)	$\varepsilon^{+/0}$ (eV)	$\varepsilon^{0/-}$ (eV)
LDA	0.07	0.14
GW	0.54	0.64

$$\varepsilon^{+/0} = \underbrace{E_0^{\mathrm{v}}(+) - E_+^{\mathrm{v}}(+)}_{\text{relaxation energy}} + \underbrace{E_0^{\mathrm{v}}(0) - E_0^{\mathrm{v}}(+) - \varepsilon_{\mathrm{VBM}}}_{\text{electron affinity}}$$

$$\varepsilon^{0/-} = \underbrace{E_-^{\mathrm{v}}(-) - E_0^{\mathrm{v}}(-)}_{\text{relaxation energy}} + \underbrace{E_0^{\mathrm{v}}(-) - E_0^{\mathrm{v}}(0) - \varepsilon_{\mathrm{VBM}}}_{\text{ionization potential}}$$

Conclusions

- Unlike the Kohn-Sham eigenvalues, the Green-function approach properly describes electron removal and addition energies as measured in photoemission spectroscopy.

- The *GW* approximation for the self-energy combines exact exchange with the dominant correlation contributions (RPA) for materials with delocalised electrons.

- It correctly describes the band gap of semiconductors, the band width of metals and the finite lifetime of quasiparticle excitations.

- The *GW* approximation is usually applied perturbatively in combination with a standard density-functional calculation.

Literature:
1. F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).
2. W. G. Aulbur, L. Jönsson and J. W. Wilkins, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, San Diego, 2000), Vol. 54, p. 1.