

Quasiparticle band structures and the *GW* approximation

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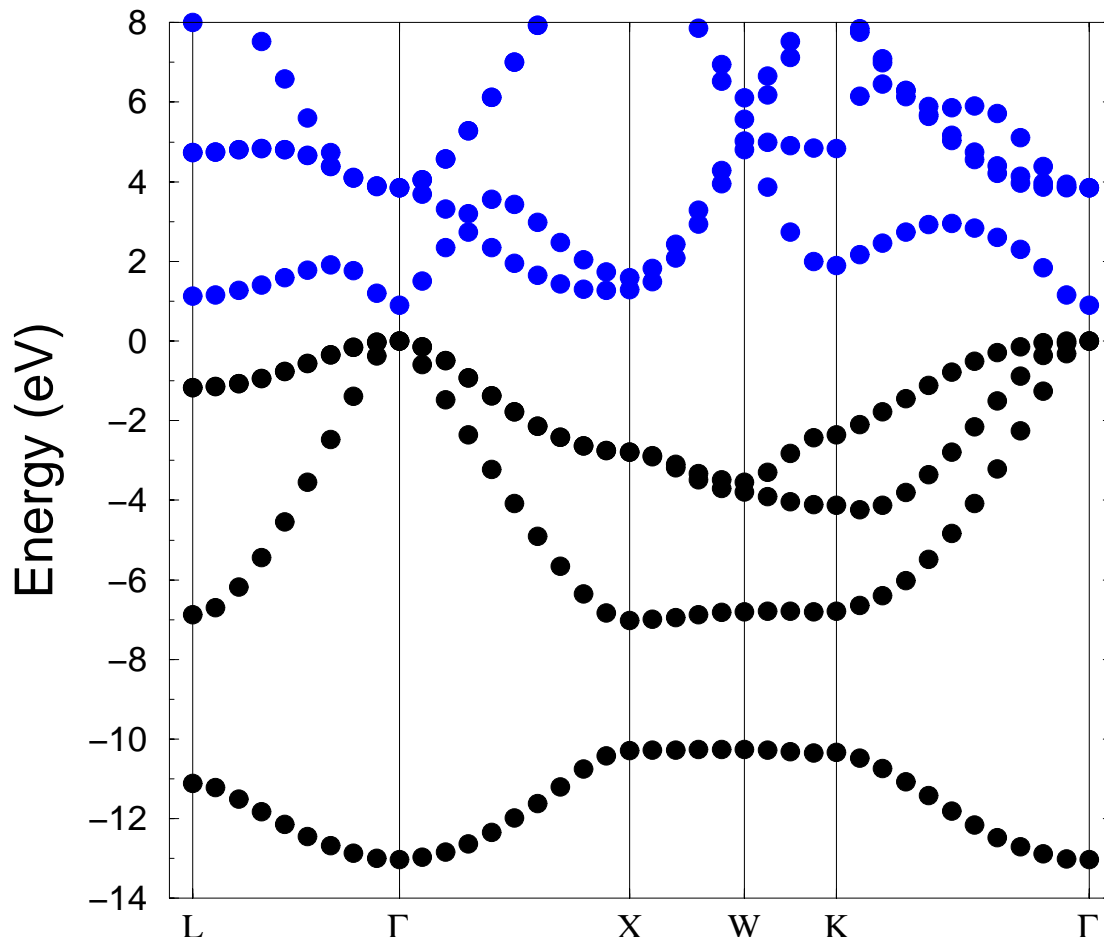
L12



Workshop on Application of Density–Functional Theory in Condensed Matter Physics,
Surface Physics, Chemistry, Engineering and Biology, Berlin, 23 July – 1 August 2001

Electronic structure in Kohn–Sham theory

GaAs band structure

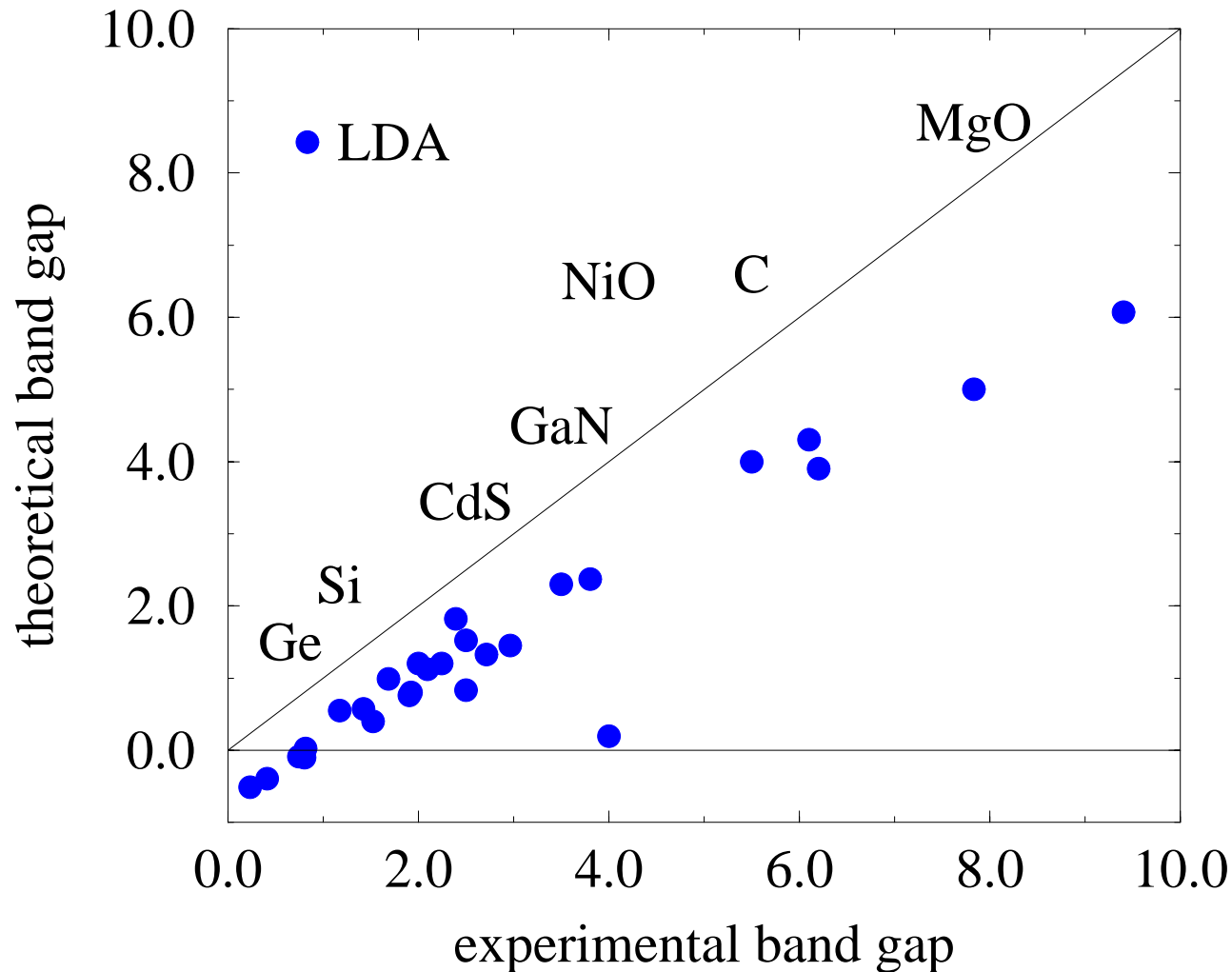


Direct band gap at Γ in LDA

nonrelativistic	1.1 eV
scalar-relativistic	0.6 eV
fully relativistic (SO)	0.5 eV
core relaxation (AE)	0.2 eV
experimental	1.5 eV

The band gap is also very sensitive to small variations in the lattice constant (up to 0.5 eV for a 2% error in a).

The band-gap problem



The LDA systematically underestimates the band gap of semiconductors and insulators.

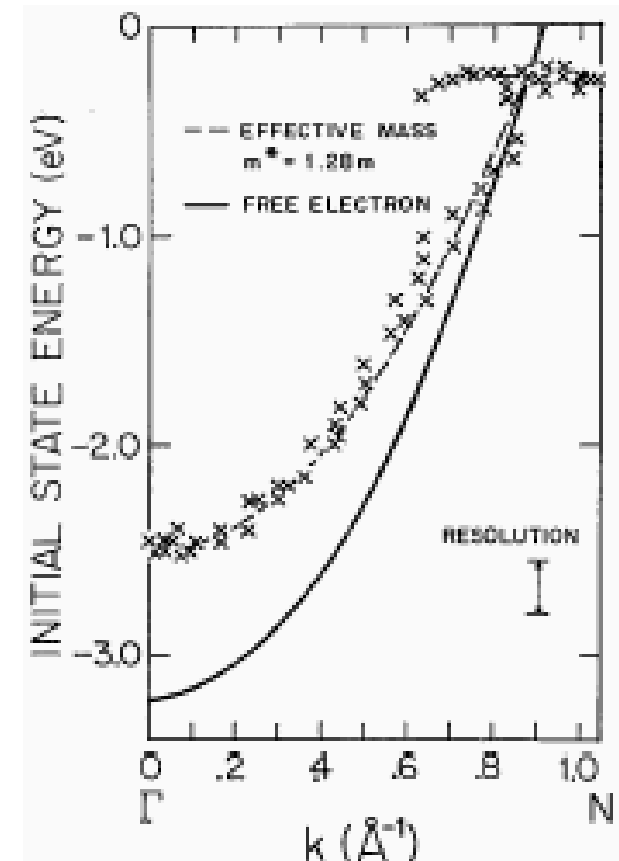
Note that in some cases, like Ge, LDA even fails qualitatively ($E_g < 0$).

The band width of metals

Free electron gas: $\epsilon_k = \frac{1}{2}k^2$, band width = $\frac{1}{2}k_F^2$

The LDA systematically overestimates the occupied band width, which is reduced by correlation compared to the electron gas.

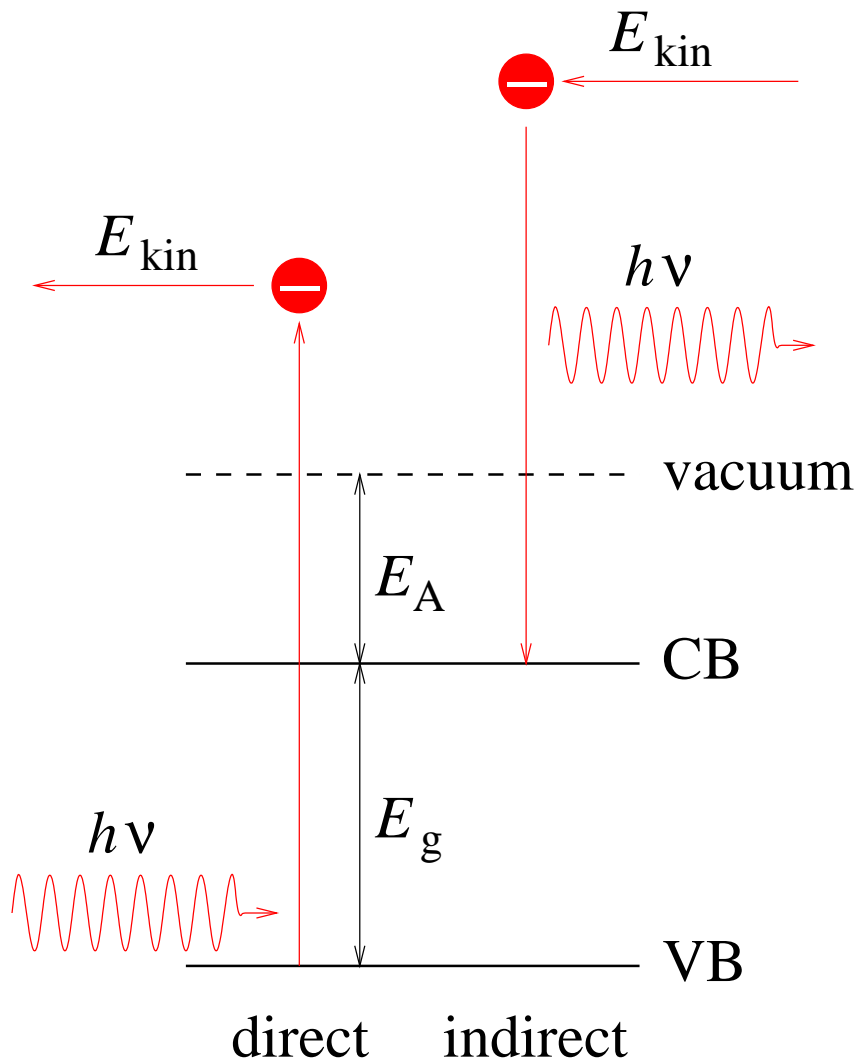
Band width	LDA	Expt.
Li	3.5 eV	3.0 eV
Na	3.2 eV	2.6 eV
K	2.3 eV	1.4 eV



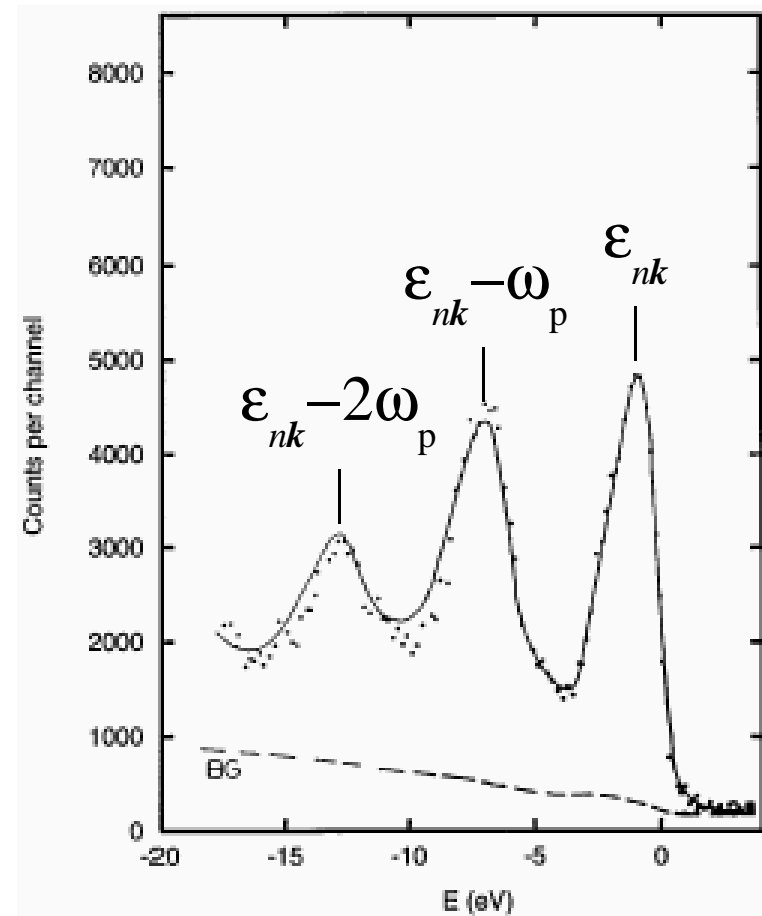
Band structure of Na

J. E. Northrup, M. S. Hybertsen and S. G. Louie,
Phys. Rev. Lett. **59**, 819 (1987)

Experimental determination of the band structure



Direct photoemission spectrum of Na



Definition of the band structure

The electronic band structure corresponds to the total-energy difference between two systems with different particle numbers.

$$\varepsilon_{n\mathbf{k}} = E(N) - E^*(N-1) \quad \text{for occupied states}$$

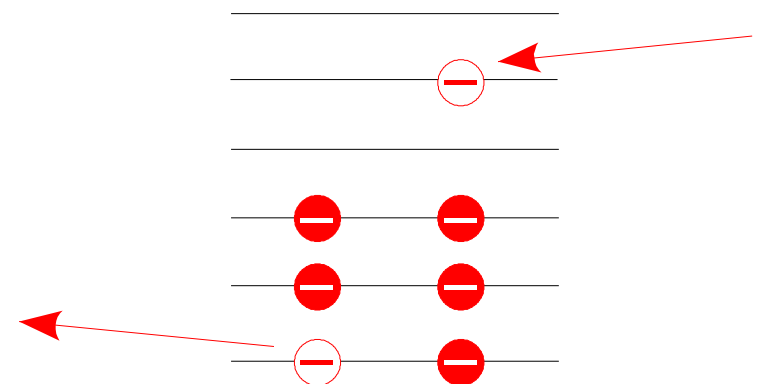
$$\varepsilon_{n\mathbf{k}} = E^*(N+1) - E(N) \quad \text{for unoccupied states}$$

In order to obtain reliable numerical results, we must find a way to calculate the band structure directly, because $\varepsilon_{n\mathbf{k}} \ll E(N)$.

Example: noninteracting systems

$$E(N) = \sum_i \int \varphi_i^*(\mathbf{r}) [-1/2 \nabla^2 + V_{\text{ext}}(\mathbf{r})] \varphi_i(\mathbf{r}) d^3 r = \sum_i \varepsilon_i$$

$$-1/2 \nabla^2 \varphi_i(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$



Koopmans' theorem (Hartree–Fock)

$$E(N) = \sum_i \int \varphi_i^*(\mathbf{r}) [-1/2 \nabla^2 + V_{\text{ext}}(\mathbf{r})] \varphi_i(\mathbf{r}) d^3 r + E_{\text{H}}(N) + E_{\text{F}}(N) \neq \sum_i \varepsilon_i$$

$$E_{\text{H}}(N) = 1/2 \sum_i \int \varphi_i^*(\mathbf{r}) V_{\text{H}}(\mathbf{r}) \varphi_i(\mathbf{r}) d^3 r$$

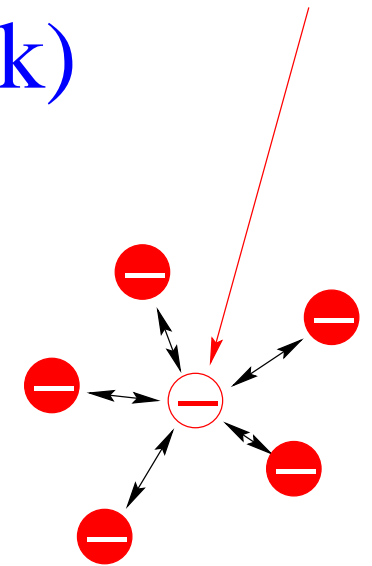
$$E_{\text{F}}(N) = 1/2 \sum_i \int \varphi_i^*(\mathbf{r}) V_{\text{F}}(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}') d^3 r d^3 r'$$

$$[-1/2 \nabla^2 + V_{\text{ext}}(\mathbf{r})] \varphi_i(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \varphi_i(\mathbf{r}) + \int V_{\text{F}}(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}') d^3 r' = \varepsilon_i \varphi_i(\mathbf{r})$$

$$V_{\text{H}}(\mathbf{r}) = \sum_j \int \varphi_j^*(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \varphi_j(\mathbf{r}') d^3 r'$$

$$V_{\text{F}}(\mathbf{r}, \mathbf{r}') = \sum_j \varphi_j^*(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \varphi_j(\mathbf{r})$$

$$E(N+1, i^*) - E(N) \approx \varepsilon_{i^*}$$



GaAs	E_g
HF	9.1 eV
Expt.	1.5 eV

Koopmans' theorem allows us to identify the Hartree–Fock eigenvalues with the electronic band structure, but the neglect of correlation grossly overestimates the fundamental band gap.

The Kohn–Sham scheme

$$E(N) = \sum_i \int \varphi_i^*(\mathbf{r}) [-1/2 \nabla^2] \varphi_i(\mathbf{r}) d^3 r + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d^3 r + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

$$E_{\text{H}}[n] = 1/2 \int n(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') n(\mathbf{r}) d^3 r d^3 r'$$

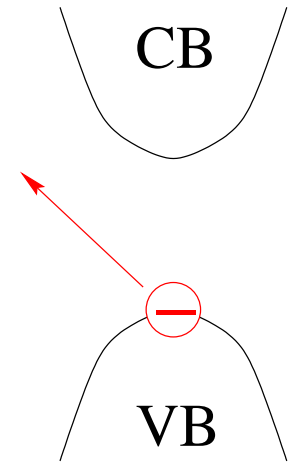
$$E_{\text{xc}}[n] = \int e_{\text{xc}}(\mathbf{r}) n(\mathbf{r}) d^3 r$$

$$[-1/2 \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$V_{\text{H}}(\mathbf{r}) = \delta E_{\text{H}}[n] / \delta n(\mathbf{r}) = \int n(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') d^3 r'$$

$$V_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n] / \delta n(\mathbf{r}) = e_{\text{xc}}(\mathbf{r}) + \int \delta e_{\text{xc}}(\mathbf{r}') / \delta n(\mathbf{r}) n(\mathbf{r}') d^3 r'$$

$$E(N+1, i^*) - E(N) \neq \varepsilon_{i^*} \text{ in general, but } E(N) - E(N-1) \equiv \mu(N) = \varepsilon_N$$



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

Origin of the band-gap problem

$$E_g = [E(N+1) - E(N)] - [E(N) - E(N-1)] \equiv \mu(N+1) - \mu(N) = \varepsilon_{N+1}(N+1) - \varepsilon_N(N)$$

But in Kohn–Sham theory we take $E_g^{\text{KS}} = \varepsilon_{N+1}(N) - \varepsilon_N(N)$

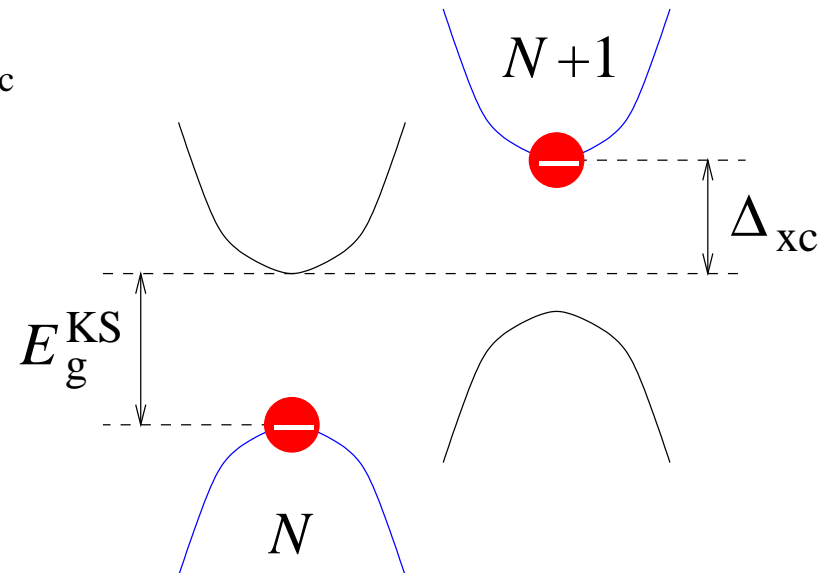
Discontinuity of the exchange–correlation potential:

$$V_{\text{xc}}(N, \mathbf{r}) = \delta E_{\text{xc}}[n] / \delta n(\mathbf{r}) \Big|_N$$

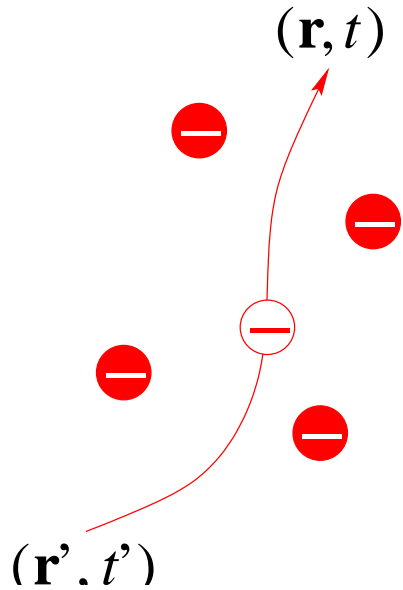
$$V_{\text{xc}}(N+1, \mathbf{r}) = \delta E_{\text{xc}}[n] / \delta n(\mathbf{r}) \Big|_{N+1} = V_{\text{xc}}(N, \mathbf{r}) + \Delta_{\text{xc}}$$

$$\Rightarrow \varepsilon_{N+1}(N+1) = \varepsilon_{N+1}(N) + \Delta_{\text{xc}}$$

$$E_g = E_g^{\text{KS}} + \Delta_{\text{xc}} \approx E_g^{\text{LDA}} + \Delta_{\text{xc}}$$



Green function theory



$$G(\mathbf{r}t, \mathbf{r}'t') = -i \langle \Psi_N | \psi(\mathbf{r}t) \psi^\dagger(\mathbf{r}'t') | \Psi_N \rangle \text{ if } t > t' \text{ (electron)}$$

$$+i \langle \Psi_N | \psi^\dagger(\mathbf{r}'t') \psi(\mathbf{r}t) | \Psi_N \rangle \text{ if } t < t' \text{ (hole)}$$

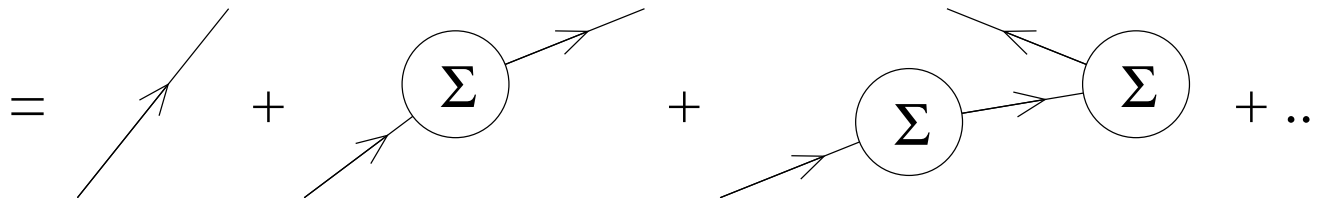
Noninteracting system:

$$G_0(\mathbf{r}t, \mathbf{r}'t') = -i \sum_{n\mathbf{k}, \text{unocc}} \varphi_{n\mathbf{k}}(\mathbf{r}) \varphi_{n\mathbf{k}}^*(\mathbf{r}') \exp\{-i\varepsilon_{n\mathbf{k}}(t-t')\} \text{ if } t > t'$$

$$+i \sum_{n\mathbf{k}, \text{occ}} \varphi_{n\mathbf{k}}(\mathbf{r}) \varphi_{n\mathbf{k}}^*(\mathbf{r}') \exp\{-i\varepsilon_{n\mathbf{k}}(t-t')\} \text{ if } t < t'$$

Interacting system:

$$G(\mathbf{r}t, \mathbf{r}'t') = G_0(\mathbf{r}t, \mathbf{r}'t') + \int G_0(\mathbf{r}t, \mathbf{r}_1 t_1) \Sigma(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) G_0(\mathbf{r}_2 t_2, \mathbf{r}'t') d^3 r_1 dt_1 d^3 r_2 dt_2 + \dots$$



The GW approximation

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

$$iG(\mathbf{r}t, \mathbf{r}'t')v(\mathbf{r}-\mathbf{r}')\delta(t^+-t') = \sum_{n\mathbf{k}, \text{occ}} \psi_{n\mathbf{k}}^*(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}) = V_{\text{F}}(\mathbf{r}, \mathbf{r}')$$

The GW approximation is an extended Hartree–Fock approximation with dynamically screened exchange. Physically, it describes the coupling of quasiparticles to single plasmons, which is appropriate for most solids.

$$\Sigma = \text{Diagram: } \begin{array}{c} \text{Wavy line } W \\ \text{Fermion line } G \end{array}$$

For consistency with the level of the GW approximation for the self–energy, W is constructed in the so–called random–phase or time–dependent Hartree approximation.

$$\epsilon(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r}-\mathbf{r}') - \int P(\mathbf{r}t, \mathbf{r}_1t')v(\mathbf{r}_1-\mathbf{r}')d^3r_1$$

Quasiparticles

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

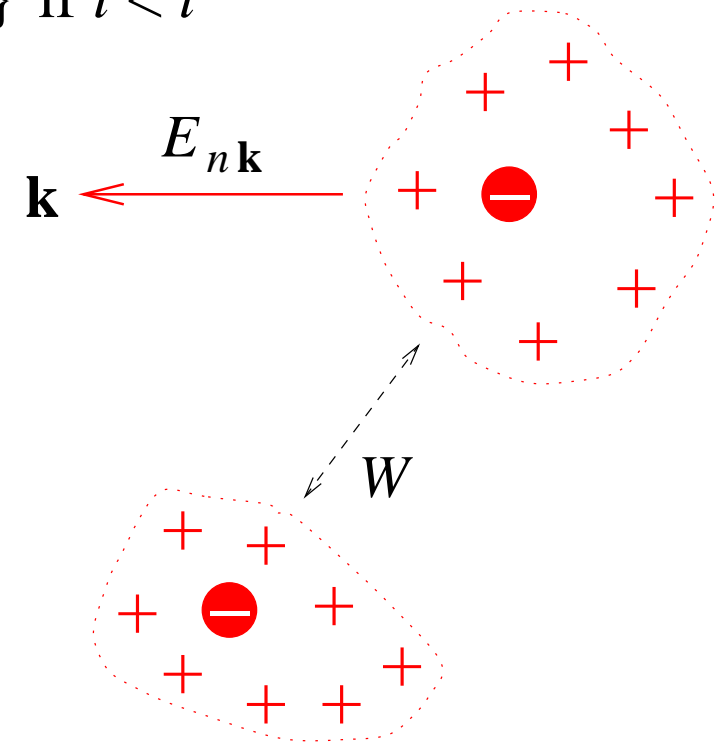
$$G(\mathbf{r}t, \mathbf{r}'t') = -i \sum_{n\mathbf{k}, \text{occ}} \psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}^*(\mathbf{r}')\exp\{-iE_{n\mathbf{k}}(t-t')\} \quad \text{if } t > t'$$

$$+i \sum_{n\mathbf{k}, \text{unocc}} \psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}^*(\mathbf{r}')\exp\{-iE_{n\mathbf{k}}(t-t')\} \quad \text{if } t < t'$$

Quasiparticles are approximate eigenstates of the many-body Hamiltonian with a long but finite lifetime. Like particles, they have a well-defined energy and momentum.

Dynamically screened Coulomb interaction:

$$W(\mathbf{r}t, \mathbf{r}'t') = \int v(\mathbf{r}-\mathbf{r}_1)\epsilon^{-1}(\mathbf{r}_1t, \mathbf{r}'t')d^3r_1$$



What quantities can be calculated from Σ ?

Spectral function:

$$A(\mathbf{k}, \omega) = \pi^{-1} \text{Im}|G(\mathbf{k}, \omega)|$$

Quasiparticle band structure:

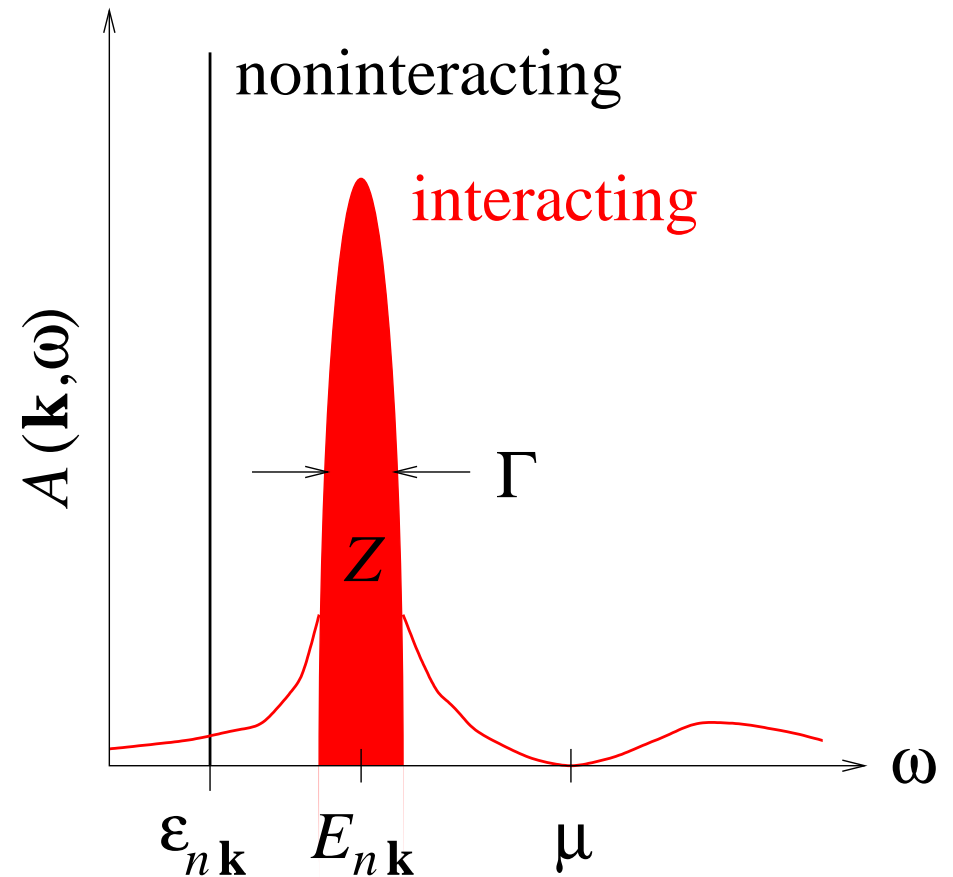
$$E_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} + \text{Re}\langle \Sigma(\mathbf{k}, E_{n\mathbf{k}}) \rangle$$

Spectral weight:

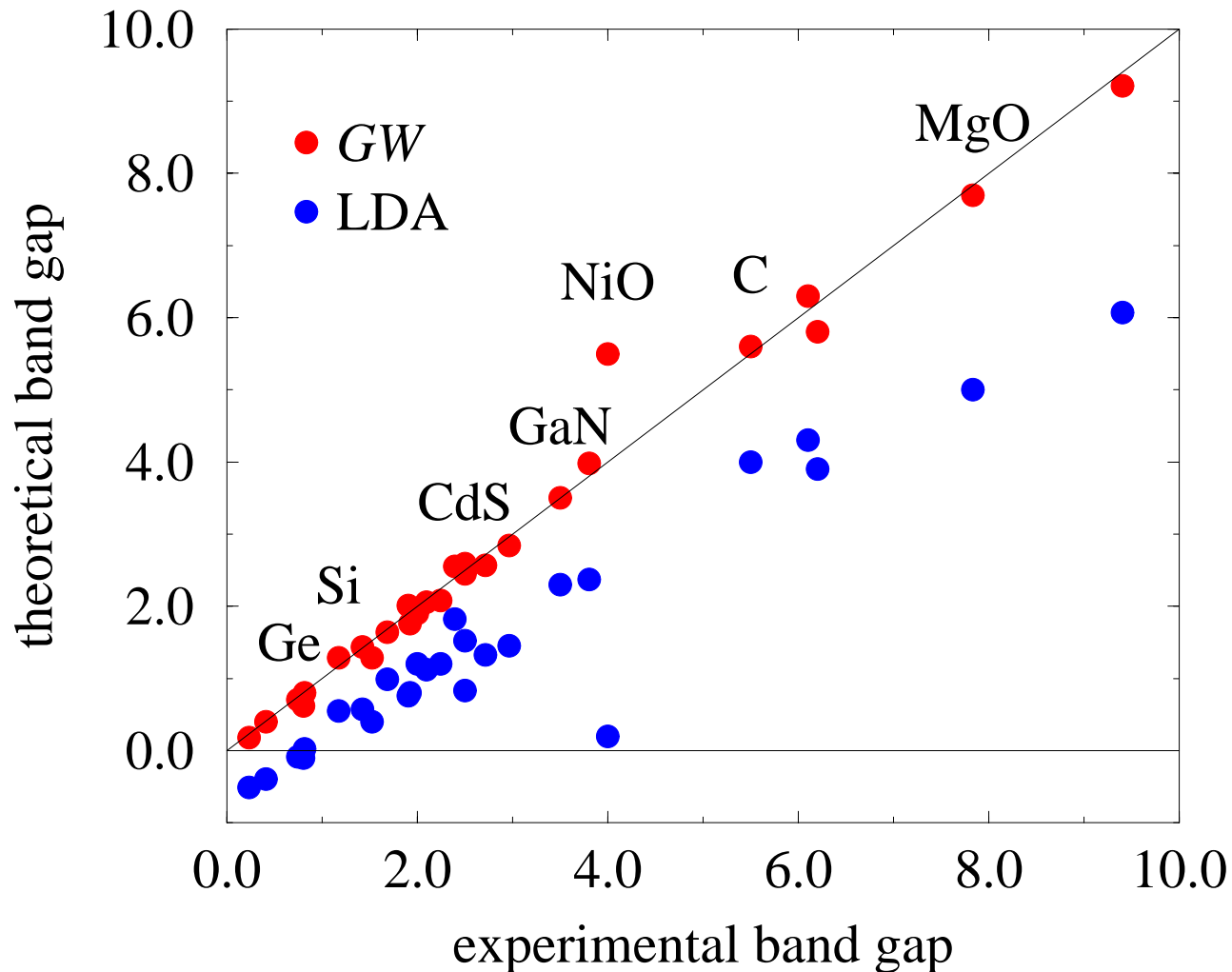
$$Z_{n\mathbf{k}} = [1 - \partial \text{Re}\langle \Sigma(\mathbf{k}, \omega) \rangle / \partial \omega]^{-1} \Big|_{\omega = E_{n\mathbf{k}}}$$

Quasiparticle lifetime:

$$1/\tau_{n\mathbf{k}} \propto \Gamma_{n\mathbf{k}} = \text{Im}\langle \Sigma(\mathbf{k}, E_{n\mathbf{k}}) \rangle$$



Performance of the *GW* approximation



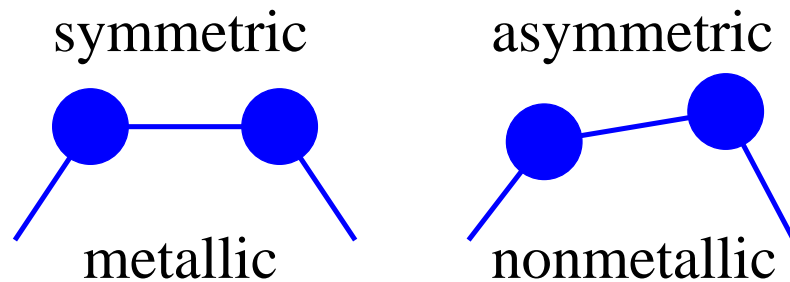
Band width of alkali metals

	LDA	<i>GW</i>	Expt.
Li	3.5	2.9	3.0 eV
Na	3.2	2.5	2.7 eV
K	2.3	1.6	1.4 eV

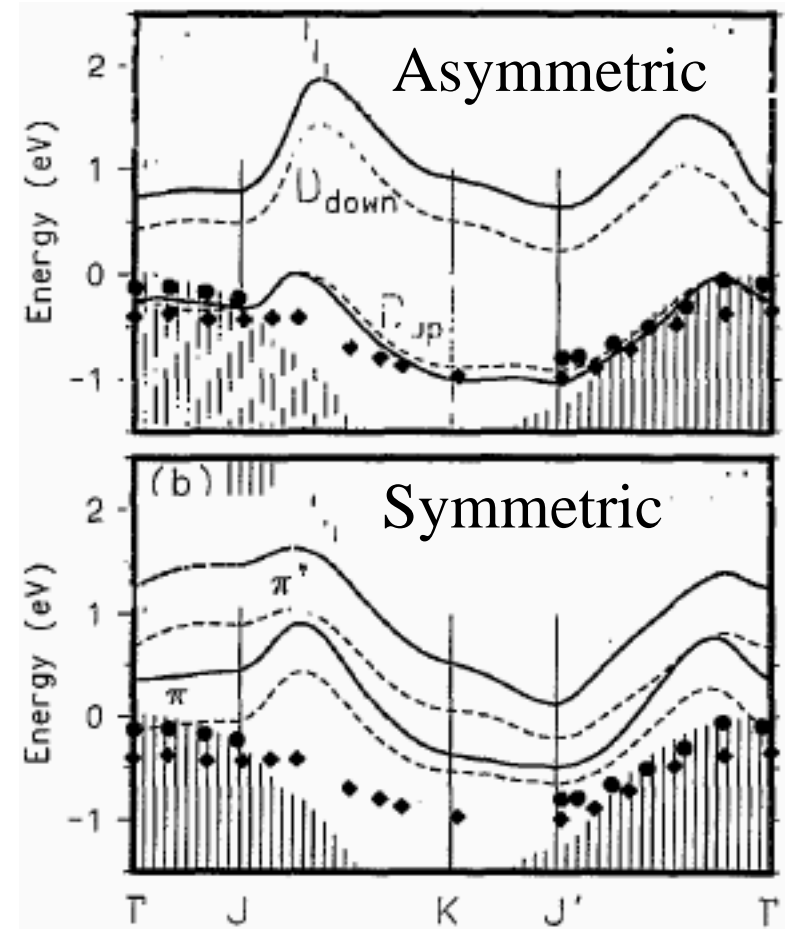
The *GW* approximation resolves the band-gap problem of LDA and also yields good band widths.

Crystal geometry and electronic structure

The very small energy difference between the Si(100) surface with symmetric and asymmetric dimers makes it difficult to determine the correct geometry. However, the electronic structure differs qualitatively.



As experiments show a nonmetallic surface, *GW* band-structure calculations strongly suggest asymmetric dimers.



Practical GW calculations

Quasiparticle equations

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

Kohn–Sham equations

$$[-1/2\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})]\varphi_{n\mathbf{k}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\varphi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{r})$$

First–order approximation with $\psi_{n\mathbf{k}}(\mathbf{r}) \approx \varphi_{n\mathbf{k}}(\mathbf{r})$

$$E_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} + \int \varphi_{n\mathbf{k}}^*(\mathbf{r})[\Sigma(\mathbf{r}, \mathbf{r}'; E_{n\mathbf{k}}) - V_{\text{xc}}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')] \varphi_{n\mathbf{k}}(\mathbf{r}')d^3r d^3r'$$

The self–energy is calculated without self–consistency

$$\Sigma(\mathbf{r}t, \mathbf{r}'t') = iG_0(\mathbf{r}t, \mathbf{r}'t')W(\mathbf{r}t^+, \mathbf{r}'t')$$

Besides, plasmon–pole models are frequently employed for W .

The GW space–time method

$$G_0(\mathbf{r}, \mathbf{r}'; i\tau) = -i \sum_{n\mathbf{k}, \text{occ}} \varphi_{n\mathbf{k}}(\mathbf{r}) \varphi_{n\mathbf{k}}^*(\mathbf{r}') \exp\{\varepsilon_{n\mathbf{k}} \tau\} \quad \text{if } \tau > 0$$

$$+ i \sum_{n\mathbf{k}, \text{unocc}} \varphi_{n\mathbf{k}}(\mathbf{r}) \varphi_{n\mathbf{k}}^*(\mathbf{r}') \exp\{\varepsilon_{n\mathbf{k}} \tau\} \quad \text{if } \tau < 0$$

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

FFT

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

FFT

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

$$\Sigma(\mathbf{r}, \mathbf{r}'; i\tau) = i G_0(\mathbf{r}, \mathbf{r}'; i\tau) W(\mathbf{r}, \mathbf{r}'; i\tau)$$

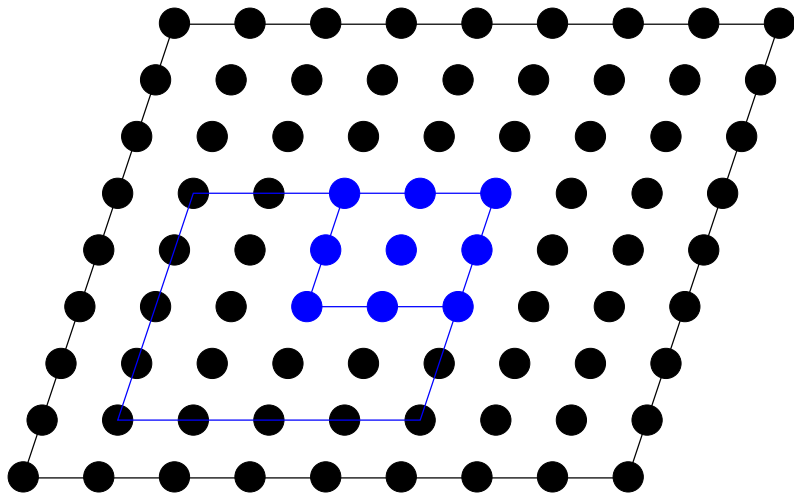
FFT

$$E_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} + \text{Re} \langle \varphi_{n\mathbf{k}} | \Sigma(E_{n\mathbf{k}}) - V_{\text{xc}} | \varphi_{n\mathbf{k}} \rangle$$

Discretizing the equations

Real space

$$F(\mathbf{r}, \mathbf{r}') \sim |\mathbf{r} - \mathbf{r}'|^2$$

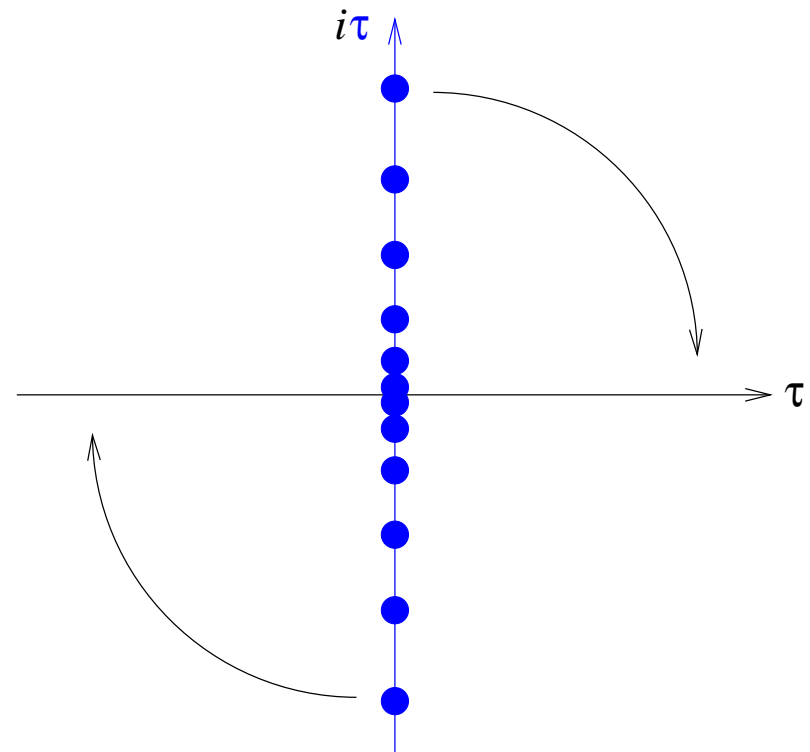


Unit cell

Interaction cell

Imaginary time

$$F(i\tau) \sim \exp(\varepsilon_{n\mathbf{k}} \tau)$$



The plasmon–pole approximation

Traditional GW implementations used a reciprocal–space representation for all operators.

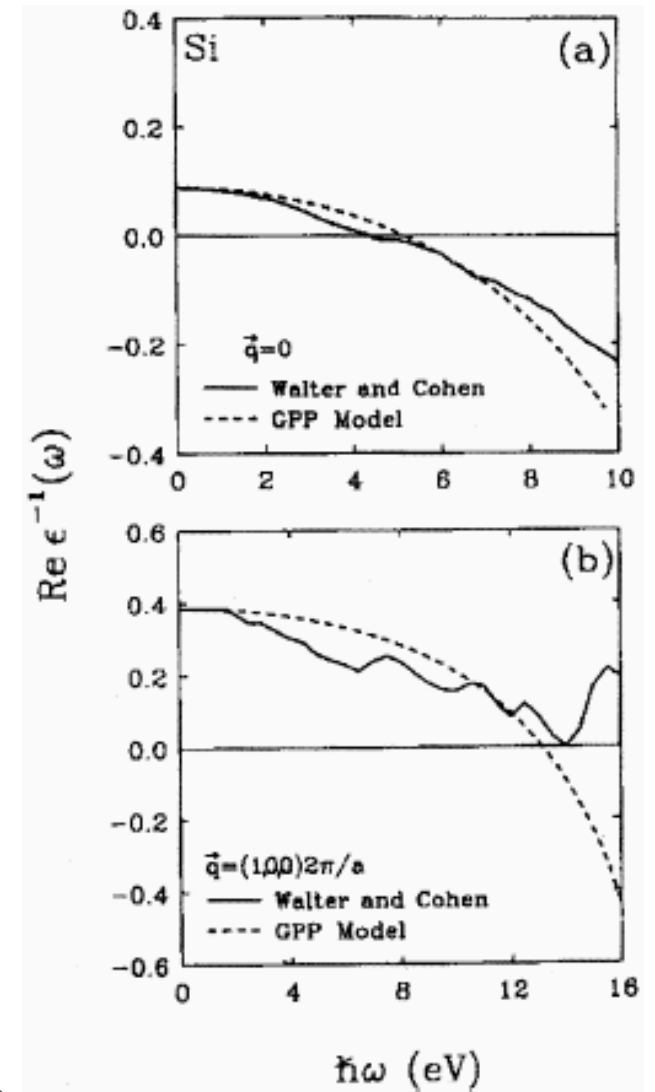
$$\Sigma(\mathbf{k},\omega) = i/(2\pi)^4 \int G_0(\mathbf{k}+\mathbf{k}',\omega+\omega')W(\mathbf{k}',\omega')d^3k' d\omega'$$

The frequency integral could be done analytically if the mathematical form of W was known. Ansatz:

$$\text{Re } \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{k},\omega) = \delta_{\mathbf{G}\mathbf{G}'} + \Omega_{\mathbf{G}\mathbf{G}'}(\mathbf{k})/[\omega^2 - \omega_{\mathbf{G}\mathbf{G}'}(\mathbf{k})^2]$$

This plasmon–pole model contains two parameters, which must be determined by fitting or sum rules.

The accuracy is good for states near the Fermi edge and decreases with increasing quasiparticle energy.



Summary

- The Kohn–Sham eigenvalues show systematic deviations from experimental band structures and may occasionally yield qualitatively incorrect results.
- A closer look at the underlying theory reveals that there is in fact no rigorous foundation for relating the Kohn–Sham eigenvalues to the band structure.
- The Green function properly describes electron addition and removal processes and thus gives access to the relevant excitation spectrum.
- The *GW* approximation for the electronic self–energy contains the dominant scattering processes that are expected in systems with delocalized states.
- It resolves the band–gap problem and yields band structures in very good agreement with experiment.
- In practice, the *GW* approximation is applied perturbatively after a standard density–functional calculation.