Faculty of Physics,
University of Warsaw

Summer Semester 2014

Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 8 – *April 14, 2014*

- **Band Gap energies in DFT**
- **Further Developments of DFT methods**

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Band Gaps in Solids
The DFT & the GW Method

DFT- The Kohn- Sham Method

W. Kohn and L. J. Sham, Phys. Rev. ***140****, A1133 (1965)*

System of interacting electrons with density $\rho(\vec{r})$ ⟷ **System of non-interacting electrons with the same density** $\rho(\vec{r})$

"Real" system

$\rho(\vec{r}) \quad T[\rho]$

"Fictitious" or Kohn-Sham reference system

$T_S[\rho] \quad \rho_S(\vec{r}) = \rho(\vec{r})$

$$\boxed{E[\rho] = \int d\vec{r}\, \upsilon_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]}$$

unknown!!!

- $\rho(\vec{r}) = \sum_{i=1}^{N} \varphi^*_i(\vec{r})\varphi_i(\vec{r})$
- $T_s[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\,\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r})$
- $E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}d\vec{r}\,'\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_i(\vec{r}\,')$

The Kohn- Sham Method – The Kohn-Sham Equations

- **Schrödinger-like equations with local potential**

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \qquad \frac{\delta E_x[\rho]}{\delta\rho} \qquad \frac{\delta E_c[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

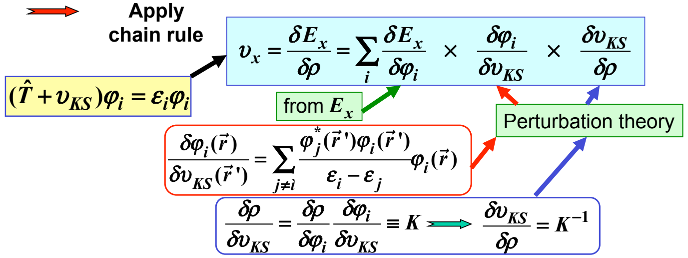
- **These equation are nonlinear and must be solved iteratively (self-consistently)**

Exact Exchange Method (EXX) [Optimized Effective Potential (OEPx)]

Solution: υ_x **is the first functional derivative of** E_x

→ **First order perturbation theory determines exactly** $\frac{\delta E_x}{\delta\rho}$

→ **Apply chain rule**



$$(\hat{T}+\upsilon_{KS})\varphi_i = \varepsilon_i\varphi_i$$

$$\upsilon_x = \frac{\delta E_x}{\delta\rho} = \sum_i \frac{\delta E_x}{\delta\varphi_i} \times \frac{\delta\varphi_i}{\delta\upsilon_{KS}} \times \frac{\delta\upsilon_{KS}}{\delta\rho}$$

from E_x

Perturbation theory

$$\frac{\delta\varphi_i(\vec{r})}{\delta\upsilon_{KS}(\vec{r}\,')} = \sum_{j\neq i}\frac{\varphi^*_j(\vec{r}\,')\varphi_i(\vec{r}\,')}{\varepsilon_i-\varepsilon_j}\varphi_j(\vec{r})$$

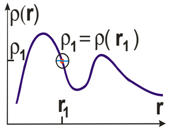
$$\frac{\delta\rho}{\delta\upsilon_{KS}} = \frac{\delta\rho}{\delta\varphi_i}\frac{\delta\varphi_i}{\delta\upsilon_{KS}} \equiv K \Longrightarrow \frac{\delta\upsilon_{KS}}{\delta\rho} = K^{-1}$$

M. Städele et al., Phys. Rev. B ***59****, 10031 (1999).*

LDA & GGA Approximations

Local Density Approximation (LDA):

the density is treated *locally* as constant



$$E_{xc}^{LDA}[\rho] = \int d\vec{r}\,\rho(\vec{r})\varepsilon_{xc}^{\text{hom}}(\rho(\vec{r}))$$

$$\varepsilon_{xc}^{\text{hom}} = \varepsilon_x^{\text{hom}} + \varepsilon_c^{\text{hom}}$$

Generalized Gradient Approximation (GGA)

J. P. Perdew & Y. Wang, Phys. Rev. B ***33****, 8800 (1986)*

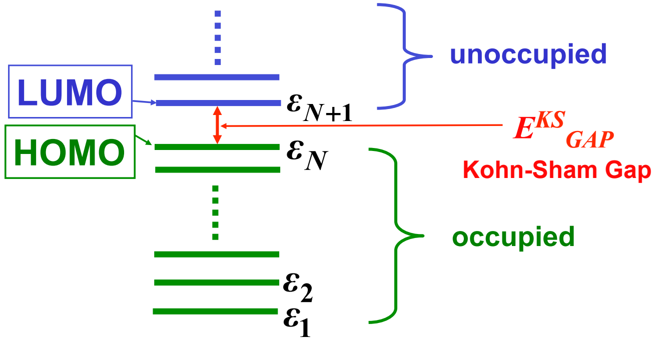
$$E_{xc}^{GGA}[\rho] = \int d\vec{r}\, f_{xc}(\rho(\vec{r}),\nabla\rho(\vec{r}))$$

f_{xc} **-constructed to fulfill maximal number of "summation rules"**

Exchange-correlation potential can be calculated very easily, since explicit dependence of E_{xc} on the density ρ is known.

$$\Rightarrow \upsilon_{xc} = \frac{\delta E_{xc}}{\delta\rho}$$

The Kohn - Sham Method – One particle energies



The occupied states are used to calculate one particle density (Aufbau principle) and the total energy

The Kohn- Sham Method – The Total Energy

$$\boxed{E[\rho]=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec r\varphi_i^*(\vec r)\vec\nabla^2\varphi_i(\vec r)+U[\rho]+E_x[\rho]+E_c[\rho]+\int d\vec r\upsilon_{ext}(\vec r)\rho(\vec r)}$$

$$E=\sum_{i=1}^{N}\varepsilon_i\underbrace{-\frac{1}{2}\iint d\vec r\,d\vec r'\frac{\rho(\vec r)\rho(\vec r')}{|\vec r-\vec r'|}+E_x[\rho]+E_c[\rho]-\int d\vec r(\upsilon_x(\vec r)+\upsilon_c(\vec r))\rho(\vec r)}_{\text{so-called double counting correction}}$$

Sum of the one-particle Kohn-Sham energies

$$\sum_{i=1}^{N}\varepsilon_i=\sum_{i=1}^{N}\left\langle\varphi_i\left|-\frac{\hbar^2}{2m}\vec\nabla^2+\vartheta_{KS}(\vec r)\right|\varphi_i\right\rangle=T_S[\rho]+\int d\vec r\vartheta_{KS}(\vec r)\rho(\vec r)$$

Energy of the reference system

differs from the energy of 'real' system

The Kohn- Sham Method – Physical meaning of one particle energies

- The Kohn-Sham orbital energy of the highest occupied level is equal to the minus of the ionization energy,

$$\boxed{\varepsilon_{max}=\mu=-I}$$

- Extension to non-integer occupation numbers

$$\rho(\vec r)=\sum_i f_i\varphi_i^*(\vec r)\varphi_i(\vec r)\qquad 0\le f_i\le 1$$

$$\boxed{\frac{\partial E}{\partial f_i}=\varepsilon_i}$$

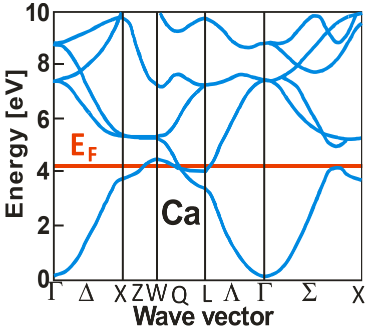
Janak theorem (1978)

Band structure of metals and semiconductors

$$\rho(\vec r)=\sum_{n,\vec k}\Theta(E_F-\varepsilon_n(\vec k))\varphi_n^*(\vec k,\vec r)\varphi_n(\vec k,\vec r)$$

Fermi energy

Band structure of simple metal (Calcium)



In metals:

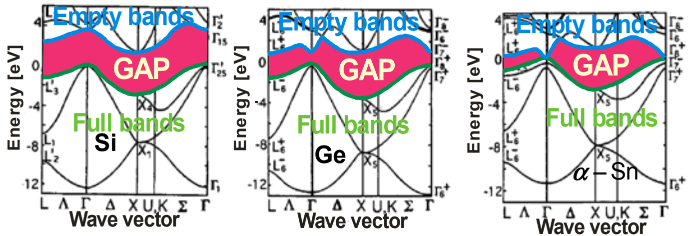
- Fermi energy lies in a band
- Fermi energy must be calculated in each iteration of the self-consistent procedure

$$N=\int_{\Omega_0}d^3\vec r\rho(\vec r)\quad\Rightarrow\quad E_F$$

Band structure of metals and semiconductors

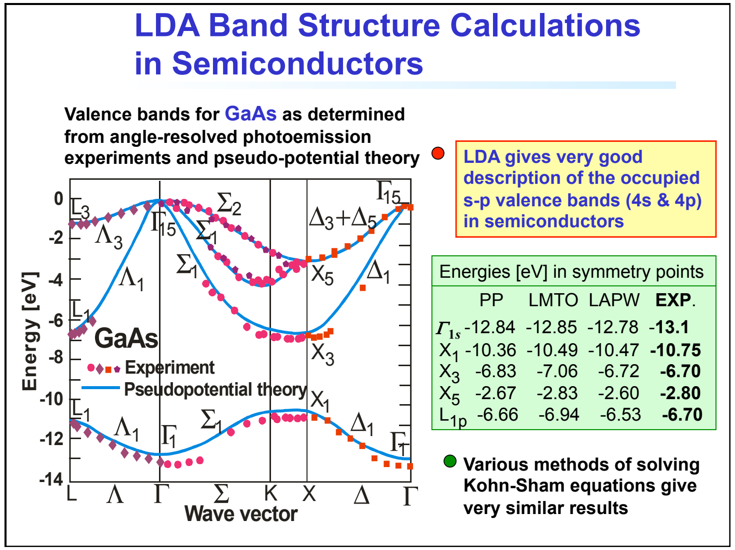
Semiconductors — Semi-metal

Silicon — Germanium — Alpha-Tin



In an ***ideal pure semiconductors at 0 K*** there are

- fully occupied valence bands & completely empty conduction bands separated by the ***energy gap***
- ***Fundamental band gap*** = Energy difference between the ***lowest unoccupied*** state and the ***highest occupied*** state
- Fundamental energy gap can be ***direct*** (Ge) or ***indirect*** (Si)
- Fermi level lies in the energy gap
- ***Insulator*** – like semiconductor with very flat bands and huge energy gap



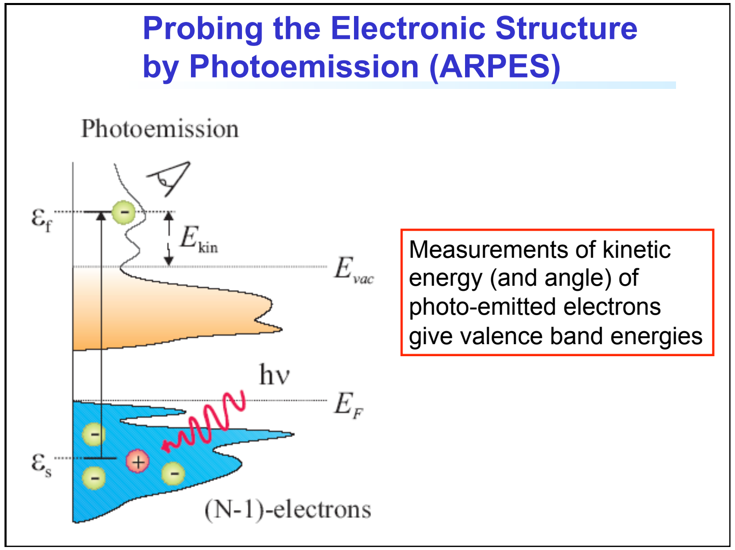
LDA Band Structure Calculations in Semiconductors

Valence bands for GaAs as determined from angle-resolved photoemission experiments and pseudo-potential theory

- **LDA gives very good description of the occupied s-p valence bands (4s & 4p) in semiconductors**

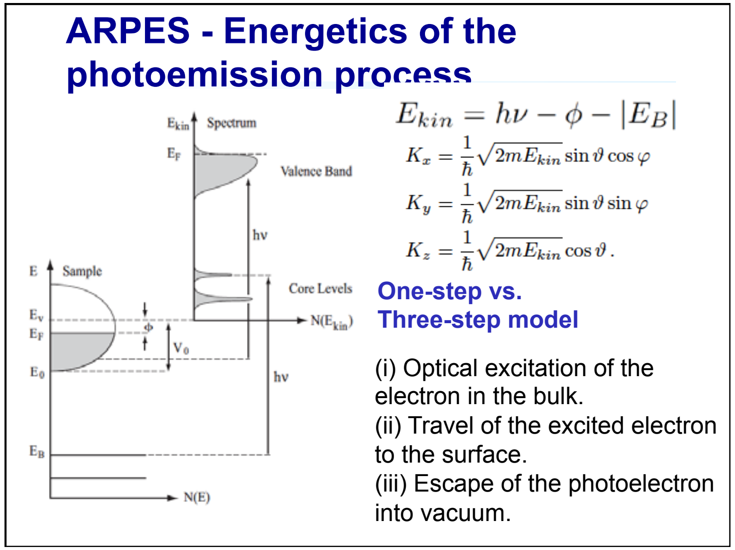
Energies [eV] in symmetry points	PP	LMTO	LAPW	**EXP.**
Γ_{1s}	-12.84	-12.85	-12.78	**-13.1**
X_1	-10.36	-10.49	-10.47	**-10.75**
X_3	-6.83	-7.06	-6.72	**-6.70**
X_5	-2.67	-2.83	-2.60	**-2.80**
L_{1p}	-6.66	-6.94	-6.53	**-6.70**

- **Various methods of solving Kohn-Sham equations give very similar results**



Probing the Electronic Structure by Photoemission (ARPES)

Measurements of kinetic energy (and angle) of photo-emitted electrons give valence band energies



ARPES - Energetics of the photoemission process

$$E_{kin} = h\nu - \phi - |E_B|$$

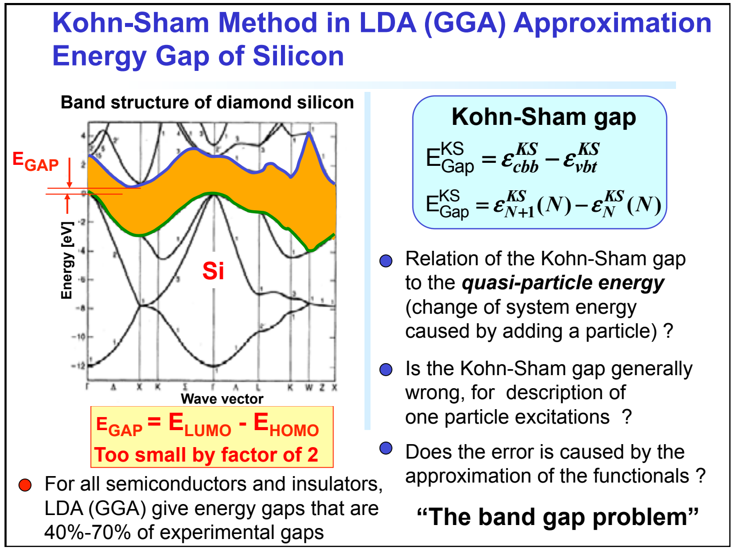
$$K_x = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi$$

$$K_y = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi$$

$$K_z = \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta\,.$$

One-step vs. Three-step model

(i) Optical excitation of the electron in the bulk.
(ii) Travel of the excited electron to the surface.
(iii) Escape of the photoelectron into vacuum.



Kohn-Sham Method in LDA (GGA) Approximation Energy Gap of Silicon

$E_{GAP} = E_{LUMO} - E_{HOMO}$
Too small by factor of 2

- For all semiconductors and insulators, LDA (GGA) give energy gaps that are 40%-70% of experimental gaps

Kohn-Sham gap

$$E^{KS}_{Gap} = \varepsilon^{KS}_{cbb} - \varepsilon^{KS}_{vbt}$$

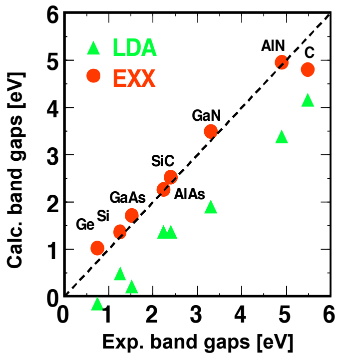
$$E^{KS}_{Gap} = \varepsilon^{KS}_{N+1}(N) - \varepsilon^{KS}_{N}(N)$$

- Relation of the Kohn-Sham gap to the ***quasi-particle energy*** (change of system energy caused by adding a particle) ?
- Is the Kohn-Sham gap generally wrong, for description of one particle excitations ?
- Does the error is caused by the approximation of the functionals ?

“The band gap problem”

Fundamental band gaps in semiconductors:
Local Density Approximation & Exact Exchange

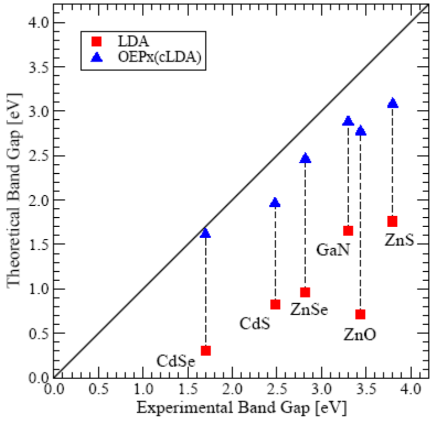
Fundamental Band Gaps



- **EXX Method leads to Kohn-Sham gaps that agree very well with experiment**

➡ Large part of the error in the fundamental gaps is connected to the approximated functionals (LDA, GGA)

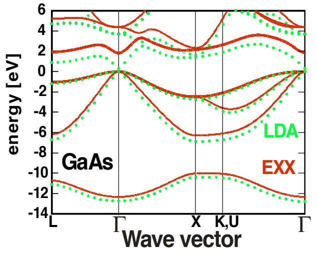
Band Gap of Semiconductors in Exact-Exchange OEP



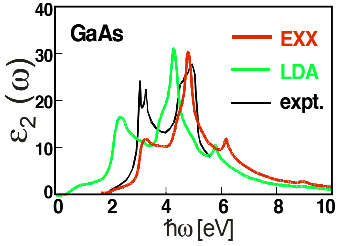
P. Rinke *et al.*
New J. Phys. **7**, 126 (2005)

Band structure of semiconductors:
Local Density Approximation & Exact Exchange Method

Band structure



Dielectric function



GaAs: electron effective mass: LDA = $0.03m_0$, EXP = $0.07m_0$, EXX = $0.10m_0$

- The most pronounced difference between band structure calculated with LDA and EXX methods – rigid shift of the conduction bands

➡ Concerning energy differences – LDA should give valuable predictions

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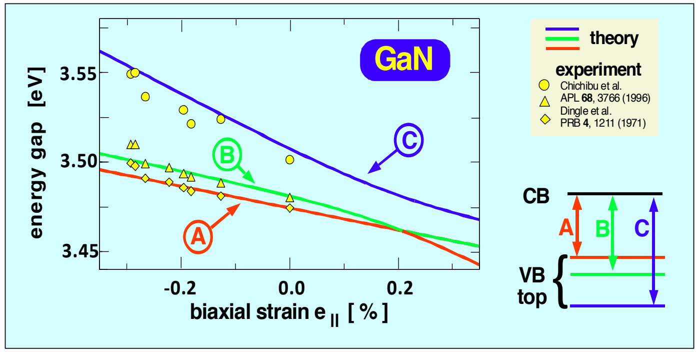
LDA calculations in wurtzite GaN:
Change of A, B, C exciton energy gaps with biaxial strain



- Gives a reference scale to determine strain in an epitaxially grown sample

LDA calculation in wurtzite nitrides:

Energy gap deformation potentials for biaxial strain and hydrostatic pressure

	GaN (theory)	GaN (expt.)	AlN (theory)
$\left.\frac{dE(\text{A exciton})}{de}\right\|_0$	-6.1	-8.2 -8.4	-8.0
= $\left.\frac{dE(\text{C exciton})}{de}\right\|_0$	-15.8	-17.2	-22.2
= $\left.\frac{dE(\text{A exciton})}{d\ln V}\right\|_{V_0}$	-8.0	-8.0 -8.2	-9.5

theory

expt.

(all data in eV)

Very good agreement with experiment

Ionisation Potential and Electron Affinity

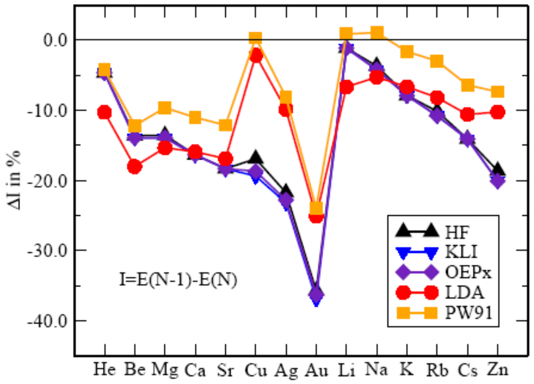
Ionisation potential:
minimal energy to remove an electron

$$I = E(N-1) - E(N)$$

Electron affinity:
minimal energy to add an electron

$$A = E(N) - E(N+1)$$

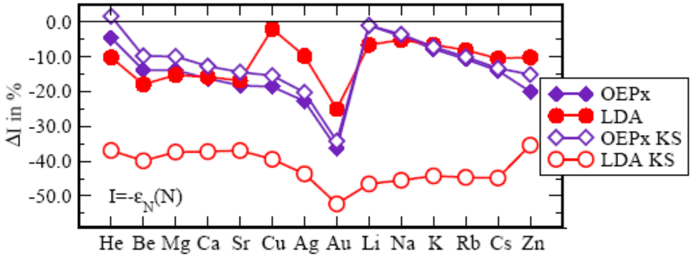
Ionisation Potential for Atoms



E. Engel in A Primer in DFT, Springer 2003

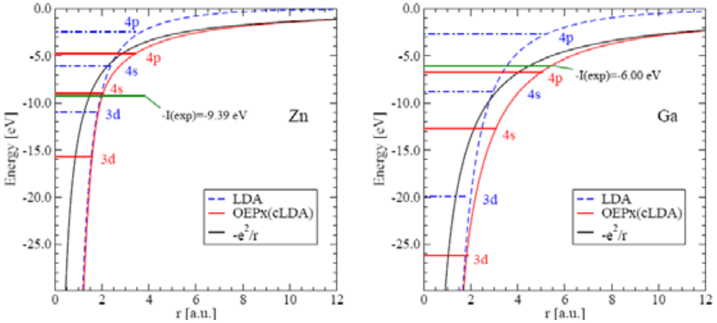
Ionisation Potential vs. Kohn-Sham HOMO

- ***Kohn-Sham:*** eigenvalue of the highest occupied Kohn-Sham level $I_{KS} = -\varepsilon_N(N)$
- **For exact density functional –** $I_{KS} = I = E(N\text{-}1) - E(N)$
- How this relation is fulfilled for approximate functionals ?



- **Much better for EXX than for LDA !**

EXX versus LDA: Zn and Ga Atoms

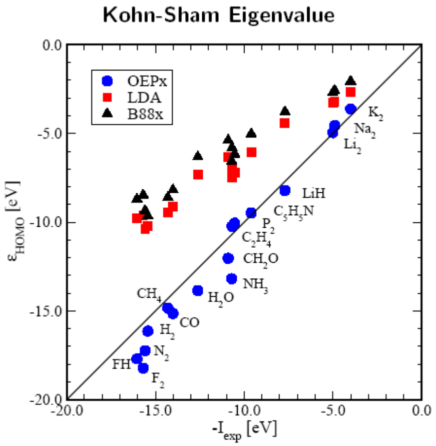


$$v_x^{\mathrm{OEPx}}(\mathbf{r}) \xrightarrow{r\to\infty} -\frac{1}{\mathbf{r}}$$

$$v_{xc}^{\mathrm{LDA}}(\mathbf{r}) \xrightarrow{r\to\infty} e^{-\beta r/3}$$

- **Correct asymptotic decay of potential in DFT-EXX**

Ionisation Potential - Small Molecules



Comparison of Kohn-Sham HOMO with experimental values of ionization potential

Very good agreement for EXX (OEPx) !

S. Hamel *et al.*,
J. Chem. Phys.
116, 8276 (2002)

Band Gaps in Solids
The DFT & the GW Method

Band Gap of Semiconductors

Band gap:

$$E_{gap} = I - A = E(N+1) - 2E(N) + E(N-1)$$

→ For solids, $E(N+1)$ and $E(N-1)$ cannot be reliable computed in DFT, yet !

- In Kohn-Sham the highest occupied state is exact

→ $$\varepsilon_N^{KS}(N) = -I_N = E(N) - E(N-1)$$

$$\varepsilon_{N+1}^{KS}(N+1) = -I_{N+1} = E(N+1) - E(N)$$

$$E_{gap} = \{E(N+1) - E(N)\} - \{E(N) - E(N-1)\}$$

$$\boxed{E_{gap} = \varepsilon_{N+1}^{KS}(N+1) - \varepsilon_N^{KS}(N)}$$

Band Gap of Semiconductors

$$E_{gap} = \epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N}(N)$$
$$= \underbrace{\epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N+1}(N)}_{\Delta_{xc}} + \underbrace{\epsilon^{\mathrm{KS}}_{N+1}(N) - \epsilon^{\mathrm{KS}}_{N}(N)}_{E^{\mathrm{KS}}_{gap}}$$

Discontinuity **Kohn-Sham gap**

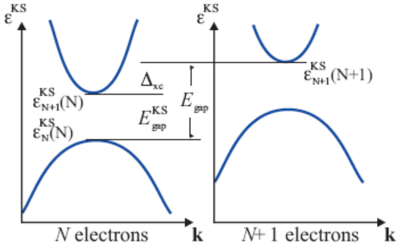
- For solids: $N \gg 1 \quad \Rightarrow \quad \Delta n(\mathbf{r}) \to 0$ for $N \to N+1$

$\Rightarrow$ discontinuity in v_{xc} upon changing the particle number

$$\Delta_{xc} = \left(\left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N+1} - \left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N} \right) + \mathcal{O}\left(\frac{1}{N}\right)$$

Band Gap of Semiconductors - Discontinuity in V_{xc}

Band gap: $E_{gap} = E^{\mathrm{KS}}_{gap} + \Delta_{xc}$



After the addition of an electron into the conduction band (right) the xc potential and the whole band-structure shift up by a quantity Δ_{xc} .

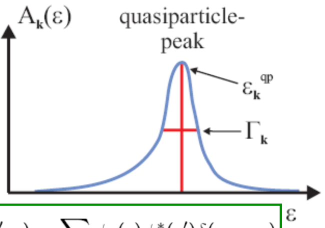
R.W. Godby *et al.*,
in *A Primer in DFT*,
Springer 2003

The Quasi-particle Concept

Quasiparticle:

- single-particle like excitation
- $$A_{\mathbf{k}}(\epsilon) \approx \frac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$$

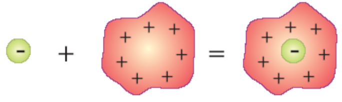
$\epsilon_{\mathbf{k}}$: excitation energy
$\Gamma_{\mathbf{k}}$: lifetime
$Z_{\mathbf{k}}$: renormalisation



Spectral function $A(\mathbf{r},\mathbf{r}';\epsilon) = \frac{1}{\pi}\mathrm{Im}\; G(\mathbf{r},\mathbf{r}';\epsilon) = \sum_s \psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')\delta(\epsilon - \epsilon_s)$

Quasiparticle:

- electron acquires polarisation cloud
- new entity



Quasi-particle energies in many-particle theory

L. Hedin & S. Lundquist, *Solid State Physics* **23**, 1 (1969)

- **Energy of quasi-particle = energy of one-particle excitation = Change of system energy caused by adding a particle to the system**
  Difference between total energy of a system with ***N+1*** and ***N*** particles
  $$E_{tot}(N+1) - E_{tot}(N)$$

Dyson equation

$$\left(\frac{\hbar^2}{2m}\vec{\nabla}^2 - \upsilon_{ext}(\vec{r}) - \upsilon_H(\vec{r}) + E\right)G(\vec{r},\vec{r}';E) - \\ - \int d^3\vec{r}'' \sum(\vec{r}',\vec{r}'';E) G(\vec{r},\vec{r}';E) = \delta(\vec{r}-\vec{r}')$$

$\sum(\vec{r}',\vec{r}'';E)$ -self- energy operator
$G(\vec{r},\vec{r}';E)$ - one particle Green's function

- **Energies of one-particle excitations = poles of** $G(\vec{r},\vec{r}';E)$

can be complex
Real part – energy of the quasiparticle
Imaginary part - Life time

Quasi-particle energies in many-particle theory
Green's function for a non-interacting system

- Self-energy operator $\sum$ - independent on energy
- It is possible to introduce one particle functions u_s

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2+\upsilon_{ext}(\vec{r})+\upsilon_H(\vec{r})\right)u_s(\vec{r})+\int d^3\vec{r}\,'\sum(\vec{r},\vec{r}\,')u_s(\vec{r}\,')=\varepsilon_s u_s(\vec{r})$$

- $G(\vec{r},\vec{r}\,';E)=\sum_s \frac{u_s(\vec{r})u_s^*(\vec{r}\,')}{E-\varepsilon_s \pm i\delta}$
- Self-energy operator $\sum(\vec{r},\vec{r}\,')=V_x^{HF}(\vec{r},\vec{r}\,')$

Quasi-particle energies in many-particle theory
GW- method

- $\sum(E) \Longrightarrow$ introduce functions $\psi_{n\vec{k}}(\vec{r})$
- $$\boxed{\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2+\upsilon_{ext}(\vec{r})+\upsilon_H(\vec{r})\right)\psi_{n\vec{k}}(\vec{r})+\int d^3\vec{r}\,'\sum(\vec{r},\vec{r}\,';E_{n\vec{k}})\psi_{n\vec{k}}(\vec{r}\,')=E_{n\vec{k}}\psi_{n\vec{k}}(\vec{r})}$$

$\mathrm{Re}(E_{n\vec{k}})$ $\mathrm{Im}(E_{n\vec{k}})$

If one is interested in energies of excitation and not their lifetimes, one can neglect imaginary part of the self-energy operator $\mathrm{Im}(\sum)=0$

There exists series expansion for self-energy operator

- Take the first term $\sum(\vec{r},\vec{r}\,';E)=\frac{i}{2\pi}\int d\omega e^{-i\omega o^+}G(\vec{r},\vec{r}\,';E-\omega)W(\vec{r},\vec{r}\,';\omega)$
- $G(\vec{r},\vec{r}\,';E)=\sum_{n\vec{k}}\frac{\psi_{n\vec{k}}(\vec{r})\psi^*_{n\vec{k}}(\vec{r}\,')}{E-E_{n\vec{k}}+io^+\,\mathrm{sgn}(E_{n\vec{k}}-\mu)}$
- $W(\vec{r},\vec{r}\,';\omega)=\int d^3\vec{r}\,''\varepsilon^{-1}(\vec{r},\vec{r}\,',\omega)\frac{e^2}{|\vec{r}\,''-\vec{r}\,'|}$ **Screened Coulomb potential**

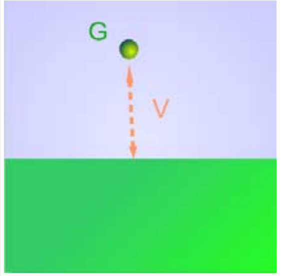
Inverse of dielectric function

GW - method

Hedin & Lundqist

- **Self-consistent solution gives energies of single particle excitations**

The GW Method – Green's Function

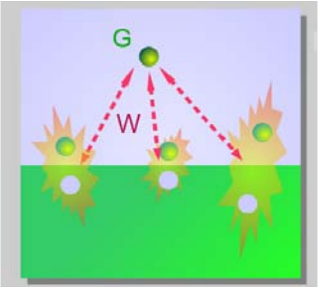


● We make the problem simpler by considering one electron in an effective potential

● The effective potential is the **Coulomb interaction, V**, between the electron and the average of all the others

● We describe the electron's motion with the **Green's function, G**

The GW Method –
Screened Coulomb Interaction



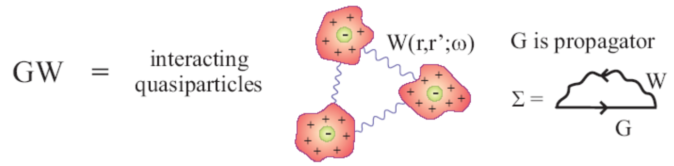
● In order to make the model better we model the excited states and their interactions.

● The electron polarizes the system, making effective electron-hole pairs.

● This screens the Coulomb interaction.

● This means that the electron now interacts with a **screened coulomb interaction, W**

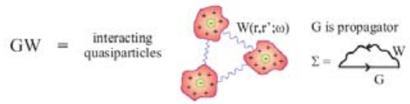
GW Approximation - Interacting Quasiparticles



Self-Energy:

- energy response of the system that the quasiparticle experiences due to its own presence
- *GW*: $\Sigma(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int d\epsilon' e^{i\epsilon'\delta} G(\mathbf{r},\mathbf{r}';\epsilon+\epsilon')W(\mathbf{r},\mathbf{r}';\epsilon')$

GW Approximation - Formalism



- *GW* self-energy: $\Sigma(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int d\epsilon' e^{i\epsilon'\delta} G(\mathbf{r},\mathbf{r}';\epsilon+\epsilon')W(\mathbf{r},\mathbf{r}';\epsilon')$
- Screened interaction: $W(\mathbf{r},\mathbf{r}',\epsilon) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r},\mathbf{r}'';\epsilon)v(\mathbf{r}''-\mathbf{r}')$
- Dielectric function: $\varepsilon(\mathbf{r},\mathbf{r}',\epsilon) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}-\mathbf{r}'')\chi_0(\mathbf{r}'',\mathbf{r}';\epsilon)$
- Polarisability: $\chi_0(\mathbf{r},\mathbf{r}';\epsilon) = -\frac{i}{2\pi}\int d\epsilon' G(\mathbf{r},\mathbf{r}';\epsilon'-\epsilon)G(\mathbf{r}',\mathbf{r};\epsilon')$
- Quasiparticle equation: $\hat{h}_0(\mathbf{r})\psi_s(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';\epsilon_s^{qp})\psi_s(\mathbf{r}') = \epsilon_s^{qp}\psi_s(\mathbf{r})$

Quasi-particle energies in many-particle theory Connection to Kohn-Sham energies

Self-consistent calculations show that $\psi_{n\vec{k}}(\vec{r}) \approx \varphi_{n\vec{k}}^{KS}(\vec{r})$

Kohn-Sham energies

Kohn-Sham orbitals

$$E_{n\vec{k}} = \varepsilon_{n\vec{k}}^{KS} + \left\langle \varphi_{n\vec{k}}^{KS}(\vec{r}) \,|\, \sum(E_{n\vec{k}}) - \upsilon_{xc}^{KS} \,|\, \varphi_{n\vec{k}}^{KS}(\vec{r}) \right\rangle$$

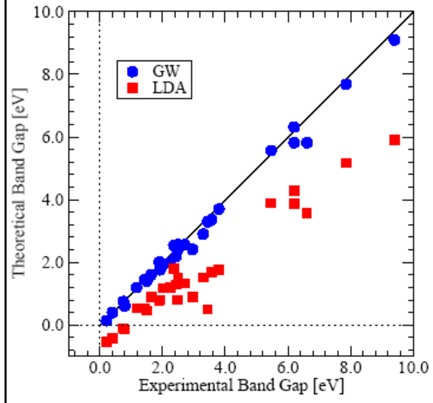
$$Z_{n\vec{k}} = \left(1 - \frac{\partial \sum(E)}{\partial E}\bigg|_{E=E_{n\vec{k}}} \right)^{-1}$$

So-called renormalization

$$\boxed{E_{n\vec{k}} = \varepsilon_{n\vec{k}}^{KS} + \left\langle \varphi_{n\vec{k}}^{KS}(\vec{r}) \,|\, \sum(E_{n\vec{k}}) - \upsilon_{xc}^{KS} \,|\, \varphi_{n\vec{k}}^{KS}(\vec{r}) \right\rangle Z_{n\vec{k}}}$$

- **Relation between quasi-particle and Kohn-Sham energies**

GW Approximation for Solids

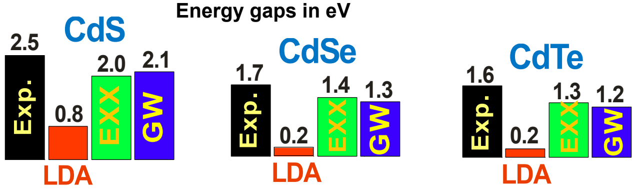


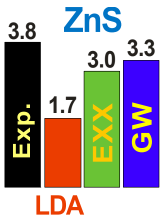
General improvement of the energy gaps in comparison to DFT-LDA

Aulbur *et al.*
Solid State Phys. **54** (2000)

Fundamental band gaps in II-VI semiconductors: LDA, EXX, and GW calculations

Energy gaps in eV

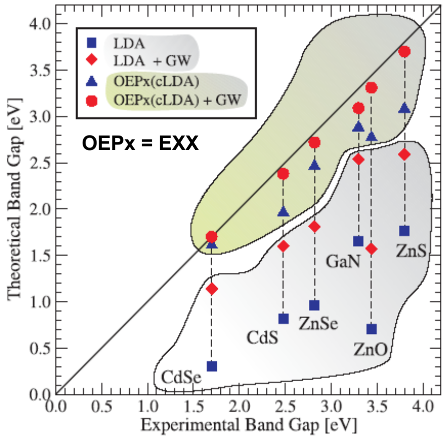




- **LDA** gives dramatically too small band gaps
- **LDA + GW** – large corrections to LDA gaps
  - corrected gaps are of order of EXX gaps
- **EXX + GW** – very small correction of order (0.1 - 0.2 eV)

➡ **Still some work to do !**

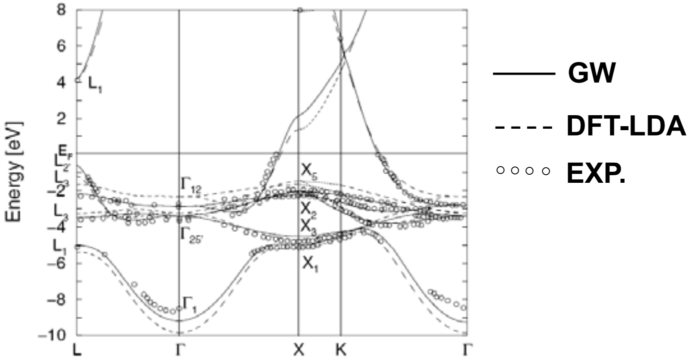
Quasi-particle (GW) Band Gaps



EXX better than LDA basis for quasi-particle calculations

P. Rinke *et al.*
New J. Phys.
7, 126 (2005)

Electronic Structure of Copper in the *GW* Approximation



Andrea Marini *et al.*, Phys. Rev. Lett. **88**, 016403 (2001)

GW Approximation - Merits

- Gives accurate band gaps for many materials
- Allows for calculation of lifetimes
- Successfully applied to
  - bulk materials
  - surfaces
  - nanotubes
  - clusters
  - defects
  - defects on surfaces

Additional reading

- *A Primer in Density Functional Theory*, C. Fiolhais, F. Nogueira and M. Marques, Springer 2003 (ISBN 3-540-03083-2).
- "Quasiparticle Calculations in Solids",
  W. G. Aulbur and L. Jönsson and J. W. Wilkins,
  Solid State Phys. : Advances in Research and Applications **54**, 1 (2000).
- "Electronic Excitations: Density-Functional Versus Many-Body Green's Function Approaches",
  G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys.* **74**, p601 (2002).
- "Combining GW calculations with exact-exchange density-functional theory: An analysis of valence-band photoemission for compound semiconductors",
  P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt and M. Scheffler,
  New J. Phys. **7**, 126 (2005).

DFT (LDA, GGA, EXX) for weakly correlated systems

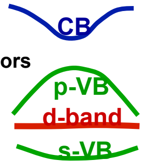
Accuracy of Common DFT implementations

- ☐ **Accuracy of geometries is better than 0.1 A**
- ☐ **Accuracy of calculated energies (relative) is usually better than 0.2 eV**
  Very often better than 0.01 eV

May we reach so-called chemical accuracy within DFT?

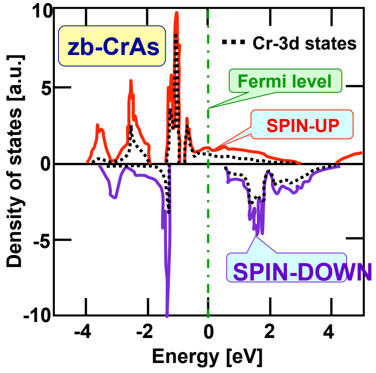
- **Exact Exchange Kohn-Sham Method – a step in this direction**
  - **Systematic improvement of existing Kohn-Sham schemes**
  - **Computationally very demanding**
    - **Bulk systems up to now**
    - **Implementations for larger systems going on**
- **Crucial - Better correlation energy functionals**

Failures of LSDA for strongly correlated systems



- **Band Gap Problem**
- **Positions of the cationic d-bands in semiconductors are by 3-4 eV too high in energy**
  ➡ **overestimation of p-d hybridization**
  (in Cu d-bands are 0.5 eV too high)
- **LSDA predicts negative ions (e.g. F^-) to be unstable**
- ***For strongly correlated* systems, LSDA consistently <u>underestimates</u> the tendency to magnetism (e.g., cuprates, NiO)**
- ***For strongly fluctuating* systems, LSDA consistently <u>overestimates</u> the tendency to magnetism**
  FeAl : M = 0.7 m_B (Exp. – paramagnetic)
  $Sr_3Ru_2O_7$: M = 0.6 m_B (Exp. – paramagnetic)

Spin-polarized LDA (LSDA) prediction: zinc-blende CrAs is ferromagnetic

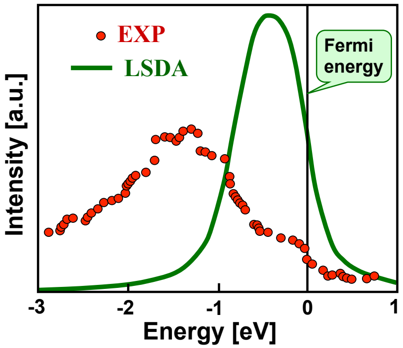


M. Shirai et al., J. Magn. & Magn. Mater. **177-181**, 1383 (1998)

- ➢ Previously nonexistent compound
- ➢ Later thin films grown by MBE
- ➢ Curie temperature larger than 400 K
- ➢ Magnetic moment = $3m_B$
  Agreement between theory and experiment

Photoemission spectrum of $La_{0.94}Sr_{0.06}TiO_3$

6% hole doping



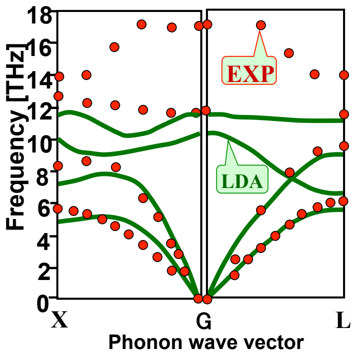
Spectra are Gauss-broadened (0.3 eV broadening parameter) to simulate the experimental accuracy

LDA band structure calculations clearly fail to reproduce the broad band observed in the experiment at energies 1-2 eV below the Fermi energy.

Exp.: *A. Fujimori et al., PRL **69**, 1796 (1992)*

LSDA: *I.A.Nekrasov et al., Euro. Phys.J B **8**, 55 (2000)*

Phonon dispersion curves for NiO
Comparison of LDA results with experiment



- **LDA overestimates the electronic screening effects by large amount**
- **⇨ causing**
  - **the artificial softening of optical phonons &**
  - **lowering of the LO-TO splitting.**
- **LDA overestimates the value of ε_∞ by a factor of 6.**

Savrasov & Kotliar (2002)

Beyond LDA approach to correlated electron systems

$$\hat H = \overbrace{\int d^3\vec r\,\hat\Psi^\dagger(\vec r)[-\Delta+V^{ext}(\vec r)]\hat\Psi(\vec r)}^{\hat H_{kin}} + \underbrace{+\frac{1}{2}\int d^3\vec r\, d^3\vec r\,'\,\hat\Psi^\dagger(\vec r)\hat\Psi^\dagger(\vec r\,')\upsilon^{ee}(\vec r-\vec r\,')\hat\Psi(\vec r)\hat\Psi(\vec r\,')}_{\hat H_{e-e}}$$

$$\boxed{\hat H = \underbrace{\int d^3\vec r\,\hat\Psi^\dagger(\vec r)[-\Delta+V_{KS}(\vec r)]\hat\Psi(\vec r)}_{\hat H_{LDA}} + \hat H_{corr}}$$

- **Expansion of field operators in basis Φ_{ilm} (LMTO, LAPW, ….)**

$$\hat\Psi^\dagger(\vec r) = \sum_{ilm}\hat c^\dagger_{ilm}\Phi_{ilm}(\vec r) \qquad \hat H_{LDA} = \sum_{ilm,jl'm',\sigma} t_{ilm,jl'm',\sigma}\hat c^{\sigma\dagger}_{ilm}\hat c^{\sigma}_{jl'm'}$$

- **How to deal with $\hat H_{corr}$?**

LDA + local Coulomb correlations

$$\hat H = \underbrace{\hat H_{LDA} + \hat H^{local}_{corr} - \hat H^{\mathrm{LDA}}_{corr}}_{\mathcal H} + \hat H_{res}$$

$$\hat H^{local}_{corr}: \quad \frac{1}{2}\sum_{i,l=l_d,m,\sigma,m',\sigma'} U^{\sigma\sigma'}_{mm'}\hat n_{ilm\sigma}\hat n_{ilm'\sigma'}$$

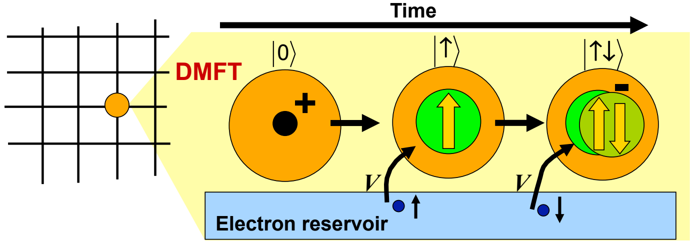
$$\hat H^{\mathrm{LDA}}_{corr}: \quad \frac{1}{2}U n_d(n_d-1)$$

$\mathcal H$ ***Ab-initio* correlated electron model**

- **Needed basis where interacting orbitals can be identified**
- **U can be calculated via constraint LDA:** $U = \dfrac{\partial^2 E_{LDA}(n_d)}{\partial n_d^2}$
- **Hund's rule coupling can be calculated similarly**
- $LDA + U$**: solve $\mathcal H$ with Hartree-Fock**
- $LDA + DMFT$**: solve $\mathcal H$ with Dynamical Mean-Field Theory**

Dynamical Mean-Field Theory

G. Kotliar & D. Vollhardt, Physics Today, March 2004



DMTS in the simplest case of an *s* orbital occupying an atom

- **DMFT replaces the full lattice of atoms and electrons with a single impurity atom imagined to exist in a bath of electrons**
- **DMFT captures the dynamics of electrons on a central atom as it *fluctuates* among different atomic configurations, shown here as snapshots in time.**

Dynamical Mean-Field Theory –
Basic Mathematical Description

- **To treat strongly correlated electrons, one has to introduce a *frequency resolution* for the electron occupancy at a particular lattice site**
- **Green function specifies the probability amplitude to create electron with spin σ at site i at time τ' and destroy it at the same site at a later time τ**

$$\boxed{G_{i\sigma}(\tau-\tau') \equiv -\left\langle \hat{c}_{i\sigma}(\tau)\hat{c}^{\dagger}_{i\sigma}(\tau') \right\rangle}$$

- **The dynamical mean field theory (DMFT) can be used to investigate the full many-body problem of interacting quantum mechanical particles or effective treatments such as the Hubbard model**

$$\hat{H} = \sum_{ij,\sigma} t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$$

Dynamical Mean-Field Theory –
Basic Mathematical Description (2)

- **The Anderson impurity model**

$$\boxed{\hat{H}_{AIM} = \hat{H}_{atom} + \sum_{\nu,\sigma}\varepsilon^{bath}_{\nu,\sigma}n^{bath}_{\nu,\sigma} + \sum_{\nu,\sigma}(V_{\nu}c^{\dagger}_{0,\sigma}a^{bath}_{\nu,\sigma} + h.c.)}$$

- **The *hybridization function*** $\Delta(\omega) = \sum_{\nu,\sigma}\frac{|V_{\nu}|^{2}}{\omega-\varepsilon^{bath}_{\nu,\sigma}}$

  plays the role of *dynamic mean field*.

- $\Delta(\omega)$ **has to be determined from the self-consistency condition:**

$$\boxed{G[\Delta(\omega)] = \sum_{\vec{k}}\left\{\omega - \Sigma[\Delta(\omega)] - t_{\vec{k}}\right\}^{-1}}$$

Self-energy term $\Sigma[\Delta(\omega)] \equiv \Delta(\omega) - \left(G[\Delta(\omega)]\right)^{-1} + \omega$

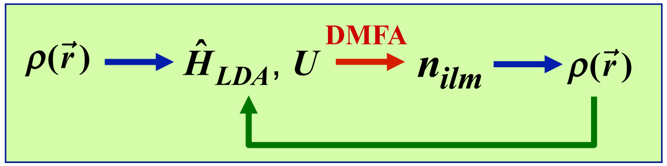
takes on the meaning of a *frequency dependent potential*

LDA+DMFA – Functional Formulation

A functional of both the charge density and the local Green function of the correlated orbital

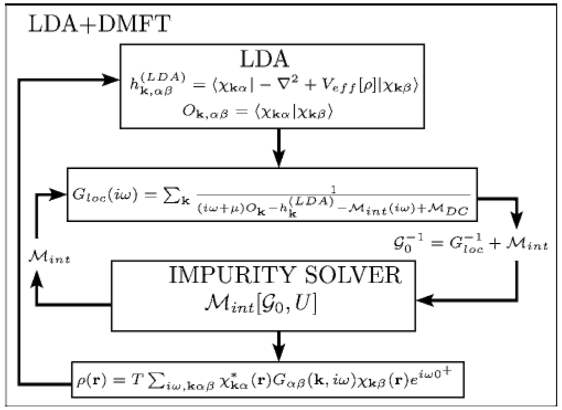
$$\boxed{\Gamma[\rho,G] = T[\rho,G] + \int V^{ext}(\vec{r})\rho(\vec{r})d^{3}\vec{r} + \frac{1}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^{3}\vec{r}d^{3}\vec{r}\,' + E_{xc}[\rho,G]}$$

Self-consistent cycle of LDA+DMFA



$$\rho(\vec{r}) \rightarrow \hat{H}_{LDA}, U \xrightarrow{DMFA} n_{ilm} \rightarrow \rho(\vec{r})$$

LDA+DMFA – Computational Scheme



LDA+DMFT

LDA

$h^{(LDA)}_{\mathbf{k},\alpha\beta} = \langle \chi_{\mathbf{k}\alpha} | -\nabla^2 + V_{eff}[\rho] | \chi_{\mathbf{k}\beta} \rangle$

$O_{\mathbf{k},\alpha\beta} = \langle \chi_{\mathbf{k}\alpha} | \chi_{\mathbf{k}\beta} \rangle$

$G_{loc}(i\omega) = \sum_{\mathbf{k}} \frac{1}{(i\omega+\mu)O_{\mathbf{k}} - h^{(LDA)}_{\mathbf{k}} - \mathcal{M}_{int}(i\omega) + \mathcal{M}_{DC}}$

$\mathcal{G}_0^{-1} = G_{loc}^{-1} + \mathcal{M}_{int}$

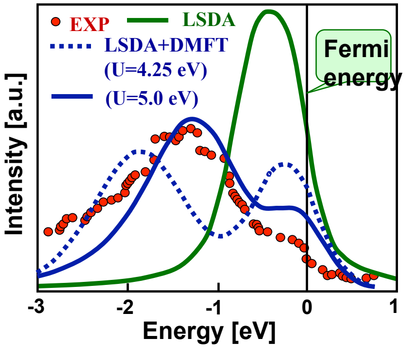
$\mathcal{M}_{int}$

IMPURITY SOLVER

$\mathcal{M}_{int}[\mathcal{G}_0, U]$

$\rho(\mathbf{r}) = T \sum_{i\omega,\mathbf{k}\alpha\beta} \chi^*_{\mathbf{k}\alpha}(\mathbf{r}) G_{\alpha\beta}(\mathbf{k}, i\omega) \chi_{\mathbf{k}\beta}(\mathbf{r}) e^{i\omega 0^+}$

Photoemission spectrum of $La_{0.94}Sr_{0.06}TiO_3$



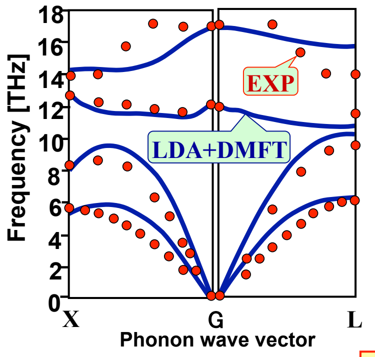
LSDA+DMFT dramatically improves the photoemission spectrum

Exp.: *A. Fujimori et al., PRL* ***69****, 1796 (1992)*

LSDA: *I.A.Nekrasov et al., Euro. Phys.J B* ***8****, 55 (2000)*

Phonon dispersion curves for NiO

Results of LDA + DMFT



$$\omega_{LO}^2 - \omega_{TO}^2 \propto |Z^*|^2 / \varepsilon_\infty$$

Born effective charge

	LDA	LDA+ DMFT	EXP
ε_∞	35.7	7.2	5.7, 6.1
$\|Z^*\|$	2.17	2.33	2.22

Accidental agreement with experiment !!

Savrasov & Kotliar (2002)

Importance of correlations in lattice dynamics of NiO

Dynamical Mean Field Theory

- **DMFT** is an intrinsically ***many body electronic theory***.
- It simultaneously handles the atomic and band character of electrons. This is at the heart of correlation physics.
- The approach leads to a non trivial but tractable problem.
- Misses out on spatial correlations. CDMFT can handle them.
- From a curiosity in the early 90’s, it has become now an indispensable part of the theorists training.

Dynamical Mean Field Theory

References:

A. Georges, et al., Rev. Mod. Phys. (1996)
T. Maier, et al., Rev. Mod. Phys. (2005)
G. Kotliar, et al., Rev. Mod. Phys. (2006)
A. Georges, review, cond-mat. (2004)
M. Civelli, Rutgers thesis, cond-mat (2007)

Thank you !