Novel Functionals and the *GW* Approach

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IPAM 2005 - Workshop III: Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions

Exchange-Correlation Exactly

- exchange-corrleation:

$$\begin{aligned} \text{energy} \quad &: \quad E_{xc} = E_{tot} - T - E_{ext} - E_H \\ \text{potential} \quad &: \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \end{aligned}$$

- exact v_{xc}:

$$\iiint d\epsilon d\mathbf{r}' d\mathbf{r}'' G_0(\mathbf{r},\mathbf{r}';\epsilon)\left[\Sigma_{xc}(\mathbf{r},\mathbf{r}';\epsilon) - v_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right] G(\mathbf{r}'',\mathbf{r};\epsilon) = 0$$

with G_0 : non-interacting Green's function
G : interacting Green's function
Σ_{xc} : self-energy

- alternative: Görling-Levy perturbation theory (*Phys. Rev. B* **47**, 13105 (1993), *Phys. Rev. A* **50**, 196 (1994))

Overview

- Novel functionals and optimised effective potentials
- Exact-exchange
- Performance of exact-exchange
- Photo-electron spectroscopy
- Quasiparticles and the *GW* method
- DFT and many-body theory

Local, Jellium Based Functionals and Self-Interaction

- total energy: $E_{tot}[n] = T + E_{ext}[n] + E_H[n] + E_{xc}[n]$
- Hartree energy:

$$E_H = \frac{1}{2}\sum_{ij}^{occ}\int d\mathbf{r}\int d\mathbf{r}'\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')$$

- Local-Density approximation (LDA):

$$E_{xc}^{\mathrm{LDA}}[n] = \int d\mathbf{r}\;\; n(\mathbf{r})\epsilon_{xc}^{\mathrm{HEG}}(n)\big|_{n=n(\mathbf{r}))}$$

$\epsilon_{xc}^{\mathrm{HEG}}(n(\mathbf{r}))$: exchange-correlation energy density of the homogeneous electron gas (HEG)

- Generalised Gradient Corrections (GGA):

$$E_{xc}^{\mathrm{GGA}}[n] = \int d\mathbf{r}\;\; n(\mathbf{r})\epsilon_{xc}^{\mathrm{HEG}}(n, \nabla n)\big|_{n=n(\mathbf{r}))}$$

- Self-interaction for $i = j$ if $\delta_i \neq 0$:

$$\delta_i = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'|\phi_i(\mathbf{r})|^2 v(\mathbf{r}-\mathbf{r}')|\phi_i(\mathbf{r}')|^2 + E_{xc}[|\phi_i(\mathbf{r})|^2]$$

Orbital Functionals and the Optimised Effective Potential Method

- orbital dependent functionals: $E_{xc} = E_{xc}[\{\phi_k\}]$
- functional derivative by chain rule:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\{\phi_k\}]}{\delta n(\mathbf{r})} = \sum_k \int d\mathbf{r}' \frac{\delta E_{xc}[\{\phi_k\}]}{\delta \phi_k(\mathbf{r}')} \frac{\delta \phi_k(\mathbf{r}')}{\delta n(\mathbf{r})} + \mathrm{c.c.}$$

- chain rule applied a 2^{nd} time:

$$v_{xc}(\mathbf{r}) = \sum_k \int d\mathbf{r}' \int d\mathbf{r}'' \left(\frac{\delta E_{xc}[\{\phi_k\}]}{\delta \phi_k(\mathbf{r}')} \frac{\delta \phi_k(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} + \mathrm{c.c.} \right) \frac{\delta v_s(\mathbf{r}'')}{\delta n(\mathbf{r})}$$

  with $v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$
- inverse of the static density response function $\chi_s(\mathbf{r}, \mathbf{r}')$:

$$\chi_s^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta v_s(\mathbf{r}')}{\delta n(\mathbf{r})}$$

Optimised Effective Potential Method

- integral equation for v_{xc}:

$$\int d\mathbf{r}'\chi_s(\mathbf{r},\mathbf{r}')v_{xc}(\mathbf{r}) = \Lambda_{xc}(\mathbf{r})$$

$$= \sum_k \int d\mathbf{r}' \left(\frac{\delta E_{xc}[\{\phi_k\}]}{\delta\phi_k(\mathbf{r}')} \frac{\delta\phi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \text{c.c.} \right)$$

- using first-order perturbation theory:

$$\frac{\delta\phi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{i\neq k}^{\infty} \frac{\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r})}{\epsilon_k - \epsilon_i}\phi_k(\mathbf{r}) =: G_k(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r})$$

⇒ for response function:

$$\chi_s(\mathbf{r},\mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \frac{\delta}{\delta v_s(\mathbf{r}')} \left(\sum_k^N \phi_k^*(\mathbf{r})\phi_k(\mathbf{r}) \right)$$

$$= \sum_k^N \sum_{i\neq k}^{\infty} \frac{\phi_k^*(\mathbf{r})\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\epsilon_k - \epsilon_i} + \text{c.c.}$$

Optimised Effective Potential Method

- optimised effective potential v_{xc}:

$$\int d\mathbf{r}'\chi_s(\mathbf{r},\mathbf{r}')v_{xc}(\mathbf{r}) = \Lambda_{xc}(\mathbf{r})$$

- can also be obtained by *optimising* the potential $v_s(\mathbf{r})$ in

$$\left[-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right]\phi_k(\mathbf{r}) = \epsilon_k\phi_k(\mathbf{r})$$

  such that the orbitals $\{\phi_k\}$ minimise $E_{tot}[n,\{\phi_k\}]$, i.e. that

$$\left.\frac{\delta E_{tot}}{\delta v_s(\mathbf{r})}\right|_{v_s=v^{\mathrm{OEP}}} = 0$$

- hence the name *optimised effective potential (OEP) method* (OPM)

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Exact-Exchange Formalism

- exchange only: $E_{xc} = E_x \quad \Rightarrow \quad E_{tot} = T + E_{ext} + E_H + E_x$
- Hartree energy:

$$E_H = \frac{1}{2} \sum_{ij}^{occ} \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}')$$

- Exchange energy:

$$E_x = -\frac{1}{2} \sum_{ij}^{occ} \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')$$

- self-interaction free!

Exact-Exchange OEP Formalism (OEPx)

- derivative:

$$\frac{\delta E_x}{\delta \phi_k(\mathbf{r}')} = f_k \sum_l f_l \phi_l(\mathbf{r}') \int d\mathbf{r} \phi_l^*(\mathbf{r}) v(\mathbf{r}-\mathbf{r}') \phi_k(\mathbf{r})$$

with $f_k = 1$ if occupied and 0 otherwise

- exchange potential:

$$v_x(\mathbf{r}) = \int d\mathbf{r}' \sum_k^{occ} \sum_j^{unocc} \left[\langle \phi_k | \Sigma_x | \phi_j \rangle \frac{\phi_j(\mathbf{r}')\phi_k(\mathbf{r}')}{\epsilon_k - \epsilon_j} + c.c. \right] \chi_s^{-1}(\mathbf{r}', \mathbf{r})$$

- Fock operator or exchange self-energy:

$$\Sigma_x(\mathbf{r}, \mathbf{r}') = -\sum_i^{occ} \phi_i(\mathbf{r}) v(\mathbf{r}-\mathbf{r}') \phi_i^*(\mathbf{r}')$$

- $v_x(\mathbf{r})$ best local potential to non-local exchange-self energy $\Sigma_x(\mathbf{r}, \mathbf{r}')$

Comparison between OEPx and Hartree-Fock

- total energy: $E_{tot}[n,\{\phi_k\}] = T[\{\phi_k\}] + E_{ext}[n] + E_H[n] + E_x[\{\phi_k\}]$
- Hartree-Fock: interacting particles
  - Hartree-Fock equation:

$$\left[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r})\right]\phi_k^{\mathrm{HF}}(\mathbf{r}) + \int d\mathbf{r}'\Sigma_x(\mathbf{r},\mathbf{r}')\phi_k^{\mathrm{HF}}(\mathbf{r}') = \epsilon_k^{\mathrm{HF}}\phi_k^{\mathrm{HF}}(\mathbf{r})$$

  - orbital decay: $\phi_k^{\mathrm{HF}}(\mathbf{r}) \xrightarrow{r\to\infty} e^{-\beta r} \quad \forall i \leq N$
- exchange-only OEP (OEPx): non-interacting particles
  - Kohn-Sham equation:

$$\left[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r})\right]\phi_k^{\mathrm{OEPx}}(\mathbf{r}) = \epsilon_k^{\mathrm{OEPx}}\phi_k^{\mathrm{OEPx}}(\mathbf{r})$$

  - orbital decay: $\phi_k^{\mathrm{OEPx}}(\mathbf{r}) \xrightarrow{r\to\infty} e^{-\beta_k r} \quad \forall \quad k$
- due to variational principle: $E_{tot}[n^{\mathrm{HF}},\{\phi_k^{\mathrm{HF}}\}] \leq E_{tot}[n^{\mathrm{OEPx}},\{\phi_k^{\mathrm{OEPx}}\}]$

Exact-Exchange Formalism with Local Correlation

- total energy: $E_{tot} = T + E_{ext} + E_H + E_x + E_c$
- Exchange energy:

$$E_x = -\frac{1}{2}\sum_{ij}^{occ}\int d\mathbf{r}\int d\mathbf{r}'\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')$$

- local LDA correlation - OEPx(cLDA):

$$E_c^{\mathrm{LDA}}[n] = \int d\mathbf{r}\;\; n(\mathbf{r})\epsilon_c^{\mathrm{HEG}}(n)\big|_{n=n(\mathbf{r}))}$$

$\epsilon_c^{\mathrm{HEG}}(n(\mathbf{r}))$: correlation energy density of the homogeneous electron gas (HEG)

- local GGA correlation - OEPx(cGGA):

$$E_c^{\mathrm{GGA}}[n] = \int d\mathbf{r}\;\; n(\mathbf{r})\epsilon_c^{\mathrm{HEG}}(n,\nabla n)\big|_{n=n(\mathbf{r}))}$$

Asymptotic Decay of v_x and v_{xc}

- exact (C. O. Almbladh and U. von Barth *Phys. Rev. B* **31**, 3231 (1985)):

$$v_x(\mathbf{r}) \xrightarrow{r\to\infty} -\frac{1}{\mathbf{r}}$$
$$v_{xc}(\mathbf{r}) \xrightarrow{r\to\infty} -\frac{\alpha}{2\mathbf{r}^4}$$

  with α the static polarisability
- OEPx:

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

- LDA:

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

  with β the exponential decay constant of the density

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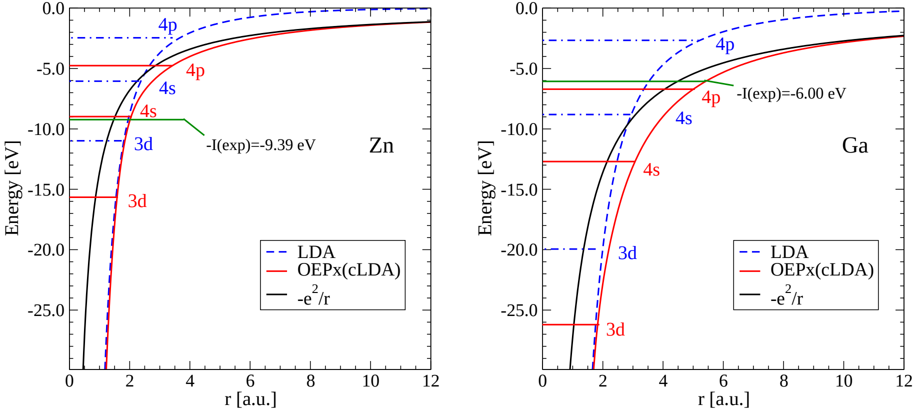
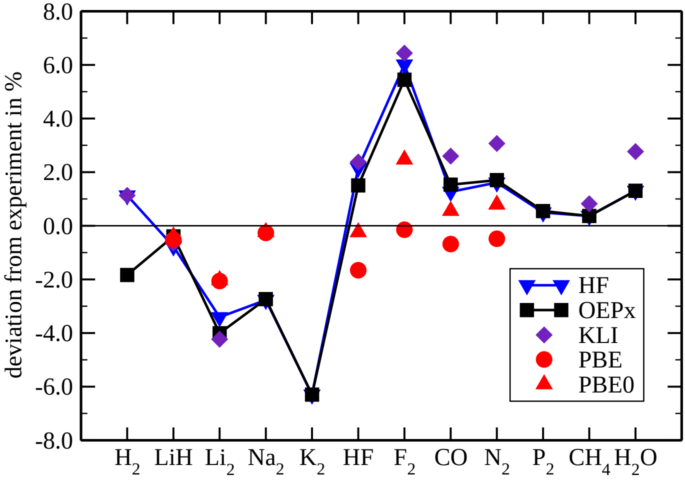
OEPx versus LDA: Zn and Ga Atoms



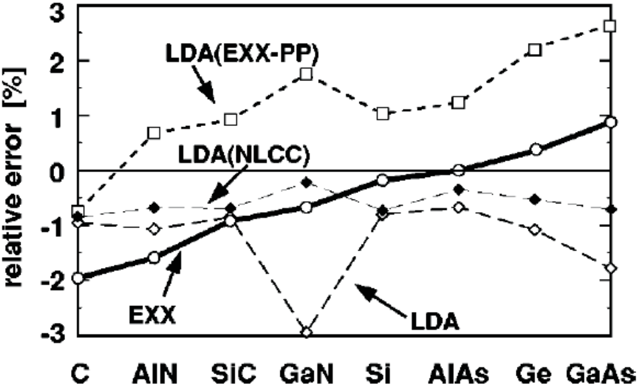
from P. Rinke *et al.* *New J. Phys.* **7**, 126 (2005). The calculations were performed with the pseudopotential generator of Moukara *et al.* J. Phys. Cond. Mat. **12** (2000)

Small Molecules - Bond Length



data from:
S. Hamel *et al.*, *J. Chem. Phys.* **116**, 8276 (2002)
J. Paier *et al.*, *J. Chem. Phys.* **122**, 234102 (2005)

Semidconductor Lattice Constant



Here EXX denotes calculations including LDA correlation and NLCC refers to non-linear core corrections.

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

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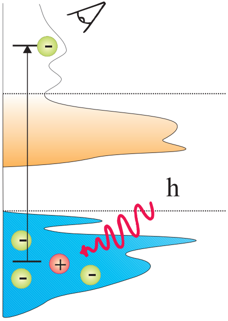
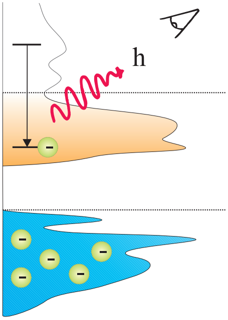
Photo-Electron Spectroscopy

Photoemission



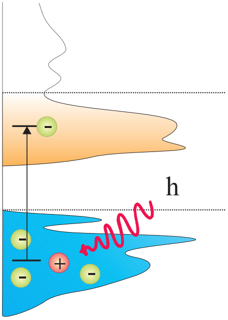
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

Photo-Electron Excitation Energies

- Photoemission
  - electron removal

    $$\psi_s(\mathbf{r}) = \langle N-1, s|\hat{\psi}(\mathbf{r})|N\rangle$$

  - removal energy

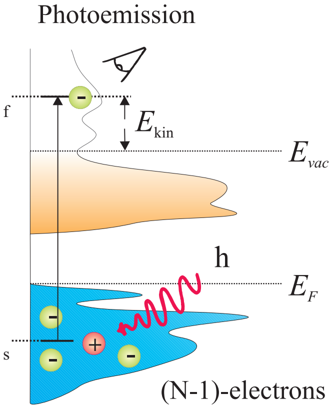
    $$\epsilon_s = E(N) - E(N-1, s)$$

- Inverse Photoemission
  - electron addition

    $$\psi_s(\mathbf{r}) = \langle N|\hat{\psi}(\mathbf{r})|N+1, s\rangle$$

  - addition energy

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



$\|N\rangle$	:	N-particle ground state
$\|N-1, s\rangle$	:	$(N-1)$-particle excited state s
$E(N, s)$	:	total energy in state s

Ionisation Potential and Electron Affinity

Ionisation potential:

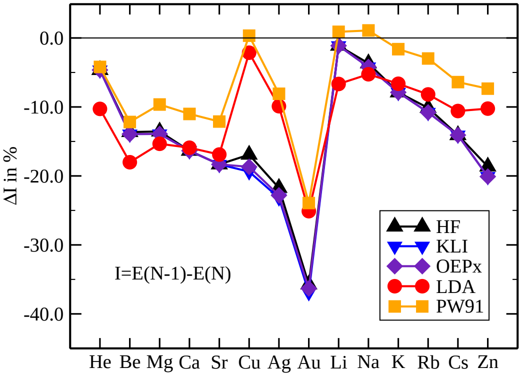
minimal energy to remove an electron

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

Electron affinity:

minimal energy to add an electron

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



E. Engel in *A Primer in DFT*, Springer 2003

Ionisation Potential - Kohn-Sham

Ionisation potential:

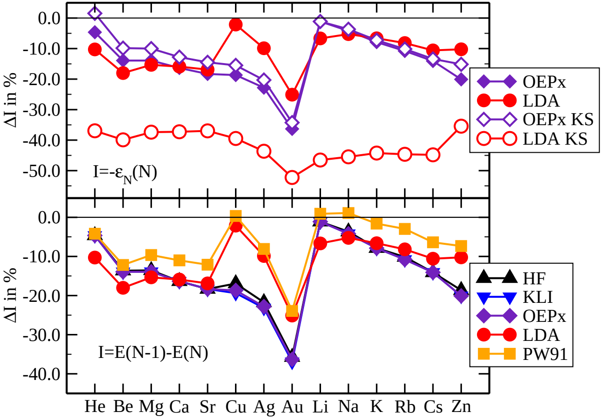
minimal energy to remove an electron

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

Kohn-Sham:

eigenvalue of the highest occupied Kohn-Sham level

$$I_{\mathrm{KS}} = -\epsilon_N(N)$$



E. Engel in *A Primer in DFT*, Springer 2003
NIST: Atomic reference data

Ionisation Potential - Small Molecules

Total Energy Difference

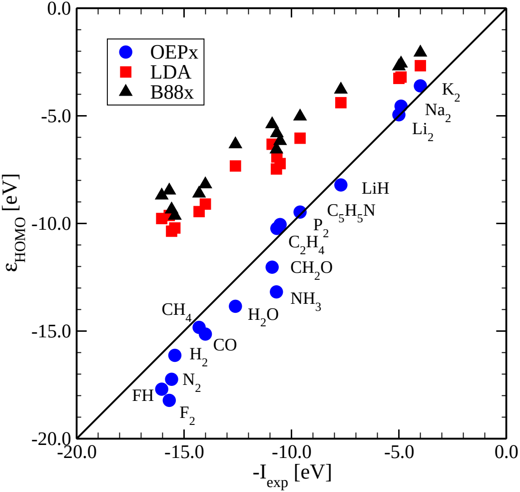
Method	deviation from exp. mean	 absolute
HF	-0.958	1.028
LSDA	0.048	0.232
PW91	-0.047	0.221
PBE	-0.105	0.235
B3LYP	0.009	0.184
PBE0	-0.064	0.199

Table: IP in eV for 86 molecules of the G3/99 test set, calculated by total energy differences, V. N. Staroverov *et al.*, *J. Chem. Phys.* **119**, 12129 (2003)

HOMO: highest occupied molecular orbital

LUMO : lowest unoccupied molecular orbital

Kohn-Sham Eigenvalue



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

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 (Janak's theorem):

$\Rightarrow$

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

- 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: $$E_{gap} = E_{gap}^{\mathrm{KS}} + \Delta_{xc}$$

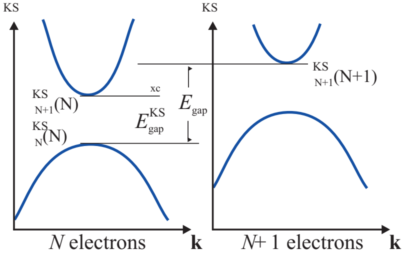


Figure: After the addition of an electron into the conduction band (right) the *xc* potential and the whole band-structure shift up by a quantity Δ_{xc}. Figure after R. W. Godby *et al.*, in *A Primer in DFT*, Springer 2003

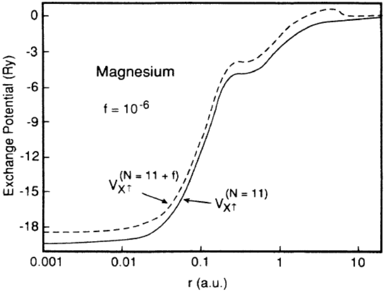


Figure: Exact-exchange potential (KLI) shifts up almost uniformly by ≈ 1 eV upon adding 10^{-6} electrons. J. B. Krieger *et al.*, Phys. Rev. A **45**, 101 (1992)

Band Gap of Semiconductors in Exact-Exchange OEP

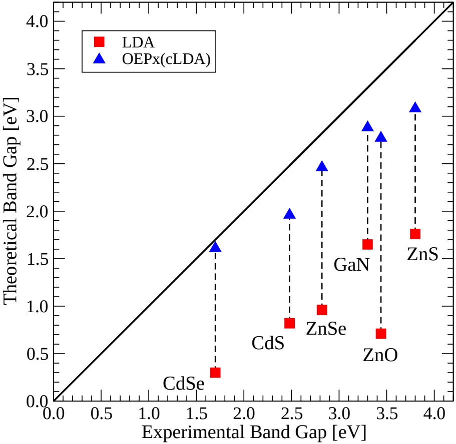
	LDA	OEPx	Exp.
Si	0.66	1.51	1.17
SiC	1.31	2.50	2.40
AlAs	1.32	2.26	2.23
AlN	3.20	5.03	5.11
C	4.17	4.92	5.50

Table: Kohn-Sham band gap for selected semiconductors (OEPx calculations include LDA correlation), W. G. Aulbur *et al.*, *Phys. Rev. B* **62**, 7121 (2000)

$$\begin{aligned}\Delta_x &= \langle CBM|\Sigma_x - v_x|CBM\rangle \\ &\quad -\langle VBM|\Sigma_x - v_x|VBM\rangle\end{aligned}$$

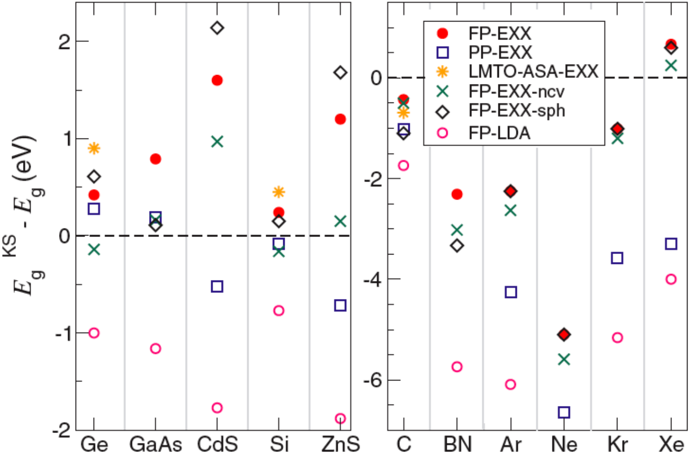
$$\Delta_x(\mathrm{Si}) = 5.48\ \mathrm{eV}$$

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



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

Exact-Exchange OEP - Pseudopotential versus All-Electron



S. Sharma *et al.* *Phys. Rev. Lett.* **95**, 136402 (2005)

Photo-Electron Excitation Energies

- Photoemission
  - electron removal

    $$\psi_s(\mathbf{r}) = \langle N-1, s|\hat{\psi}(\mathbf{r})|N\rangle$$

  - removal energy

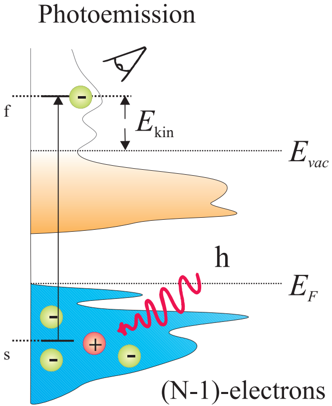
    $$\epsilon_s = E(N) - E(N-1, s)$$

- Inverse Photoemission
  - electron addition

    $$\psi_s(\mathbf{r}) = \langle N|\hat{\psi}(\mathbf{r})|N+1, s\rangle$$

  - addition energy

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



$|N\rangle$: N-particle ground state
$|N-1, s\rangle$: $(N-1)$-particle excited state s
$E(N, s)$: total energy in state s

Photo-Electron Spectroscopy and Green's Functions

- ϵ_s and $\psi_s(\mathbf{r})$ are solutions to the many-body Hamiltonian $\hat{H}$
- $\hat{H}$ can be transformed into single-particle form:

$$\hat{H}(\mathbf{r},\mathbf{r}';\epsilon) = \hat{h}_0(\mathbf{r}) + \Sigma(\mathbf{r},\mathbf{r}';\epsilon)$$

- self-enery Σ contains all electron-electron interactions
- Green's function G solution to Schrödinger equation:

$$G(\mathbf{r},\mathbf{r}';\epsilon) = \langle\mathbf{r}|[\hat{H}(\epsilon)-\epsilon]^{-1}|\mathbf{r}'\rangle = \lim_{\eta\to 0^+}\sum_s \frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\epsilon - (\epsilon_s + i\eta\,\mathrm{sgn}(E_f - \epsilon_s))}$$

- spectroscopically relevant quantity: photocurrent
- photocurrent weighted surface integral over diagonal part of the spectral function A:

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

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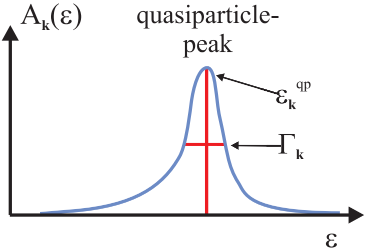
The Quasiparticle Concept

Quasiparticle:

- single-particle like excitation
-

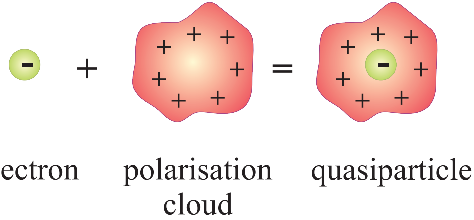
$$A_{\mathbf{k}}(\epsilon) \approx \frac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$$

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



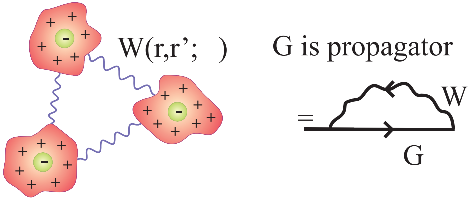
Quasiparticle:

- electron acquires polarisation cloud
- new entity



GW Approximation - Interacting Quasiparticles

GW = interacting quasiparticles

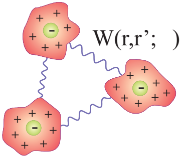


Self-Energy:

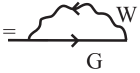
- energy response of the system that the quasiparticle experiences due to its own presence
- *GW*: $$\Sigma(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int d\epsilon' e^{i\epsilon'\delta} G(\mathbf{r},\mathbf{r}';\epsilon+\epsilon')W(\mathbf{r},\mathbf{r}';\epsilon')$$

GW Approximation - Formalism

GW = interacting quasiparticles



G is propagator

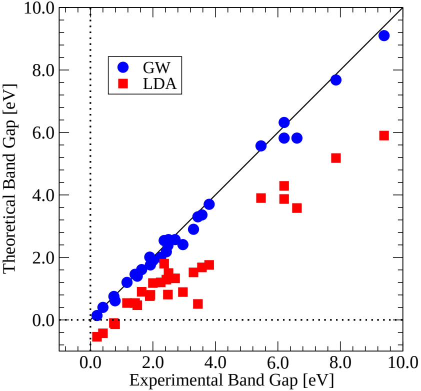


- *GW* self-energy: $\Sigma(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int d\epsilon' e^{i\epsilon'\delta} G(\mathbf{r},\mathbf{r}';\epsilon+\epsilon') W(\mathbf{r},\mathbf{r}';\epsilon')$
- Screened interaction: $W(\mathbf{r},\mathbf{r}',\epsilon) = \int d\mathbf{r}''\varepsilon^{-1}(\mathbf{r},\mathbf{r}'';\epsilon)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

GW - Merits

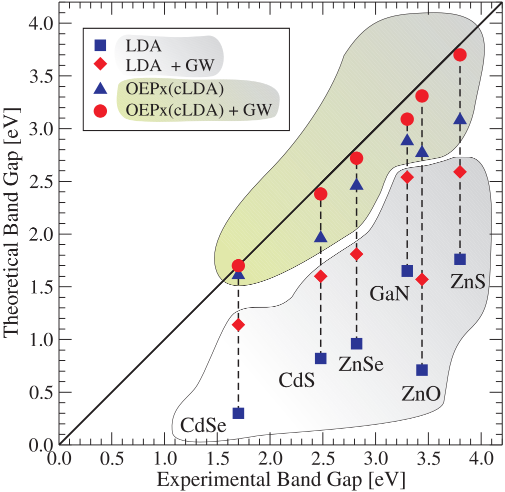
GW:

- gives accurate band gaps for many materials
- allows to calculate lifetimes
- successfully applied to
  - bulk materials
  - surfaces
  - nanotubes
  - clusters
  - defects
  - defects on surfaces



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

Quasiparticle Band Gaps



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

Overview

- Novel functionals and optimised effective potentials
- Exact-exchange
- Performance of exact-exchange
- Photo-electron spectroscopy
- Quasiparticles and the *GW* method
- DFT and many-body theory

Connection between DFT and Green's Function Theory

Many-Body Green's Function Theory:

- non-interacting electrons: Density-Functional Theory

$$G^{-1}_{\mathrm{DFT}}(\mathbf{r},\mathbf{r}';\epsilon) = [\epsilon - h_0(\mathbf{r}) - v_{xc}(\mathbf{r})]\,\delta(\mathbf{r}-\mathbf{r}')$$

- interacting electrons: self-energy (Σ_{xc})

$$G^{-1}(\mathbf{r},\mathbf{r}';\epsilon) = [\epsilon - h_0(\mathbf{r})]\,\delta(\mathbf{r}-\mathbf{r}') - \Sigma_{xc}(\mathbf{r},\mathbf{r}';\epsilon)$$

Perturbation Theory:

- adiabatic connection between non-interacting and interacting system
- Dyson equation: $G^{-1} = G^{-1}_{\mathrm{DFT}} - [\Sigma_{xc} - v_{xc}]$

Density:

$$n(\mathbf{r}) = \frac{1}{2\pi}\mathrm{Im}\int_{-\infty}^{\mu} d\epsilon\, G(\mathbf{r},\mathbf{r};\epsilon)$$

Connection between DFT and Green's Function Theory

Density condition (recap: density in DFT is exact):

$$0 = n(\mathbf{r}) - n_{\mathrm{DFT}}(\mathbf{r}) = \frac{1}{2\pi}\mathrm{Im}\int d\epsilon \left[G(\mathbf{r},\mathbf{r};\epsilon) - G_{\mathrm{DFT}}(\mathbf{r},\mathbf{r};\epsilon)\right]$$

Dyson equation:

$$\begin{aligned} & G^{-1} && = G_{\mathrm{DFT}}^{-1} - [\Sigma_{xc} - v_{xc}] \\ \Leftrightarrow \quad & G_{\mathrm{DFT}} && = G - G_{\mathrm{DFT}}\,[\Sigma_{xc} - v_{xc}]\,G \\ \Leftrightarrow \quad & G - G_{\mathrm{DFT}} && = G_{\mathrm{DFT}}\,[\Sigma_{xc} - v_{xc}]\,G \end{aligned}$$

Sham-Schlüter equation connects exact v_{xc} with Σ:

$$\iiint d\epsilon d\mathbf{r}' d\mathbf{r}''\, G_{\mathrm{DFT}}(\mathbf{r},\mathbf{r}';\epsilon)\left[\Sigma_{xc}(\mathbf{r},\mathbf{r}';\epsilon) - v_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right] G(\mathbf{r}'',\mathbf{r};\epsilon) = 0$$

Further Reading

- *A Primer in Density Functional Theory*, C. Fiolhais, F. Nogueira and M. Marques, Springer 2003 (ISBN 3-540-03083-2)
- *Many-Particle Theory*, E. K. U. Gross and E. Runge and O. Heinonen, Adam Hilger 1991
- *Quasiparticle Calculations in Solids*, W. G. Aulbur and L. Jönsson and J. W. Wilkins, Solid State Phys. : Advances in Research and Applications **54**, p1 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
- *Orbital functionals in density-functional theory: the optimized effective potential method*, R. Grabo, T. Kreibich, S. Kurth and E. K. U. Gross, in *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation* edited by V. I. Anisimov (Gordon and Breach, New York, 2000)
- *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)

Krieger-Li-Iafrate Approximation (KLI)

- OPM and OEPx are computationally demanding! Is there a more efficient way?
- Krieger-Li-Iafrate common energy denominator approximation: $(\epsilon_k - \epsilon_l) \rightarrow \Delta\bar{\epsilon}$:

$$G_k^{\mathrm{KLI}}(\mathbf{r},\mathbf{r}') \approx \sum_{l\neq k} \frac{\phi_l(\mathbf{r})\phi_l^*(\mathbf{r}')}{\Delta\bar{\epsilon}} = \frac{\delta(\mathbf{r}-\mathbf{r}') - \phi_k^*(\mathbf{r})\phi_k(\mathbf{r}')}{\Delta\bar{\epsilon}}$$

$$\chi_s^{\mathrm{KLI}}(\mathbf{r},\mathbf{r}') \approx \sum_k^N \sum_{l\neq k}^{\infty} \frac{\phi_k^*(\mathbf{r})\phi_l(\mathbf{r})\phi_l^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\Delta\bar{\epsilon}} + \mathrm{c.c.}$$

$$= \sum_k^N \frac{\phi_k^*(\mathbf{r})\phi_k(\mathbf{r}')\left[\delta(\mathbf{r}-\mathbf{r}') - \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')\right]}{\Delta\bar{\epsilon}} + \mathrm{c.c.}$$

Krieger-Li-Iafrate Approximation (KLI)

- inserting $G_k^{\mathrm{KLI}}(\mathbf{r},\mathbf{r}')$ and $\chi_s^{\mathrm{KLI}}(\mathbf{r},\mathbf{r}')$ into OPM equation:

$$v_{xc}^{\mathrm{KLI}}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})}\sum_k^N |\phi_k(\mathbf{r})|^2 \left[u_{xck}(\mathbf{r}) + \bar{v}_{xck}^{\mathrm{KLI}} - \bar{u}_{xck}\right] + \mathrm{c.c.}$$

with

$$\begin{aligned} u_{xck}(\mathbf{r}) &:= \frac{1}{\phi_k^*(\mathbf{r})}\frac{\delta E_{xc}[\{\phi_k\}]}{\delta\phi_k(\mathbf{r})} \\ \bar{v}_{xck}^{\mathrm{KLI}} &:= \int d\mathbf{r}\phi_k^*(\mathbf{r})v_{xc}^{\mathrm{KLI}}(\mathbf{r})\phi_k(\mathbf{r}) \\ \bar{u}_{xck} &:= \int d\mathbf{r}\phi_k^*(\mathbf{r})u_{xck}(\mathbf{r})\phi_k(\mathbf{r}) \end{aligned}$$

- advantage: only occupied states are needed