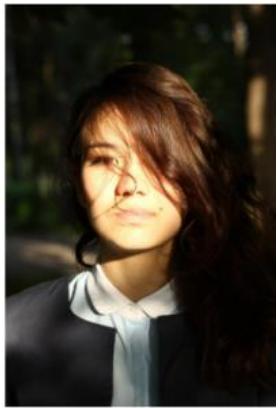


Advanced Materials Modeling

*Center for Energy Science and Technology (CEST)
Skolkovo Institute of Science and Technology
Moscow, Russia*

Introduction

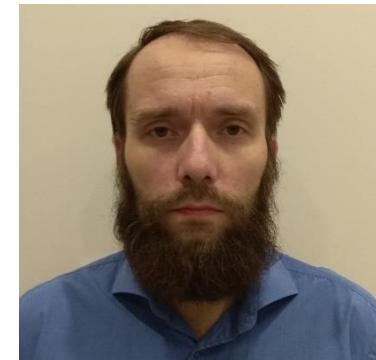
Instructors and teaching assistant



Dr. Dina Fazlizhanova



Prof. Dmitry Aksenov



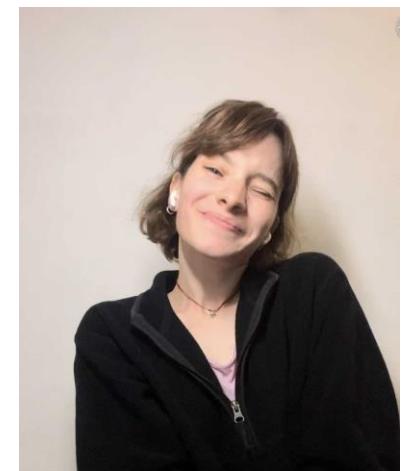
Prof. Alexander Shapeev



Dr. Ivan Novikov



**Prof. Sergey
Levchenko - lead
instructor**



TA: Ekaterina Anisimova

Course content

Schedule: <https://cms-lab.github.io/edu/AMM2025/Schedule.htm>

Adjusted/refined topics based on your interests

Discussion of your research projects

Final projects according to your interests

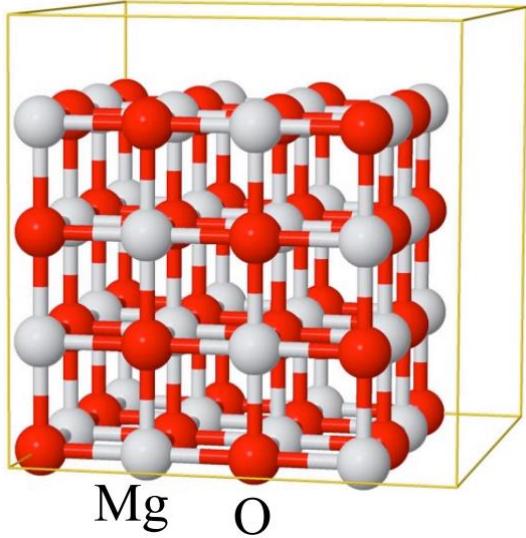
Course content: Prerequisites

- 1) Quantum mechanics**
- 2) Basic solid state theory (periodic boundary conditions, Brillouin zones, k-points)**
- 3) Basic electronic-structure concepts (many-body Schrödinger equation, Born-Oppenheimer approximation, density functional theory, Hartree-Fock approximation)**

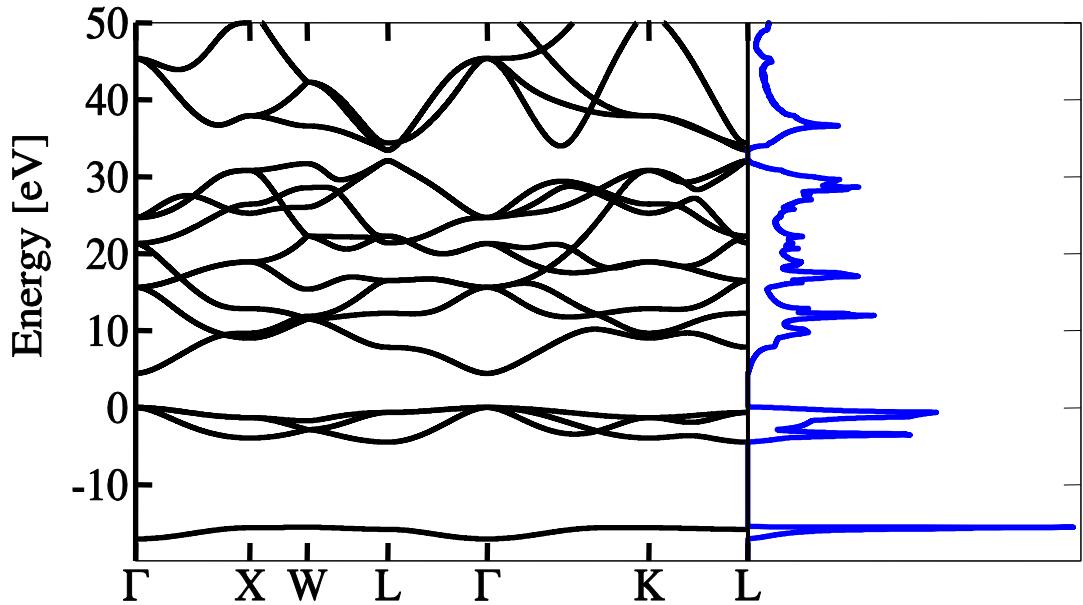
We will briefly review some of the background topics for you

Course content: What it is about

Goal: Teach advanced concepts and tools in materials modeling



Atomic structure



Electronic structure

Materials modeling:

- + Interpretation of experiments at the atomic scale
- + Prediction of unexplored materials' properties

Course content: What it is about

$$i \frac{\partial \Psi}{\partial t} = \left(-\frac{1}{2} \sum_j \frac{\partial^2}{\partial \mathbf{r}_j^2} + \frac{1}{2} \sum_{j \neq k} \frac{Q_j Q_k}{|\mathbf{r}_j - \mathbf{r}_k|} + V^{\text{ext}}(\{\mathbf{r}_j\}, t) \right) \Psi$$

non-relativistic Schrödinger equation

$\Psi(\{\mathbf{r}_i\}, \{\sigma_i\}, t)$ – wave function, depends on spatial (\mathbf{r}_i) and spin (σ_i) coordinates of ALL particles in the system, and time t

No analytic solutions for more than two particles → need approximations!

Course content: What it is about

- The Born-Oppenheimer approximation has separated the nuclear degrees of freedom, but we are still left with a many-body problem.

$$\sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I_0}^M \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_{I_0}|} \right] \Phi(\{\mathbf{r}_i\}) = E^e \Phi(\{\mathbf{r}_i\})$$

- How to simplify the problem further?

Course content: What it is about

□ The Hartree-Fock approximation

Slater determinant fulfills the Pauli principle

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{N!} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_2) \\ \dots & & & \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

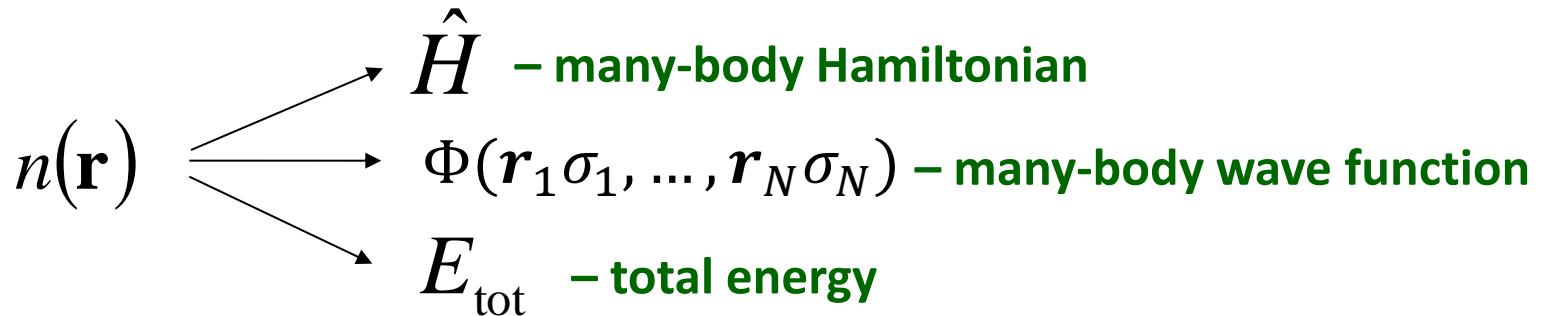
Variational principle → Hartree-Fock equations:

$$\begin{aligned} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) + e^2 \sum_j \int \frac{\psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_i(\mathbf{r}) \\ - e^2 \sum_j \int \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_j(\mathbf{r}) = E_i \psi_i(\mathbf{r}) \end{aligned}$$

No self-interaction, but also no correlation

Course content: What it is about

Density functional theory: Hohenberg-Kohn theorem

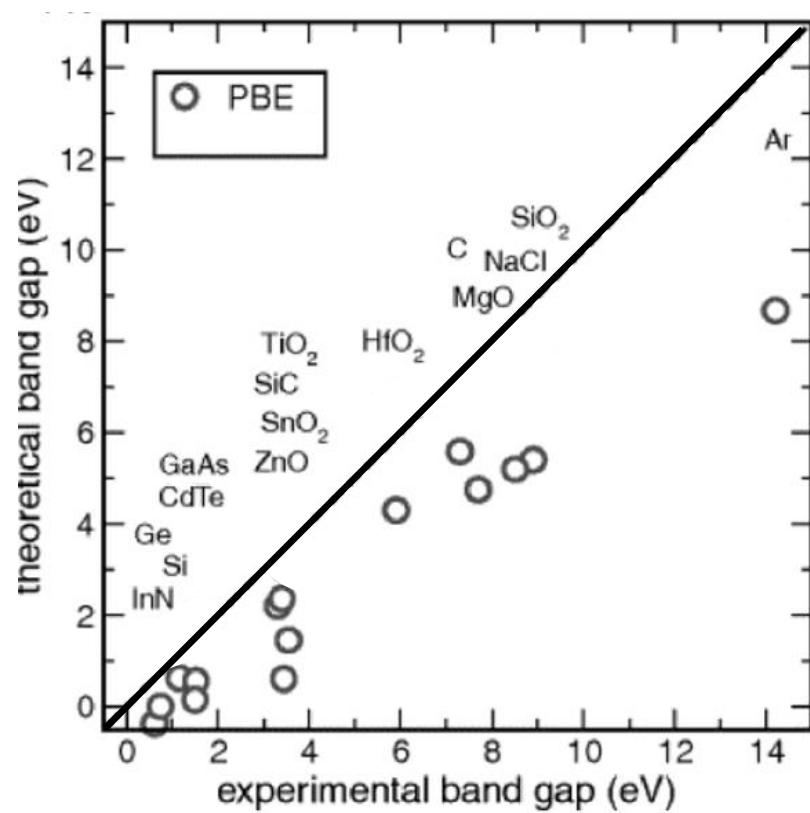
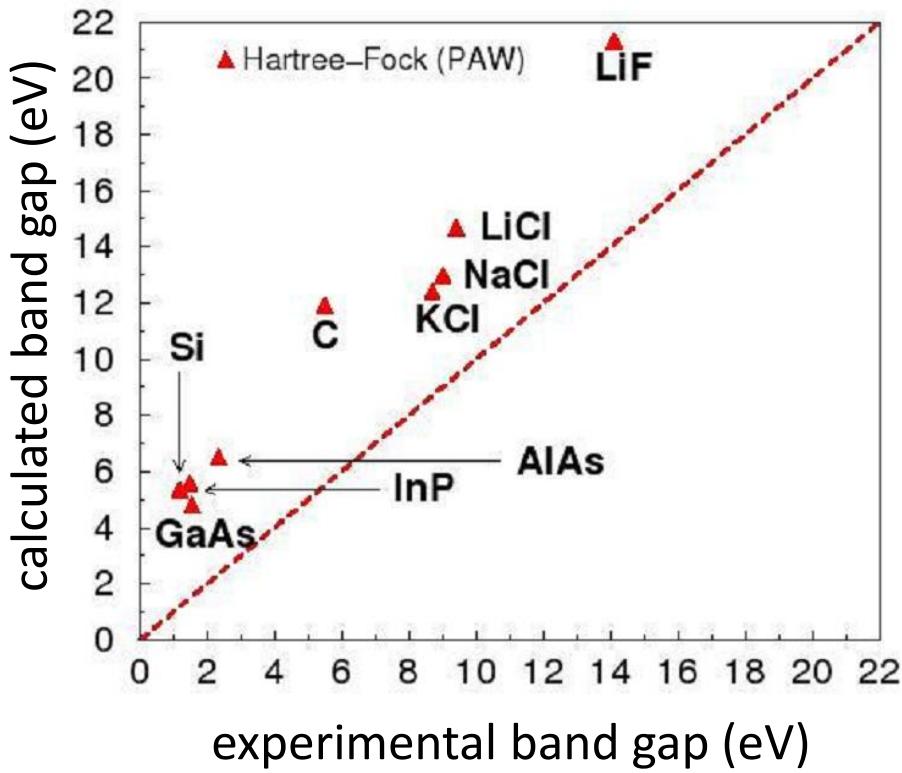


$$E_{\text{tot}} = T[n] - \sum_{I=1}^M Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d^3r + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \boxed{\frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3rd^3r'} + E_{\text{XC}}[n]$$

Standard approximations to $E_{\text{XC}}[n]$: Local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA

Correlation is included (approximately), but also self-interaction

Course content: What it is about



What can we do?

Course content: What it is about

Advanced topics:

Hybrid functionals, many-body perturbation theory (GW , Bethe-Salpeter equation)

Density functional perturbation theory (phonons, electron-phonon coupling)

Optical spectroscopy

Course content: What it is about

Advanced topics:

A DFT calculation corresponds to $T = 0$ K and $p = 0$ atm. We explain how to go beyond this approximation (molecular dynamics, *ab initio* atomistic thermodynamics, kinetic Monte Carlo)

Bridging materials gap (*ab initio* modeling versus real materials) → use data analysis and machine learning

Assignments and assessment

1) Homeworks: based on the lectures, multiple-choice or free question-and-answer format.

Assessment: number of correctly answered questions

2) Lab reports: based on computational labs.

Assessment: Task completion, understanding, writing

3) Quizzes: based on the lectures, simple questions on the discussed topics

Assesment: number of correct answers

4) Progress reports on your final projects.

Assessment: Quality of presentation, understanding of the subject

5) Final project (<https://cms-lab.github.io/edu/AMM2024/FinalProject.htm>).

Assessment: Scientific quality, quality of presentation, answering questions

First homework: Introduce yourself

Homework assignment:

[https://cms-](https://cms-lab.github.io/edu/AMM2025/homeworks/Homework1.pdf)

[lab.github.io/edu/AMM2025/homeworks/Homework1.pdf](https://cms-lab.github.io/edu/AMM2025/homeworks/Homework1.pdf)

1. Give a 10-min presentation of your research project most relevant to the course using the following plan:
 - Introduce yourself (1 min)
 - Why are you interested in the course (1 min)
 - Present your most relevant research projects (3-5 min)
 - Speculate on possible final project (1-3 min)

2. Look at the list of lectures (<https://cms-lab.github.io/edu/AMM2025/Schedule.htm>) and mark the most interesting from your point of view.

Due date: Friday 4.04 at 12:30 (presentations)

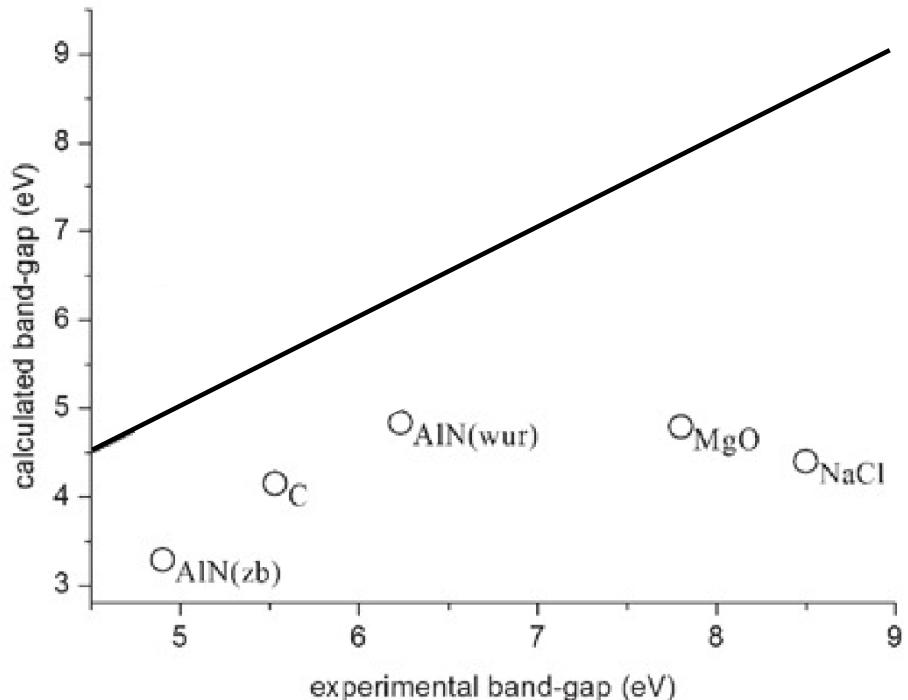
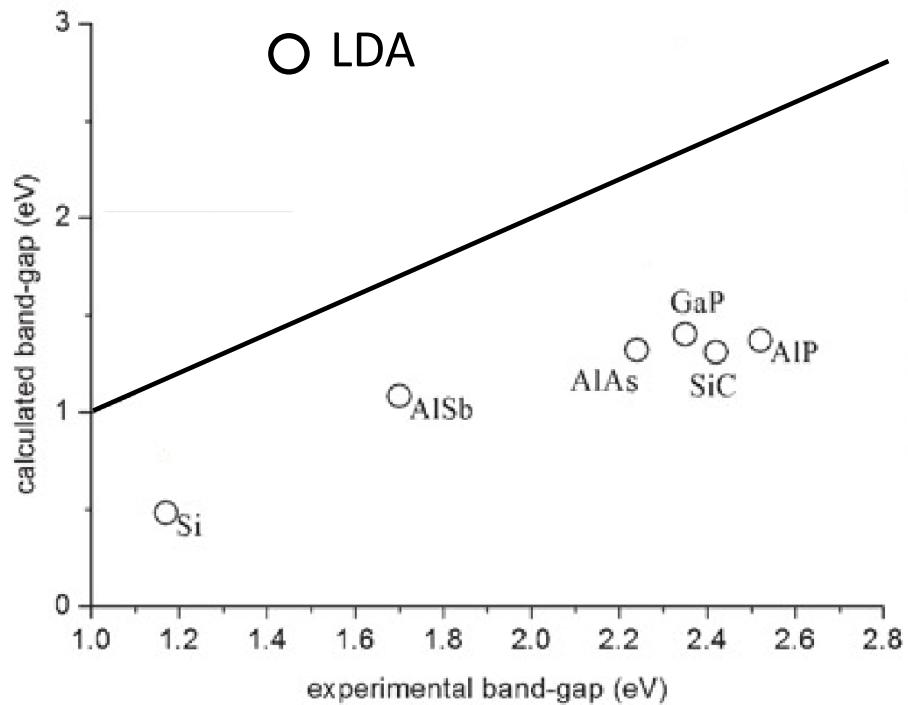
Office hours

No fixed office hours

Simply send me and Ekaterina an email if you have a question or want to discuss something, we will answer by email or arrange an online or offline meeting

Lecture 1: Advanced DFT for solids 1

DFT approximations: What is missing?



Philipsen and Baerends, Phys. Rev. B, 54, p. 5326 (1996)

We do not know the exact exchange-correlation functional
but we can determine some of its properties!

Exact DFT functional properties: $E(N)$

□ Fractional occupations

Time average → statistical mixture of *pure states*:

Ψ_1 , probability p_1 ; Ψ_2 , probability p_2 ; etc. - ensemble Γ

Exact DFT functional properties: $E(N)$

□ Fractional occupations

Time average → statistical mixture of *pure states*:

Ψ_1 , probability p_1 ; Ψ_2 , probability p_2 ; etc. - ensemble Γ

$$\langle \hat{O} \rangle_{\Gamma} = \sum_i p_i \langle \Psi_i | \hat{O} | \Psi_i \rangle \text{ - for any operator } \hat{O}$$

$$E[n] = \min_{\Gamma \rightarrow n} \langle \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} + \hat{V}_{xc} \rangle_{\Gamma} \text{ [minimize over all } \Gamma \text{ giving the same } n(\mathbf{r})]$$

Exact DFT functional properties: $E(N)$

□ Fractional occupations

Time average → statistical mixture of *pure states*:

Ψ_1 , probability p_1 ; Ψ_2 , probability p_2 ; etc. - ensemble Γ

$$\langle \hat{O} \rangle_{\Gamma} = \sum_i p_i \langle \Psi_i | \hat{O} | \Psi_i \rangle \text{ - for any operator } \hat{O}$$

$$E[n] = \min_{\Gamma \rightarrow n} \langle \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} + \hat{V}_{xc} \rangle_{\Gamma} \text{ [minimize over all } \Gamma \text{ giving the same } n(\mathbf{r})]$$

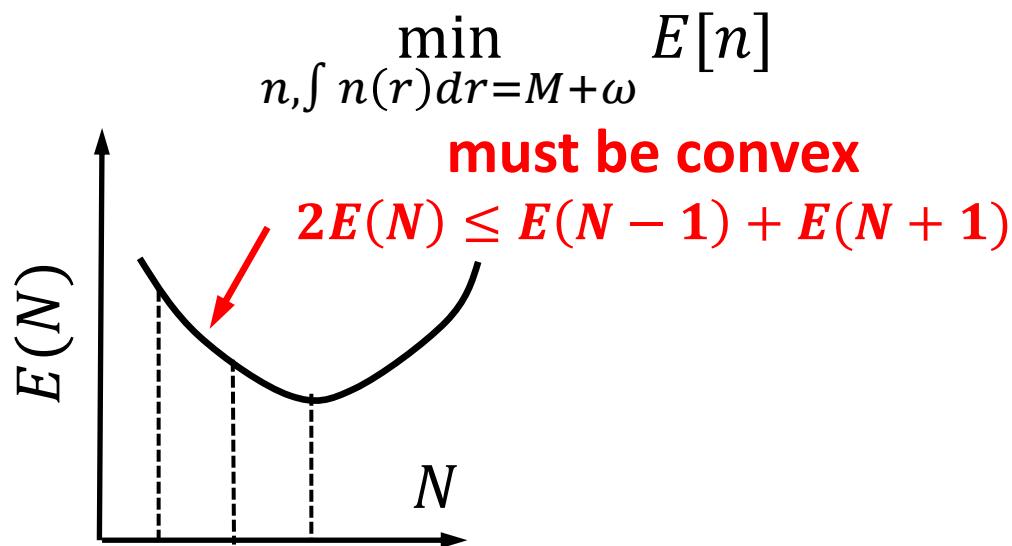
Fractional number of electrons - ensemble of pure states with different integer charges:

$$p_1 M + p_2(M-1) + p_3(M+1) + \dots = M + \omega, 0 < \omega < 1,$$
$$E[n] = p_1 E_M + p_2 E_{M-1} + p_3 E_{M+1} + \dots, \quad p_1 + p_2 + \dots = 1$$

Exact DFT functional properties: $E(N)$

□ Fractional occupations

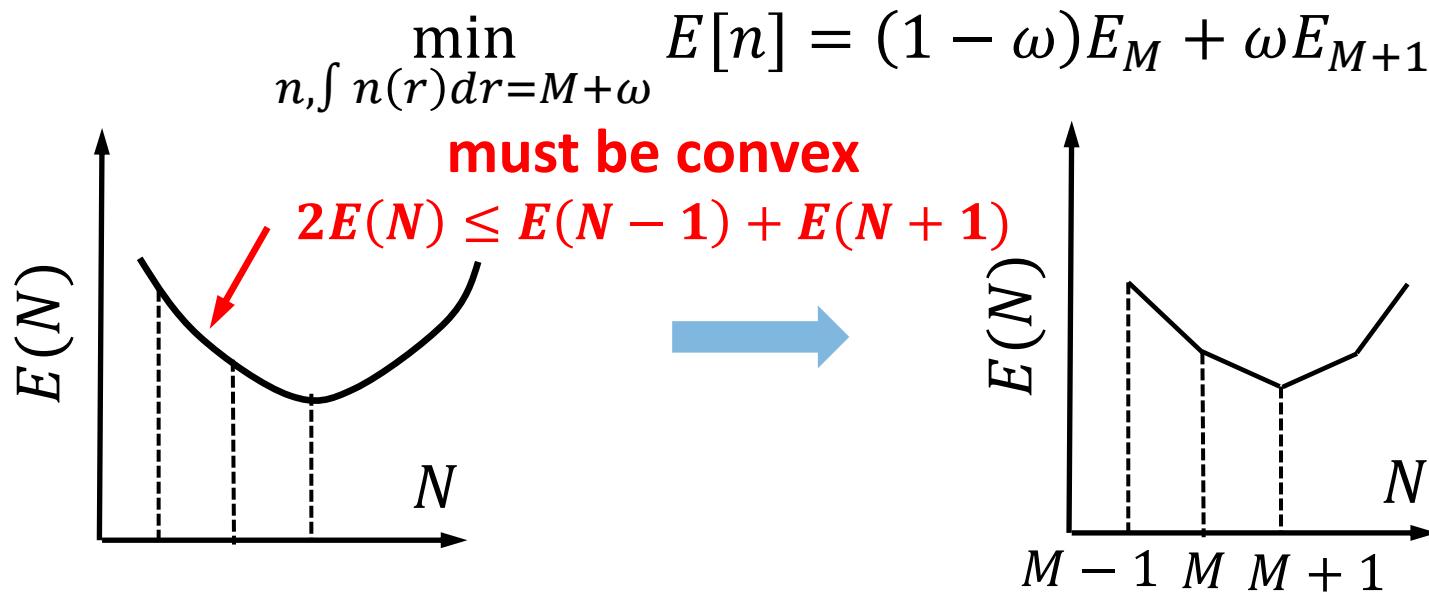
$$p_1M + p_2(M - 1) + p_3(M + 1) + \dots = M + \omega, 0 < \omega < 1,$$
$$E[n] = p_1E_M + p_2E_{M-1} + p_3E_{M+1} + \dots, \quad p_1 + p_2 + \dots = 1$$



Exact DFT functional properties: $E(N)$

□ Fractional occupations

$$p_1M + p_2(M - 1) + p_3(M + 1) + \dots = M + \omega, 0 < \omega < 1,$$
$$E[n] = p_1E_M + p_2E_{M-1} + p_3E_{M+1} + \dots, \quad p_1 + p_2 + \dots = 1$$



The exact energy changes piece-wise linearly with N

Perdew *et al.*, Phys. Rev. Lett. 49, 1691 (1982)

Fractional occupations

□ Fractional occupations in Kohn-Sham formalism

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

sum over occupied states

$$E_{\text{KS}}(\{\psi_i\}, \{f_i\}) = \sum_i t_i + E_C[n] + E_{\text{XC}}[n],$$

kinetic energy

Coulomb energy

exchange-correlation
energy

$$t_i = -\frac{1}{2} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

$$\begin{aligned} & \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' \\ & - \int d^3r \sum_J \frac{Z_J}{|\mathbf{r}-\mathbf{R}_J|} n(\mathbf{r}) \end{aligned}$$

Fractional occupations

□ Fractional occupations in Kohn-Sham formalism

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad \text{sum over occupied states}$$

$$E_{\text{KS}}(\{\psi_i\}, \{f_i\}) = \sum_i t_i + E_C[n] + E_{\text{XC}}[n], \quad t_i = -\frac{1}{2} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

Let us define: sum over ALL states

$$n(\mathbf{r}) = \sum_i \textcolor{red}{f}_i |\psi_i(\mathbf{r})|^2, \quad \sum_{i=1}^{\infty} f_i = N, \quad 0 \leq f_i \leq 1$$

$$\tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i \textcolor{red}{f}_i t_i + E_C[n] + E_{\text{XC}}[n]$$

Fractional occupations

□ Fractional occupations in Kohn-Sham formalism

Let us define:

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \sum_{i=1}^{\infty} f_i = N, 0 \leq f_i \leq 1$$

$$\tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i f_i t_i + E_C[n] + E_{XC}[n]$$

Lagrangian:

$$Q[\{\psi_i\}, \{f_i\}] = \tilde{E}(\{\psi_i\}, \{f_i\}) + \sum_i \lambda_i \left(\int |\psi_i|^2 d\mathbf{r} - 1 \right) - \mu (\sum_i f_i - N),$$

$$\min_{\psi_i, f_i} Q \rightarrow n, \tilde{E}[n], \psi_i$$

Fractional occupations

□ Fractional occupations in Kohn-Sham formalism

Let us define:

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \sum_{i=1}^{\infty} f_i = N, 0 \leq f_i \leq 1$$

$$\tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i f_i t_i + E_C[n] + E_{XC}[n]$$

Lagrangian:

$$Q[\{\psi_i\}, \{f_i\}] = \tilde{E}(\{\psi_i\}, \{f_i\}) + \sum_i \lambda_i \left(\int |\psi_i|^2 d\mathbf{r} - 1 \right) - \mu (\sum_i f_i - N),$$

$\frac{\delta Q}{\delta \psi_i^*} = 0 \rightarrow$ Kohn-Sham equations by choosing $\lambda_i = f_i \varepsilon_i$

$$-\frac{1}{2} \nabla^2 \psi_i + \left(\int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_J \frac{Z_J}{|\mathbf{r}-\mathbf{R}_J|} \right) \psi_i + \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \psi_i = \varepsilon_i \psi_i$$

Fractional occupations

□ Fractional occupations in Kohn-Sham formalism

Let us define:

$$n(\mathbf{r}) = \sum_i \mathbf{f}_i |\psi_i(\mathbf{r})|^2, \sum_{i=1}^{\infty} f_i = N, 0 \leq f_i \leq 1$$

$$\tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i \mathbf{f}_i t_i + E_C[n] + E_{XC}[n]$$

Lagrangian:

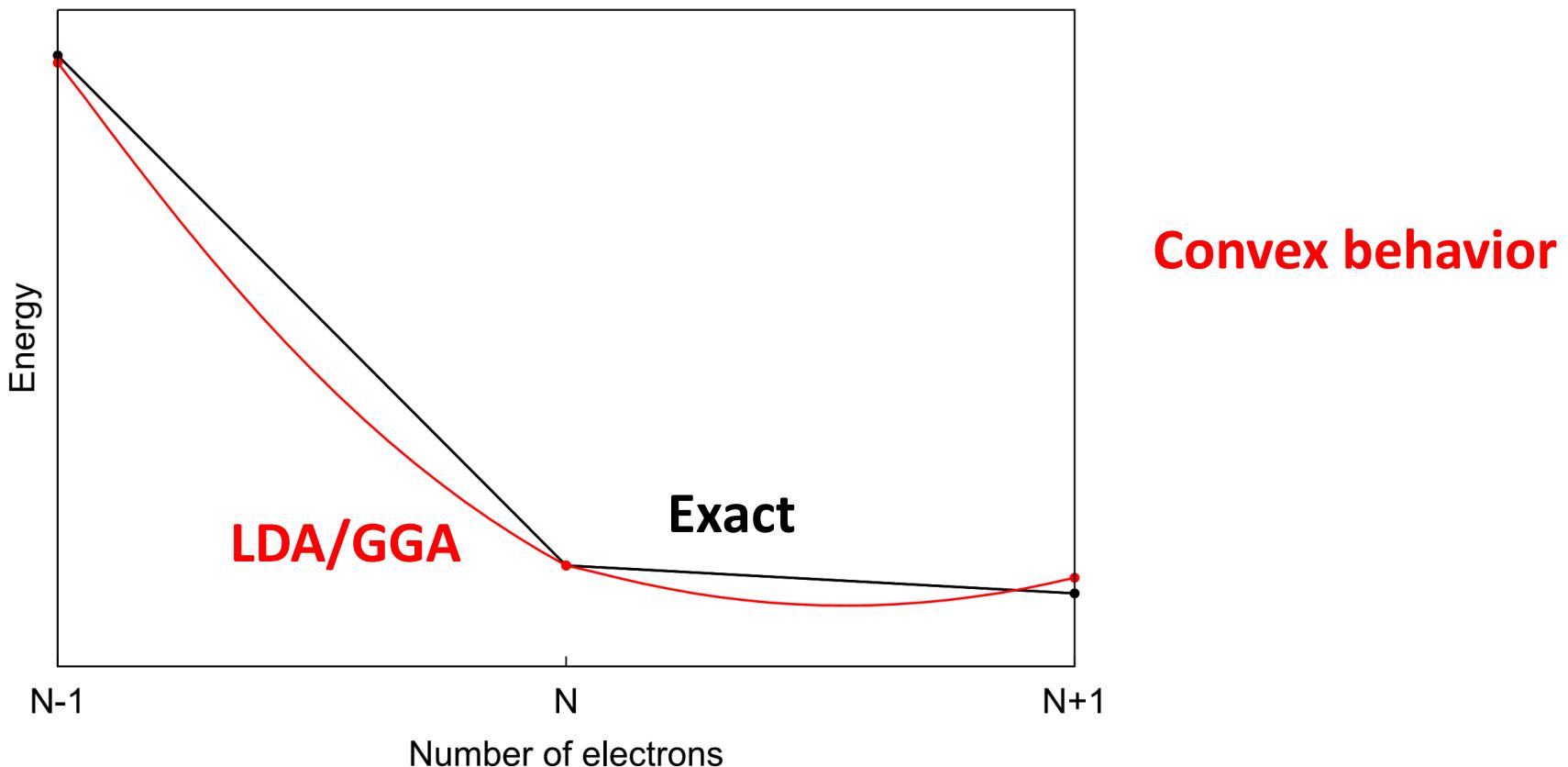
$$Q[\{\psi_i\}, \{f_i\}] = \tilde{E}(\{\psi_i\}, \{f_i\}) + \sum_i \lambda_i (\int |\psi_i|^2 d\mathbf{r} - 1) - \mu (\sum_i f_i - N),$$

$$\frac{\partial Q}{\partial f_i} = 0 \rightarrow \text{set } f_i = \cos^2 \theta_i \rightarrow \frac{\partial Q}{\partial \theta_i} = - \left(\frac{\partial \tilde{E}}{\partial f_i} - \mu \right) \sin 2\theta_i = 0$$

$$\frac{\partial \tilde{E}}{\partial f_i} = \mu, 0 \leq f_i \leq 1, \quad \frac{\partial \tilde{E}}{\partial f_i} \neq \mu, f_i = 1, \quad \frac{\partial \tilde{E}}{\partial f_i} \neq \mu, f_i = 0$$

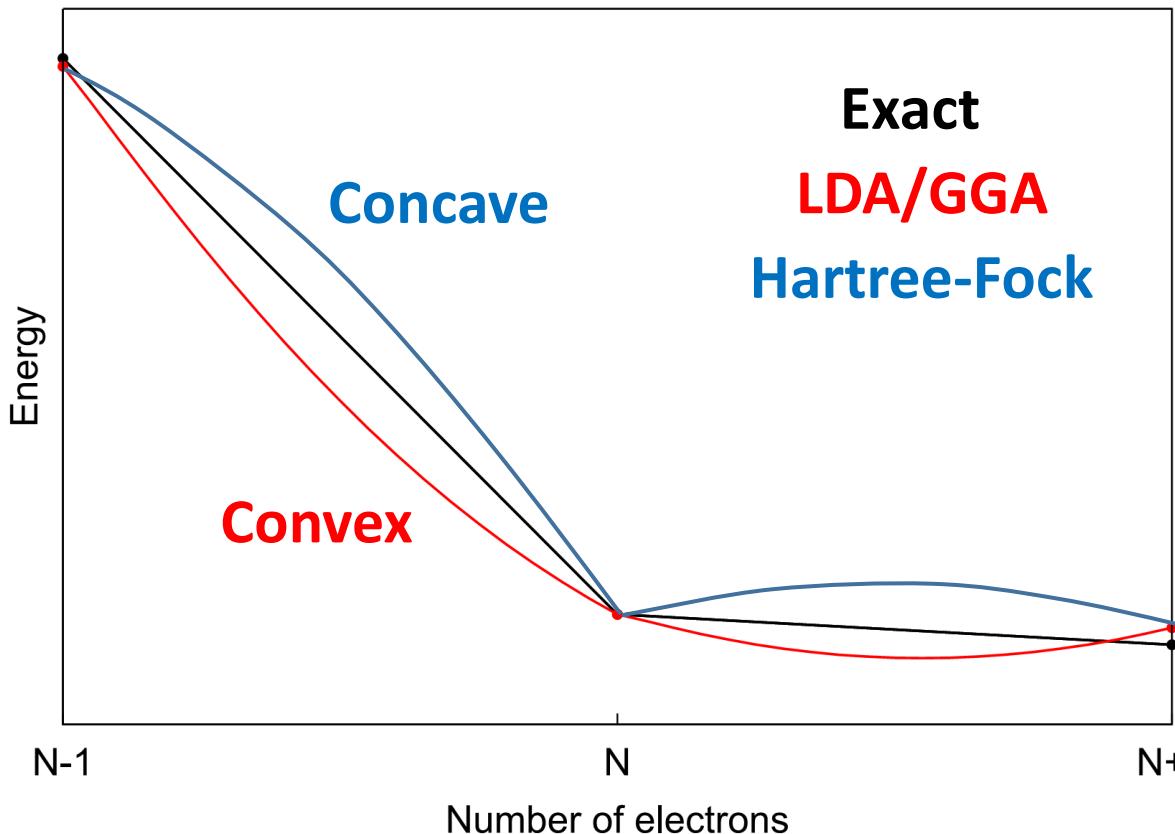
Approximate functionals

- Dependence $E(N)$ for an approximate functional:



Approximate functionals

□ Dependence $E(N)$ for an approximate functional:

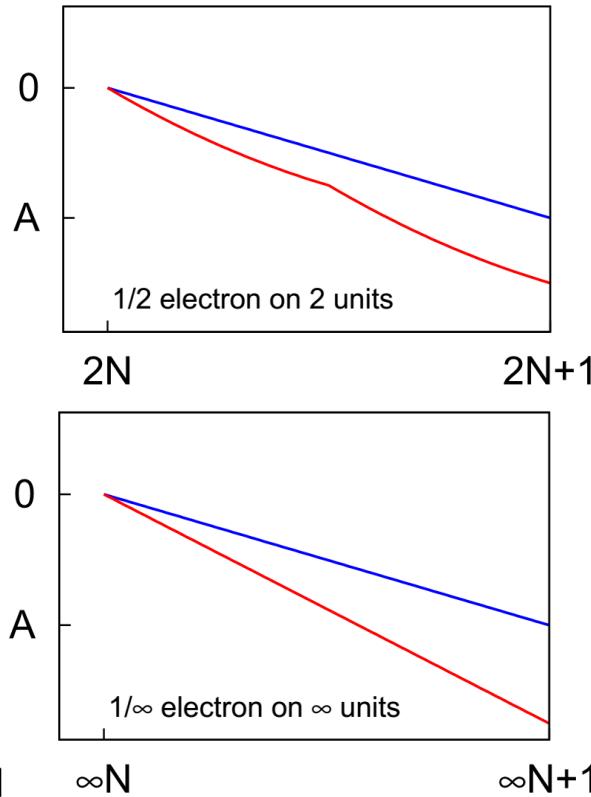
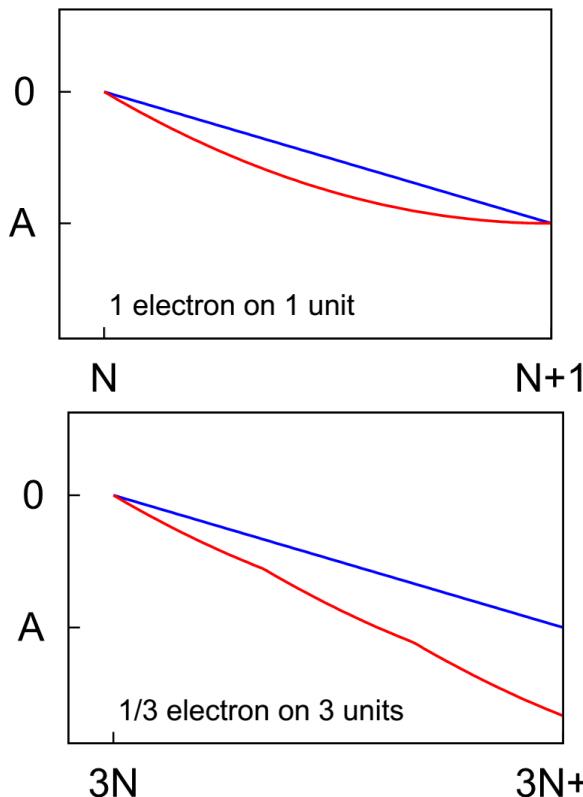


Hartree-Fock is a functional within generalized Kohn-Sham scheme: $E = E[\{\psi\}]$

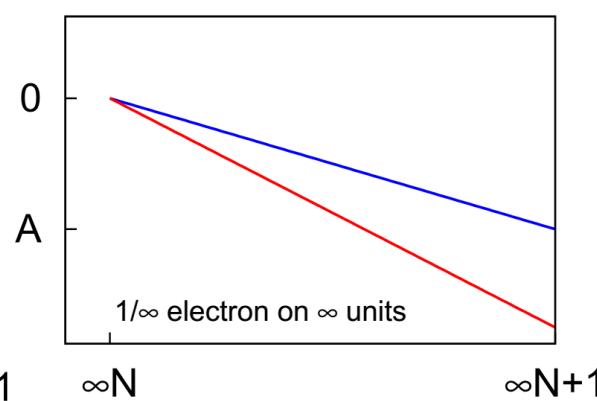
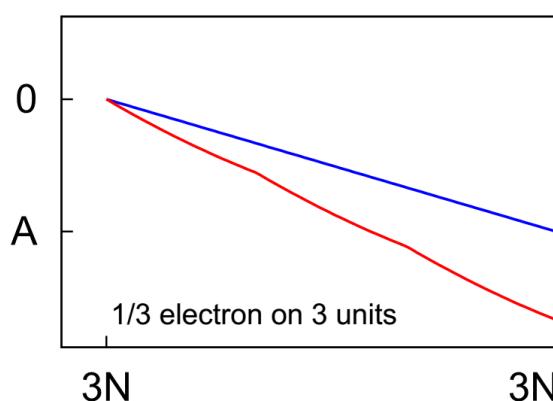
More “DFT-like”: Optimized effective potentials (local potentials that approximate the non-local HF exchange)
- numerically complex and computationally expensive

Approximate functionals

□ Connection between the self-interaction (delocalization) error (SIE) and the convex behavior



Dependence $E(N)$ for
1, 2, 3, and ∞
separated molecules



$E^{LDA/GGA}(N)$ is convex
because of SIE

Band gap problem

□ Observable gap:

$$E_{gap}^{obs} = (E(M+1) - E(M)) - (E(M) - E(M-1))$$

□ Kohn-Sham gap:

$$E_{gap}^{KS} = \varepsilon_{LUMO}^M - \varepsilon_{HOMO}^M$$

Are they the same?

Janak's theorem

□ Fractional occupations in Kohn-Sham formalism

Let us define:

$$n(\mathbf{r}) = \sum_i \mathbf{f}_i |\psi_i(\mathbf{r})|^2, \sum_{i=1}^{\infty} f_i = N, 0 \leq f_i \leq 1$$

$$\tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i \mathbf{f}_i t_i + E_C[n] + E_{XC}[n]$$

Lagrangian:

$$Q[\{\psi_i\}, \{f_i\}] = \tilde{E}(\{\psi_i\}, \{f_i\}) + \sum_i \lambda_i (\int |\psi_i|^2 d\mathbf{r} - 1) - \mu (\sum_i f_i - N),$$

$$\frac{\partial Q}{\partial f_i} = 0 \rightarrow \text{set } f_i = \cos^2 \theta_i \rightarrow \frac{\partial Q}{\partial \theta_i} = - \left(\frac{\partial \tilde{E}}{\partial f_i} - \mu \right) \sin 2\theta_i = 0$$

$$\frac{\partial \tilde{E}}{\partial f_i} = \mu, 0 \leq f_i \leq 1, \quad \frac{\partial \tilde{E}}{\partial f_i} \neq \mu, f_i = 1, \quad \frac{\partial \tilde{E}}{\partial f_i} \neq \mu, f_i = 0$$

Janak's theorem

□ Fractional occupations in Kohn-Sham formalism

Derivative w.r.t. f_i :

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \quad \tilde{E}(\{\psi_i\}, \{f_i\}) = \sum_i f_i t_i + E_C[n] + E_{XC}[n]$$

$$E_C[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' - \int d^3r \sum_J \frac{Z_J}{|\mathbf{r}-\mathbf{R}_J|} n(\mathbf{r})$$

$$-\frac{1}{2} \nabla^2 \psi_i + \left(\int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_J \frac{Z_J}{|\mathbf{r}-\mathbf{R}_J|} \right) \psi_i + \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \psi_i = \varepsilon_i \psi_i$$

$$\frac{\partial \tilde{E}}{\partial f_i} = t_i + \int d^3r |\psi_i(\mathbf{r})|^2 V_C(\mathbf{r}) + \int d^3r \frac{\delta E_{XC}}{\delta n(\mathbf{r})} |\psi_i|^2 = \varepsilon_i = \frac{d\tilde{E}}{df_i}$$

from KS equations

from stationary condition
with respect to ψ_i^*

Janak's theorem

□ Fractional occupations in Kohn-Sham formalism

Lagrangian:

$$Q[\{\psi_i\}, \{f_i\}] = \tilde{E}(\{\psi_i\}, \{f_i\}) + \sum_i \lambda_i \left(\int |\psi_i|^2 dr - 1 \right) - \mu (\sum_i f_i - N),$$

$$\frac{\partial Q}{\partial f_i} = 0 \rightarrow \text{set } f_i = \cos^2 \theta_i \rightarrow \frac{\partial Q}{\partial \theta_i} = -(\varepsilon_i - \mu) \sin 2\theta_i = 0$$

Three cases:

$$\varepsilon_i = \mu, 0 \leq f_i \leq 1$$

$$\varepsilon_i \neq \mu, f_i = 1$$

$$\varepsilon_i \neq \mu, f_i = 0$$

Note: There can be additional constraints on f_i
(electronic smearing for metals, finite temperature)

Janak's theorem

□ Fractional occupations in Kohn-Sham formalism

Janak's theorem:

$$\frac{dE[n]}{df_i} = \varepsilon_i$$

Also: $E[n]$ is minimized when the fractional occupation is in ε_{HOMO} , and

$$\left. \frac{dE[n]}{dN} \right|_{M-\delta} = \frac{dE[n]}{df_{HOMO}} = \varepsilon_{HOMO} = \mu(M - \delta)$$

From the piece-wise linear behavior of the exact functional $\rightarrow \varepsilon_{HOMO}(M - \delta) = \text{const}$ for $0 < \delta < 1$ for exact KS potential (IP theorem)

What's up with the band gap?

Band gap problem

□ Observable gap:

$$E_{gap}^{obs} = (E(M+1) - E(M)) - (E(M) - E(M-1))$$

□ From Janak's theorem and the exact functional condition:

$$E(M+1) - E(M) = \int_0^1 \varepsilon_{M+1}(f) df = \varepsilon_{M+1}^{M+1} = \varepsilon_{HOMO}^{M+1}$$

$$E(M) - E(M-1) = \int_0^1 \varepsilon_M(f) df = \varepsilon_M^M = \varepsilon_{HOMO}^M$$



$$E_{gap}^{obs} = \varepsilon_{HOMO}^{M+1} - \varepsilon_{HOMO}^M$$

BUT!

$$E_{gap}^{KS} = \varepsilon_{LUMO}^{\textcolor{red}{M}} - \varepsilon_{HOMO}^M$$

Band gap problem

□ Derivative discontinuity

$$E_{gap}^{obs} - E_{gap}^{KS} = \varepsilon_{HOMO}^{M+1} - \varepsilon_{LUMO}^M = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \Big|_{M+\delta} - \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \Big|_{M-\delta}$$

For the exact functional, the KS gap is not the same as the observable gap!

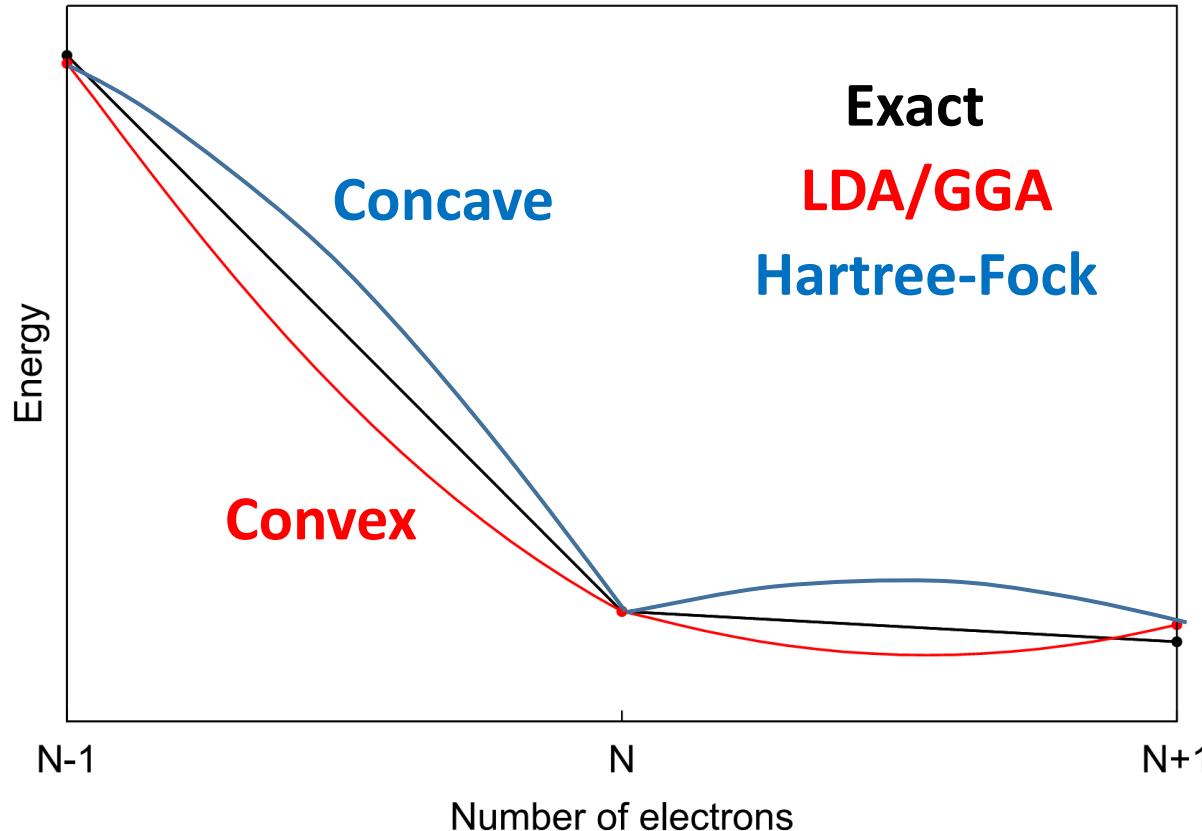
Thus, there are TWO problems:

- 1) non-straight-line behavior of the total energy with number of electrons for approximate functionals
- 2) $E_{gap}^{obs} \neq E_{gap}^{KS}$ for exact functional, and we do not know how large the difference is

Observation: improving $E(N)$ behavior improves the KS gaps compared to experiment

Band gap problem

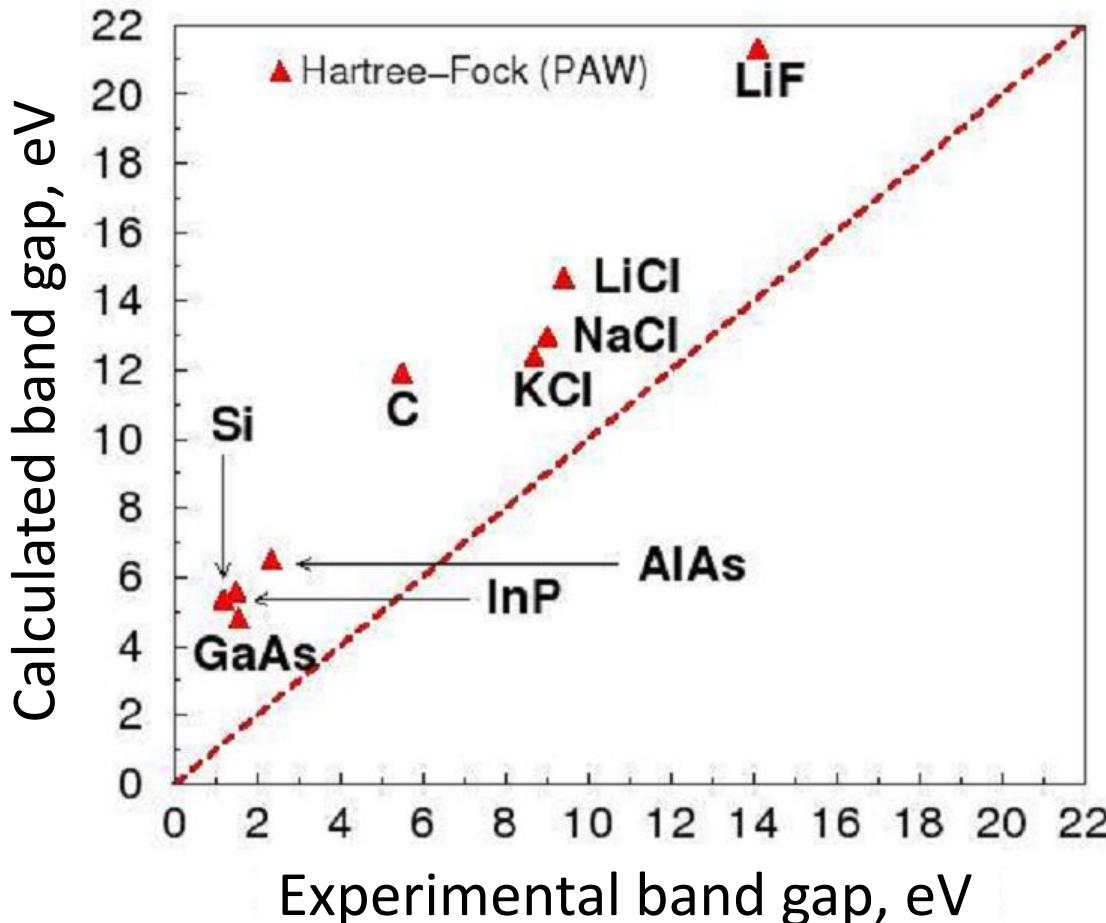
□ Generalized Kohn-Sham (GKS):



Hartree-Fock “overcorrects” the discontinuity (correlation part is missing)

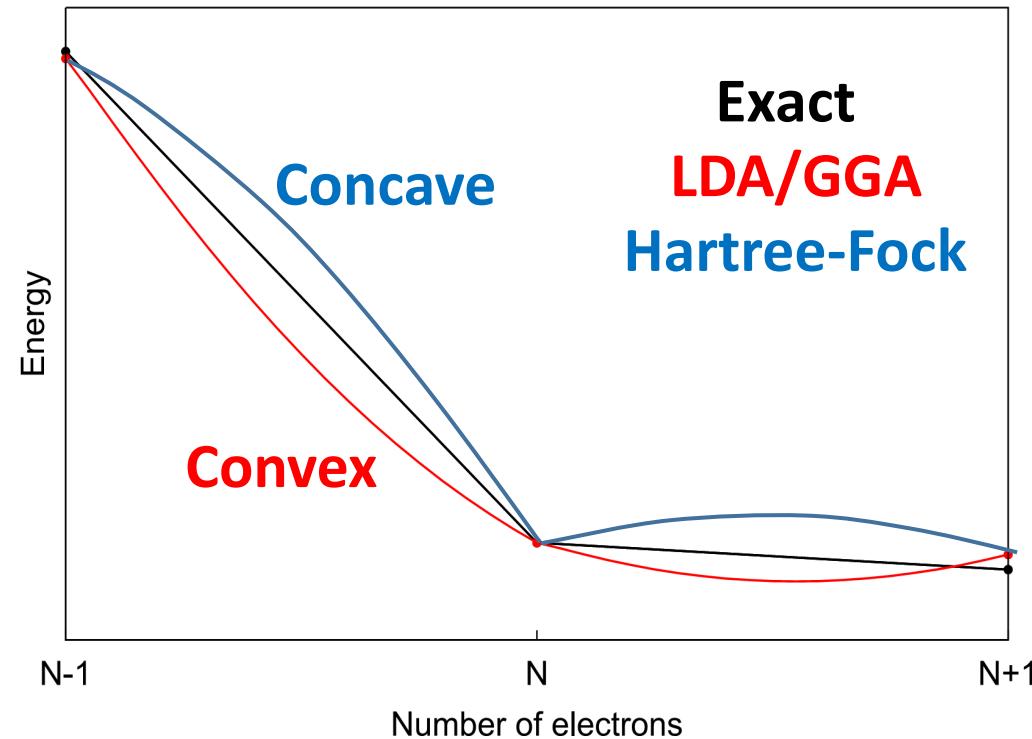
Band gap problem

- Hartree-Fock is self-interaction free, but...



Band gap problem

□ Hybrid functionals



Idea: combine HF with GGA to reduce the self-interaction error:

$$E[\{\psi\}] = \alpha E_X^{HF} + (1 - \alpha) E_X^{GGA} + E_C^{GGA}, \quad 0 < \alpha \leq 1$$

Approximate $E(N)$ is not exactly straight and may have a different slope: some errors remain

Hybrid functionals

□ **Hybrid functionals** $E = \alpha E_X^{HF} + (1 - \alpha) E_X^{LDA/GGA} + E_C^{LDA/GGA}$

The mixing parameter α depends on the choice of
(semi)local exchange/correlation

$E^{PBE0} = 0.25E_X^{HF}(\{\psi^{KS}\}) + 0.75E_X^{PBE} + E_C^{PBE}$ (choice of α is based on perturbation theory (MP4))

Perdew, Ernzerhof, and Burke, J. Chem. Phys. 105, 9982 (1996)

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Perdew, Ernzerhof, and Burke, J. Chem. Phys. 105, 9982 (1996)

There can be other parameters

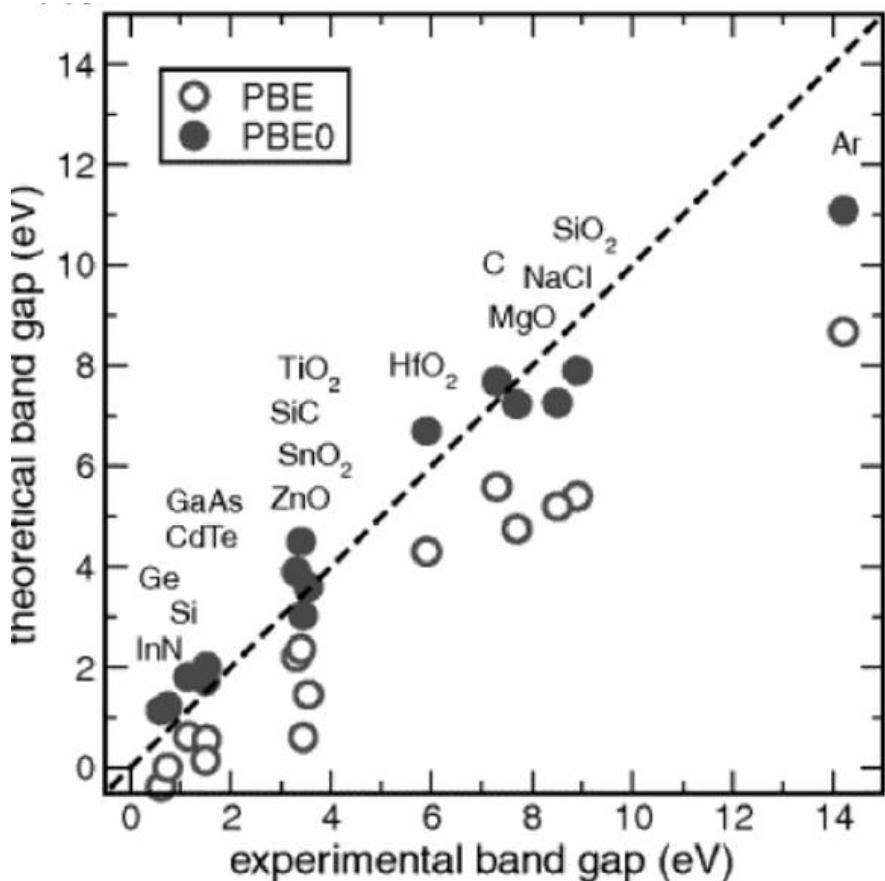
$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$
$$\frac{1}{r} = SR_\omega(r) + LR_\omega(r) = \frac{\text{erfc}(\omega r)}{r} + \frac{1 - \text{erfc}(\omega r)}{r}$$

J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

Hybrid functionals

□ Hybrid functionals

$$E^{PBE0} = 0.25E_X^{HF}(\{\psi^{KS}\}) + 0.75E_X^{PBE} + E_C^{PBE}$$



From: “Advanced Calculations for Defects in Materials: Electronic Structure Methods”, Alkauskas, Deák, Neugebauer, Pasquarello, Van de Walle (eds.), Wiley-VCH (2011)

Hybrid functionals

□ Hybrid functionals

“An ideal hybrid would be sophisticated enough to optimize n [SVL: $\alpha = 1/n$] for each system and property...”

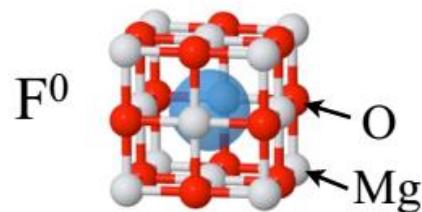
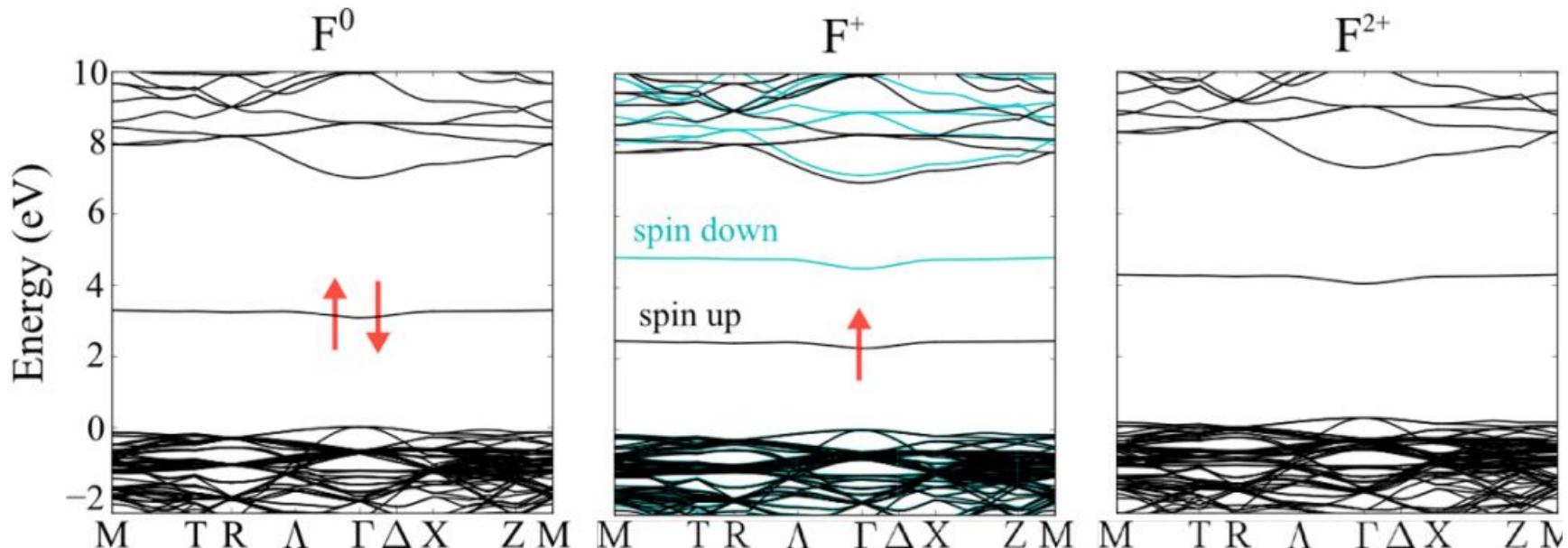
Perdew, Ernzerhof, and Burke, J. Chem. Phys. 105, 9982 (1996)

How can we do this?

Tuning hybrids: A practical approach

- Determine the best α by comparing to more accurate approaches

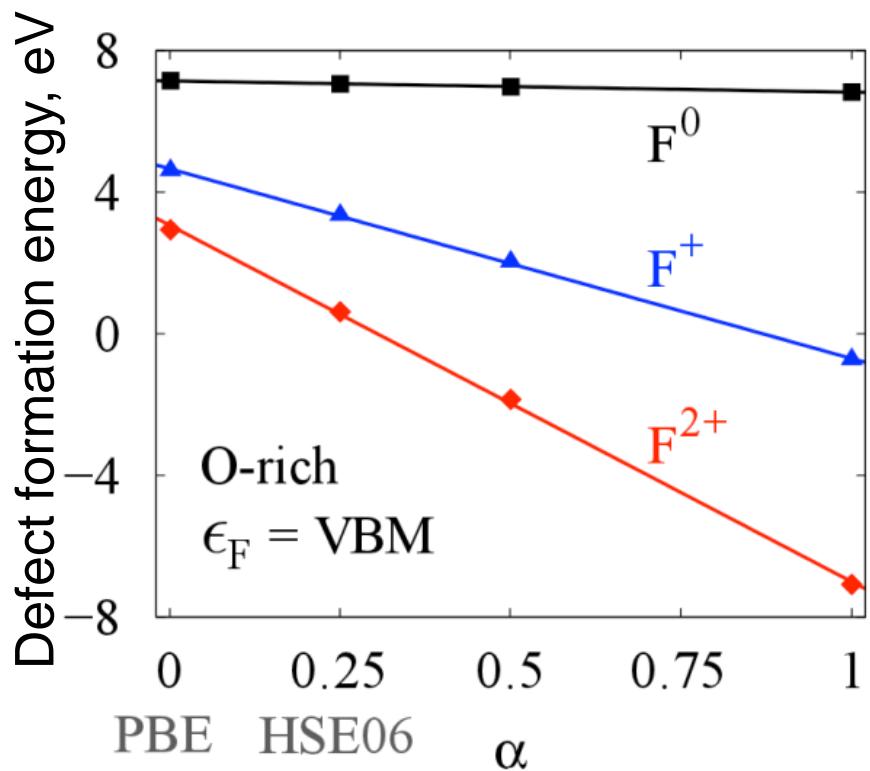
$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$



Tuning hybrids: A practical approach

Determine the best α

$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$



HSE formation energies for varying α :
strong dependence for F^+ and F^{2+} !

Which α to use?

Tuning hybrids: A practical approach

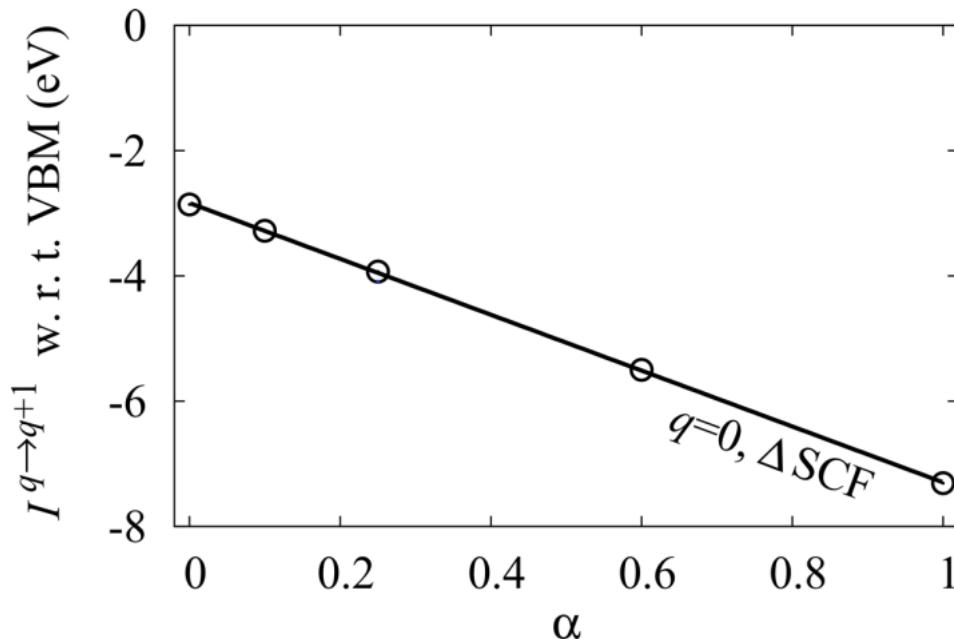
□ Determine the best α

$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$

Request:

Ionization energies with opt-HSE and with $G_0W_0@\text{opt-HSE}$ should agree

calculated using an Mg_6O_9 embedded cluster



From total energy differences

Tuning hybrids: A practical approach

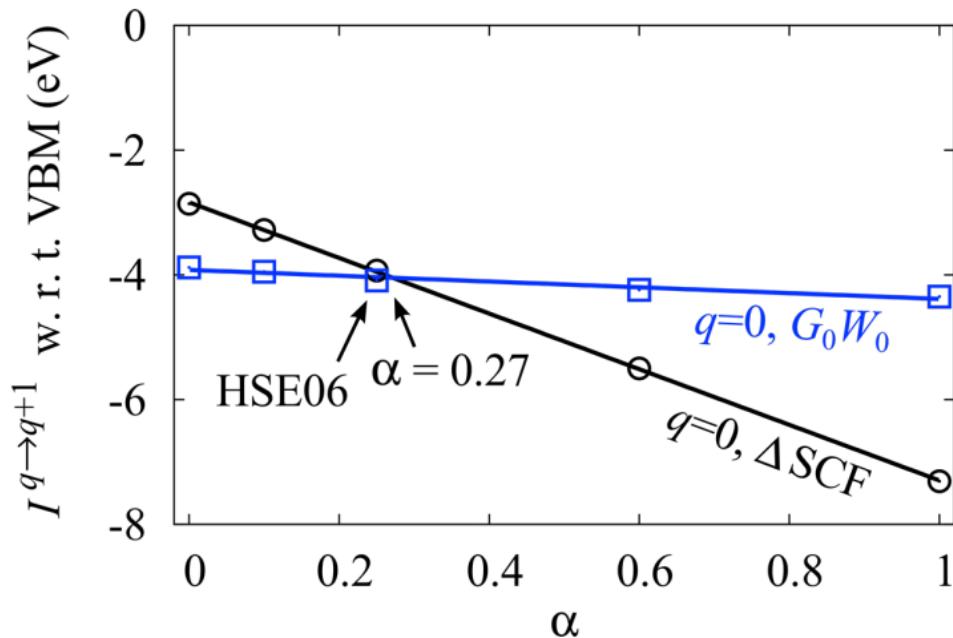
□ Determine the best α

$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$

Request:

Ionization energies with opt-HSE and with G_0W_0 @opt-HSE should agree

calculated using an Mg_6O_9 embedded cluster



From highest occupied orbital

From total energy differences

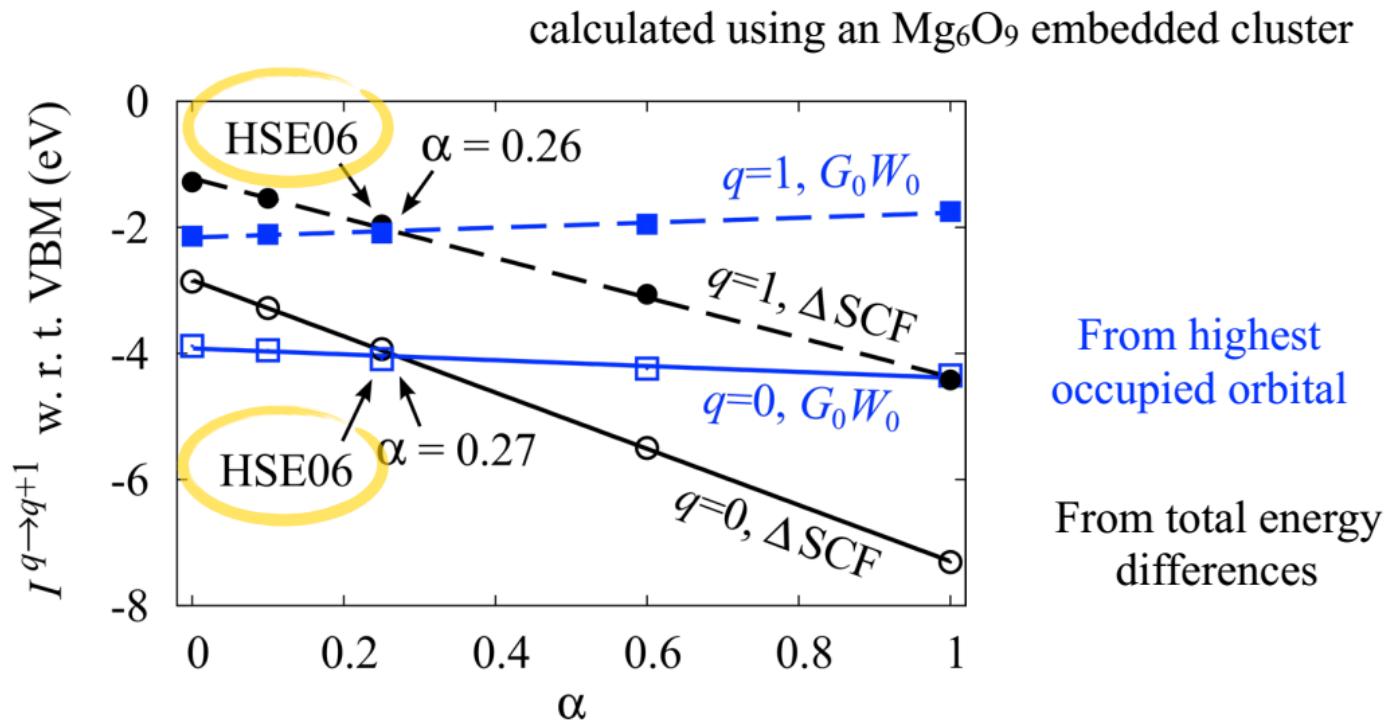
Tuning hybrids: A practical approach

□ Determine the best α

$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$

Request:

Ionization energies with opt-HSE and with G_0W_0 @opt-HSE should agree

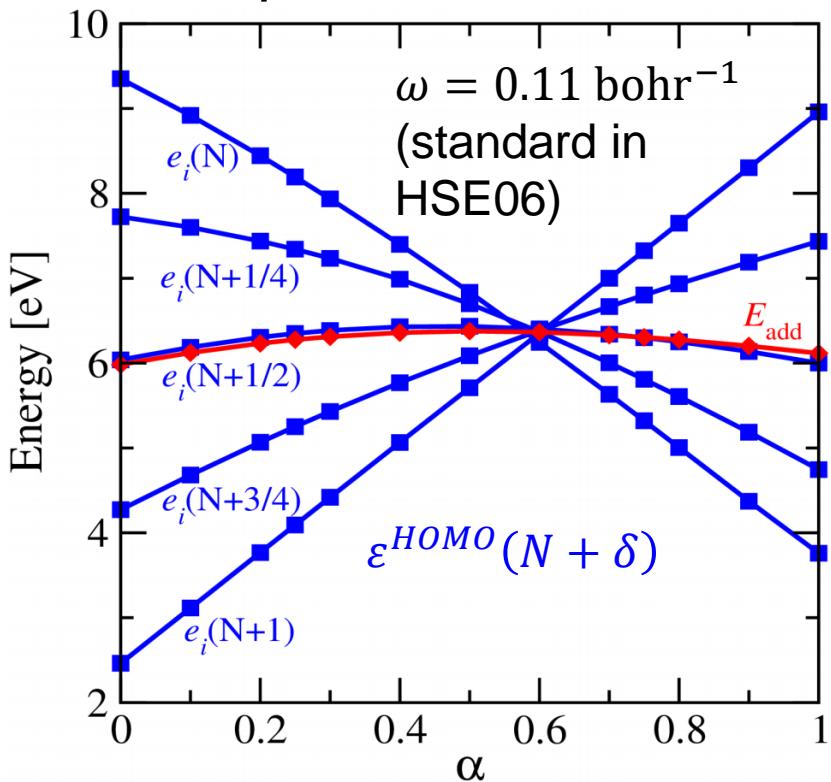


Tuning hybrids: A practical approach

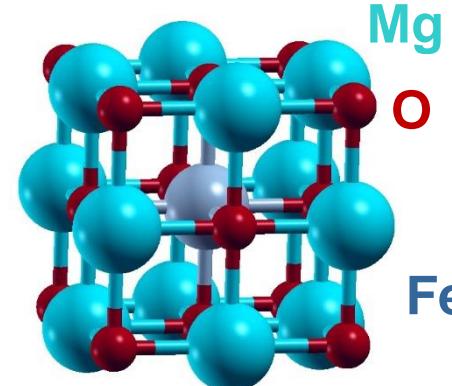
Example: Fe_{Mg} substitutional defects in MgO

□ Is $\alpha = 0.25$ always good?

$$E^{HSE} = 0.25E_X^{HF,SR}(\omega) + 0.75E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$
$$\frac{1}{r} = SR_\omega(r) + LR_\omega(r) = \frac{\text{erfc}(\omega r)}{r} + \frac{1 - \text{erfc}(\omega r)}{r}$$



Electron addition energy $E_{add} = E(N + 1) - E(N)$ for the Fe_{Mg} defect



Optimal $\alpha \approx 0.6$

There IS an α for which $\epsilon^{HOMO} \approx const$

Hybrid functionals

□ Hybrid functionals

“An ideal hybrid would be sophisticated enough to optimize n [SVL: $\alpha = 1/n$] for each system and property...”

Perdew, Ernzerhof, and Burke, J. Chem. Phys. 105, 9982 (1996)

How can we do this?

1) $\alpha = 1/\epsilon_\infty$ (self-consistent or not)

Skone, Govoni, and Galli, Phys. Rev. B 89, 195112 (2014)

2) $\alpha \rightarrow \alpha(r)$ - local hybrids

Maier, Arbuznikov, and Kaupp, WIREs Comput Mol Sci. 9, 1 (2019)

Other approaches: Self-interaction correction

Hybrids are a consistent way to improve accuracy, but they are computationally expensive (30-40 times PBE)

□ Perdew-Zunger self-interaction correction:

$$E^{PZ-SIC} = E^{DFA} - \frac{1}{2} \sum_{i\sigma} \left(\int d^3r d^3r' \frac{n_{i\sigma}(\mathbf{r})n_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[n_{i\sigma}] \right)$$

where $n_{i\sigma}$ are single-orbital densities

Perdew and Zunger, Phys. Rev. B 23, 5048 (1981)

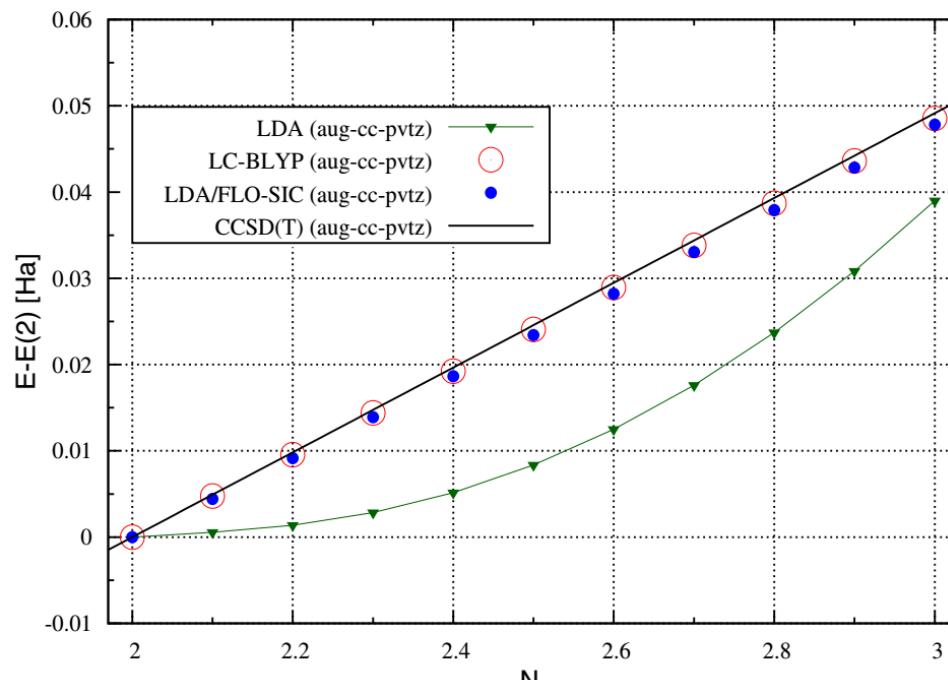
+ exact for any one-electron density

+ fast

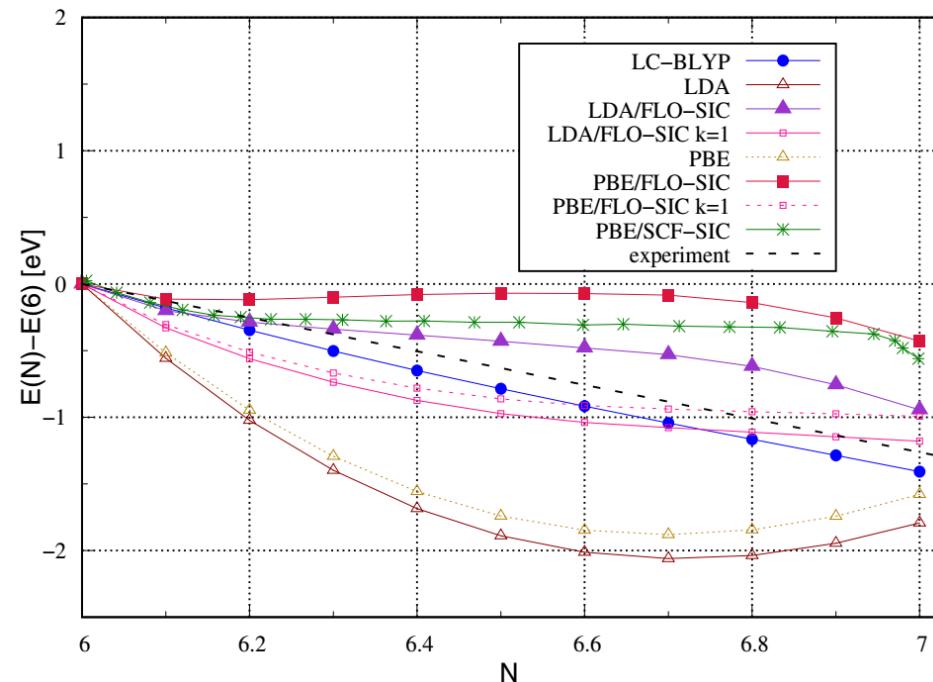
- depends on the choice of orbitals representing the density

- not good for many-electron densities in general

Other approaches: Self-interaction correction



charged H_2 molecule



charged carbon atom

Aquino, Shinde, and Wong, J. Comput. Chem. 41, 1200 (2020)

Locally scaled SIC: reduce SIC in many-electron regions

Vydrov and Scuseria, J. Chem. Phys. 124, 094108 (2006)

Other approaches: DFA+U

Transition-metal atoms with **LOCALIZED** orbitals (d, f)



Self-interaction error → dramatic effects on electronic structure

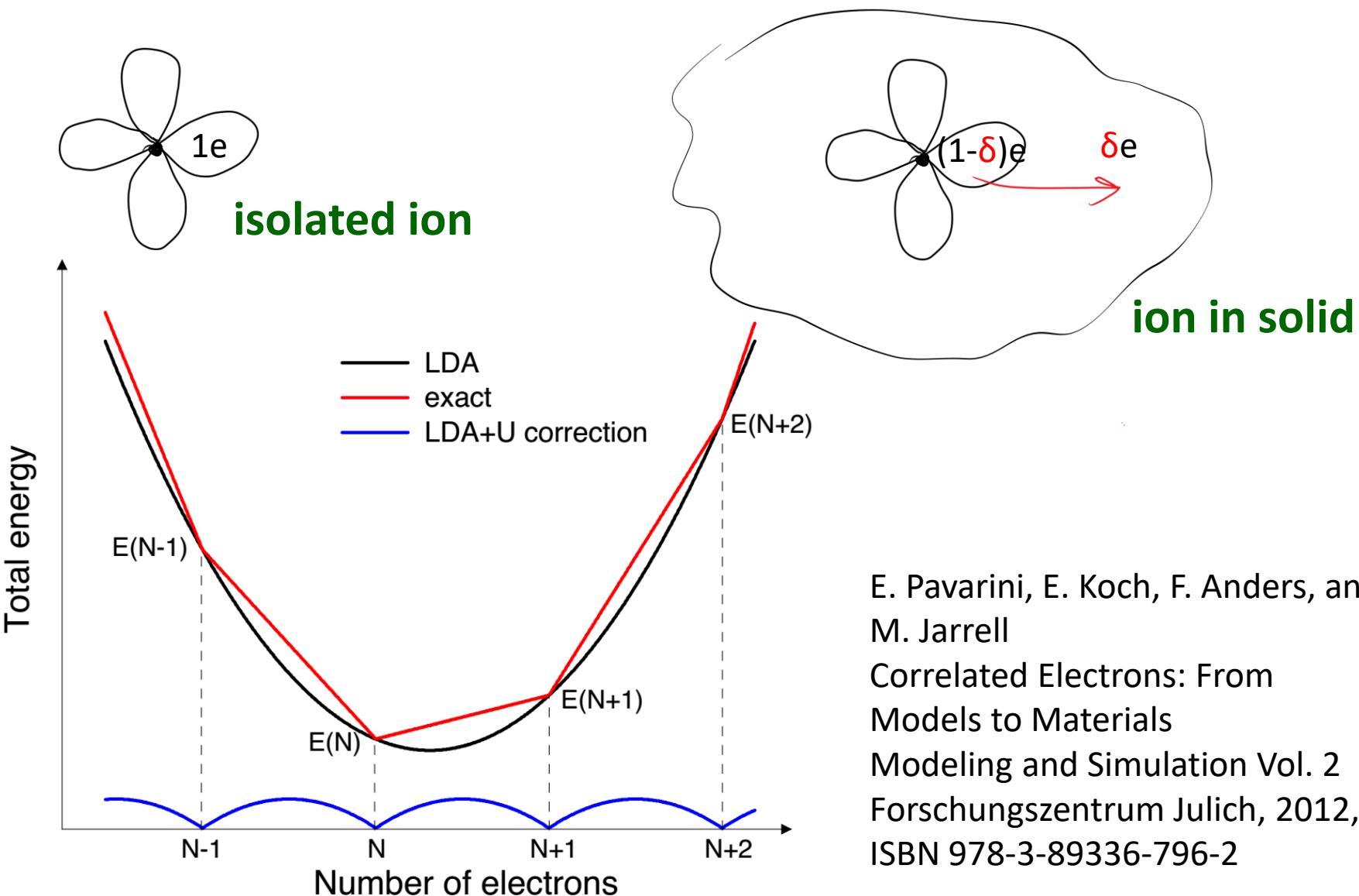


Idea: Correct ON-SITE errors (locally on each atom) only

How?

Other approaches: DFA+U

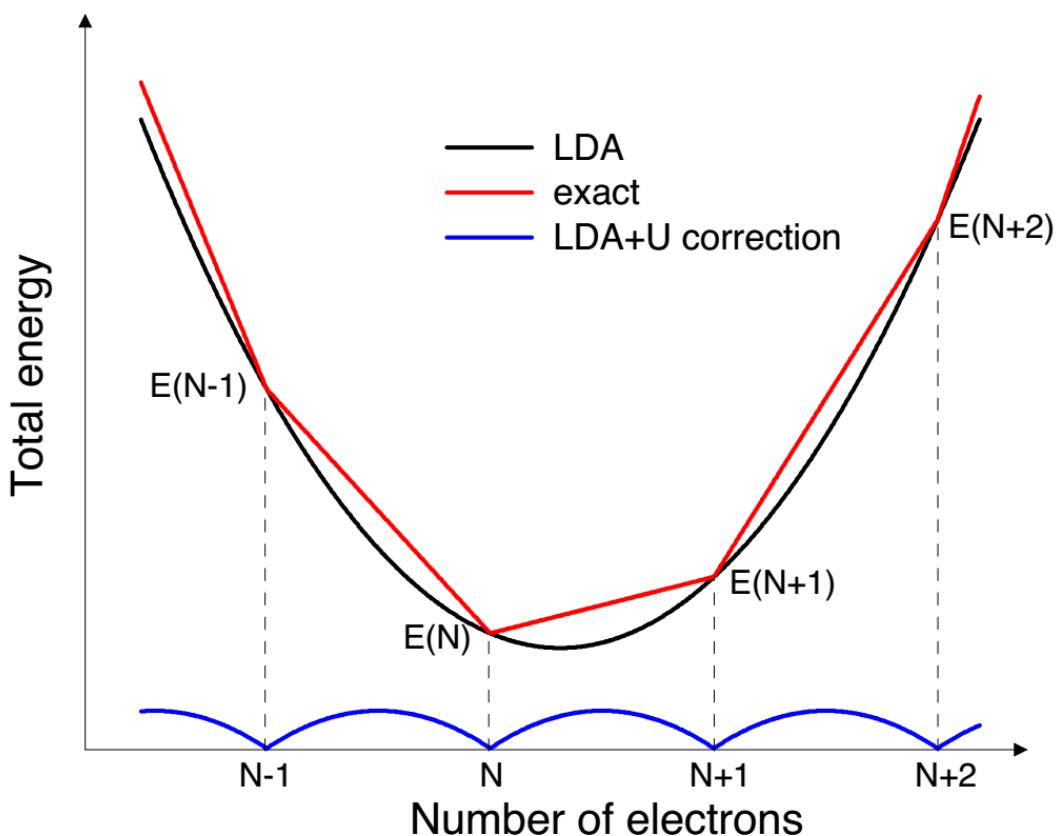
Idea: Penalize fractional occupations of localized atomic orbitals



Other approaches: DFA+U

Idea: Penalize fractional occupations of localized atomic orbitals

Electron-electron interaction of localized electrons in mean-field approximation (Hartree-Fock) → concave



Use as penalty!

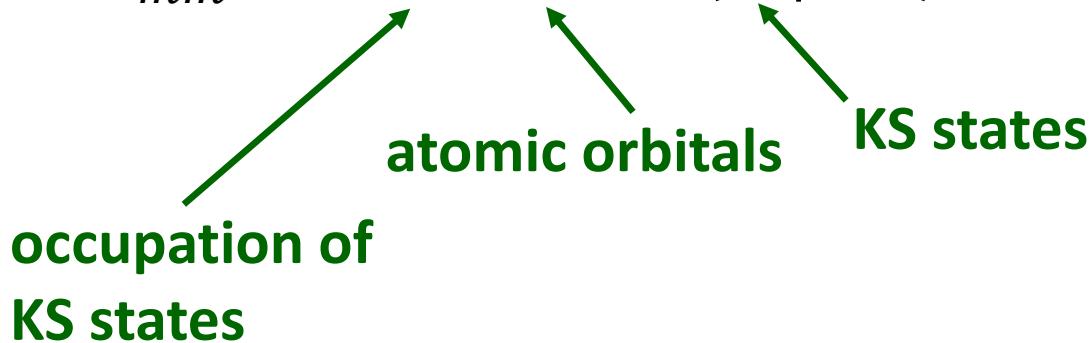
E. Pavarini, E. Koch, F. Anders, and
M. Jarrell
Correlated Electrons: From
Models to Materials
Modeling and Simulation Vol. 2
Forschungszentrum Julich, 2012,
ISBN 978-3-89336-796-2

Other approaches: DFA+U

Hartree-Fock energy of localized electrons in a solid:

$$E^{loc} = \frac{1}{2} \sum_{\{m\}\sigma} \{ \langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle n_{mm''}^{\sigma} n_{m'm''}^{-\sigma} + \\ (\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle - \langle \phi_m \phi_{m'} | V | \phi_{m'''} \phi_{m''} \rangle) n_{mm''}^{\sigma} n_{m'm''}^{\sigma} \}$$

$$n_{mm'}^{\sigma} = \sum_i f_{i\sigma} \langle \phi_m | \psi_i \rangle \langle \psi_i | \phi_{m'} \rangle \text{ -- occupation matrix}$$

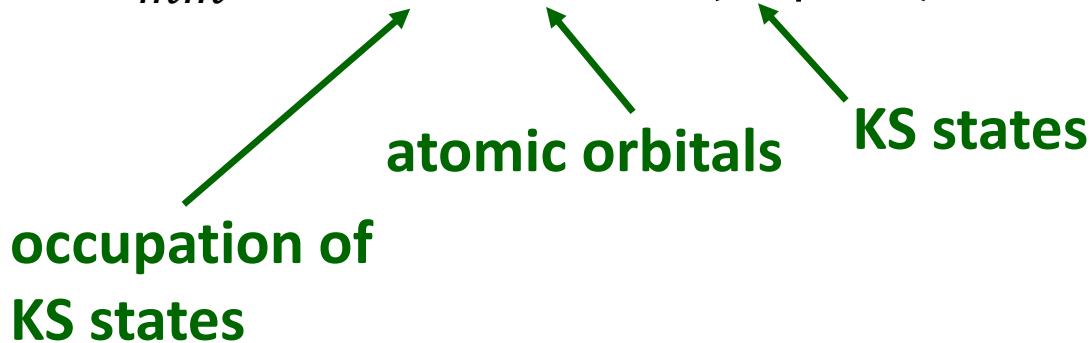


Other approaches: DFA+U

Hartree-Fock energy of localized electrons in a solid:

$$E^{loc} = \frac{1}{2} \sum_{\{m\}\sigma} \{ \langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle n_{mm''}^{\sigma} n_{m'm'''}^{-\sigma} + \\ (\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle - \langle \phi_m \phi_{m'} | V | \phi_{m'''} \phi_{m''} \rangle) n_{mm''}^{\sigma} n_{m'm'''}^{\sigma} \}$$

$$n_{mm'}^{\sigma} = \sum_i f_{i\sigma} \langle \phi_m | \psi_i \rangle \langle \psi_i | \phi_{m'} \rangle \text{ -- occupation matrix}$$



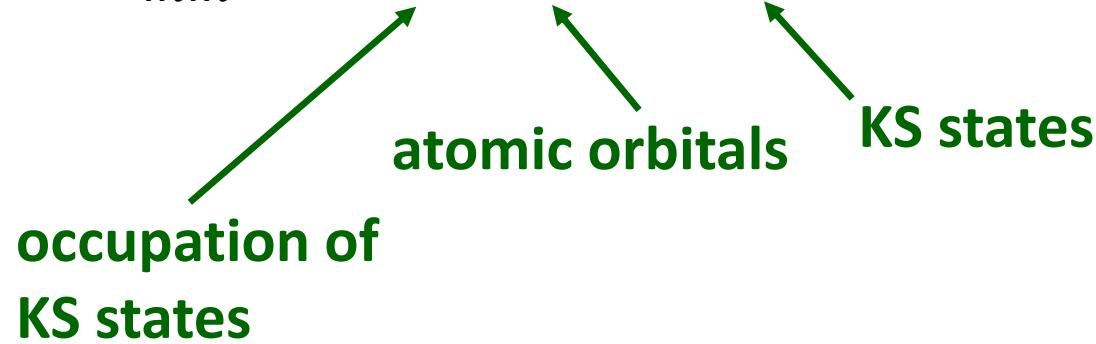
V - screened Coulomb interaction (due to other atomic orbitals s, p, \dots)

Other approaches: DFA+U

Hartree-Fock energy of localized electrons in a solid:

$$E^{loc} = \frac{1}{2} \sum_{\{m\}\sigma} \{ \langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle n_{mm''}^\sigma n_{m'm''}^{-\sigma} + \\ (\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle - \langle \phi_m \phi_{m'} | V | \phi_{m'''} \phi_{m''} \rangle) n_{mm''}^\sigma n_{m'm''}^\sigma \}$$

$$n_{mm'}^\sigma = \sum_i f_{i\sigma} \langle \phi_m | \psi_i \rangle \langle \psi_i | \phi_{m'} \rangle \text{ -- occupation matrix}$$



Approximating $\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle \approx U \delta_{mm''} \delta_{m'm'''}$

$$\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle - \langle \phi_m \phi_{m'} | V | \phi_{m'''} \phi_{m''} \rangle \approx (U - J)(\delta_{mm''} \delta_{m'm'''} - \delta_{mm'''} \delta_{m'm''})$$

$$\rightarrow E^{loc} \approx \frac{1}{2} \sum_{\{m\}\sigma} \{ U n_{mm}^\sigma n_{m'm'}^{-\sigma} + (U - J) n_{mm}^\sigma n_{m'm'}^\sigma - (U - J) n_{mm'}^\sigma n_{m'm'}^\sigma \}$$

Other approaches: DFA+U

$$E^{loc} \approx \frac{1}{2} \sum_{\{m\}\sigma} \{ Un_{mm}^{\sigma} n_{m'm'}^{-\sigma} + (U - J) n_{mm}^{\sigma} n_{m'm'}^{\sigma} - (U - J) n_{mm'}^{\sigma} n_{m'm}^{\sigma} \}$$



Hubbard-like parameter ($U \sum_i \hat{n}_i^{\uparrow} \hat{n}_i^{\downarrow}$)

Penalty for fractional occupations:

$$\Delta E = E^{loc}(n_{mm'}^{\sigma}, \text{in solid}) - E^{loc}(n_{mm'}^{\sigma}, \text{in ion})$$

$$E^{loc}(n_{mm'}^{\sigma}, \text{in ion})$$

$$= \frac{1}{2} \sum_{\{m\}\sigma} \{ Un_{mm}^{\sigma} n_{m'm'}^{-\sigma} + (U - J) n_{mm}^{\sigma} n_{m'm'}^{\sigma} \} - \frac{(U - J)}{2} \sum_{m\sigma} n_{mm}^{\sigma}$$

Other approaches: DFA+U

$$E^{loc} \approx \frac{1}{2} \sum_{\{m\}\sigma} \{ Un_{mm}^{\sigma} n_{m'm'}^{-\sigma} + (U - J) n_{mm}^{\sigma} n_{m'm'}^{\sigma} - (U - J) n_{mm'}^{\sigma} n_{m'm}^{\sigma} \}$$



Hubbard-like parameter ($U \sum_i \hat{n}_i^{\uparrow} \hat{n}_i^{\downarrow}$)

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$$E^{loc}(n_{mm'}^{\sigma}, \text{in ion})$$

$$= \frac{1}{2} \sum_{\{m\}\sigma} \{ Un_{mm}^{\sigma} n_{m'm'}^{-\sigma} + (U - J) n_{mm}^{\sigma} n_{m'm'}^{\sigma} \} - \frac{(U - J)}{2} \sum_{m\sigma} n_{mm}^{\sigma}$$

$$E_{DFA+U} = E_{DFA} + \Delta E$$

$$= E_{DFA} + \frac{(U - J)}{2} \left\{ \sum n_{mm}^{\sigma} - \sum n_{mm'}^{\sigma} n_{m'm}^{\sigma} \right\}$$

Other approaches: DFA+U

$$\begin{aligned} E_{DFA+U} &= E_{DFA} + \Delta E \\ &= E_{DFA} + \frac{(U - J)}{2} \left\{ \sum_{m\sigma} n_{mm}^\sigma - \sum_{mm'\sigma} n_{mm'}^\sigma n_{m'm}^\sigma \right\} \end{aligned}$$

Notes:

- $U - J$ can be considered as an effective U
- First derivations were not rotationally invariant
- One can go beyond mean-field, then need both U and J
- $E^{loc}(n_{mm'}^\sigma \text{ in ion})$ is called double-counting term
- Depends on the choice of atomic basis ϕ_m
- U depends on atom, orbital (d, f), atom environment

How to determine U ?

Other approaches: DFA+U

$$E_{DFA+U} = E_{DFA} + \Delta E$$
$$= E_{DFA} + \frac{(U - J)}{2} \left\{ \sum_m n_{mm}^\sigma - \sum_{m'm'\sigma} n_{mm'}^\sigma n_{m'm}^\sigma \right\}$$

How to determine U ?

- Compare DFA+U with experiment (band gap, structure) - often unavailable
- Compare DFA+U with accurate methods (GW) - expensive
- Ensure linear $E(N)$ - done using linear-response DFT
- From constrained random-phase approximation calculations - expensive, complex formalism

Pavarini, Koch, Vollhardt, and Lichtenstein, The LDA+DMFT approach to strongly correlated materials Modeling and Simulation Vol. 1 Forschungszentrum Juelich, 2011, ISBN 978-3-89336-734-4

- Calculate U using HF for localized orbitals (pseudo-hybrid ACBN0)

U depends on atom, orbital (d, f), atom environment

Take-home messages:

Know what you are doing!

Non-linearity of $E(N) \rightarrow$ DFA failures

Functional development - active field of research (SIC, DFA+U, local hybrids, $\alpha = \frac{1}{\varepsilon_\infty}$, meta-GGA)

Strongly constrained and appropriately normed semilocal density functional
J Sun, A Ruzsinszky, JP Perdew
Physical review letters 115 (3), 036402

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2015