Advanced Materials Modeling

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

Introduction

Instructors and teaching assistant

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TA: Maria Pogodaeva

Course content

Schedule: https://cms-lab.github.io/edu/AMM2021/Schedule.htm

We are here for you!

Adjusted/refined topics based on your interests

Discussion of your research projects

Final projects according to your interests

Course content: Prerequisites

1) Quantum mechanics

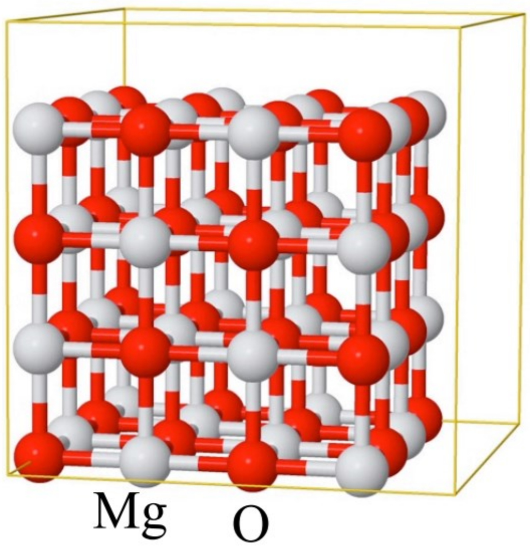
2) Basic solid state theory (periodic boundary conditions, Brillouin zones, k-points)

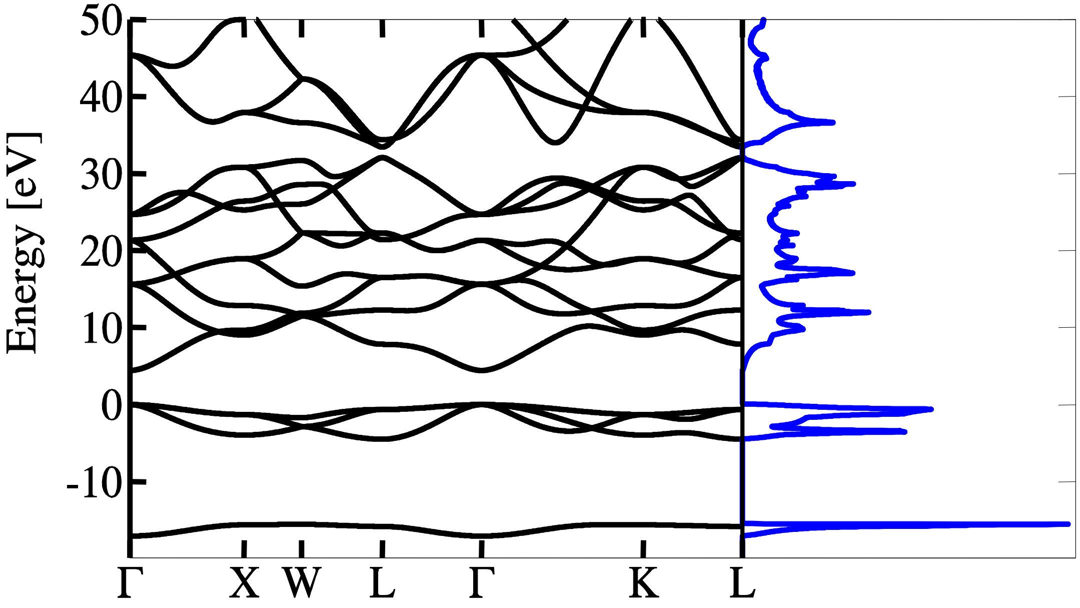
3) Basic electronic-structure concepts (many-body Schrödinger equation, Born-Oppenheimer approximation, density functional theory, Hartree-Fock approximation)

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

$$i\frac{\partial\Psi}{\partial t}=\left(-\frac{1}{2}\sum_{j}\frac{\partial^2}{\partial\boldsymbol{r}_j^2}+\frac{1}{2}\sum_{j\neq k}\frac{Q_jQ_k}{|\boldsymbol{r}_j-\boldsymbol{r}_k|}+V^{\mathrm{ext}}(\{\boldsymbol{r}_j\},t)\right)\Psi$$

non-relativistic Schrödinger equation

$\Psi\left(\{\mathbf{r}_i\},\{\sigma_i\},t\right)$ – 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.

- How to simplify the problem further?

Course content: What it is about

❒ The Hartree-Fock approximation

Slater determinant fulfills the Pauli principle

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

Hartree-Fock equation

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

No self-interaction, but also no correlation

Course content: What it is about

Density functional theory: Hohenberg-Kohn theorem

$n(\mathbf{r}) \rightarrow \hat{H}$ – many-body Hamiltonian

$n(\mathbf{r}) \rightarrow \Phi(\boldsymbol{r}_1\sigma_1, \ldots, \boldsymbol{r}_N\sigma_N)$ – many-body wave function

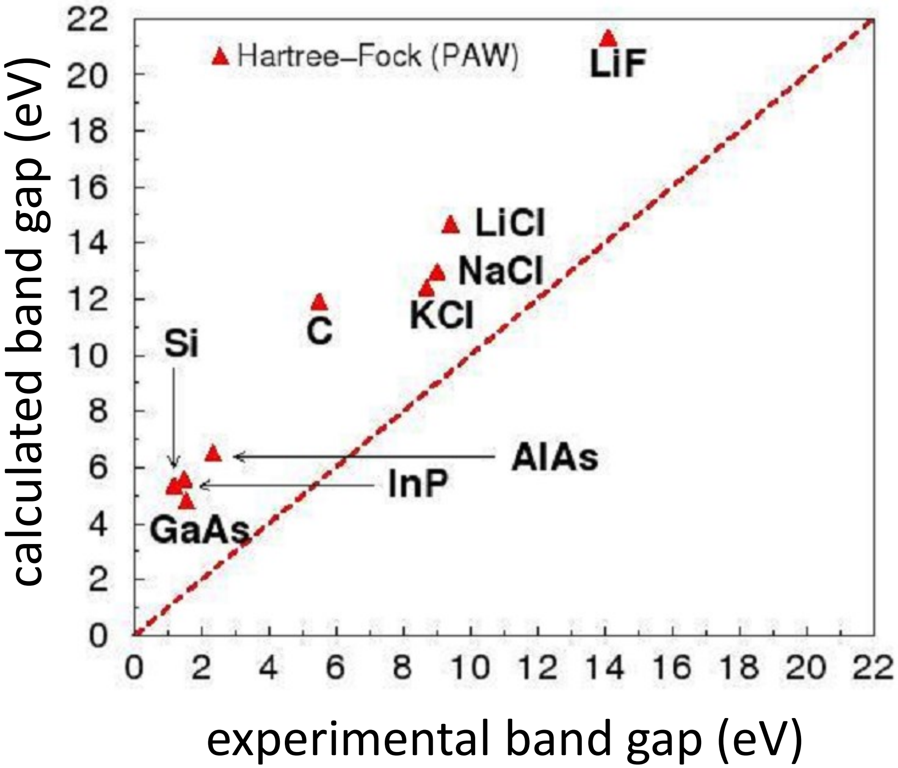
$n(\mathbf{r}) \rightarrow E_{\text{tot}}$ – total energy

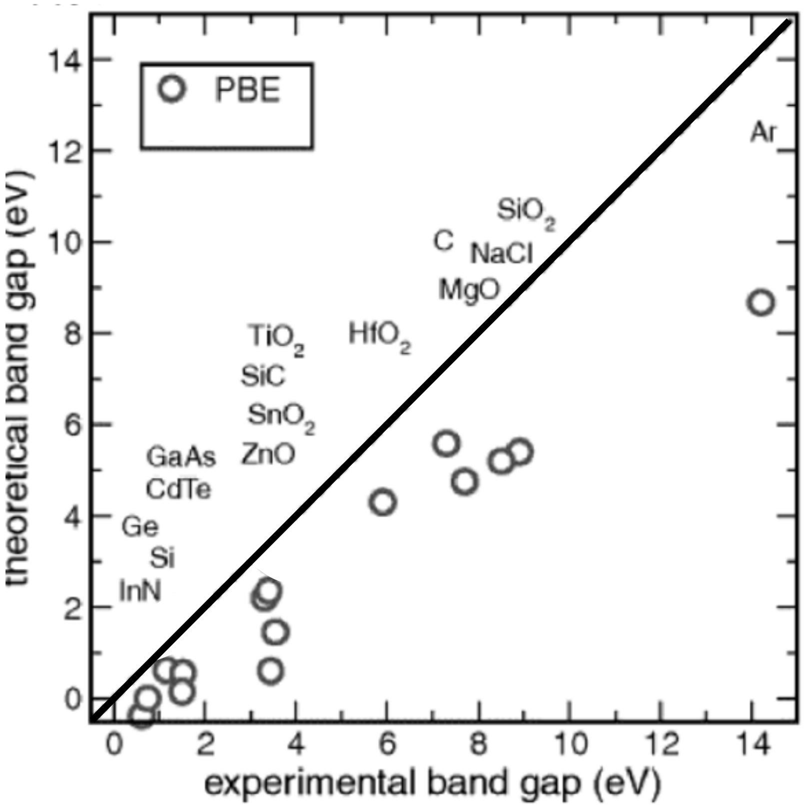
$$E_{\text{tot}} = T[n] - \sum_{I=1}^{M} Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_I|} d^3r + \frac{1}{2}\sum_{I=1}^{M}\sum_{J=1}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \boxed{\frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'} + E_{\text{XC}}[n]$$

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, spectroscopy, electron transport)

Excited state dynamics

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) Progress reports on your final projects.

Assessment: Quality of presentation, understanding of the subject

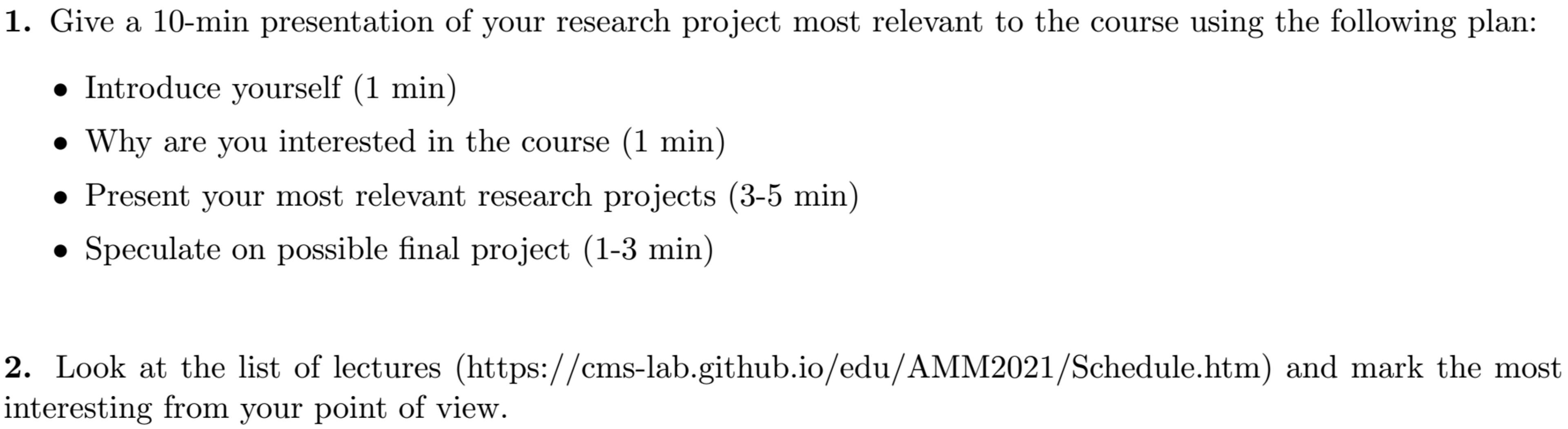
4) Final project (https://cms-lab.github.io/edu/AMM/FinalProject.htm).

Assessment: Scientific quality, quality of presentation, answering questions

First homework: Introduce yourself

Homework assignment:

https://cms-lab.github.io/edu/AMM2021/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/AMM2021/Schedule.htm) and mark the most interesting from your point of view.

Due date: Thursday 1.04 at 9:00 (presentations)

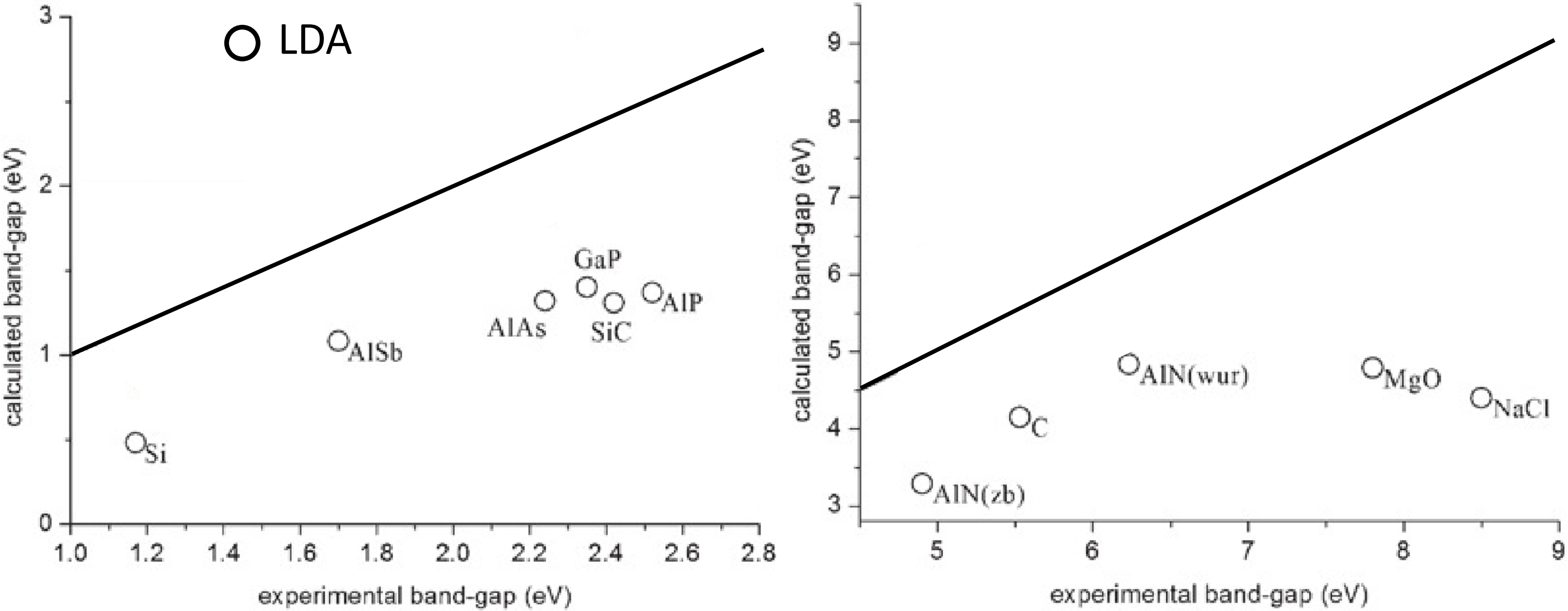
Office hours

No fixed office hours

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

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

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

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

$E[n] = \min\limits_{\Gamma \to n} \langle \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} + \hat{V}_{xc} \rangle_\Gamma$ [minimize over all Γ giving the same $n(\boldsymbol{r})$]

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

Exact DFT functional properties: *E*(*N*)

❒ Fractional occupations

Time average → statistical mixture of *pure* states:

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

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

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

Exact DFT functional properties: *E*(*N*)

❒ Fractional occupations

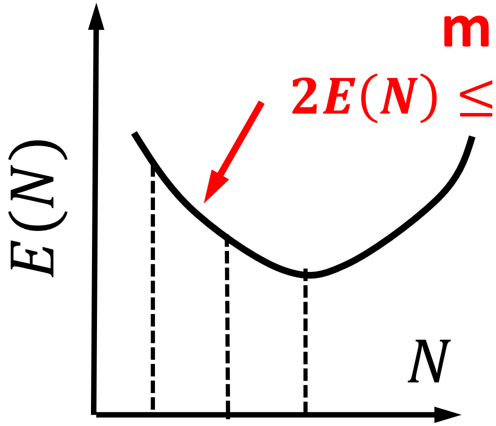
$$p_1 M + p_2(M-1) + p_3(M+1) + \cdots = M + \omega, 0 < \omega < 1,$$

$$E[n] = p_1 E_M + p_2 E_{M-1} + p_3 E_{M+1} + \cdots , \qquad p_1 + p_2 + \cdots = 1$$

$$\min_{n,\int n(r)dr = M+\omega} E[n]$$

must be convex

$$\mathbf{2E(N) \le E(N-1) + E(N+1)}$$



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

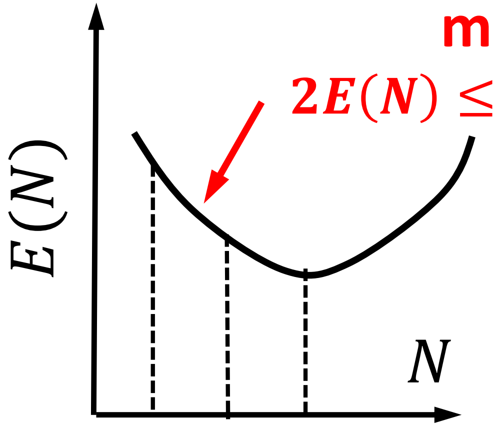
Exact DFT functional properties: *E*(*N*)

❐ Fractional occupations

$$p_1 M + p_2(M-1) + p_3(M+1) + \cdots = M + \omega, 0 < \omega < 1,$$

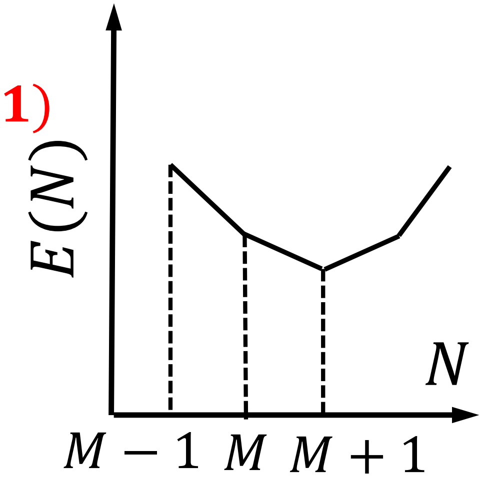
$$E[n] = p_1 E_M + p_2 E_{M-1} + p_3 E_{M+1} + \cdots, \qquad p_1 + p_2 + \cdots = 1$$

$$\min_{n,\int n(r)dr=M+\omega} E[n] = (1-\omega)E_M + \omega E_{M+1}$$



must be convex

$$2E(N) \le E(N-1) + E(N+1)$$



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

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

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

kinetic energy

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

Coulomb energy

$$\frac{1}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d^3r\, d^3r' - \int d^3r \sum_J \frac{Z_J}{|\boldsymbol{r}-R_J|}\, n(\boldsymbol{r})$$

exchange-correlation energy

Janak, Phys. Rev. B 18, 7165 (1978)

Fractional occupations

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❒ Fractional occupations in Kohn-Sham formalism

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

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

Let us define:

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

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

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Lagrangian:

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

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

Janak, Phys. Rev. B 18, 7165 (1978)

Fractional occupations

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

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

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

Janak, Phys. Rev. B 18, 7165 (1978)

Fractional occupations

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

$$\frac{\partial \tilde{E}}{\partial f_i} = \mu, 0 \le f_i \le 1, \qquad \frac{\partial \tilde{E}}{\partial f_i} \ne \mu, f_i = 1, \qquad \frac{\partial \tilde{E}}{\partial f_i} \ne \mu, f_i = 0$$

Janak, Phys. Rev. B 18, 7165 (1978)

Approximate functionals

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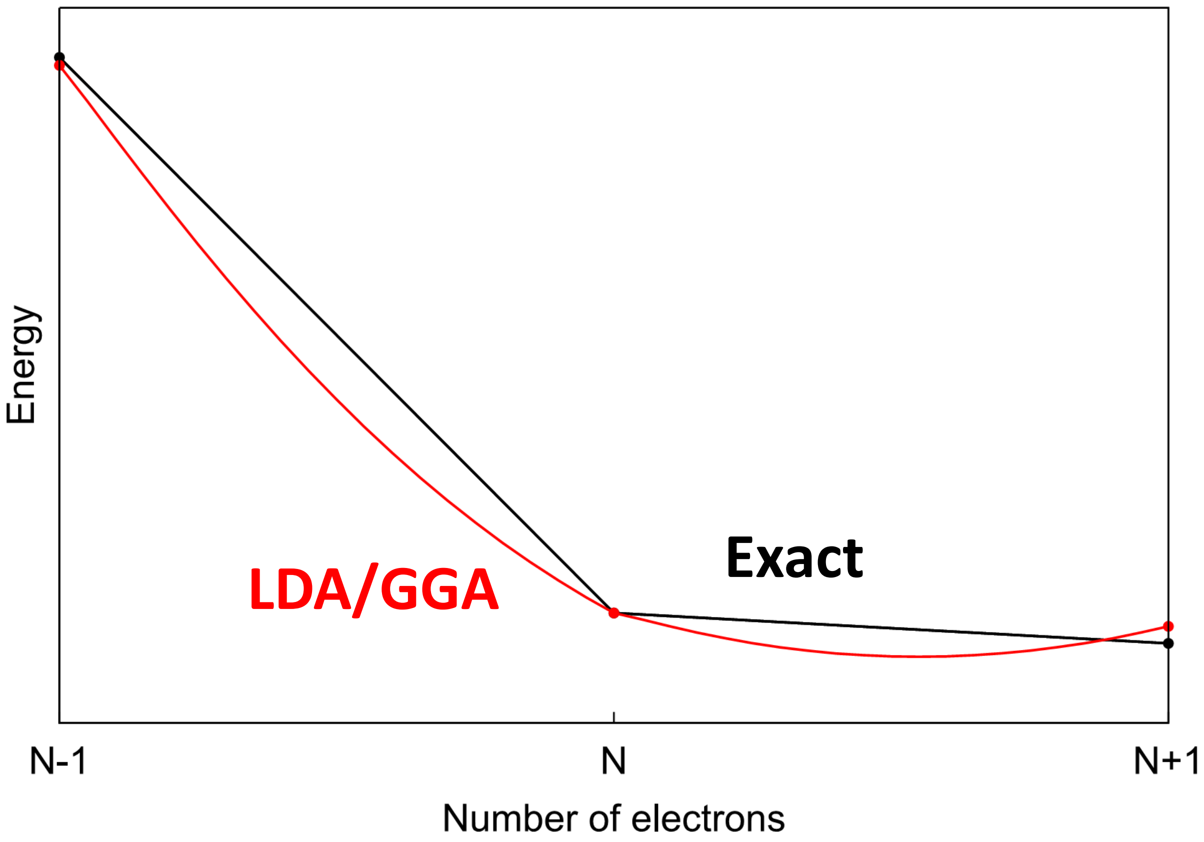
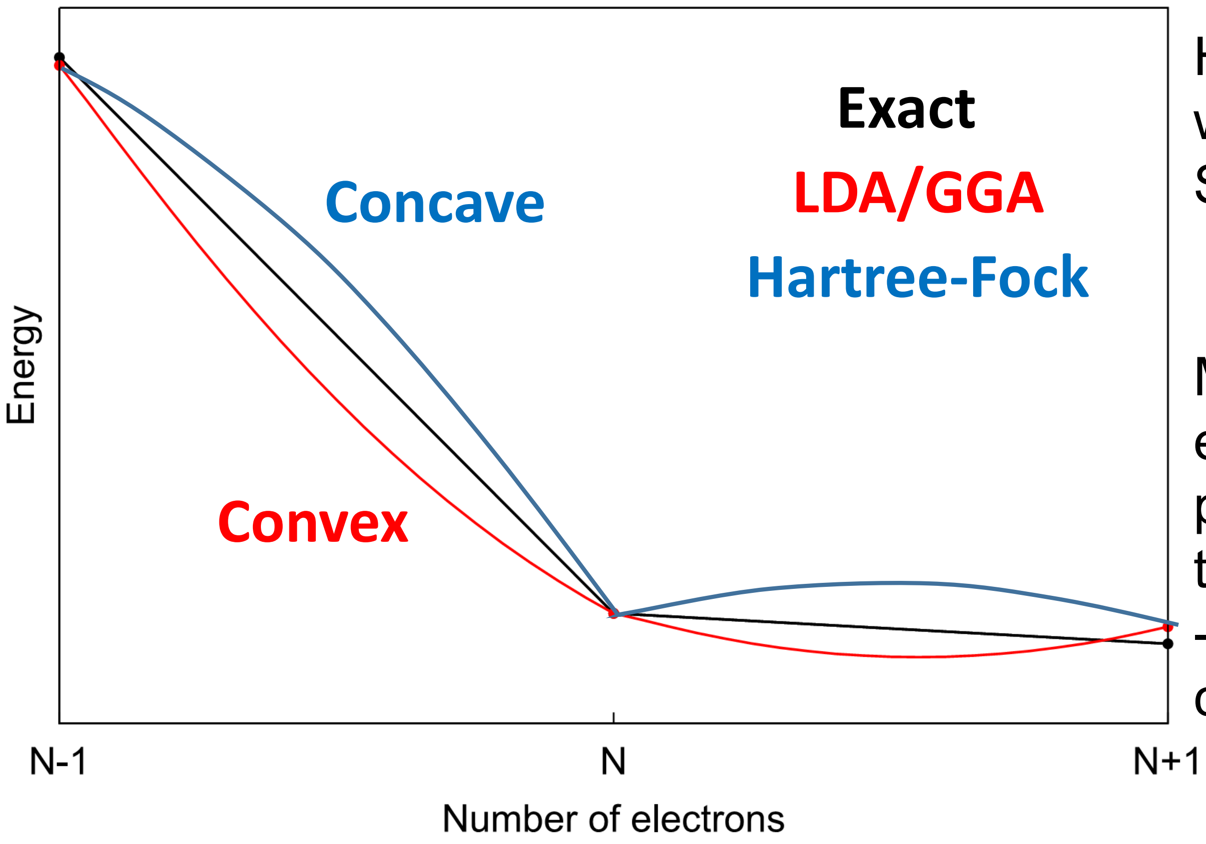
- **Dependence $E(N)$ for an approximate functional:**



Convex behavior

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

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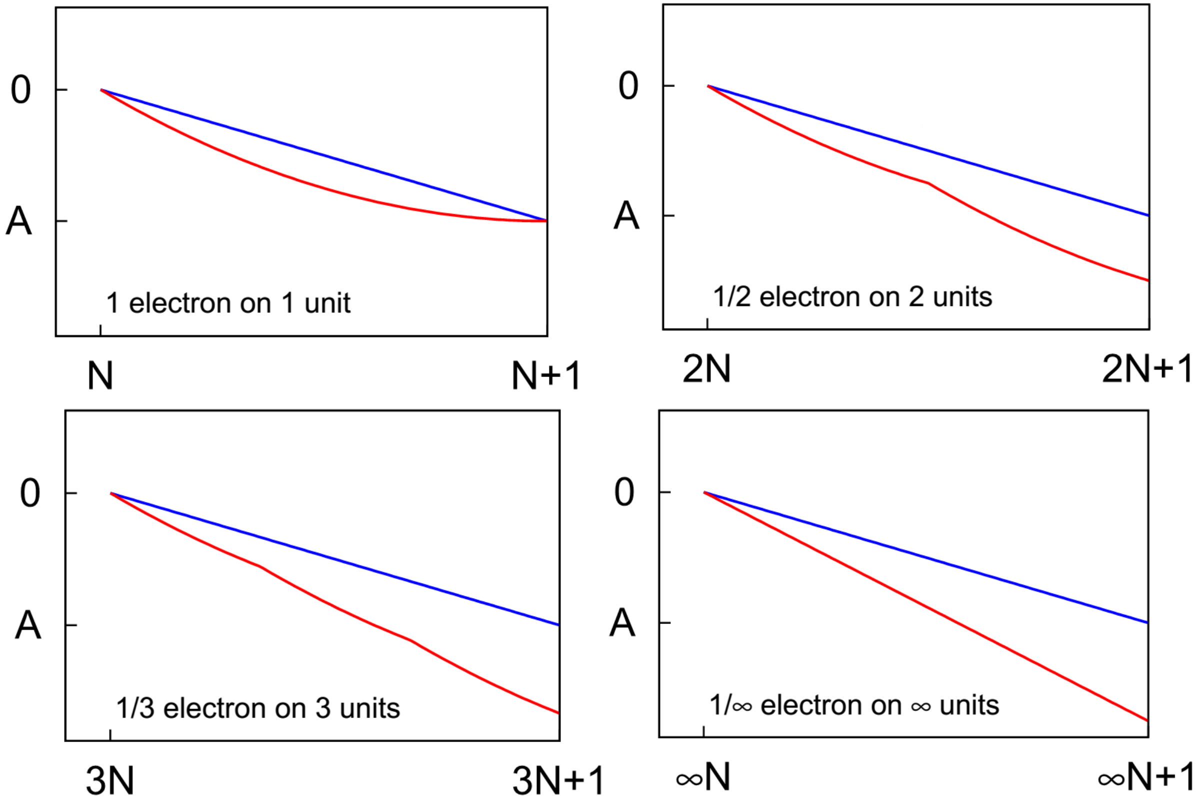
- **Connection between the self-interaction (delocalization) error (SIE) and the convex behavior**



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

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

Mori-Sánchez, Cohen, Yang, Phys. Rev. Lett. 100, 146401 (2008)

Band gap problem

- ❒ **Observable gap:**

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

- ❒ **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:

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

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

Lagrangian:

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

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

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

Janak, Phys. Rev. B 18, 7165 (1978)

Janak's theorem

❒ Fractional occupations in Kohn-Sham formalism

Derivative w.r.t. f:

$$n(\boldsymbol{r}) = \sum_i f_i |\psi_i(\boldsymbol{r})|^2 \qquad \tilde{E}(\{\psi_i\},\{f_i\}) = \sum_i f_i t_i + E_{\mathrm{C}}[n] + E_{\mathrm{XC}}[n]$$

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

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

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

from KS equations

from stationary condition with respect to ψ_i^*

Janak, Phys. Rev. B 18, 7165 (1978)

Janak's theorem

.

❒ Fractional occupations in Kohn-Sham formalism

Lagrangian:

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

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

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, Phys. Rev. B 18, 7165 (1978)

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 → $\varepsilon_{HOMO}(M-\delta) = const$ for $0 < \delta < 1$ for exact KS potential (IP theorem)

What‘s up with the band gap?

Band gap problem

- **Observable gap:**

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

- **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!

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

Band gap problem

❒ Derivative discontinuity

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

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

Thus, there are TWO problems:

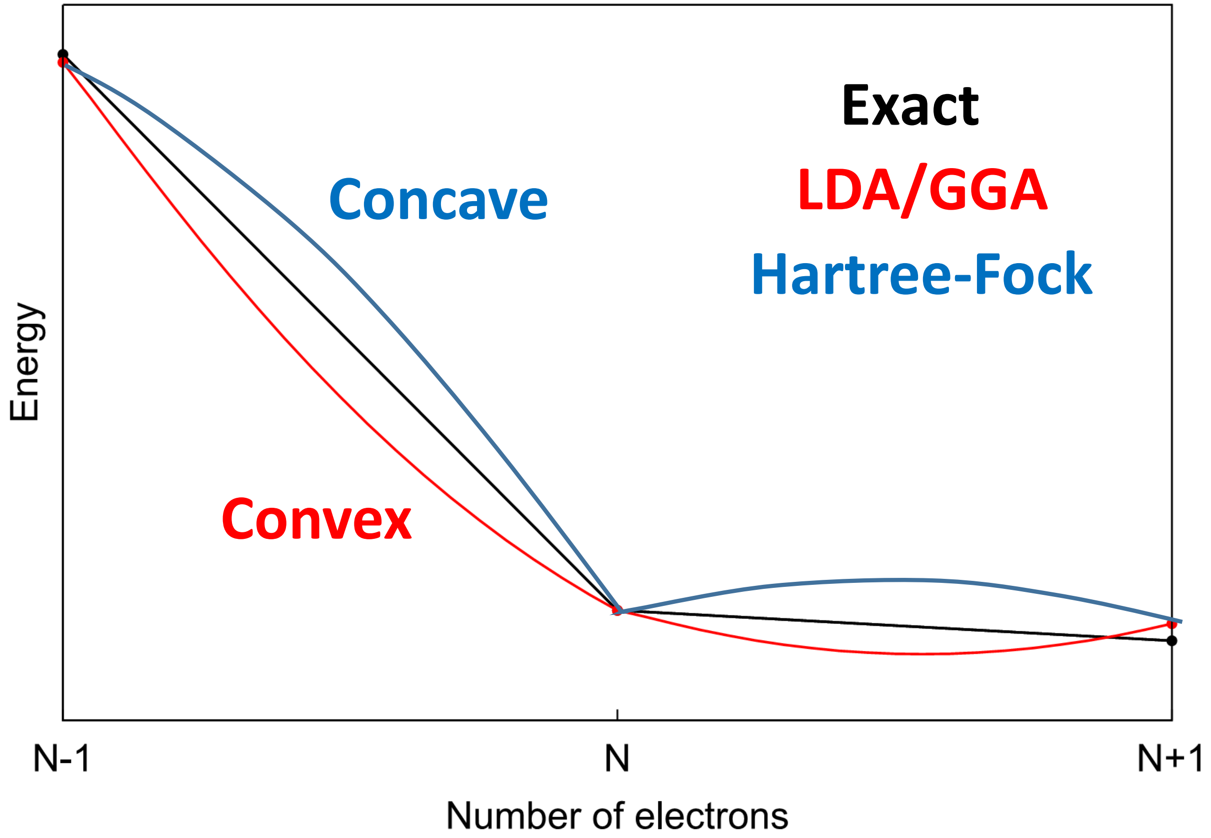
1) non-straight-line behavior of the total energy with number of electrons for approximate functionals

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)

Mori-Sánchez, Cohen, Yang, Phys. Rev. Lett. 100, 146401 (2008)

Band gap problem

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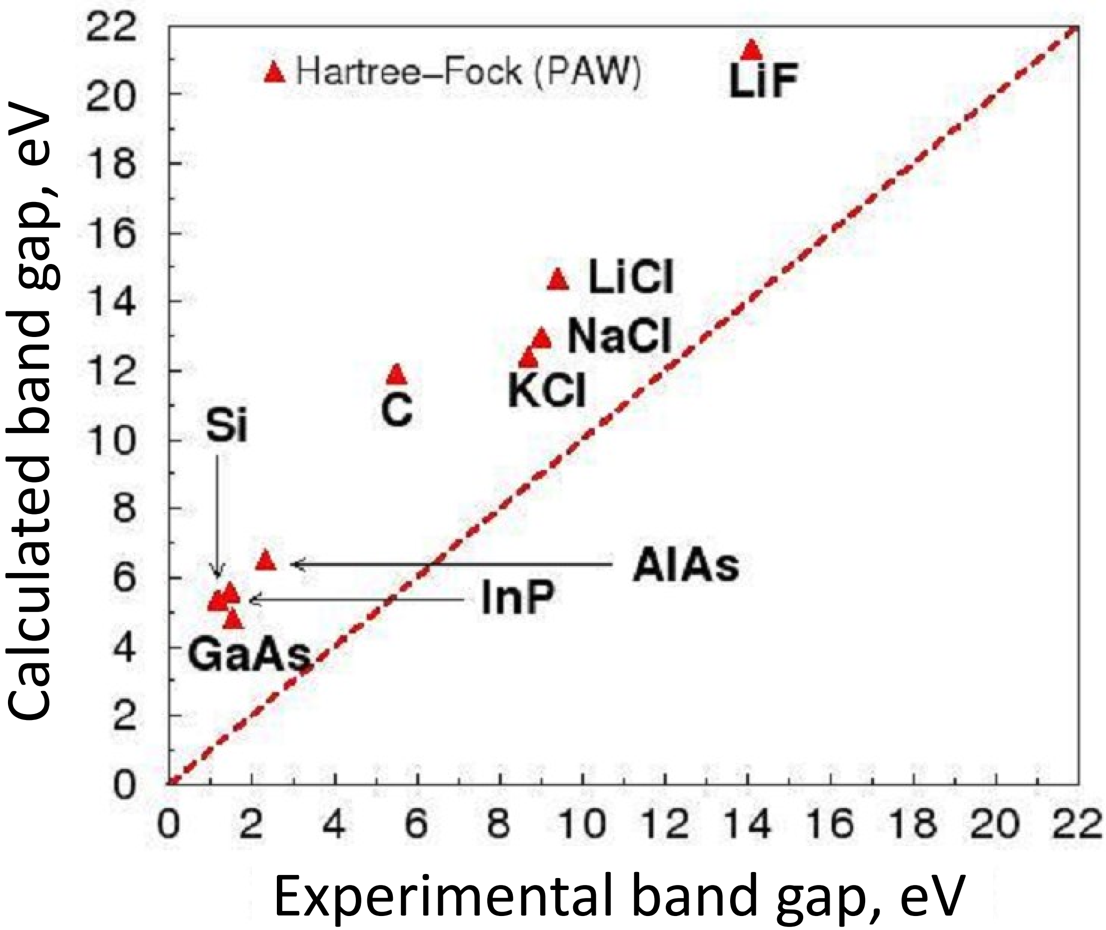
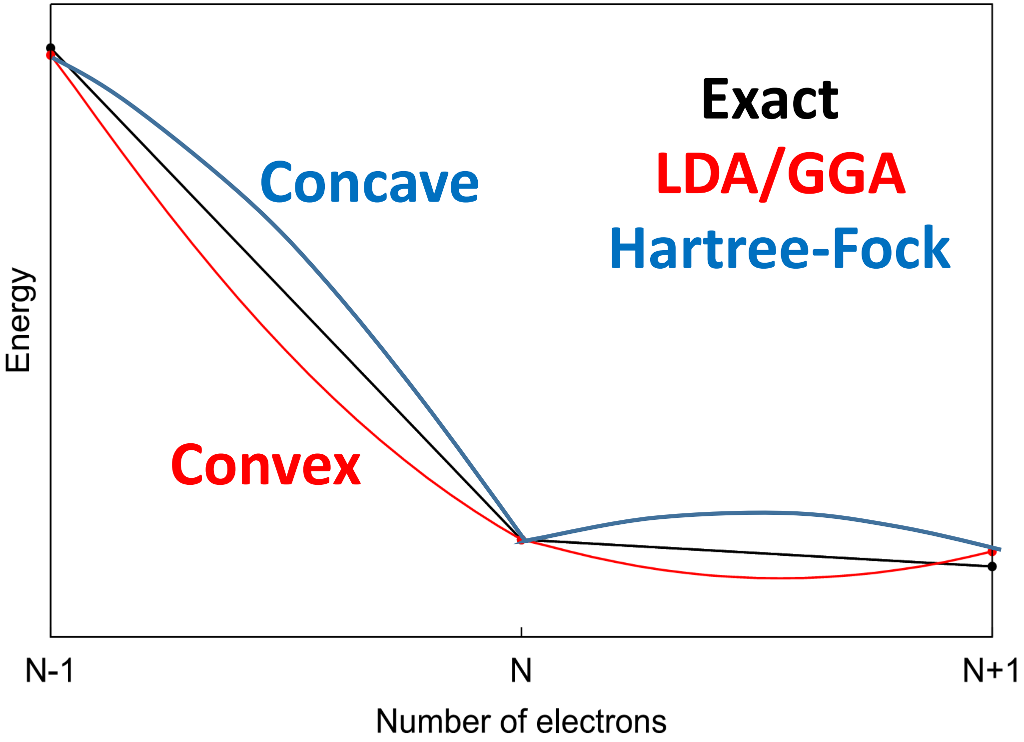
- Hartree-Fock is self-interaction free, but…



Brice Arnaud, Universit´e de Rennes, France

Band gap problem

❒ Hybrid functionals



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

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

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

Mori-Sánchez, Cohen, Yang, Phys. Rev. Lett. 100, 146401 (2008)

Hybrid functionals

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- ❒ **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

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

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

Hybrid functionals

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

There can be other parameters

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

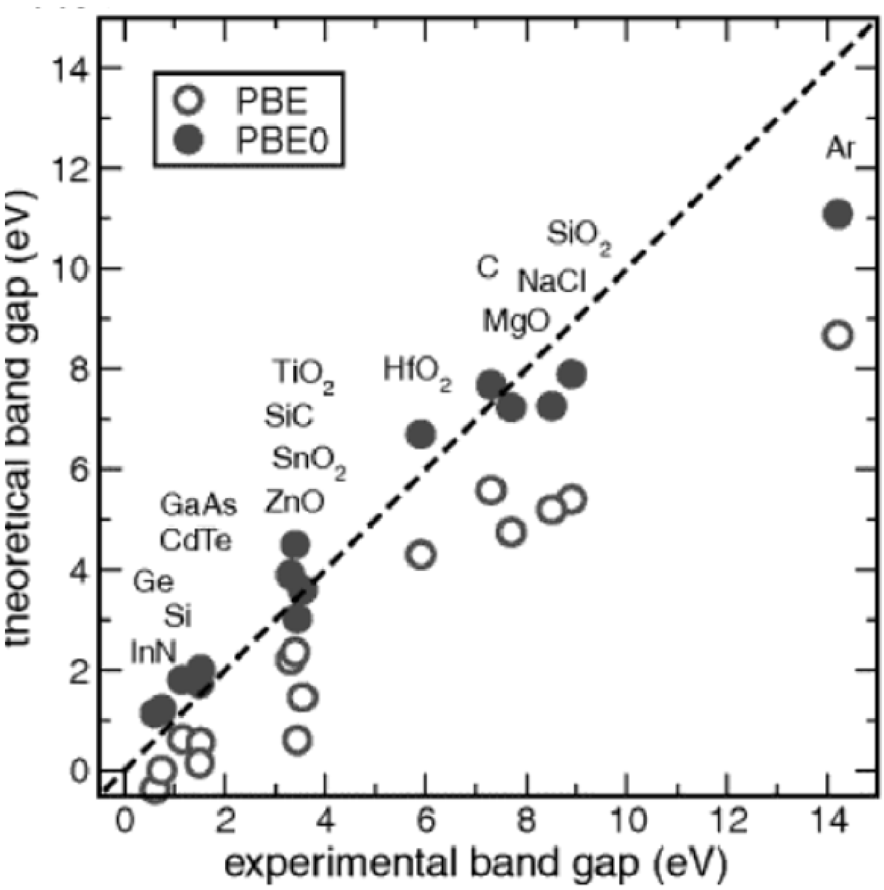
$$\frac{1}{r} = SR_\omega(r) + LR_\omega(r) = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{1 - \mathrm{erfc}(\omega r)}{r}$$

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.), Willey-VCH (2011)

Hybrid functionals

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- ❐ **Hybrid functionals**

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

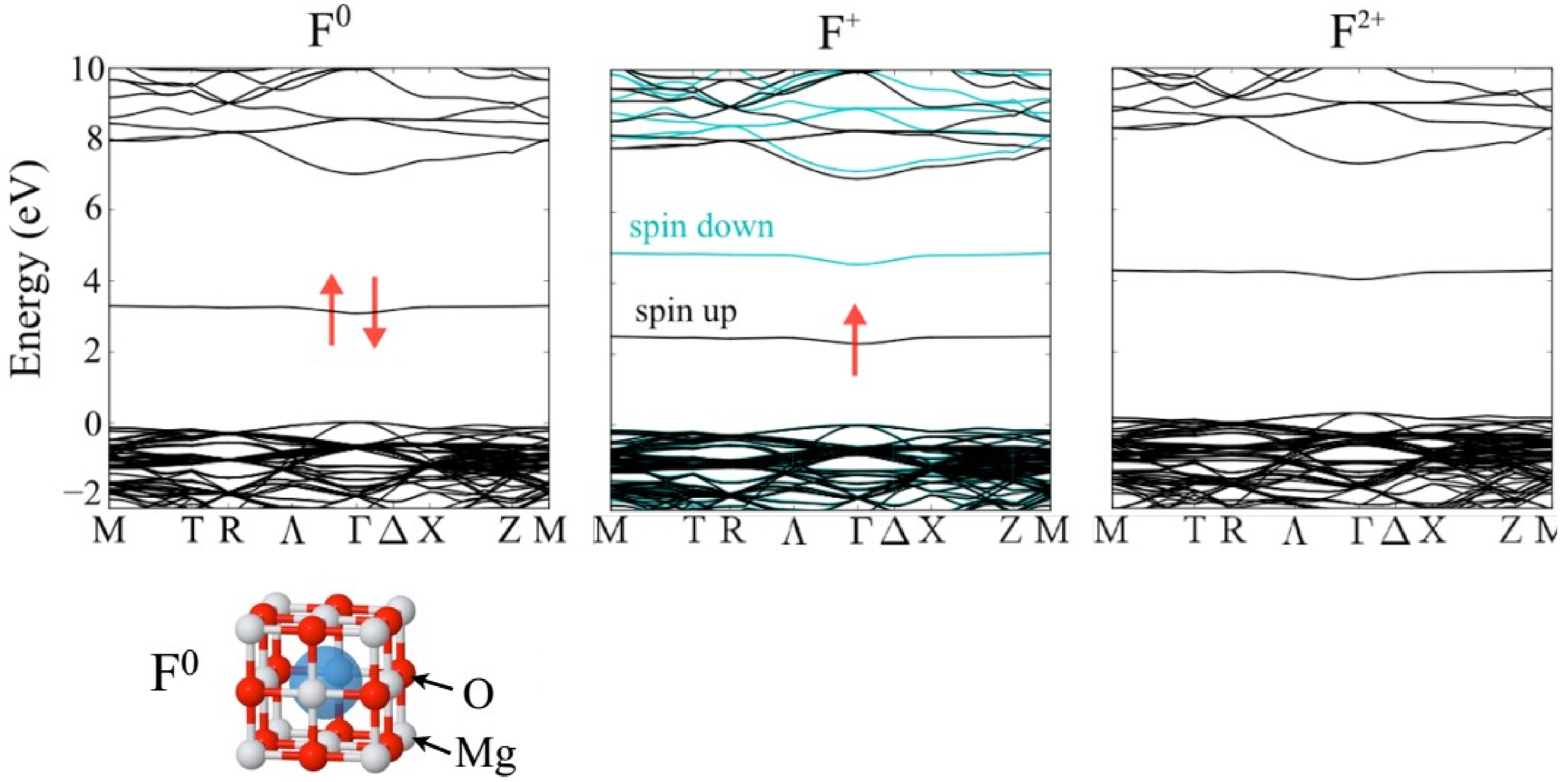
  Perdew, Ernzerhof, and Burke, J. Chem. Phys. 105, 9982 (1996)

  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

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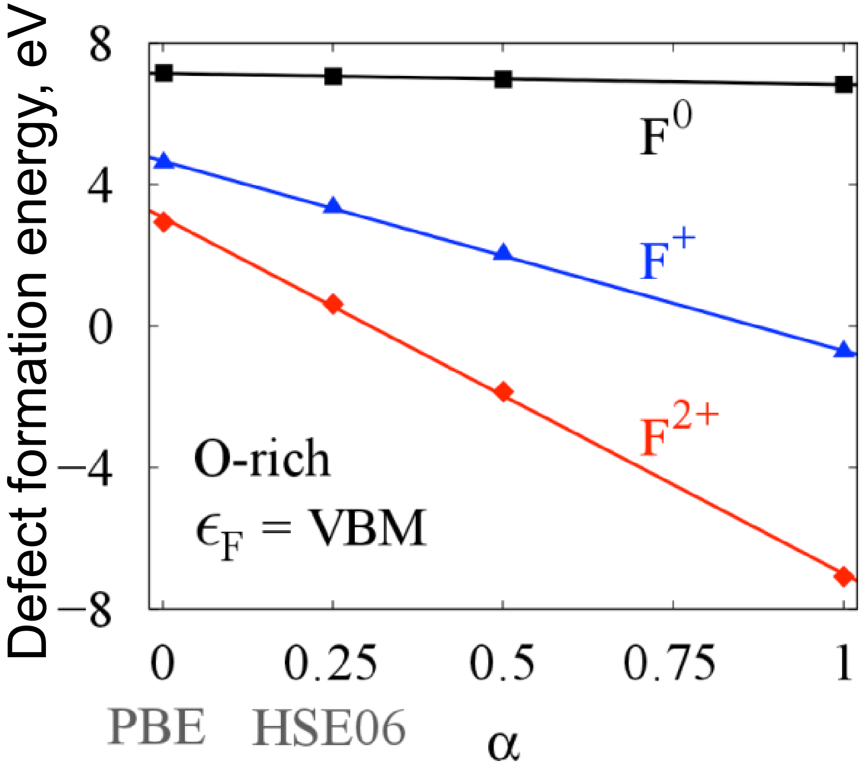
☐ Determine the best α

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



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

Which α to use?

Tuning hybrids: A practical approach

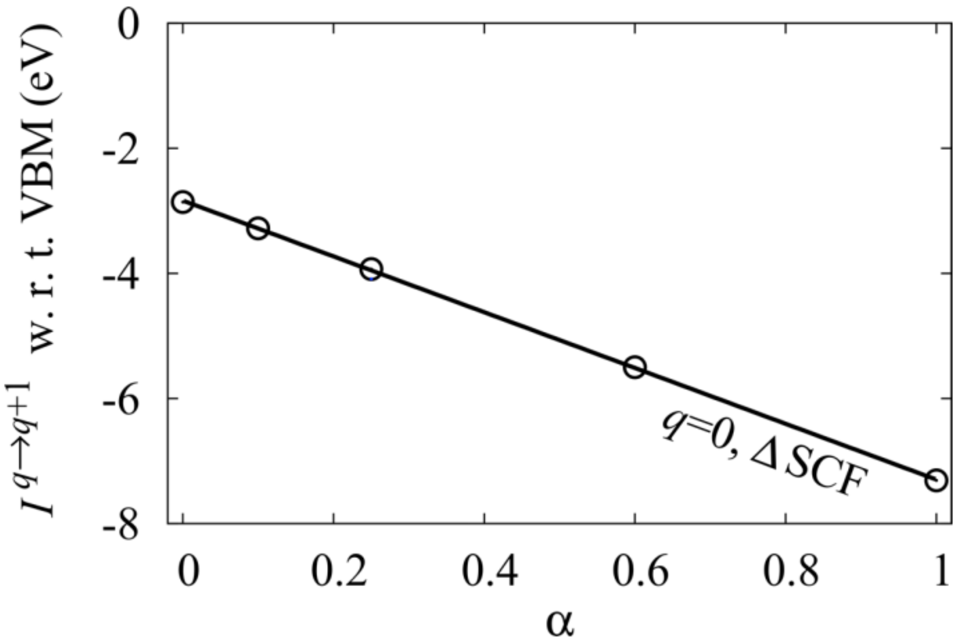
- ❐ **Determine the best α**

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

Request:

Ionization energies with opt-HSE and with G_0W_0@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

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

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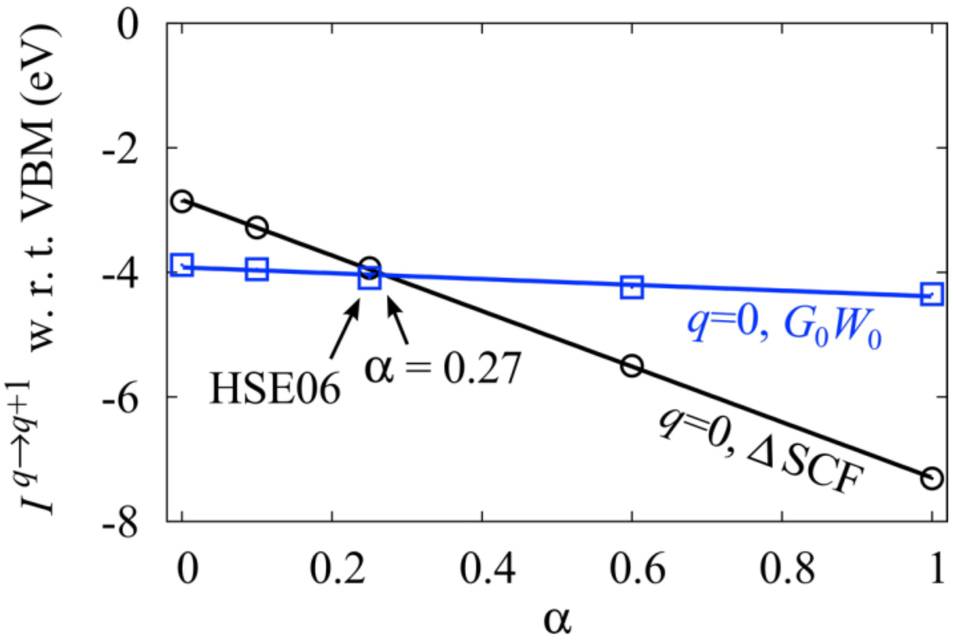

From highest occupied orbital

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:

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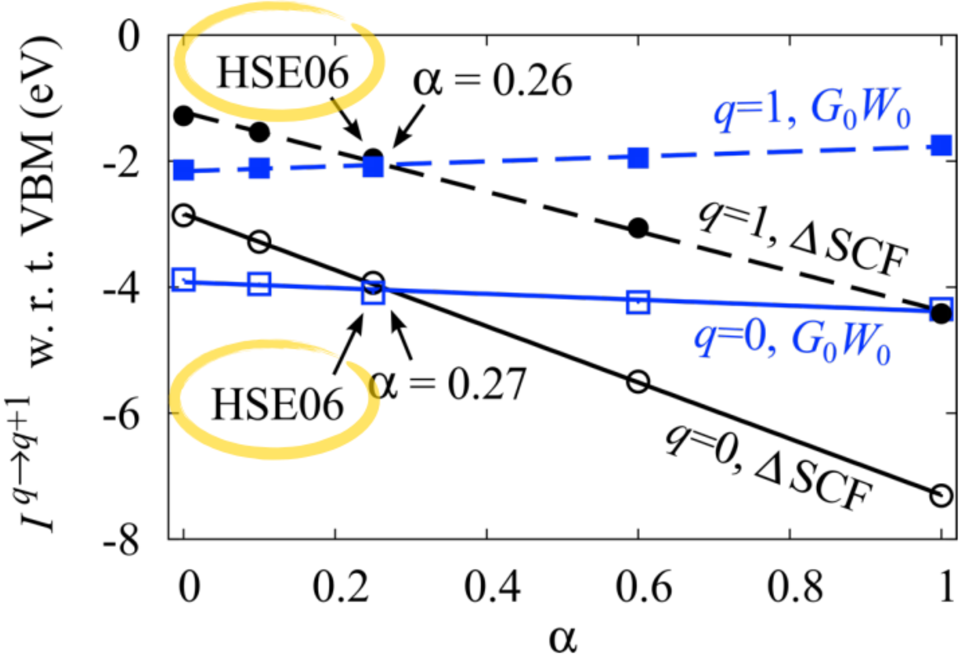


From highest occupied orbital

From total energy differences

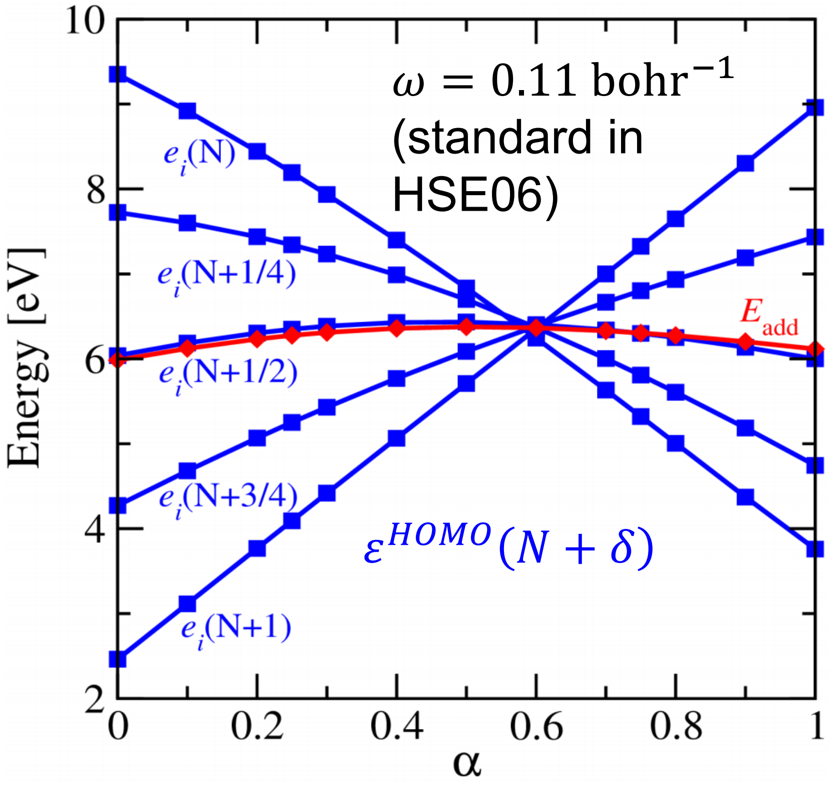
Tuning hybrids: A practical approach

Example: $\mathrm{Fe_{Mg}}$ substitutional defects in MgO

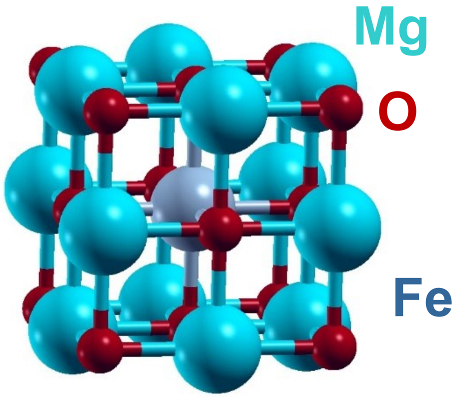
- **Is $\alpha = 0.25$ always good?**

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

$$\frac{1}{r} = SR_\omega(r) + LR_\omega(r) = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{1-\mathrm{erfc}(\omega r)}{r}$$



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



Optimal $\alpha \approx 0.6$

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

Hybrid functionals

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- ## 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) $\alpha = 1/\varepsilon_\infty$ (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:

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

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

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

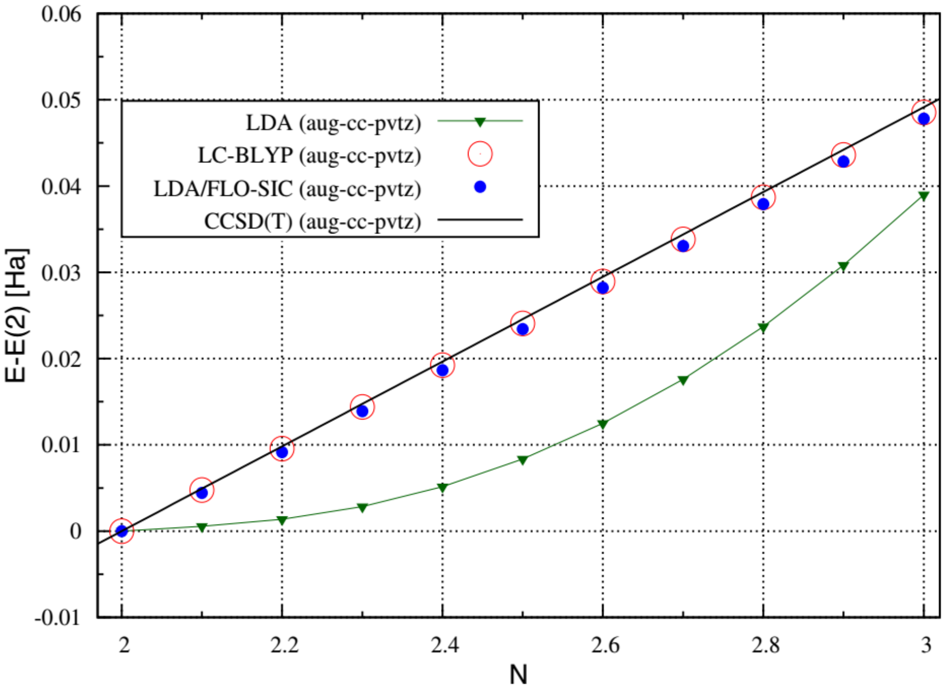
+ exact for any one-electron density

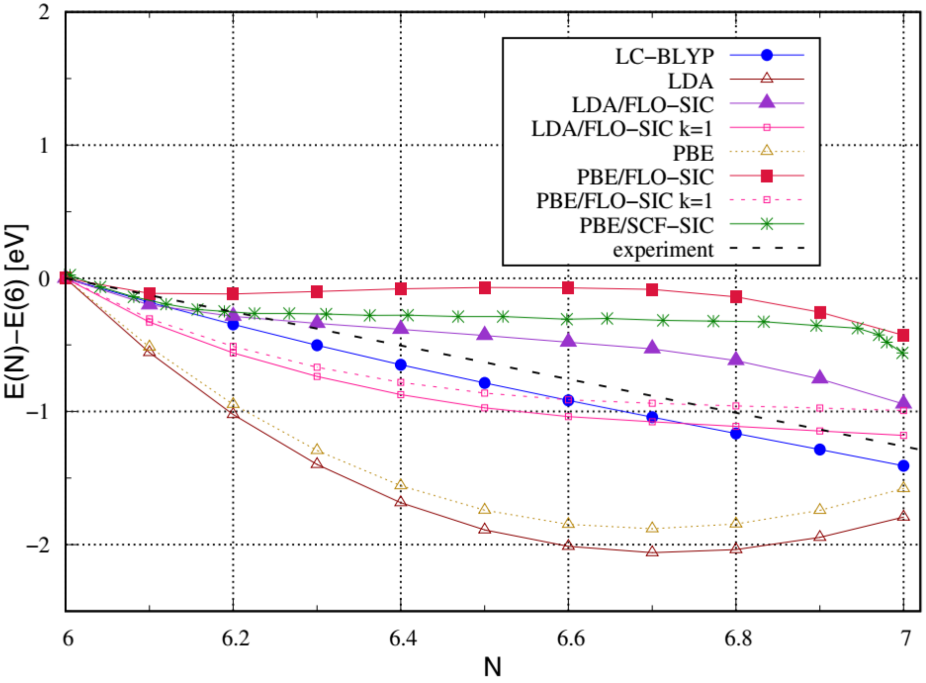
+ fast

- 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*

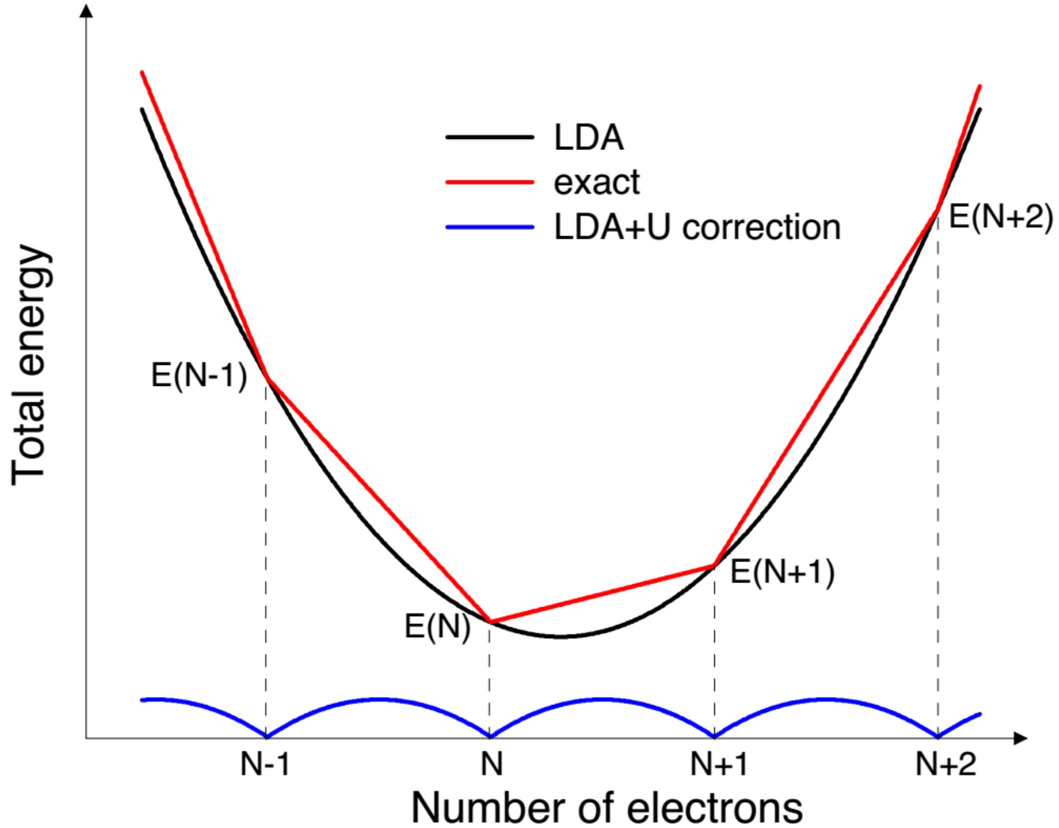
Idea: Penalize fractional occupations of localized atomic orbitals

1e

(1-δ)e δe

isolated ion

ion in solid

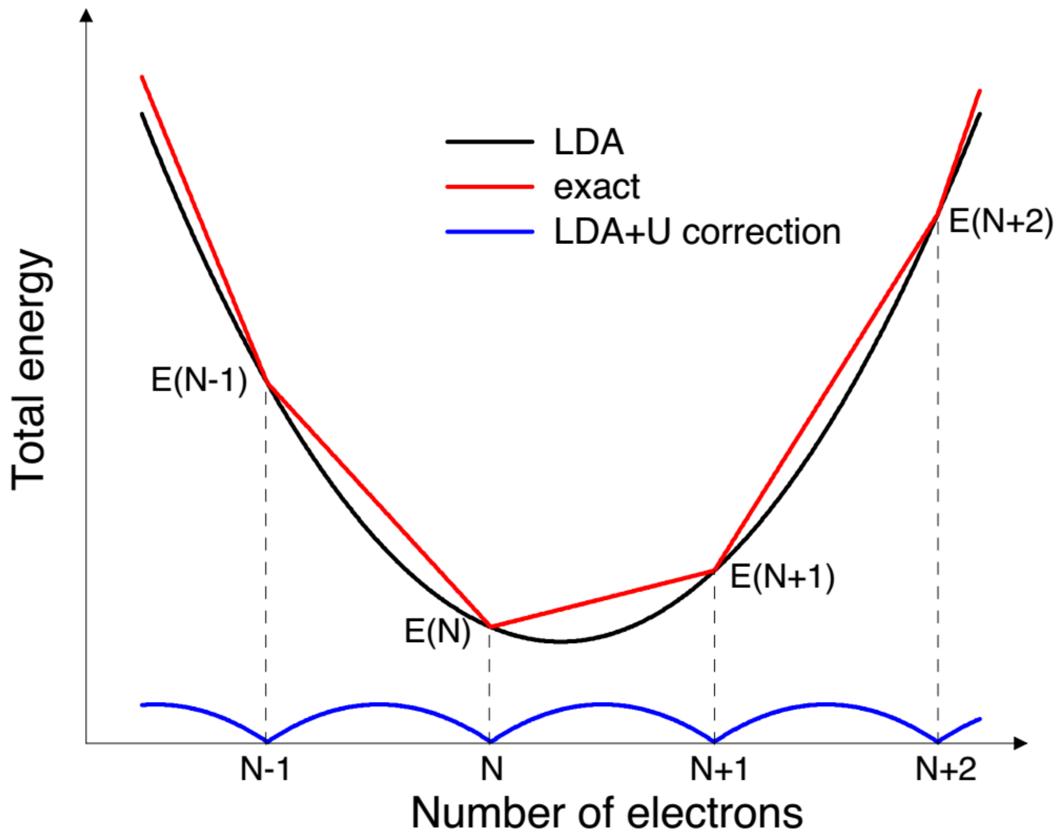


E. Pavarini, E. Koch, F. Anders, and M. Jarrell
Correlated Electrons: From Models to Materials
Modeling and Simulation Vol. 2
Forschungszentrum Julich, 2012,
ISBN 978-3-89336-796-2

Other approaches: DFA+*U*

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
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Other approaches: DFA+*U*

Hartree-Fock energy of localized electrons in a solid:

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

$$(\langle \phi_m \phi_{m'} | V | \phi_{m''} \phi_{m'''} \rangle - \langle \phi_m \phi_{m'} | V | \phi_{m'''} \phi_{m''} \rangle) n^{\sigma}_{mm''} n^{\sigma}_{m'm'''} \}$$

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

atomic orbitals

KS states

occupation of KS states

Liechtenstein, Anisimov, and Zaanen, Phys. Rev. B **52**, R5467 (1995)

Other approaches: DFA+*U*

Hartree-Fock energy of localized electrons in a solid:

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

atomic orbitals

KS states

occupation of KS states

V **- screened Coulomb interaction (due to other atomic orbitals *s*,*p*,...)**

Liechtenstein, Anisimov, and Zaanen, Phys. Rev. B **52**, R5467 (1995)

Other approaches: DFA+*U*

Hartree-Fock energy of localized electrons in a solid:

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

atomic orbitals

KS states

occupation of KS states

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

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

$$\Rightarrow \quad E^{loc} \approx \frac{1}{2}\sum_{\{m\}\sigma}\{Un^{\sigma}_{mm}n^{-\sigma}_{m'm'} + (U-J)n^{\sigma}_{mm}n^{\sigma}_{m'm'} - (U-J)n^{\sigma}_{mm'}n^{\sigma}_{m'm}\}$$

Other approaches: DFA+U

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

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

Penalty for fractional occupations:

$$\Delta E = E^{loc}\left(n^{\sigma}_{mm'} \text{ in solid}\right) - E^{loc}\left(n^{\sigma}_{mm'} \text{ in ion}\right)$$

$$E^{loc}\left(n^{\sigma}_{mm'} \text{ in ion }\right)$$
$$= \frac{1}{2}\sum_{\{m\}\sigma}\{U n^{\sigma}_{mm} n^{-\sigma}_{m'm'} + (U-J) n^{\sigma}_{mm} n^{\sigma}_{m'm'}\} - \frac{(U-J)}{2}\sum_{m\sigma} n^{\sigma}_{mm}$$

Other approaches: DFA+*U*

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

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

Penalty for fractional occupations:

$$\Delta E = E^{loc}\left(n^{\sigma}_{mm'} \text{ in solid}\right) - E^{loc}\left(n^{\sigma}_{mm'} \text{ in ion}\right)$$

$$E^{loc}\left(n^{\sigma}_{mm'} \text{ in ion }\right) = \frac{1}{2}\sum_{\{m\}\sigma}\{U n^{\sigma}_{mm} n^{-\sigma}_{m'm'} + (U-J) n^{\sigma}_{mm} n^{\sigma}_{m'm'}\} - \frac{(U-J)}{2}\sum_{m\sigma} n^{\sigma}_{mm}$$

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

Other approaches: DFA+*U*

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

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
- $E^{loc}\left(n^{\sigma}_{mm'} \text{ in ion}\right)$ **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*

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

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

_U_ depends on atom, orbital (*d*, *f*), atom environment

Take-home messages:

Know what you are doing!

Non-linearity of *E*(*N*) → 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 1307 2015

J Sun, A Ruzsinszky, JP Perdew

Physical review letters 115 (3), 036402