Computational Chemistry and Materials Modeling

Lecture 3

Density Functional Theory

Sergey Levchenko

Center for Energy Science and Technology (CEST)

Skolkovo Institute of Science and Technology

Moscow, Russia

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Hartree-Fock Theory

- **The Hartree-Fock approximation**

Slater determinant fulfills the Pauli principle

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

Hartree-Fock equation

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

Hartree-Fock Theory

- **Configuration interaction (CI)**

  Linear combination of Slater determinants

  Correlation effects taken into account

  Leads to the energetically preferred solution

  Leads generally to the exacte solution

  Only for small systems doable

  Van Vleck catastrophy

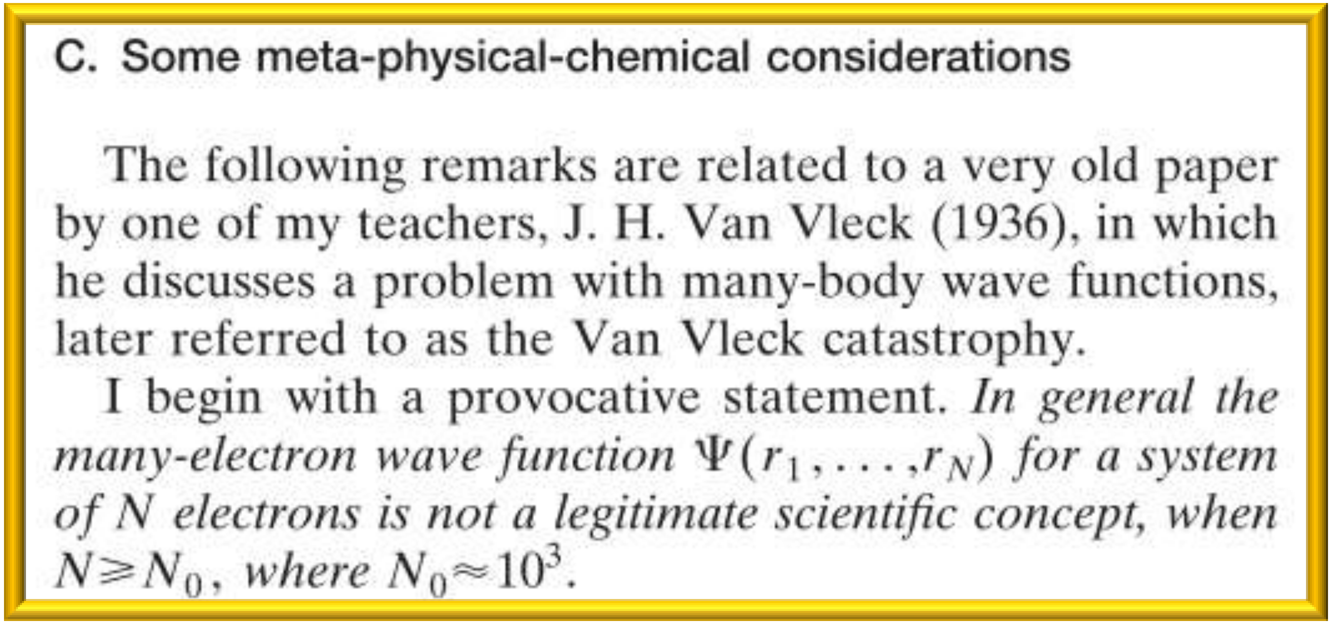
Nobel lecture …

$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$

- ☐ **The many-body wavefunction of 1000 electrons cannot be stored in the whole universe**

Van Vleck catastrophy (1936)

W. Kohn, Rev. Mod. Phys. 11, 1253 (1999).



C. Some meta-physical-chemical considerations

The following remarks are related to a very old paper by one of my teachers, J. H. Van Vleck (1936), in which he discusses a problem with many-body wave functions, later referred to as the Van Vleck catastrophy.

I begin with a provocative statement. *In general the many-electron wave function* $\Psi(r_1, \ldots, r_N)$ *for a system of N electrons is not a legitimate scientific concept, when* $N \geqslant N_0$, *where* $N_0 \approx 10^3$.

A simpler example

- **Ne atom**

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_6, \mathbf{r}_7, \mathbf{r}_8, \mathbf{r}_9, \mathbf{r}_{10})$$

10 electrons	
30 coordinates	
10 entries for each coordinate	10^{30} entries
1 byte per entry	10^{30} bytes
5 x 10^9 bytes per DVD	2 x 10^{20} DVDs
16 GB per smartphone	~10^{20} smartphones
7 x 10^9 people on earth	1.5 x 10^{10} smartphones / person

- **Storing is not an option (maybe calculating on demand is)**

Density-functional theory

- ☐ **In principle, we need to know the many-electron wave function**

$$\Phi(\{\mathbf{r}_i\}) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$$

depending on the coordinates of all electrons

- ☐ **According to Hohenberg and Kohn, only the electron density is required**

$$n(\mathbf{r})$$

depending on three coordinates: x, y, z

Questions

- ❒ **Do we really need the many-body wave function?**
- ❒ **Can we compute the electron distribution without explicitly knowing the WF?**

$$n(\mathbf{r}) = \left\langle \mathbf{\Phi}(\{\mathbf{r}_i\}) \middle| \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \middle| \mathbf{\Phi}(\{\mathbf{r}_i\}) \right\rangle$$

$$n(\boldsymbol{r}) = N \int \Phi^*(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \Phi\,(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) d^3 r_2 \ldots d^3 r_N$$

Density-functional theory

❒ Literature

P. Hohenberg, W. Kohn, Phys. Rev. 136 , B864 (1964)

W. Kohn, L. Sham, Phys. Rev. A 140,1133 (1965)

R.M. Dreizler, E.K.U. Gross, Density Functional Theory (Spinger,1990)

R .G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules (Oxford University Press 1994)

R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989)

K. Burke, ABC of DFT: http://dft.uci.edu/sites/default/files/g1.pdf

Hohenberg-Kohn theorem

P. Hohenberg, W. Kohn, Phys. Rev. 136 , B864 (1964)

- **I: The total energy of an interacting system of electrons is a unique functional of the density**

$$\boxed{E = F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}$$

The functional *F* does not depend on the external potential!

- **II: The energy takes its minimum at the ground-state density**

Proof of HK theorem

- **I: Uniqueness: We need to show that there is only one potential that leads to a certain density**

Proof of HK theorem

- **I: Uniqueness: We need to show that there is only one potential that leads to a certain density**

Given H^e, V_{ext}, $E = \langle \Phi(\{\mathbf{r}_i\}) | H^e | \Phi(\{\mathbf{r}_i\}) \rangle$, $n(\mathbf{r})$

Assume there is another potential such that we have

$$\tilde{H}^e, \tilde{V}_{ext}, \tilde{E} = \left\langle \tilde{\Phi}(\{\mathbf{r}_i\}) \middle| \tilde{H}^e \middle| \tilde{\Phi}(\{\mathbf{r}_i\}) \right\rangle, \boxed{\tilde{n}(\mathbf{r}) = n(\mathbf{r})}$$

$$\tilde{E} = \left\langle \tilde{\Phi} \middle| \tilde{H}^e \middle| \tilde{\Phi} \right\rangle < \left\langle \Phi \middle| \tilde{H}^e \middle| \Phi \right\rangle = \left\langle \Phi \middle| H^e - V_{ext} + \tilde{V}_{ext} \middle| \Phi \right\rangle$$

$$+\begin{array}{l} \tilde{E} < E + \left\langle \Phi \middle| \tilde{V}_{ext} - V_{ext} \middle| \Phi \right\rangle \\ E < \tilde{E} + \left\langle \Phi \middle| V_{ext} - \tilde{V}_{ext} \middle| \Phi \right\rangle \end{array} \Longrightarrow \tilde{E} + E < E + \tilde{E}$$

impossible!

Two potentials cannot lead to the same density

Proof of HK theorem

$$\tilde{E} < E + \left\langle \Phi \middle| \tilde{V}_{ext} - V_{ext} \middle| \Phi \right\rangle = E + \int d\mathbf{r} \left(\tilde{V}_{ext} - V_{ext} \right) n(\mathbf{r})$$

$+$

$$E < \tilde{E} + \left\langle \tilde{\Phi} \middle| V_{ext} - \tilde{V}_{ext} \middle| \tilde{\Phi} \right\rangle = \boxed{\tilde{E} + \int d\mathbf{r} \left(V_{ext} - \tilde{V}_{ext} \right) \tilde{n}(\mathbf{r})}$$

$$\Updownarrow \quad \tilde{n}(\mathbf{r}) = n(\mathbf{r})$$

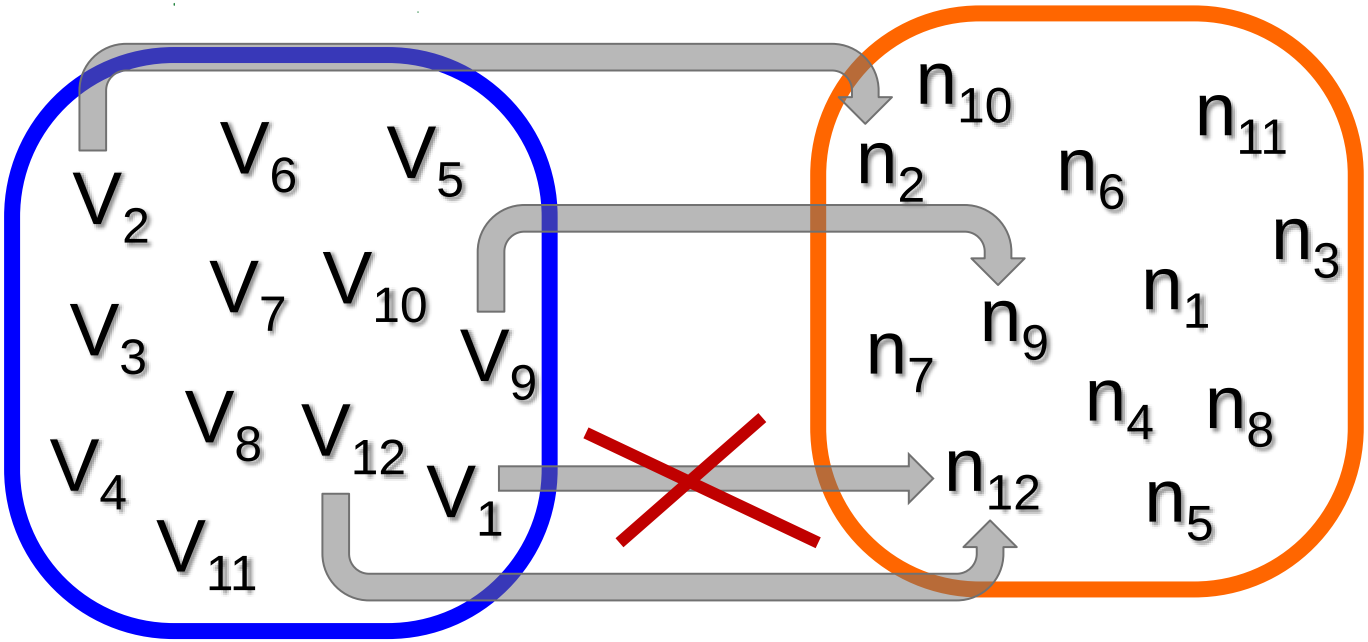
$$\boxed{\tilde{E} + \int d\mathbf{r} \left(V_{ext} - \tilde{V}_{ext} \right) n(\mathbf{r})}$$

$$\tilde{E} + E < E + \tilde{E} \quad \Longrightarrow \quad \boxed{\tilde{n}(\mathbf{r}) \neq n(\mathbf{r})}$$

impossible!

Proof of HK theorem

- ❒ **There is a one-to-one correspondence between density and potential**



Proof of HK theorem

- **Part II: The ground state energy can be obtained variationally: The density that minimizes the total energy is the ground-state density**

Proof of HK theorem

- **Part II: The ground state energy can be obtained variationally: The density that minimizes the total energy is the ground-state density**

$$n(\boldsymbol{r}) \rightarrow \hat{V}_{ext} \rightarrow \hat{H}^{e} = \hat{F} + \hat{V}_{ext} \rightarrow \Phi(\{\boldsymbol{r}_i\}) \Rightarrow \langle\Phi|\hat{F}|\Phi\rangle \equiv F[n(\boldsymbol{r})]$$

The total energy is a functional of the density:

$$E[n(\boldsymbol{r})] = F[n(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n(\boldsymbol{r})d\boldsymbol{r}$$

A density that is a ground state of some external potential is called *V*-representable

$$E[n'(\boldsymbol{r})] = F[n'(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n'(\boldsymbol{r})d\boldsymbol{r} = \langle\Phi'|\hat{F}|\Phi'\rangle + \langle\Phi'|\hat{V}_{ext}|\Phi'\rangle$$

Proof of HK theorem

- **Part II: The ground state energy can be obtained variationally: The density that minimizes the total energy is the ground-state density**

$$E[n'(\boldsymbol{r})] = F[n'(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n'(\boldsymbol{r})d\boldsymbol{r} = \langle\Phi'|\hat{F}|\Phi'\rangle + \langle\Phi'|\hat{V}_{ext}|\Phi'\rangle$$

For a ground state density:

$$E[n(\boldsymbol{r})] = F[n(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n\,(\boldsymbol{r})d\boldsymbol{r} = \langle\Phi|\hat{F}|\Phi\rangle + \langle\Phi|\hat{V}_{ext}|\Phi\rangle$$

From variational principle:

$$\langle\Phi'|\hat{F}|\Phi'\rangle + \langle\Phi'|\hat{V}_{ext}|\Phi'\rangle > \langle\Phi|\hat{F}|\Phi\rangle + \langle\Phi|\hat{V}_{ext}|]\Phi\rangle$$

$$E[n'(\boldsymbol{r})] > E[n(\boldsymbol{r})]$$

Kohn-Sham theory

- **The HK theorem is exact for the ground state**
- **It is beautiful as we only need to know one = *THE* functional to describe any system**

  Atoms, molecules, solids, surfaces, nano-structures
- **The only problem is that we don't know this functional**

  Thus DFT is not practical so far
- **Kohn and Sham set the stage for the practicality of DFT**

  W. Kohn, L. Sham, Phys. Rev. A 140,1133 (1965)

Kohn-Sham theory

- One can divide the energy functional into three contributions:

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

- We still don't have a good expression for the kinetic energy

This problem is, however, diminished by introducing single-particle functions which give the exact density:

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

Kohn-Sham theory

- **We will now carry out the variation with respect to the density through a variation with respect to the single-particle functions.**

Kohn-Sham equations

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'\boxed{\sum_j u_j^*(\mathbf{r}')u_j(\mathbf{r}')}\frac{1}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})-\epsilon_i\right\}u_i(\mathbf{r})=0$$

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})-\epsilon_i\right\}u_i(\mathbf{r})=0$$

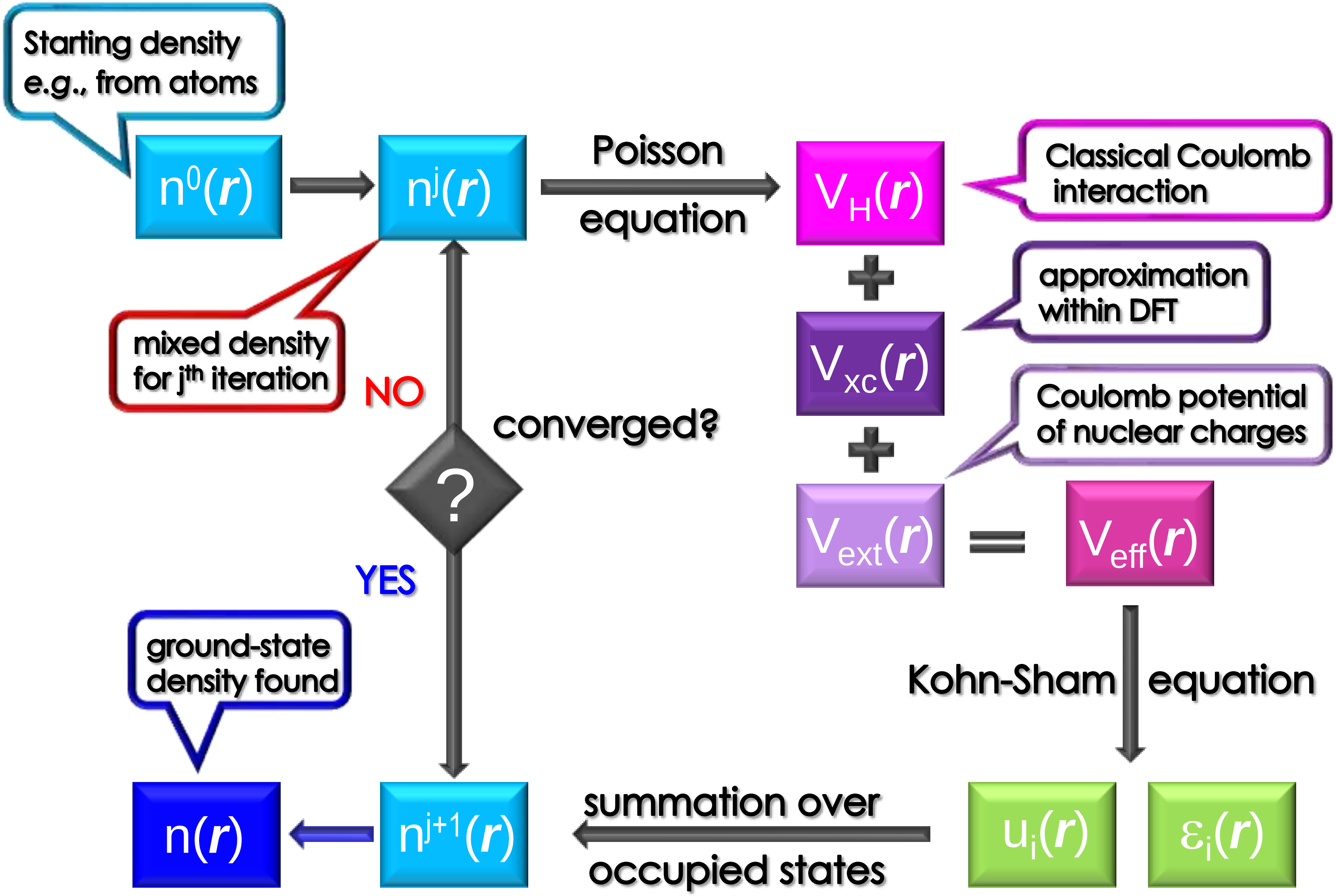
$$\boxed{\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\boxed{V_{xc}[n(\mathbf{r})]}-\epsilon_i\right\}u_i(\mathbf{r})=0}$$

approximation needed – only approximation!
contains xc effects and corrections to kinetic energy

Kohn-Sham theory

- **Caution: The** Kohn-Sham eigenvalues **were derived as Lagrange parameters of the variation procedure and cannot *a priori* be interpreted as single-particle energies.**
- **The** Kohn-Sham orbitals **are auxiliary quantities which produce the exact density.**
- **The** only approximation **required for the ground state is V_{xc}.**
- **The potential is a functional of the density which is obtained from the KS orbitals; these, in turn, give the density. Thus the** KS equation **must be solved** self-consistently**.**

Self-consistent field cycle



Starting density e.g., from atoms

$n^0(\boldsymbol{r})$

$n^j(\boldsymbol{r})$

mixed density for jth iteration

Poisson equation

$V_H(\boldsymbol{r})$

Classical Coulomb interaction

+

$V_{xc}(\boldsymbol{r})$

approximation within DFT

+

$V_{ext}(\boldsymbol{r})$

Coulomb potential of nuclear charges

=

$V_{eff}(\boldsymbol{r})$

Kohn-Sham equation

$u_i(\boldsymbol{r})$

$\varepsilon_i(\boldsymbol{r})$

summation over occupied states

$n^{j+1}(\boldsymbol{r})$

converged?

?

NO

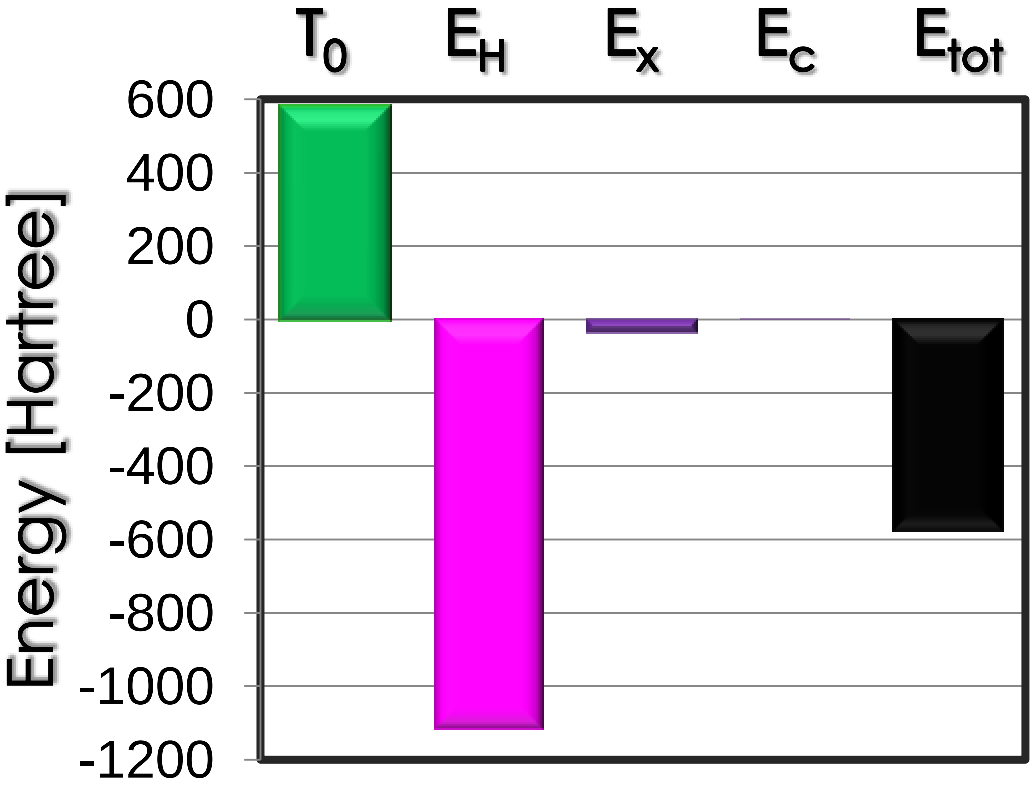
YES

$n(\boldsymbol{r})$

ground-state density found

Energy contributions

- **Example: Si**



Exchange-correlation functionals

- **Local-density approximation (LDA)**

xc effects taken from homogenous electron gas

$$E_{xc}^{LDA} = \int d\mathbf{r} \; n(\mathbf{r}) \epsilon_{xc}^{unif}[n(\mathbf{r})]$$

Exchange is known analytically:

$$\epsilon_x(r_s) = -\frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} \qquad r_s = \left[\frac{3}{4\pi n(\mathbf{r})}\right]^{\frac{1}{3}}$$

Correlation: high- and low-density limits are known analytically:

$$\epsilon_c = A \ln(r_s) + B + r_s(C \ln(r_s) + D)$$ - high density

Exchange-correlation functionals

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Correlation: high- and low-density limits are known analytically:

$$\epsilon_c = -\frac{0.438}{r_s} + \frac{1.33}{r_s^{3/2}} - \frac{1.47}{r_s^2}$$

- low-density (electrons form a BCC lattice called Wigner crystal)

Exchange-correlation functionals

❐ Local-density approximation (LDA)

Neither the high nor the low-density limits are useful for ordinary matter

For the intermediate densities, one can parametrize an exact numerical solution (e.g., obtained with quantum Monte Carlo)

e.g., Hedin & Lundquist, 1971

$$\epsilon_c[n(\mathbf{r})] = 0.045\left[\left(1+x^3\right) ln\left(1+\frac{1}{x}\right)+\frac{x}{2}-x^2-\frac{1}{3}\right] \qquad x=\frac{r_s}{21}$$

Exchange-correlation functionals

- ☐ **Many features of the exact $E_{XC}[n]$ are known → constraints on the approximate functional**

Limiting behavior for $n(r) \to \infty$ and $n(r) \to 0$

Lieb-Oxford bound:

$$\left\langle \Phi \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \Phi \right\rangle - \frac{1}{2} \int \frac{n_\Phi(\boldsymbol{r}) n_\Phi(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' \geq 1.68 \int n_\Phi(\boldsymbol{r})^{\frac{4}{3}} d\boldsymbol{r}$$

- ☐ **LDA satisfies these constraints**

Exchange-correlation functionals

- **Many features of the exact $E_{XC}[n]$ are known → constraints on the approximate functional**

  Express $E_{XC}[n]$ through *exchange-correlation hole* (change due to XC of probability to find an electron at r when another electron is at r', can be measured!):

Exchange-correlation functionals

- ❐ **Many features of the exact $E_{XC}[n]$ are known → constraints on the approximate functional**

Express $E_{XC}[n]$ through *exchange-correlation hole* (change due to XC of probability to find an electron at r when another electron is at r'):

$$E_{XC}[n] = \frac{1}{2}\int d\boldsymbol{r}\, n(\boldsymbol{r})\int d\boldsymbol{u}\, \frac{h_{XC}(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u}\,)}{|\boldsymbol{u}|}$$

Sum rules:

$$\int d\boldsymbol{u}\, h_X(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u}\,) = -1, \qquad \int d\boldsymbol{u}\, h_C(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u}\,) = 0$$

Local conditions:

$$h_X(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u}\,) \le 0\ \forall \boldsymbol{r},\boldsymbol{u}, \qquad h_X(\boldsymbol{r},\boldsymbol{r}\,) = -\frac{n(\boldsymbol{r})}{2}\ \text{(no spin)}$$

- ❐ **LDA satisfies all these constraints!**

Exchange-correlation functionals

- **What about spin?**

Exchange-correlation functionals

- ❒ **Local spin density approximation (LSDA)**

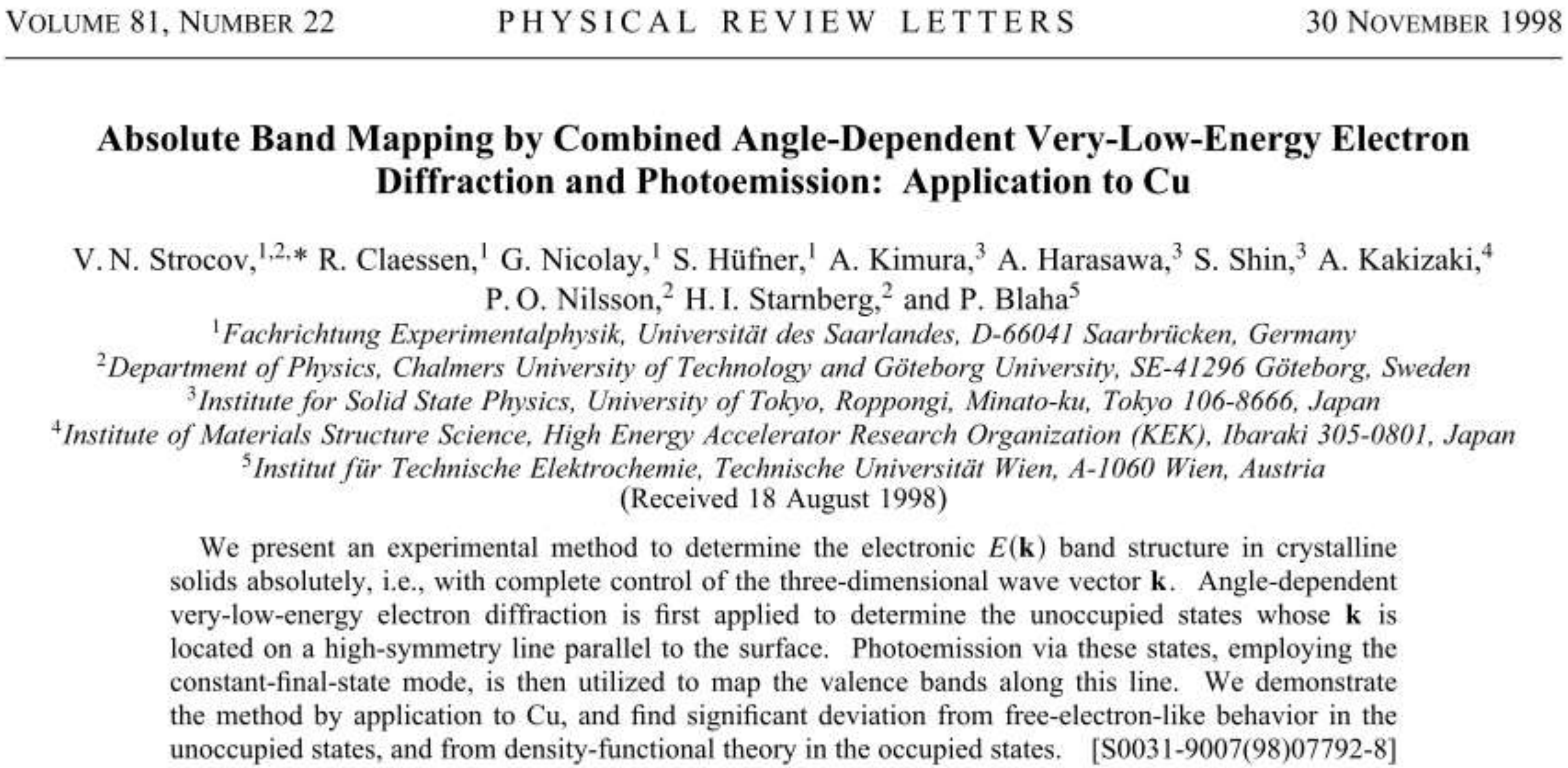
  The total energy is a unique functional of the density, but the wave function is not - any normalized linear combination of wave functions with the same energy gives the same density

  If $\hat{H}$ does not depend on spin, there are $2S + 1$ wave functions with the same energy and the same total spin S

  Constrain number of spin-up and spin-down electrons separately →$E[n_\alpha, n_\beta] = \langle \Phi | \hat{H} | \Phi \rangle_{\Phi \to n_\alpha, n_\beta}$

  Generalizations of the HK theorem to $E[n_\alpha, n_\beta]$ exist

Example: Cu



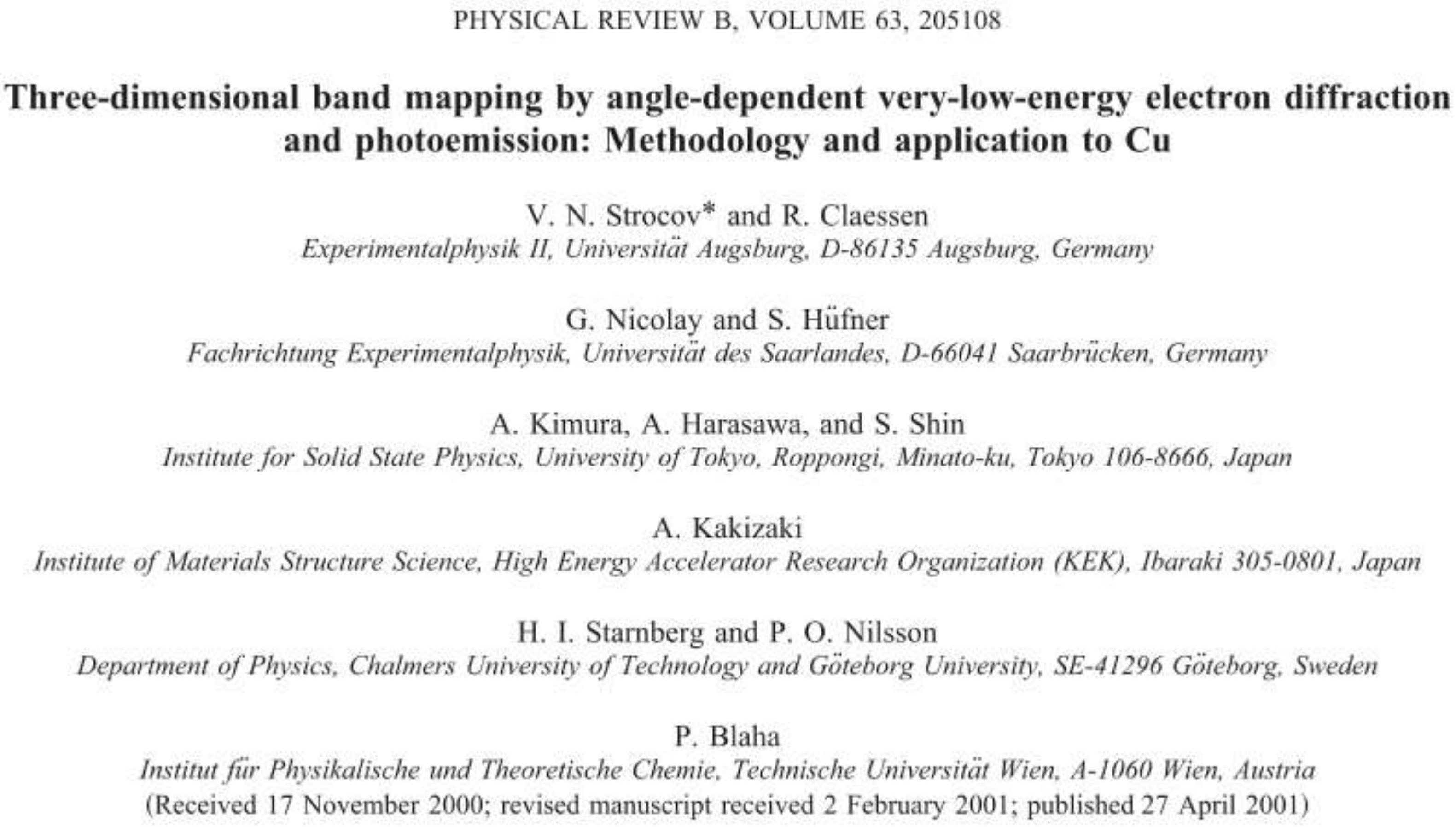
VOLUME 81, NUMBER 22 PHYSICAL REVIEW LETTERS 30 NOVEMBER 1998

Absolute Band Mapping by Combined Angle-Dependent Very-Low-Energy Electron Diffraction and Photoemission: Application to Cu

V. N. Strocov,[1,2,*] R. Claessen,[1] G. Nicolay,[1] S. Hüfner,[1] A. Kimura,[3] A. Harasawa,[3] S. Shin,[3] A. Kakizaki,[4]
P. O. Nilsson,[2] H. I. Starnberg,[2] and P. Blaha[5]
[1]*Fachrichtung Experimentalphysik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*
[2]*Department of Physics, Chalmers University of Technology and Göteborg University, SE-41296 Göteborg, Sweden*
[3]*Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan*
[4]*Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Ibaraki 305-0801, Japan*
[5]*Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Wien, Austria*
(Received 18 August 1998)

We present an experimental method to determine the electronic $E(\mathbf{k})$ band structure in crystalline solids absolutely, i.e., with complete control of the three-dimensional wave vector $\mathbf{k}$. Angle-dependent very-low-energy electron diffraction is first applied to determine the unoccupied states whose $\mathbf{k}$ is located on a high-symmetry line parallel to the surface. Photoemission via these states, employing the constant-final-state mode, is then utilized to map the valence bands along this line. We demonstrate the method by application to Cu, and find significant deviation from free-electron-like behavior in the unoccupied states, and from density-functional theory in the occupied states. [S0031-9007(98)07792-8]

Example: Cu



PHYSICAL REVIEW B, VOLUME 63, 205108

Three-dimensional band mapping by angle-dependent very-low-energy electron diffraction and photoemission: Methodology and application to Cu

V. N. Strocov* and R. Claessen
Experimentalphysik II, Universität Augsburg, D-86135 Augsburg, Germany

G. Nicolay and S. Hüfner
Fachrichtung Experimentalphysik, Universität des Saarlandes, D-66041 Saarbrücken, Germany

A. Kimura, A. Harasawa, and S. Shin
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan

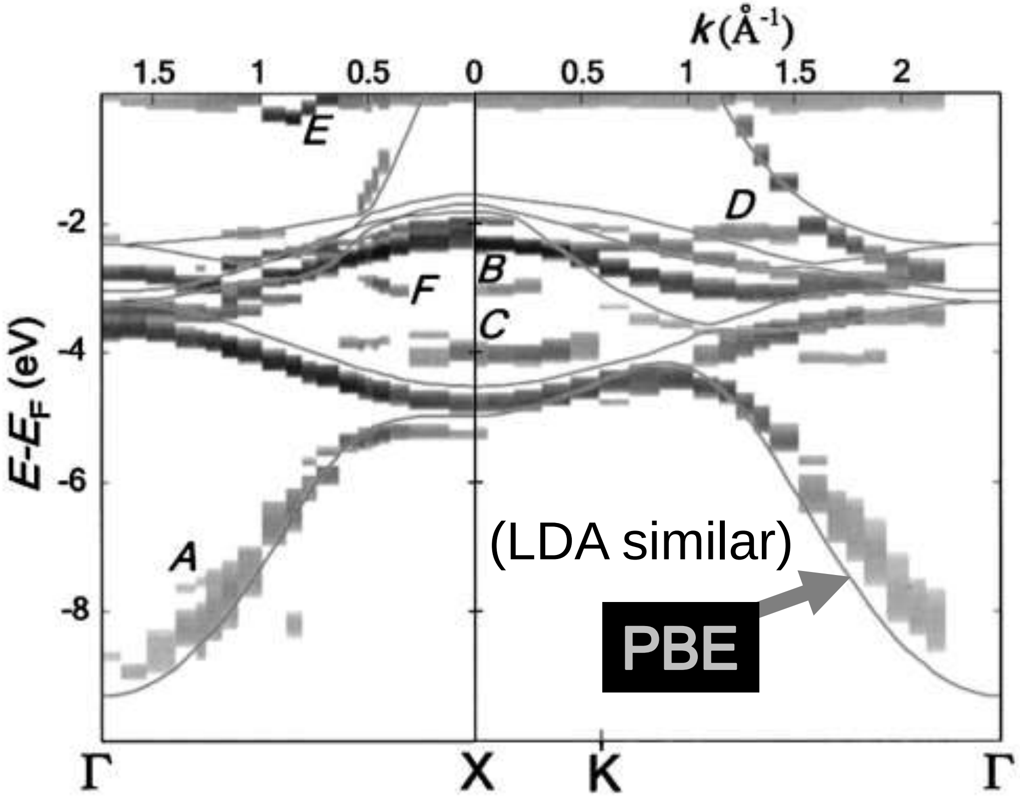
A. Kakizaki
Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Ibaraki 305-0801, Japan

H. I. Starnberg and P. O. Nilsson
Department of Physics, Chalmers University of Technology and Göteborg University, SE-41296 Göteborg, Sweden

P. Blaha
Institut für Physikalische und Theoretische Chemie, Technische Universität Wien, A-1060 Wien, Austria

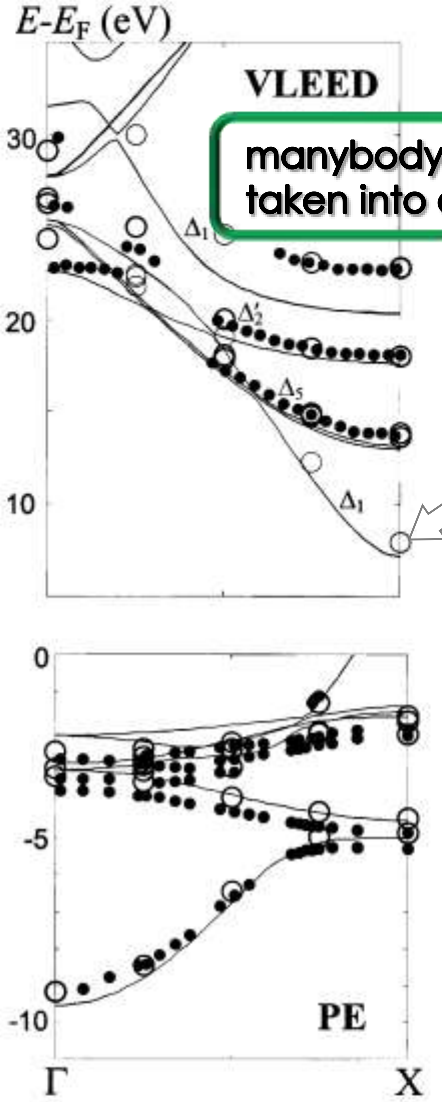
(Received 17 November 2000; revised manuscript received 2 February 2001; published 27 April 2001)

Example: Cu



(LDA similar)

PBE



manybody effects taken into account

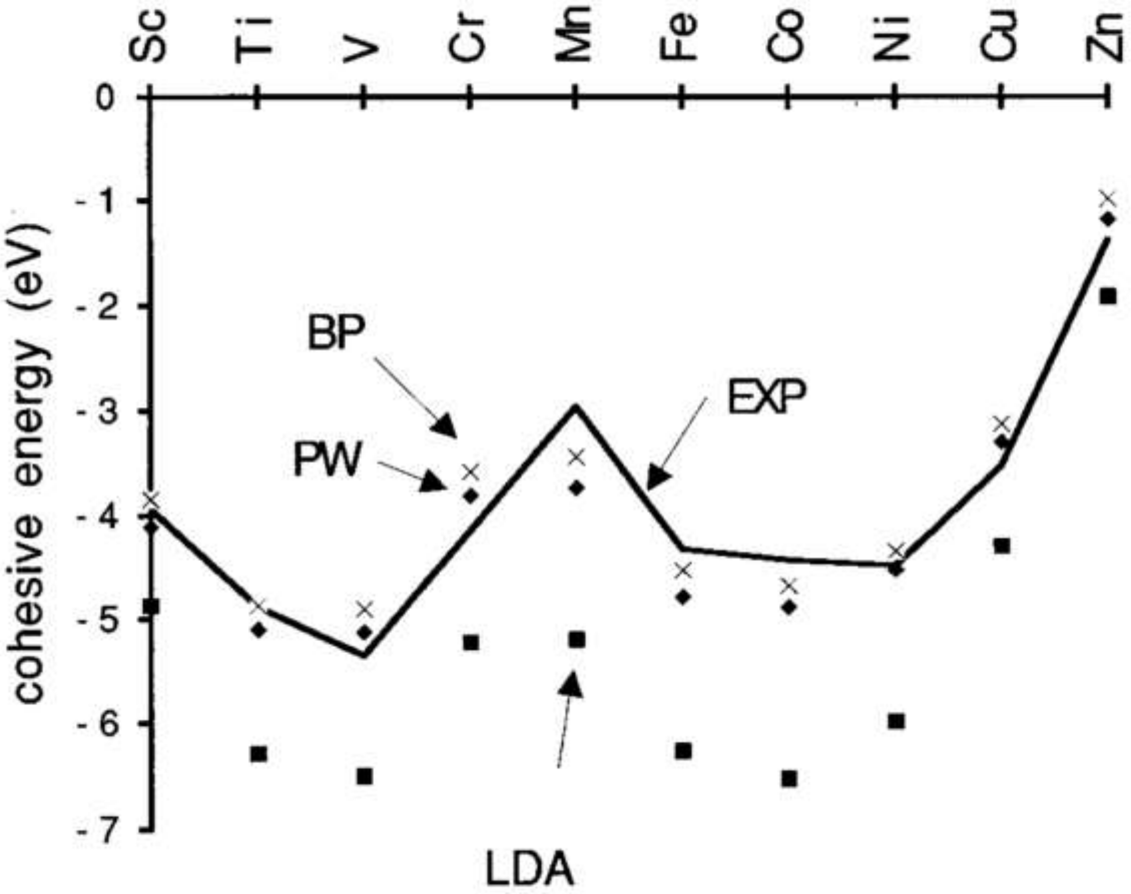
GW

V. N. Strocov, et al.,
Phys. Rev. B 63, 205108 (2001).

V. N. Strocov, et al.,
Surface Rev. and Lett. 9, 1281 (2002).

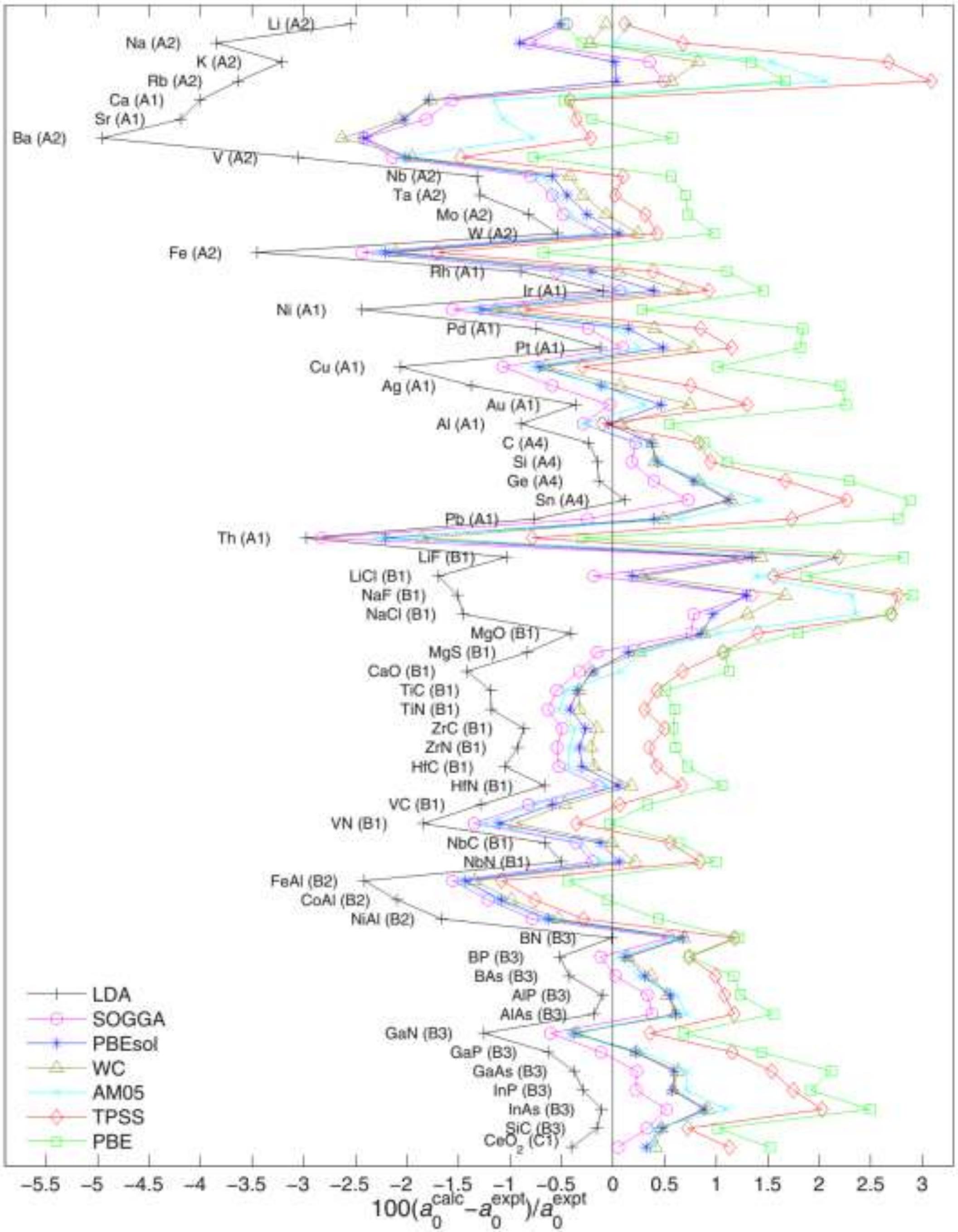
Exchange-correlation functionals

- **How well (or badly) does LDA work?**



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

Equilibrium lattice constant compared to experiment



P. Haas, F. Tran, and P. Blaha,

Phys. Rev. B 79, 085104 (2009)

Exchange-correlation functionals

- ❐ **How well (or badly) does LDA work?**

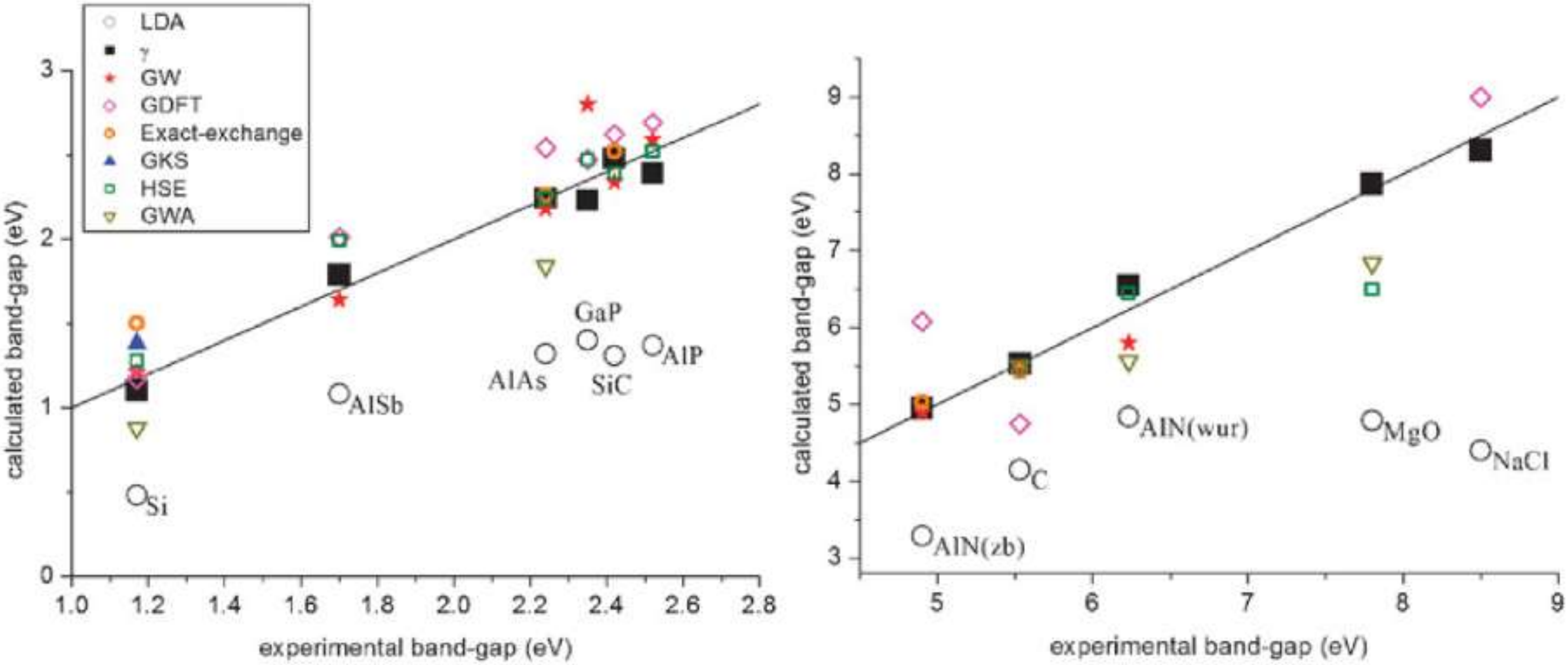
  For total energies, E_X is underestimated by about 10%, E_C is overestimated by about 200%, so E_{XC} is good to about 7% (mysterious cancellation of errors).

  For bond dissociation energies, LDA overbinds by about 1 eV/bond (30 kcal/mol), so no good for thermochemistry.

  Typical bond lengths are underestimated by 1% (unless involving an H atom), so excellent geometries and vibrations. So still used for structure.

Exchange-correlation functionals

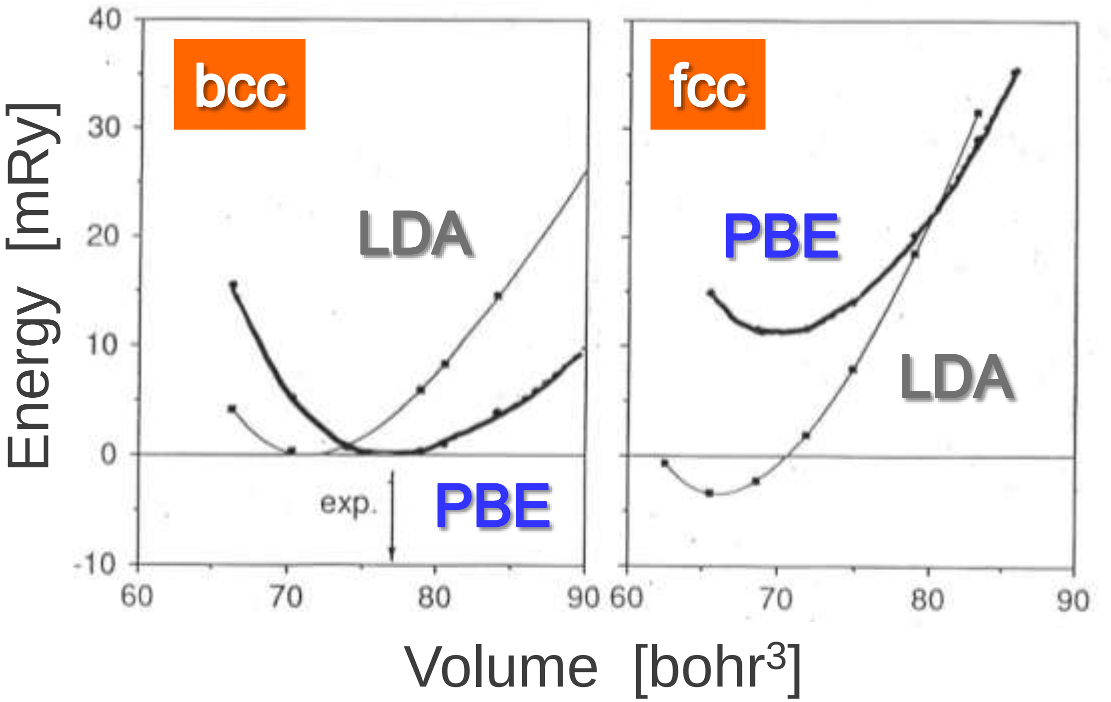
- **How well (or badly) does LDA work?**



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

Example: Fe

- **It took until 1996 that the proper crystallographic phase of Fe could be correctly obtained by DFT**



calculations
by P. Blaha

J. **P**erdew, K. **B**urke, and M. **E**rnzerhof, Phys. Rev. Lett. 77, 3865 (1996).
More than 137000 citations

Exchange-correlation functionals

- ☐ **Generalized gradient approximation (GGA)**

  Take into account local variations of the density:

$$E_{XC}^{GGA} = \int d\boldsymbol{r}\, n(\boldsymbol{r})(\epsilon_X^{GGA}[n, |\nabla n|] + \epsilon_C^{GGA}[n, |\nabla n|])$$

  Gradient expansion approximation: expand E_{XC} for slowly varying electron gas in terms of ∇n -- slow convergence

Exchange-correlation functionals

- **Generalized gradient approximation (GGA)**

Take into account local variations of the density:

$$E_{XC}^{GGA} = \int d\mathbf{r}\, n(\mathbf{r})(\epsilon_X^{GGA}[n, |\nabla n|] + \epsilon_C^{GGA}[n, |\nabla n|])$$

Gradient expansion approximation: expand E_{XC} for slowly varying electron gas in terms of ∇n -- slow convergence

$$\epsilon_X^{GGA} = \epsilon_X^{HES}[n] F_X[n, \nabla n]$$ (enhancement factor)

PBE: $$F_X = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}, \qquad s = \frac{|\nabla n(\mathbf{r})|}{2\kappa n(\mathbf{r})}$$

$$\epsilon_C^{GGA} = \epsilon_C^{LDA} + \frac{\beta^2}{2\alpha} \ln\left(1 + \frac{2\alpha}{\beta} \frac{s^2 + As^4}{1 + As^2 + A^2 s^4}\right)$$

Exchange-correlation functionals

- **Generalized gradient approximation (GGA)**

  Take into account local variations of the density:

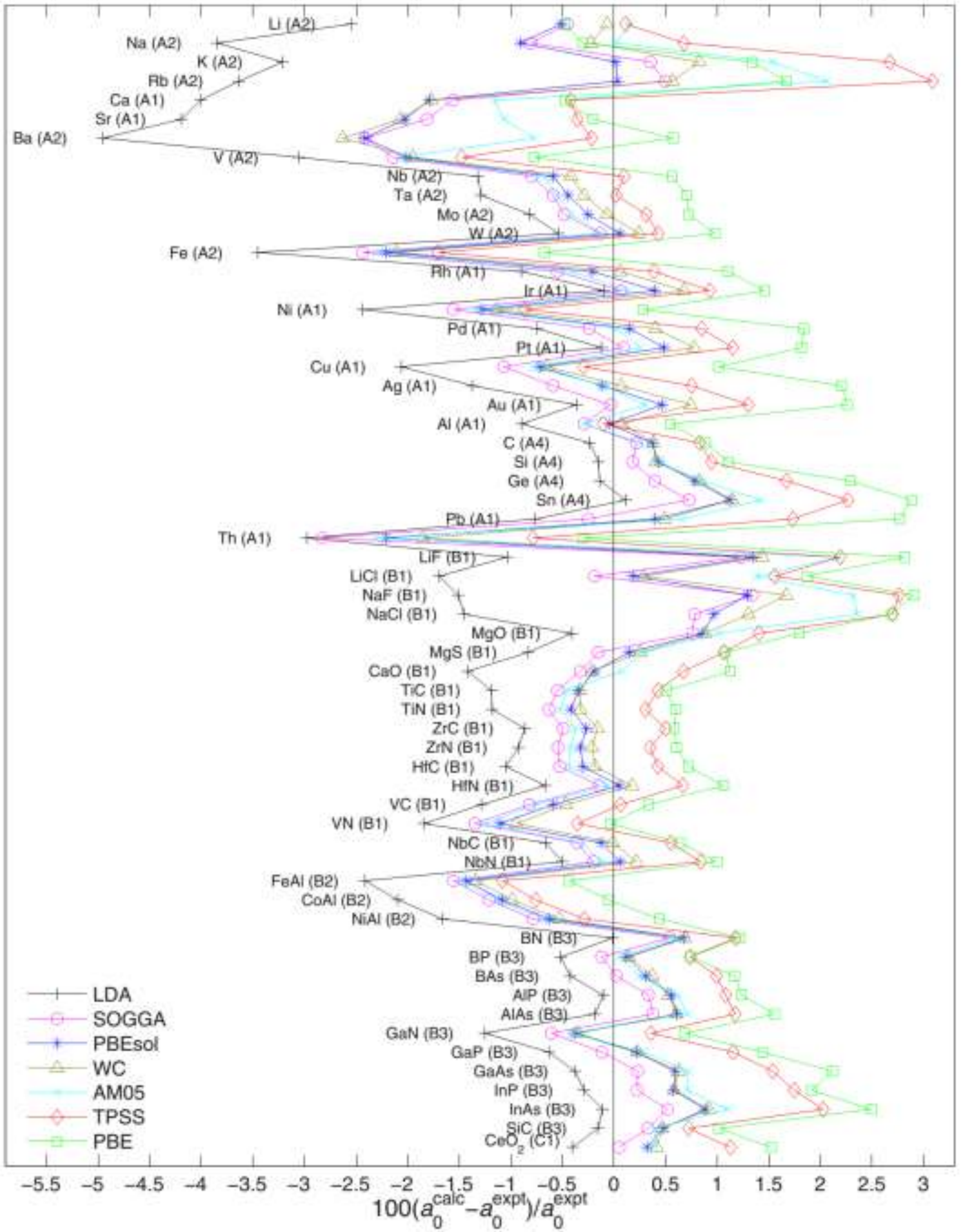
$$E_{XC}^{GGA} = \int d\mathbf{r}\, n(\mathbf{r})(\epsilon_X^{GGA}[n,|\nabla n|] + \epsilon_C^{GGA}[n,|\nabla n|])$$

PBE: $\epsilon_X^{GGA} = \epsilon_X^{HES}[n]F_X[n,\nabla n]$ (enhancement factor)

$$F_X = 1 + \kappa - \frac{\kappa}{1+\mu s^2/\kappa}, \qquad s = \frac{|\nabla n(\mathbf{r})|}{2\kappa n(\mathbf{r})}$$

$$\epsilon_C^{GGA} = \epsilon_C^{LDA} + \frac{\beta^2}{2\alpha}\ln\left(1 + \frac{2\alpha}{\beta}\frac{s^2 + As^4}{1 + As^2 + A^2 s^4}\right)$$

- **The parameters are chosen to satisfy the constraints (PBE: exchange hole sum rule and local, and Lieb-Oxford bound)**



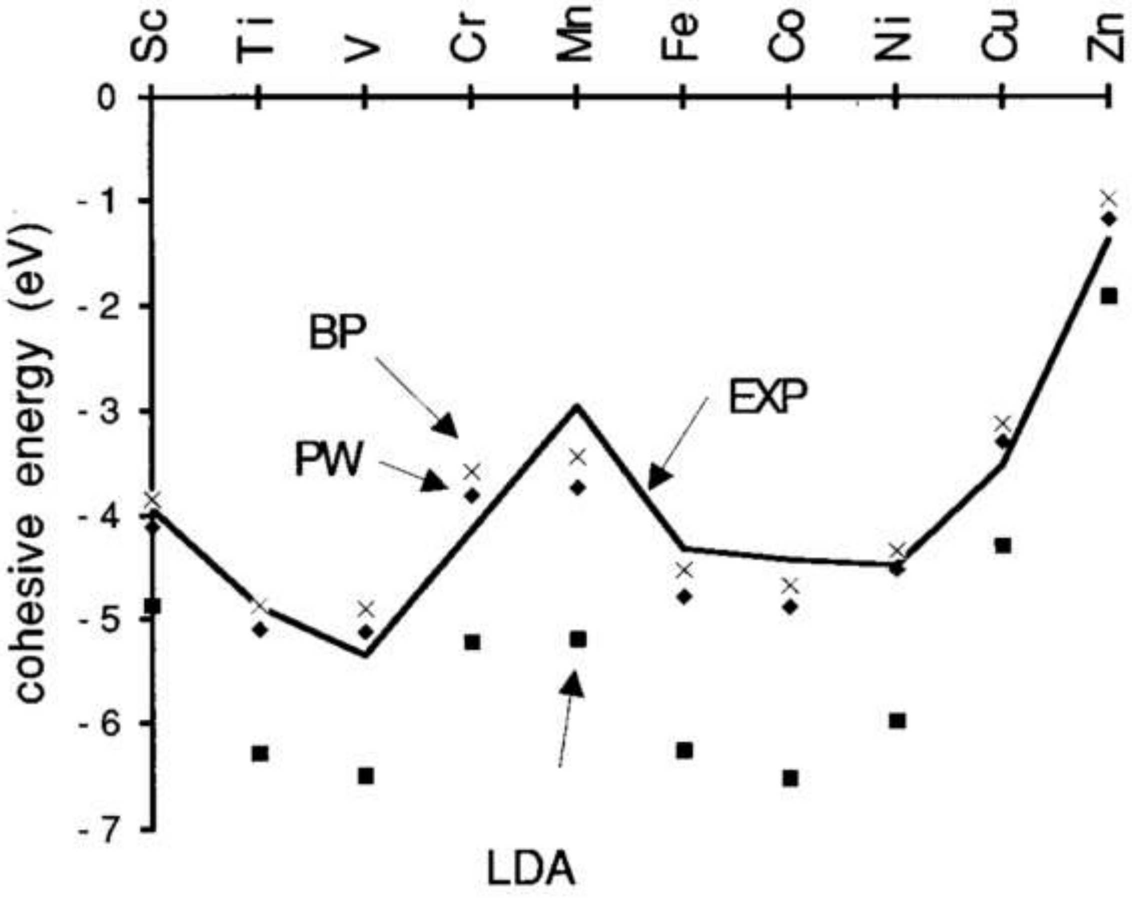
Equilibrium lattice constant compared to experiment

P. Haas, F. Tran, and P. Blaha,

Phys. Rev. B 79, 085104 (2009)

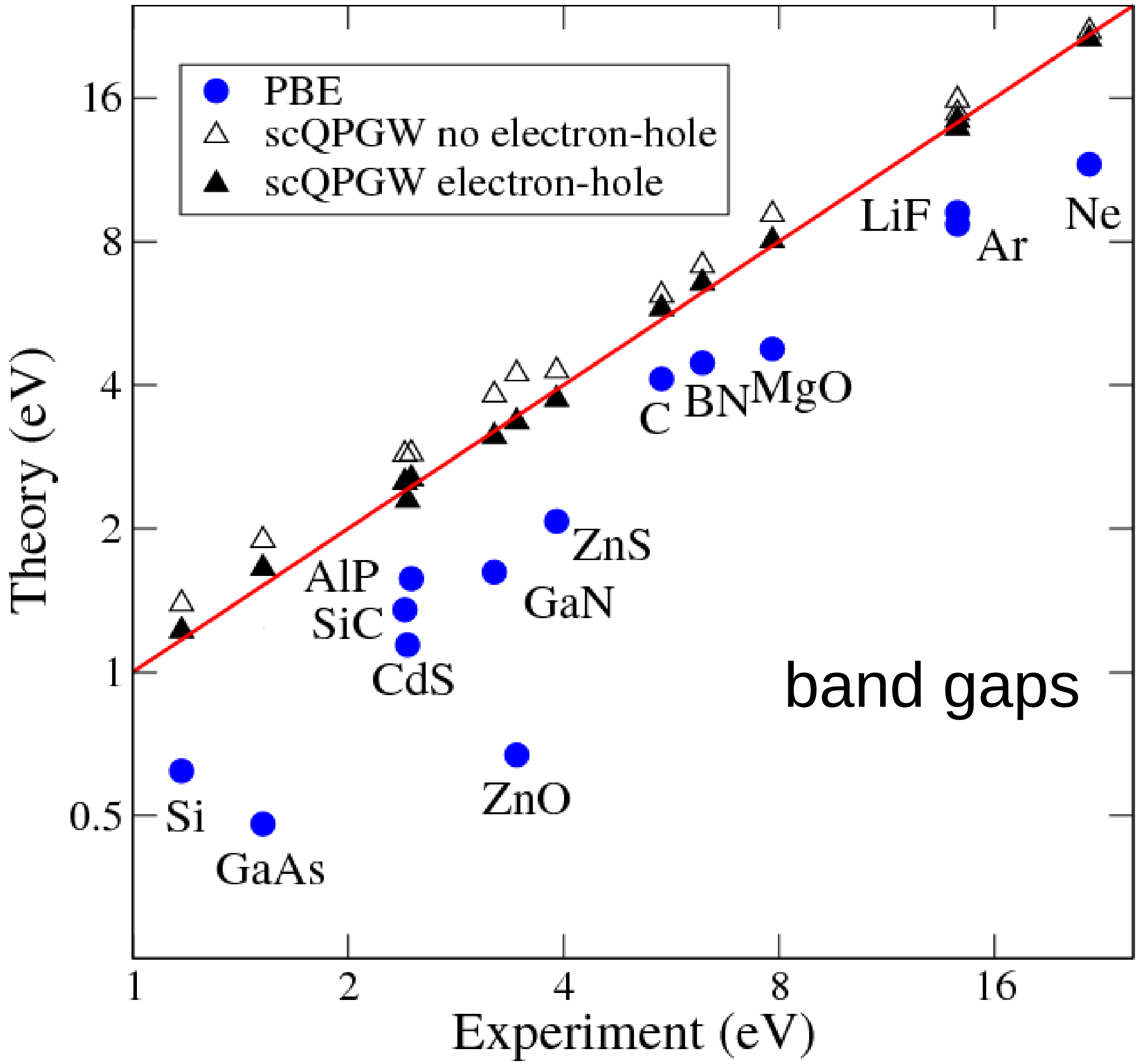
Exchange-correlation functionals

❒ Performance of GGAs



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

Exchange-correlation functionals



band gaps

M. Shishkin, M. Marsman, Phys. Rev. Lett. 95, 246403 (2007)

Exchange-correlation functionals

☐ Meta-GGAs

$$E_{XC}^{GGA} = \int d\boldsymbol{r}\, n(\boldsymbol{r}) \epsilon_{XC}^{MGGA}(n, \nabla n, \tau)$$

with *kinetic energy density* $\tau(\boldsymbol{r}) = \sum_i^{occup} \frac{1}{2} |\nabla \psi_i(\boldsymbol{r})|^2$

Although τ is a non-local functional of n, it is available in standard calculations

For a 1-electron system, τ is known exactly (Weizsäcker):

$$\tau^W = \frac{|\nabla n|^2}{8n}$$

Gradient expansion motivates use of τ

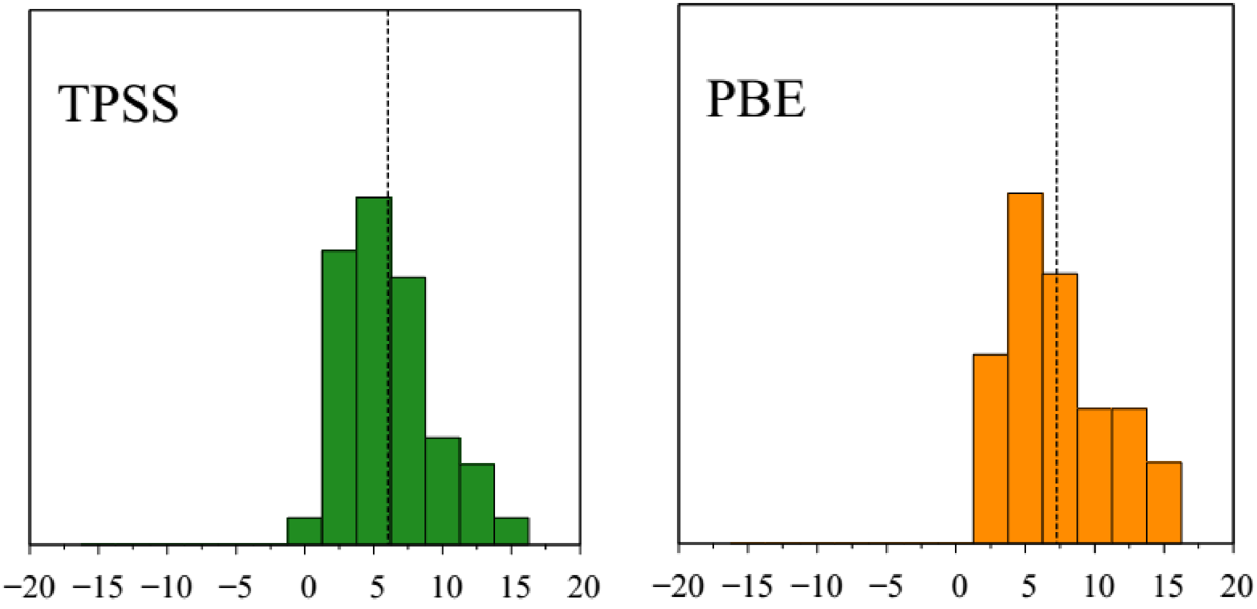
Functional is constructed similar to GGAs

Exchange-correlation functionals

- **Meta-GGAs**

$$E_{XC}^{GGA} = \int d\boldsymbol{r}\, n(\boldsymbol{r})\epsilon_{XC}^{MGGA}(n, \nabla n, \tau)$$

Histogram of lattice constatnt errors for a set of semiconductors (units: 0.01 A)

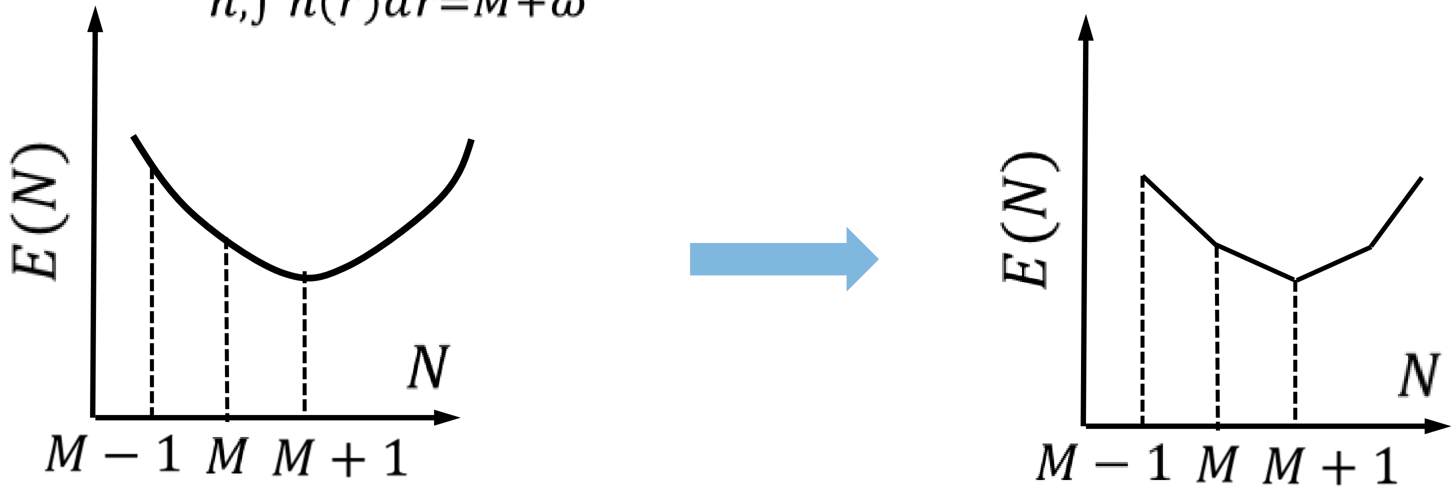


Lucero, Henderson, and Scuseria, J. Phys.: Cond. Matter 24, 145504 (2012)

Exchange-correlation functionals

☐ Fractional occupations

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

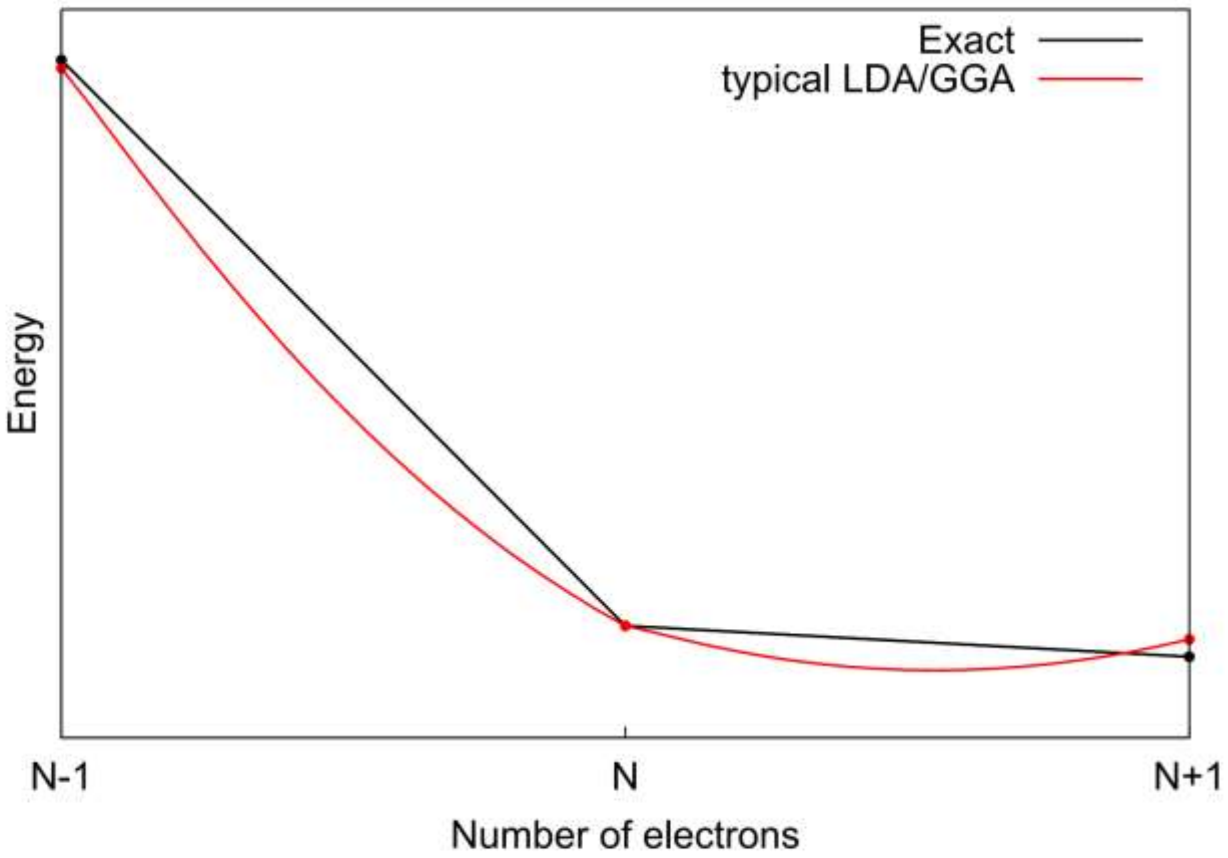


The exact energy changes piece-wise linear with *N*

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

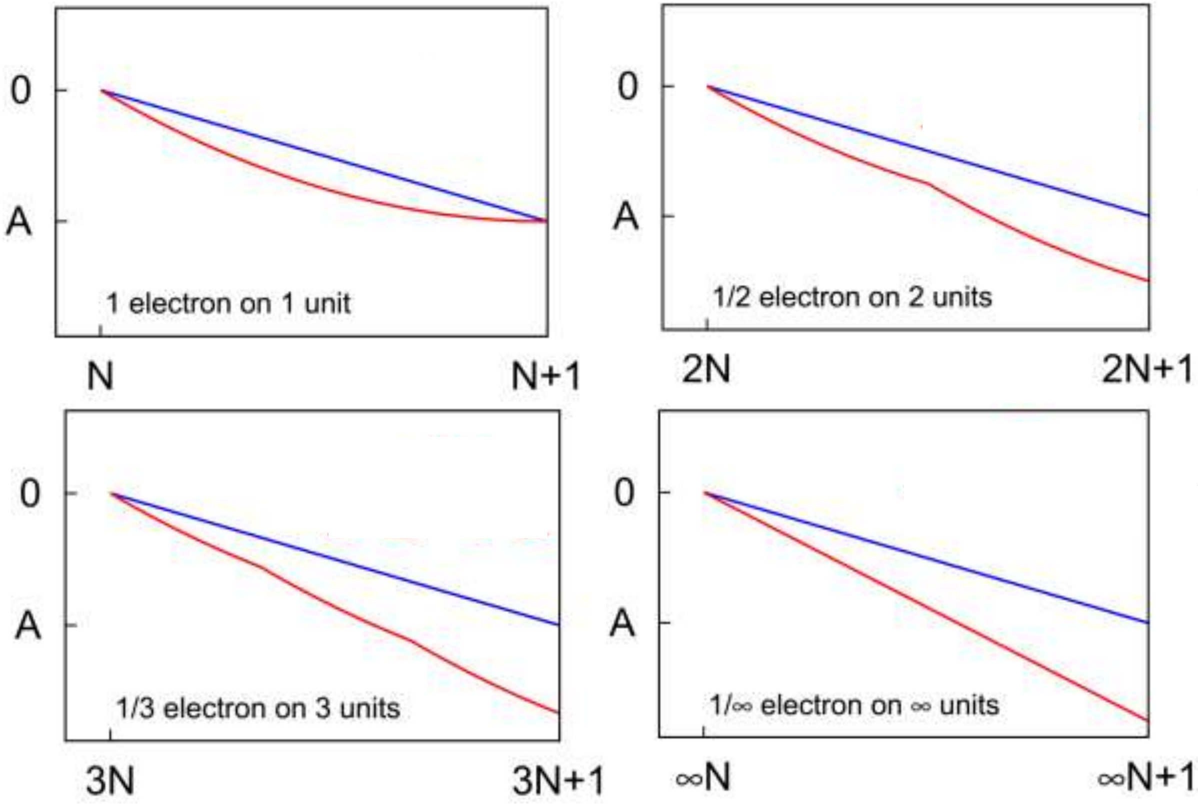
Exchange-correlation functionals

- Dependence of approximate DFT on the occupation



Exchange-correlation functionals

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



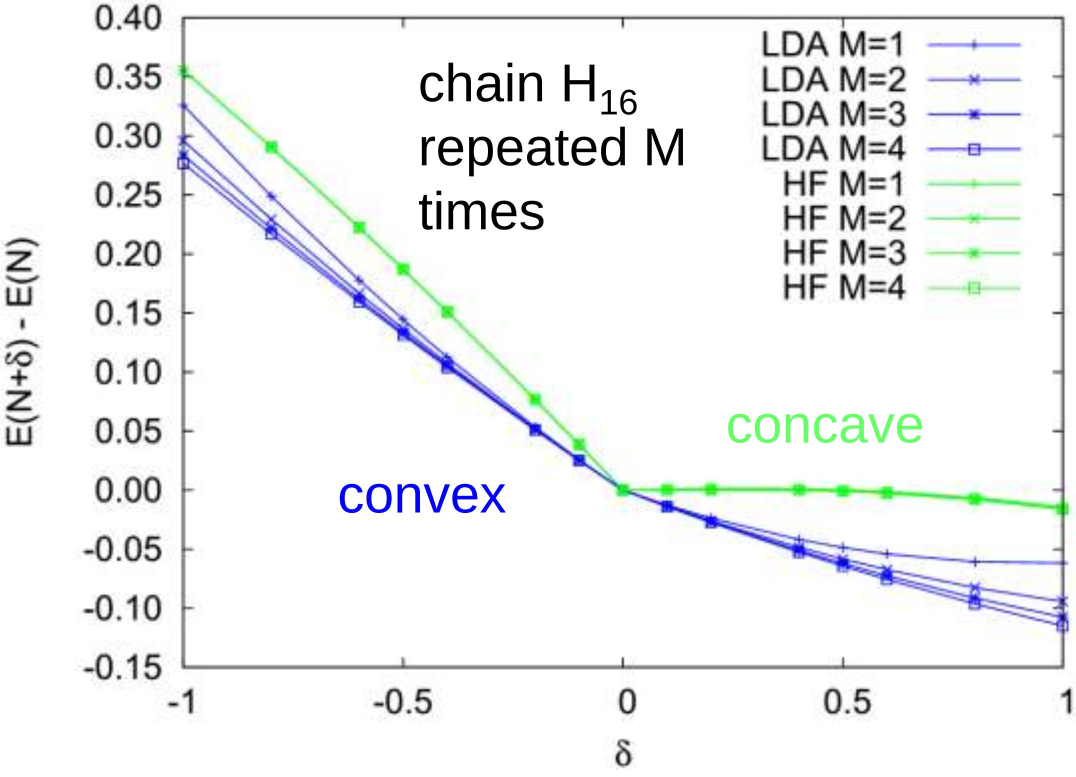
Dependence $E(N)$ for 1, 2, 3, and ∞ separated molecules

$E^{LDA/GGA}(N)$ is convex because $\varepsilon^{HOMO}(\delta)$ increases with δ, mainly due to SIE

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

Exchange-correlation functionals

- **Generalized Kohn-Sham (GKS):** $E = E[\{\psi\}]$


chain H_{16} repeated M times

convex

concave

Hartree-Fock is a functional within GKS

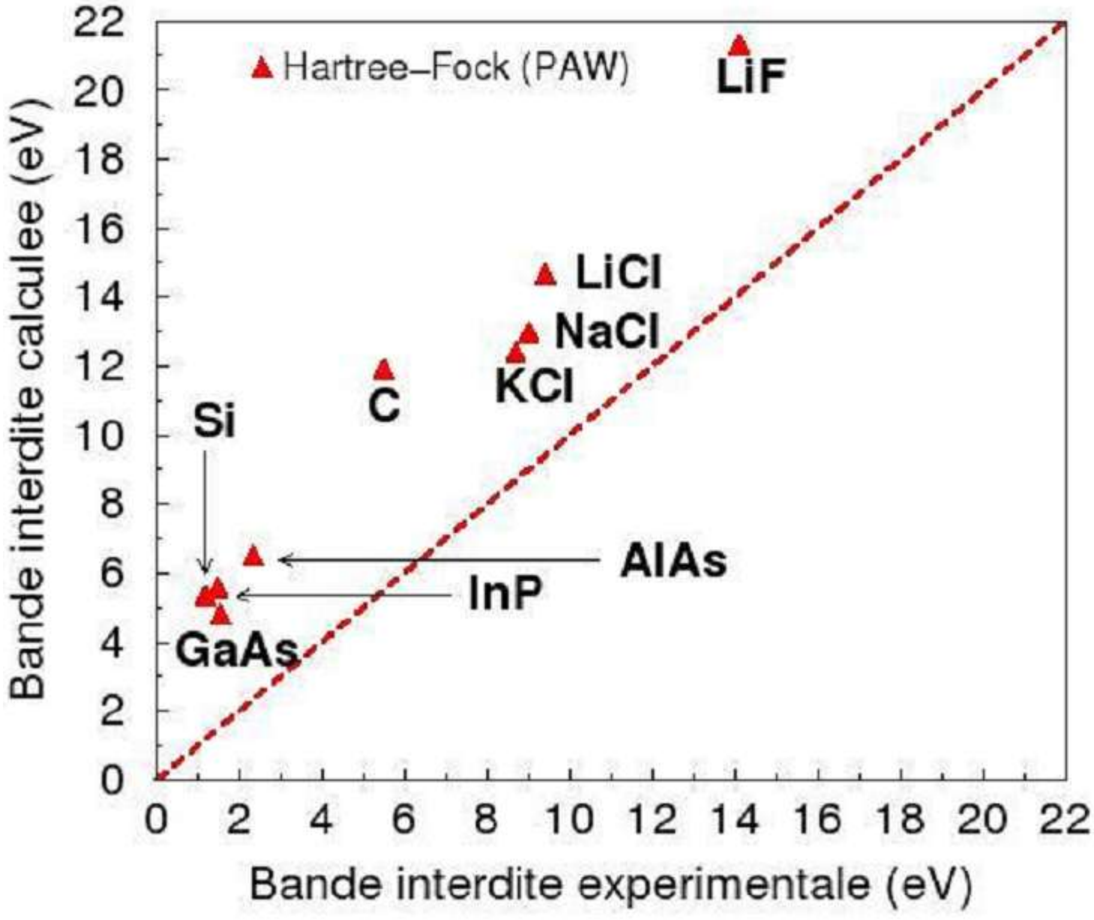
More “DFT-like”: Optimized effective potentials (local potentials that approximate the non-local HF exchange) - numerically complex and computationally expensive

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

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

Exchange-correlation functionals

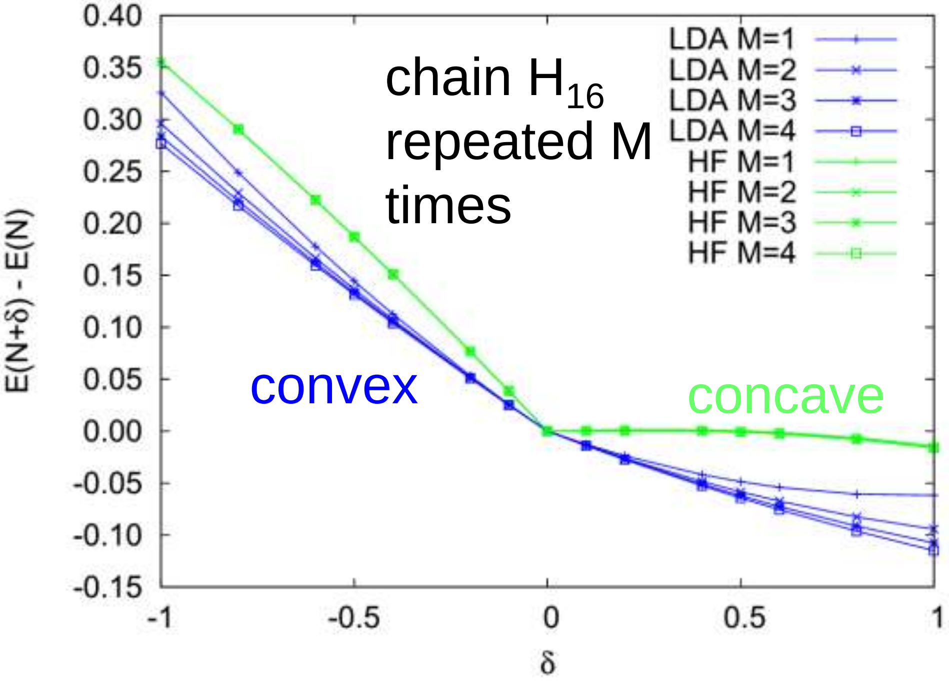
- Hartree-Fock is self-interaction free, but…



Brice Arnaud, Universit´e de Rennes, France

Exchange-correlation functionals

❐ Hybrid functionals



chain H_{16} repeated M times

convex

concave

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

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

$\alpha \neq 1$ because a non-local expression for correlation functional would otherwise be needed, but we don't know it, therefore - a balance

How to choose α?

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

Exchange-correlation 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

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

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

There can be other parameters

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

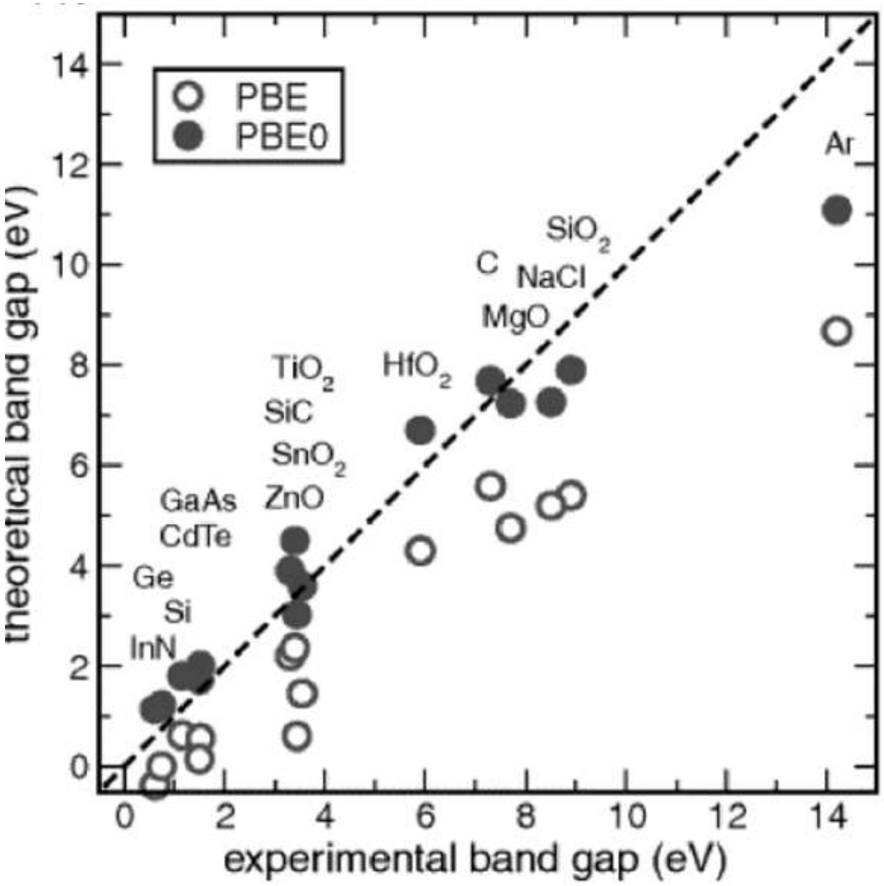
$$\frac{1}{r} = SR_\omega(r) + LR_\omega(r) = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{1-\mathrm{erfc}(\omega r)}{r}$$

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

Exchange-correlation 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)

Exchange-correlation functionals

- **Hybrid functionals**

  "An ideal hybrid would be sophisticated enough to optimize n for each system and property…"

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

  How can we do this?

Example: Fe_{Mg} defect in MgO

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

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

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

Example: Fe_{Mg} defect in MgO

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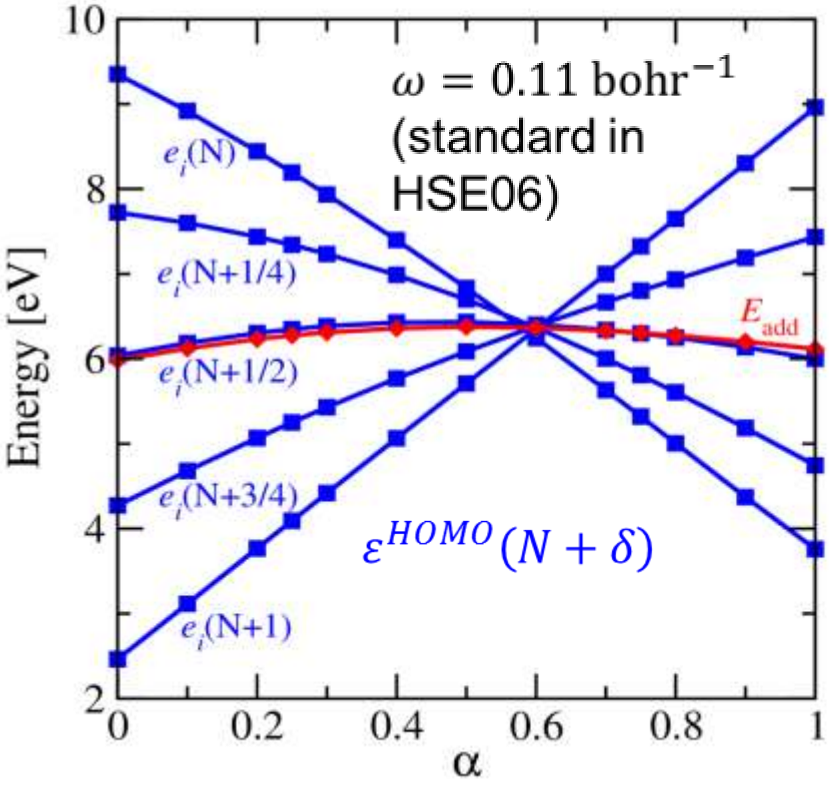
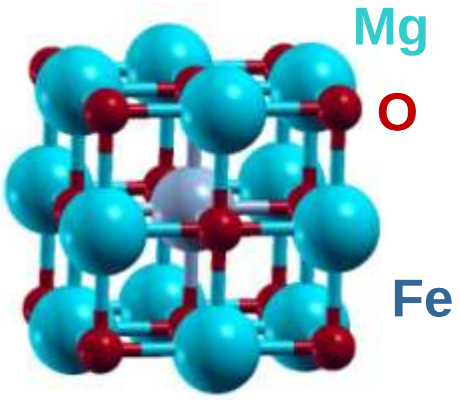


$\omega = 0.11\ \text{bohr}^{-1}$ (standard in HSE06)

$\varepsilon^{HOMO}(N + \delta)$

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



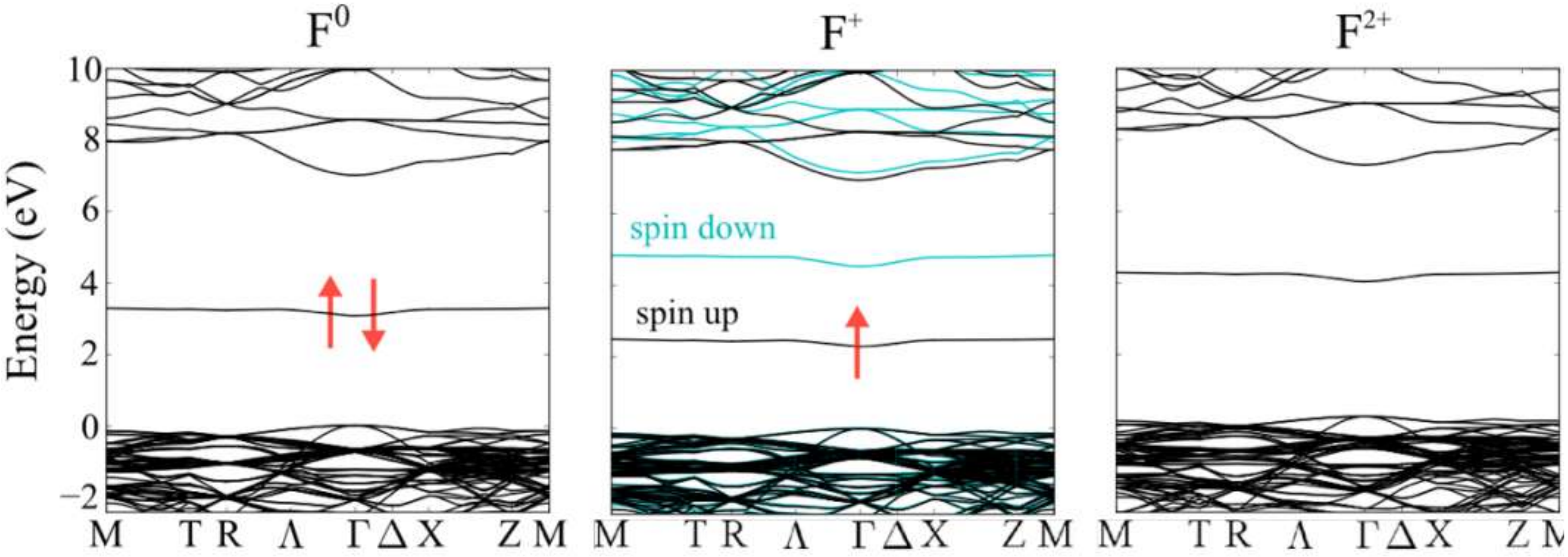
Optimal $\alpha \approx 0.6$

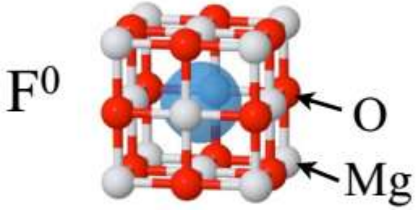
There IS an α for which $\varepsilon^{HOMO} = const$

Example: O vacancy in MgO

- **Determine the best α**

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

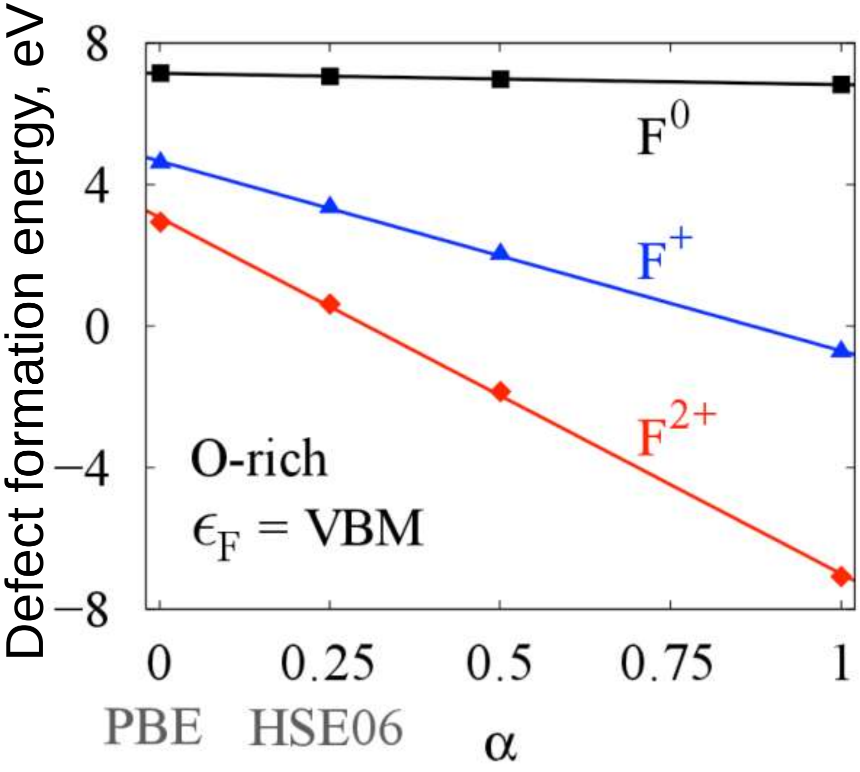




Example: O vacancy in MgO

- ☐ **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?

Example: O vacancy in MgO

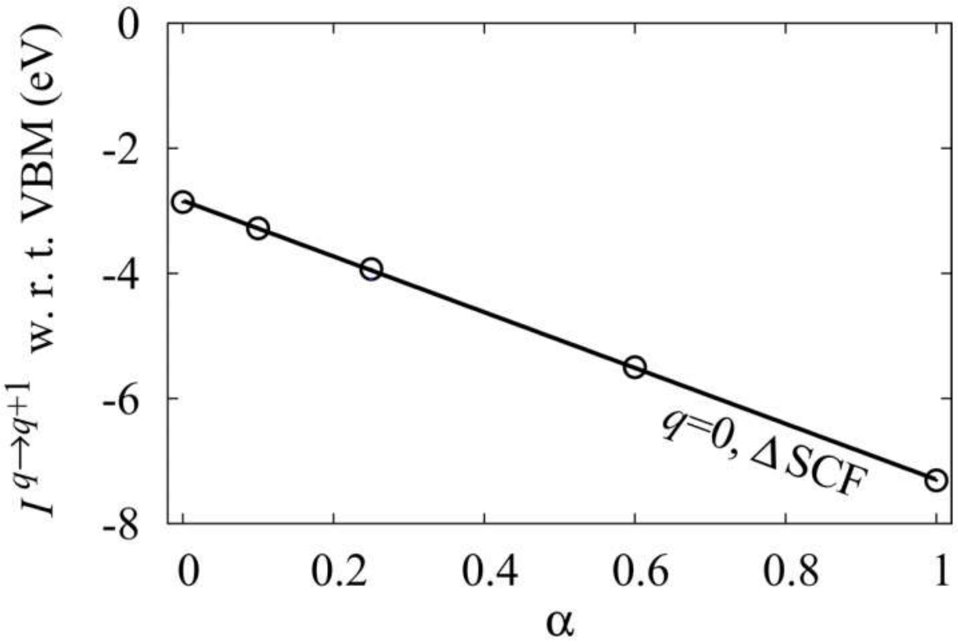
- **Determine the best α**

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

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

Example: O vacancy in MgO

- ❒ **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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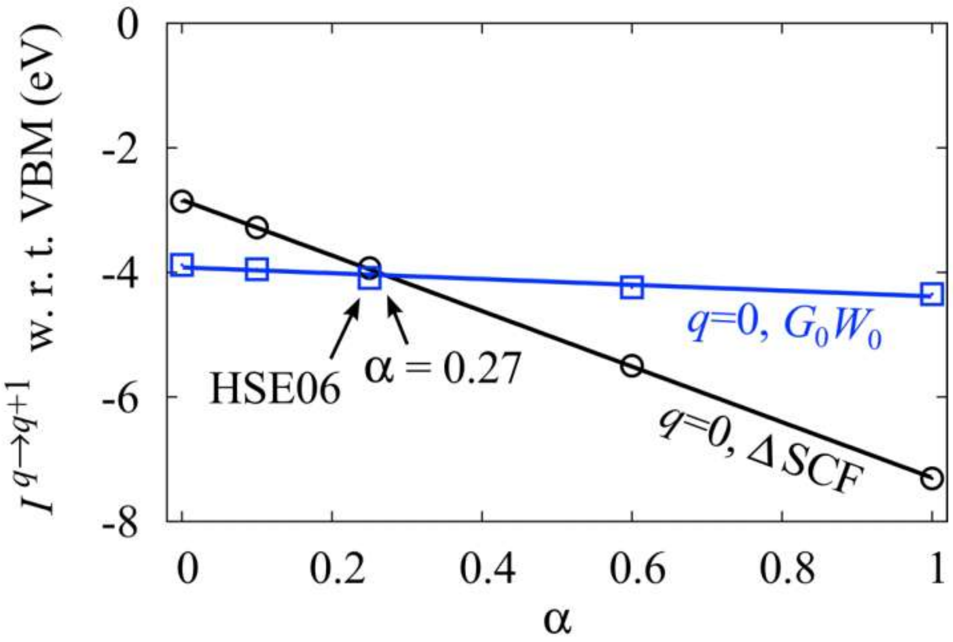

From highest occupied orbital

From total energy differences

Example: O vacancy in MgO

- **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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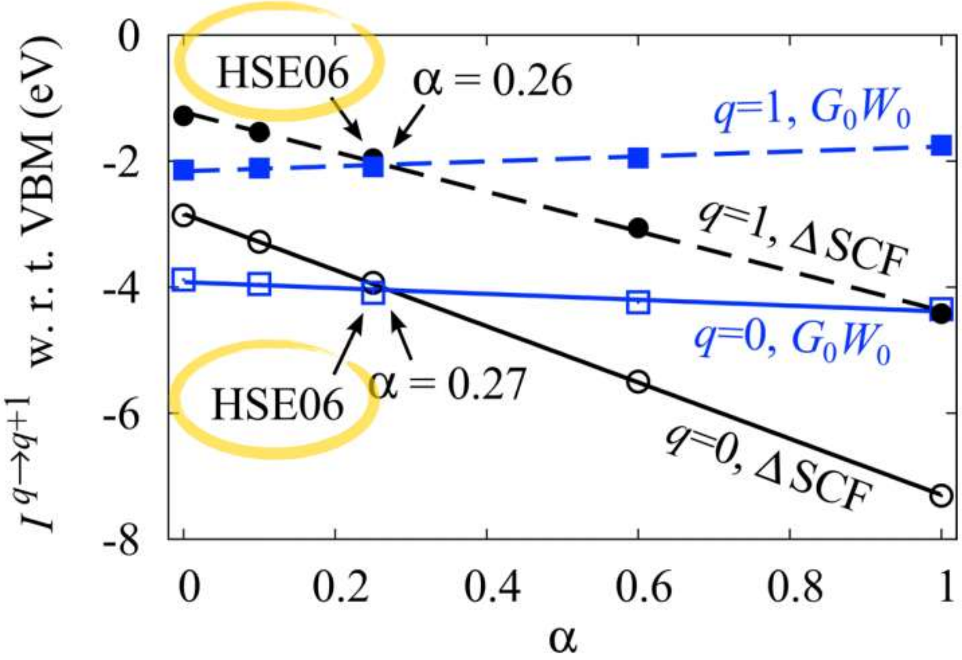


From highest occupied orbital

From total energy differences

Exchange-correlation functionals

- **Gradient-corrected density functionals**

$$E_{xc}^{GGA} = \int d\mathbf{r}\ f[n(\mathbf{r}), \nabla n(\mathbf{r})]$$

- **Meta- GGA's**

$$E_{xc}^{meta-GGA} = \int d\mathbf{r}\ g[n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(r)]$$

- **Orbital-dependent functionals**

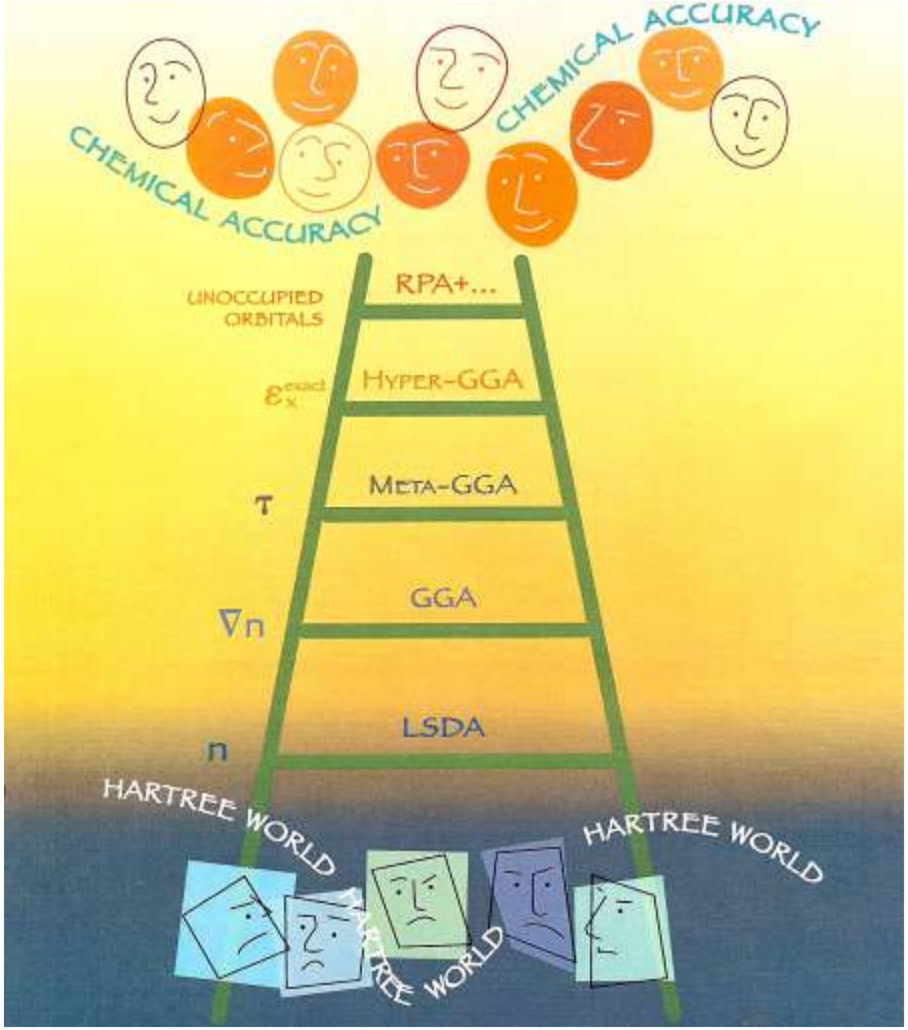
  E.g., *exact* exchange

$$E_x^{EX} = -\frac{1}{2}\sum_{i,j}^{\mathrm{occ}} \int d\mathbf{r}\ d\mathbf{r}' \frac{u_i^*(\mathbf{r})u_j^*(\mathbf{r}')u_j(\mathbf{r})u_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Exchange-correlation functionals

- **Jacob's ladder**

  John Perdew



from Kieron Burke

The End …