

Beyond LDA and GGA - Tackling exact exchange, hybrid functional, MP2, and RPA with numeric atom-centered orbitals

Xinguo Ren

Fritz Haber Institute (Berlin)

DFT meets Solid State Chemistry & 8th Tutorial Hands-on-FPLO,
at MPI CPfS Dresden, October 29, 2009

The Fritz-Haber-Institute *ab initio* molecular simulations package

$$\phi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

"LAPW-like accuracy and reliability -
plane wave pseudopotential-like speed"

- all-electron
- Periodic, cluster systems on equal footing
- good scaling (system size and CPUs)
- Hartree-Fock, hybrid functionals, MP2, RPA
- Quasiparticle self-energies: GW, MP2

<http://www.fhi-berlin.mpg.de/aims>

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler,
Computer Physics Communications, **180**, 2175 (2009).

Problems with LDA and GGA

- Total energy in Kohn-Sham DFT

$$E_{\text{tot}}[n(\mathbf{r})] = T_s + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n(\mathbf{r})]$$

- $E_{\text{xc}}[n(\mathbf{r})]$ has to be approximated !

LDA and GGA: very useful, but have problems in certain applications.

Problems with LDA and GGA

- Total energy in Kohn-Sham DFT

$$E_{\text{tot}}[n(\mathbf{r})] = T_s + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n(\mathbf{r})]$$

- $E_{\text{xc}}[n(\mathbf{r})]$ has to be approximated !

LDA and GGA: very useful, but have problems in certain applications.

- Deficiencies of LDA and GGA:

- ▶ Self-interaction error (delocalization error [1]) \implies
 - Underestimated band-gaps, wrong dissociation behavior of molecular ions, etc.
 - Failure to describe localized electrons in both solids and molecules.
- ▶ Absence of van der Waals interaction
- ▶ Unable to treat excited states
- ▶ ...

[1] A. J. Cohen, P Mori-Sánchez, W. Yang, Science, **321**, 792 (2008).

LDA and GGA errors for atomization energy

Unit: kcal/mol (= 43.4 meV)

Atomization energy

$$\Delta E = - \left[E_{\text{mol}} - \sum_i E_{\text{atom}}(i) \right]$$

Desired accuracy: 1 kcal/mol

Data from

Perdew, Burke, Erzenhof,

Phys. Rev. Lett. **77**, 3565 (1996).

Molecules	LDA	PBE-GGA	EXP
H2	113	105	109
LiH	60	52	58
CH4	462	420	419
NH3	337	302	297
OH	124	110	107
H2O	267	234	232
HF	162	142	141
Li2	23	19	24
LiF	153	136	139
Be2	13	10	3
C2H2	460	415	405
C2H4	633	571	563
HCN	361	326	312
CO	299	269	259
N2	267	243	229
NO	199	172	153
O2	175	144	121
F2	78	53	39
P2	142	120	117
Cl2	81	63	58
Mean abs. error	31.4	7.9	

Wave-function based methods: systematically increasing accuracy

Quantum Chemistry approach

(43.4 meV)

↑
accuracy
computation time

↑
CCSD(T) – Gold standard,
higher order correlations

↑
MP2 – Correlation is treated up to
2nd order of Coulomb interaction

↑
Hartree-Fock – Exchange treated exactly,
but no correlation

MP2: 2nd order Møller-Plesset (many-body) Perturbation Theory

CCSD(T): Coupled-Cluster Theory with Single, Double and perturbative Triple excitations

Perdew's construction: Jacob's ladder in DFT

(43.4 meV)

↑
accuracy?
computation time

5	unoccupied $\psi_n(\mathbf{r})$, e.g., ACFD-RPA
4	occupied $\psi_n(\mathbf{r})$, hybrid functional (e.g., PBE0)
3	$\tau(\mathbf{r})$, meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$, GGA (e.g., PBE)
1	$n(\mathbf{r})$, LDA

$\tau(\mathbf{r})$: KS kinetic energy density

ACFD: Adiabatic Connection Fluctuation-Dissipation theorem

RPA: Random Phase Approximation

Underlying principle of constructing Jacob's ladder

"Adiabatic Connection": a formally exact way for constructing E_{XC}

Imagine a continuum of fictitious systems governed by

$$\hat{H}_\lambda = \hat{T} + \hat{v}_{\text{ext}}^\lambda + \lambda \hat{V}_{\text{ee}} \quad (\text{where } 0 \leq \lambda \leq 1), \quad \text{and} \quad V_{\text{ee}} = \sum_{i < j}^N \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

Hohenberg-Kohn theorem holds for every $\lambda \implies \hat{v}_{\text{ext}}^\lambda(\mathbf{r})$ can be chosen such that $n_\lambda(\mathbf{r}) = n_{\lambda=1}(\mathbf{r}) = n(\mathbf{r})$

$$\hat{H}_\lambda |\Phi_\lambda[n]\rangle = E_\lambda |\Phi_\lambda[n]\rangle .$$

D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

Underlying principle of constructing Jacob's ladder

"Adiabatic Connection": a formally exact way for constructing E_{XC}

Imagine a continuum of fictitious systems governed by

$$\hat{H}_\lambda = \hat{T} + \hat{v}_{\text{ext}}^\lambda + \lambda \hat{V}_{\text{ee}} \quad (\text{where } 0 \leq \lambda \leq 1), \quad \text{and} \quad V_{\text{ee}} = \sum_{i < j}^N \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

Hohenberg-Kohn theorem holds for every $\lambda \implies \hat{v}_{\text{ext}}^\lambda(\mathbf{r})$ can be chosen such that $n_\lambda(\mathbf{r}) = n_{\lambda=1}(\mathbf{r}) = n(\mathbf{r})$

$$\hat{H}_\lambda |\Phi_\lambda[n]\rangle = E_\lambda |\Phi_\lambda[n]\rangle.$$

Exchange-correlation (XC) part of the interaction energy

$$U_{XC}^\lambda = \langle \Phi_\lambda[n] | V_{\text{ee}} | \Phi_\lambda[n] \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Exact E_{XC} : $E_{XC}^{\text{exact}} = \int_0^1 d\lambda U_{XC}^\lambda$

D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

Two limits of the connection

- $\lambda = 0$, $\hat{v}_{\text{ext}}^{\lambda=0}(\mathbf{r}) = v_{\text{KS}}(\mathbf{r})$ (KS system)

$$\begin{aligned} U_{\text{XC}}^{\lambda=0} &= \langle \Phi_0 | V_{\text{ee}} | \Phi_0 \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\frac{1}{2} \sum_{mn} \int d\mathbf{r} \int d\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n(\mathbf{r}')^*\psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} := E_{\text{x}}^{\text{exact}} \end{aligned}$$

Exchange-only limit, LDA/GGA are least accurate. \implies Instead exact exchange is needed

Two limits of the connection

- $\lambda = 0$, $\hat{v}_{\text{ext}}^{\lambda=0}(\mathbf{r}) = v_{\text{KS}}(\mathbf{r})$ (KS system)

$$\begin{aligned} U_{\text{XC}}^{\lambda=0} &= \langle \Phi_0 | V_{\text{ee}} | \Phi_0 \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\frac{1}{2} \sum_{mn} \int d\mathbf{r} \int d\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n(\mathbf{r}')^*\psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} := E_{\text{x}}^{\text{exact}} \end{aligned}$$

Exchange-only limit, LDA/GGA are least accurate. \implies Instead exact exchange is needed

- $\lambda = 1$, $\hat{v}_{\text{ext}}^{\lambda=1} = v_{\text{ext}}$ (Full interacting system)

LDA/GGA work well.

Correlation is crucial, and exchange-only treatment will not work!

Two limits of the connection

- $\lambda = 0$, $\hat{v}_{\text{ext}}^{\lambda=0}(\mathbf{r}) = v_{\text{KS}}(\mathbf{r})$ (KS system)

$$\begin{aligned} U_{\text{XC}}^{\lambda=0} &= \langle \Phi_0 | V_{\text{ee}} | \Phi_0 \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\frac{1}{2} \sum_{mn} \int d\mathbf{r} \int d\mathbf{r}' \frac{\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n(\mathbf{r}')^*\psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} := E_{\text{x}}^{\text{exact}} \end{aligned}$$

Exchange-only limit, LDA/GGA are least accurate. \implies Instead exact exchange is needed

- $\lambda = 1$, $\hat{v}_{\text{ext}}^{\lambda=1} = v_{\text{ext}}$ (Full interacting system)

LDA/GGA work well.

Correlation is crucial, and exchange-only treatment will not work!

- $E_{\text{XC}}^{\text{hyb}} = \alpha E_{\text{x}}^{\text{exact}} + (1 - \alpha) E_{\text{x}}^{\text{GGA}} + E_{\text{c}}^{\text{GGA}}$

A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

Contents

- 1 Hartree-Fock theory, hybrid functionals
- 2 Second-order Möller-Plesset Perturbation Theory
- 3 Random Phase Approximation
- 4 Applications

Hartree-Fock Theory

N-electron interacting hamiltonian

$$\hat{H} = - \sum_i^N \left[\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right] + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H} \Phi_0^{\text{exact}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_0^{\text{exact}} \Phi_0^{\text{exact}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Hartree-Fock approximation (single Slater determinant)

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

$\psi_m(\mathbf{r}) = |m\rangle$: spin-orbital

$$E_c = E_0^{\text{exact}} - E_{\text{HF}} = E_0^{\text{exact}} - \langle \Phi_{\text{HF}} | \hat{H} | \Phi_{\text{HF}} \rangle$$

Hartree-Fock (HF) vs Kohn-Sham (KS) DFT

HF equation: $\delta E_{\text{HF}}[\{\psi_n(\mathbf{r})\}]/\delta\psi_n(\mathbf{r}) = 0$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r})\right) \psi_n(\mathbf{r}) + \int d\mathbf{r}' v_{\text{x}}(\mathbf{r}, \mathbf{r}') \psi_n(\mathbf{r}') = \epsilon_n^{\text{HF}} \psi_n(\mathbf{r})$$

Nonlocal HF exchange potential: $v_{\text{x}}(\mathbf{r}, \mathbf{r}') = - \sum_{m=1}^N \frac{\psi_m(\mathbf{r}) \psi_m^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

KS equation: $\delta E_{\text{KS}}[n(\mathbf{r})]/\delta n(\mathbf{r}) = 0$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r})\right) \psi_n(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \psi_n(\mathbf{r}) = \epsilon_n^{\text{KS}} \psi_n(\mathbf{r})$$

Local KS XC potential: $v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$

$E_{\text{xc}}[n(\mathbf{r})]$: DFT exchange-correlation (XC) energy functional

Solving HF equation in practice

- Introduce a set of basis function $\phi_i(\mathbf{r})$

$$\psi_n(\mathbf{r}) = \sum_i c_{in} \phi_i(\mathbf{r}).$$

Solving HF equation in practice

- Introduce a set of basis function $\phi_i(\mathbf{r})$

$$\psi_n(\mathbf{r}) = \sum_i c_{in} \phi_i(\mathbf{r}).$$

- HF Eq. becomes a matrix (Roothaan) Eq.

$$\sum_j F_{ij} c_{jn} = \epsilon_n^{\text{HF}} \sum_j S_{ij} c_{jn}. \quad (F_{ij} : \text{Fock matrix})$$

$$F_{ij} = \langle \phi_i | \hat{H}_{\text{HF}} | \phi_j \rangle = \langle \phi_i | -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) | \phi_j \rangle \\ - \langle \phi_i | v_{\text{x}}(\mathbf{r}, \mathbf{r}') | \phi_j \rangle$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

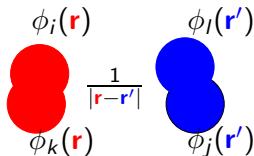
- Exchange matrix requires a special treatment

Evaluating HF exchange matrix

$$\begin{aligned}v_{x,ij} &= - \langle \phi_i | v_x(\mathbf{r}, \mathbf{r}') | \phi_j \rangle \\ &= - \sum_{m=1}^N \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_i^*(\mathbf{r}) \psi_m(\mathbf{r}) \psi_m^*(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = - \sum_{kl} D_{kl} (ik|lj) \\ D_{kl} &= - \sum_{m=1}^N c_{km} c_{lm}. \quad (\text{density matrix})\end{aligned}$$

Two electron Coulomb repulsion integral

$$(ik|lj) = \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_i^*(\mathbf{r}) \phi_k(\mathbf{r}) \phi_l^*(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



Two electron Coulomb integral in practice

- Gaussian-type orbital $\phi(\mathbf{r}) = x^l y^m z^n e^{-\alpha r^2}$

- Gaussian product theorem

$$e^{-\alpha_1 |\mathbf{r} - \mathbf{R}_A|^2} e^{-\alpha_2 |\mathbf{r} - \mathbf{R}_B|^2} = \exp \left[-\alpha_1 \alpha_2 |\mathbf{R}_A - \mathbf{R}_B|^2 / \gamma \right] \exp \left[-\gamma |\mathbf{r} - \mathbf{P}|^2 \right]$$

$$\gamma = \alpha_1 + \alpha_2, \quad \mathbf{P} = (\alpha_1 \mathbf{R}_A + \alpha_2 \mathbf{R}_B) / \gamma$$

- Analytical evaluation

Two electron Coulomb integral in practice

- Gaussian-type orbital $\phi(\mathbf{r}) = x^l y^m z^n e^{-\alpha r^2}$
 - Gaussian product theorem

$$e^{-\alpha_1 |\mathbf{r} - \mathbf{R}_A|^2} e^{-\alpha_2 |\mathbf{r} - \mathbf{R}_B|^2} = \exp \left[-\alpha_1 \alpha_2 |\mathbf{R}_A - \mathbf{R}_B|^2 / \gamma \right] \exp \left[-\gamma |\mathbf{r} - \mathbf{P}|^2 \right]$$

$$\gamma = \alpha_1 + \alpha_2, \quad \mathbf{P} = (\alpha_1 \mathbf{R}_A + \alpha_2 \mathbf{R}_B) / \gamma$$

- Analytical evaluation
- Numerical atomic orbital $\phi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\vartheta, \varphi)$

$(ik|lj)$: $O(N_{\text{basis}}^4)$ many 6-dimensional integrals: \implies
very expensive to calculate and to store !

But, do we have to do this ?

Auxiliary basis to two electron Coulomb integral (Resolution of Identity (RI))

- Observation:

- N_{basis}^2 many pair products $\{\phi_i(\mathbf{r})\phi_j(\mathbf{r})\}$, where $i, j = 1, 2, \dots, N_{\text{basis}}$, are heavily linear dependent

Auxiliary basis to two electron Coulomb integral (Resolution of Identity (RI))

- Observation:

- N_{basis}^2 many pair products $\{\phi_i(\mathbf{r})\phi_j(\mathbf{r})\}$, where $i, j = 1, 2, \dots, N_{\text{basis}}$, are heavily linear dependent

- There must exist an auxiliary basis set $\{P_\mu(\mathbf{r})\}$

- ▶ Linear independent, (hence $N_{\text{aux}} \ll N_{\text{basis}}^2$)
- ▶ Sufficiently accurate to represent $\{\phi_i(\mathbf{r})\phi_j(\mathbf{r})\}$

$$\phi_i(\mathbf{r})\phi_k(\mathbf{r}) \approx \sum_{\mu} C_{ik}^{\mu} P_{\mu}(\mathbf{r})$$

- ▶ It follows

$$(ik|lj) \approx \sum_{\mu\nu} C_{ik}^{\mu} \langle P_{\mu} | v | P_{\nu} \rangle C_{lj}^{\nu} = \sum_{\mu\nu} C_{ik}^{\mu} V_{\mu\nu} C_{lj}^{\nu}$$

$$C_{ij}^{\nu} = \sum_{\mu} O_{ij}^{\mu} S_{\mu\nu}^{-1}, \quad \text{where} \quad O_{ij}^{\mu} = \int d\mathbf{r} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) P_{\mu}(\mathbf{r}), \text{ and}$$

$$S_{\mu\nu} = \int d\mathbf{r} P_{\mu}(\mathbf{r}) P_{\nu}(\mathbf{r})$$

Construction of auxiliary basis

A very simple procedure, but it works!

- Should also be atom-centered orbitals

$$P(\mathbf{r}) = \xi_{ql}(r) Y_{lm}(\vartheta, \varphi) \quad (\text{"normal" basis: } \phi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\vartheta, \varphi))$$

numerically easy to manipulate

Construction of auxiliary basis

A very simple procedure, but it works!

- Should also be atom-centered orbitals

$$P(\mathbf{r}) = \xi_{ql}(\mathbf{r}) Y_{lm}(\vartheta, \varphi) \quad (\text{"normal" basis: } \phi(\mathbf{r}) = R_{nl}(\mathbf{r}) Y_{lm}(\vartheta, \varphi))$$

numerically easy to manipulate

- Determine the shape of $\xi_{ql}(\mathbf{r})$

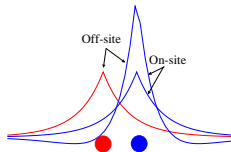
For every atom, l

$$\begin{array}{c} \boxed{R_{n_1 l_1}(\mathbf{r}) R_{n_2 l_2}(\mathbf{r})} \\ |l_1 - l_2| \leq 1 \leq |l_1 + l_2| \end{array}$$

Gram-Schmidt Orthonormalization

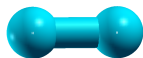
$$\boxed{\xi_{ql}}$$

- $\{P_\mu(\mathbf{r})\}$ are orthonormal on each atom, but nonorthogonal between different atoms.



- "On-site" pairs $\phi_i(\mathbf{r} - \mathbf{R}_A) \phi_j(\mathbf{r} - \mathbf{R}_A)$ "exactly" represented by $P_\mu(\mathbf{r})$!
- But how about "off-site" pairs $\phi_i(\mathbf{r} - \mathbf{R}_A) \phi_j(\mathbf{r} - \mathbf{R}_B)$?

On the accuracy of RI approximation (for off-site pairs)

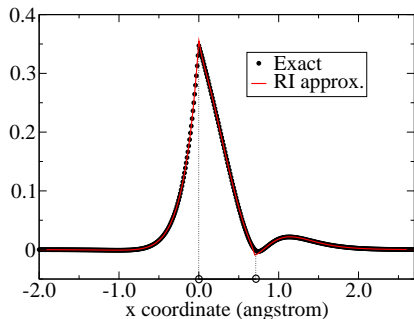
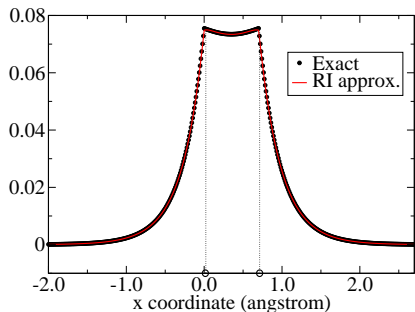


A B

(H₂: d = 0.7 Å)

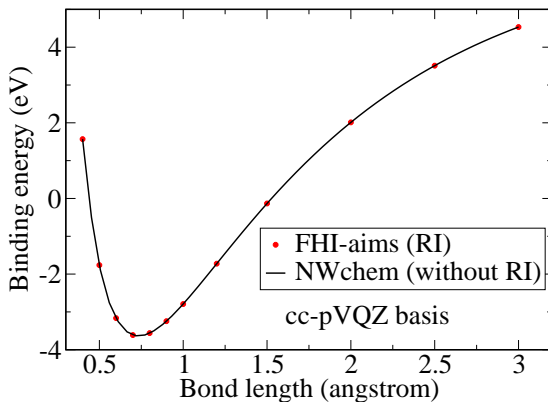
$$\phi_{1s}(x - X_A)\phi_{1s}(x - X_B)$$

$$\phi_{2s}(x - X_A)\phi_{2p_x}(x - X_B)$$



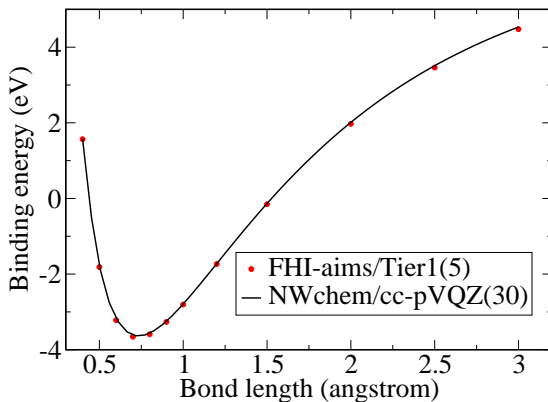
On the accuracy of RI approximation

HF binding energy curve for H₂



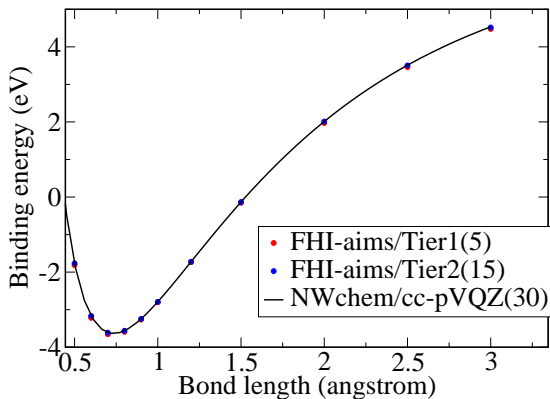
On the convergence of NAO basis set

HF binding energy curve for H₂



On the convergence of NAO basis set

HF binding energy curve for H₂



Hybrid functional

General principle:

Mixing a fraction of “exact exchange” with GGA semilocal exchange

Hybrid functional

General principle:

Mixing a fraction of “exact exchange” with GGA semilocal exchange

- B3LYP (semi-empirical)

$$E_{XC}^{B3LYP} = E_{XC}^{LSDA} + a_0(E_X^{\text{exact}} - E_X^{LSDA}) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{LYP}$$

$$a_0 = 0.20, a_X = 0.72, a_C = 0.81$$

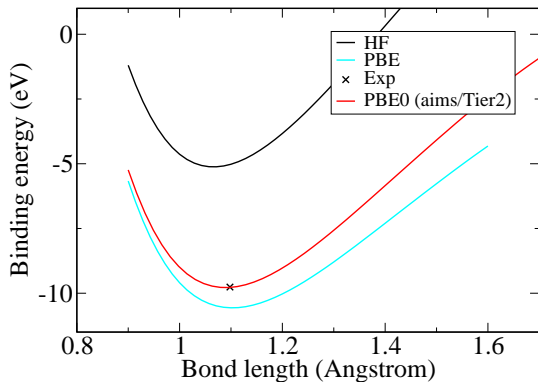
- PBE0 (non-empirical)

$$E_{XC}^{PBE0} = 0.25 * E_X^{\text{exact}} + 0.75 * E_X^{PBE} + E_C^{PBE}$$

A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

Binding energy for N₂

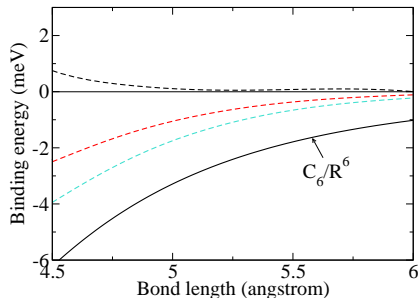
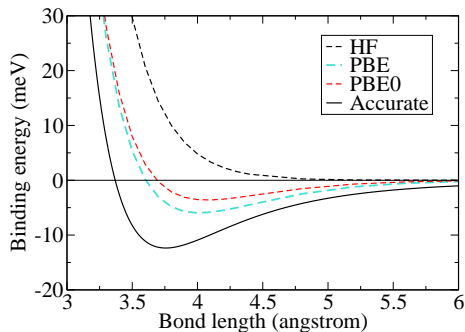


Vibrational frequency
(cm⁻¹)

HF:	2729.7 (371.1)
PBE:	2347.9 (-10.7)
PBE0:	2478.3 (119.7)
EXP:	2358.6

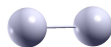
PBE0 improves over PBE for the atomization energy, but not the vibrational frequency

Argon dimer: importance of the vdW interaction



"Accurate" result:

K. T. Tang and J. P. Toennies, J. Chem. Phys.
118, 4976 (2003).



Nonlocal correlation is needed for
describing the asymptotic behavior.

Contents

- 1 Hartree-Fock theory, hybrid functionals
- 2 Second-order Möller-Plesset Perturbation Theory
- 3 Random Phase Approximation
- 4 Applications

Second Order Møller-Plesset perturbation theory (MP2)

- Rayleigh-Schrödinger perturbation theory

$$\hat{H} = \hat{H}^{(0)} + \hat{V}; \quad \hat{H}^{(0)}|n\rangle = E_n^{(0)}|n\rangle$$

$$E_0^{(1)} = \langle 0|\mathcal{V}|0\rangle, \quad E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}}, \quad \dots$$

Second Order Møller-Plesset perturbation theory (MP2)

- Rayleigh-Schrödinger perturbation theory

$$\hat{H} = \hat{H}^{(0)} + \hat{V}; \quad \hat{H}^{(0)}|n\rangle = E_n^{(0)}|n\rangle$$

$$E_0^{(1)} = \langle 0|\mathcal{V}|0\rangle, \quad E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}}, \quad \dots$$

- MP2

$$\hat{H}^{(0)} = \hat{H}_{\text{HF}}; \quad E_{\text{HF}} = E_0^{(0)} + E_0^{(1)}$$

$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{[(ia|jb)^* - (ib|ja)^*](ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Second Order Møller-Plesset perturbation theory (MP2)

- Rayleigh-Schrödinger perturbation theory

$$\hat{H} = \hat{H}^{(0)} + \hat{V}; \quad \hat{H}^{(0)}|n\rangle = E_n^{(0)}|n\rangle$$

$$E_0^{(1)} = \langle 0|\mathcal{V}|0\rangle, \quad E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}}, \quad \dots$$

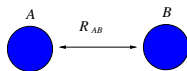
- MP2

$$\hat{H}^{(0)} = \hat{H}_{\text{HF}}; \quad E_{\text{HF}} = E_0^{(0)} + E_0^{(1)}$$

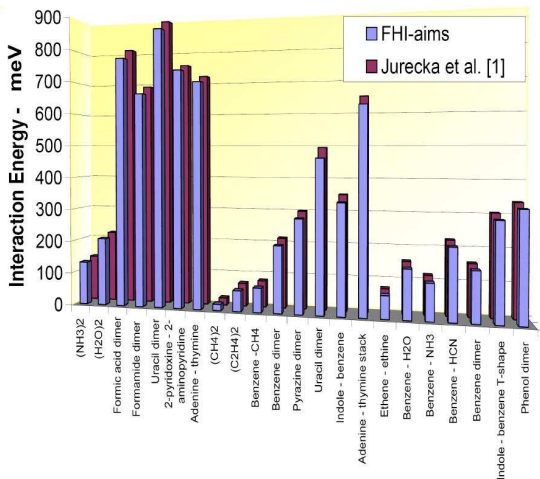
$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{[(ia|jb)^* - (ib|ja)^*](ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- Nonlocal correlation \implies van der Waals (vdW) interaction

$$E_c^{\text{MP2}} \longrightarrow \frac{C_6^{\text{MP2}}}{R_{AB}^6} \text{ when } R_{AB} \rightarrow \infty$$



MP2 calculations for a benchmark database S22

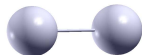
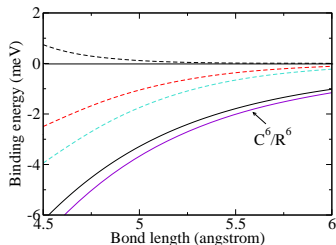
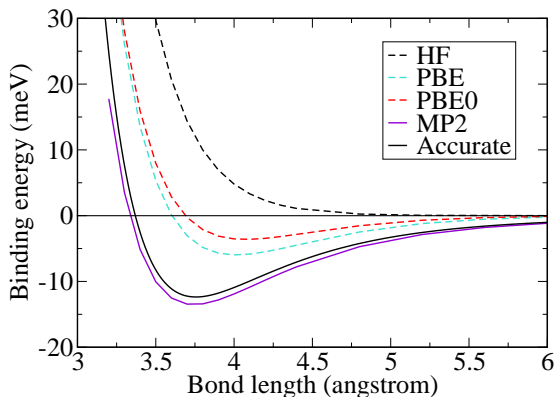


- **S22**: Benchmark database containing 22 weakly bonded molecular complex [1]
- The **complete basis set limit** is approached with Tier4 basis set (remaining error about **5%** on average).

FHI-aims calculations performed by Alexandre Tkatchenko

[1] Jurečka, Šponer, Černý, and Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006)

MP2 for Argon dimer



"Accurate" result:

K. T. Tang and J. P. Toennies, J. Chem. Phys. **118**, 4976 (2003).

Nonlocal correlation in MP2 is crucial for a quantitative description.

Successes and limitations of MP2

Pros

- + “Cheapest” *ab-initio* post-HF method for incorporating non-local correlation effect;
- + Good for properties of organic molecule
- + Very good for hydrogen bonding
- + Good for charge transfer barriers (which LDA/GGA strongly underestimate)

Successes and limitations of MP2

Pros

- + “Cheapest” *ab-initio* post-HF method for incorporating non-local correlation effect;
- + Good for properties of organic molecule
- + Very good for hydrogen bonding
- + Good for charge transfer barriers (which LDA/GGA strongly underestimate)

Cons

- Bad for small-gap systems, molecules containing transition metal/rare earth ions, and completely fails (diverges) for 3D metals
- Reason: HF reference, and perturbation based on bare Coulomb interaction

Contents

- 1 Hartree-Fock theory, hybrid functionals
- 2 Second-order Möller-Plesset Perturbation Theory
- 3 Random Phase Approximation
- 4 Applications

Adiabatic connection fluctuation dissipation theorem

- Exact XC energy via “adiabatic connection”

$$E_{XC}^{\text{exact}} = \int_0^1 d\lambda U_{XC}^\lambda$$

U_{XC}^λ is related to the **density-density fluctuation** of the system.

D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

Adiabatic connection fluctuation dissipation theorem

- Exact XC energy via “adiabatic connection”

$$E_{\text{XC}}^{\text{exact}} = \int_0^1 d\lambda U_{\text{XC}}^\lambda$$

U_{XC}^λ is related to the **density-density fluctuation** of the system.

- Fluctuation-dissipation theorem

$$\underbrace{U_{\text{XC}}^\lambda}_{\text{Fluctuation}} = -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \left[-\frac{1}{\pi} \int_0^\infty d\omega \underbrace{\text{Im} \chi_\lambda(\mathbf{r}, \mathbf{r}', \omega)}_{\text{Dissipation}} - n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right]$$

$\chi_\lambda(\mathbf{r}, \mathbf{r}', t - t') = \delta n(\mathbf{r}, t) / \delta v_{\text{ext}}^\lambda(\mathbf{r}', t')$: Response function
(the imaginary part of which describe the dissipation process)

\implies **Opens a new route to construct E_{XC}**

D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

RPA formulated within DFT framework

- Dyson equation for χ_λ (in TDDFT)

$$\begin{aligned}\chi_\lambda &= \chi_0 + \chi_0(\lambda v + f_{xc}^\lambda)\chi_\lambda \\ f_{xc}^\lambda(\mathbf{r}, \mathbf{r}', t - t') &= \frac{\delta v_{xc}^\lambda(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}\end{aligned}$$

- RPA: $f_{xc} = 0$

$$\begin{aligned}E_{xc}^{\text{RPA}} &= E_x^{\text{exact}} + E_c^{\text{RPA}} \\ E_c^{\text{RPA}} &= \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} [\ln(1 - \chi_0(i\omega)v) + \chi_0(i\omega)v]\end{aligned}$$

$$\text{Tr} = \int d\mathbf{r} \int d\mathbf{r}'$$

- RPA is done *non-self-consistently* as a post-correction to LDA/GGA.

Some attractive features of RPA

The application of RPA to realistic systems is just at the beginning. Its further development and systematic assessment is underway.

$$E_{\text{tot}}^{\text{RPA}} = T_s + E_{\text{ext}} + E_{\text{H}} + E_x^{\text{exact}} + E_c^{\text{RPA}}$$

- “Exact exchange” incorporated, self-interaction error is dramatically reduced.
- Nonlocal vdW interactions are included automatically (and seamlessly).
- Screening effect is taken into account, thus works for metals/small gap systems, in contrast to MP2.

RPA in FHI-aims

RPA correlation energy

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} [\ln(1 - \chi_0(i\omega)v) + \chi_0(i\omega)v]$$

- Noninteracting response function in real space

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{mn} \frac{(f_n - f_m) \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \psi_m(\mathbf{r}')}{i\omega - \epsilon_m + \epsilon_n}$$

$0 \leq f_m \leq 1$: Fermi occupation number

RPA in FHI-aims

RPA correlation energy

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} [\ln(1 - \chi_0(i\omega)v) + \chi_0(i\omega)v]$$

- Noninteracting response function in real space

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{mn} \frac{(f_n - f_m) \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \psi_m(\mathbf{r}')}{i\omega - \epsilon_m + \epsilon_n}$$

$0 \leq f_m \leq 1$: Fermi occupation number

- Matrix representation with auxiliary basis

$$\chi_{0,\mu\nu} = \langle P_\mu | \chi_0 | P_\nu \rangle = 2 \sum_{mn} \frac{(f_n - f_m) O_{mn}^\mu O_{nm}^\nu}{i\omega - \epsilon_m + \epsilon_n}$$

where $O_{mn}^\mu = \int d\mathbf{r} \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) P_\mu(\mathbf{r})$.

RPA in FHI-aims

RPA correlation energy

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} [\ln(1 - \chi_0(i\omega)v) + \chi_0(i\omega)v]$$

- Noninteracting response function in real space

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{mn} \frac{(f_n - f_m) \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \psi_m(\mathbf{r}')}{i\omega - \epsilon_m + \epsilon_n}$$

$0 \leq f_m \leq 1$: Fermi occupation number

- Matrix representation with auxiliary basis

$$\chi_{0,\mu\nu} = \langle P_\mu | \chi_0 | P_\nu \rangle = 2 \sum_{mn} \frac{(f_n - f_m) O_{mn}^\mu O_{nm}^\nu}{i\omega - \epsilon_m + \epsilon_n}$$

where $O_{mn}^\mu = \int d\mathbf{r} \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) P_\mu(\mathbf{r})$.

- $v_{\mu\nu} = \int d\mathbf{r} \int d\mathbf{r}' \frac{P_\mu(\mathbf{r}) P_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

Atomization energy for small molecules

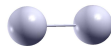
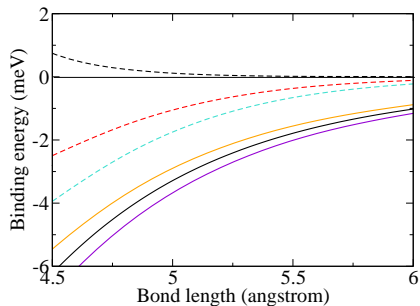
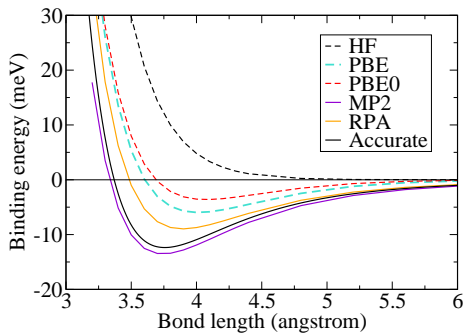
Table: Unit in eV

Molecule	PBE	PBE0	RPA*	EXP
H ₂	4.54	4.53	4.73	4.73
N ₂	10.58	9.75	9.67	9.88
O ₂	6.24	5.36	4.86	5.03
F ₂	2.30	1.48	1.30	1.65
CO	11.70	11.09	10.58	11.23
HF	6.16	5.93	5.74	6.11
H ₂ O	10.17	9.84	9.67	10.06
C ₂ H ₂	18.00	17.54	16.52	17.56
mean abs. error	0.48	0.17	0.45	

* Gaussian basis extrapolated to basis set limit

- The accuracy achieved by hybrid functionals for atomization energies is hard to beat. A simple RPA does not improve over PBE0.

RPA for Argon dimer

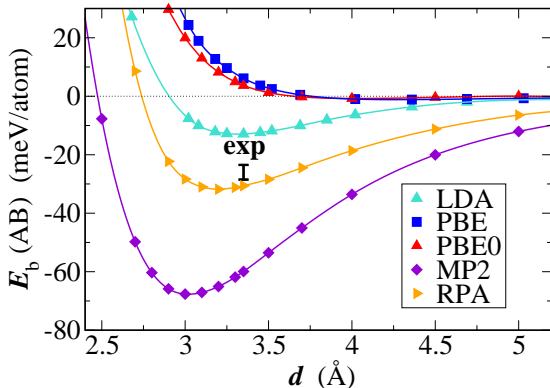


Both RPA and MP2 give the correct asymptotic behavior.

Contents

- 1 Hartree-Fock theory, hybrid functionals
- 2 Second-order Möller-Plesset Perturbation Theory
- 3 Random Phase Approximation
- 4 Applications

Binding energy of two graphene layers

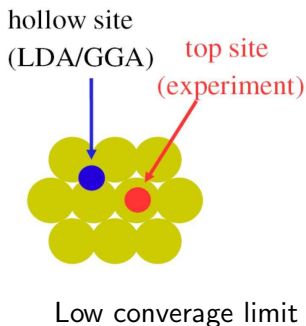


Calculations done by A. Sanfilippo with FHI-aims

CO adsorption puzzle

CO adsorbed on transition metal surfaces

- LDA and GGAs (PW91, PBE, RPBE, AM05) predict the wrong adsorption site, and the adsorption energies are largely overestimated.
- For Cu, Pt, Rh, hollow site is preferred in LDA/GGA; for Ag, Au, hollow and top site are almost degenerate.



P.J. Feibelman *et al.*, J. Phys. Chem. B **105**, 4018 (2001).

A. Stroppa and G. Kresse, New J. Phys, **10**, 063030 (2008).

RPA adsorption energy for CO@Cu(111)

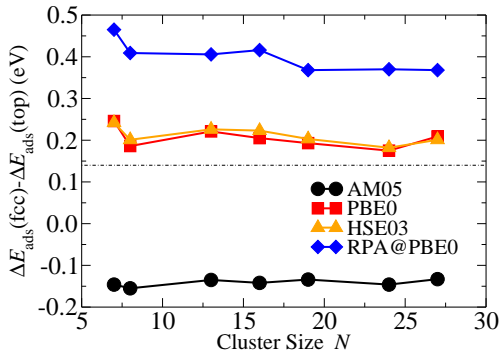
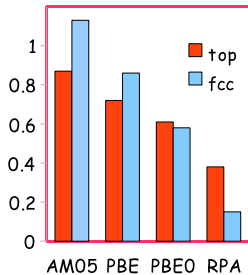
$$\Delta E_{\text{ads}} = \lim_{\text{cluster} \rightarrow \infty} \left[E_{\text{ads}}^{\text{cluster}}(\text{XC}) - E_{\text{ads}}^{\text{cluster}}(\text{PBE}) \right]$$

Q.-M. Hu, K. Reuter, and M. Scheffler, Phys. Rev. Lett., **98**, 176103 (2007)

XC = AM05

PBE0, HSE03

RPA



CO@Cu(111) adsorption Energies: A Comparison

E_{ads}	top (eV)	fcc (eV)	Δ (eV)
PBE[1]	-0.71	-0.87	0.16
PBE0[1]	-0.61	-0.58	-0.03
CASSCF[2]	-0.49	>0	<-0.49
EXP	-0.46, -0.49	/	/
this work [3]			
PBE	-0.72	-0.86	0.14
PBE0	-0.58 ± 0.04	-0.54 ± 0.01	-0.04 ± 0.01
RPA@PBE	-0.35 ± 0.02	-0.17 ± 0.02	0.18 ± 0.02
RPA@PBE0	-0.37 ± 0.02	-0.15 ± 0.02	0.22 ± 0.02

[1] A. Stroppa and G. Kresse, New J. Phys, **10**, 063030 (2008)

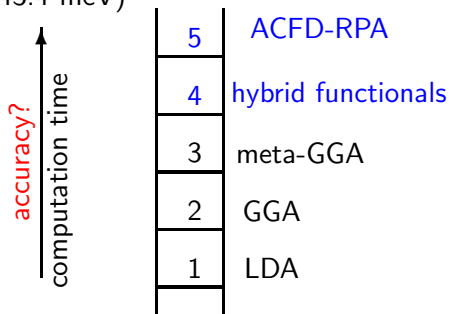
[2] Sharifzadeh, P. Huang, and E. Carter, J. Phys. Chem. C **112**, 4649 (2008)

[3] X. Ren, P. Rinke, and M. Scheffler, Phys. Rev. B, **80**, 045402 (2009)

Summary

Quantum chemistry method HF, MP2

and in the DFT world
(43.4 meV)



- Post-LDA/GGA approaches improve things in one way or another, but they have their own limitations.
- Present higher rungs (hybrid functionals and RPA) are promising, but the improvement is not (yet) systematic. **More work are needed to construct these rungs, and FHI-aims provides such a platform.**

Many thanks to

- [Concept, algorithm](#)
Volker Blum and Patrick Rinke
- [MP2](#)
Andrea Sanfilippo
- [Bilayer graphene](#)
Andrea Sanfilippo, Karsten Reuter, Alexandre Tkatchenko,
Volker Blum, and Patrick Rinke
- [Support and Funding](#)
Matthias Scheffler
DFG, Nanoquanta/ETSF