第一性原理计算中的杂化泛函和无规相近似方法

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Outline

- Background – basics of density functional theory
- The concept of hybridizing DFT and Hartree-Fock and the popular hybrid functionals
- Random phase approximation as a method to compute the ground-state total energy of interacting electron systems
- Recent progresses and perspectives
- Implementation and computer codes

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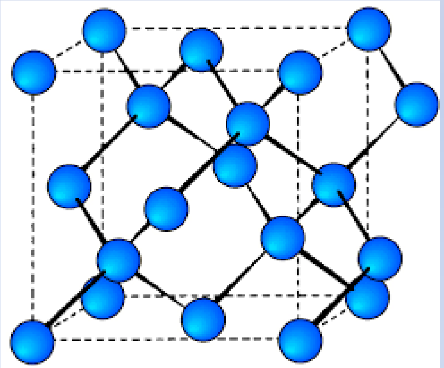
The idea of first-principles computations

Atomic positions and nuclear changes



$$\{Z_\alpha,\ \boldsymbol{R}_\alpha\}$$

"Electronic structure"

Physical and chemical properties

Ground-state energy
Charge density
Energy gap
Optical spectra
Transport properties
Hardness
……

Many-body interacting Hamiltonian for condensed matter physics, chemistry, and materials science

$$\hat{H} = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

The electron part

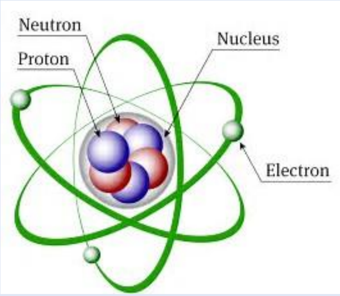
$$-\sum_{\alpha=1}^{N_{nul}} \frac{\nabla_\alpha^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha \neq \beta}^{N_{nul}} \frac{Z_\alpha Z_\beta e^2}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}$$

The nuclei part

$$-\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_{nul}} \frac{Z_\alpha e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|}$$

The electron-nuclei attraction

Different systems differ by their atomic species $\{Z_\alpha\}$ and positions $\{\boldsymbol{R}_\alpha\}$.



The Born-Oppenheimer approximation and interacting many-electron problem

$$\hat{H}^e = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i}^{N_e} V^{ext}_{\{\boldsymbol{R}_\alpha, Z_\alpha\}}(\boldsymbol{r}_i)$$

$$V^{ext}_{\{R_\alpha, Z_\alpha\}}(\boldsymbol{r}) = -\sum_{\alpha=1}^{N_{nul}} \frac{Z_\alpha e^2}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|}$$

is the external potential due to the nuclei.

The "*external*" potential contains the information about the positions and species of the constituted atoms, and hence specifies the actual systems: atoms, molecules, solids, surfaces, clusters, nanostructures ……

The Born-Oppenheimer (BO) approximation is not always valid. To describe non-adiabatic process, one needs to go beyond BO approximation.

The *ab-initio* electronic many-body Hamiltonian

$$\hat{H}^e = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i}^{N_e} V_{\{\boldsymbol{R}_i, Z_i\}}^{ext}(\boldsymbol{r}_i)$$

$$= \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

The ground state and excited states of the electronic Hamiltonian determine most properties of materials.

Despite the considerable simplification that the Born-Oppenheimer approximation brings, the computational challenge remains. The exact solution of the interacting many-body Hamiltonian is not possible even numerically for *O(N)*>10.

Further simplification/approximation is a must!

The Hartree-Fock approximation

The ground-state many-body electronic wave function is approximated by a single Slater determinant:

$$\Psi_{\mathrm{HF}}(\boldsymbol{r}_1\sigma_1,\boldsymbol{r}_2\sigma_2,\cdots,\boldsymbol{r}_N\sigma_N)=\frac{1}{\sqrt{N!}}\begin{bmatrix}\psi_1(\boldsymbol{r}_1)\zeta_1(\sigma_1) & \psi_1(\boldsymbol{r}_2)\zeta_1(\sigma_2) & \cdots & \psi_1(\boldsymbol{r}_N)\zeta_1(\sigma_N)\\ \psi_2(\boldsymbol{r}_1)\zeta_2(\sigma_1) & \psi_2(\boldsymbol{r}_2)\zeta_2(\sigma_2) & \cdots & \psi_2(\boldsymbol{r}_N)\zeta_2(\sigma_N)\\ \cdots & \cdots & \cdots & \cdots\\ \psi_N(\boldsymbol{r}_1)\zeta_N(\sigma_1) & \psi_N(\boldsymbol{r}_2)\zeta_N(\sigma_2) & \cdots & \psi_N(\boldsymbol{r}_N)\zeta_N(\sigma_N)\end{bmatrix}$$

$$\min_{\{\psi_n\}}\langle\Psi_{\mathrm{HF}}|\hat{H}^e|\Psi_{\mathrm{HF}}\rangle \Rightarrow \left(-\frac{\nabla^2}{2m}+V^{ext}(\boldsymbol{r})+\sum_{m=1}^{N}\int d\boldsymbol{r}'\frac{\psi_m^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\psi_n(\boldsymbol{r})$$

$$-\sum_{m=1}^{N}\int d\boldsymbol{r}'\frac{\psi_m^*(\boldsymbol{r}')\psi_n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\delta_{\sigma_i\sigma_j}\psi_m(\boldsymbol{r})=\epsilon_n\psi_n(\boldsymbol{r})$$

The interacting many-body problem is reduced to an effective single-particle problem that should be solved self-consistently.

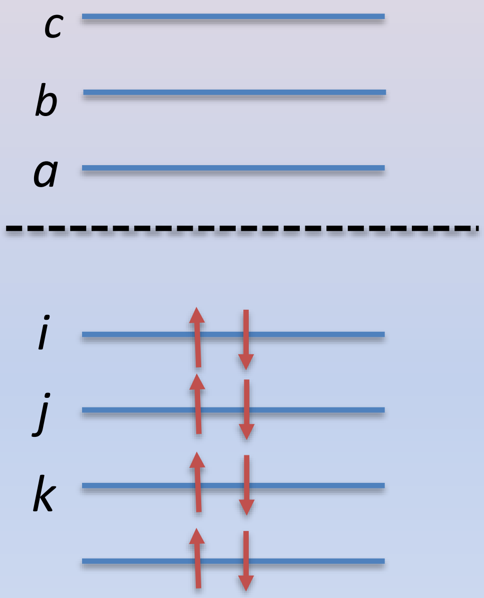
The Hartree-Fock equation

The Hartree-Fock equation can also be written as

$$\left[-\frac{\nabla^2}{2m} + v_{ext}(\boldsymbol{r}) + \int d\boldsymbol{r}' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right]\psi_{n,\sigma}(\boldsymbol{r})$$

$$+\sum_{m}^{occ.} \int d\boldsymbol{r}' \frac{\psi_{n,\sigma}(\boldsymbol{r}')\psi^*_{m,\sigma}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_{m,\sigma}(\boldsymbol{r}) = \epsilon_n\psi_{n,\sigma}(\boldsymbol{r})$$

$$n(\boldsymbol{r}) = \sum_{n,\sigma}^{occ.} \left|\psi_{n,\sigma}(\boldsymbol{r})\right|^2$$



The Hartree-Fock equations are a set of non-linear equations that need to be solved self-consistently. The resultant set of eigenstates are called Hartree-Fock orbitals.

Orbital energies $\{\epsilon_n\}$ describe approximately the energy cost to remove or the energy gain to add an electron to the system. (Koopman's theorem)

Correlation: effect beyond Hartree-Fock

Exact ground-state wave function

$$E_c = \langle \Psi_0 | \widehat{H}^e | \Psi_0 \rangle - \langle \Psi_{\mathrm{HF}} | \widehat{H}^e | \Psi_{\mathrm{HF}} \rangle$$

Hartree-Fock wave function

The different ways to treat the correlation effects underlines the different electronic structure methods in quantum chemistry and condensed matter physics.

HF is insufficiently accurate for most applications, especially for extended systems (no screening!).

Approaches to solve the electronic Hamiltonian

Interacting electron Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

Wave function methods

(quantum chemistry)

Configuration Interaction
Coupled Cluster Theory
Møller-Plesset Perturbation Theory

(Generalized) Kohn-Sham DFT, TDDFT

LDA, GGA. meta-GGA
hybrid functional
vdW-DF, …

Model Hamiltonian

Model:

Tight-binding, Anderson, Kondo,
Heisenberg, t-J model, Hubbard, …

Numerical algorithm:

ED, NRG, DMRG, QMC, DMFT,
Guzwiller, Tensor Network, …

The Nobel prize in chemistry (1998)

John Pople for his contribution to wave-function methods

Walter Kohn for his contribution to density functional theory

Basic idea behind density functional theory

The many-body Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} = \sum_{i}^{N} -\frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j}^{N} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i=1}^{N} V_{ext}(\boldsymbol{r}_i)$$

How to compute the ground-state energy?

1. From the wave function (3*N*-dimensional variable)

$$E_0[\Psi] = \langle \Psi \mid \hat{H} \mid \Psi \rangle$$

2. From the electron density (3-dimensional variable)

$$E_0 = E_0[n]$$

$$E_0 = E_0[\Psi] \xrightarrow{?} E_0 = E_0[n]$$

If one can avoid complex many-body wavefunction, and express the ground-state energy as a function of the electron density, then the problem will be significantly simplified.

Energy functional of interacting many-particle system

$$E_{v_{ext}}[n] = T[n] + V_{ee}[n] + \int d^3 r v_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) \geq E_0$$

Re-expressing the functional as：

$$E_{v_{ext}}[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d^3 r v_{ext}(\boldsymbol{r}) n(\boldsymbol{r})$$

$T[n]$: Kinetic energy functional of interacting system;

$T_s[n]$: Kinetic energy functional of noninteracting system;

$E_H[n]$: The Hartree energy functional;

$$E_{xc}[n] = T[n] + V_{ee}[n] - T_s[n] - E_H[n]$$

Exchange-correlation energy functional (everything unknown).

The Kohn-Sham equation (1965)

$$\left(-\frac{\nabla^2}{2\mathrm{m}}+v_{eff}(\boldsymbol{r})\right)\psi_l(\boldsymbol{r})=\epsilon_l\psi_l(\boldsymbol{r})$$

$$v_{eff}(\mathbf{r})=V_{ext}(\boldsymbol{r})+\int d^3r'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+\frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}$$

$$n(\boldsymbol{r})=\sum_{l=1}^{N}|\psi_l(\boldsymbol{r})|^2$$

To be solved
self-consistently

$n(\boldsymbol{r}) \rightarrow n_0(\boldsymbol{r})$

$$E_0=-\frac{1}{2m}\sum_{l=1}^{N}\langle\psi_l|\nabla^2|\psi_l\rangle+E_H[n_0]+E_{xc}[n_0]+\int d^3r\,v_{ext}(\boldsymbol{r})n_0(\mathbf{r})$$

By solving the Kohn-Sham equation, one can in principle obtain the exact ground-state energy and density of interacting systems, if $E_{xc}[n]$ is known exactly.

The exchange-correlation energy

$$E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$$

Exact-exchange energy in KS-DFT

Slater determinant formed by occupied Kohn-Sham orbitals

$$E_{\mathrm{x}} = \langle \Phi_{\mathrm{KS}} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{KS}} \rangle - E_{\mathrm{Hartree}} = -\sum_{m,n}^{occ.} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$= \frac{1}{2}\sum_{i,j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

The Hartree energy

Electron-electron interaction operator

Correlation energy in KS-DFT

$$E_c = \langle \Psi_0 | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi_0 \rangle - \langle \Phi_{\mathrm{KS}} | \hat{T} + \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{KS}} \rangle = T_{\mathrm{c}} + U_{\mathrm{c}}$$

$$T_c = T - T_s, \qquad U_c = \langle \Psi_0 | \hat{V}_{\mathrm{ee}} | \Psi_0 \rangle - E_{\mathrm{Hartree}} - E_{\mathrm{x}}$$

The exchange-correlation energy

$$E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$$

Exact-exchange energy in KS-DFT

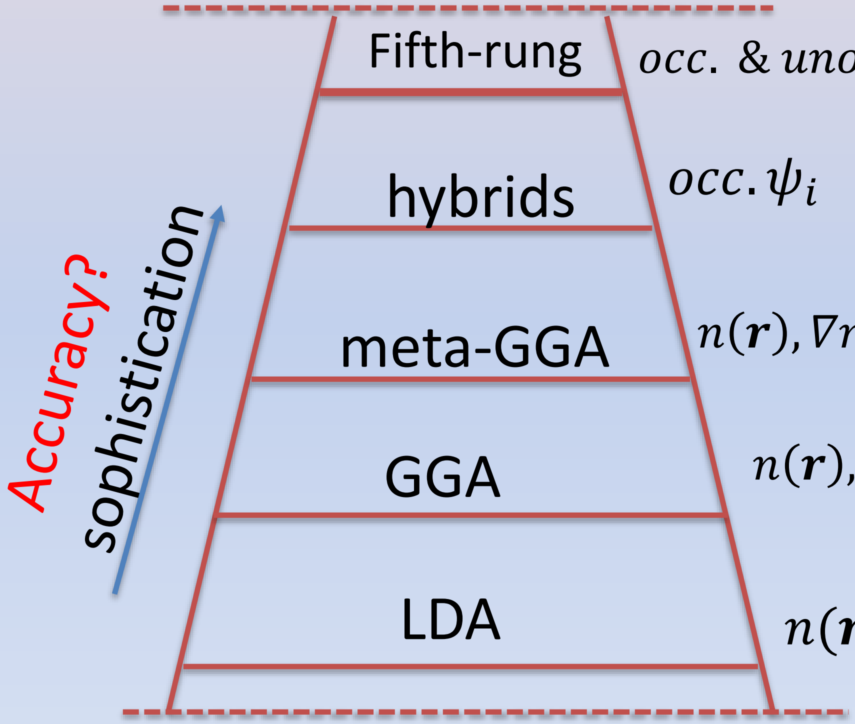
- Approximation must be made for E_{c}.
- E_{x} and E_{c} are often approximated together to achieve error compensation.
- Approximate E_{x} as an explicit density-dependent functional introduces “self-interaction error”.

Correlation energy in KS-DFT

$$E_c = \langle \Psi_0 | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi_0 \rangle - \langle \Phi_{\mathrm{KS}} | \hat{T} + \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{KS}} \rangle = T_{\mathrm{c}} + U_{\mathrm{c}}$$

$$T_c = T - T_s, \qquad U_c = \langle \Psi_0 | \hat{V}_{\mathrm{ee}} | \Psi_0 \rangle - E_{\mathrm{Hartree}} - E_{\mathrm{x}}$$

Jacob’s ladder in DFT



Chemical accuracy

Fifth-rung $occ.\ \&\ unocc\ \psi_i$ e.g., RPA, double hybrids

hybrids $occ.\,\psi_i$ e.g., B3LYP, PBE0, HSE

meta-GGA $n(\boldsymbol{r}), \nabla n(\boldsymbol{r}), \tau(\boldsymbol{r})$ e.g., TPSS, SCAN

GGA $n(\boldsymbol{r}), \nabla n(\boldsymbol{r})$ e.g., BLYP, PBE

LDA $n(\boldsymbol{r})$

Accuracy?

sophistication

Hartree

J. Perdew & K. Schmidt, in Density functional theory and its application to materials, edited by Van Doren e al. (2001).

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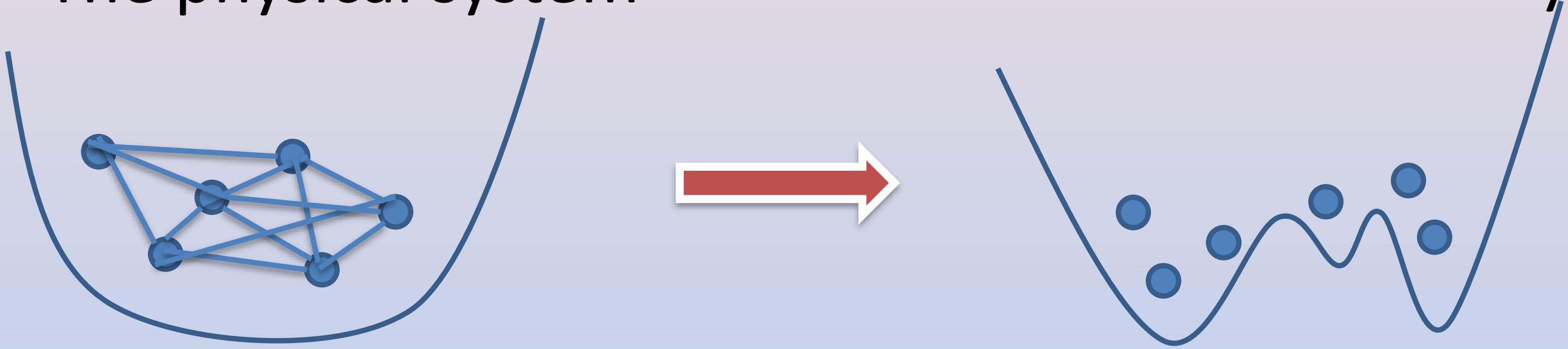
The adiabatic connection construction

The physical system

The Kohn-Sham system



$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

$$\hat{H}_{KS} = \hat{T} + \hat{V}_{aux}$$

Define a series of fictitious systems with scaled interparticle interactions:

$$\hat{H}_{\lambda} = \hat{T} + \lambda\hat{V}_{ee} + \hat{V}^{\lambda}_{ext}$$

$$\hat{H}_{\lambda=1} = \hat{H}$$

$$\hat{H}_{\lambda=0} = \hat{H}_{KS}$$

The electron density $n(r)$ is kept fixed for $0 \leq \lambda \leq 1$.

$$E^{\text{exact}}_{\text{xc}} = \int_0^1 d\lambda U^{\lambda}_{\text{xc}}$$

$$U^{\lambda}_{xc} = \langle \Psi^{\lambda}_0 | \hat{V}_{ee} | \Psi^{\lambda}_0 \rangle - \frac{1}{2} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

Two limits in the adiabatic connection path

- $\lambda = 0, v_{aux}^{\lambda=0}(r) = v_{\mathrm{KS}}(r), \left|\Psi_0^{\lambda=0}\right\rangle = |\Psi_{\mathrm{KS}}\rangle$ (the KS system)

$$U_{xc}^{\lambda=0} = \langle\Psi_{\mathrm{KS}}|\hat{V}_{ee}|\Psi_{\mathrm{KS}}\rangle - \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$= -\frac{1}{2}\sum_{m,n}^{occ.}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} := E_x^{\mathrm{HF}}$$

Exchange-only limit, where LDA/GGAs are least accurate. => exact exchange is needed.

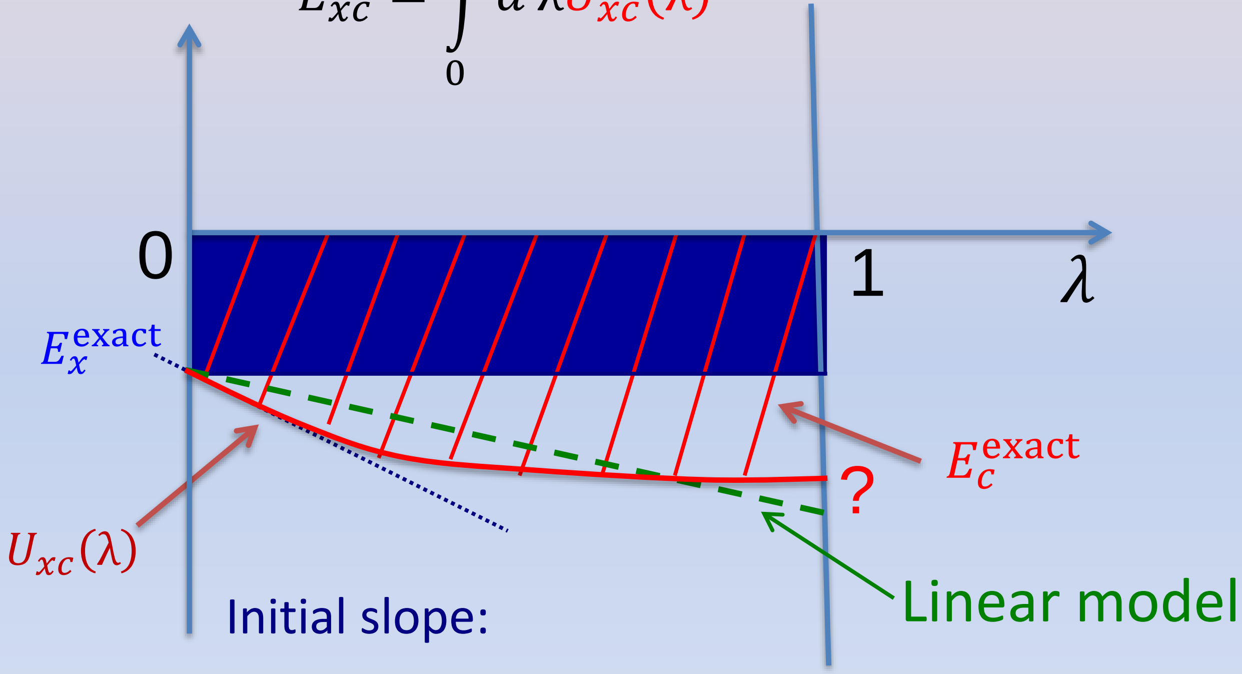
- $\lambda = 1, v_{aux}^{\lambda=1}(r) = v_{\mathrm{ext}}(r), \left|\Psi_0^{\lambda=1}\right\rangle = |\Psi_0\rangle$ (fully interacting system)

$$U_{xc}^{\lambda=1} = \langle\Psi_0|\hat{V}_{ee}|\Psi_0\rangle - \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} = E_x^{\mathrm{HF}} + U_c$$

LDA/GGAs work reasonably well. Correlation effect is crucial, and exact-exchange-only treatment will not work.

Adiabatic connection path

$$E_{xc} = \int_0^1 d\lambda\, U_{xc}(\lambda)$$



Initial slope:

$$\frac{dU_{xc}(\lambda)}{d\lambda}\Big|_{\lambda=0} = 2E_c^{\text{PT2}}$$

Second-order perturbation theory

The milestone: Becke's half-half theory

*A. D. Becke, JCP **98**, 1372 (1993)*

$$E_{xc} = \int_0^1 d\lambda U_{xc}^{\lambda} \approx 1/2\left(U_{xc}^{\lambda=0} + U_{xc}^{\lambda=1}\right)$$

$$U_{xc}^{\lambda=0} = E_x^{\mathrm{exact}}, \quad U_{xc}^{\lambda=1} \approx U_{xc}^{\mathrm{LSDA}}$$

Becke's half-half (HH) theory : ⇨

$$E_{xc}^{\mathrm{HH}} = 1/2\left(E_x^{\mathrm{exact}} + U_{xc}^{\mathrm{LSDA}}\right)$$

Performance of the half-half method

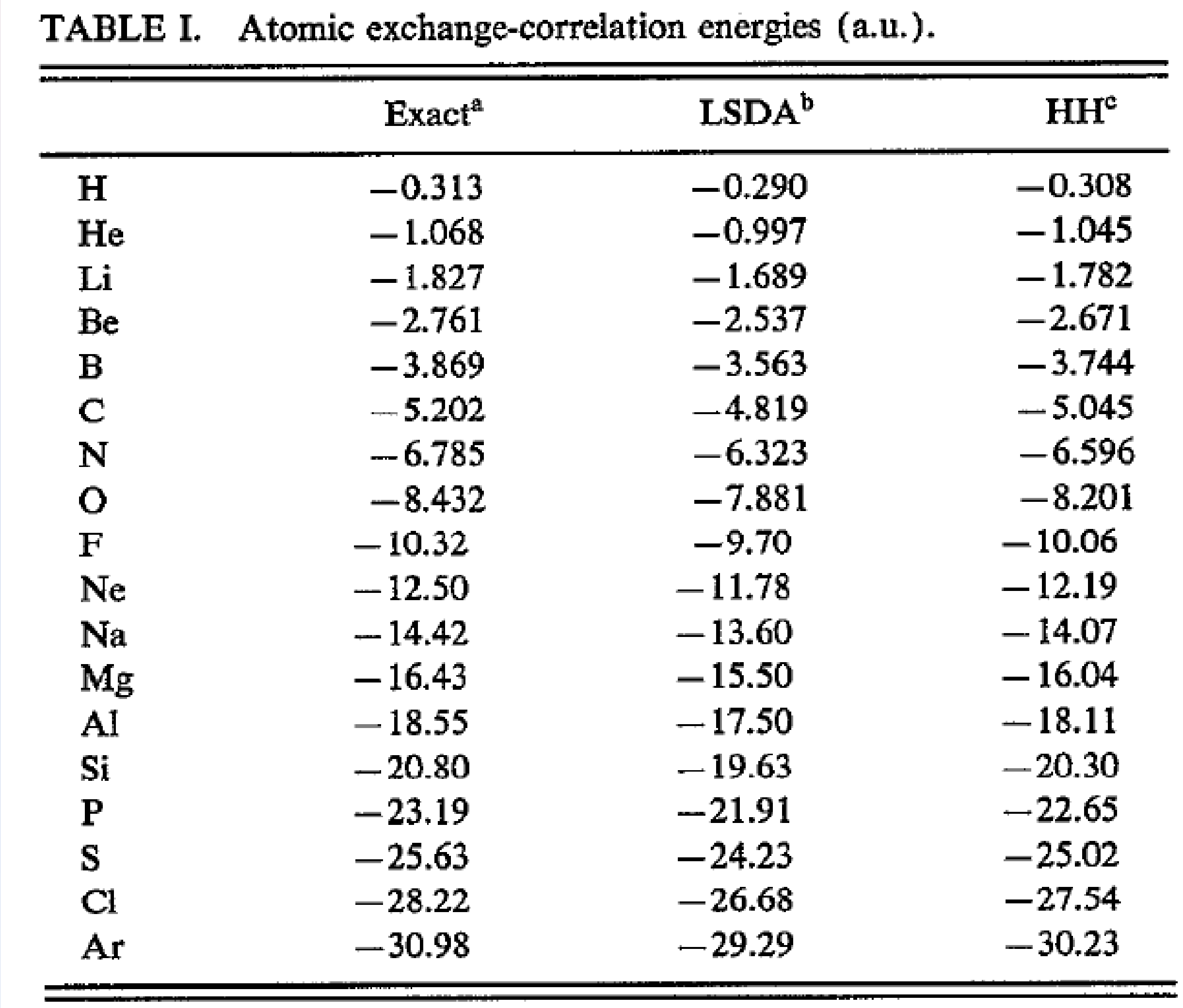


TABLE I. Atomic exchange-correlation energies (a.u.).

	Exact[a]	LSDA[b]	HH[c]
H	−0.313	−0.290	−0.308
He	−1.068	−0.997	−1.045
Li	−1.827	−1.689	−1.782
Be	−2.761	−2.537	−2.671
B	−3.869	−3.563	−3.744
C	−5.202	−4.819	−5.045
N	−6.785	−6.323	−6.596
O	−8.432	−7.881	−8.201
F	−10.32	−9.70	−10.06
Ne	−12.50	−11.78	−12.19
Na	−14.42	−13.60	−14.07
Mg	−16.43	−15.50	−16.04
Al	−18.55	−17.50	−18.11
Si	−20.80	−19.63	−20.30
P	−23.19	−21.91	−22.65
S	−25.63	−24.23	−25.02
Cl	−28.22	−26.68	−27.54
Ar	−30.98	−29.29	−30.23

A. D. Becke, JCP ***98****, 1372 (1993)*

Further development: the B3LYP functional

A. D. Becke, *J. Chem. Phys.* ***98***, *5648 (1993)* (# of citations >900,000)

The original form:

Perdew-Wang 1991 GGA correlation correction

$$E_{xc}^{\mathrm{B3PW91}} = E_{xc}^{\mathrm{LSDA}} + a_0\left(E_x^{\mathrm{exact}} - E_x^{\mathrm{LSDA}}\right) + a_x \Delta E_x^{\mathrm{B88}} + a_c \Delta E_c^{\mathrm{PW91}}$$

Becke 1988 GGA exchange correction

$$\Delta E_x^{\mathrm{B88}} = E_x^{\mathrm{B88}} - E_x^{\mathrm{LSDA}}, \qquad \Delta E_c^{\mathrm{PW91}} = E_c^{\mathrm{PW91}} - E_c^{\mathrm{LSDA}}$$

Empiricalparameters: $a_0 = 0.20, a_x = 0.72, a_c = 0.81$

Later, implemented in GAUSSIAN:

$$E_{xc}^{\mathrm{B3LYP}} = E_{xc}^{\mathrm{LSDA}} + a_0\left(E_x^{\mathrm{exact}} - E_x^{\mathrm{LSDA}}\right) + a_x \Delta E_x^{\mathrm{B88}} + a_c \Delta E_c^{\mathrm{LYP}}$$

Lee-Yang-Parr 1991 GGA correlation correction

Simplification to one parameter

The B3LYP functional:

$$E_{xc}^{\mathrm{B3LYP}} = E_{xc}^{\mathrm{LSDA}} + a_0\left(E_x^{\mathrm{exact}} - E_x^{\mathrm{LSDA}}\right) + a_x \Delta E_x^{\mathrm{B88}} + a_c \Delta E_c^{\mathrm{LYP}}$$

Choosingparameters: $a_x = 1 - a_0,\ \ a_c = 1$

<u>B1LYP:</u>

$$E_{xc}^{\mathrm{B1LYP}} = E_{xc}^{\mathrm{BLYP}} + a_0\left(E_x^{\mathrm{exact}} - E_x^{\mathrm{B88}}\right)$$

$$\downarrow$$

$$\left(= E_x^{\mathrm{B88}} + E_c^{\mathrm{LYP}}\right)$$

In general, one-parameter hybrid functional :

$$E_{xc}^{\mathrm{hyd}} = E_{xc}^{\mathrm{GGA}} + a_0\left(E_x^{\mathrm{exact}} - E_x^{\mathrm{GGA}}\right)$$

$a_0 \sim 0.25$ performs best for atomization energies!

Rationale for the best mixing parameter

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

$$E_{xc,\lambda}^{\text{hyd}}(n) = E_{xc,\lambda}^{\text{DFA}} + \left(E_x^{\text{exact}} - E_x^{\text{DFA}}\right)(1-\lambda)^{n-1}$$

$$E_{xc}^{\text{hyd}}(n) = \int_0^1 E_{xc,\lambda}(n) = E_{xc}^{\text{DFA}} + \frac{1}{n}\left(E_x^{\text{exact}} - E_x^{\text{DFA}}\right)$$

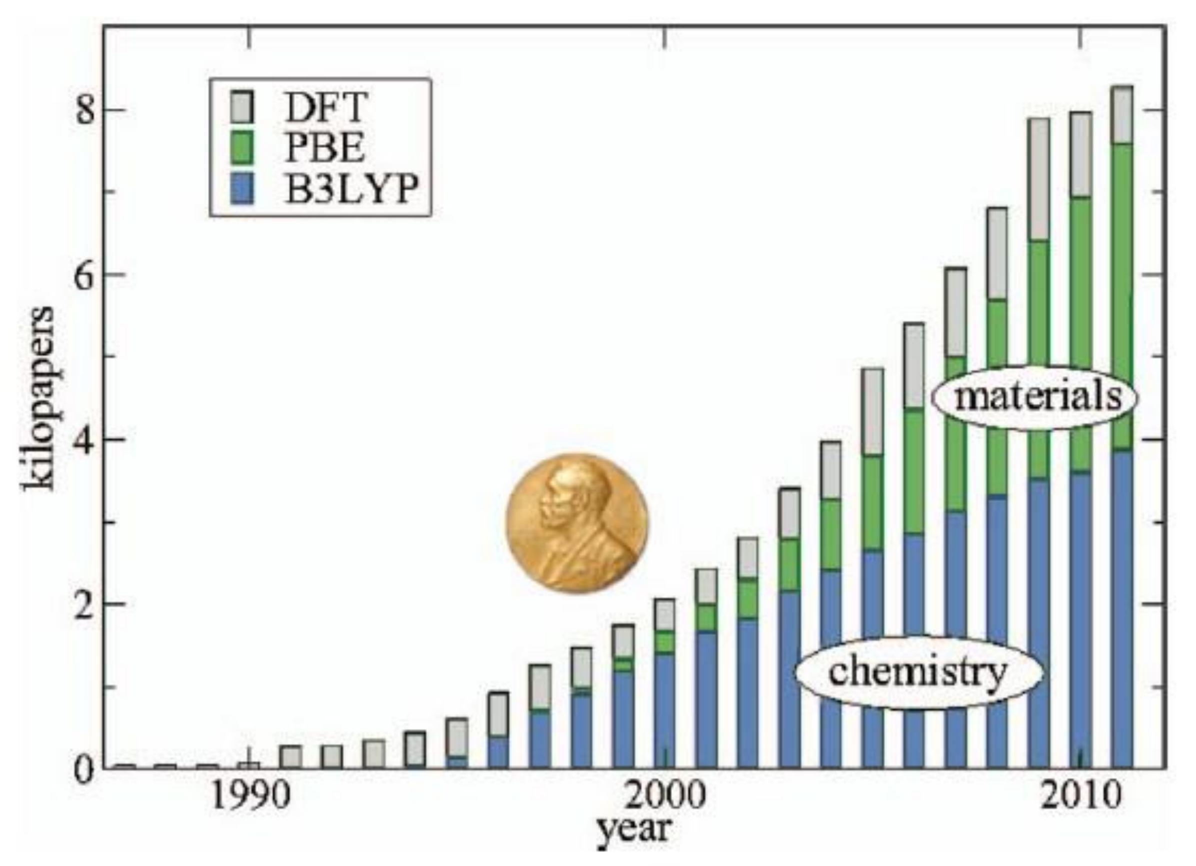
n=4 ⟺ The 4th-order Møller-Plesset perturbation theory

The PBE0 functional :

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{PBE}} + 0.25\left(E_x^{\text{exact}} - E_x^{\text{PBE}}\right)$$

$a_0 = 0.25$ is good for atomization energies!

Number of Publications on Topics “DFT”

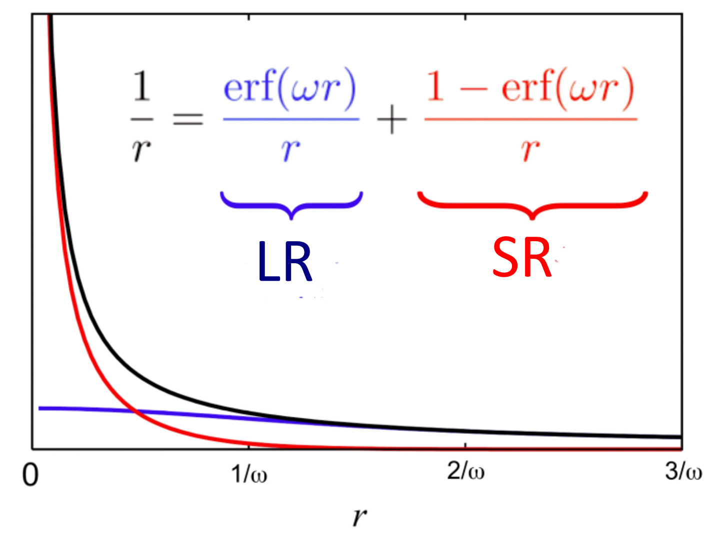


K. Burke, J. Chem. Phys. ***136****, 150901 (2012)*

Application to solids: the HSE functional

Heyd, Scuseria, Ernzerhof, J. Chem. Phys. ***118****, 8207 (2003)*

$$\frac{1}{r} = \underbrace{\frac{erfc(\omega r)}{r}}_{\text{Short-range(SR)}} + \underbrace{\frac{erf(\omega r)}{r}}_{\text{Long-range (LR)}}$$



$$E_x^{\mathrm{HF,SR}} = -\sum_{l,m}^{occ} \int d^3r d^3r' \frac{\psi_l^*(\mathbf{r})\psi_m(\mathbf{r}) erfc(\omega|\mathbf{r}-\mathbf{r}'|)\psi_m^*(\mathbf{r}')\psi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{xc}^{\mathrm{PBE0}} = E_{xc}^{\mathrm{PBE}} + 0.25\left(E_x^{\mathrm{HF}} - E_x^{\mathrm{PBE}}\right) \quad \Rightarrow$$

$$E_{xc}^{\mathrm{HSE}} = E_{xc}^{\mathrm{PBE}} + 0.25\left(E_x^{\mathrm{HFt,SR}} - E_x^{\mathrm{PBE,SR}}\right)$$

Lattice constants

40 Semiconductors

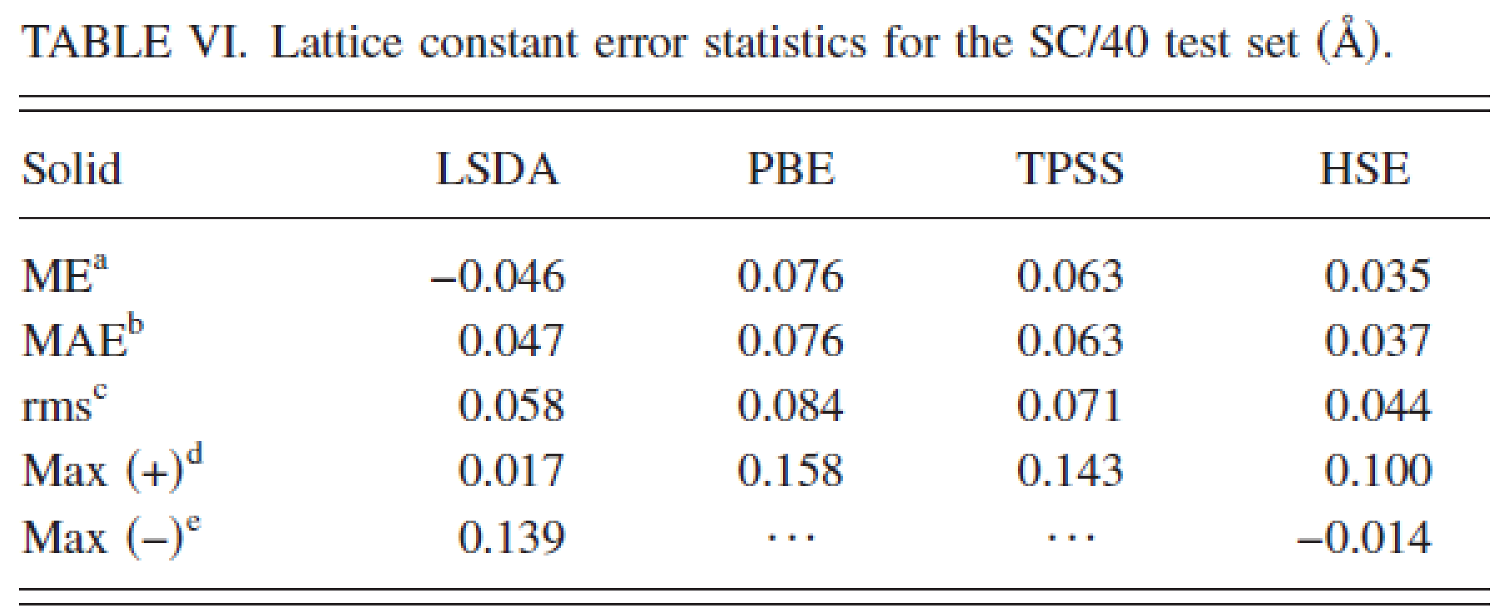
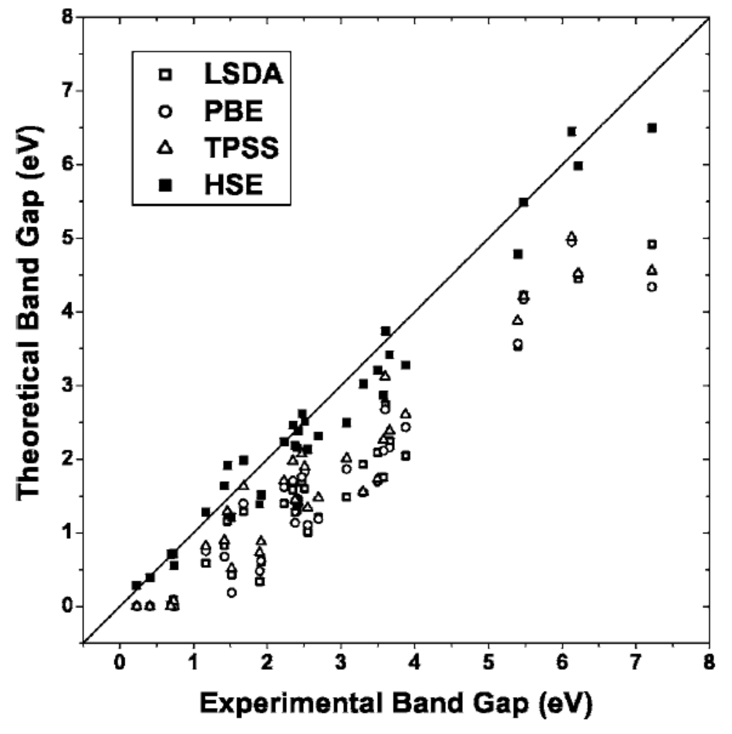


TABLE VI. Lattice constant error statistics for the SC/40 test set (Å).

Solid	LSDA	PBE	TPSS	HSE
ME[a]	–0.046	0.076	0.063	0.035
MAE[b]	0.047	0.076	0.063	0.037
rms[c]	0.058	0.084	0.071	0.044
Max (+)[d]	0.017	0.158	0.143	0.100
Max (–)[e]	0.139	···	···	–0.014

Heyd, Peralta, Scuseria, and Martin, J. Chem. Phys. ***123****, 174101 (2005)*

Band gaps



Heyd, Peralta, Scuseria,and Martin, J. Chem. Phys. ***123****, 174101 (2005)*

T. M. Henderson, J. Paier, G.E., Scuseria, Phys. Status. Solidi B ***248****, 767 (2011)*

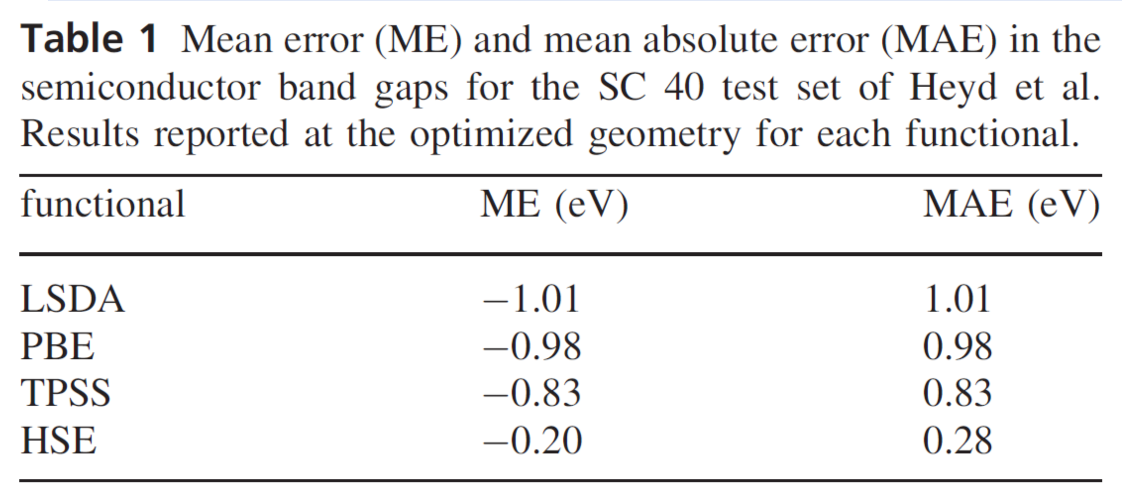
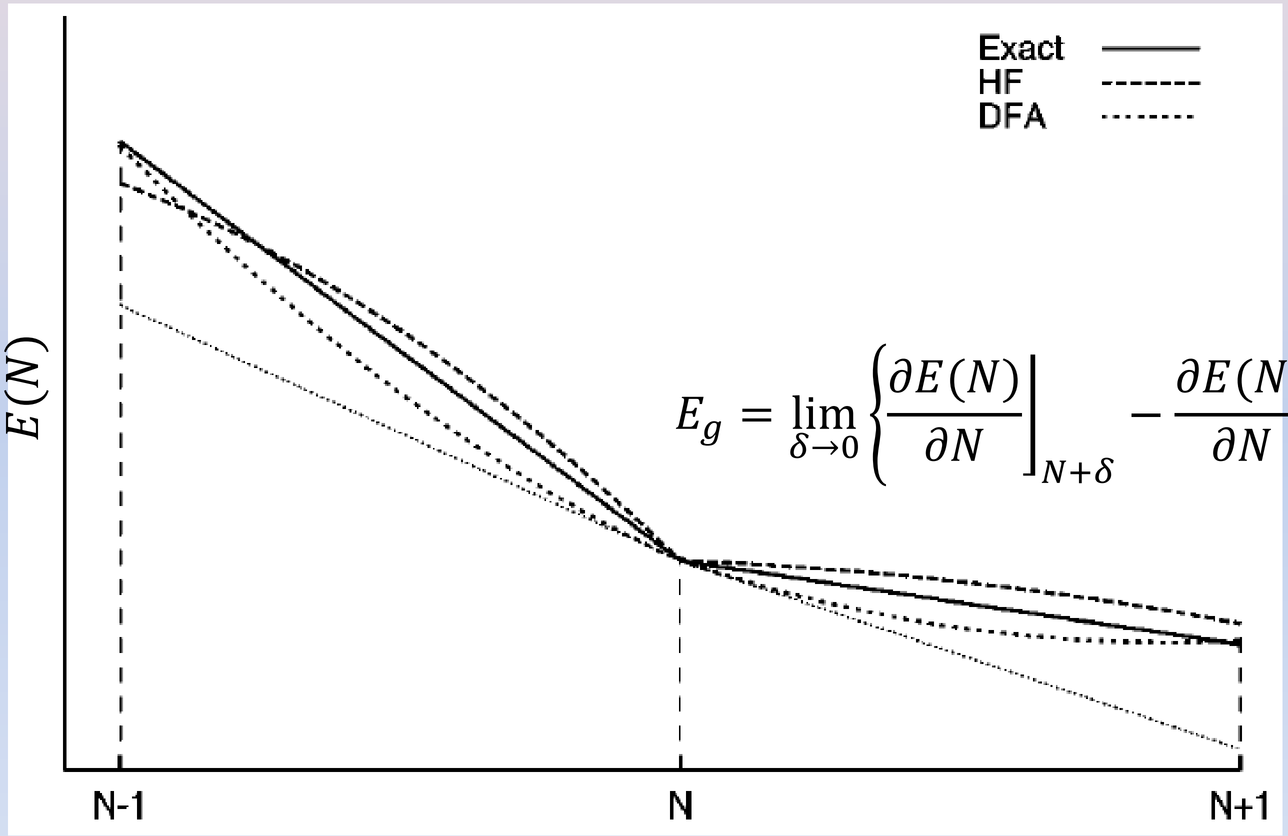


Table 1 Mean error (ME) and mean absolute error (MAE) in the semiconductor band gaps for the SC 40 test set of Heyd et al. Results reported at the optimized geometry for each functional.

functional	ME (eV)	MAE (eV)
LSDA	−1.01	1.01
PBE	−0.98	0.98
TPSS	−0.83	0.83
HSE	−0.20	0.28

Band gap problem: another perspective



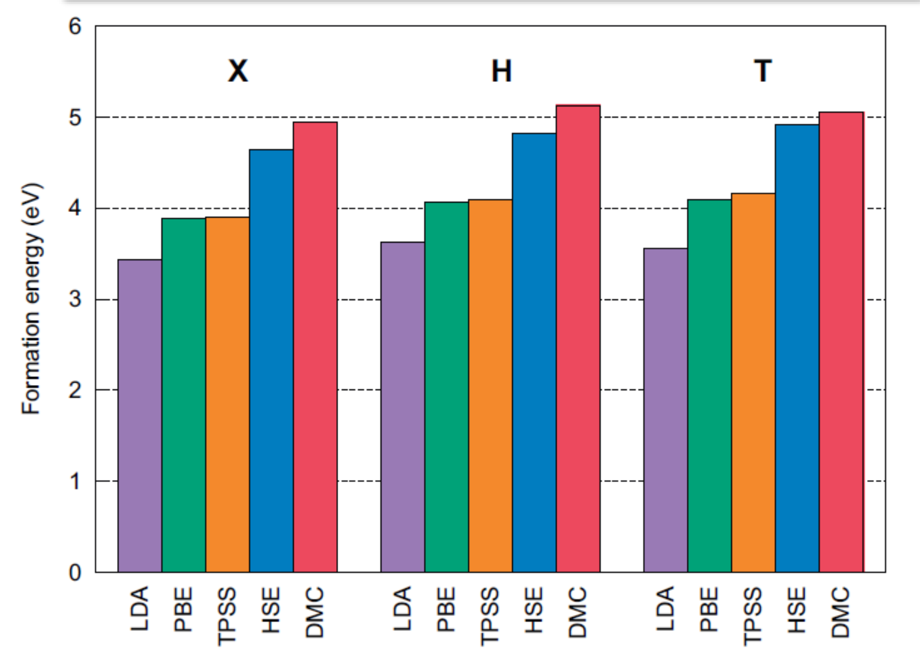
$$E_g = \lim_{\delta \to 0} \left\{ \left. \frac{\partial E(N)}{\partial N} \right|_{N+\delta} - \left. \frac{\partial E(N)}{\partial N} \right|_{N-\delta} \right\}$$

$$\boxed{E_{\mathrm{g}}^{\mathrm{HF}} > E_{\mathrm{g}}^{\mathrm{exp}}, \quad E_{\mathrm{g}}^{\mathrm{DFA}} < E_{\mathrm{g}}^{\mathrm{exp}}}$$

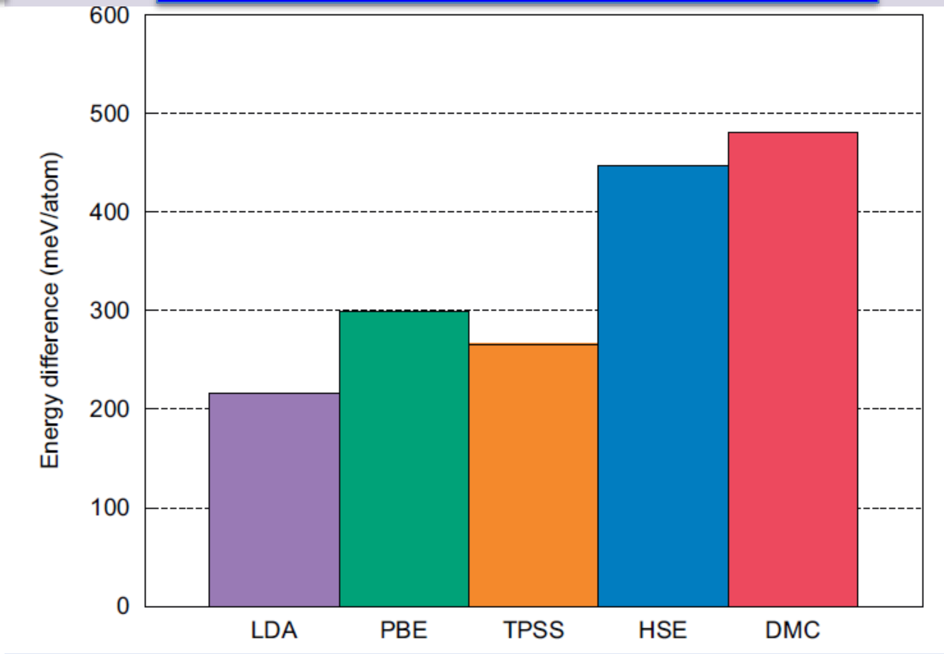
$$\Rightarrow \quad \boxed{E_{\mathrm{g}}^{\mathrm{hy}b} \approx E_{\mathrm{g}}^{\mathrm{exp}}}$$

Formation energy

Formation energies of different defects in Si



Energy difference of the diamond and β-tin phases of Si



DMC: diffusion Monte Carlo

*T. M. Henderson, J. Paier, G.E., Scuseria, Phys. Status. Solidi B **248**, 767 (2011)*

Outline

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- Implementation and computer codes

RPA as a first-principles method

- With the framework of adiabatic-connection fluctuation-dissipation (ACFD) theorem, RPA can be formulated as an approximate, but fully nonlocal exchange-correlation (XC) energy functional.

The XC energy

The density response function

$$E_{\mathrm{xc}} = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty d\omega \iint d\mathbf{r}d\mathbf{r}'\left[\chi_\lambda(\mathbf{r},\mathbf{r}',i\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]v(\mathbf{r},\mathbf{r}')$$

The coupling constant

Coulomb interaction

*Langreth & Perdew, Phys. Rev. B **15**, 2884 (1977).*
*Gunnarsson & Lundqvist, Phys. Rev. B **13**, 4274 (1976).*

$$\chi_\lambda(\mathbf{r},\mathbf{r}',t-t') = \delta n_\lambda(\mathbf{r},t)/\delta v_\lambda^{ext}(\mathbf{r}',t')$$

Dyson equation for the linear response function:

$$\chi_\lambda = \boxed{\chi_0} + \lambda\chi_0(v + f_{xc})\chi_\lambda\,, \qquad f_{xc} = 0 \rightarrow \chi_\lambda \approx \chi_\lambda^{\mathrm{RPA}}$$

Explicitly known in terms of KS (both occupied and virtual) orbitals and orbital energies

$$\Rightarrow \quad E_c^{\mathrm{RPA}} = E_c^{\mathrm{RPA}}[\epsilon_i, \psi_i]$$

RPA as a first-principles method

- With the framework of adiabatic-connection fluctuation-dissipation (ACFD) theorem, RPA can be formulated as an approximate, but fully nonlocal exchange-correlation (XC) energy functional.

The XC energy

The RPA density response function

$$E_{\mathrm{xc}}^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty d\omega \iint d\mathbf{r}\,d\mathbf{r}'\left[\chi_\lambda^{\mathrm{RPA}}(\mathbf{r},\mathbf{r}',i\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]v(\mathbf{r},\mathbf{r}')$$

The coupling constant

Coulomb interaction

Langreth & Perdew, Phys. Rev. B ***15****, 2884 (1977).*
Gunnarsson & Lundqvist, Phys. Rev. B ***13****, 4274 (1976).*

- First application to real molecules.

Furche, Phys. Rev. B ***64****, 195120 (2001).*
Fuchs & Gonze, Phys. Rev. B ***65*** *235109 (2002).*

- Applications to molecules, solids, surfaces, molecules on surfaces, and layered materials (2006-2012).

For a review, see *XR, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci.* ***47****, 7447 (2012)*

Why is RPA interesting for materials science?

- Automatic and seamless inclusion of van der Waals (vdW) interactions; non-additive, anisotropic, and many-body screening effects are properly accounted for.
- Compatible with exact exchange; exact exchange plus RPA correlation makes the self-interaction error insignificant.
- Different bonding (ionic, covalent, metallic, vdW) types are treated on an equal footing.
- Static correlation (partly) captured => Correct dissociation of H_2; excellent chemical reaction barrier heights

RPA calculations in practice (so far …)

In practical calculations, RPA is most often carried out as a single-point post-SCF approach, based on references from a preceding semi-local (or hybrid) calculation.

RPA correlation energy

$$E^{\mathrm{RPA}} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + E_c^{\mathrm{RPA}}[\epsilon_i, \psi_i]$$

Hartree-Fock energy
with (generalized) KS orbitals

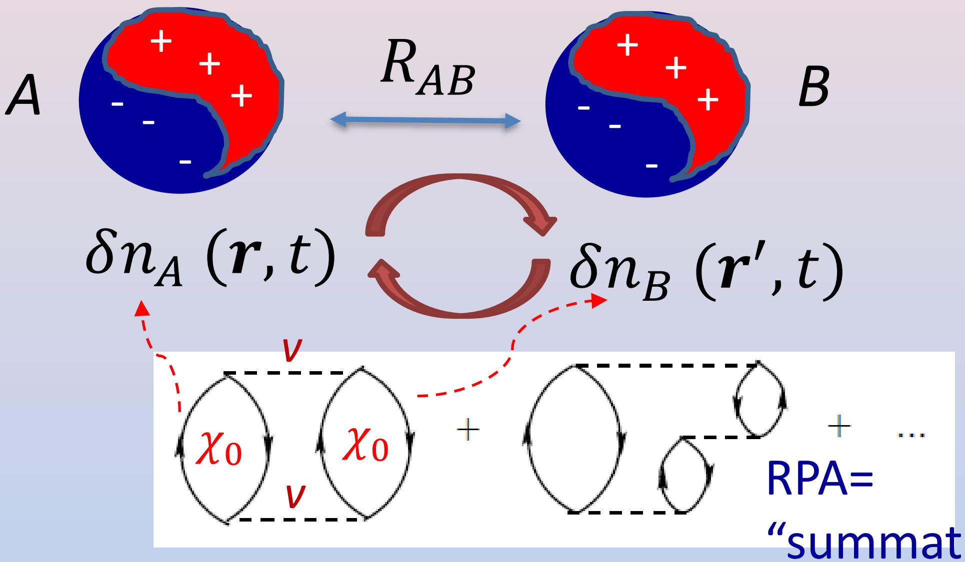
ϵ_i, ψ_i: (generalized) Kohn-Sham orbitals and orbital energies

Φ_0: Slater determinant formed with occupied ψ_i

Typical choices for reference: LDA, PBE, TPSS, PBE0, HSE

Consequently, RPA results show a slight dependence on the starting point, denoted e.g., by “RPA@PBE”.

RPA description of vdW interactions



RPA=
“summation of ring diagrams”

- RPA captures the non-local coupling between spontaneous quantum charge fluctuations separated in space.
- It can be shown analytically

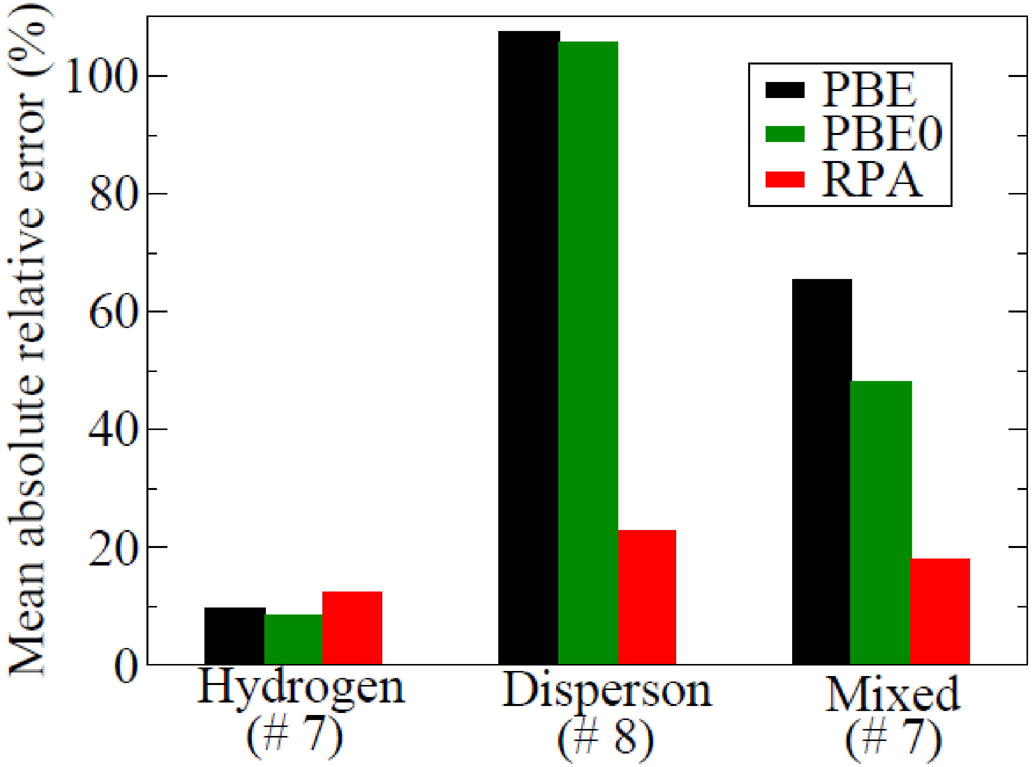
$$\Delta E_c^{\mathrm{RPA}} \rightarrow C_6^{\mathrm{RPA}}/R^6 \quad \text{for large } R \rightarrow \infty$$

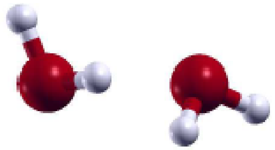
$$C_6^{RPA} = \frac{3}{\pi}\int d\omega\, \alpha_A^{RPA}(i\omega)\alpha_B^{RPA}(i\omega) \quad \text{“Dispersion consistent”}$$

J. Dobson, in “Topics in Condensed Matter Physics”, Ed. M. P. Das (Nova, New York, 1994)

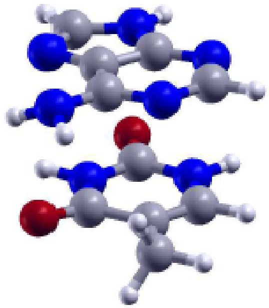
Y. Gao, W. Zhu, and XR, Phys. Rev. B. ***101****, 035113 (2020).*

RPA for the S22 test set

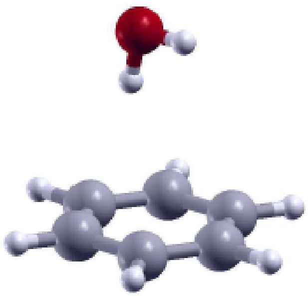




H_2O-H_2O



Adenine-Thymine

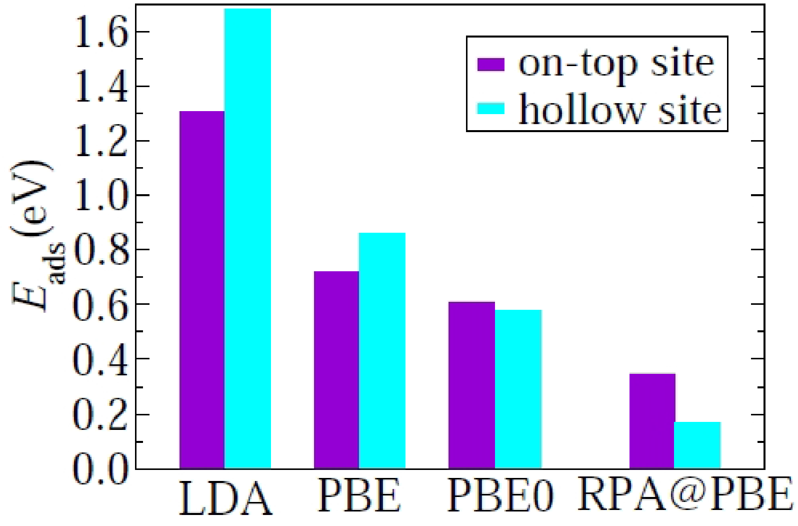


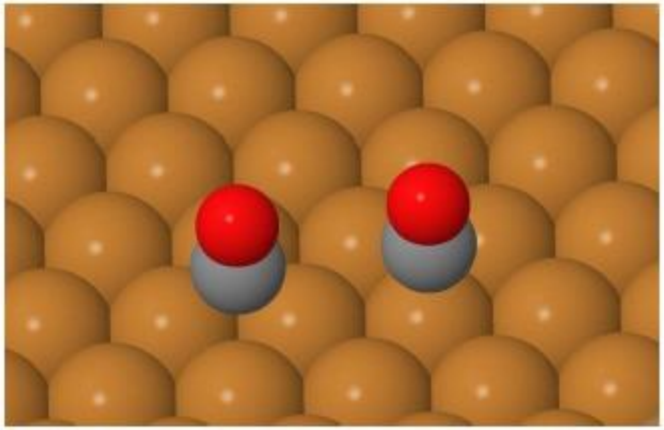
H_2O-C_6H_6

XR, A. Tkatchenko, P. Rinke, and M. Scheffler, Phys. Rev. Lett. 106, 153003 (2011)

S22 test set: P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

RPA applied to the “CO adsorption puzzle”





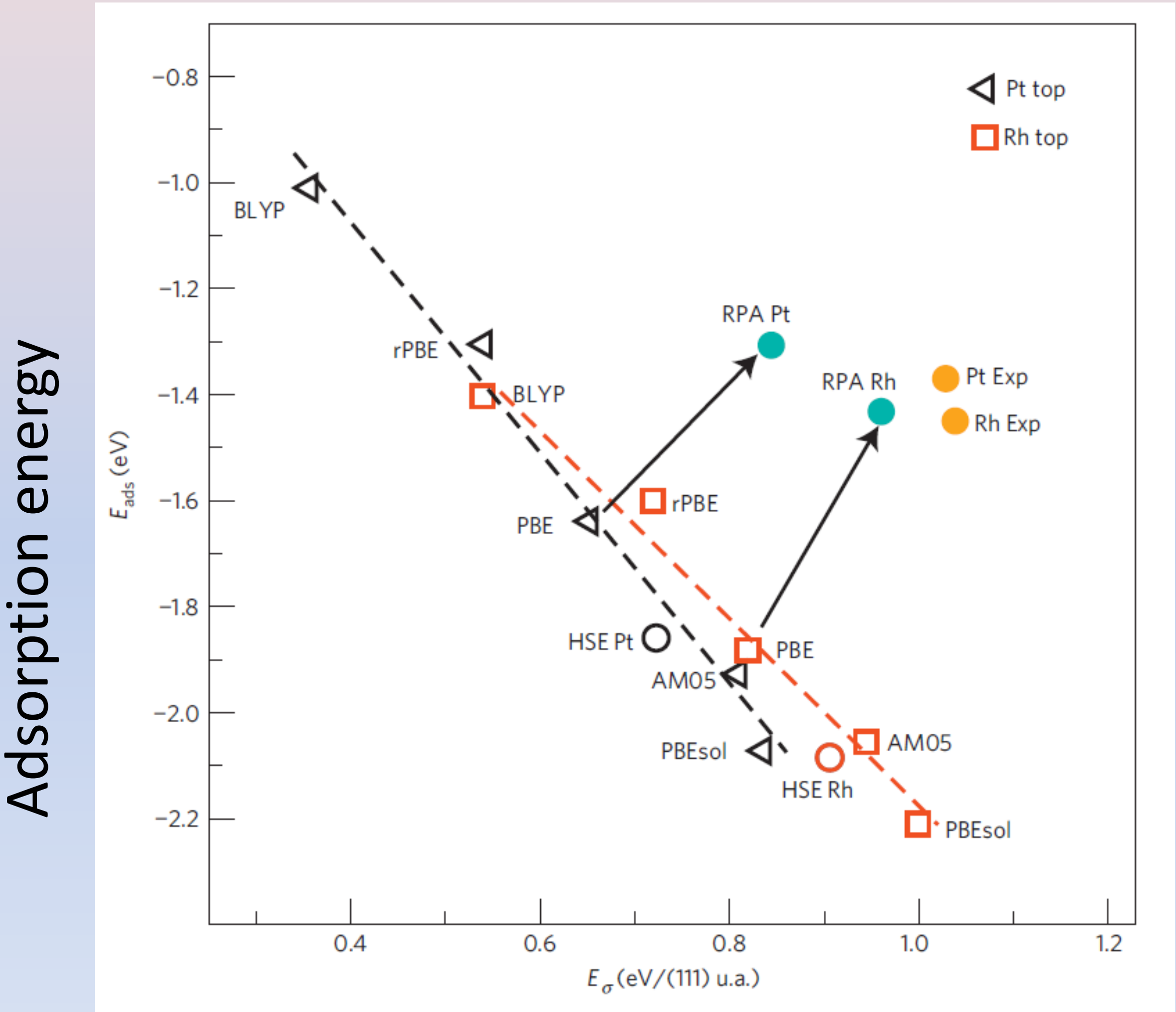
CO@Cu(111)

LDA/GGA => hollow site
Exp/RPA => on-top site

XR, P. Rinke, and M. Scheffler, Phys. Rev. B 80, 045402 (2009)

See also *L. Schimka et al., Nature Materials 9, 741 (2010).*

CO adsorption energy versus surface energy

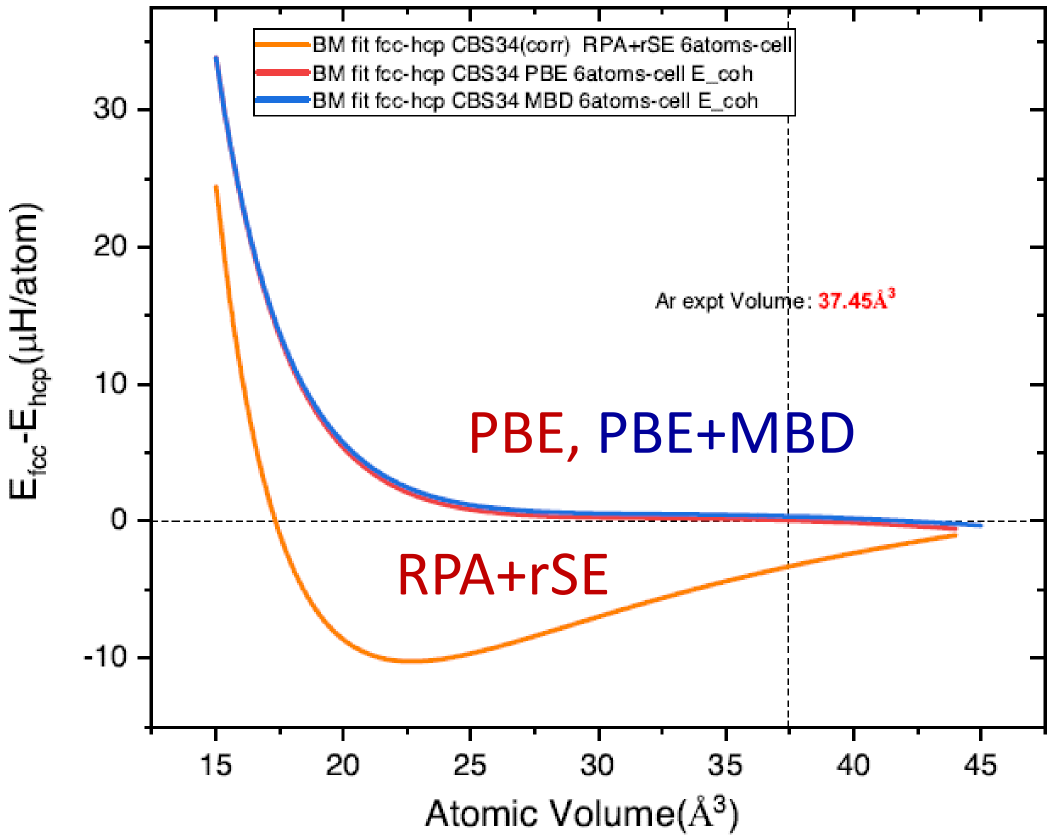


Surface energy

L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nature Materials ***9****, 741 (2010)*

Energy difference between fcc and hcp phases of Ar crystal

$$\Delta E = E_{fcc} - E_{hcp}$$



RPA+rSE (renormalized singles excitations) method:

X. Ren et al. Phys. Rev. Lett. *106, 153003 (2011)*

S. Yang & X. Ren, New J. Phys. ***24****, 033049 (2022)*

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Recent developments: local hybrids

- Local hybrids (LH): position-dependent admixture of HFX and semi-local exchange

$$E_{\mathrm{xc}}^{\mathrm{LH}} = \int d^3 r \left[\alpha(\mathbf{r}) \epsilon_x^{\mathrm{HF}}(\mathbf{r}) + \left(1 - \alpha(\mathbf{r})\right) \epsilon_x^{\mathrm{GGA}}(\mathbf{r}) \right] + E_c^{\mathrm{GGA}}$$

$$\alpha(\mathbf{r}) = \boldsymbol{c} \frac{\tau_W(\boldsymbol{r})}{\tau(\boldsymbol{r})}$$

$$\tau(\boldsymbol{r}) = \sum_n |\nabla \psi_n(\boldsymbol{r})|^2$$: kinetic energy density

$$\tau_W(\boldsymbol{r}) = \frac{|\nabla n(\boldsymbol{r})|^2}{8n(\boldsymbol{r})} = \begin{cases} 0, & \text{Constant density region} \\ \tau(\boldsymbol{r}) & \text{One-electron region} \end{cases}$$

System-dependent hybrid functionals

The mixing parameter α, and the screening parameter ω are related to the dielectric function of the system.

Dielectric (insulating) screening

$$W(\mathbf{r},\mathbf{r}') = \frac{1}{\varepsilon_M}\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

$$W(q) = \frac{v(q)}{\varepsilon(q)}$$

Metallic (Thomas-Fermi) screening

$$W(\mathbf{r},\mathbf{r}') = \frac{e^{-\lambda_{\mathrm{TF}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

$$\epsilon(q) = 1 + \left[(\epsilon_{\mathrm{M}}-1)^{-1} + \alpha\left(\frac{q}{q_{\mathrm{TF}}}\right)^2\right]^{-1}$$

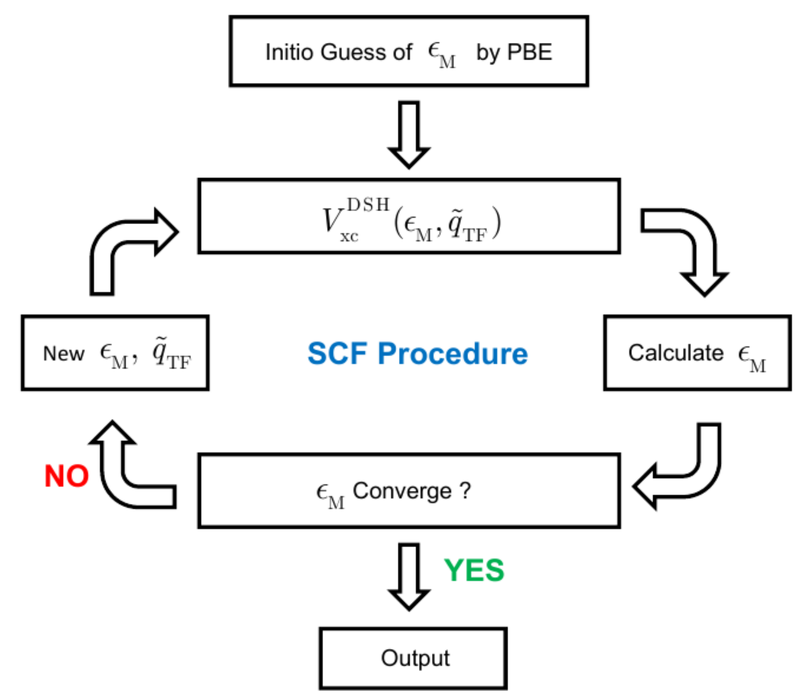
$$v_{\mathrm{sc}}(\mathbf{r},\mathbf{r}') \approx \frac{1}{\epsilon_{\mathrm{M}}}\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \left(1-\frac{1}{\epsilon_{\mathrm{M}}}\right)\frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

*Shimazaki, T.; Asai, Y. Chem. Phys. Lett. 2008, **466**, 91–94.*

Doubly screened hybrid (DSH) functional

$$v_{\mathrm{sc}}(\mathbf{r},\mathbf{r}') \approx \frac{1}{\epsilon_{\mathrm{M}}}\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \left(1-\frac{1}{\epsilon_{\mathrm{M}}}\right)\frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

$$V_{\mathrm{xc}}^{\mathrm{DSH}}(\mathbf{r},\mathbf{r}') = \frac{1}{\epsilon_{\mathrm{M}}}V_{\mathrm{x}}^{\mathrm{HF}}(\mathbf{r},\mathbf{r}') + \left(1-\frac{1}{\epsilon_{\mathrm{M}}}\right)V_{\mathrm{x}}^{\mathrm{HF,SR}}(\mathbf{r},\mathbf{r}';\mu) + \left(1-\frac{1}{\epsilon_{\mathrm{M}}}\right)V_{\mathrm{x}}^{\mathrm{PBE,LR}}(\mathbf{r};\mu) + V_{\mathrm{c}}^{\mathrm{PBE}}(\mathbf{r}).$$



Initio Guess of ϵ_{M} by PBE

$V_{\mathrm{xc}}^{\mathrm{DSH}}(\epsilon_{\mathrm{M}}, \tilde{q}_{\mathrm{TF}})$

Calculate ϵ_{M}

SCF Procedure

ϵ_{M} Converge ?

NO

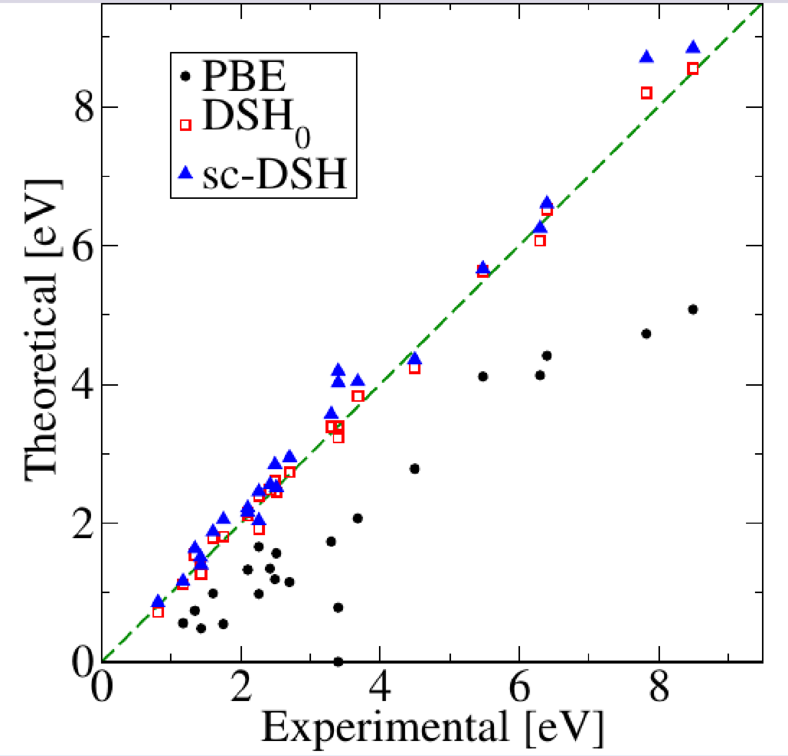
New ϵ_{M}, $\tilde{q}_{\mathrm{TF}}$

YES

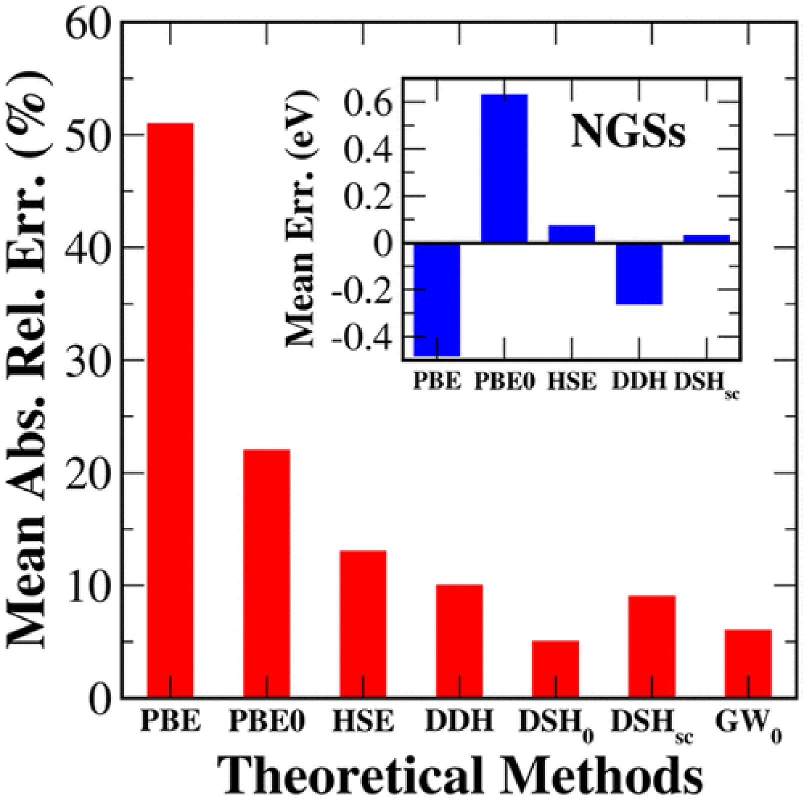
Output

Cui, Wang, Zhang, Xu, Hong Jiang,*
J. Phys. Chem. Lett. ***9****, 2338(2018)*

DSH: Performances



NGSs: narrow gap semiconductors



Cui, Wang, Zhang, Xu, Hong Jiang, J. Phys. Chem. Lett. ***9****, 2338 (2018)*

Doubly hybrid functionals

$$E_{xc} = \alpha E_x^{\mathrm{HF}} + (1-\alpha) E_x^{\mathrm{GGA}} + \beta E_c^{\mathrm{PT2}} + (1-\beta) E_c^{\mathrm{GGA}}$$

$$E_c^{\mathrm{PT2}} = \frac{1}{4} \sum_{p,q}^{occ} \sum_{r,s}^{unocc} \frac{|\langle pq|rs\rangle|^2}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s}$$

Second-order (non-local) correlation energy

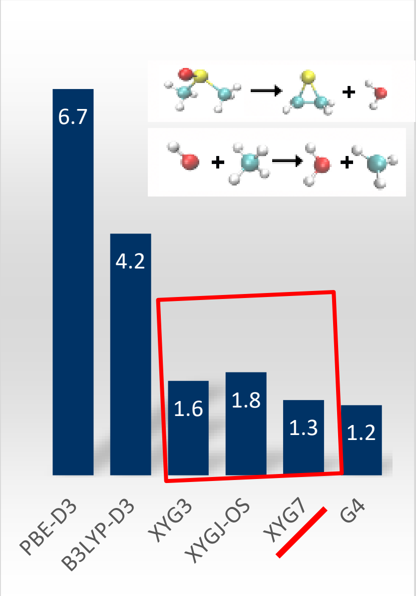
One successful functional: XYG3

$$E_{xc}^{\mathrm{XYG3}} = a_1 E_x^{\mathrm{HF}} + (1-a_1) E_x^{\mathrm{LDA}} + a_2 \left(E_x^{\mathrm{B88}} - E_x^{\mathrm{LDA}}\right) + a_3\, E_c^{\mathrm{PT2}} + (1-a_3) E_c^{\mathrm{GGA}}$$

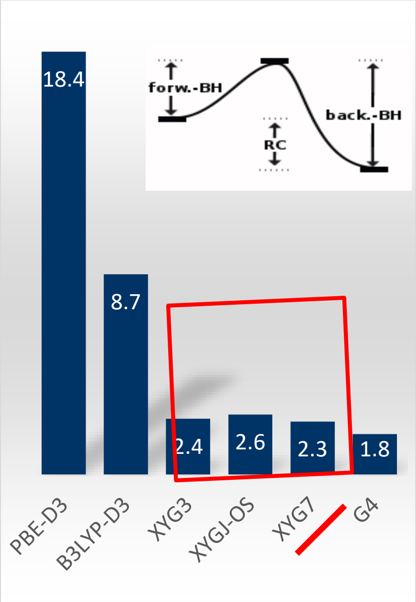
Y. Zhang, X. Xu, W. A. Goddard III, PNAS 106, 4963 (2009)

XYG7: the highest accuracy record of current density functional approximation

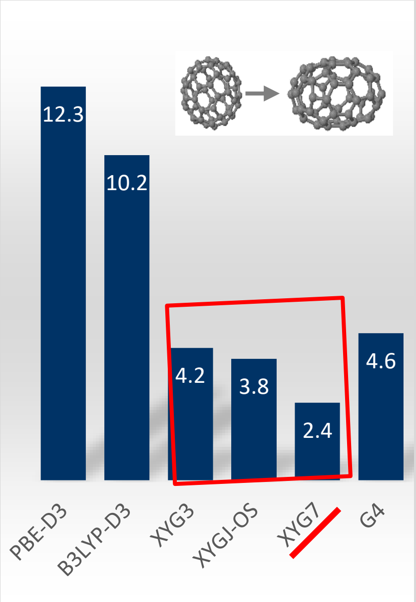
权重绝对平均偏差（kcal/mol）



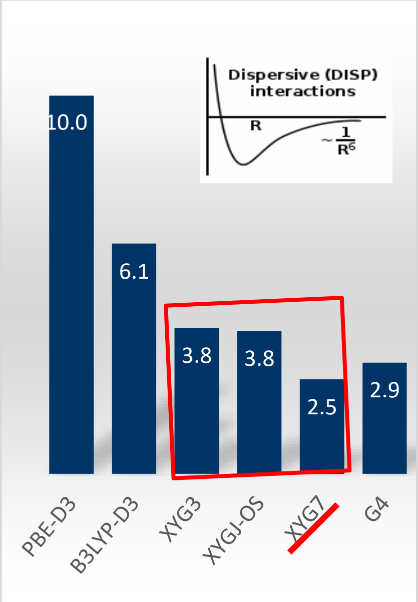
小分子体系
18测试集（473个反应能）



过渡态能垒
7测试集（194个能垒）



大分子体系
9测试集（304个反应能）

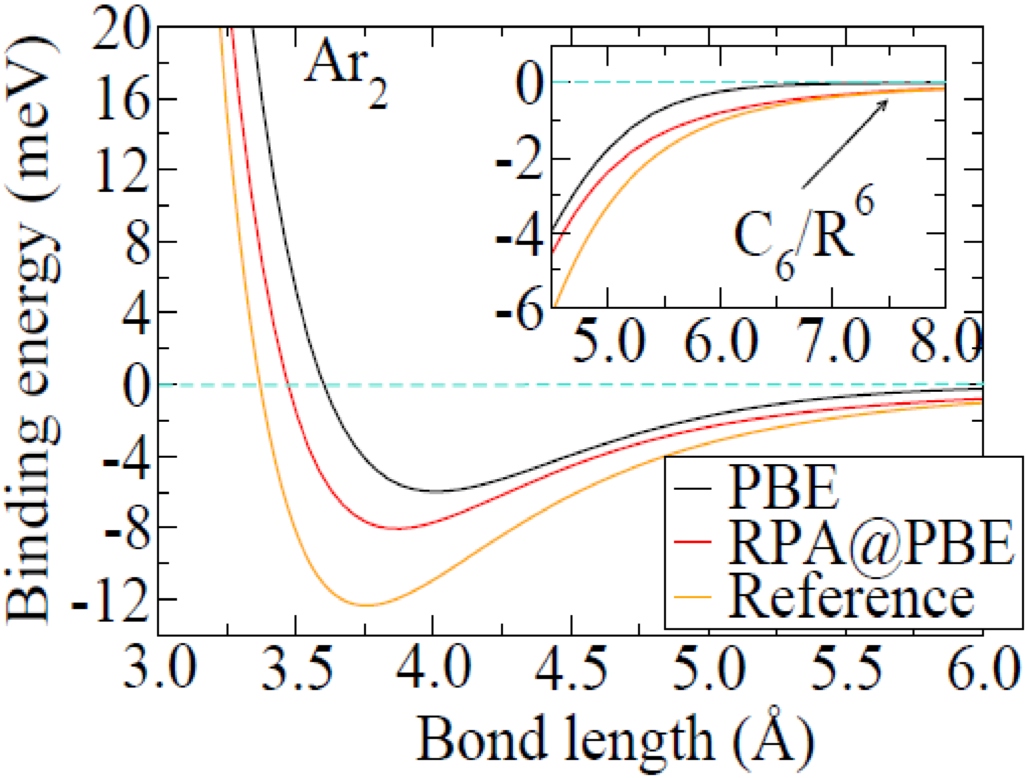


弱相互作用
21测试集（595个数据）

Accuracy significantly beyond B3LYP and PBE.

I.Y. Zhang and X. Xu* J. Phys. Chem. Lett. 12:2638 （2021）*

Problem of RPA for Ar_2



Reference: Tang and Toennies, J. Chem. Phys. **118**, 4976 (2003)

+ Correct asymptotic behavior, crucial for large molecules

– Underbinding around the equilibrium distance

The singles correction: A many-body perturbation analysis

$$\hat{H}^e = \hat{H}_0^{\mathrm{KS}} + \hat{H}_1, \quad \hat{H}_0^{\mathrm{KS}} = \sum_{k=1}^{N}\left(-\frac{\nabla_k^2}{2} + v_{\mathrm{ext}}(\boldsymbol{r}_k) + v_{\mathrm{Hxc}}(\boldsymbol{r}_k)\right), \qquad \hat{H}_0^{\mathrm{KS}}\left|\Phi_n\right\rangle = E_n^{(0)}\left|\Phi_n\right\rangle$$

$$E_0^{(0)} = \left\langle \Phi_0^{\mathrm{KS}} \middle| \hat{H}_0 \middle| \Phi_0^{\mathrm{KS}} \right\rangle, \quad E_0^{(1)} = \left\langle \Phi_0^{\mathrm{KS}} \middle| \hat{H}' \middle| \Phi_0^{\mathrm{KS}} \right\rangle,$$

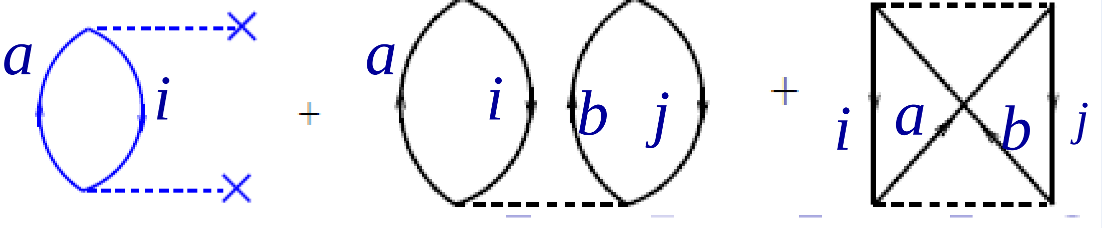
$$E_{\mathrm{KS}}^{\mathrm{EXX}} = E_0^{(0)} + E_0^{(1)}$$

Now

$$E_0^{(2)} = \sum_{i,a} \frac{\left|\left\langle \Phi_0^{\mathrm{KS}} \middle| H' \middle| \Phi_i^a \right\rangle\right|^2}{\varepsilon_i - \varepsilon_a} + \sum_{i,j,a,b} \frac{\left|\left\langle \Phi_0 \middle| H' \middle| \Phi_{i,j}^{a,b} \right\rangle\right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$\neq 0$

$$\left\langle i \,|\, v_{\mathrm{x}}^{\mathrm{HF}} - v_{\mathrm{xc}}^{\mathrm{KS}} \,|\, a \right\rangle$$



The computation of singles correction

Fock operator

$$E_{\mathrm{c}}^{\mathrm{SE}} = \sum_{i}^{occ} \sum_{a}^{unocc} \frac{\left| \left\langle \psi_i \mid \hat{f} \mid \psi_a \right\rangle \right|^2}{\varepsilon_i - \varepsilon_a} = \sum_{i}^{occ} \sum_{a}^{unocc} \frac{\left| \left\langle \psi_i \mid V_{\mathrm{x}}^{\mathrm{HF}} - V_{\mathrm{x}}^{\mathrm{KS}} \mid \psi_a \right\rangle \right|^2}{\varepsilon_i - \varepsilon_a}$$

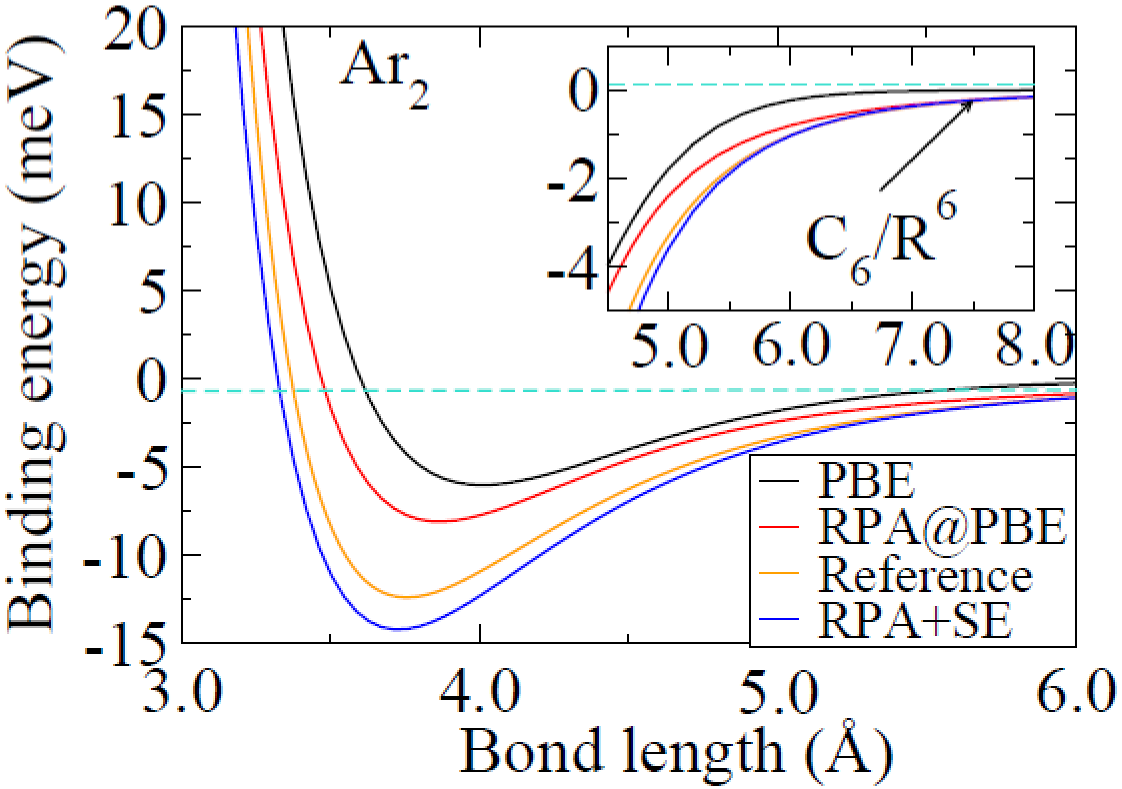
Kohn-Sham orbitals

- Originally derived within the framework of Rayleigh-Schrödinger perturbation theory

XR, A. Tkatchenko, P. Rinke, M. Scheffler, PRL 106, 153003 (2011)

- This term accounts for the fact that the orbitals used in RPA calculations are not “optimal”.

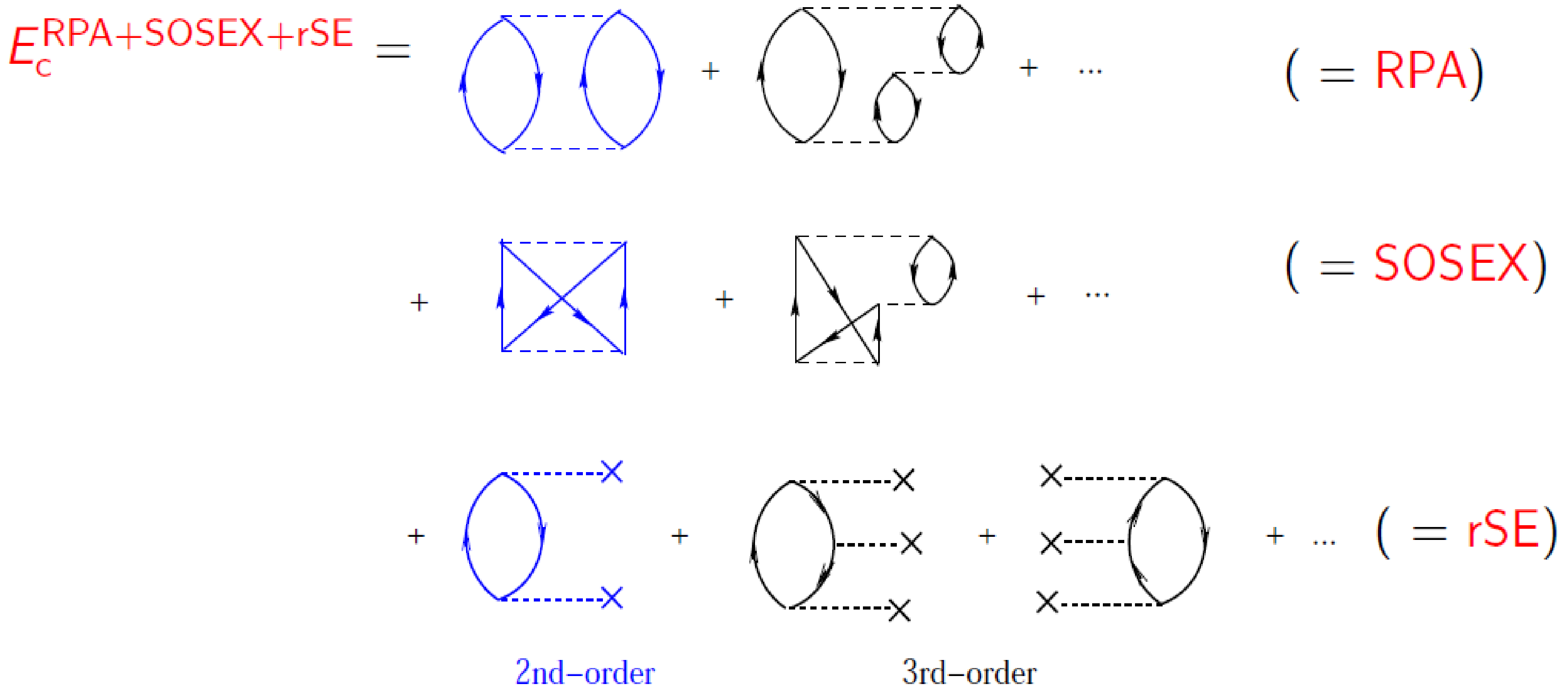
RPA+SE for Ar_2



Singles contributions correct the too strong Pauli repulsion arising from the too extended semi-local DFT charge density.

XR, A. Tkatchenko, P. Rinke, and M. Scheffler, Phys. Rev. Lett. ***106****, 153003 (2011).*

The concept of renormalized second-order perturbation theory (rPT2)



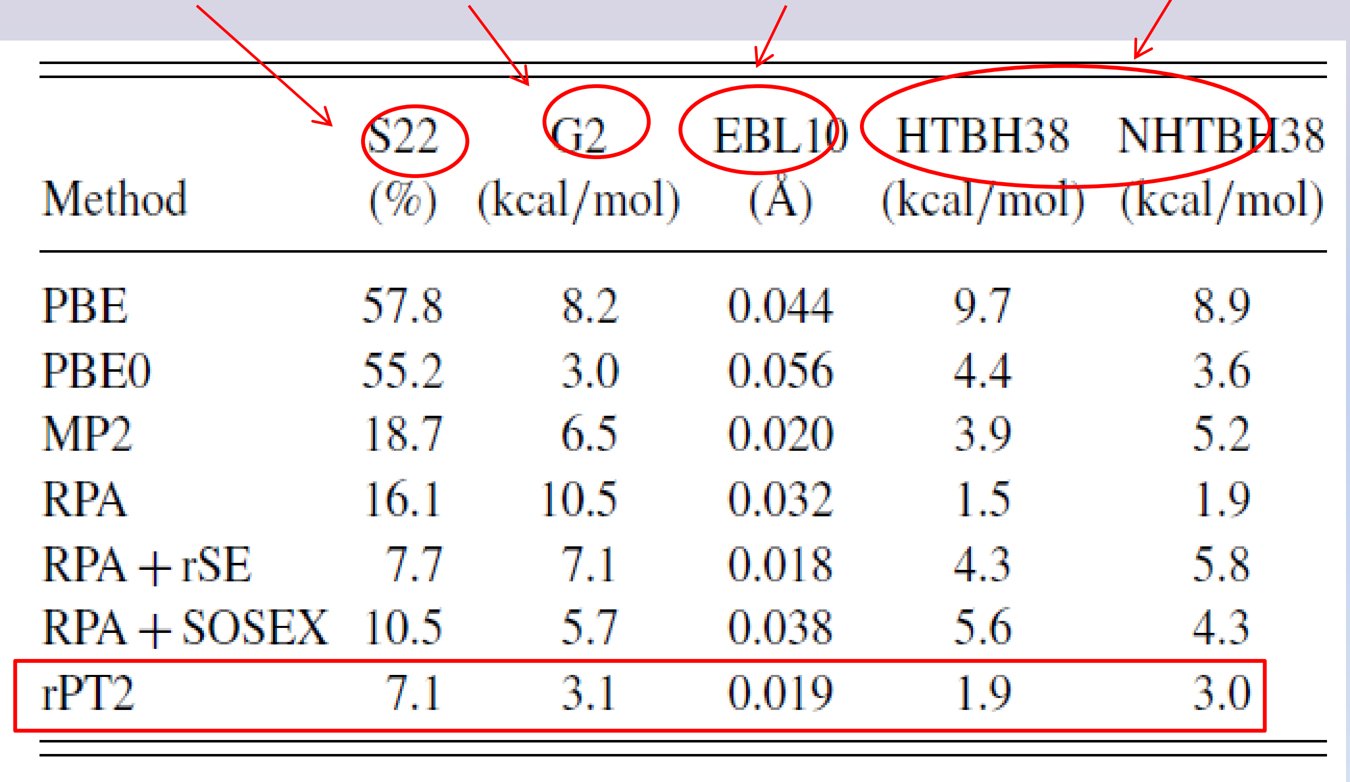
(PT2)

rPT2 = “RPA+SOSEX+rSE”

XR, P. Rinke, G.E. Scuseria, M. Scheffler, Phys Rev. B ***88****, 035120 (2013).*

The performance of rPT2

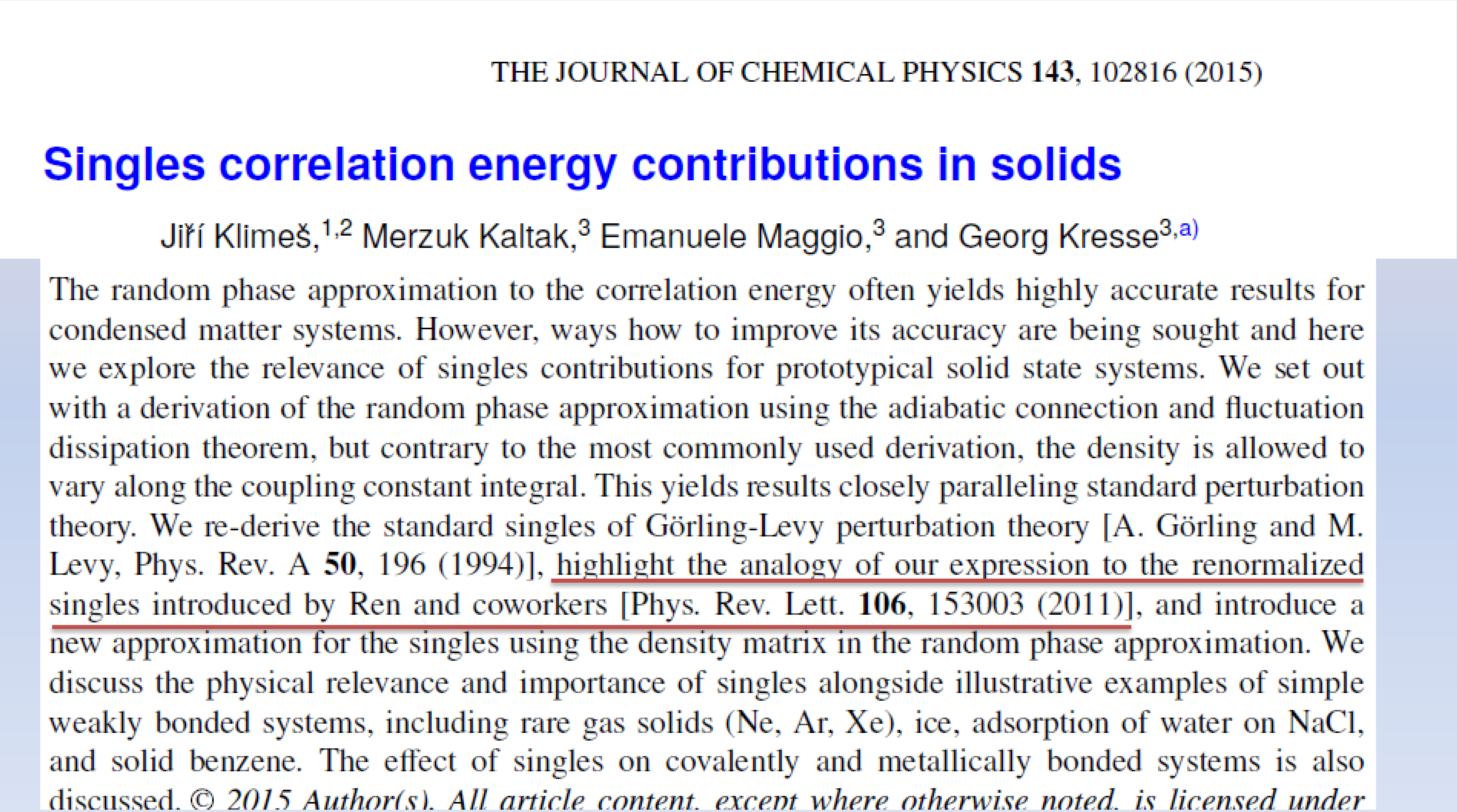
Van der Waals Cohesive energy Bond length Barrier heights



Method	S22 (%)	G2 (kcal/mol)	EBL10 (Å)	HTBH38 (kcal/mol)	NHTBH38 (kcal/mol)
PBE	57.8	8.2	0.044	9.7	8.9
PBE0	55.2	3.0	0.056	4.4	3.6
MP2	18.7	6.5	0.020	3.9	5.2
RPA	16.1	10.5	0.032	1.5	1.9
RPA + rSE	7.7	7.1	0.018	4.3	5.8
RPA + SOSEX	10.5	5.7	0.038	5.6	4.3
rPT2	7.1	3.1	0.019	1.9	3.0

rPT2: most balanced approach for atomization energy, van der Waals interaction, and chemical reaction barrier heights !

RPA + Singles for Solids



THE JOURNAL OF CHEMICAL PHYSICS **143**, 102816 (2015)

Singles correlation energy contributions in solids

Jiří Klimeš,[1,2] Merzuk Kaltak,[3] Emanuele Maggio,[3] and Georg Kresse[3,a)]

The random phase approximation to the correlation energy often yields highly accurate results for condensed matter systems. However, ways how to improve its accuracy are being sought and here we explore the relevance of singles contributions for prototypical solid state systems. We set out with a derivation of the random phase approximation using the adiabatic connection and fluctuation dissipation theorem, but contrary to the most commonly used derivation, the density is allowed to vary along the coupling constant integral. This yields results closely paralleling standard perturbation theory. We re-derive the standard singles of Görling-Levy perturbation theory [A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994)], highlight the analogy of our expression to the renormalized singles introduced by Ren and coworkers [Phys. Rev. Lett. **106**, 153003 (2011)], and introduce a new approximation for the singles using the density matrix in the random phase approximation. We discuss the physical relevance and importance of singles alongside illustrative examples of simple weakly bonded systems, including rare gas solids (Ne, Ar, Xe), ice, adsorption of water on NaCl, and solid benzene. The effect of singles on covalently and metallically bonded systems is also discussed. *© 2015 Author(s). All article content, except where otherwise noted, is licensed under*

rSE fixed the problem of RPA!

On-going community-wide activities

- Low-scaling $[\mathrm{O}(N^3 - N)]$ RPA algorithm and implementations

  -- Georg Kresse (VASP), up to 256 Si atoms
  -- Joerg Hutter (CP2K), up to 500 water molecules
  -- Rong Shi, Xinguo Ren etal (LibRPA), up to 1000 atoms for solids

- Analytical gradient of RPA energy, allowing for geometry determination

  -- Filipp Furche (Turbomole) for molecules
  -- Georg Kresse (VASP) for solids
  -- M. Tahir, X. Ren et al. (FHI-aims) for molecules, working towards for solids

- Self-consistent RPA within a generalized Kohn-Sham (GKS) framework

  -- Weitao Yang, optimizing the orbitals for RPA (similar to the Bruckner theory)
  -- Filipp Furche, GKS-RPA, defining a static "RPA Hamiltonian"

How to relax geometries with RPA?

The RPA forces:

(gradients of the RPA total energy with respect to the atomic displacement):

Energy: $E^{\mathrm{RPA}} = E^{\mathrm{DFA}} - E_{\mathrm{xc}}^{\mathrm{DFA}} + E_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{RPA}}$

Force: $\boldsymbol{F}_I^{\mathrm{RPA}} = -\frac{dE^{\mathrm{RPA}}}{d\boldsymbol{R}_I}$

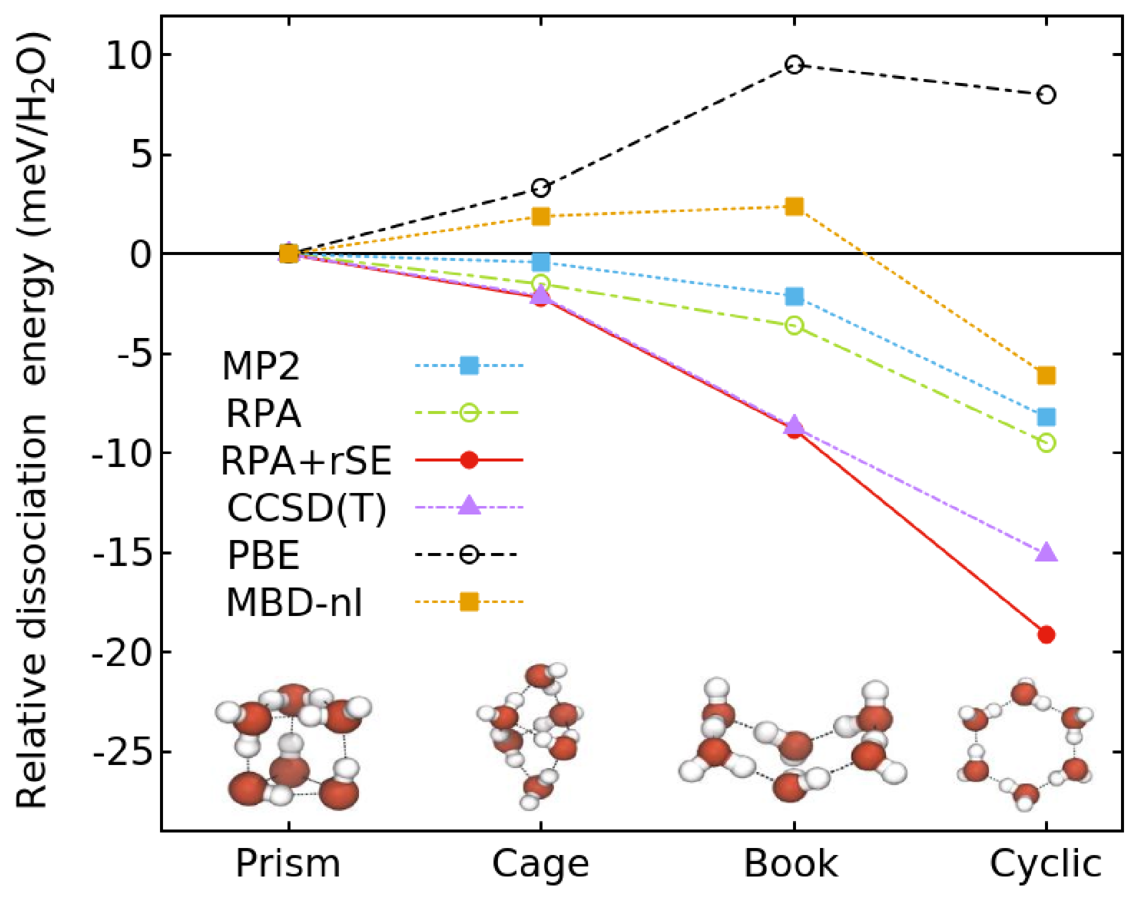
$$= -\frac{dE^{\mathrm{DFA}}}{d\boldsymbol{R}_I} + \frac{dE_{\mathrm{xc}}^{\mathrm{DFA}}}{d\boldsymbol{R}_I} - \frac{dE_{\mathrm{x}}^{\mathrm{HF}}}{d\boldsymbol{R}_I} - \frac{dE_{\mathrm{c}}^{\mathrm{RPA}}}{d\boldsymbol{R}_I}$$

Already available in the DFT code

Need to be evaluated in this work.

$$\frac{dE_{\mathrm{c}}^{\mathrm{RPA}}}{d\boldsymbol{R}_I} = \left\langle \frac{dE_c^{RPA}}{dC} \frac{dC}{dR_I} \right\rangle + \left\langle \frac{dE_c^{RPA}}{dV} \frac{dV}{dR_I} \right\rangle + \left\langle \frac{dE_{\mathrm{c}}^{\mathrm{RPA}}}{dc} \frac{dc}{d\boldsymbol{R}_I} \right\rangle + \left\langle \frac{dE_{\mathrm{c}}^{\mathrm{RPA}}}{d\epsilon} \frac{d\epsilon}{d\boldsymbol{R}_I} \right\rangle$$

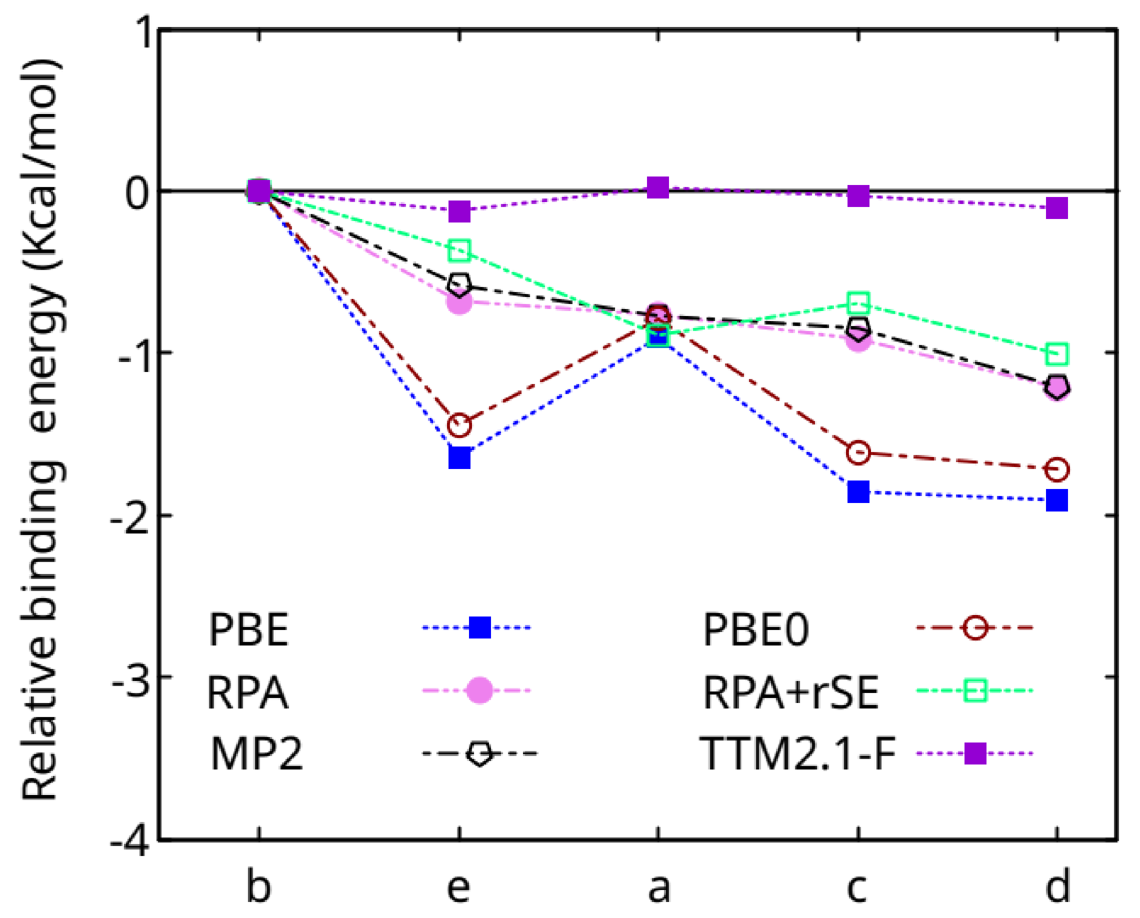
Energy hierarchy of water hexamers



M.N. Tahir, T. Zhu, H. Shang, J. Li, V. Blum, and X. Ren, J. Chem. Theory Comput. 18, 5297 (2022)

Energy hierarchy of $(H_2O)_{25}$

Energy ordering of five low-lying isomers of $(H_2O)_{25}$



M.N. Tahir, , H. Shang, J. Li, and X. Ren, submitted

Outline

- Background – basics of density functional theory
- The concept of hybridizing DFT and Hartree-Fock and the popular hybrid functionals
- Random phase approximation as a method to compute the ground-state total energy of interacting electron systems
- Recent progresses and perspectives
- Implementation and computer codes

Key component: the exact-exchange matrix

$$E_{xc}^{hyd}[\{\psi_n\}] = \alpha E_x^{\mathrm{HF}}[\{\psi_n\}] + (1-\alpha\,)E_x^{GGA}[n,\nabla n] + E_c^{GGA}[n,\nabla n]$$

$$E_x^{\mathrm{HF}}[\{\psi_n\}] = -\frac{1}{2}\sum_{m,n}^{occ.}\iint d\boldsymbol{r}d\boldsymbol{r}'\,\frac{\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$\psi_n(\boldsymbol{r}) = \sum_i \varphi_i(\boldsymbol{r})c_{in}$$

$$\Sigma_{ij}^x = -\sum_n^{occ.}\iint d\boldsymbol{r}d\boldsymbol{r}'\,\frac{\varphi_i(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$E_x^{\mathrm{HF}}[\{\psi_n\}] = \frac{1}{2}\sum_{i,j}\Sigma_{ij}^x D_{ij}^*$$

$$D_{ij} = \sum_n^{occ} c_{in}c_{jn}^*$$ (Density matrix)

Construction of the exact-exchange matrix

$$\Sigma_{ij}^{x} = -\sum_{n}^{occ.} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{\varphi_i(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

- Plane wave basis set

$$\varphi_i(\boldsymbol{r}) \rightarrow \frac{1}{\sqrt{\Omega}} e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}} \qquad \psi_n(\boldsymbol{r}) \rightarrow \psi_{n\boldsymbol{q}}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} c_{n,q}(\boldsymbol{G})\, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

$$\Sigma_{ij}^{x} \rightarrow \Sigma_{\boldsymbol{k}}^{x}(\boldsymbol{G},\boldsymbol{G}') = -\frac{1}{N_{\boldsymbol{q}}} \sum_{n,\boldsymbol{q}}^{occ} \sum_{G''} \frac{c_{\boldsymbol{n},\boldsymbol{q}}(\boldsymbol{G}-\boldsymbol{G}'')c_{\boldsymbol{n},\boldsymbol{q}}^{*}(\boldsymbol{G}'-\boldsymbol{G}'')}{|\boldsymbol{k}-\boldsymbol{q}-\boldsymbol{G}''|}$$

- Atomic-orbital basis set

$$\Sigma_{ij}^{x}[D] = -\sum_{k.l} D_{kl} \iint d\boldsymbol{r} d\boldsymbol{r}' \underbrace{\frac{\varphi_i(\boldsymbol{r})\varphi_k(\boldsymbol{r})\varphi_l(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}}_{\text{Two-electron Coulomb integrals}}$$

Compute codes that support hybrid functional calculations

- Plane wave codes:

VASP

QUANTUMESPRESSO

PWMAT

- Gaussian orbital codes:

CRYSTAL17 (Crystal)

CP2K

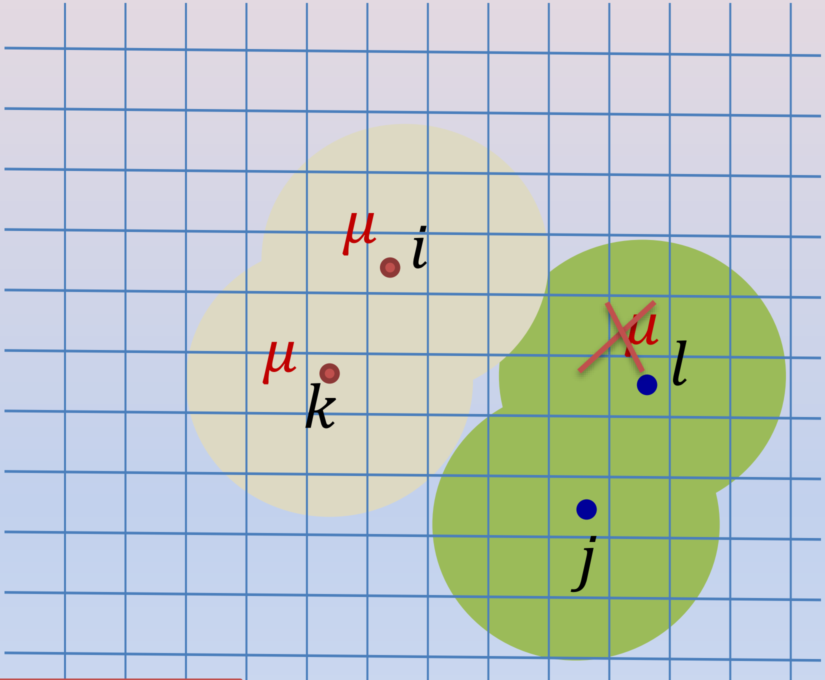
- Numerical atomic orbital (NAO) codes

FHI aims
The ab initio molecular simulations package
(FHI-aims)

ABACUS

Localized resolution of identity (LRI)

$$(ik|lj) = \iint d\boldsymbol{r}d\boldsymbol{r}'\,\frac{\varphi_i(\boldsymbol{r})\varphi_k(\boldsymbol{r})\varphi_l(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



Challenge: Too many 4-center integrals to compute and store

- Localized resolution of identity technique

$$\varphi_i(\boldsymbol{r})\varphi_k(\boldsymbol{r}) \approx \sum_{\mu\in I,K} C_{ik}^{\mu}\, P_{\mu}(\boldsymbol{r})$$

Auxiliary basis function

$$(ik|lj) = \sum_{\mu\in I,K}\sum_{\upsilon\in J,L} C_{ik}^{\mu} V_{\mu\nu} C_{lj}^{\nu}$$

$$V_{\mu\nu} = \iint d\boldsymbol{r}d\boldsymbol{r}'\,\frac{P_{\mu}(\boldsymbol{r})P_{\nu}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

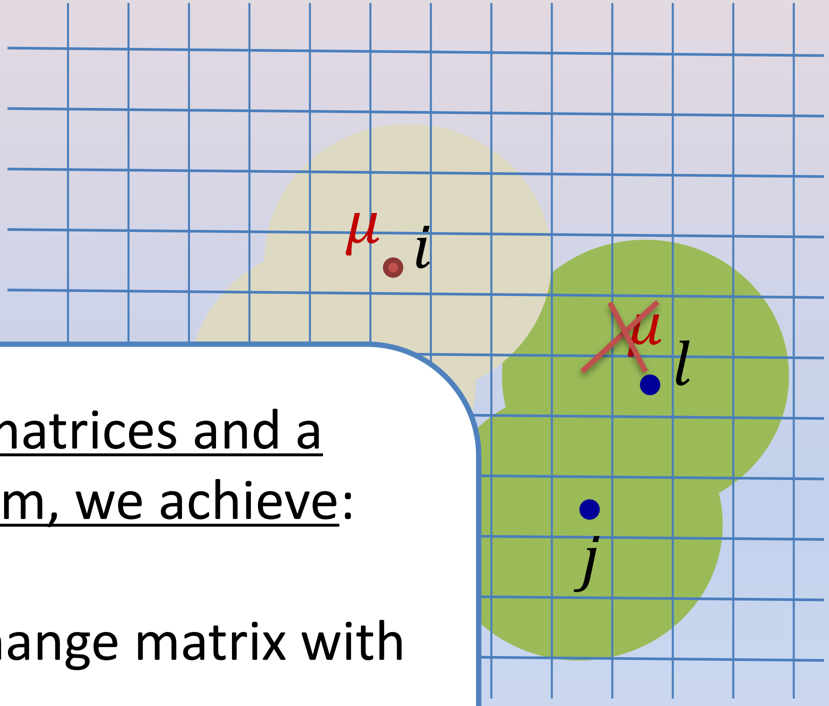
Target: Compute the HF exchange matrix:

$$\Sigma_{ij}^{x}[D] = \sum_{kl}\sum_{\mu\in I,K}\sum_{\upsilon\in J,L} C_{ik}^{\mu} V_{\mu\nu} C_{lj}^{\nu}\, D_{kl}$$

Localized resolution of identity (LRI)

$$(ik|lj) = \iint d\boldsymbol{r}d\boldsymbol{r}' \frac{\varphi_i(\boldsymbol{r})\varphi_k(\boldsymbol{r})\varphi_l(\boldsymbol{r}')\varphi_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Challenge: Too many 4-center integrals to compute and store



By exploiting the sparsity of C, V, D matrices and a careful design of the parallel algorithm, we achieve:

- Linear scaling build of the HF exchange matrix with respect to the system size
- Nearly perfect scalability up to 1000 CPU cores
- No more expensive than GGA calculations for system size with 1000 atoms or larger

$$V_{\mu\nu} = \iint d\boldsymbol{r}d\boldsymbol{r}' \frac{P_\mu(\boldsymbol{r})P_\nu(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

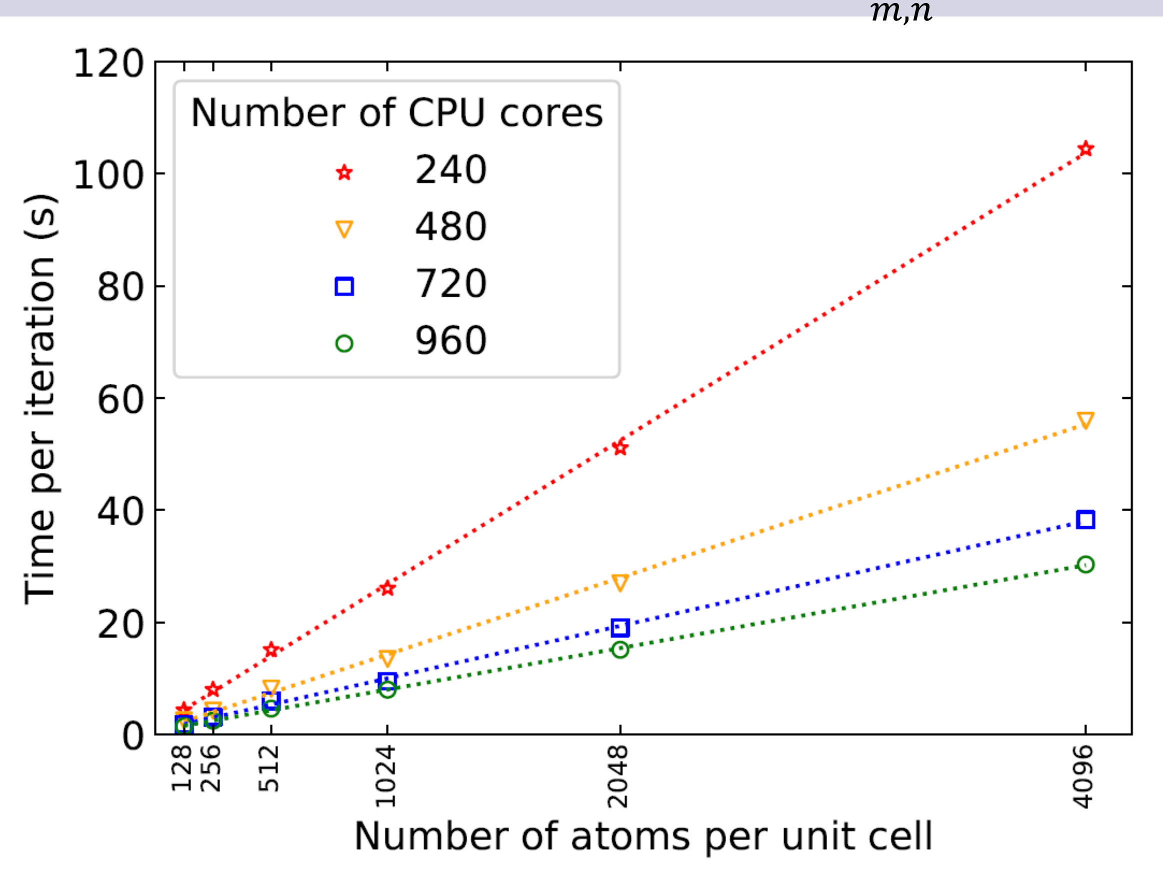
exchange matrix:

$$\Sigma_{ij}[D] = \sum_{kl} \sum_{\mu\in I,K} \sum_{\nu\in J,L} C_{ik}^{\mu} V_{\mu\nu} C_{lj}^{\nu} D_{kl}$$

Linear-scaling hybrid functional implementation (@ABACUS)

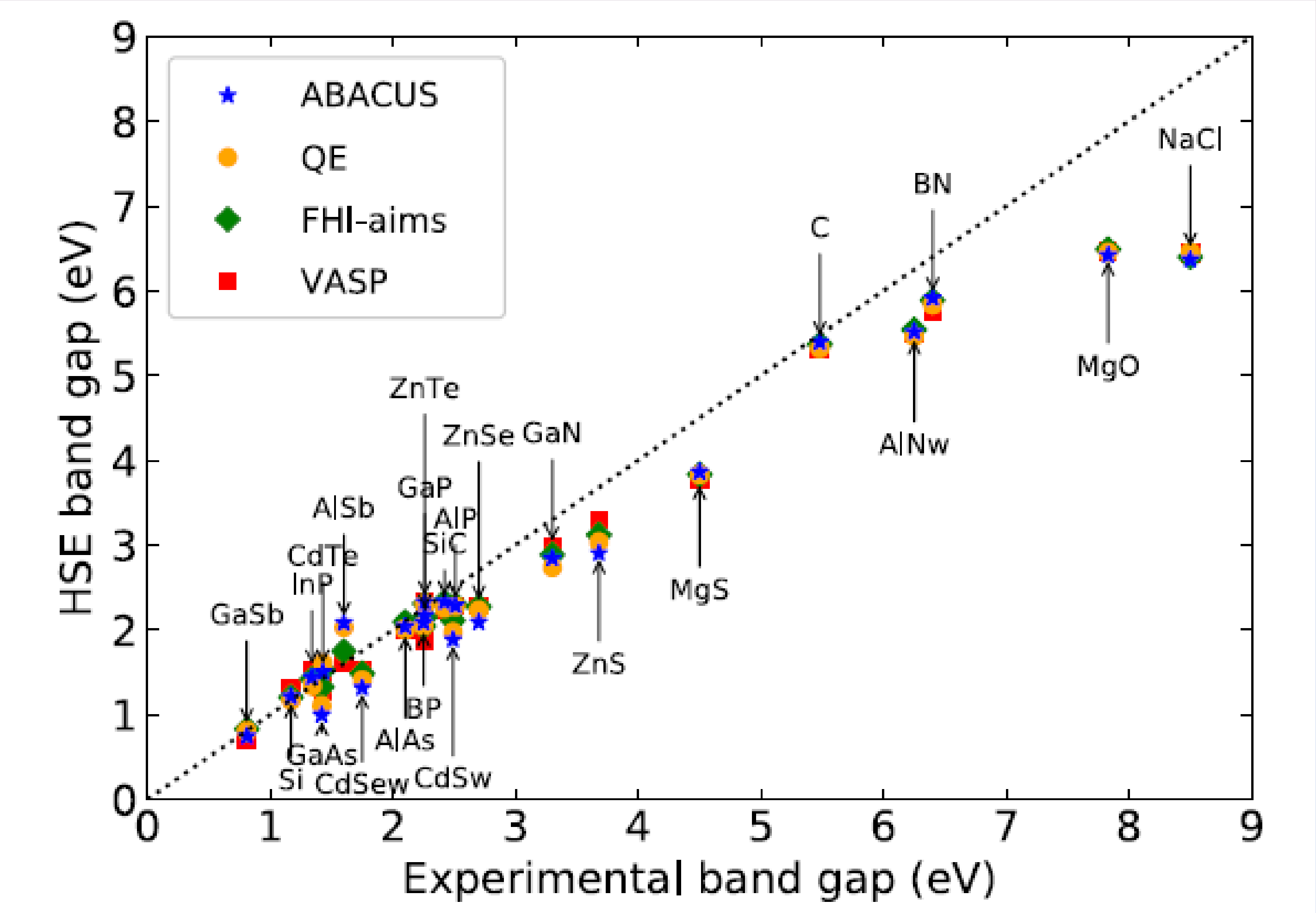
Time of Fock build per iteration

$$E_x^{\mathrm{HF}}[\psi] = \frac{1}{2}\sum_{m,n}^{occ.}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\psi_m(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



P. Lin, X. Ren, L. He, J. Chem. Theory Comput. ***17****, 222 (2021)*

Accuracy of the HSE hybrid functional implemented in ABACUS



P. Lin, X. Ren, L. He, J. Phys. Chem. Lett., ***11****, 3082 (2020).*

Released in ABACUS 3.0.

Real-space implementation of RPA

(1) Preparation

Atom-centered auxiliary basis functions

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\tau) = -iG^0(\boldsymbol{r},\boldsymbol{r}',i\tau)G^0(\boldsymbol{r}',\boldsymbol{r},-i\tau)$$

$$= \sum_{\boldsymbol{R}}\sum_{\mu,\nu} P_\mu(\boldsymbol{r}-\boldsymbol{\tau}_\mu)\chi^0_{\mu\nu}(\boldsymbol{R},i\tau)P_\nu(\boldsymbol{r}'-\boldsymbol{R}-\boldsymbol{\tau}_\nu)$$

$$G^0(\boldsymbol{r},\boldsymbol{r}',i\tau) = \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,i,j} \varphi_i(\boldsymbol{r}-\boldsymbol{R}_1-\boldsymbol{\tau}_i)\,G^0_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1,i\tau)\varphi_j(\boldsymbol{r}'-\boldsymbol{R}_2-\boldsymbol{\tau}_j)$$

$$\varphi_i(\boldsymbol{r}-\boldsymbol{R}_1-\boldsymbol{\tau}_i)\varphi_j(\boldsymbol{r}-\boldsymbol{R}_2-\boldsymbol{\tau}_j) = \sum_{\boldsymbol{R},\mu} C^{\mu\boldsymbol{R}}_{i\boldsymbol{R}_1,j\boldsymbol{R}_2} P_\mu(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{\tau}_\mu)$$

$$C^{\mu\boldsymbol{R}}_{i\boldsymbol{R}_1,j\boldsymbol{R}_2} = C^{\mu\boldsymbol{0}}_{i\boldsymbol{R}_1-\boldsymbol{R},j\boldsymbol{R}_2-\boldsymbol{R}}$$

highly sparse under LRI

(2) Constructing the response function matrix

$$\chi^0_{\mu\nu}(\boldsymbol{R},i\tau) = -i\sum_{i,j,k,l}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3,\boldsymbol{R}_4} C^{\mu\boldsymbol{0}}_{i\boldsymbol{R}_1,j\boldsymbol{R}_3} G^0_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1,i\tau)G^0_{lk}(\boldsymbol{R}_3-\boldsymbol{R}_4,-i\tau)C^{\boldsymbol{\nu}\boldsymbol{0}}_{j(\boldsymbol{R}_2-\boldsymbol{R}),l(\boldsymbol{R}_4-\boldsymbol{R})}$$

Computational cost:

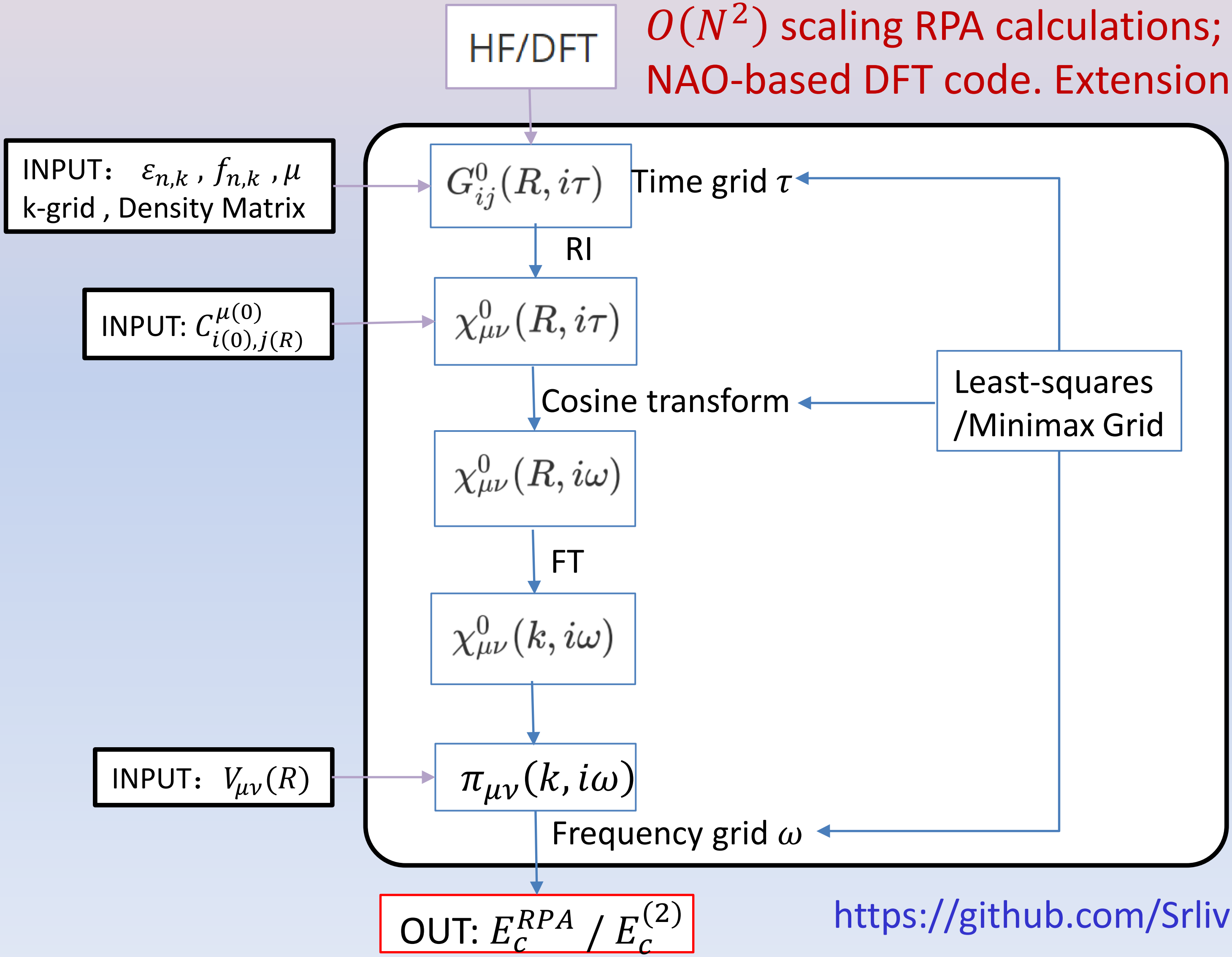
$O(N^2_{basis}N_{\boldsymbol{k}})$ with a large prefactor

(3) Fourier transform to $(\boldsymbol{q},i\omega)$ domain

$$\chi^0_{\mu\nu}(\boldsymbol{R},i\tau) \xrightarrow{\text{FT}} \chi^0_{\mu\nu}(\boldsymbol{q},i\omega)$$

LibRPA: A stand-alone library for low-scaling RPA & *GW* calculations

$O(N^2)$ scaling RPA calculations; interfaced with NAO-based DFT code. Extension to *GW* is ongoing.



HF/DFT

INPUT: $\varepsilon_{n,k}$, $f_{n,k}$, μ
k-grid , Density Matrix

INPUT: $C^{\mu(0)}_{i(0),j(R)}$

INPUT: $V_{\mu\nu}(R)$

$G^0_{ij}(R, i\tau)$

Time grid τ

RI

$\chi^0_{\mu\nu}(R, i\tau)$

Cosine transform

Least-squares /Minimax Grid

$\chi^0_{\mu\nu}(R, i\omega)$

FT

$\chi^0_{\mu\nu}(k, i\omega)$

$\pi_{\mu\nu}(k, i\omega)$

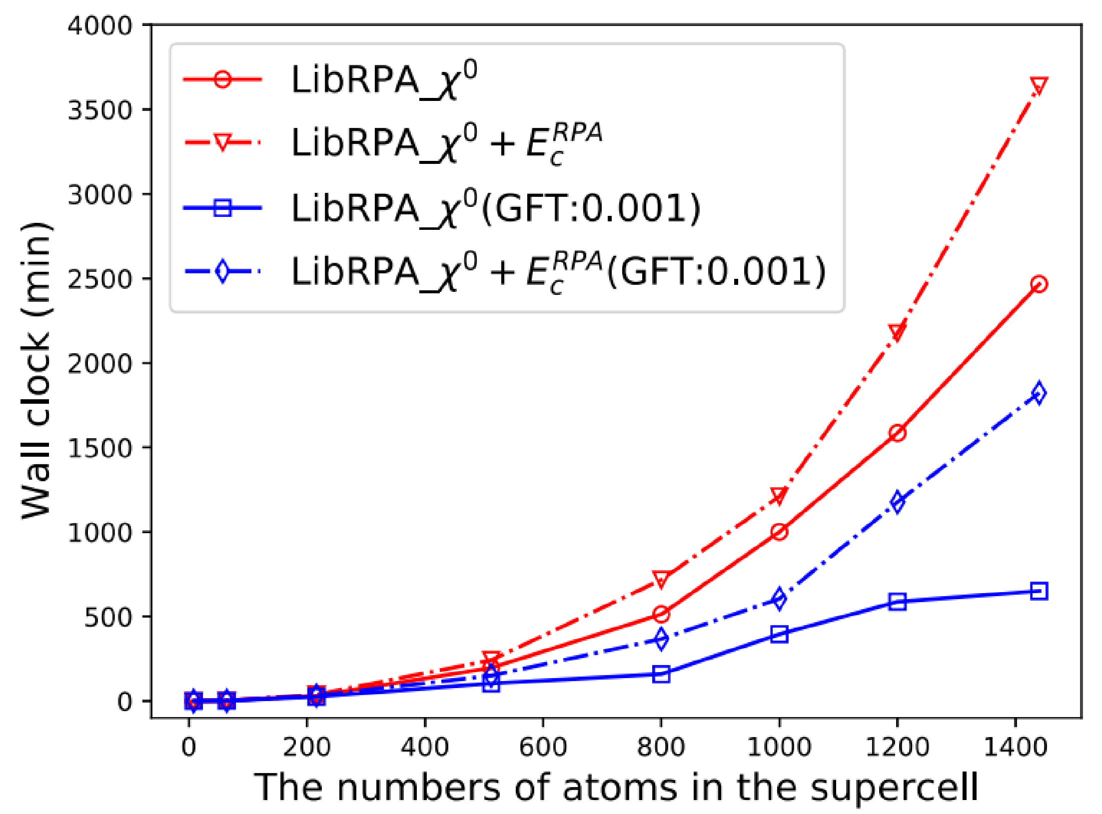
Frequency grid ω

OUT: E_c^{RPA} / $E_c^{(2)}$

https://github.com/Srlive1201/LibRPA

Scaling behavior of real-space RPA implementation

ABACUS+LibRPA: C diamond with increasing supercell size



R. Shi, P. Lin, M. Zhang, L. He, and X. Ren, Phys. Rev. B ***109****, 035103 (2024).*

Summary

Hybrid functionals

- Hybrid functionals deliver accuracy that is systematically better than GGAs (better band gaps, structure and energetics).

- Typically one or two orders of magnitude more expensive than local/semi-local functionals; for large systems (>1000 atoms), the difference in cost gets small.

RPA

- With rapid advance of new concepts and algorithms, RPA-based methods can be developed into a viable approach that bridges the conventional DFT and quantum-chemistry methods

- Routinely tackle system size of a few hundred atoms

- Provide unprecedented accuracy for computational materials science