Hybrid Functionals, van der Waals Corrections and ASE Interface to CP2K

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Part I: Hybrid Functionals

What are hybrid functionals?

$$E_{xc}[\rho] = \alpha E_x^{HFX}[\{\psi_i\}] + (1 - \alpha)E_x^{DFT}[\rho] + E_c^{DFT}[\rho]$$

Hybrid functionals:

mixing non-local Hartree-Fock exchange with local/semi-local DFT/GGA exchange

Why do we need hybrid DFT?

- Improved description of the thermochemistry (e.g. atomisation energy, heats of formation, etc) of molecular systems

- Improved description of the lattice constants, surface energies, ionisation potentials and band gaps of semiconductors and insulators

Why do we need hybrid DFT?

	Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
SVWN [a]	121.2	39.6	229	94
LSD(SVWN5)	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP [a]	7.1	4.7	28	15
VSXC [b]	2.7	2.5	12	8
B3LYP [a]	3.1	2.4	20	10
PBE1PBE/PBE0	4.8	3.5	24	10

Mean absolute errors (Mae) for atomisation energies (kcal/mol)

Why do we need hybrid DFT?

Solid	LSDA	PBE	TPSS	HSE
ME[a]	−1.14	−1.13	−0.98	−0.17
MAE[b]	1.14	1.13	0.98	0.26
rms[c]	1.24	1.25	1.12	0.34
Max (+)[d]	⋯	⋯	⋯	0.32
Max (−)[e]	−2.30	−2.88	−2.66	−0.72

Band gap error (eV) statistics for the SC/40 test set

Scuseria et al., J. Chem. Phys., 123, 174101 (2005)

Hybrid DFT Calculations with CP2K

- Total energy as a functional of the electron density

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\, \rho(\mathbf{r})\, \mathrm{d}\mathbf{r}$$

- Exchange-correlation energy with a hybrid functional

$$E_{xc}[\rho] = \alpha E_x^{HFX}[\{\psi_i\}] + (1 - \alpha)E_x^{DFT}[\rho] + E_c^{DFT}[\rho]$$

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Hybrid DFT Calculations with CP2K

- Hartree-Fock exchange energy

$$E_{\text{x}}^{\text{HFX}}[P] = -\frac{1}{2} \sum_{\lambda\sigma\mu\nu} P^{\mu\sigma} P^{\nu\lambda} (\mu\nu|\lambda\sigma)$$

$$P^{\mu\nu} = \sum_i C^{\mu i} C^{\nu i} \Leftrightarrow P = CC^T$$

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r}_1)\,\phi_\nu(\mathbf{r}_1)\,g(|\mathbf{r}_2 - \mathbf{r}_1|)\,\phi_\lambda(\mathbf{r}_2)\,\phi_\sigma(\mathbf{r}_2)\,d\mathbf{r}_1\mathbf{r}_2$$

Four-centre two-electron integrals (ERIs): $O(N^4)$ scaling

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Interaction potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r}_1)\,\phi_\nu(\mathbf{r}_1)\,\boxed{g(|\mathbf{r}_2 - \mathbf{r}_1|)}\,\phi_\lambda(\mathbf{r}_2)\,\phi_\sigma(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\mathbf{r}_2$$

- Standard Coulomb potential

$$g(r) = \frac{1}{r}$$

(used in B3LYP, PBE0, etc)

(see POTENTIAL_TYPE keyword in &INTERACTION_POTENTIAL subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

Interaction potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r}_1)\,\phi_\nu(\mathbf{r}_1)\,\boxed{g(|\mathbf{r}_2 - \mathbf{r}_1|)}\,\phi_\lambda(\mathbf{r}_2)\,\phi_\sigma(\mathbf{r}_2)\,d\mathbf{r}_1\mathbf{r}_2$$

- Range-separated Coulomb potential

parameter

$$\frac{1}{r} = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{\mathrm{erf}(\omega r)}{r}$$

short-range   **long-range**

(used in HSE06, etc)

(see POTENTIAL_TYPE keyword in &INTERACTION_POTENTIAL subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)
Heyd & Scuseria, J. Chem. Phys., 118, 8207 (2003)

Interaction potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r}_1)\,\phi_\nu(\mathbf{r}_1)\,\boxed{g(|\mathbf{r}_2 - \mathbf{r}_1|)}\,\phi_\lambda(\mathbf{r}_2)\,\phi_\sigma(\mathbf{r}_2)\,d\mathbf{r}_1\mathbf{r}_2$$

- Truncated Coulomb potential

parameter

$$g_{\mathrm{TC}}(r_{12}) = \begin{cases} \dfrac{1}{r_{12}}, & r_{12} \leq R_c \\[2mm] 0, & r_{12} > R_c \end{cases}$$

(used in PBE0-TC-LRC, etc)

(see POTENTIAL_TYPE keyword in &INTERACTION_POTENTIAL subsection)

Guidon et al., J. Chem. Theory Comput., 5, 3010 (2008)

Spencer & Alavi, Phys. Rev. B, 77, 193110 (2008)

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Auxiliary Density Matrix Methods

$$E_{xc}[\rho] = \alpha E_x^{HFX}[\{\psi_i\}] + (1 - \alpha)E_x^{DFT}[\rho] + E_c^{DFT}[\rho]$$

$$E_x^{HFX}[P] = -\frac{1}{2} \sum_{\lambda\sigma\mu\nu} P^{\mu\sigma} P^{\nu\lambda} (\mu\nu|\lambda\sigma)$$

- Introducing auxiliary density matrix $\hat{P} \approx P$

$$E_x^{HFX}[P] = \quad E_x^{HFX}[\hat{P}] + (E_x^{HFX}[P] - E_x^{HFX}[\hat{P}])$$
$$\approx \quad E_x^{HFX}[\hat{P}] + (E_x^{DFT}[P] - E_x^{DFT}[\hat{P}])$$

approximation

original density matrix

auxiliary density matrix

$$P^{\mu\nu} = \sum_i C^{\mu i} C^{\nu i} \Leftrightarrow P = CC^T \qquad \hat{P}^{\mu\nu} = \sum_i \hat{C}^{\mu i} \hat{C}^{\nu i} \Leftrightarrow \hat{C}\hat{C}^T$$

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

ADMM basis sets

(see $CP2K/cp2k/data/BASIS_ADMM)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010) 13

ADMM basis sets

Choice of auxiliary basis set for ADMM

- FIT3: three Gaussian exponents for each valence orbital

- cFIT3: a contraction of FIT3

- pFIT3: FIT3 + polarization functions

- cpFIT3: cFIT3 + polarization functions

- aug-FIT3, aug-cFIT3, aug-pFIT3, aug-cpFIT3: augmented with a "diffuse" function

(see $CP2K/cp2k/data/BASIS_ADMM)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

ADMM basis sets

(see $CP2K/cp2k/data/**BASIS_ADMM_MOLOPT**)

ADMM basis sets

Uncontracted basis sets

- FIT10: $4s + 3p + 3d$
- <u>FIT11</u>: $4s + 3p + 3d + 1f$ $\longrightarrow$ **recommended for solids**
- FIT12: $4s + 3p + 4d + 1f$
- FIT13: $4s + 4p + 4d + 1f$

Contracted basis sets (double-ζ quality)

- cFIT10 / <u>cFIT11</u> / cFIT12 / cFIT13

Names of the ADMM basis sets for main group elements will differ slightly, and usually the first ADMM basis set will not contain polarisation function.

(see $CP2K/cp2k/data/**BASIS_ADMM_MOLOPT**)   16

Some general suggestions

➢ **Always check the convergence of <u>CUTOFF</u>**

(see http://www.cp2k.org/howto:converging_cutoff)

➢ **Always check the convergence of properties (e.g. lattice parameters, band gaps) with respect to <u>supercell sizes</u>**

➢ **Always start from pre-converged GGA (e.g. PBE) wavefunction and geometry**

➢ **Always check the convergence of <u>primary and ADMM basis sets</u> (start from a small basis and gradually increase the size)**

➢ **ADMM has only been implemented for use with GPW**

Work Flow

1. Convergence test (primary basis, CUTOFF, supercell, etc)

2. GGA optimisation with selected primary basis

3. Name GGA wave function file for use with ADMM

4. Construct ADMM input with auxiliary basis (e.g. FIT3)

5. Run calculations and check convergence of ADMM basis

Input Structure: ADMM

```
&DFT
            …
            BASIS_SET_FILE_NAME ./BASIS_MOLOPT            (files can be found in $CP2K/cp2k/data)
            BASIS_SET_FILE_NAME ./BASIS_ADMM
            WFN_RESTART_FILE_NAME ${project}-RESTART.wfn
            &SCF
                    SCF_GUESS RESTART

                    …
            &END SCF
            &AUXILIARY_DENSITY_MATRIX_METHOD
                    METHOD BASIS_PROJECTION
                    ADMM_PURIFICATION_METHOD MO_DIAG
            &END AUXILIARY_DENSITY_MATRIX_METHOD

            …
            &XC

            …
            &END XC
&END DFT
&SUBSYS
            &KIND Si
                    BASIS_SET DZVP-MOLOPT-SR-GTH
                    AUX_FIT_BASIS_SET FIT3
                    POTENTIAL GTH-PBE-q4
            &END KIND
&END SUBSYS
```
(see examples in $CP2K/cp2k/tests/QS/regtest-admm-1/2/3/4)

Which functional to use?

- ## PBE0-TC-LRC

$$E_{xc}^{PBE0-TC-LRC} = aE_x^{HF,TC}(R_C) + aE_x^{PBE,LRC}(R_C)$$
$$+(1-a)E_x^{PBE} + E_c^{PBE}$$

Guidon et al., J. Chem. Theory Comput., 5, 3010 (2008)
Spencer & Alavi, Phys. Rev. B, 77, 193110 (2008)

- ## HSE06

$$E_{xc}^{HSE06} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega)$$
$$+E_x^{PBE,LR}(\omega) + E_c^{PBE}$$

Scuceria et al., J. Chem. Phys., 125, 224106 (2006)

"Empirical" parameters: a, R_c, and ω

Input Structure: PBE0 vs. HSE06

```
&XC
   &XC_FUNCTIONAL
    &PBE
      SCALE_X 0.75
      SCALE_C 1.0
    &END PBE
    &PBE_HOLE_T_C_LR
      CUTOFF_RADIUS 2.0
      SCALE_X 0.25
    &END PBE_HOLE_T_C_LR
   &END XC_FUNCTIONAL
   &HF
    &SCREENING
      EPS_SCHWARZ 1.0E-6
      SCREEN_ON_INITIAL_P FALSE
    &END SCREENING
    &INTERACTION_POTENTIAL
      POTENTIAL_TYPE TRUNCATED
      CUTOFF_RADIUS 2.0
      T_C_G_DATA ./t_c_g.dat
    &END INTERACTION_POTENTIAL
    &MEMORY
      MAX_MEMORY 2400
      EPS_STORAGE_SCALING 0.1
    &END MEMORY
    FRACTION 0.25
   &END HF
  &END XC
```

PBE0-TC-LRC

(**t_c_g.dat** can be found in $CP2K/cp2k/data)

```
&XC
   &XC_FUNCTIONAL
    &PBE
     SCALE_X 0.0
     SCALE_C 1.0
    &END PBE
    &XWPBE
     SCALE_X -0.25
     SCALE_X0 1.0
     OMEGA 0.11
    &END XWPBE
   &END XC_FUNCTIONAL
   &HF
    &SCREENING
      EPS_SCHWARZ 1.0E-6
      SCREEN_ON_INITIAL_P FALSE
    &END SCREENING
    &INTERACTION_POTENTIAL
      POTENTIAL_TYPE SHORTRANGE
      OMEGA 0.11
    &END INTERACTION_POTENTIAL
    &MEMORY
      MAX_MEMORY  2400
      EPS_STORAGE_SCALING 0.1
    &END MEMORY
    FRACTION 0.25
   &END HF
  &END XC
```

HSE06

(see examples in $CP2K/cp2k/tests/QS/regtest-admm-1/2/3/4)

A few more remarks …

➢ **Libint library is used to calculate ERIs and their analytic derivatives, see $CP2K/cp2k/INSTALL for more details on installation and linking with CP2K**

➢ **Hybrid DFT calculations of large systems are memory demanding, try to increase MAX_MEMORY or run the job with more MPI processes**

➢ **For extremely large hybrid DFT calculations, try hybrid MPI/OpenMP binary (i.e. cp2k.psmp)**

Example: Diamond Band Gap

method	number of integrals	gap [eV]
PBE (PBS)		4.17
PBE (ABS)		4.37
PBE0 (PBS)	40 787 850 778 591	6.07
PBE0 (ABS)	23 561 509 497	6.25
PBE0 ADMM1	24 816 897 009	6.03
PBE0 ADMM2	24 795 460 638	6.02

3x3x3 supercell

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Part II: Van der Waals Corrections

Where does van der Waals force come from?
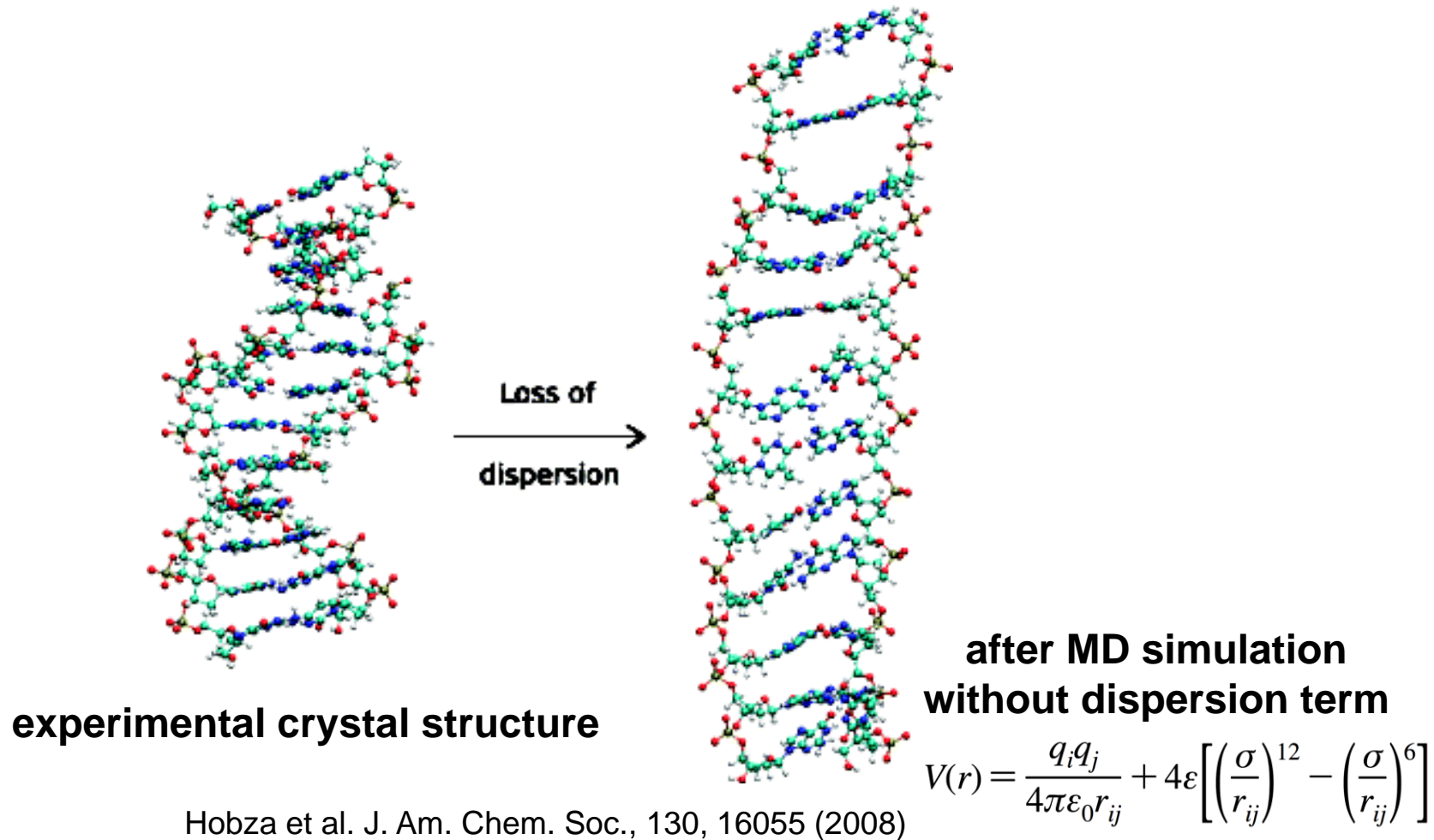
http://www.youtube.com/watch?v=G1jGeeSWhXY
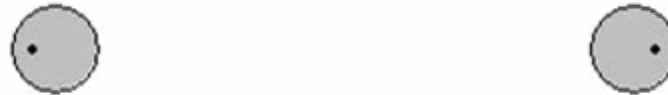
vdW force results from interaction of fluctuating charge distributions in one particle with those in an adjacent particle

(particle = atom, molecule, molecular fragment, etc)

Why van der Waals force is important?

Loss of dispersion

experimental crystal structure

after MD simulation without dispersion term

$$V(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Hobza et al. J. Am. Chem. Soc., 130, 16055 (2008)

helical to ladder structural transition in DNA

Conventional DFT Fails for vdW Force
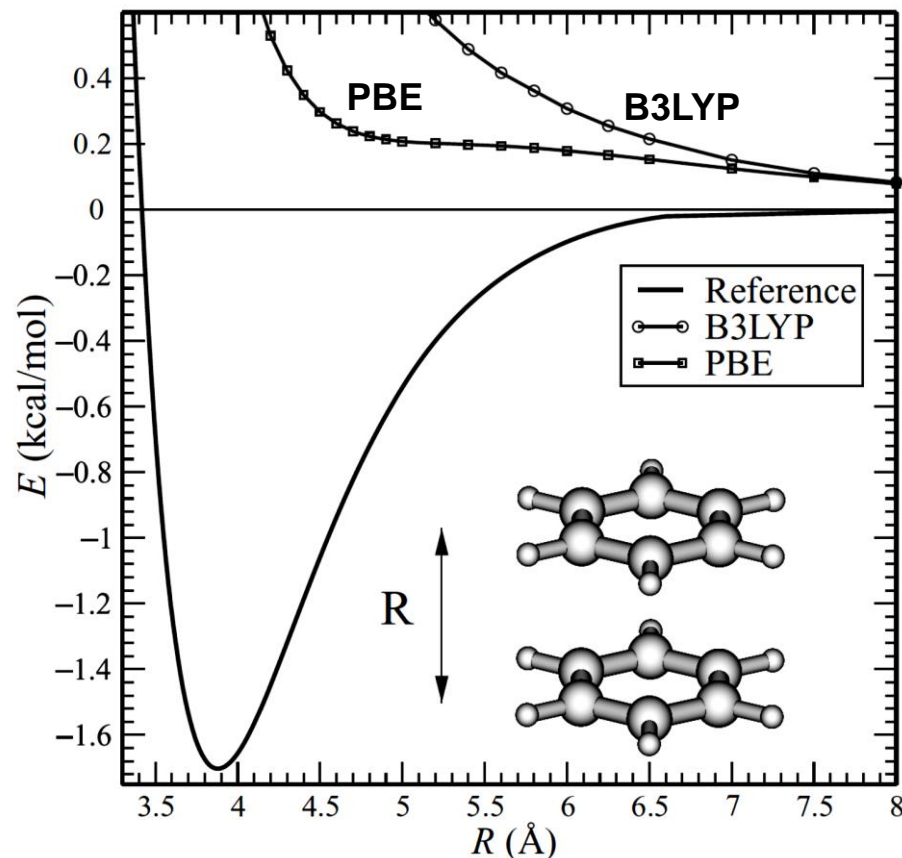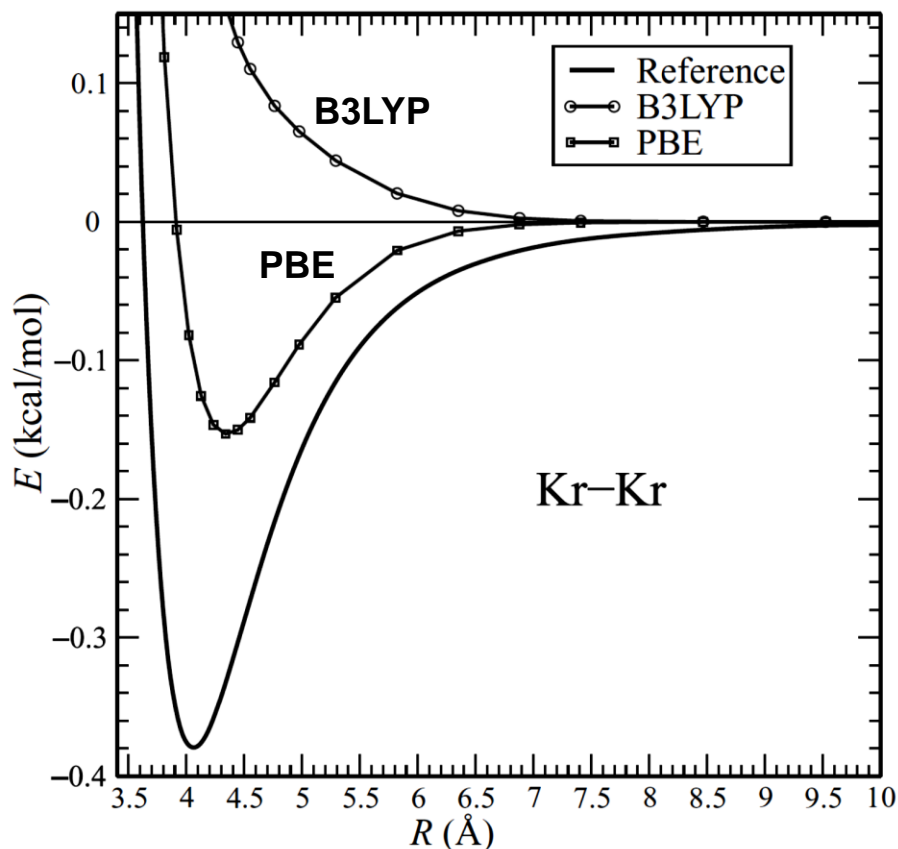
Reference: CCSD(T), see Grimme, WIREs Comput. Mol. Sci., 1, 211 (2011)

Conventional DFT methods cannot provide correct $-1/R^6$ dependence of vdW force on R

Methods to include vdW force in Conventional DFT
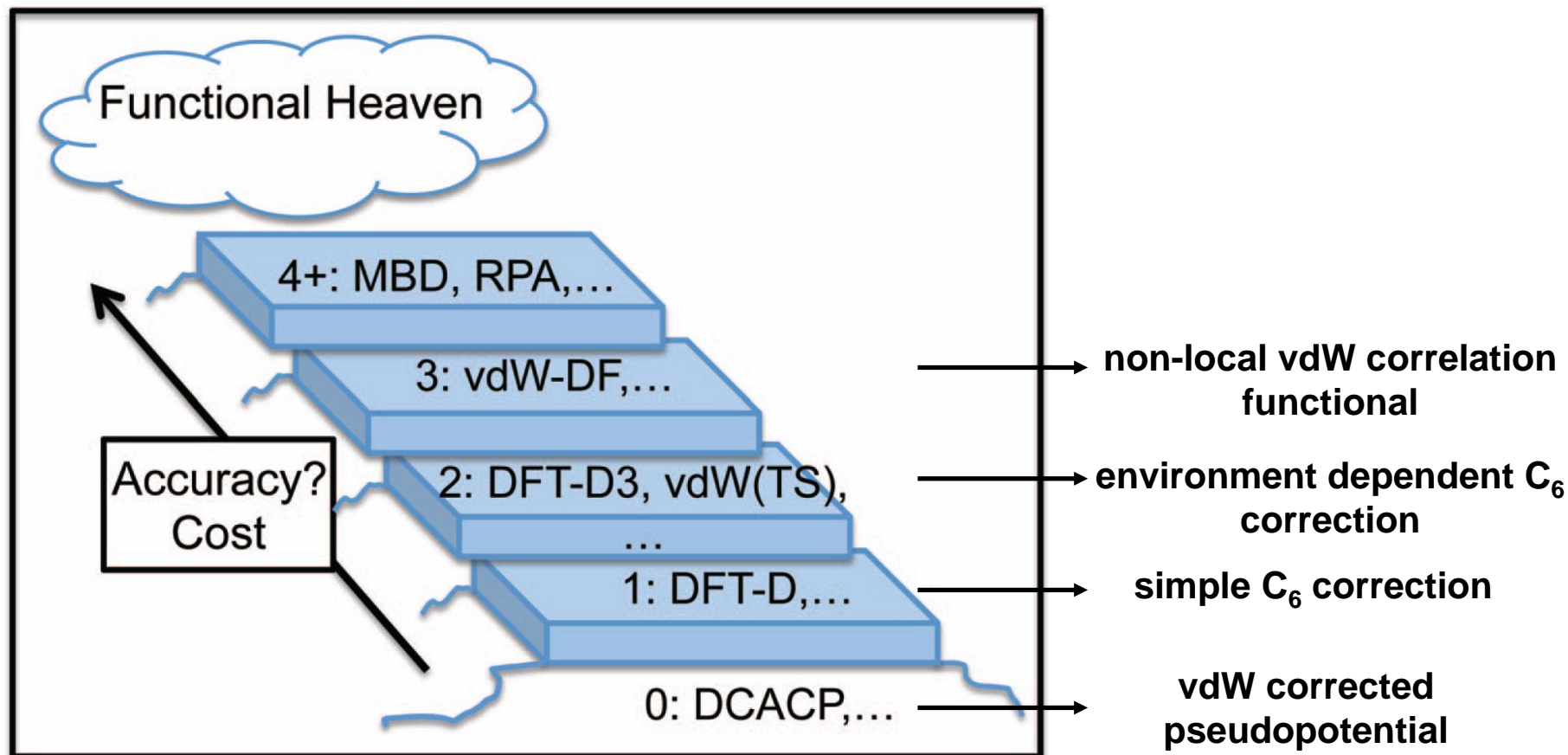
Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

"stairway to heaven" for long range dispersion interactions

Simple C$_6$ Correction

$$E_{\text{disp}} = -\sum_{A,B} C_6^{AB} / r_{AB}^6$$

pairwise additive

dispersion coefficients

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{disp}}$$

conventional DFT

Damped C$_6$ Correction
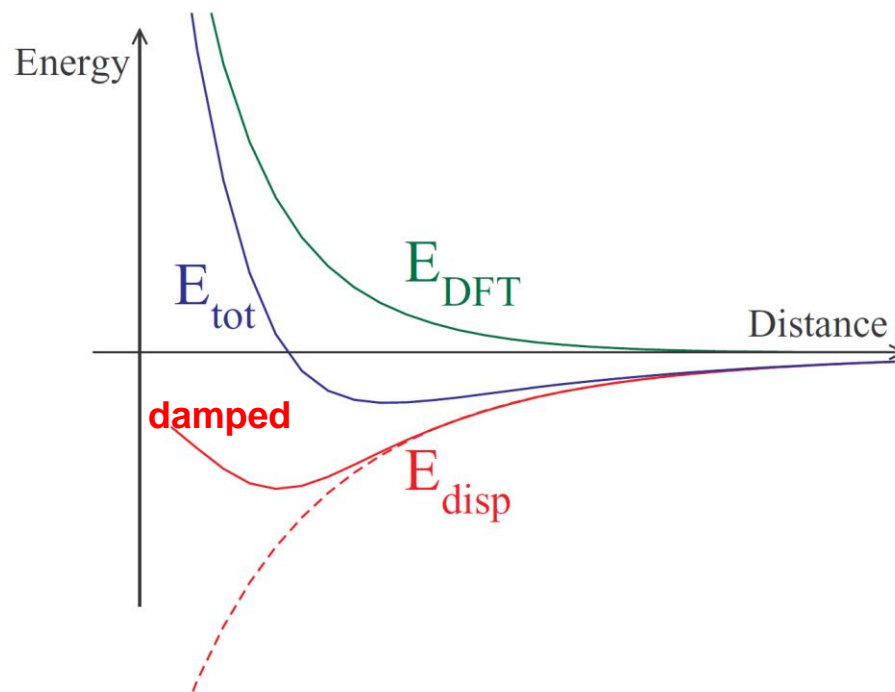
$$E_{\text{disp}} = - \sum_{A,B} f(r_{AB}, A, B) C_6^{AB} / r_{AB}^6$$

Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

DFT+D2

$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$

$$C_6^a = 0.05 N I_p^a \alpha^a$$

atomic ionization potentials   **static polarizability**

Grimme, J. Comput. Chem., 27, 1787 (2006)

DFT+D2

```
&XC
   &XC_FUNCTIONAL PBE
   &END XC_FUNCTIONAL
   &vdW_POTENTIAL
     DISPERSION_FUNCTIONAL PAIR_POTENTIAL
     &PAIR_POTENTIAL
       TYPE DFTD2
       REFERENCE_FUNCTIONAL PBE
       SCALING  ???      ←——   XC-dependent
       R_CUTOFF ???    ←——    cutoff radius to calculate E_disp
     &END PAIR_POTENTIAL
   &END vdW_POTENTIAL
&END XC
```

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-1)

Methods to include vdW force in Conventional DFT
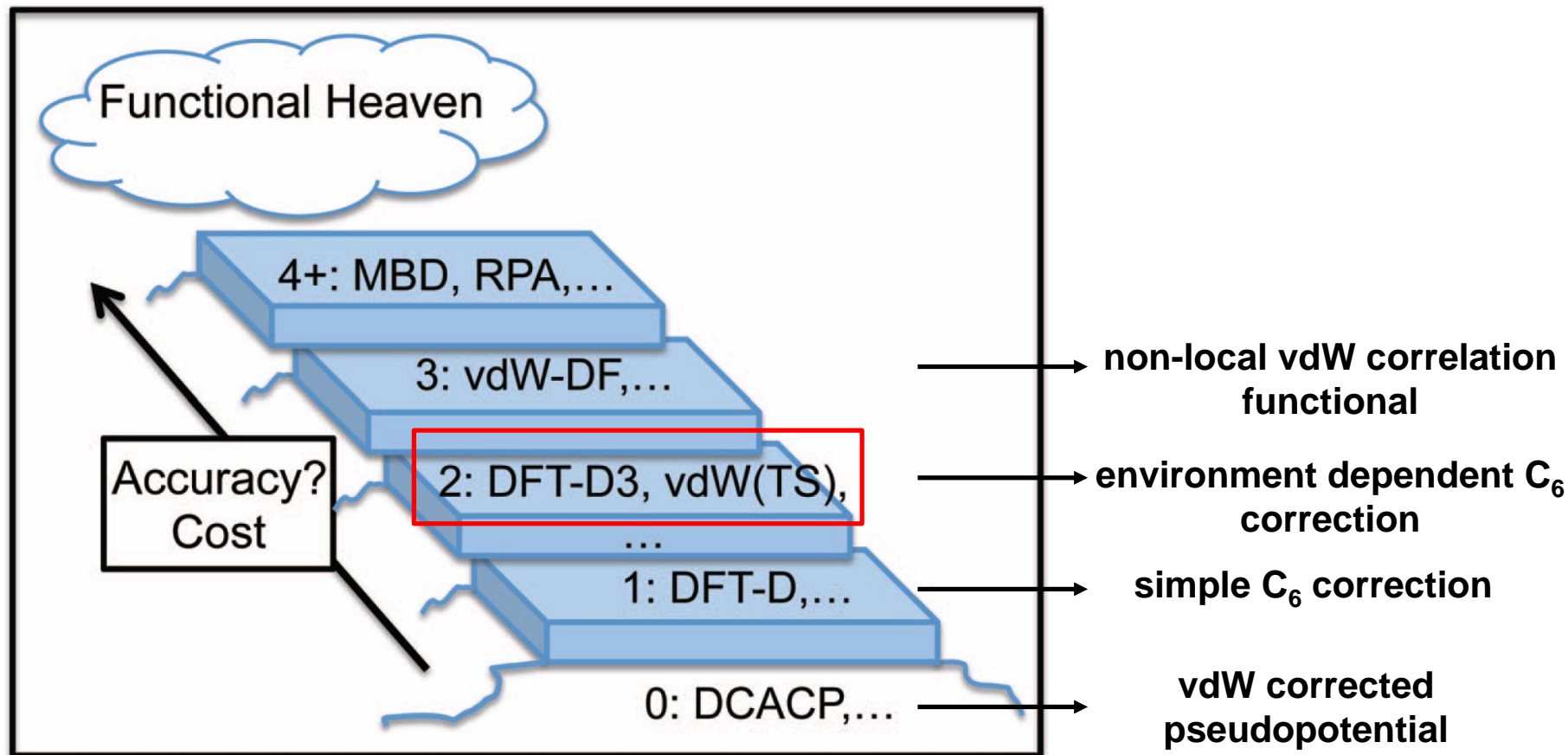
Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

"stairway to heaven" for long range dispersion interactions

# **Environment Dependent C_6 Correction**

DFT-D3: pre-calculated C_6 coefficients for various pairs of elements in different hybridisation states

Grimme et al., J. Chem. Phys, 132, 154104 (2010)

DFT-TS: Hirshfeld partitioning of the molecular electron density, compare effective atomic volume with a free atom, and then scale the C_6 coefficients of a free-atom reference

Tkatchenko & Scheffler, Phys. Rev. Letts., 102, 073005 (2009)

DFT+D3

$$C_6^{AB}(\text{CN}^A, \text{CN}^B) = \frac{Z}{W},$$

$$Z = \sum_i^{N_A} \sum_j^{N_B} C_{6,\text{ref}}^{AB}(\text{CN}_i^A, \text{CN}_j^B) L_{ij},$$

$$W = \sum_i^{N_A} \sum_j^{N_B} L_{ij},$$

$$L_{ij} = e^{-k_3[(\text{CN}^A - \text{CN}_i^A)^2 + (\text{CN}^B - \text{CN}_j^B)^2]},$$

$$\text{CN}^A = \sum_{B \neq A}^{N_{at}} \frac{1}{1 + e^{-k_1(k_2(R_{A,\text{cov}} + R_{B,\text{cov}})/r_{AB} - 1)}}$$

coordination number

DFT+D3

$$E^{ABC} = \frac{C_9^{ABC}(3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3}$$ **three-body term**

$$C_9^{ABC} \approx - \sqrt{C_6^{AB} C_6^{AC} C_6^{BC}}$$

Grimme et al., J. Chem. Phys, 132, 154104 (2010)

DFT+D3

```
&XC
   &XC_FUNCTIONAL PBE
   &END XC_FUNCTIONAL
   &vdW_POTENTIAL
     DISPERSION_FUNCTIONAL PAIR_POTENTIAL
     &PAIR_POTENTIAL
       TYPE DFTD3 ### or DFTD3(BJ)     ⟵  type of damping
       CALCULATE_C9_TERM .TRUE.     ⟵   include three-body term
       PARAMETER_FILE_NAME dftd3.dat
       REFERENCE_FUNCTIONAL PBE
       D3_SCALING ???      ⟵    XC and basis set dependent
       R_CUTOFF ???   ⟵   cutoff radius to calculate E_disp
     &END PAIR_POTENTIAL
   &END vdW_POTENTIAL
&END XC
```

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-2;
for additional scaling parameters optimised for **moderate** basis set
calculations, see Supporting Information of the D3 paper)

Methods to include vdW force in Conventional DFT
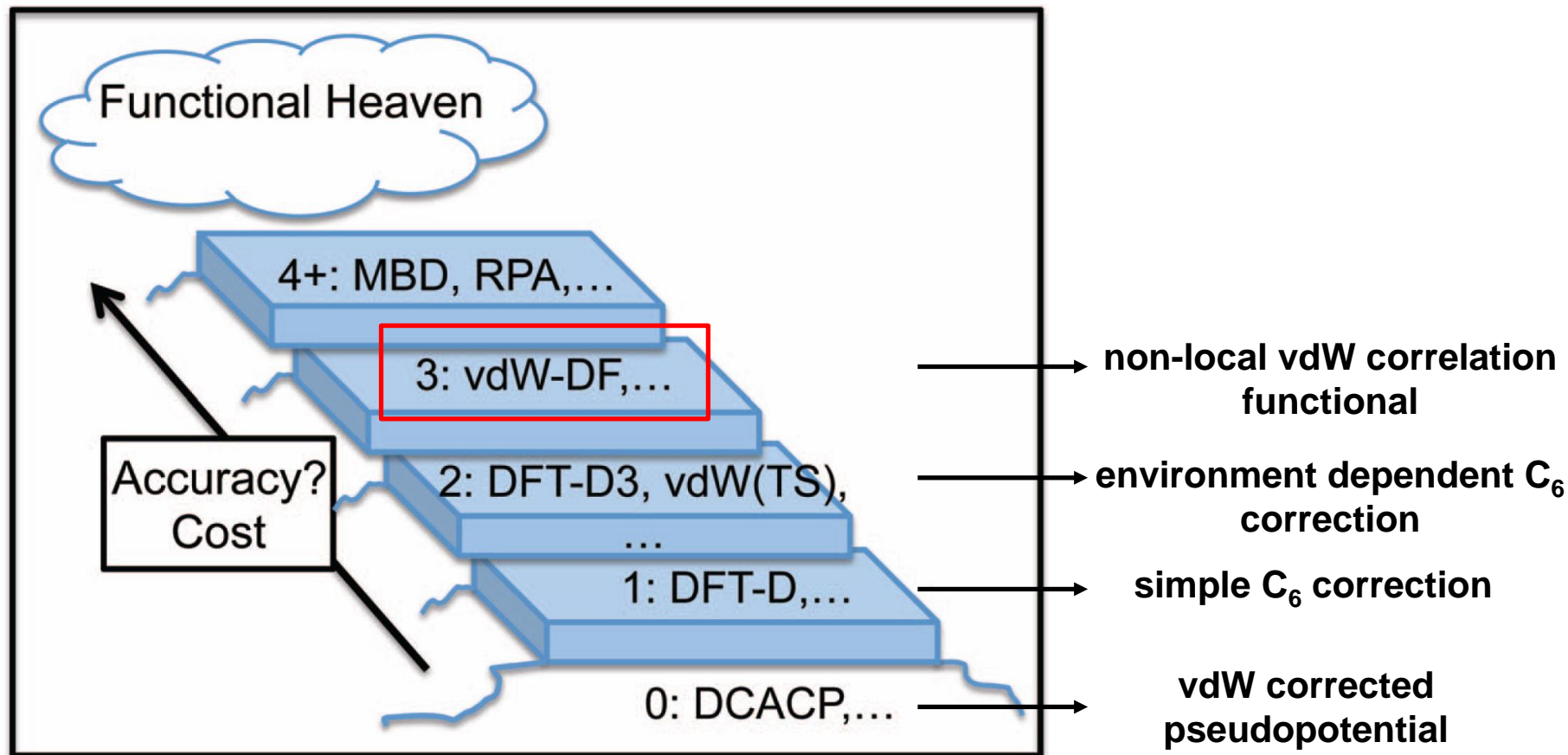
Functional Heaven

4+: MBD, RPA,…

3: vdW-DF,… → **non-local vdW correlation functional**

Accuracy? Cost

2: DFT-D3, vdW(TS), … → **environment dependent C_6 correction**

1: DFT-D,… → **simple C_6 correction**

0: DCACP,… → **vdW corrected pseudopotential**

Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

"stairway to heaven" for long range dispersion interactions

Non-local vdW Correlation Functional

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}$$

$$E_c^{nl} = \frac{1}{2} \int \int \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d^3r \, d^3r'$$

$$\Phi(\mathbf{r}, \mathbf{r}') = \Phi(\rho(\mathbf{r}), \rho(\mathbf{r}'), |\nabla \rho(\mathbf{r})|, |\nabla \rho(\mathbf{r}')|, |\mathbf{r} - \mathbf{r}'|)$$

Michaelides et al., J. Chem. Phys., 137, 120901 (2012)
Hutter et al., J. Chem. Phys., 138, 204103 (2013)

Non-local vdW Correlation Functional
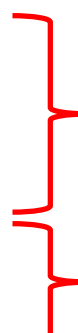
Functional	Reference	Exchange	Correlation
LDA	1 and 33	LDA	LDA
PBE	5	PBE	PBE
vdW-DF	19	revPBE	LDA+DRSLL
vdW-DF2	26	PW86R	LDA+LMKLL
$C09_x$-vdW	29	$C09_x$	LDA+DRSLL
optB88-vdW	30	optB88	LDA+DRSLL
RPBEc2/3+nl	31	RPBE	$\frac{1}{3}$LDA+$\frac{2}{3}$PBE+DRSLL
rVV10	34	PW86R	PBE+rVV10
PBE-D3	18	PBE	PBE+D3
revPBE-D3	18	revPBE	PBE+D3
B97D-D3	18	B97D	B97D+D3

Hutter et al., J. Chem. Phys., 138, 204103 (2013)

vdW-DF

```
&XC
   &XC_FUNCTIONAL
    &PBE
     PARAMETRIZATION revPBE                    revPBE exchange
     SCALE_C 0.0
    &END PBE
    &VWN
    &END VWN                                   LDA correlation
   &END XC_FUNCTIONAL
   &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL NON_LOCAL
    &NON_LOCAL
     TYPE DRSLL  ⟵——  type of non-local vdW correlation functional
     KERNEL_FILE_NAME vdW_kernel_table.dat
     CUTOFF  ???  ⟵——  cutoff of FFT grid used to calculate $E_c^{nl}$
    &END NON_LOCAL
   &END vdW_POTENTIAL
&END XC
```

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-3)

rVV10

```
&XC
   &XC_FUNCTIONAL
    &LIBXC
     FUNCTIONAL XC_GGA_X_RPW86 XC_GGA_C_PBE
    &END LIBXC
   &END XC_FUNCTIONAL
   &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL NON_LOCAL
    &NON_LOCAL
     TYPE RVV10          ←——  type of non-local vdW correlation functional
     PARAMETERS 6.3 0.0093   ←——   parameters relevant to rVV10
     KERNEL_FILE_NAME rVV10_kernel_table.dat
     CUTOFF  ???        ←——   cutoff of FFT grid used to calculate $E_c^{nl}$
    &END NON_LOCAL
   &END vdW_POTENTIAL
&END XC
```

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-3)

meta-GGA: M06-L

```
&XC
    &XC_FUNCTIONAL
     &LIBXC  T
      FUNCTIONAL XC_MGGA_X_M06_L XC_MGGA_C_M06_L
     &END LIBXC
    &END XC_FUNCTIONAL
&END XC
```

Truhlar et al., J. Chem. Phys., 125, 194101 (2006)

➢ **maybe combined with D3 correction**

➢ **analytical stress tensor has not been implemented, i.e.**

cannot be used for CELL_OPT

A few more remarks …

➢ **use higher planewave cutoff and tighter energy/force convergence criteria for meta-GGAs and functionals from Libxc**

➢ **to use functionals from Libxc, you will need to install Libxc and link CP2K with Libxc, see $CP2K/cp2k/INSTALL for more details**

➢ **Basis set superposition error may "mimick" the missing dispersion interactions by DFT; check convergence on basis sets**

Part III: ASE interface

How to use CP2K/ASE interface?

A sample CP2K/ASE job script (e.g. on ARCHER):

```
#!/bin/bash --login
#PBS -N CP2K-ASE
#PBS -l select=20
#PBS -l walltime=01:00:00
#PBS -A XXX-XXX ──────▶ account number, replace with your own
#PBS -j oe

# modules that need to be loaded
module load cp2k
module load python-compute
module load pc-numpy
module load pc-scipy
module load pc-ase/3.11.0

# environment variables that need to be set
export ASE_CP2K_COMMAND="aprun -n 480 cp2k_shell.popt"
export CP2K_DATA_DIR=/work/y07/y07/cp2k/3.0.16521/data

# go to the job directory
cd $PBS_O_WORKDIR

# execute the CP2K-ASE job
python job.py
```

How to use CP2K/ASE interface?

A sample CP2K/ASE job input file:

```python
#!/usr/bin/python
from __future__ import division, print_function
import os

from ase.structure import molecule
from ase.optimize import BFGS
from ase.calculators.cp2k import CP2K

def main():

    calc = CP2K(label='test_H2_GOPT')
    atoms = molecule('H2', calculator=calc)
    atoms.center(vacuum=2.0)

    # Run Geo-Opt
    gopt = BFGS(atoms, logfile=None)
    gopt.run(fmax=1e-6)

    # check distance
    dist = atoms.get_distance(0, 1)
    dist_ref = 0.7245595
    assert (dist - dist_ref) / dist_ref < 1e-7

    # check energy
    energy_ref = -30.7025616943
    energy = atoms.get_potential_energy()
    assert (energy - energy_ref) / energy_ref < 1e-10
    print('passed test "H2_GEO_OPT"')

main()
```

Setting up the system:

```python
calc = CP2K(label='sys')
sys = io.read('sys.xyz')
sys.set_cell([(8.0, 0.0, 0.0), (4.3, 7.0, 0.0), (0.0, 0.0, 21.4)],
scale_atoms=False)
sys.set_pbc((True, True, True))
sys.set_calculator(calc)
```

(see more examples in $ASE/ase/test/cp2k)

How to use CP2K/ASE interface?

More advanced settings:

```
…

inp = """
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    &MGRID
      CUTOFF 400
    &END MGRID
    &XC
      &XC_FUNCTIONAL LDA
      &END XC_FUNCTIONAL
    &END XC
    &POISSON
      PERIODIC NONE
      PSOLVER  MT
    &END POISSON
  &END DFT
   &SUBSYS
    &KIND H
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-LDA
    &END KIND
  &END SUBSYS
&END FORCE_EVAL
"""
```

```
…

    # Basically, the entire CP2K input is passed in explicitly.
    # Disable ASE's input generation by setting everything to None.
    # For default settings, see $ASE/ase/calculators/cp2k.py.
    # ASE should only add the CELL and the COORD section.
    calc = CP2K(basis_set=None,
            basis_set_file=None,
            max_scf=None,
            cutoff=None,
            force_eval_method=None,
            potential_file=None,
            poisson_solver=None,
            pseudo_potential=None,
            stress_tensor=False,
            xc=None,
            label='test_H2_inp', inp=inp)
    h2 = molecule('H2', calculator=calc)
    h2.center(vacuum=2.0)
    energy = h2.get_potential_energy()
    energy_ref = -30.6989595886
    diff = abs((energy - energy_ref) / energy_ref)
    assert diff < 1e-10
    print('passed test "H2_None"')

main()
```

(see more examples in $ASE/ase/test/cp2k)

Further Reading

Hybrid functionals in CP2K (by Sanliang Ling)
https://www.cp2k.org/_media/events:2015_cecam_tutorial:ling_hybrids.pdf

Van der Waals corrected DFT (by Sanliang Ling)
https://www.cp2k.org/_media/events:2015_cecam_tutorial:ling_vdw.pdf

and references therein.

For Atomic Simulation Environment, see
https://wiki.fysik.dtu.dk/ase/_downloads/ase-talk.pdf