van der Waals corrected DFT

Sanliang Ling

University College London

Where does van der Waals force come from?

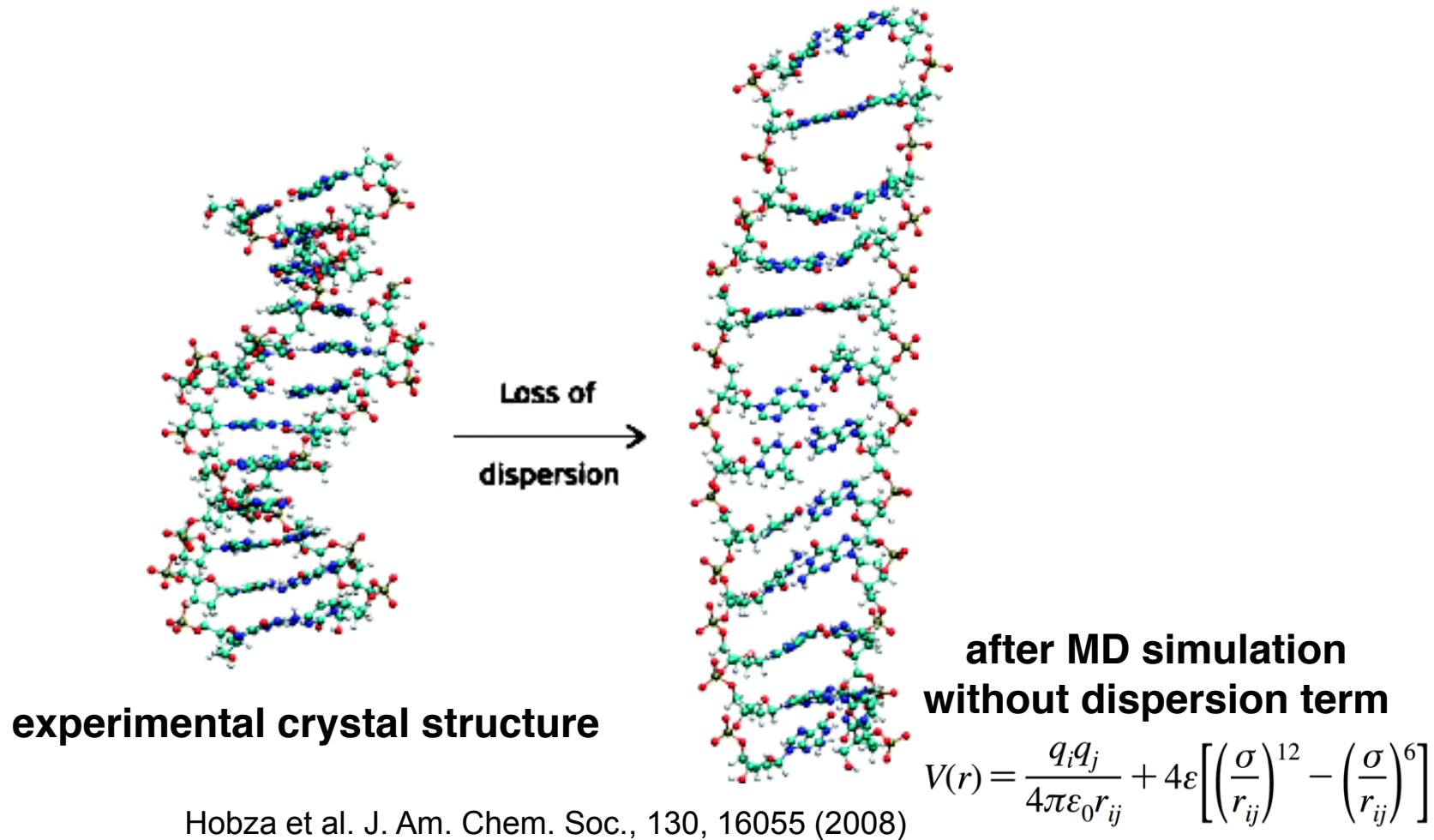

http://www.youtube.com/watch?v=G1jGeeSWhXY

vdW force results from interaction of fluctuating charge distributions in one particle with those in an adjacent particle
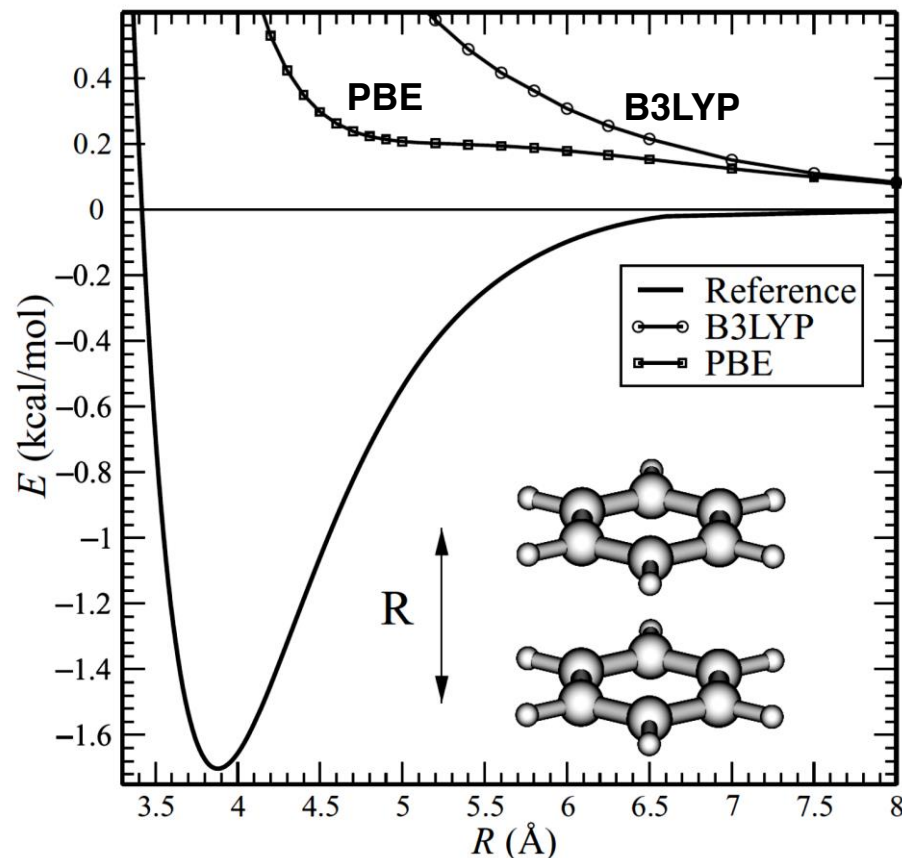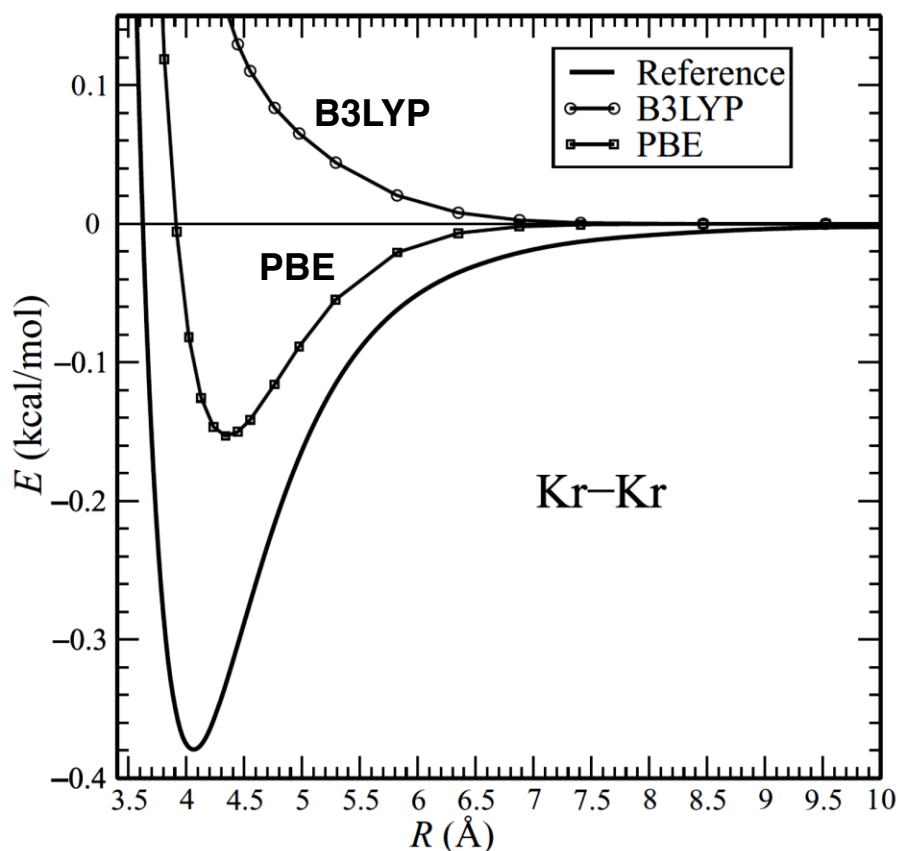
(particle = atom, molecule, molecular fragment, etc)

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)

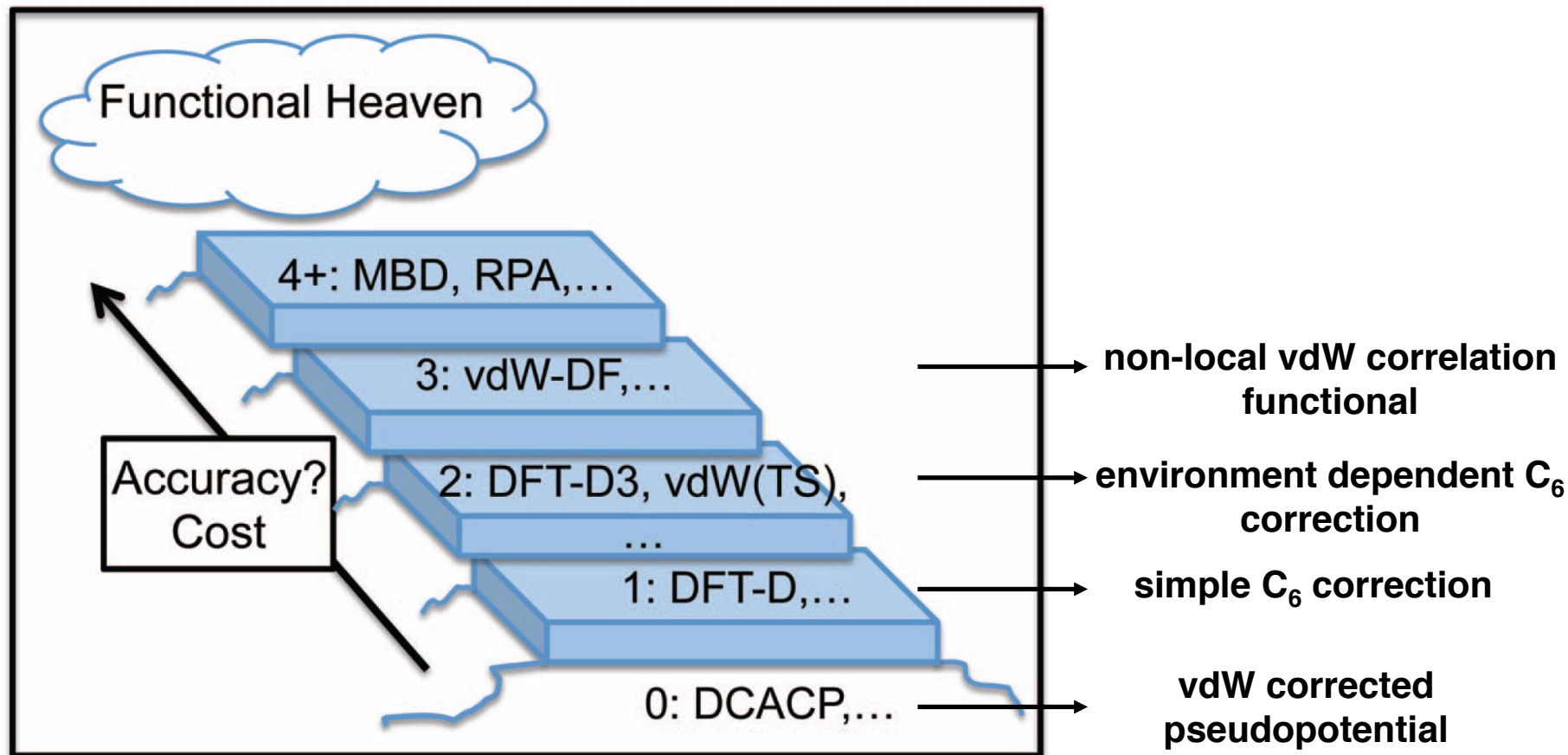**helical to ladder structural transition in DNA**

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

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
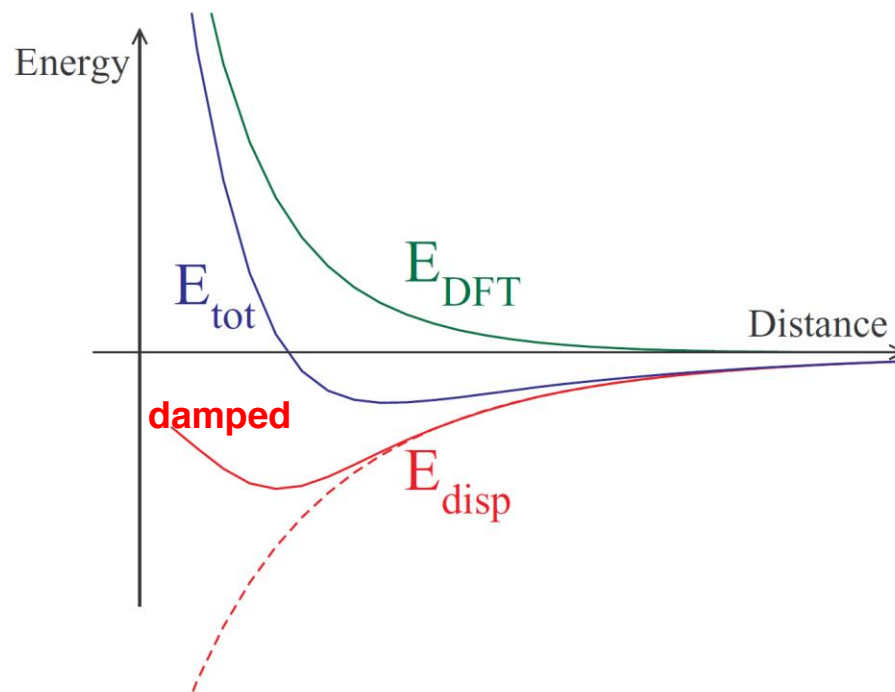
5

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)

8

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 Edisp
     &END PAIR_POTENTIAL
   &END vdW_POTENTIAL
&END XC
```

SCALING ??? ⟵ **XC-dependent**

R_CUTOFF ??? ⟵ **cutoff radius to calculate E_{disp}**

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

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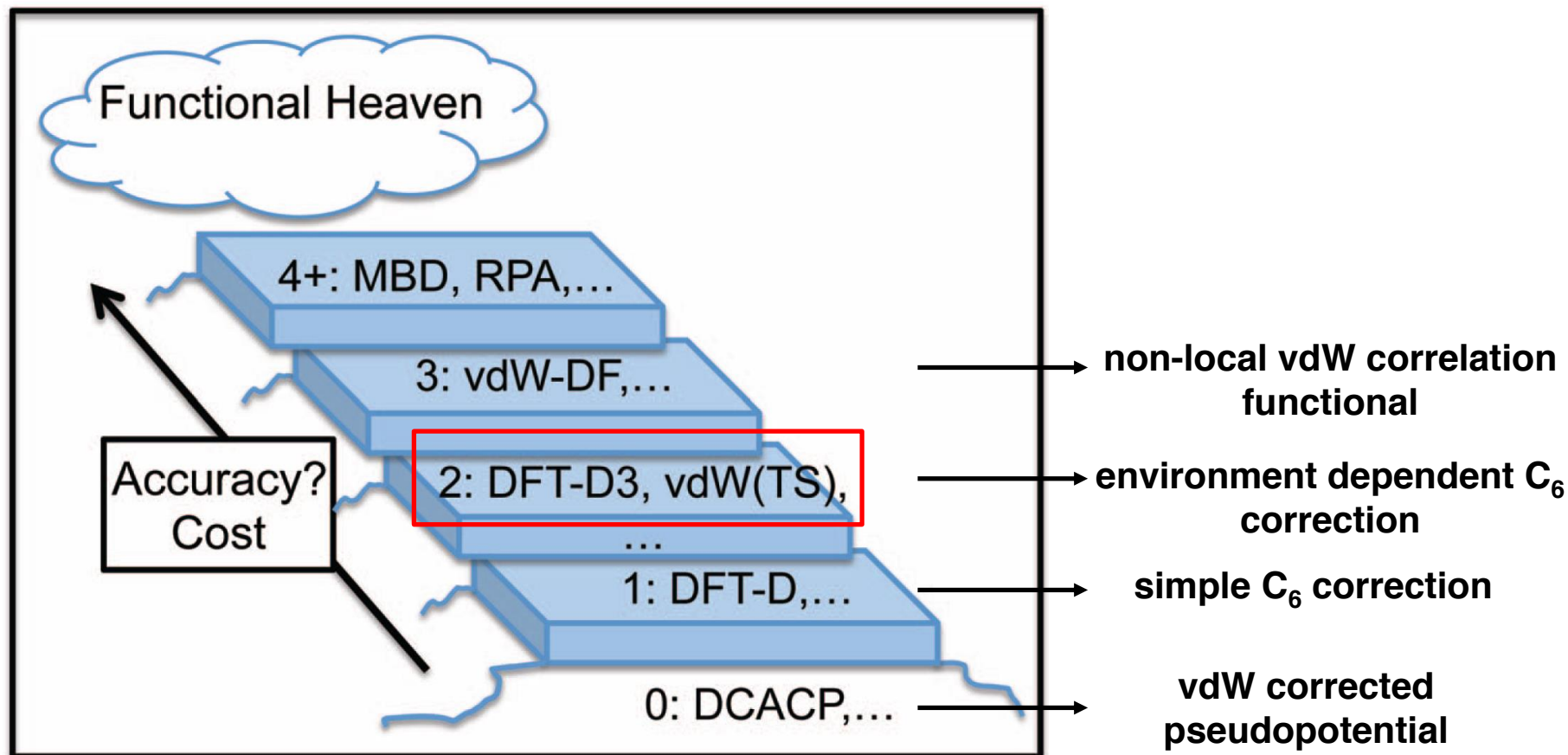
Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

"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

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

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

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

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

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

**coordination
number**

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

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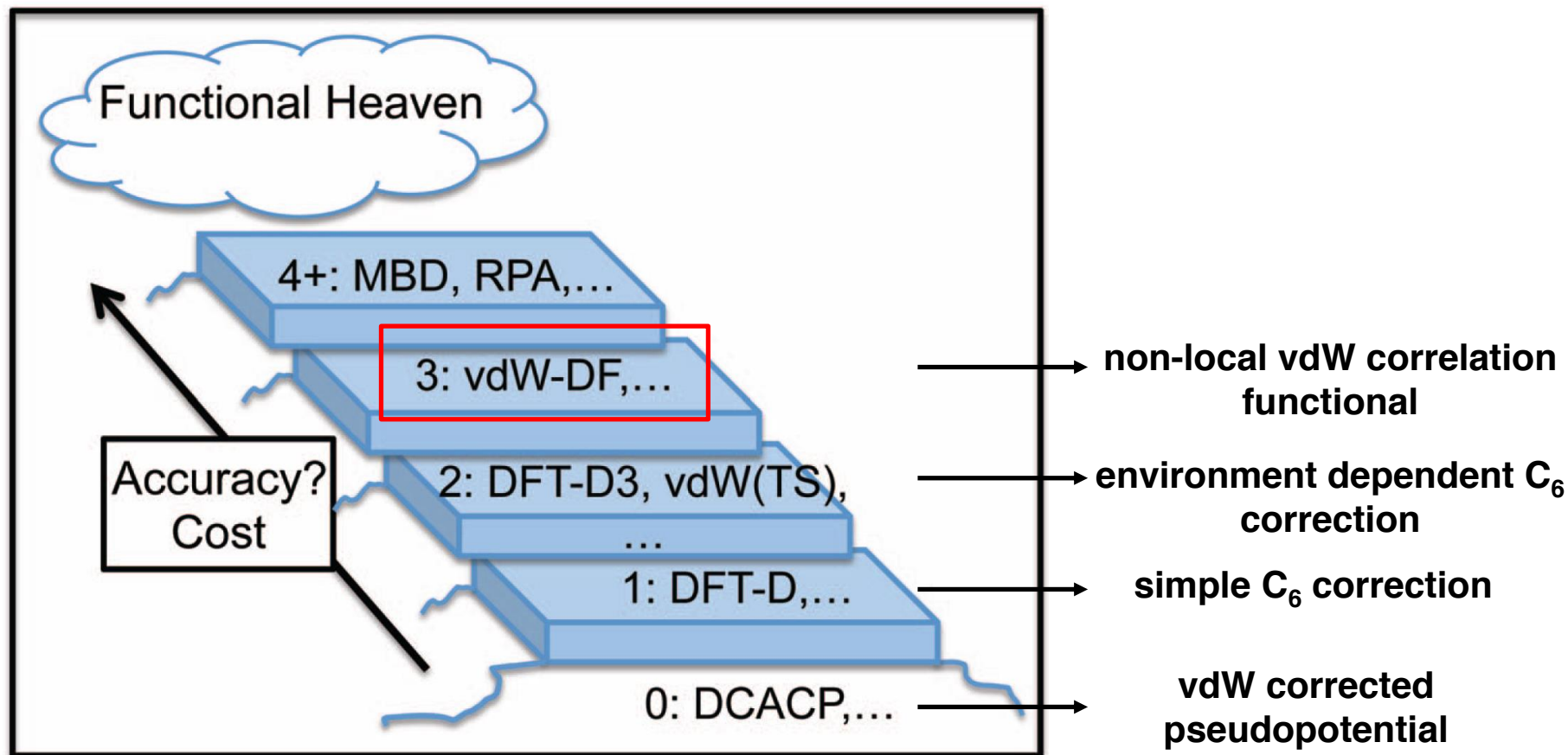
(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-2;
for additional scaling parameters optimised for **moderate** basis set
calculations, see Supporting Information of the D3 paper)

14

Semi-empirical+D3

```
&QS
   METHOD PM3
   &SE
     DISPERSION              T
     DISPERSION_RADIUS       15.
     D3_SCALING              1.0 1.2 1.4
     DISPERSION_PARAMETER_FILE   dftd3.dat
   &END SE
&END QS
```

(see more examples in $CP2K/cp2k/tests/SE/regtest-2)

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

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

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

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

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
     SCALE_C 0.0
    &END PBE
    &VWN
    &END VWN
   &END XC_FUNCTIONAL
   &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL NON_LOCAL
    &NON_LOCAL
     TYPE DRSLL
     KERNEL_FILE_NAME vdW_kernel_table.dat
     CUTOFF  ???
    &END NON_LOCAL
   &END vdW_POTENTIAL
&END XC
```

revPBE exchange

LDA correlation

type of non-local vdW correlation functional

cutoff of FFT grid used to calculate E_c^{nl}

(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)

BEEF-vdW

$$E_{xc} = \sum_{m=0}^{M_x-1} a_m E_m^{\text{GGA-x}} + \alpha_c E^{\text{LDA-c}}$$

$$+ (1 - \alpha_c) E^{\text{PBE-c}} + E^{\text{nl-c}},$$

BEEF: Bayesian error estimation functional
(with a total of 31 parameters)

Jacobsen et al., Phys. Rev. B, 85, 235149 (2012)

```
&XC
   &XC_FUNCTIONAL  BEEFVDW
   &END XC_FUNCTIONAL
   &VDW_POTENTIAL
    &NON_LOCAL
       TYPE LMKLL
       KERNEL_FILE_NAME vdW_kernel_table.dat
     &END NON_LOCAL
   &END VDW_POTENTIAL
&END XC
```

Role of different exchange functionals
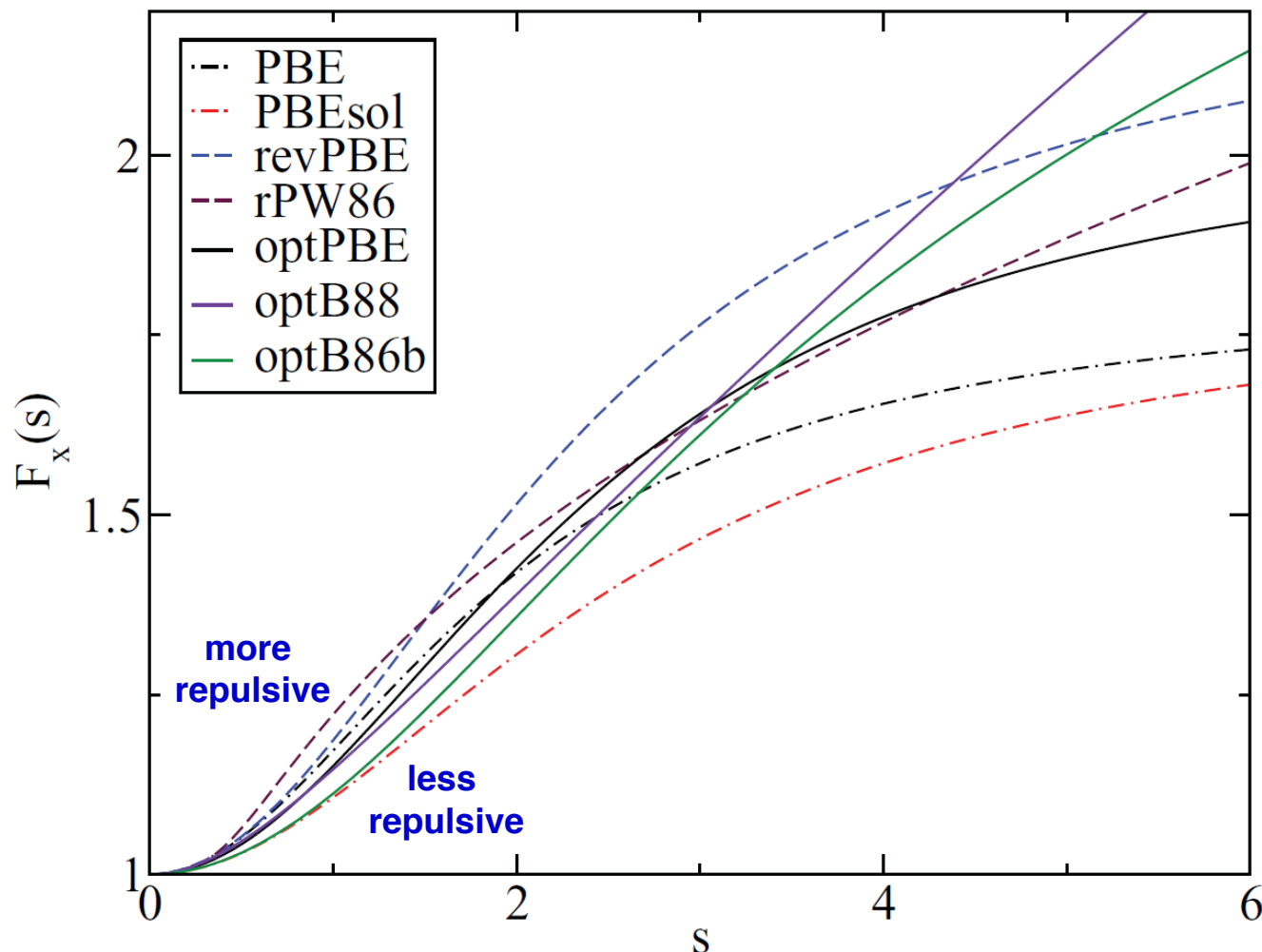
exchange enhancement factor (F_x) vs. reduced density gradient (s)

Michaelides et al., Phys. Rev. B, 83, 195131 (2011)

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

Comparison of various methods

Method	Step	Reference for C_6	C_6 depend on	Additional computational cost[a]
Minnesota	0	None	N/A	None
DCACP	0	None	N/A	Small
DFT-D	1	Various	Constant	Small
DFT-D3	2	TDDFT	Structure	Small
vdW(TS)	2	Polarizabilities and atomic C_6	Atomic volume	Small
BJ	2	Polarizabilities	Atomic volume, X hole	Large
LRD	3	C_6 calculated	Density	Small
vdW-DF	3	C_6 calculated	Density	$\approx 50\%$
Dbl. hybrids	4	None or as "-D"	Orbitals	Large

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

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**

Methods beyond DFT

Available in CP2K

➢ **Random phase approximation**

➢ **Møller–Plesset perturbation theory**

(see tomorrow's presentation by Jan Wilhelm)

Not available in CP2K

➢ **quantum Monte Carlo**

➢ **Symmetry adapted perturbation theory (SAPT) based on DFT**

➢ **Coupled cluster theory**

Further Reading

Self-Interaction Energy and Dispersion (by Prof Juerg Hutter)
http://www.cecam.org/upload/talk/presentation_2988.pdf

Van der Waals Corrections to DFT (by Dr Ari Paavo Seitsonen)
http://www.cecam.org/upload/talk/presentation_5738.pdf