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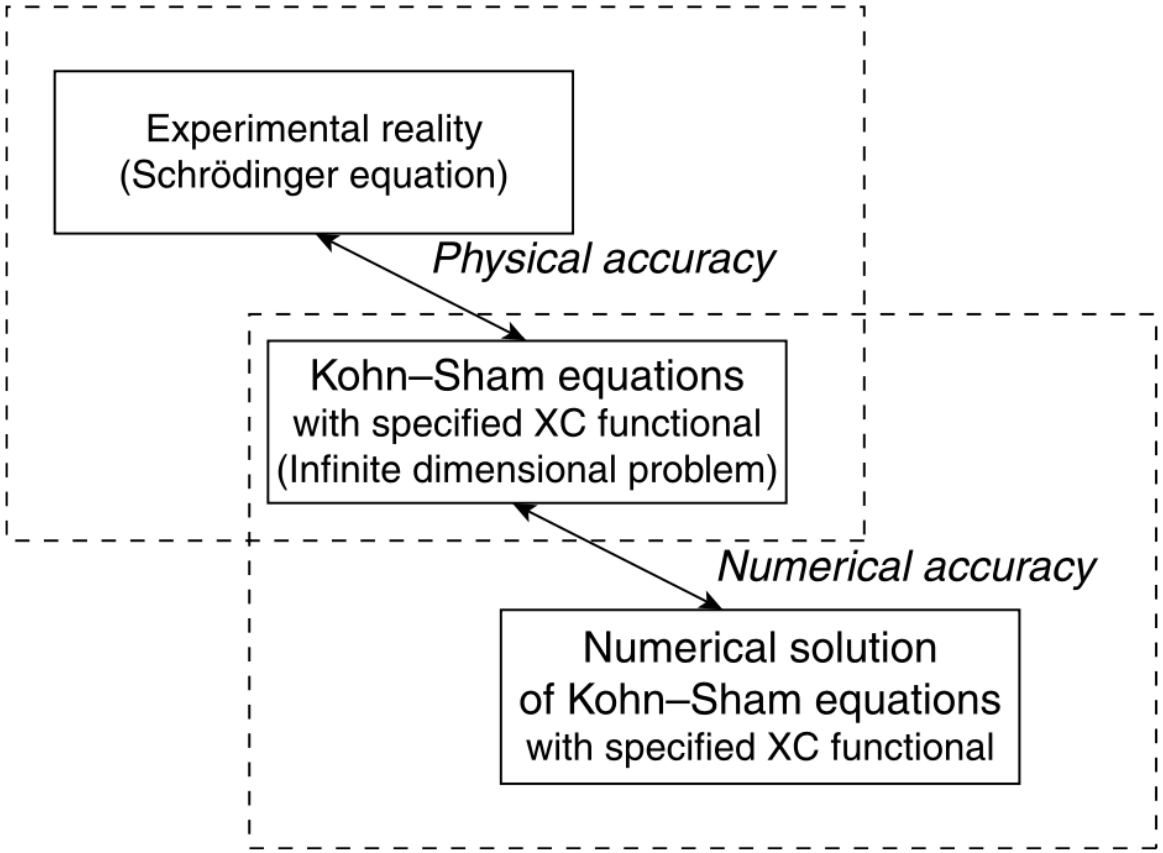
DFT Methods for van der Waals Interactions

Chemnitz // 18 April 2023

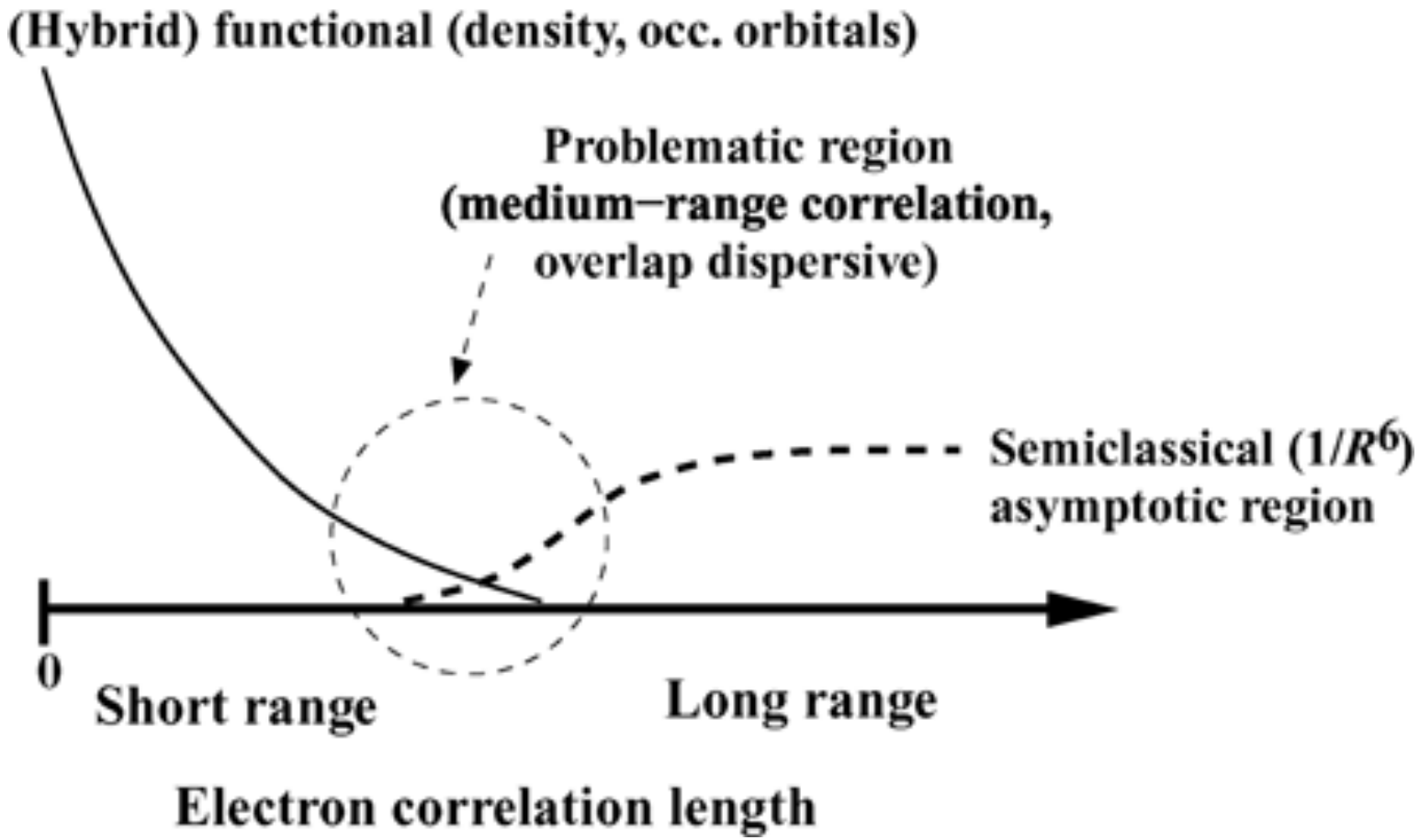
How accurate are DFT calculations?

- $E_{\mathrm{DFT}}[\rho] = T_{\mathrm{S}}[\rho] + \int \mathrm{d}\boldsymbol{r}\, v_{ext}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho]$

- Excited states
- Self-interaction error
- Local and semi-local XC
- …

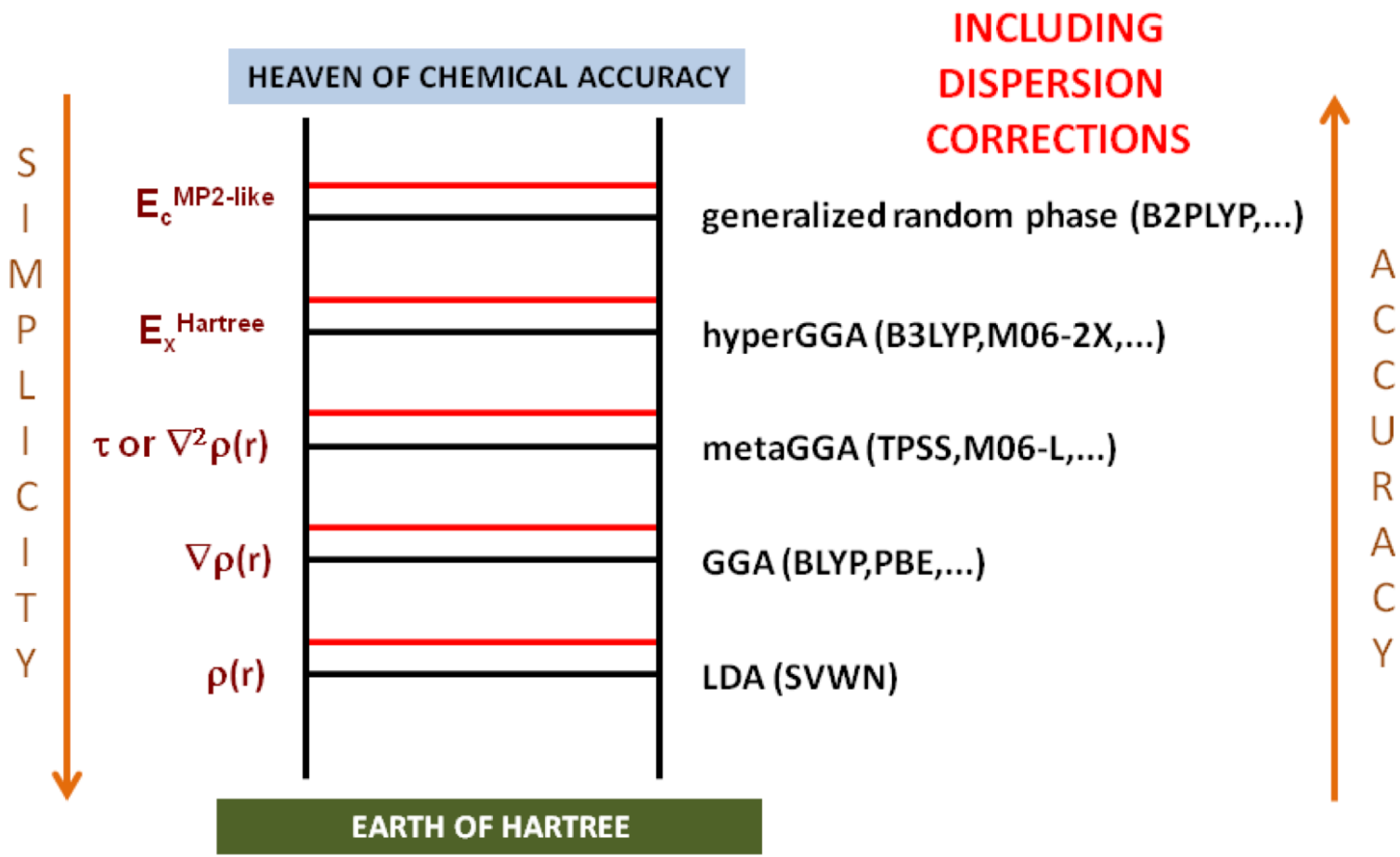


Short- and long-range correlation in DFT



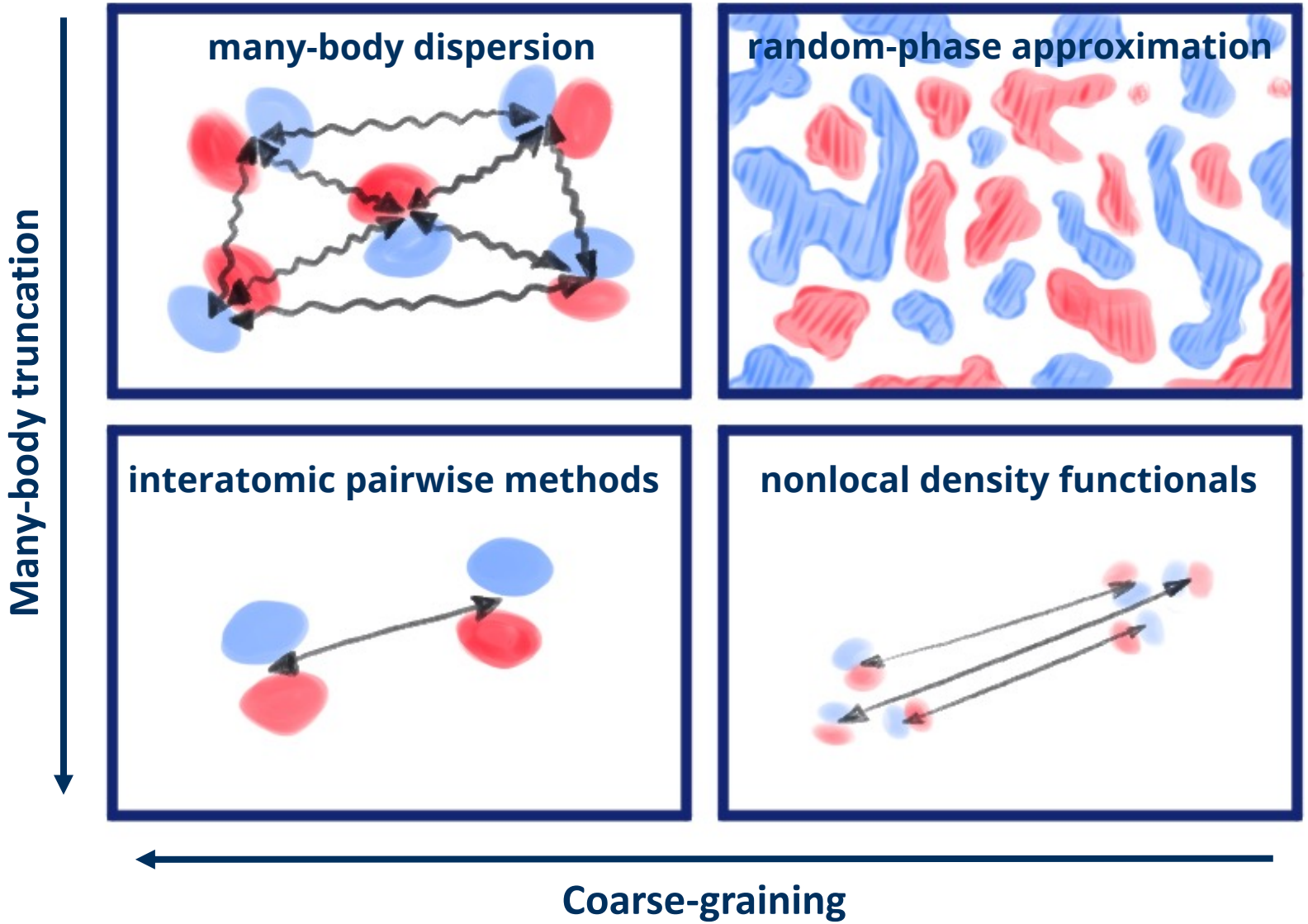
S. Grimme; Wiley Interdiscip. Rev. Comput. Mol. Sci., **2011**, *1*, 211

Choosing a functional



J. P. Perdew; K. Schmidt; *AIP Conf. Proc.*, **2001**, *577*, 1

Models for vdW interaction



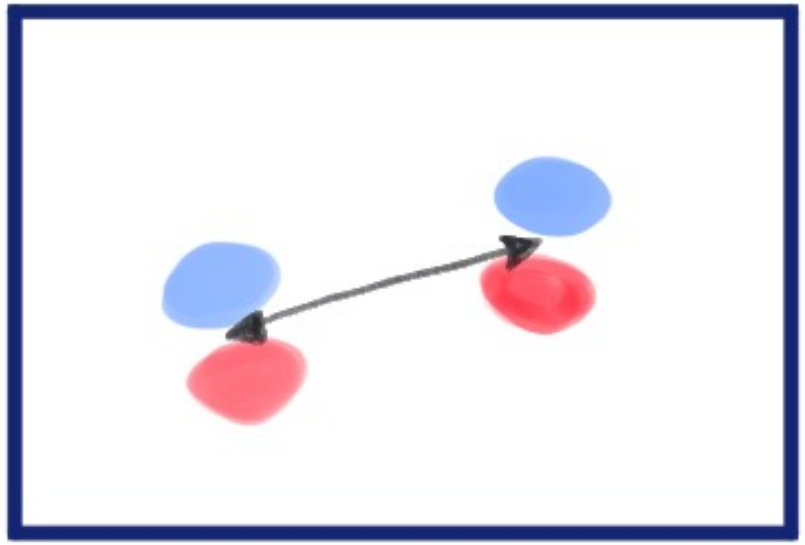
J. Hermann; R. A. DiStasio; A. Tkatchenko; Chem. Rev., **2017**, *117*, 4714.

Fragment-based pairwise methods

- London dispersion
  - $V_{dispersion} = -\frac{C}{r_6}$
- Add an empirical damped dispersion
  - $E_{DFT-D} = E_{DFT} + S \sum_{i \neq j} \frac{C_{ij}}{r_{ij}^6} f_{damp}(r_{ij})$

empirical parameter

  - Including DFT-D*n*, XDM, TS…



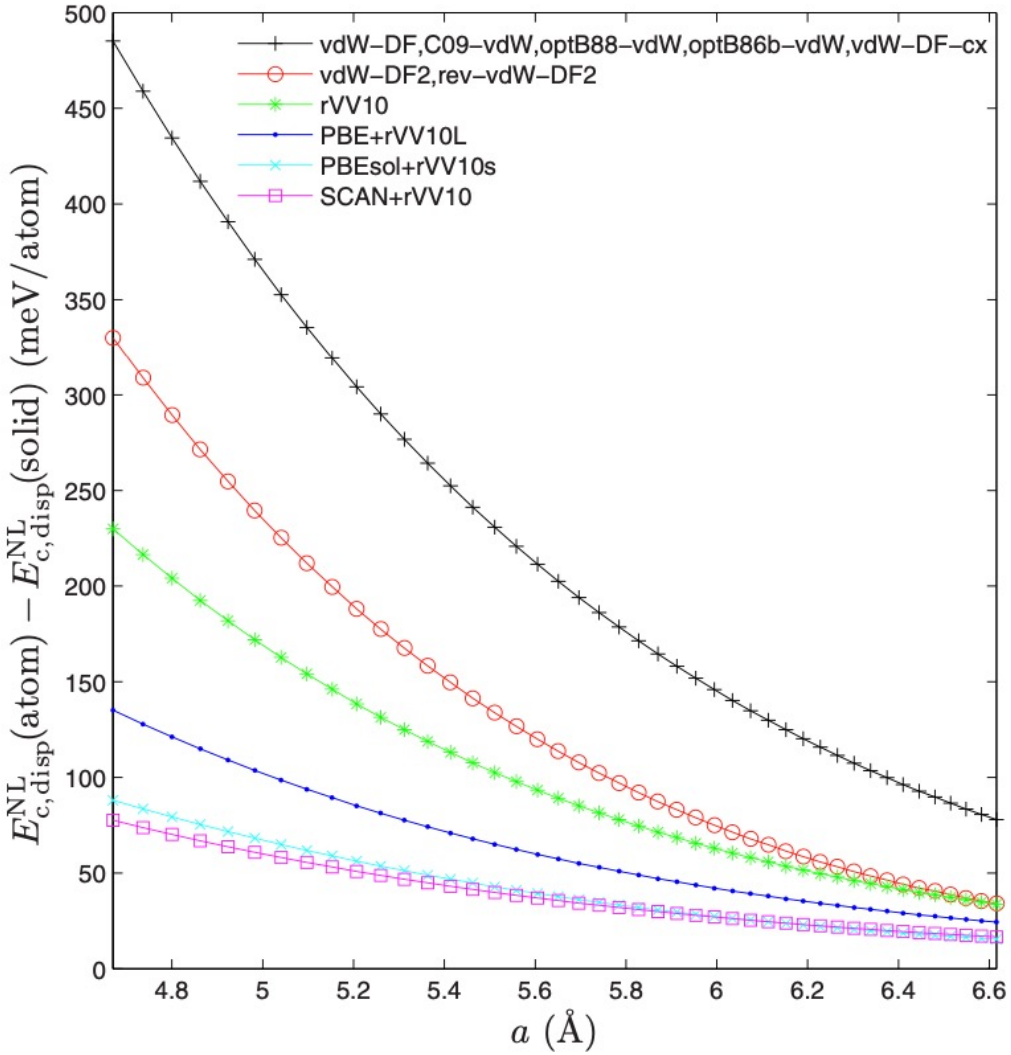
Nonlocal vdW Density Functionals

- London dispersion is not included in XC

$$E_{\mathrm{xc}}^{\mathrm{vdW-DF}} = E_{\mathrm{xc}}^{\mathrm{SL/hybrid}} + E_{\mathrm{c}}^{\mathrm{NL}}$$

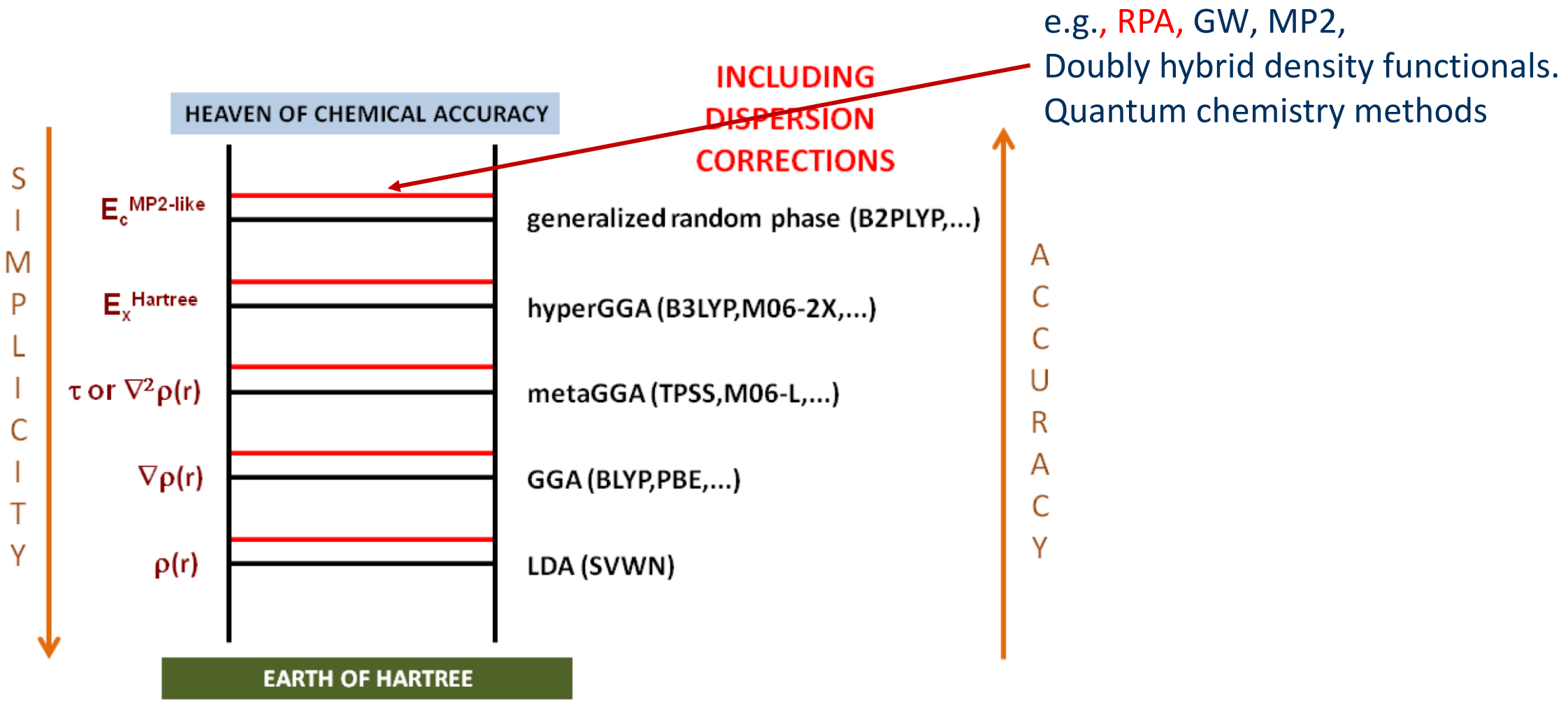
$$E_{\mathrm{c}}^{\mathrm{NL}} = \frac{1}{2}\int\int \rho(\boldsymbol{r})\Phi(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}'$$

- Dispersion correction affects density



F. Tran, L. Kalantari, B. Traoré, X. Rocquefelte, P. Blaha, *Phys. Rev. Materials* **2019**, *3*, 063602.

What is random phase approximation (RPA)?



The concept of RPA

Two kinds of response of the electrons to a wave

- In phase with the wave
  - position-independent
  - behavior of the system

- A phase difference with the wave
  - position-dependent
  - random location of the particles -> response to zero

D. Bohm and D Pines, *Phys. Rev.* **1950**, 82, 625.

RPA correlation energy

- With the framework of adiabatic-connection fluctuation-dissipation (ACFD) theorem:

$$E_{\mathrm{C}} = -\frac{1}{2\pi}\int_0^{\infty} du\, \mathrm{Tr}\left[\ln\left(1-\chi_0(\boldsymbol{r},\boldsymbol{r}',u)v(\boldsymbol{r},\boldsymbol{r}')\right) - \chi_0(\boldsymbol{r},\boldsymbol{r}',u)v(\boldsymbol{r},\boldsymbol{r}')\right]$$

Density response function

Coulomb interaction

- RPA captures the non-local coupling between spontaneous quantum charge fluctuations separated in space.
- If you're interested, you may check:

Langreth & Perdew, *Phys. Rev. B* **1977**, 15, 2884.
Gunnarsson & Lundqvist, *Phys. Rev. B* **1976**, 13, 4274.
XR, P. Rinke, C. Joas, and M. Scheffler, *J. Mater. Sci*. **2012**, 47, 7447.
...

RPA calculations in practice

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

$$E^{\mathrm{RPA}} = \langle \phi_0 | \hat{H} | \phi_0 \rangle + E_c^{\mathrm{RPA}}[\epsilon_n, \psi_n]$$

Hartree-Fock energy

ϵ_n, ψ_n : (generalized) KS orbitals and orbital energies

ϕ_0 : Slater determinant formed with occupied ψ_i

- RPA results show a slight dependence on the starting point, denoted e.g., by "RPA@PBE".

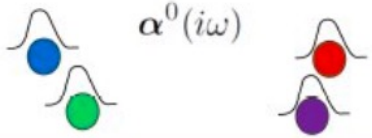
Coarse-grained MBD based on RPA and TS

- Shortcomings in TS approach
  - Only pairwise interactions
  - Only the local electron density for polarizability

- Many-body dispersion
  - Many-body interaction
  - Long-range screening effects
  - Using model response functions in ACFD-RPA
  - MBD@rsSCS(/FI), MBD-NL
  - More details:
    - A. Tkatchenko, R. DiStasio, R. Car, and M. Scheffler, *Phys. Rev. Lett.* **2012**, 108, 236402
    - J. Hermann, A. Tkatchenko, *Phys. Rev. Lett.* **2020**, 124, 146401.

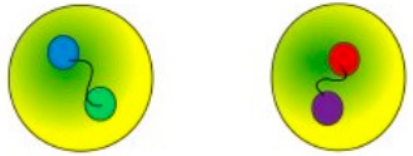
STEP 1: Tkatchenko-Scheffler atomic polarizabilities from DFT electron density and free atom reference data

$$\boldsymbol{\alpha}^0(i\omega)$$



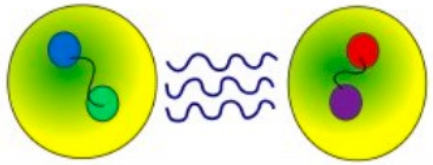
STEP 2: Short-range (SR) range-separated self-consistent screening (rsSCS)

$$\boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega) = \boldsymbol{\alpha}^0(i\omega) - \boldsymbol{\alpha}^0\mathbf{T}_{\mathrm{SR}}\boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega)$$



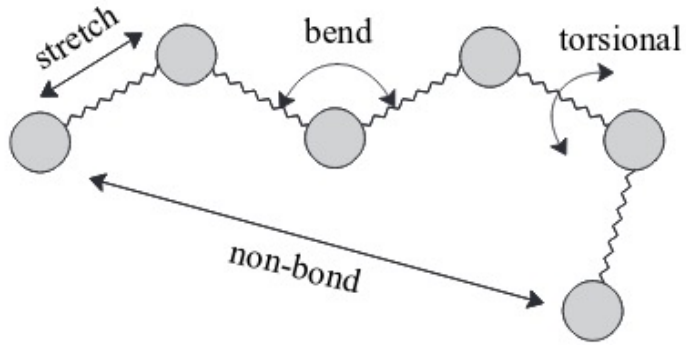
STEP 3: Long-range (LR) correlation energy from rsSCS polarizabilities

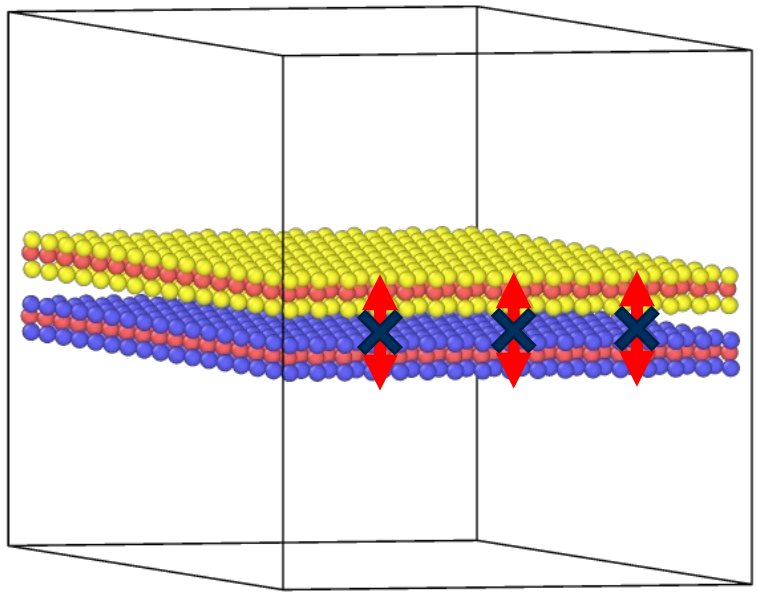
$$E_{\mathrm{c,MBD@rsSCS}} = \frac{1}{2\pi}\int_0^\infty \mathrm{d}\omega \mathrm{Tr}[\ln(\mathbf{1} - \mathbf{A}\mathbf{T}_{\mathrm{LR}})]$$



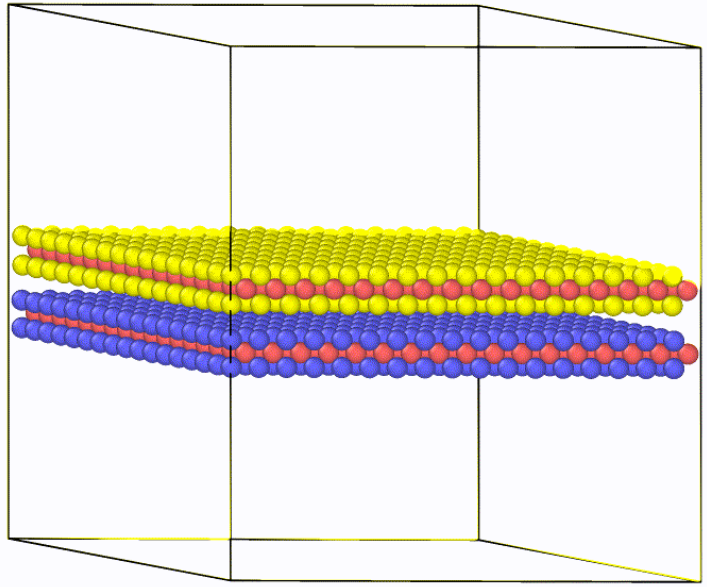
Force Field

$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{bend} + E_{el} + E_{cross} + E_{vdw} + \cdots$$





Only interlayer potential

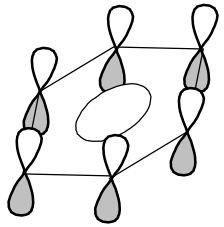


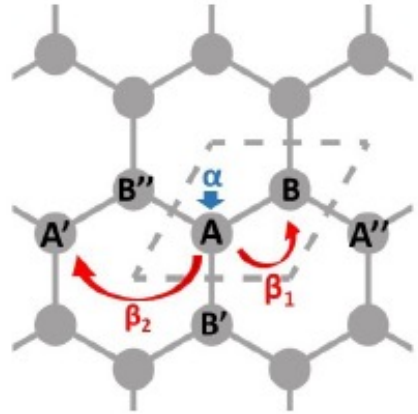
+ intralayer potential

Tight-Binding (TB) Approach

Conjugated System

- π-electron
- One-site-one-orbital model





Periodic version of "Hückel model" …

$$H = \sum_i \alpha_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} \beta_1 c_i^\dagger c_j + \sum_{\langle\langle i,j \rangle\rangle} \beta_2 c_i^\dagger c_j + H_{\mathrm{soc}}$$

$$\begin{array}{c} \\ 1 \\ 2 \\ \vdots \\ N \end{array} \begin{array}{c} \begin{array}{cccc} 1 & 2 & \cdots & N \end{array} \\ \begin{bmatrix} \alpha & \beta_i & \square & \square \\ \beta_i & \ddots & \square & \square \\ \square & \square & \ddots & \square \\ \square & \square & \square & \alpha \end{bmatrix} \end{array}$$

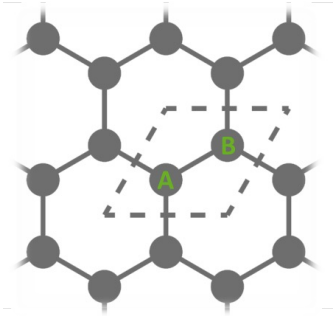
$$\begin{array}{c} \\ A \\ B \end{array} \begin{array}{c} \begin{array}{cc} A & B \end{array} \\ \begin{bmatrix} \alpha & \beta_1 + \cdots \\ \beta_1 + \cdots & \alpha \end{bmatrix} \end{array}$$

parameters???

fit parameters from the other method?

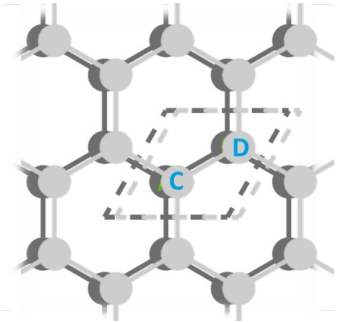
dftb slako parameters? (carbon, ppπ)

How about having a second layer?



$$\begin{array}{c} \\ A \\ B \end{array} \begin{array}{c} \begin{array}{cc} A & B \end{array} \\ \begin{bmatrix} \alpha & \beta_1 + \cdots \\ \beta_1 + \cdots & \alpha \end{bmatrix} \end{array}$$

$$H = H_{\parallel} + H_{\perp},\ H_{\perp} = \sum_{i,j,\alpha,m} \beta_{inter} C^{\dagger}_{i,\alpha,m} C_{j,\alpha,m+1}$$



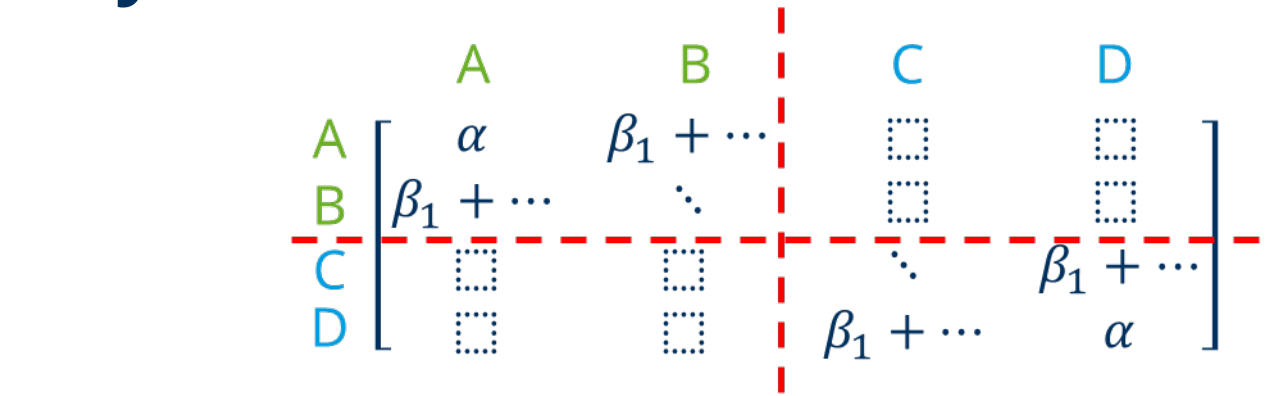
$$\begin{array}{c} \\ A \\ B \\ C \\ D \end{array} \begin{array}{c} \begin{array}{cccc} A & B & C & D \end{array} \\ \left[\begin{array}{cccc} \alpha & \beta_1 + \cdots & \square & \square \\ \beta_1 + \cdots & \ddots & \square & \square \\ \square & \square & \ddots & \beta_1 + \cdots \\ \square & \square & \beta_1 + \cdots & \alpha \end{array}\right] \end{array}$$

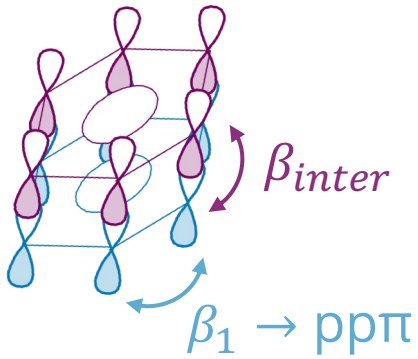
It's still a matter of how to fill the matrix, and what parameters to use…

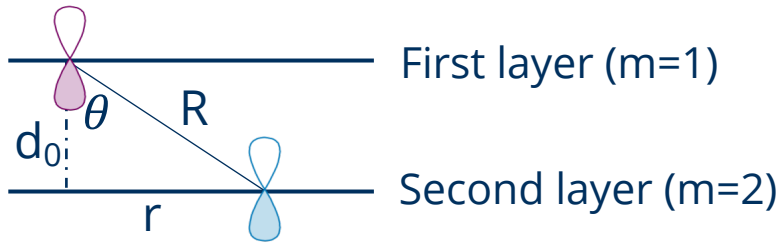
How about having a second layer?

Adding interlayer interaction:

$$H = H_{\parallel} + H_{\perp},\ H_{\perp} = \sum_{i,j,\alpha,m} \beta_{inter} C^{\dagger}_{i,\alpha,m} C_{j,\alpha,m+1}$$







$$\beta_{inter}(r) = V_{pp\sigma}(R)\frac{d_0^2}{r^2+d_0^2} = V_{pp\sigma}(R)\cos^2\theta$$

dftb slako parameters again, but ppσ.

X. Lin; D. Tománek; Phys. Rev. B, **2018**, *98*, 081410

DFT and DFTB

$$E_{\mathrm{DFT}}[\rho] = T_{\mathrm{S}}[\rho] + \int \mathrm{d}\boldsymbol{r}\, v_{ext}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho]$$

calculate directly → **RPA**

(DFTB also has pp-DFTB)

↓ expand at ρ_0

$$E_{\mathrm{DFTB}}[\rho_0 + \delta\rho] = E^0[\rho_0] + E^1[\rho_0, \delta\rho] + E^2[\rho_0, (\delta\rho)^2]$$

Include in the functional

The effect is not included in the equation!!

↓

Dispersion Correction

Dispersion Correction

Empirical correction for London dispersion

$$E_{\text{total}} = E_{\text{DFT/DFTB}} + E_{\text{disp}}$$

Options:

- Lennard-Jones $\longrightarrow$ $U_{ij}(r) = d_{ij}\left[-2\left(\frac{r_{ij}}{r}\right)^6 + \left(\frac{r_{ij}}{r}\right)^{12}\right], r \geq r_0$

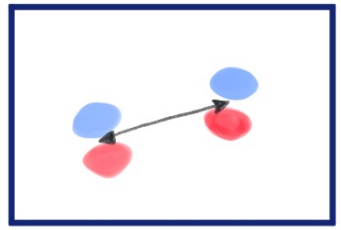
  $U_{ij}(r) = U_0 + U_1 r^5 + U_2 r^{10}, r < r_0$ $\longrightarrow$ parameter from UFF

- Grimme's correction (Dn)
- Tkatchenko-Scheffler model (TS)

} Fragment-based pairwise methods

- many-body dispersion (Mbd)
- etc...

Fragment-based pairwise methods



- Grimme's correction (Dn)

Parameters differ in different methods!!

D2: $E_{\text{disp}} = -\frac{1}{2}\sum_{i=1}^{N_{at}}\sum_{j=1}^{N_{at}}\sum_{\boldsymbol{L}}{}'\left(\frac{C_{6ij}}{r_{ij,L}^{6}}\right) f_{d,6}(r_{ij,\boldsymbol{L}})$

D3: $+\left(\frac{C_{8ij}}{r_{ij,L}^{8}}\right) f_{d,8}(r_{ij,\boldsymbol{L}})$

D4: $+\left(\frac{C_{10ij}}{r_{ij,L}^{10}}\right) f_{d,10}(r_{ij,\boldsymbol{L}}) + \mathrm{E}^{(3)}$

(D3BJ→Becke–Johnson damping)

(3-body term)

$$\left(\frac{C_{nij}}{r_{ij,L}^{n} + f_{d,n}(r_{ij,\boldsymbol{L}})}\right)$$

- Tkatchenko-Scheffler model (TS)

  similar idea but different expressing for C_6 and damping term

Many-body Dispersion (Mbd)

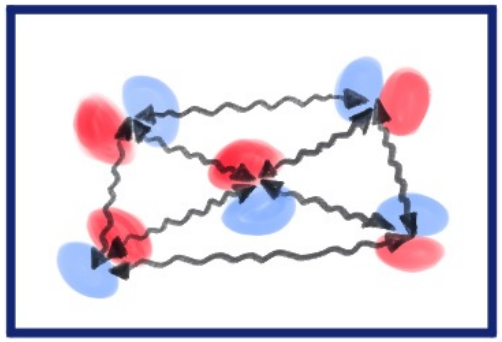
approximation from **RPA**

↓

Mbd (Empirical correction)

↑

atoms-in-molecule as in **TS**



underbinding

↓ separate short-range

MBD@rsSCS

↓ fractional ionic polarizabilities

MBD@rsSCS/FI

↓ smeared-out dipole

uMBD

nonlocal functional

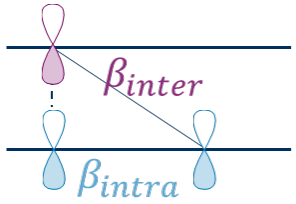
↓

MBD-NL

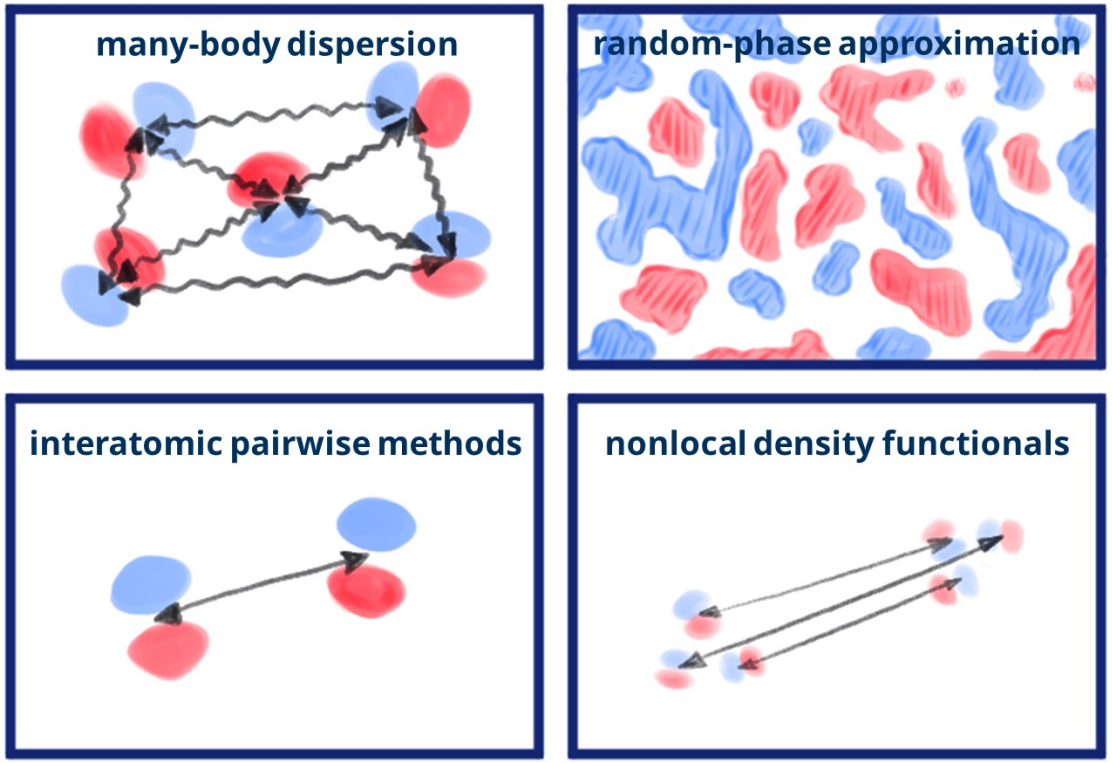
P. Xu; M. Alkan; M. S. Gordon; Chem. Rev., **2020**, *120*, 22, 12343–12356

Short Summary

- Force Field: direct term E_{vdw}
- Tight-Binding: add hoppings for interlayer sites



- DFTB/DFT:



Method	Ions/ Oxidation		DFT Package
Grimme	separate param	molecules	Vasp, Crystal, AMS, QE, QATK
TS	Yes (strong char needs paramete	molecules	FHI-aims, Vasp, QE
Mbd	Yes (strong char needs paramete	tals	FHI-aims, Vasp, ADF, QE
vdW-DFn	Yes	nd bulk solids, nge functional	FHI-aims, Vasp, QE, QATK
VV10	Yes	molecules	Vasp, AMS
RPA	Yes		FHI-aims, Vasp, AMS, QATK

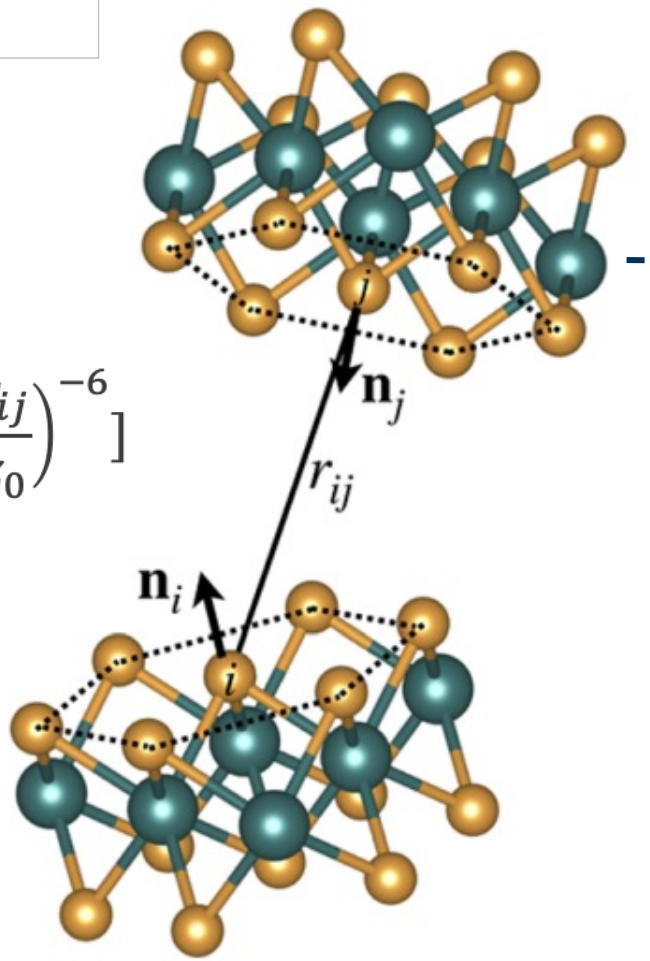
J. Hermann; R. A. DiStasio; A. Tkatchenko; *Chem. Rev.*, **2017**, *117*, 4714.

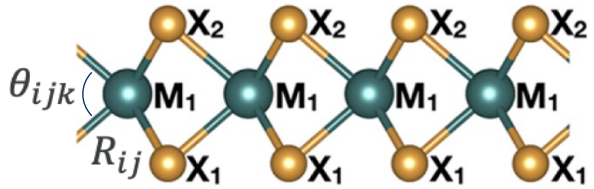
Questions?

Backup: geometry optimization in Force-field method

$$\frac{1}{2}\sum_i \sum_{j\neq i} [e^{-\lambda(r_{ij}-z_0)} V_\rho - A\left(\frac{r_{ij}}{z_0}\right)^{-6}]$$

Interlayer





$$\sum_i \sum_{j>i} \phi_2(R_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(R_{ij}, R_{ik}, \theta_{ijk})$$

bond stretching + angle bending

Intralayer

Backup: 3-body term in D4 method

$$E_{\text{disp}} = -\frac{1}{2}\sum_{i=1}^{N_{at}}\sum_{j=1}^{N_{at}}\sum_{\boldsymbol{L}}{}'\left(\frac{C_{6ij}}{r_{ij,L}^{6}}\right) f_{d,6}(r_{ij,\boldsymbol{L}}) \quad + \left(\frac{C_{8ij}}{r_{ij,L}^{8}}\right) f_{d,8}(r_{ij,\boldsymbol{L}}) \quad + \left(\frac{C_{10ij}}{r_{ij,L}^{10}}\right) f_{d,10}(r_{ij,\boldsymbol{L}}) \; + \mathrm{E}^{(3)}$$

$$E^{(3)} = -\frac{1}{2}\sum_{i=1}^{N_{at}}\sum_{j=1}^{N_{at}}\sum_{k=1}^{N_{at}} s_9 \frac{\left(3\cos\theta_i \cos\theta_j \cos\theta_k + 1\right)\sqrt{C_{6ij}C_{6ik}C_{6jk}}}{\left(r_{ij}r_{ik}r_{jk}\right)^3} f^{(3)}(r_{ij})$$

Backup: functional

Table 6.1 Perdew classification of exchange–correlation functionals

Level	Name	Variables	Examples
1	Local density	ρ	LDA, LSDA, X_α
2	GGA	ρ, $\nabla\rho$	BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
3	Meta-GGA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ	BR, B95, VSXC, PKZB, TPSS, τ-HCTH
4	Hyper-GGA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ *HF exchange*	H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, τ-HCTH-hybrid
5	Generalized RPA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ *HF exchange* *Virtual orbitals*	OEP2

Table 1. Approximate vdW Methods in Terms of Their General Properties and the Degree to Which They Incorporate Some Effects Influencing vdW Interactions

Method[a]	Hybridization, coordination and chemical environment	Ions/oxidation states	Accuracy of C_6 coefficients of small organic molecules	Polarization in materials	Nonadditive polarizability
D1/D2	No	No	20%	No	No
D3	Only coord. effects	Requires separate parametrization	5−10%	No	No
XDM	Yes	Yes, but strong charge transfer requires parametrization	12%	No	Short-range
TS	Yes	Yes, but strong charge transfer requires parametrization	5.5%	No	Short-range
MBD	Yes	Yes, but strong charge transfer requires parametrization	6.2%	Yes	All ranges
vdW-DF1	Yes	Yes	20%	No	Short-range
vdW-DF2	Yes	Yes	60%	No	Short-range
VV10	Yes	Yes	12%	No	Short-range
RPA	Yes	Yes	10%	Yes	All ranges

Method	Anisotropy in vdW parameters	Many-body vdW energy	Computational cost	Amount of fitting	Applicability
D1/D2	No	No	Very low	High	Small molecules
D3	No	Three-body Axilrod−Teller can be added	Very low	Intermediate	Small and midsize molecules
XDM	No	Three-body Axilrod−Teller can be added	Low	Low	Small and midsize molecules
TS	No	Three-body Axilrod−Teller can be added	Low	Low	Small and midsize molecules
MBD	Yes	Infinite order	Low	Low	Broadly applicable. Take care with metals
vdW-DF1	No	No	Intermediate	None	Small molecules and bulk solids, sensitive to exchange functional
vdW-DF2	No	No	Intermediate	Low	Small molecules and bulk solids, sensitive to exchange functional
VV10	No	No	Intermediate	Low	Small and midsize molecules
dRPA	Yes	Infinite order	High	None	Broadly applicable

[1] J. Hermann, R. A. DiStasio, A. Tkatchenko, *Chem. Rev.* **2017**, *117*, 4714.

Backup: Coarse-grained MBD based on RPA and TS

$$E_c^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty du\,\mathrm{Tr}\left[\ln\left(1-\chi_0(\boldsymbol{r},\boldsymbol{r}',u)v(\boldsymbol{r},\boldsymbol{r}')\right)-\chi_0(\boldsymbol{r},\boldsymbol{r}',u)v(\boldsymbol{r},\boldsymbol{r}')\right]$$

approximated

- MBD@rsSCS

$$E_c = -\frac{1}{2\pi}\int_0^\infty du\,\mathrm{Tr}\left[\ln\left(1-\alpha_{\mathrm{eff}}(iu)T_{ij}\right)\right]$$

dynamic polarizability

long-range dipole tensor

an atoms-in-molecule approach as employed in TS