

vdW-DF in STATE

Ikutaro Hamada

Input variables (section &VDW-DF ... &END)

- VDW-DF/VDW-DF 2
 - Choice of correlation energy functional
 - Default: VDW-DF
- EXCHANGE
 - Choice of exchange energy functional
 - | revPBE | RPBE | PBE | C09 | optPBE | OptB88 | (latter two are not fully tested)
 - Default for VDW-DF: revPBE
 - Default for VDW-DF2:PW86R
- CUTOFF
 - Interaction cutoffs (three-dimensional array) along the directions of basic lattice vectors (in Bohr)
 - Default: $0.5 \cdot |\mathbf{a}_1|$, $0.5 \cdot |\mathbf{a}_2|$, $0.5 \cdot |\mathbf{a}_3|$
- EXCHANGE-ONLY
 - Calculate exchange-only total energy
 - No default for the exchange energy functional

Choice of interaction cutoff

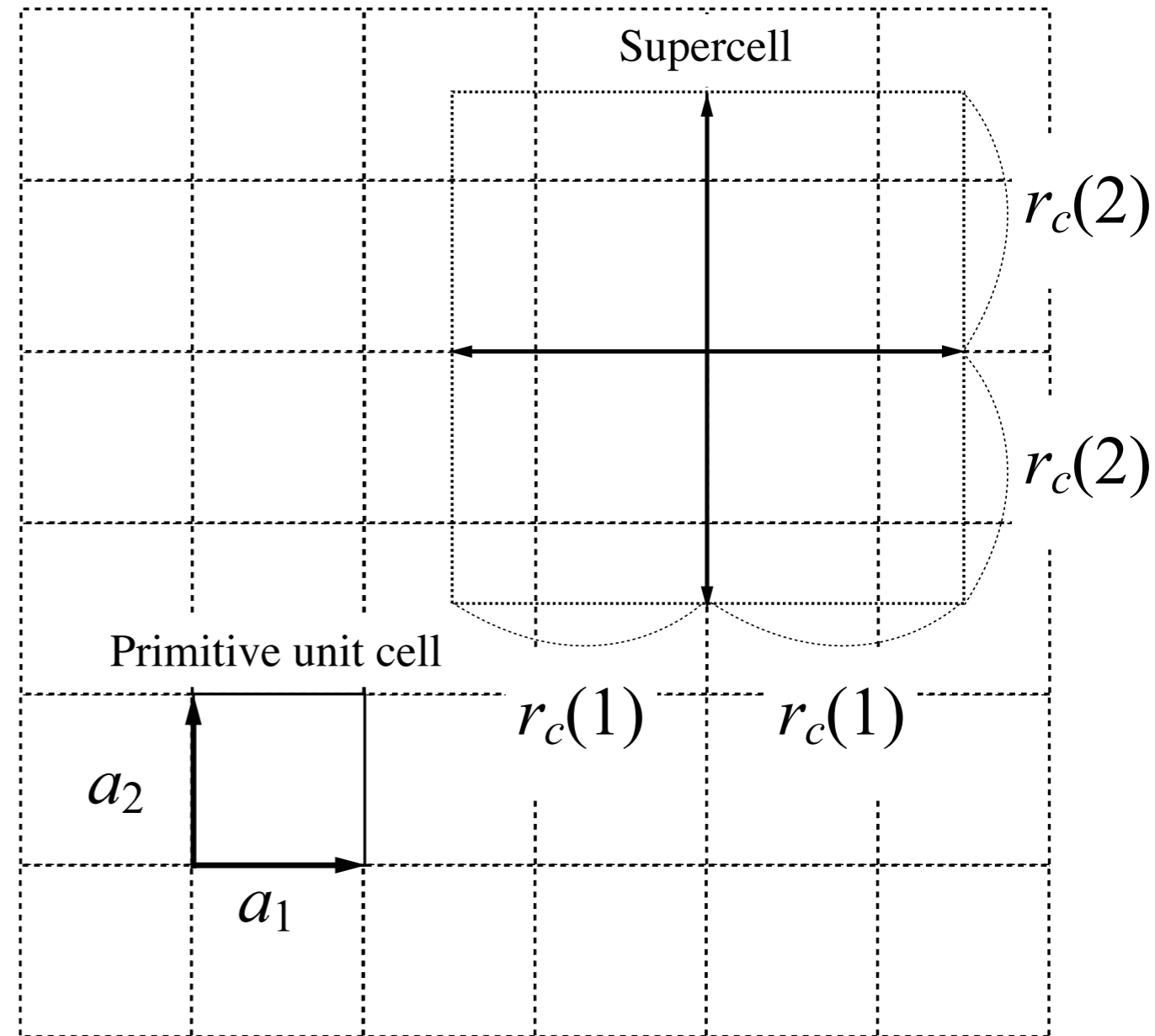
In a calculation of the nonlocal correlation energy for a periodic system, one needs to use a supercell which is defined by the interaction distance cutoff r_c (keyword CUTOFF(1:3)).

The cutoff distance must be chosen such that the nonlocal correlation energy is converged with respect to the cutoff distance

Sometimes we write “cutoff radius”, but the keyword CUTOFF is used to specify the interaction cutoff distance r_c in the nonlocal correlation (the equation below), or to specify the range of real-space integration in the nonlocal correlation energy in the directions along the basic lattice vectors

In modeling a finite system with supercell approach, CUTOFF should be chosen such that interactions with periodic images are eliminated.

$$E_c^{\text{nl}} = \int_{\text{unit cell}} n(\mathbf{r}_1) d\mathbf{r}_1 \int_{r_c} d\mathbf{r}_2 \phi(q_1, q_2, r_{12}) n(\mathbf{r}_2)$$



$$\text{CUTOFF}(1:3) = r_c(1:3)$$

Calculation procedure

- Self-consistent field (SCF) calculation within GGA (ICOND=0 or 1)
- Post-GGA (non-SCF) vdW-DF calculation (ICOND=26)
 - kernel.dat (included in the source directory) is necessary, which is a tabulated vdW kernel Φ
- Post process: Calculation of interaction energy or binding energy (see below)

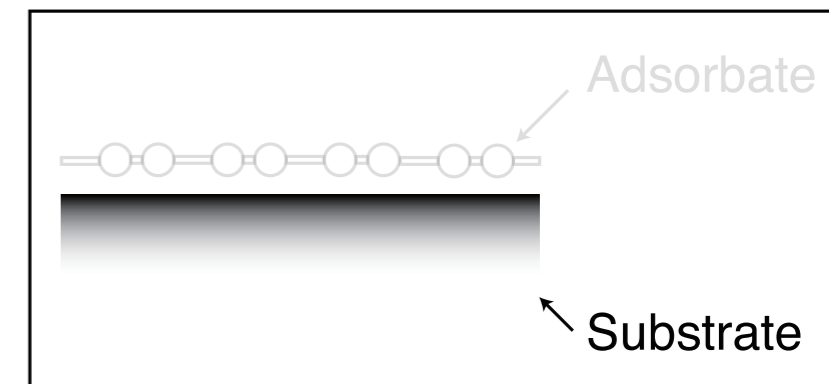
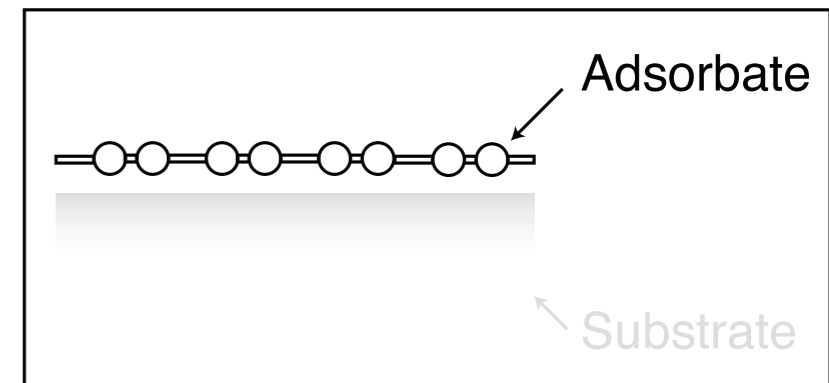
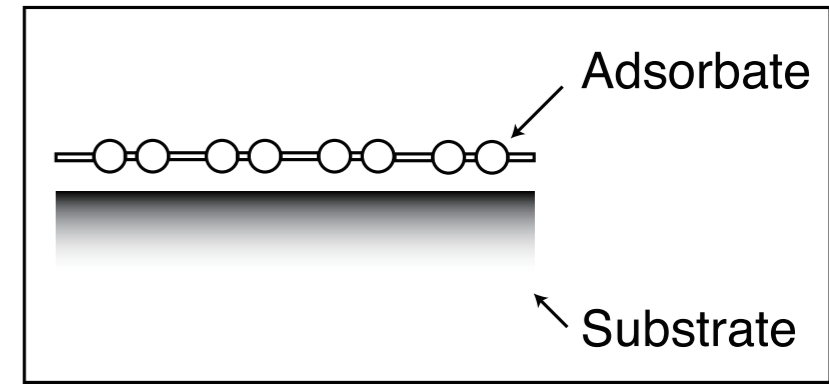
Calculation of binding energy in vdW-DF

1. Calculate the vdW-DF total energy of the adsorption system (E_{tot})
2. Calculate the vdW-DF total energy of adsorbate at exactly the same position and with exactly the same unit cell in the adsorption system [$E_{\text{tot}}(\text{ads})$]
3. Calculate the vdW-DF total energy of substrate at exactly the same position and with exactly the same unit cell in the adsorption system [$E_{\text{tot}}(\text{sub})$]
4. calculate the binding energy $E_b = E_{\text{tot}} - E_{\text{tot}}(\text{ads}) - E_{\text{tot}}(\text{sub})$
5. (optional) in a non-SCF vdW-DF calculation, relaxation energy is calculated in GGA (PBE or revPBE), i.e. after the steps 2, 3, isolated substrate and adsorbate are relaxed, and the energy difference between relaxed and unrelaxed fragments are added to the binding energy calculated in the step 4

NOTE: the error in the absolute value of vdW-DF total energy is large, therefore the above procedure is mandatory to cancel the error in the total energy and to calculate accurate binding energy

Reference

1. S. D. Chakarova-Kack et al., PRL 96, 146107 (2006).
2. E. Ziambaras and E. Schroder, PRB 68, 064112 (2003).
3. K. Johnston, et al., PRB 77, 121404(R) (2008).
4. I. Hamada, K. Lee, and Y. Morikawa, PRB 81, 115452 (2010).



Calculation of binding energy of solid in vdW-DF: an example of graphite



Convergence of adsorption energy with respect to cutoff distance

