# *van der Waals forces in density functional theory*

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(Many-body) Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

(Many-body) wave function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_{N_\mathrm{e}}; \mathbf{R}_1, \mathbf{R}_2, \cdots \mathbf{R}_{N_\mathrm{I}})$$

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Electron density

$$n(\mathbf{r}) = N_{\mathrm{e}} \int \cdots \int d\mathbf{r}_2 \cdots d\mathbf{r}_{N_{\mathrm{e}}} |\Psi_{\mathbf{R},\mathbf{R}_2,\cdots,\mathbf{R}_{N_{\mathrm{I}}}}(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_{N_{\mathrm{e}}})|^2$$

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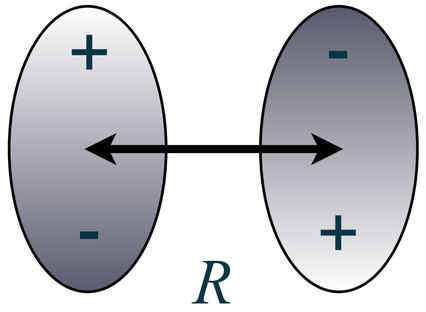
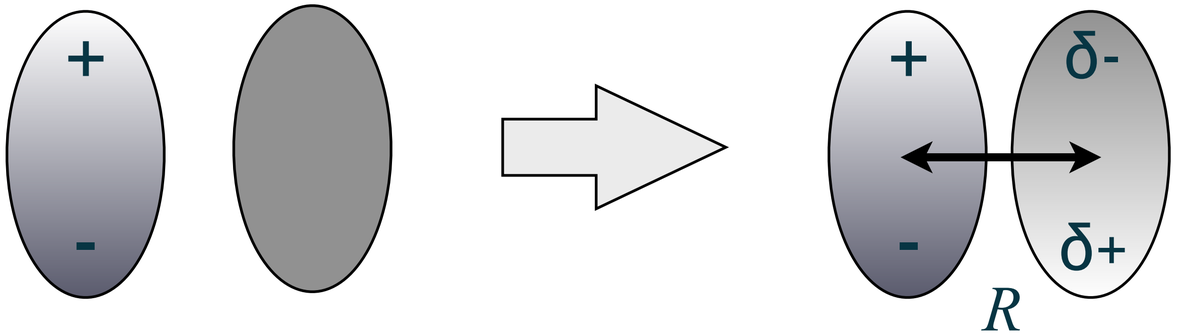
→ Semiempirical correction (DFT-Dx, TS-vdW, XDM, LRD, …)

# Van der Waals forces

Dipole-dipole interaction
(Keesom force)




Dipole-induced dipole interaction
(Debye force)




Induced dipole-induced dipole interaction
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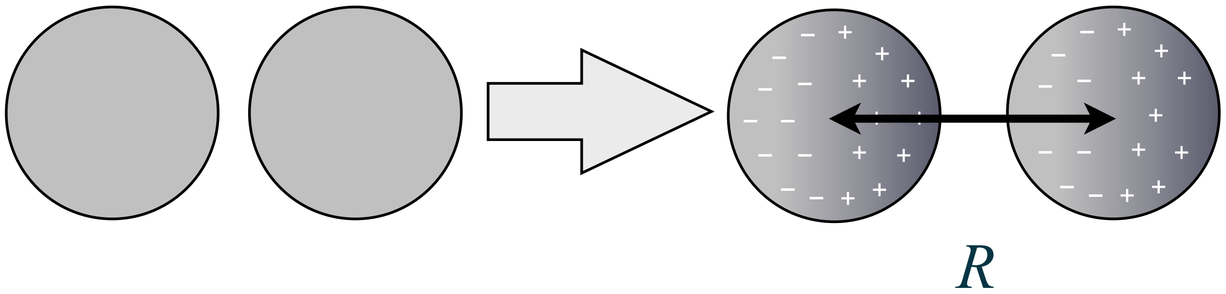

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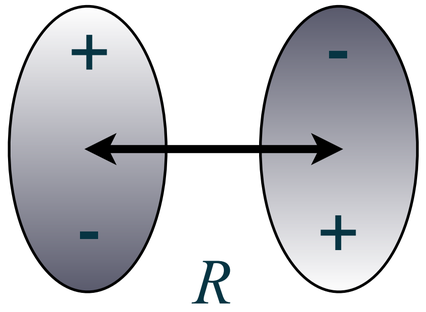
$$1/R^3$$

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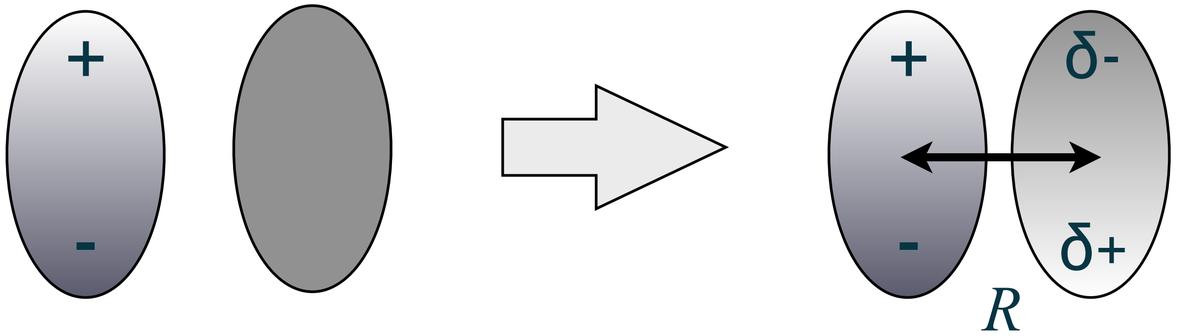


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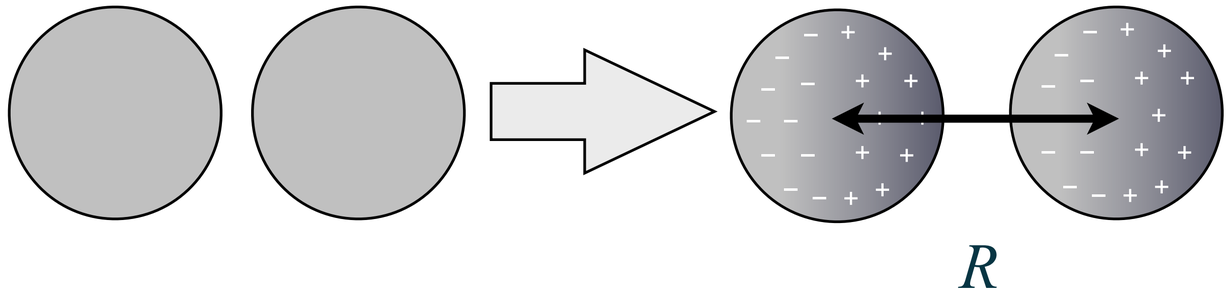

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Dipole-dipole interaction
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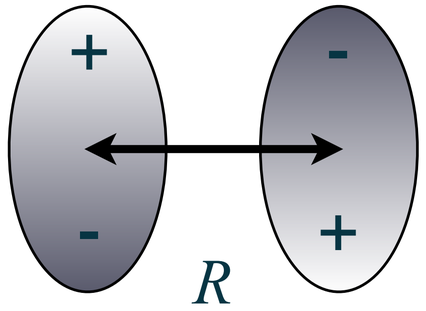
☺ LDA/GGA works

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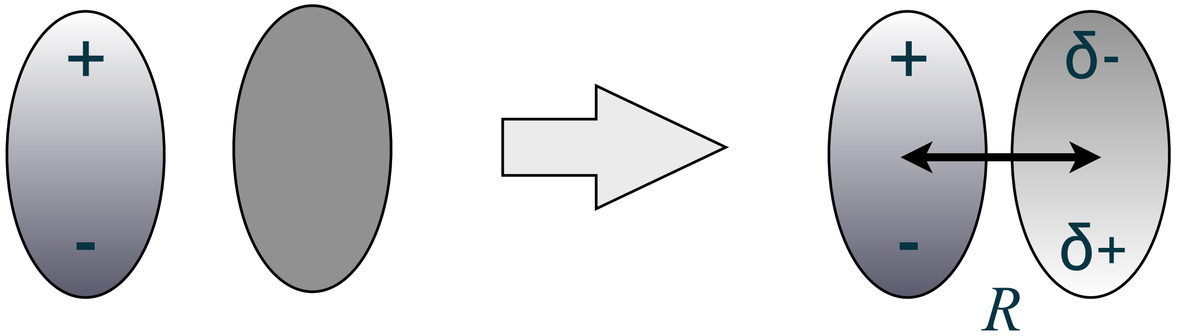


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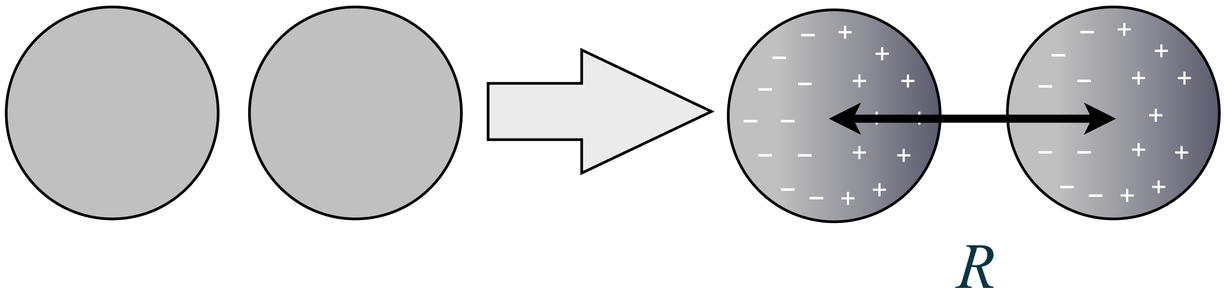

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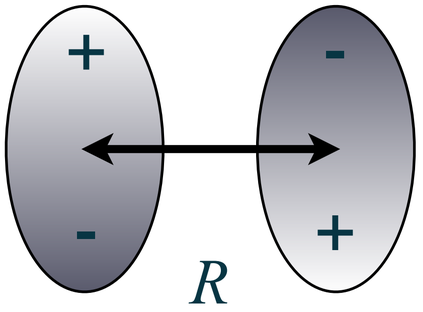


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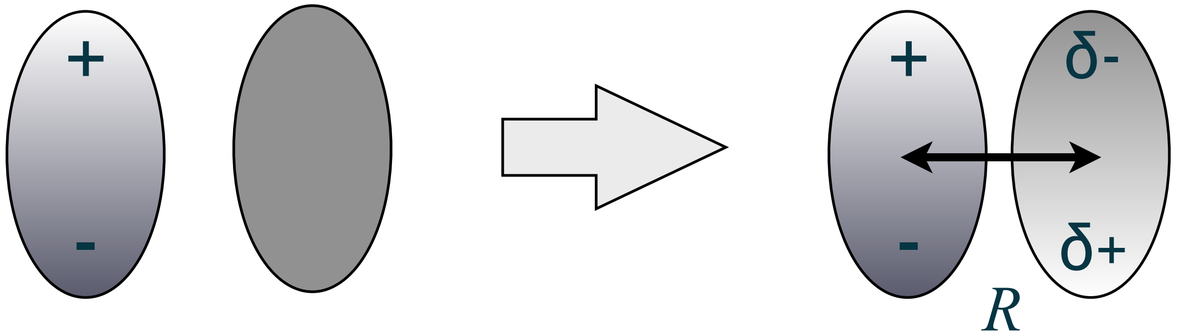


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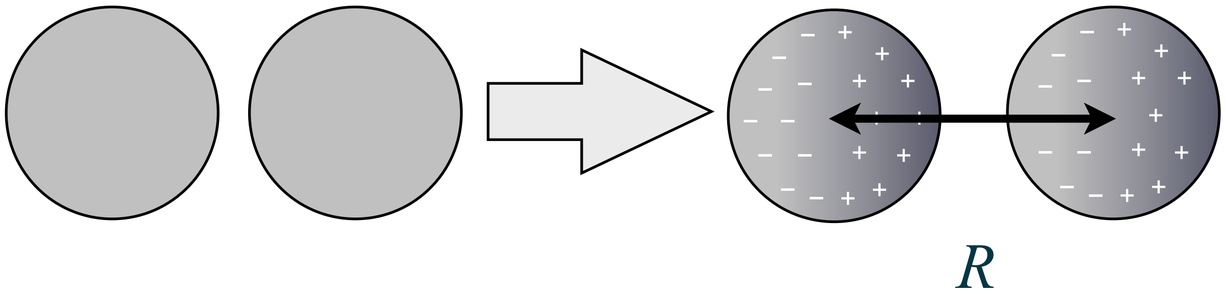

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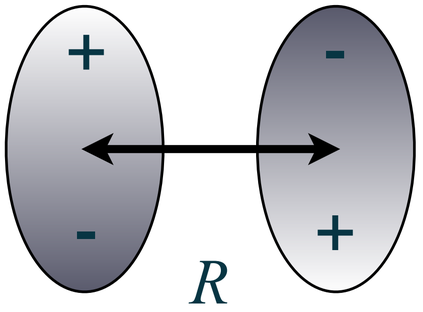


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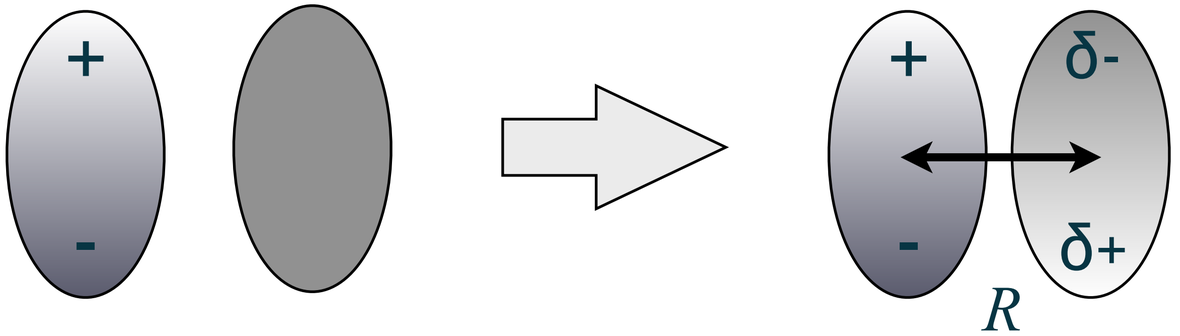


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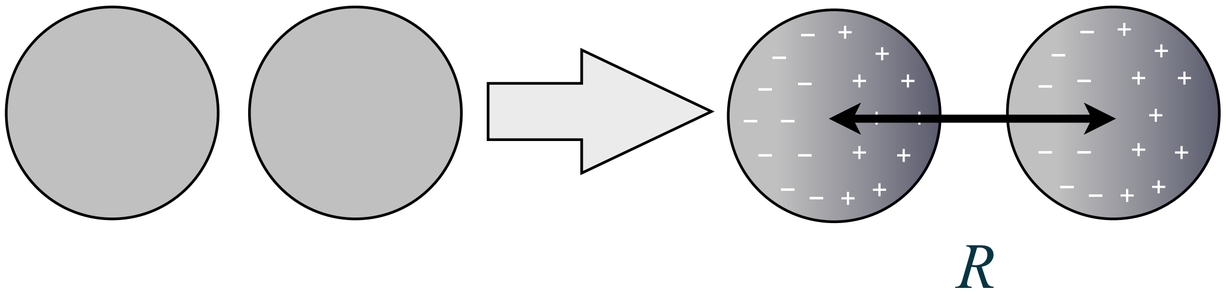

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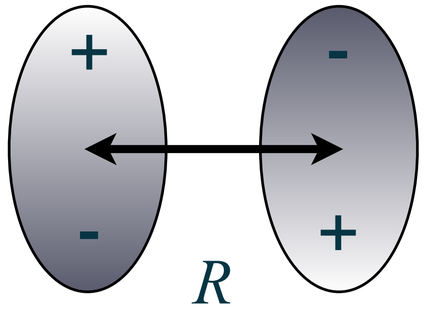


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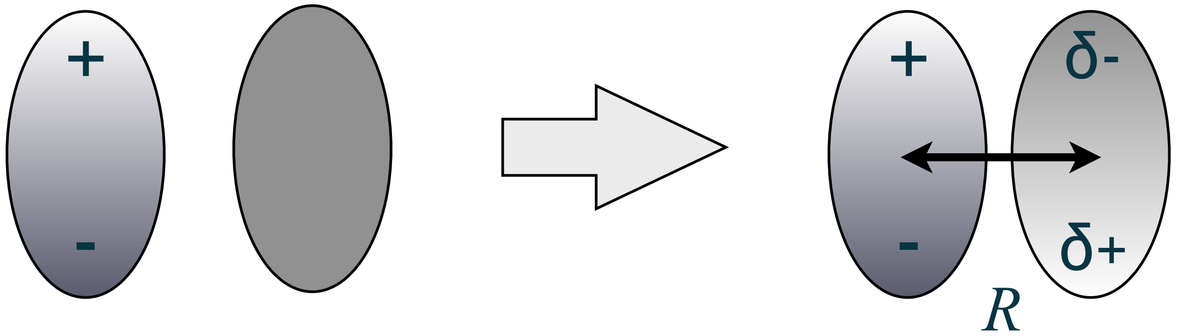


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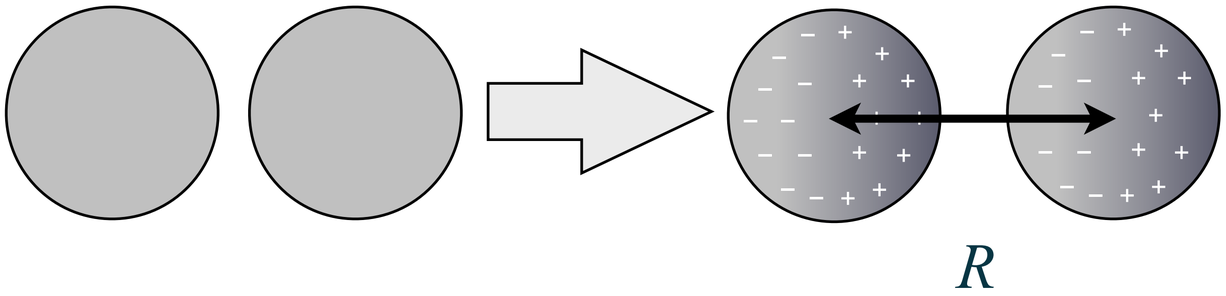


$$1/R^6$$

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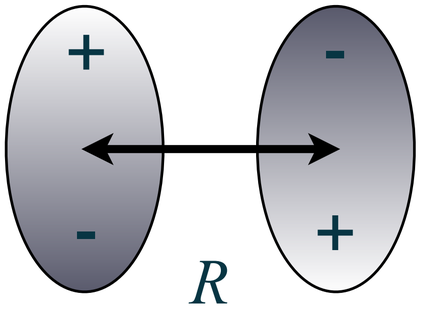


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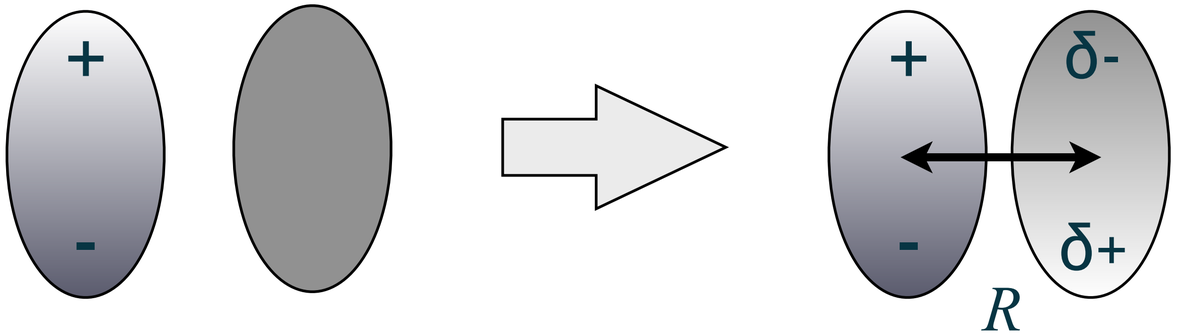


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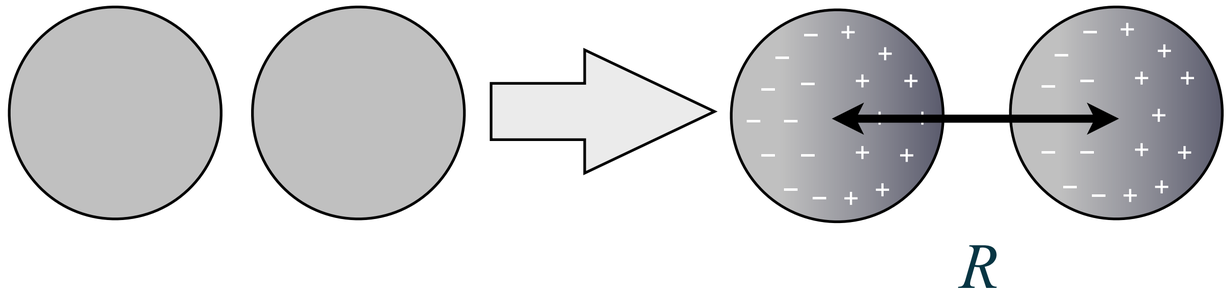


# Simple derivation of the dispersion interaction

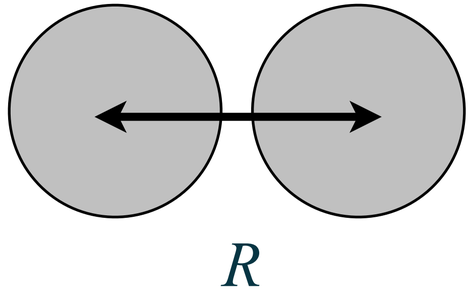
A pair of neutral atoms

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

$$\hat{H}^{(0)} = \hat{H}_1 + \hat{H}_2$$

$$\hat{H}_i = -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{eff}}(\hat{\mathbf{r}}_i)$$

$$\hat{H}' = V(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2; \hat{\mathbf{R}})$$



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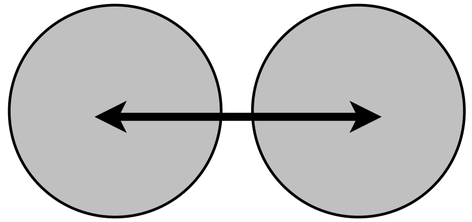

$R$

$R \gg 1$

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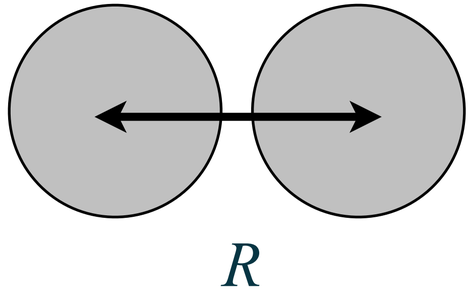


Unperturbed state (non-interacting atoms)

$$E^{(0)} = 2E_0,\ \hat{H}_i|\psi_0\rangle = E_0|\psi_0\rangle$$

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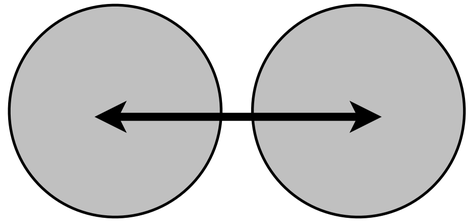

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First-order energy

$$E^{(1)} = 0$$

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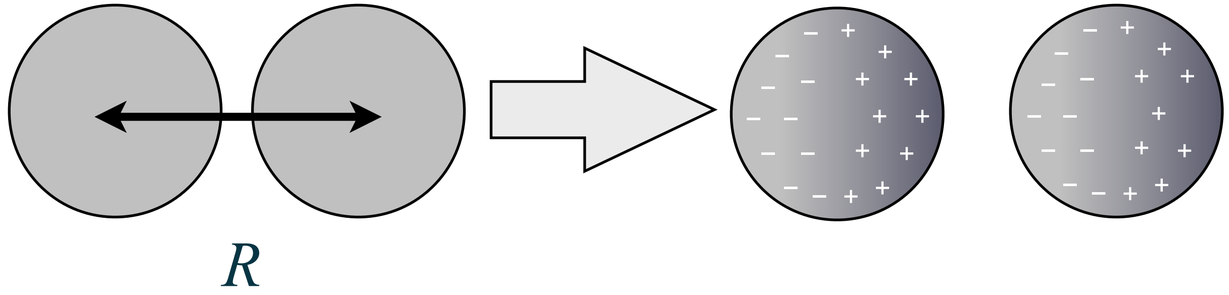


$$R \gg 1$$

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First-order energy

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Second-order energy

$$E^{(2)} \propto 1/R^6$$

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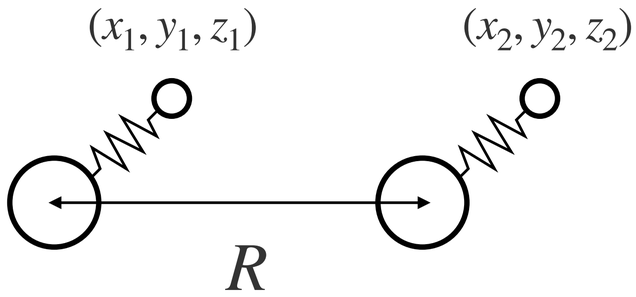
A pair of model hydrogen atoms



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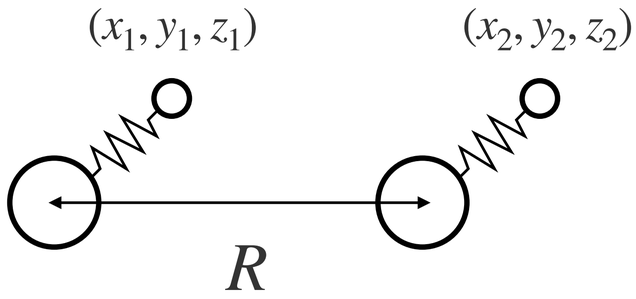
$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

$$\hat{H}^{(0)} = \frac{\hat{p}_1^2}{2m} + \frac{1}{2}\hbar\omega\hat{x}_1^2 + \frac{\hat{p}_2^2}{2m} + \frac{1}{2}\hbar\omega\hat{x}_2^2$$



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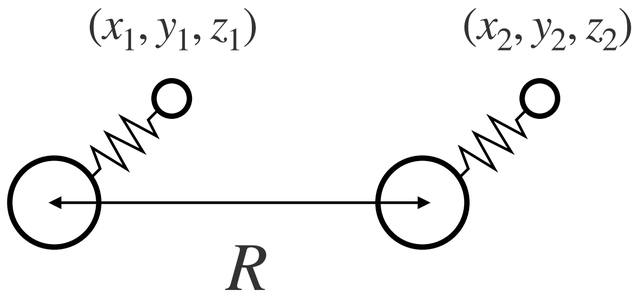
$$\hat{H}' \approx e^2 \frac{x_1 x_2 + y_1 y_2 - 2 z_1 z_2}{R^3}$$




$$R \gg 1$$

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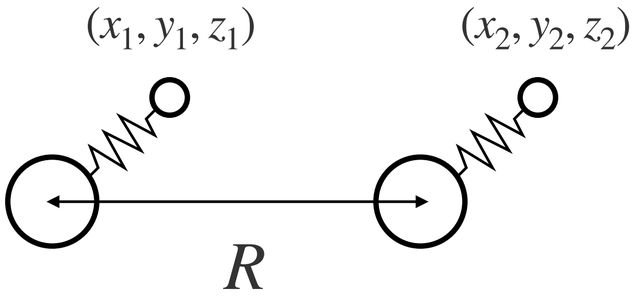


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$$\hat{H}' \approx e^2 \frac{x_1 x_2 + y_1 y_2 - 2 z_1 z_2}{R^3}$$

$$E^{(2)} = -\frac{3\hbar\omega}{4}\left(\frac{e^2}{m\omega^2}\right)\frac{1}{R^6}$$

Dispersion interaction is inverse proportional to $R^6$

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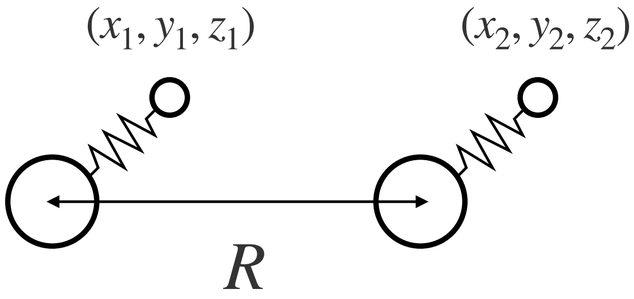


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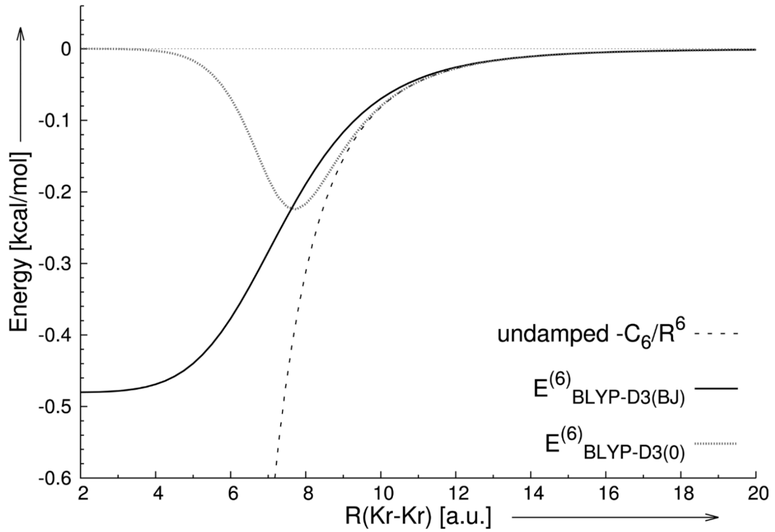
Dispersion interaction originates from nonlocal many-body interaction

# Semiempirical dispersion corrected DFT

Grimme's DFT-D2

$$E_{\mathrm{DFT-D}} = E_{\mathrm{LDA/GGA}} - \frac{1}{2} s_6 \sum_{I \neq J} f_{\mathrm{dmp}}(|R_I - R_J|) \frac{C_6^{A(I)B(J)}}{|R_I - R_J|^6}$$

Damping function $f_{\mathrm{dmp}}$




Grimme, *et al*., C*hem. Rev*. **116**, 5105 (2016).



Grimme, Antony, Ehrlich, & Krieg, *J. Chem. Phys*. **132**, 154104 (2010).

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$$+(\text{higher term})$$

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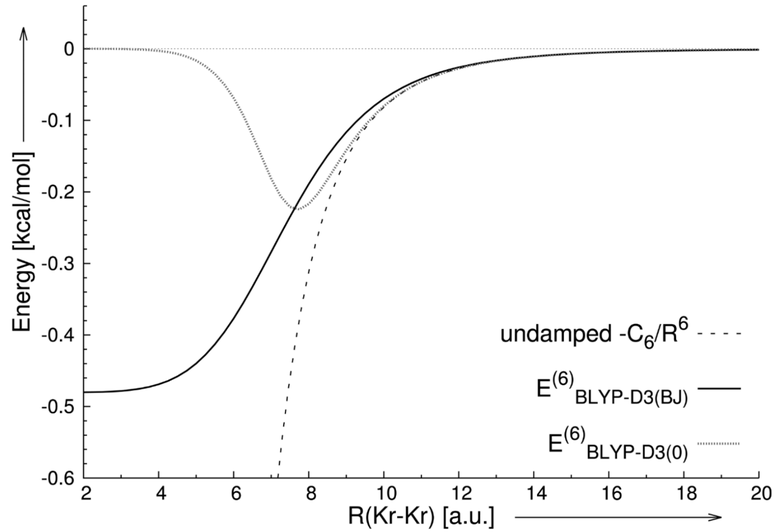


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# Semiempirical dispersion corrected DFT

Grimme's DFT-D3

$$E_{\mathrm{DFT-D}} = E_{\mathrm{LDA/GGA}} - \frac{1}{2} s_6 \sum_{I \neq J} f_{\mathrm{dmp}}(|R_I - R_J|) \frac{C_6^{A(I)B(J)}}{|R_I - R_J|^6}$$

$$+(\text{higher term})$$

Dispersion coefficient from the Casimir–Polder formula

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty d\omega \alpha^A(i\omega) \alpha^B(i\omega)$$



Grimme, Antony, Ehrlich, & Krieg, *J. Chem. Phys*. **132**, 154104 (2010).

# Semiempirical dispersion corrected DFT

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Dispersion coefficient from the modified Casimir–Polder formula

$$C_{6,\mathrm{ref}}^{AB} = \frac{3}{\pi} \int_0^\infty d\omega \frac{1}{m} \left[ \alpha^{\mathrm{A}_m\mathrm{H}_n}(i\omega) - \frac{n}{2} \alpha^{\mathrm{H}_2}(i\omega) \right] \times \frac{1}{k} \left[ \alpha^{\mathrm{B}_k\mathrm{H}_l}(i\omega) - \frac{l}{2} \alpha^{\mathrm{H}_2}(i\omega) \right]$$



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System specific dispersion coefficient via the coordination number (CN)

$$C_6^{\mathrm{AB}}(\mathrm{CN}^A, \mathrm{CN}^B) = \frac{\sum_I^{N_A} \sum_J^{N_B} C_{6,\mathrm{ref}}(\mathrm{CN}^A, \mathrm{CN}^B) L_{IJ}}{\sum_I^{N_A} \sum_I^{N_B} L_{IJ}}$$

$$L_{IJ} = \exp\left[ -4 \left( \left( \mathrm{CN}^A - \mathrm{CN}_I^A \right)^2 + \left( \mathrm{CN}^B - \mathrm{CN}_J^B \right)^2 \right) \right]$$

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☹ Accuracy can depend on DFT XC functional

(e.g., PBE+D3 tends to overestimate the binding energy)



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# van der Waals density functional (vdW-DF)

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys*. **78**, 066501 (2015).

# van der Waals density functional (vdW-DF)

Nonempirical exchange-correlation functional

No orbital dependency - pure density functional

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XC functional — sum of semilocal exchange-correlation and nonlocal correlation

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{sl}} + E_{\mathrm{c}}^{\mathrm{nl}}$$

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# van der Waals density functional (vdW-DF)

XC energy from the adiabatic connection fluctuation dissipation theorem

$$E_{\mathrm{xc}} = -\int_0^1 \frac{d\lambda}{\lambda} \int \frac{du}{2\pi} \iint d\mathbf{r} d\mathbf{r}' \chi^{\lambda}(\mathbf{r}, \mathbf{r}'; iu) \frac{\lambda e^2}{|\mathbf{r} - \mathbf{r}'|} - E_{\mathrm{self}}$$

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

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Density-density response function at $\lambda$

Coulomb kernel $V(\mathbf{r}, \mathbf{r}')$ at $\lambda$

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Density-density response function at $\lambda$

Coulomb kernel $V(\mathbf{r}, \mathbf{r}')$ at $\lambda$

- Full potential approximation — Exact at the van der Waals asymptote
- Second-order expansion in the response function
- Plasmon-pole approximation to the response function

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

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XC energy from the adiabatic connection fluctuation dissipation theorem

$$E_{\mathrm{xc}} = -\int_0^1 \frac{d\lambda}{\lambda} \int \frac{du}{2\pi} \mathrm{tr}\left[\tilde{\chi}^{\lambda}(iu) V^{\lambda}\right] - E_{\mathrm{self}}$$

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Full potential approximation (FPA)

$$\tilde{\chi} \equiv \tilde{\chi}^{\lambda=1}$$

$$E_{\mathrm{xc}}^{\mathrm{FPA}} = \int \frac{du}{2\pi} \mathrm{tr}\left[\ln\left(1 - \tilde{\chi}V\right)\right] - E_{\mathrm{self}}$$

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LDA-like approximation to local XC to extract the nonlocal correlation

$$E_{\mathrm{c}}^{\mathrm{nl}} = E_{\mathrm{xc}}^{\mathrm{FPA}} - E_{\mathrm{xc}}^{\mathrm{FPA}}(\mathrm{HEG})$$

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015).

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LDA-like approximation to local XC to extract the nonlocal correlation

$$E_{\mathrm{c}}^{\mathrm{nl}} = \int \frac{du}{2\pi}\mathrm{tr}\left[\ln\left(1-\tilde{\chi}V\right) - \ln\epsilon\right]$$

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# van der Waals density functional (vdW-DF)

Nonlocal correlation in terms of the dielectric function $\epsilon$

$$E_{\mathrm{c}}^{\mathrm{nl}} = \int \frac{du}{2\pi} \mathrm{tr} \left[ \ln \left( -\frac{1}{4\pi} \nabla \cdot \epsilon \nabla V \right) - \ln \epsilon \right]$$

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# van der Waals density functional (vdW-DF)

Nonlocal correlation in terms of the dielectric function $\epsilon$

$$E_c^{nl} = \int \frac{du}{2\pi} \mathrm{tr} \left[ \ln \left( -\frac{1}{4\pi} \nabla \cdot \epsilon \nabla V \right) - \ln \epsilon \right]$$

Second-order expansion wrt $S$

$$S = 1 - \epsilon^{-1}$$

$$E_c^{nl} \approx \int \frac{du}{4\pi} \mathrm{tr} \left[ S^2 - \left( \frac{\nabla S \cdot \nabla V}{4\pi} \right)^2 \right]$$

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# van der Waals density functional (vdW-DF)

Plasmon-pole approximation to $S$

$$S(\mathbf{r},\omega) = \frac{\omega_p^2(\mathbf{r})}{\omega_{\mathbf{q}}^2(\mathbf{r}) - \omega^2}$$

$$\omega_p(\mathbf{r}) = \sqrt{4\pi n(\mathbf{r})}$$

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Dispersion function

$$\omega_{\mathbf{q}} = \frac{q^2}{2m}\frac{1}{h[q/q_0]}$$

$$h(x) = 1 - e^{-\frac{4\pi}{9}x^2}$$

$$q_0(\mathbf{r}) = -\frac{4\pi}{3}\varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}(n(\mathbf{r})) - \frac{Z_{ab}}{9}s^2(\mathbf{r})k_F(\mathbf{r})$$

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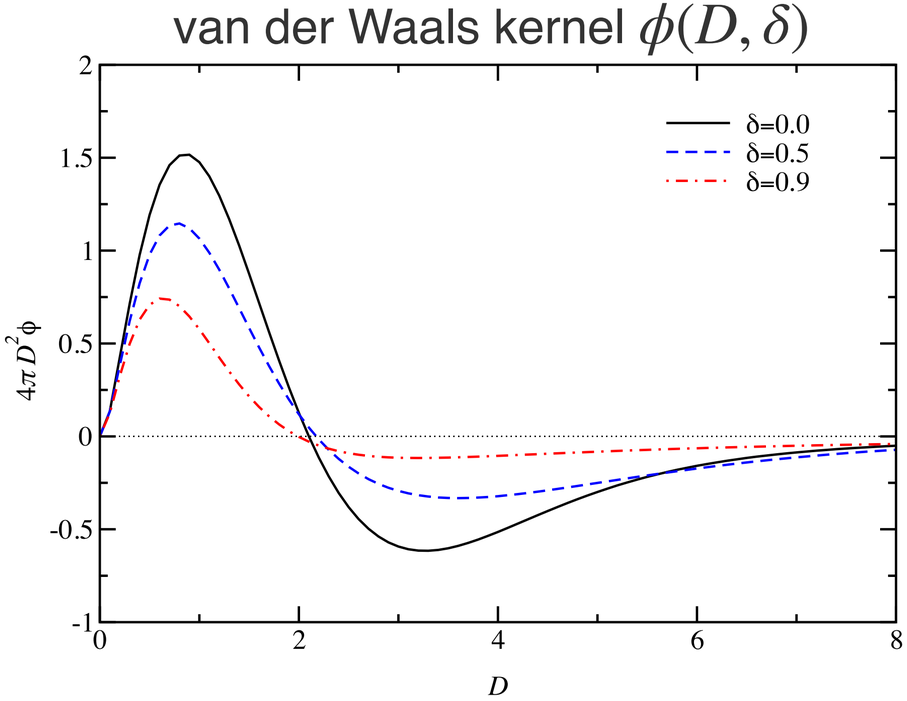
# van der Waals density functional (vdW-DF)

Nonlocal correlation

$$E_c^{nl} = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|)n(\mathbf{r}_2)$$

$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

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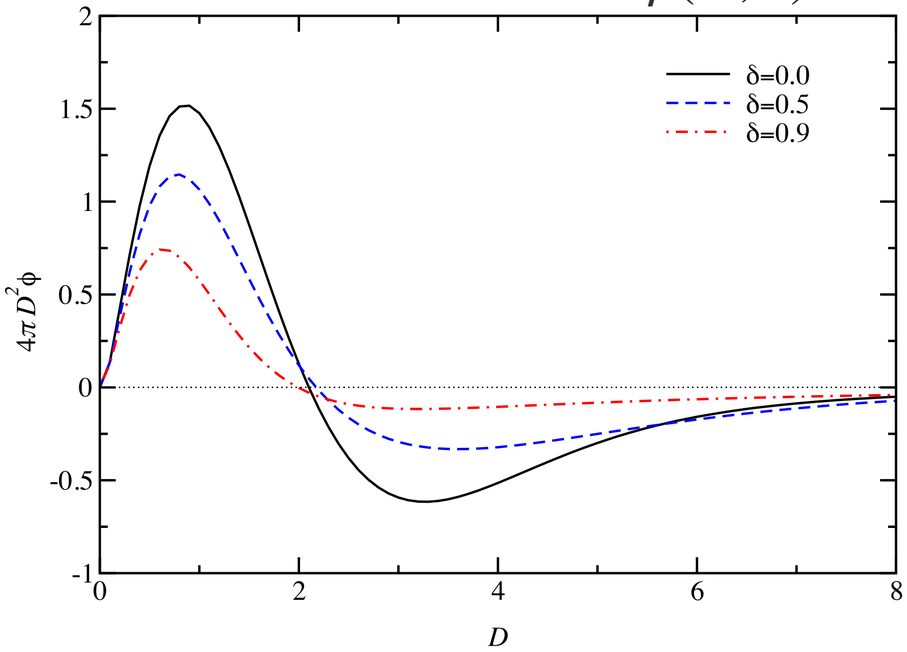
$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

$$|r_1 - r_2| \to \infty$$

$$\phi \to -\frac{3}{2}\frac{1}{|r_1 - r_2|^6}\frac{1}{q_0^2(\mathbf{r}_1)q_0^2(\mathbf{r}_2)[q_0^2(\mathbf{r}_1) + q_0^2(\mathbf{r}_2)]}$$

van der Waals kernel $\phi(D, \delta)$

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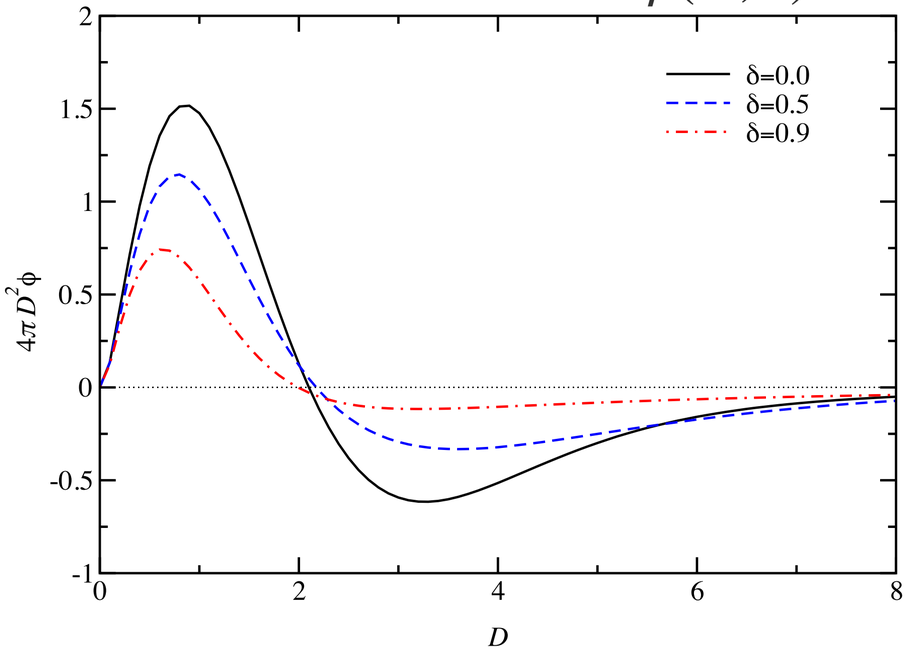
Uniform (homogeneous) limit

$$E_c^{nl} \to 0$$

van der Waals kernel $\phi(D, \delta)$

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XC functional in vdW-DF

$$E_{\mathrm{xc}}^{\mathrm{vdW-DF}} = E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{LDA}} + E_{\mathrm{c}}^{\mathrm{nl}}$$

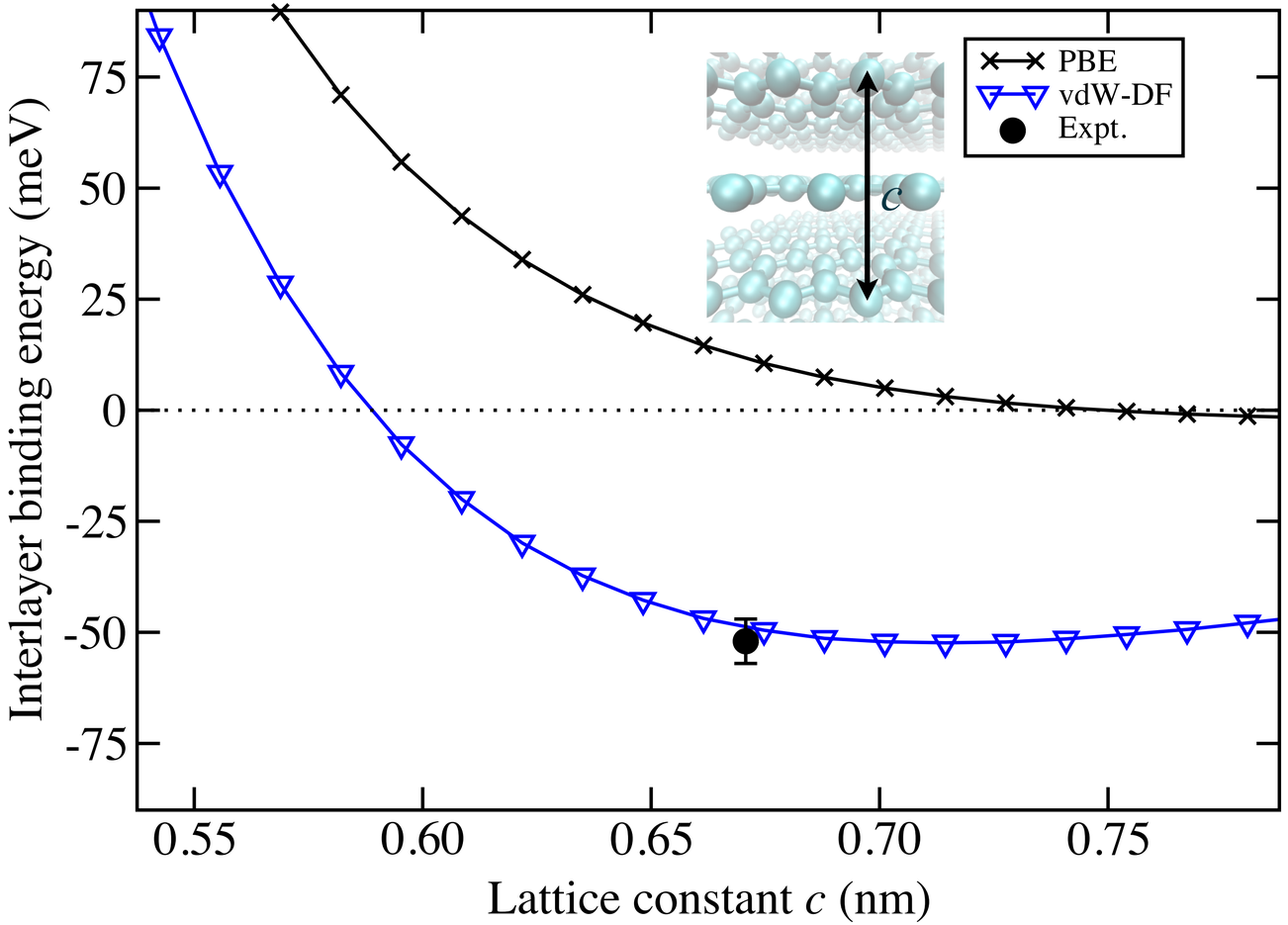
$$E_{\mathrm{c}}^{\mathrm{nl}} = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|)n(\mathbf{r}_2)$$

$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

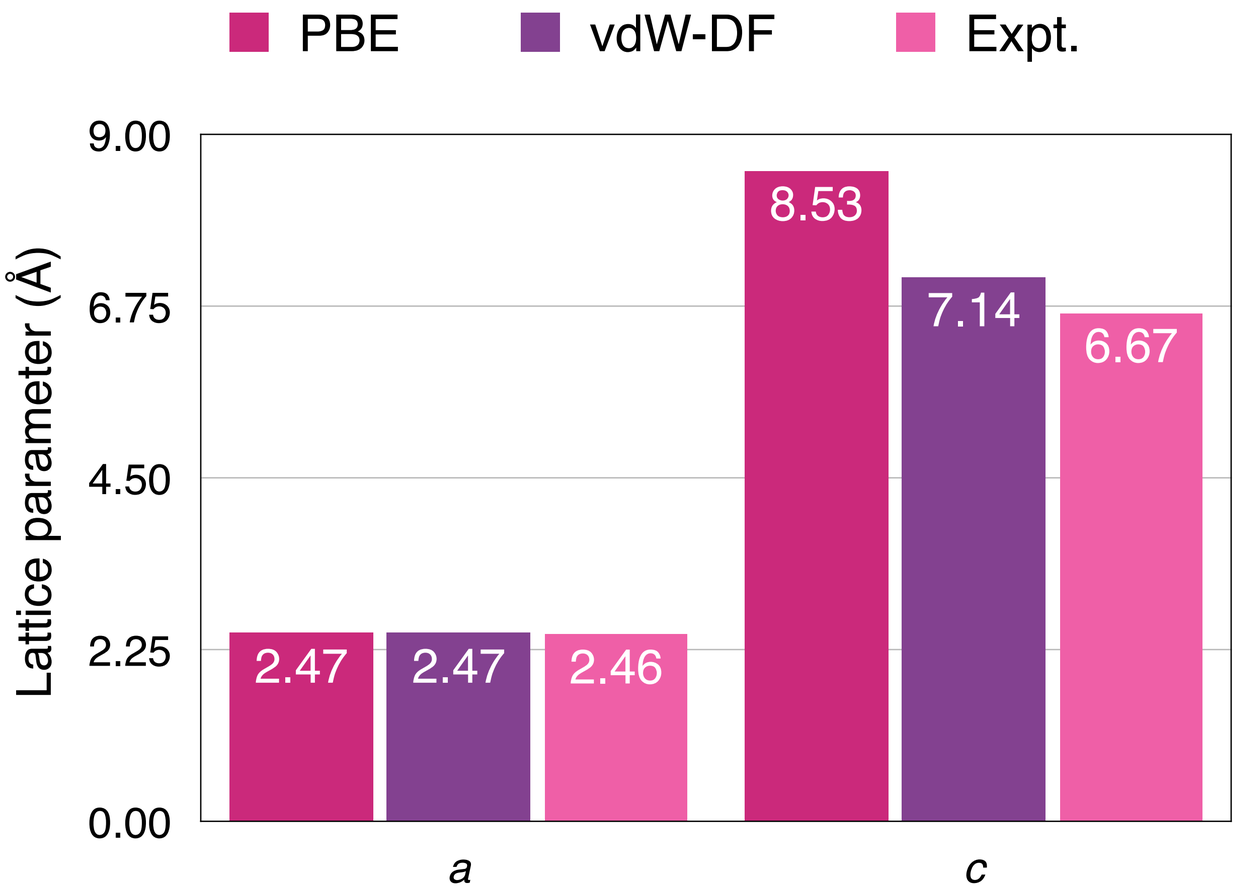
- ☻ No empirical parameters
- ☻ Seamless description of covalent and van der Waals bondings

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015).

# Graphite


PBE
vdW-DF
Expt.
c
Interlayer binding energy (meV)
75
50
25
0
-25
-50
-75
0.55
0.60
0.65
0.70
0.75
Lattice constant c (nm)

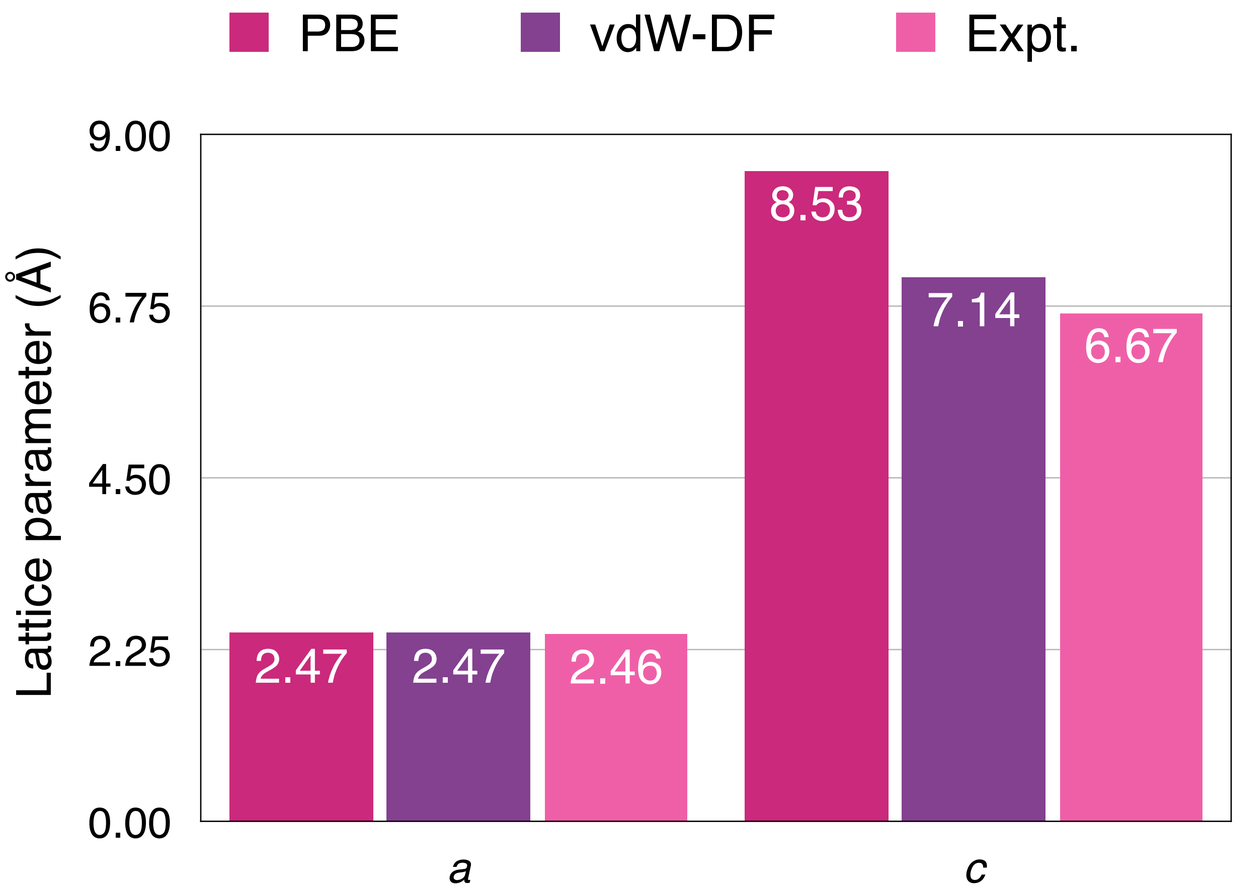
# Graphite





- vdW-DF can describe both intra- and interlayer bindings

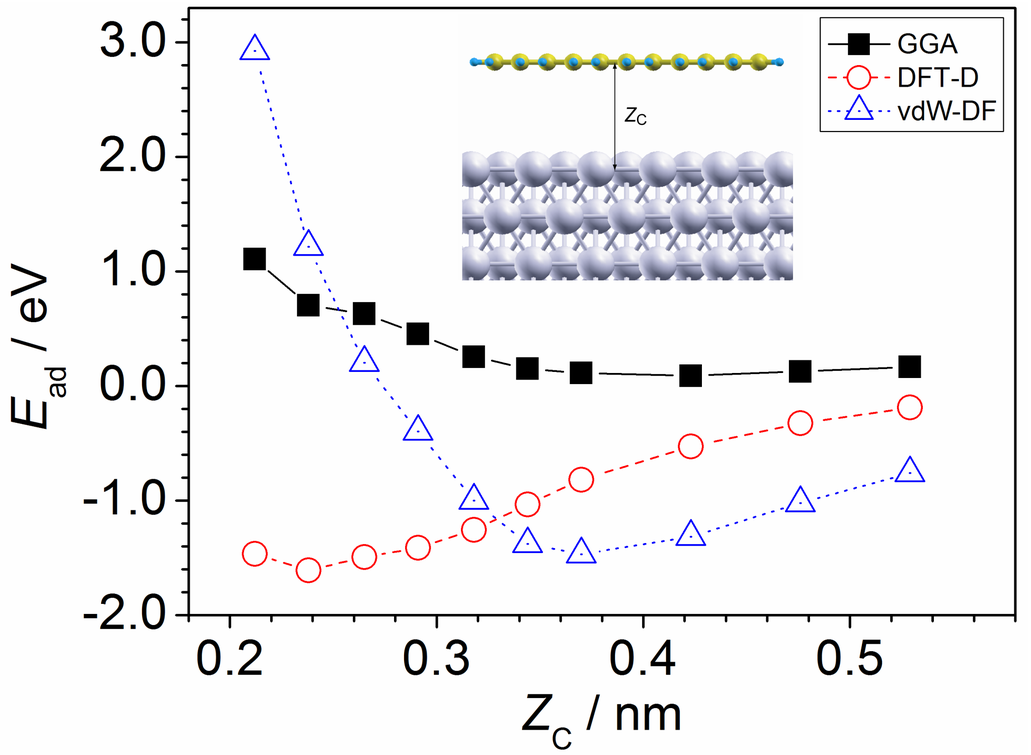
# Graphite





- vdW-DF can describe both intra- and interlayer bindings
- Binding energy is accurate, but interlay distance is overestimated

# Work-function change in pentacene/Cu(111)




Toyoda, IH, Lee, Yanagisawa, & Morikawa, *J. Chem. Phys*. **132**, 134703 (2010).

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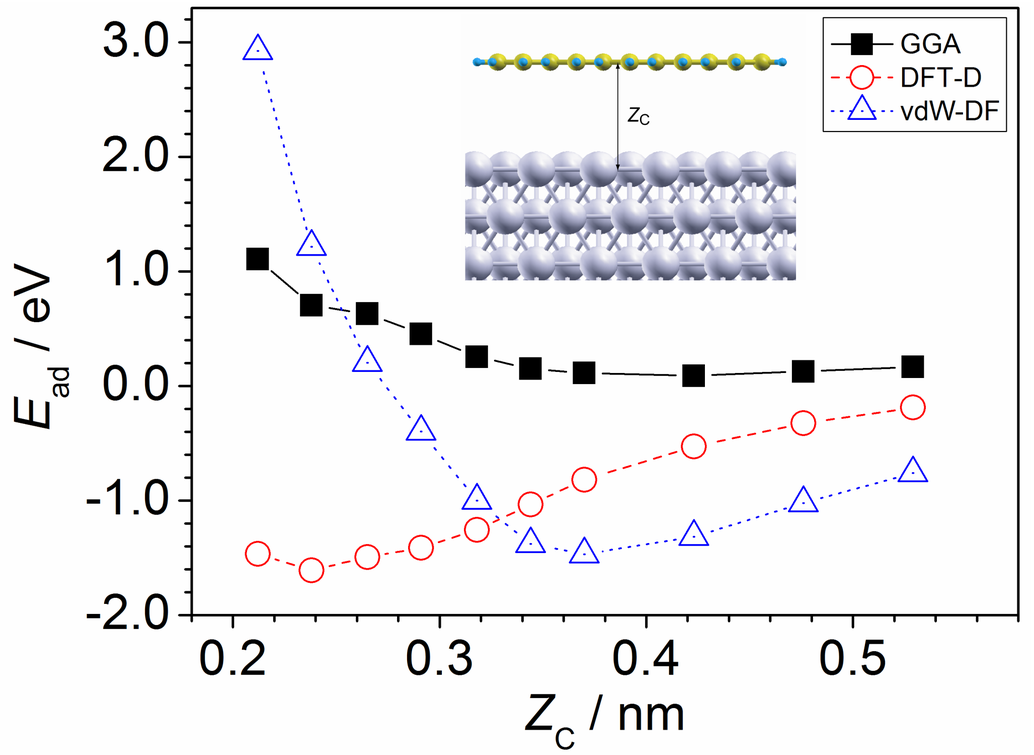


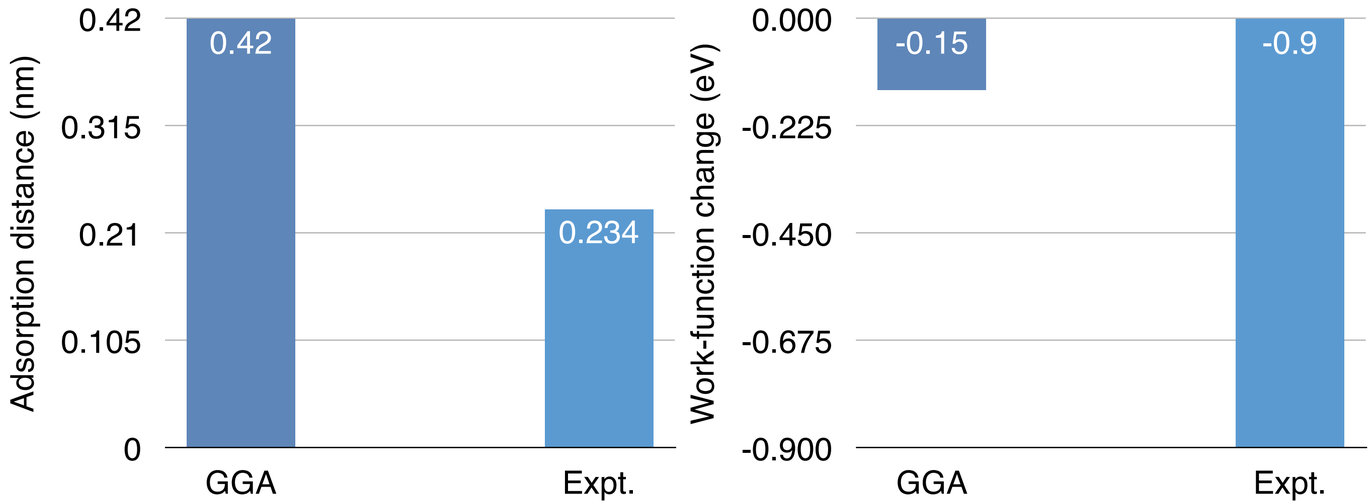


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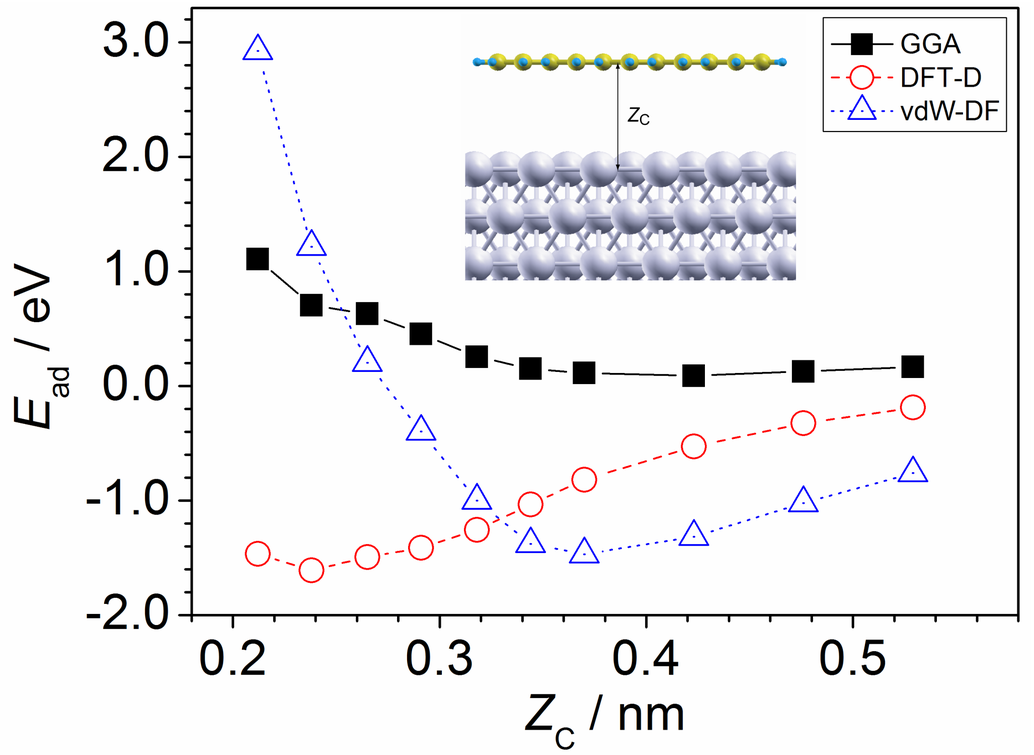


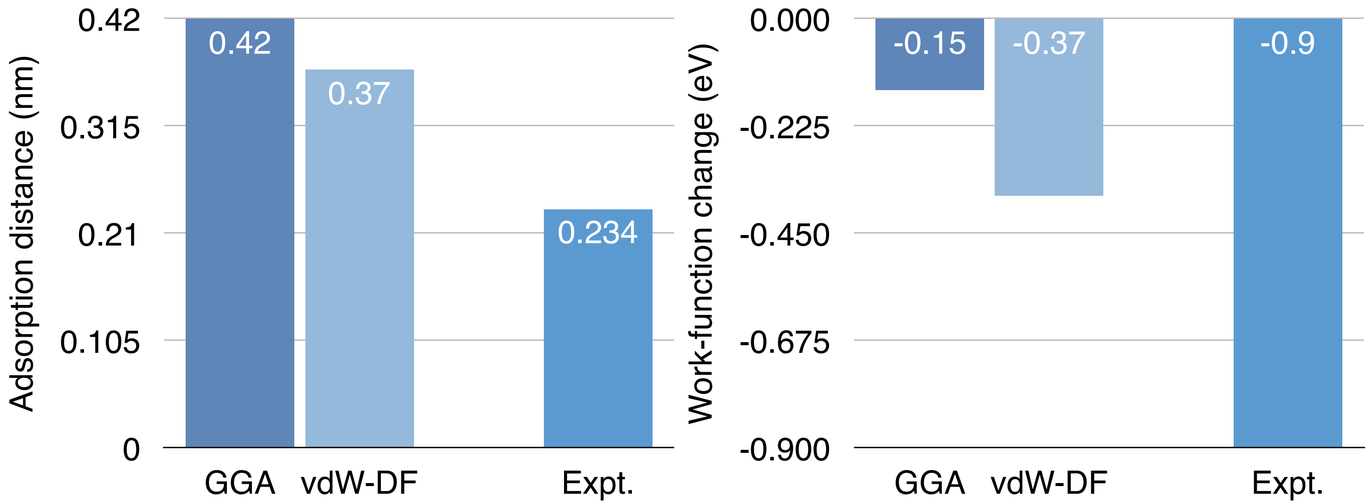


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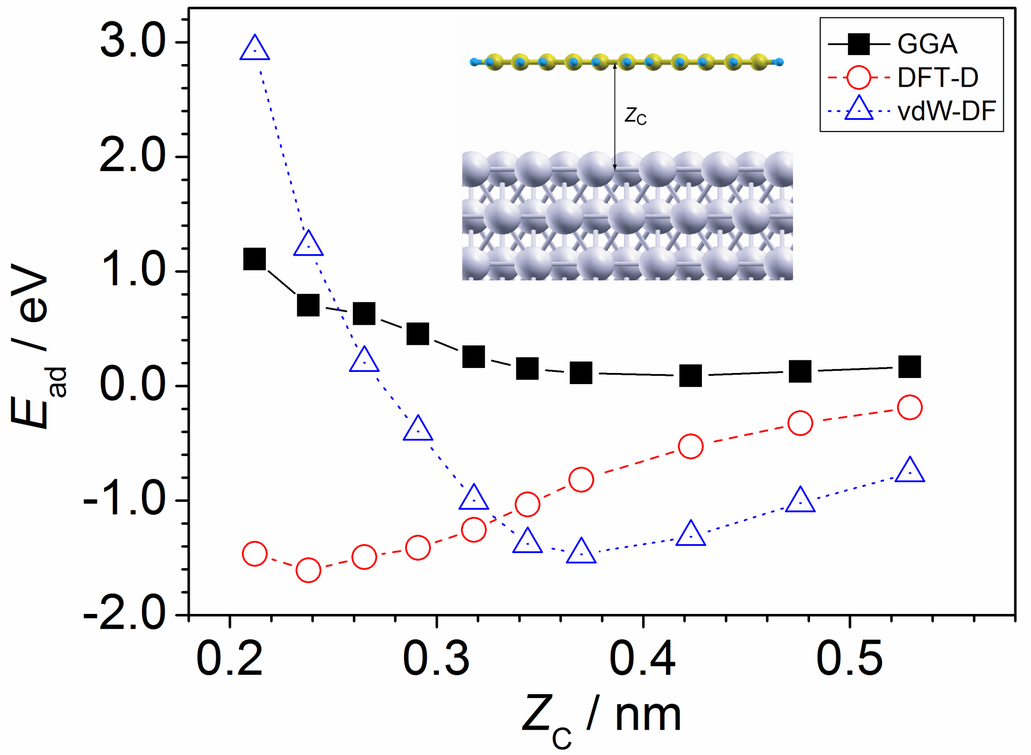


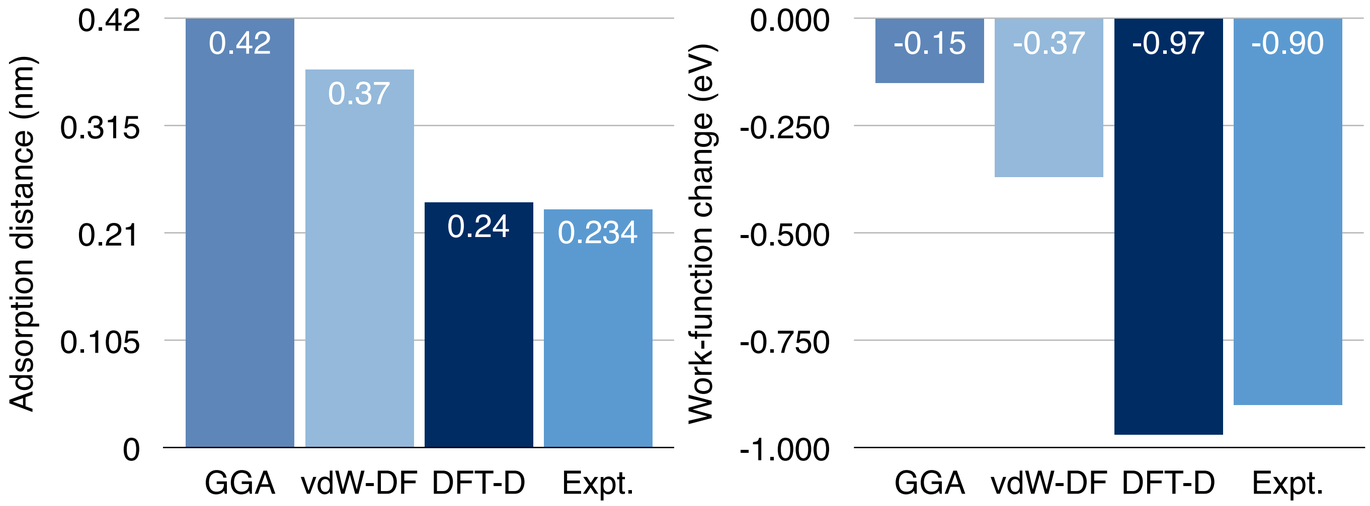


☹ Overestimated binding distance, leading to incorrect interface electronic structure

Toyoda, IH, Lee, Yanagisawa, & Morikawa, *J. Chem. Phys*. **132**, 134703 (2010).

# Band-gap opening at the *K* point of graphene on Ni(111)

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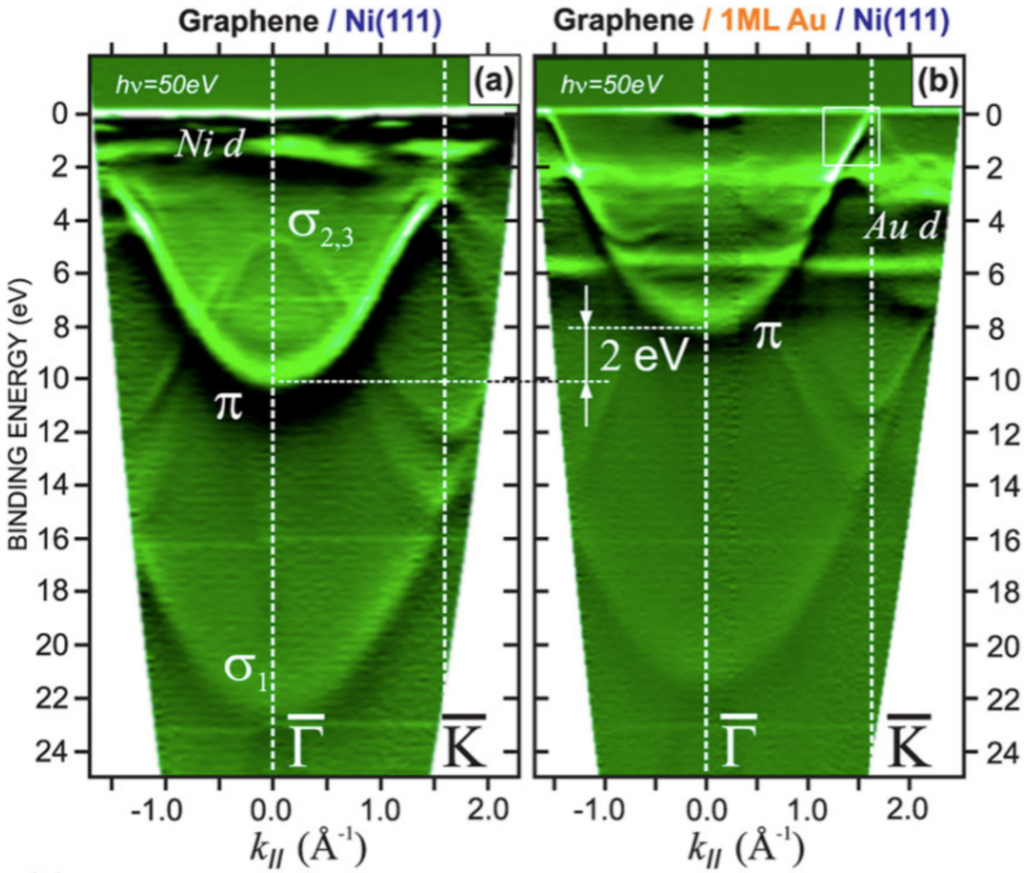
ARPES Expt.




Varykhalov *et al.*, *Phys. Rev. Lett.* **101**, 157601 (2008).

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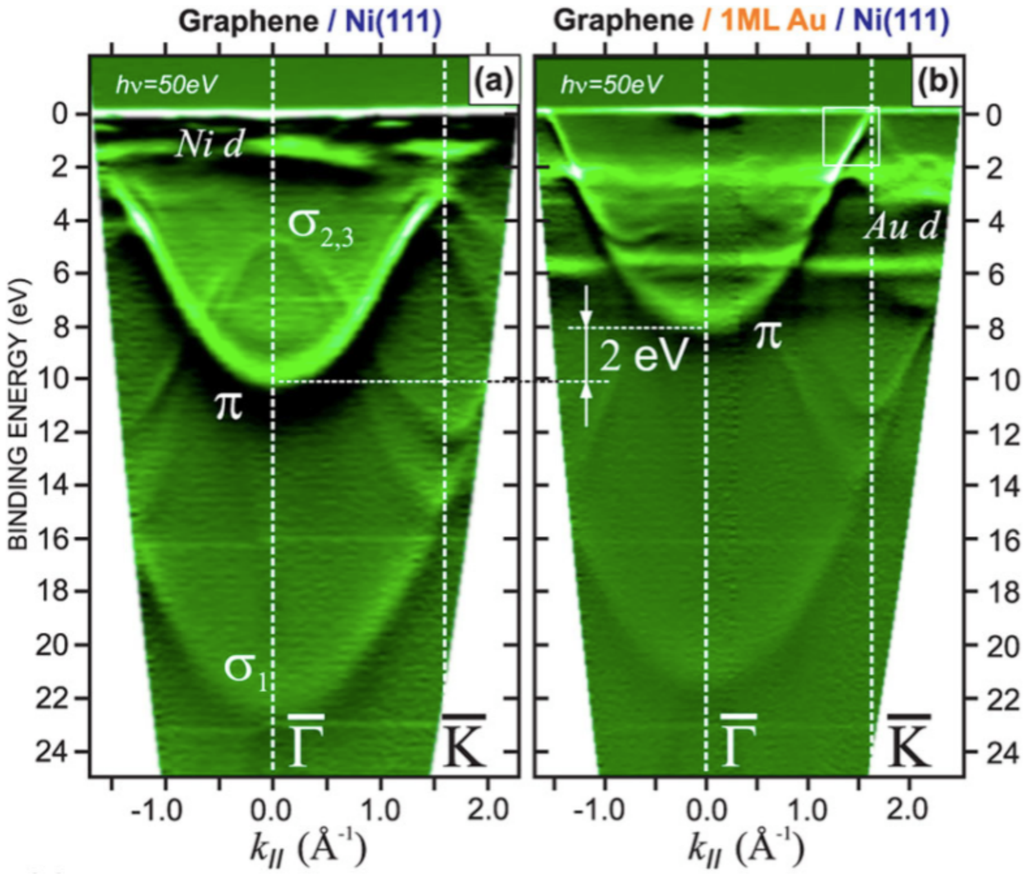
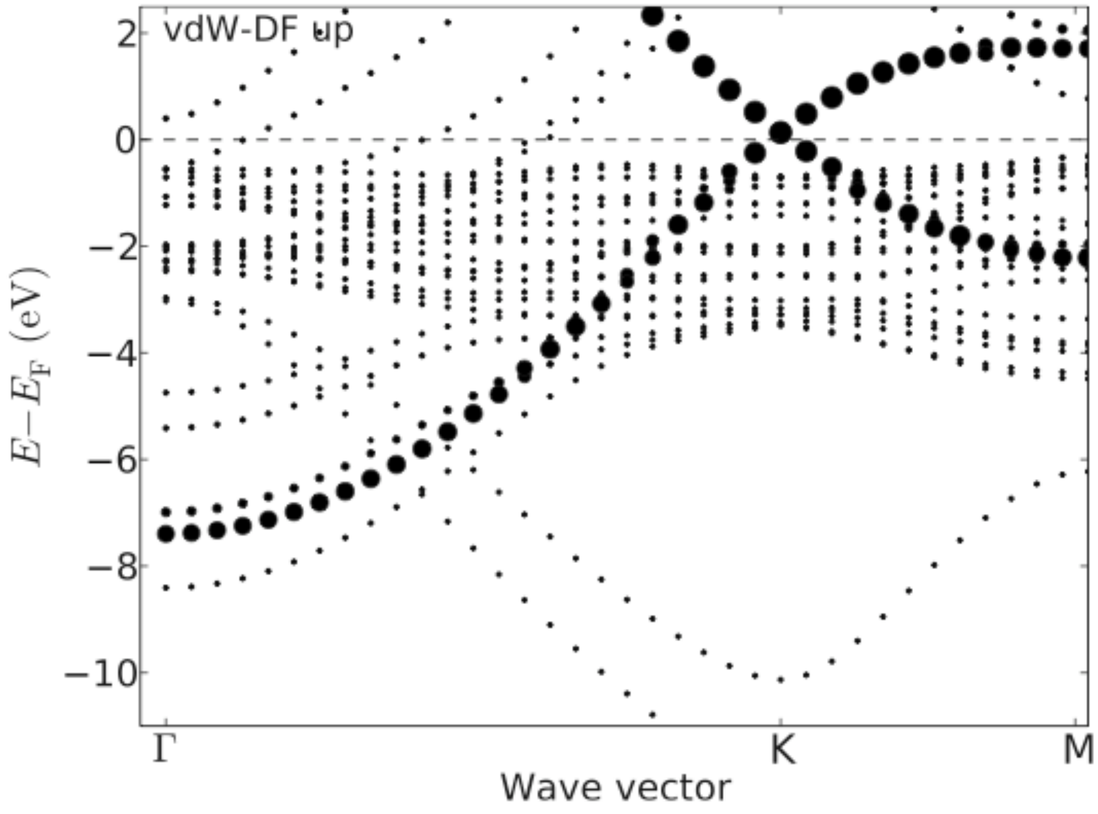


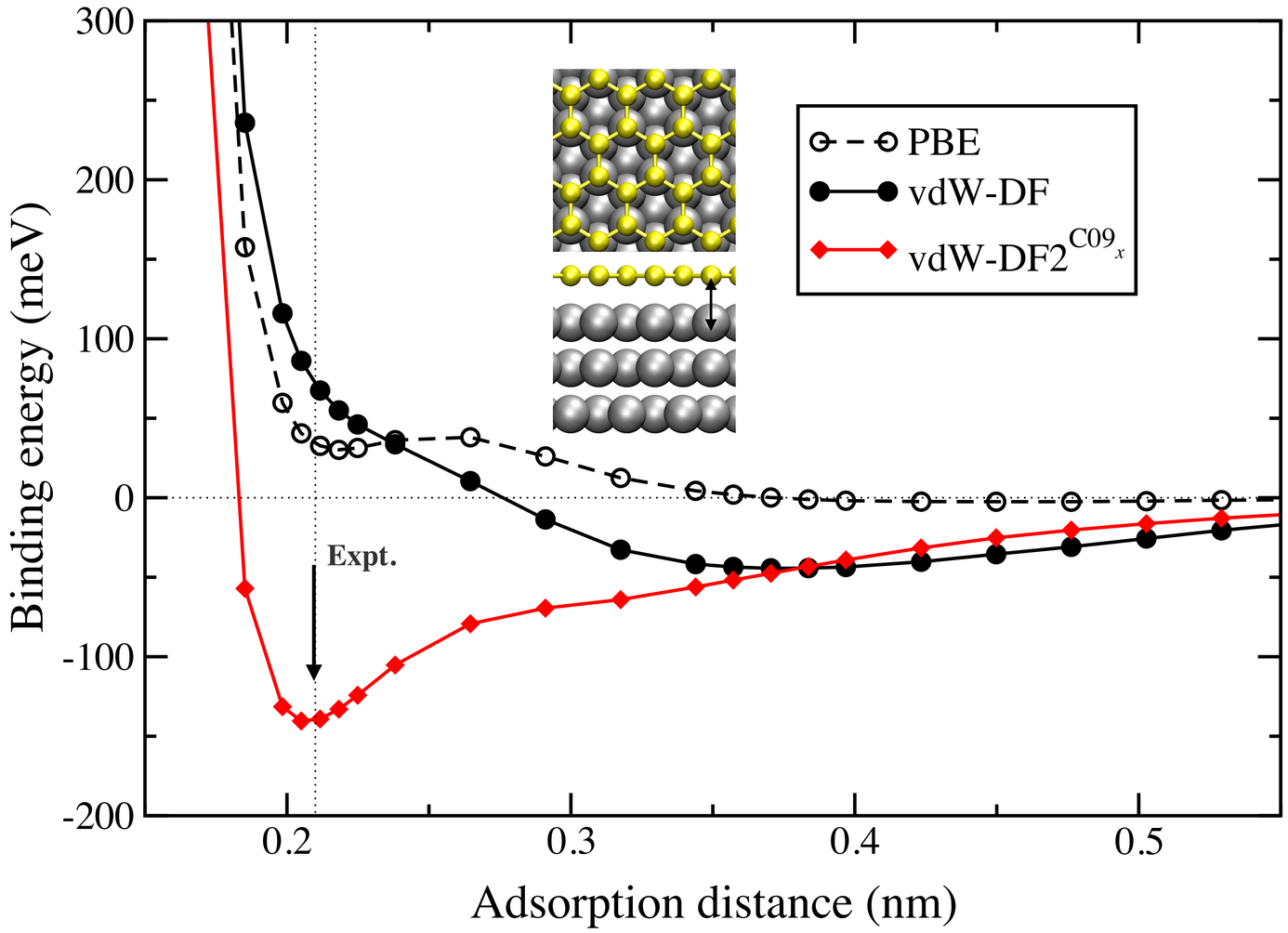

Varykhalov *et al.*, *Phys. Rev. Lett.* **101**, 157601 (2008).

vdW-DF Calc.




Vanin *et al.*, *Phys. Rev. B* **81**, 081408(R) (2010).

# Binding energy curves of graphene on Ni(111)




vdW-DF2-C09 improves the adsorption distance of graphene on Ni(111)

*IH and* M. Otani, *Phys. Rev. B* **82**, 153412 (2010).

# Band structure of graphene on Ni(111)

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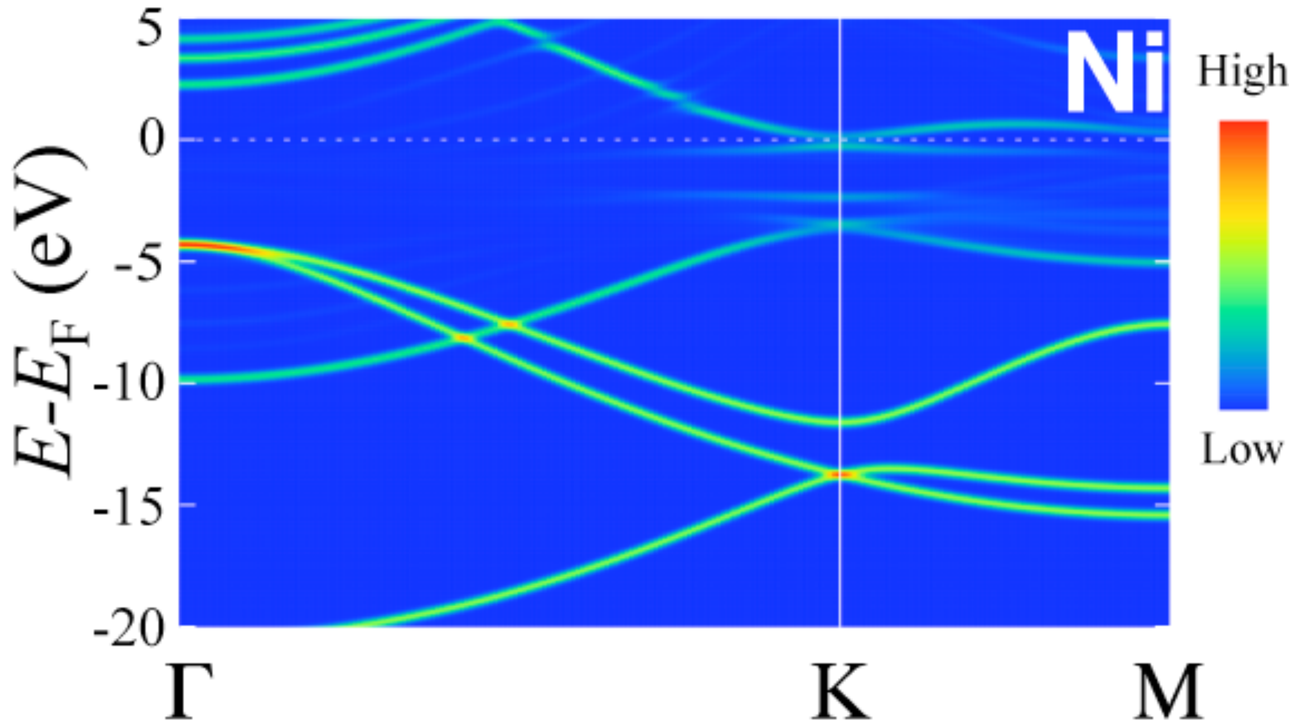


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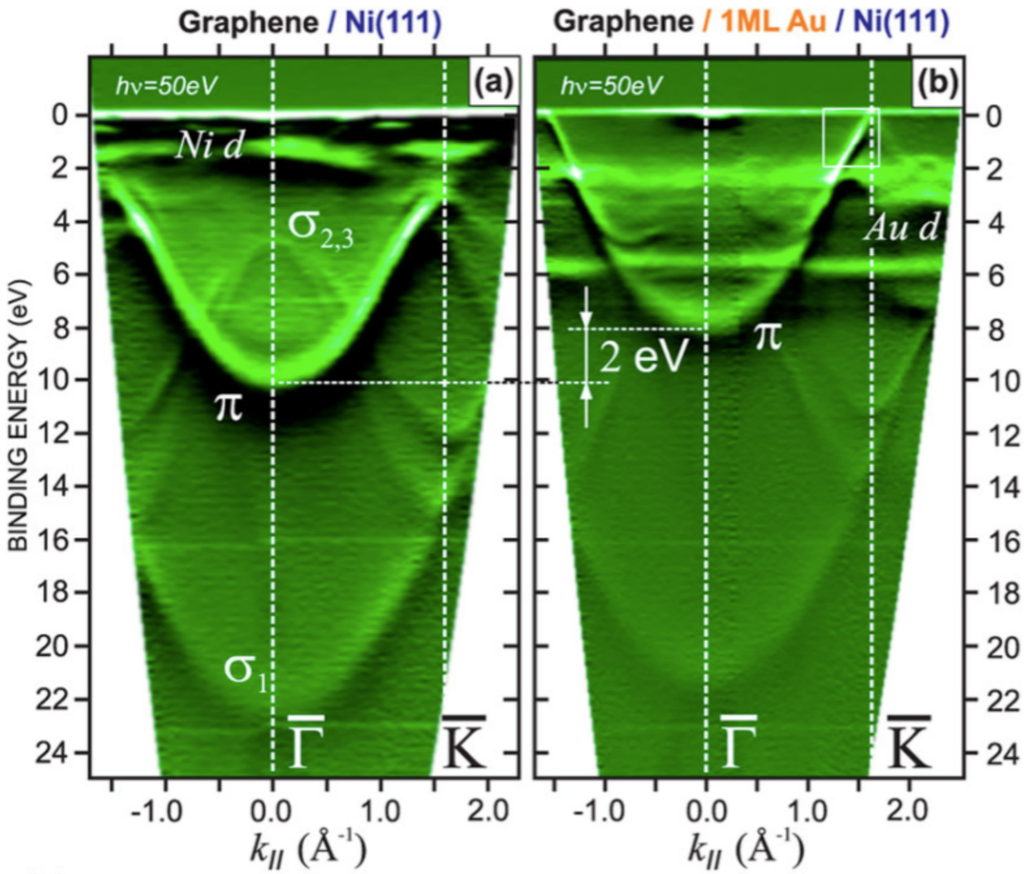


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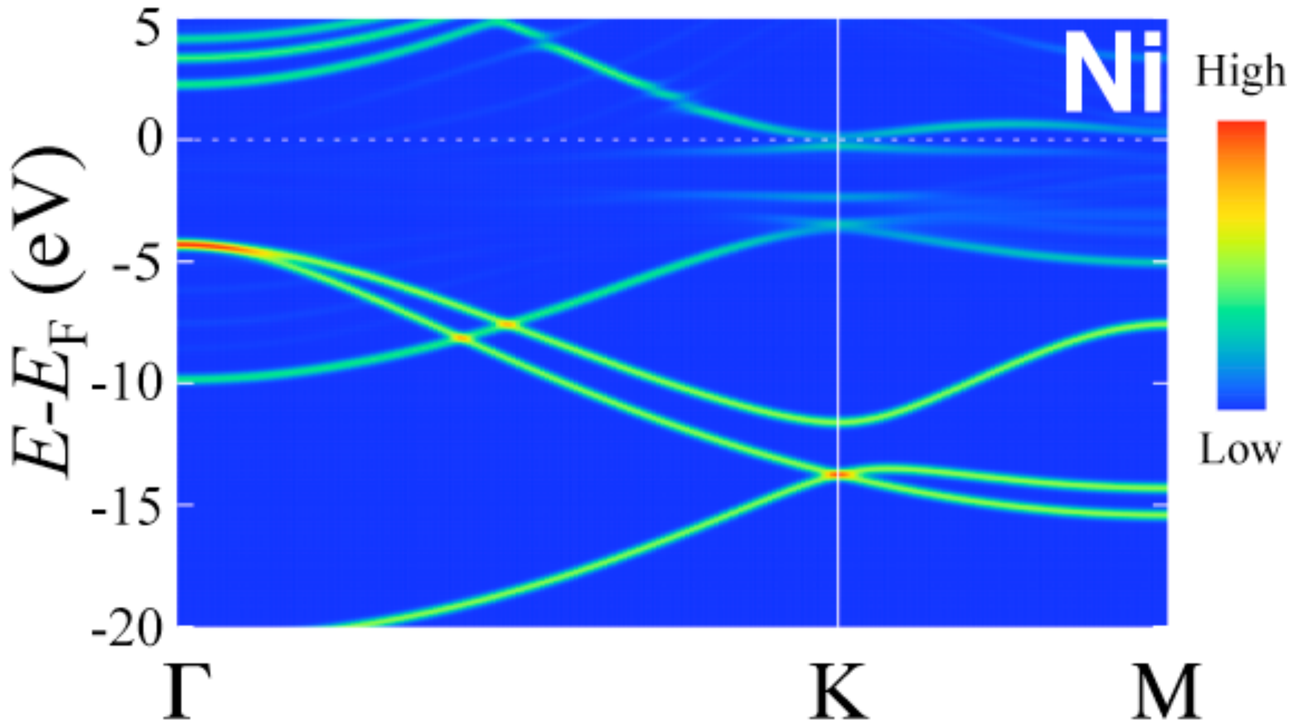


**Calculated band structure with vdW-DF2-C09 agrees well with experiment when the correct adsorption distance is used**

*IH and* M. Otani, *Phys. Rev. B* **82**, 153412 (2010).

# van der Waals density functional (vdW-DF)

XC functional in vdW-DF

$$E_{\mathrm{xc}}^{\mathrm{vdW-DF}} = E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{LDA}} + E_{\mathrm{c}}^{\mathrm{nl}}$$

$$E_{\mathrm{c}}^{\mathrm{nl}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1) \phi(q_1 |r_1 - r_2|, q_2 |r_1 - r_2|) n(\mathbf{r}_2)$$

$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015).

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- ☻ No empirical parameters
- ☻ Seamless description of covalent and van der Waals bondings

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☹ No unique choice of local exchange and correlation to be accurate functional

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1st generation: vdW-DF(1), optB88-vdW, optB86b-vdW, vdW-DF-C09, vdW-DF-cx

2nd generation: vdW-DF2, vdW-DF2-C09, rev-vdW-DF2 (vdW-DF2-B86R)

3rd generation: vdW-DF3-opt1, vdW-DF3-opt2

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015).

# van der Waals density functional (vdW-DF)

XC functional in rev-vdW-DF2 (vdW-DF2-B86R)

$$E_{\mathrm{xc}}^{\mathrm{rev-vdW-DF2}} = E_{\mathrm{x}}^{\mathrm{B86R}} + E_{\mathrm{c}}^{\mathrm{LDA}} + E_{\mathrm{c,nl}}^{\mathrm{vdW-DF2}}$$

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Hamada, *Phys. Rev. B* **89**, 121103 (2014).

Dion, *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004); Berland *et al.*, *Rep. Prog. Phys.* **78**, 066501 (2015).

# Revised B86b exchange functional (B86R)

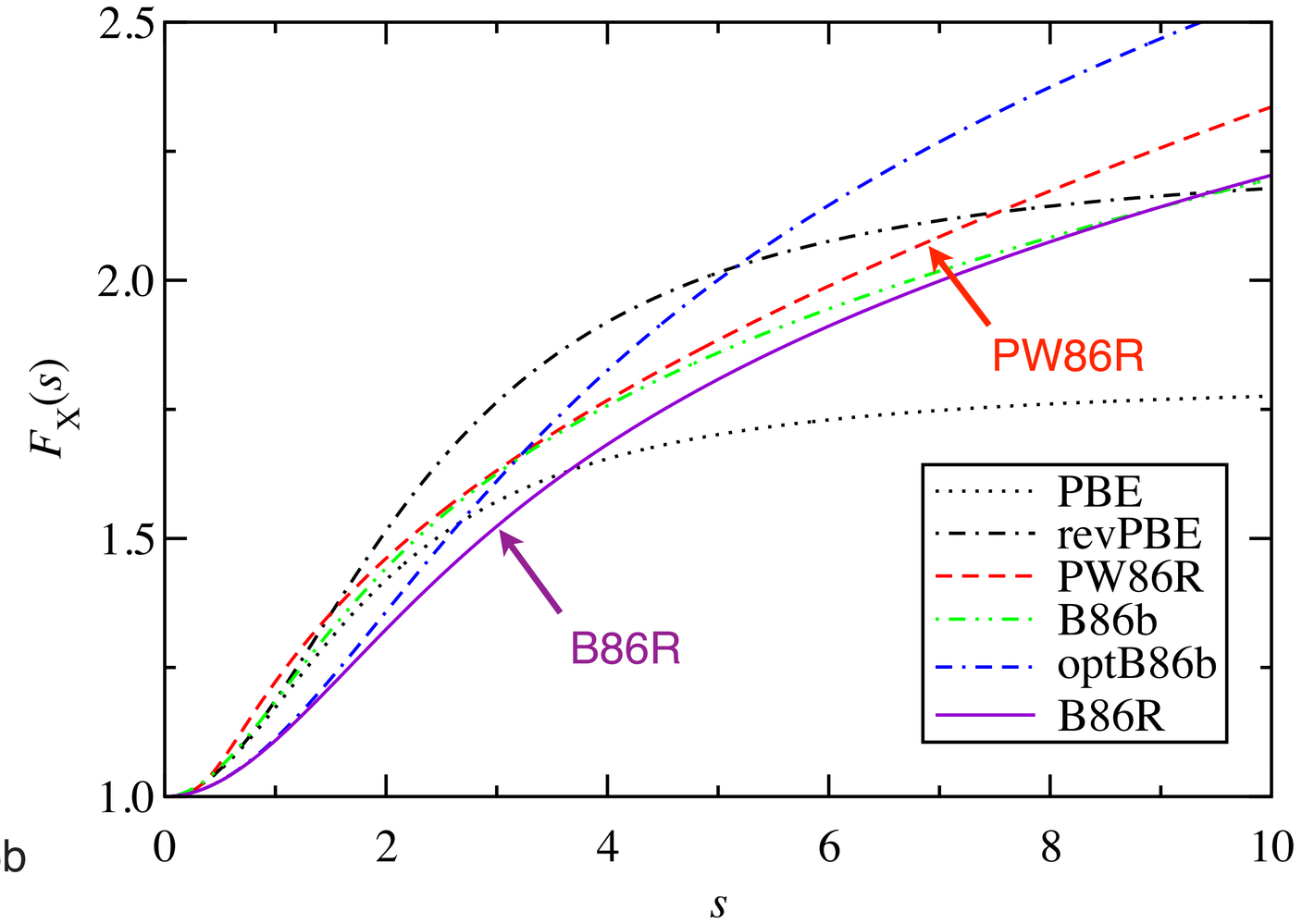
$$E_{\mathrm{X}}^{\mathrm{GGA}} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{\mathrm{X}}^{\mathrm{unif}}(n) F_{\mathrm{X}}(s)$$

$$F_{\mathrm{X}}^{\mathrm{B86b}}(s) = 1 + \frac{\mu s^2}{(1+\mu s^2/\kappa)^{4/5}}$$

$$s = |\nabla n| / (2 k_{\mathrm{F}} n)$$

Becke, *J. Chem. Phys.* **85**, 7184 (1986).

- $\mu$ and $\kappa$ are determined so as to match
  - -GEA at the slowly varying density limit (important for covalent bonding)
  - -Large density gradient behavior in the B86b (important for the vdW bonding)



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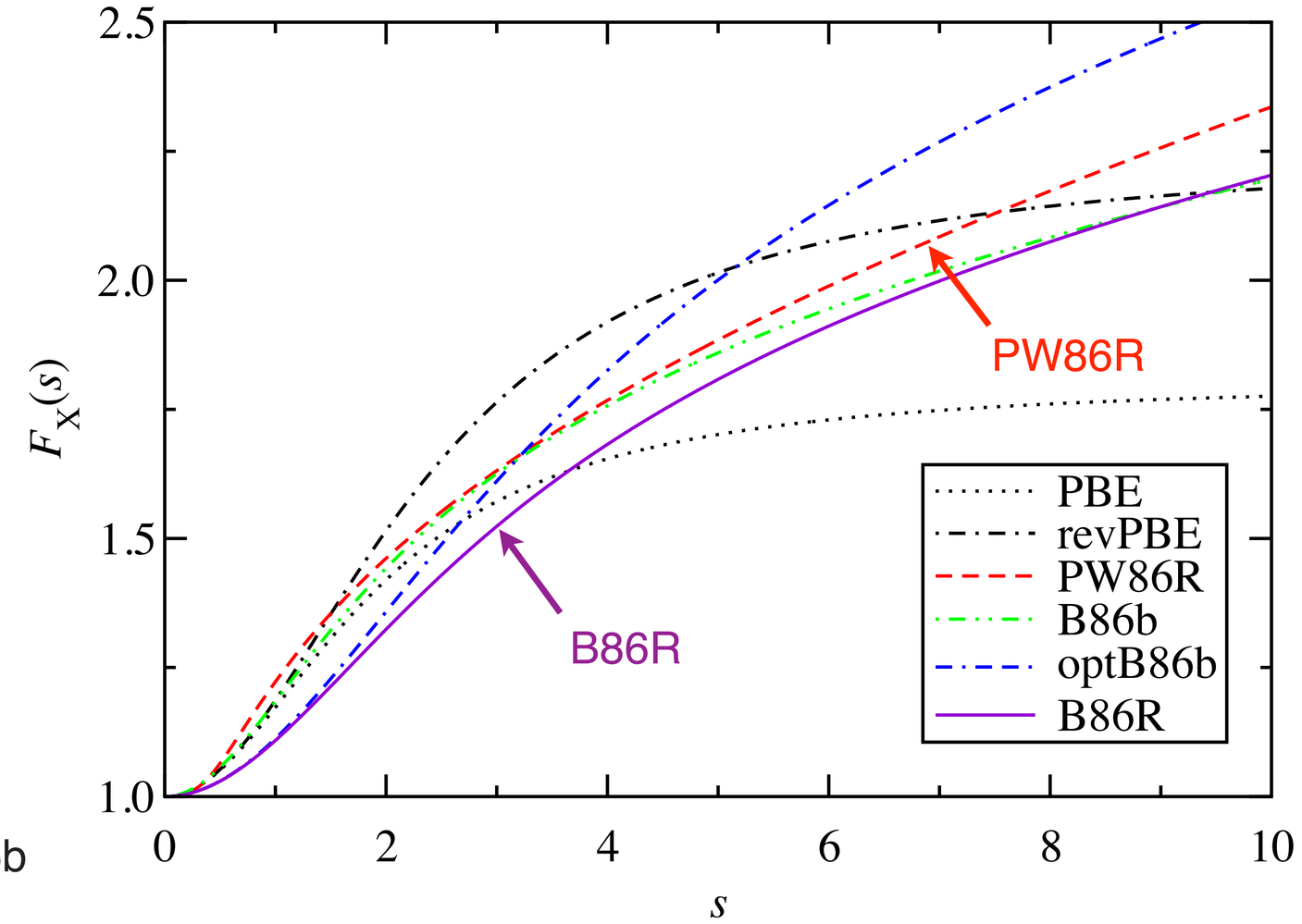


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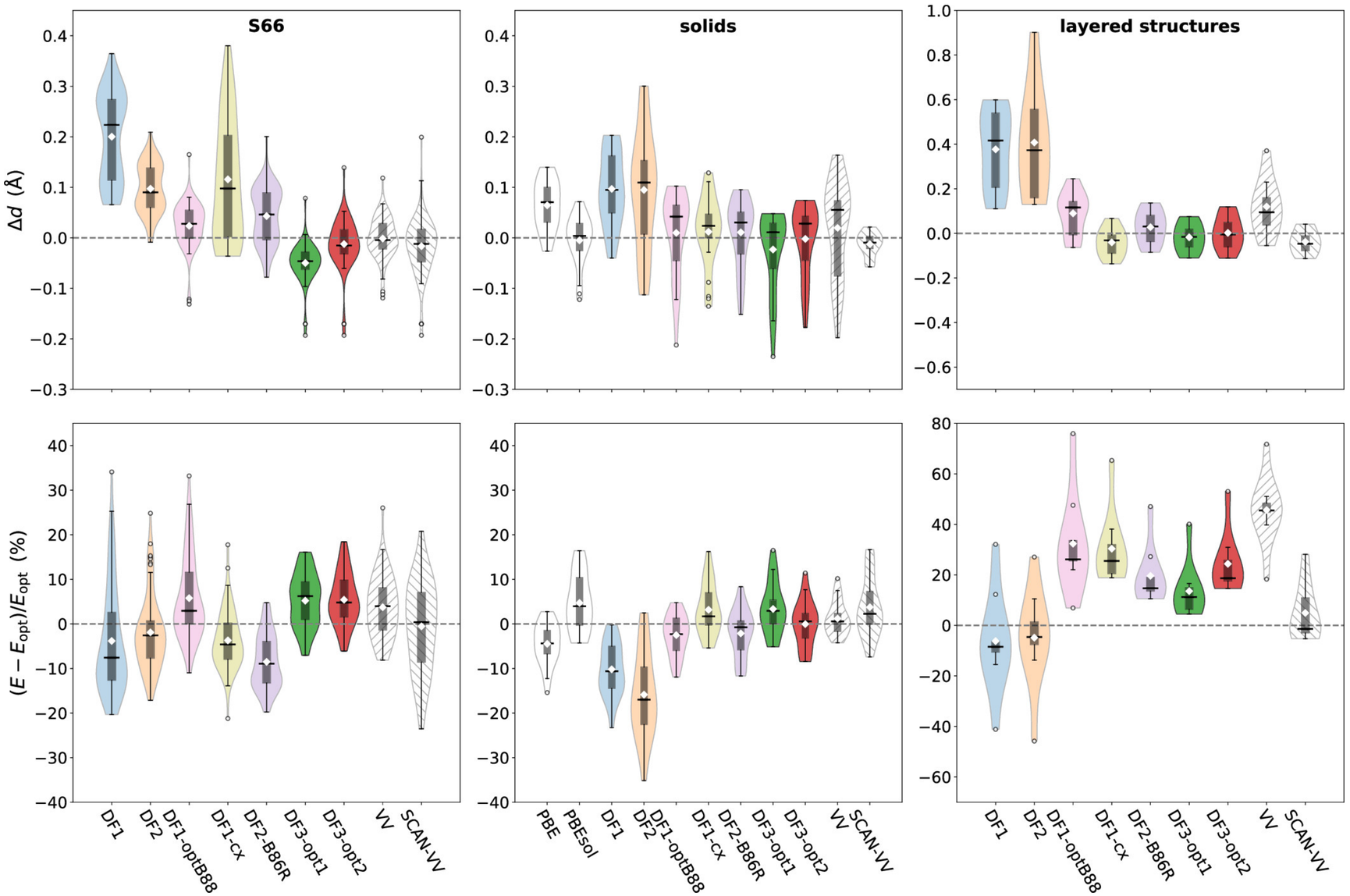
# Outline

- Background: Dispersion forces in density functional theory
- Theory and application of van der Waals density functional (vdW-DF)
  - Benchmark for molecules, materials, and interfaces
  - Case study
    - Layered materials
    - Organic crystals
  - Recent development
- Summary

# Comparison of vdW-DFs for molecules and solids




Chakraborty, Berland, Thonhauser, *J. Chem. Theory Comput.* **16**, 5893 (2020).

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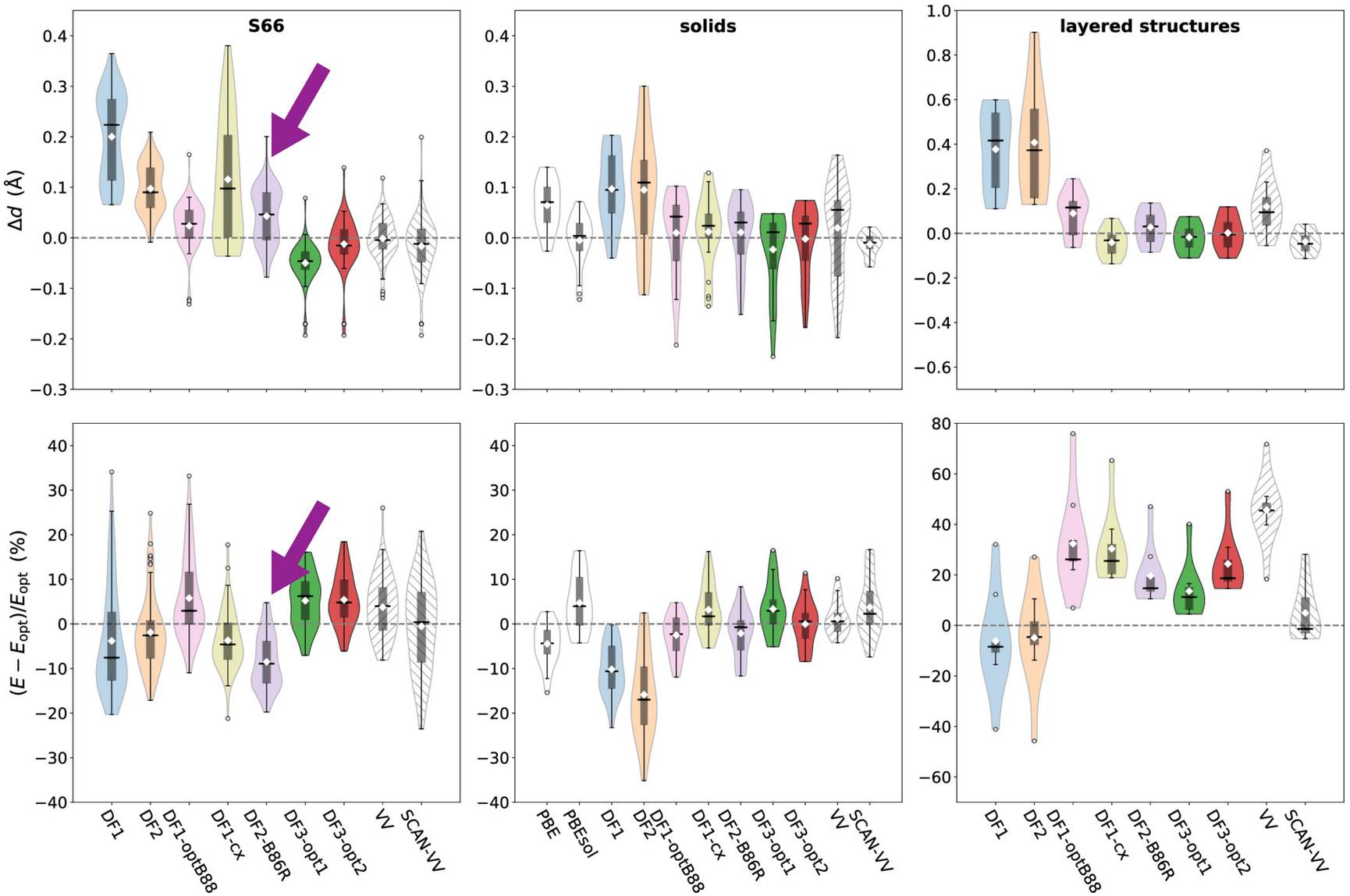


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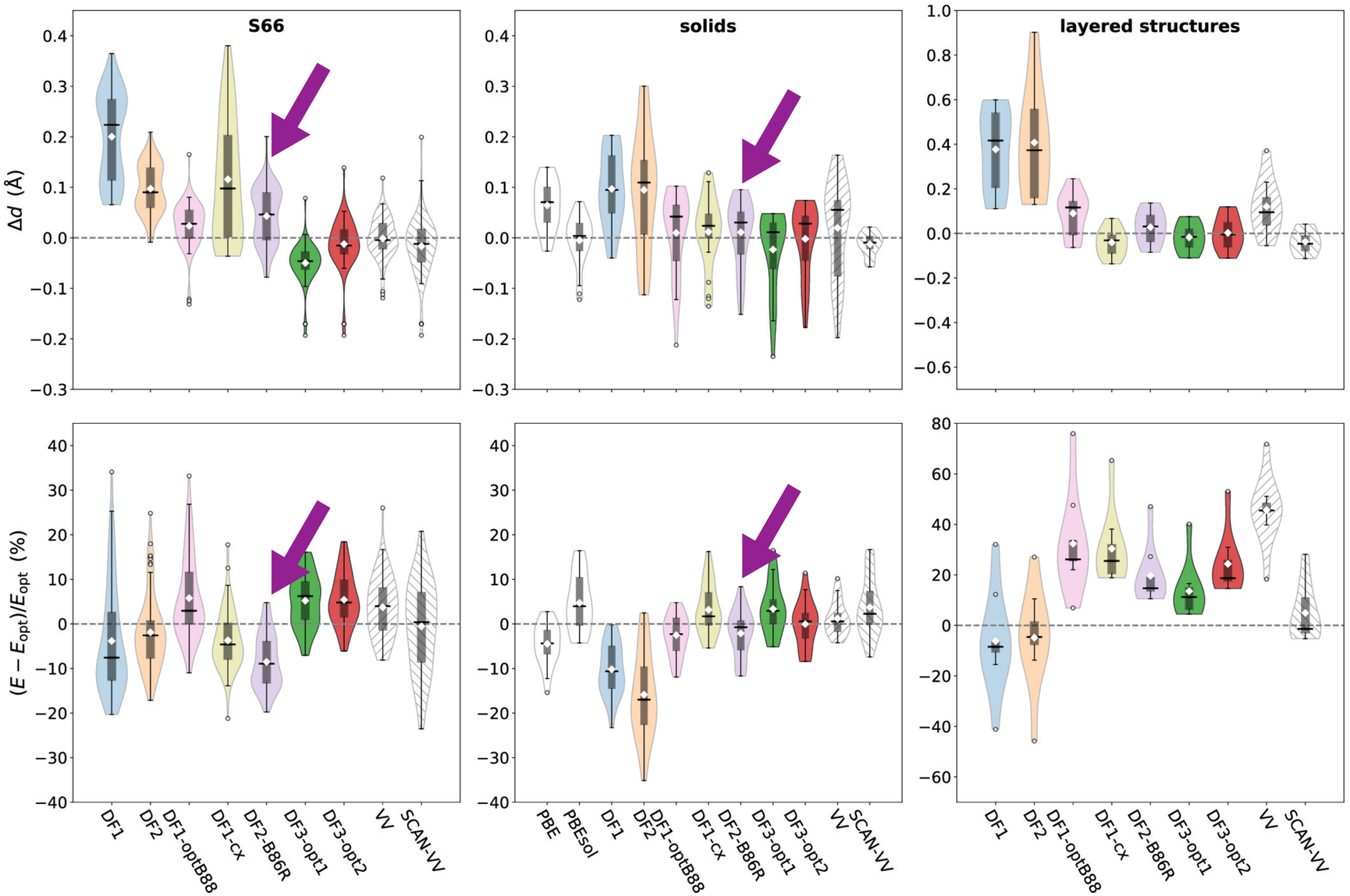


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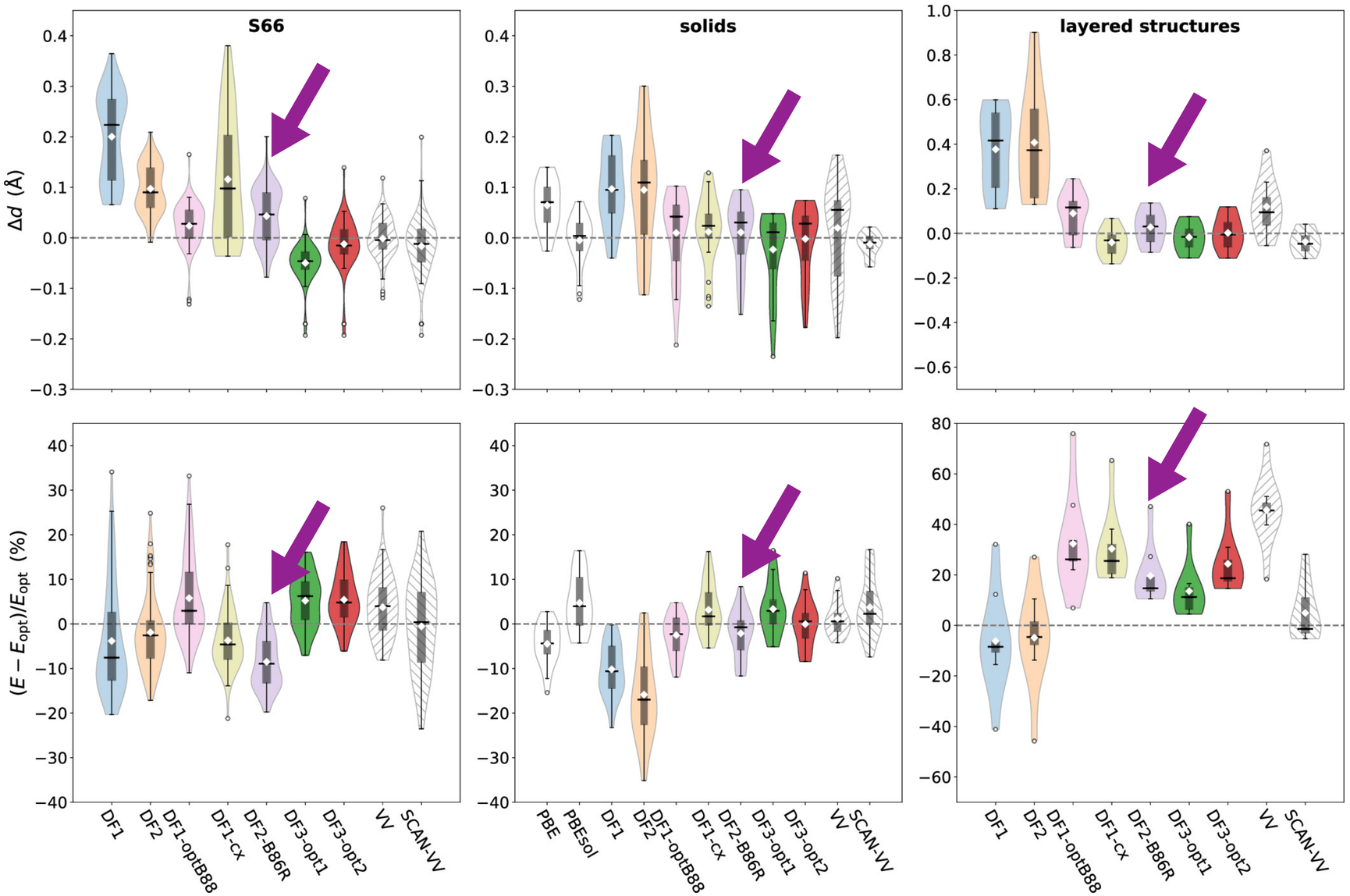


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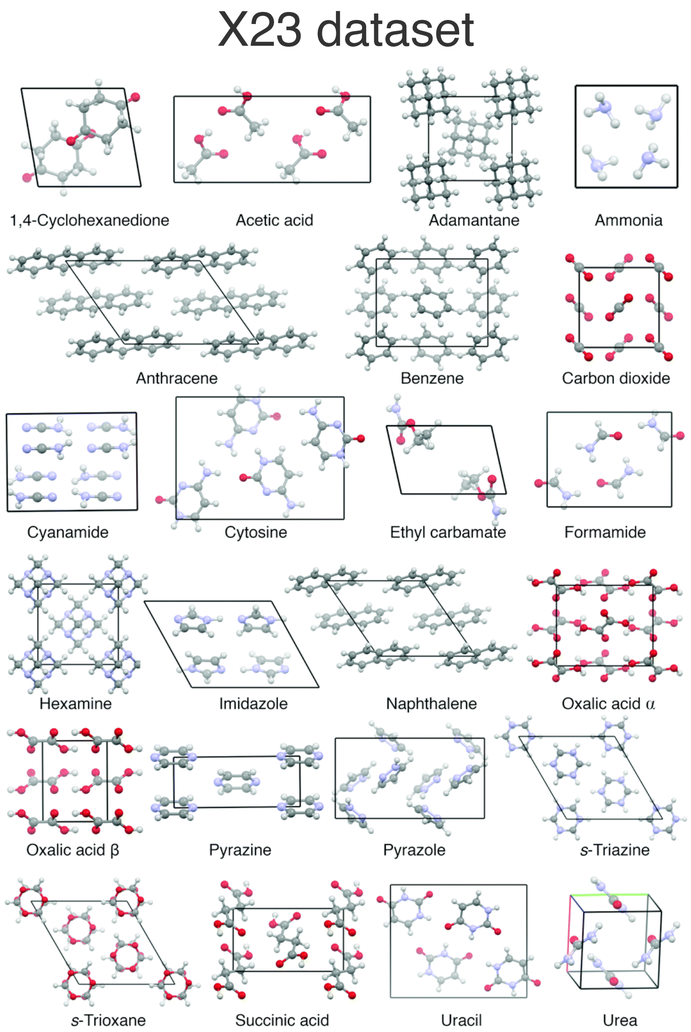


Reilly and Tkatchenko, *J. Chem. Phys*. **139**, 024705 (2013);
G. A. Dolgonos, J. Hoja, D. Boese, *Phys. Chem. Chem. Phys*. **21**, 24333 (2019).

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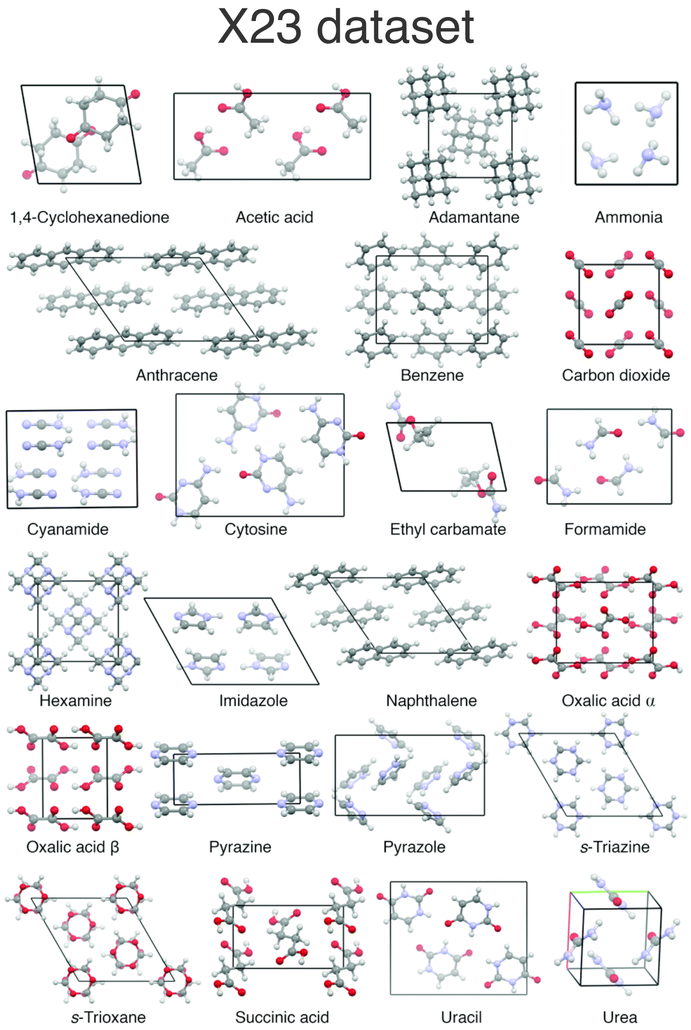


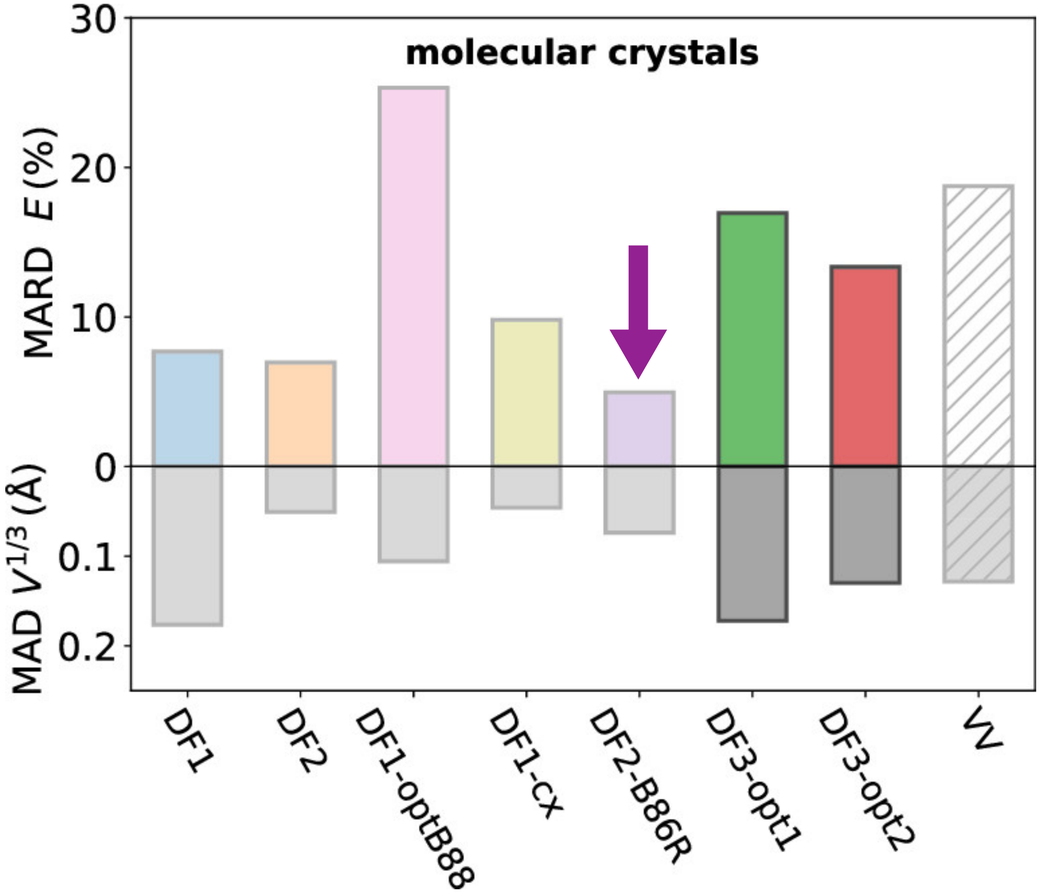


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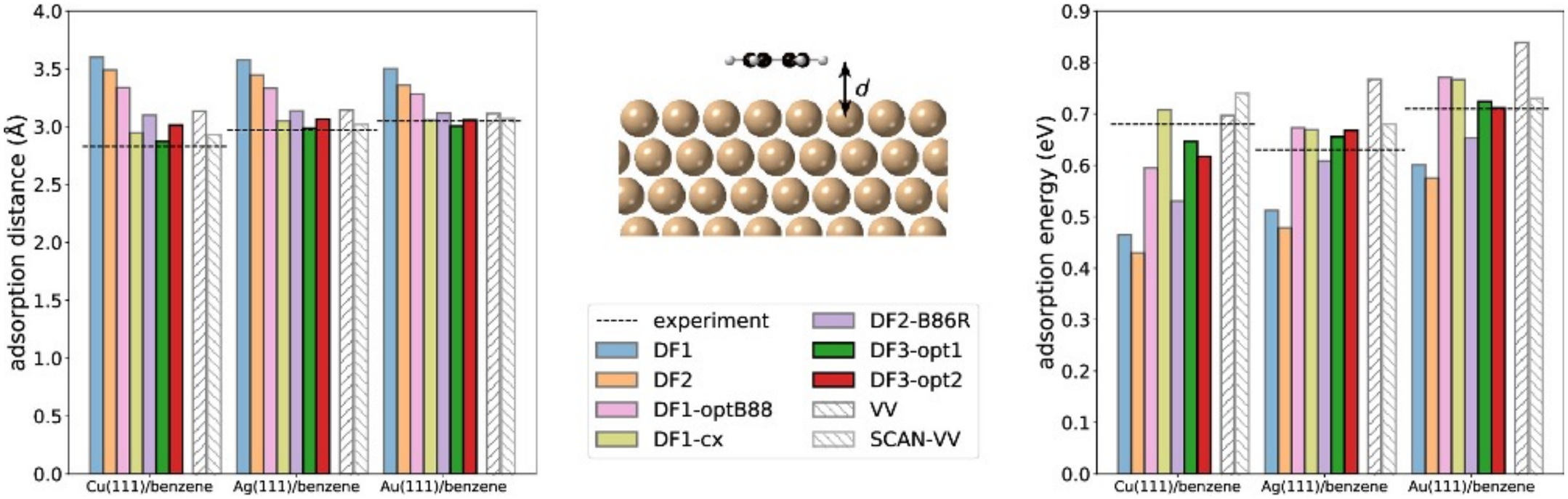
# Comparison of vdW-DFs for adsorption systems

Benzene on Cu, Ag, and Au(111) surfaces

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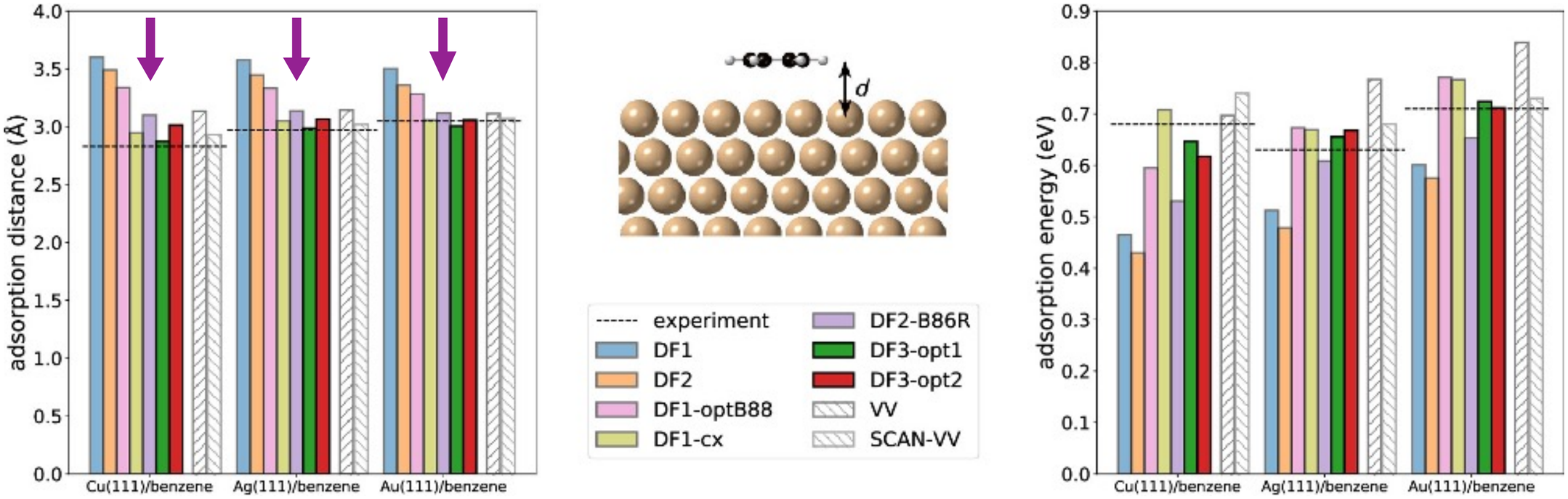


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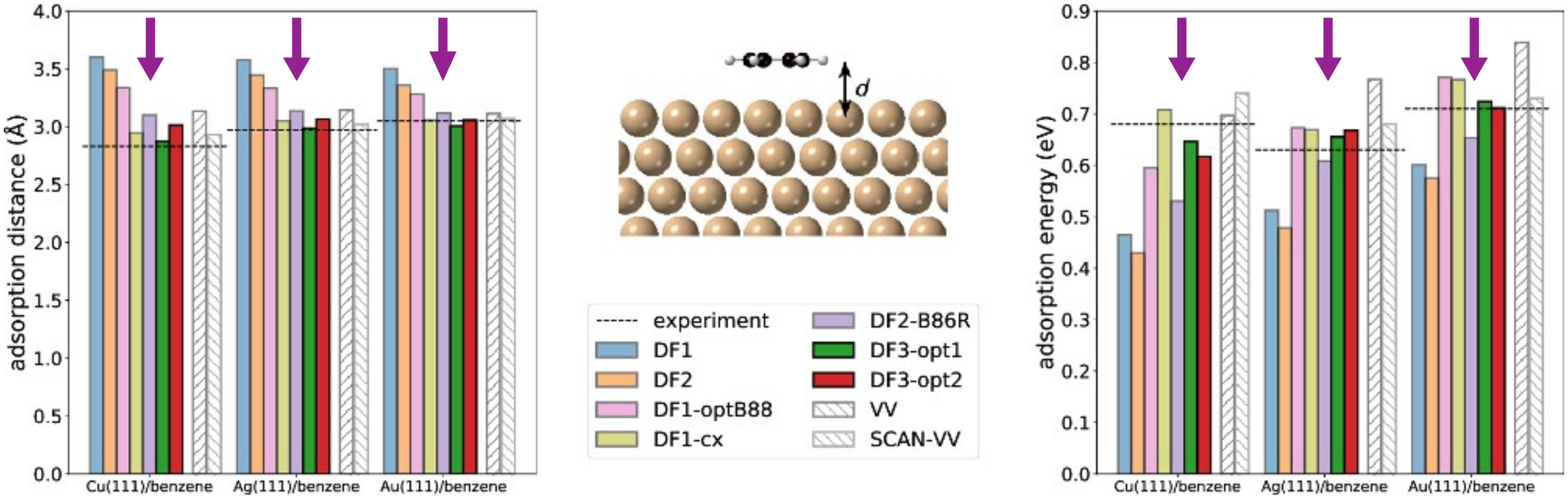


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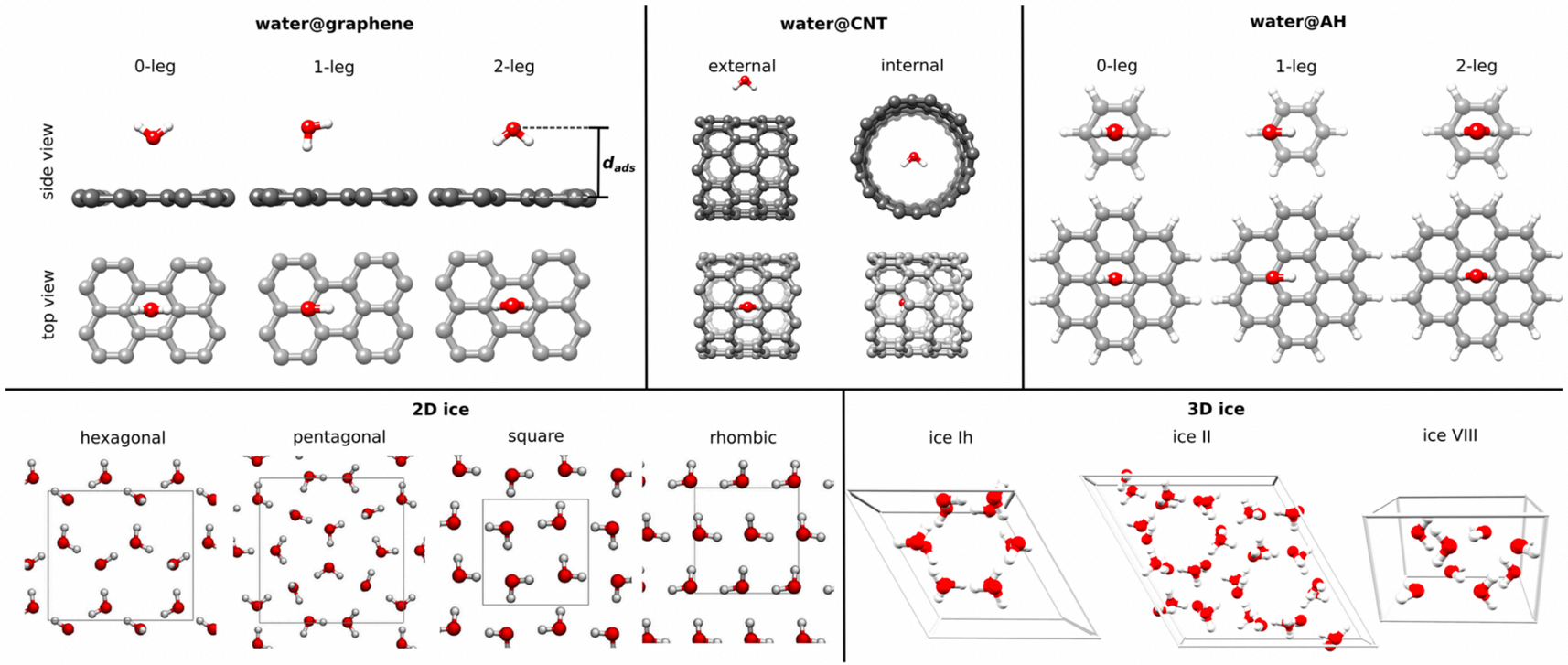


Benchmark quantum Monte Carlo results of
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Brandenburg et al. *J. Chem. Phys.* **151**, 164702 (2019).

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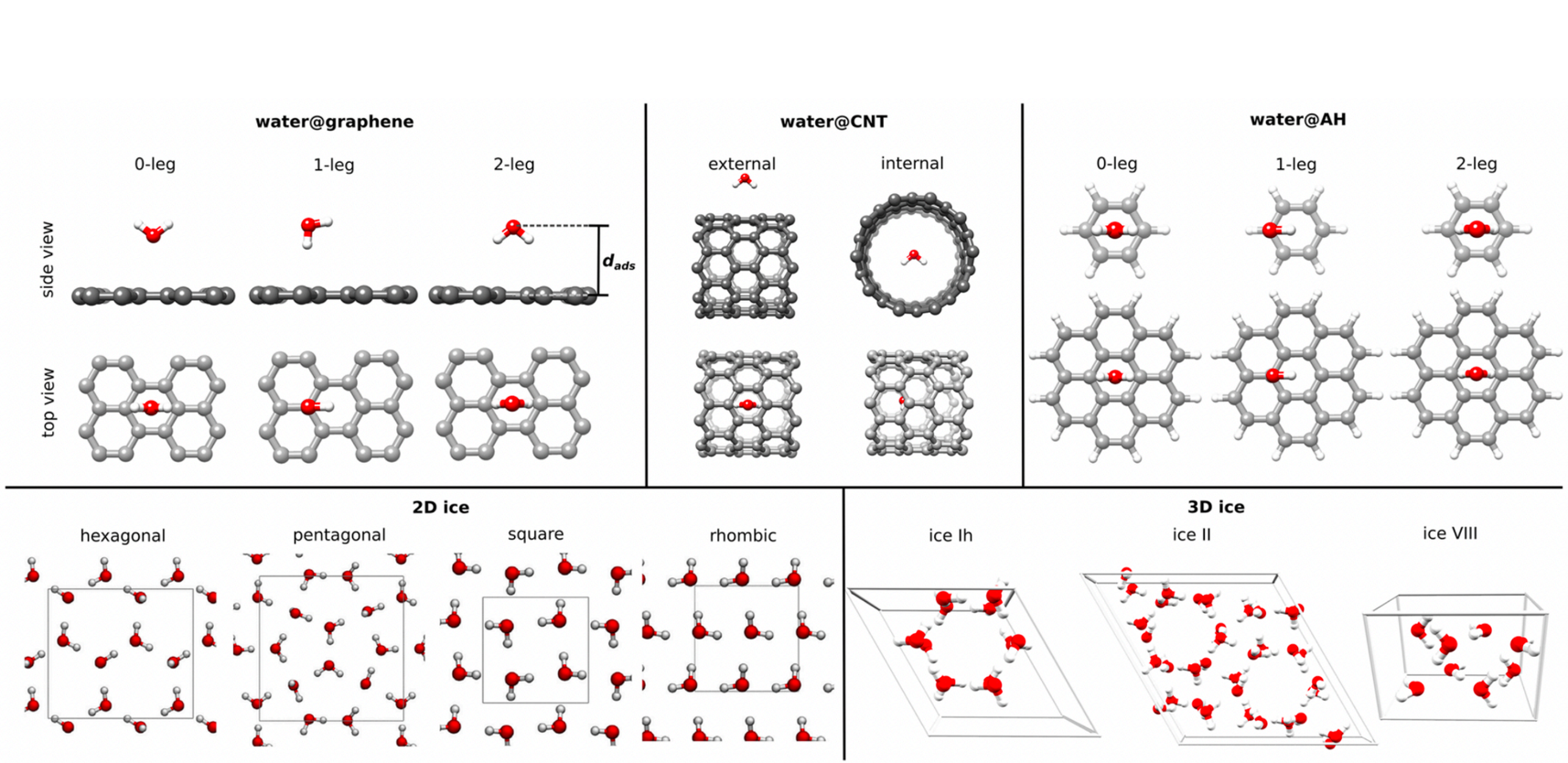


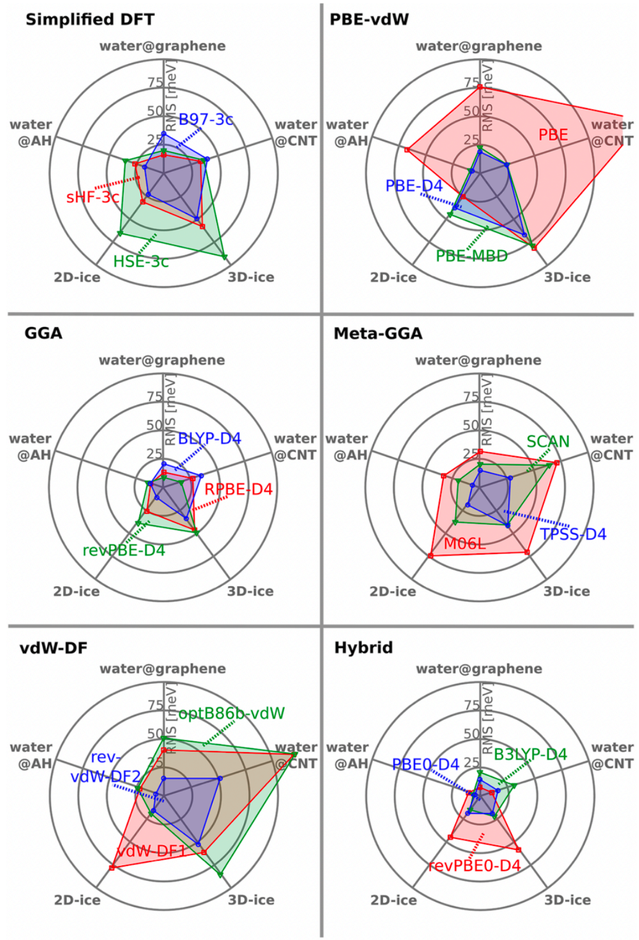


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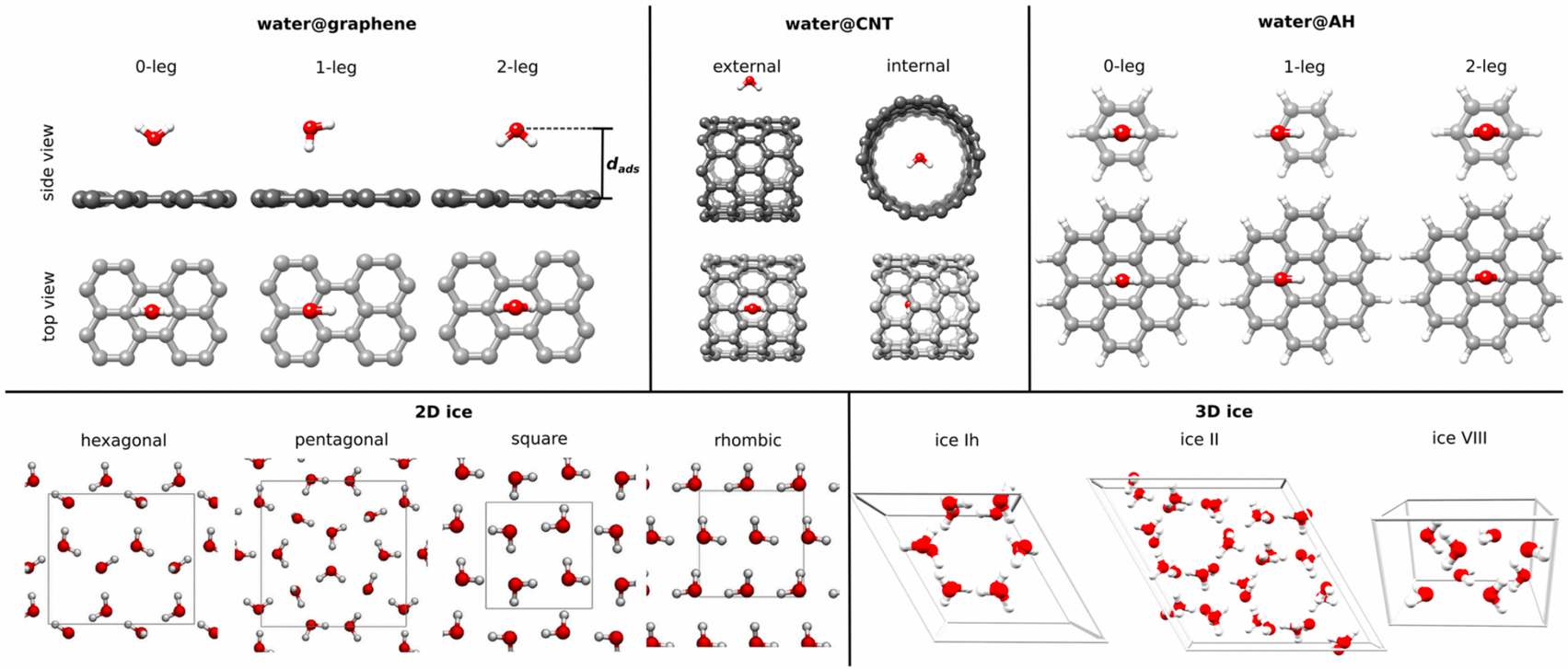


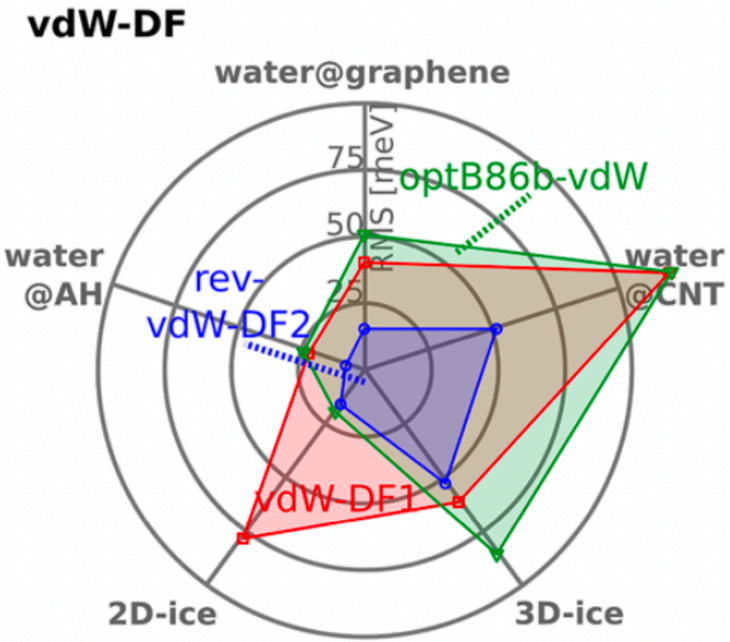


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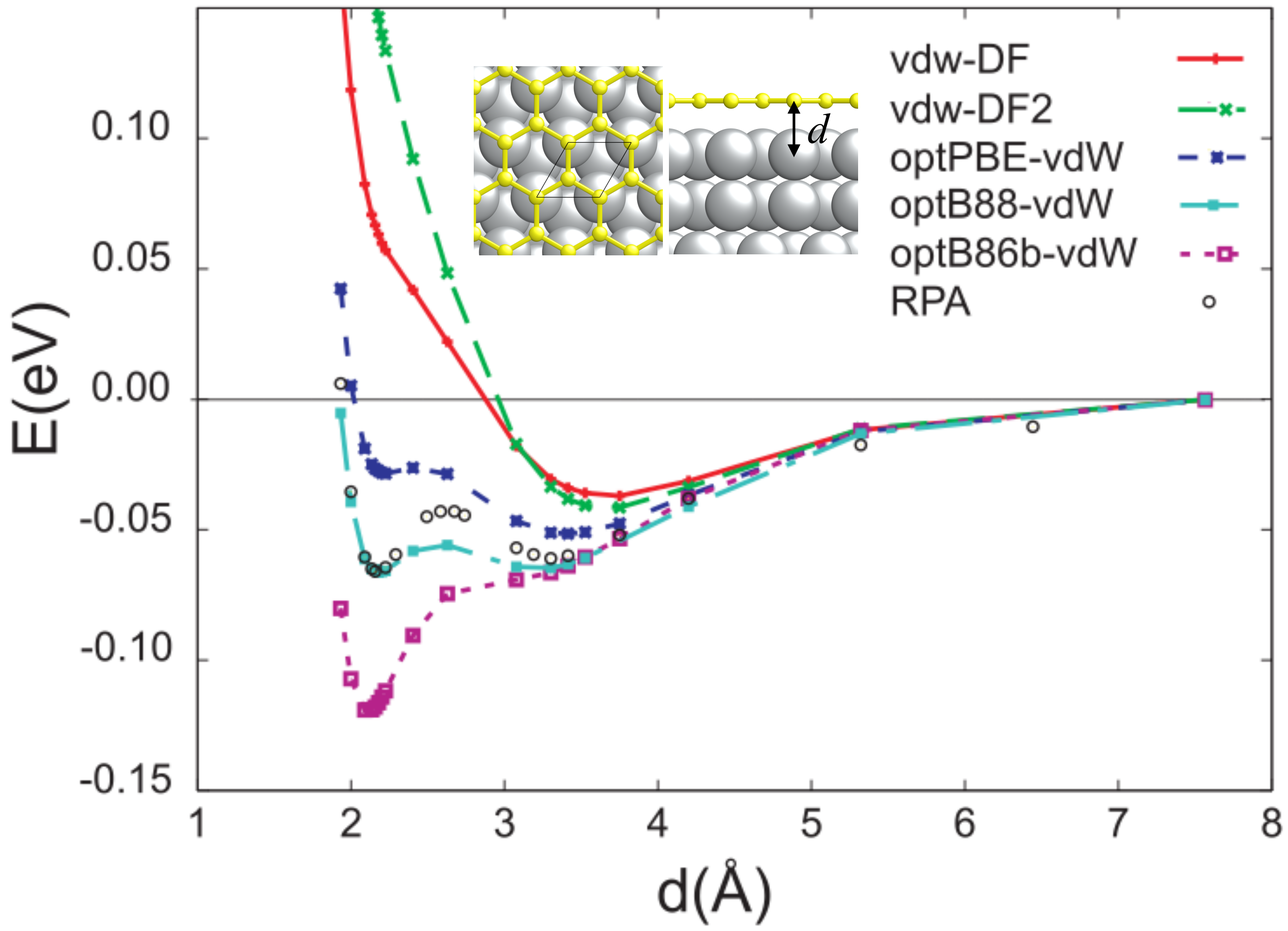
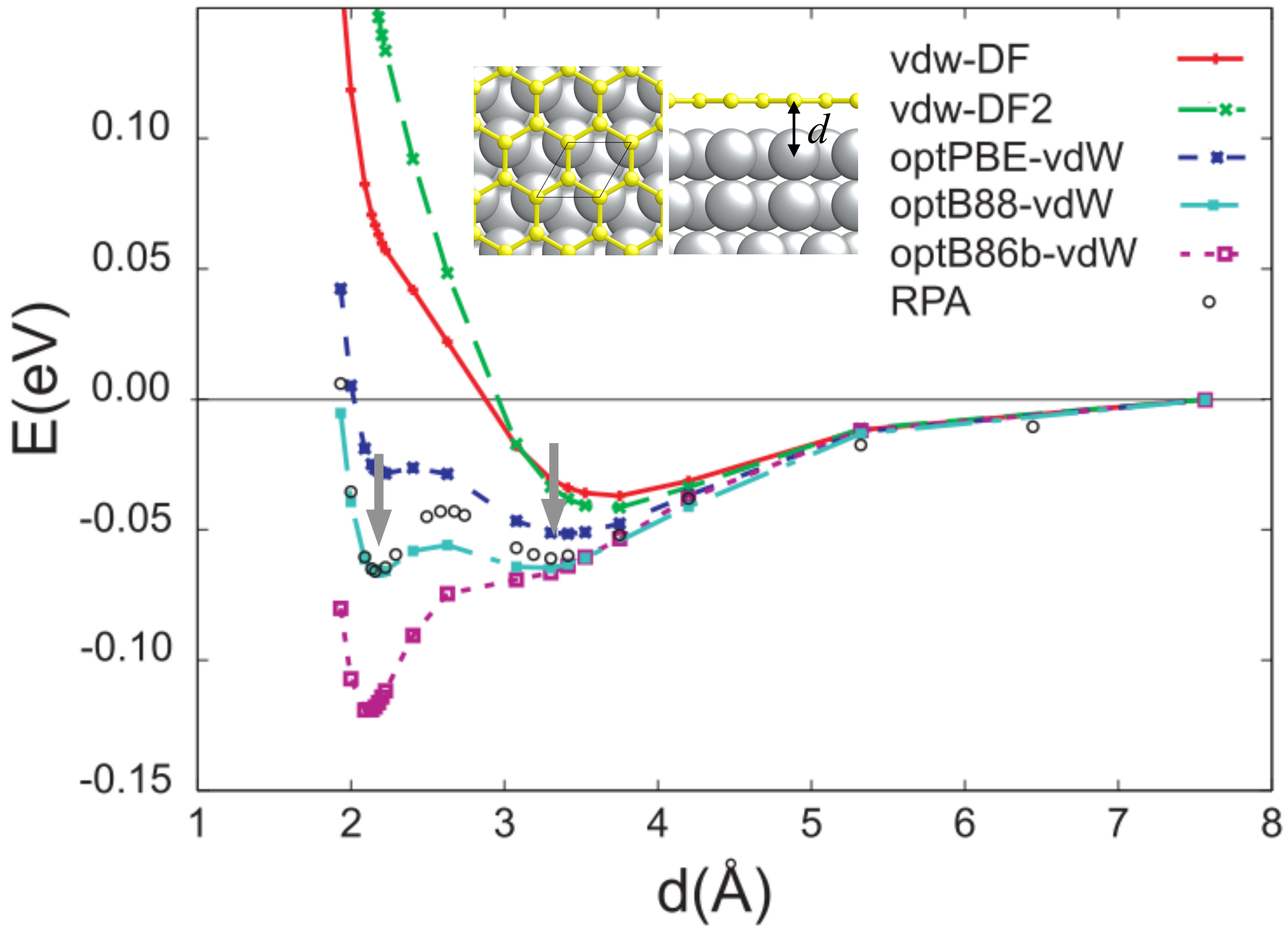



Mittendorfer, Garhofer, Redinger, Klimeš, Harl, and Kresse, *Phys. Rev. B* **84**, 201401(R) (2011).

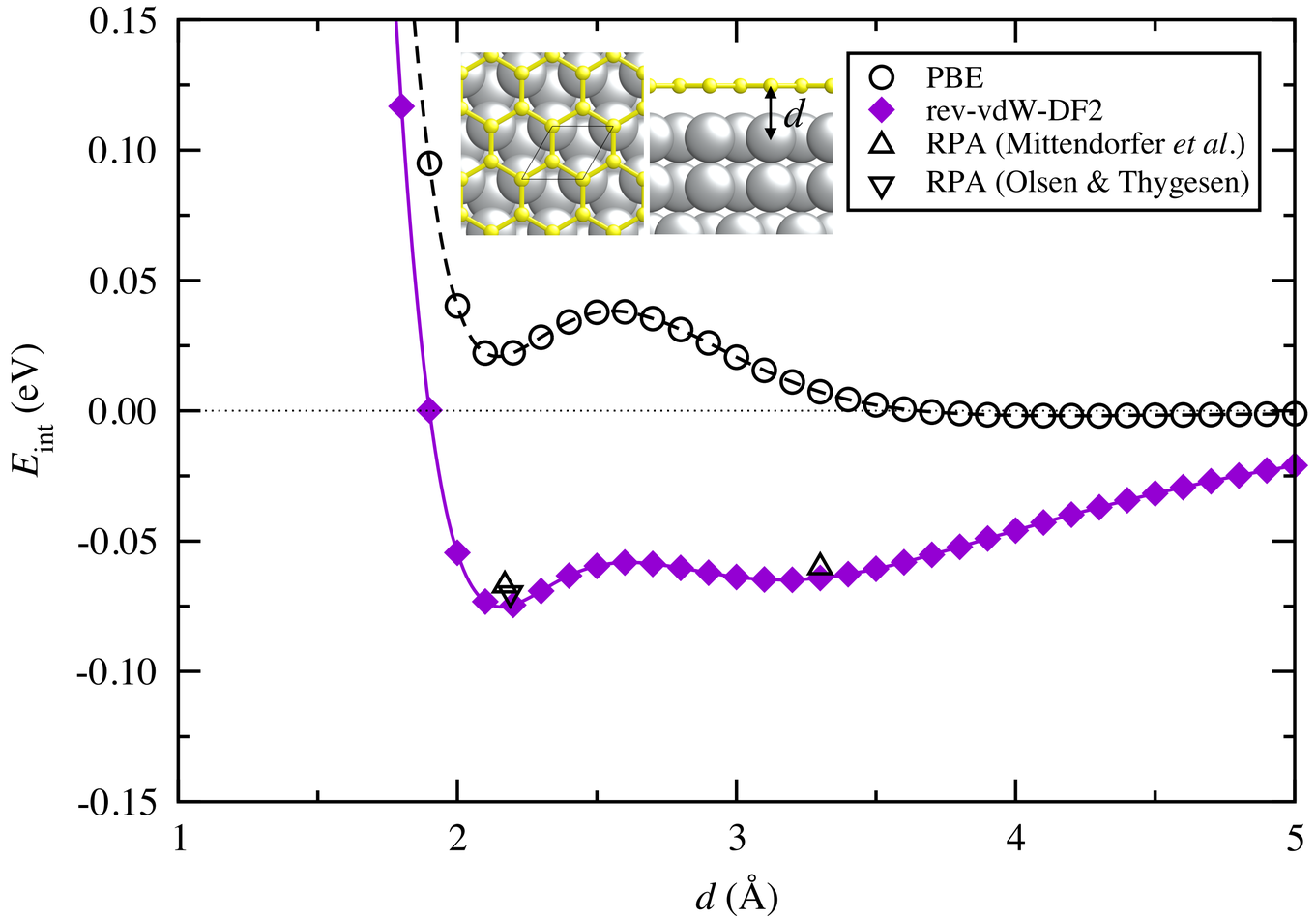
# Graphene/Ni(111)




- Two minima in the binding energy curve for chemisorption and physisorption
- Good system to test the accuracy to describe both strong and weak interactions

Mittendorfer, Garhofer, Redinger, Klimeš, Harl, and Kresse, *Phys. Rev. B* **84**, 201401(R) (2011).

# Graphene/Ni(111)




- rev-vdW-DF2 Interaction energies are in good agreement with the RPA ones
- Two minima in the interaction energy curve are nicely reproduced.

RPA: Mittendorfer, *et al*, *Phys. Rev. B* **84**, 201401(R) (2011), Olsen & Thygesen, *Phys. Rev. B* **87**, 075111 (2013).

# Outline

- Background: Dispersion forces in density functional theory
- Theory and application of van der Waals density functional (vdW-DF)
  - Benchmark for molecules, materials, and interfaces
  - Case study
    - Layered materials
    - Organic semiconductors
  - Recent development
- Summary

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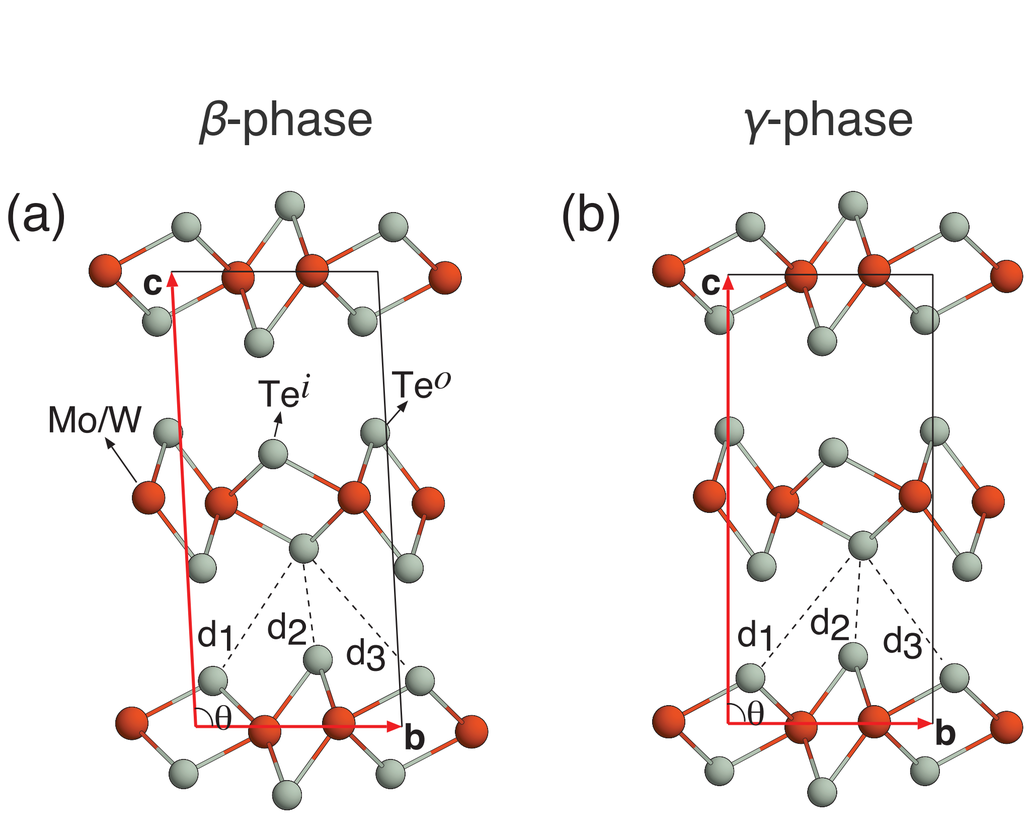
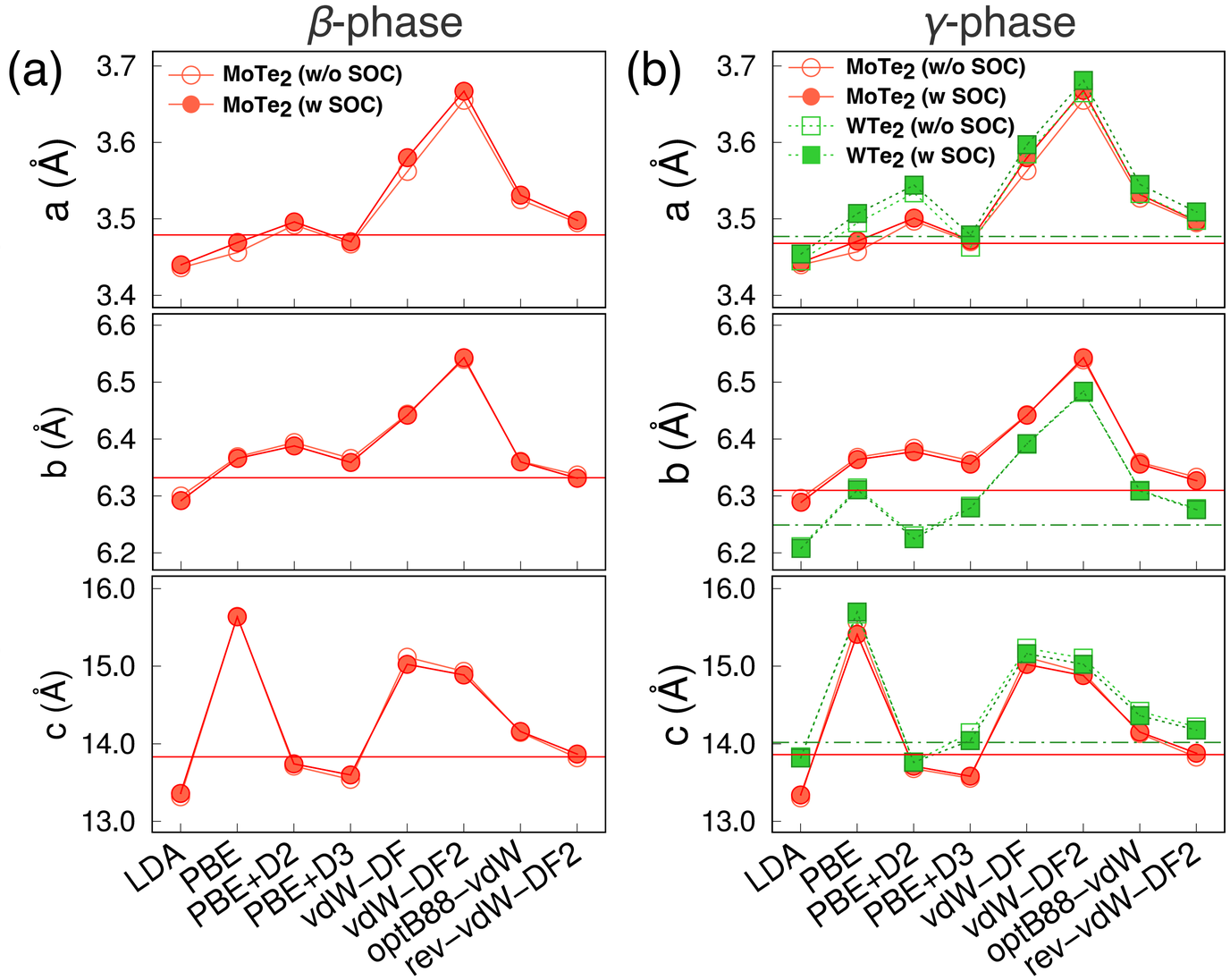
# Layered transition metal dichalcogenides

## $MoTe_2$ and $WTe_2$




Kim, Kang, IH, and Son, *Phys. Rev. B*. **95**, 180101 (R) (2017).

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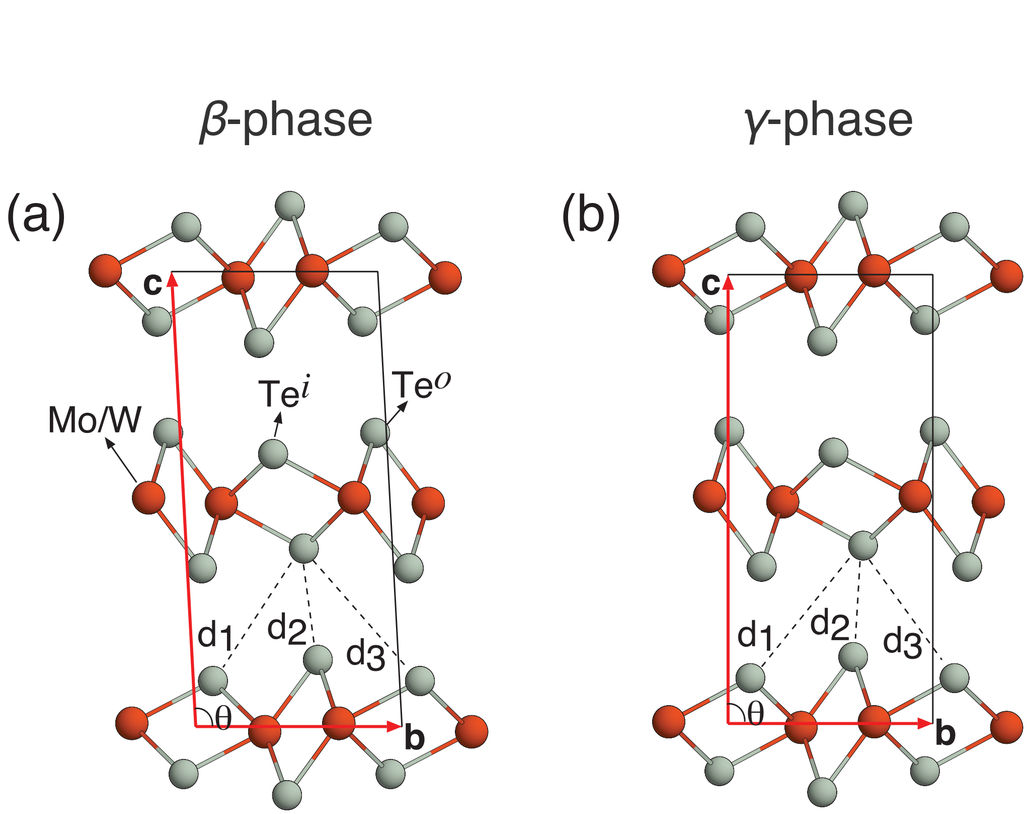


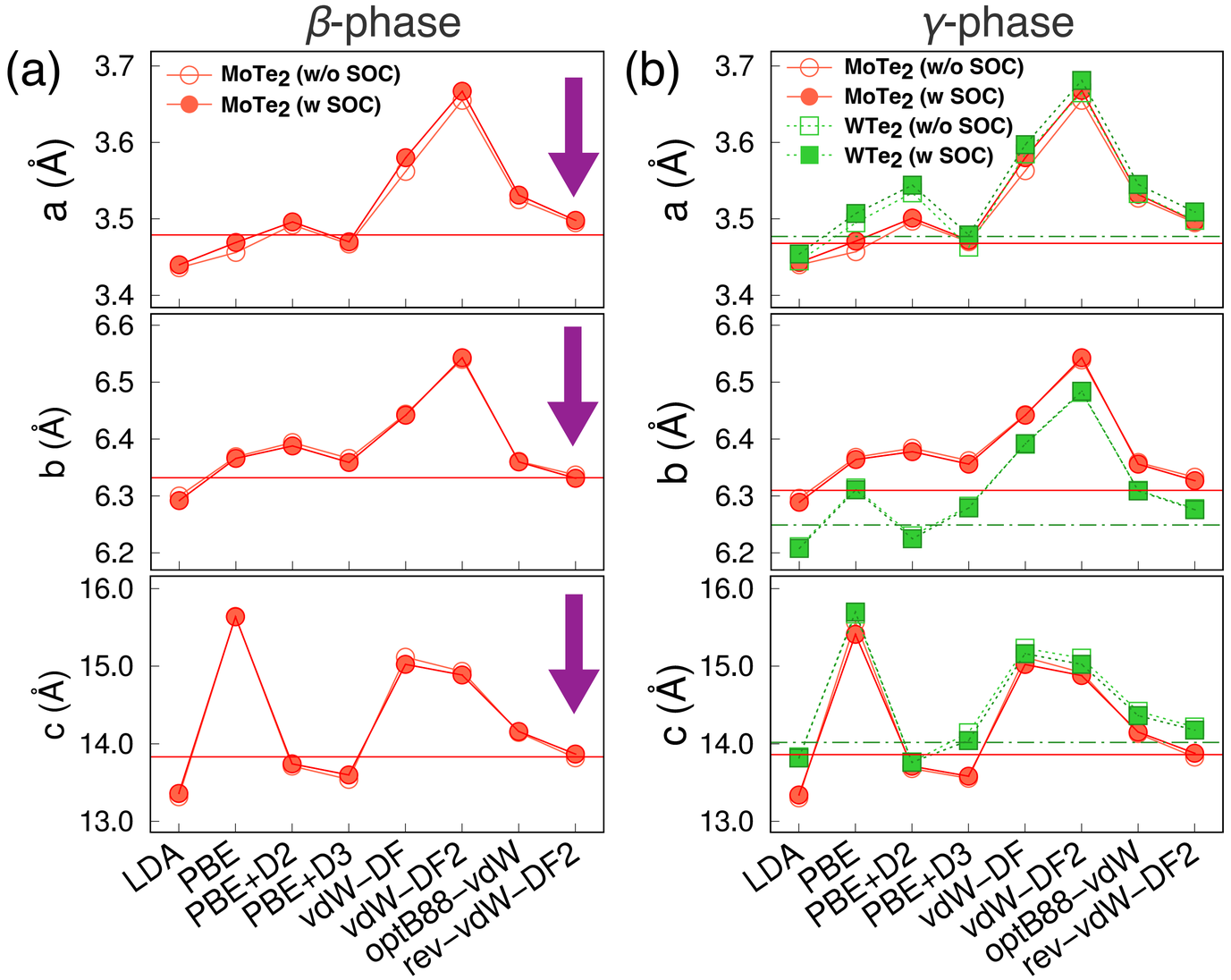


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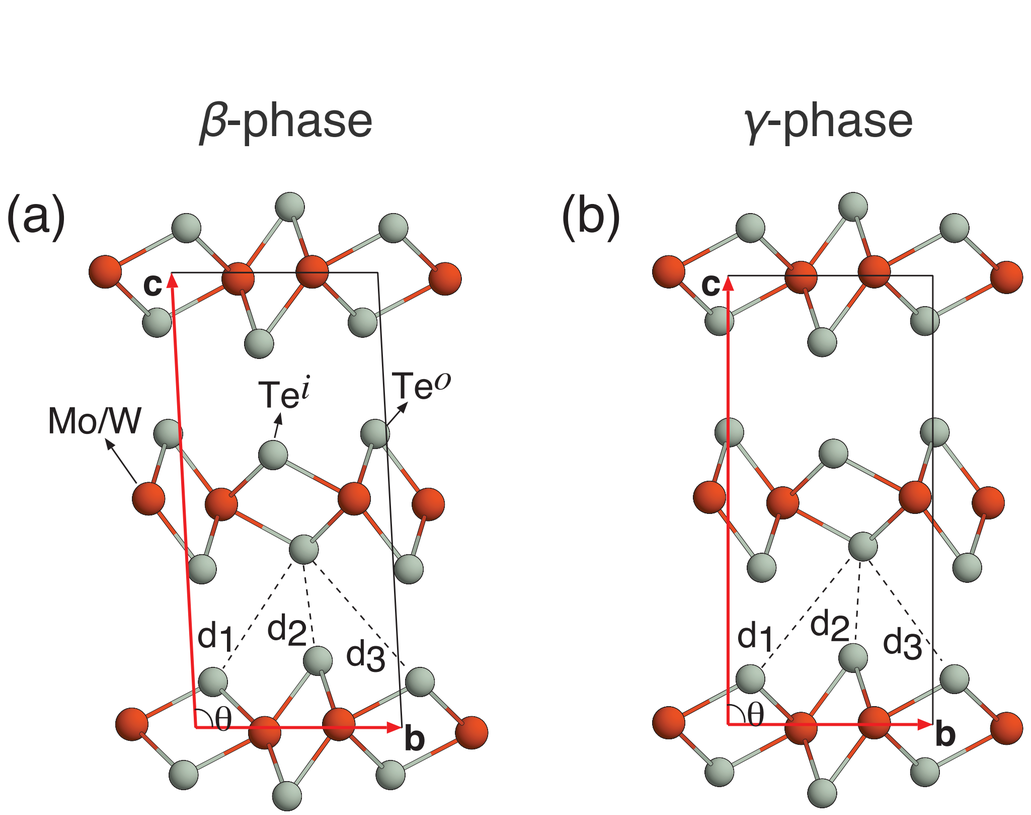


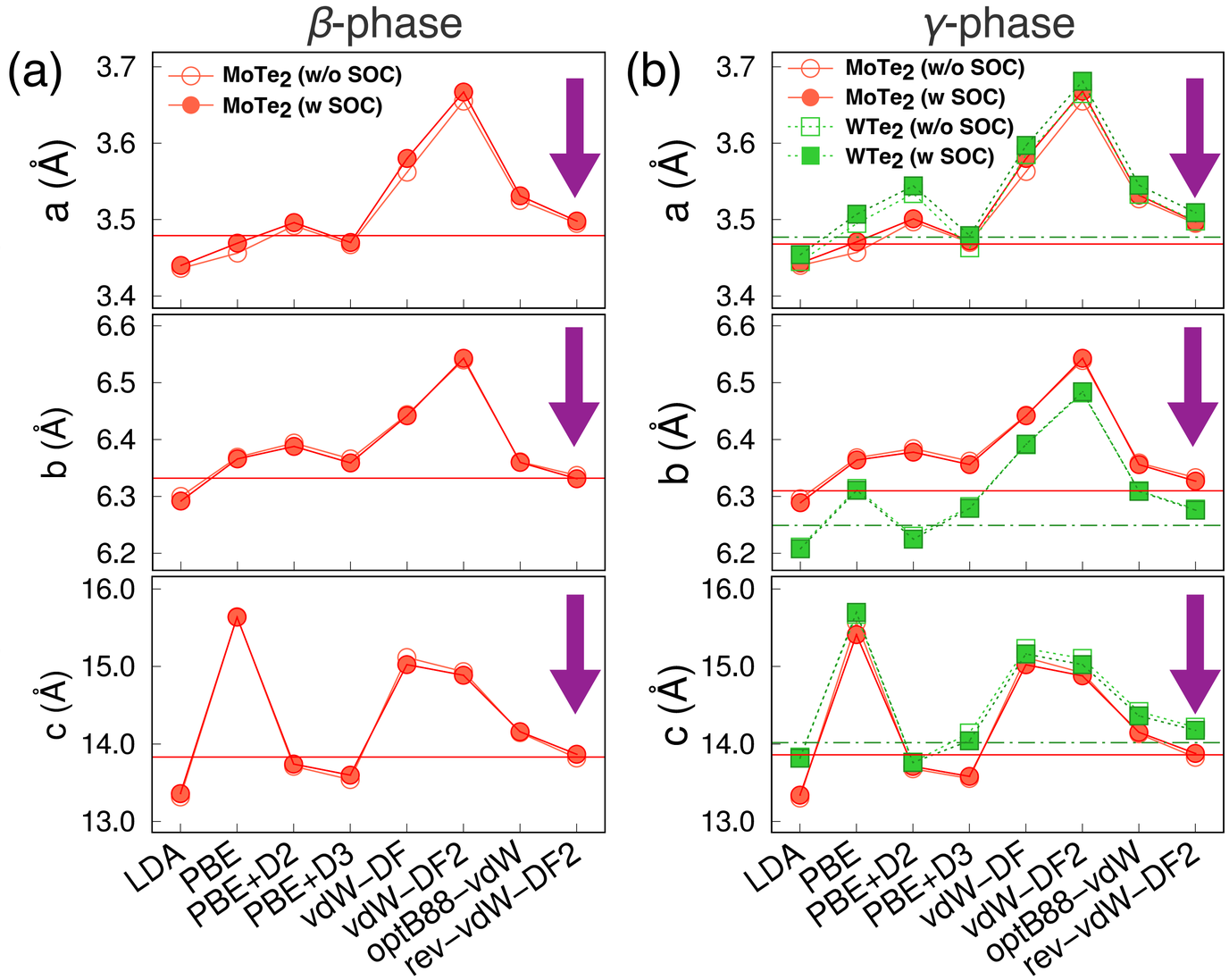


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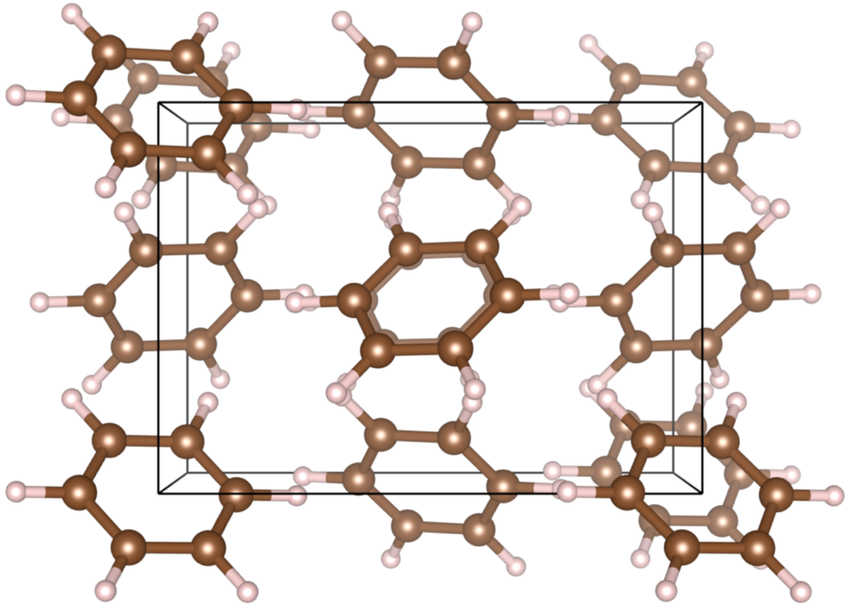
# Structure of an organic solid: Benzene crystal (*Pbca*)



Expt. : Cox, *Rev. Mod. Phys*. **30**, 159 (1958)
RPA: Lu, Li, Rocca, & Galli, *Phys. Rev. Lett*. **102**, 206411 (2009).
DMC: Zen *et al*., *Proc. Natl. Acad. Sci*. **115**, 1724 (2018).

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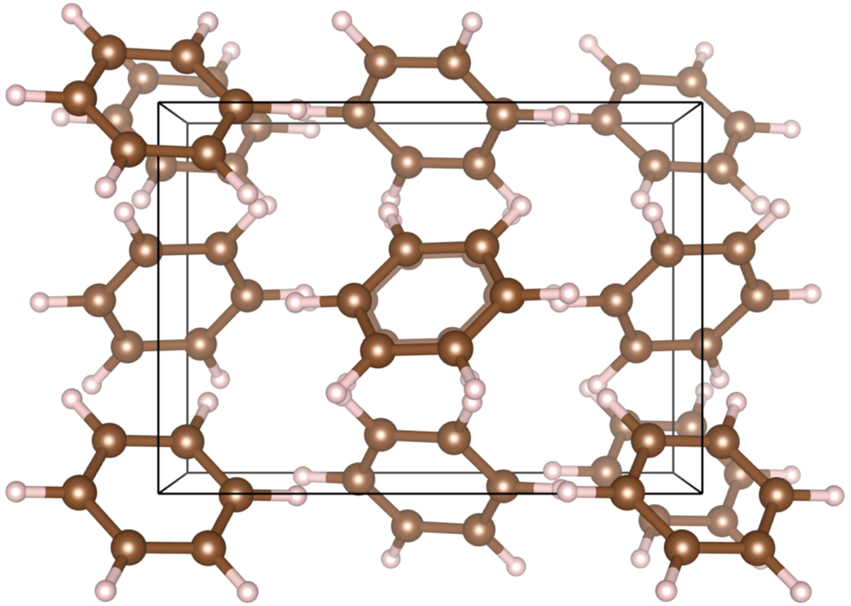

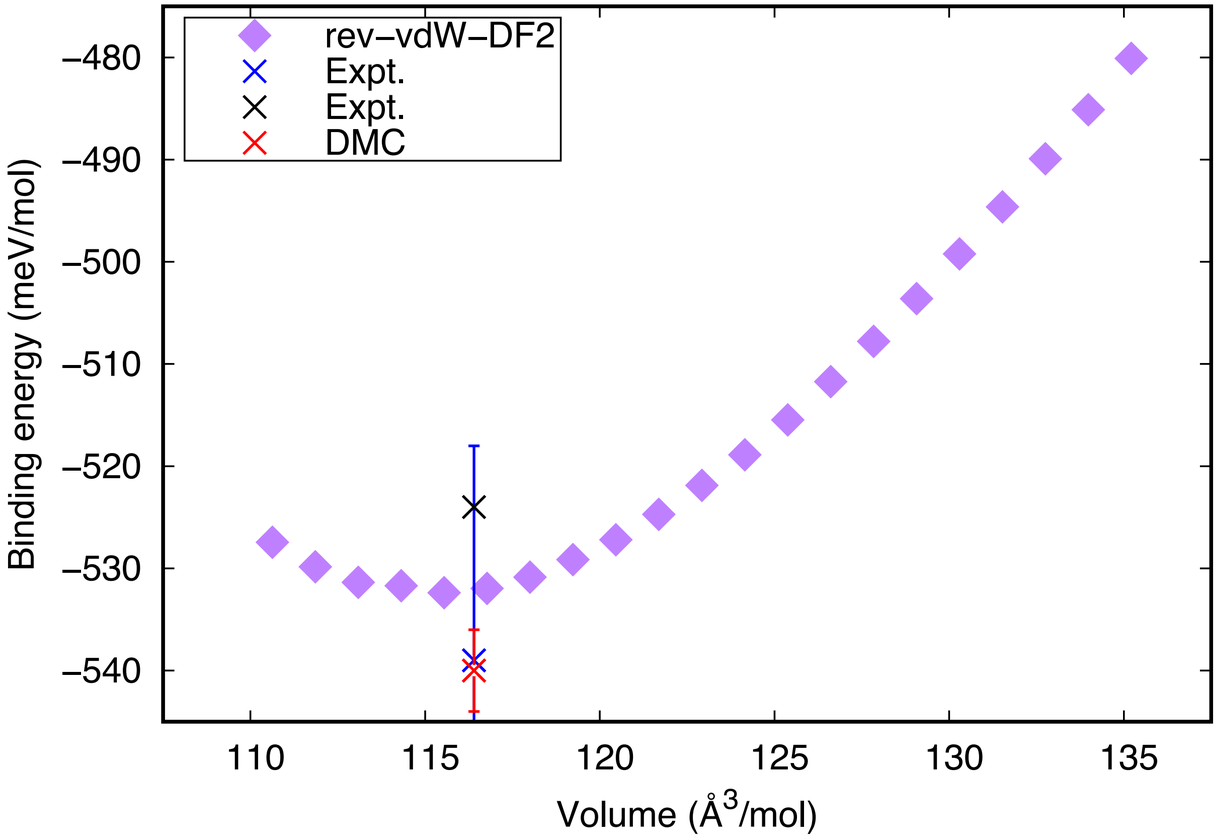


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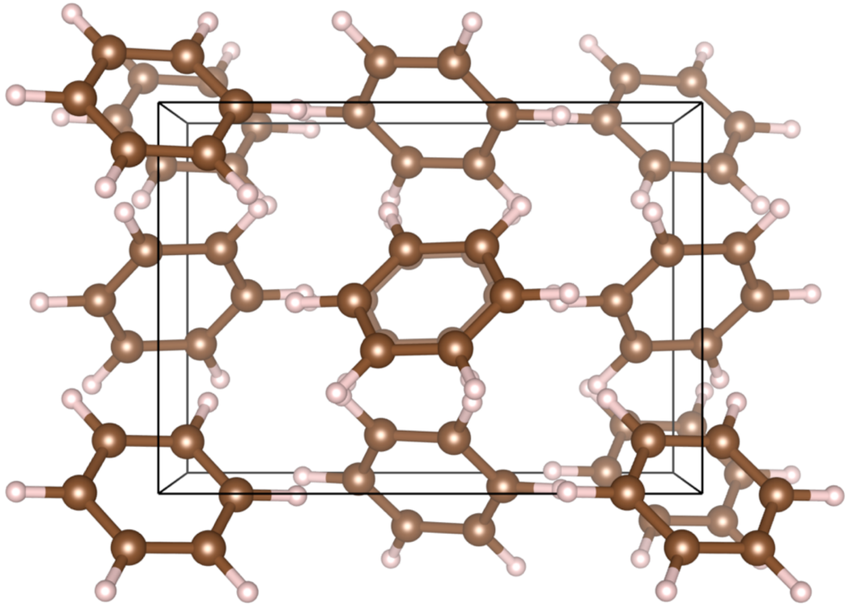

| | *a* (Å) | *b* (Å) | *c* (Å) | $V_0$ (Å$^3$) | $E_b$ (eV/mol) |
|---|---|---|---|---|---|
| PBE | 8.19 | 10.118 | 7.541 | 624.9 | |
| vdW-DF2 | 7.477 | 9.496 | 6.872 | 487.9 | 0.563 |
| rev-vdW-DF2 | 7.33 | 9.38 | 6.734 | 463 | 0.53 |
| RPA@PBE | | | | 1.00×$V_0$ | 0.487 |
| DMC | | | | | 0.540±4 |
| Expt. (-195°C) | 7.292 | 9.471 | 6.742 | 465.6 | 0.542 |


Expt. : Cox, *Rev. Mod. Phys*. **30**, 159 (1958)
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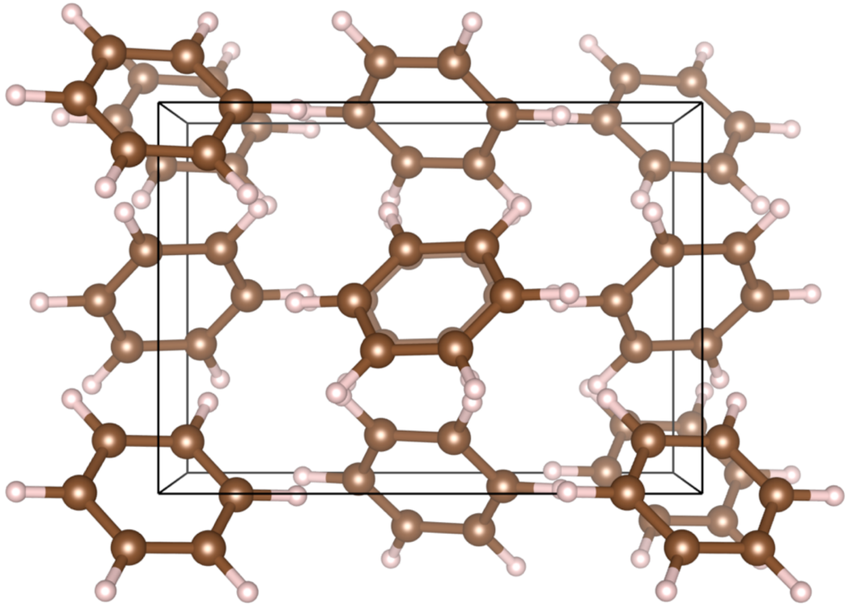

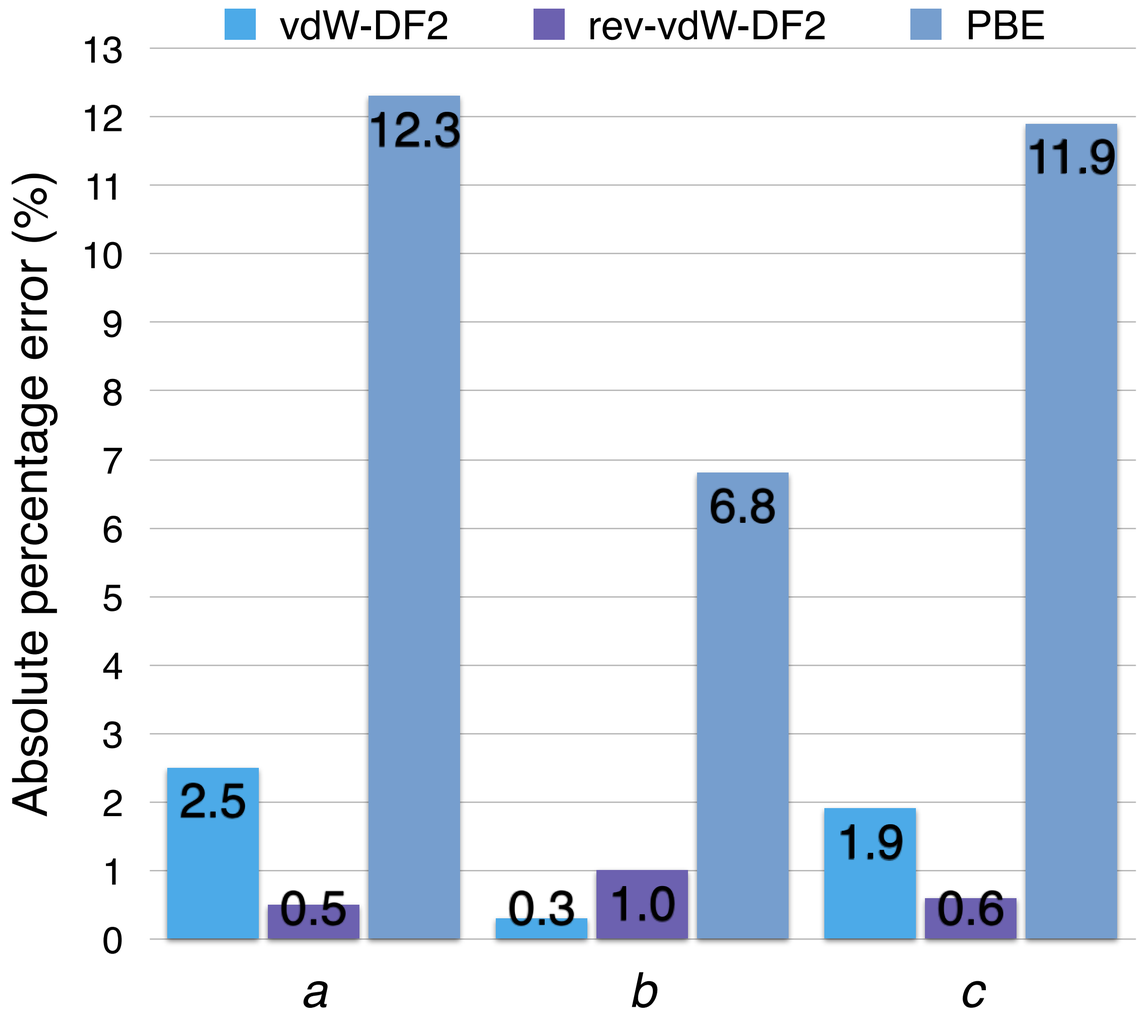


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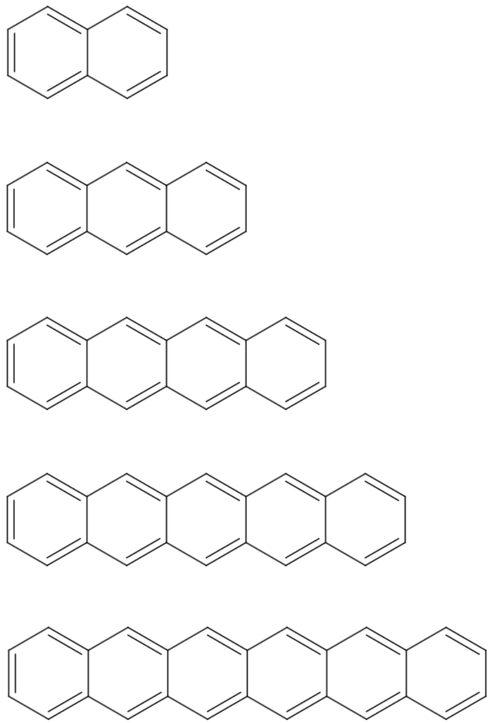
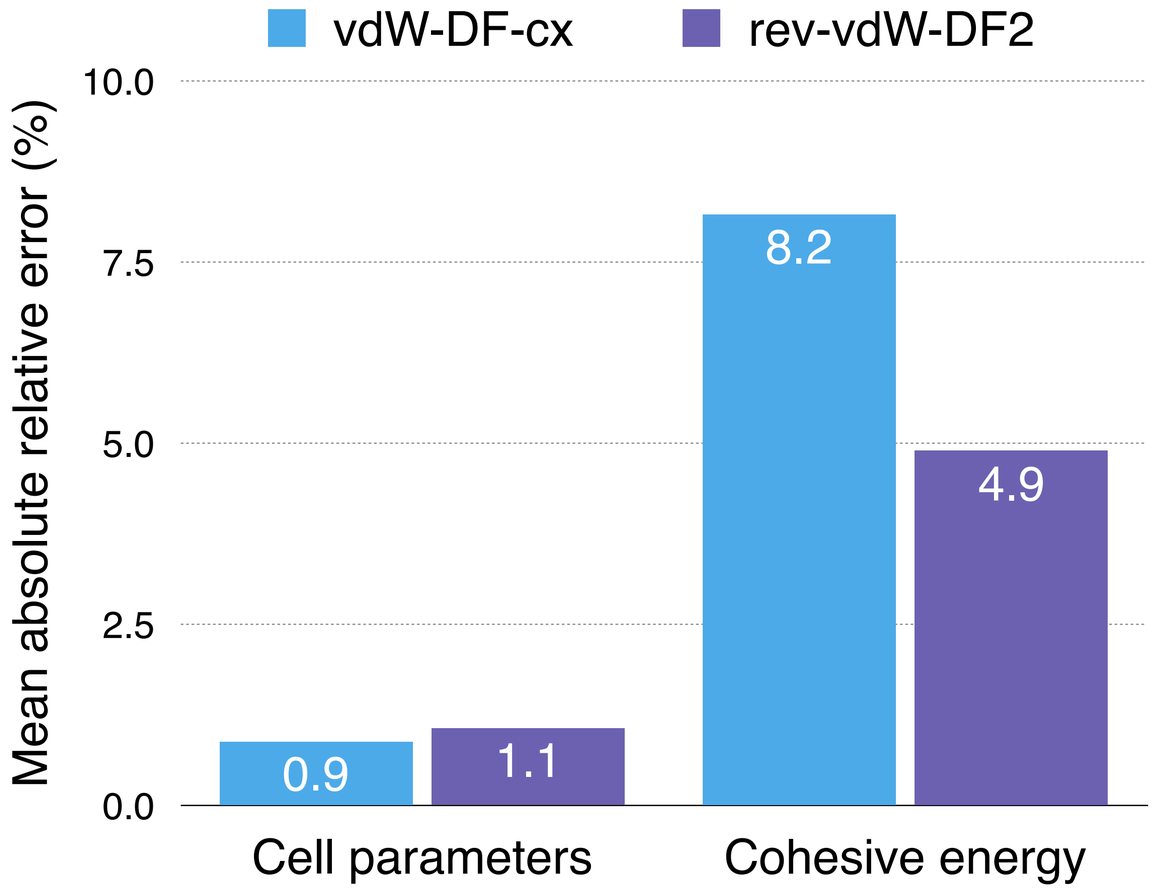
# Structures of organic solids: Oligoacene crystals






Yanagisawa and IH in *Theoretical Chemistry for Advanced Nanomaterials - Functional Analysis by Computation and Experiment*. (Springer-Nature, 2020)

# Electronic structure — Band gaps of oligoacene crystals

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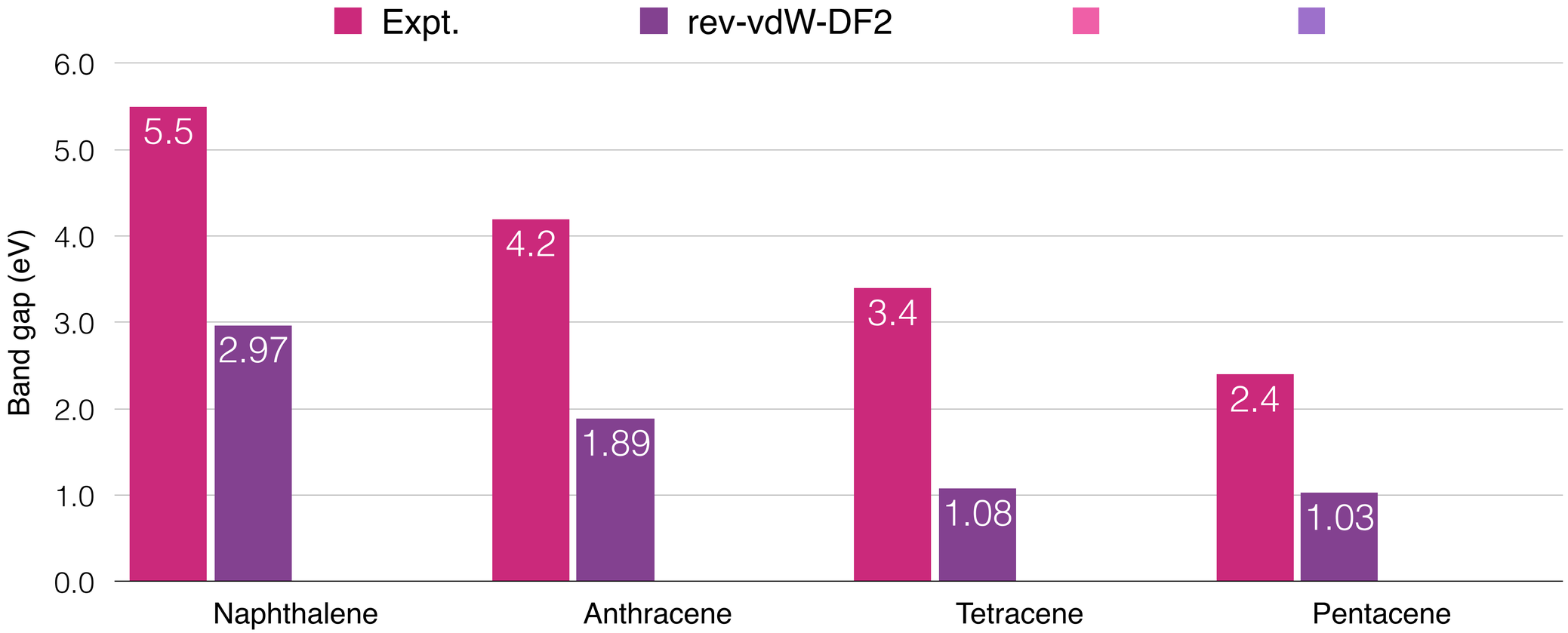



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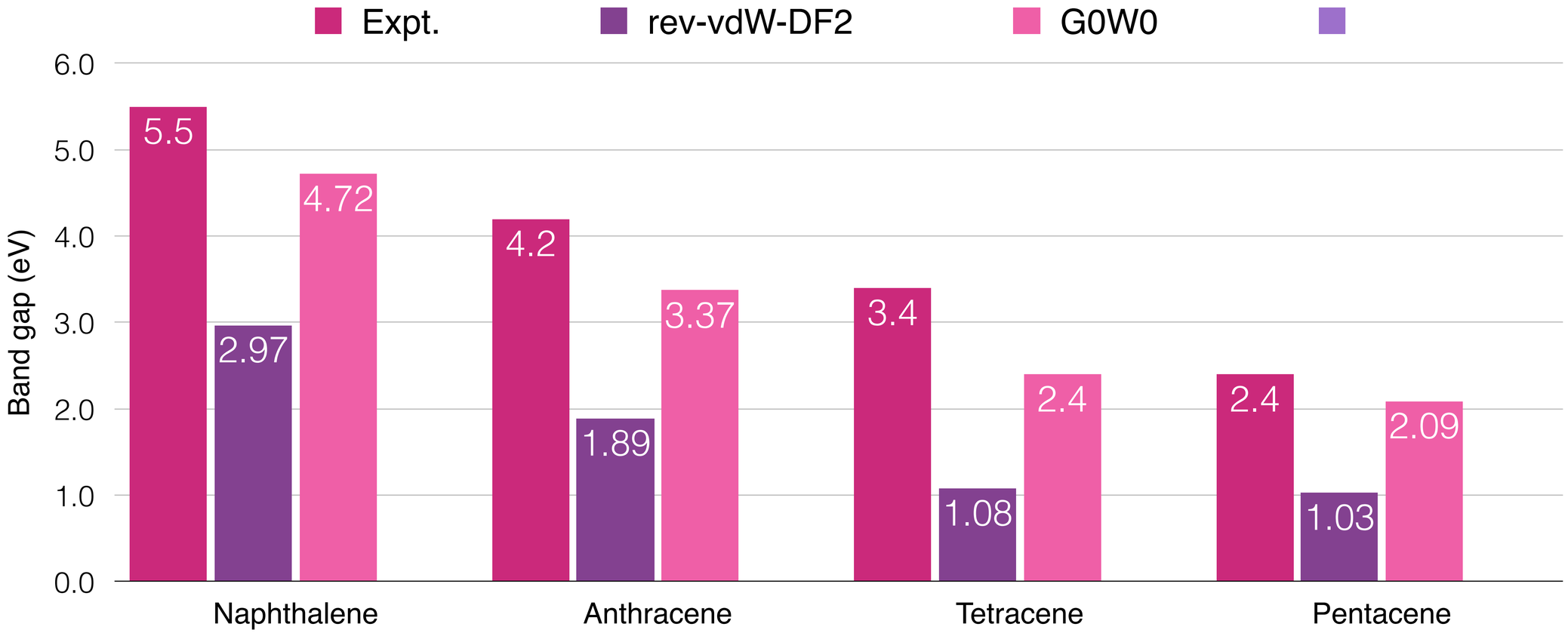



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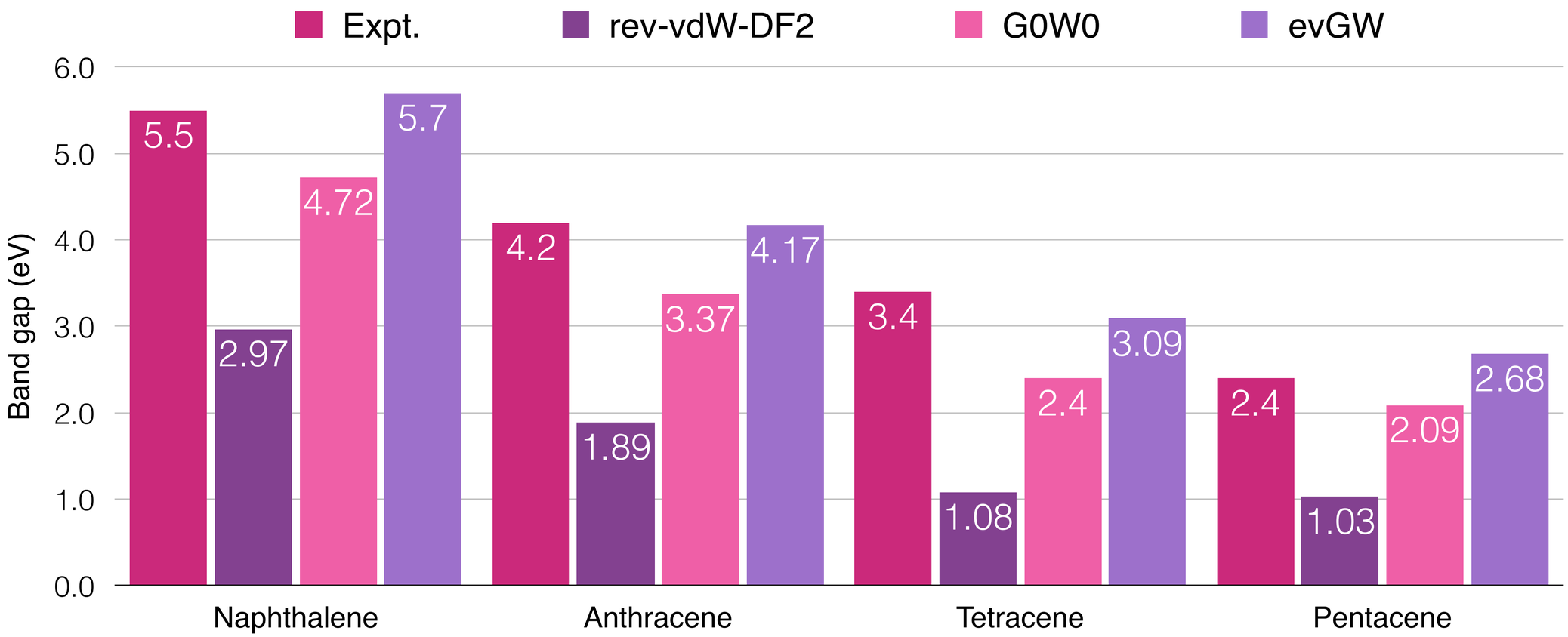


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# Lattice dynamics

# Lattice dynamics

Diagonalization of the dynamical matrix

$$|D_{s\alpha,t\beta}(\mathbf{q}) - \omega_{\mathbf{q}}^2 \delta_{s,t}\delta_{\alpha,\beta}| = 0$$

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \tilde{C}_{s\alpha,t\beta}(\mathbf{q})$$

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Fourier transform of the interatomic force constant [$C_{s\alpha,t\beta}(I,J)$]

$$\tilde{C}_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{N} \sum_{I,J} C_{s\alpha,t\beta}(I,J) e^{-i\mathbf{q}\cdot(\mathbf{R}_I - \mathbf{R}_J)}$$

# Lattice dynamics from the perturbation theory

Diagonalization of the dynamical matrix

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Fourier transform of atomic displacement

# Lattice dynamics from the perturbation theory

Diagonalization of the dynamical matrix

$$|D_{s\alpha,t\beta}(\mathbf{q}) - \omega_{\mathbf{q}}^2 \delta_{s,t}\delta_{\alpha,\beta}| = 0$$

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$$\frac{\partial^2 E_{\text{tot}}}{\partial u_{s,\mathbf{q}}^{\alpha *} \partial u_{t,\mathbf{q}}^{\beta}} = \sum_{m}^{\text{occ}} \sum_{\mathbf{k}\in \text{BZ}} \left( 2 \left\langle \frac{\partial \psi_{m,\mathbf{k}}}{\partial u_{s,\mathbf{q}}^{\alpha}} \middle| \frac{\partial v_{\text{ext}}}{\partial u_{t,\mathbf{q}}^{\beta}} \middle| \psi_{m,\mathbf{k}} \right\rangle + \left\langle \psi_{m,\mathbf{k}} \middle| \frac{\partial^2 v_{\text{ext}}}{\partial u_{s,\mathbf{q}}^{\alpha *} \partial u_{t,\mathbf{q}}^{\beta}} \middle| \psi_{m,\mathbf{k}} \right\rangle \right) + \frac{\partial^2 E_{\text{II}}}{\partial u_{s,\mathbf{q}}^{\alpha *} \partial u_{t,\mathbf{q}}^{\beta}}$$

↑

First-order change in the wave function (modulated by ***q***)

# Density functional perturbation theory

Linearized Kohn-Sham equation wrt external perturbation $\lambda_{\mathbf{q}}$ (Sternheimer equation)

$$\left(\hat{H} - \varepsilon_{m,\mathbf{k}}\right) \left| \frac{\partial \psi_{m,\mathbf{k}}}{\partial u^{\alpha}_{s,\mathbf{q}}} \right\rangle = -\left( \frac{\partial \hat{H}}{\partial u^{\alpha}_{s,\mathbf{q}}} - \frac{\partial \varepsilon_{m,\mathbf{k}}}{\partial u^{\alpha}_{s,\mathbf{q}}} \right) \left| \psi_{m,\mathbf{k}} \right\rangle$$

# Density functional perturbation theory

Linearized Kohn-Sham equation wrt external perturbation $\lambda_{\mathbf{q}}$ (Sternheimer equation)

$$\left(\hat{H} - \varepsilon_{m,\mathbf{k}}\right) \hat{P}_{\mathrm{c},\mathbf{k}+\mathbf{q}} \left| \frac{\partial \psi_{m,\mathbf{k}}}{\partial u^{\alpha}_{\mathbf{q}}} \right\rangle = - \hat{P}_{\mathrm{c},\mathbf{k}+\mathbf{q}} \frac{\partial \hat{H}}{\partial u^{\alpha}_{s,\mathbf{q}}} \left| \psi_{m,\mathbf{k}} \right\rangle$$

$$\hat{P}_{\mathrm{c},\mathbf{k}+\mathbf{q}} = 1 - \sum_{m}^{\mathrm{occ}} |\psi_{m,\mathbf{k}+\mathbf{q}}\rangle\langle\psi_{m,\mathbf{k}+\mathbf{q}}|$$

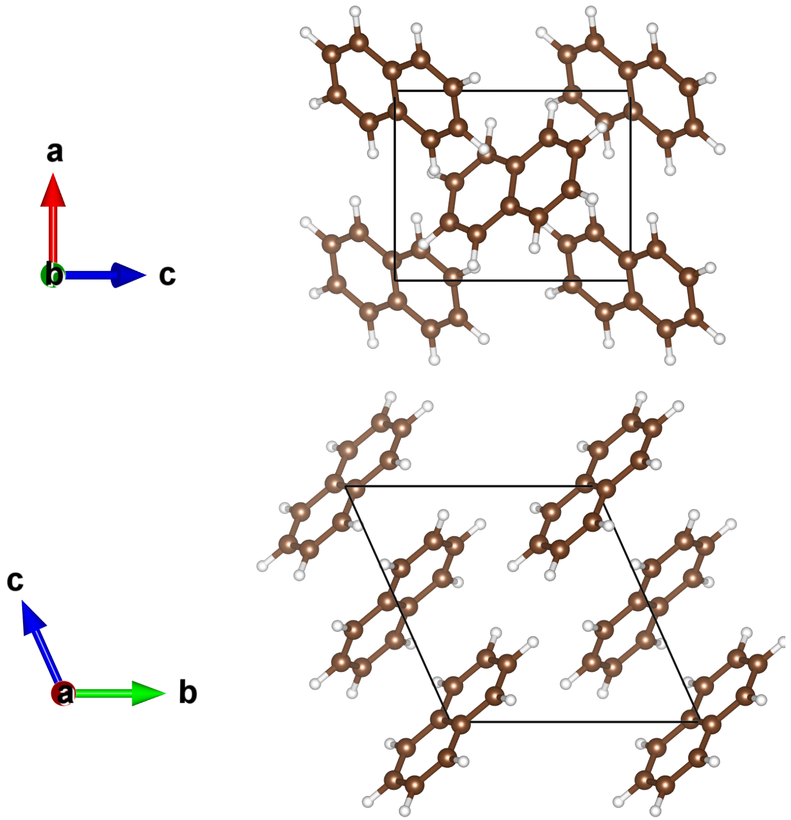
Treatment of incommensurate perturbations (arbitrary ***q***) allowed,
in contrast to the finite difference method

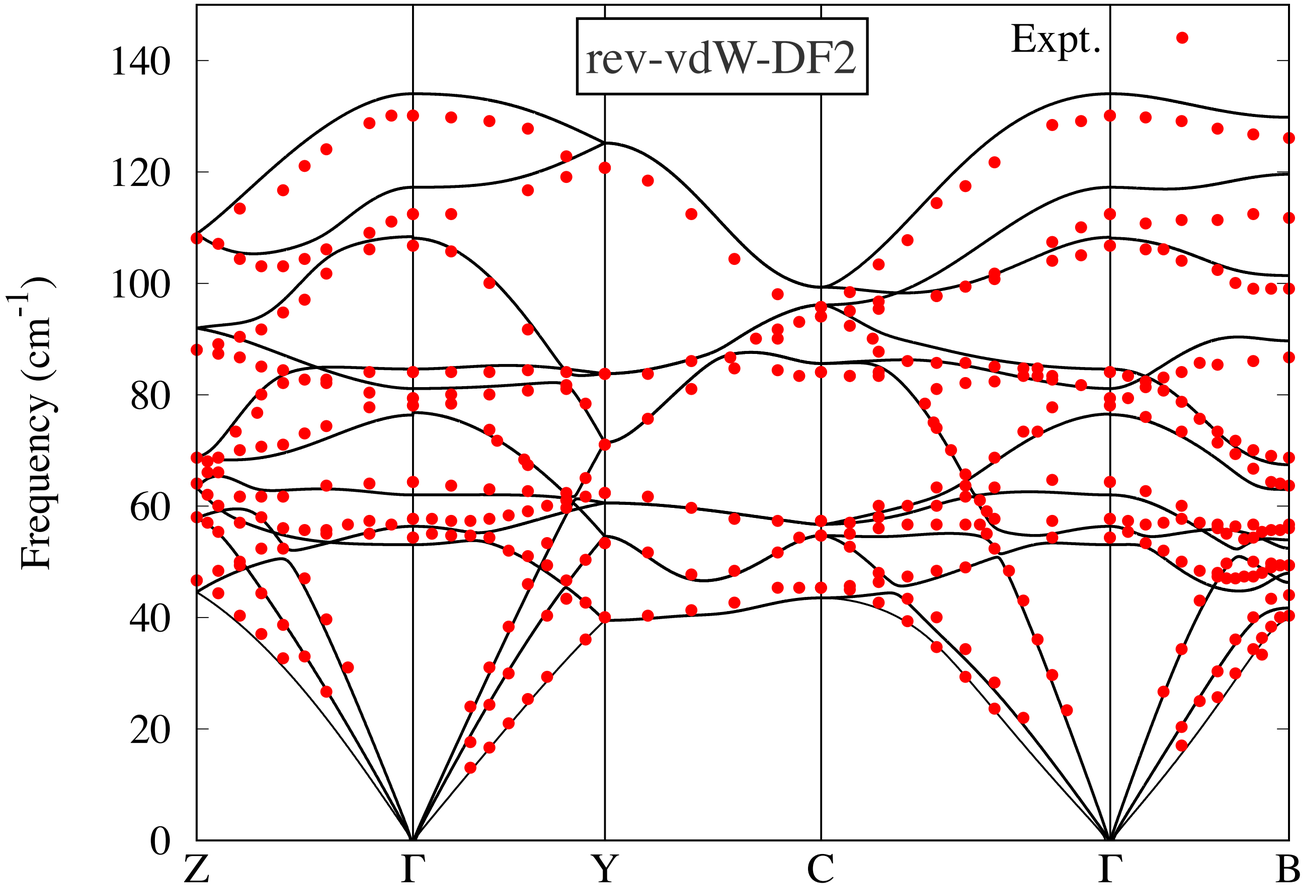
# Lattice dynamics

Phonon band structure of $d_8$-naphthalene

# Lattice dynamics

Phonon band structure of $d_8$-naphthalene




rev-vdW-DF2: IH (unpublished).

Expt. Natkaniec *et al.*, *J. Phys. C: Solid State Phys.* **13**, 4265 (1980).

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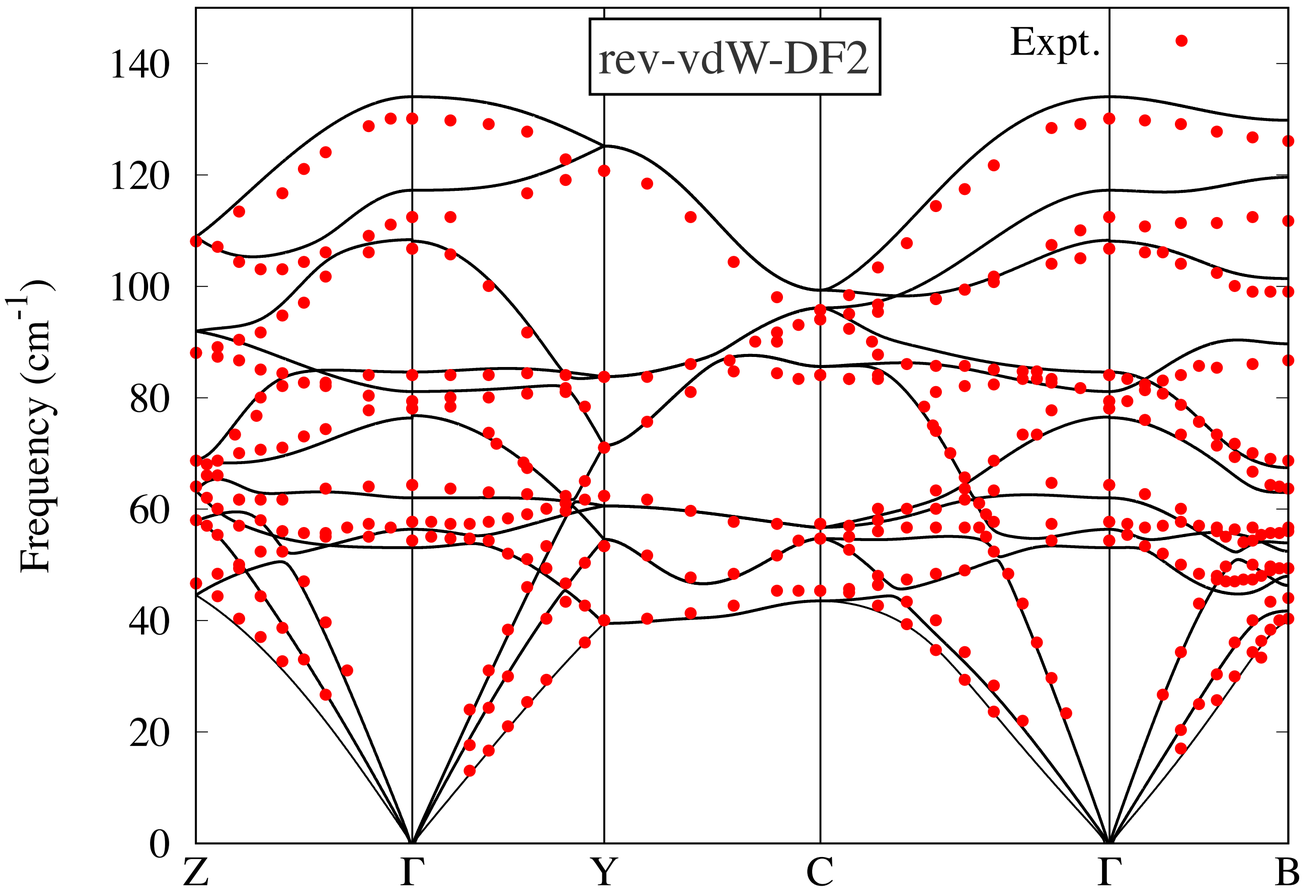
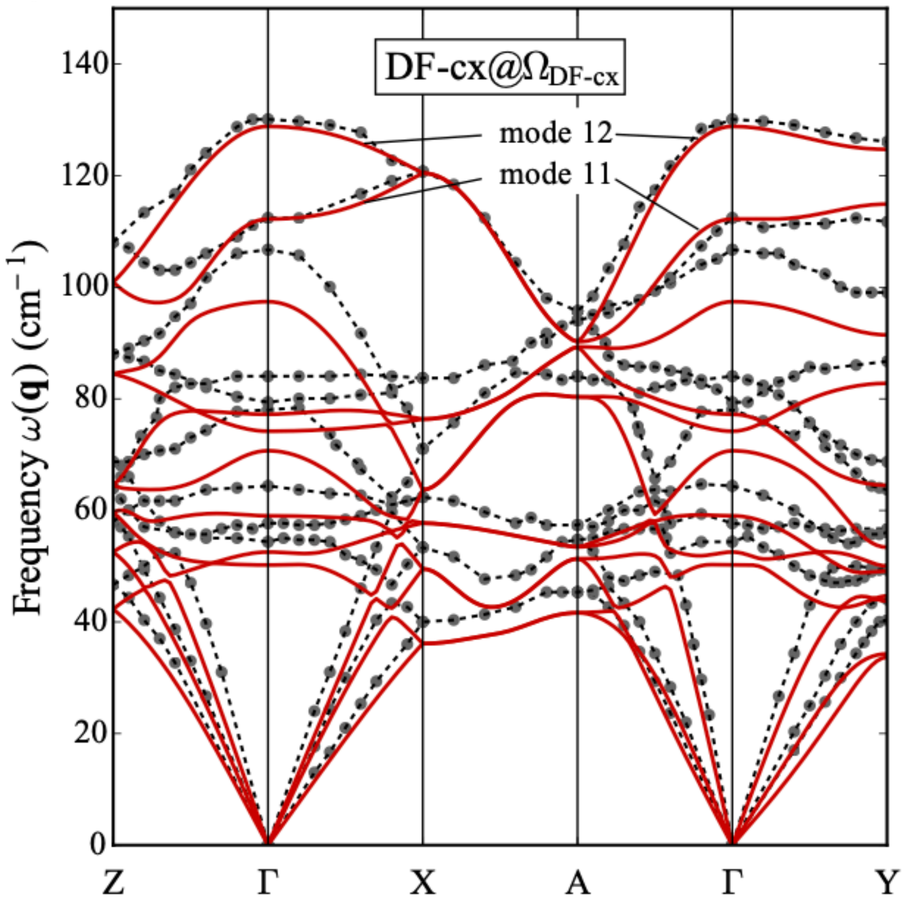
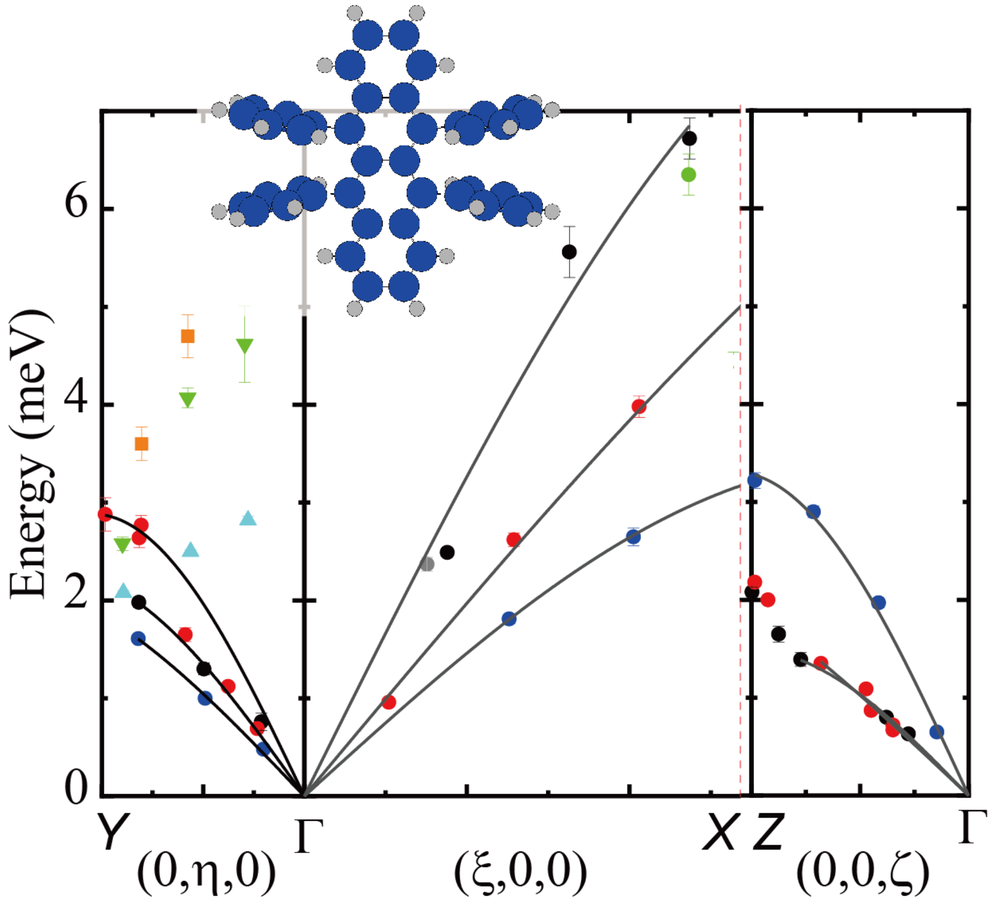


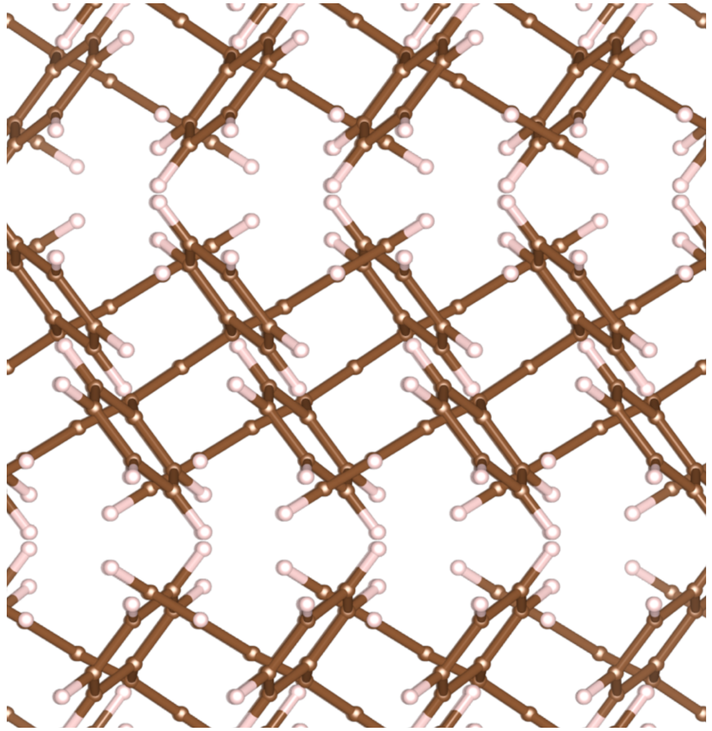

rev-vdW-DF2: IH (unpublished).
vdW-DF-cx (DF-cx): Brown-Altvater *et al.*, *Phys. Rev. B* **93**, 195206 (2016).
Expt. Natkaniec *et al.*, *J. Phys. C: Solid State Phys.* **13**, 4265 (1980).

# Phonon dispersion of the organic semiconductor rubrene




Takada, *et al.*, *Phys. Rev. B* **105**, 205205 (2022).

# Crystal structure of rubrene



| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V_0$ (Å$^3$) | $E_b$ (eV/mol) |
|---|---|---|---|---|---|
| PBE | 27.989 | 7.804 | 16.585 | 1811.1 | 0.234 |
| vdW-DF2 | 26.969 | 7.167 | 14.523 | 1403.5 | 2.319 |
| rev-vdW-DF2 | 26.828 | 7.134 | 14.04 | 1354.3 | 2.18 |
| Expt. (100K) | 26.789 | 7.17 | 14.211 | 1364.8 | |

Expt. : O. D. Jurchescu, A. Meetsma, T. T. M. Palstra, *Acta Cryst. B* **62**, 330 (2006).

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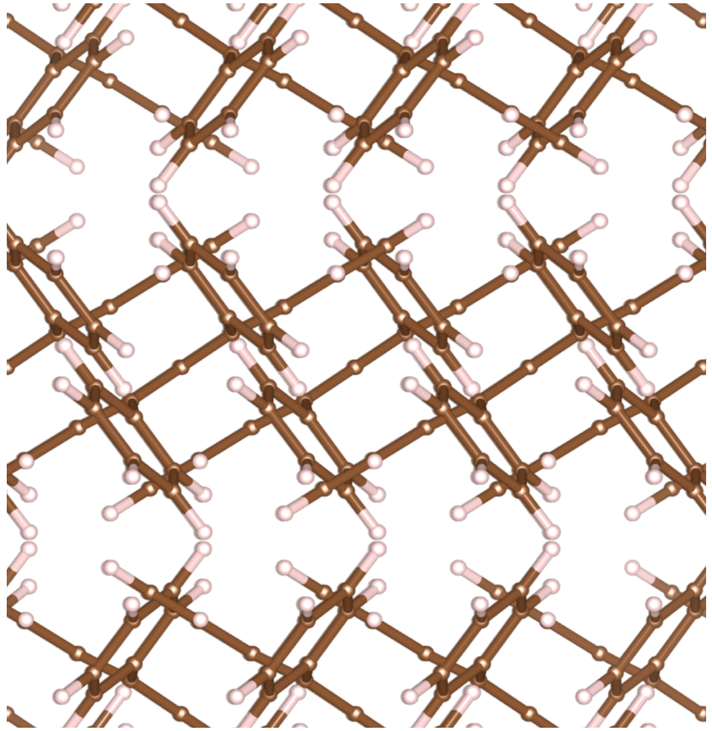

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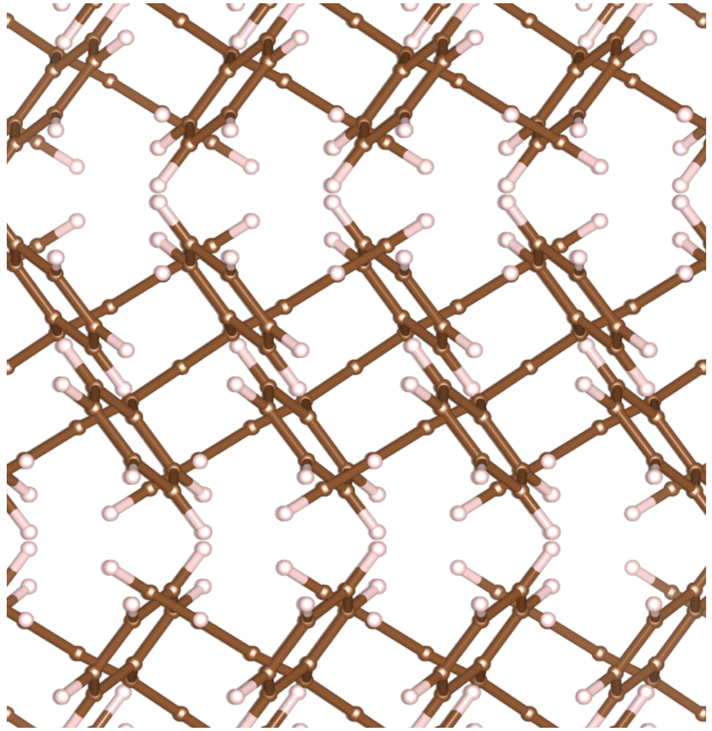

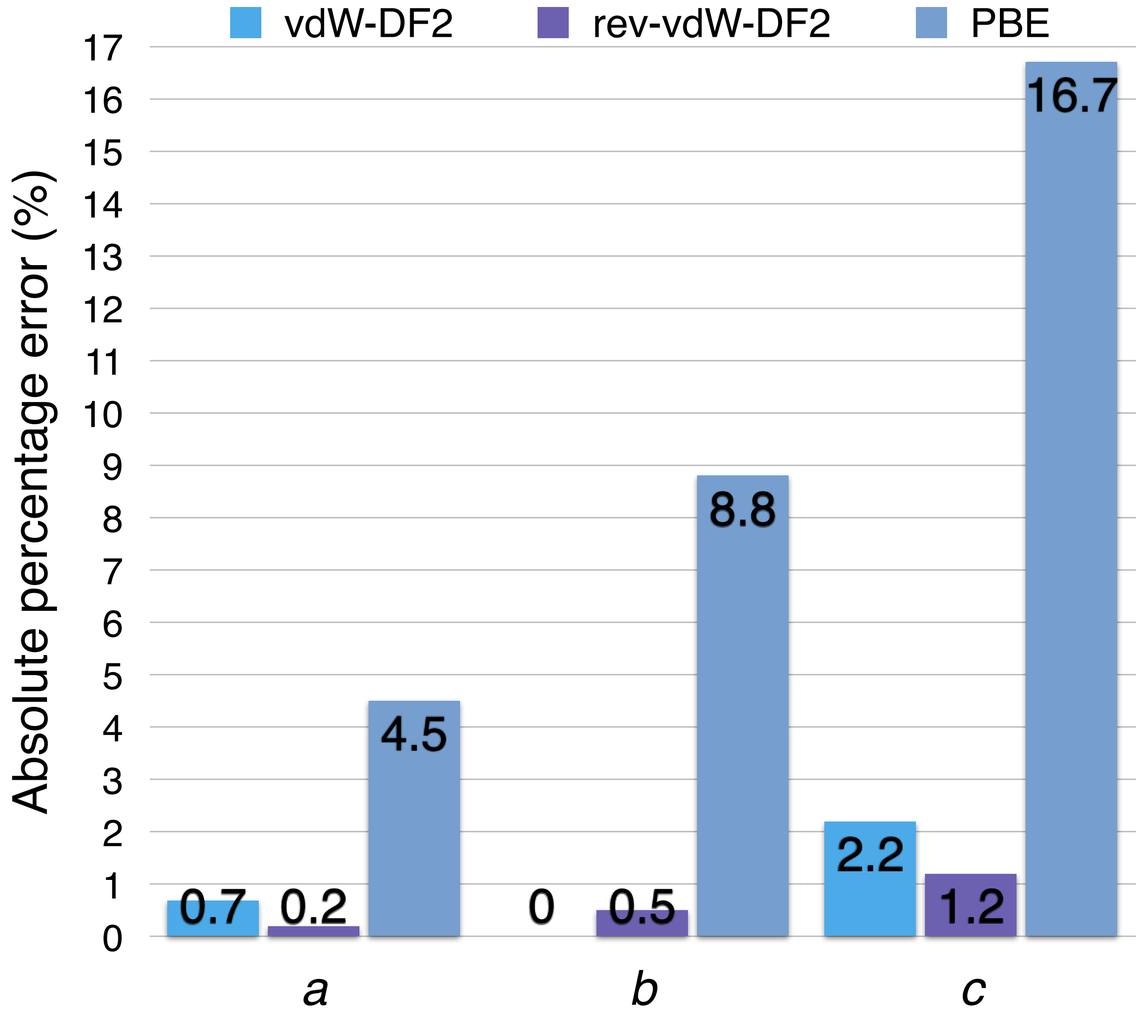


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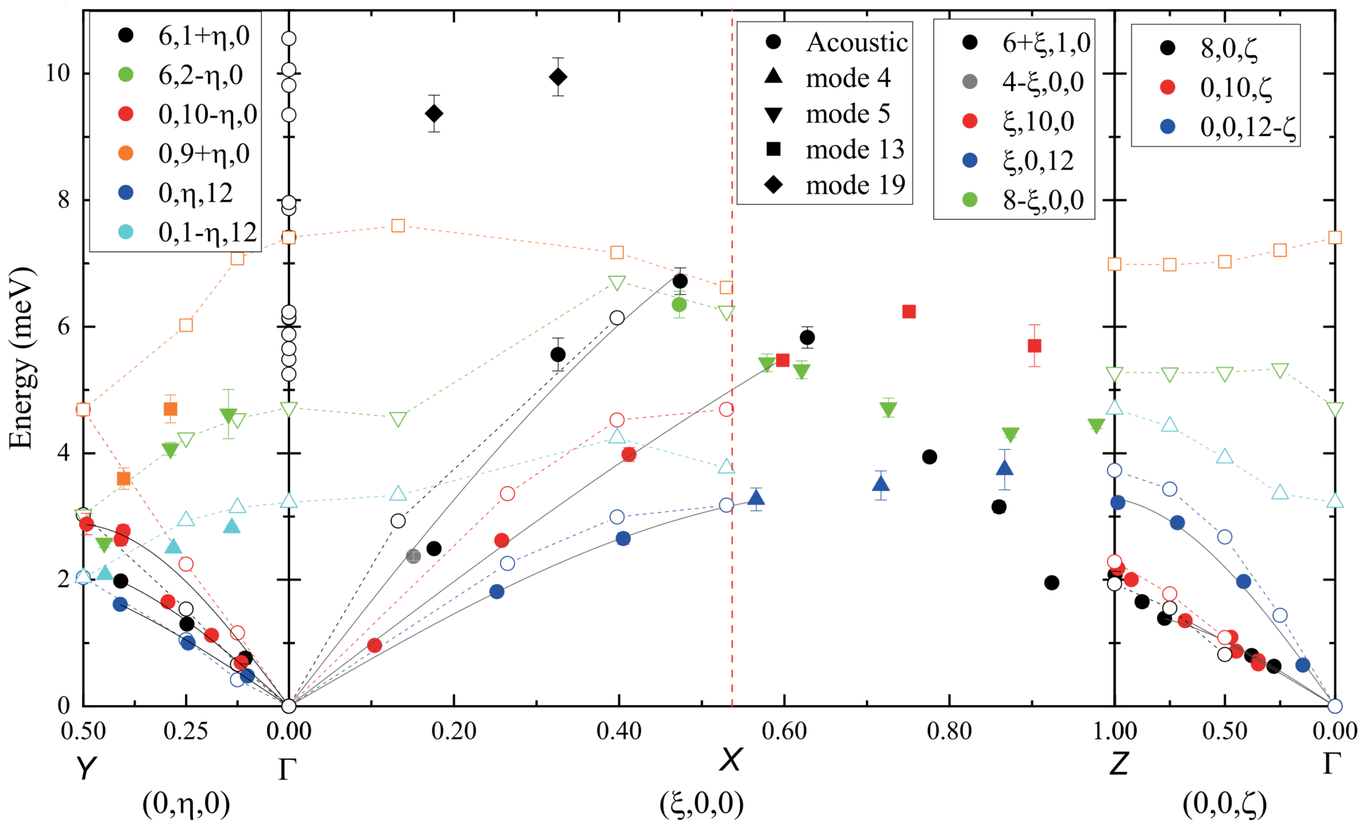
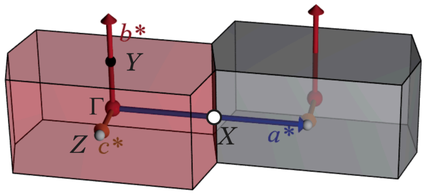
# Phonon band structure of rubrene




Filled circle: Expt.
Open circle: Calc.

Calculated phonon frequencies overestimated —temperature (unharmonic) effect?

Takada, *et al.*, *Phys. Rev. B* **105**, 205205 (2022).

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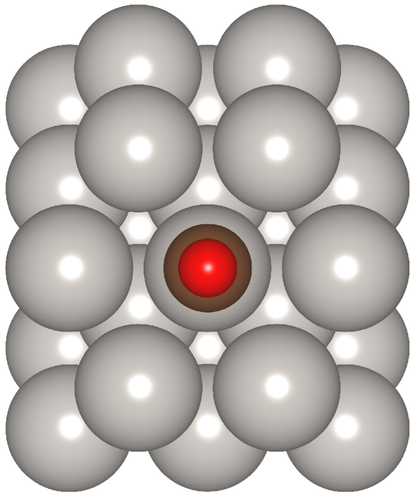
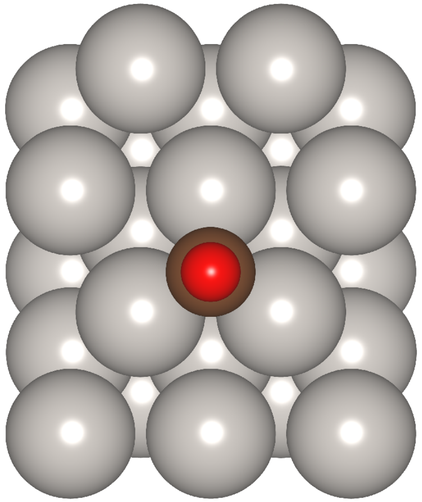
# CO puzzle: CO adsorption on Pt(111)

$$\Delta E_{\text{site}} = E_{\text{ads}}^{\text{top}} - E_{\text{ads}}^{\text{fcc}}$$

Top



Fcc-hollow



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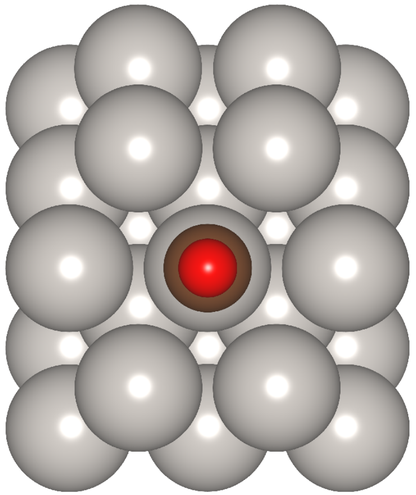
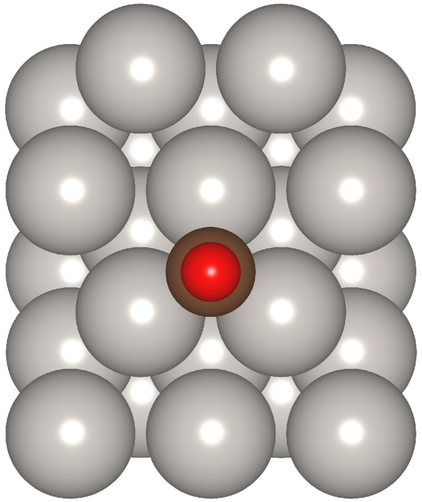
Top



Fcc-hollow

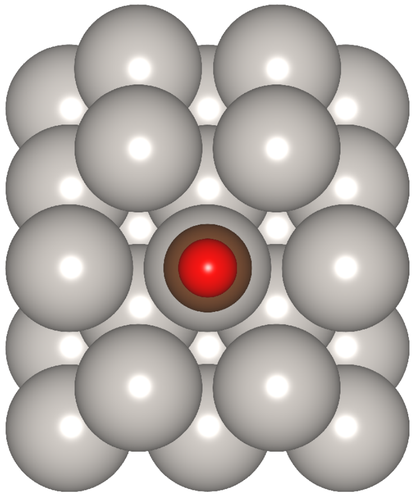


Semilocal DFT (PBE, RPBE, …) predicts wrong adsorption site (fcc)

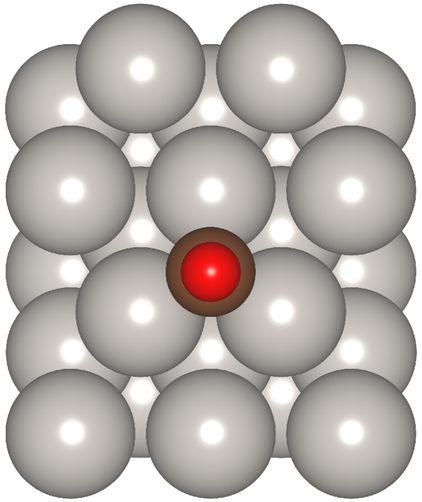
# CO puzzle: CO adsorption on Pt(111)

$$\Delta E_{\text{site}} = E_{\text{ads}}^{\text{top}} - E_{\text{ads}}^{\text{fcc}}$$

Top



Fcc-hollow

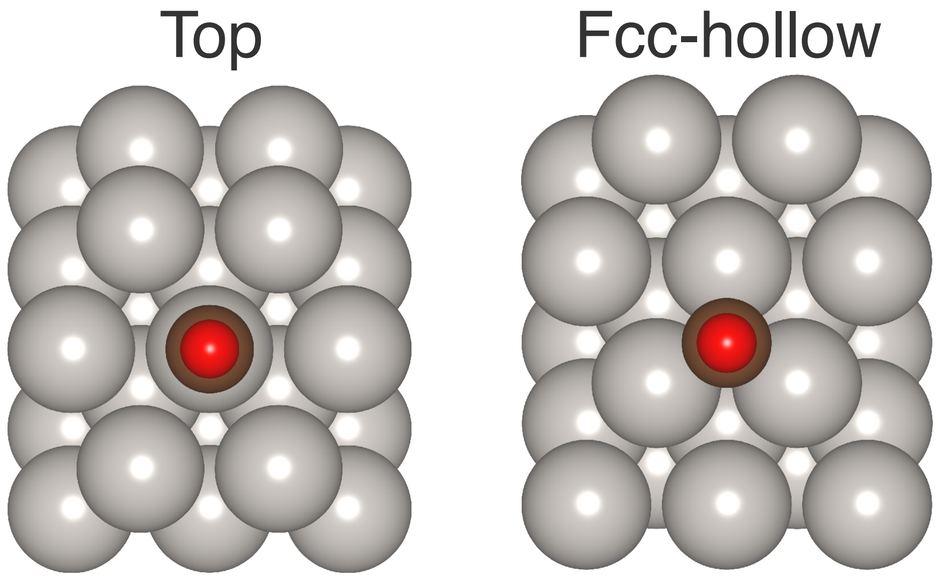


| | vdW-DF2-B86R | Expt |
|---|---|---|
| Top | -1.683 | -1.32 |
| Fcc-hollow | **-1.78** | - |

Shulka, Jiao, *et al.*, *Phys. Rev. X* **12**, 041003 (2022).

# CO puzzle: CO adsorption on Pt(111)

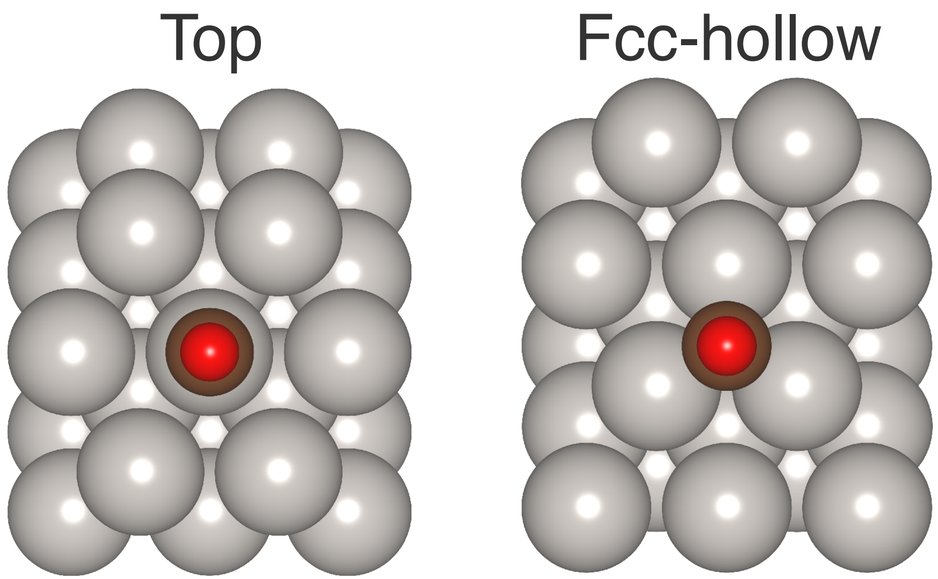
$$\Delta E_{\text{site}} = E_{\text{ads}}^{\text{top}} - E_{\text{ads}}^{\text{fcc}}$$

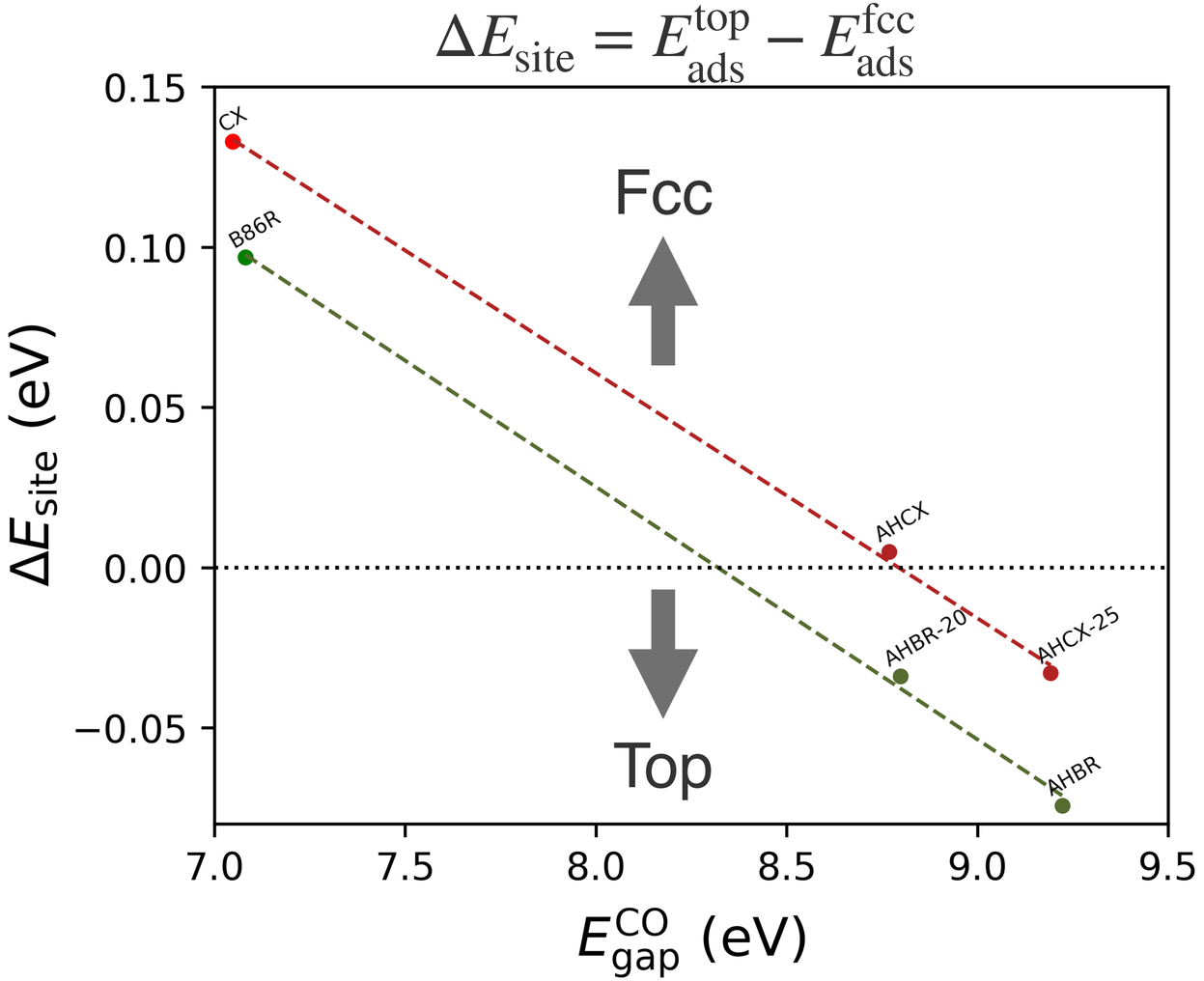



| | vdW-DF2-B86R | vdW-DF2-AHBR (hybrid vdW-DF) | Expt |
|---|---|---|---|
| Top | -1.683 | **-1.824** | -1.32 |
| Fcc-hollow | **-1.78** | -1.752 | - |

Shulka, Jiao, *et al.*, *Phys. Rev. X* **12**, 041003 (2022).

# CO puzzle: CO adsorption on Pt(111)




vdW-DF2-B86R predicts the wrong adsorption site (fcc),
but (range-separate) hybrid vdW-DF2-AHBR corrects it (top)

Shulka, Jiao, *et al.*, *Phys. Rev. X* **12**, 041003 (2022).

# Summary

- rev-vdW-DF2 / vdW-DF2-B86R
  - Accurate for energetics, geometries, and dynamics of variety systems
  - Accurate as PBE / PBEsol, but with the dispersion force included
  - Less accurate for band / HOMO-LUMO gap and related problem

- Further improvement is being underway, e.g., hybrid vdW-DF2-AHBR, but (periodic) quantum chemistry and/or many-body methods are highly desirable

# References


- vdW-DF
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  - Lee *et al*., *Phys. Rev. B* **82**, 081101 (2010).
  - Berland *et al*., *Rep. Prog. Phys*. **78**, 066501 (2015).
  - Hamada, Activity Report 2021, Supercomputer Center, ISSP, Univ. of Tokyo.

    https://mdcl.issp.u-tokyo.ac.jp/scc/wp/wp-content/uploads/2022/08/2021_0301_invited1.pdf
- rev-vdW-DF2
  - Hamada, *Phys. Rev. B* **89**, 121103 (2014).
  - Callsen and Hamada, *Phys. Rev. B* **91**, 195103 (2015).

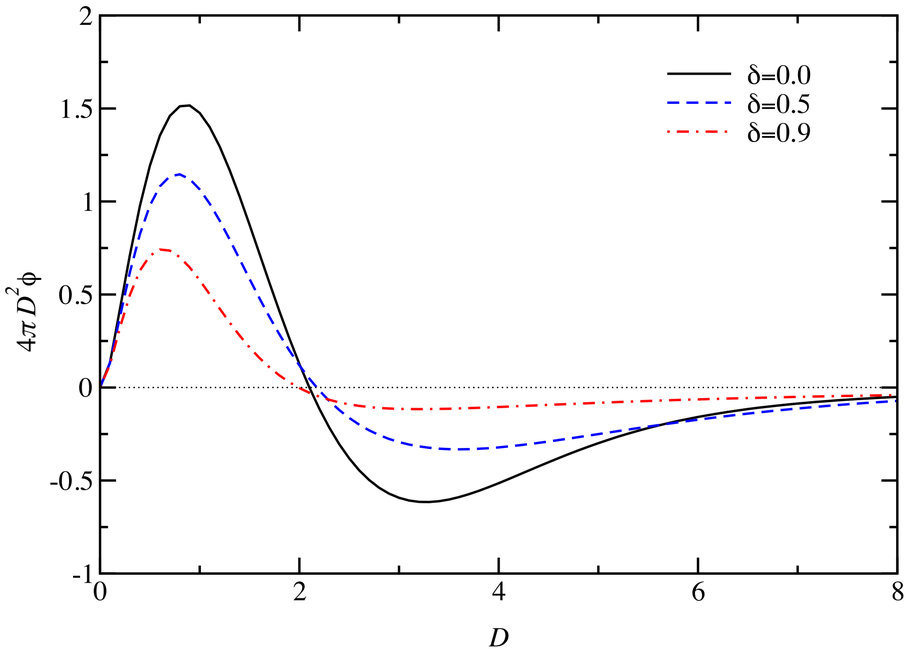
# Backup

# Efficient implementation of vdW-DF

Nonlocal correlation

$$E_c^{nl} = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|)n(\mathbf{r}_2)$$

$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$





Román-Pérez and Soler, *Phys. Rev. Lett.* **103**, 096102 (2009).
Wu and Gygi, *J. Chem. Phys*. **136**, 224107 (2012).
Hamamoto *et al*., *Phys. Rev. B* **93**, 245440 (2016).

# Efficient implementation of vdW-DF

## Nonlocal correlation

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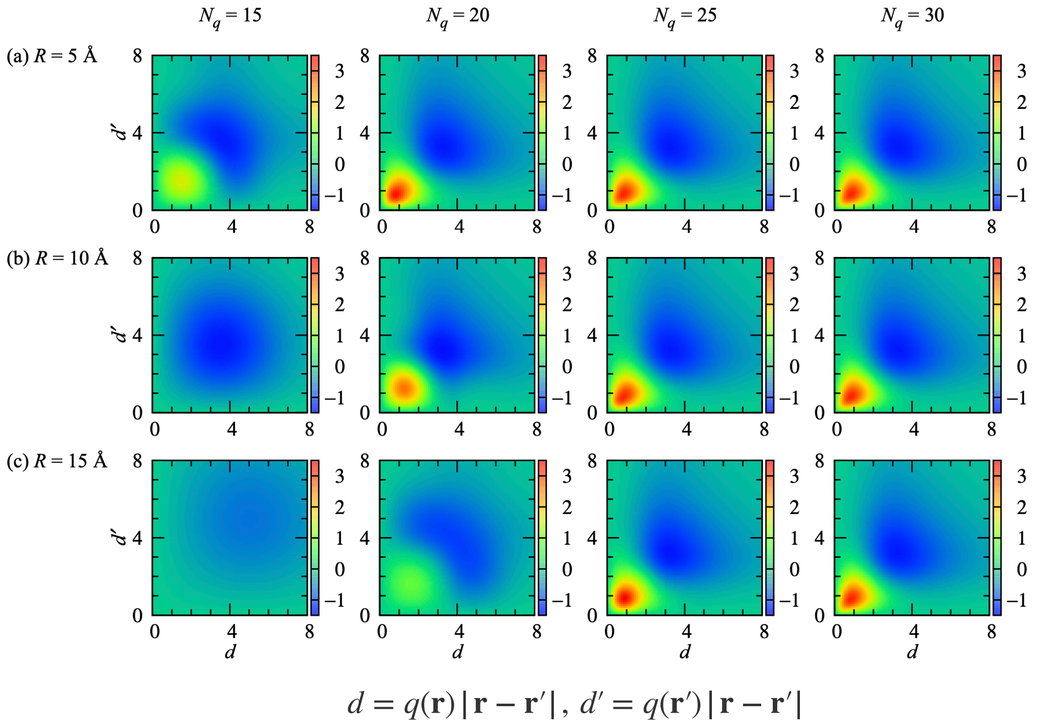



Román-Pérez and Soler, *Phys. Rev. Lett.* **103**, 096102 (2009).
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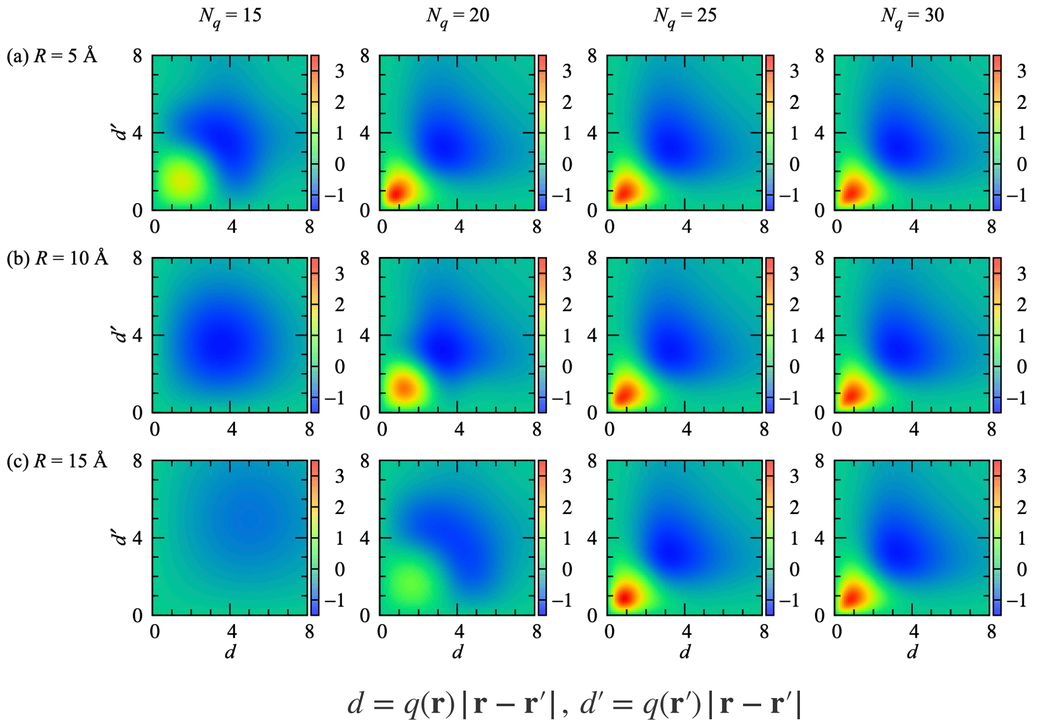
$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

$$\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|) \approx \sum_{\alpha,\beta} p_\alpha(q_1)\phi_{\alpha\beta}(|r_1 - r_2|)p_\beta(q_2)$$

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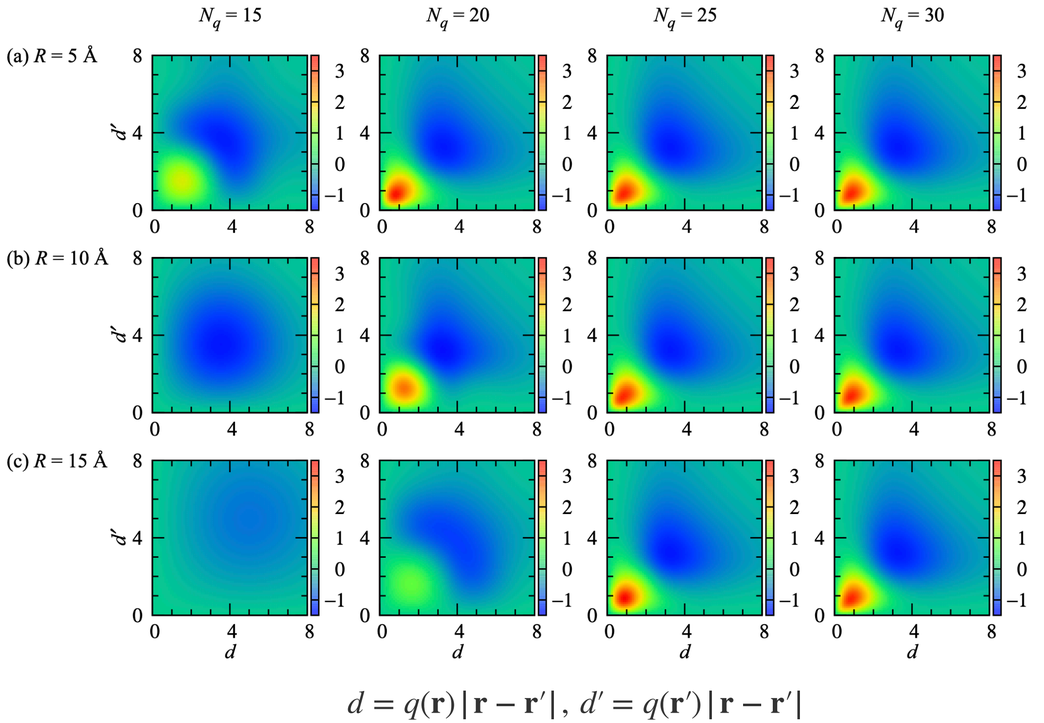
## Nonlocal correlation

$$E_c^{nl} = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|)n(\mathbf{r}_2)$$

$$q_i = q_0(n(\mathbf{r}_i), |\nabla n(\mathbf{r}_i)|)$$

$$\phi(q_1|r_1 - r_2|, q_2|r_1 - r_2|) \approx \sum_{\alpha,\beta} p_\alpha(q_1)\phi_{\alpha\beta}(|r_1 - r_2|)p_\beta(q_2)$$

$$E_c^{nl} = \frac{1}{2}\sum_{\alpha\beta}\int d\mathbf{k}\theta_\alpha^*(\mathbf{k})\phi_{\alpha\beta}(k)\theta_\beta(\mathbf{k})$$

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Wu and Gygi, *J. Chem. Phys.* **136**, 224107 (2012).
Hamamoto *et al.*, *Phys. Rev. B* **93**, 245440 (2016).

# Graphite

| | In-plane lattice constant (Å) | Interlayer distance (Å) | Binding energy (meV) |
|---|---|---|---|
| PBE | 2.47 | 4.38 | 1 |
| optB88-vdW | 2.46 | 3.35 | 52 |
| vdW-DF2 | 2.48 | 3.52 | 70 |
| vdW-DF2-C09 | 2.48 | 3.27 | 56 |
| rev-vdW-DF2 | 2.47 | 3.32 | 60 |
| Expt. | 2.4589 | 3.34 | 50±5 |

Hamada, *Phys. Rev. B* **89**, 121103 (2014).