

Lecture on First-principles Computations (18): van der Waals Interactions

任新国 (Xinguo Ren)

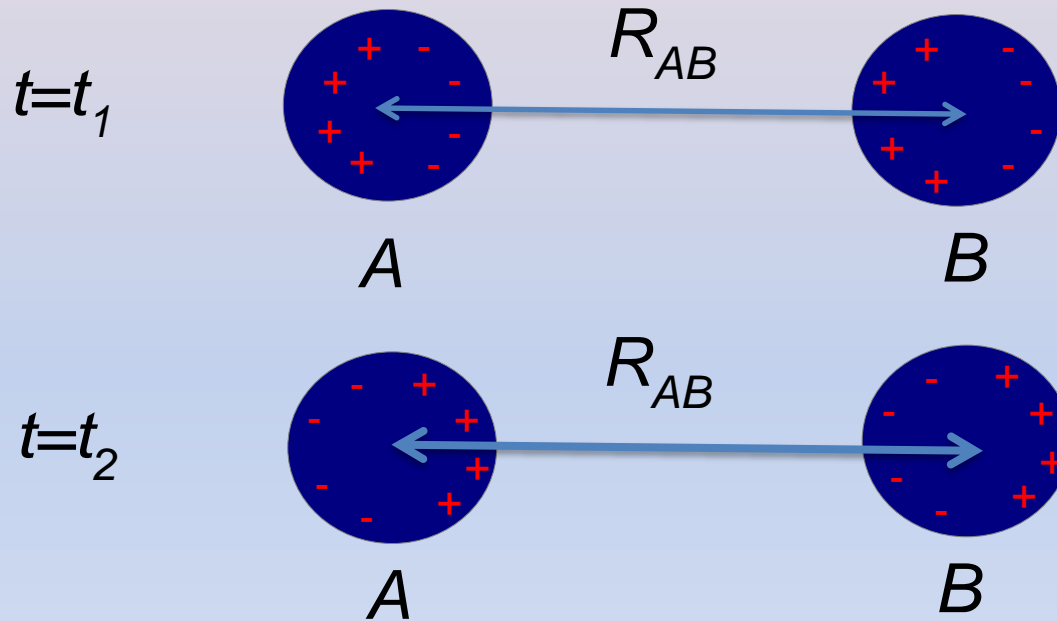
中国科学技术大学
量子信息重点实验室

Key Laboratory of Quantum Information, USTC

Hefei, 2018.11.16

Van der Waals (vdW) interactions

Interaction between fluctuating multipoles (dispersion forces)

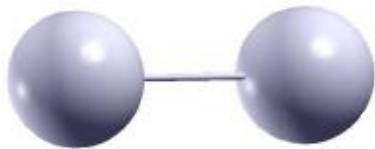


$$C_6^{AB} = \frac{3}{\pi} \int d\omega \alpha_A(i\omega) \alpha_B(i\omega)$$

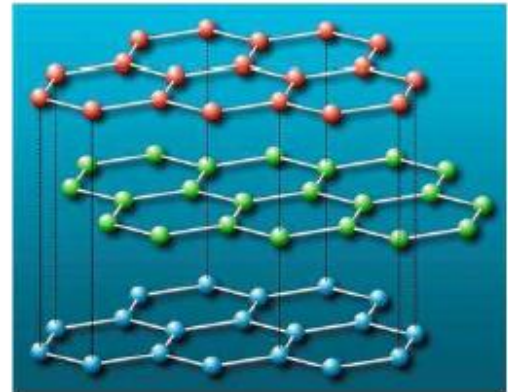
$$E_{disp} = -\frac{C_6}{R_{AB}^6} - \frac{C_8}{R_{AB}^8} - \frac{C_{10}}{R_{AB}^{10}} + \dots$$

Electric dipole polarizability

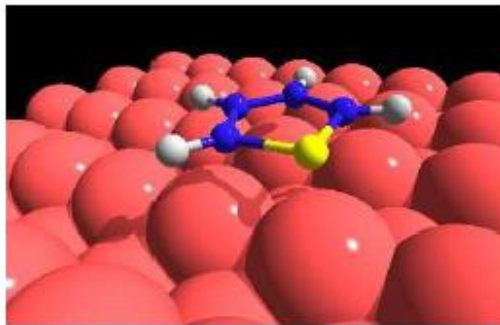
vdW interactions are ubiquitous



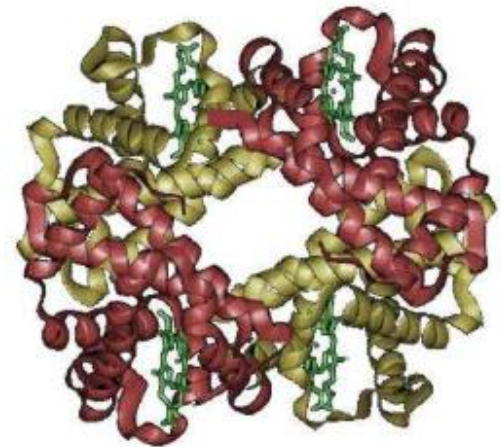
Rare gas dimer



Graphite

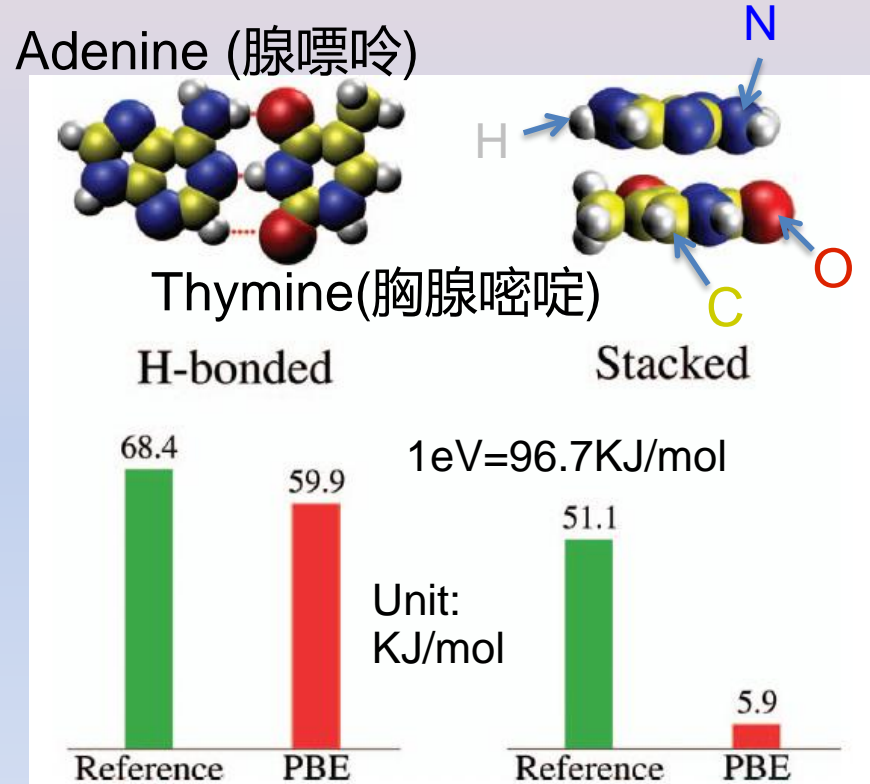
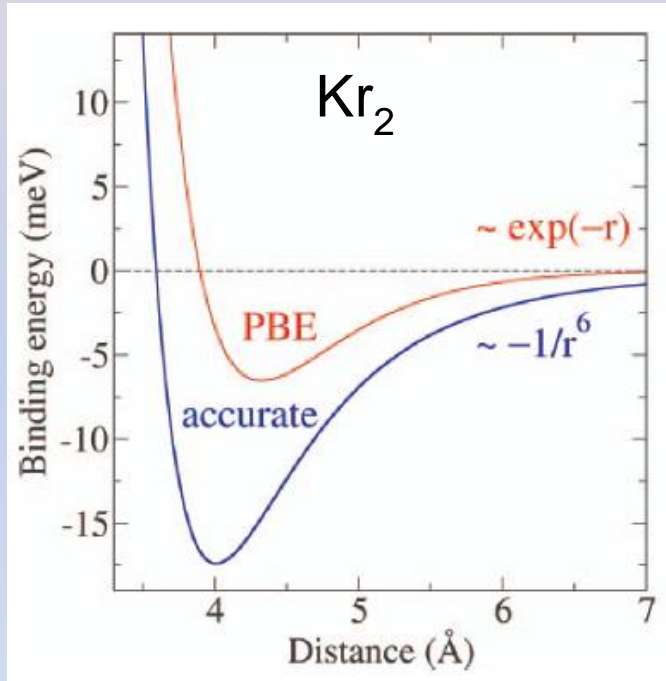


Physisorption



Biomolecules

Describing vdW interactions within DFT is a challenge



LDA, GGAs, and hybrid functions don't capture the $1/R^6$ vdW tail!

The DFT-D method

Dispersion force

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$$

DFT under conventional local/semi-local approximations, no long-range vdW tail.

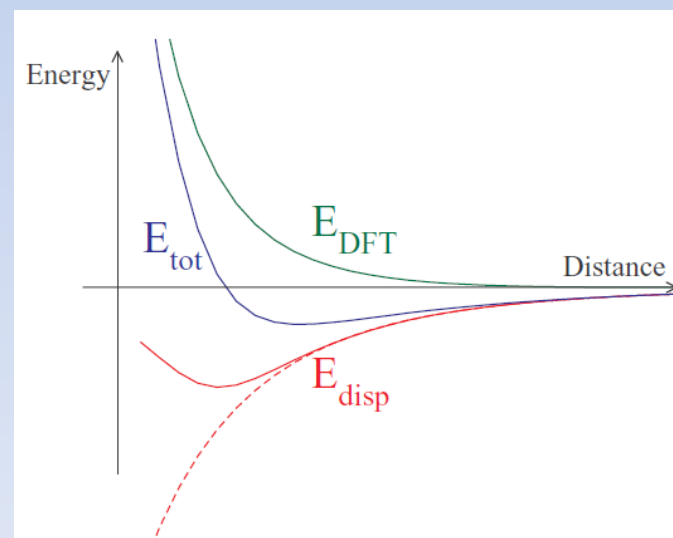
$$E_{\text{disp}} = - \sum_{AB} f_{\text{damp}}(R_{AB}, A, B) \frac{C_6^{AB}}{R_{AB}^6}$$

(all atom pairs)

vdW radius

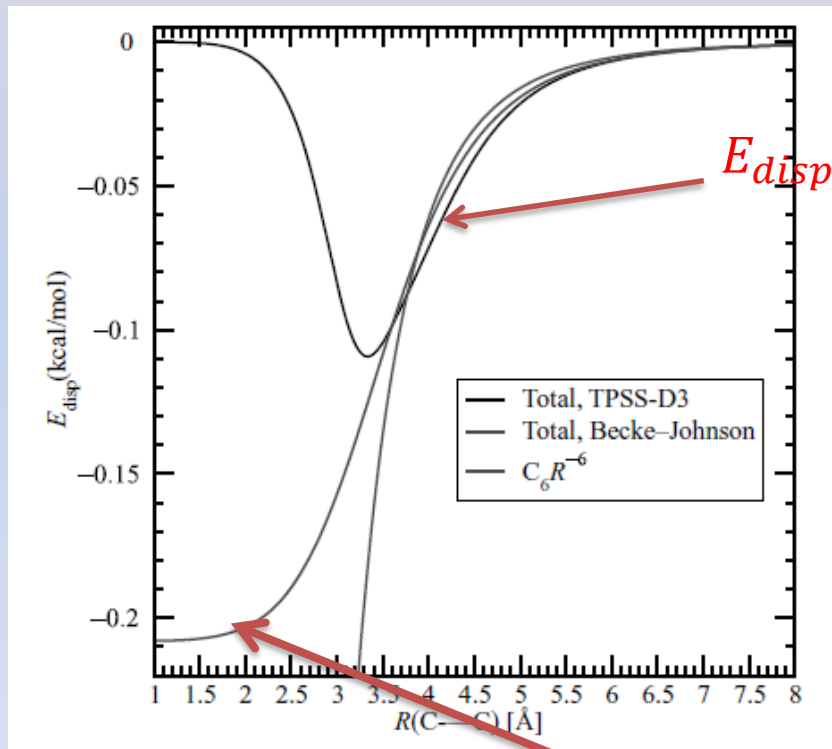
Damping function

$$f_{\text{damp}}(R_{AB}, A, B) = \frac{1}{1 + e^{-\gamma[R_{AB}/(R_A^0 + R_B^0) - 1]}}$$



The damping function

$$f_{damp}(R_{AB}, A, B) = \frac{1}{1 + e^{-\gamma[R_{AB}/(R_A^0 + R_B^0) - 1]}}$$



Grimme

$$E_{disp} = - \sum_{AB} f_{damp}(R_{AB}, A, B) \frac{C_6^{AB}}{R_{AB}^6}$$

Becke-Johnson

$$E_{disp} = - \sum_{AB} \frac{C_6^{AB}}{R_{AB}^6 + const}$$

DFT-D2 (Grimme's method)

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

Global scaling factor, depending on the DFT functional

$$E_{\text{disp}} = -s_6 \sum_{AB} f_{\text{damp}}(R_{AB}, A, B) \frac{C_6^{AB}}{R_{AB}^6}$$

$$f_{\text{damp}}(R_{AB}, A, B) = \frac{1}{1 + e^{-\gamma[R_{AB}/(R_A^0 + R_B^0) - 1]}}$$

$$C_6^{AB} = \sqrt{C_6^{AA} C_6^{BB}}$$

Atomic ionization energy

$$C_6^{AA} = 0.05 N I_p^A \alpha_A$$

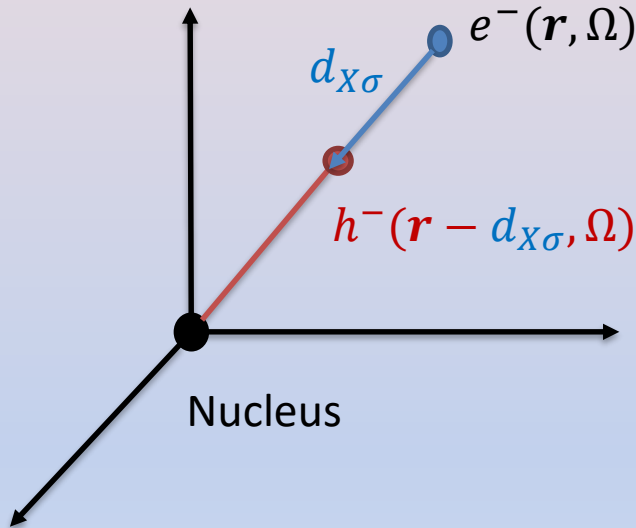
Atomic dipole polarizability

2, 10, 18, 36, ...

Element	C_6 (Jnm^6/mol)	R_0 (\AA)
H	0.14	1.001
He	0.08	1.012
Li	1.61	0.825
Be	1.61	1.408
B	3.13	1.485
C	1.75	1.452
N	1.23	1.397
O	0.70	1.342
F	0.75	1.287
Ne	0.63	1.243
Na	5.71 ^c	1.144
Mg	5.71 ^c	1.364

Becke-Johnson scheme

A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **127**, 154108 (2007)



The exchange hole:

$$h_{X\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{n_\sigma(\mathbf{r}_1)} \sum_{i,j}^{occ.} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2)$$

Electron plus its exchange hole define a non-zero dipole moment

$$d_{X\sigma}(\mathbf{r}_1) = \left[\int h_{X\sigma}(\mathbf{r}_1, \mathbf{r}_2) \mathbf{r}_2 d^3 r_2 \right] - \mathbf{r}_1$$

$$M_{l\sigma} = -[\mathbf{r}^l - (\mathbf{r} - d_{X\sigma}^l(\mathbf{r}))^l]$$

$$\langle M_l^2 \rangle = \sum_\sigma \int n_\sigma(\mathbf{r}) M_{l\sigma}^2 d^3 r$$

$$C_6 = \frac{2 \langle M_1^2 \rangle_A \langle M_1^2 \rangle_B}{3 \Delta E_{av}}$$

$$C_8 = \frac{\langle M_1^2 \rangle_A \langle M_2^2 \rangle_B + \langle M_2^2 \rangle_A \langle M_1^2 \rangle_B}{\Delta E_{av}}$$

ΔE_{av} : average excitation energy

TS-vdW scheme

A. Tkatchenko and M. Scheffler, PRL **102**, 073005 (2009)

The C_6 coefficients depend on the chemical environment!

$$C_6^{AB} = \frac{3}{\pi} \int d\omega \alpha_A(i\omega) \alpha_B(i\omega)$$

$$\alpha_A(\omega) \approx \frac{\alpha_A^0}{1 - (\omega/\eta_A)^2}$$

Plasmon-pole approximation

$$C_6^{AB} = \frac{3}{2} \frac{\eta_A^0 \eta_B^0}{(\eta_A^0 + \eta_B^0)} \alpha_A^0 \alpha_B^0$$



$$C_6^{AB} = \frac{2C_6^{AA} C_6^{BB}}{\frac{\alpha_B^0}{\alpha_A^0} C_6^{AA} + \frac{\alpha_A^0}{\alpha_B^0} C_6^{BB}}$$

(Hirshfeld partitioning)

$$C_6^{AA} = \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}} \right)^2 C_{6, \text{free}}^{AA}$$

Free C_6 coefficient

$$w_A(\mathbf{r}) = n_A^{\text{free}}(\mathbf{r}) / \sum_B n_B^{\text{free}}(\mathbf{r})$$

$$\frac{V_A^{\text{eff}}}{V_A^{\text{free}}} = \frac{\int d^3 r r r^3 w_A(\mathbf{r}) n(\mathbf{r})}{\int d^3 r r r^3 n_A^{\text{free}}(\mathbf{r})}$$

DFT-D3

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

$$E_{disp} = E_{disp}^{(2)} + E_{disp}^{(3)}$$

Pair-wise two-body terms

Three-body terms

$$E_{disp}^{(2)} = - \sum_{AB} \sum_{n=6,8} s_n f_{damp}^n(R_{AB}, A, B) \frac{C_n^{AB}}{R_{AB}^n}$$

Depends on the chemical environment, e.g., the coordination numbers.

$$E_{disp}^{(3)} = - \sum_{ABC} f_{damp,3}(\bar{R}_{ABC}) \frac{C_9^{ABC} (3 \cos\theta_A \cos\theta_B \cos\theta_C - 1)}{R_{AB}^3 R_{BC}^3 R_{AC}^3}$$

Axilrod-Teller-Muto term

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

Remarks on the DFT-D type method

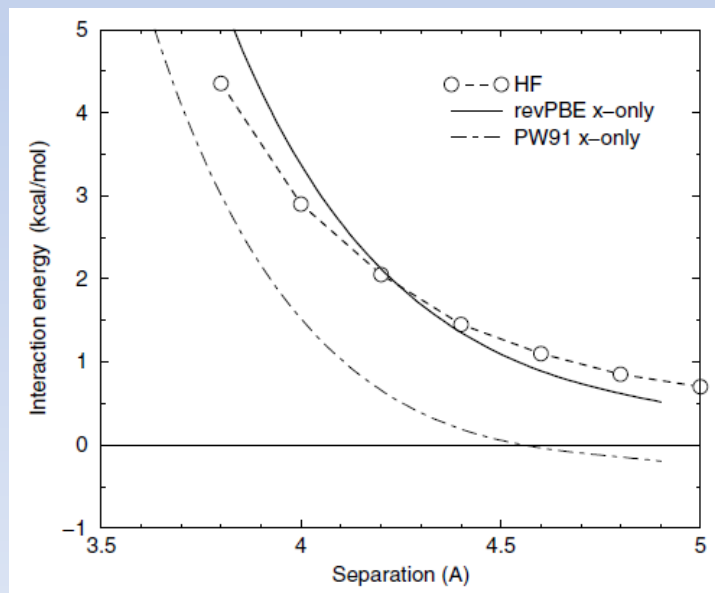
- + Very efficient (tiny extra computational cost)
- + Usefully accurate for many applications
- Non-additive effects not captured
- Empiricism of different levels
- “Double-counting” in the overlapping density regime
- **Not true density functional (relying on geometries)**

van der Waals density functional (vdW-DF)

M. Dion, H. Rydberg, E. Schroeder, D. C. Langreth,
and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004).

$$E_{xc}[n] = E_x^{GGA}[n] + E_c^{LDA}[n] + E_c^{non-local}[n]$$

E_x^{GGA} as close to Hartree-Fock as possible, choose E_x^{revPBE}



van der Waals density functional (vdW-DF)

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$$E_{xc}[n] = E_x^{\text{GGA}}[n] + E_c^{\text{LDA}}[n] + E_c^{\text{non-local}}[n]$$

$$E_c^{\text{non-local}} = \frac{1}{2} \int d^3 r d^3 r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

$$\phi(\mathbf{r}, \mathbf{r}') = \phi(q_0(\mathbf{r}), q_0(\mathbf{r}'), |\mathbf{r} - \mathbf{r}'|), \quad q_0(\mathbf{r}) = \frac{\epsilon_{xc}^0(\mathbf{r})}{\epsilon_x^{\text{LDA}}(\mathbf{r})} k_F(\mathbf{r})$$

$$\phi(\vec{r}, \vec{r}') = \frac{2me^4}{\pi^2} \int_0^\infty a^2 da \int_0^\infty b^2 db W(a, b) \\ \times T(v(a), v(b), v'(a), v'(b)),$$

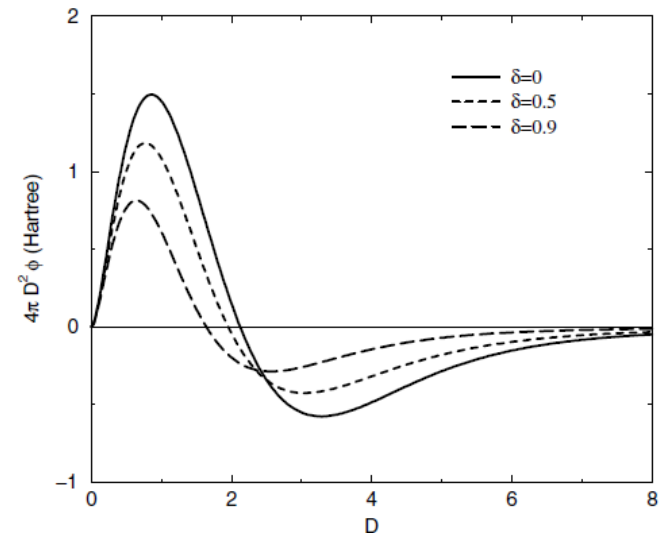
$$T(w, x, y, z) = \frac{1}{2} \left[\frac{1}{w+x} + \frac{1}{y+z} \right] \left[\frac{1}{(w+y)(x+z)} + \frac{1}{(w+z)(y+x)} \right]$$

$$W(a, b) = 2[(3 - a^2)b \cos b \sin a + (3 - b^2)a \cos a \sin b \\ + (a^2 + b^2 - 3) \sin a \sin b - 3ab \cos a \cos b] / a^3 b^3.$$

$$v(y) = \frac{y^2}{2h\left(\frac{y}{d}\right)}, \quad v'(y) = \frac{y^2}{2h\left(\frac{y}{d'}\right)}$$

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

$$d = |r - r'|q_0(\mathbf{r}), \quad d' = |r - r'|q_0(\mathbf{r}') \\ d = D(1 + \delta), \quad d' = D(1 - \delta)$$



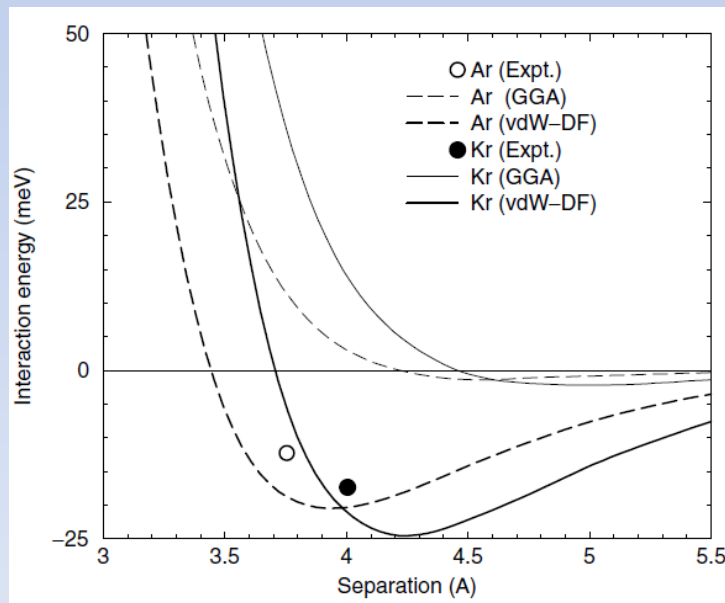
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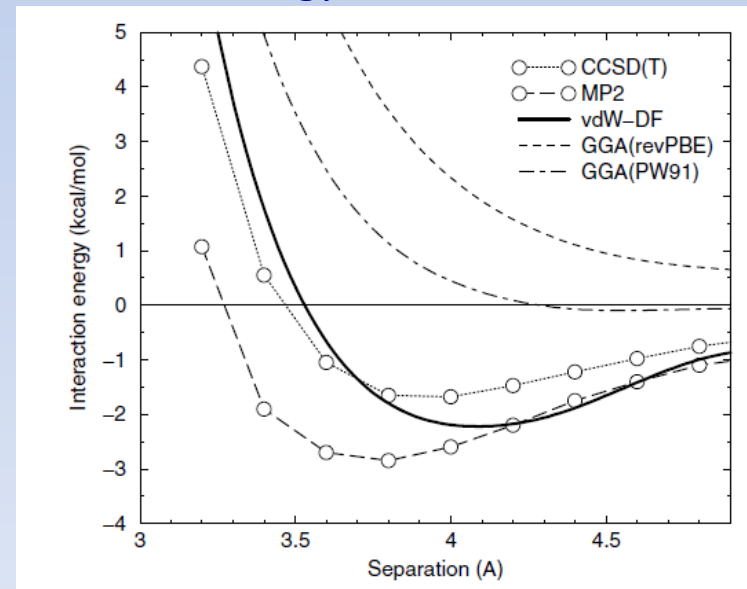
$$E_{xc}[n] = E_x^{\text{GGA}}[n] + E_c^{\text{LDA}}[n] + E_c^{\text{non-local}}[n]$$

$$E_c^{\text{non-local}} = \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

$$\phi(\mathbf{r}, \mathbf{r}') = \phi(q_0(\mathbf{r}), q_0(\mathbf{r}'), |\mathbf{r} - \mathbf{r}'|), \quad q_0(\mathbf{r}) = \frac{\epsilon_{xc}^0(\mathbf{r})}{\epsilon_x^{\text{LDA}}(\mathbf{r})} k_F(\mathbf{r})$$



Interaction energy between benzene dimer



Vydrov-Van Voorhis functional (VV09)

Nonlocal van der Waals Density Functional Made Simple

Oleg A. Vydrov and Troy Van Voorhis

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 13 May 2009; published 6 August 2009)

We derive a nonlocal correlation functional that adequately describes van der Waals interactions not only in the asymptotic long-range regime but also at short range. Unlike its precursor, developed by Langreth, Lundqvist, and co-workers, the new functional has a simple analytic form, finite for all interelectron separations, well behaved in the slowly varying density limit, and generalized to spin-polarized systems.

Phys. Rev. Lett. **103**, 063004 (2009)

Vydrov-Van Voorhis functional (VV09)

$$E_c^{\text{VV09}} = E_c^{\text{nl-VV}} + E_c^{\text{LSDA}}$$

$$E_c^{\text{nl-VV}} = \frac{3\hbar}{64\pi^2} \iint dr dr' \frac{\omega_p^2(\mathbf{r})\omega_p^2(\mathbf{r}')D(K)}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')[\omega_0(\mathbf{r}) + \omega_0(\mathbf{r}')]| \mathbf{r} - \mathbf{r}'|^6}$$


$$\omega_p = \sqrt{\frac{4\pi^2 n}{m}} : \text{plasmon frequency} \quad \omega_0^2 = \omega_g^2 + \omega_p^2/3 \quad \omega_g^2(r) = C \frac{\hbar^2}{m^2} \left| \frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \right|^4$$

$$D(K) = \frac{4}{3} K^2 AB - B^2 \quad C: 0.0089 \text{ (fitting parameter)}$$

$$K(\mathbf{r}, \mathbf{r}') = \frac{|\mathbf{r} - \mathbf{r}'|}{2} \left[\frac{\kappa(\mathbf{r})\kappa(\mathbf{r}')}{\kappa(\mathbf{r}) + \kappa(\mathbf{r}')} \right]^{1/2} \quad A = \frac{2K}{\sqrt{\pi}} e^{-K^2}, B = \text{erf}(K) - A$$

$$\kappa(\mathbf{r}) = k_s^2(\mathbf{r}) \phi^2(\mathbf{r}) \quad \phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] / 2 : \text{spin scaling factor}$$

$$k_s(r) = \sqrt{4k_F / \pi a_0} : \text{Thomas-Fermi screening parameter.}$$


 Bohr radius

Comparison: the S66 test set

S66: 66 vdW-bonded dimolecular complex set

	vdW-DF2	VV10	LC-VV10	ω B97X-D	M06-2X
<i>hydrogen bonds (23)</i>					
MPE (%)	-5.6	6.4	-0.4	-0.4	-3.3
MAPE (%)	5.8	6.4	2.3	2.2	3.9
MAE	0.62	0.53	0.20	0.16	0.32
<i>dispersion (23)</i>					
MPE (%)	-2.8	7.5	-2.1	17.0	-9.2
MAPE (%)	8.7	7.9	3.3	17.2	10.1
MAE	0.33	0.20	0.10	0.50	0.29
<i>others (20)</i>					
MPE (%)	-12.8	1.0	0.0	3.8	-4.6
MAPE (%)	13.1	4.3	4.5	5.6	7.3
MAE	0.49	0.15	0.17	0.20	0.26
<i>total (66)</i>					
MPE (%)	-6.8	5.1	-0.9	6.9	-5.8
MAPE (%)	9.0	6.3	3.3	8.5	7.1
MAE	0.48	0.30	0.15	0.29	0.29

Comparison of different methods

TABLE I. Overview of current DFT methods to account for London dispersion interactions.

Property	DFT-D	vdW-DF	DCACP	DF ^a
Correct R^{-6}	Yes	Yes	No	No
Good thermochemistry	Yes	?	?	Yes
Numerical complexity	Low	High	Low	Medium
Simple forces	Yes	No	Yes	Yes
System dependency	No (yes ^b)	Yes	No ^c	Yes
Electronic effect	No	Yes	Yes	Yes
Empiricism	Medium (low ^b)	No	High	Medium
Analysis/insight	Good	?	?	No

DCACP: Dispersion-corrected atom-centered potentials

G. Grimme, WIREs Comput. Mol. Sci. **1**, 212 (2011)