Van-der-Waals interactions: Incorporation in the DFT framework

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PHASG473 - UCL - ELECTRONIC STRUCTURE METHODS FOR MATERIALS MODELLING

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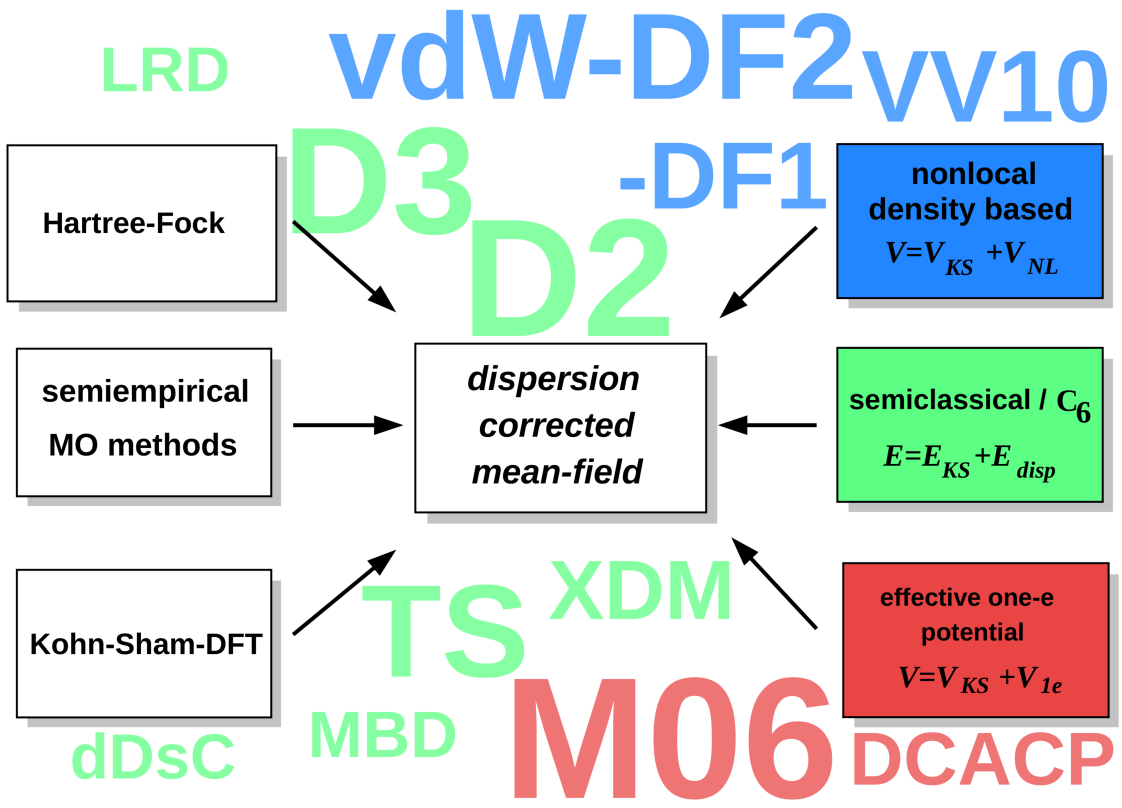
Outline of talk

Many good dispersion corrections exist



- local electronic structure often sufficiently accurate by effective mean field
- combine with vdW correction (long-range correlation)

[1] S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016)

[2] K, Berland, V. Cooper, K. Lee, E. Schröder, T Thonhauser, P. Hyldgaard, B. Lundqvist, Rep. Prog. Phys. **78** 066501 (2015).

Outline of talk

Local model for response function

- density response function for homogeneous electron gas

$$\chi(\omega) = \frac{1}{4\pi} \frac{\omega_p^2}{\omega_p^2 - \omega^2}$$

- plasmon frequency $\omega_p = \sqrt{4\pi\rho}$
- use local approximation $\omega_p(\mathbf{r}) = \sqrt{4\pi\rho(\mathbf{r})}$
- for non-overlapping densities in r and r'

$$E_c^{DD/ALL} = -\frac{3}{32\pi^2} \int d\mathbf{r}\, d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|^{12}} \frac{\omega_p(\mathbf{r})\omega_p(\mathbf{r}')}{\omega_p(\mathbf{r}) + \omega_p(\mathbf{r}')}$$

- general form of density based long-range correlation energy

$$E_c = -\frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$$

Modern nonlocal vdW density functionals

Class 1:

- vdW-DF0, vdW-DF1, vdW-DF1, optPBE-vdW, optB86b-vdW
- generalize DD/ALL form to seamlessly interpolate between long-range and short range regime
- fulfill local density limit

Class 2:

- VV09, VV10
- introduce empirical parameter (C, b) to simplify nonlocal kernel

$$\Phi(\mathbf{r},\mathbf{r}') = -\frac{1}{2gg'(g+g')}$$

$$g = g(\mathbf{r},\mathbf{r}') = \sqrt{C\left|\frac{\nabla\rho(\mathbf{r})}{\rho(\mathbf{r})}\right|^4 + \frac{\omega_p(\mathbf{r})}{3}|\mathbf{r}-\mathbf{r}'|^2 + b\frac{3\pi}{2}\left(\frac{\rho}{9\pi}\right)^{1/6}}$$

Outline of talk

Coarse-graining to atomic contributions leads to significant simplifications

- coarse-grain ACFDT to fragment contributions

$$E_{\text{disp}}^{AB} = -\frac{1}{2\pi}\int \mathrm{d}\omega \int \mathrm{d}\mathbf{r}_a \mathrm{d}\mathbf{r}'_a \mathrm{d}\mathbf{r}_b \mathrm{d}\mathbf{r}'_b \frac{\chi(\mathbf{r}_a, \mathbf{r}'_a, i\omega)\chi(\mathbf{r}_b, \mathbf{r}'_b, i\omega)}{|\mathbf{r}_a - \mathbf{r}'_a||\mathbf{r}_b - \mathbf{r}'_b|}$$

- assume vanishing overlap to factorize response function
- integrate fragment response to dynamic polarizabilities

$$\alpha_{ij}(i\omega) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \mathbf{r}_i \mathbf{r}'_j \chi(\mathbf{r}, \mathbf{r}', i\omega)$$

- expansion of Coulomb operator in multipoles

$$E_{\text{disp}}^{AB} = -\frac{2}{\pi}\sum_{\substack{\alpha,\beta \\ \gamma,\delta}} \left(\nabla_\alpha \nabla_\beta \frac{1}{R}\right)\left(\nabla_\gamma \nabla_\delta \frac{1}{R}\right) \int \mathrm{d}\omega\, \alpha^A_{\alpha\beta}(i\omega)\alpha^B_{\gamma\delta}(i\omega)$$

[3] H. B. G. Casimir. D. Polder, *Phys. Rev.* **73**, 360 (1948)

Spherical averaging and higher order terms beyond dipole-dipole

- spherical averaging of dyn. polarizabilities

$$E_{\text{disp}}^{AB} = -\underbrace{\frac{3}{\pi}\int \mathrm{d}\omega\, \alpha_A(i\omega)\alpha_B(i\omega)}_{C_6^{AB}} \times \frac{1}{R_{AB}^6} + \mathcal{O}(R^{-8})$$

- beyond dipole terms from higher multipole expansion, e.g. C_8 dipole-quadrupole, C_{10} quadrupole-quadrupole, etc

$$E_{\text{disp}}^{AB} = -\frac{C_6^{AB}}{R_{AB}^6} - \frac{C_8^{AB}}{R_{AB}^8} - \frac{C_{10}^{AB}}{R_{AB}^{10}} + \mathcal{O}(R^{-12})$$

- beyond pair-wise terms from multi-fragment terms, e.g C_9 dipole-dipole-dipole

$$C_9^{ABC} = -\frac{3}{\pi}\int \mathrm{d}\omega\, \alpha_A(i\omega)\alpha_B(i\omega)\alpha_C(i\omega)$$

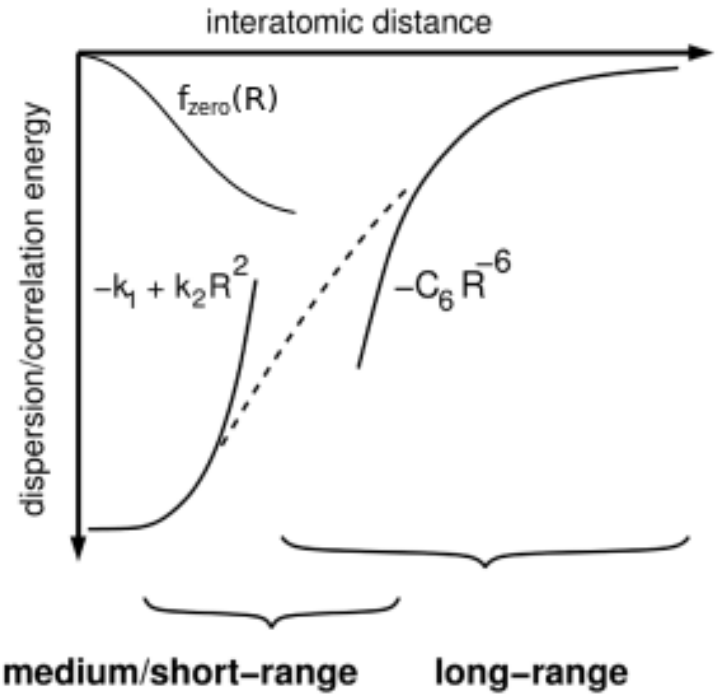
Combining vdW correction with mean field model

- sum of fragment contributions for total London dispersion energy

$$E_{\text{disp}} = -\frac{1}{2}\sum_{A,B}^{\text{pairs}}\sum_{n}\frac{C_n^{AB}}{R_{AB}^n} - \frac{1}{6}\sum_{A,B,C}^{\text{triples}}\sum_{n}\frac{C_n^{ABC}}{R_{ABC}^n}F^{\text{geom}} + \mathcal{O}(\text{quadruples})$$

- singularity at short-range (and expansion not valid)
- introduce short-range damping, motivated by range separation of Coulomb operator

$$E_{\text{tot}}^{AB} = E_{\text{DFT}}^{AB}\text{erf}(\omega R_{AB}) + E_{\text{disp}}^{AB}\text{erfc}(\omega R_{AB})$$



Outline of talk

How to classify different vdW methods?

Classifications according to

- order in many-body perturbation theory
- order in multipole expansion
- estimation and partitioning of C_6 coefficients
- shape of damping function (empiricism)
- use of precalculated, values (empiricism)

D2: First generally dispersion correction with general applicability

$$E_{disp}^{(D2)} = -\sum_{AB} \frac{C_6^{AB}}{R^6} f_{dmp}^{Fermi}(R)$$

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

$$C_6^{AA} = \frac{N}{20} I_A \alpha_A(0)$$

- only atom-pairwise (two-body)
- lowest order multipoles
- C_6 estimated from ionization potential and static polarizability
- Fermi type zero damping

D3: Environment dependent C_6 computed from first principles

$$E_{\text{disp}}^{(\text{D3})} = -\frac{1}{2} \sum_{n=6,8} \sum_{A,B}^{\text{pair}} \frac{C_n^{AB}}{R_{AB}^n} \cdot f_n^d(R_{AB}) - \frac{1}{6} \sum_{A,B,C}^{\text{triples}} \frac{C_9^{ABC}}{R_{ABC}^9} \cdot f_9^d(R_{ABC}, \theta_{ABC})$$

neglect all terms decaying faster than $\frac{1}{R^9}$

- third order in many-body expansion
- quadrupole terms in multipole expansion
- C_6 calculated (for model systems) via TD-DFT
  partitioned to atoms via fractional coordination number
- rational Becke-Johnson damping

D3: Dynamic polarizability via linear response DFT

- use frequency domain formalism to get excitation frequencies[7]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{A}^* & \mathbf{B}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

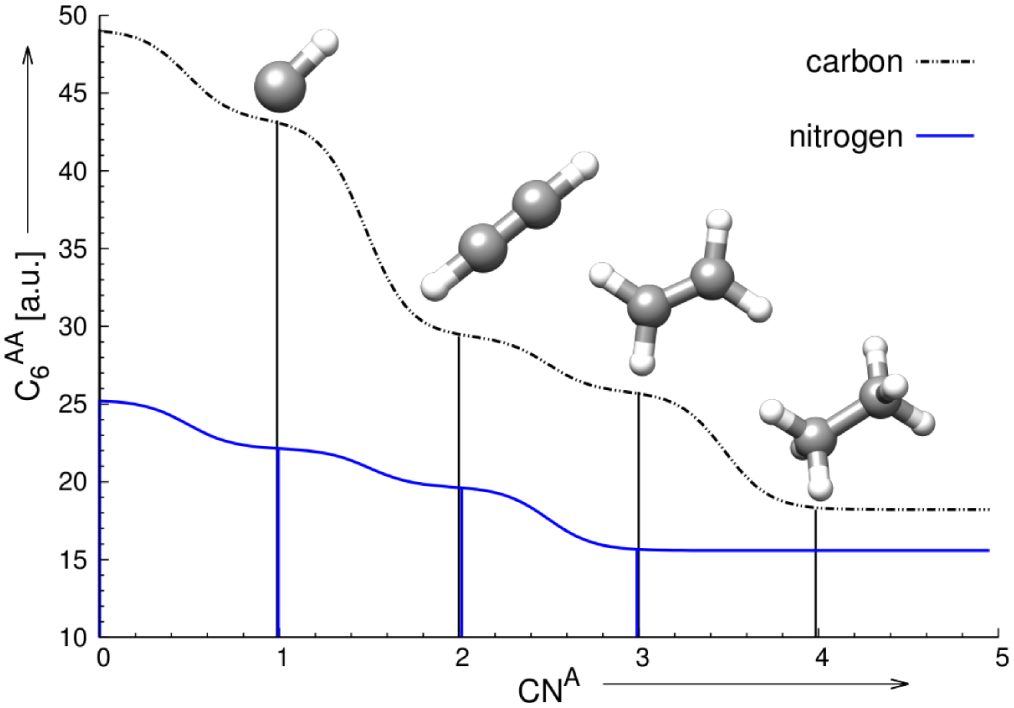
- orbital rotation matrices

$$A_{ia.jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \langle ab|1/r|ij\rangle + \langle ab|f_{xc}|ij\rangle$$
$$B_{ia.jb} = \langle aj|1/r|ib\rangle + \langle aj|f_{xc}|ib\rangle$$

- approximation: neglect frequency dependence of f_{xc} and use ground state functional (PBE38)
- similar to random phase approximation with exchange

[4] M. E. Casida, *Recent Advances in Density Functional Methods*, D. P. Chong (World Scientific, Singapore), 155 (1995)

D3: Geometric coordination number for interpolations of reference C_6



- atoms-in-molecules C_6 by TD-DFT of $\alpha(i\omega)$ on model hydrides
- reference C_6 are mapped to real system via geometrical coordination

TS: Hirshfeld partitioning for C_6 scaling

$$E_{disp}^{(TS)} = -\sum_{AB} \frac{C_6^{AB}}{R^6} f_{dmp}^{Fermi}(R)$$

$$C_6^{AB} = \frac{2 C_6^{AA} C_6^{BB}}{(\alpha^B(0)/\alpha^A(0)) C_6^{AA} + (\alpha^A(0)/\alpha^B(0)) C_6^{BB}}$$

$$C_6^{AA} = \frac{V_{eff}^A}{V_{free}^A} C_{6,free}^{AA}$$

- only atom-pairwise (two-body)
- lowest order multipoles
- C_6 estimated from effective atomic volumes
- Fermi type zero damping

TS+MBD: summing all orders in a Drude model of oscillating dipoles

$$E_{disp}^{(TS+MBD)} = \frac{1}{2}\sum_{p=1}^{3N}\sqrt{\lambda_p} - \frac{3}{2}\sum_{A}^{N}\omega_A^{TS+SCS} \tag{1}$$

$$V_{CFDM} = \sum_{A\neq B}^{N}\sum_{p\in A}^{3}\sum_{q\in B}^{3}\chi_p T_{pq}^{LR}\chi_q \tag{2}$$

$$T_{pq}^{LR} = \nabla_p \otimes \nabla_q W'(R) \tag{3}$$

- all many body orders (coupled fluctuating dipole Hamiltonian)
- lowest order multipoles
- C_6 estimated from screened effective atomic volumes
- Fermi type zero damping

XDM: Estimate C_6 from locally integrated exchange hole

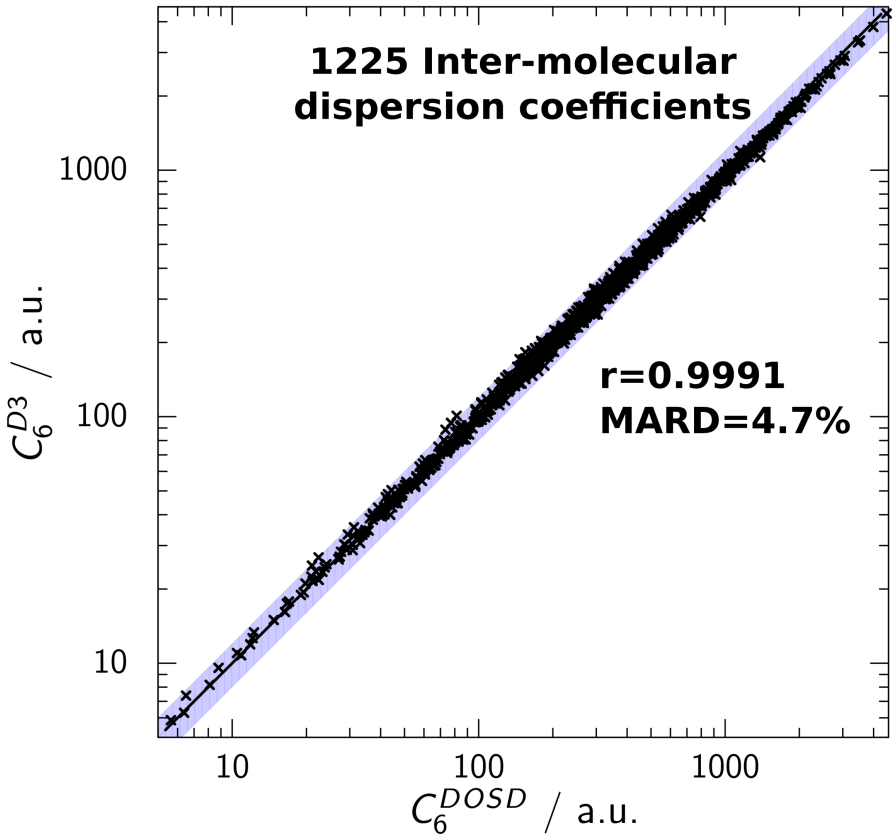
$$E_{\mathrm{disp}}^{(\mathrm{XDM})} = -\frac{1}{2}\sum_{n=6,8,10}\sum_{A,B}^{\mathrm{atoms}}\frac{C_n^{AB}}{r_{AB}^n}\cdot f_n^d(r_{AB})$$

$$h_{X,\sigma}(r_1,r_2) = -\frac{1}{\rho_\sigma(r_1)}\sum_{ij}\phi_{i\sigma}(r_1)\phi_{j\sigma}(r_1)\phi_{i\sigma}(r_2)\phi_{j\sigma}(r_2)$$

$$C_6^{AB} = \frac{\langle\mu_X^2\rangle_A\langle\mu_X^2\rangle_B\alpha_A^0\alpha_B^0}{\langle\mu_X^2\rangle_A\alpha_B^0 + \langle\mu_X^2\rangle_B\alpha_A^0}$$

- lowest order in many-body expansion (higher orders exist, but are seldom used)
- quadrupole terms in multipole expansion
- C_6 calculated from exchange dipole
- rational Becke-Johnson damping

Semi-classical schemes yield highly accurate dispersion coefficients



D3 correction

- dipole oscillator strength distribution (DOSD) yield $C_6^{\text{exptl.}}$ (compiled by A. Tkatchenko)
- residual long-range mean absolute relative deviation (MARD) of D3 $< 5\%$ [9]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

[9] S. Grimme, *WIREs Comput. Mol. Sci.* **1**, 211-228 (2011)

Summary C_6 based dispersion

model	complexity[a]	ρ based	limit[b]	multipoles[c]	many-body[d]
non-local density based					
vdw-DF	high	✓	✓	X	X
VV10	medium	✓	✓	X	X
C_6 **based**					
D2	low	X	✓	X	X
D3	low	X[e]	✓	✓	✓
TS	low	✓	✓	X	X
MBD	medium	✓	✓	X	✓[f]
XDM	medium	✓	✓	✓	✓[g]
one electron potentials					
DCP	medium	✓	X	?	X
M06L	medium	✓	X	?	X

D3 'advertisement': High accuracy at force field speed

Advantages of D3 model

- intermolecular C_6 coefficients are very accurate
- no electronic structure input needed
- computation is extremely fast D3(two-body) $\sim$ FF speed
- analytical first (and second) derivatives

Possible shortcomings

- no automatic adjustment to unusual electronic structures[*]
- missing anisotropy of dispersion interaction
- no many-body contributions beyond Axilrod-Teller-Muto term
- high empiricism in short-range damping