Van der Waals corrections in the DFT framework

Gerit Brandenburg <g.brandenburg@ucl.ac.uk> | 20th of Sept. 2018
Outline of talk

1. Introduction
2. H2 model system
3. Adiabatic connection fluctuation dissipation theorem (ACFDT)
4. Van der Waals inclusive density functional approximations
5. Show-cases
6. Conclusions
Recommended literature


Other review articles

Understanding phenomena in nature

How can a Gecko stick to a glass wall?
- cannot be explained by classical mechanics
- London dispersion ($C_6$)

Why does a tablet change its properties?
- van der Waals interaction stabilizes tablet dependent on its form
- relevant for production process and dosage
Possible theoretical ansatz

\[ H |\psi\rangle = E |\psi\rangle \]

- **exact in principle**
- **semi-local, easier to solve**
- **complicated to solve**
- **no London dispersion**
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Definition of the model system

- nuclei fixed, Hilbert space $\mathcal{H}_A = \mathcal{H}_B = \mathcal{L}^2(\mathbb{R}^d)$
- Hamiltonian $\hat{H} = \hat{H}_0^A + \hat{H}_0^B + \hat{H}_I$
- interaction $\hat{H}_I = \frac{1}{R} + \frac{1}{|\mathbf{R} - \mathbf{r}_A + \mathbf{r}_B|} + \frac{1}{|\mathbf{R} - \mathbf{r}_A|} + \frac{1}{|\mathbf{R} + \mathbf{r}_B|}$
- assume $R$ large enough to ignore Fermionic symmetry
- specific form of $\hat{H}_0^{A/B}$ not relevant, only assume rotational symmetry, i.e.
  
  \[ [\hat{H}_0^A, \hat{U}] = 0, \text{ and } \hat{U}|\psi(\mathbf{r}_A, \mathbf{r}_B)\rangle = |\psi(U\mathbf{r}_A, \mathbf{r}_B)\rangle \]
  rotation matrix $U$ ($\pm 1$ for one dimension)
Second order perturbation theory

- expand $\hat{H}_I$ in powers of $1/R$:

$$\hat{H}_I = \frac{(r_A r_B) R^2 - 3(r_A R)(r_B R)}{R^5} = \frac{r_A r_B - 3 x_A x_B}{R^3} + \mathcal{O}(R^{-4})$$

- zero order ground state from direct product $|0\rangle = |0_A\rangle |0_B\rangle$

- rotational symmetry $\langle 0_A | r_A | 0_A \rangle = 0$

- zero order energy

$$E_0^0 = \langle 0 | \hat{H}_0 | 0 \rangle = E_A^0 + E_B^0$$

- first order energy

$$E_0^1 = \langle 0 | \hat{H}_I | 0 \rangle = \langle 0 | \frac{1}{R^3} (r_A r_B - 3 x_A x_B) | 0 \rangle + \mathcal{O}(R^{-4}) = 0 + \mathcal{O}(R^{-4})$$
Second order perturbation theory

- second order energy

\[ E_0^2 = - \sum_n \frac{|\langle n | \hat{H}_I | 0 \rangle|^2}{E_n - E_0} \]

\[ = - \frac{1}{R^6} \sum_n \frac{|\langle n | \mathbf{r}_A \mathbf{r}_B - 3x_Ax_B | 0 \rangle|^2}{E_n - E_0} + \mathcal{O}(R^{-8}) \]

\[ = - \frac{1}{R^6} \sum_{n_A} \sum_{n_B} \frac{|\langle n_A n_B | \mu_A \mu_B | 0_A 0_B \rangle|^2}{E_n^A - E_0^A + E_n^B - E_0^B} + \mathcal{O}(R^{-8}) \]

\[ = - \frac{6}{R^6} \sum_{n_A} \sum_{n_B} \frac{1}{\omega_{0n}^A + \omega_{0n}^B} \left( |\langle n_A | \mu_A | 0_A \rangle|^2 |\langle n_B | \mu_B | 0_B \rangle|^2 \right) + \mathcal{O}(R^{-8}) \]

- excitation energies \( \omega_{0n}^A = E_n^A - E_0^A \), spherical dipole operators \( \mu_A \)

- MacLachlan integral identity \( \frac{1}{A+B} = \frac{2}{\pi} \int d\omega \frac{\omega_{AB}}{(A^2+\omega^2)(B^2+\omega^2)} \)
Second order perturbation theory

- second order energy

\[ E_0^2 = - \frac{1}{R^6} \frac{3}{\pi} \int d\omega \left[ \sum_{n_A} \frac{\omega_0^A n_A \langle n_A | \mu_A | 0_A \rangle^2}{\omega_0^A - (i\omega)^2} \right] \left[ \sum_{n_B} \frac{\omega_0^B n_B \langle n_B | \mu_B | 0_B \rangle^2}{\omega_0^B - (i\omega)^2} \right] \]

\[ = - \frac{1}{R^6} \frac{3}{\pi} \int d\omega \alpha^A(i\omega) \alpha^B(i\omega) \]

- dynamical dipole polarizabilities \( \alpha^A/B \)

- dispersion coefficients \( C_{AB}^6 = \frac{3}{\pi} \int d\omega \alpha^A(i\omega) \alpha^B(i\omega) \)

- well known expression for London dispersion energy

\[ E_0^2 = - \frac{C_{AB}^6}{R^6} \]
Absence of $1/R^7$ terms

- Inversion operator: $\hat{l}|\psi(r_A, r_B)\rangle = |\psi(-r_A, -r_B)\rangle$
- $\hat{l}$ is symmetry of system: $[\hat{l}, \hat{H}] = 0$
- $|n\rangle$ are eigenstates of $\hat{l}$, $\hat{l}^2 = 1$, $\hat{l}r_A\hat{l} = -r_A$
- Split perturbation sum

$$E_0^2 = -\sum_n \left| \frac{\langle n|\hat{H}_l|0\rangle}{E_n - E_0} \right|^2$$

$$= -\sum_n \left| \frac{\langle n|\hat{H}_l|0\rangle}{E_n - E_0} \right|^2 - \sum_n \left| \frac{\langle n|\hat{H}_l|0\rangle}{E_n - E_0} \right|^2$$

- No mixed terms of even and uneven power of $R$ possible
  $\rightarrow$ No $R^{-7}$ term in second order expansion
Consistency of perturbation expansion

- for consistency, higher order expansion of $\hat{H}_i$ in first order energy needed
- rewrite first order energy

$$E^1_0 = \langle 0 | \hat{H}_i | 0 \rangle = \langle 0_B | V_A(R) - V_A(R + r_B) | 0_B \rangle$$

$$V_A(r) = \langle 0_A | \frac{1}{r} - \frac{1}{|r - r_A|} | 0_A \rangle$$

$$= \langle 0_A | - \frac{rr_A}{r^3} + \frac{r_A^2}{2r^3} - \frac{3(rr_A)^2}{2r^5} + \mathcal{O}(r^{-4}) | 0_A \rangle$$

- employ identity $\langle 0_A | |r_A|^2 | 0_A \rangle |r|^2 = d \langle 0_A | |rr_A|^2 | 0_A \rangle$
- characteristic length $a^2 = \frac{\langle 0_A | |r_A|^2 | 0_A \rangle}{d}$
Consistency of perturbation expansion

- first order energy

\[ E_0^1 = \frac{3(3 - d)(5 - d)a^2}{4} \frac{1}{R^5} + O(R^{-7}) \]

- for \( d = 3 \), first order term vanishes and attractive \( R^{-6} \) is the leading order
- for \( d = 1, 2 \), \( E_0^1 \) is nonzero and repulsive \( R^{-5} \) is the leading order

Summary: \( \text{H}_2 \) model

- leading order energy: attractive \( R^{-6} \) in 3D and repulsive \( R^{-5} \) in 1D/2D
- \( C_6 \) dispersion coefficients can be computed from dynamical polarizabilities of separated atoms
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Exact expression for correlation energy from response function

\[ E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int dr dr' \frac{1}{|r - r'|} \times \int_0^\infty d\omega [\chi_\lambda(r, r', i\omega) - \chi_0(r, r', i\omega)] \]

- from adiabatic connection fluctuation dissipation theorem\(^1\)
- Coulomb interaction scaled by \(\lambda\)
- linear response of the electron density with respect to local perturbation

\[ \delta \rho(r, \omega) = \int dr' \chi(r, r', i\omega) \delta V^{\text{ext}}(r', \omega) \]

- relation to dynamic polarizability

\[ \alpha_{ij}(i\omega) = \int dr dr' r_i r'_j \chi(r, r', i\omega) \]

In practice not solvable for many-particle systems

\[ E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \int_0^\infty d\omega \left[ \chi_\lambda (\mathbf{r}, \mathbf{r}', i\omega) - \chi_0 (\mathbf{r}, \mathbf{r}', i\omega) \right] \]

- analytical expression for non-interaction Kohn-Sham system

\[ \chi_0 (\mathbf{r}, \mathbf{r}', i\omega) = -4 \sum_{i}^{\text{occ}} \sum_{a}^{\text{virt}} \frac{\omega_{ai}}{\omega_{ai}^2 + \omega^2} \varphi_i (\mathbf{r}) \varphi_a (\mathbf{r}) \varphi_a (\mathbf{r}') \varphi_i (\mathbf{r}') , \]

- occupied and virtual KS orbitals \( \varphi_i \) and \( \varphi_a \)

- \( \chi_\lambda \) too complicated to compute in practice

\[ \rightarrow \text{approximation needed} \]

Coarse-graining to atomic contributions leads to significant simplifications

- coarse-grain ACFDT to fragment contributions
  
  $$E_{\text{disp}}^{AB} = -\frac{1}{2\pi} \int d\omega \int dr_a dr'_a dr_b dr'_b \frac{\chi(r_a, r'_a, i\omega) \chi(r_b, r'_b, i\omega)}{|r_a - r'_a||r_b - r'_b|}$$

- assume vanishing overlap to factorize response function

- integrate fragment response to dynamic polarizabilities
  
  $$\alpha_{ij}(i\omega) = \int dr dr' r_i r'_j \chi(r, r', i\omega)$$

- expansion of Coulomb operator in multipoles

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

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Spherical averaging and higher order terms beyond dipole-dipole

- spherical averaging of dyn. polarizabilities

\[
E_{\text{disp}}^{AB} = - \frac{3}{\pi} \int \frac{d\omega}{\omega} \alpha_A(\omega) \alpha_B(\omega) \times \frac{1}{R_{AB}^6} + O(R^{-8})
\]

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

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

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

\[
C_9^{ABC} = - \frac{3}{\pi} \int \frac{d\omega}{\omega} \alpha_A(i\omega) \alpha_B(i\omega) \alpha_C(i\omega)
\]
Combining vdW correction with mean field model

- sum of fragment contributions for total London dispersion energy

\[ E_{\text{disp}} = -\frac{1}{2} \sum_{A,B} \sum_n C_{n}^{AB} \frac{R_{n}^{AB}}{} - \frac{1}{6} \sum_{A,B,C} \sum_n C_{n}^{ABC} \frac{R_{n}^{ABC}}{} F^{\text{geom}} + \mathcal{O}(\text{quadruples}) \]

- singularity at short-range (and expansion not valid)

- introduce short-range damping, motivated by range separation of Coulomb operator

\[ E_{\text{tot}}^{AB} = E_{\text{DFT}}^{AB} \text{erf}(\omega R_{AB}) + E_{\text{disp}}^{AB} \text{erfc}(\omega R_{AB}) \]
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Many good dispersion corrections exist. Focus on D3 scheme as it can be used at all computational levels. Own work started with extension of D3 type corrections.

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Introduction

H2 model

ACFDT

vdW inclusive DFA

Show-cases

Conclusions

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20th of Sept. 2018

Coarse-graining to atomic contributions leads to significant simplifications

- Coarse-grain to atomic contributions

\[ \alpha_{ij}(i\omega) = \int \, drdr' \, r_i r'_j \chi(r, r', i\omega) \]

- Expansion of Coulomb operator in multipoles

\[ E_{\text{disp}}^{AB} = -\frac{3}{\pi} \int d\omega \alpha_A(i\omega)\alpha_B(i\omega) \times \frac{1}{R_{AB}^6} \]

\[ C_6^{AB} \]

- \( C_8^{AB} \) and \( C_9^{AB} \) from recursion relations and averages

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


Dynamic polarizability via linear response DFT

- use frequency domain formalism to get excitation frequencies\[^5\]

\[
\begin{pmatrix}
A & B \\
A^* & B^*
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix} = \omega
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\]

- 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

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
- short-range damping avoids double counting \[^{[6]}\]

Semi-classical scheme yields 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 $< 5\%$ [7]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

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## Advantages of D3 model

- intermolecular $C_6$ coefficients are very accurate
- no electronic structure input needed
- computation is extremely fast $\sim$ 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
## Multilevel methodologies: finding the right compromise

<table>
<thead>
<tr>
<th>task/property</th>
<th>example method</th>
</tr>
</thead>
<tbody>
<tr>
<td>accurate QM</td>
<td>L-CCSD(T)</td>
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<tr>
<td></td>
<td>DMC[^8], FCIQMC</td>
</tr>
<tr>
<td>cheap QM</td>
<td>metaGGA (SCAN-D3[^9])</td>
</tr>
<tr>
<td></td>
<td>HSE-3c[^10]</td>
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<tr>
<td>very cheap QM</td>
<td>semi-empirical</td>
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<tr>
<td></td>
<td>HF-3c[^11,12], DFTB3-D3[^13]</td>
</tr>
<tr>
<td>force field</td>
<td>transferable or molecule specific (QM derived) FF</td>
</tr>
</tbody>
</table>

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Simple input of D3 dispersion correction in CRYSTAL17

old calculation

MOLECULE
40
2
6 1.209708 0.698426 0.000000
1 2.152747 1.242889 0.000000
BASISSET
def2−mTZVP
DFT
PBE
END
END

new D3 inclusive calculation

MOLECULE
40
2
6 1.209708 0.698426 0.000000
1 2.152747 1.242889 0.000000
BASISSET
def2−mTZVP
DFT
PBE−D3
END
END

*****************************************************************************

DFT−D3 DISPERSION ENERGY CORRECTION

D3 DISPERSION ENERGY (AU) −1.0948042757474E−02
TOTAL ENERGY + DISP (AU) −2.3201130812713E+02

*****************************************************************************

- combinable with geometry optimization, frequencies, QHA, etc.
- impact of D3 should be tested for all DFT applications
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Numerical convergence & different functional approximations

- check literature if similar systems have been studied
- are high-level theory data available?
  → use those or generate your own
- are experimental references available?
  → be careful to compare the right observables
- converge all numerical thresholds
  (basis set, \( k \)-point sampling, SCF/geometry thresholds)
- different methods in terms of computational efficiency and accuracy
  → influence of XC treatment (PBE vs. BLYP vd. SCAN vs. PBE0)
  → vdW correction should always be included (D3, MBD, XDM, vdW-DF2)
- use affordable method with acceptable accuracy
  if none exist abandon project
Guinea pig for testing vdW interactions

Noble gas assemblies

- binding solely from electron correlation effects
Guinea pig for testing vdW interactions

Benzene dimer and crystal

- zero-point and thermal effects crucial for comparing to measurement
- error bar in volume mainly from QHA back-correction (about 1%)

Introduction  ······· H2 model  ······· ACFDT  ······· vdW inclusive DFA  ········ Show-cases  ········ Conclusions
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20th of Sept. 2018  28/39
High-level QM data needed to test DFT for organic solids

- substantial uncertainties in $H_{\text{sub}}^{\text{exp}}$ and thermodynamic corrections \footnote{W. Acree, J. S. Chickos, J. Phys. Chem. Ref. Data 39, 043101 (2010).}
- high-level data needed to judge approximate methods
High-level QM data needed to test DFT for organic solids

- substantial uncertainties in $H_{\text{sub}}^{\text{exp}}$ and thermodynamic corrections \[14\]
- high-level data needed to judge approximate methods

Modern DFT-D methods have excellent accuracy

- benzene crystal purely vdW bonded
- significant effect of many-body dispersion
Choosing the right functional and basis set combination

- effect of semi-local functional as important as many-body dispersion
- significant BSSE up to triple-ζ basis sets
Choosing the right functional and basis set combination

- ice VIII: high-density phase
- BSSE even stronger in H-bonded systems
Many properties depend on the polymorphic form of a crystal

Polymorphism

- ability of a molecule to crystallize in more than one structure\(^{[15]}\)
- properties change with crystal packing, e.g. solubility, color, etc.\(^{[16]}\)

- late appearing polymorph disrupted supply of antiviral drug ritonavir\(^{[17]}\)

→ Tools to predict possible polymorphs would be valuable

→ High accuracy \(~1\) kJ/mol needed


Sampling and energetic ranking for crystal structure prediction

molecular diagram of ROY

CSP

Crystal Structure Prediction

crystal energy landscape

-130
-125
-120
-115

lattice energy / kJ mol⁻¹

1.3
1.4
1.5

density / g cm⁻³

Properties of ROY polymorphs

categorized

Red prism
P-1, θ=21.7°

Orange Red Plate
Pbca, θ=39.4°

Orange Needle
P2₁/c, θ=52.6°

Yellow prism
P2₁/n, θ=104.7°

H2 model

ACFDT

vdW inclusive DFA

Show-cases

Conclusions

Introduction

FF

size of sampling space

>1,000,000

>1,000

<100

methodology

classical force fields

semiempirical

ab-initio

most stable

most stable

improve lattice energy model

reduce polymorph space

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Promising results in the 6th blind test

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<thead>
<tr>
<th>Method</th>
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<td>4</td>
<td>13</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

lattice energy on fixed TPSS-D3 structures

- good lattice energy based ranking of PBE-D3
- impact of free energy contributions estimated to $\sim 1-3$ kJ/mol\textsuperscript{[20,21]}

Crystal packing dependent properties II

bond isomerization\textsuperscript{[22]}

spin crossover\textsuperscript{[23]}

co-adsorption on graphite

Fast electronic structure for large systems

- fast computer code CRYS\[26\]TAL17 with cost-efficient methods\[11\]
- enabling routine electronic structure calculation of large systems

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Summary

Take-home messages

- D3 London dispersion interaction arises in second order perturbation theory.
- \( C_6 \) based dispersion corrections are most efficient in DFT framework.
- DFT-D methods show excellent performance for organic crystals.
- D3, gCP, and composite methods implemented in CRYSTAL17.
Key references

- Dispersion corrections:

- DFT development

- DFA-DISP for crystal structure prediction:
  DOI: 10.1039/C8FD00010G
  S. L. Price, JGB, Molecular Crystal Structure Prediction, G. DiLabio, A.

- homepage: gerit-brandenburg.de