Methods for van der Waals Interactions

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Van der Waals (dispersion) energy
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\[
\begin{align*}
\delta^- & \quad \delta^+ \\
\text{A} & \quad \text{A} \\
\delta^- & \quad \delta^+ \\
\text{B} & \quad \text{B}
\end{align*}
\]
Van der Waals (dispersion) energy

- Ubiquitous interatomic and intermolecular interaction
- Scales linearly with system size
- Weak compared to hydrogen or covalent bonds

... but is a significant component of intermolecular binding energies!

\[ E^{\text{disp}}(R) = - \left( f_6(R) \frac{C_6}{R^6} + f_8(R) \frac{C_8}{R^8} + f_{10}(R) \frac{C_{10}}{R^{10}} + \ldots \right) \]
VdW Interactions Are Ubiquitous ...
Current state-of-the-art of modeling

\[ H\Psi = E\Psi \]

- Empirical potentials ("force fields")
- Semi-empirical methods (based on DFT or Q.C.)
- Hybrid DFT (Semi)-local DFT: LDA and GGA
- Post Hartree-Fock (MP2, CCSD(T), RPA)
- Full CI

Accuracy, Reliability and Predictive Power vs. Computational Cost
Current state-of-the-art of modeling

\[ H \Psi = E \Psi \]

- Empirical potentials ("force fields")
- Semi-empirical methods (based on DFT or Q.C.)
- Density-functional theory with approximate functionals
  - Post Hartree-Fock (MP2, CCSD(T), RPA)
- Full CI

Accuracy, Reliability and Predictive Power

Computational Cost
Correlated methods:
MP2, RPA, CCSD(T)

- Compute the correlation energy based on a Hartree-Fock or DFT wavefunction
- Include different many-body diagrams for the correlation energy

- **MP2**: Minimal level for correlation energy
- **RPA**: Doubles to infinite order, no singles
- **CCSD(T)**: Quantum chemistry “gold standard”
DFT and vdW interaction: Rare-gas dimers

\[ E^{\text{disp}}(R) = - \left( f_6(R) \frac{C_6}{R^6} + f_8(R) \frac{C_8}{R^8} + f_{10}(R) \frac{C_{10}}{R^{10}} + \ldots \right) \]
Why existing methods are not sufficient?

Polymorphism in drugs

**Ritonavir (HIV protease inhibitor)**

1996 (launch) 1998 (recall)
2001 (*trans* form found)

Polymorph energies are typically within 1 kcal/mol per molecule
Why existing methods are not sufficient?

Polymorphism in drugs

Ritonavir (HIV protease inhibitor)

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Polymorph energies are typically within 1 kcal/mol per molecule

Molecular switches at surfaces

Standard DFT yields wrong adsorption structure.
No available method gives quantitative energetics!

Accurate First-Principles Modeling of vdW Interactions is Challenging

\[ E_{vdW}^{(2)} = -\frac{C_{6}^{AB}}{R_{AB}^{6}} \]

\[ C_{6}^{AB} = \frac{3}{\pi} \int \alpha_{A}(i\omega)\alpha_{B}(i\omega) d\omega \]
Accurate First-Principles Modeling of vdW Interactions is Challenging

\[ E_c = - \int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left( (\chi_\lambda(r_1, r_2; i\omega) - \chi_0(r_1, r_2; i\omega)) \frac{1}{|r_1 - r_2|} \right) \]

Extremely expensive!
Accurate First-Principles Modeling of vdW Interactions is Challenging

Accurate Microscopic Modeling of Coulomb Screening

Full (All-Order) Many-Body van der Waals Energy

\[ E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left( (\chi_\lambda(r_1, r_2; i\omega) - \chi_0(r_1, r_2; i\omega)) \frac{1}{|r_1 - r_2|} \right) \]
VdW-corrected DFT methods
Concepts and methods for dispersion in DFT

\[ E_{xc} = E_{\text{ex}}^{\text{GGA}} \text{ or } E_{\text{X}} + E_{\text{corr}}^{\text{LDA,GGA}} + E_{\text{corr}}^{\text{non-local}} \]
Concepts and methods for dispersion in DFT

\[ E_{xc} = E^{GGA}_{ex} \text{ or } E^{EX} + E^{LDA,GGA}_{corr} + E^{\text{non-local}}_{corr} \]

- Non-local functionals (depend explicitly on \( r \) and \( r' \)) \((\text{Langreth, Lundqvist et al.})\).
- Modified pseudopotentials \((\text{von Lilienfeld et al.})\)
- Highly empirical (hybrid) meta-GGA functionals \((\text{Truhlar et al.})\)
- Interatomic (pairwise or beyond) dispersion corrections (Many people)

\textbf{Wu and Yang JCP (2002); Grimme J. Comp. Chem. (2004,2006); Dion et al. PRL (2004); Zhao and Truhlar JCP (2006); von Lilienfeld et al. PRL (2004); Johnson and Becke JCP (2005-2007); Tkatchenko and Scheffler PRL (2009); and many others ...}
S22 benchmark database

Hydrogen bonding

A•••T WC
2-pyridoxine•••2-aminopyridine
Hydrogen bonded uracil dimer

(NH₃)₂
(H₂O)₂
(HCONH₂)₂
(HCOOH)₂

Hydrogen bonding

S22 benchmark database

VdW bonding

S22 benchmark database

T-shaped indole···benzene  
T-shaped benzene dimer  
Phenol dimer  

Benzene···H2O  
Benzene···NH3  
Benzene···HCN  
Ethene···ethyne

Mixed bonding

Langreth-Lundqvist functional
(vdW-DF-04 and vdW-DF-10)
Langreth-Lundqvist functional

\[
E_{xc} = E_{ex}^{GGA}[n(r)] + E_{corr}^{LDA}[n(r)] + E_{corr}^{non-local}[n(r)]
\]

\[
E_{corr}^{non-local}[n(r)] = \frac{1}{2} \int d^3rd^3r'n(r)K(r,r')n(r')
\]

Langreth-Lundqvist functional (vdW-DF-04 and vdW-DF-10)

\[ E_{xc} = E_{ex}^{GGA}[n(r)] + E_{corr}^{LDA}[n(r)] + E_{corr}^{non-local}[n(r)] \]

\[ E_{corr}^{non-local}[n(r)] = \frac{1}{2} \int d^3 r d^3 r' n(r) K(r, r') n(r') \]

vdW-DF-04
- Exchange: revPBE
- Local corr.: LDA
- No free parameters
- \( C_6 \) error: \( \sim 20\% \)

vdW-DF-10
- Exchange: PW86
- Local corr.: LDA
- 2 parameters
- \( C_6 \) error: \( \sim 60\% \)

Approximations for $E^\text{non-local}_{\text{corr}}$ in vdW-DF

1) Local approximation for the response function
2) Only pairwise point-point interaction, ignoring non-additive many-body energy
Performance of vdw-DF on the S22 database
Performance of vdW-DF on the S22 database

The chart shows the mean absolute relative error to CCSD(T) (%) for different types of interactions: H-bond, vdW, Mixed, and Overall. The errors are compared for different methods: PBE, MP2, vdW-DF-04, and vdW-DF-10.
Limitations of the Langreth-Lundqvist functional

- **vdW-DF-04** is a general purpose functional, however its performance is not optimal (errors significantly larger than chemical accuracy).

- **vdW-DF-10** is a special purpose functional with good performance for molecules. Asymptotic vdW interactions are significantly underestimated (~60%), so no good performance should be expected for larger systems.

- The **vdW-DF** concept does not have flexibility for the coupling to semi-local DFT functional. This is being improved by Vydrov and van Voorhis (*PRL* 2009, *JCP* 2010).
Empirical Minnesota functionals
(Zhao-Truhlar, M06 family)
Empirical Minnesota functionals (Zhao-Truhlar, M06 family)

- Highly flexible (and empirical) form for a functional (20-40 parameters) trained on a broad set of benchmark (theory and experiment) data

- A family of functionals:
  - M06: Hybrid meta-GGA functional
  - M06-L: GGA (non-hybrid) version of M06
  - M06-2X: M06 with twice the amount of HF exchange
  - M06-HF: M06 with 100% HF exchange
The description of vdw in M06

Flexible meta-GGA form allows for an approximate modeling of vdw interactions at short-range whenever there is a non-negligible electron density overlap

M06 converges to zero interaction at ~ 5 Å separation between atoms, in the same way as LDA and GGA

Thus, M06 does not include the correct physics of vdw interactions, typically leading to underbinding of vdw-bound systems
The description of vdW in M06

Marom, Tkatchenko, Gobre, Rossi, Hod, Scheffler, Kronik, to be submitted.
Performance of M06(-L) for S22
Interatomic vdW correction methods
Interatomic vdW methods

\[ E_{xc} = E_{ex}^{\text{GGA}} \text{ or } EX + E_{corr}^{\text{LDA,GGA}} + E_{\text{non-local}}^{\text{corr}} \]

\[ E^{\text{vdW}}(R) = - \left( f_6(R) \frac{C_6}{R^6} + f_8(R) \frac{C_8}{R^8} + f_{10}(R) \frac{C_{10}}{R^{10}} + \ldots \right) \]

- Two parameters per atomic pair: (1) \textbf{VdW} \( C_6 \) interaction coefficient and (2) \textbf{vdW} radius.
- Clearly, if (1) and (2) are empirical, this leads to many fitting parameters. This was frequently the case before 2008.
Damping function for vDW-corrected DFT

\[ f_{damp}(R_{AB}, R_{AB}^0) = \left[1 + \exp\left(-d\left(s_{R}R_{AB}^0 - 1\right)\right)\right]^{-1} \]

- Steep damping function required to separate the short range from vDW energy
- About 5 different functional forms proposed
- Fermi function (above) among the most popular ones
- Works for molecules, but the functional form is arbitrary!
Evolution of interatomic vdW methods

- Grimme's D1,D2 (2004-2006): Parameterization for many elements in the periodic table
  - Highly empirical, some approximations unfounded
- Jurečka et al. (2007): Accurate parameterization for organic molecules
  - Better theoretical ground, but still very empirical
- Johnson and Becke (2005-2008), Silvestrelli (2008): $C_6$ and vdW radii from HF or DFT orbitals
  - Reduced empiricism, errors of ~ 20%-40% in $C_6$ coefficients
- Tkatchenko and Scheffler (2009): $C_6$ coefficients and vdW radii from ground-state electron density
  - First-principles $C_6$ accurate to 5%
- ....
Highlights of TS-vdW method

- VdW asymptotics with an accuracy of 5%
- Transparent partitioning of vdW coefficients over atoms
- Reduced empiricism (1 parameter in the damping function)
- Polarizability is directly proportional to volume
- Computationally efficient
- Valid for the whole periodic table

\[
C_{6AA}[n(r)] = \left( \frac{V_A[n(r)]}{V_A^{free}[n^{free}(r)]} \right)^2 C_{6AA}^{free}
\]

Tkatchenko and Scheffler, *PRL* (2009)
Performance of TS-vdW method for molecules

Mean absolute error of 5.5% for 1225 molecular $C_6$ from reference DOSD data of W. J. Meath et al.
Performance of TS-vdW method for molecules

Results depend negligibly (1% deviation) on the employed $xc$ functional
$C_6$ is a functional of the density
(Carbon-Carbon $C_6$ coefficient / Hartree Bohr$^6$)
DFT+\text{vdW}

Leading dispersion term is added to DFT total energy, damped at short interatomic distance,

\[ E_{\text{vdW}} = - \sum_A \sum_{B>A} f_{\text{damp}}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6} \]

\[ R_{\text{eff}}^0 = \left( \frac{V_{\text{eff}}}{V_{\text{free}}} \right)^{1/3} R_{\text{free}}^0 \]

- Effective vdW parameters are functionals of the electron density:

\[ C_6 = C_6[n(r)], \quad R_{\text{vdW}} = R_{\text{vdW}}[n(r)] \]

\textbf{DFT+vdW: Tkatchenko and Scheffler, PRL (2009)}
Performance of DFT+vdW for S22
Performance of DFT+vdW for S22 (Mean Absolute Error)
Performance of DFT+vdW for S22: Different functionals

![Graph showing the performance of DFT+vdW for S22 with different functionals]
What is missing in DFT+vdW?

1) Long-range electrostatic screening among fluctuating dipoles
2) Non-additive many-body vdW energy beyond two-body

\[ E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left( \chi_\lambda (\mathbf{r}_1, \mathbf{r}_2; i\omega) - \chi_0 (\mathbf{r}_1, \mathbf{r}_2; i\omega) \right) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \]
DFT+vdW$^{\text{SCS+MB}}$: Screening and Many-Body vdW Energy

Benzene crystal

**PBE+vdW**
690 meV/molecule

**PBE+vdW$^{\text{SCS+MB}}$**
565 meV/molecule

**Experiment**
518-560 meV/molecule

2.9 kcal/mol due to screening and many-body VdW effects

 Tkatchenko, DiStasio Jr., Car, Scheffler, to be submitted.
DFT+vdW: Challenges

- DFT+vdW treats intra- and intermolecular interactions accurately. Recent extension permits the treatment of insulators, ionic, and semiconductor solids.
- Coupling of (short-range) DFT and (long-range) vdW remains empirical, and one of the biggest issues to address.
- No satisfactory model for metallic bulk systems yet.
- Interatomic potentials may not work for highly anisotropic low-dimensional systems (Dobson, Rubio, et al.)
Applications
Unraveling the Role of vdW Interactions for Peptide Secondary Structure

- $\text{Ala}_{15}\text{LysH}^+$ forms stable helices \textit{in vacuo} up to $\sim 700$ $K$ (in solution only up to $\sim 340$ $K$)

- Direct first-principles folding simulations are not feasible, but unfolding dynamics could provide similar insight!

Experiments: \textit{Kohtani, Jones, Schneider, Jarrold, JACS} (2004)
DFT-PBE+vdW

DFT-PBE

Tkatchenko, Rossi, Blum, Ireta, Scheffler, PRL (2011)
Van der Waals and Inorganic/Organic Interfaces

perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA)
Van der Waals and Interfaces: Which theoretical method?

Van der Waals and Interfaces: Which theoretical method?


LDA/PBE: (semi-)local DFT. Can be applied to > 1000 atoms

![Graph showing the relationship between adsorption energy (E_{ads}) and distance (d) for LDA and PBE methods. The graph indicates the expected behavior for both methods at various distances. The LDA method shows a more pronounced adsorption energy increase with distance, while the PBE method shows a gentler trend. The graph highlights the difference between the two methods, with the LDA curve starting lower and rising more sharply compared to the PBE curve.](PTCDA.png)
Van der Waals and Interfaces: Which theoretical method?

Experiment:

vDW-DF: Non-local Langreth-Lundqvist functional. Can be applied to > 1000 atoms


Van der Waals and Interfaces: Which theoretical method?


PBE-D: PBE+Pairwise correction by Grimme. Can be applied to > 1000 atoms
Van der Waals and Interfaces: Which theoretical method?

**Experiment:**

**PBE+vdW:**
- PBE+Pairwise correction by Tkatchenko-Scheffler.
  - Can be applied to > 1000 atoms

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**Graph:**
- E$_{ads}$ (eV) vs. d (Å)
- Lines represent different methods: PBE-D, LDA, PBE+vdW, PBE, vdW-DF
- Experimental data (Exp.)

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**Notes:**
- PTCDA
- Ag(111)
Van der Waals and Interfaces: Which theoretical method?


EX+cRPA:
Exact exchange + approximate many-body correlation energy.
Can be applied to < 200 atoms
PTCDA@Ag(111): PBE+vdW(ZK)
PTCDA@Cu/Ag/Au: PBE+vdW(ZK)

Joint work with V. Ruiz, E. Zojer, M. Scheffler.
VdW Interactions Are Ubiquitous ...
Thank you!