Evaluating van der Waals energies from dielectric response functions

Deyu Lu
Department of chemistry, UC Davis

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Motivation

- **vdW forces** play important roles in many processes such as physical absorption, adhesion, assembly of organic molecules, wetting...

- In order to describe the vdW energies accurately, a central ingredient of the theory is the **dielectric response function**, which is **dynamical and non-local** in nature.

- From the practical aspect, evaluation of the dielectric response function from first principles is usually **computationally demanding**. Thus it is important to develop efficient **numerical implementations** suitable for the application to large systems.
Outline

- Existing vdW methods
- ACFDT theory and numerical implementation
  - RPA correlation energy using dielectric eigenmode expansion technique
  - Examples
    - Benzene crystal
    - Methane phase I
    - PDI SAM on Au(111) surface
- ACFDT with local basis sets
  - Dielectric eigenmodes from linear combination of local basis functions
  - Classification of dielectric eigenmodes of a rare gas atom
van der Waals interaction

\[ \chi(r, r') = \frac{\delta \rho(r)}{\delta V_{\text{ext}}(r')} \]

\[ E(d) \sim -c_6 \ d^6 \]

at large distance

- Standard DFT XC-functionals are short-ranged and fail to describe the very non-local nature of electron-electron correlation in vdW systems.
- LDA sometimes provides fortuitous good agreements with experiments; GGA very often fails to bind vdW systems.

Empirical methods

- Adding \( c_6 \) pairwise potential gives qualitative improvement, but it assumes additivity and has issues with transferability.

Functional based methods

- vdW functional
- Range-separated KS

General theories

- Quantum chemistry methods (CCSD, MP2, SAPT, etc) are very expensive and not feasible for large systems and extended systems.
- QMC (Poster by Leonardo Spanu)
- Adiabatic connection fluctuation-dissipation theorem (ACFDT), which contains EXX and correlation energy formulated on density-density response function
RPA correlation energy through ACFDT

ACFDT: \[ E_{xc} = E_{xx} + E_c \]

\[ E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int dr \int dr' \frac{1}{|r - r'|} \int_0^\infty du \left( \chi^\lambda(r, r', iu) - \chi_{KS}(r, r', iu) \right) \]

\[ \chi^\lambda(1,2) - \chi_{KS}(1,2) = \chi_{KS}(1,3) f_H(34) \chi^\lambda(42) \]

Under RPA: \[ \chi^\lambda = \frac{\chi_{KS}}{1 - \lambda \chi_{KS} v_H} \]

\[ \chi_{KS,G,G'}(q, iu) = \frac{2}{\Omega} \sum_k \sum_{n,m} (f_n - f_m) \frac{\rho_{k,q}(G)\rho_{k,q}^*(G')}{iu + \epsilon_n(k) - \epsilon_m(k + q)} \]

\[ \rho_{k,q}(G) = \langle k,n | e^{-i(q+G)\cdot r} | k + q,m \rangle \]

Short range correction: \[ E_{c}^{RPA+} = E_{c}^{RPA} + \left( E_{c}^{LDA/GGA} - E_{c}^{RPA_{model}} \right) \]


Features of the EXX/RPA approach

- It is **self-interaction free** due to the use of exact exchange.
- **RPA correlation** (ACFDT) treats long-range correlation accurately
- **Short-range correction** of correlation (RPA+)
  - RPA+ usually does not significantly affect the binding curve and cohesive energy due to error cancellation
- Because exchange and correlation are calculated **separately**, they both need to be converged very well, in contrast to LDA or GGA xc energies, which have huge error cancellation.
- The standard implementation is computationally quite demanding, which scales as $N_v N_{pw}^3$.
- We apply density functional perturbation theory to improve the scaling to $N_v^2 N_{eig} N_{pw}$, which makes it possible for the calculation of large systems.


Existing Works

**Jellium**

**Isolated molecule**
M. Fuchs and X. Gonze, *Phys. Rev. B*, 65, 235109 (2002); (H2, Be2)
F. Furche and T. V. Voorhis, J. Chem. Phys. 122, 164106 (2005); (He2 and HeNe)

**Compact solid**
Layered material


Noble gas solid


Physisorption on metal surface


vdW Crystal


Formulation based on excitation energies

Eigenmode expansion of $E_c^{\text{RPA}}$

$\nu^{1/2}(q) = \sqrt{4\pi/q}$

$\tilde{\epsilon} = 1 - \nu^{1/2}\chi_{KS}\nu^{1/2}$

$= \sum_i |i\rangle \epsilon_i \langle i|$

$-\int_0^1 d\lambda \nu^{1/2}\chi^\lambda\nu^{1/2} = \log(I - \nu^{1/2}\chi_{KS}\nu^{1/2})$

$= \sum_i |i\rangle \log(\epsilon_i) \langle i|$  

$E_c = \frac{1}{2\pi N_q} \int_0^\infty du \sum_q \sum_i \{ \log(\epsilon_i(q,iu)) - \epsilon_i(q,iu) + 1 \}$

remove the $\lambda$ integration

Need to compute $\epsilon_i$!
Solving the dielectric eigenmodes with an iterative method

- Eigenpotentials are found by repeated application of the operator $\tilde{\mathcal{E}}$
- Effect of XC kernel (not in RPA) in the perturbation can be easily included
- Implemented through a modified version of the phonon code in the Quantum Espresso package*


* P. Giannozzi et al., http://www.quantum-espresso.org
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Benzene Crystal

- One of the simplest organic crystals bound by vdW forces
- Experimental lattice constants (4K) [1]:
  - Four monomers per cell
  - Pbca symmetry
    \[ a=7.360 \text{ Å}, \quad b=9.375\text{Å}, \]
    \[ c=6.70 \text{ Å}, \quad \alpha=\beta=\gamma=90^\circ \]
- LDA overestimates the equilibrium density by 13%; PBE underestimates the equilibrium density by 27% and severely under-binds [2].

EXX/RPA from LDA ground states
EXX/RPA from PBE ground states

![Graph showing EXX/RPA from PBE ground states](image-url)
EXX/RPA predicts equilibrium density, cohesive energy, and bulk modulus in good agreement with experiment.

The binding curve is insensitive to the exchange-correlation functional in the ground state calculation.

Short-range correction (EXX/RPA+) does not change the binding curve but reduces the cohesive energy by about 2 kJ/mol.

Semi-empirical DFT+D (pair-potential correction), e.g., Grimme06 parameterization, yields excellent cohesive energy but the equilibrium density is about 10% too large.


Phase I: fcc structure, with one freely rotating molecule in the unit cell.

Existing theoretical work ignored rotational degree of freedom \[3-4\]
Is the orientation important?
EXX/RPA binding curve

config. 1

config. 2

$E_{\text{coh}}$ (kJ/mol) vs. lattice constant (Å)

ACFDT/LDA
ACFDT/PBE
EXX/RPA (PBE) results

<table>
<thead>
<tr>
<th>config.</th>
<th>EXX/RPA</th>
<th>PBE+D&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PBE+D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>MP2&lt;sup&gt;c&lt;/sup&gt;</th>
<th>exp.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>≥6</td>
<td>5.84</td>
<td>5.80</td>
<td>6.00</td>
<td>plastic phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.8</td>
<td>11.35</td>
<td>10.3</td>
<td>a&lt;sub&gt;0&lt;/sub&gt; ~5.84&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>5.80</td>
<td>5.50</td>
<td>–</td>
<td>–</td>
<td>E&lt;sub&gt;coh&lt;/sub&gt;=10.4-11.4&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>8.8</td>
<td>14.9</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
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</table>

a: This work from PBE ground state. Dispersion corrections were evaluated with Grimme2006 parametrization scheme. [S. Grimme, *J. Comp. Chem.* 27, 1787 (2006)].


d: a<sub>0</sub> = 5.84 Å was measured at 29K.

e: The measured heat of sublimation (in kJ/mol) is corrected for temperature effects. ZPE is not included.
Summary on methane crystal

- Orientations of methane molecules in the fcc structure were found to contribute significantly to the intermolecular interaction energy, both at the DFT level and the EXX/RPA level.

- The cohesive energy from EXX/RPA (LDA) is about 2 kJ/mol smaller than EXX/RPA (PBE).

- Comparing to EXX/RPA, semi-empirical DFT+D method underestimates the lattice constant and overestimates the cohesive energy.

- Quantum effects may need to be incorporated to recover experimentally observed plastic phase (random orientations).

PDI SAM on Au(111) surface: Is Isocyanide group a good linker?

- The presence of the triple bond in the isocyanide group may effectively connect the \( p\text{π} \) electrons in the aromatic moiety and the \( d\text{π} \) electrons on the gold surface.
- However, no ordered monolayers of PDI or BPDI has been observed in either AFM or STM experiments.
- DFT (LDA or GGA) does not describe well vdW interactions among SAMs.

Which one is more stable?

- full coverage: \( \sqrt{3} \times \sqrt{3} \): 1 PDI / 3 Au
- full coverage: Herringbone
- low coverage (1/3): 1 PDI / 9 Au
DFT(PBE) results for PDI/Au(111)

\[ E_{ad} = -(E_{mol/Au} - E_{Au} - E_{mol}) = E_{mol-Au} + E_{mol-mol} \]

<table>
<thead>
<tr>
<th>coverage</th>
<th>( E_{mol-Au} ) (eV)</th>
<th>( E_{mol-mol} ) (eV)</th>
<th>( E_{ad} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \ (\sqrt{3} \times \sqrt{3}) )</td>
<td>0.44</td>
<td>-0.38</td>
<td><strong>0.06</strong></td>
</tr>
<tr>
<td>( 1 \ (Herringbone) )</td>
<td>0.46</td>
<td>-0.22</td>
<td>0.24</td>
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<tr>
<td>( 1/3 )</td>
<td>0.59</td>
<td>-0.05</td>
<td>0.54</td>
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</table>

1. Is PDI intermolecular interaction indeed repulsive?
2. Is the low coverage structure more stable?

EXX/RPA greatly improves the under-binding in PBE for PDI SAMs at high packing density.

Contrary to the case of methane, PBE+D agrees reasonably well with EXX/RPA.

The adsorption energy of the gas phase and the high coverage herringbone structure are nearly identical.

The lack of ordering in experiments may arise from the close competition between vdW interactions at high density and stronger surface binding at low density.

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DEMns of gas phase water monomer

DEM of water clusters
DEMs of water clusters resemble linear combinations of those of the monomers.
DEMs from local basis functions

- Represent DEMs in groups I - IV of water clusters by linear combination of local basis functions derived from dielectric response of a monomer.

- Compute the elements of coupling matrix and overlap matrix for only once.

- Solving the eigenvalues of $\varepsilon$ from the secular equation:

$$\langle U_i | \tilde{\varepsilon} | U_j \rangle - \lambda \langle U_i | U_j \rangle = 0$$
DEMs from local basis functions

Linear combination of:

- dimer
- pentamer
Summary

- We have developed a new implementation of EXX/RPA with the scaling of \( N_v^2 N_{eig} N_{pw} \), which allows the theory to be applied to reasonably large systems.

- The feasibility of the implementation is demonstrated by applications to a variety of systems with different geometries and bonding properties.

- Good agreement has been found between the ACFDT and experimental results, with EXX/RPA (PBE) yielding slightly better results.

- We found that the empirical method gives qualitative improvement over LDA(GGA), but the quantitative results need to be taken with caution.

Work in progress

- The computational cost of ACFDT may be further reduced by considering the dielectric eigenpotentials as the linear combination of the local response basis functions, analogous to the tight-binding type of models.

- Preliminary study on water clusters shows very promising results.

- Application and validation of the local basis approach for rare gas dimers may provide further insight of vdW theory from a microscopic point of view.
Acknowledgement

Collaborators

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- Dr. Hugh Wilson
- Dr. Dario Rocca
- Dr. Huy-Viet Nguyen
- Prof. François Gygi
- Prof. Giulia Galli
- the Angstrom group
See also related posters

1. van der Waals interactions in weakly-bonded molecular systems from first principles: An *adiabatic-connection fluctuation-dissipation theorem* approach

2. Optical properties of nanostructures from novel density matrix based methods

3. The nature and strength of inter-layer binding in graphene