Intermolecular Interactions

The Perturbation Theory Approach

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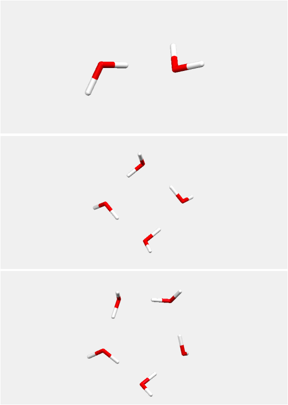
Small clusters (high accuracy):

Helium:

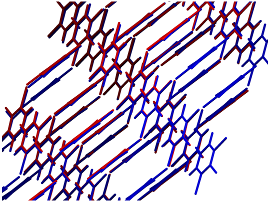
$$-11.009(8)\ \mathrm{K}$$

(Cencek *et al.* 2004)

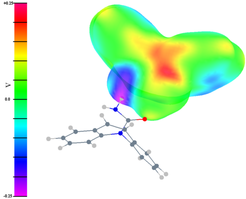
Water:



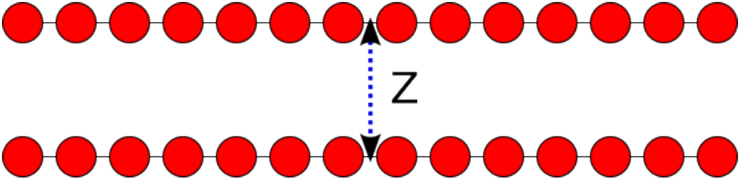
Infinite systems consisting of finite elements:

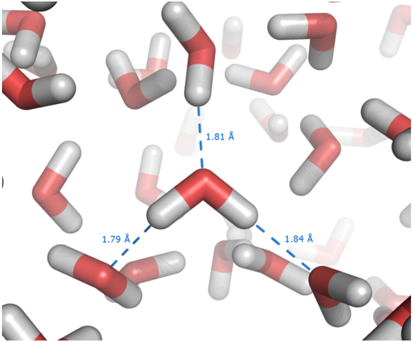


Understanding interactions (interpretation):



We may want to probe the fundamental nature of intermolecular interactions:





- Evolution on a potential energy surface (PES). Finite T.
- Born-Oppenheimer
- Energy differences (MC) (& gradients (MD)):

$$V(\mathit{every\ atom\ in\ cell})$$

Electronic structure methods

$$V(every\ atom\ in\ cell)$$

All electron calculations:

- DFT
    1. Efficient. Flexible. Superb codes.
    2. Accuracy? Dispersion? Interpretation?
- QMC, CCSD(T)
    1. Accurate (in principle). Also superb codes.
    2. Impossible (or very hard?)!
- Perturbation theory (PT):
    - Generally formulated for two or three bodies.
    - So use the many-body expansion...

Many-body expansion I

$$V = V(2) + \Delta V(3) + \Delta V(4) + \cdots$$

where

$$\begin{aligned} V(2) &= \sum_{A>B} V(2)_{AB} \\ &= \sum_{A>B} E^{AB} - E^{A} - E^{B} \end{aligned}$$

$$\begin{aligned} \Delta V(3) &= \sum_{A>B>C} \Delta V(3)_{ABC} \\ &= \sum_{A>B>C} E^{ABC} - E^{AB} - E^{AC} - E^{BC} \\ &\qquad + E^{A} + E^{B} + E^{C} \end{aligned}$$

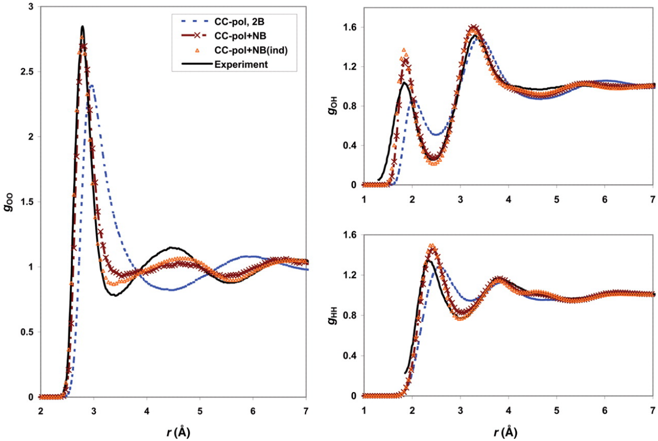
Many-body expansion II

$$V = V(2) + \Delta V(3) + \Delta V(4) + \cdots$$

- Efficient if converges quickly.
- Hierachy of theory-levels possible: PT/QMC/CCSD(T) for $V(2)$ and $\Delta V(3)$, DFT/polarizable model for the rest.
- Though $V(2)$ dominates (basis for all potentials), the many-body terms contribute as much as 30% for polar systems. Polarizable potentials are needed.
- Can be cumbersome.
- Gradients are difficult.
- On-the-fly methods only now becoming possible.

Many-body expansion III

An example: liquid water



Bukowski *et al.* Science 2007

$V(2)_{AB}$

Let us now focus on the two-body energy for *rigid* molecules:

$$V(2)_{AB} = V(AB) = E^{AB} - E^{A} - E^{B}.$$

Supermolecular method

1. Variety: MP2, CCSD(T),...
2. Lots of efficient codes
3. BSSE
4. Little interpretation

Perturbation Theory

$$\mathcal{H} = \mathcal{H}^{A} + \mathcal{H}^{B} + \lambda\mathcal{V}$$

1. Physical decomposition into electrostatic, exchange, dispersion, etc.
2. Basis for all model building.
3. Higher-order terms complicated, but possible.

Raleigh-Schrödinger PT I

$$\mathcal{H} = \mathcal{H}^A + \mathcal{H}^B + \lambda \mathcal{V}$$

Let's assume we know the eigenfunctions and eigenvalues of the unperturbed Hamiltonians:

$$\begin{aligned} \mathcal{H}_A |m_A\rangle &= E_m^A |m_A\rangle, \\ \mathcal{H}_B |n_B\rangle &= E_n^B |n_B\rangle. \end{aligned} \tag{1}$$

For $\lambda = 0$: $\psi^{(0)} = |0_A 0_B\rangle$ and $E^{(0)} = E_0^A + E_0^B$.
For $\lambda > 0$: perturbation expansion for the wavefunction and energy:

$$\begin{aligned} \psi &= \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \cdots, \\ E^{AB} &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \end{aligned} \tag{2}$$

Raleigh-Schrödinger PT II

The interaction energy is given by

$$V(AB) = E^{(1)} + E^{(2)} + \cdots . \tag{3}$$

At first-order,

$$\begin{aligned} E^{(1)} &= \langle 0_A 0_B | \mathcal{V} | 0_A 0_B \rangle & (4) \\ &= \iint \rho_A(\mathbf{r}_1) \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2) \rho_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 . & (5) \end{aligned}$$

where $\rho_A = N \int \cdots \int |\phi_A(1,2,...,N)|^2 d\mathbf{r}_2 ... \mathbf{r}_N$ is the electron density. This is called the electrostatic energy, $E^{(1)}_{\text{elst}}$.

Raleigh-Schrödinger PT III

At second-order:

$$E^{(2)} = -\sum_{mn\neq 00} \frac{|\langle 0_A 0_B|\mathcal{V}|m_A n_B\rangle|^2}{E^A_m + E^B_n - E^A_0 - E^B_0}. \tag{6}$$

We can separate this into:

$$E^{(2)}_{\rm ind}(A) = -\sum_{m\neq 0} \frac{|\langle 0_A 0_B|\mathcal{V}|m_A 0_B\rangle|^2}{E^A_m - E^A_0}, \tag{7}$$

$$E^{(2)}_{\rm ind}(B) = -\sum_{n\neq 0} \frac{|\langle 0_A 0_B|\mathcal{V}|0_A n_B\rangle|^2}{E^B_n - E^B_0}, \tag{8}$$

$$E^{(2)}_{\rm disp} = -\sum_{m\neq 0}\sum_{n\neq 0} \frac{|\langle 0_A 0_B|\mathcal{V}|m_A n_B\rangle|^2}{E^A_m + E^B_n - E^A_0 - E^B_0}. \tag{9}$$

Raleigh-Schrödinger PT IV

$E^{(2)}_{\rm ind}(A)$ describes the change in energy of molecule A in response to the electric field of molecule B. It is the *induction energy* of molecule A. Similarly $E^{(2)}_{\rm ind}(B)$ is the induction energy of molecule B. The final term, $E^{(2)}_{\rm disp}$, is the *dispersion energy*.

Some comments on the induction energy

- *At long-range*: $E^{(2)}_{\rm ind}(A)$ depends on polarizability of A and permanent multipole moments of B. So $E^{(2)}_{\rm ind}(A)$ is zero if B has no permanent multipole moments.
- Always non-zero at short range where charge-densities overlap.
- Dominant contributor to many-body effects.
- Also exists at 3^{rd} and higher-orders of perturbation theory. Can be significantly large (10% for the water dimer).

SAPT I

A few points:

- Of course, we do not know E_m^A and $|m_A\rangle$. So we need a different partitioning of the Hamiltonian. For example:

  $$\mathcal{H} = \mathcal{F}^A + \mathcal{F}^B + \xi^A(\mathcal{H}^A - \mathcal{F}^A) + \xi^B(\mathcal{H}^B - \mathcal{F}^B) + \lambda\mathcal{V}$$

  This leads to a triple perturbation theory.
- Exchange: Antisymmetrize. Many ways of doing this.

The combination leads to:
Symmetry-Adapted Perturbation Theory (SAPT).

SAPT II

SAPT

Jeziorski, Szalewicz & Moszynski (1994).

- Interpretative power!
- Very accurate. Lots of applications. Often spectroscopic accuracy.
- Very poor scaling with system size: $\mathcal{O}(N^7)$.
- Worst scaling for dispersion.
- Very hard to extend to higher orders in PT.

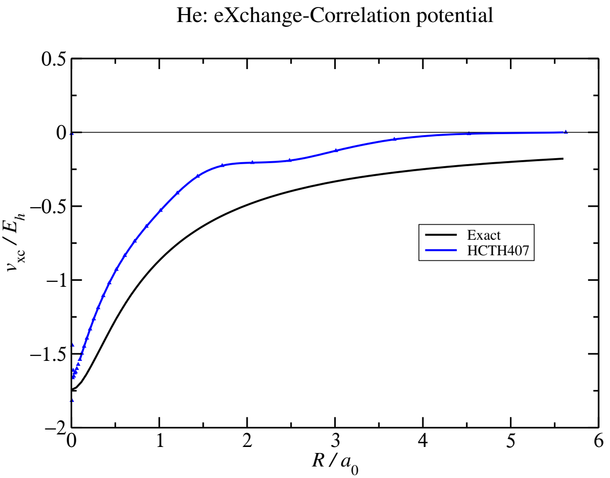
SAPT(KS) I

Chabalowski & Williams (2001).

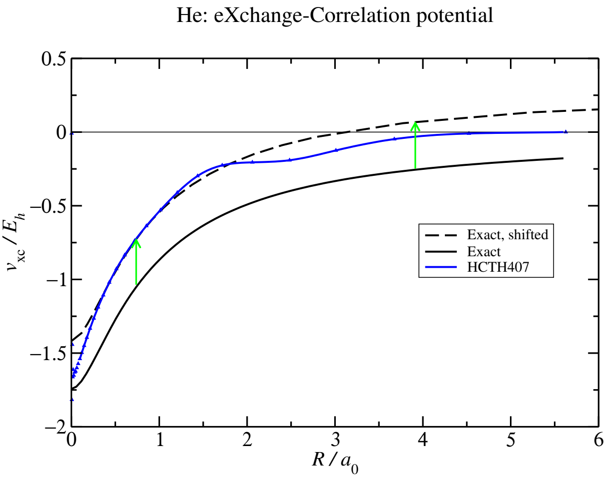
$$\mathcal{H}^{\mathrm{KS}} = \mathcal{K}^{A} + \mathcal{K}^{B} + \lambda \mathcal{V}$$

- Formally justified only for $E^{(1)}_{\mathrm{elst}}$ as this depends on the unperturbed densities of the interacting molecules.
- In practice, even this fails miserably if the exchange-correlation potential is not asymptotically correct...

SAPT(KS) II

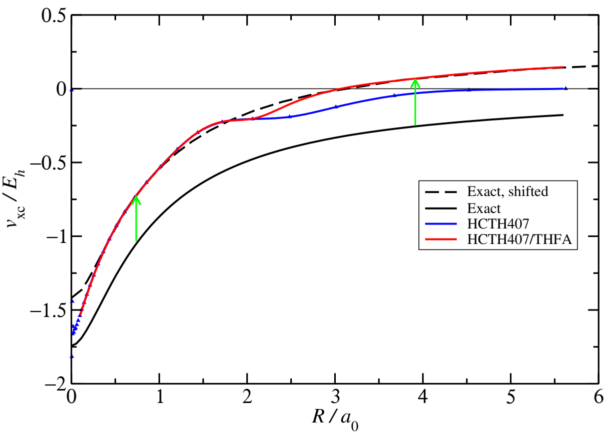

He: eXchange-Correlation potential
0.5
0
−0.5
−1
−1.5
−2
0
1
2
3
4
5
6
v_{xc} / E_h
R / a_0
Exact
HCTH407

SAPT(KS) III


He: eXchange-Correlation potential
0.5
0
−0.5
−1
−1.5
−2
0
1
2
3
4
5
6
v_{xc} / E_h
R / a_0
Exact, shifted
Exact
HCTH407

SAPT(KS) IV

He: eXchange-Correlation potential



SAPT(KS) V

Misquitta & Szalewicz (2001).

- This fixed $E^{(1)}_{\mathrm{elst}}$.
- And, *amazingly*, $E^{(2)}_{\mathrm{ind}}(A)$ and $E^{(2)}_{\mathrm{ind}}(B)$.
- Even the exchange energies came out correct.

However,
the dispersion was still wrong!.

By the way, standard DFT doesn't even get $E^{(1)}_{\mathrm{elst}}$ correct!

The Dispersion I

$$E^{(2)}_{\rm disp} = -\sum_{m\neq 0}\sum_{n\neq 0} \frac{|\langle 0_A 0_B|\mathcal{V}|m_A n_B\rangle|^2}{E^A_m + E^B_n - E^A_0 - E^B_0}.$$

Using the identity

$$\frac{1}{A+B} = \frac{2}{\pi}\int_0^\infty \frac{AB}{(A^2+u^2)(B^2+u^2)}\, du.$$

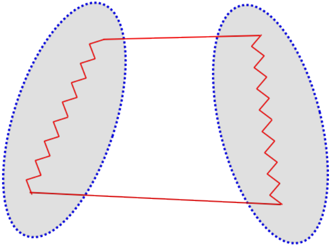
the dispersion can be written in terms of the density response functions

$$E^{(2)}_{\rm disp} = -\frac{1}{2\pi}\int_0^\infty {\rm d}u \int {\rm d}^3\mathbf{r}_1\, {\rm d}^3\mathbf{r}'_1\, {\rm d}^3\mathbf{r}_2\, {\rm d}^3\mathbf{r}'_2 \frac{\alpha_A(\mathbf{r}_1,\mathbf{r}'_1;{\rm i}u)\alpha_B(\mathbf{r}_2,\mathbf{r}'_2;{\rm i}u)}{|\mathbf{r}_1-\mathbf{r}_2||\mathbf{r}'_1-\mathbf{r}'_2|}.$$

H. C. Longuet-Higgins (1965).

The Dispersion II

$$E^{(2)}_{\rm disp} = -\frac{1}{2\pi}\int_0^\infty {\rm d}u \int {\rm d}^3\mathbf{r}_1\,{\rm d}^3\mathbf{r}'_1\,{\rm d}^3\mathbf{r}_2\,{\rm d}^3\mathbf{r}'_2\,\frac{\alpha_A(\mathbf{r}_1,\mathbf{r}'_1;{\rm i}u)\alpha_B(\mathbf{r}_2,\mathbf{r}'_2;{\rm i}u)}{|\mathbf{r}_1-\mathbf{r}_2||\mathbf{r}'_1-\mathbf{r}'_2|}.$$



- $\alpha(\mathbf{r},\mathbf{r}';{\rm i}u)$ describes the first-order change in the density at $\mathbf{r}$ due to a frequency-dependent poke (delta-function perturbation) at point $\mathbf{r}'$.
- The dispersion arises from correlations in density fluctuations.

The Dispersion III

So what went wrong with SAPT(KS)?

- We had calculated the density response function *without including orbital relaxation*.
- This over-estimated the density response, and therefore, the dispersion.

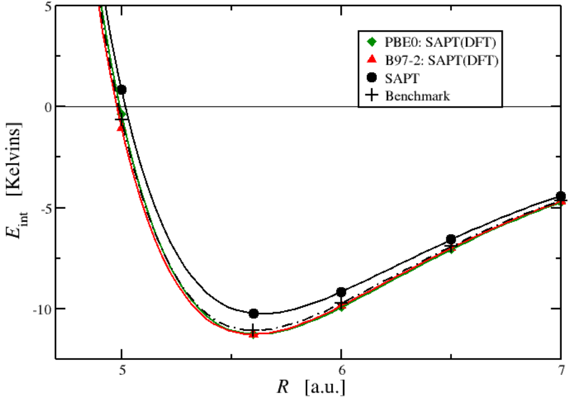
The proper way to calculate $\alpha(\mathbf{r}, \mathbf{r}'; \mathrm{i}u)$ is to use LR-TDDFT. Casida (1995), Gross (1996), Colwell, Handy & Lee (1995).

- Proven to be very accurate on small molecules.
- Use density-fitting to improve scaling of the dispersion which now becomes $\mathcal{O}(M^3)$.
- Also calculate the induction energy using this response function.

This theory is called SAPT(DFT) or DFT-SAPT (Jansen & Hesselmann).

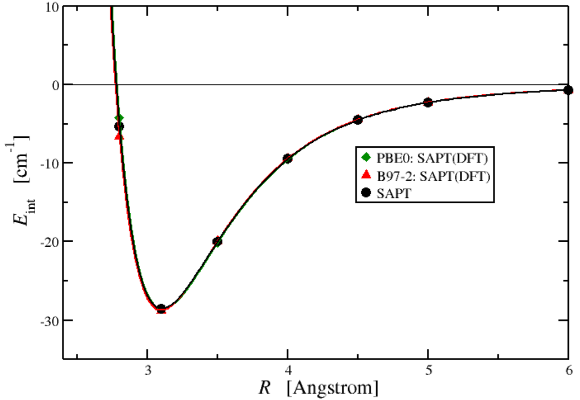
SAPT(DFT) I

Helium dimer



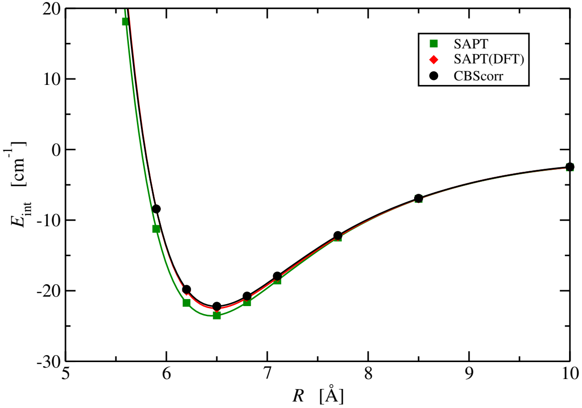
SAPT(DFT) II

Neon dimer



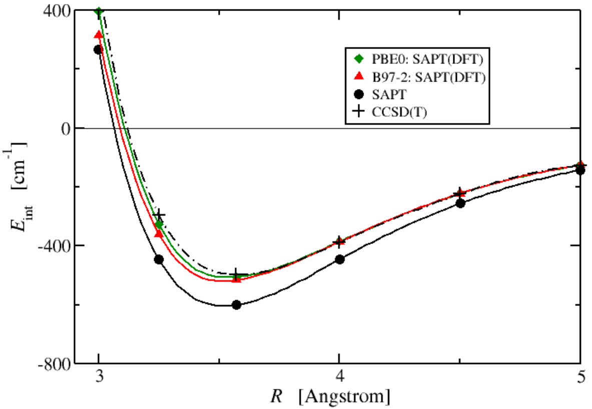
SAPT(DFT) III

He$\cdots$CO



SAPT(DFT) IV

CO_2 dimer

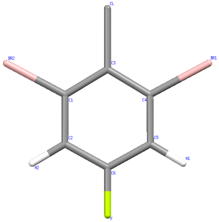


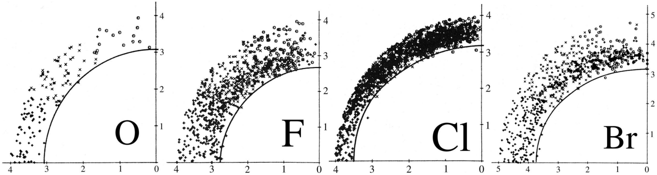
CamCASP

The Cambridge package for Calculation of Anisotropic Site Properties
or
CamCASP

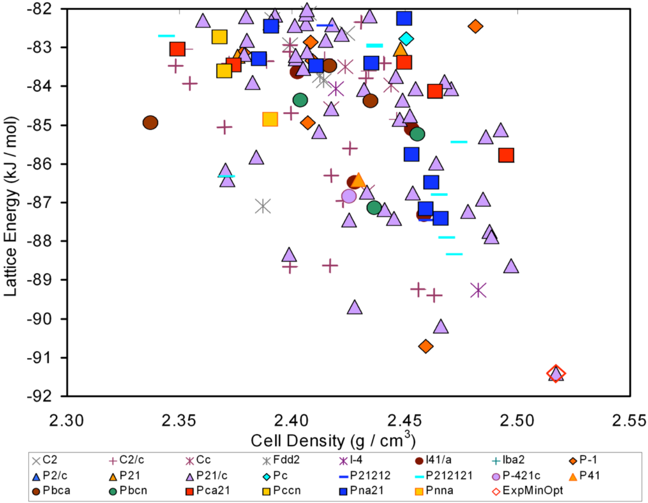
- Interaction energies
- Molecular properties: multipoles, polarizabilities, dispersion coefficients. *All distributed.*
- Tools to assemble it all into an analytic potential of arbitrary complexity.

CCDC Blind Test I

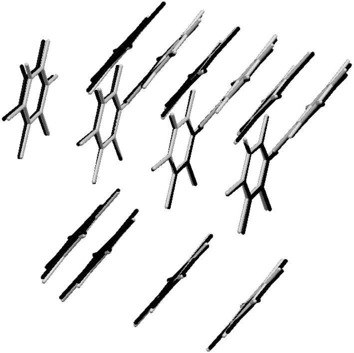




CCDC Blind Test II



CCDC Blind Test III



- First ever fully *ab initio* prediction of a crystal structure.
- About 200 stable minima (within $10\,\mathrm{kJ\,mol^{-1}}$ of the minima) on the *ab initio* surface, but *1200 on the empirical surface*.

CCDC Blind Test IV

What else have we been up to?

- How important is polarization in organic crystals? (UCL)
- Efficient routes to creating accurate polarizable force fields.
- Investigations in the fundamental theory of van der Waals interactions. (Cambridge,Chem & TCM?)
- Pyridine. (UCL)
- Formation of soot particles in combustion engines. (Cambridge,Chem & ChemEngg)
- Constant improvement of CamCASP.

The People behind this work

- SAPT(DFT)
    - Krysztof Szalewicz (U. Del)
    - Bogumil Jeziorski (Warsaw)
- Organic Crystals
    - Sally Price (UCL)
    - Gareth Welch (UCL)
- CamCASP & many developments too numerous to list
    - Anthony Stone