Long-range Correlation Energy from Isotropically Damped Coupled Quantum Harmonic Oscillators

A. Ambrosetti, R. A. DiStasio Jr., A. Tkatchenko

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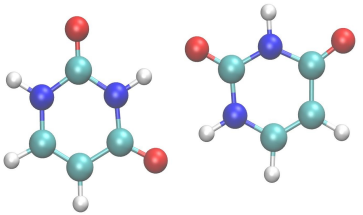
- BERLIN -

Ab Initio description of molecules and solids

Complex quantum mechanical Many-Body problem due to the e-e Coulomb interaction.



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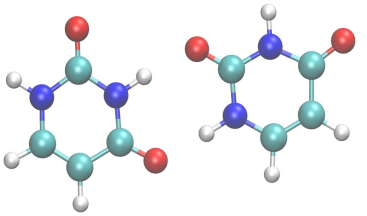
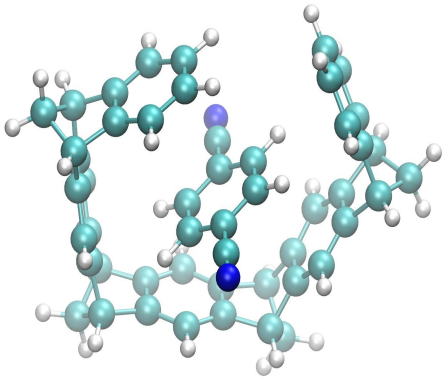


Possible (highly accurate) approaches:

- High level correlated **Quantum Chemistry** methods (CI,CCSD(T)) : N^5-N^7 scalings ~ few dozens of atoms



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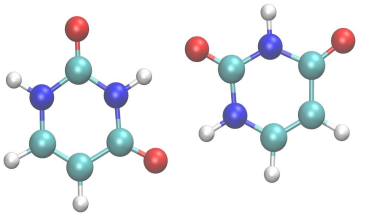

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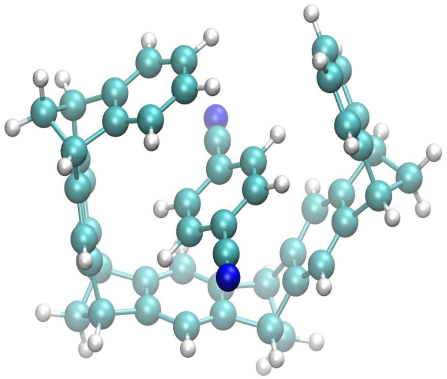

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Larger systems?

Molecular dynamics?

Fast computation of trial wave functions?

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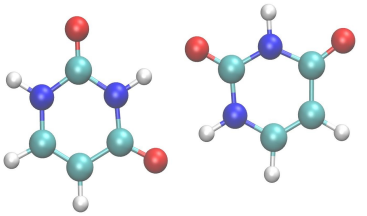

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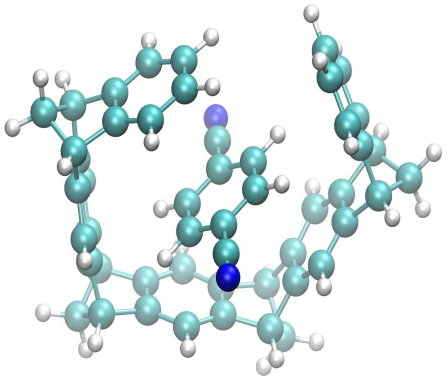

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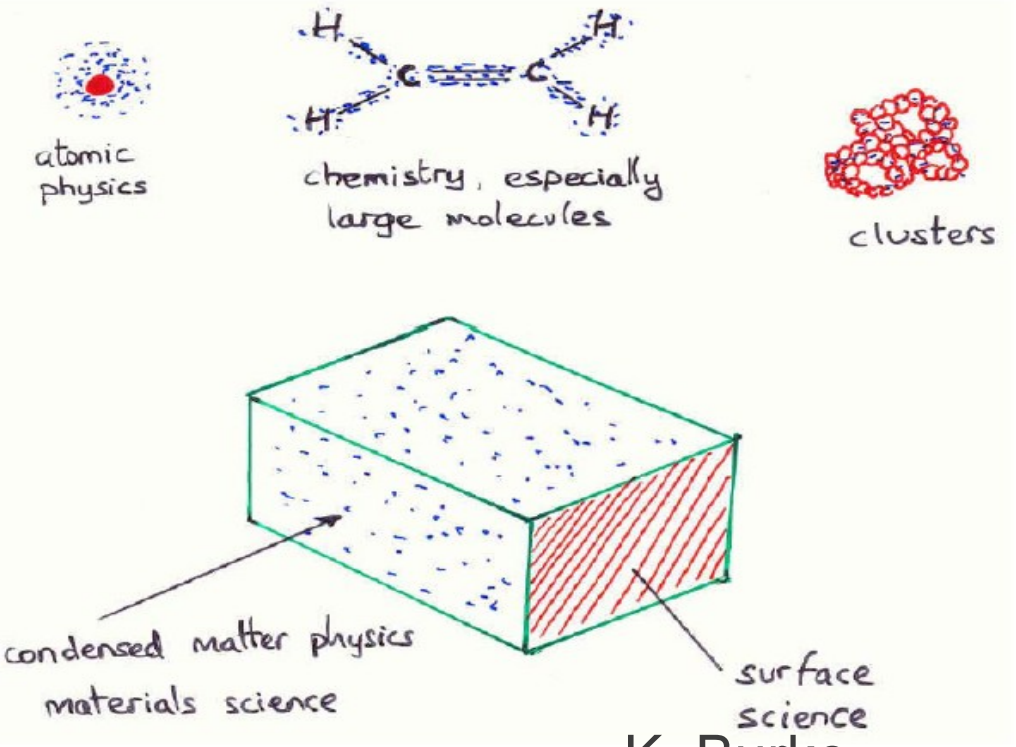
➡ **Efficient complementary method desirable**

Density Functional Approximations

- Favorable ratio of accuracy to computational cost
- Limitations of widely used xc functionals: **self-interaction** error and lack of **long-range electron correlation** effects



K. Burke
[JCP 136 150901 (2012)]

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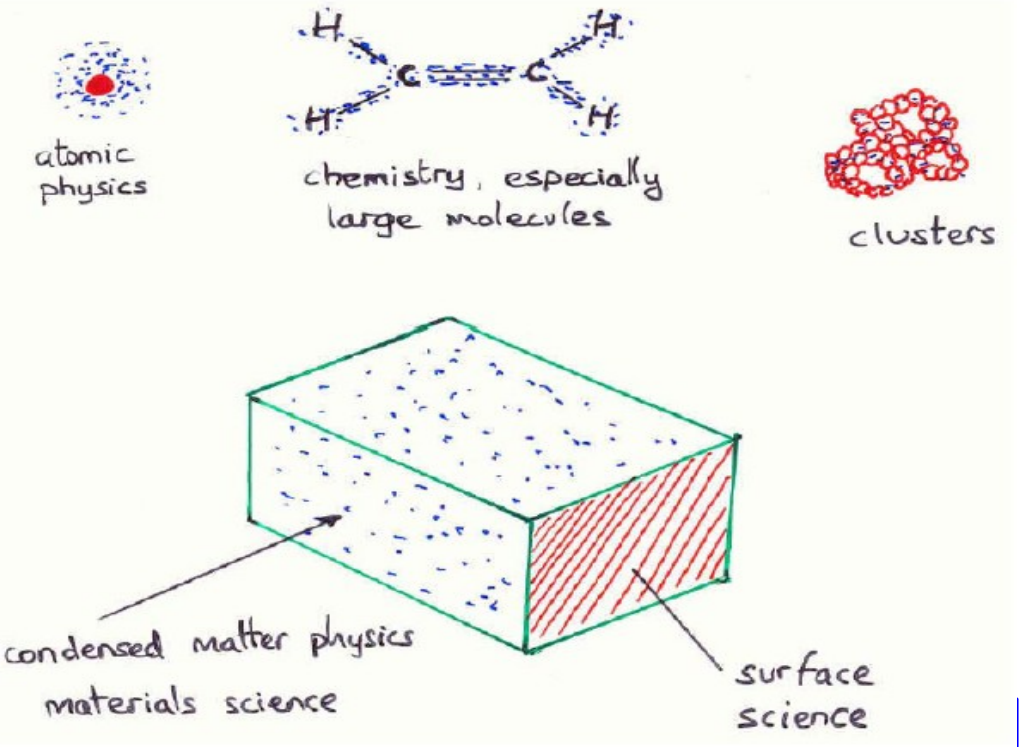
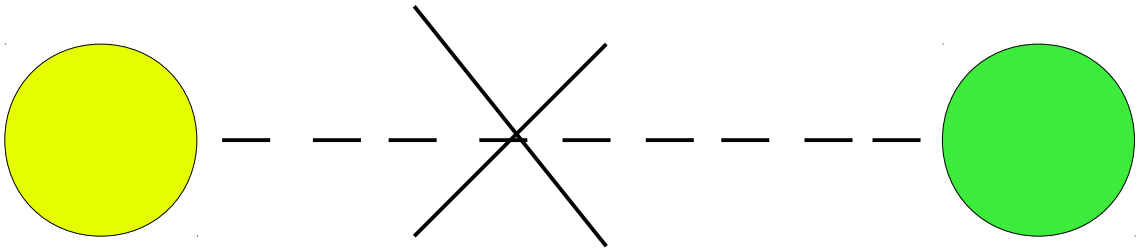


Semi-local and hybrid functionals lack long range correlation for non-overlapping fragments



No interaction in absence of charge overlap

Approaches to long range correlation

vdW energy methods:

$$\int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

- Non local correlation functionals:

  vdW-DF [PRL 92 246401 (2004)], VV10 [JCP 133 244103 (2010)]

- Effective core potentials

  v. Lilienfeld et al. [PRL 93 153004 (2004)],

- Pairwise approaches

$$E_{vdW} = -\frac{1}{2}\sum_{i,j} f_{damp}(R_{ij})\frac{C_6^{ij}}{R_{ij}^6}$$

  Grimme [JCP 132 154104 (2010)],

  Silvestrelli [PRL 100 053002 (2008)], Johnson [JCP 123 124101 (2005)], TS [PRL 102 073005 (2009)], ….

- MBD [Tkatchenko et al. PRL 108 236402 (2012)]

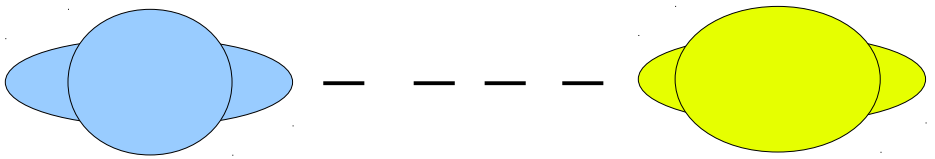
Long range correlation methods:

- Range separation using long-range correlation from QC [Savin et al. PRA 70 062505 (2004)]
- Range separated RPA, … [Toulouse et al. PRL 102 096404 (2012); de Gironcoli et al. PRB 79 205114 (2009); Paier et al. JCP 132 094103 (2010); Ren et al. PRL 106 153003 (2011); …]

vdW interaction

The vdW energy is a part of the correlation energy

$$E_c = -\frac{1}{2}\sum_i \sum_j \frac{C_6^{ij}}{R_{ij}^6} \qquad C_6^{ij} = \frac{3}{\pi}\int_0^\infty d\omega \alpha_i(i\omega)\alpha_j(i\omega)$$



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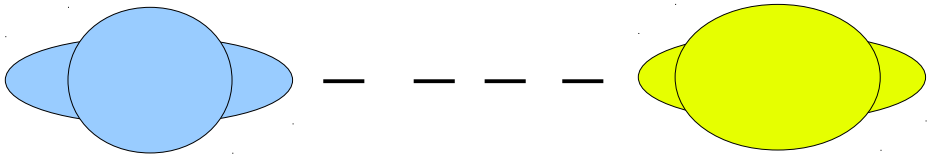

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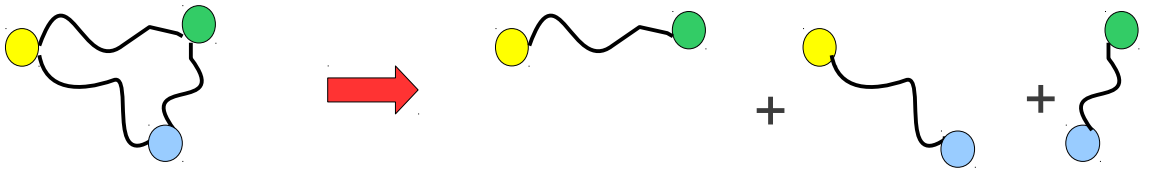
Intrinsic limitations:

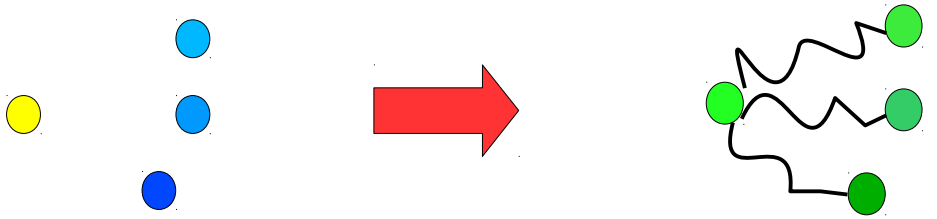
- Additive expression



- Sum of pure 2 body terms - absence of Many Body effects

Long range Many Body effects

The mutual interaction induces a “self consistent” modification of the polarizabilities.



Consequences:

- **Higher than pairwise** energy contributions (3,4,..,N-body terms) [Axilrod-Teller, JCP 11 299 (1943) ; Bade JCP 27 1280 (1957)]
- **Screening effects:** modification of interaction due to the medium

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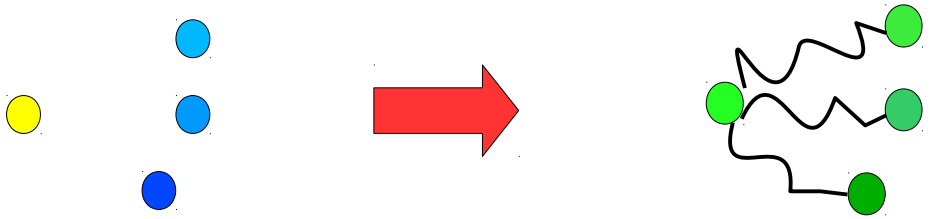

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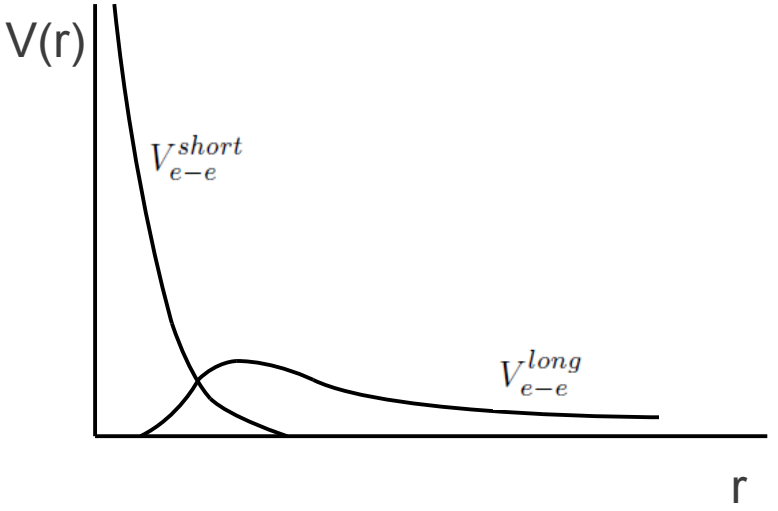
MB effects are obtained from high order perturbation theory

➡ **need to go beyond a 2nd order pairwise approach**

Long-range correlation energy in DFT from range-separated Coulomb potential

Separation of the e-e interaction into long and short range parts [Savin et al. PRA 70, 062505 (2004); Paier et al. JCP 132 094103 (2010)]:

$$V_{e-e} = V_{e-e}^{short} + V_{e-e}^{long}$$



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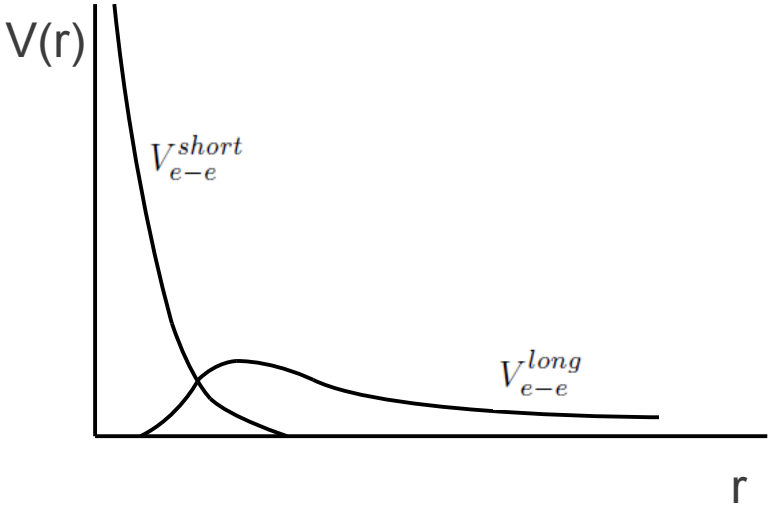

$$E = E_{kin} + E_{el.stat.} + E_x + E_c$$

$$E_c \sim E_c^{short} + E_c^{long}$$ ← Contains VdW!

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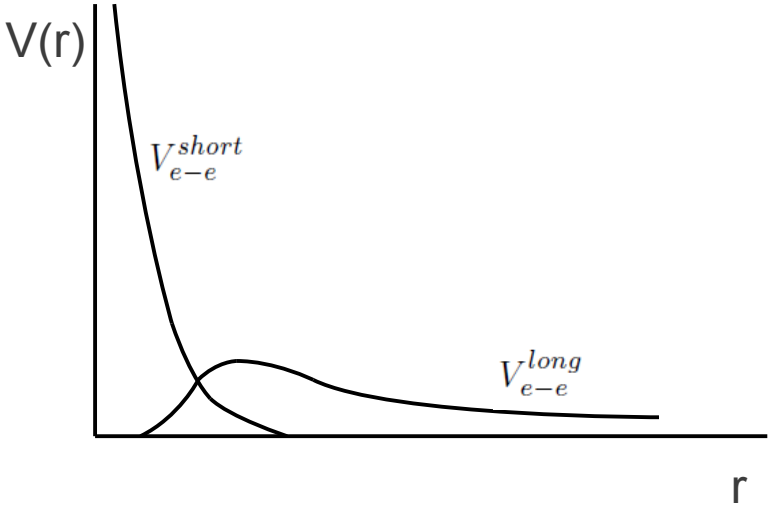

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$$E_{PBE} \sim E_{kin} + E_{el.stat.} + E_x + E_c^{short} \Rightarrow E \sim E_{PBE} + E_c^{long}$$

Need accurate and efficient approximation for E_c^{long}

How to compute the MB long range correlation energy?

Adiabatic Connection Fluctuation-Dissipation formula (formally exact)

$$E_c = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 d\lambda \mathrm{Tr}[\chi_\lambda v - \chi_0 v]$$

Long range interaction

dressed

bare

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Problems:

- The dressed response function is unknown → approximation needed
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Approach:

- Only retain the **key ingredients**:

1) Interaction v

2) Response function χ_0

- Take **appropriate approximations for the long range**

Approximations for the long range

1) Interaction

Dipole-dipole approximation to **long range Coulomb** (at large distances higher multipoles decay faster)

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2) Response function

In dipole approx. only the **polarizability** is needed
→ we model it with **one QHO per atom**
(finite gap systems)

Static polarizability

$$\alpha(\mathrm{i}\omega) = \frac{\alpha_0}{1 + (\omega/\omega_0)^2}$$

QHO frequency

MODEL HAMILTONIAN

Long range correlation made simple using coupled QHOs

Effective hamiltonian for the computation of E_c^{long}

dipole interaction tensor

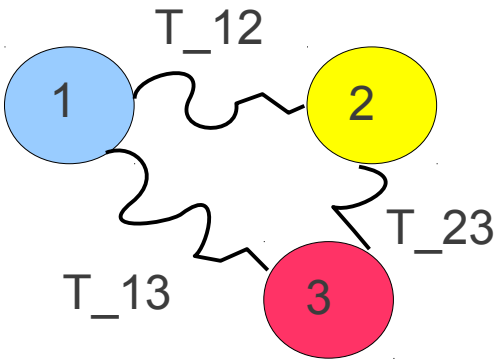
$$H_{cQHO} = -\sum_{p}^{N} \frac{\nabla_{\xi_p}^2}{2} + \sum_{p}^{N} \frac{\omega_p^2 \xi_p^2}{2} + \sum_{p>q}^{N} \omega_p \omega_q \sqrt{\alpha_p \alpha_q} \xi_p T_{p,q} \xi_q$$

Coupled QHOs in dipole approximation centered on atoms

TS input polarizabilities

$$\alpha = \alpha\left(n(\mathbf{r})\right)$$

$$\omega = \omega\left(n(\mathbf{r})\right)$$



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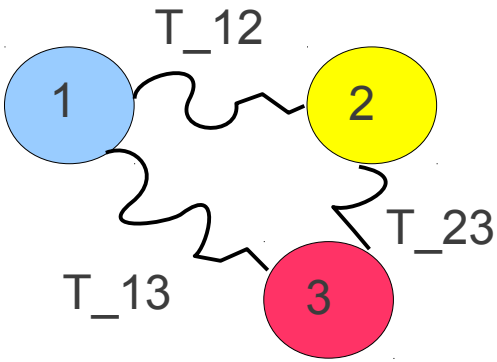

Quadratic hamiltonian → exactly solvable

Interaction energy:

$$E_{c,\mathrm{QHO}} = \frac{1}{2} \sum_p^N \left(\sqrt{\bar{\omega}_p^2} - \omega_p \right)$$

Coupled

Uncoupled

Which MB effects do we include through CFDM?

cQHO is a MB hamiltonian (due to interaction)**, and can be solved exactly and efficiently** (single 3Nx3N matrix diagonalization)

But:

- Could we recover higher than pairwise contributions such as Axilrod-Teller-Muto from CFDM?
- Does CFDM provide screening?

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What we proved : RPA is exact for the cQHO model

[Tkatchenko,Ambrosetti,di Stasio JCP 138, 074106 (2013)]

→ **cQHO** naturally includes all RPA higher than pairwise and screening contributions

Effective RPA long range correlation with single matrix diagonalization

RPA correlation energy for cQHO

The RPA correlation energy is obtained using in the ACFD formula the RPA dressed response function (summation of ring diagrams)

$$E_c^{RPA} = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 d\lambda Tr\left[\chi_\lambda^{RPA} v - \chi_0 v\right]$$

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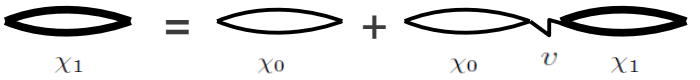

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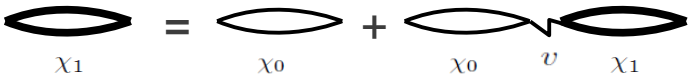

RPA naturally contains:

- vdW (second order)
- Axilrod-Teller-Muto (third order)
- Higher MB effects and long range screening

Good candidate for the MB correlation

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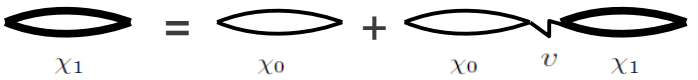

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After space integration (localized charge fragments) it is possible to substitute $\chi_0 v$ with $A_0 T$

T : dipole-dipole interaction tensor

A_0 : diagonal matrix of the free QHO polarizabilities

Efficient discrete matrix formulation

Exactness of RPA in the cQHO model

$$E^{c}_{\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty d\omega \mathrm{Tr}[ln(1-\chi_0 v) + \chi_0 v]$$

No “self interaction”

$$\chi_0 v \longrightarrow A_0 T$$

$$\chi_\lambda^{RPA} = \frac{\chi_0}{1-\chi_0 v}$$

$$E^{cQHO}_{\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty d\omega \mathrm{Tr}[ln(A_0) - ln(A_1^{\mathrm{RPA}})]$$

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Constant factors cancel out

$$E^{cQHO}_{\mathrm{RPA}} = \frac{1}{2\pi}\sum_{p=1}^{N}\int_0^\infty d\omega \ \ln\left(\frac{\bar{\omega}_p^2+\omega^2}{\omega_p^2+\omega^2}\right)$$

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$\bar{\omega}_p$: **dressed** QHO frequencies. Contribute with $|\bar{\omega}_i|/2$ — Coupled QHO energy

ω_p : **free** QHO frequencies. Contribute with $-\omega_i/2$ — Free QHO energy

Within the cQHO model the RPA correlation energy exactly corresponds to the total binding energy

$$E_{c,cQHO}^{RPA} = E_{cQHO}^{bind-exact}$$

Coupling to short-range DFT correlation

V_{e-e}^{long} should be computed from the DFT electron density (ongoing)

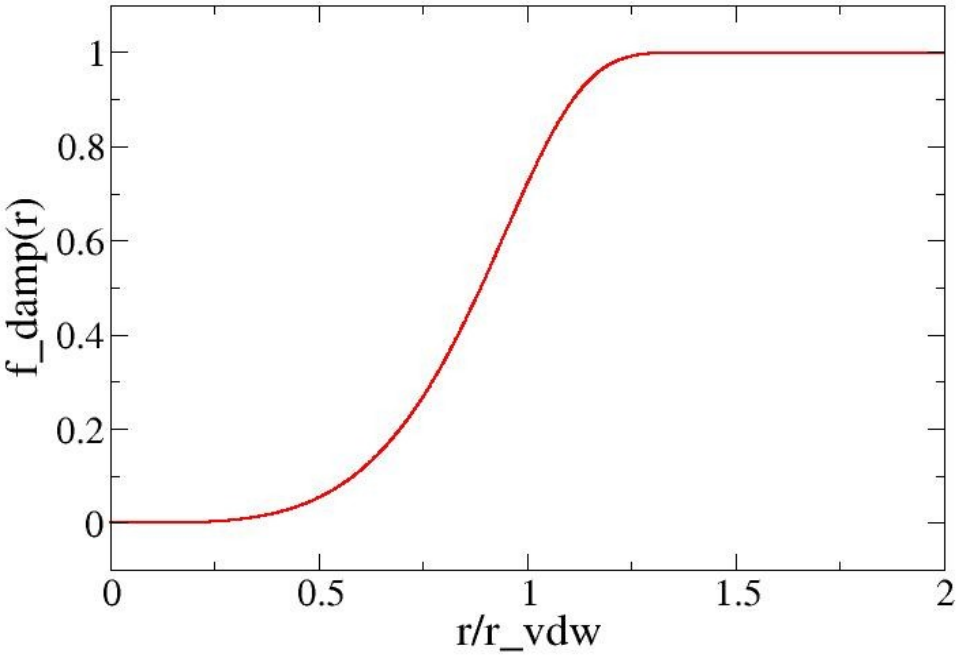
Simplification:

Use an isotropic damping function

$$T_{ij}^{ab} = f_{damp}(r_{ij}) \frac{-3r_{ij}^a r_{ij}^b + r_{ij}^2 \delta_{ab}}{r_{ij}^5}$$

$$f_{damp}(r) = erf\left((r/(\beta r_{vdW}))^4\right)$$

- Single parameter β obtained fitted over s66x7
- Weak variation of β from PBE to PBE0 (1.07 to 1.08)
- Possibility of using other functional forms for the damping - analogous performance



$$E \sim E_{PBE} + E_{cQHO}^{bind-long}$$

Polarizability screening - MBD

- In cQHO same screening for polarizability and energy
- Need to cut the energy “steeply” in order to avoid double countings of the DFT energy.
- Better screened polarizabilities are obtained from smoother range separation.

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- Need to cut the energy "steeply" in order to avoid double countings of the DFT energy.
- Better screened polarizabilities are obtained from smoother range separation.

➡ Good candidate: potential due to **gaussian-gaussian** charge distribution:

$$T_{ij}^{lm} = \partial_{\mathbf{r}_i^l} \partial_{\mathbf{r}_j^m} v_{gg}(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$v_{gg}(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{erf\left(|\mathbf{r}_i - \mathbf{r}_j|/\sigma_{ij}\right)}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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MBD method (Tkatchenko et al. PRL 2012):

1) Classical electrodynamic "SCS" screening of TS polarizabilities

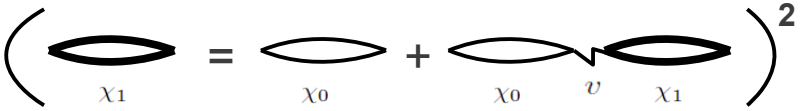
$$\alpha^{self-cons}(\mathbf{r}, i\omega) = \alpha^{free}(\mathbf{r}, i\omega) + \alpha^{free}(\mathbf{r}, i\omega) \int d\mathbf{r}' T(\mathbf{r} - \mathbf{r}') \alpha^{self-cons}(\mathbf{r}', i\omega)$$

2) Plug screened parameters in the cQHO hamiltonian to get the energy

MBD – double screening

- MBD often improves wrt cQHO, **BUT** problems in highly anisotropic systems
- **Double screening**:

  Both SCS and cQHO introduce RPA screening → double counting



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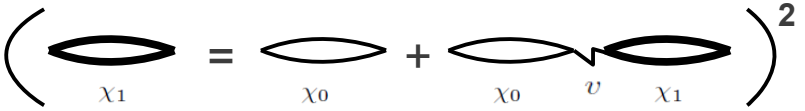

Solution:

- Start from gaussian-gaussian potential $T_{ij}^{gauss,ab}$
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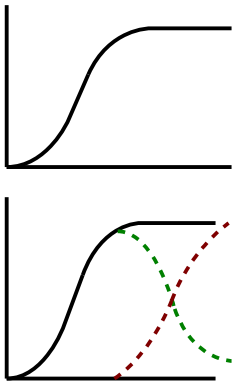

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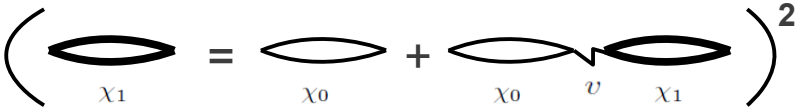

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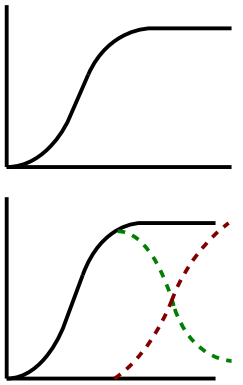

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dRFA method:

1) "Short range" SCS from TS polarizabilities
2) Plug screened parameters in "long range" cQHO and compute the energy

- Soft polarizability screening
- Avoids double counting
- RPA at long range

Benchmarking

- S66 database [Hobza et al. JCTC 7, 2427 (2011)] : **66 dimers** CCSD(T) reference energies - estimated accuracy ~ 2-3% (~ 0.2 Kcal/Mol)

	MARE	MAE (Kcal/mol)
PBE0+TS	9.7 %	0.40
PBE0+cQHO	8.2 %	0.38
PBE0+MBD	7.0 %	0.32
PBE0+dRFA	8.1 %	0.40
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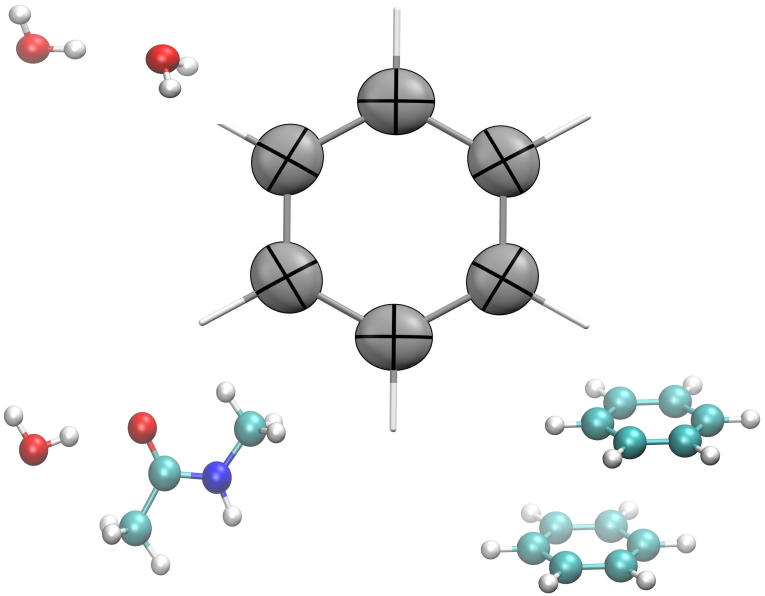

[Vydrov, van Voorhis JTCT 8 1929 (2012); Grimme et al. ChemPhysChem 2011, 12, 3421]

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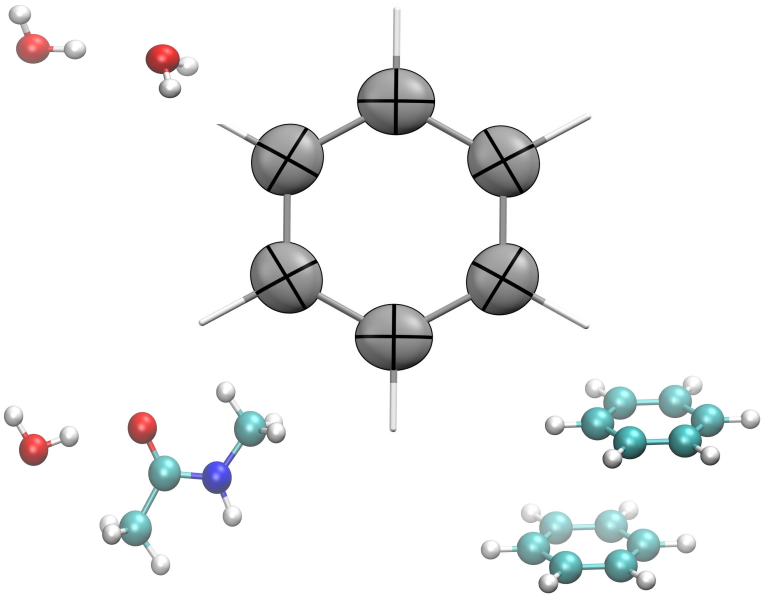

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- **Graphite** (unbound with PBE0+MBD – meV/C atom)

PBE0+TS	PBE0+cQHO	PBE0+dRFA	vdW-DF2	DFT-D3+$E^{(3)}$ PBE
87	60	53	48	35
Exp	52±5			
QMC	56±5			

[Graziano et al. J. Phys. Cond. Mat. 24 424216 (2012) ; Grimme et al. JCP 132 154104 (2010) ; Zacharia et al. PRB 69 155406 (2004) ; Sorella et al. PRL 103 196401 (2009)]

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- Bosonic problem (QHOs distinguishable and singly occupied)
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First tests suggest a slight binding increase (order ~10%) at mid range (4-6 A) ← very preliminar & qualitative

Still in Progress:

- Parametrization of QHO for higher response
- Coulomb range separation
- Study of overlap effects

Conclusions

- **Range-separated** DFT + long-range correlation is a promising electronic structure method, beyond (semi)local approximations

- **Long-range correlation** can be **reliably** and **efficiently** computed by mapping KS electronic system to coupled QHOs

- **Accurate** results are obtained with **PBE(0)+dRFA** for a wide range of small and large molecules, as well as molecular crystals

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Outlook

- Analytical derivation of interatomic forces
- Inclusion of **higher multipoles** through **DMC**
- Ongoing investigations on **metallic systems**