Two different approaches to include van der Waals interactions within ABINIT

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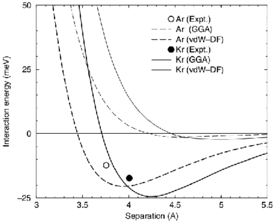
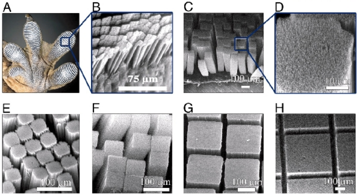
5^{th} ABINIT developers workshop, Han Sur Lesse, 2011

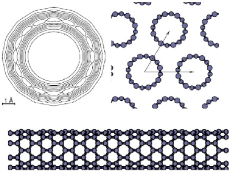
Outline

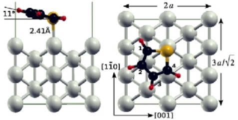
Relevance of vdW interactions

- Gas law.
- surface tension.
- Hydrocarbon sublimation heats.
- Organic molecules adsorption(OLEDs, OFETs)
- Crystal packing of Org. Mol.
- Protein folding.
- CNT interactions.







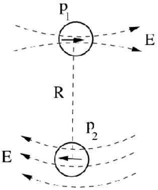


van der Waals Interactions

All molecular interactions other than those due to: *Covalent bonds*, *Ionic attractions* and *Permanent dipoles*:

- Permanent dipole - Induced dipole.
- Instantaneous induced dipole - dipole. Charge distributions on the atoms are not rigid $\rightarrow$ *London dispersion forces*.

London Dispersion Formula (Classical model):



Electric field at R $\quad E = 2p_1/R^3$

Placing another atom at R $\quad p_2 = \alpha E$

$$p_2 = 2\alpha p_1/R^3$$

Potential energy: $\quad U \sim -\frac{2p_1 p_2}{R^3} = -\frac{4\alpha p_1^2}{R^6}$

From Quantum Mechanics

It is needed as molecules or atoms without permanent dipoles are considered! From a series expansion of the potential energy and perturbation theory, London showed that the second[1] term (associated with dipolar transitions):

$$E_{1,2} = \frac{3e^4\hbar^4}{2R_{1,2}^6 m^2} \times \sum_{k,l} \frac{f_{o,l}^1 f_{o,k}^2}{\Delta E_{0,l}\Delta E_{o,k}[\Delta E_{0,l} + \Delta E_{o,k}]}$$

which can be expressed in terms of atomic polarizabilities and ionization energies

$$E_{1,2}^{London} = -\frac{3h}{2R^6}\frac{\nu_1\nu_2}{\nu_1+\nu_2}\alpha_1\alpha_2 = -\frac{3}{2R^6}\frac{I_1 I_2}{I_1+I_2}\alpha_1\alpha_2$$

$$E_{1,2}^{London} = -\frac{C_6^{i,j}}{R^6}$$

[1] The first is null if there is not permanent dipoles

Proposed schemes to treat vdW in DFT

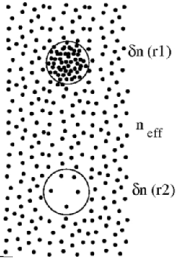
London dipersion interactions are naturally out of range for commonly used LDA and GGA xc functionals. Attempts to solve this shortcoming:

- *Ad hoc* methods:
  1. Fitting of C_6 coefficients: DFT-D (Grimme).
  2. Obtaining C_6 from the interaction between localized electronic densities of the fragments: Sato (constituent atoms), Silvestrelli (MLWF), Tkatchenko-Sheffler (atomic densities).
- First principles methods.
  1. LC-DFT (Long range correction).
  2. Seamless van der Waals Density Functional.
  3. Meta-GGAs
  4. ACFDT (Adiabatic connection Fluctuation Disipation Theorem)
- Midway methods.
  Take partially into account the electronic nature of the vdW interactions.
  1. DFT+LAP (Local Atomic Potentials.)
  2. DCAC (Dispersion Corrected Atom Centered.)

First principles methods

1) LC Scheme (Long range Correction) *Phys.Rev.Lett.***76**:102 (1996)
xc energy associated with two distant charge disturbances of an uniform electron gas:

$$E_{\rm xc} = \int d^3 r_1 \int d^3 r_2 K_{\rm xc}(\mathbf{r}_1, \mathbf{r}_2)\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)$$



With:

$$n_{eff} = \left[\sqrt{n(\mathbf{r}_1)n(\mathbf{r}_2)}(\sqrt{n(\mathbf{r}_1)} + \sqrt{n(\mathbf{r}_2)})\right]^{2/3}$$

and taking the long range limit:

$$E_{\rm xc}^{l-r} = -\frac{3e^4\hbar^4}{2m^2} \frac{1}{\omega_p(\mathbf{r}_1)\omega_p(\mathbf{r}_2)[\omega_p(\mathbf{r}_1) + \omega_p(\mathbf{r}_2)]|\mathbf{r}_1 - \mathbf{r}_2|^6}$$

where $\omega_p(r) = \sqrt{4\pi e^2 n(r)/m}$ (plasma freq.) Like if *e* in each atom respond as a uniform eg.

First principles methods

Finally, in terms of charge densities:

$$E_{\mathrm{xc}}^{\mathrm{l-r}} = \frac{6e}{4(4\pi)^{3/2}m^{1/2}} \int_{V_1} \mathrm{d}^3 r_1 \times \int_{V_2} \mathrm{d}^3 r_2 \frac{\sqrt{n_1(\mathbf{r}_1) n_2(\mathbf{r}_2)}}{\sqrt{n_1(\mathbf{r}_1)} + \sqrt{n_2(\mathbf{r}_2)}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6}$$

In the case of two distant atoms, $|\mathbf{r}_1 - \mathbf{r}_2|^{-6}$ can be left outside the integral. The latter implies that the xc energy of the the system takes the shape:

$$-\frac{C_6}{R^6}$$

providing a way to evaluate dispersion coefficients from electronic density only!.

	He	Ne	Ar	Kr	Xe	H_2
He	4 (3)	7 (6)	22 (20)	31 (27)	44 (37)	10 (8)
Ne		12 (12)	37 (41)	50 (57)	71 (76)	17 (16)
Ar			126 (134)	175 (187)	253 (258)	60 (54)
Kr				245 (266)	356 (368)	84 (76)
Xe					520 (522)	123 (114)
H	6 (6)	10 (11)	37 (40)	52 (57)	76 (82)	18 (17)
Li	46 (82)	67 (88)	292 (350)	434 (518)	669 (808)	154 (159)
Na	51 (48)	74 (95)	325 (378)	486 (562)	750 (876)	
K	92 (76)	136 (150)	580 (584)	862 (866)	1327 (1338)	

Anderson, Langreth and Lundqvist
Phys.Rev.Lett. ***76***:102 (1996)

First principles methods

2) Seamless vdW Density Functional.

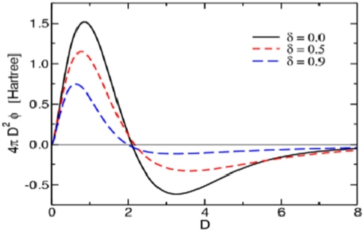
$$E_{\mathrm{xc}}[n] = E_{\mathrm{x}}^{revPBE}[n] + E_{\mathrm{c}}^{\mathrm{LDA}}[n] + E_{\mathrm{c}}^{\mathrm{nl}}[n]$$

where:

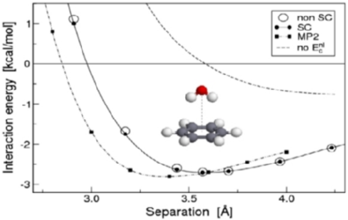
$$E_{\mathrm{c}}^{\mathrm{nl}}[n] = \frac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, n(r)\phi(r,r')n(r')$$

$\phi(r,r') = \phi(q(r),q(r'))$ and $q(r) = q(n(r), \nabla n(r))$:

$$D = \frac{q+q'}{2}|r-r'| \quad \delta = \frac{q-q'}{2(q+q')}$$



J. Phys.: Condens. Matter **21** (2009) 084203



vdw-DF

Long range correlation derived from:

1. Adiabatic connection formula.
2. Approximate coupling-constant integration —¿ exact for the long range limit.
3. Use of an approximated dielectric function (single pole form).
4. Pole position scaled to give exact electron gas ground state energy locally.

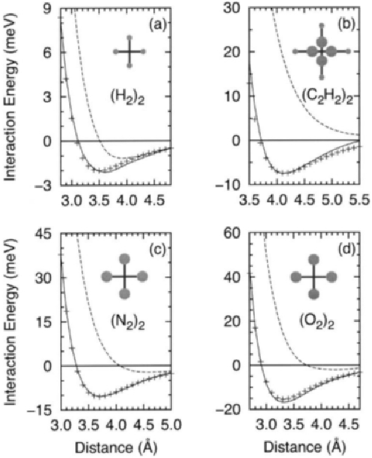
Midway methods

LAP and DCAC:
In both schemes the vdW interaction is represented either by a local or by a non local parameterized contributions added to atomic pseudopotentials. The parameters are determined by comparison with high level calculations on simple vdW systems.

$$v(r) = \begin{cases} -C_0/r^n & \text{if } r > r_{cut} \\ -v_{const} & \text{if} \leq r_{cut} \end{cases}$$

Comparison to 165 complexes (vdW and H-bonded):
Mean abs dev of 0.5Kcal/mol Great transferability!

J. Chem. Phys. **129**, 154102 (2008)



Ad hoc methods

vdW: electron-electron → atom-atom interactions mediated by pair contributions of the form:

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

Damping function (to avoid both singularity and *c* double counting for short distances:

$$f_{i,j}(R_{i,j}) = \frac{1}{1+\exp(-a(R_{i,j}/R_s - 1))}$$

where $R_s = R_i^{vdW} + R_j^{vdW}$

Ad hoc methods

C_6 coefficients can be obtained from:

- Fitting to benchmark calculations or experimental data when available. (*J.Comp.Chem.***25**:1463)
  The drawback here lies in its lack of transferability $\rightarrow$ Dependence of coeffiecients to the bonding enviroment of atoms.
- Calculated in somehow.

C_6 from Maximally Localized Wannier Functions

MLWF are obtained from a unitary transformation over the occupied K-S orbitals, to minimize:

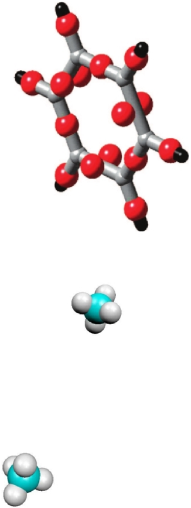
$$\Omega = \sum_n \left(\langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2 \right)$$

Silvestrelli proposed to decompose the electronic density in terms of maximally localized Wannier functions (MLWF).

$$w_n(|\mathbf{r} - \mathbf{r}_n|) = \frac{3^{3/4}}{\sqrt{\pi} S_n^{3/2}} e^{-(\sqrt{3}/S_n)|\mathbf{r}-\mathbf{r}_n|}$$

Substituting $n(r) = w^2(r)$ in the LC expression:

J. Phys. Chem. A, Vol. 113, No. 17, 2009



C_6 from Wannier Functions

Dispersion coefficient:

$$C_6^{\mathrm{nl}} = \frac{3}{32\pi^{3/2}} \int_{|r|\leq \mathbf{r_c}} \mathrm{d}\mathbf{r} \int_{|r'|\leq \mathbf{r'_c}} \mathrm{d}\mathbf{r}' \frac{w_n(\mathbf{r}) w_l(\mathbf{r}')}{w_n(\mathbf{r}) + w_l(\mathbf{r}')}$$

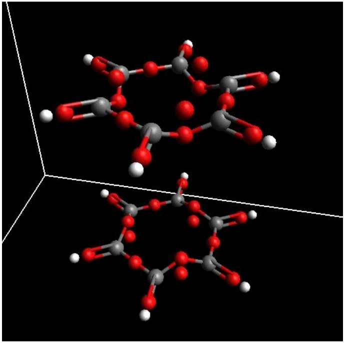
The cutoff radius and are calculated equating the length scale for density change to the electron gas screening length:

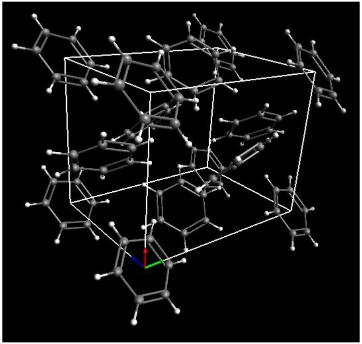
$$r_c = S_n \sqrt{3}[0.769 + 1/2 \ln S_n].$$

The vdW correction is then:

$$E_{vdW} = -\sum_{n,l} \frac{f_{n,l}(r_{n,l}) C_6^{n,l}}{r_{n,l}^6}$$

MLWFs method to vdW. What is needed?





- Definition of interacting fragments in terms of atoms rather than MLWFs.

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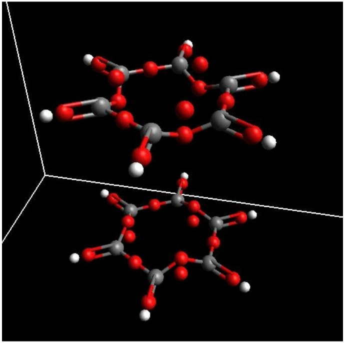

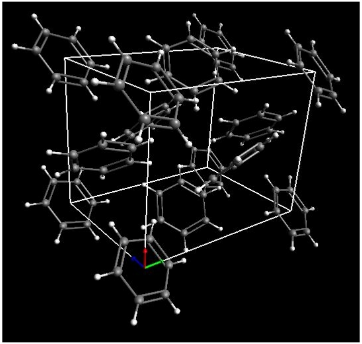

- Definition of interacting fragments in terms of atoms rather than MLWFs.
- Molecular and crystalline systems in the same ground.

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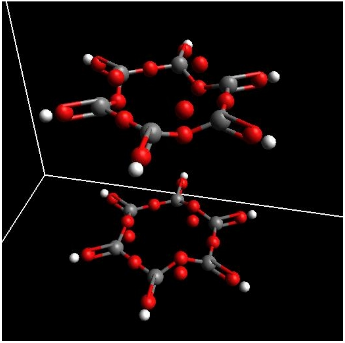

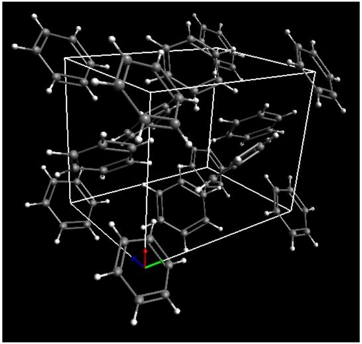

- Definition of interacting fragments in terms of atoms rather than MLWFs.
- Molecular and crystalline systems in the same ground.
- Handling of vdW interactions anisotropy (layered systems).

vdW-MLWFs into ABINIT. New imput variables.

1. **vdw_xc**: Selects the type of vdW scheme to be used. MLWFs approach is chosen with `vdw_xc`=10. Default value 0, no vdW correction.

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1. **vdw_xc**: Selects the type of vdW scheme to be used. MLWFs approach is chosen with `vdw_xc`=10. Default value 0, no vdW correction.
2. **vdw_nfrag**: Its absolute value is the number of interacting vdW fragments in the unit cell. If `vdw_nfrag` $\geq$ 1 then MLWFs are translated to the original unit cell, otherwise the program will keep the positions obtained by **Wannier90**. Default is zero.

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3. **vdw_typfrag**: Integer array of `natom` components. Associate each atom with one of the `vdw_nfrag` vdW interacting fragments. No default.

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3. **vdw_typfrag**: Integer array of natom components. Associate each atom with one of the vdw_nfrag vdW interacting fragments. No default.
4. **vdw_supercell**: Three component integer array. Determine the number of neighbor cells along positive and negative directions of each primitive vector for which vdW interactions will be taken into account. Default value $(0, 0, 0)$.

Some results and testing:Ar_2

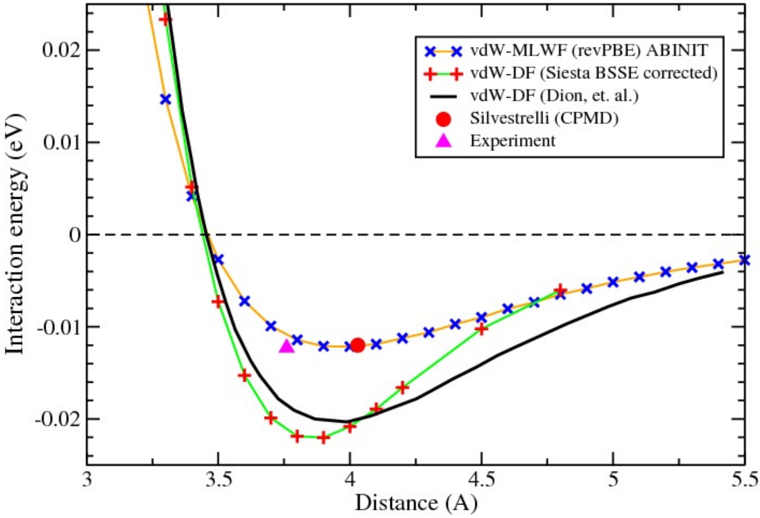

Figure: vdW-DF (taken from Phys.Rev.Lett. **92**:246401), Silvestrelli's Phys.Rev.Lett. **100**:053002

Some results and testing:

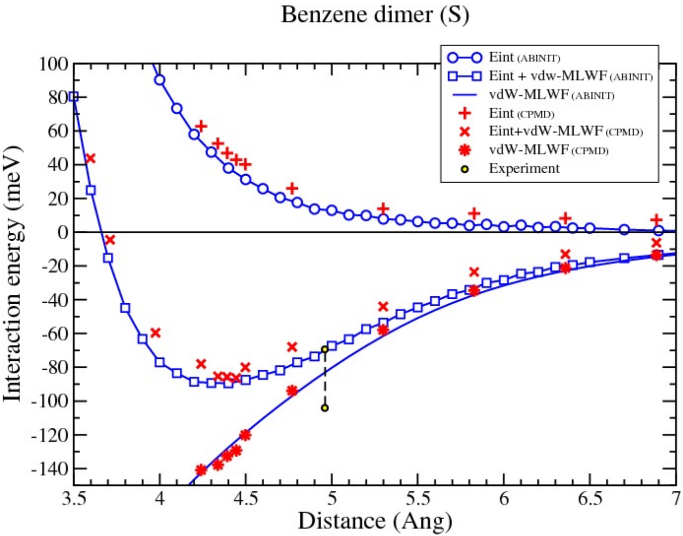

Figure: Comparison between ABINIT implementation to Silvestrelli results and experiment.

Solid Argon (FCC)

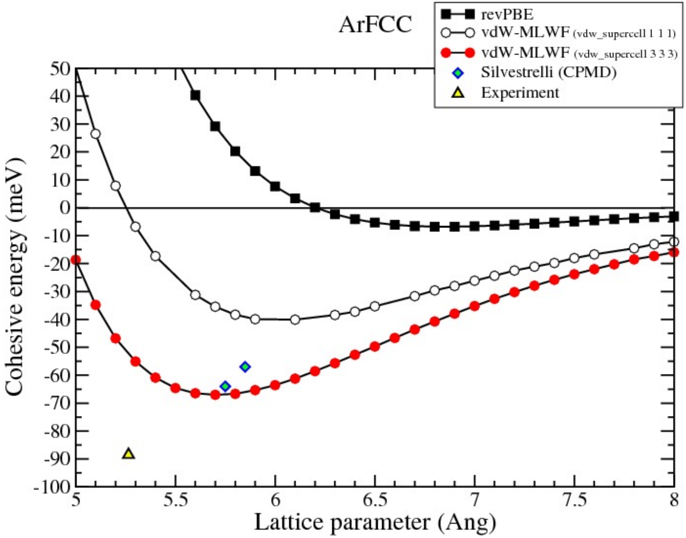

Figure: Cohesive energy of Ar FCC, convergence of vdW correction.

Benzene crystal

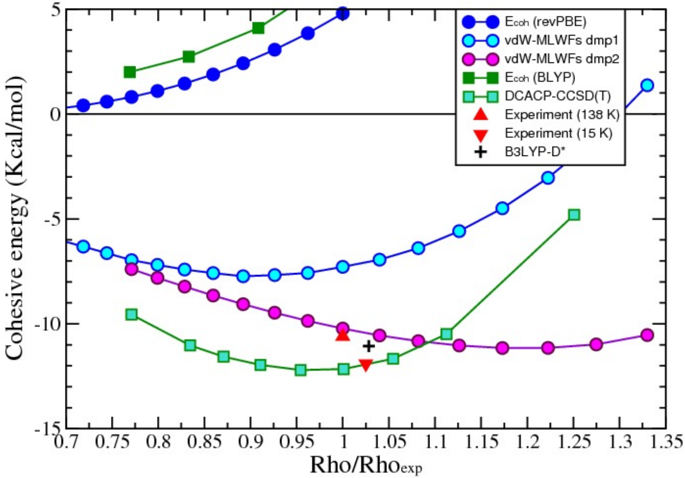

Figure: DFT-D (Crys.Eng.Comm.**10**:405.), DCACP (J.Chem.Theo.Comp. **3**:1673) and experiment (J.Phys.Chem.Ref.Data **31**:537).

First principles methods

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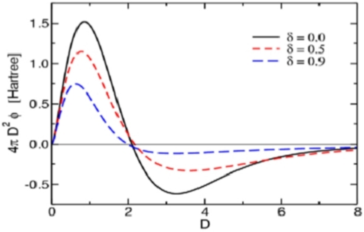

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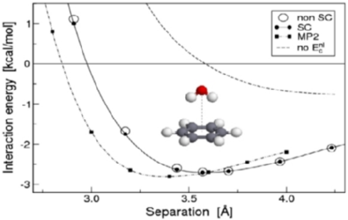

New Developments in vdW-DF

- Numerical Efficiency: Guillermo Román-Pérez and José Soler. Efficient implementation of a van der Waals Density Functional: Application to Double-Wall Carbon Nanotubes. *Phys. Rev. Lett.* ***103****: 096102* (2009). Currently being implemented into ABINIT.

$$E_{\mathrm{xc}}[n] = E_{\mathrm{x}}^{revPBE}[n] + E_{\mathrm{c}}^{\mathrm{LDA}}[n] + E_{\mathrm{c}}^{\mathrm{nl}}[n]$$

where

$$E_{\mathrm{c}}^{\mathrm{nl}}[n] = \frac{1}{2}\int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 n(r_1)\phi(r_1, r_2, r_{12})n(r_2)$$

the proposal is:

$$\phi(q_1, q_2, r_{12}) \simeq \sum_{\alpha\beta} \phi(q_\alpha, q_\beta, r_{12}) p_\alpha(q_1) p_\beta(q_2)$$

which allows to factorize the kernel and obtain a sum of convolution like integrals.

New Developments in vdW-DF

- Accuracy: Kyuho Lee, Éamonn D. Murray, Lingzhu Kong, Bengt I. Lundqvist and David. C. Langreth. A Higher-Accuracy van der Waals Density Functional. *arXiv:1003.5255v1* (2010). Also known as vdW-DF2. vdW-DF drawbacks:
  1. Understimation of hydrogen bond strenght.
  2. Overestimation of bond lenghts.
- Valentino R. Cooper. Van der Waals Density Functional: An appropiate exchange functional. *Phys. Rev. B.* ***81****: 161104(R)* (2010).

Summary

1. Work done
   - The method based on MLWFs to evaluate has been coded: **`/abinit/src/67_common/evdw_wannier.F90`**.
   - Currently the spin polarized version is under testing.
   - vdW-DF is in development and also under testing: Coded module: **`/Src/56_xc/m_xc_vdw.F90`**:
     xc_vdw_aggregate, xc_vdw_dft, xc_vdw_done,
     xc_vdw_get_params, xc_vdw_init,
     xc_vdw_memcheck, xc_vdw_read, xc_vdw_set_functional,
     xc_vdw_show,
     xc_vdw_write, vdw_df_filter, vdw_fft, vdw_ldaxc
   - V09 exchange coded as native functional in ABINIT (ixc 24).

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   - The method based on MLWFs to evaluate has been coded: **`/abinit/src/67_common/evdw_wannier.F90`**.
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     xc_vdw_show,
     xc_vdw_write, vdw_df_filter, vdw_fft, vdw_ldaxc
   - V09 exchange coded as native functional in ABINIT (ixc 24).
2. Work to do
   - Automatic tests for the vdW-MLWF spin polarized implementation.
   - Debugging and testing of the vdW-DF non local functional.
   - Atomatic tests for vdW-DF.
   - Update documentation.

Acknowledgements

Profs: Aldo Romero, Xavier Gonze, Angel Rubio, P. L. Silvestrelli.
Dr. Yann Pouillon, and Tonatiuh Rangel.
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Thank You!!