Implementation of vdW-DF functional in ABINIT

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Outline

vdW-DF, Definition and implementation

$$E_{xc}[n(\mathbf{r})] = E_x^{\mathrm{GGA}}[n(\mathbf{r})] + E_c^{\mathrm{LDA}}[n(\mathbf{r})] + E_c^{\mathrm{nl}}[n(\mathbf{r})]$$

Where

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' n(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

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Approximations:

- Full Potential Approx to ACF: $\tilde{\chi}_\lambda \simeq \tilde{\chi}_{\lambda=1}$, RPA:$\tilde{\chi}_\lambda = \tilde{\chi}_{\lambda=0}$

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- From the subtraction of the XC energy at FPA level and the XC for the HEG in the same approximation it is obtained:

$$E_c^{\mathrm{nl}} = \int_0^\infty \frac{\mathrm{d}u}{2\pi}\mathrm{Tr}\left[\ln\left(1-(1-\frac{1}{\epsilon})-\frac{\tilde{\chi}}{\epsilon}V\right)\right].$$

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- Expand the logarithm to a low order in $S = 1 - \frac{1}{\epsilon}$:

$$E_c^{\mathrm{nl}} = \int_0^\infty \frac{\mathrm{d}u}{4\pi}\mathrm{Tr}\Big[S^2 - \Big(\frac{\nabla S\cdot\nabla - V}{4\pi}\Big)^2\Big]\,.$$

vdW-DF, Definition and implementation

Approximations:

- Model dielectric function:

$$S = 1 - \frac{1}{\epsilon} \text{ with } S_{\mathbf{q}}(u) = \frac{\omega_p^2}{\omega_q^2 + u^2}$$

- Pole position scaled to give exact electron gas ground state energy locally:

$$\omega_q = \frac{q^2}{2h(q/q_0(\mathbf{r}))} \text{ with } q_0(\mathbf{r}) = k_F(\mathbf{r}) \frac{\epsilon_{xc}^0(\mathbf{r})}{\epsilon_x^{HEG}(\mathbf{r})}$$

- The function $h(x) = 1 - \exp(-\eta x^2/2)$, with $\eta = 8\pi/9$. which obeys the limits: $\omega_q = q^2/2$ for large q and $\omega_{q=0} = q_0^2/2$.

The vdW-DF kernel

Phys. Rev. Lett. 92, 246401 (2004)

$$\phi(\mathbf{r},\mathbf{r}') = \frac{2}{\pi^2}\int_0^\infty a^2 \mathrm{d}a \int_0^\infty b^2 \mathrm{d}b W(a,b) T(\nu(a),\nu(b),\nu(a)',\nu(b)') \quad (1)$$

$$T(w,x,y,z) = \frac{1}{2}\left[\frac{1}{w+x}+\frac{1}{y+z}\right]\left[\frac{1}{(w+y)(x+z)}+\frac{1}{(w+z)(y+x)}\right] \quad (2)$$

$$W(a,b) = \left[2[(3-a^2)b\cos b\sin a+(3-b^2)a\cos a\sin b+(a^2+b^2-3)\sin a\sin b-3ab\cos a\cos b]\right]/a^3b^3 \quad (3)$$

$$\nu(y) = \frac{y^2}{2h(y/d)}, \nu'(y) = \frac{y^2}{2h(y/d')}$$

$$d = |\mathbf{r}-\mathbf{r}'|q_0(\mathbf{r}), h(x) = 1-\exp\left(-\frac{8\pi}{9}x^2/2\right) \rightarrow \phi(d,d')$$

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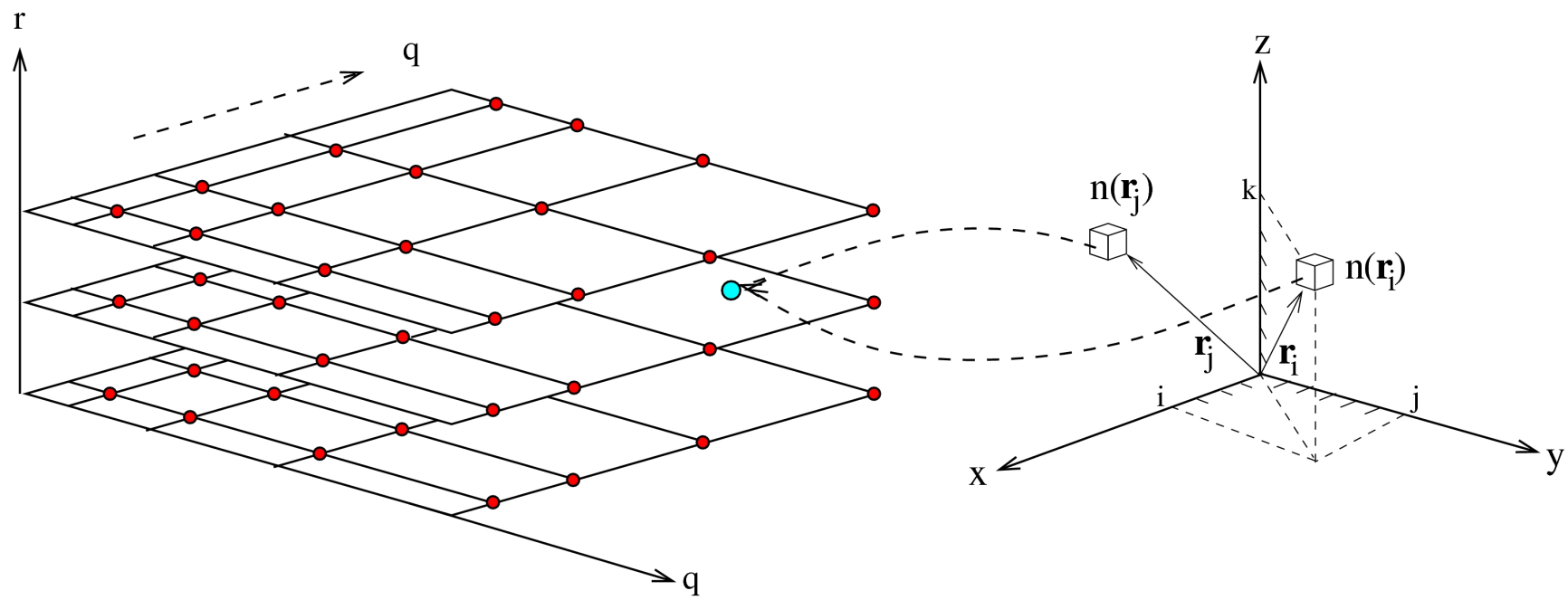
Direct computation of vdW-DF n-l energy $\rightarrow$ N^2 double integrals (elec. density stored on N spatial mesh points.)

Efficient implementation of vdW-DF

Phys. Rev. Lett. 103, 096102 (2009)



Rewrite the kernel as

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

Factorized kernel $\rightarrow$ easier computation of both kernel values (interpolation) and integrals.

$$E_c^{nl} = \frac{1}{2} \sum_{ij} \int \int \theta_i(\mathbf{r}_1)\theta_j(\mathbf{r}_2)\phi_{ij}(r_{12}) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \ , \ \theta_i(\mathbf{r}) = n(\mathbf{r}) p_i[q_0(n(\mathbf{r}), \nabla n(\mathbf{r}))]$$

vdW-DF non-local potential

Phys. Rev. Lett. 103, 096102 (2009)

Given the rewriting of nl energy as a sum rather than an intergal, the expression for the potential:

$$\nu_c^{\mathrm{nl}}(\mathbf{r}) = \frac{\delta E_c^{\mathrm{nl}}}{\delta n(\mathbf{r})}$$

can be approximated by (following White and Bird Phys. Rev. B. 50:4954)

$$\tilde{\nu}_c^{\mathrm{nl}}(\mathbf{r_i}) = \frac{N}{\Omega}\frac{\mathrm{d}\tilde{E}_c^{\mathrm{nl}}}{\mathrm{d}n(\mathbf{r_i})}$$

Since

$$\tilde{E}_c^{nl} = \frac{1}{2}\left(\frac{\Omega}{N}\right)^2 \sum_{\alpha\beta}\sum_{ij} \theta_{\alpha i}\theta_{\beta j}\phi_{\alpha\beta}(r_{ij})$$

vdW-DF non-local potential

Phys. Rev. Lett. 103, 096102 (2009)

The vdW-DF potential at a grid point is finally:

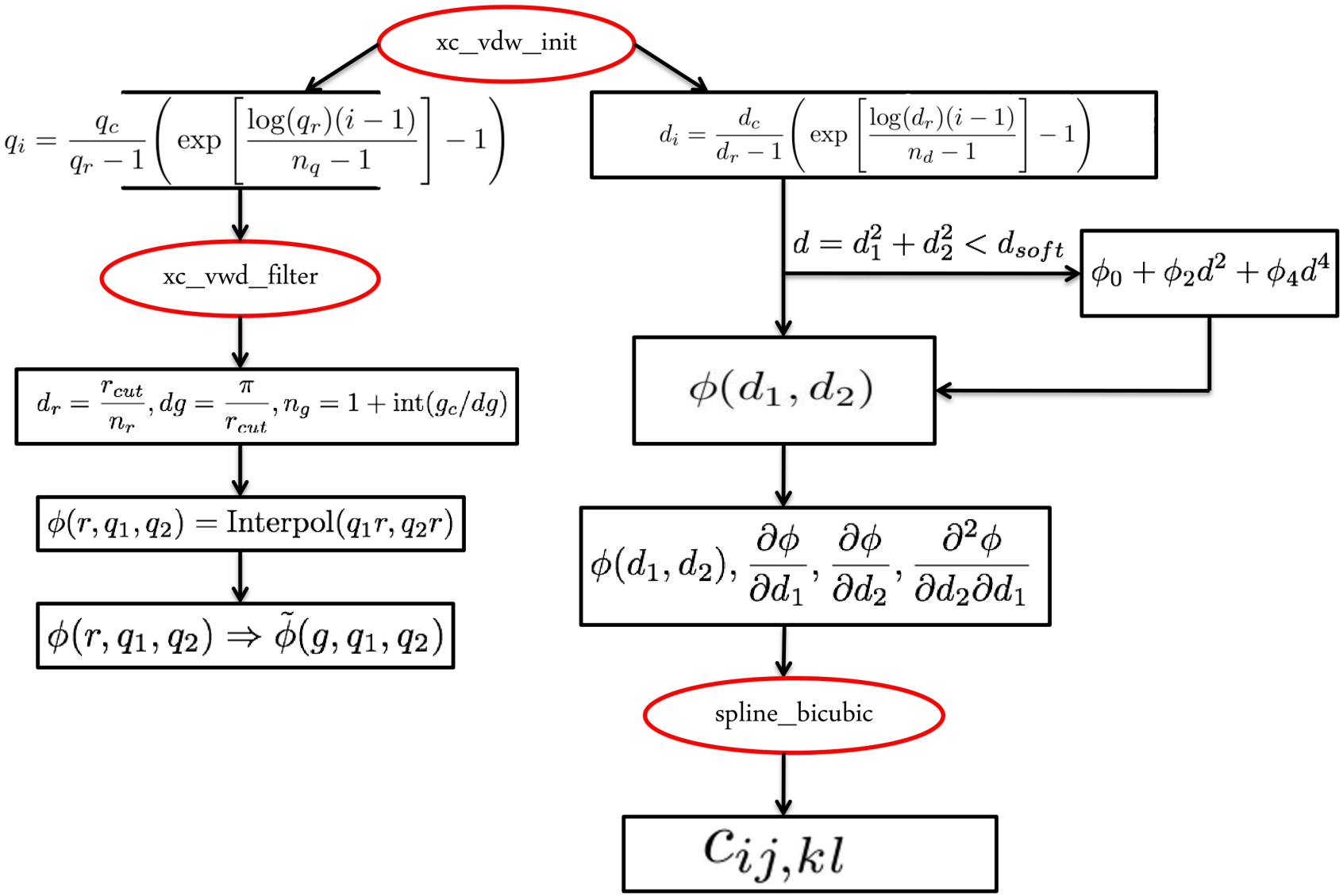
$$\tilde{\nu}_i^{\mathrm{nl}} = \sum_\alpha \left(u_{\alpha i} \frac{\partial \theta_{\alpha i}}{\partial n_i} + \sum_j u_{\alpha j} \frac{\partial \theta_{\alpha j}}{\partial \nabla n_j} \frac{\partial \nabla n_j}{\partial n_i} \right)$$

where

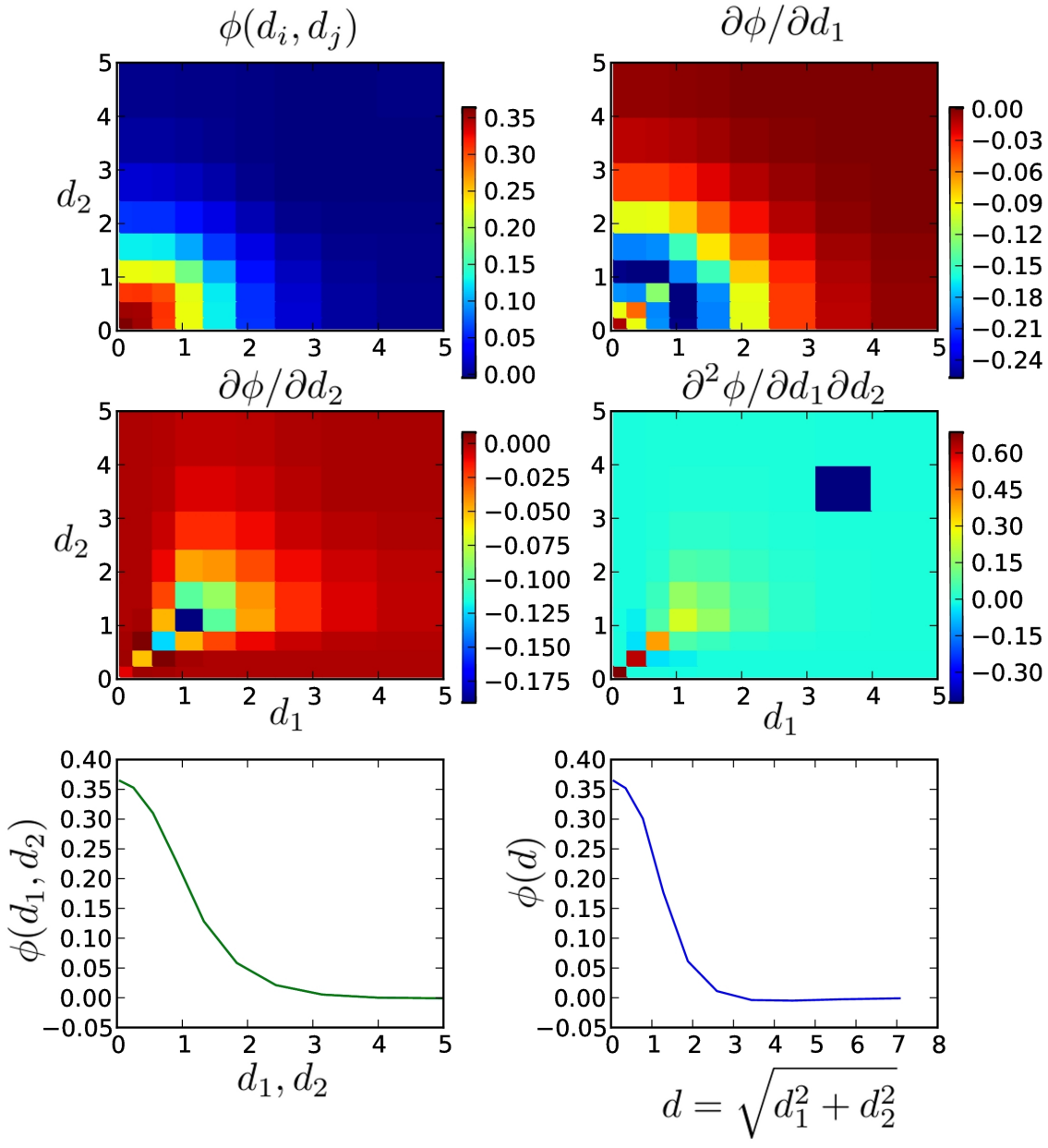
$$u_{\alpha i} = \frac{\Omega}{N} \sum_\beta \sum_j \theta_{\beta j} \phi_{\alpha\beta}(r_{ij})$$

Efficient implementation in Abinit

Kernel generation Flow chart

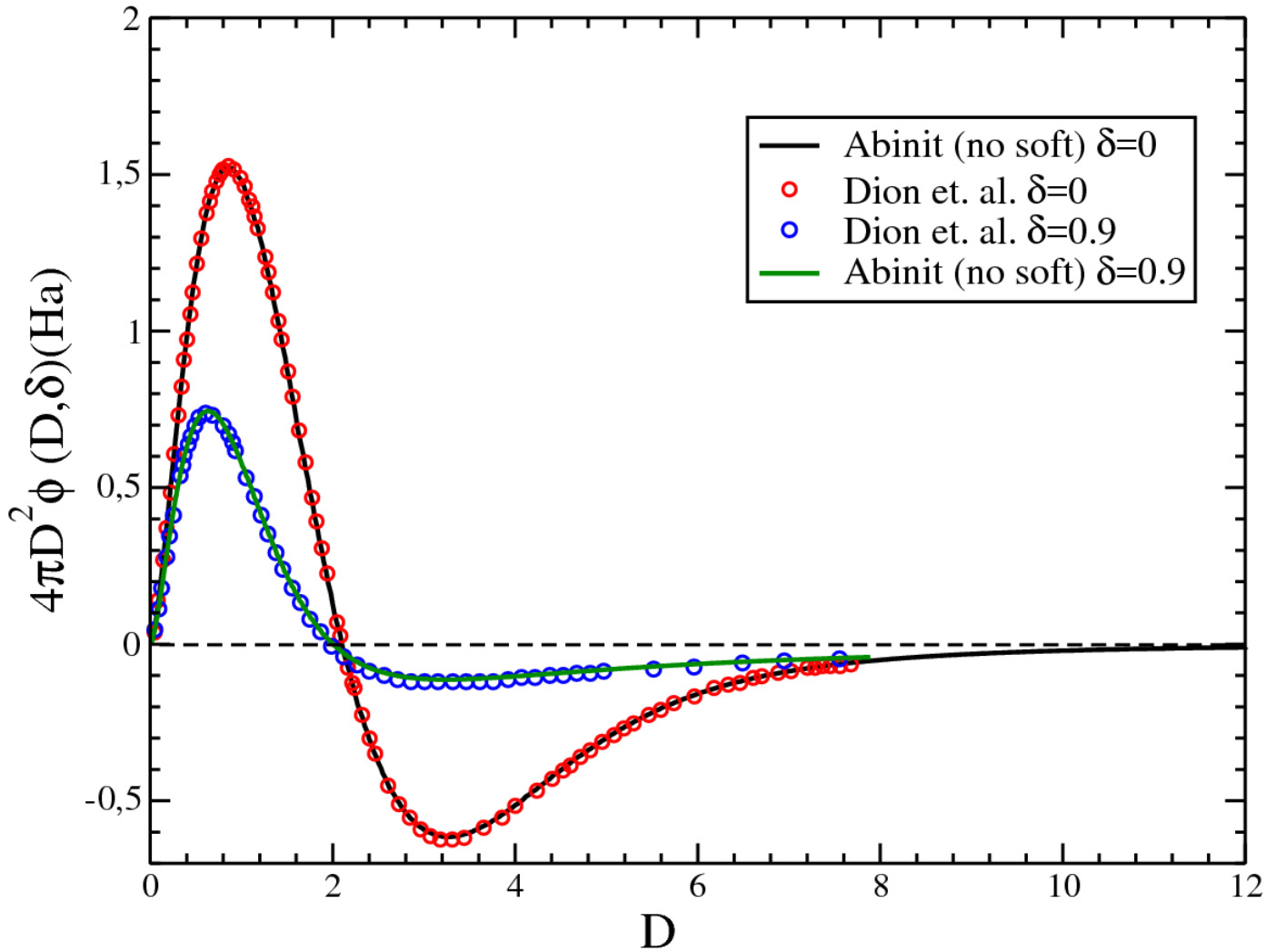


Visualizing Kernel



Kernel comparison

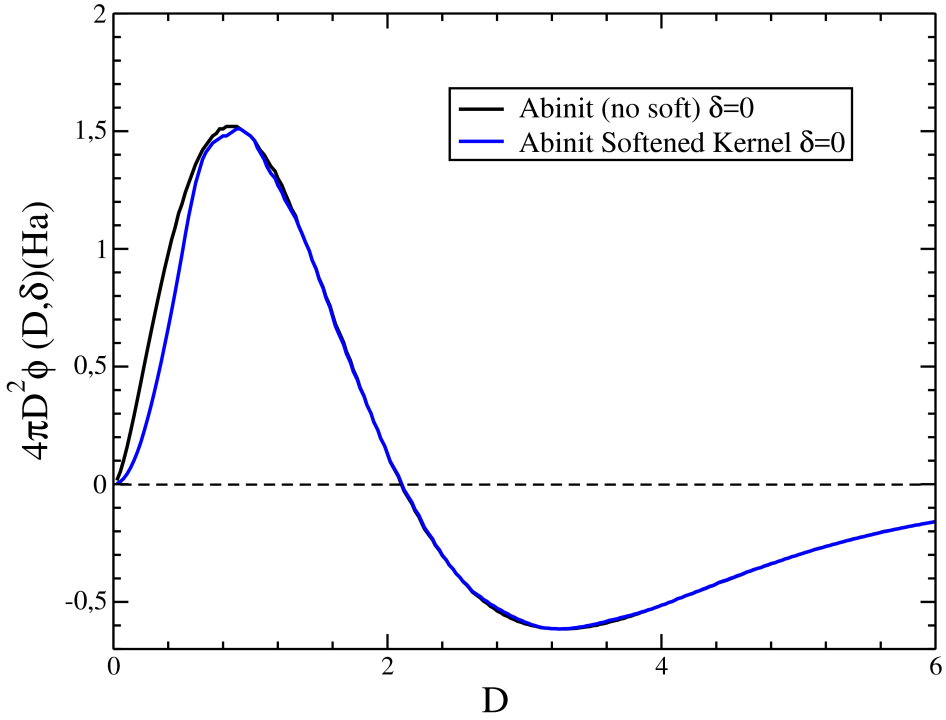
$D = \frac{d+d'}{2}$, $\delta = \frac{d-d'}{d+d'}$



Reference data from Rep. Prog. Phys. 78:066501 (2015).

Effect of kernel softening

$D = \frac{d+d'}{2}$, $\delta = \frac{d-d'}{d+d'}$



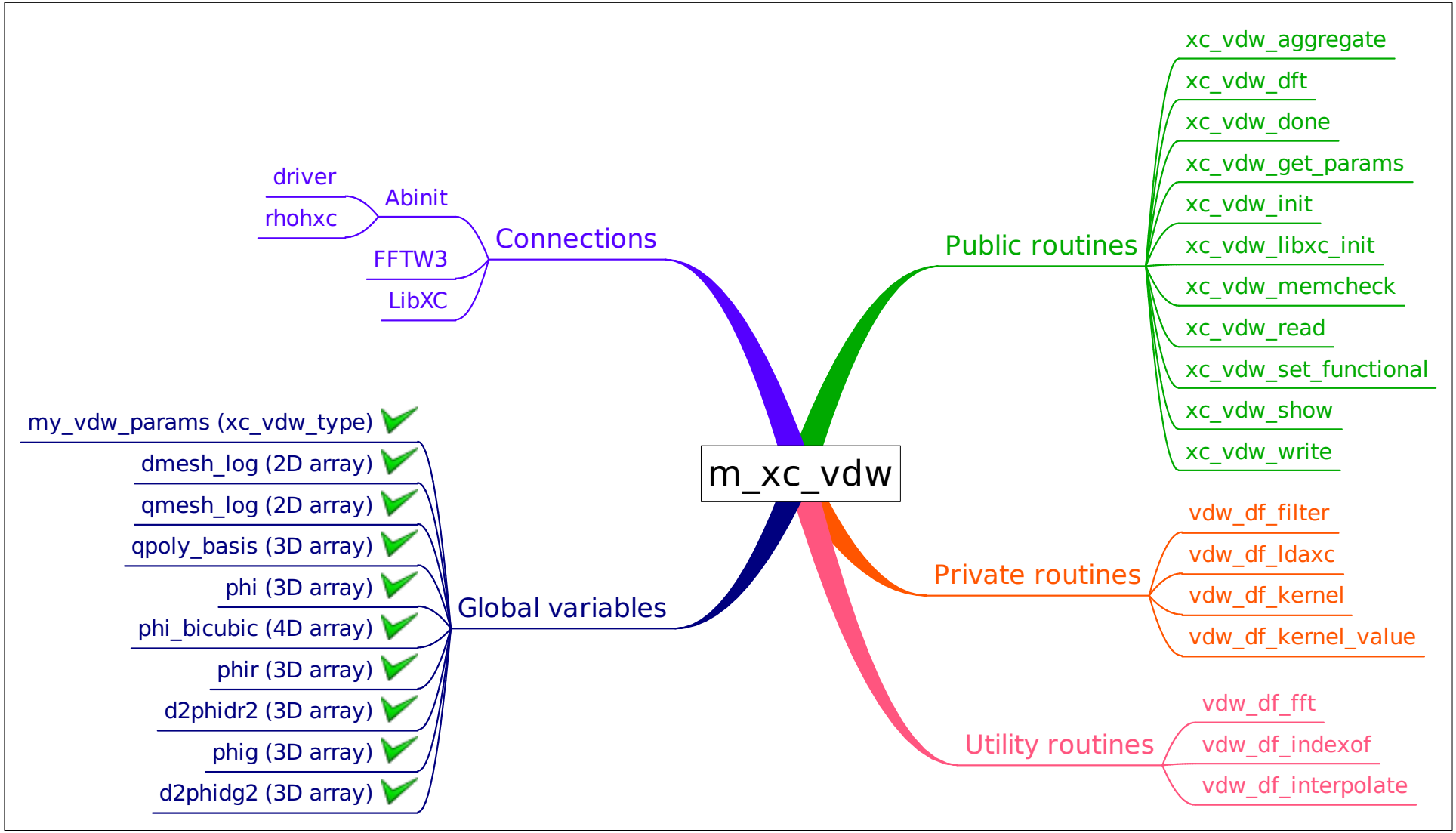
Need for a correction:

$$\Delta E_c^{nl} = \int \mathrm{d}\mathbf{r} n(\mathbf{r}) \Delta\epsilon_c^{nl}(\mathbf{r})$$

where

$$\Delta\epsilon_c^{nl}(\mathbf{r}) = \frac{n(\mathbf{r})}{2} \int_0^\infty 4\pi r'^2 \mathrm{d}r' [phi(q,q,r') - phi_s(q,q,r')]$$

Structure of module m_xc_vdw



VYM - xc_vdw_structure.vym

Wed Jun 1 2011

vdw_kernelgen

Input file sample:

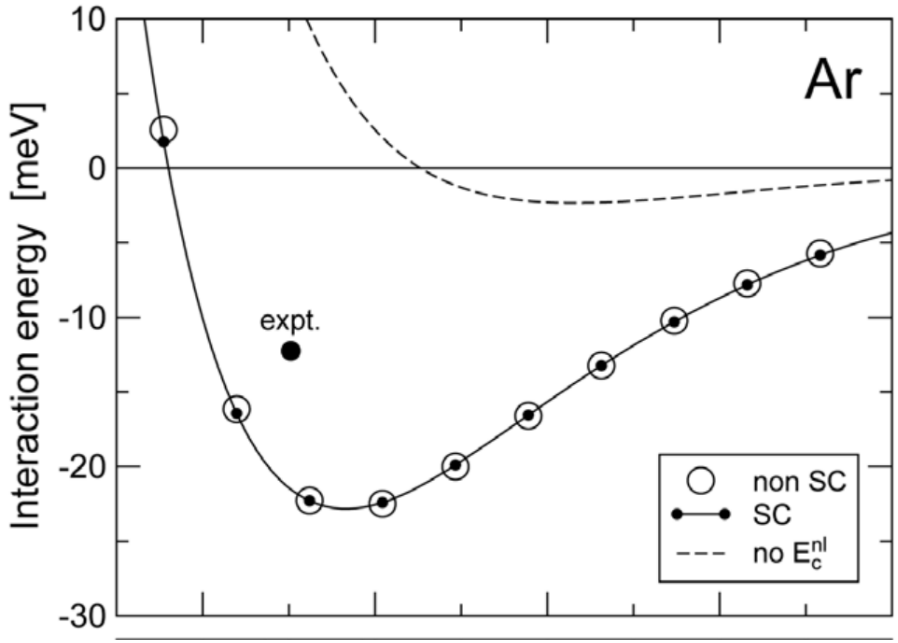
```
1          vdw_xc: functional - 1=DF1, 2=DF2, 3=C09x
-0.8491    vdw_df_zab (should not be changed, see biblio for details)
20         vdw_df_ndpts
30.0       vdw_df_dcut
20.0       vdw_df_dratio
1.0        vdw_df_dsoft
-1.0       vdw_df_phisoft
30         vdw_df_nqpts
5.0        vdw_df_qcut
20.0       vdw_df_qratio
2048       vdw_df_nrpts
100.0      vdw_df_rcut
0.0        vdw_df_rsoft
-1         vdw_df_ngpts
5.0        vdw_df_gcut
10.0       vdw_df_acutmin
30.0       vdw_df_aratio
0.5        vdw_df_damax
1.0e-2     vdw_df_damin
12         vdw_df_nsmooth
1.0e-15    vdw_df_tolerance
1391       vdw_df_tweaks
t01o_VDW
```

Computing time: 15 min on 1 processor, output in a NetCDF file

Execution of vdW-DF

selfconsistent Vs non-selfconsistent runs

- Input variables: `vdw_xc, irdvdw, vdw_df_threshold`
- Once difference in total energy reaches `vdw_df_threshold` rhohxc calls for vdW-DF.
- SCF will stop as usual (toldfe)
- if `vdw_df_threshold` < `toldfe` then vdW-DF is called at the end of SCF.



Rep. Prog. Phys. 78:066501 (2015)

Non-local term of the vdW-DF potential in plave-wave basis

Since

$$\nabla n(\mathbf{r}) = \sum_{\mathbf{G}} i\mathbf{G} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{1}{N} \sum_{\mathbf{G}} \sum_{\mathbf{R}} i\mathbf{G} n(\mathbf{R}) e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R})}$$

we get

$$\frac{\partial \nabla n_j}{\partial n_i} = \frac{1}{N} \sum_{\mathbf{G}} i\mathbf{G} e^{i\mathbf{G}\cdot(\mathbf{r}_j-\mathbf{r}_i)}$$

plugging the latter in nl potential we finally obtain:

$$\tilde{\nu}_i^{\mathrm{nl}} = \sum_{\alpha} \left(u_{\alpha i} \frac{\partial \theta_{\alpha i}}{\partial n_i} + \sum_j u_{\alpha j} \frac{\partial \theta_{\alpha j}}{\partial \nabla n_j} \cdot \left(\frac{1}{N} \sum_{\mathbf{G}} i\mathbf{G} e^{i\mathbf{G}\cdot(\mathbf{r}_j-\mathbf{r}_i)} \right) \right)$$

Getting the non-local term implies performing $2 \times \alpha$ FFTs:

$$\tilde{\nu}_i^{\mathrm{nl}} = \sum_{\alpha} \left(u_{\alpha i} \frac{\partial \theta_{\alpha i}}{\partial n_i} + \frac{1}{N} \sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}_i} \sum_j u_{\alpha j} \frac{\partial \theta_{\alpha j}}{\partial \nabla n_j} \cdot i\mathbf{G} e^{i\mathbf{G}\cdot\mathbf{r}_j} \right)$$

Currently under implementation

Warnings and Opportunities

- Literature is lacking of a systematic study on how the ”efficient implementation” modify the resulting energies as compared to the direct calculation.
- Need to stablish optimal implementation parameters.
- Transferability of the implementation parameters with the systems under study is not guaranteed.
- How good is the performance of vdW-DF for intra-molecular dispersion interactions? (Grimme’s difficult systems: Branching energy of Octane, dimerization of Anthracene.)
- The coded routines can be used for other non-local functionals, just change the definition of the Kernel. (VV09 and VV10).
- LibXC will allow a thorough study of the effect of the semilocal XC functional on the vdW correction.
- Implement a recet proposal for extending vdW-DF to include spin ().

Near future

- Finish and test the non local part of the vdW-DF potential.
- Enable parallelization, `paral_kgb`, in particular for FFTs.
- Complete a set of automatic tests on molecular and solid state systems.
- Define a set of ”universal” implementation parameters.
- Documentation and tutorial for the users.

Acknowledgements

Yann Pouillon, Aldo Romero, Xavier Gonze

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Thank You!!