Going beyond Local Density and Gradient Corrected XC functionals in Quantum-ESPRESSO

Stefano de Gironcoli
SISSA and INFM DEMOCRITOS
Jacob's ladder of Density Functional Theory

Chemical Accuracy

unoccupied $\psi_\alpha(r')$  ↓  exact exchange and exact partial correlation
occupied $\psi_\alpha(r')$  ↓  exact exchange and compatible correlation
$\tau(r)$  ↓  meta-generalized gradient approximation
$\nabla n(r)$  ↓  generalized gradient approximation
$n(r)$  ↑  local spin density approximation

Hartree World

**FIGURE 1.** Jacob’s ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.
LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META GGA: PKZB, TPSS,

SIC, DFT+U, hybrids

van der Waals functionals

... 

exact DFT
van der Waals

van der Waals interaction is relatively weak but widespread in nature. An important source of stability for molecular solids and physisorption of molecules on surfaces.

It is due to truly non-local correlation effects. It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.
vdW : non local correlation

Two neutral atoms separated by $R$ much larger than the atomic size, a limit that ensures that the corresponding wavefunctions are not overlapping.
vdW : non local correlation

Instantaneous dipole $d_A$ generated from charge fluctuations.

Two neutral atoms separated by $R$ much larger than the atomic size, a limit that ensures that the corresponding wavefunctions are not overlapping.
vdW : non local correlation

Instantaneous dipole $d_A$ generated from charge fluctuations.

Induced dipole

$$d_B = \alpha_B d_A R^{-3}$$

Two neutral atoms separated by $R$ much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

$$E = (K \hbar \omega_0 \alpha_A \alpha_B) R^{-6}$$

$$C_6^{AB}$$
DFT within LDA and GGA functionals has been extremely successful in predicting structural, elastic, vibrational properties of materials bound by metallic, ionic, covalent bonds.

These functionals focus on the properties of the electron gas around a single point in space.

$$E_{xc}^{LDA} = \int n(r)\epsilon_{xc}^{hom}(n(r))dr$$

$$E_{xc}^{GGA} = \int n(r)F_{xc}^{GGA}(n(r)), |\nabla n(r)||dr$$

As such they do not describe vdW interaction.

The same is true for Hybrids, DFT+U and SIC etc...
Failure of semilocal functionals

Graphite
How to deal with van der Waals?

- neglect it

- add an empirical damped dispersion correction
  Grimme, Tatckenko-Scheffler

- develop a truly non local XC functional
  Vdw-DF, vdw-DF2, VV09, VV10

- RPA and beyond RPA
How to deal with van der Waals?

- add an empirical damped dispersion correction


$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}$$

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_{ij}^6}{R_{ij}^6} f_{\text{dmp}}(R_{ij}).$$

Here, $N_{at}$ is the number of atoms in the system, $C_{ij}^6$ denotes the dispersion coefficient for atom pair $ij$, $s_6$ is a global scaling factor that only depends on the DF used, and $R_{ij}$ is an interatomic distance. In order to avoid near-singularities for small $R$, a damping function $f_{\text{dmp}}$ must be used

$$C_{ij}^6 = \sqrt{C_i^j C_j^i}$$

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r-1)}}$$
$C_6H_6-C_6H_6$ interaction energy as a function of the distance between centers of mass: red (black) lines refer to Gaussian (PWscf) calculations. GTO results were not corrected for BSSE.

Density Functional Theory

\[ E(\{R\}) = T_s[n(r)] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} drdr' + E_{xc}[n(r)] + \int V_{ext}(r)n(r)dr + E_N(\{R\}) \]

KS self consistent eqs.

\[ n(r) = 2 \sum_{i=1}^{N/2} |\phi_n(r)|^2 \]

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) \right] \phi_n(r) = \varepsilon_n n(r) \]

\[ v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \]

\[ V_{KS}(r) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) \]

\[ E^{LDA}_{xc} = \int n(r)\epsilon^{hom}_{xc}(n(r))dr \]

\[ E^{GGA}_{xc} = \int n(r)F^{GGA}_{xc}(n(r)),|\nabla n(r)|)dr \]
vdW : non local correlation

Instantaneous dipole $d_A$ generated from charge fluctuations.

Induced dipole

$$d_B = \alpha_B d_A R^{-3}$$

Two neutral atoms separated by $R$ much larger than the atomic size, a limit that ensures that the corresponding wavefunctions are not overlapping.

$$E = (K \hbar \omega_0 \alpha_A \alpha_B) \frac{C_6^{AB}}{R^6}$$
Truly non-local functionals

\[ E^{(2)} = -\frac{3\hbar}{\pi} \int_0^\infty du \int_A dr \int_B dr' \frac{\alpha(r, iu)\alpha(r', iu)}{|r - r'|^6} \]

\[ \bar{\alpha}(iu) = \int \alpha(r, iu) \]

\[ u \to \infty : \bar{\alpha}(iu) = Ne^2/mu^2 \]

\[ \alpha(r, iu) = \frac{e^2}{m} \frac{n(r)}{\omega_0^2(r) + u^2} \]

\[ E^{(2)} = -\frac{3\hbar e^4}{2m^2} \int dr \int dr' \frac{n(r)n(r')}{\omega_0(r)\omega_0(r')[\omega_0(r) + \omega_0(r')]|r - r'|^6} \]

\[ E_c = E_c^0 + E_c^{nl} \]

\[ E_c^{nl} = \frac{\hbar}{2} \int dr \int dr' n(r)\Phi(r, r')n(r') \]

\[ 6 \text{ dim integral} ! \]

\[ \Phi \to -\frac{3e^4}{2m^2} \frac{1}{\omega_0(r)\omega_0(r')[\omega_0(r) + \omega_0(r')]|r - r'|^6} \]
How to deal with van der Waals in DFT?

- develop a truly non local XC functional

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

\[ \Phi(n(r), \text{grad} \, n, \, n(r'), \, \text{grad} \, n', \, |r-r'|) \]

A number of functionals have been proposed

- vdw-DF2 : Lee et al, PRB 82, 081101 (2010)

- VV09 : Vydrov and Van Voorhis, PRL 103, 063004 (2009)
- VV10 : Vydrov and Van Voorhis, JCP 133, 244103 (2010)
How to deal with van der Waals in DFT?
- develop a truly non local XC functional

\[ E^{nl}_{c} = \frac{1}{2} \int d^3r \, d^3r' \, n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'), \]

\[ \Phi(n(\vec{r}), \text{grad } n, n(\vec{r}'), \text{grad } n', |\vec{r} - \vec{r}'|) \]
How to compute efficiently van der Waals functionals?

- for

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

\[ \Phi( n(r), \text{grad } n, n(r'), \text{grad } n', |r-r'| ) \]

If the kernel depends separately on densities and gradients in the two points the integral is a 6-dimensional object very expensive to calculate.
How to compute efficiently van der Waals functionals?

- for

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

\[
\text{Phi}( n(\vec{r}), \text{grad} \, n, n(\vec{r}'), \text{grad} \, n', |\vec{r}-\vec{r}'| )
\]

If the kernel does not depend separately on the densities and gradient in the two points but only through a combined function \( q(n(\vec{r}), \text{grad} \, n) \) (true for vDW-DF/vdW-dF2)

\[
\text{Phi}( q(n(\vec{r}), \text{grad} \, n), q(n(\vec{r}'), \text{grad} \, n'), |\vec{r}-\vec{r}'| )
\]

one can precalculate the value of the kernel for a number of Points in a 2D \( q \)-grid and interpolate in between

an efficient integration

Roman-Perez & Soler interpolation scheme
If it's possible to express the complex density dependence on r, r' via a single q(r) (and q(r')) function then...

$$\Phi(q_1, q_2, r_{12}) \approx \sum_{\alpha, \beta} \Phi(q_\alpha, q_\beta, r_{12}) P_\alpha(q_1) P_\beta(q_2)$$

$$E_{c}^{nl} = \frac{1}{2} \sum_{\alpha, \beta} \int \int \Theta_\alpha(r) \Phi(q_\alpha, q_\beta, |r - r'|) \Theta_\beta(r') \, dr \, dr'$$

$$= \frac{\Omega}{2} \sum_{\alpha, \beta} \sum_{G} \Theta_\alpha^*(G') \Phi(q_\alpha, q_\beta, |G|) \Theta_\beta(G)$$

$$\Theta_\alpha(r) = n(r) P_\alpha(q(r))$$

The vdW energy can be expressed as a sum of a number of convolutions i.e. simple 3d integrals

The grid dimension determines the accuracy: 20 x 20 is ok
Glycine polymorphs

\[ \gamma < \alpha < \beta < \ldots \]
Alanine evolution with P
Alanine evolution with Pressure
# Several Non-Local Functionals

<table>
<thead>
<tr>
<th>Functional</th>
<th>$\omega_0$ in $E^{(2)}_c$</th>
<th>$E_{xc}^{LDA/GGA}$</th>
<th>$C_6$ error</th>
</tr>
</thead>
<tbody>
<tr>
<td>vdWDF</td>
<td>$\frac{9\hbar}{8\pi m} \left[ k_F(1 + \mu s^2) \frac{4\pi}{3e^2} \varepsilon_{c}^{LDA} \right]$ with $\mu = 0.09434$</td>
<td>SLA+PW+RPBE- 18.5%</td>
<td></td>
</tr>
<tr>
<td>vdWDF2</td>
<td>$\frac{9\hbar}{8\pi m} \left[ k_F(1 + \mu s^2) \frac{4\pi}{3e^2} \varepsilon_{c}^{LDA} \right]$ with $\mu = 0.20963$</td>
<td>SLA+PW+RPW86- 60.9%</td>
<td></td>
</tr>
<tr>
<td>vdWDF-09</td>
<td>$\frac{\hbar}{3m} k_F^2 (1 + \mu s^2)$ with $\mu = 0.22$</td>
<td>SLA+PW+RPBE- 10.4%</td>
<td></td>
</tr>
<tr>
<td>vv10</td>
<td>$\sqrt{\frac{\omega_p^2}{3} + C \frac{\hbar^2}{m^2} \left</td>
<td>\nabla n \right</td>
<td>^{4}}$ with $C = 0.0089$</td>
</tr>
</tbody>
</table>

vdWDF – functional can exploit the Roman-Perez Soler interpolation
Vv10 – functional does not fulfill the needed conditions
$\Phi_{VV10}^{V}(r, r') = -\frac{3e^4}{2m^2 gg'(g + g')}$

$g = \omega_0(r) R^2 + k(r)$

$k(r) = 3\pi b \left( \frac{n}{9\pi} \right)^{\frac{1}{6}}$

$\omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C \left( \frac{\hbar^2}{m^2} \right) \left| \nabla n \right|^4, \quad \omega_p^2 = \frac{4\pi n e^2}{m}$

The original expression cannot be separated in a function of two auxiliary functions $q(n, \nabla n)$
\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2 \, gg'(g + g')} \]

\[ g = \omega_0(r) R^2 + k(r) \quad k(r) = 3\pi b \left( \frac{n}{9\pi} \right)^{\frac{1}{6}} \]

\[ \omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C \left( \frac{\hbar^2}{m^2} \right) \left| \nabla n \frac{\nabla n}{n} \right|^4, \quad \omega_p^2 = \frac{4\pi ne^2}{m} \]

reordering the terms...

\[ z(r) = \frac{\omega_0(r)}{k(r)} R^2 + 1 \]

\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2 \, k^{3/2} \, k^{3/2}} \frac{1}{zz' \left( \sqrt{\frac{k}{k'}} z + \sqrt{\frac{k'}{k}} z' \right)} \]
\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{gg'(g + g')} \]

\[ g = \omega_0(r) R^2 + k(r) \quad k(r) = 3\pi b \left( \frac{n}{9\pi} \right)^{\frac{1}{6}} \]

\[ \omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C \left( \frac{\hbar^2}{m^2} \right) \left| \nabla n \right|^4, \quad \omega_p^2 = \frac{4\pi ne^2}{m} \]

reordering the terms...

\[ z(r) = \frac{\omega_0(r)}{k(r)} R^2 + 1 \]

\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{k^{3/2}k'^{3/2}} \frac{1}{zz'\left(\sqrt{\frac{k}{k'}} + \sqrt{\frac{k'}{k}}\right)} \]

\[ \sqrt{k/k'} \]
\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{gg'(g + g')} \]

\[ g = \omega_0(r) R^2 + k(r) \quad k(r) = 3\pi b \left( \frac{n}{9\pi} \right)^{\frac{1}{6}} \]

\[ \omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C \left( \frac{\hbar^2}{m^2} \right) \left| \nabla n \frac{n}{n} \right|^{4}, \quad \omega_p^2 = \frac{4\pi ne^2}{m} \]

reordering the terms...

\[ z(r) = \frac{\omega_0(r)}{k(r)} R^2 + 1 \]

\[ \Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{kk'^{3/2}k'^{3/2}} \]

\[ zz' \left( \sqrt{\frac{k}{k'}} + \sqrt{\frac{k'}{k}} \right) \]

setting \( \sqrt{\frac{k}{k'}} = 1 \) and \( q(r) = \omega_0(n(r), \nabla n(r))/k(n(r)) \)
\[
\Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{gg'(g + g')}
\]

\[
g = \omega_0(r)R^2 + k(r) \quad \quad k(r) = 3\pi b \left( \frac{n}{9\pi} \right)^{\frac{1}{6}}
\]

\[
\omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C \left( \frac{\hbar^2}{m^2} \right) \left| \nabla n \right|^4, \quad \omega_p^2 = \frac{4\pi ne^2}{m}
\]

reordering the terms...

\[
z(r) = \frac{\omega_0(r)}{k(r)} R^2 + 1
\]

setting \( \sqrt{\frac{k}{k'}} = 1 \) and \( q(r) = \omega_0(n(r), \nabla n(r))/k(n(r)) \)

\[
\Phi_{VV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{k^{3/2}k'^{3/2}} \frac{1}{zz'(\sqrt{\frac{k}{k'}}) + \sqrt{\frac{k'}{k}}}
\]

\[
\Phi_{rVV10}(r, r') = -\frac{3e^4}{2m^2} \frac{1}{k^{3/2}k'^{3/2}} \frac{1}{(qR^2 + 1)(q'R^2 + 1)(qR^2 + q'R^2 + 2)}
\]

Separable!

Sabatini, Gorni & de Gironcoli, PRB 87, 041108(R) (2013)
VV10 vs rVV10

\[ \Delta \Phi^{VV10} = \Phi^{VV10}(r, r') - \Phi^{rVV10}(r, r') \]

The error in the kernel is small except when the density itself is very small!
rVV10 validation

S22 – hydrogen bonded

- Adenine–thymine WC (C1)
- 2-pyridone–2-aminopyridine (C1)
- Uracil dimer (C2h) planar
- Formamide dimer (C2h)
- Formic acid dimer (C2h)
- H2O dimer (Cs)
- NH3 dimer (C2h)

S22 – Mixed complexes

- Phenol dimer (C1)
- Indole–benzene (Cs)
- Benzene dimer (C2v) (t-shaped)
- Benzene–HCN (Cs)
- Benzene–NH3 (Cs)
- Benzene–H2O (Cs)
- C2H4–C2H2 (C2v)

S22 – dispersion dominated

- Adenine–thymine (C1)
- Indole–benzene (Cs)
- Uracil dimer (C2) stacked
- Pyrazine dimer (Cs)
- Benzene cimer (C2h) parallel
- Benzene–CH4 (C3)
- C2H4 dimer (D2d)
- CH4 dimer (C3d)

Graph showing mean absolute error (%) for various methods: VV10, rVV10, EX+crPA, vDW-DF2, MP2, PBE-D3, PBE+TS-vdW.
rVV10 applications

Noble gas dimers are classical examples of dispersion dominated systems where the quality of different functionals can be explored.

<table>
<thead>
<tr>
<th>Graphite cell parameters (Å)</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>vdW-DF</td>
<td>2.48</td>
<td>7.19</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>2.47</td>
<td>7.06</td>
</tr>
<tr>
<td>rVV10</td>
<td>2.46</td>
<td>6.72</td>
</tr>
<tr>
<td>exp</td>
<td>2.46</td>
<td>6.71</td>
</tr>
</tbody>
</table>
Phonons in Graphite

Comparison of DFPT results at high symmetry points

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>vdW-DF</th>
<th>vdW-DF2</th>
<th>rVV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAE (cm⁻¹)</td>
<td>39.86</td>
<td>24.57</td>
<td>28.29</td>
<td>18.29</td>
</tr>
<tr>
<td>MARE (%)</td>
<td>3.21</td>
<td>1.85</td>
<td>2.04</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Stiff intralayer modes
Phonons in Graphite

Soft interlayer modes

<table>
<thead>
<tr>
<th>Method</th>
<th>MAE (cm⁻¹)</th>
<th>MARE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>5.50</td>
<td>10.51</td>
</tr>
<tr>
<td>vdW-DF</td>
<td>13.50</td>
<td>28.17</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>10.00</td>
<td>22.50</td>
</tr>
<tr>
<td>rVV10</td>
<td>7.50</td>
<td>13.63</td>
</tr>
</tbody>
</table>
LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META GGA: PKZB, TPSS,

SIC, DFT+U, hybrids

van der Waals functionals

...