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FROM RESEARCH TO INDUSTRY

Exchange and correlation functionals in ABINIT: New features

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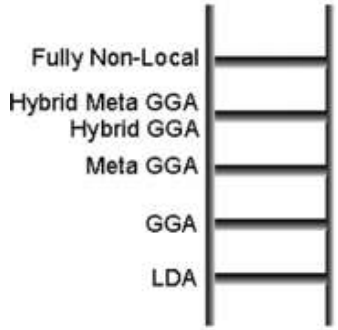
OUTLINE

- MetaGGA
- MetaGGA + PAW
- MetaGGA + 1^{st} order DFPT
- 3^{rd} order DFPT + GGA
- Unitary tests for exchange-correlation

- A bit of non-locality in Exchange-Correlation
- Intermediate level in the « Jacob's ladder »
- Low computational cost (but not negligible)



- XC energy density $\mathcal{E}_{xc}(r)$ depends on $n, \vec{\nabla}n, \vec{\nabla}^2 n, \tau$
- $\int \tau(r)\, dr = E_{KIN}$, $\int \vec{\nabla}^2 n(r)\, dr = 0$ (finite or periodic syst.)
- Kinetic energy density and Laplacian are usually exclusive

$$f_{xc}(r) = n(r)\varepsilon_{xc}(r) \qquad V_\tau(r) = \frac{\partial f_{xc}(r)}{\partial \tau}$$

Hamiltonian

$$H = -\frac{1}{2}\vec{\nabla}^2 - \frac{1}{2}\vec{\nabla}\cdot\left(\frac{\partial f_{xc}}{\partial \tau}\vec{\nabla}\right)$$

Non-locality

$$+ V_{ext} + V_H$$

$$+ \frac{\partial f_{xc}(\ldots,\tau)}{\partial n} - \vec{\nabla}\cdot\left(\frac{\partial f_{xc}}{\partial|\vec{\nabla}n|}\frac{\vec{\nabla}n}{|\vec{\nabla}n|}\right) + \vec{\nabla}^2\left(\frac{\partial f_{xc}}{\partial(\vec{\nabla}^2 n)}\right)$$

Additional term in XC

Energy

$$E^{\mathrm{mGGA}} = \sum_i f_i \left\langle \psi_i \middle| -\frac{1}{2}\vec{\nabla}\cdot\left(\frac{\partial f_{xc}}{\partial \tau}\vec{\nabla}\psi_i\right)\right\rangle = \int \tau(r)\, V_\tau(r) dr$$

$$\psi = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$

$$-\frac{1}{2}\vec{\nabla}\cdot\left(\frac{\partial f_{xc}}{\partial \tau}\vec{\nabla}\psi\right) \longrightarrow \psi = \sum_i iG_i \times \mathbf{FFT}[\mathbf{FFT}^{-1}(iG_i C_{\mathbf{G}}) \times V_\tau]$$

2 FFTs per direction
(« coarse » grid)

$$\vec{\nabla}^2\left(\frac{\partial f_{xc}}{\partial(\vec{\nabla}^2 n)}\right) \longrightarrow \vec{\nabla}^2 n = \mathbf{FFT}^{-1}\left[-\sum_i G_i^2 \times \mathbf{FFT}(n(\mathbf{r}))\right]$$

2 FFTs (« fine » grid)

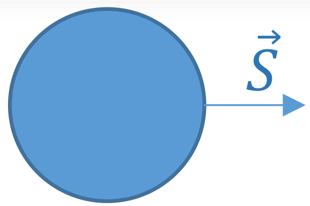
Numerical stability?

Cost of FFTs?

META-GGA FUNCTIONALS – TESTING PROCEDURE

- Take advantage of the integration by parts

$$\int \frac{1}{2}\sum_i \left|\vec{\nabla}\psi_i(\mathbf{r})\right|^2 d\Omega = \cancel{\int \psi_i^*(\mathbf{r})\,\vec{\nabla}\psi_i(\mathbf{r})\,d\vec{S}} - \int \frac{1}{2}\sum_i \psi_i^*(\mathbf{r})\,\vec{\nabla}^2\psi_i(\mathbf{r})\,d\Omega$$



$$\left[\psi_i^*(\mathbf{r})\,\vec{\nabla}\psi_i(\mathbf{r}) - \tilde{\psi}_i^*(\mathbf{r})\,\vec{\nabla}\tilde{\psi}_i(\mathbf{r})\right] = \mathbf{0} \text{ on } \vec{S}$$

Plane-wave part is zero
because of periodicity

On-site PAW parts are zero
at augmentation region boundaries

META-GGA FUNCTIONALS – TESTING PROCEDURE

Testing the kinetic energy density functional against LDA or GGA

$$\varepsilon_{xc}^{MGGA1}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + \alpha\,\vec{\nabla}^2 n(\mathbf{r})$$

Integration by parts

$$\varepsilon_{xc}^{GGA}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) - \alpha \frac{\left|\vec{\nabla} n(\mathbf{r})\right|^2}{n(\mathbf{r})}$$

$$\varepsilon_{xc}^{MGGA2}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + 2\alpha\,\tau(\mathbf{r})$$

$$E_{xc}^{MGGA21} = E_{xc}^{LDA} + \alpha \int n(\mathbf{r})\vec{\nabla}^2 n(\mathbf{r})d\mathbf{r} = E_{xc}^{LDA} - \alpha \int \left|\vec{\nabla} n(\mathbf{r})\right|^2 d\mathbf{r} = E_{xc}^{GGA} = E_{xc}^{MGGA2}$$

$$\varepsilon_{xc}^{MGGA3}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + \left(1 - \frac{1}{\widetilde{m}_e}\right)\frac{\tau(\mathbf{r})}{n(\mathbf{r})}$$

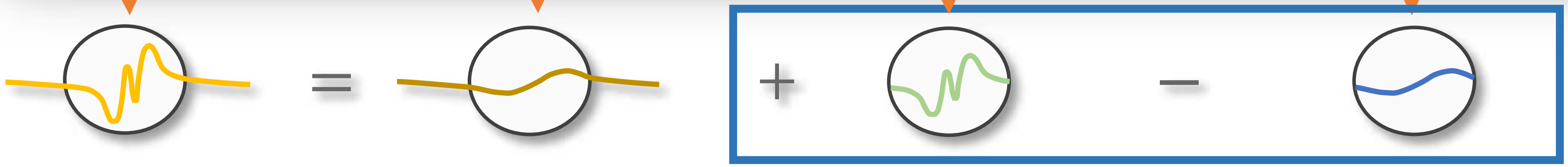
Modified value for the electron mass:
$m_e = \widetilde{m}_e$ *instead of* $m_e = 1$ *(a.u.)*

$$E^{KIN+XC\,(MGGA3)} = \frac{1}{\widetilde{m}_e} E^{KIN} + E_{xc}^{LDA} + \int \left(1 - \frac{1}{\widetilde{m}_e}\right)\tau(\mathbf{r})\,d\mathbf{r} = E^{KIN+XC\,(LDA)}$$

META-GGA + PAW

See: Sun, Mársman *et al*, *Phys. Rev. B*. **84**, 035117 (2011)

$$|\psi_n\rangle = T\,|\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle\langle\tilde{p}_i^R|\tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle\langle\tilde{p}_i^R|\tilde{\psi}_n\rangle$$



PAW on-site contributions

$$\mathbf{H}_{PAW} = -½\Delta + \tilde{v}_{Hxc} + \sum_{R,i,j} \left|\tilde{p}_i^R > D_{ij}^R < \tilde{p}_j^R\right|$$

$$D_{ij}^R \coloneqq \langle\phi_i^R|H(n_1^R;n_c)|\phi_j^R\rangle - \langle\tilde{\phi}_i^R|\tilde{H}(\tilde{n}_1^R;\tilde{n}_c)|\tilde{\phi}_j^R\rangle$$

$$n_1^R(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R\,\phi_i(\mathbf{r})\,\phi_j(\mathbf{r}) \qquad \rho_{ij}^R = \sum_n f_n\,\langle\tilde{\psi}_n|\tilde{p}_i^R\rangle\langle\tilde{p}_j^R|\tilde{\psi}_n\rangle$$

$$\boldsymbol{D_{ij}^{R,MGGA}} = \left\langle \vec{\nabla}\phi_i^R \middle| \frac{\partial f_{xc}}{\partial \tau}(n_1^R; n_c) \middle| \vec{\nabla}\phi_j^R \right\rangle - \left\langle \vec{\nabla}\tilde{\phi}_i^R \middle| \frac{\partial f_{xc}}{\partial \tau}(\tilde{n}_1^R; \tilde{n}_c) \middle| \vec{\nabla}\tilde{\phi}_j^R \right\rangle$$

$$\boldsymbol{\tau_1^R}(\mathbf{r}) = \frac{1}{2}\sum_{i,j} \rho_{ij}^R \, \vec{\nabla}\phi_i(\mathbf{r}) \cdot \vec{\nabla}\phi_j(\mathbf{r}) = \sum_{i,j} Y_L(\hat{r}) \;\; \tau_{1,L}^R(r)$$

$$\boldsymbol{\tau_{1,L}^R}(r) = \frac{1}{2}\sum_{i,j} \frac{\rho_{ij}^R}{r^2}\left[G_{ijL}\,\overline{\phi}_i^R(r)\overline{\phi}_j^R(r) + \boldsymbol{H_{ijL}}\,\phi_i^R(r)\phi_j^R(r)\right]$$

$$\overline{\phi}_i^R(r) = \frac{d\varphi_i^R}{dr} - \frac{\varphi_i^R(r)}{r} \qquad G_{ijL} = \int Y_L \, Y_{l_i m_i} \, Y_{l_j m_j} \, d\Omega$$

$$\phi_i^R(r) = Y_{l_i m_i} \frac{\varphi_i^R(r)}{r} \qquad H_{ijL} = \int Y_L \, \vec{\nabla}Y_{l_i m_i} \cdot \vec{\nabla}Y_{l_j m_j} \;\, d\Omega$$

META-GGA IN ABINIT – HOW TO USE IT?

- Use a GGA pseudopotential file
  No core correction at present
  or a PAW dataset including the core kinetic energy density
  JTH table - Soon metaGGA PAW datasets – See N. Holzwarth's talk

- Put a metaGGA value for ***ixc*** input parameter
  This value is from libXC and has to be negative
  Examples: -202231=TPSS, -263267=SCAN, -497498=R2SCAN

- No more need of ***usekden*** input parameter
  Automatically set. Only useful to print out KDEN.

- R2SCAN only available in libXC v5.1.
  Soon available in ABINIT

We definitively have to find something more user-friendly!

- You should increase slightly FFT grid sizes:
  - increase ***ecut***, or (better) increase ***ngfft***
  - increase ***pawecutdg*** or inscrease ***ngfftdg***
- KED-based XC functionals require more CPU time because of the additional FFTs
- Laplacian-based XC functionals do not need more resources than GGA

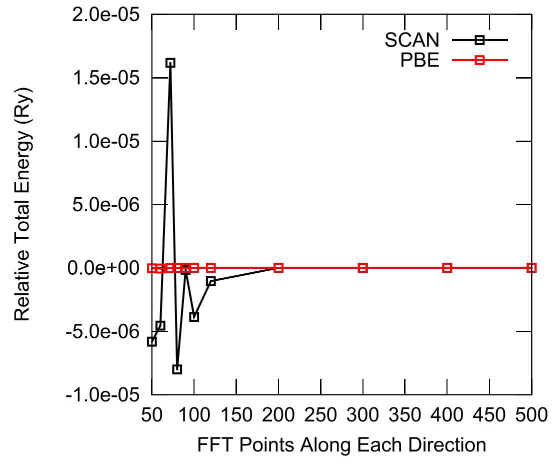


FIG. 2. Convergence of the total energy of the crystalline silicon in the semi-conducting diamond phase with respect to the FFT grids. The y-axis shows the relative energy to the converged total energy. The black line is for the SCAN functional and the red line is for the PBE functional.

From: Yao, Kanai, *J. Chem . Phys.* **146**, 224105 (2017)

META-GGA + PAW IN ABINIT - CHECK

Yao, Kanai, *J. Chem . Phys.* **146**, 224105 (2017)

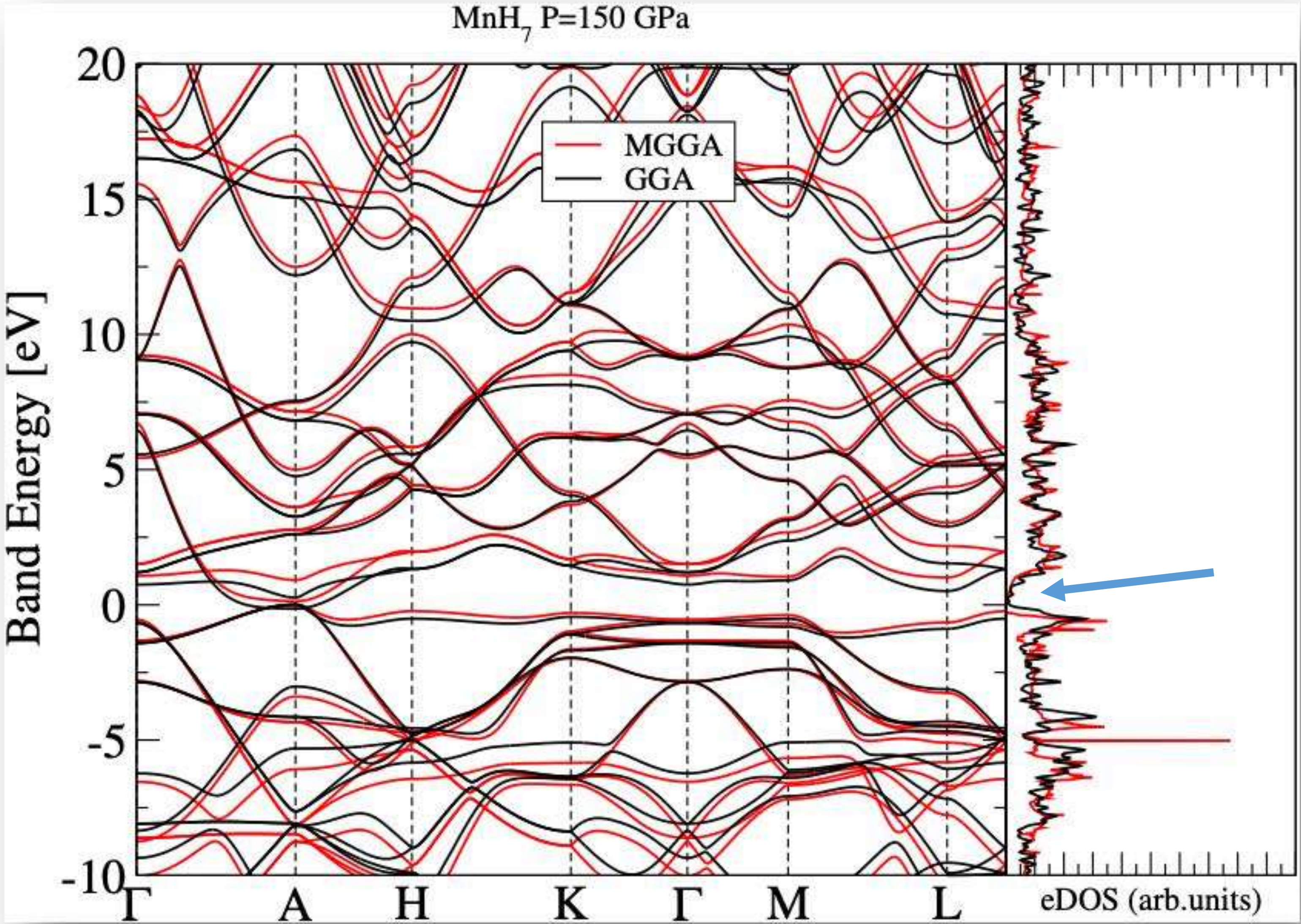
TABLE III. Bulk modulus (GPa) of silicon and germanium in the diamond phase.

	Silicon		Germanium	
PBE	87.95	**88.6**	58.73	**58.9**
TPSS	90.71		57.15	
SCAN	99.30	**99.4**	73.38	**72.8**
SCAN w/PBE pp	95.03		62.76	
LDA[a]	96.8		72.6	
PBE[a]	89.2		59.7	
PBE0[b]	100		75	
Experiment[a]	99.2		75.8	

[a]Reference 4.
[b]Reference 7.

ABINIT **ABINIT**

EXAMPLE: MnH7 SUPERHYDRIDE AT 150 GPA



See J.-B. Charraud's talk

Forces

- Just need to add a contribution from the **core** kinetic energy density

$$V_\tau(r) = \frac{\partial f_{xc}(r)}{\partial \tau}$$

$$F_{R,\alpha}^{mGGA} = F_{R,\alpha}^{GGA} - \int \tilde{V}_\tau(\mathbf{r}) \frac{\partial \tilde{\tau}_c(\mathbf{r})}{\partial R_\alpha} d\mathbf{r} = F_{R,\alpha}^{GGA} - \sum_{\mathbf{G}} iG_\alpha \tilde{V}_\tau(G)\tilde{\tau}_c(G)\, e^{i\mathbf{G}\cdot\mathbf{R}}$$

Stress tensor

- Apply same procedure as in: dal Corso, Resta, PR*B* **50**, 4327 (1994)
- Use the fact that : $\sum_i f_i \left\langle \psi_i \middle| \left[\mathbf{H}, r_\beta \frac{\partial}{r_\alpha}\right] \middle| \psi_i \right\rangle = 0$

$$\sigma_{\alpha\beta}^{mGGA} = \sigma_{\alpha\beta}^{GGA} - \frac{1}{\Omega}\Bigg[\delta_{\alpha\beta} \int \tilde{V}_\tau(\mathbf{r})\,(\tau + \tau_c)(\mathbf{r}) d\mathbf{r} + 2 \int \frac{\partial f_{xc}}{\partial \vec{\nabla}^2 n}(\mathbf{r}) \frac{\partial^2 \tilde{n}_c}{\partial r_\alpha \partial r_\beta}(\mathbf{r})\, d\mathbf{r}$$

$$+ \sum_i f_i \left\langle \frac{\partial \psi_i}{\partial r_\alpha} \middle| \tilde{V}_\tau \middle| \frac{\partial \psi_i}{\partial r_\beta} \right\rangle \Bigg]$$

Using WF plane wave coefs

From XC routine

Computed with finite-differences in other codes

- *Why?* : **Raman efficiencies** computation within DFPT

Raman tensor:

$$\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\beta}} = -\frac{1}{\Omega_0}\frac{\partial^3 E}{\partial \tau_{\kappa\beta}\partial \mathcal{E}_i \partial \mathcal{E}_j}$$

Non-linear susceptibility:

$$\chi^{(2)}_{ijk} = -\frac{1}{2\Omega_0}\frac{\partial^3 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k}$$

- Need several **derivatives of the XC energy**:
  « Grid » version (plane waves) and « spherical » version

- First order: $$E^{(1)}_{xc} = \int d\mathbf{r}' n^{(1)}(\mathbf{r}') \frac{\delta E_{xc}}{\delta n(\mathbf{r}')} = \int d\mathbf{r}' n^{(1)}(\mathbf{r}') V_{xc}(\mathbf{r}')$$

- Second order: $$E^{(2)}_{xc} = \int d\mathbf{r} \left(n^{(2)}(\mathbf{r}) V_{xc}(\mathbf{r}) + n^{(1)}(\mathbf{r}) (V_{xc}(\mathbf{r}))^{(1)} \right)$$

- Third order: $$E^{(3)}_{xc} = \int d\mathbf{r} \left(n^{(3)}(\mathbf{r}) V_{xc}(\mathbf{r}) + 2n^{(2)}(\mathbf{r}) (V_{xc}(\mathbf{r}))^{(1)} + n^{(1)}(\mathbf{r}) (V_{xc}(\mathbf{r}))^{(2)} \right)$$

- Remember that: $n(r) = n_v(\mathbf{r}) + n_c(\mathbf{r})$

Need order n

Need order 2n or 2n+1

Non polarized version…

- LDA functional $\varepsilon_{xc}^{LDA}(n(\mathbf{r}))$

$$V_{xc}^{LDA}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n}$$

$$E_{xc,n^{(1)}}^{(1)} = \int d\mathbf{r}\, n^{(1)}(\mathbf{r}) \frac{\partial f_{xc}}{\partial n}(\mathbf{r})$$

$$E_{xc,n^{(1)}}^{(2)} = \int d\mathbf{r}\, d\mathbf{r}'\, n^{(1)}(\mathbf{r})\, n^{(1)}(r') \frac{\partial^2 f_{xc}(\mathbf{r})}{\partial n\,(r) \partial n\,(\mathbf{r}')}$$

$$E_{xc,n^{(1)}}^{(3)} = \int d\mathbf{r}\, dr' dr''\, n^{(1)}(\mathbf{r})\, n^{(1)}(r')\, n^{(1)}(r'') \frac{\partial^3 f_{xc}(\mathbf{r})}{\partial n(r) \partial n(\mathbf{r}') \partial n(r'')}$$

Currently implemented in ABINIT

AND NOW GGA – ORDER 2

- GGA functional $\varepsilon_{xc}^{LDA}\left(n(\mathbf{r}),\vec{\nabla}n(\mathbf{r})\right)$

$$V_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \vec{\nabla}\cdot\left(\frac{\partial f_{xc}}{\partial|\vec{\nabla}n|}\frac{\vec{\nabla}n}{|\vec{\nabla}n|}\right)$$

$$E_{xc}^{(1)} = \int d\mathbf{r} n^{(1)}(\mathbf{r})\frac{\partial f_{xc}}{\partial n}(\mathbf{r}) + \int d\mathbf{r}\frac{\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|}\frac{\partial f_{xc}}{\partial|\nabla n|}(\mathbf{r})$$

$$\begin{aligned}E_{xc,n^{(1)}}^{(2)} &= \int d\mathbf{r} n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r})\frac{\partial^2 f_{xc}}{\partial n\partial n}(\mathbf{r}) + 2\int d\mathbf{r} n^{(1)}(\mathbf{r})\frac{\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|}\frac{\partial^2 f_{xc}}{\partial n\partial|\nabla n|}(\mathbf{r})\\ &+ \int d\mathbf{r}\frac{\nabla_1 n^{(1)}(\mathbf{r}).\nabla_1 n(\mathbf{r})}{|\nabla n(\mathbf{r})|}\frac{\nabla_2 n^{(1)}(\mathbf{r}).\nabla_2 n(\mathbf{r})}{|\nabla n(\mathbf{r})|}\left(\frac{\partial^2 f_{xc}}{\partial|\nabla n|\partial|\nabla n|}(\mathbf{r}) - \frac{1}{|\nabla n(\mathbf{r})|}\frac{\partial f_{xc}}{\partial|\nabla n|}(\mathbf{r})\right)\\ &+ \int d\mathbf{r}\nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r})\frac{1}{|\nabla n(\mathbf{r})|}\frac{\partial f_{xc}}{\partial|\nabla n|}(\mathbf{r})\end{aligned}$$

Currently implemented in ABINIT

AND NOW THIRD ORDER

$$
\begin{aligned}
E^{(3)}_{xc,n^{(1)}} = & \int d\mathbf{r} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) \frac{\partial^3 f_{xc}}{\partial n \partial n \partial n}(\mathbf{r}) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) \frac{\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\partial^3 f_{xc}}{\partial n \partial n \partial |\nabla n|}(\mathbf{r}) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) \frac{\nabla_1 n^{(1)}(\mathbf{r}).\nabla_1 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\nabla_2 n^{(1)}(\mathbf{r}).\nabla_2 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \left(\frac{\partial^3 f_{xc}}{\partial n \partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) - \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^2 f_{xc}}{\partial n \partial |\nabla n|}(\mathbf{r}) \right) \\
& + \int d\mathbf{r} \frac{\nabla_1 n^{(1)}(\mathbf{r}).\nabla_1 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\nabla_2 n^{(1)}(\mathbf{r}).\nabla_2 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\nabla_3 n^{(1)}(\mathbf{r}).\nabla_3 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \\
& \times \left(\frac{\partial^3 f_{xc}}{\partial |\nabla n| \partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) - \frac{3}{|\nabla n(\mathbf{r})|} \left(\frac{\partial^2 f_{xc}}{\partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) - \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_{xc}}{\partial |\nabla n|}(\mathbf{r}) \right) \right) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) \frac{\nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\partial^2 f_{xc}}{\partial n \partial |\nabla n|}(\mathbf{r}) \\
& \\
& + 3 \int d\mathbf{r} \frac{\nabla_1 n^{(1)}(\mathbf{r}).\nabla_1 n^{(1)}(\mathbf{r})}{|\nabla n(\mathbf{r})|} \frac{\nabla_2 n^{(1)}(\mathbf{r}).\nabla_2 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \left(\frac{\partial^2 f_{xc}}{\partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) - \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_{xc}}{\partial |\nabla n|}(\mathbf{r}) \right)
\end{aligned}
$$

ABINIT REFORMULATION

$$
\begin{aligned}
E^{(3)}_{xc,n^{(1)}} = & \int d\mathbf{r} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) K_{3xc}(\mathbf{r},1) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) K_{3xc}(\mathbf{r},2) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) \left(K_{3xc}(\mathbf{r},3) - \frac{1}{|\nabla n(\mathbf{r})|^2} K_{xc}(\mathbf{r},3) \right) \\
& + \int d\mathbf{r} \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) \left(K_{3xc}(\mathbf{r},4) - \frac{3}{|\nabla n(\mathbf{r})|^2} K_{xc}(\mathbf{r},4) \right) \\
& + 3 \int d\mathbf{r} n^{(1)}(\mathbf{r}) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r}) \right) K_{xc}(\mathbf{r},3) \\
& + 3 \int d\mathbf{r} \left(\nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r}) \right) \left(\nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \right) K_{xc}(\mathbf{r},4)
\end{aligned}
$$

$$
\begin{aligned}
K_{xc}(\mathbf{r},1) &= \frac{\partial^2 f_{xc}}{\partial n \partial n}(\mathbf{r}) \\
K_{xc}(\mathbf{r},2) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_{xc}}{\partial |\nabla n|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},3) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^2 f_{xc}}{\partial n \partial |\nabla n|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},4) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial}{\partial |\nabla n|} \left(\frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_{xc}}{\partial |\nabla n|}(\mathbf{r}) \right) \\
K_{xc}(\mathbf{r},5:7) &= \nabla n(\mathbf{r})
\end{aligned}
$$

$$
\begin{aligned}
K_{3xc}(\mathbf{r},1) &= \frac{\partial^3 f_{xc}}{\partial n \partial n \partial n}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},2) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^3 f_{xc}}{\partial n \partial n \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},3) &= \frac{1}{|\nabla n(\mathbf{r})|^2} \frac{\partial^3 f_{xc}}{\partial n \partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},4) &= \frac{1}{|\nabla n(\mathbf{r})|^3} \frac{\partial^3 f_{xc}}{\partial |\nabla n| \partial |\nabla n| \partial |\nabla n|}(\mathbf{r})
\end{aligned}
$$

JUST FOR FUN: SPIN-POLARIZED VERSION!

$$
\begin{aligned}
E^{(3)}_{xc,n^{(1)}} = & \int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) n^{(1)}_\uparrow(\mathbf{r}) n^{(1)}_\uparrow(\mathbf{r}) K_{3xc}(\mathbf{r},1) + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) n^{(1)}_\uparrow(\mathbf{r}) n^{(1)}_\downarrow(\mathbf{r}) K_{3xc}(\mathbf{r},2) \\
& + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) n^{(1)}_\downarrow(\mathbf{r}) n^{(1)}_\uparrow(\mathbf{r}) K_{3xc}(\mathbf{r},3) + \int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) n^{(1)}_\downarrow(\mathbf{r}) n^{(1)}_\downarrow(\mathbf{r}) K_{3xc}(\mathbf{r},4) \\
& + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) \left(n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) K_{3xc}(\mathbf{r},5) + n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) K_{3xc}(\mathbf{r},7) + n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) K_{3xc}(\mathbf{r},8) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) \left(n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) K_{3xc}(\mathbf{r},6) + n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) K_{3xc}(\mathbf{r},8) + n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) K_{3xc}(\mathbf{r},9) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) \left(K_{3xc}(\mathbf{r},10) - \frac{1}{|\nabla n_\uparrow(\mathbf{r})|^2} K_{xc}(\mathbf{r},6) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) \left(K_{3xc}(\mathbf{r},11) - \frac{1}{|\nabla n_\downarrow(\mathbf{r})|^2} K_{xc}(\mathbf{r},7) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \left(K_{3xc}(\mathbf{r},12) - \frac{1}{|\nabla n(\mathbf{r})|^2} K_{xc}(\mathbf{r},11) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \left(K_{3xc}(\mathbf{r},13) - \frac{1}{|\nabla n(\mathbf{r})|^2} K_{xc}(\mathbf{r},12) \right) \\
& + \int d\mathbf{r} \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) \left(K_{3xc}(\mathbf{r},14) - \frac{3}{|\nabla n_\uparrow(\mathbf{r})|^2} K_{xc}(\mathbf{r},8) \right) \\
& + \int d\mathbf{r} \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) \left(K_{3xc}(\mathbf{r},15) - \frac{3}{|\nabla n_\downarrow(\mathbf{r})|^2} K_{xc}(\mathbf{r},9) \right) \\
& + \int d\mathbf{r} \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) \left(K_{3xc}(\mathbf{r},16) - \frac{3}{|\nabla n(\mathbf{r})|^2} K_{xc}(\mathbf{r},13) \right) \\
& + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n^{(1)}_\uparrow(\mathbf{r}) K_{xc}(\mathbf{r},6) + 3\int d\mathbf{r} n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r}) K_{xc}(\mathbf{r},11) \\
& + 3\int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n^{(1)}_\downarrow(\mathbf{r}) K_{xc}(\mathbf{r},7) + 3\int d\mathbf{r} n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r}) K_{xc}(\mathbf{r},12) \\
& + 3\int d\mathbf{r} \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n^{(1)}_\uparrow(\mathbf{r}) \nabla n^{(1)}_\uparrow(\mathbf{r}).\nabla n_\uparrow(\mathbf{r}) K_{xc}(\mathbf{r},8) \\
& + 3\int d\mathbf{r} \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n^{(1)}_\downarrow(\mathbf{r}) \nabla n^{(1)}_\downarrow(\mathbf{r}).\nabla n_\downarrow(\mathbf{r}) K_{xc}(\mathbf{r},9) \\
& + 3\int d\mathbf{r} \nabla n^{(1)}(\mathbf{r}).\nabla n^{(1)}(\mathbf{r}) \nabla n^{(1)}(\mathbf{r}).\nabla n(\mathbf{r}) K_{xc}(\mathbf{r},13)
\end{aligned}
\tag{7.26}
$$

$$
\begin{aligned}
K_{xc}(\mathbf{r},1) &= \frac{\partial^2 f_{xc}}{\partial n_\uparrow \partial n_\uparrow}(\mathbf{r}) \\
K_{xc}(\mathbf{r},2) &= \frac{\partial^2 f_{xc}}{\partial n_\uparrow \partial n_\downarrow}(\mathbf{r}) \\
K_{xc}(\mathbf{r},3) &= \frac{\partial^2 f_{xc}}{\partial n_\downarrow \partial n_\downarrow}(\mathbf{r}) \\
K_{xc}(\mathbf{r},4) &= \frac{1}{|\nabla n_\uparrow(\mathbf{r})|} \frac{\partial f_x}{\partial |\nabla n_\uparrow|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},5) &= \frac{1}{|\nabla n_\downarrow(\mathbf{r})|} \frac{\partial f_x}{\partial |\nabla n_\downarrow|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},6) &= \frac{1}{|\nabla n_\uparrow(\mathbf{r})|} \frac{\partial^2 f_x}{\partial n_\uparrow \partial |\nabla n_\uparrow|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},7) &= \frac{1}{|\nabla n_\downarrow(\mathbf{r})|} \frac{\partial^2 f_x}{\partial n_\downarrow \partial |\nabla n_\downarrow|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},8) &= \frac{1}{|\nabla n_\uparrow|^2} \left(\frac{\partial^2 f_x}{\partial |\nabla n_\uparrow| \partial |\nabla n_\uparrow|}(\mathbf{r}) - \frac{1}{|\nabla n_\uparrow(\mathbf{r})|} \frac{\partial f_x}{\partial |\nabla n_\uparrow|}(\mathbf{r}) \right) \\
K_{xc}(\mathbf{r},9) &= \frac{1}{|\nabla n_\downarrow|^2} \left(\frac{\partial^2 f_x}{\partial |\nabla n_\downarrow| \partial |\nabla n_\downarrow|}(\mathbf{r}) - \frac{1}{|\nabla n_\downarrow(\mathbf{r})|} \frac{\partial f_x}{\partial |\nabla n_\downarrow|}(\mathbf{r}) \right) \\
K_{xc}(\mathbf{r},10) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_c}{\partial |\nabla n|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},11) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^2 f_c}{\partial n_\uparrow \partial |\nabla n|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},12) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^2 f_c}{\partial n_\downarrow \partial |\nabla n|}(\mathbf{r}) \\
K_{xc}(\mathbf{r},13) &= \frac{1}{|\nabla n|^2} \left(\frac{\partial^2 f_c}{\partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) - \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial f_x}{\partial |\nabla n|}(\mathbf{r}) \right)
\end{aligned}
$$

$$
\begin{aligned}
K_{3xc}(\mathbf{r},1) &= \frac{\partial^3 f_{xc}}{\partial n_\uparrow \partial n_\uparrow \partial n_\uparrow}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},2) &= \frac{\partial^3 f_{xc}}{\partial n_\uparrow \partial n_\uparrow \partial n_\downarrow}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},3) &= \frac{\partial^3 f_{xc}}{\partial n_\uparrow \partial n_\downarrow \partial n_\downarrow}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},4) &= \frac{\partial^3 f_{xc}}{\partial n_\downarrow \partial n_\downarrow \partial n_\downarrow}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},5) &= \frac{1}{|\nabla n_\uparrow(\mathbf{r})|} \frac{\partial^3 f_x}{\partial n_\uparrow \partial n_\uparrow \partial |\nabla n_\uparrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},6) &= \frac{1}{|\nabla n_\downarrow(\mathbf{r})|} \frac{\partial^3 f_x}{\partial n_\downarrow \partial n_\downarrow \partial |\nabla n_\downarrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},7) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^3 f_c}{\partial n_\uparrow \partial n_\uparrow \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},8) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^3 f_c}{\partial n_\uparrow \partial n_\downarrow \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},9) &= \frac{1}{|\nabla n(\mathbf{r})|} \frac{\partial^3 f_c}{\partial n_\downarrow \partial n_\downarrow \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},10) &= \frac{1}{|\nabla n_\uparrow(\mathbf{r})|^2} \frac{\partial^3 f_x}{\partial n_\uparrow \partial |\nabla n_\uparrow| \partial |\nabla n_\uparrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},11) &= \frac{1}{|\nabla n_\downarrow(\mathbf{r})|^2} \frac{\partial^3 f_x}{\partial n_\downarrow \partial |\nabla n_\downarrow| \partial |\nabla n_\downarrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},12) &= \frac{1}{|\nabla n(\mathbf{r})|^2} \frac{\partial^3 f_c}{\partial n_\uparrow \partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},13) &= \frac{1}{|\nabla n(\mathbf{r})|^2} \frac{\partial^3 f_c}{\partial n_\downarrow \partial |\nabla n| \partial |\nabla n|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},14) &= \frac{1}{|\nabla n_\uparrow(\mathbf{r})|^3} \frac{\partial^3 f_x}{\partial |\nabla n_\uparrow| \partial |\nabla n_\uparrow| \partial |\nabla n_\uparrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},15) &= \frac{1}{|\nabla n_\downarrow(\mathbf{r})|^3} \frac{\partial^3 f_x}{\partial |\nabla n_\downarrow| \partial |\nabla n_\downarrow| \partial |\nabla n_\downarrow|}(\mathbf{r}) \\
K_{3xc}(\mathbf{r},16) &= \frac{1}{|\nabla n(\mathbf{r})|^3} \frac{\partial^3 f_c}{\partial |\nabla n| \partial |\nabla n| \partial |\nabla n|}(\mathbf{r})
\end{aligned}
$$

IMPLEMENTATION FEASIBLE THANKS TO LIBXC V5

$$\sigma[0] = \nabla\rho_\uparrow \cdot \nabla\rho_\uparrow \qquad \sigma[1] = \nabla\rho_\uparrow \cdot \nabla\rho_\downarrow \qquad \sigma[2] = \nabla\rho_\downarrow \cdot \nabla\rho_\downarrow$$

$$\mathbf{vsigma}_\alpha \quad ; \quad \frac{\partial\epsilon}{\partial\sigma_\alpha}$$

$$\mathbf{v2rhosigma}_{\alpha\beta} \quad ; \quad \frac{\partial\epsilon}{\partial\rho_\alpha\partial\sigma_\beta}$$

$$\mathbf{v2sigma2}_{\alpha\beta} \quad ; \quad \frac{d^2\epsilon}{\partial\sigma_\alpha\partial\sigma_\beta}$$

$$\mathbf{v3rho2sigma}_{\alpha\beta\gamma} \quad ; \quad \frac{d^3\epsilon}{\partial\rho_\alpha\partial\rho_\beta\partial\sigma_\gamma}$$

$$\mathbf{v3rhosigma2}_{\alpha\beta\gamma} \quad ; \quad \frac{d^3\epsilon}{\partial\rho_\alpha\partial\sigma_\beta\partial\sigma_\gamma}$$

$$\mathbf{v3sigma3}_{\alpha\beta\gamma} \quad ; \quad \frac{d^3\epsilon}{\partial\sigma_\alpha\partial\sigma_\beta\partial\sigma_\gamma} \quad ;$$

Need to convert libXC objects into ABINIT ones…

$$\frac{1}{|\vec{\nabla}n|}\frac{\partial f_x}{\partial|\vec{\nabla}n|} = \frac{1}{|\vec{\nabla}n|}\frac{\partial f_x}{\partial\sigma}\frac{\partial\sigma}{\partial|\vec{\nabla}n|} = \frac{1}{|\vec{\nabla}n|}\frac{\partial f_x}{\partial\sigma}2|\vec{\nabla}n| = 2\frac{\partial f_x}{\partial\sigma}$$

$$\frac{1}{|\vec{\nabla}n^\uparrow|}\frac{\partial}{\partial|\vec{\nabla}n^\uparrow|}\left(\frac{1}{|\vec{\nabla}n^\uparrow|}\frac{\partial^2 f_x}{\partial|\vec{\nabla}n^\uparrow|\partial n^\uparrow}\right) = 64\frac{\partial^2 f_x}{\partial n\partial\sigma^2}$$

HOW TO CHECK?

$$E^{(3)}_{xc,n^{(1)}} = \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}''\, n^{(1)}(\mathbf{r})\, n^{(1)}(\mathbf{r}')\, n^{(1)}(\mathbf{r}'')\, \frac{\delta^3 f_{xc}(\mathbf{r})}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}$$

Number of terms to implement :

functional polarization	LDA unpola.	LDA pola.	GGA unpola.	GGA pola.
$(V_{xc}(\mathbf{r}))^{(1)}$	1	2×2	5	2×11
$E^{(3)}_{xc,n^{(1)}}$	1	8	6	24

- with real or complex densities
- with or without core correction
- with or without compensating charge (PAW)
- on FFT grids or PAW spheres (for the latter : 3 different implementations !)

Problem with the usual finite difference tests :

- test only the *total* energy : hard to test individual terms...
- not so cheap in some situations
- precision is not high in PAW, and many terms could be small...

Need of a very quick and precise test for the validation of $E^{(3)}_{xc,n^{(1)}}$ in GGA

HOW TO CHECK?

We define a fictive density (here a distorded gaussian) depending on fictive parameters :

$$n(\mathbf{r}) = Ae^{-B(\mathbf{r}-\mathbf{R})^T M(\mathbf{r}-\mathbf{R})} = Ae^{-B\sum_{\alpha\beta}(r_\alpha - R_\alpha)M_{\alpha\beta}(r_\beta - R_\beta)}$$

we can compute the first derivative of the XC energy analytically or by finite difference :

$$E_{xc}^{(R_\alpha)} = \int d\mathbf{r} n^{(R_\alpha)}(\mathbf{r})V_{xc}(\mathbf{r}) \qquad E_{xc}^{(\Delta R_\alpha)} = \frac{E_{xc}[n_{+\Delta R_\alpha}] - E_{xc}[n_{-\Delta R_\alpha}]}{2R_\alpha}$$

Input :

```
# DFPT TEST : LDA,PAW,unpolarized

#**********************************
# Necessary to activate DFPT_TEST:
optdriver    5
useria       900
#**********************************

# Relevant parameters for DFPT_TEST
#**********************************
   acell 3*10
   rprim 0.8 -0.2  0.0
         0.2 -0.7  0.1
         0.0  0.0 -0.9

   nsym 1

# Only for Norm Conserving pseudos:
     ecut  10
# Only for PAW:
pawecutdg  40

pawxcdev 0

# Irrelevant for DFPT_TEST but mandatory for abinit
#**************************************************
   natom 1
   znucl 13
   xred  0.00  0.00  0.00
```

Output :

```
---------------------------------------------------------
DFPT TEST SUMMARY:
---------------------------------------------------------
cplex  = 1
PAW Pseudo-potlential (without usexcnhat)
With core correction
LDA functional
Unpolarized system
pawxcdev = 0
---------------------------------------------------------
 FFT grid   : densities : success : tol=1.E-09)
 FFT grid   : exc1      : success : tol=1.E-07)
 FFT grid   : vxc1      : success : tol=1.E-04)
 FFT grid   : exc2      : success : tol=1.E-09)
 FFT grid   : exc3      : success : tol=1.E-07)
---------------------------------------------------------
 FFT grid   : all       : success
---------------------------------------------------------
 PAW Sphere : densities : success : tol=1.E-09)
 PAW Sphere : exc1      : success : tol=1.E-09)
 PAW Sphere : vxc1      : success : tol=1.E-05)
 PAW Sphere : exc2      : success : tol=1.E-09)
 PAW Sphere : exc3      : success : tol=1.E-09)
---------------------------------------------------------
 PAW Sphere : all       : success
---------------------------------------------------------
```

A set of 18 tests is added to the testsuite ("dfpt_test") : different functionals, polarization, etc...
The 18 tests are done in 35 seconds on a laptop (1 CPU), for a relative error of 10^{-7} or lower on energies (10^{-4} on potentials).
⇒ Can be easily extended to magnetic case (nspden=4) or metaGGA functionals (local part only).

CONCLUSION

Current status

- metaGGA + PAW in the next ABINIT version
- Including stress tensor (was not available in NCPP)
- Link with libXC 5.1 in the next version
- A set of automatic tests for XC derivatives

Next to come

- Raman intensities + GGA
- Need to finish the implementation and check

Upcoming plans

- metaGGGA + 2nd order DFPT

Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr

- Every function which integrates as E^{KIN} is a kinetic energy density
  Choose which one?

$$\tau_1(\mathbf{r}) = -\frac{1}{2}\sum_i \psi_i^*(\mathbf{r})\,\vec{\nabla}^2\psi_i(\mathbf{r})$$

From kinetic operator

$$\tau_2(\mathbf{r}) = +\frac{1}{2}\sum_i \left|\vec{\nabla}\psi_i(\mathbf{r})\right|^2$$

Commonly Used

$$\int \vec{\nabla}^2 n(\mathbf{r})\, d\mathbf{r} = 0$$

$$\tau_1(\mathbf{r}) = \tau_2(\mathbf{r}) - \frac{1}{4}\vec{\nabla}^2 n(\mathbf{r})$$

- Within (scalar-)relativistic scheme, what is the definition of $\tau(\mathbf{r})$?

$$\tau_{rel}(\mathbf{r}) = \sum_i [\varepsilon_i - V_{xc}(\mathbf{r}) - V_H(\mathbf{r}) - V_{ext}(\mathbf{r})]\, |\psi_i(\mathbf{r})|^2$$

Like τ_1

$$\tau_{rel}(\mathbf{r}) \simeq c^2\, n(\mathbf{r}) \left[1 + \frac{2\tau(\mathbf{r})}{c^2\, n(\mathbf{r})}\right]^{\frac{1}{2}}$$

Like τ_2

See: Sim, Larkin, Burke, Bock, *J. Chem. Phys*. **118**, 8140 (2003)
Becke, *J. Chem. Phys*. **131**, 244118 (2009)

Testing the kinetic energy density functional against LDA

Use a modified value for the electron mass:
$m_e = \widetilde{m}_e$ *instead of* $m_e = 1$ *(a.u.)*

$$\varepsilon_{xc}^{MGGA}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + \left(1 - \frac{1}{\widetilde{m}_e}\right)\frac{\tau(\mathbf{r})}{n(\mathbf{r})}$$

$$\frac{\partial f_{xc}^{MGGA}}{\partial \tau}(\mathbf{r}) = \left(1 - \frac{1}{\widetilde{m}_e}\right) \qquad \frac{\partial f_{xc}^{MGGA}}{\partial n}(\mathbf{r}) = V_{xc}^{LDA}(\mathbf{r})$$

$$E^{KIN+XC\,(MGGA)} = \frac{1}{\widetilde{m}_e}E^{KIN} + E_{xc}^{LDA} + \int \left(1 - \frac{1}{\widetilde{m}_e}\right)\tau(\mathbf{r})\,d\mathbf{r} = E^{KIN+XC\,(LDA)}$$

Testing MGGA(Laplacian) against MGGA(KED) against GGA

Use 1 or 2 electronic bands

$$\varepsilon_{xc}^{MGGA1}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + \alpha\,\vec{\nabla}^2 n(\mathbf{r})$$

$$\frac{\partial f_{xc}^{MGGA1}}{\partial n}(\mathbf{r}) = V_{xc}^{LDA}(\mathbf{r}) + \alpha\,\vec{\nabla}^2 n(\mathbf{r})$$

$$\frac{\partial f_{xc}^{MGGA2}}{\partial n}(\mathbf{r}) = V_{xc}^{LDA}(\mathbf{r}) + 2\alpha\,\tau(\mathbf{r})$$

Integration by parts

$$\varepsilon_{xc}^{GGA}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) - \alpha\,\frac{\left|\vec{\nabla} n(\mathbf{r})\right|^2}{n(\mathbf{r})}$$

$$\frac{\partial f_{xc}^{GGA}}{\partial n}(\mathbf{r}) = V_{xc}^{LDA}(\mathbf{r})$$

$$\frac{\partial f_{xc}^{GGA}}{\partial\left|\vec{\nabla} n(\mathbf{r})\right|}(\mathbf{r}) = -2\alpha\left|\vec{\nabla} n(\mathbf{r})\right|$$

$$\varepsilon_{xc}^{MGGA2}(\mathbf{r}) = \varepsilon_{xc}^{LDA}(\mathbf{r}) + 2\alpha\,\tau(\mathbf{r})$$

$$\frac{\partial f_{xc}^{MGGA2}}{\partial\,\vec{\nabla}^2 n}(\mathbf{r}) = \alpha\,n(\mathbf{r})$$

$$\frac{\partial f_{xc}^{MGGA2}}{\partial \tau(\mathbf{r})}(\mathbf{r}) = 2\alpha\,n(\mathbf{r})$$

Can mix all approaches

$$E_{xc}^{MGGA1} = E_{xc}^{LDA} + \alpha\int n(\mathbf{r})\vec{\nabla}^2 n(\mathbf{r})d\mathbf{r} = E_{xc}^{LDA} - \alpha\int\left|\vec{\nabla} n(\mathbf{r})\right|^2 d\mathbf{r} = E_{xc}^{GGA} = E_{xc}^{MGGA2}$$