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FROM RESEARCH TO INDUSTRY

DFPT: Extending the 1st-order PAW Hamiltonian to GGA+SOC

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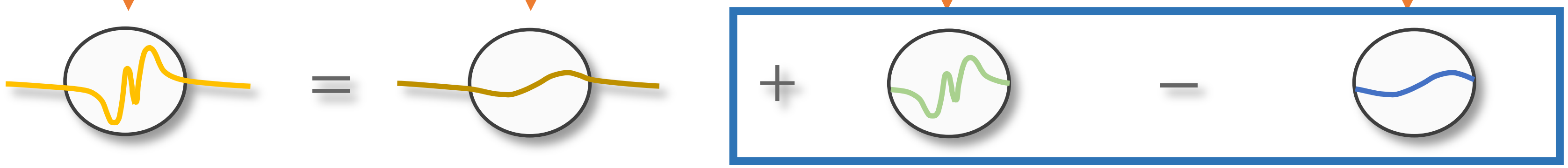
OUTLINE

- PAW on-site contributions
- Non-collinear magnetism within PAW
- DFPT within PAW
- Symmetries issue
- DFPT and GGA within PAW
- Taylor expansion of PAW exchange-correlation potential

PROJECTOR AUGMENTED-WAVE

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



PAW on-site contributions

From Norm-Conserving Pseudo-potentials to PAW

- Non-orthogonality of the pseudo-wavefunctions
- Use of a compensation charge density
- Self-consistency of the non-local operator
- Additional on-site contributions on partial wave basis

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

D_{ij}^R is the expression of **H** in the partial wave basis

$$\boldsymbol{D_{ij}^R} \coloneqq \langle \phi_i^R | -½\Delta + v_{Hxc}(n_1^R; n_c) | \phi_j^R \rangle - \langle \tilde{\phi}_i^R | -½\Delta + \tilde{v}_{Hxc}(\tilde{n}_1^R; \tilde{n}_c) | \tilde{\phi}_j^R \rangle$$

$n_1^R(\mathbf{r})$ and $\tilde{n}_1^R(\mathbf{r})$ are « on-site densities »

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \tilde{\psi}_n^*(\mathbf{r})\, \tilde{\psi}_n(\mathbf{r})$$

$$n_1^R(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R\, \phi_i(\mathbf{r})\, \phi_j(\mathbf{r})$$

$$\tilde{n}_1^R(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R\, \tilde{\phi}_i(\mathbf{r})\, \tilde{\phi}_j(\mathbf{r})$$

$\rho_{\mathrm{ij}}^{\mathrm{R}}$ is the occupancy matrix

$$\boldsymbol{\rho_{ij}^R} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i^R \rangle \langle \tilde{p}_j^R | \tilde{\psi}_n \rangle$$

PAW ON-SITE KEY QUANTITIES

$$\boldsymbol{\rho^R_{ij}} = \sum_n f_n \langle\tilde{\psi}_n|\tilde{p}^R_i\rangle\langle\tilde{p}^R_j|\tilde{\psi}_n\rangle$$

→ Time consuming!

$$\boldsymbol{D^R_{ij}} := \langle\phi^R_i| -½\Delta + \boldsymbol{v_{Hxc}(n^R_1; n_c)}|\phi^R_j\rangle - \langle\tilde{\phi}^R_i| -½\Delta + \tilde{v}_{Hxc}(\tilde{n}^R_1;\tilde{n}_c)|\tilde{\phi}^R_j\rangle$$

$$v_{xc}(n^R_1 + n_c)(\mathbf{r}) = v_{xc}\left(\sum_{i,j} \rho^R_{ij}\,\phi_i(\mathbf{r})\,\phi_j(\mathbf{r}) + n_c\right) = \sum_{lm} v^R_{xc\,lm}(r)\,Y_{lm}(\hat{r})$$

- ρ^R_{ij} is hermitian (only real part needed) and D^R_{ij} is symmetric
- The PAW on-site energy $E_{PAW} = \sum_{R,ij} \rho^R_{ij} D^R_{ij}$ is real!

packed

- ρ^R_{ij} in ABINIT: `pawrhoij(atom)%rhoijp(ij,spin)`
- D^R_{ij} in ABINIT: `paw_ij(atom)%dij(ij,spin)`

Wave function

$$|\psi_n\rangle = \sum_{\alpha} \psi_n^{\alpha} \, |\alpha> = \begin{pmatrix} |\psi_n^1 > \\ |\psi_n^2 > \end{pmatrix} \qquad \sum_{\beta} \mathbf{H}_{PAW}^{\alpha\beta} \left|\psi_n^{\beta} > \right. = \varepsilon_n \, \mathbf{S}^{\alpha\alpha} \, |\psi_n^{\alpha} >$$

Density

$$\tilde{n}(\mathbf{r}) = \sum_{n} f_n \, \tilde{\psi}_n^*(\mathbf{r}) \, \tilde{\psi}_n(\mathbf{r}) = \begin{pmatrix} \tilde{n}^{11}(\mathbf{r}) & \tilde{n}^{12}(\mathbf{r}) \\ \tilde{n}^{21}(\mathbf{r}) & \tilde{n}^{22}(\mathbf{r}) \end{pmatrix} \qquad \tilde{n}^{\alpha\beta}(\mathbf{r}) = \sum_{n} f_n \, \tilde{\psi}_n^{\beta\,*}(\mathbf{r}) \, \tilde{\psi}_n^{\alpha}(\mathbf{r})$$

Magnetization

$$\begin{cases} \tilde{n}(\mathbf{r}) = \sum_{\alpha} \tilde{n}^{\alpha\alpha}(\mathbf{r}) \\ \vec{\tilde{m}}(\mathbf{r}) = \sum_{\alpha\beta} \tilde{n}^{\alpha\beta}(\mathbf{r}) \, \vec{\sigma}^{\beta\alpha} \end{cases} \Rightarrow \begin{cases} \tilde{n}(\mathbf{r}) = \sum_{\alpha} \tilde{n}^{\alpha\alpha}(\mathbf{r}) \\ \vec{\tilde{m}}(\mathbf{r}) = \sum_{\alpha\beta} \tilde{n}^{\alpha\beta}(\mathbf{r}) \, \vec{\sigma}^{\beta\alpha} \end{cases}$$

$\vec{\sigma}^{\beta\alpha}$ → Pauli Matrixes

NON-COLLINEAR MAGNETISM AND PAW

Hobbs, Kresse, Hafner, PRB **62**, 11556 (2000)

On-site densities

$$\begin{cases} n_1^R(\mathbf{r}) = \sum_{\alpha} n_1^{R,\alpha\alpha}(\mathbf{r}) \\ \vec{m}_1^R(\mathbf{r}) = \sum_{\alpha\beta} n_1^{R,\alpha\beta}(\mathbf{r})\, \vec{\sigma}^{\beta\alpha} \end{cases} \Rightarrow \begin{cases} n_1^R(\mathbf{r}) = \sum_{\alpha}\sum_{i,j} \rho_{ij}^{R\,\alpha\alpha}\, \phi_i(\mathbf{r})\, \phi_j(\mathbf{r}) \\ \vec{m}_1^R(\mathbf{r}) = \sum_{\alpha\beta}\sum_{i,j} \rho_{ij}^{R\,\alpha\beta}\, \phi_i(\mathbf{r})\, \phi_j(\mathbf{r})\; \vec{\sigma}^{\beta\alpha} \end{cases}$$

Occupancy matrix

$$\boldsymbol{\rho}_{ij}^{\alpha\beta\,R} = \sum_n f_n \left\langle \tilde{\psi}_n^{\beta} \middle| \tilde{p}_i^R \right\rangle \left\langle \tilde{p}_j^R \middle| \tilde{\psi}_n^{\alpha} \right\rangle \;\Rightarrow\; \boldsymbol{\rho}_{ij}^{R} = \sum_\alpha \rho_{ij}^{R\,\alpha\alpha}\,,\quad \vec{\boldsymbol{m}}_{ij}^{R} = \sum_{\alpha\beta} \rho_{ij}^{R\,\alpha\beta}\, \vec{\sigma}^{\beta\alpha}$$

NL Hamiltonian

$$\begin{aligned} \boldsymbol{D}_{ij}^{\alpha\beta\,R} := & \left\langle \phi_i^R \middle| [-\tfrac{1}{2}\Delta + v_H(n_1^R + n_c)]\delta_{\alpha\beta} + \boldsymbol{v}_{xc}\left(\boldsymbol{n}_1^{R\,\alpha\beta} + \boldsymbol{n}_c\right) \middle| \phi_j^R \right\rangle \\ & - \left\langle \tilde{\phi}_i^R \middle| [-\tfrac{1}{2}\Delta + v_H(\tilde{n}_1^R + \tilde{n}_c + \hat{n})]\delta_{\alpha\beta} + \tilde{v}_{xc}\left(\tilde{n}_1^{R\,\alpha\beta} + \tilde{n}_c\right) \middle| \tilde{\phi}_j^R \right\rangle \end{aligned}$$

Hamiltonian

$$\boldsymbol{D_{ij}^{\alpha\beta\,R}} := \left\langle \phi_i^R \middle| [-½\Delta \ + v_H(n_1^R + n_c)]\delta_{\alpha\beta} + v_{xc}\left(n_1^{R\,\alpha\beta} + n_c\right) \middle| \phi_j^R \right\rangle$$
$$- \left\langle \tilde{\phi}_i^R \middle| [-½\Delta + v_H(\tilde{n}_1^R + \tilde{n}_c + \hat{n})]\delta_{\alpha\beta} + \tilde{v}_{xc}\left(\tilde{n}_1^{R\,\alpha\beta} + \tilde{n}_c\right) \middle| \tilde{\phi}_j^R \right\rangle$$
$$+ \left\langle \phi_i^R \middle| \boldsymbol{v_{SOC}^{\alpha\beta}(n_1^R + n_c)} \middle| \phi_j^R \right\rangle$$

$$\left\langle \boldsymbol{\alpha, \phi_i^R} \middle| \boldsymbol{\frac{\hbar^2}{2m_e^2c^2} \frac{1}{r} \frac{dV(n_1^R)}{dr} (\vec{L}\cdot\vec{S})} \middle| \boldsymbol{\beta, \phi_j^R} \right\rangle$$

2 approximations:

- Potential is quasi-spherical
- Density is mainly in PAW regions

$$\frac{\hbar^2}{2m_e^2c^2} \frac{1}{\sqrt{4\pi}} \left\langle \alpha, Y_{l_i m_i} \middle| (\vec{L}\cdot\vec{S}) \middle| \beta, Y_{l_j m_j} \right\rangle \int_{\Omega_R} dr \, \frac{1}{r}\frac{dV_0(r)}{dr} \, \phi_i^R(r)\phi_j^R(r)$$

Complex quantity

PAW KEY QUANTITIES AND SOC

- The PAW on-site energy should be real:

$$\sum_{R,ij}\sum_{\alpha,\beta}\rho_{ij}^{R\,\alpha\beta}D_{ij}^{R\,\beta\alpha}$$

- The symmetry relations are:

$$\boldsymbol{\rho_{ij}^{R\,\alpha\beta} = \rho_{ji}^{R\,\beta\alpha} \Rightarrow \rho_{ij}^{R} = \rho_{ji}^{R}\,,\vec{m}_{ij}^{R} = \vec{m}_{ji}^{R}}$$

$$\boldsymbol{D_{ij}^{R\,\alpha\beta} = D_{ji}^{R\,\beta\alpha}}$$

- $\rho_{ij}^{R}, \vec{m}_{ij}^{R}$ in ABINIT: `pawrhoij(atom)%rhoijp(2× ij,1:4)`
- $D_{ij}^{\alpha\beta\,R}$ in ABINIT: `paw_ij(atom)%dij(2× ij,1:4)`

Complex

DFPT basics

λ small perturbation

$$X^{(i)} = \frac{1}{i!}\frac{d^i X}{d\lambda^i}$$

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \cdots$$

2N+1 theorem

$$E^{(2p)} = \min_{\psi^{(p)}_{m,trial}} \left(E\left[\sum_{i=0}^{p-1} \lambda^i \psi_m^{(i)} + \lambda^p \psi^{(p)}_{m,trial}, \lambda \right] \right)$$

Sternheimer equation

$$P_c^* \left(\mathbf{H}^{(0)}_{PAW} - \varepsilon_n^{(0)} \mathbf{S}^{(0)} \right) P_c \left| \tilde{\psi}_n^{(1)} \right\rangle = -P_c^* \left(\mathbf{H}^{(1)}_{PAW} - \varepsilon_n^{(0)} \mathbf{S}^{(1)} \right) P_c \left| \tilde{\psi}_n^{(0)} \right\rangle$$

Parallel transport gauge

$$\sum_{i=0}^{p} \left\langle \tilde{\psi}_n^{(p-i)} \middle| \tilde{\psi}_m^{(i)} \right\rangle = 0$$

$$v_{\mathrm{ext}}^{(0)}(\mathbf{r}+\mathbf{R}_a,\mathbf{r}'+\mathbf{R}_a) = v_{\mathrm{ext}}^{(0)}(\mathbf{r},\mathbf{r}')$$

$$v_{\mathrm{ext},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a,\mathbf{r}'+\mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a}\ v_{\mathrm{ext},\mathbf{q}}^{(1)}(\mathbf{r},\mathbf{r}')$$

$$\psi_{n,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a) = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_a}\ \psi_{n,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})$$

$$X(\lambda) = X^{(0)} + \left(\lambda X_{\mathbf{q}}^{(1)} + \lambda^* X_{-\mathbf{q}}^{(1)}\right) + \left(\lambda^2 X_{\mathbf{q},\mathbf{q}}^{(2)} + \lambda\lambda^* X_{\mathbf{q},-\mathbf{q}}^{(2)} + \lambda^*\lambda X_{-\mathbf{q},\mathbf{q}}^{(2)} + \lambda^{*2} X_{-\mathbf{q},-\mathbf{q}}^{(2)}\right) + \cdots$$

Trick:
Factorisation of the phase

$$\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) = e^{-i\mathbf{q}\cdot\mathbf{r}} n_{\mathbf{q}}^{(1)}(\mathbf{r})$$

$$\boldsymbol{\rho}_{ij,\mathbf{q}}^{R\,(1)} = \sum_n f_n \left[\left\langle \tilde{\psi}_{n,\mathbf{q}}^{(1)} \middle| \tilde{p}_i^R \right\rangle \left\langle \tilde{p}_j^R \middle| \tilde{\psi}_n^{(0)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{p}_i^R \right\rangle \left\langle \tilde{p}_j^R \middle| \tilde{\psi}_{n,\mathbf{q}}^{(1)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| \left(\tilde{p}_i^R >< \tilde{p}_j^R \right)_{\mathbf{q}}^{(1)} \middle| \tilde{\psi}_n^{(0)} \right\rangle \right]$$

- $\mathbf{q}$-periodicity of $\tilde{\psi}_{n,\mathbf{q}}^{(1)}$
- Factorisation of the phase

$$\Rightarrow \quad \bar{\rho}_{ij,\mathbf{q}}^{R\,(1)} = e^{-i\mathbf{q}\cdot\mathbf{R}_a} \rho_{ij,\mathbf{q}}^{R\,(1)}$$

$$\Rightarrow \quad \bar{D}_{ij,\mathbf{q}}^{R\,(1)} = e^{-i\mathbf{q}\cdot\mathbf{R}_a} D_{ij,\mathbf{q}}^{R\,(1)}$$

Complex

- The PAW 2nd-order on-site energy is:

$$E^{(2)}_{PAW,\mathbf{q}} = \sum_{R,ij} \bar{\rho}^{R\,(1)}_{ij,\mathbf{q}}\ \bar{D}^{R\,(1)}_{ij,\mathbf{q}} + \left.\frac{\partial \rho^R_{ij}}{\partial\lambda}\right|^{(2)}_{\psi^{(0)}} D^R_{ij} + \rho^R_{ij}\left.\frac{\partial D^R_{ij}}{\partial\lambda}\right|^{(2)}_{\psi^{(0)}}$$

- The symmetry relations are:

$$\bar{\boldsymbol{\rho}}^{R\,(1)}_{ij,\mathbf{q}} = \bar{\boldsymbol{\rho}}^{R\,(1)}_{ji,-\mathbf{q}}$$

$$\bar{\boldsymbol{D}}^{R\,(1)}_{ij,\mathbf{q}} = \bar{\boldsymbol{D}}^{R\,(1)}_{ji,-\mathbf{q}}$$

$\Longrightarrow$ Problem!
To have the full matrixes, we need to compute two **q**-vectors

or… change the structure of the PAW code

Using a trick related to the symmetry of the imaginary part

- $\rho^{R\,(1)}_{ij,\mathbf{q}}$ in ABINIT: `pawrhoij1(atom)%rhoijp(2× ij,spin)`
- $D^{R\,(1)}_{ij,\mathbf{q}}$ in ABINIT: `paw_ij1(atom)%dij(2× ij,spin)`

Complex

AND NOW: PAW QUANTITIES AND NC MAGNETISM (SOC) AND DFPT!

- How to have a storage compatible with symmetries and imaginary numbers?

  How to use existing routines?

  And mix

$$\rho_{ij}^{R\,\alpha\beta} = \rho_{ji}^{R\,\beta\alpha} \Rightarrow \rho_{ij}^{R} = \rho_{ji}^{R}\,,\ \vec{m}_{ij}^{R} = \vec{m}_{ji}^{R}$$

$$D_{ij}^{R\,\alpha\beta} = D_{ji}^{R\,\beta\alpha}$$

→ Complex due to SOC

and

$$\overline{\rho}_{ij,\mathrm{q}}^{R\,(1)} = \overline{\rho}_{ji,-\mathrm{q}}^{R\,(1)}$$

$$\overline{D}_{ij,\mathrm{q}}^{R\,(1)} = \overline{D}_{ji,-\mathrm{q}}^{R\,(1)}$$

→ Complex phase

$$\rho_{ij,\mathrm{q}}^{R\,\alpha\beta\,(1)} = \rho_{ji,-\mathrm{q}}^{R\,\beta\alpha\,(1)} \Rightarrow \rho_{ij,\mathrm{q}}^{R\,(1)} = \rho_{ji,\mathrm{q}}^{R\,(1)}\,,\ \vec{m}_{ij,\mathrm{q}}^{R\,(1)} = \vec{m}_{ji,\mathrm{q}}^{R\,(1)}$$

$$D_{ij,\mathrm{q}}^{R\,\alpha\beta\,(1)} = D_{ji,-\mathrm{q}}^{R\,\beta\alpha\,(1)}$$

$$\boldsymbol{\rho}_{\boldsymbol{ij},\mathbf{q}}^{\boldsymbol{R}\,(\mathbf{1})} = \left[\boldsymbol{A}_{\boldsymbol{ij}}^{\mathbf{R}} + \boldsymbol{i}\boldsymbol{A}_{\boldsymbol{ij}}^{\mathbf{I}}\right]\cos(q\mathbf{R}_{\boldsymbol{a}}) + i\cdot\left[\boldsymbol{B}_{\boldsymbol{ij}}^{\mathbf{R}} + \boldsymbol{i}\boldsymbol{B}_{\boldsymbol{ij}}^{\mathbf{I}}\right]\sin(q\mathbf{R}_{\boldsymbol{a}})$$

Imaginary number due to SOC

DFPT phase

Similar storage for $\vec{m}_{ij,\boldsymbol{q}}^{R\,(1)}$ and $D_{ij,\boldsymbol{q}}^{R\,\alpha\beta\,(1)}$

- $\boldsymbol{A}_{\boldsymbol{ij}}^{\mathbf{R}}, \boldsymbol{A}_{\boldsymbol{ij}}^{\mathbf{I}}, \boldsymbol{B}_{\boldsymbol{ij}}^{\mathbf{R}}, \boldsymbol{B}_{\boldsymbol{ij}}^{\mathbf{I}}$ have the single *ij* symmetry of the initial coding
- All initial routines can be reused, with small changes
- The ρ_{ij}^{R} symmetrization routine is applied on each 4 components

- $\rho_{ij,\mathbf{q}}^{R\,(1)}, \vec{m}_{ij,\mathbf{q}}^{R\,(1)}$ in ABINIT

  `pawrhoij1(atom)%rhoijp(`**`cplex_rhoij`**`×` **`qphase`**`× nlmn,1:nspden)`

- $D_{ij,\mathbf{q}}^{R\,\alpha\beta\,(1)}$ in ABINIT

  `paw_ij1(atom)%dij(`**`cplex_dij`**`×` **`qphase`**`× nlmn,1:nspden)`

With this internal representation…

- We do not change libPAW interfaces
  Other codes do not have to change (for single GS calc.)
- A generic `pawaccenergy` routine has been created and is used for all $\sum_{ij} \rho_{ij} D_{ij}$-like accumulations.
- Changes in existing code have been few

- First-order change of the XC potential (factorized phase)

$$\bar{v}_{xc,\mathbf{q}}^{(1)}(\mathbf{r}) = \left.\frac{dv_{xc}}{dn}\right|_{n^{(0)}(\mathbf{r})} \left(\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) + \bar{n}_{c,\mathbf{q}}^{(1)}(\mathbf{r})\right)$$

- Spin-polarized LDA

$$\bar{v}_{xc,\mathbf{q}}^{\uparrow\,(1)}(\mathbf{r}) = \left.\frac{d^2 f_{xc}}{dn^{\uparrow} dn^{\uparrow}}\right|_{n^{(0)}(\mathbf{r})} \bar{n}_{\mathbf{q}}^{\uparrow\,(1)}(\mathbf{r}) + \left.\frac{d^2 f_{xc}}{dn^{\uparrow} dn^{\downarrow}}\right|_{n^{(0)}(\mathbf{r})} \bar{n}_{\mathbf{q}}^{\downarrow\,(1)}(\mathbf{r})$$

- Non-collinear LDA – *See E. Bousquet's talk*

$$v_{xc,\mathbf{q}}^{(1)}(\mathbf{r}) = \frac{1}{2}\left(\left.\frac{d^2 f_{xc}}{dn^{\uparrow} dn^{\uparrow}}\right|_{n^{(0)}} \left(\frac{\bar{n}_{\mathbf{q}}^{\uparrow\,(1)} + \bar{m}_{z,\mathbf{q}}^{\uparrow\,(1)}}{2}\right) + \left.\frac{d^2 f_{xc}}{dn^{\downarrow} dn^{\downarrow}}\right|_{n^{(0)}} \left(\frac{\bar{n}_{\mathbf{q}}^{\uparrow\,(1)} - \bar{m}_{z,\mathbf{q}}^{\uparrow\,(1)}}{2}\right) + \left.\frac{d^2 f_{xc}}{dn^{\uparrow} dn^{\downarrow}}\right|_{n^{(0)}} \bar{n}_{\mathbf{q}}^{(1)} \right)$$

- XC potential

$$\bar{v}_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \vec{\nabla} \cdot \frac{\partial f_{xc}}{\partial \vec{g}} \qquad \vec{g} = \vec{\nabla} n$$

- 1st-order change of XC potential (factorized phase, polarized)

$$\bar{v}_{xc,\mathbf{q}}^{\uparrow(1)} =$$

$$\left[\frac{\partial^2 f_{xc}}{\partial n^\uparrow \partial n^\uparrow} \bar{n}_{\mathbf{q}}^{\uparrow\,(1)} + \frac{\partial^2 f_{xc}}{\partial n^\uparrow \partial n^\downarrow} \bar{n}_{\mathbf{q}}^{\downarrow\,(1)} + \frac{\partial^2 f_{xc}}{\partial n^\uparrow \partial g^\uparrow} \frac{\vec{g}^\uparrow \cdot \vec{\bar{g}}_{\mathbf{q}}^{\uparrow\,(1)}}{g^\uparrow} + \frac{\partial^2 f_{xc}}{\partial n^\uparrow \partial g^\downarrow} \frac{\vec{g}^\downarrow \cdot \vec{\bar{g}}_{\mathbf{q}}^{\downarrow\,(1)}}{g^\downarrow}\right]$$

$$-\vec{\nabla} \cdot \left[\begin{array}{c} \left(\frac{1}{g^\uparrow}\frac{\partial f_x}{\partial g^\uparrow} + \frac{1}{g}\frac{\partial f_c}{\partial g}\right) \vec{\bar{g}}_{\mathbf{q}}^{\uparrow\,(1)} + \frac{1}{g}\frac{\partial f_c}{\partial g} \vec{\bar{g}}_{\mathbf{q}}^{\downarrow\,(1)} \\ + \left(\frac{1}{g^\uparrow}\frac{\partial^2 f_x}{\partial g^\uparrow \partial n^\uparrow} \bar{n}_{\mathbf{q}}^{\uparrow\,(1)} + \frac{\partial}{\partial g^\uparrow}\left[\frac{1}{g^\uparrow}\frac{\partial f_x}{\partial g^\uparrow}\right] \frac{\vec{g}^\uparrow \cdot \vec{\bar{g}}_{\mathbf{q}}^{\uparrow\,(1)}}{g^\uparrow}\right) \vec{g}^\uparrow \\ + \left(\frac{1}{g}\frac{\partial^2 f_c}{\partial g \partial n^\uparrow} \bar{n}_{\mathbf{q}}^{\uparrow\,(1)} + \frac{1}{g}\frac{\partial^2 f_c}{\partial g \partial n^\downarrow} \bar{n}_{\mathbf{q}}^{\downarrow\,(1)} + \frac{\partial}{\partial g}\left[\frac{1}{g}\frac{\partial f_c}{\partial g}\right] \frac{\vec{g} \cdot \vec{\bar{g}}_{\mathbf{q}}^{(1)}}{g}\right) \vec{g} \end{array}\right]$$

19 GS terms to store

- « Brute force » approach

$$v_{xc}(\mathbf{r}) = v_{xc}(r,\theta,\varphi) = v_{xc}[n(r,\theta,\varphi)]$$

Same formulae as previous slide

- « Taylor development » approach (LDA/GGA version, non polarized)

$$v_{xc}(\mathbf{r}) = v_{xc}[n_s(\mathbf{r})] + [n(\mathbf{r}) - n_s(\mathbf{r})]\frac{dv_{xc}}{dn}\bigg|_{n_s} + \frac{1}{2}[n(\mathbf{r}) - n_s(\mathbf{r})]^2\frac{d^2v_{xc}}{dn^2}\bigg|$$

$$v_{xc}(\mathbf{r}) = \sum_{lm} v_{xc\,lm}(r)\, Y_{lm}(\theta,\varphi)$$

Finite differences

ABINIT keyword **pawxdev**

$$v_{xc\,lm}(r) = \sqrt{4\pi}\, v_{xc}[n_s(\mathbf{r})] + \frac{1}{2\sqrt{4\pi}}\frac{d^2v_{xc}}{dn^2}\bigg|_{n_s} \sum_{l'>0} n_{l'm'}(r)^2 \qquad \text{if } l=0$$

$$v_{xc\,lm}(r) = n_{lm}(r)\,\frac{dv_{xc}}{dn}\bigg|_{n_s} + \frac{1}{2}\frac{d^2v_{xc}}{dn^2}\bigg|_{n_s} \sum_{l'l''>0} n_{l'm'}(r)\, n_{l''m''}(r)\, g^{lm}_{l'm',l''m''}$$

- « Taylor development » approach

$$v_{xc}(\mathbf{r}) = v_{xc}[n_s, \vec{m}_s] + [n - n_s]\left.\frac{dv_{xc}}{dn}\right|_{\substack{n_s \\ \vec{m}_s}} + \frac{[\vec{m} - \vec{m}_s]\cdot\vec{m}_s}{m_s}\left.\frac{dv_{xc}}{dn}\right|_{\substack{n_s \\ \vec{m}_s}}$$
$$+\frac{1}{2}[n(\mathbf{r}) - n_s(\mathbf{r})]^2\left.\frac{d^2v_{xc}}{dn^2}\right|_{\substack{n_s \\ \vec{m}_s}} + \frac{1}{2}\left[\frac{[\vec{m} - \vec{m}_s]\cdot\vec{m}_s}{m_s}\right]^2\left.\frac{d^2v_{xc}}{dn^2}\right|_{\substack{n_s \\ \vec{m}_s}}$$
$$+[n - n_s]\left[\frac{[\vec{m} - \vec{m}_s]\cdot\vec{m}_s}{m_s}\right]^2\left.\frac{d^2v_{xc}}{dndm}\right|_{\substack{n_s \\ \vec{m}_s}}$$

$$v_{xc\,lm}(r) = n_{lm}\left.\frac{dv_{xc}}{dn}\right|_{\substack{n_s \\ \vec{m}_s}} + \frac{\vec{m}_{lm}\cdot\vec{m}_s}{m_s}\left.\frac{dv_{xc}}{dm}\right|_{\substack{n_s \\ \vec{m}_s}} +$$
$$\frac{1}{2}\left.\frac{d^2v_{xc}}{dn^2}\right|_{\substack{n_s \\ \vec{m}_s}}\sum_{l'l''>0}\left[n_{l'm'}\,n_{l''m''}\,g^{lm}_{l'm',l''m''}\right] +$$
$$\frac{1}{2}\left.\frac{d^2v_{xc}}{dm^2}\right|_{\substack{n_s \\ \vec{m}_s}}\sum_{l'l''>0}\left[\frac{(\vec{m}_{l'm'}\cdot\vec{m}_s)(\vec{m}_{l''m''}\cdot\vec{m}_s)}{m_s^2}\,g^{lm}_{l'm',l''m''}\right]$$
$$+\left.\frac{d^2v_{xc}}{dndm}\right|_{\substack{n_s \\ \vec{m}_s}}\sum_{l'l''>0}\left[\frac{n_{l'm'}(\vec{m}_{l''m''}\cdot\vec{m}_s)}{m_s}\,g^{lm}_{l'm',l''m''}\right] \qquad \text{if } l>0$$

$$\bar{v}_{xc,\mathbf{q}}^{\uparrow(1)} = \left[\frac{\partial^2 f_{xc}}{\partial n \partial n}\bar{n}_{\mathbf{q}}^{(1)} + \frac{\partial^2 f_{xc}}{\partial n \partial g}\frac{\vec{g}\cdot\vec{\bar{g}}_{\mathbf{q}}^{(1)}}{g}\right] - \vec{\nabla}\cdot\left[\frac{1}{g}\frac{\partial f_{xc}}{\partial g}\vec{\bar{g}}_{\mathbf{q}}^{\uparrow(1)} + \left(\frac{1}{g}\frac{\partial^2 f_{xc}}{\partial g \partial n}\bar{n}_{\mathbf{q}}^{\uparrow(1)} + \frac{\partial}{\partial g}\left[\frac{1}{g}\frac{\partial f_{xc}}{\partial g}\right]\frac{\vec{g}\cdot\vec{\bar{g}}_{\mathbf{q}}^{(1)}}{g}\right)\vec{g}\right]$$

$$v_{xc,\mathbf{q}\,lm}^{\uparrow(1)}(r) = \int d\Omega\ \bar{v}_{xc,\mathbf{q}}^{\uparrow(1)}(r,\theta,\varphi)Y_{lm}(\theta,\varphi)$$

Non polarized!

- « Taylor development » approach

$$v_{xc,\mathbf{q}\,lm}^{\uparrow(1)}(r) = \sum_{l'm',l''m''}\left\{\left[K_{xc\,l'm'}^{1}\,\bar{n}_{\mathbf{q}\ l''m''}^{(1)} + K_{xc\,l'm'}^{2}\left(\vec{g}\cdot\vec{\bar{g}}_{\mathbf{q}}^{(1)}\right)_{l''m''}\right]\mathcal{G}_{l'm',l''m''}^{lm}\right\}$$

$$-\vec{\nabla}\cdot\left[\sum_{l'm',l''m''}\left\{\left[\left(K_{xc\,l'm'}^{2}\,\bar{n}_{\mathbf{q}\ l''m''}^{(1)} + K_{xc\,l'm'}^{3}\left(\vec{g}\cdot\vec{\bar{g}}_{\mathbf{q}}^{(1)}\right)_{l''m''}\right)\vec{g} + V_{xc\,l'm'}^{g}\left(\vec{\bar{g}}_{\mathbf{q}}^{(1)}\right)_{l''m''}\right]\mathcal{G}_{l'm',l''m''}^{lm}\right\}\right]$$

$$V_{xc}^{g} = \frac{1}{g}\frac{\partial f_{xc}}{\partial g} \qquad K_{xc}^{1} = \frac{\partial^2 f_{xc}}{\partial n \partial n} \qquad K_{xc}^{2} = \frac{1}{g}\frac{\partial^2 f_{xc}}{\partial n \partial g} \qquad K_{xc}^{3} = \frac{1}{g}\frac{\partial}{\partial g}\left[\frac{1}{g}\frac{\partial f_{xc}}{\partial g}\right]$$

PAW WITH DFPT AND GGA AND NC MAGNETISM!

$$\bar{v}_{xc,\mathbf{q}}^{\uparrow(1)}\left(n, n_{\mathbf{q}}^{(1)}, \vec{m}, \vec{m}_{\mathbf{q}}^{(1)}\right)_{lm} = \ \dots$$

FINALLY… A PHONON SPECTRUM

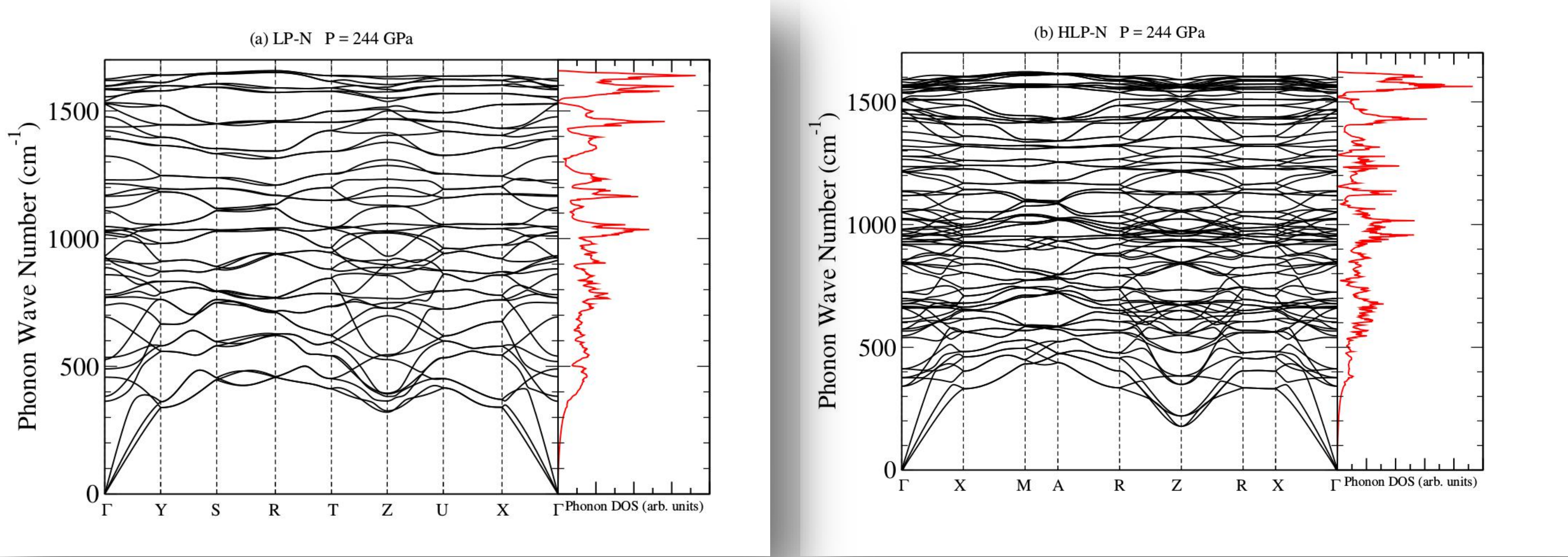
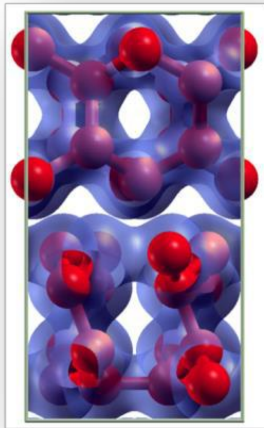


Figure S9: Phonon band structure of the LP-N (a) and HLP-N (b) phases at 244 GPa along with their vibrational DOS. The optical phonons in HLP-N (all but three lowest-frequency modes) at the Γ point are at frequencies between ~340 and ~1600 cm^{-1}.



2 dynamically phases (polymeric) stable
1 is seen experimentally

PAW+DFPT+GGA

Hexagonal Layered Polymeric Nitrogen Phase Synthesized near 250 Gpa,
Laniel, Geneste, Weck, Mezouar, Loubeyre, PRL **122**, 066001 (2019)

- Current status of PAW+DFPT implementation:
  - DFPT+GGA= in ABINIT official version 8.10
  - DFPT+SPINORS= in private version, only for nspden=1
  - DFPT+SOC= in private version, only for nspden=1
  - DFPT+SOC+GGA= in private version, only for nspden=1
- Private version will be merged soon, after more checking
- Available for all perturbations, except strain perturbation, including incommensurate perturbations
- Separately, each formalism is not so complicated
  But all together, implementation becomes heavy:
  PAW+DFPT+SPINORS+SOC+GGA
- Change of internal PAW datastructures was necessary
- On-going developments (first in “brute force” approach)
  - meta-GGA
  - GGA+3rd order DFPT