*3rd International ABINIT developer Workshop*

*January 29 – 31, 2007*
*LIEGE, Belgium*

# IMPLEMENTATION OF THE LINEAR RESPONSE WITHIN PAW

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# Summary

- ✓ Recalls: DFPT formalism — PAW method
- ✓ DFTP and PAW
- ✓ Implementation in ABINIT
- ✓ Example: Frozen WF term of dynamical matrix
- ✓ Conclusion — *Done / To be done*

# The DFPT formalism – 1

*Density-functional Perturbation Theory*

From a non-perturbed system ( $E^{(0)}, \psi_m^{(0)}, n^{(0)}(r)$ ), we want to get the responses with respect to a perturbation λ...

Any physical quantity X is expanded as:

$$X[\lambda] = X^{(0)} + \lambda \cdot X^{(1)} + \lambda^2 \cdot X^{(2)} + \cdots \quad \text{with } X^{(i)} = \frac{1}{i!}\left(\frac{d^i}{d\lambda^i} X\right)_{\lambda=0}$$

Have to compute: $E^{(i)}, \psi_m^{(i)}, n^{(i)}(r), \quad \forall i \geq 1$

DFPT, *2n+1* theorem (Gonze et al, 1995):

$$E^{(2n+1)} = \left( E\left[ \sum_{i=0}^{n} \lambda^i \psi_m^{(i)}, \lambda \right] \right)^{(2n+1)}$$

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

*Normalization condition:*

$$\sum_{i=0}^{n} \left\langle \psi_m^{(n-i)} \middle| \psi_{m'}^{(i)} \right\rangle = 0$$

# The DFPT formalism - 2

Application: *from* $\psi_n^{(0)}$ get $E^{(0)}$, $E^{(1)}$

*from* $\psi_n^{(0)}$ and $\psi_n^{(1)}$ get $E^{(0)}$, $E^{(1)}$, $E^{(2)}$

$\psi_{nk}^{(0)}$ comes from DFT calculation;

How to get $\psi_{nk}^{(1)}$ ?

*Sternheimer* equations

First order Schrodinger equation: $\left(H^{(0)}-\varepsilon_n^{(0)}\right)\left|\psi_n^{(1)}\right\rangle = -\left(H^{(1)}-\varepsilon_n^{(1)}\right)\left|\psi_n^{(0)}\right\rangle$

and projection on subspace $\perp$ to $\psi_n^{(0)}$:

$$P_c\left(H^{(0)}-\varepsilon_n^{(0)}\right)P_c\left|\psi_n^{(1)}\right\rangle = -P_c\left(H^{(1)}-\varepsilon_n^{(1)}\right)\left|\psi_n^{(0)}\right\rangle$$

$$P_c = I - \sum_{m=1}^{N}\left|\psi_m^{(0)}\right\rangle\left\langle\psi_m^{(0)}\right|$$

# The DFPT formalism and norm-conserving PS

Total energy and derivatives

$$E^{(0)} = \sum_n^{occ} \left\{ \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}^{(0)} \middle| \tilde{\psi}_n^{(0)} \right\rangle \right\} + \frac{1}{2} \int V_{Hxc}^{(0)}\left(\tilde{n}^{(0)}\right) \cdot \tilde{n}^{(0)}(\vec{r}\,')\, d\vec{r}\,' d\vec{r}$$

$$E^{(2)} = \sum_n^{occ} \left\{ \left\langle \tilde{\psi}_n^{(1)} \middle| \tilde{H}^{(0)} - \varepsilon_n^{(0)} \middle| \tilde{\psi}_n^{(1)} \right\rangle + \left\langle \tilde{\psi}_n^{(1)} \middle| \tilde{H}^{(1)} \middle| \tilde{\psi}_n^{(0)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}^{(1)} \middle| \tilde{\psi}_n^{(1)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| V_{PS}^{(2)} \middle| \tilde{\psi}_n^{(0)} \right\rangle \right\}$$
$$+ \frac{1}{2} \int V_{Hxc}^{(1)}\left(\tilde{n}^{(0)}\right) \cdot \tilde{n}^{(1)}(\vec{r}\,')\, d\vec{r}\,' d\vec{r}$$

$$\tilde{H}^{(0)} = T + V_{Hxc}^{(0)}\left(\tilde{n}^{(0)}\right) + \underbrace{V_{loc}^{(0)} + \sum_{\mathrm{R},i} \left| \tilde{p}_i^{\mathrm{R}} \right\rangle D_i^0 \left\langle \tilde{p}_i^{\mathrm{R}} \right|}_{V_{PS}^{(0)}}$$

$D_i^0 \rightarrow E_i^{KB}$

$$\tilde{H}^{(1)} = V_{Hxc}^{(1)} + V_{loc}^{(1)} + \int \frac{\delta V_{Hxc}}{\delta \tilde{n}}\left(\tilde{n}^{(0)}\right) \cdot \tilde{n}^{(1)} + \left( \sum_{\mathrm{R},i} \left| \tilde{p}_i^{\mathrm{R}} \right\rangle D_i^0 \left\langle \tilde{p}_i^{\mathrm{R}} \right| \right)^{(1)}$$

$$V_{PS}^{(2)} = V_{Hxc}^{(2)} + V_{loc}^{(2)} + \left( \sum_{\mathrm{R},i} \left| \tilde{p}_i^{\mathrm{R}} \right\rangle D_i^0 \left\langle \tilde{p}_i^{\mathrm{R}} \right| \right)^{(2)}$$

# PAW – Magic formulas

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle \tilde{p}_i | \tilde{\psi}_n\rangle$$

$$\tilde{H}|\tilde{\psi}_n\rangle = \varepsilon_n S |\tilde{\psi}_n\rangle$$

$$S = 1 + \sum_{R,ij} |\tilde{p}_i\rangle s_{ij} \langle \tilde{p}_j|$$

$$\tilde{H} = T + V_{Hxc} + V_{loc} + \sum_{i,j} |\tilde{p}_i\rangle D_{ij} \langle \tilde{p}_j|$$

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

$$D_{ij} = D_{ij}^0 + \sum_{kl} \rho_{kl} E_{ijkl} + D_{ij}^{xc} + \sum_L \int_{R^3} [V_{Hxc} + V_{loc}](\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

$$E = \tilde{E} + \sum_R \left( E_R^1 - \tilde{E}_R^1 \right)$$

$$\tilde{E} = \sum_n \langle \tilde{\psi}_n | T | \tilde{\psi}_n \rangle + E_{Hxc}[\tilde{n} + \hat{n}] + \int V_{loc} \cdot (\tilde{n} + \hat{n})$$

$$E_R^1 = \sum_{ij} \rho_{ij} \langle \phi_i | T | \phi_i \rangle + E_{Hxc}[n_1] + \int_{\Omega_R} V_{loc} \cdot (n_1)$$

$$\tilde{E}_R^1 = \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | T | \tilde{\phi}_i \rangle + E_{Hxc}[\tilde{n}_1 + \hat{n}] + \int_{\Omega_R} V_{loc} \cdot (\tilde{n}_1 + \hat{n})$$

$$n_1 = \sum_{ij} \rho_{ij} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \qquad \hat{n}(\mathbf{r}) = \sum_{ij,L} \rho_{ij} \hat{Q}_{ij}^L(\mathbf{r})$$

# DFPT+PAW – 1

Complete description in:

*C. Audouze, F. Jollet, M. Torrent, X. Gonze, Phys. Rev. B **73**, 235101 (2006)*

*For simplicity,*

*The following quantities are omitted...*

- ✓ Ewald, ion-ion and NLCC contributions to the total energy
- ✓ $V^{ext}$ potential
- ✓ Electronic occupations
- ✓ Core or pseudo-core density in Hartree and XC potentials or energies formulations:

$$V_{Hxc}(n) \quad \text{means} \quad V_H(n) + V_{xc}(n + n_c)$$

$$V_{Hxc}(\tilde{n}) \quad \text{means} \quad V_H(\tilde{n}) + V_{xc}(\tilde{n} + \tilde{n}_c)$$

# DFPT+PAW – 2

First, rewrite total Hamiltonian and total energy in a suitable form for the application of the variation-perturbation theory:

$$E^{(0)} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}_{KV}^{(0)} \middle| \tilde{\psi}_n^{(0)} \right\rangle + \tilde{E}_{Hxc}^{(0)} + E_{Hxc}^{1(0)} - \tilde{E}_{Hxc}^{1(0)}$$

$$\tilde{H}_{KV}^{(0)} = T + V_{loc}^{(0)} + \sum_{R,ij} \left| \tilde{p}_i \right\rangle D_{ij}^{KV} \left\langle \tilde{p}_j \right|$$

$$D_{ij}^{KV} = D_{ij}^0 + \sum_L \int_{R^3} V_{loc}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

$$= D_{ij} - \sum_{kl} \rho_{kl} E_{ijkl} - D_{ij}^{xc} - \sum_L \int_{R^3} V_{Hxc}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

$$\tilde{E}_{Hxc}^{(0)} = \int_{R^3} V_{Hxc}^{(0)}(\tilde{n} + \hat{n}) \cdot (\tilde{n} + \hat{n})$$

$$\tilde{E}_{Hxc}^{1(0)} = \int_{\Omega} V_{Hxc}^{(0)}(\tilde{n}_1 + \hat{n}) \cdot (\tilde{n}_1 + \hat{n})$$

$$E_{Hxc}^{1(0)} = \int_{\Omega} V_{Hxc}^{(0)}(n_1) \cdot n_1$$

$$\rho_{ij} = \sum_n \left\langle \tilde{\psi}_n \middle| \tilde{p}_i \right\rangle \left\langle \tilde{p}_j \middle| \tilde{\psi}_n \right\rangle$$

$$\hat{n}(\mathbf{r}) = \sum_{ij,L} \rho_{ij} \hat{Q}_{ij}^L(\mathbf{r})$$

# DFPT+PAW - 3

$$E^{(1)} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}_{KV}^{(1)} - \varepsilon_n^{(0)} S^{(1)} \middle| \tilde{\psi}_n^{(0)} \right\rangle + \int_{R^3} V_{Hxc}^{(0)}\left(\tilde{n}^{(0)} + \hat{n}^{(0)}\right) \cdot \hat{n}^{(1)} + \int_{\Omega} V_{Hxc}^{(0)}\left(n_1^{(0)}\right) \cdot n_1^{(1)} - \int_{\Omega} V_{Hxc}^{(0)}\left(\tilde{n}_1^{(0)} + \hat{n}^{(0)}\right) \cdot \left(\tilde{n}_1^{(1)} + \hat{n}^{(1)}\right)$$

First order change of total energy

$$\tilde{H}_{KV}^{(1)} = V_{loc}^{(1)} + \left( \sum_{ij} | p_i \rangle D_{ij}^{KV} \langle p_j | \right)^{(1)}$$

$$\sum_{ij} D_{ij}^{KV} \left( | p_i \rangle \langle p_j | \right)^{(1)}$$

$$\sum_{ij} \sum_L \left( \int_{R^3} V_{loc}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \right)^{(1)} | p_i \rangle \langle p_j |$$

# DFPT+PAW - 4

**Second order change of total energy**

$$E^{(2)} = \sum_n \left\{ \begin{aligned} &\left\langle \tilde{\psi}_n^{(1)} \middle| \tilde{H}^{(0)} - \varepsilon_n S^{(0)} \middle| \tilde{\psi}_n^{(1)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}_{KV}^{(1)} - \varepsilon_n^{(0)} S^{(1)} \middle| \tilde{\psi}_n^{(1)} \right\rangle \\ &+ \left\langle \tilde{\psi}_n^{(1)} \middle| \tilde{H}_{KV}^{(1)} - \varepsilon_n^{(0)} S^{(1)} \middle| \tilde{\psi}_n^{(0)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| \tilde{H}_{KV}^{(2)} - \varepsilon_n^{(0)} S^{(2)} \middle| \tilde{\psi}_n^{(0)} \right\rangle \end{aligned} \right\}$$

$$+ \tilde{E}_{Hxc}^{(2:1,1)} + \int_{R^3} V_{Hxc}^{(0)}\left(\tilde{n}^{(0)} + \hat{n}^{(0)}\right) \cdot \left(\tilde{n}^{(2:1)} + \hat{n}^{(2:0)}\right)$$

$$+ \int_{\Omega} V_{Hxc}^{(0)}\left(n_1^{(0)}\right) \cdot \left(n_1^{(2:1)} + n_1^{(2:0)}\right)$$

$$- \int_{\Omega} V_{Hxc}^{(0)}\left(\tilde{n}_1^{(0)} + \hat{n}^{(0)}\right) \cdot \left(\tilde{n}_1^{(2:1)} + \tilde{n}_1^{(2:0)} + \hat{n}^{(2:1)} + \hat{n}^{(2:0)}\right)$$

With the notation:
$$X^{(2)} = \underbrace{\frac{\delta X}{\delta Y} Y^{(2)}}_{X^{(2:2)}} + \underbrace{\frac{1}{2}\frac{\delta^2 X}{\delta Y^2}\left(Y^{(1)}\right)^2}_{X^{(2:1,1)}} + \underbrace{\left(\frac{\partial}{\partial \lambda}\frac{\delta X}{\delta Y}\right)_{\lambda=0}}_{X^{(2:1)}} + \underbrace{\frac{1}{2}\left(\frac{\partial^2 X}{\partial \lambda^2}\right)_{\lambda=0}}_{X^{(2:0)}}$$

# DFPT+PAW - 5

Generalized Stermheimer equation

First-order wave equation:

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

and projection on subspace S⊥ to $\psi_n^{(0)}$:

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

with:

$$P_c = I - \sum_{m=1}^{N} \left|\tilde{\psi}_m^{(0)}\right\rangle\left\langle\tilde{\psi}_m^{(0)}\right| S^{(0)}$$

$$P_c^* = I - \sum_{m=1}^{N} S^{(0)} \left|\tilde{\psi}_m^{(0)}\right\rangle\left\langle\tilde{\psi}_m^{(0)}\right|$$

# DFPT+PAW – Implementation in ABINIT

What has to be done in the code:

- ✓ All PAW data structures in « RESPFN » tree
- ✓ Double FFT grid definitions in « RESPFN » tree
- ✓ Perturbed PAW datastructures
- ✓ Generalized Sternheimer equation (CGWF3)
- ✓ Second order derivative of Hamiltonian (DYFNL3, DYFRO3, ...)
- ✓ Application of first-order derivative of Hamiltonian on $\psi_n^{(1)}$
- ✓ Perturbed compensation charge density
- ✓ Perturbed version of « on-site » contributions to energy
- ✓ Mixing of perturbed $\rho_{ij}$ (SCFCV3, NEWVTR3,... )
- ✓ ...

# Response to atomic displacement: frozen WF term - 1

Example

$$\chi^a_{\alpha\beta} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \right| \frac{\partial^2}{\partial R^a_\alpha \partial R^a_\beta} \left( \tilde{H}_{KV} - \varepsilon_n^{(0)} S \right) \left| \tilde{\psi}_n^{(0)} \right\rangle$$

**A**

$$\tilde{H}_{KV} = T + V_{loc} + \sum_{R,ij} \left| \tilde{p}_i \right\rangle D^{KV}_{ij} \left\langle \tilde{p}_j \right|$$

$$\frac{\partial^2 \tilde{H}_{KV}}{\partial R^a_\alpha \partial R^a_\beta} = \frac{\partial^2 V_{loc}}{\partial R^a_\alpha \partial R^a_\beta} + \frac{\partial^2}{\partial R^a_\alpha \partial R^a_\beta} \left( \sum_{ij} \left| p_i \right\rangle D^{KV}_{ij} \left\langle p_j \right| \right)$$

**C**

**B** $$\sum_{ij} D^{KV}_{ij} \frac{\partial^2}{\partial R^a_\alpha \partial R^a_\beta} \left( \left| p_i \right\rangle \left\langle p_j \right| \right)$$

$$\sum_{ij} \sum_L \frac{\partial^2}{\partial R^a_\alpha \partial R^a_\beta} \left( \int_{R^3} V_{loc}(\mathbf{r}) \hat{Q}^L_{ij}(\mathbf{r}) d\mathbf{r} \right) \left| p_i \right\rangle \left\langle p_j \right|$$ **D**

$$\sum_{ij} \left[ \sum_L \frac{\partial}{\partial R^a_\alpha} \left( \int_{R^3} V_{loc}(\mathbf{r}) \hat{Q}^L_{ij}(\mathbf{r}) d\mathbf{r} \right) \frac{\partial}{\partial R^a_\beta} \left( \left| p_i \right\rangle \left\langle p_j \right| \right) + \sum_L \frac{\partial}{\partial R^a_\beta} \left( \int_{R^3} V_{loc}(\mathbf{r}) \hat{Q}^L_{ij}(\mathbf{r}) d\mathbf{r} \right) \frac{\partial}{\partial R^a_\alpha} \left( \left| p_i \right\rangle \left\langle p_j \right| \right) \right]$$ **E**

# Response to atomic displacement: frozen WF term - 2

$$\rho_{ij} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle$$

$$\overline{\rho}_{ij} = \sum_n \varepsilon_n^{(0)} \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle$$

$$\mathbf{A} = \sum_{ij} \frac{\partial^2 \overline{\rho}_{ij}}{\partial R_\alpha^a \partial R_\beta^a} \cdot s_{ij}$$

$$\mathbf{B} = \sum_{ij} \frac{\partial^2 \rho_{ij}}{\partial R_\alpha^a \partial R_\beta^a} \cdot D_{ij}^{KV}$$

$$\mathbf{C} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \middle| \frac{\partial^2 V_{loc}}{\partial R_\alpha^a \partial R_\beta^a} \middle| \tilde{\psi}_n^{(0)} \right\rangle = \left( \int_{R^3} \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial R_\alpha^a \partial R_\beta^a} \cdot \tilde{n}^{(0)}(\mathbf{r}) d\mathbf{r} \right)$$

$$\mathbf{D} = \sum_{ij} \sum_L \rho_{ij} \cdot \frac{\partial^2}{\partial R_\alpha^a \partial R_\beta^a} \left( \int_{R^3} V_{loc}(\mathbf{r}) \cdot \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \right)$$

$$\mathbf{E} = \sum_{ij} \sum_L \frac{\partial \rho_{ij}}{\partial R_\alpha^a} \cdot \frac{\partial}{\partial R_\beta^a} \left( \int_{R^3} V_{loc}(\mathbf{r}) \cdot \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \right) + \frac{\partial \rho_{ij}}{\partial R_\beta^a} \cdot \frac{\partial}{\partial R_\alpha^a} \left( \int_{R^3} V_{loc}(\mathbf{r}) \cdot \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \right)$$

# Response to atomic displacement: frozen WF term - 3

$$\frac{\partial}{\partial R_\alpha^a}\left(\int_{R^3} V_{loc}(\mathbf{r})\cdot \hat{Q}_{ij}^L(\mathbf{r})d\mathbf{r}\right) = \int_{R^3} \frac{\partial V_{loc}(\mathbf{r})}{\partial R_\alpha^a}\cdot \hat{Q}_{ij}^L(\mathbf{r})d\mathbf{r} + \int_{R^3} V_{loc}(\mathbf{r})\cdot \frac{\partial \hat{Q}_{ij}^L(\mathbf{r})}{\partial R_\alpha^a} d\mathbf{r}$$

$$\frac{\partial^2}{\partial R_\alpha^a \partial R_\beta^a}\left(\int_{R^3} V_{loc}(\mathbf{r})\cdot \hat{Q}_{ij}^L(\mathbf{r})d\mathbf{r}\right) = \cdots$$

$$\mathbf{D} = \int_{R^3} \frac{\partial^2 V_{loc}}{\partial R_\alpha^a \partial R_\beta^a} \underbrace{\sum_{ij,L} \rho_{ij} q_{ij}^L g_L Y_L}_{\hat{n}^{(0)}(\mathbf{r})} d\mathbf{r} + \sum_{ij,L} q_{ij}^L \rho_{ij} \int_{R^3} \left[ V_{loc} \frac{\partial^2 (g_L Y_L)}{\partial R_\alpha^a \partial R_\beta^a} + \frac{\partial V_{loc}}{\partial R_\alpha^a} \frac{\partial (g_L Y_L)}{\partial R_\beta^a} + \frac{\partial V_{loc}}{\partial R_\beta^a} \frac{\partial (g_L Y_L)}{\partial R_\alpha^a} \right] d\mathbf{r}$$

↓

Spherical terms; so $\frac{\partial}{\partial \vec{R}^a} = -\frac{\partial}{\partial \vec{r}}$

Derivatives of $\hat{Q}_{ij}^L(\mathbf{r}) = q_{ij}^L g_L(r) Y_L(\hat{\mathrm{r}})$ ⟶ Need 1st and 2nd derivatives of $Y_L$

# Response to atomic displacement: frozen WF term - 4

$$\chi^{a}_{\alpha\beta}=\sum_{ij}\left\{\begin{aligned}&\boxed{D^{KV}_{ij}\frac{\partial^2\rho_{ij}}{\partial R^a_\alpha\partial R^a_\beta}}^{(*)}-s_{ij}\frac{\partial^2\overline{\rho}_{ij}}{\partial R^a_\alpha\partial R^a_\beta}\boxed{+\int_{R^3}\frac{\partial^2 V_{loc}}{\partial r_\alpha\partial r_\beta}(\tilde{n}+\hat{n})^{(0)}(\mathbf{r})d\mathbf{r}}^{(*)}\\&+\sum_L q^L_{ij}\rho_{ij}\int_{R^3}\left[V_{loc}\frac{\partial^2(g_LY_L)}{\partial r_\alpha\partial r_\beta}+\frac{\partial V_{loc}}{\partial r_\alpha}\frac{\partial(g_LY_L)}{\partial r_\beta}+\frac{\partial V_{loc}}{\partial r_\beta}\frac{\partial(g_LY_L)}{\partial r_\alpha}\right]d\mathbf{r}\\&-\sum_L q^L_{ij}\frac{\partial\rho_{ij}}{\partial R^a_\alpha}\int_{R^3}\left[\frac{\partial V_{loc}}{\partial r_\beta}g_LY_L+V_{loc}\frac{\partial(g_LY_L)}{\partial r_\beta}\right]d\mathbf{r}\\&-\sum_L q^L_{ij}\frac{\partial\rho_{ij}}{\partial R^a_\beta}\int_{R^3}\left[\frac{\partial V_{loc}}{\partial r_\alpha}g_LY_L+V_{loc}\frac{\partial(g_LY_L)}{\partial r_\alpha}\right]d\mathbf{r}\end{aligned}\right\}$$

**(*)** Norm-conserving psps term (with $D_{ij}=E_i^{KB}\,\delta_{ij}$ and $\hat{n}=0$)

# Response to atomic displacement: frozen WF term - 5

$$\rho_{ij}, \bar{\rho}_{ij}, \frac{\partial \rho_{ij}}{\partial R^a_\alpha}, \frac{\partial^2 \rho_{ij}}{\partial R^a_\alpha \partial R^a_\beta}, \frac{\partial^2 \bar{\rho}_{ij}}{\partial R^a_\alpha \partial R^a_\beta}$$

are computed by nonlop_ylm, pawmkrhoij and symrhoij routines

$$\int_{R^3} \left[ \frac{\partial^2 V_{loc}}{\partial r_\alpha \partial r_\beta} (\tilde{n} + \hat{n})^{(0)} \right] d\mathbf{r}$$

is computed in RECIPROCAL SPACE by pawcorloc routine

$$\int_{R^3} \left[ \frac{\partial V_{loc}}{\partial r_\alpha} g_L Y_L \right] d\mathbf{r}, \int_{R^3} \left[ V_{loc} \frac{\partial (g_L Y_L)}{\partial r_\alpha} \right] d\mathbf{r}, \cdots$$

and analog integrals
are computed in REAL SPACE
by pawgrnhat routine

$$\frac{\partial (g_L Y_L)}{\partial r_\alpha}, \frac{\partial^2 (g_L Y_L)}{\partial r_\alpha \partial r_\beta}, \frac{\partial V_{loc}}{\partial r_\alpha}$$

are computed on each point of the fine FFT grid by nhatgrid routine

# Response to atomic displacement: frozen WF term - 6

Computation of: $\dfrac{\partial^2 \rho_{ij}}{\partial R_\alpha^a \partial R_\beta^a}$

nonlop_ylm + pawmkrhoij +symrhoij

$$\frac{\partial^2 \rho_{ij}}{\partial R_\alpha^a \partial R_\beta^a} = \sum_n \left\langle \tilde{\psi}_n^{(0)} \right| \frac{\partial^2}{\partial R_\alpha^a \partial R_\beta^a} \left( \left| p_i \right\rangle \left\langle p_j \right| \right) \left| \tilde{\psi}_n^{(0)} \right\rangle$$

opernld_ylm

$$= \sum_n \frac{\partial^2 \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle}{\partial R_\alpha^a \partial R_\beta^a} \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle + \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle \frac{\partial^2 \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle}{\partial R_\alpha^a \partial R_\beta^a} + \frac{\partial \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle}{\partial R_\alpha^a} \frac{\partial \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle}{\partial R_\beta^a} + \frac{\partial \left\langle \tilde{\psi}_n^{(0)} \middle| p_i \right\rangle}{\partial R_\beta^a} \frac{\partial \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle}{\partial R_\alpha^a}$$

$$\left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle = \frac{4\pi}{\sqrt{\Omega}} (-i)^{l_j} \sum_G C_G \cdot f_{l_j n_j}(G) \cdot Y_{l_j m_j}(\hat{G}) \cdot e^{2i\pi \vec{G}\cdot\vec{R}^a}$$

$$\frac{\partial \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle}{\partial R_\alpha^a} = \frac{4\pi}{\sqrt{\Omega}} (-i)^{l_j} \sum_G -2i\pi \cdot G_\alpha \cdot C_G \cdot f_{l_j n_j}(G) \cdot Y_{l_j m_j}(\hat{G}) \cdot e^{-2i\pi \vec{G}\cdot\vec{R}^a}$$

$$\frac{\partial^2 \left\langle p_j \middle| \tilde{\psi}_n^{(0)} \right\rangle}{\partial R_\alpha^a \partial R_\beta^a} = \frac{4\pi}{\sqrt{\Omega}} (-i)^{l_j} \sum_G -4\pi^2 \cdot G_\alpha \cdot G_\beta \cdot C_G \cdot f_{l_j n_j}(G) \cdot Y_{l_j m_j}(\hat{G}) \cdot e^{-2i\pi \vec{G}\cdot\vec{R}^a}$$

opernla_ylm

*Note: for atomic displacement perturbation, no need of $Y_{lm}$ derivatives; this is not the case for strain pêrturbation*

# Response to atomic displacement: frozen WF term - 7

**Frozen WF term of dynamical matrix has been implemented in Abinit (v5.3.2+)**

From tutorial RF1:

- AlAs
- Al atom perturbed in first direction

**Displ. +$10^{-5}$**

```
-------------------------------------------
 ponents of total free energy (in Hartree) :
    Kinetic energy  =  3.23574233470892E+00
    Hartree energy  =  1.30633814042893E-01
    XC energy       = -2.22536699596815E+00
    Ewald energy    = -8.47988979410789E+00
    PspCore energy  =  2.66021488770152E-01
    Loc. psp. energy=  1.07918258823726E+00
    Spherical terms =  1.41329594719218E-01
    >>>>>>>>> Etotal= -5.85234696959759E+00
```

**Unperturbed**

```
-----------------------------------------------
 Components of total free energy (in Hartree) :
    Kinetic energy  =  3.23574233470892E+00
    Hartree energy  =  1.30633814160560E-01
    XC energy       = -2.22536699592924E+00
    Ewald energy    = -8.47988991313938E+00
    PspCore energy  =  2.66021488770152E-01
    Loc. psp. energy=  1.07918258604830E+00
    Spherical terms =  1.41329583121884E-01
    >>>>>>>>> Etotal= -5.85234710225880E+00
```

**Displ. -$10^{-5}$**

```
-------------------------------------------
   ents of total free energy (in Hartree) :
    Kinetic energy  =  3.23574233470892E+00
    Hartree energy  =  1.30633814284781E-01
    XC energy       = -2.22536699586992E+00
    Ewald energy    = -8.47989003098646E+00
    PspCore energy  =  2.66021488770152E-01
    Loc. psp. energy=  1.07918258201017E+00
    Spherical terms =  1.41329572614893E-01
    >>>>>>>>> Etotal= -5.85234723446746E+00
```

$$\frac{\partial E}{\partial t^2} = \left(E(t+dt) + E(t+dt) - 2E(t)\right)/\,dt^2$$

→

```
Ewald:   11.8440723895219
Local:  -18.4916970624727
Total :   4.52549997476126
```

**Abinit GS runs**

**Abinit RF run**

```
Ewald frozen wf part of 2DTE:    11.8439985635023
local frozen wf part of 2DTE:    18.4916991569321
n-loc frozen wf part of 2DTE:   -25.8102045047232
total frozen wf part of 2DTE:     4.5254932157112
```

# PAW+RF in ABINIT – Done / To be done

Done in v5.3.2
To be done in v5.4

- ✓ All PAW data structure in « RESPFN » tree
- ✓ Double FFT grid definitions in « RESPFN » tree
- ✓ Perturbed PAW datastructures
- ✓ Generalized Sternheimer equation (CGWF3)
- ✓ Second order derivative of Hamiltonian (DYFNL3, DYFRO3, ...)
- ✓ Application of first-order derivative of Hamiltonian on $\psi_n^{(1)}$
- ✓ Perturbed compensation charge density
- ✓ Perturbed version of « on-site » contribution to energy
- ✓ Mixing of perturbed $\rho_{ij}$ (SCFCV3, NEWVTR3,... )
- ✓ ...

# PAW+RF in ABINIT – Roadmap

- ✓ $2^{nd}$ order response to atomic displacements (phonons) → ABINIT v5.4
- ✓ $2^{nd}$ order response to **k** perturbation
- ✓ $2^{nd}$ order response to $V^{ext}$ perturbation

  (these two → ABINIT v5.5 or v5.6)
- ✓ $2^{nd}$ order response to strain perturbation → ABINIT v?.?
- ✓ ...