Ab-initio Computation of Raman spectra within the DFPT formalism coupled with the PAW method

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Table of Contents

1 Theory of non-resonant Raman scattering

2 Implementation of 3rd order DFPT in ABINIT
   - 2nd order Sternheimer equation
   - Expression of 3rd derivatives (norm conserving)
   - Expression of 3rd derivatives (PAW)
   - Validation on AlAs

3 Computation of Raman Intensities
   - Workflow
   - An exemple: $\alpha$ – Quartz

4 Raman spectra in PAW+U
   - A simple reformulation of the PAW+U formalism
   - Preliminary results on LiCoO2

5 Conclusion and Perspectives
Table of contents

1 Theory of non-resonant Raman scattering

2 Implementation of 3\textsuperscript{rd} order DFPT in ABINIT
   - 2\textsuperscript{nd} order Sternheimer equation
   - Expression of 3\textsuperscript{rd} derivatives (norm conserving)
   - Expression of 3\textsuperscript{rd} derivatives (PAW)
   - Validation on AlAs

3 Computation of Raman Intensities
   - Workflow
   - An exemple : $\alpha$ – Quartz

4 Raman spectra in PAW+U
   - A simple reformulation of the PAW+U formalism
   - Preliminary results on LiCoO2

5 Conclusion and Perspectives
Stokes scattering: inelastic scattering of an *incident photon* interacting with a *phonon*.

⇒ Frequency shift between the incident and scattered light:
\[ \Delta \omega = \omega_m \]

We treat only *non resonant* scattering: \( E_\gamma < E_{\text{gap}} \)

⇒ Relevant only for insulators

Only *active* phonon modes contribute:
- \( \mathbf{q} \approx 0 \) (as \( \lambda_\gamma \gg a \))
- Selection rules depending on crystal symmetries

Measured intensity \( \approx \) sum of Lorentzian functions:
\[
I(\omega) \approx \sum_m^{\text{active}} \frac{l_m}{\pi} \frac{\Gamma_m}{(\omega - \omega_m)^2 + \Gamma_m^2}
\]
- Position: \( \omega_m \) (phonon frequency)
  ⇒ 2\textsuperscript{nd} derivatives of \( E \):
  \[
  E^{(\tau\kappa\alpha\tau\kappa'\beta)}_m \equiv \frac{\partial^2 E}{\partial\tau\kappa\alpha \partial\tau\kappa'\beta}
  \]
- Intensity: \( l_m \)
  ⇒ 3\textsuperscript{rd} derivatives of \( E \):
  \[
  E^{(\tau\kappa\alpha\varepsilon\beta\varepsilon\gamma)}_m \equiv \frac{\partial^3 E}{\partial\tau\kappa\alpha \partial\varepsilon\beta \partial\varepsilon\gamma}
  \]
- Width: \( \Gamma_m \)
  ⇒ other 3\textsuperscript{rd} derivatives (not computed)

In ABINIT: \( \omega_m \) (available in PAW), \( l_m \Rightarrow \) To adapt to PAW
Table of contents

1 Theory of non-resonant Raman scattering

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   • 2nd order Sternheimer equation
   • Expression of 3rd derivatives (norm conserving)
   • Expression of 3rd derivatives (PAW)
   • Validation on AlAs

3 Computation of Raman Intensities
   • Workflow
   • An exemple : $\alpha$ – Quartz

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   • A simple reformulation of the PAW+U formalism
   • Preliminary results on LiCoO2

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2n + 1 theorem: $E^{(\tau\kappa\beta E_i E_j)}$ depends only on ground-state ($\psi_n^{(0)}$) and first-order WFs ($\psi_n^{(\tau\kappa\beta)}, \psi_n^{(E_i)}, \psi_n^{(E_j)}$).

⇒ They are obtained solving 1st order Sternheimer equations.

The electric field perturbation brings a difficulty: $V(\mathcal{E}) = \mathcal{E} \cdot \mathbf{r} = \mathcal{E} \cdot i \nabla_k$.

In the expression of $E^{(\tau\kappa\beta E_i E_j)}$:

$$\langle \psi_n^{(\tau\kappa\beta)} | H(E_i) | \psi_n^{(E_j)} \rangle = i \langle \psi_n^{(\tau\kappa\beta)} | \psi_n^{(k_i E_j)} \rangle + \ldots$$

⇒ We need to solve a 2nd order Sternheimer equation.

**Note:** Previous ABINIT implementation (Veithen et al PRB 71, 125107 (2005)) uses a formalism (“PEAD”) where “ $\nabla_k$ ” is kind of discretised: no need of 2nd derivatives.

However, difficult to adapt to PAW, decreases the convergence with respect to the $k$ point grid.
The electric field perturbation brings a difficulty: \( V(\mathcal{E}) = \mathcal{E} \cdot r = \mathcal{E} \cdot i \nabla_k \).

In the expression of \( E^{(\tau \kappa \beta \mathcal{E}_i \mathcal{E}_j)} \):

\[
\langle \psi_n^{(\tau \kappa \beta \mathcal{E}_i)} | H^{(\mathcal{E}_j)} | \psi_n^{(\mathcal{E}_j)} \rangle = i \langle \psi_n^{(\tau \kappa \beta)} | \psi_n^{(k_i \mathcal{E}_j)} \rangle + \ldots
\]

\( \Rightarrow \) We need to solve a 2\textsuperscript{nd} order Sternheimer equation.

**Note:** Previous ABINIT implementation (Veithen et al PRB 71, 125107 (2005)) uses a formalism ("PEAD") where " \( \nabla_k \) " is kind of discretised: no need of 2\textsuperscript{nd} derivatives.

However, difficult to adapt to PAW, decreases the convergence with respect to the \( k \) point grid.

The Sternheimer equations have the form \( Ax = b \) where \( A^\dagger = A \Rightarrow \) Solved with a conjugate gradient algorithm.

\[1\textsuperscript{st} \text{ order: } \left( P^c \right)^\dagger \left( H^{(0)} - \epsilon_n S^{(0)} \right) P^c | \psi_n^{(\lambda_1)} \rangle = - \left( P^c \right)^\dagger \left( H^{(\lambda_1)} - \epsilon_n S^{(\lambda_1)} \right) | \psi_n^{(0)} \rangle\]

\[2\textsuperscript{nd} \text{ order: } \left( P^c \right)^\dagger \left( H^{(0)} - \epsilon_n S^{(0)} \right) P^c | \psi_n^{(\lambda_1 \lambda_2)} \rangle = - \left( P^c \right)^\dagger \left( H^{(\lambda_1 \lambda_2)} - \epsilon_n S^{(\lambda_1 \lambda_2)} \right) | \psi_n^{(0)} \rangle - \left( P^c \right)^\dagger \left( H^{(\lambda_1)} - \epsilon_n S^{(\lambda_1)} \right) | \psi_n^{(\lambda_2)} \rangle - \left( P^c \right)^\dagger \left( H^{(\lambda_2)} - \epsilon_n S^{(\lambda_2)} \right) | \psi_n^{(\lambda_1)} \rangle + \sum_m \Lambda_m^{(\lambda_1 \lambda_2)} \left( P^c \right)^\dagger \left( S^{(\lambda_2)} | \psi_m^{(0)} \rangle + S^{(0)} | \psi_m^{(\lambda_2)} \rangle \right) \]

+ \sum_m \Lambda_m^{(\lambda_2 \lambda_1)} \left( P^c \right)^\dagger \left( S^{(\lambda_1)} | \psi_m^{(0)} \rangle + S^{(0)} | \psi_m^{(\lambda_1)} \rangle \right)
\[ |\psi_n\rangle \approx |\tilde{\psi}_n\rangle \quad \langle \tilde{\psi}_n|\tilde{\psi}_m\rangle = \delta_{nm} \]

\[ E^{(\lambda_1 \lambda_2 \lambda_3)} = (I) + (II) + (III) \]

\[ (I) = \sum_n \langle \tilde{\psi}_n^{(\lambda_1)} | \tilde{H}^{(\lambda_2)} | \tilde{\psi}_n^{(\lambda_3)} \rangle \]

\[ (II) = -\sum_{nm} \Lambda_{nm}^{(\lambda_2)} \langle \tilde{\psi}_m^{(\lambda_1)} | \tilde{\psi}_n^{(\lambda_3)} \rangle \]

\[ (III) = \frac{1}{6} \int dr \, F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\tilde{\rho}] (r) \]

\[ F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\rho] (r) = \rho^{(\lambda_1)}(r) \rho^{(\lambda_2)}(r) \rho^{(\lambda_3)}(r) \frac{d^2 \mu xc}{d\rho^2} (\rho^{(0)}(r)) \]
\[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{\kappa} \sum_i \left( |\phi_{\kappa,i}\rangle - |\tilde{\phi}_{\kappa,i}\rangle \right) \langle \tilde{\phi}_{\kappa,i}|\tilde{\psi}_n\rangle \]
\[ \langle \tilde{\psi}_n| S|\tilde{\psi}_m\rangle = \delta_{nm} \]

\[ E^{(\lambda_1 \lambda_2 \lambda_3)} = (I) + (II) + (III) + (IV) + (V) + (VI) + (VII) + (VIII) + (IX) \]

\[ (I) = \sum_n \langle \tilde{\psi}_n^{(\lambda_1)} | \left( \tilde{H}^{(\lambda_2)} - \epsilon_n^{(0)} S^{(\lambda_2)} \right) |\tilde{\psi}_n^{(\lambda_3)} \rangle \]

\[ (II) + (III) = - \sum_{nm} \Lambda_{nm}^{(\lambda_2)} \left( \langle \tilde{\psi}_m^{(\lambda_1)} | S^{(0)} |\tilde{\psi}_n^{(\lambda_3)} \rangle + \langle \tilde{\psi}_m^{(0)} | S^{(\lambda_1)} |\tilde{\psi}_n^{(\lambda_3)} \rangle + \langle \tilde{\psi}_m^{(\lambda_3)} | S^{(\lambda_1)} |\tilde{\psi}_n^{(0)} \rangle \right) \]

\[ (IV) + (V) = \sum_n \left( \langle \tilde{\psi}_n^{(0)} | \tilde{H}_K^{(\lambda_1 \lambda_3)} |\tilde{\psi}_n^{(\lambda_2)} \rangle + \langle \tilde{\psi}_n^{(\lambda_2)} | \tilde{H}_K^{(\lambda_1 \lambda_3)} |\tilde{\psi}_n^{(0)} \rangle \right) \]

\[ (VI) = \sum_{\kappa} \int_{\Omega_{\kappa}} dr \left( (V_{Hxc}[\tilde{\rho}_{\kappa}])^{(\lambda_1 \lambda_3)}(r) \tilde{\rho}_{\kappa}^{(\lambda_1 \lambda_3)}(r) - (V_{Hxc}[\tilde{\rho}_{\kappa}])^{(\lambda_2)}(r) \tilde{\rho}_{\kappa}^{(\lambda_1 \lambda_2)}(r) \right) \]

\[ (VII) = \int dr \left( V_{Hxc}[\tilde{\rho}] \right)^{(\lambda_2)}(r) \tilde{\rho}^{(\lambda_1 \lambda_3)}(r) \]

\[ (VIII) + (IX) = \frac{1}{6} \int dr F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\tilde{\rho}] (r) + \frac{1}{6} \sum_{\kappa} \int_{\Omega_{\kappa}} dr \left( F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\tilde{\rho}_{\kappa}] (r) - F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\tilde{\rho}_{\kappa}] (r) \right) \]

\[ F_{\mu xc}^{\lambda_1 \lambda_2 \lambda_3} [\rho] (r) = \rho^{(\lambda_1)}(r) \rho^{(\lambda_2)}(r) \rho^{(\lambda_3)}(r) \frac{d^2 \mu xc}{d\rho^2} (\rho^{(0)}(r)) \]
System: AlAs – Due to symmetries: only 1 degree of liberty in the third derivative tensor:

\[ a_{xyz}(Al) = -E^{(\tau_{Al}, xy)} \]

\[ N_k : \text{number of k-points in the Brillouin zone} \]

DFPT: current work

PEAD: previous ABINIT implementation

FDM: Finite Difference Method:

\[ E_{FDM}^{(\tau_{Al}, xy)} = \frac{E_{Al=+\Delta x}^{(\varepsilon_y \varepsilon_z)} - E_{Al=-\Delta x}^{(\varepsilon_y \varepsilon_z)}}{2\Delta x} \]

Upper frames: norm conserving results

Lower frames: PAW results

Right-handed frames: \(|X - X_{\text{conv}}|\)

where \(X_{\text{conv}}\) is the value corresponding to \(N_k \approx 180000\)

Black lines: \(|X_{\text{DFPT}} - X_{\text{FDM}}|\)
# Table of contents

1. Theory of non-resonant Raman scattering

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   - Expression of 3\textsuperscript{rd} derivatives (norm conserving)
   - Expression of 3\textsuperscript{rd} derivatives (PAW)
   - Validation on AlAs

3. Computation of Raman Intensities
   - Workflow
   - An exemple: $\alpha - Quartz$

4. Raman spectra in PAW+U
   - A simple reformulation of the PAW+U formalism
   - Preliminary results on LiCoO$\textsubscript{2}$

5. Conclusion and Perspectives
(I) : ABINIT : compute DDB: $E^{(\tau \kappa \alpha \tau' \kappa' \beta)}(\mathbf{q} = 0), E^{(\tau \kappa \beta \mathcal{E}_i \mathcal{E}_j)}$
(I) : ABINIT : compute DDB: \( E^{(\tau_\kappa \alpha \tau_{\kappa'} \beta)}(q = 0), E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)} \)

(II) : MRGDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor \( \alpha^m \) for every phonon mode \( m \):

\[
\alpha^m_{ij}(q = 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa, \beta} E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)} u_{m, q=0}(\kappa, \beta)
\]
(I) : ABINIT : compute DDB: $E^{(\tau_\kappa \alpha \tau_\kappa' \beta)}(q = 0), E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)}$

(II) : MRGDDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor $\alpha^m$ for every phonon mode $m$:

$$\alpha^m_{ij}(q = 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa, \beta} E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)} u_{m,q=0}(\kappa,\beta)$$

(III) : RAMAN_SPEC.PY : compute Raman intensities (from the Raman tensor)

Parameters depending on experimental setup : laser frequency ($\omega_0$) and polarization ($e_I, e_S$), temperature ($T$)

$$I_m = \frac{\hbar}{2\omega_m} (n_m + 1) \frac{(\omega_0 - \omega_m)^4}{c^4} |e_S . \alpha^m . e_I|^2$$

$$n_m = \frac{1}{e^{\hbar \omega_m / k_B T} - 1}$$
(I) : ABINIT : compute DDB: $E^{(\tau_\kappa \alpha \tau_{\kappa'} \beta)}(q = 0) = E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)}$

(II) : MRGDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor $\alpha^m$ for every phonon mode $m$:

$$\alpha^m_{ij}(q = 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa, \beta} E^{(\tau_\kappa \beta \varepsilon_i \varepsilon_j)} u_{m, q = 0}(\kappa, \beta)$$

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$$n_m = \frac{1}{e^{\hbar \omega_m / k_B T} - 1}$$

Can also compute the intensity of a powder.

**NOTE** : We are interested in relative intensities only : $I_m$ are normalized (highest value = 1)
Taking into account LO modes:

(I) : ABINIT : compute DDB: $E^{(\tau_{\kappa' \alpha} \tau_{\kappa' \beta})} (q = 0)$, $E^{(\tau_{\kappa' \beta} \varepsilon_i \varepsilon_j)}$, $E^{(\varepsilon_i \varepsilon_j)}$, $E^{(\tau_{\kappa' \beta} \varepsilon_i \varepsilon_j)}$, $E^{(\varepsilon_i \varepsilon_j \varepsilon_k)}$

(II) : MRGDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor $\alpha^m$ for every phonon mode $m$:

TO : $\alpha^m_{ij} (q = 0) = - \frac{1}{\sqrt{\Omega_0}} \sum_{\kappa, \beta} E^{(\tau_{\kappa \beta} \varepsilon_i \varepsilon_j)} u_{m, q=0} (\kappa \beta)$

For different $q$ directions:

LO : $\alpha^m_{ij} (q \rightarrow 0) = - \frac{1}{\sqrt{\Omega_0}} \sum_{\kappa, \beta} E^{(\tau_{\kappa \beta} \varepsilon_i \varepsilon_j)} u_{m, q \rightarrow 0} (\kappa \beta) + \sum_{\kappa, \beta} \frac{4\pi}{\Omega_0^2} \left( \sum_k E^{(\varepsilon_i \varepsilon_j \varepsilon_k)} q_k \frac{\sum_{k, l} Z^*_{\kappa \beta, k} q_k q_l}{\sum_{k, l, \epsilon} \epsilon_{kl} q_k q_l} u_{m, q \rightarrow 0} (\kappa \beta) \right)$

(III) : RAMAN_SPEC.PY : compute Raman intensities (from the Raman tensor)

Parameters depending on experimental setup : laser frequency ($\omega_0$) and polarization ($e_I, e_S$), temperature ($T$)

$$I_m = \frac{\hbar}{2\omega_m} \left( n_m + 1 \right) \left( \omega_0 - \omega_m \right)^4 \frac{|e_S \cdot \alpha^m \cdot e_I|^2}{c^4}$$

$$n_m = \frac{1}{e^{\hbar \omega_m / k_B T} - 1}$$

WARNING : For LO modes, $I_{\text{powder}}$ cannot be obtained directly from RAMAN_SPEC.PY : numerical integration on $q$ directions is needed!
\[ I(\omega) \approx \sum_m^{\text{active}} \frac{I_m}{\pi} \frac{\Gamma_m}{(\omega - \omega_m)^2 + \Gamma_m^2} \]

**Blue line** (offset=0.4): theoretical spectrum - PAW+LDA \( (\Gamma_m = 4 \text{ cm}^{-1}) \)

**Grey dots** (offset=0.2): experimental spectrum (Handbook of Minerals Raman Spectra)

**Black dots** (no offset): experimental spectrum (RRUFF project)

**Red line**: Fit of RRUFF data

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<tr>
<th>PAW+LDA</th>
<th>Fit of RRUFF</th>
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</tbody>
</table>
Table of contents

1 Theory of non-resonant Raman scattering

2 Implementation of 3\textsuperscript{rd} order DFPT in ABINIT
   - 2\textsuperscript{nd} order Sternheimer equation
   - Expression of 3\textsuperscript{rd} derivatives (norm conserving)
   - Expression of 3\textsuperscript{rd} derivatives (PAW)
   - Validation on AlAs

3 Computation of Raman Intensities
   - Workflow
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4 Raman spectra in PAW+U
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   - Preliminary results on LiCoO2

5 Conclusion and Perspectives
In the “LDA+U” formalism, one combines DFT with a Hubbard model that corrects the $e^{-}e^{-}$ interaction of orbitals localized around the ions (generally used for $d$ or $f$ bands):

$$E_{\text{LDA}+U}[n_{\text{LDA}+U}] = E_{\text{LDA}}[n_{\text{LDA}+U}] + \sum_{a}^{+U} (E_{a}(U, J) - E_{a,dc}(U, J))$$

$$E_{a}(U, J) = \frac{1}{2} \sum_{m_{1}m_{2}} \sum_{\sigma} \left[ A(U, J)n_{L,m_{1}m_{2}}^{\sigma}n_{L,m_{3}m_{4}}^{\bar{\sigma}} + B(U, J)n_{L,m_{1}m_{2}}^{\bar{\sigma}}n_{L,m_{3}m_{4}}^{\sigma} \right]$$

where $U$ and $J$ are the Hubbard model parameters.

In the "PAW+U" formulation, the occupation matrices $n_{L,m_{1}m_{2}}^{\sigma}$ are:

$$n_{Lmm'}^{\sigma} = \sum_{k} \sum_{n_{i},n_{j}} \langle \psi_{nk\sigma} | \hat{P}_{a,n_{i}Lm} \rangle \langle \hat{P}_{a,n_{j}Lm'} | \psi_{nk\sigma} \rangle \langle \phi_{a,n_{i}Lm} | \phi_{a,n_{j}Lm'} \rangle$$

(3)
In the "LDA+U", formalism, one combines DFT with a Hubbard model that corrects the $e^- e^-$ interaction of orbitals localized around the ions (generally used for $d$ or $f$ bands):

\[
E_{\text{LDA+U}}[n_{\text{LDA+U}}] = E_{\text{LDA}}[n_{\text{LDA+U}}] + \sum_a \left( E_a(U, J) - E_a,dc(U, J) \right) + U \sum_a (A(U, J)n_{L, m_1 m_2}^{a, \sigma} n_{L, m_3 m_4}^{a, -\sigma} + B(U, J)n_{L, m_1 m_2}^{a, \sigma} n_{L, m_3 m_4}^{a, \sigma}) \quad (1)
\]

where $U$ and $J$ are the Hubbard model parameters.

In the "PAW+U" formulation, the occupation matrices $n_{L, m_1 m_2}^{a, \sigma}$ are:

\[
n_{L, m_1 m_2}^{a, \sigma} = \sum_k \sum_{n, j} \sum_{n, j} \langle \psi_{n k \sigma} | \tilde{p}_{a, n_j Lm} | \psi_{n k \sigma} \rangle \langle \phi_{a, n_j Lm | \phi_{a, n_j Lm} \rangle \quad (3)
\]

Following PAW notations: $i \equiv n_i, l_i, m_i, j \equiv n_j, l_j, m_j$, we note: $\rho_{a, ij \sigma} = \sum_k \sum_n \langle \psi_{n k \sigma} | \tilde{p}_{a, i} | \psi_{n k \sigma} \rangle$

In terms of the PAW vocabulary, $E_a(U, J)$ is a "on-site" term, like the Hartree "on-site" term:

\[
E_a(U, J) = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i, j, i', j'} \rho_{a, ij \sigma} \rho_{a, i' j' \sigma'} e_a,_{ij \sigma', i'j'}(U, J) \quad (4)
\]

\[
E_a^H = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i, j, i', j'} \rho_{a, ij \sigma} \rho_{a, i' j' \sigma'} e_a^H,_{ij \sigma, i'j'} \quad (5)
\]

where $e_a,_{ij \sigma', i'j'}(U, J)$ and $e_a^H,_{ij \sigma, i'j'}$ are constants, depending only on the PAW pseudo-potential.
In the “LDA+U”, formalism, one combines DFT with a Hubbard model that corrects the $e^{-} e^{-}$ interaction of orbitals localized around the ions (generally used for $d$ or $f$ bands):

$$E_{LDA+U}[n_{LDA+U}] = E_{LDA}[n_{LDA+U}] + \sum_a \left( E_a(U, J) - E_{a,dc}(U, J) \right)$$

$$E_a(U, J) = \frac{1}{2} \sum_{m_1 m_2} \sum_{m_3 m_4} \left[ A(U, J)n^{a\sigma}_{L, m_1 m_2} n^{a-\sigma}_{L, m_3 m_4} + B(U, J)n^{a\sigma}_{L, m_1 m_2} n^{a\sigma}_{L, m_3 m_4} \right]$$

where $U$ and $J$ are the Hubbard model parameters.

In the "PAW+U" formulation, the occupation matrices $n^{a\sigma}_{L, m_1 m_2}$ are:

$$n^{a\sigma}_{Lmm'} = \sum_k \sum_{n_i, n_j} \sum_n \langle \psi_{nk\sigma} | \tilde{p}_{a,njLm} \rangle \langle \tilde{p}_{a,njLm'} | \psi_{nk\sigma} \rangle$$

Following PAW notations : $i \equiv n_i, l_i, m_i, j \equiv n_j, l_j, m_j$, we note: $\rho_{a,ij\sigma} = \sum_k \sum_n \langle \psi_{nk\sigma} | \tilde{p}_{a,i} \rangle \langle \tilde{p}_{a,j} | \psi_{nk\sigma} \rangle$

In terms of the PAW vocabulary, $E_a(U, J)$ is a "on-site" term, like the Hartree "on-site" term:

$$E_a(U, J) = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i, j, i', j'} \rho_{a,ij\sigma} \rho_{a,i'j'\sigma'} e_{a,\sigma\sigma',ij,i'j'}(U, J)$$

$$E_a^H = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i, j, i', j'} \rho_{a,ij\sigma} \rho_{a,i'j'\sigma'} e_{a,ij,i'j'}^H$$

where $e_{a,\sigma\sigma',ij,i'j'}(U, J)$ and $e_{a,ij,i'j'}^H$ are constants, depending only on the PAW pseudo-potential.

In DFPT:

$$\left( E_a(U, J) \right)^{(n)} = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i, j, i', j'} \left( \rho_{a,ij\sigma} \rho_{a,i'j'\sigma'} \right)^{(n)} e_{a,\sigma\sigma',ij,i'j'}(U, J)$$

Similar derivation for the double-counting term $E_{a,dc}(U, J)$. 
Preliminary results on LiCoO₂:

With "+U", relative error between DFPT and finite difference (FD) on the Raman tensor: $|\alpha_{ij}^{DFPT} - \alpha_{ij}^{FD}| / |\alpha_{ij}^{DFPT}| < 0.2\%$
Preliminary results on LiCoO₂:

With "+U", relative error between DFPT and finite difference (FD) on the Raman tensor: $|\alpha_{ij}^{DFPT} - \alpha_{ij}^{FD}| / |\alpha_{ij}^{DFPT}| < 0.2\%$

Comparison between PAW LDA / LDA+U (this work) and Ultrasoft (USPP) GGA / GGA+U (Miwa PRB 97, 075143 (2018)):

- U and J not computed for LDA+U, chosen as the same values than GGA+U ($U = 5.6$ eV, $J = 0.8$ eV).
- Cell optimization for LDA and LDA+U


Theoretical spectra: lorentzian width $= 5$ cm$^{-1}$, depend on three parameters only: $\omega_1, \omega_2, I_1/I_2$. 

![Graph showing theoretical spectra comparison between different methods]
Table of contents

1 Theory of non-resonant Raman scattering

2 Implementation of 3rd order DFPT in ABINIT
   • 2nd order Sternheimer equation
   • Expression of 3rd derivatives (norm conserving)
   • Expression of 3rd derivatives (PAW)
   • Validation on AlAs

3 Computation of Raman Intensities
   • Workflow
   • An exemple: $\alpha$ – Quartz

4 Raman spectra in PAW+U
   • A simple reformulation of the PAW+U formalism
   • Preliminary results on LiCoO2

5 Conclusion and Perspectives
In conclusion:

- Raman intensities in PAW are available in **ABINIT v8.10**!
- Raman intensities in PAW+U will be released soon, hopefully.

What could be done:

- Current implementation needs to write $\psi_{nk}^{(\tau_{\kappa\beta})}$ on disk, could be avoided (becomes problematic for large systems).
- Implementation of GGA (for both norm-conserving and PAW)
- Computation of Raman peak width: needs other third-derivatives of the energy (three atomic displacements, at $\mathbf{q} \neq 0$)