Ab-initio Computation of Raman spectra

within the DFPT formalism coupled with the PAW method

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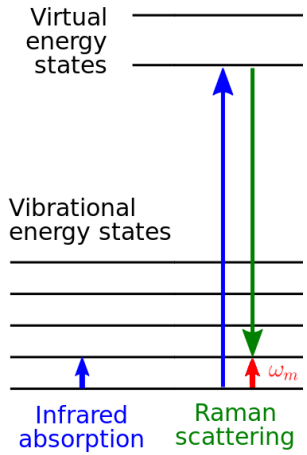

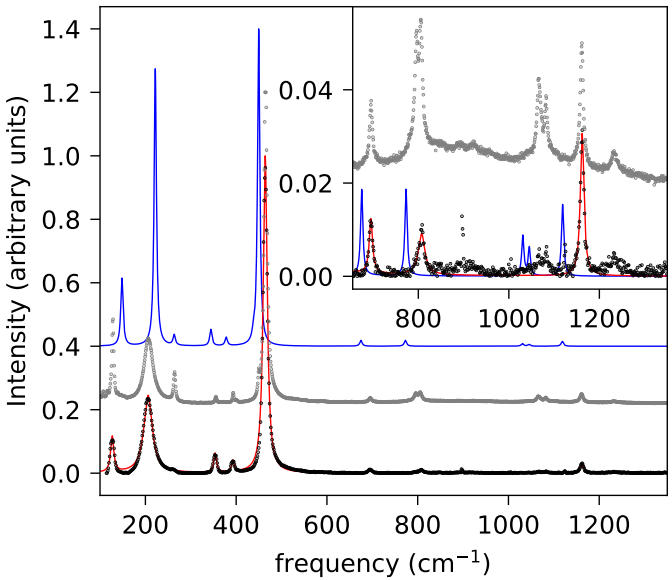

Stokes scattering : inelastic scattering of an *incident photon* interacting with a *phonon*.

$\Rightarrow$ Frequency shift between the incident and scattered light : $\Delta\omega = \omega_m$

We treat only *non resonant* scattering : $E_\gamma < E_{\mathrm{gap}}$

$\Rightarrow$ 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 :

$$I(\omega) \approx \sum_m^{\mathrm{active}} \frac{I_m}{\pi} \frac{\Gamma_m}{(\omega - \omega_m)^2 + \Gamma_m^2}$$

- position : ω_m (= phonon frequency)
  $\Rightarrow 2^{\mathrm{nd}}$ derivatives of E : $E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})} \equiv \frac{\partial^2 E}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\beta}}$
- intensity : I_m
  $\Rightarrow 3^{\mathrm{rd}}$ derivatives of E : $E^{(\tau_{\kappa\alpha}\mathcal{E}_\beta\mathcal{E}_\gamma)} \equiv \frac{\partial^3 E}{\partial\tau_{\kappa\alpha}\partial\mathcal{E}_\beta\partial\mathcal{E}_\gamma}$
- width : Γ_m
  $\Rightarrow$ other 3^{rd} derivatives (not computed)

In ABINIT : ω_m (available in PAW), $I_m \Rightarrow$ To adapt to PAW

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$2n+1$ theorem : $E^{(\tau_\kappa\beta\mathcal{E}_i\mathcal{E}_j)}$ depends only on ground-state ($\psi^{(0)}_{n\mathbf{k}}$) and first-order WFs ($\psi^{(\tau_\kappa\beta)}_{n\mathbf{k}}$,$\psi^{(\mathcal{E}_i)}_{n\mathbf{k}}$,$\psi^{(\mathcal{E}_j)}_{n\mathbf{k}}$).

$\Rightarrow$ They are obtained solving 1^{st} order Sternheimer equations.

The electric field perturbation brings a difficulty : $V(\mathcal{E}) = \mathcal{E}.\mathbf{r} = \mathcal{E}.\text{“ } i\nabla_{\mathbf{k}} \text{ ”}$.
In the expression of $E^{(\tau_\kappa\beta\mathcal{E}_i\mathcal{E}_j)}$:

$$\langle\psi^{(\tau_\kappa\beta)}_{n\mathbf{k}}|H^{(\mathcal{E}_i)}|\psi^{(\mathcal{E}_j)}_{n\mathbf{k}}\rangle = i\langle\psi^{(\tau_\kappa\beta)}_{n\mathbf{k}}|\psi^{(k_i\mathcal{E}_j)}_{n\mathbf{k}}\rangle + \dots$$

$\Rightarrow$ We need to solve a 2^{nd} order Sternheimer equation.

Note: Previous ABINIT implementation (Veithen *et al* PRB 71, 125107 (2005)) uses a formalism (“PEAD”) where “ $\nabla_{\mathbf{k}}$ ” is kind of discretised : no need of 2^{nd} derivatives.
However, difficult to adapt to PAW, decreases the convergence with respect to the k point grid.

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

$$1^{\mathrm{st}} \text{ order : } \left(P^c\right)^\dagger\left(H^{(0)} - \epsilon_n\mathcal{S}^{(0)}\right)P^c|\psi^{(\lambda_1)}_n\rangle = -\left(P^c\right)^\dagger\left(H^{(\lambda_1)} - \epsilon_n\mathcal{S}^{(\lambda_1)}\right)|\psi^{(0)}_n\rangle$$

$$\begin{aligned}2^{\mathrm{nd}} \text{ order : } &\left(P^c\right)^\dagger\left(H^{(0)} - \epsilon_n\mathcal{S}^{(0)}\right)P^c|\psi^{(\lambda_1\lambda_2)}_n\rangle = -\left(P^c\right)^\dagger\left(H^{(\lambda_1\lambda_2)} - \epsilon_n\mathcal{S}^{(\lambda_1\lambda_2)}\right)|\psi^{(0)}_n\rangle \\ &-\left(P^c\right)^\dagger\left(H^{(\lambda_1)} - \epsilon_n\mathcal{S}^{(\lambda_1)}\right)|\psi^{(\lambda_2)}_n\rangle - \left(P^c\right)^\dagger\left(H^{(\lambda_2)} - \epsilon_n\mathcal{S}^{(\lambda_2)}\right)|\psi^{(\lambda_1)}_n\rangle \\ &+\sum_m^{\mathrm{occ}}\Lambda^{(\lambda_1)}_{mn}\left(P^c\right)^\dagger\left(\mathcal{S}^{(\lambda_2)}|\psi^{(0)}_m\rangle + \mathcal{S}^{(0)}|\psi^{(\lambda_2)}_m\rangle\right) + \sum_m^{\mathrm{occ}}\Lambda^{(\lambda_2)}_{mn}\left(P^c\right)^\dagger\left(\mathcal{S}^{(\lambda_1)}|\psi^{(0)}_m\rangle + \mathcal{S}^{(0)}|\psi^{(\lambda_1)}_m\rangle\right)\end{aligned}$$

$$|\psi_n\rangle \approx |\tilde{\psi}_n\rangle \qquad \langle\tilde{\psi}_n|\tilde{\psi}_m\rangle = \delta_{nm}$$

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

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

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

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

$$F_{\mu xc}^{\lambda_1\lambda_2\lambda_3}\,[\rho]\,(\mathbf{r}) = \rho^{(\lambda_1)}(\mathbf{r})\rho^{(\lambda_2)}(\mathbf{r})\rho^{(\lambda_3)}(\mathbf{r})\,\frac{d^2\mu_{xc}}{d\rho^2}(\rho^{(0)}(\mathbf{r}))$$

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_\kappa \sum_i \left(|\phi_{\kappa,i}\rangle - |\tilde{\phi}_{\kappa,i}\rangle \right) \langle \tilde{p}_{\kappa,i} | \tilde{\psi}_n \rangle \qquad \langle \tilde{\psi}_n | \mathcal{S} | \tilde{\psi}_m \rangle = \delta_{nm}$$

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

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

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

$$(IV) + (V) = \sum_n \left(\langle \tilde{\psi}_n^{(0)} | \tilde{\mathcal{H}}_{KV}^{(\lambda_1 \lambda_3)} | \tilde{\psi}_n^{(\lambda_2)} \rangle + \langle \tilde{\psi}_n^{(\lambda_2)} | \tilde{\mathcal{H}}_{KV}^{(\lambda_1 \lambda_3)} | \tilde{\psi}_n^{(0)} \rangle \right)$$

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

$$(VII) = \int d\mathbf{r} \, (V_{Hxc}[\tilde{\rho}])^{(\lambda_2)}(\mathbf{r}) \hat{\rho}^{(\lambda_1 \lambda_3)}(\mathbf{r})$$

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

$$F_{\mu_{xc}}^{\lambda_1 \lambda_2 \lambda_3}[\rho](\mathbf{r}) = \rho^{(\lambda_1)}(\mathbf{r}) \rho^{(\lambda_2)}(\mathbf{r}) \rho^{(\lambda_3)}(\mathbf{r}) \frac{d^2 \mu_{xc}}{d\rho^2}(\rho^{(0)}(\mathbf{r}))$$

System : AlAs – Due to symmetries : only 1 degree of liberty in the third derivative tensor :

$$a_{xyz}(Al) = -E^{(\tau_{Al,x}\mathcal{E}_y\mathcal{E}_z)}$$

$N_{\mathbf{k}}$: number of k-points in the Brillouin zone

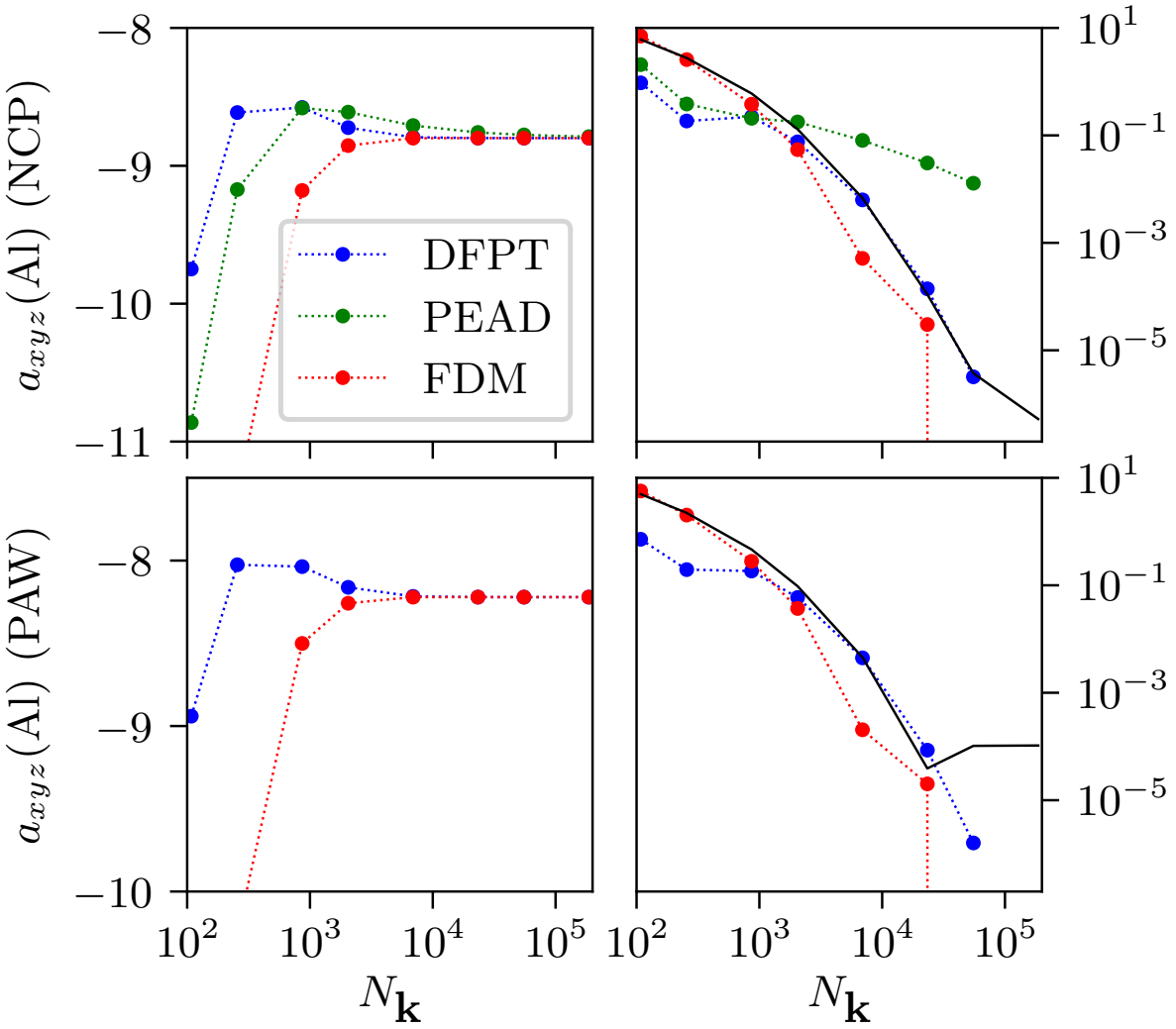
DFPT : current work
PEAD : previous ABINIT implementation
FDM : Finite Difference Method :

$$E^{(\tau_{Al,x}\mathcal{E}_y\mathcal{E}_z)}_{FDM} \equiv \frac{E^{(\mathcal{E}_y\mathcal{E}_z)}_{Al=+\Delta x} - E^{(\mathcal{E}_y\mathcal{E}_z)}_{Al=-\Delta x}}{2\Delta x}$$

Upper frames : norm conserving results
Lower frames : PAW results

Right-handed frames : $|X - X_{\mathrm{conv}}|$ where X_{conv} is the value corresponding to $N_{\mathbf{k}} \approx 180000$

Black lines : $|X_{\mathrm{DFPT}} - X_{\mathrm{FDM}}|$



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(I) : ABINIT : compute DDB: $E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})}(\mathbf{q}=0)$, $E^{(\tau_{\kappa\beta}\mathcal{E}_i\mathcal{E}_j)}$

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

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

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

Parameters depending on experimental setup : laser frequency (ω_0) and polarization ($\mathbf{e}_I$, $\mathbf{e}_S$), temperature (T)

$$I_m = \frac{\hbar}{2\omega_m}(n_m+1)\frac{(\omega_0-\omega_m)^4}{c^4}\left|\mathbf{e}_S.\alpha^m.\mathbf{e}_I\right|^2 \qquad n_m = \frac{1}{e^{\hbar\omega_m/k_BT}-1}$$

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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: $E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})}(\mathbf{q}=0)$, $E^{(\tau_{\kappa\beta}\mathcal{E}_i\mathcal{E}_j)}$, $E^{(\mathcal{E}_i\mathcal{E}_j)}$, $E^{(\tau_{\kappa\beta}\mathcal{E}_i)}$, $E^{(\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k)}$

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

For different **q** directions:

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

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Parameters depending on experimental setup : laser frequency (ω_0) and polarization ($\mathbf{e}_I$, $\mathbf{e}_S$), temperature (T)

$$I_m = \frac{\hbar}{2\omega_m}(n_m+1)\frac{(\omega_0-\omega_m)^4}{c^4}\left|\mathbf{e}_S.\alpha^m.\mathbf{e}_I\right|^2 \qquad n_m = \frac{1}{e^{\hbar\omega_m/k_BT}-1}$$

WARNING : For LO modes, I_{powder} cannot be obtained directly from *RAMAN_SPEC.PY* : numerical integration on **q** directions is needed!

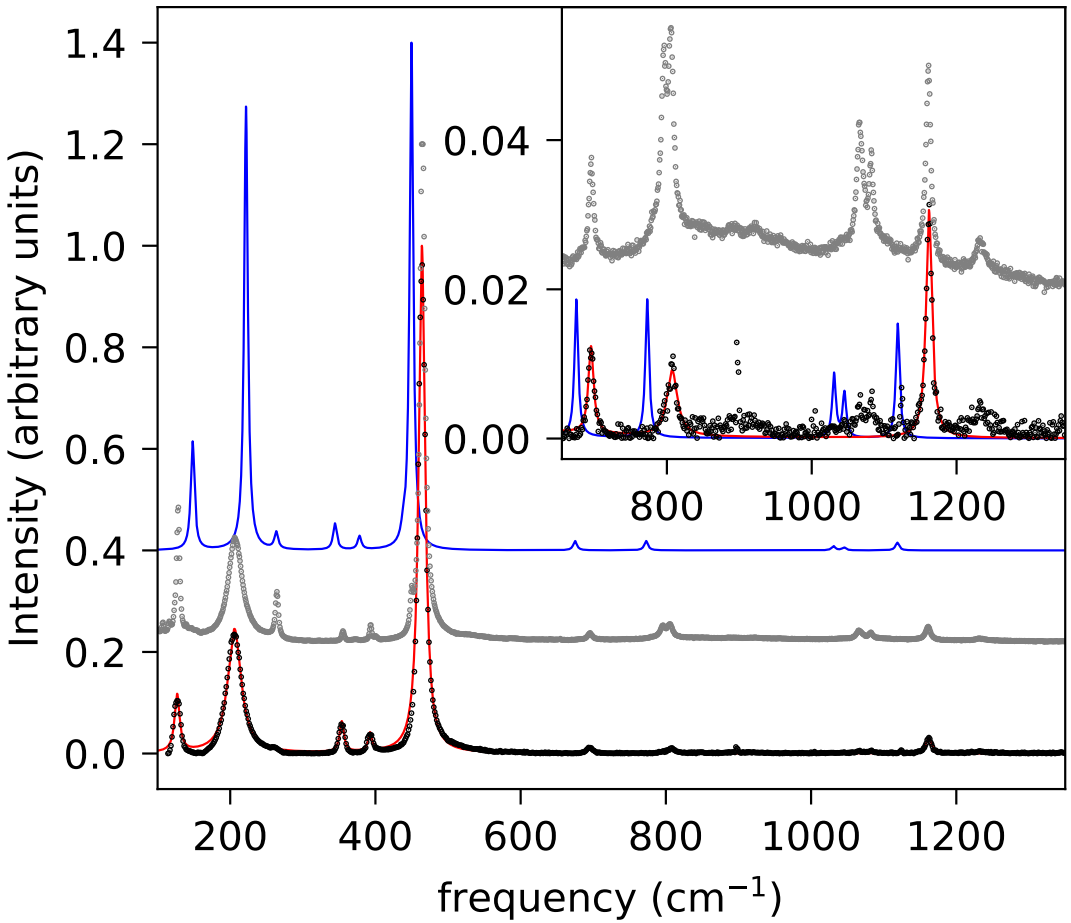
$$I(\omega) \approx \sum_{m}^{\text{active}} \frac{I_m}{\pi} \frac{\Gamma_m}{(\omega - \omega_m)^2 + \Gamma_m^2}$$

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



PAW+LDA		Fit of RRUFF		
ω	I/I_{ref}	ω	I/I_{ref}	Γ
148	0.214	127	0.089	4.1
222	0.875	206	0.521	11.1
263	0.033			
344	0.052	354	0.040	3.5
378	0.027	393	0.021	3.0
438	0.019			
450	1.000	464	1.000	5.2
675	0.018	695	0.010	4.4
773	0.019	807	0.014	8.6
1031	0.009			
1045	0.006			
1119	0.015	1162	0.028	4.8

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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):

$$E_{LDA+U}[n_{LDA+U}] = E_{LDA}[n_{LDA+U}] + \sum_{a}^{+U} \left(E_a(U,J) - E_{a,dc}(U,J)\right) \tag{1}$$

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

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:

$$n^{a\sigma}_{Lmm'} = \sum_{\mathbf{k}} \sum_{n_i,n_j} \sum_{n} \langle \psi_{n\mathbf{k}\sigma} | \tilde{p}_{a,n_i Lm} \rangle \langle \tilde{p}_{a,n_j Lm'} | \psi_{n\mathbf{k}\sigma} \rangle \langle \phi_{a,n_i Lm} | \phi_{a,n_j Lm'} \rangle \tag{3}$$

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

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

$$E_a(U,J) = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j,i',j'} \rho_{a,ij\sigma} \rho_{a,i'j'\sigma'} e_{a,\sigma\sigma',ij,i'j'}(U,J) \tag{4}$$

$$E^H_a = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j,i',j'} \rho_{a,ij\sigma} \rho_{a,i'j'\sigma'} e^H_{a,ij,i'j'} \tag{5}$$

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

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

$$(E_a(U,J))^{(n)} = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j,i',j'} \left(\rho_{a,ij\sigma} \rho_{a,i'j'\sigma'}\right)^{(n)} e_{a,\sigma\sigma',ij,i'j'}(U,J) \tag{6}$$

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 : $|\alpha_{ij}^{DFPT} - \alpha_{ij}^{FD}|/|\alpha_{ij}^{DFPT}| < 0.2\%$

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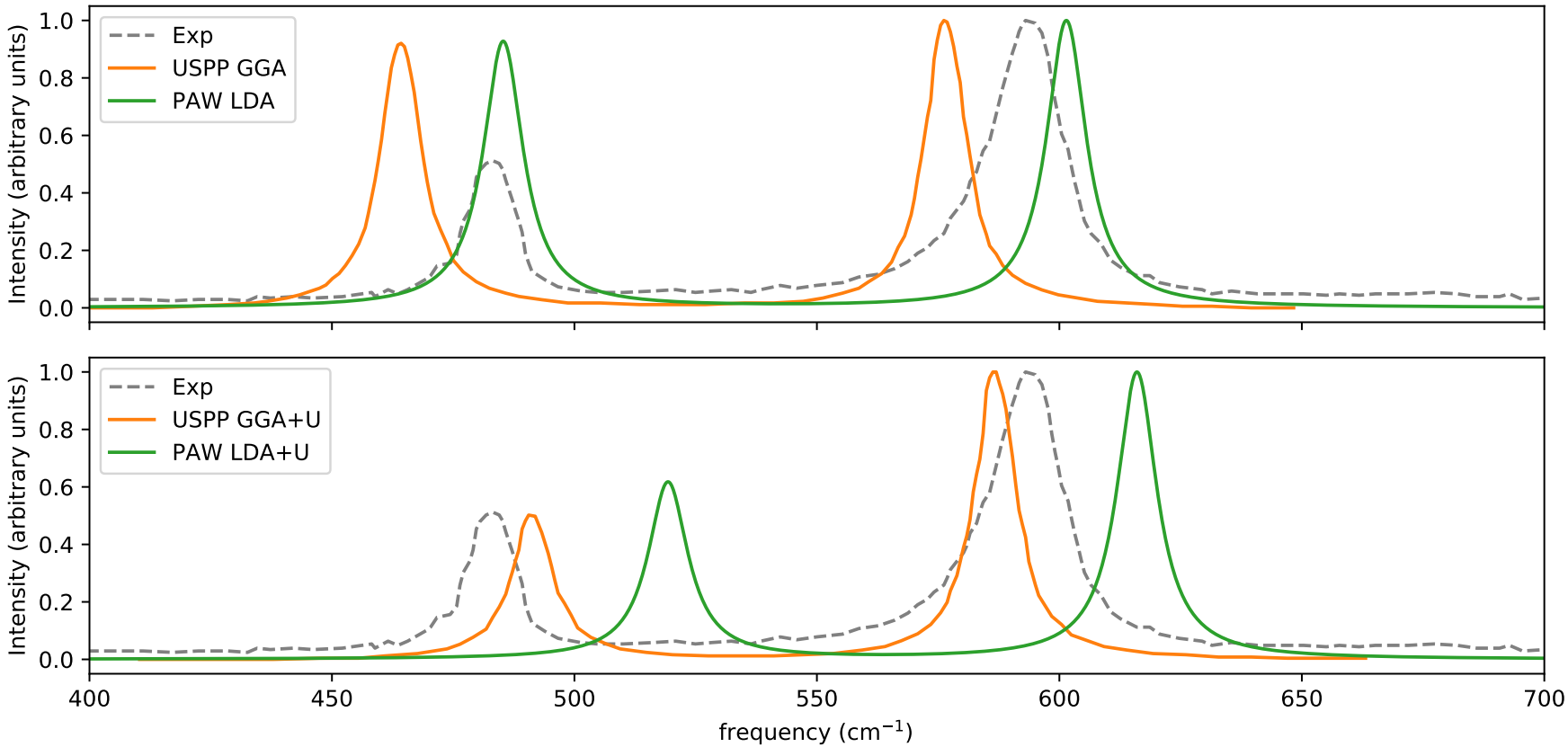
Comparison between PAW LDA / LDA+U (this work) and Ultrasoft (USPP) GGA / GGA+U (Miwa PRB 97, 075143 (2018)):

- 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

Experimental values also taken from Inaba *et al*, Chem. Lett. 24, 889 (1995).

Theoretical spectra : lorentzian width = 5 cm^{-1}, depend on three parameters only : ω_1 , ω_2, I_1 / I_2.



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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 $\psi_{n\mathbf{k}}^{(\tau_{\kappa\beta})}$ 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 $\mathbf{q} \neq 0$)