Ab Initio Simulation of Infrared and Raman Spectroscopy

Advanced Workshop on High-Performance & High-Throughput Materials Simulations using Quantum ESPRESSO

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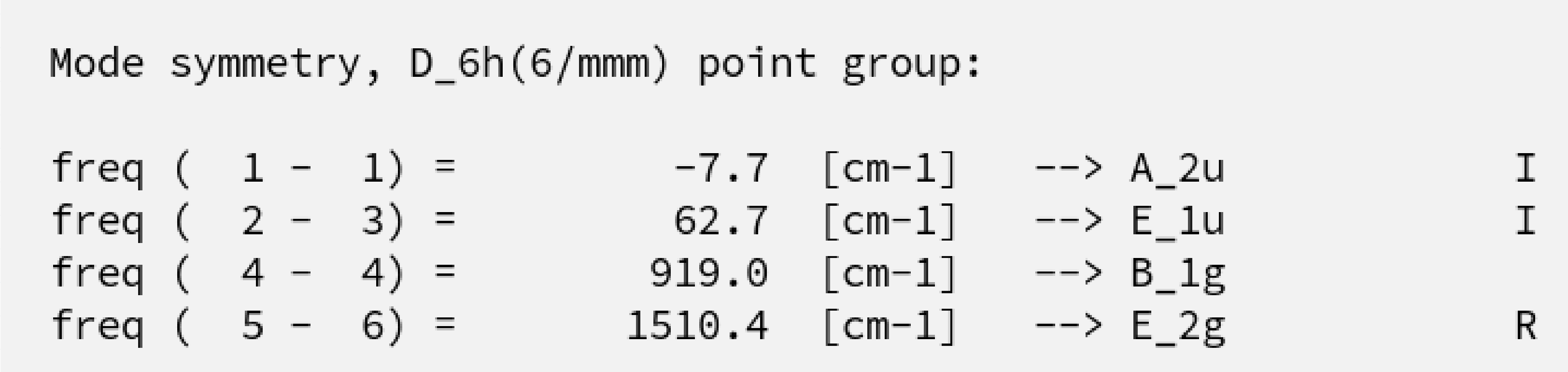
What do we want to say about IR/Raman spectroscopy?

- They are both methods to measure the phonon spectrum
- Which phonon modes can measured by IR/Raman?
- Can we predict the relative intensity of modes?
- We’re not going to threat more advanced techniques: 2nd order Raman, resonant Raman

Which modes can be measured

- If a mode is Infrared or Raman active, depends only on the mode symmetry, it is printed out by phonon:

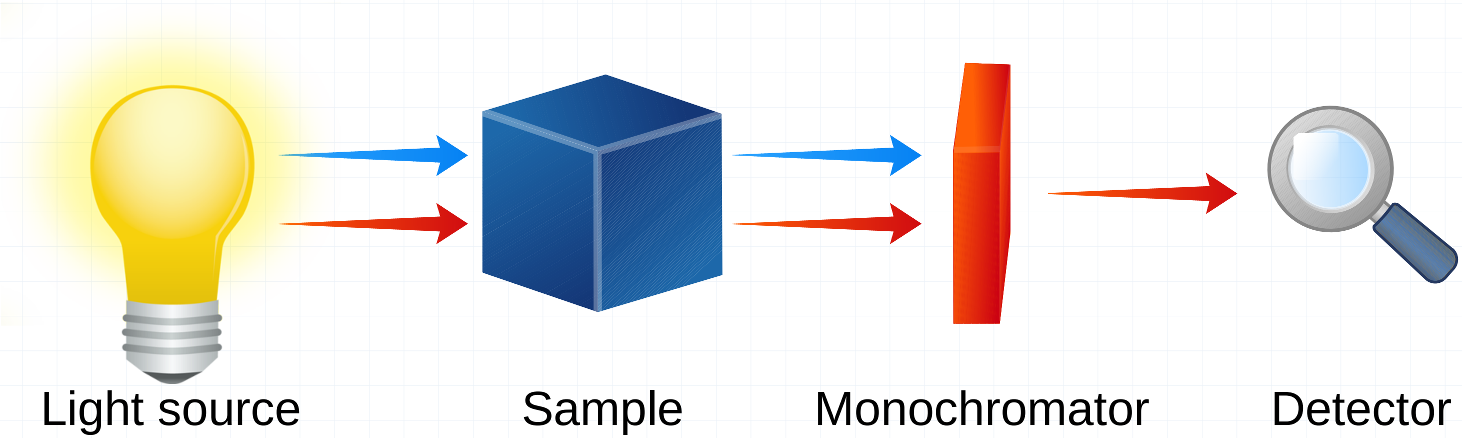


```
Mode symmetry, D_6h(6/mmm) point group:

freq (  1 -  1) =        -7.7  [cm-1]   --> A_2u           I
freq (  2 -  3) =        62.7  [cm-1]   --> E_1u           I
freq (  4 -  4) =       919.0  [cm-1]   --> B_1g
freq (  5 -  6) =      1510.4  [cm-1]   --> E_2g           R
```

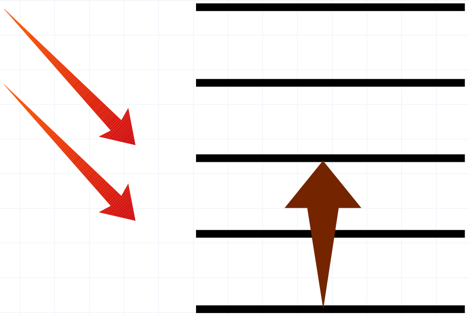
- It depends only on symmetry

What is IR spectroscopy?



- A known-wavelength and constant intensity light is shined through a sample, the outcoming light intensity is measured

What is IR spectroscopy?



- A photon is absorbed to excite a phonon
- Energy and momentum must be conserved

- Photon: $E = \hbar\omega, \lambda = \omega/c, p = \hbar/\lambda$
- Phonon: $\mathrm{E} = \hbar\omega_{\mathbf{n},\mathbf{q}}$, $\mathrm{p} = \hbar(\mathbf{q} + \mathbf{G})$ $\lambda = 1/\mathrm{q}$

What is IR spectroscopy?

- Phonon: $E = \hbar\omega_{n,\mathbf{k}}$, $p = \hbar(\mathbf{q} + \mathbf{G})$ $\lambda = 1/q$
- Photon: $E = \hbar\omega$, $\lambda = \omega/c$, $p = \hbar/\lambda$

In practice:

- Phonon: $E \simeq 1000\mathrm{cm}^{-1}, p \simeq 0 \to .1\hbar\mathrm{nm}^{-1}$
- Photon: $E \simeq 1000\mathrm{cm}^{-1}, p \simeq 10^{-5}\hbar\mathrm{nm}^{-1}$
  - wavelength of at least 10 μm:

E field is constant over many unit cells

Response to a finite E field

- The naïve approach: add an external field:

  $V_E(r) = e\,\mathbf{E}\cdot\mathbf{r}$

- In an infinite crystal V_E diverges at long range
- The operator ***r*** is ill-defined in PBC
- The potential can cause Zener tunneling of valence electrons to conduction band

Gonze PRB 55, 10336 – Gonze & Lee PRB 55, 10355

Baroni, *et al*, Rev.Mod.Phys 73, 515

Response to finite E field

- We can avoid the problem with ***r*** by observing that:

$$\Delta\psi_n(\mathbf{r}) = \sum_{m\neq n} \psi_m(\mathbf{r}) \frac{\langle\psi_m|\Delta V_{SCF}|\psi_n\rangle}{\epsilon_n-\epsilon_m}$$

- In this specific case we have:

$$\langle\psi_m|\mathbf{r}|\psi_n\rangle = \frac{\langle\psi_m|[H_{SCF},\mathbf{r}]|\psi_n\rangle}{\epsilon_m-\epsilon_n}, \quad \forall m\neq n. \qquad [H_{SCF},\mathbf{r}] = -\frac{\hbar^2}{m}\frac{\partial}{\partial\mathbf{r}}$$

- With additional terms if H is non-local

Response to finite E field

- The screened electric field is defined as:

  $\boldsymbol{E} = \boldsymbol{E}_0 - 4\pi\, \boldsymbol{P}$

- The polarization ***P*** induced by the scf field ***E*** is:

$$\mathbf{P} = -\frac{e}{V}\int_V \mathbf{r}\Delta^{\mathsf{E}} n(\mathbf{r})\, d\mathbf{r}. \qquad \Delta^{\mathsf{E}} n(\mathbf{r}) = 4\sum_{n=1}^{N/2} \psi_n^*(\mathbf{r})\Delta^{\mathsf{E}}\psi_n(\mathbf{r})$$

- Note that ***P*** is ill-defined in PBC, because it depends on charge on the surface

Response to finite E field

- We can recast ***P*** in a form that does not depend on the boundaries:

$$\mathrm{P}_\alpha = -\frac{4e}{V}\sum_{n=1}^{N/2}\langle\psi_n|r_\alpha|\Delta^{\mathbf{E}}\psi_n\rangle$$

$$= -\frac{4e}{V}\sum_{n=1}^{N/2}\sum_{m=N/2+1}^{\infty}\frac{\langle\psi_n|[H_{SCF},r_\alpha]||\psi_m\rangle}{(\epsilon_n-\epsilon_m)}\langle\psi_m|\Delta^{\mathbf{E}}\psi_n\rangle$$

- We define an auxiliary wfc

$$\bar{\psi}_n^\alpha(\mathbf{r}) = \sum_{m\neq n}\psi_m(\mathbf{r})\frac{\langle\psi_m|[H_{SCF},r_\alpha]|\psi_n\rangle}{(\epsilon_m-\epsilon_n)}$$

Response to finite E field

- We set-up a self-consistent system of eqs.

$$(H_{SCF}-\epsilon_n)|\Delta^{\mathsf{E}}\psi_n\rangle=-e\sum_{\alpha}\mathsf{E}_\alpha|\bar{\psi}_n^{\alpha}\rangle-P_c\Delta V^{lf}|\psi_n\rangle$$

$$\Delta V^{lf}(\mathbf{r})=e^2\int\frac{\Delta^{\mathsf{E}}n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\left.\frac{dv_{xc}(n)}{dn}\right|_{n=n(\mathbf{r})}\Delta^{\mathsf{E}}n(\mathbf{r})$$

$$\Delta^{\mathsf{E}}n(\mathbf{r})=4\sum_{n=1}^{N/2}\psi_n^*(\mathbf{r})\Delta^{\mathsf{E}}\psi_n(\mathbf{r})$$

- We get the response to the screened field **E**

Dielectric constant

- The long wavelength limit of the dielectric tensor can be computed from these ingredients:

$$\mathsf{E}_{0\alpha} = (\mathsf{E}_{\alpha} + 4\pi \mathsf{P}_{\alpha}) = \sum_{\beta} \epsilon_{\infty}^{\alpha\beta} \mathsf{E}_{\beta}$$

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} - \frac{16\pi e}{V \mathsf{E}_{\beta}} \sum_{n=1}^{N/2} \langle \bar{\psi}_{n}^{\alpha} | \Delta^{\mathsf{E}_{\beta}} \psi_{n} \rangle$$

Variational formulation

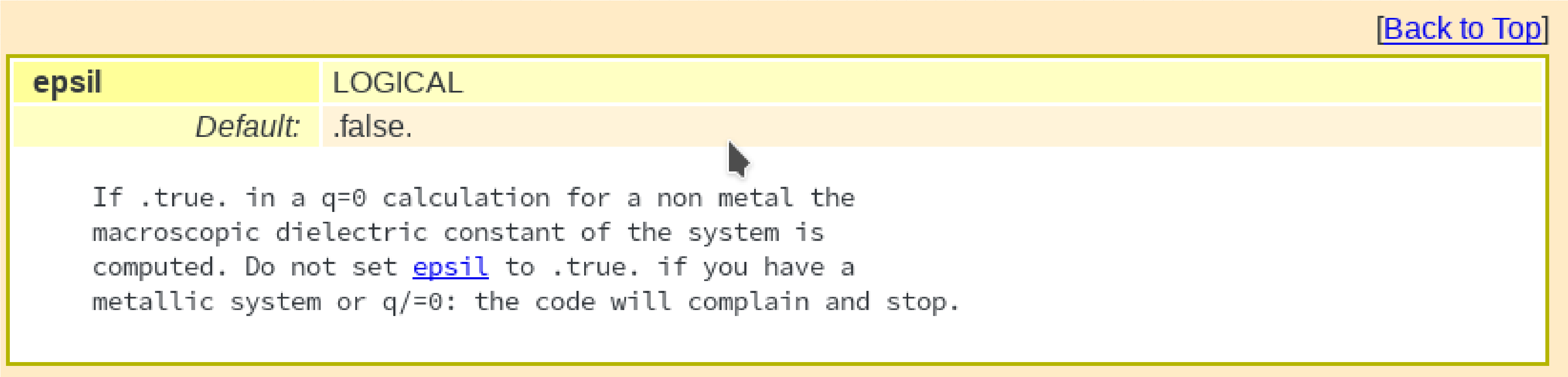
- Gonze: variational formulation, minimize an approximate functional

$$\epsilon^{\infty}_{\alpha\beta} = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} 2 \frac{\partial^2 \mathsf{E}_{\mathsf{KS}}}{\partial \mathsf{E}_{\alpha} \partial \mathsf{E}_{\beta}}$$

$$\frac{\partial^2 \mathsf{E}_{\mathsf{KS}}}{\partial \mathsf{E}_{\alpha} \partial \mathsf{E}_{\beta}} = \frac{\Omega}{(2\pi)^3} \int_{\mathsf{BZ}} \sum_{\mathsf{v}} \mathsf{i} < \delta^{\mathsf{E}_{\alpha}} \psi_{\mathsf{v}} | \delta^{\mathsf{k}_{\beta}} \psi_{\mathsf{v}} > \mathrm{d}\mathbf{k}$$

- ph.x does not normally use this formula

ph.x input for epsilon



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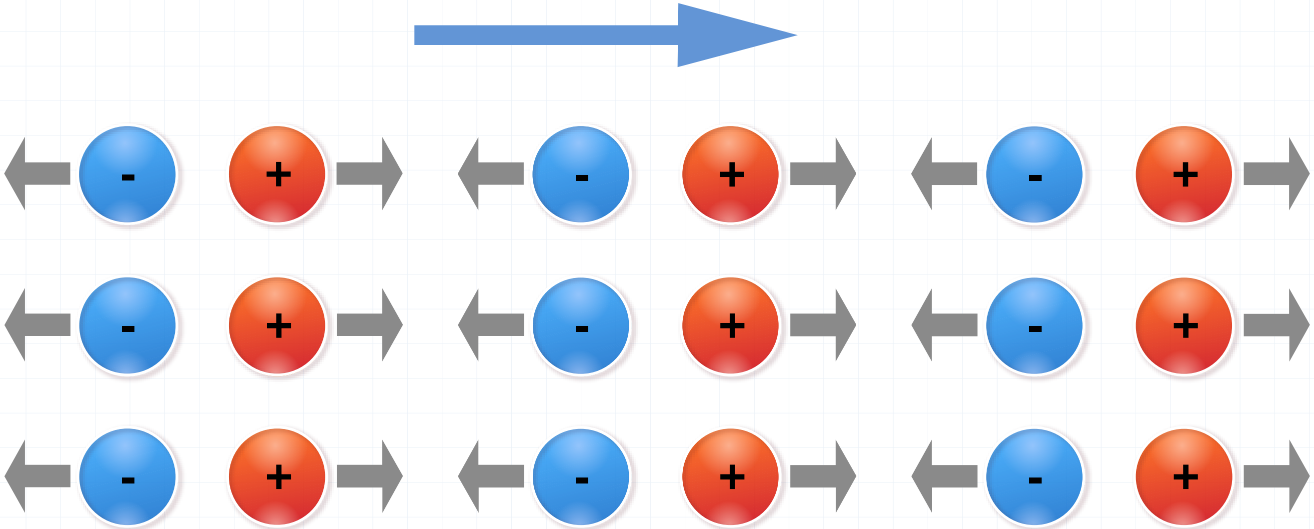
epsil	LOGICAL
Default:	.false.

If .true. in a q=0 calculation for a non metal the macroscopic dielectric constant of the system is computed. Do not set epsil to .true. if you have a metallic system or q/=0: the code will complain and stop.

- It takes quite a bit of time!
- You do not need to compute also the phonons in the same run
- Not available for metals (either real or fake)

Optical phonons in a ionic crystal

- Let’s consider a simple ionic crystal, the atoms move according to a LO long-wavelength phonon:



- Coupling of charges with macroscopic polarization:

$$z^{\star}_{\mathsf{I}\beta\alpha} = \Omega \frac{\partial \mathsf{P}_{\mathsf{mac},\beta}}{\partial \tau_{\mathsf{I}\alpha}}$$

R.P. Tulip PhD Thesis, Durham, 2004

Optical phonons in a ionic crystal

- We consider the electric enthalpy (internal energy + interaction with ext.)

$$\tilde{\mathsf{H}}[\mathsf{u}_{\mathbf{nk}}, \mathsf{E}] = \mathsf{E}_{\mathsf{KS}} - \Omega \mathbf{P}_{\mathsf{mac}} \cdot \mathbf{E}$$

$$\mathsf{P}_{\mathsf{mac},\alpha} = -\frac{1}{\Omega} \frac{\partial \tilde{\mathsf{H}}}{\partial \mathsf{E}_\alpha}$$

$$\mathsf{z}^{\star}_{\mathsf{I}\alpha\beta} = -\frac{\partial^2 \tilde{\mathsf{H}}}{\partial \mathsf{E}_\beta \partial \tau_{\mathsf{I}\alpha}} = \frac{\mathsf{F}_{\mathsf{I}\alpha}}{\mathsf{E}_\beta}\Big|_{\tau_{\mathsf{I}\alpha}=0}$$

Z*$_{\text{ue}}$ vs. Z*$_{\text{eu}}$

- ph.x can compute z* in two ways:
- Derive w.r.t the E field first

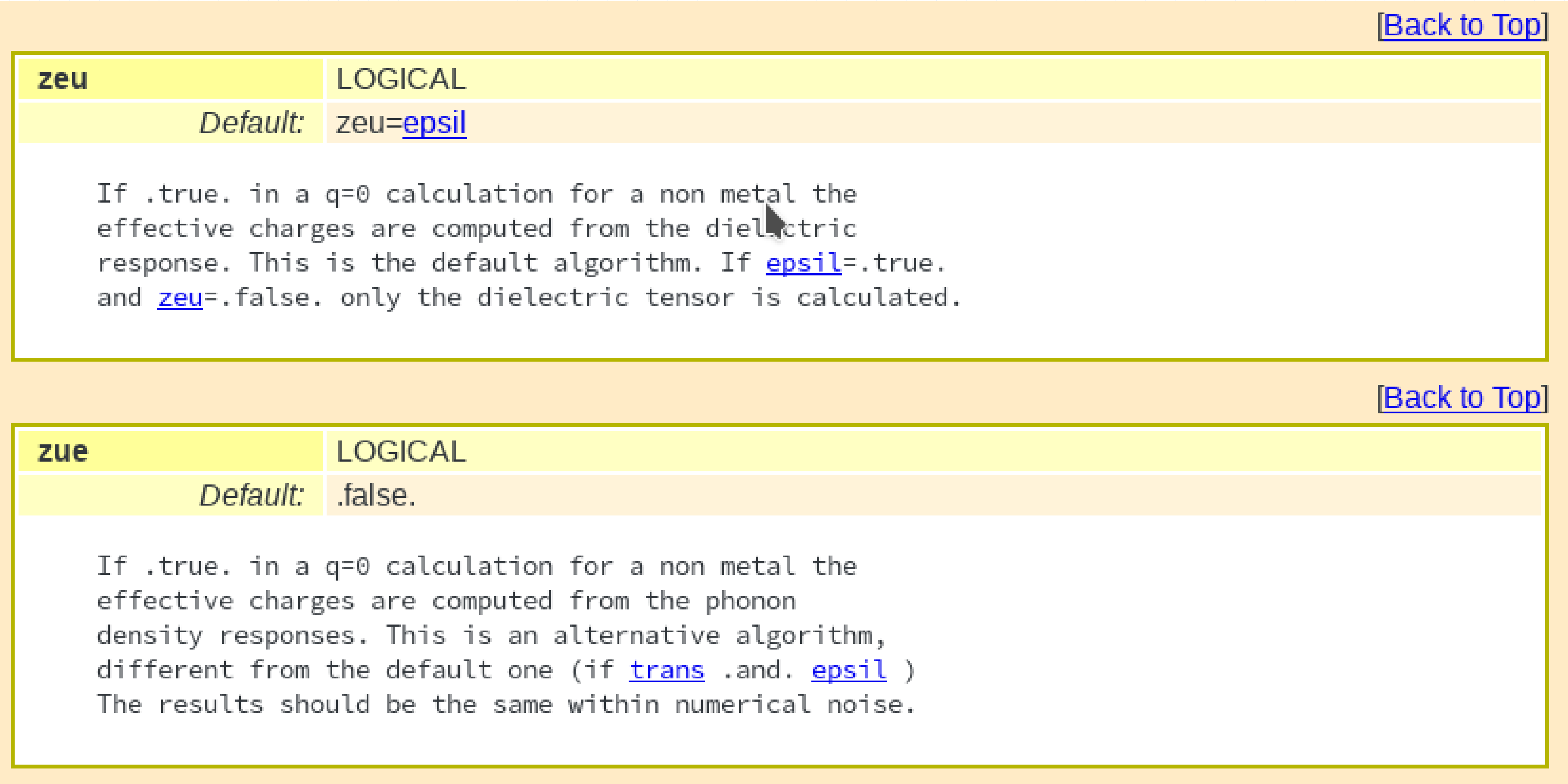
$$\mathsf{z}^{\star}_{\mathsf{ue}} = -2 < \delta^{\tau_\alpha}\psi|\delta^{\mathsf{E}_\beta}\mathsf{H}|\psi >$$

- Derive w.r.t the displacements first

$$\mathsf{z}^{\star}_{\mathsf{ue}} = \left.\frac{\mathsf{F}_{\mathsf{I}\alpha}}{\mathsf{E}_\beta}\right|_{\tau_{\mathsf{I}\alpha}=0} = -2 < \delta^{\mathsf{E}_\beta}\psi|\delta^{\tau_\alpha}\mathsf{H}|\psi >$$

Check that they give the same result!

ph.x input for zeu/zue



zeu	LOGICAL
Default:	zeu=epsil

If .true. in a q=0 calculation for a non metal the effective charges are computed from the dielectric response. This is the default algorithm. If epsil=.true. and zeu=.false. only the dielectric tensor is calculated.

zue	LOGICAL
Default:	.false.

If .true. in a q=0 calculation for a non metal the effective charges are computed from the phonon density responses. This is an alternative algorithm, different from the default one (if trans .and. epsil) The results should be the same within numerical noise.

ph.x input for zeu/zue

- They do not cost much more than the phonon/epsilon calculation respectively
- They cannot be computed for metals (either real or fake)
- They are zero in high symmetry materials

Non-analytical contribution to LO

- The most generic equation of motion for ions with a macroscopic electric field:

$$E(\mathbf{u},\mathbf{E})=\frac{1}{2}M\omega_0^2u^2-\frac{\Omega}{8\pi}\epsilon_\infty \mathsf{E}^2-eZ^\star\mathbf{u}\cdot\mathbf{E}$$

- Conjugate variables to u, E: force and el. induction

$$\mathbf{F}\equiv-\frac{\partial E}{\partial\mathbf{u}}=-M\omega_0^2\mathbf{u}+eZ^\star\mathbf{E},$$

$$\mathbf{D}\equiv-\frac{4\pi}{\Omega}\frac{\partial E}{\partial\mathbf{E}}=\frac{4\pi}{\Omega}eZ^\star\mathbf{u}+\epsilon_\infty\mathbf{E}$$

Non-analytical contribution to LO

- The most generic equation of motion for ions with a macroscopic electric field:

$$E(\mathbf{u},\mathbf{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathrm{E}^2 - e Z^\star \mathbf{u} \cdot \mathbf{E}$$

- We setup Maxwell equation w/o ext. charges

$$\mathrm{rot}\, \mathbf{E} \sim i\mathbf{q} \times \mathbf{E} = 0 \qquad \mathrm{div}\, \mathbf{D} \sim i\mathbf{q} \cdot \mathbf{D} = 0$$

Non-analytical contribution to LO

$$E(\mathbf{u},\mathbf{E}) = \frac{1}{2}M\omega_0^2 u^2 - \frac{\Omega}{8\pi}\epsilon_\infty \mathbf{E}^2 - eZ^\star \mathbf{u}\cdot \mathbf{E}$$

$$\mathbf{F} \equiv -\frac{\partial E}{\partial \mathbf{u}} = -M\omega_0^2\mathbf{u} + eZ^\star\mathbf{E}, \qquad \mathrm{rot}\,\mathbf{E} \sim i\mathbf{q}\times\mathbf{E} = 0$$

$$\mathbf{D} \equiv -\frac{4\pi}{\Omega}\frac{\partial E}{\partial \mathbf{E}} = \frac{4\pi}{\Omega}eZ^\star\mathbf{u} + \epsilon_\infty\mathbf{E} \qquad \mathrm{div}\,\mathbf{D} \sim i\mathbf{q}\cdot\mathbf{D} = 0$$

- Solve for transverse/longitudinal field:

$$\omega_L = \sqrt{\omega_0^2 + 4\pi e^2 Z^{\star 2}/\Omega\epsilon_\infty M}$$

$$\omega_T = \omega_0$$

Computing the IR cross section

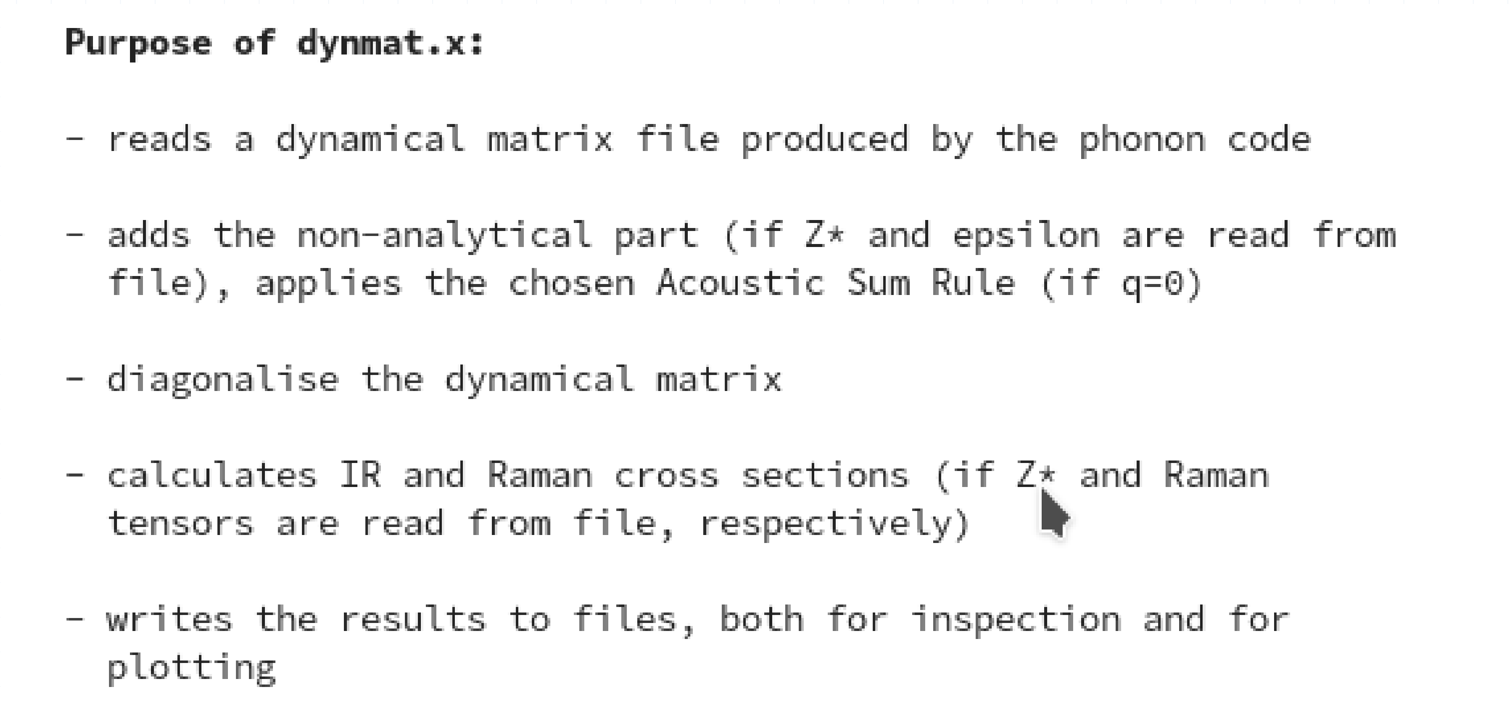
- One the effective charges are done, computing the IR cross section is trivial:

$$\mathcal{I}_{\nu\alpha} = \sum_{\alpha} \mathsf{z}^{\star}_{\mathsf{I}\alpha\beta} \mathsf{u}_{\nu,\mathsf{I}\beta}$$

- In the case of molecules, or powdered crystals, the average I is just the square modulus
- In case of polarized light, talk with the experimentalist!

Computing the IR cross section

- *dynmat.x* code (Phonon/Doc/IPUT_DYNMAT.html)
- It reads the dynamical matrix at Gamma

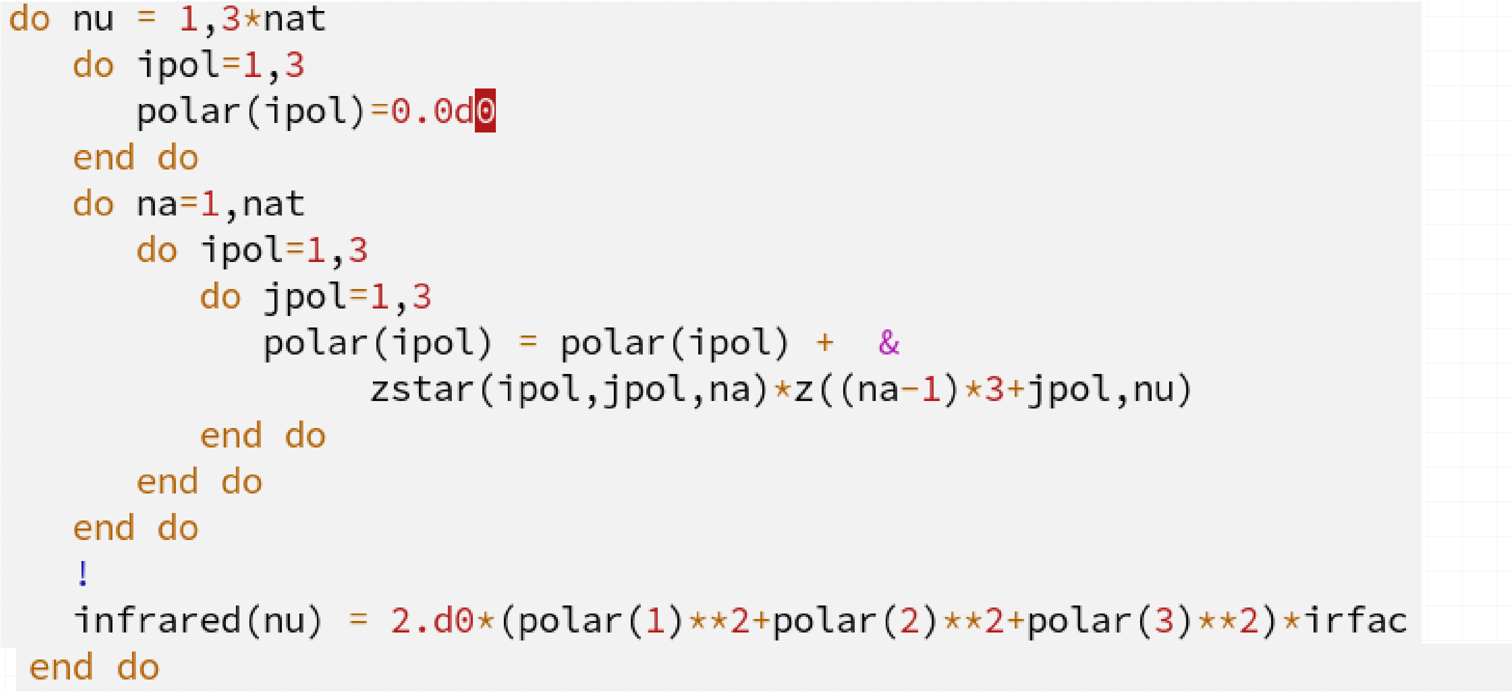


Purpose of dynmat.x:

- reads a dynamical matrix file produced by the phonon code
- adds the non-analytical part (if Z* and epsilon are read from file), applies the chosen Acoustic Sum Rule (if q=0)
- diagonalise the dynamical matrix
- calculates IR and Raman cross sections (if Z* and Raman tensors are read from file, respectively)
- writes the results to files, both for inspection and for plotting

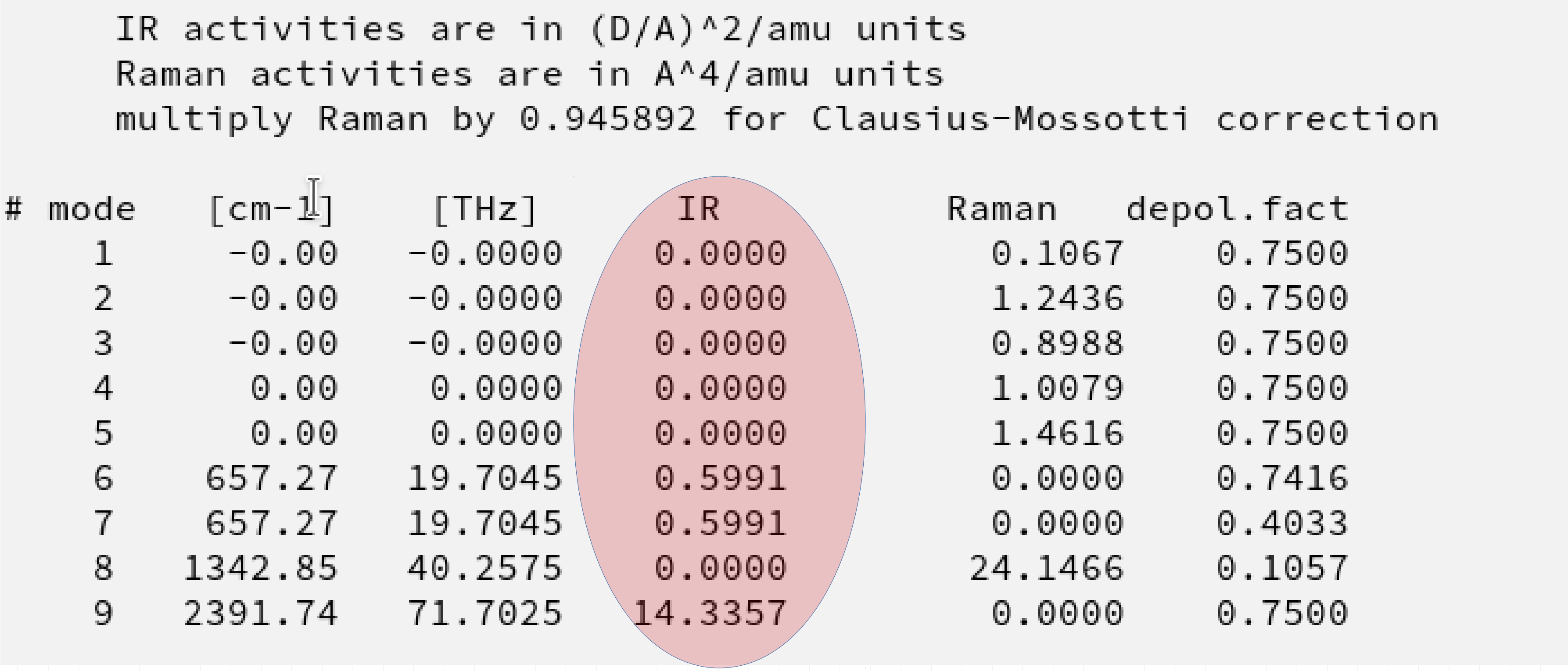
Computing the IR cross section

- It is also possible to compute the cross section by hand, taking the information from the dynamical matrix file with a simple scripting language (matlab, python..)



```
do nu = 1,3*nat
   do ipol=1,3
      polar(ipol)=0.0d0
   end do
   do na=1,nat
      do ipol=1,3
         do jpol=1,3
            polar(ipol) = polar(ipol) +  &
                 zstar(ipol,jpol,na)*z((na-1)*3+jpol,nu)
         end do
      end do
   end do
   !
   infrared(nu) = 2.d0*(polar(1)**2+polar(2)**2+polar(3)**2)*irfac
 end do
```

Computing the IR cross section



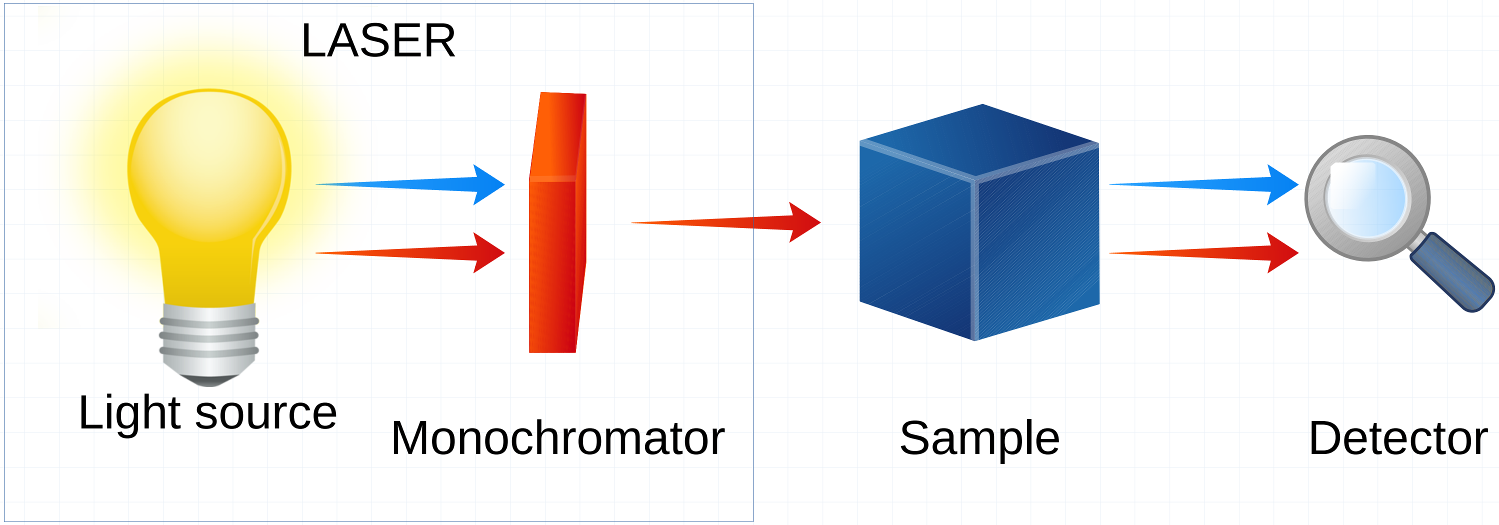
```
     IR activities are in (D/A)^2/amu units
     Raman activities are in A^4/amu units
     multiply Raman by 0.945892 for Clausius-Mossotti correction

# mode   [cm-1]    [THz]      IR          Raman   depol.fact
    1     -0.00   -0.0000     0.0000         0.1067    0.7500
    2     -0.00   -0.0000     0.0000         1.2436    0.7500
    3     -0.00   -0.0000     0.0000         0.8988    0.7500
    4      0.00    0.0000     0.0000         1.0079    0.7500
    5      0.00    0.0000     0.0000         1.4616    0.7500
    6    657.27   19.7045     0.5991         0.0000    0.7416
    7    657.27   19.7045     0.5991         0.0000    0.4033
    8   1342.85   40.2575     0.0000        24.1466    0.1057
    9   2391.74   71.7025    14.3357         0.0000    0.7500
```

What is Raman spectroscopy

- Sir Chandrasekhara Venkata Raman
- ~ 1928
- Nobel Prize 1930
- W/ K. S. Krishnan and independently by Grigory Landsberg and Leonid Mandelstam

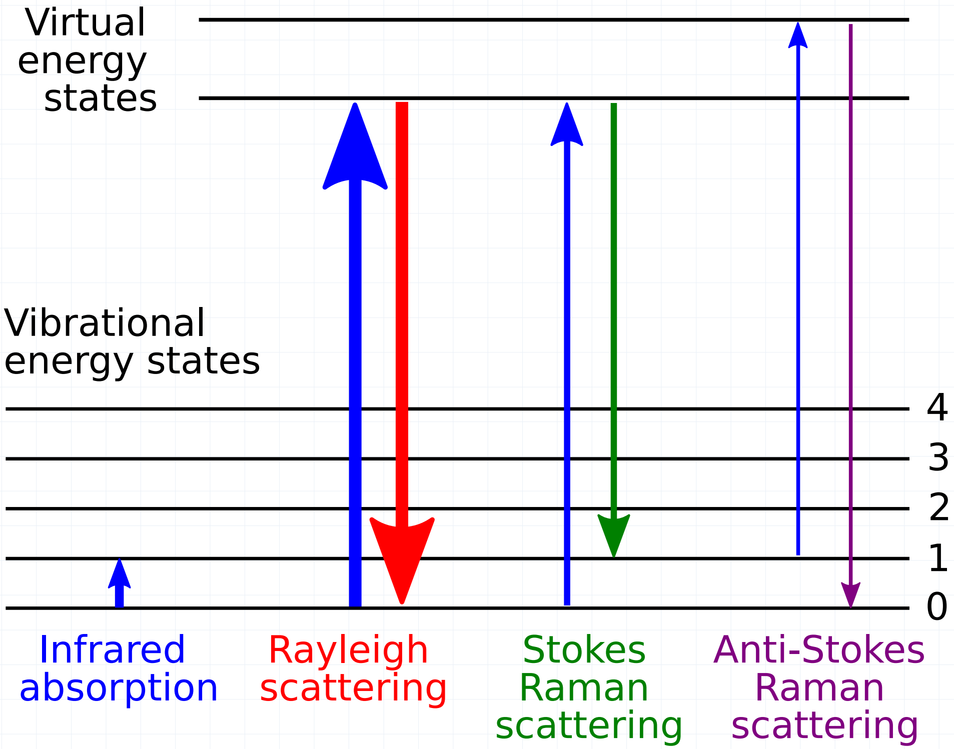
What is Raman spectroscopy



- The sample is excited with a monochromatic light (nowadays a laser) the spectrum of the outcoming light is measured

What is Raman spectroscopy

- How can this be related to phonons?



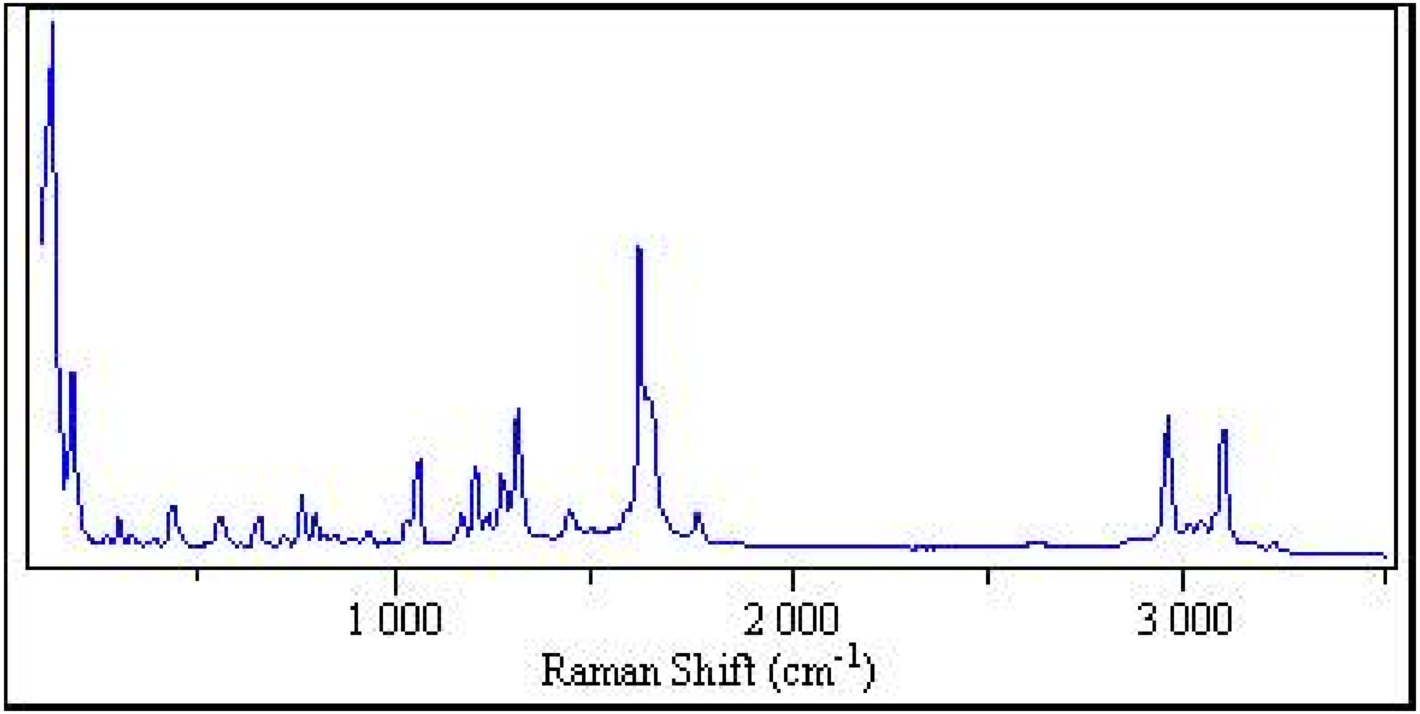
e.g. *Raman shift / Elastic peak*

Image: Raman_energy_levels.svg/Wikipedia

What is Raman spectroscopy

- Photon excites the solid to an unstable state
- The excitation relaxes:
  - Directly, emitting photon on the same wavelength
  - Indirectly, emitting a phonon and photon of a shifted wavelength

What is Raman spectroscopy



Spectrum of aspirin (4-acetylsalicylic acid) acquired in 1 second

Image from Horiba scientific

What is Raman spectroscopy

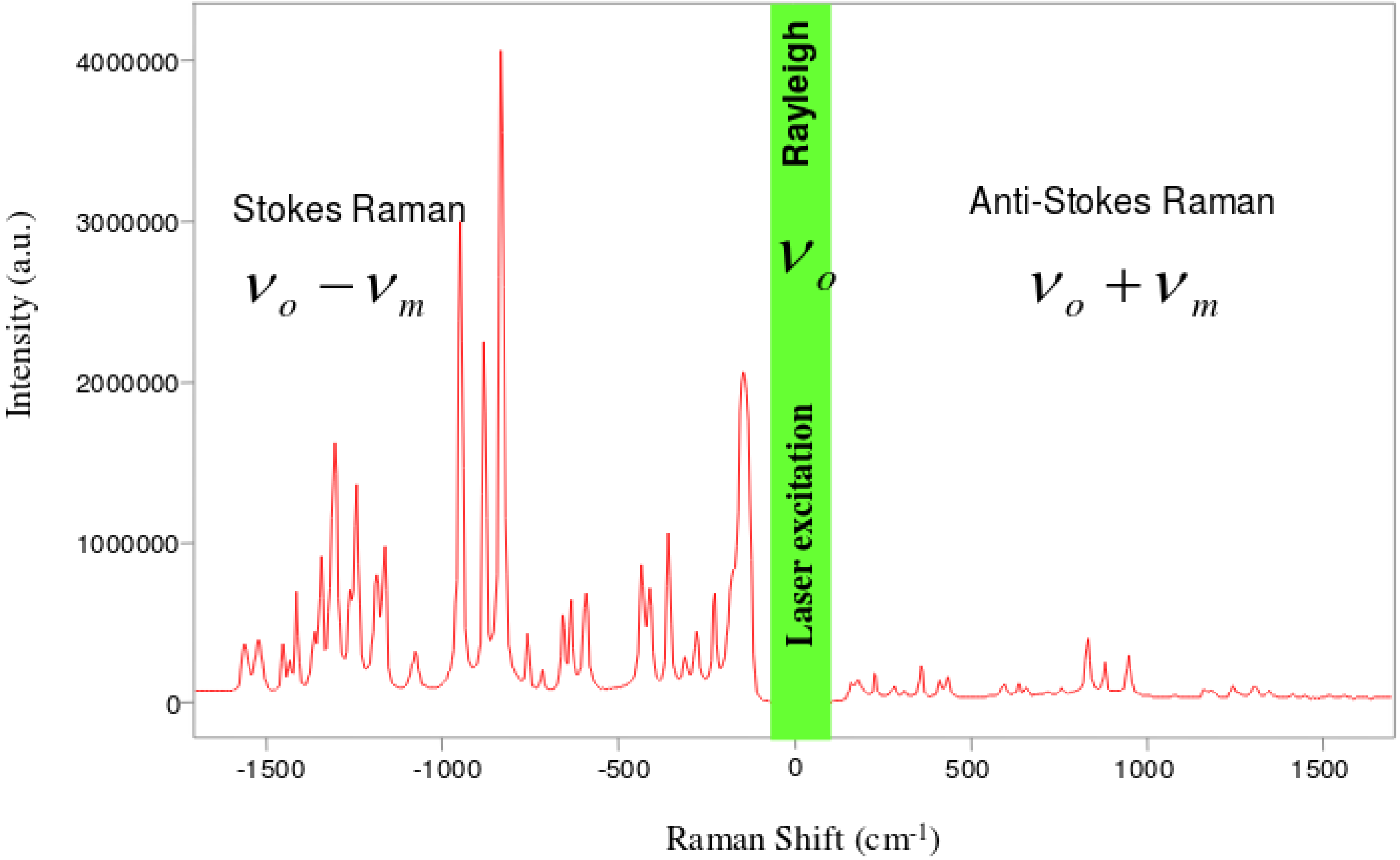


Image: Anupan Misra, HIGP, Honolulu

Computing the Raman x section

- The intensity is proportional to:

$$\mathrm{I}^{\nu} \propto \left| \mathbf{e}_{\mathrm{i}} \overleftrightarrow{\mathbf{A}} \mathbf{e}_{\mathrm{s}} \right|^{2} \frac{\mathrm{n}_{\nu}+1}{\omega_{\nu}}$$

- Where the tensor **A** is the response w.r.t one phonon and two electric fields

$$\mathrm{A}^{\nu}_{\alpha\beta} = \sum_{\mathrm{I}\gamma} \frac{\partial^{3}\mathrm{E}_{\mathrm{KS}}}{\partial \mathrm{E}_{\alpha} \partial \mathrm{E}_{\beta} \partial \mathrm{u}_{\mathrm{I}\gamma}} \frac{\mathrm{w}^{\nu}_{\mathrm{I}\gamma}}{\sqrt{\mathrm{M}_{\mathrm{I}}}}$$

Porezag&Pederson PRB 54, 7830 (1996) – Lazzeri&Mauri PRL 90, 036401 (2003)

Computing the Raman tensor

- Simpler approach:
  - finite derivation of the dielectric matrix
- Advantages: readily available, does not require a super-cell
- Disadvantages: bad scaling, very expensive for large systems

Computing the Raman tensor

- Smarter approach:
  - Density matrix $\rho = \sum |\psi >< \psi|$
  - Energy derivative

$$\frac{\partial \mathrm{E}_{\mathrm{KS}}}{\partial \mathrm{u}_{\mathrm{I}\gamma}} = 2\mathrm{Tr}\left[\rho \frac{\partial \mathrm{v}_{\mathrm{ext}}}{\partial \mathrm{u}_{\mathrm{I}\gamma}}\right]$$

  - $\mathrm{V}_{\mathrm{ext}}$ does not change with an ext **E** field

$$\frac{\partial^3 \mathrm{E}_{\mathrm{KS}}}{\partial \mathrm{u}_{\mathrm{I}\gamma} \partial \mathrm{E}_\alpha \partial \mathrm{E}_\beta} = 2\mathrm{Tr}\left[\frac{\partial^2 \rho}{\partial \mathrm{E}_\alpha \partial \mathrm{E}_\beta} \frac{\partial \mathrm{v}_{\mathrm{ext}}}{\partial \mathrm{u}_{\mathrm{I}\gamma}}\right]$$

Computing the Raman tensor

- We still need the 2nd derivative of ρ

$$\frac{\partial^2 \rho}{\partial\lambda\partial\mu} = \sum_{\nu} \Bigg(|\mathsf{P_c}\eta^{\lambda\mu} >< \psi_{\mathsf{n}}\mathsf{u}| + |\mathsf{P_c}\frac{\partial\psi}{\partial\lambda} >< \mathsf{P_c}\frac{\partial\psi}{\partial\mu}| - \sum_{\nu'} |\psi_{\nu'} >< \mathsf{P_c}\frac{\partial\psi}{\partial\lambda}|\mathsf{P_c}\frac{\partial\psi}{\partial\mu} >< \psi_\nu| \Bigg) + \mathsf{c.c.}$$

- We have all the ingredients, except $\eta^{\lambda\mu}$, the second derivative of Ψ in the parallel transport gauge

Computing the Raman tensor

- Solving with a Green function method

$$|\mathsf{P_c}\frac{\partial\psi_\nu}{\partial\lambda}> = \tilde{\mathsf{G}}_\nu\left[\frac{\partial\mathsf{V}^{\mathsf{KS}}}{\partial\lambda},\rho\right]|\psi_\nu>$$

$$\begin{aligned}|\mathsf{P_c}\eta_\nu^{\lambda\mu}> = \tilde{\mathsf{G}}_\nu\Big\{&\frac{\partial^2\mathsf{V}^{\mathsf{KS}}}{\partial\lambda\partial\mu}+\left[\frac{\partial\mathsf{V}^{\mathsf{KS}}}{\partial\lambda},\frac{\partial\rho}{\partial\mu}\right]\\&+\left[\frac{\partial\mathsf{V}^{\mathsf{KS}}}{\partial\mu},\frac{\partial\rho}{\partial\lambda}\right]\Big\}|\psi_\nu>\end{aligned}$$

$$\tilde{\mathsf{G}}_\nu = \sum_{\mathsf{c}}\frac{|\psi_{\mathsf{c}}><\psi_{\mathsf{c}}|}{\epsilon_{\mathsf{v}}-\epsilon_{\mathsf{c}}}$$

Computing the Raman tensor

- In periodic boundary condition, the **r** operator can be expressed as a derivative w.r.t the wavevector

$$\langle \psi_c^{\mathbf{k}} | [r_l, \rho] | \psi_\upsilon^{\mathbf{k}} \rangle = i \sum_{\upsilon'} \langle u_c^{\mathbf{k}} | \frac{\partial | u_{\upsilon'}^{\mathbf{k}} \rangle \langle u_{\upsilon'}^{\mathbf{k}} |}{\partial k_l} | u_\upsilon^{\mathbf{k}} \rangle,$$

$$\langle \psi_c^{\mathbf{k}} | \left[r_l, \frac{\partial \rho}{\partial E_m} \right] | \psi_\upsilon^{\mathbf{k}} \rangle = i \sum_{\upsilon'} \langle u_c^{\mathbf{k}} | \frac{\partial | P_{\mathbf{k}} \frac{\partial u_{\upsilon'}^{\mathbf{k}}}{\partial E_m} \rangle \langle u_{\upsilon'}^{\mathbf{k}} |}{\partial k_l} | u_\upsilon^{\mathbf{k}} \rangle,$$

- We can compute ε with the Gonze formula

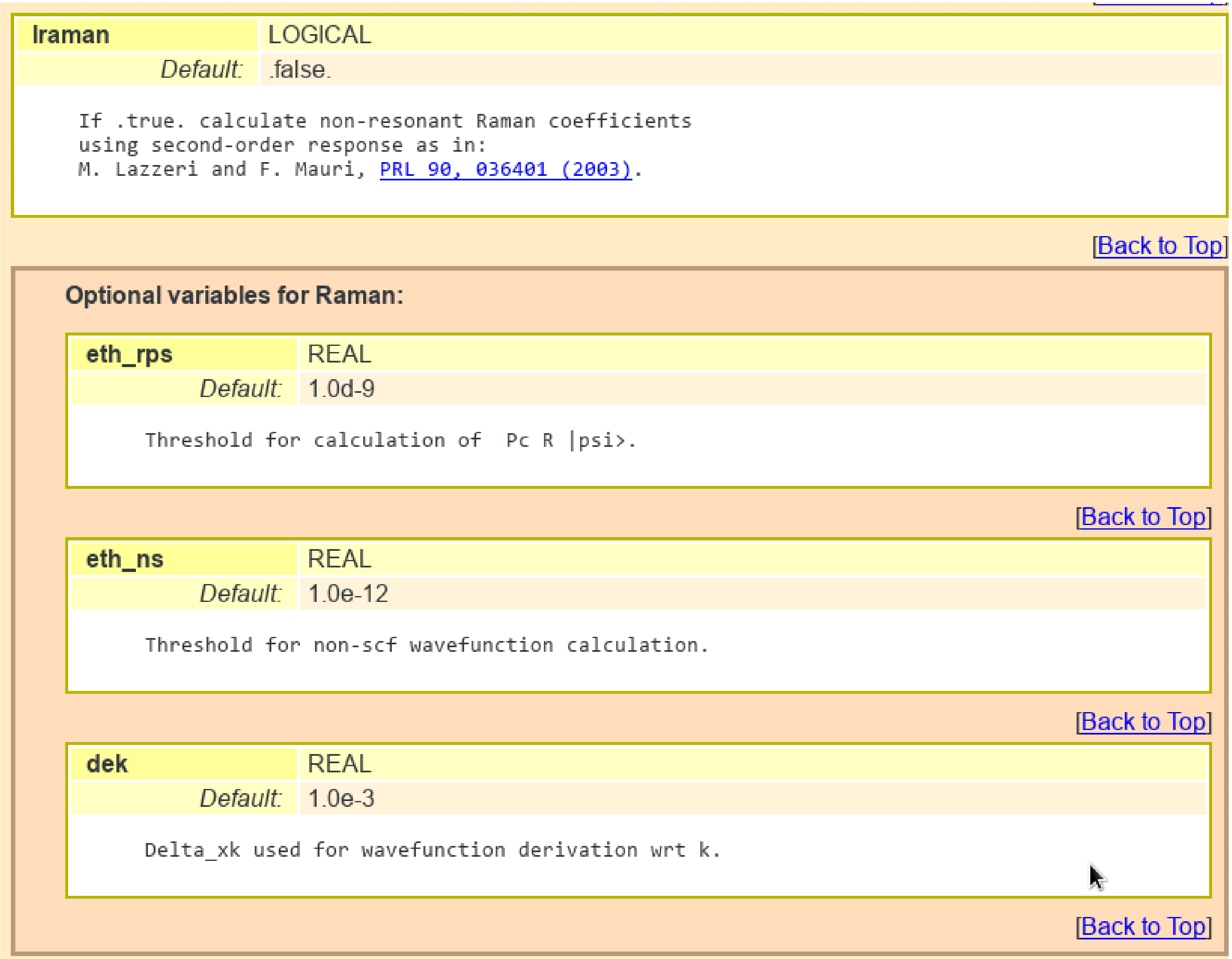
Computing the Raman tensor

- One critical component of the calculation in practice is the convergence with the k-points grid
- Convergence of this method is usually much faster than the finite differences method
- Check that ε computed with the two formulas is consistent (finite difference derivative w.r.t the wavevector)

Computing the Raman tensor

- If you are familiar with Berry phase formalism, you will notice that we are using more or less the same “ingredients”
- This theory can be also formulated in terms of Berry phase (see Gonze)
- It is possible to do finite differences w.r.t **E** using the modern theory of polarization

Computing the Raman tensor



lraman	LOGICAL
Default:	.false.

```
If .true. calculate non-resonant Raman coefficients
using second-order response as in:
M. Lazzeri and F. Mauri, PRL 90, 036401 (2003).
```

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Optional variables for Raman:

eth_rps	REAL
Default:	1.0d-9

```
Threshold for calculation of  Pc R |psi>.
```

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eth_ns	REAL
Default:	1.0e-12

```
Threshold for non-scf wavefunction calculation.
```

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dek	REAL
Default:	1.0e-3

```
Delta_xk used for wavefunction derivation wrt k.
```

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Computing the Raman tensor

- Some important limitations:
  - Only norm-conserving pseudopotentials
  - Only LDA (PBE wip?)
  - Limited support for spin-polarization
  - Not for metals (you could enable it for semimetals at your own risk)

Computing the Raman tensor

- You do not need to compute the phonons in the same run
  - *only the derivative of the external potential w.r.t the harmonic perturbation is needed*
  - *But you will have to re-assemble the dynamical matrix file by hand*

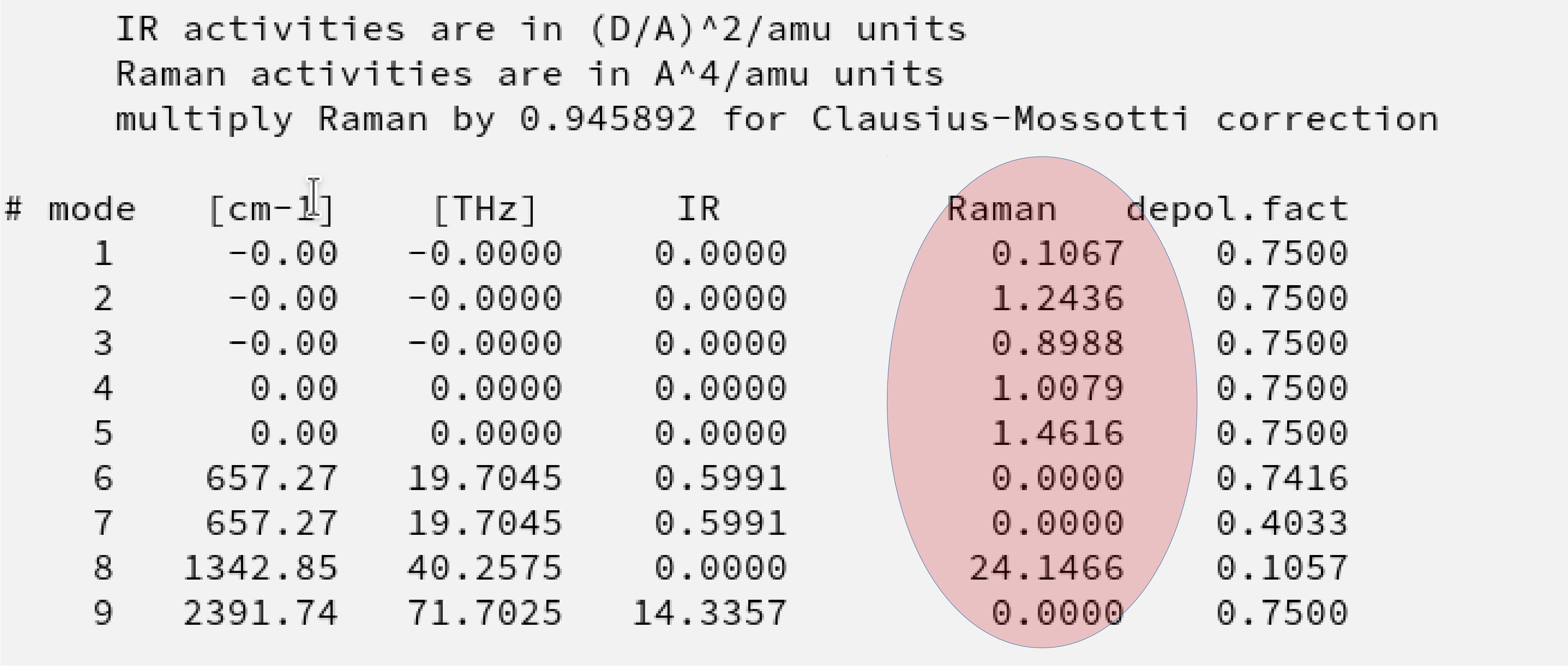
Computing the Raman X section

- dynmat.x can read the dynamical matrix file and compute the cross section if **A** is available
- It uses the non-polarized formula (e.g. good for molecule, powder samples)

$$\mathsf{I}^{\nu} \propto \left| \mathbf{e}_{\mathsf{i}} \overleftrightarrow{\mathbf{A}} \mathbf{e}_{\mathsf{s}} \right|^2 \frac{\mathsf{n}_{\nu} + 1}{\omega_{\nu}}$$

- LR_Modules/dynmat_sub.f90

Computing the Raman X section



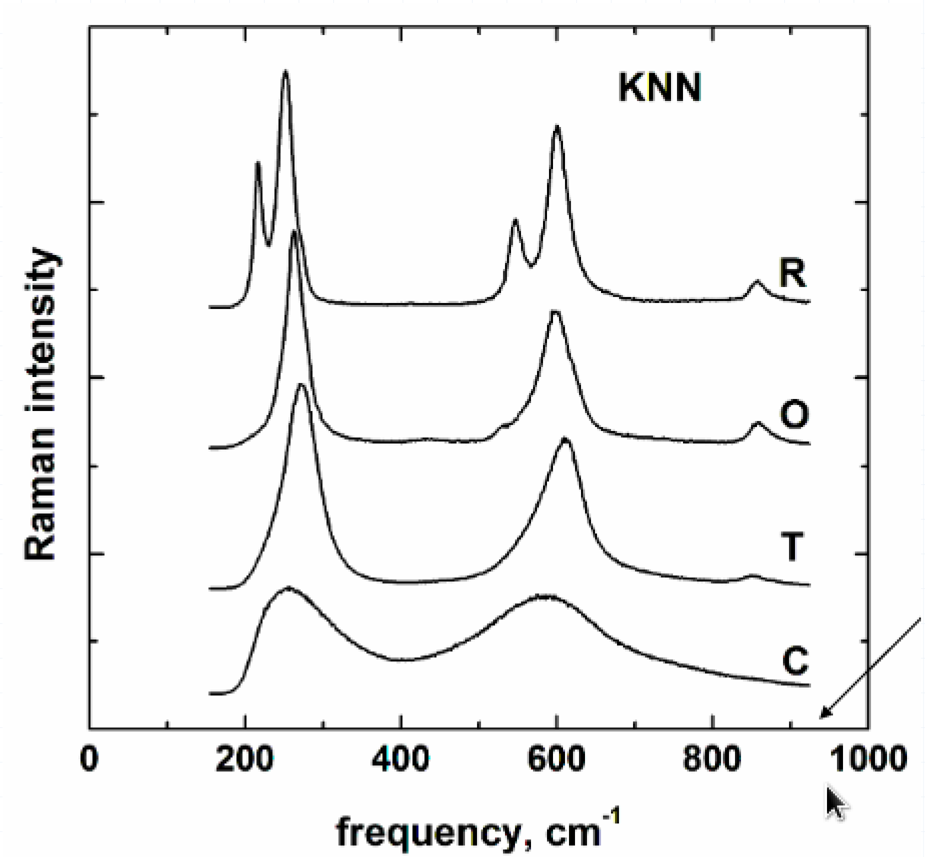
```
     IR activities are in (D/A)^2/amu units
     Raman activities are in A^4/amu units
     multiply Raman by 0.945892 for Clausius-Mossotti correction

# mode    [cm-1]     [THz]       IR            Raman    depol.fact
    1      -0.00    -0.0000    0.0000          0.1067      0.7500
    2      -0.00    -0.0000    0.0000          1.2436      0.7500
    3      -0.00    -0.0000    0.0000          0.8988      0.7500
    4       0.00     0.0000    0.0000          1.0079      0.7500
    5       0.00     0.0000    0.0000          1.4616      0.7500
    6     657.27    19.7045    0.5991          0.0000      0.7416
    7     657.27    19.7045    0.5991          0.0000      0.4033
    8    1342.85    40.2575    0.0000         24.1466      0.1057
    9    2391.74    71.7025   14.3357          0.0000      0.7500
```

Special cases for Raman

- As seen here, Raman can only measure phonons at Γ
- In second order Raman, two phonons are emitted with opposite momentum
- Raman can be resonant, when the laser frequency is tuned (willingly or not) to the energy of some transition

Phonon linewidth

- In reality a Raman spectrum looks more like this:



Joe Trodhal - Raman-Workshop-Lecture-1-Notes.pdf

Phonon linewidth

- Each peak is not a perfect energy delta
- In the best case it is a narrow Lorentzian
  - its FWHM is temperature dependent
- In the case of anharmonic materials the main peaks can have *satellites*
- These features can appear/disappear with T

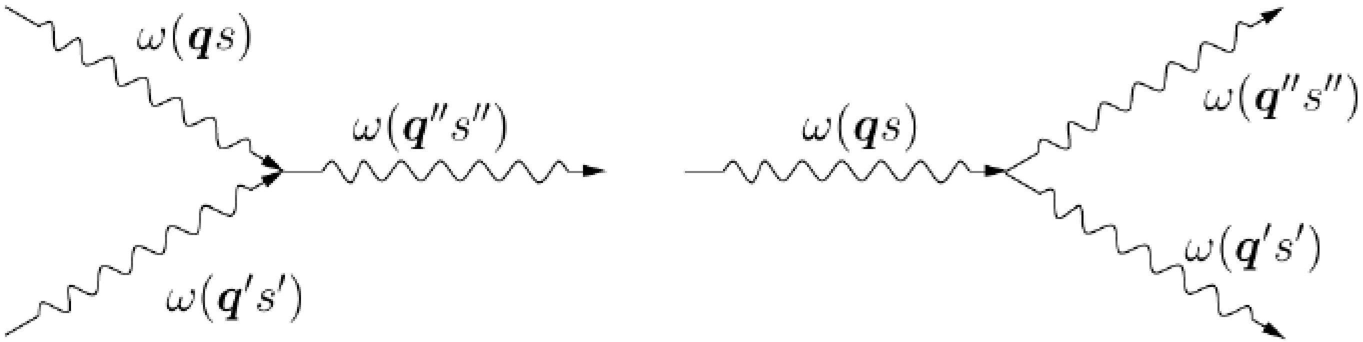
Phonon linewidth

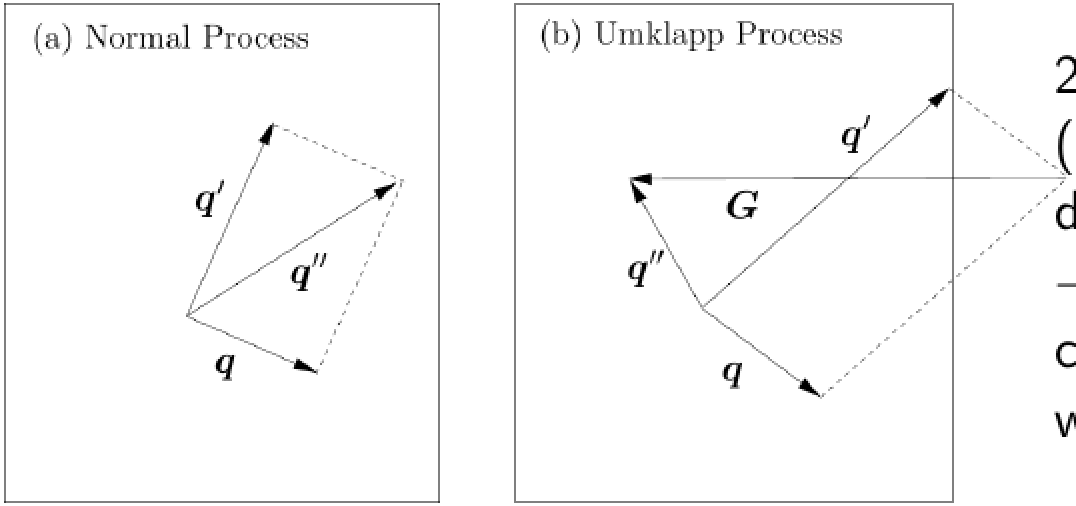
- We expand the total energy around its minimum as a function of a perturbation (harmonic phonons)

$$E[\lambda] \;=\; E^0 - \sum_i f_i\lambda_i + \frac{1}{2}\sum_{ij} h_{ij}\lambda_i\lambda_j + \frac{1}{3!}\sum_{ijk} d_{ijk}\lambda_i\lambda_j\lambda_k + \ldots$$

- We will treat the orders beyond the 2nd as a perturbation on top of harmonic phonons

Phonon linewidth



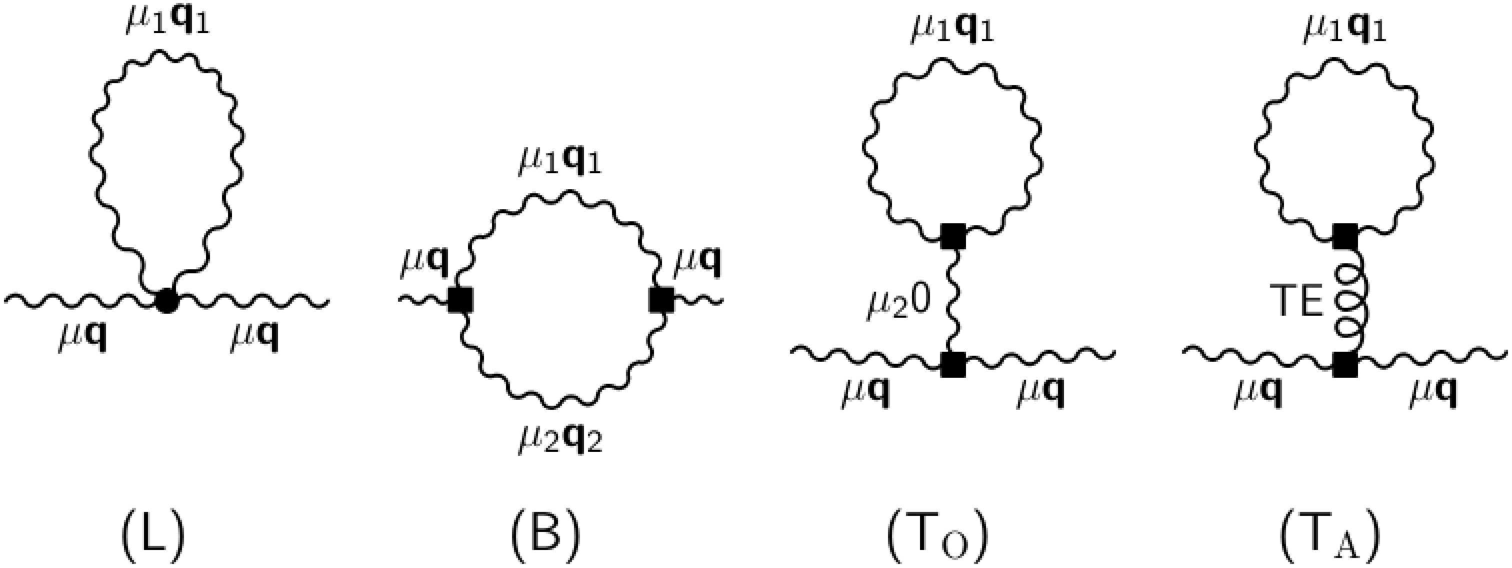


2 phonons can merge in one (coalescence) or one can divide in 2 (decay)
→ momentum has to be conserved ($\pm G$ for PBC) as well as energy

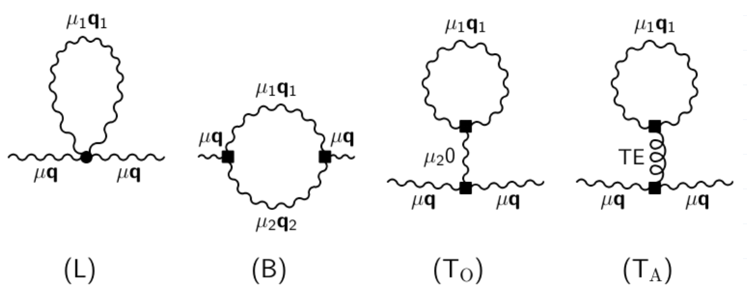
These interactions are *not* possible in the simple harmonic model

Phonon linewidth

- These features are due to the breakdown of the quasi-particle of phonons

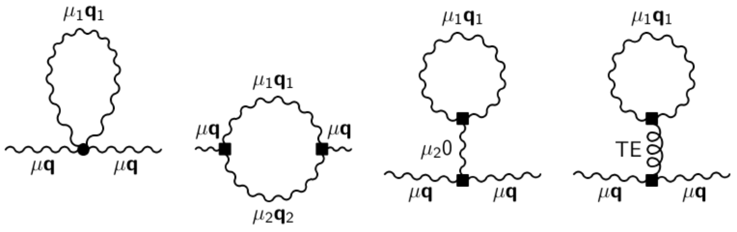


Phonon linewidth



- The **T**adpole diagram is treated in QHA (T_0 = internal coords, T_A = cell volume)
- The **L**oop diagram only contributes a shift to the phonon frequency
- The **B**ubble diagram is responsible for the lineshift+linewidth

Phonon linewidth



(L) (B) ($\mathrm{T_O}$) ($\mathrm{T_A}$)

$$\Pi^L_\mu(\mathbf{q},\omega) = \frac{1}{2N\hbar}\sum_{\mathbf{q}_1\mu_1}\phi^{(4)}_{\mu\mu\mu_1\mu_1}(-\mathbf{q},\mathbf{q},\mathbf{q}_1,-\mathbf{q}_1)[2n_B(\omega_{\mu_1}(\mathbf{q}_1))+1]$$

$$\Pi^T_\mu(\mathbf{q},\omega) = -\frac{1}{N\hbar^2}\sum_{\substack{\mathbf{q}_1\\ \mu_1\mu_2}}\phi^{(3)}_{\mu\mu\mu_2}(-\mathbf{q},\mathbf{q},0)\phi^{(3)}_{\mu_1\mu_1\mu_2}(-\mathbf{q}_1,\mathbf{q}_1,0)[2n_B(\omega_{\mu_1}(\mathbf{q}_1))+1]$$

$$\Pi^B_\mu(\mathbf{q},\omega) = -\frac{1}{2N\hbar^2}\sum_{\substack{\mathbf{q}_1\\ \mu_1\mu_2}}|\phi^{(3)}_{\mu\mu_1\mu_2}(-\mathbf{q},\mathbf{q}_1,\mathbf{q}-\mathbf{q}_1)|^2$$

$$\times\frac{1}{\hbar}\left[\frac{2(\omega_1+\omega_2)[1+n_B(\omega_1)+n_B(\omega_2)]}{(\omega_1+\omega_2)^2-(\omega+i\delta)^2}+\frac{2(\omega_1-\omega_2)[n_B(\omega_2)-n_B(\omega_1)]}{(\omega_2-\omega_1)^2-(\omega+i\delta)^2}\right]$$

Phonon linewidth

- The phonon linewidth (HWHM=γ) is the Imaginary part of Π^B:

$$\begin{aligned}\frac{1}{\tau_{\mathbf{q}j}(T)} = \gamma_{\mathbf{q}j}(T) = \frac{2\pi}{\hbar^2 N_q} & \sum_{\mathbf{q}',j',j''} \left| V^{(3)}_{\mathbf{q}j,\mathbf{q}'j',\mathbf{q}''j''} \right|^2 \times \\ & \Big[(1+\overline{n}_{\mathbf{q}'j'}+\overline{n}_{\mathbf{q}''j''})\delta(\omega_{\mathbf{q}j}-\omega_{\mathbf{q}'j'}-\omega_{\mathbf{q}''j''})+ \\ & 2(\overline{n}_{\mathbf{q}'j'}-\overline{n}_{\mathbf{q}''j''})\delta(\omega_{\mathbf{q}j}+\omega_{\mathbf{q}'j'}-\omega_{\mathbf{q}''j''})\Big].\end{aligned}$$

- With a bit of algebra we recast it as a sort of Fermi golden-rule

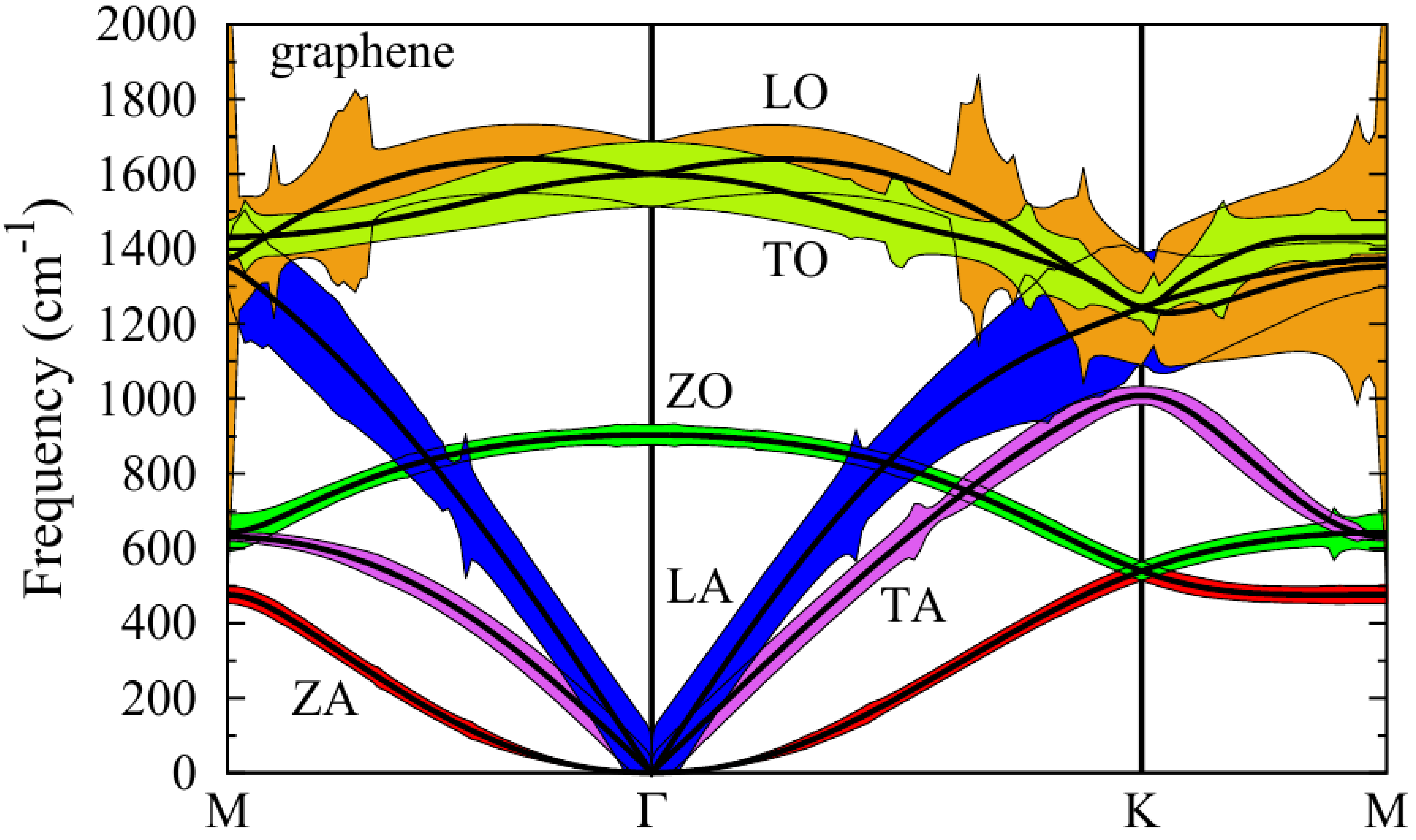
Third derivative of total energy

- It can be compute from the first variation of the wfc using the *2n+1* theorem

$$
\begin{aligned}
\frac{d^3 E}{d\lambda^3} &= \frac{\partial^3 E_{II}}{\partial\lambda^3} + 6\sum_{v}\langle \phi'_v \mid H'_{KS} - \epsilon'_v \mid \phi'_v\rangle \\
&+ 3\int v^{(2)}_{ext}(r)\mathrm{n}'(r)\mathrm{d}r + \int v^{(3)}_{ext}(r)\mathrm{n}(r)\mathrm{d}r \\
&+ \frac{1}{6}\int \frac{\delta^3 E_{xc}[\mathrm{n}]}{\delta\mathrm{n}(r)\delta\mathrm{n}(r')\delta\mathrm{n}(r'')}\mathrm{n}'(r)\mathrm{n}'(r')\mathrm{n}'(r'')\mathrm{d}r\mathrm{d}r'\mathrm{d}r''
\end{aligned}
$$

- +many additional terms (metals, psp, gga)

Phonon linewidth



Strongly anharmonic case

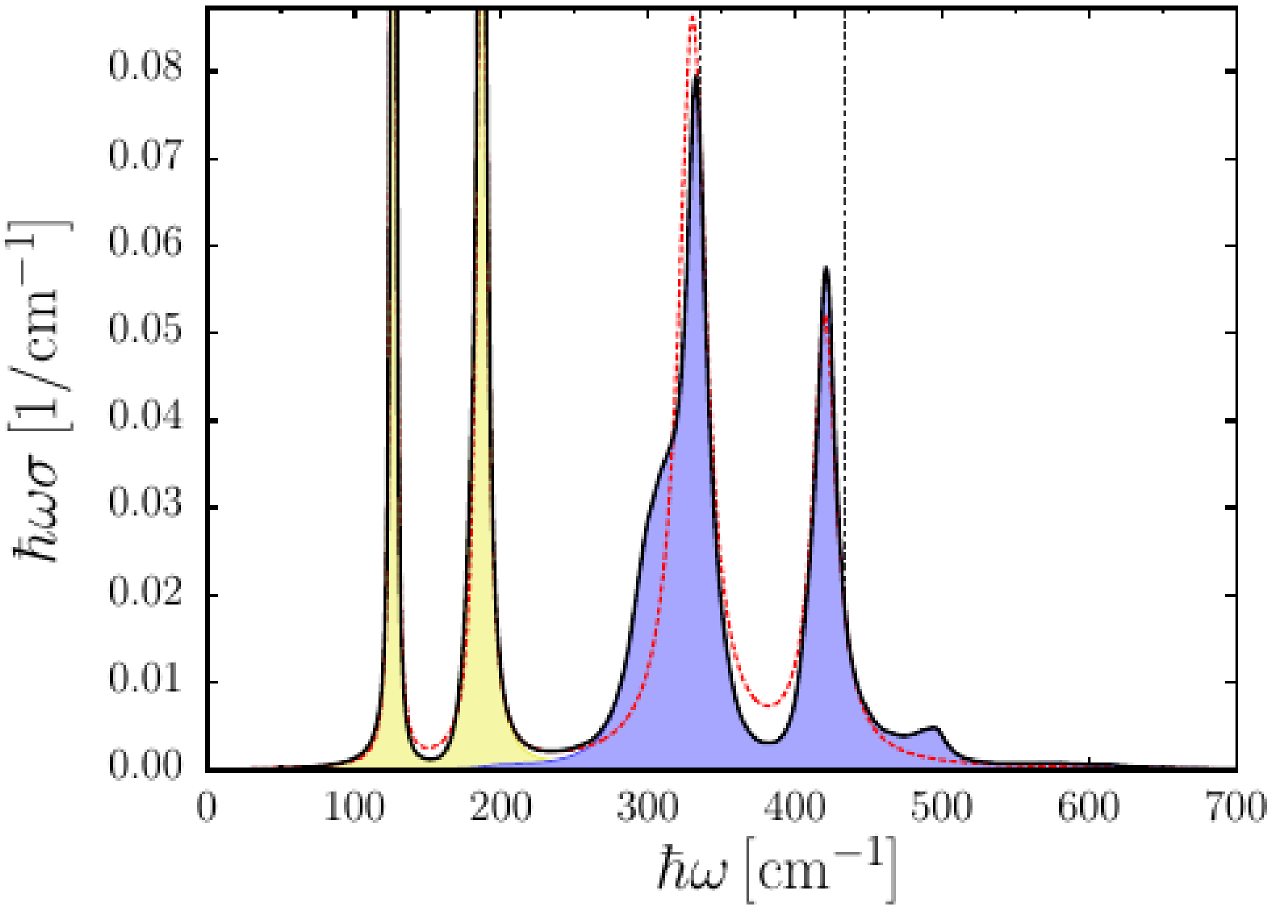
- We can drop completely the quasiparticles and compute the spectral width directly:

$$\sigma(\mathbf{q},\omega) = \sum_{\mu} \frac{-2\hbar\Omega_{\mu}(\mathbf{q})\Im\mathfrak{m}\Pi_{\mu}^{\mathcal{H}B}(\mathbf{q},\omega)}{[\hbar^2\omega^2 - \hbar^2\Omega_{\mu}^2(\mathbf{q}) - 2\hbar\Omega_{\mu}(\mathbf{q})\Re\mathfrak{e}\Pi_{\mu}^{\mathcal{H}B}(\mathbf{q},\omega)]^2 + 4\hbar^2\omega_{\mu}^2(\mathbf{q})[\Im\mathfrak{m}\Pi_{\mu}^{\mathcal{H}B}(\mathbf{q},\omega)]^2}$$

- *It is wrong to include the lineshift from* B *while ignoring that from* T *and* L*!*
- It falls back to the previous case when Π_B is constant in ω

Strongly anharmonic case

- Example: Palladium Hydride



Combining X section with SPF

- At least in the case of moderate anharmonicity → weight the contribution of each mode with its harmonic cross section
- Also in the case of strong anharmonicity, it is an unjustified but useful approach
- In any case, the complexity of the experimental conditions must be taken in account

Afternoon session

- Computing the IR and Raman cross sections for a Co2 molecule
- And for Aluminum Arsenide (AlAs)
- If there is time: we will see a script to compute the Raman tensor by finite differences, compare its convergence with DFPT

Thank you!