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The position operator in extended systems:

Application to electron localization and non-linear optics

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Outline

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Modern theory of polarization

- Interaction of electrons with an electric field $V = e\,\mathbf{r}\cdot\mathcal{E}$
- Position operator incompatible with BvK boundary conditions
- Polarization can be expressed as a Berry phase of the electronic wavefunctions
  - continuous form $\mathbf{P} = -\frac{2ie}{(2\pi)^3}\sum_n \int d\mathbf{k}\,\langle u_{n\mathbf{k}}|\,\nabla_{\mathbf{k}}|\,u_{n\mathbf{k}}\rangle$
  - discretized form $\mathbf{P}\cdot\mathbf{G}_{||} = \frac{e}{4\pi^3}\int d\mathbf{k}_\perp \sum_j \Im \ln\det\left[S(\mathbf{k}_j, \mathbf{k}_{j+1})\right]$

$$S_{nm}(\mathbf{k}, \mathbf{k}') = \langle u_{n\mathbf{k}}|u_{m\mathbf{k}'}\rangle$$

⇒ recent developments based on this formalism

- Electron localization tensor
- Non-linear optical response

Localization tensor: Background

- Characteristic length that is finite in insulators and diverges in metals
- Linear response formulation

$$\langle r_\alpha r_\beta \rangle_c = \frac{V_c}{N(2\pi)^3} \int_{BZ} dk \left[\sum_{n=1}^{N} \left\langle \frac{\partial u_{nk}}{\partial k_\alpha} \middle| \frac{\partial u_{nk}}{\partial k_\beta} \right\rangle - \sum_{n,m=1}^{N} \left\langle \frac{\partial u_{nk}}{\partial k_\alpha} \middle| u_{mk} \right\rangle \left\langle u_{mk} \middle| \frac{\partial u_{nk}}{\partial k_\beta} \right\rangle \right]$$

  - V_c = unit cell volume
  - N = number of doubly occupied bands
  - u_{nk} = periodic part of the Bloch functions

Sgiarovello, Peressi and Resta, Phys. Rev. B ***64****, 115202 (2001).*

- First order wavefunctions
  - linear response approach to density functional theory
  - diagonal gauge

Band by band decomposition

- Global characterization of the whole electron gaz
  - core and valence electrons exhibit different localization properties
  - result depends on the construction of the pseudopotentials

Band by band decomposition allows to focus on individual groups of bands

- Sum of random variables
  - u_1, u_2 □ probability density function $f(u_1, u_2)$
  - Total mean

$$\overline{u_1 + u_2} = \overline{u_1} + \overline{u_2}$$

  - Total variance

$$\underbrace{\sigma^2_{u_1+u_2}}_{\text{total variance}} = \underbrace{\sigma^2_1 + \sigma^2_2}_{\text{sum of the variances}} + 2\underbrace{\text{cov}(u_1, u_2)}_{\text{covariance}}$$

The covariance indicates how u_1 and u_2 are related together.

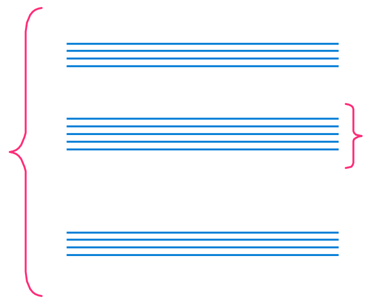
It is zero if they are independent:

$f(u_1,u_2)=f_1(u_1)f_2(u_2)$

Band by band decomposition

- Localization tensor

N_g groups of occupied bands



group i, n_i bands

  - variance

$$\langle r_\alpha r_\beta \rangle_c (i) = \frac{V_c}{n_i (2\pi)^3} \int_{BZ} dk \left[\sum_{n \in i} \left\langle \frac{\partial u_{nk}}{\partial k_\alpha} \middle| \frac{\partial u_{nk}}{\partial k_\beta} \right\rangle - \sum_{n,m \in i} \left\langle \frac{\partial u_{nk}}{\partial k_\alpha} \middle| u_{mk} \right\rangle \left\langle u_{mk} \middle| \frac{\partial u_{nk}}{\partial k_\beta} \right\rangle \right]$$

  - covariance

$$\langle r_\alpha r_\beta \rangle_c (i,j) = \frac{-V_c}{n_i n_j (2\pi)^3} \int_{BZ} dk \sum_{n \in i} \sum_{m \in j} \left\langle \frac{\partial u_{nk}}{\partial k_\alpha} \middle| u_{mk} \right\rangle \left\langle u_{mk} \middle| \frac{\partial u_{nk}}{\partial k_\beta} \right\rangle$$

Many-body wavefunction = Slater determinant of the one particle orbitals and not their product

Implementation

- Gauge for linear response computations
  - First-order wavefunctions are computed within the **parallel gauge**
  - Band by band decomposition meaningful in the **diagonal gauge**

$$\left|\frac{du_{m\mathbf{k}}}{d\lambda}\right|_d\Big\rangle = \left|\frac{du_{m\mathbf{k}}}{d\lambda}\right|_p\Big\rangle - \sum_{m\neq n} \frac{\langle u_{n,\mathbf{k}}|dH/d\lambda|u_{m,\mathbf{k}}\rangle}{\varepsilon_{n,\mathbf{k}} - \varepsilon_{m,\mathbf{k}}} \left|u_{m,\mathbf{k}}\right\rangle$$

- Relevant ABINIT routines
  - **nstwf3.f :** computation of second-order derivatives from non-stationary expressions
    - computation of the localization tensor and its band-by-band decomposition
    - band-by-band decomposition of Born effective charges (phonon-type perturbations)
  - **gaugetransfo.f :**
    - transforms first-order wavefunctions to the diagonal gauge
  - **wrtloctens.f :**
    - ouput of the localization tensor

Implementation

- New input variable
  - **prtbbb :** governs the computation of the band-by-band decomposition of the localization tensor and the Born effective charges
- Subtlety
  - the variable **getddk** has to be declared the number of the dataset where the ddk is computed (ex: getddk3 3)
- Documentation
  - Band-by-band decomposition of the Born effective charges
    - Ph. Ghosez and X. Gonze, J. Phys. Condens. Matter **12**, 9179 (2000)
  - Band-by-band decomposition of the localization tensor
    - M. Veithen and Ph. Ghosez, AIP conference proceeding **626**, 208 (2002).
    - M. Veithen, X. Gonze and Ph. Ghosez, to appear in Phys. Rev. B. (preprint available at *cond-mat/0206580*)

  \+ references therein

Electrooptic effect

- Modification of the index ellipsoid of a compound induced by a static electric field
- Electrooptic tensor r_{ijk}

$$\Delta\left(\frac{1}{n_{ij}^2}\right) = \sum_{k=1}^{3} r_{ijk}\mathcal{E}_k^{dc}$$

- Separation into a bare electronic and an ionic contribution

$$r_{ijk} = r_{ijk}^{el} + r_{ijk}^{ion}$$

  - **electronic contribution :**
    - interaction of the electric field with the electronic cloud at clamped ionic positions
    - related to the non linear optical susceptibility
  - **ionic contribution :**
    - electric field → atomic displacements → refractive index changes
    - can be computed from the Born effective charges, phonon frequencies and eigendisplacements, Raman susceptibilities

Electronic contribution

- Non linear optical susceptibility $\chi^{(2)}_{ijk}$

$$r^{el}_{ijk} = \frac{-8\pi}{n_i^2 n_j^2}\chi^{(2)}_{ijk}$$

- Third-order derivative with respect to an electric field

$$\chi^{(2)}_{ijk} = -\frac{3}{\Omega}E^{\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k}$$

- *2n + 1* theorem

$$\begin{aligned} E^{(3)} &= \sum_{\alpha}\langle\psi_\alpha^{(1)}|H^{(1)}|\psi_\alpha^{(1)}\rangle - \sum_{\alpha,\beta}\Lambda^{(1)}_{\beta\alpha}\langle\psi_\alpha^{(1)}|\psi_\beta^{(1)}\rangle \\ &+\frac{1}{6}\int\int\int\frac{\delta^3 E_{xc}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}')n^{(1)}(\mathbf{r}'')d\mathbf{r}d\mathbf{r}'d\mathbf{r}'' \end{aligned}$$

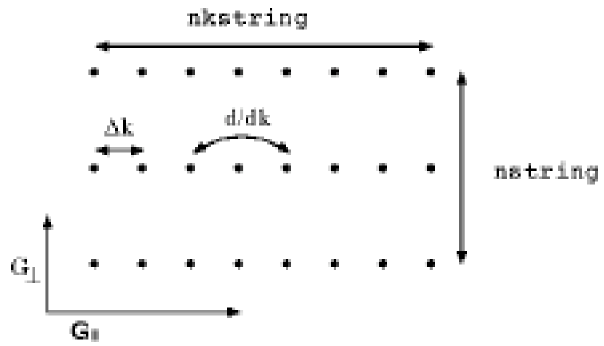
- Electric field dependent energy functional

$$E[\psi,\mathcal{E}] = E^{(0)}[\psi] - V_c\,\mathcal{E}\cdot\mathbf{P}[\mathcal{E}]$$

Perturbation expansion of the polarization: continuous form

$$E_{pol}^{(3)} = \frac{2V_c}{(2\pi)^3} \int_{BZ} d\mathbf{k} \sum_{m,n} \langle u_{n\mathbf{k}}^{(1)}| \left(ie \frac{\partial}{\partial k_{||}} |u_{m\mathbf{k}}^{(1)}\rangle\langle u_{m\mathbf{k}}| \right) |u_{n\mathbf{k}}\rangle$$

- Finite differences along **strings**



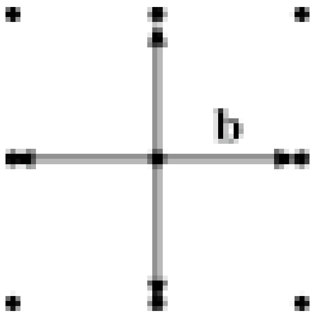
$$\frac{\partial}{\partial k}|u_{n\mathbf{k}}\rangle\langle u_{n\mathbf{k}}| = \frac{1}{2\Delta k}\left(|u_{n\mathbf{k}+\Delta\mathbf{k}}\rangle\langle u_{n\mathbf{k}+\Delta\mathbf{k}}| - |u_{n\mathbf{k}-\Delta\mathbf{k}}\rangle\langle u_{n\mathbf{k}-\Delta\mathbf{k}}|\right)$$

- Example: cristalline GaAs
  - **cartesian coordinates :** $\chi_{ijk}^{(2)} = \chi|\varepsilon_{ijk}|$
  - **reduced coordinates :**

$$\left|\frac{\chi_{ijk}^{(2)}}{\chi_{iii}^{(2)}}\right| = \frac{1}{3} \qquad i \neq j \text{ and } j \neq k$$

nstring	nkstring	$\lvert\chi_{112}^{(2)}/\chi_{111}^{(2)}\rvert$	$\lvert\chi_{121}^{(2)}/\chi_{111}^{(2)}\rvert$
16	32	0.3333	0.7735
36	48	0.3333	0.5365
64	64	0.3333	0.4293
100	80	0.3333	0.3788

- Finite difference expression of Marzari and Vanderbilt on a **regular grid** of k-points



Shells of first neighbors

- **SC** grid of k-points : 6
- **FCC** grid of k-points : 12
- **BC** grid of k-points : 8

Phys. Rev. B ***53****, 15638 (1996).*

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \left[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k}) \right]$$

$$\sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b}_\alpha \mathbf{b}_\beta = \delta_{\alpha\beta}$$

→ right symmetry

- Application to cubic semiconductors: □ in pm/V

Compound	u. cell	present	Dal Corso [a]	Deinzer [b]
GaAs	R	151	158	157
AlAs	R	69	64	74 (81)
AlP	R	41.423	39	42 (38)
	C	41.423		

[a] A. Dal Corso *et al.*, Phys. Rev. B **53**, 15638 (1996).

[b] G. Deinzer, private communication.

Perturbation expansion of the polarization: discretized form

- Regular k-point grid

$$\mathbf{P} = \frac{2e}{N_k V_c} \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \, \Im \ln \det \left[S(\mathbf{k}, \mathbf{k}+\mathbf{b}) \right]$$

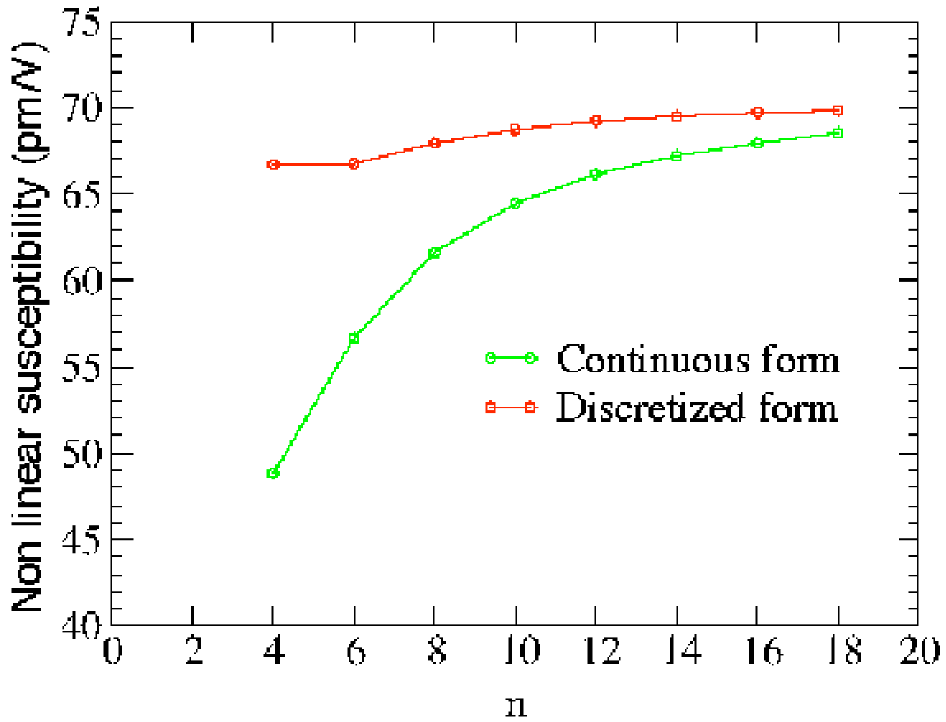
- Perturbative expansion

$$E_{pol}^{(3)} = \frac{-e}{N_k} \Im \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \left\{ 2 \sum_{m,n} S_{nm}^{(2)} Q_{mn} - \sum_{m,n,l,l'} S_{mn}^{(1)} Q_{nl} S_{ll'}^{(1)} Q_{l'm} \right\}$$

$$\begin{aligned}
Q(\mathbf{k}, \mathbf{k}+\mathbf{b}) &= S^{-1}(\mathbf{k}, \mathbf{k}+\mathbf{b}) \\
S_{mn}^{(1)}(\mathbf{k}, \mathbf{k}+\mathbf{b}) &= \langle u_{m\mathbf{k}}^{(1)} | u_{n\mathbf{k}+\mathbf{b}} \rangle + \langle u_{m\mathbf{k}} | u_{n\mathbf{k}+\mathbf{b}}^{(1)} \rangle \\
S_{mn}^{(2)}(\mathbf{k}, \mathbf{k}+\mathbf{b}) &= \langle u_{m\mathbf{k}}^{(1)} | u_{n\mathbf{k}+\mathbf{b}}^{(1)} \rangle
\end{aligned}$$

Convergence study : k-point sampling

- Case of AlAs
  - ngkpt = n n n
  - shiftk = 0.5 0.5 0.5
    0.5 0.0 0.0
    0.0 0.5 0.0
    0.0 0.0 0.5



Implementation notes

- General structure

driver.f

→ **nonlinear.f** : equivalent of *respfn.f* for 2^{nd} order derivatives

- initialization tasks
- reads pseudopotential files, GS wavefunctions + density
- computes 3^{rd} order XC kernel

→ **loop3dte.f** : loop over the 3 perturbations j_1, j_2 and j_3

- read 1^{st} order wavefunctions + densities
- compute 1^{st} order hartee and XC potential
- compute 3^{rd} order XC energy

→ **mv_3dte.f** : compute ddk-part of the 3^{rd} order energy

→ **resp3dte.f** : compute matrix elements of $v^{(1)}_{hxc}$

- Relevant input variables
  - 3rd order derivatives are computed in case **optdriver** = 5
  - The reading of the 1st order densities is controlled by **get1den**
  - At the opposite with the computation of 2nd order derivatives, the 3 perturbations j_1, j_2 and j_3 have to be specified explicitely
    - **rf1elfd, rf2elfd, rf3elfd** : electric field-type perturbations
    - **rf1phon, rf2phon, rf3phon** : phonon-type perturbations
    - **rf1dir, rf2dir, rf3dir** : direction of the perturbations
    - **rf1atpol, rf2atpol, rf3atpol** : atomic polarization

Ionic contribution

Relaxation of the atoms within an electric field

Born effective charges : $$Z^*_{\kappa,\alpha\beta} = V_c \frac{\partial P_\alpha}{\partial \tau_{\kappa\beta}}$$

→ variations of the refractive index

First-order changes of the linear susceptibility : $$\frac{\partial \chi_{ij}}{\partial \tau_{\kappa\alpha}}$$

General expression : $$r^{ion}_{ijk} = -\frac{4\pi}{\sqrt{V_c} n_i^2 n_j^2} \sum_m \frac{\alpha^m_{ij} s_{m,k}}{\omega_m^2}$$

$$\alpha^m_{ij} = \sqrt{\Omega} \sum_{\kappa,\beta} \frac{\partial \chi_{ij}}{\partial \tau_{\kappa\beta}} u_m(\kappa\beta)$$ (Raman susceptibility)

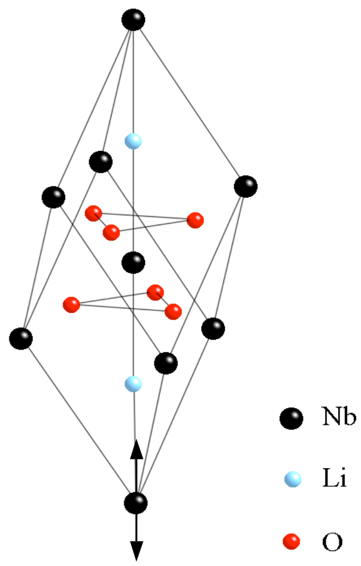
$$s_{m,k} = \sum_{\kappa,\beta} Z^*_{\kappa,k\beta} u_m(\kappa\beta)$$

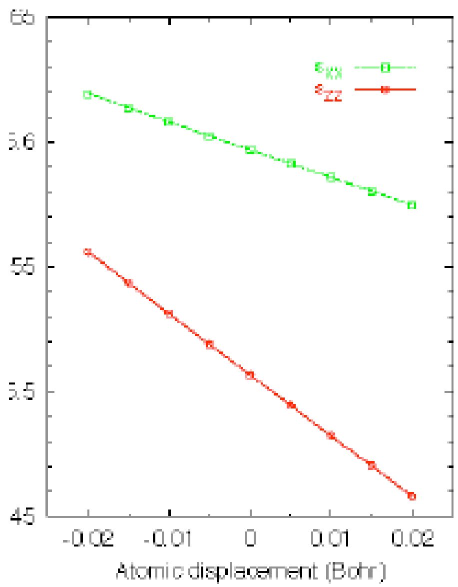
Raman susceptibilities: finite difference approach

- Individual atomic displacements
  (case of $LiNbO_3$)

$$4\pi \frac{d\chi}{d\tau} = \frac{d\varepsilon}{d\tau} = \frac{\varepsilon(\Delta\tau) - \varepsilon(-\Delta\tau)}{2\Delta\tau} + \mathcal{O}(\Delta\tau^2)$$

$\Delta\tau$ (Bohr)	$d\varepsilon_{xx}/d\tau$	$d\varepsilon_{zz}/d\tau$
0.005	-0.1101	-0.2436
0.01	-0.1112	-0.2447
0.015	-0.1109	-0.2444
0.02	-0.1114	-0.2449





- Collective displacements along the normal mode coordinates
  (case of the lowest A_1 mode in $LiNbO_3$)

$$\alpha = \begin{pmatrix} a & \cdot & \cdot \\ \cdot & a & \cdot \\ \cdot & \cdot & b \end{pmatrix}$$

	a (10^{-2} a.u.)	b (10^{-2} a.u.)
individual disp.	-0.718	-2.047
collective disp.	-0.722	-2.052

Raman susceptibilities: perturbative approaches

- Berry phase approach (1d, non self-consistent case)

$$\frac{1}{6}\frac{\partial^3 E}{\partial^2 \mathcal{E}\,\partial\tau} = \frac{1}{3}\left\{\tilde{E}^{\mathcal{E},\tau,\mathcal{E}} + \underbrace{\tilde{E}^{\mathcal{E},\mathcal{E},\tau} + \tilde{E}^{\tau,\mathcal{E},\mathcal{E}}}\right\}$$

$\tilde{E}^{\mathcal{E},\tau,\mathcal{E}} \rightarrow \frac{\partial v_{ext}}{\partial\tau}$; $\tilde{E}^{\mathcal{E},\mathcal{E},\tau} + \tilde{E}^{\tau,\mathcal{E},\mathcal{E}} \rightarrow ie\frac{\partial}{\partial k}$

$$\tilde{E}^{\mathcal{E},\tau,\mathcal{E}} = \frac{a}{\pi}\int dk \left\{\sum_n \langle u^{\mathcal{E}}_{nk}|v^{\tau}_{ext}|u^{\mathcal{E}}_{nk}\rangle - \sum_{m,n}\langle u_{nk}|v^{\tau}_{ext}|u_{mk}\rangle\langle u^{\mathcal{E}}_{mk}|u^{\mathcal{E}}_{nk}\rangle\right\}$$

$$\tilde{E}^{\mathcal{E},\mathcal{E},\tau} = \frac{iea}{\pi}\int dk \sum_n \langle u^{\mathcal{E}}_{nk}|\left(\frac{\partial}{\partial k}\sum_m |u^{\tau}_{mk}\rangle\langle u_{mk}|\right)|u_{nk}\rangle$$

$$\tilde{E}^{\tau,\mathcal{E},\mathcal{E}} = \frac{iea}{\pi}\int dk \sum_n \langle u^{\tau}_{nk}|\left(\frac{\partial}{\partial k}\sum_m |u^{\mathcal{E}}_{mk}\rangle\langle u_{mk}|\right)|u_{nk}\rangle$$

- Derivative of the linear susceptibility
  - stationary expression of the second order energy

$$
\begin{aligned}
\frac{1}{2}\frac{\partial^2 E}{\partial \mathcal{E}^2} &= \langle \psi^{\mathcal{E}} | H^{(0)} - \varepsilon^{(0)} | \psi^{\mathcal{E}} \rangle + \langle \psi^{\mathcal{E}} | i \frac{\partial}{\partial k} \psi^{(0)} \rangle + \langle i \frac{\partial}{\partial k} \psi^{(0)} | \psi^{\mathcal{E}} \rangle \\
&+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\delta^2 E_{Hxc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\mathcal{E}}(\mathbf{r}) n^{\mathcal{E}}(\mathbf{r}')
\end{aligned}
$$

  - derivative with respect to an atomic displacement □

$$
\begin{aligned}
\frac{1}{2}\frac{\partial^3 E}{\partial \tau \partial \mathcal{E}^2} &= \langle \psi^{\mathcal{E}} | H^{\tau} - \varepsilon^{\tau} | \psi^{\mathcal{E}} \rangle + \langle \psi^{\mathcal{E}} | i \frac{\partial}{\partial k} \psi^{\tau} \rangle + \langle i \frac{\partial}{\partial k} \psi^{\tau} | \psi^{\mathcal{E}} \rangle \\
&+ \langle \psi^{\mathcal{E}} | v^{\mathcal{E}}_{Hxc} | \psi^{\tau} \rangle + \langle \psi^{\tau} | v^{\mathcal{E}}_{Hxc} | \psi^{\mathcal{E}} \rangle \\
&+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta^3 E_{Hxc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{\mathcal{E}}(\mathbf{r}) n^{\mathcal{E}}(\mathbf{r}') n^{\tau}(\mathbf{r}'')
\end{aligned}
$$

  - mixed derivative of the wavefunctions : non self consistent calculation

$$
\left(H^{(0)} - \varepsilon^{(0)} \right) \frac{\partial}{\partial k} | \psi^{\tau} \rangle = - \left(\frac{\partial H}{\partial k} - \frac{\partial \varepsilon}{\partial k} \right) | \psi^{\tau} \rangle - \frac{\partial H^{\tau}}{\partial k} | \psi^{(0)} \rangle - H^{\tau} \frac{\partial}{\partial k} | \psi^{(0)} \rangle
$$

- Method of M. Lazzeri and F. Mauri

(preprint available at *cond-mat/0207039*)

$$\frac{\partial^3 E}{\partial \mathcal{E}^2 \partial \tau} = 2\,\mathrm{Tr}\left(\frac{\partial^2 \rho}{\partial \mathcal{E}^2}\frac{\partial v_{ext}}{\partial \tau}\right)$$

Density matrix of the Kohn-Sham eigenstates $\rho = |\psi\rangle\langle\psi|$

$$\frac{\partial^2 \rho}{\partial \mathcal{E}^2} = |\frac{\partial^2 \psi}{\partial \mathcal{E}^2}\rangle\langle\psi| + |\frac{\partial \psi}{\partial \mathcal{E}}\rangle\langle\frac{\partial \psi}{\partial \mathcal{E}}| + c.c.$$

The wavefunctions $|\frac{\partial \psi}{\partial \mathcal{E}}\rangle$ and $|\frac{\partial^2 \psi}{\partial \mathcal{E}^2}\rangle$ can be computed from a self-consistent calculation

Comment : the computation of $|\frac{\partial^2 \psi}{\partial \mathcal{E}^2}\rangle$ needs the operator $\frac{\partial}{\partial k}\left[|\frac{\partial \psi}{\partial \mathcal{E}}\rangle\langle\psi|\right]$

that has to be computed from *finite differences*

Conclusions and Perspectives

Implementation of 2 quantities based on the modern theory of polarization into the ABINIT package

- **Electron localization tensor**
  - Characteristic length that quantifies the degree of electron localization in crystalline solids
  - Computed from the ground-state and ddk wavefunctions
- **Electrooptic tensor**
  - **Electronic contribution :** expression based on the $2n + 1$ theorem and the modern theory of polarization has been implemented
  - **Ionic contribution (Raman susceptibilities)** :
    - Actually accessible from finite differences of the dielectric tensor
    - Perturbative approach will be implemented in the future