Abinit response-function capabilities

- Many physical properties can be formulated as derivatives of the DFT ground-state total energy with respect to parameters of the problem
- In the early days of electronic structure theory, these were generally obtained by numerical differentiation of the total energy
  - This was cumbersome, computationally costly, and often not accurate.
- Analytic methods for evaluating derivatives have been developed for many cases.
  - This is an ongoing effort.
- We've already dealt with some first derivatives which can be evaluated analytically from ground-state wave functions and densities.
- Many physical materials properties can be expressed as second derivatives, such as vibrational spectra and elastic constants.
- Some 3rd derivatives are within reach.
  - Abinit can do Raman tensors, but we're not going to go there.

Perturbations and energy first derivatives

- The simplest case – forces
  - Derivatives wrt atomic coordinates $\tau_{\kappa i}$
  - Includes all periodic replicas $\tau_{\kappa i} + R_i$
- A more subtle case – stress
  - Derivative wrt uniform strain tensor $\eta_{\alpha\beta}$
  - Correctly formulating the DFT energy as an analytic function of strain is difficult.
- A very subtle case (not yet encountered) – electric polarization $\mathbf{P}$
  - Derivative wrt uniform electric field of an extended energy functional,

    $$E = E_{\mathrm{HKS}} - \mathcal{E} \cdot \mathbf{P}$$
  - Principal difficulty – the electric field destroys the periodicity of the potential
- A simpler periodicity-destroying case – atomic displacements with a different period, $\tau_{\kappa i} + R_i \rightarrow \tau_{\kappa i} + R_i + \lambda e^{i\mathbf{q}\cdot\mathbf{R}}$
  - First derivatives wrt λ vanish
  - Second derivatives wrt one $\mathbf{q}$ and one $-\mathbf{q}$ perturbation give phonons.

Strain tensor $\eta_{\alpha\beta}$ as a perturbation

- Strain really only changes the positions of the atomic (pseudo)potentials,

$$V_{\text{ext}}(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{\boldsymbol{\tau}}^{\text{cell}} V_{\boldsymbol{\tau}}(\mathbf{r} - \boldsymbol{\tau} - \mathbf{R}) \xrightarrow[\boldsymbol{\eta}]{} V_{\text{ext}}^{\boldsymbol{\eta}}(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{\boldsymbol{\tau}}^{\text{cell}} V_{\boldsymbol{\tau}}[\mathbf{r} - (\mathbf{1} + \boldsymbol{\eta}) \cdot \boldsymbol{\tau} - (\mathbf{1} + \boldsymbol{\eta}) \cdot \mathbf{R}] .$$

- However, this causes unique problems for perturbation expansions:
  - Viewed in terms of the infinite lattice, the strain perturbation can never be small.
  - From the point of view of a single unit cell, strain changes the periodic boundary conditions, so wave functions of the strained lattice cannot be expanded in terms of those of the unstrained lattice.
- Strain appears to be qualitatively different from other perturbations such as periodicity-preserving atomic displacements.

Reduced coordinate (~) formulation

- Every lattice, unstrained or strained, is a unit cube in reduced coordinates.
  - Primitive real and reciprocal lattice vectors define the transformations:

$$X_\alpha = \sum_i R^{\mathrm{P}}_{\alpha i} \tilde{X}_i \,, \quad K_\alpha \equiv (k_\alpha + G_\alpha) = \sum_i G^{\mathrm{P}}_{\alpha i} \tilde{K}_i \,, \quad \sum_\alpha R^{\mathrm{P}}_{\alpha i} G^{\mathrm{P}}_{\alpha j} = 2\pi\delta_{ij}$$

  - Cartesian indices $\alpha, \beta, \cdots = 1,3$ and reduced indices $i, j, \cdots = 1,3$

- Every term in the DFT functional can be expressed in terms of dot products and the unit cell volume Ω
  - Dot products and Ω in reduced coordinates are computed with **metric tensors**,

$$\mathbf{X}' \cdot \mathbf{X} = \sum_{ij} \tilde{X}'_i \Xi_{ij} \tilde{X}_j \,, \quad \mathbf{K}' \cdot \mathbf{K} = \sum_{ij} \tilde{K}'_i \Upsilon_{ij} \tilde{K}_j \,, \quad \Omega = (\det[\Xi_{ij}])^{1/2}$$

- This trick reduces strain to a "simple" parameter of a density functional whose wave functions have invariant boundary conditions.
  - The only strain depencence is in the metric tensors.
  - Conveniently, Abinit uses reduced coordinates throughout its code.

Electrical polarization in insulators

- The "dipole moment" definition of the polarization of a molecule becomes ambiguous and useless in an infinite solid.
- The change in polarization when a parameter (eg., an atom position) is changed in a solid is well-defined and can be calculated by integrating the current induced when the parameter $\lambda(t)$ is changed very slowly.
- Using 1st-order time-dependent perturbation theory for the wave function, taking the matrix elements of the current operator, and taking the zero-frequency limit of $\mathbf{j}(\omega)/\omega$, one can show

$$\frac{\partial \mathbf{P}}{\partial \lambda} = \frac{-i}{\Omega} \sum_{\mathbf{k}} \sum_{i}^{\text{occ}} \sum_{j}^{\text{empty}} \frac{\left\langle \psi_{\mathbf{k}i}^{\lambda} \middle| \hat{\mathbf{p}} \middle| \psi_{\mathbf{k}j}^{\lambda} \right\rangle \left\langle \psi_{\mathbf{k}j}^{\lambda} \middle| \partial V_{\text{KS}}^{\lambda} / \partial \lambda \middle| \psi_{\mathbf{k}i}^{\lambda} \right\rangle}{\left(\varepsilon_{\mathbf{k}i}^{\lambda} - \varepsilon_{\mathbf{k}j}^{\lambda} \right)^2} + \text{c.c.}$$

  - Why is the energy denominator squared?

Polarization, continued

- Now consider just the periodic part $u_{\mathbf{k}i}^{\lambda}$ of $\psi_{\mathbf{k}i}^{\lambda}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}i}^{\lambda}(\mathbf{r})$
- It is the solution of the k-dependent Hamiltonian

$$\hat{H}_{KS}(\mathbf{k},\lambda) = -\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\mathrm{KS}}(\mathbf{r},\lambda)$$

- Two identities can be established which, along with the completeness relation for the j states, allow $\partial\mathbf{P}/\partial\lambda$ to be expressed strictly in terms of occupied states,

$$\left\langle \psi_{\mathbf{k}i}^{\lambda} \middle| \hat{\mathbf{p}} \middle| \psi_{\mathbf{k}j}^{\lambda} \right\rangle = \left\langle u_{\mathbf{k}i}^{\lambda} \middle| \left[\partial/\partial\mathbf{k}, \hat{H}_{\mathrm{KS}}(\mathbf{k},\lambda) \right] \middle| u_{\mathbf{k}j}^{\lambda} \right\rangle,$$

$$\left\langle \psi_{\mathbf{k}i}^{\lambda} \middle| \partial V_{\mathrm{KS}}^{\lambda}/\partial\lambda \middle| \psi_{\mathbf{k}j}^{\lambda} \right\rangle = \left\langle u_{\mathbf{k}i}^{\lambda} \middle| \left[\partial/\partial\lambda, \hat{H}_{\mathrm{KS}}(\mathbf{k},\lambda) \right] \middle| u_{\mathbf{k}j}^{\lambda} \right\rangle.$$

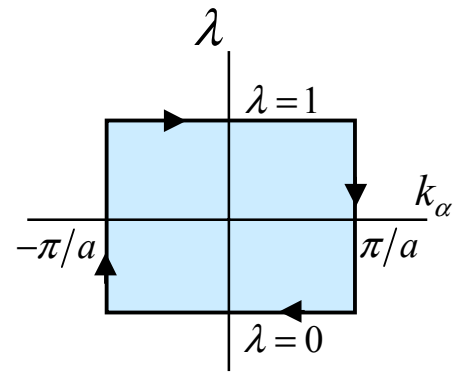
- The λ-integrated net change of the α component of the polarization is

$$\Delta P_{\alpha} = \frac{-2}{(2\pi)^3} \mathrm{Im} \int_{\mathrm{BZ}} d\mathbf{k} \int_0^1 d\lambda \sum_i^{\mathrm{occ}} \left\langle \frac{u_{\mathbf{k}i}^{\lambda}}{\partial k_{\alpha}} \middle| \frac{u_{\mathbf{k}i}^{\lambda}}{\partial\lambda} \right\rangle$$

Polarization, continued

- The 2-dimensional (λ, k_α) integral can be transformed by Stokes theorem into a contour integral. (The $k_\perp$ integrals are simple averages.)
- If the phase of $u^\lambda_{\mathbf{k}i}$ is chosen to change continuously and obey the condition

$$u^\lambda_{\mathbf{k}+\mathbf{G}i}(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}} u^\lambda_{\mathbf{k}i}(\mathbf{r})$$



where $\mathbf{G}$ is a reciprocal lattice vector, the λ integrals cancel and only the k_α integrals at the end points $\lambda = 0,1$ contribute,

$$\Delta P_\alpha = \frac{-i}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \sum_i^{\mathrm{occ}} \left[\left\langle u^{\lambda=1}_{\mathbf{k}i} \middle| \partial u^{\lambda=1}_{\mathbf{k}i} / \partial k_\alpha \right\rangle - \left\langle u^{\lambda=0}_{\mathbf{k}i} \middle| \partial u^{\lambda=0}_{\mathbf{k}i} / \partial k_\alpha \right\rangle \right]$$

- The quantity we are calculating here is called a “Berry phase.”
- When the BZ integral is replaced by a sum on a regular mesh, a finite-difference approximation to $\partial u^\lambda_{\mathbf{k}i} / \partial k_\alpha$ can be used, so the polarization can be expressed strictly in terms of ground-state wave functions.

Density Functional Perturbation Theory

- All quantities are expanded in power series in a DF energy parameter λ,

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \cdots, \quad X = E_{el}, T, V_{ext}, \psi_\alpha(\mathbf{r}), n(\mathbf{r}), \varepsilon_\alpha, H$$

- Solutions $\psi^{(0)}$ of Kohn-Sham equation minimize the usual DFT functional $E^{(0)}$

$$H^{(0)} \left| \psi_\alpha^{(0)} \right\rangle = \varepsilon_\alpha^{(0)} \left| \psi_\alpha^{(0)} \right\rangle.$$

- There is a variational functional for $E^{(2)}$

$$\begin{aligned} E_{el}^{(2)}\left\{\psi^{(0)};\psi^{(1)}\right\} = \sum_\alpha^{occ} \Big[& \left\langle \psi_\alpha^{(1)} \middle| T^{(0)} + V_{loc}^{(0)} + V_{non-loc}^{(0)} - \varepsilon_\alpha^{(0)} \middle| \psi_\alpha^{(1)} \right\rangle \\ & + \left\langle \psi_\alpha^{(1)} \middle| T^{(1)} + V_{loc}^{(1)} + V_{non-loc}^{(1)} + V_{Har}^{(1)} + V_{xc}^{(1)} \middle| \psi_\alpha^{(0)} \right\rangle \\ & + \left\langle \psi_\alpha^{(0)} \middle| T^{(1)} + V_{loc}^{(1)} + V_{non-loc}^{(1)} + V_{Har}^{(1)} + V_{xc}^{(1)} \middle| \psi_\alpha^{(1)} \right\rangle \\ & + \left\langle \psi_\alpha^{(0)} \middle| T^{(2)} + V_{loc}^{(2)} + V_{non-loc}^{(2)} \middle| \psi_\alpha^{(0)} \right\rangle \Big] \\ & + \frac{1}{2} \frac{d^2 E_{Har}}{d\lambda^2}\bigg|_{n^{(0)}} + \frac{1}{2} \frac{d^2 E_{xc}}{d\lambda^2}\bigg|_{n^{(0)}} + \frac{1}{2} \frac{d^2 E_{Ion-Ion}}{d\lambda^2} \end{aligned}$$

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DFPT, continued

- The variational functional for $E^{(2)}$ is minimized by solutions $\psi^{(1)}$ of the self-consistent Sternheimer equation

$$P_c(H^{(0)} - \varepsilon_\alpha^{(0)})P_c \left|\psi_\alpha^{(1)}\right\rangle = -P_c H^{(1)} \left|\psi_\alpha^{(0)}\right\rangle,$$

  – where P_c is the projector on unoccupied states (conduction bands) and

$$H^{(1)} = T^{(1)} + V_{ext}^{(1)} + V_{Hxc}^{(1)},$$

$$V_{Hxc0}^{(1)} = \frac{\partial}{\partial\lambda}\frac{\delta E_{Hxc}}{\delta n(\mathbf{r})}\bigg|_{n^{(0)}}$$

$$V_{Hxc}^{(1)} = V_{Hxc0}^{(1)} + \int \frac{\delta^2 E_{Hxc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}')\, d\mathbf{r}',$$

$$n^{(1)}(\mathbf{r}) = \sum_\alpha^{\text{occ}} [\psi_\alpha^{*(1)}(\mathbf{r})\psi_\alpha^{(0)}(\mathbf{r}) + \psi_\alpha^{*(0)}(\mathbf{r})\psi_\alpha^{(1)}(\mathbf{r})].$$

DFPT, continued

- Sternheimer equation for $\psi^{(1)}$ is solved using same techniques as ground-state Kohn-Sham equation
  - Minimize residuals by conjugate-gradient method
  - Constrain solutions to be orthogonal to occupied states
  - No normalization, inhomogeneous term determines amplitude
- Converge first-order potential $V_{Hxc}^{(1)}$ by conjugate-gradient or mixing method
- Iterative steps for potential and wave functions alternate
  - Wave functions never “start from scratch”
  - Accurate wave-function convergence is never “wasted” on a poorly converged potential
- Variational 2nd-order energy decreases with iterations

DFPT for metals

- Thermal smearing of the Fermi surface must be introduced for stability
- Density is defined with Fermi factor, $n(\mathbf{r}) = \sum_{\alpha} f_{\mathrm{F},\alpha} \psi_{\alpha}^{*}(\mathbf{r}) \psi_{\alpha}(\mathbf{r})$
- Correct 1st-order density can be generated from wave functions satisfying a modified Sternheimer equation (simulating a statistical ensemble of determinental wave functions).[1] Solution:

$$\left|\psi_{\alpha}^{(1)}\right\rangle = P_c (H^{(0)} - \varepsilon_{\alpha}^{(0)})^{-1} P_c H^{(1)} \left|\psi_{\alpha}^{(0)}\right\rangle$$

$$-\frac{1}{2} \sum_{\beta \neq \alpha}^{\beta < c} f_{\mathrm{F},\alpha}^{-1} \left|\psi_{\beta}^{(0)}\right\rangle \frac{\max\left(f_{\mathrm{F},\alpha} - f_{\mathrm{F},\beta}, 0\right)}{\varepsilon_{\beta}^{(0)} - \varepsilon_{\alpha}^{(0)}} \left\langle \psi_{\beta}^{(0)} \middle| H^{(1)} \middle| \psi_{\alpha}^{(0)} \right\rangle$$

$$+\frac{1}{2} f_{\mathrm{F},\alpha}^{-1} \left|\psi_{\beta}^{(0)}\right\rangle \frac{d f_{\mathrm{F},\alpha}}{d \varepsilon_{\alpha}} \left\langle \psi_{\beta}^{(0)} \middle| H^{(1)} \middle| \psi_{\alpha}^{(0)} \right\rangle$$

  - Resembles ordinary finite-temperature perturbation theory for partially occupied states $\alpha, \beta < c$, where c is chosen so that $f_{\mathrm{F},\alpha \geq c} \equiv 0$
  - Contributions from $\beta \geq c$ treated as for insulators with P_c

(1) S. de Gironcoli, Phys. Rev. B 51, 6773 (1995)

Strain perturbation for metals

- For strain (or $\mathbf{q}=0$ phonons), a first-order Fermi energy $\varepsilon_F^{(1)}$ must be introduced to preserve charge neutrality[(1)]

$$\varepsilon_{\mathrm{F}}^{(1)} = \sum_{\alpha<c} \left\langle \psi_\alpha^{(0)} \middle| H^{(1)} \middle| \psi_\alpha^{(0)} \right\rangle \frac{df_{\mathrm{F},\alpha}}{d\varepsilon_\alpha} \Bigg/ \sum_{\alpha<c} \frac{df_{\mathrm{F},\alpha}}{d\varepsilon_\alpha}$$

- $\varepsilon_{\mathrm{F}}^{(1)}$ "corrects" the 1st-order wave function found for constant ε_{F} ,

$$\left| \psi_\alpha^{(1)} \right\rangle = \left| \psi_\alpha^{(1)} \right\rangle \Big|_{\varepsilon_{\mathrm{F}}^{(0)}} - \frac{1}{2} f_{\mathrm{F},\alpha}^{-1} \left| \psi_\alpha^{(0)} \right\rangle \frac{df_{\mathrm{F},\alpha}}{d\varepsilon_\alpha} \varepsilon_{\mathrm{F}}^{(1)}$$

- $\varepsilon_{\mathrm{F}}^{(1)}$ enters into the self-consistency cycle of the Sternheimer equation

(1) S. Baroni, S. de Gironcoli, and A. Dal Corso, Rev. Mod. Phys. **73**, 515 (2001),

DFPT for elastic and piezoelectric tensors

- Mixed 2nd derivatives of the energy with respect to pairs of perturbations
  - By the "2n+1" theorem, these only require one set of 1st order wave functions,

$$E_{el}^{(\lambda_1\lambda_2)} = \sum_{\alpha}^{\text{occ}} \left\langle \psi_\alpha^{(\lambda_2)} \middle| (T^{(\lambda_1)} + V_{ext}^{(\lambda_1)} + V_{Hxc0}^{(\lambda_1)}) \middle| \psi_\alpha^{(0)} \right\rangle$$

Non-self-consistent

$$+ \sum_{\alpha}^{\text{occ}} \left\langle \psi_\alpha^{(0)} \middle| (T^{(\lambda_1\lambda_2)} + V_{ext}^{(\lambda_1\lambda_2)}) \middle| \psi_\alpha^{(0)} \right\rangle + \frac{1}{2} \frac{\partial^2 E_{Hxc}}{\partial\lambda_1 \partial\lambda_2}\bigg|_{n^{(0)}},$$

  - This expression is non-stationary (i.e., 1st-order in convergence errors)
- To include atomic relaxation, we need strain $\eta_{\alpha\beta}$, electric field $\tilde{\mathcal{E}}_j$ and atomic coordinate $\tilde{\tau}_{\kappa i}$ derivatives
  - Clamped-atom elastic tensor ---------- $\partial^2 E_{el} / \partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta}$
  - Internal strain tensor ---------- $\partial^2 E_{el} / \partial\eta_{\alpha\beta}\partial\tilde{\tau}_{\kappa j}$
  - Interatomic force constants ---------- $\partial^2 E_{el} / \partial\tilde{\tau}'_{\kappa' i}\partial\tilde{\tau}_{\kappa j}$
  - Clamped-atom piezoelectric tensor ---- $\partial^2 E_{el} / \partial\eta_{\alpha\beta}\partial\tilde{\mathcal{E}}_j$
  - Born effective charges ---------- $\partial^2 E_{el} / \partial\tilde{\tau}_{\kappa i}\partial\tilde{\mathcal{E}}_j$

Electric field derivatives (more polarization)

- The energy acquires an extra term, $E = E_{\mathrm{HKS}} - \mathcal{E} \cdot \mathbf{P}$
- Recall the Berry-phase expression for polarization,

$$\mathbf{P} = \frac{-i}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \sum_i^{\mathrm{occ}} \left[\left\langle u_{\mathbf{k}i} \middle| \nabla_{\mathbf{k}} u_{\mathbf{k}i} \right\rangle \right]$$

  where we have dropped λ.
- The response-function calculation proceeds in 2 stages
  - First, we use the RF machinery to calculate $\left| \nabla_{\mathbf{k}} u_{\mathbf{k}i} \right\rangle$ by treating it as a first-order wave function, solving the Sternheimer equation with $\left[\nabla_{\mathbf{k}} \hat{H}_{\mathrm{KS}}(\mathbf{k}) \right] \left| u_{\mathbf{k}i}^{(0)} \right\rangle$ as the inhomogeneous 1st-order perturbation term on the right-hand side
  - There in no self-consistent potential involved here.
  - Next, we take the $\mathcal{E}$ derivative and $\left| \nabla_{\mathbf{k}} u_{\mathbf{k}i} \right\rangle$ itself becomes the inhomogeneous Sternheimer term.
  - In this second step, there is a self-consistent 1st-order screening potential.

Incorporating atomic relaxation

- Introduce a model energy function quadratic in atomic displacements $u_{m\alpha}$ from a reference configuration, strain $\eta_{\alpha\beta}$, and electric field $\mathcal{E}_\alpha$

$$H(\mathbf{u},\boldsymbol{\eta},\mathcal{E}) = \begin{pmatrix}\mathbf{u} & \boldsymbol{\eta} & \mathcal{E}\end{pmatrix}\left[\begin{pmatrix}-\mathbf{F}/\Omega \\ \boldsymbol{\sigma} \\ -\mathbf{P}\end{pmatrix} + \begin{pmatrix}\mathbf{K}/\Omega & -\boldsymbol{\Lambda}/\Omega & -\mathbf{Z}/\Omega \\ -\boldsymbol{\Lambda}^T/\Omega & \mathbf{C} & -e \\ -\mathbf{Z}^T/\Omega & e^T & \boldsymbol{\chi}\end{pmatrix}\begin{pmatrix}\mathbf{u} \\ \boldsymbol{\eta} \\ \mathcal{E}\end{pmatrix}\right]$$

- Various terms, all “bare” or clamped-atom quantities with atom indices m,n and Cartesian components $\alpha,\beta,\gamma,\cdots$ are as follows:

$F_{m\alpha}$	Atomic forces	$C_{\alpha\beta,\gamma\delta}$	Elastic tensor
$\sigma_{\alpha\beta}$	Stress	$Z_{m\alpha,\gamma}$	Born effective charges
P_α	Electric polarization	$e_{\alpha,\gamma\delta}$	Piezoelectric tensor
$K_{m\alpha,n\gamma}$	Interatomic force constants	$\chi_{\alpha,\gamma}$	Dielectric susceptibility
$\Lambda_{m\alpha,\gamma\delta}$	“Force” internal strain tensor		

Incorporating atomic relaxation, continued

- The "relaxed atom" model energy function is defined as

$$\tilde{H}\left(\eta_{\alpha\beta},\mathcal{E}_{\alpha}\right)=\min_{\{u_{m\alpha}\}}H\left(u_{m\alpha},\eta_{\alpha\beta},\mathcal{E}_{\alpha}\right)$$

  - Additionally assume that $F_{m\alpha}=0$ in the reference configuration
- Strain and electric field 2nd derivatives of $\tilde{H}$ then yield the "dressed" or relaxed-atom elastic and piezoelectric tensors

$$\tilde{C}_{\alpha\beta,\gamma\delta}=C_{\alpha\beta,\gamma\delta}+\Omega^{-1}\sum_{mn=1}^{\text{natom}}\sum_{ij=1}^{3}\Lambda_{mi,\alpha\beta}(K^{-1})_{mi,nj}\Lambda_{nj,\gamma\delta}$$

$$\tilde{e}_{\alpha\beta,\gamma}=e_{\alpha\beta,\gamma}+\Omega^{-1}\sum_{mn=1}^{\text{natom}}\sum_{ij=1}^{3}\Lambda_{mi,\alpha\beta}(K^{-1})_{mi,nj}Z_{nj,\gamma}$$

  - K^{-1} is the pseudo-inverse of the interatomic force constant matrix
  - Various other quantities corresponding to differing boundary conditions such as fixed or zero polarization or stress, etc. can be calculated using the same approach

DPFT for periodic atomic displacements

- Displacement $\tau_{\kappa i} + R_i \rightarrow \tau_{\kappa i} + R_i + \lambda e^{i\mathbf{q}\cdot\mathbf{R}}$

- First-order external potential
  - PSP & model core charge contributions

$$V^{(1)}_{\text{ext},\mathbf{q}}(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \frac{\partial}{\partial \tau_{\kappa i}} \Big[v_{\text{psp},\kappa}(\mathbf{r}-\boldsymbol{\tau}_\kappa-\mathbf{R},\mathbf{r}'-\boldsymbol{\tau}_\kappa-\mathbf{R}) + \delta(\mathbf{r}-\mathbf{r}') \left.\frac{\delta V_{xc}}{\delta n(\mathbf{r})}\right|_{n^{(0)}} \rho_{\text{core},\kappa}(\mathbf{r}-\boldsymbol{\tau}_\kappa-\mathbf{R}) \Big]$$

- Sternheimer equation

$$P_{\mathbf{k}+\mathbf{q},c}(H^{(0)} - \varepsilon^{(0)}_{\mathbf{k},\alpha}) P_{\mathbf{k}+\mathbf{q},c} \left|\psi^{(1)}_{\mathbf{k}+\mathbf{q},\alpha}\right\rangle = -P_{\mathbf{k}+\mathbf{q},c} H^{(1)}_{\mathbf{q}}\left(n^{(1)}_{\mathbf{q}}\right)\left|\psi^{(0)}_{\mathbf{k},\alpha}\right\rangle,$$

- 2nd-order energy (dynamical matrix)
  - 2 atoms and directions

$$E^{(\tau_{\kappa i}\tau_{\kappa' j})}_{\text{el},-\mathbf{q},\mathbf{q}} = \int_{\text{BZ}} \sum_{\alpha}^{\text{occ}} \left(\left\langle \psi^{(\tau_{\kappa i})}_{\mathbf{k}+\mathbf{q},\alpha} \middle| V^{(\tau_{\kappa' j})}_{\text{ext},\mathbf{q}} \middle| \psi^{(0)}_{\mathbf{k},\alpha} \right\rangle + \left\langle \psi^{(0)}_{\mathbf{k},\alpha} \middle| V^{(\tau_{\kappa i},\tau_{\kappa' j})}_{\text{psp},-\mathbf{q},\mathbf{q}} \middle| \psi^{(0)}_{\mathbf{k},\alpha} \right\rangle \right) d\mathbf{k} + \frac{1}{2} \left.\frac{\partial^2 E_{xc}}{\partial \tau_{\kappa i,-\mathbf{q}} \partial \tau_{\kappa' j,\mathbf{q}}}\right|_{n^{(0)}}$$

Full phonon spectrum

- Find dynamical matrix on a uniform mesh of $\mathbf{q}$ points
  - $\mathbf{q}$ mesh should be commensurate with $\mathbf{k}$ mesh for GS wave functions
- FFT to create interatomic force constant matrix on a finite set of $\mathbf{R}$ lattice points
  - Density of $\mathbf{q}$ mesh determines maximum $\mathbf{R}$ calculated
  - Should be short-ranged (a few unit cells)
- Now do "Slow" FT to get phonon energies at any $\mathbf{q}$'s you want (such as on BZ symmetry lines)

Special treatment for polar insulators

- Dipole-dipole interactions are long-range
- This contribution to the dynamical matrix can be expressed analytically in terms of Born effective charges and the electronic dielectric tensor
- Subtract before the FFT, add back in after the Slow FT
- Contribution at $\mathbf{q} \to 0$ is non-analytic, and gives LO-TO splitting

Index to Abinit RF perturbations

ipert	idir	type	coord	_1WF*	Voigt
1	1	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_1^P$	1	
1	2	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_2^P$	2	
1	3	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_3^P$	3	
2	1	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_1^P$	4	
2	2	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_2^P$	5	
2	3	$\partial/\partial\tilde{\boldsymbol{\tau}}$	$\mathbf{R}_3^P$	6	
…				…	
natom+1	1	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+1	
natom+1	2	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+2	
natom+1	3	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+3	
natom+2	1	$\partial/\partial\mathcal{E}$	$\mathbf{R}_1^P$	3*natom+4	
natom+2	2	$\partial/\partial\mathcal{E}$	$\mathbf{R}_2^P$	3*natom+5	
natom+2	3	$\partial/\partial\mathcal{E}$	$\mathbf{R}_3^P$	3*natom+6	
natom+3	1	$\partial/\partial\eta$	xx	3*natom+7	1
natom+3	2	$\partial/\partial\eta$	yy	3*natom+8	2
natom+3	3	$\partial/\partial\eta$	zz	3*natom+9	3
natom+4	1	$\partial/\partial\eta$	yz	3*natom+10	4
natom+4	2	$\partial/\partial\eta$	xz	3*natom+11	5
natom+4	3	$\partial/\partial\eta$	xy	3*natom+12	6

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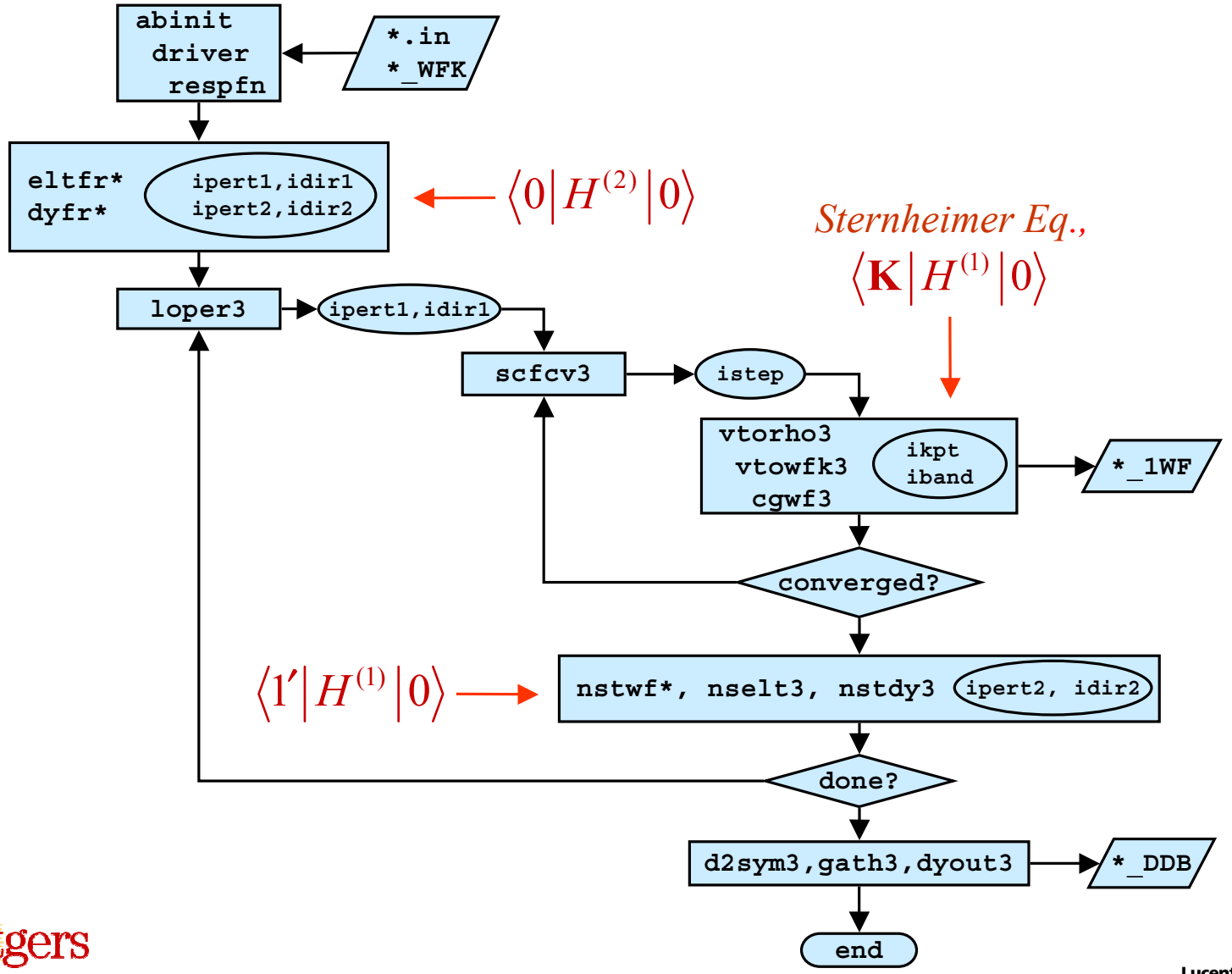
Response function code organization



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