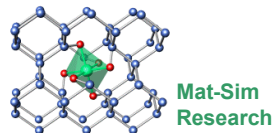# Elastic and Piezoelectric Properties in ABINIT

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History

- Bad old days (70's)
  - Murnaghan function fit to energy vs. volume results
  - Bulk moduli from 2nd derivatives of fits
  - No piezoelectricity
- Moving forward (80's +)
  - Analytic theories for stress (Nielsen & Martin) and polarization (Vanderbilt & King-Smith)
  - Numerical 1st derivatives for elastic and piezoelectric constants
- The modern era (90's +)
  - Density functional perturbation theory for analytic 2nd (& 3rd) derivatives
  - Phonons, Born effective charges, dielectric tensor
- Abinit in 2004 +
  - Strain in DFPT for analytic elastic and piezoelectric constants
  - Analytic treatment of atomic relaxation contributions

Overview

- Issues in the perturbation treatment of strain

- Reduced coordinates as the fundamental basis of an alternative approach

- <u>Brief</u> review of Density Functional Perturbation Theory

- Strain derivatives needed for DFPT – some special considerations

- Verifying DFPT results

- Incorporating atomic relaxation contributions

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Periodicity in cases studied so far

- Periodic atomic displacements
  - Derivatives wrt atomic coordinates $\tau_{\kappa i}$ including all periodic replicas
    $$\tau_{\kappa i} + R_i$$
  - Ground-state forces and response-function Q=0 phonons
- Atomic displacements with a different period $\quad \tau_{\kappa i} + R_i \rightarrow$
  $$\tau_{\kappa i} + R_i + \lambda e^{i\mathbf{q}\cdot\mathbf{R}}$$

  - "Phase-shifted replica" technique permits treatment in terms of the original periodic lattice
  - Second derivatives wrt one $\mathbf{q}$ and one $-\mathbf{q}$ perturbation give phonons.
- Uniform electric fields
  - Extended energy functional $E = E_{\text{HKS}} - \mathcal{E}\cdot\mathbf{P}$ destroys periodicity
  - Berry-phase formulation restores the ability to treat this perturbation in the original periodic framework
  - Derivatives give GS polarization, dielectric tensor, and Born effective charges

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

- Uniform strain changes the positions of the atomic (pseudo)potentials proportionally to their distances from the origin,

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

- 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.

- The boundary-condition problem can be treated by a transformation introducing a *fictitious* self-consistent Hamiltonian.[1]
  - However this changes structure of the DFPT calculation from that for "ordinary" perturbations, and has not been widely pursued.

(1) S. Baroni, P. Giannozzzi, and A. Testa, Phys. Rev. Lett. **59**, 2662 (1987).

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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 plane-wave 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**,

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

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

Reduced coordinate (~) formulation, continued

- Strain derivatives of the metric tensors are straightforward,

$$\Xi_{ij}^{(\alpha\beta)} \equiv \frac{\partial \Xi_{ij}}{\partial \eta_{\alpha\beta}} = R_{\alpha i}^{P} R_{\beta j}^{P} + R_{\beta i}^{P} R_{\alpha j}^{P}, \quad \Upsilon_{ij}^{(\alpha\beta)} \equiv \frac{\partial \Upsilon_{ij}}{\partial \eta_{\alpha\beta}} = -G_{\alpha i}^{P} G_{\beta j}^{P} - G_{\beta i}^{P} G_{\alpha j}^{P}$$

$$\Xi_{ij}^{(\alpha\beta\gamma\delta)} \equiv \frac{\partial^2 \Xi_{ij}}{\partial \eta_{\gamma\delta} \partial \eta_{\alpha\beta}} = \delta_{\alpha\gamma}(R_{\beta i}^{P} R_{\delta j}^{P} + R_{\delta i}^{P} R_{\beta j}^{P}) + \delta_{\beta\gamma}(R_{\alpha i}^{P} R_{\delta j}^{P} + R_{\delta i}^{P} R_{\alpha j}^{P})$$

$$+\delta_{\alpha\delta}(R_{\beta i}^{P} R_{\gamma j}^{P} + R_{\gamma i}^{P} R_{\beta j}^{P}) + \delta_{\beta\delta}(R_{\alpha i}^{P} R_{\gamma j}^{P} + R_{\gamma i}^{P} R_{\alpha j}^{P}),$$

- Ω has uniquely simple derivatives for Cartesian Strains

$$\frac{\partial \Omega}{\partial \eta_{\alpha\beta}} = \delta_{\alpha\beta}\Omega, \quad \frac{\partial^2 \Omega}{\partial \eta_{\alpha\beta} \partial \eta_{\gamma\delta}} = \delta_{\alpha\beta}\delta_{\gamma\delta}\Omega$$

- **Key decision**: strain will be Cartesian throughout the code
  - Existing perturbations will remain in reduced-coordinates

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Stress and strain notation

Cartesian	xx	yy	zz	yz	xz	xy
Cartesian	1 1	2 2	3 3	2 3	1 3	1 2
Voigt	1	2	3	4	5	6
ipert, idir	natom+3, 1	natom+3, 2	natom+3, 3	natom+4, 1	natom+4, 2	natom+4, 3

- Only the symmetric part of the strain tensor matters
  - Antisymmetric strains are simply rotations
- All these forms are used at various places internally and in the output

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 $E^{(0)}$

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

- 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

$$H^{(1)} = T^{(1)} + V_{ext}^{(1)} + V_{Hxc}^{(1)}, \quad V_{Hxc}^{(1)} = \left.\frac{\partial}{\partial\lambda}\frac{\delta E_{Hxc}}{\delta n(\mathbf{r})}\right|_{n^{(0)}} + \int \frac{\delta^2 E_{Hxc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}')\,d\mathbf{r}',$$

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

DFPT, continued

- Sternheimer equation for $\psi^{(1)}$ is solved using same techniques as ground-state Kohn-Sham equation
  - Residuals minimized by conjugate-gradient method
  - Solutions constrained to be orthogonal to occupied states
  - No normalization; inhomogeneous term determines amplitude
- First-order potential $V_{Hxc}^{(1)}$ converged by conjugate-gradient or mixing methods
- 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 $\psi^{(1)}$, $V^{(1)}$ convergence

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Variational 2DTE expression for strain

- Numbered breakdown of components as in Abinit output

$$
E_{el}^{(2)}\left\{\psi^{(0)};\psi^{(1)}\right\} = \sum_{\alpha}^{occ}\Bigg[\underbrace{\Big\langle \psi_{\alpha}^{(1)}\Big|}_{} \underbrace{T^{(0)}}_{1} + \underbrace{V_{Har+loc}^{(0)}}_{3} + \underbrace{V_{non-loc}^{(0)}}_{9} - \underbrace{\varepsilon_{\alpha}^{(0)}}_{2} \Big|\psi_{\alpha}^{(1)}\Big\rangle
$$

$$
+ \Big\langle \psi_{\alpha}^{(1)}\Big| \underbrace{T^{(1)}}_{7} + \underbrace{V_{loc}^{(1)}}_{4} + \underbrace{V_{non-loc}^{(1)}}_{10} + \underbrace{V_{Har}^{(1)}}_{5} + \underbrace{V_{xc}^{(1)}}_{6} \Big|\psi_{\alpha}^{(0)}\Big\rangle
$$

$$
+ \Big\langle \psi_{\alpha}^{(0)}\Big| T^{(1)} + V_{loc}^{(1)} + V_{non-loc}^{(1)} + V_{Har}^{(1)} + V_{xc}^{(1)} \Big|\psi_{\alpha}^{(1)}\Big\rangle
$$

$$
+ \Big\langle \psi_{\alpha}^{(0)}\Big| \underbrace{T^{(2)}}_{12} + \underbrace{V_{loc}^{(2)}}_{13} + \underbrace{V_{non-loc}^{(2)}}_{14} \Big|\psi_{\alpha}^{(0)}\Big\rangle \Bigg]
$$

$$
+ \underbrace{\frac{1}{2}\frac{d^2 E_{Har}}{d\lambda^2}\bigg|_{n^{(0)}}}_{11} + \underbrace{\frac{1}{2}\frac{d^2 E_{xc}}{d\lambda^2}\bigg|_{n^{(0)}}}_{15} + \underbrace{\frac{1}{2}\frac{d^2 E_{Ion-Ion}}{d\lambda^2}}_{16,\ 17}
$$

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Variational 2DTE components for strain

```
Seventeen components of 2nd-order total energy (hartree) are
1,2,3: 0th-order hamiltonian combined with 1st-order wavefunctions
    kin0=    5.45759309E+00 eigvalue=   -4.64795287E-01  local=   -3.43266023E+00
4,5,6,7: 1st-order hamiltonian combined with 1st and 0th-order wfs
loc psp =    1.38229987E+00  Hartree=    1.08631683E+00     xc=   -4.86887660E-01
    kin1=   -5.29050571E+00
8,9,10: eventually, occupation + non-local contributions
   edocc=    0.00000000E+00     enl0=    2.22543400E+00   enl1=   -4.92230408E+00
1-10 gives the relaxation energy (to be shifted if some occ is /=2.0)
   erelax=   -4.44550918E+00
11,12,13 Non-relaxation  contributions : frozen-wavefunctions and Ewald
 fr.hart=  -5.37096135E-01    fr.kin=    4.17616081E+00 fr.loc=    2.61961436E+00
14,15,16 Non-relaxation  contributions : frozen-wavefunctions and Ewald
 fr.nonl=    3.24102985E+00     fr.xc=  -2.30295282E-01  Ewald=   -3.20692684E+00
17 Non-relaxation  contributions : pseudopotential core energy
 pspcore=  -2.77394479E-01
Resulting in :
2DEtotal=    0.1339583111E+01 Ha. Also 2DEtotal=    0.364519096295E+02 eV
   (2DErelax=   -4.4455091757E+00 Ha. 2DEnonrelax=    5.7850922867E+00 Ha)
   (  non-var. 2DEtotal :    1.3395938195E+00 Ha)
```

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Derivatives for elastic and piezoelectric tensors

- We need combinations of strain $\eta_{\alpha\beta}$, electric field $\tilde{\mathcal{E}}_j$ and atomic coordinate $\tilde{\tau}_{\kappa i}$ derivatives (some for atomic relaxation corrections).

  - 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 ($\mathbf{q}$=0) ------- $\partial^2 E_{el}/\partial\tilde{\tau}'_{\kappa'i}\partial\tilde{\tau}_{\kappa j}$

  - Clamped-atom piezoelectric tensor ---- $\partial^2 E_{el}/\partial\eta_{\alpha\beta}\partial\tilde{\mathcal{E}}_j$

  - Born effective charges -------------------- $\partial^2 E_{el}/\partial\tilde{\tau}_{\kappa i}\partial\tilde{\mathcal{E}}_j$

- Calculating mixed 2nd derivatives of the energy wrt pairs of perturbations

  - By the "2n+1" theorem, these only require one set of 1st order wave functions,

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

Non-self-consistent

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

  - This expression is non-stationary (i.e., **1st-order in convergence errors**)

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Mixed derivative evaluation

- For strain – reduced atomic coordinate derivatives
  - Use 1st-order strain wave functions $\psi_\alpha^{(\eta_{\alpha\beta})}$
  - Use 1st-order reduced-atomic-coordinate Hamiltonian $H^{(\tilde{\tau}_{\kappa i})}$
  - Calculate non-variational terms (explicit 2nd derivatives with $\psi_\alpha^{(0)}$ and $n^{(0)}$) within the same framework as the strain-strain 2nd derivatives
  - All terms enter (kinetic, local psp, nonlocal psp, hartree, xc, and ion-ion)

- For strain – electric field derivatives
  - Special, simpler non-stationary expression can be derived

$$\frac{\partial^2 E_{el}}{\partial \tilde{\mathcal{E}}_j \partial \eta_{\alpha\beta}} = 2\frac{\Omega}{(2\pi)^3} \int\limits_{BZ} \sum_m^{occ} \left\langle i\,\psi_{\mathbf{k}m}^{(\tilde{k}_j)} \middle| \psi_{\mathbf{k}m}^{(\eta_{\alpha\beta})} \right\rangle d\mathbf{k} \,,$$

  - $\psi_{\mathbf{k}m}^{(\tilde{k}_j)}$ are 1st-order wave functions for the $\partial/\partial k$ perturbation which enters. through the modern theory of polarization.[1]
  - There are no explicit 2nd-derivative terms.

(1) R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**,1651 (1993)

DFPT modifications for metals

- Thermal smearing of the Fermi surface must be introduced for stability

- Density is defined with Fermi factors, $n(\mathbf{r}) = \sum_{\alpha} f_{F,\alpha} \psi_{\alpha}^{*}(\mathbf{r}) \psi_{\alpha}(\mathbf{r})$

- Correct 1st-order density can be generated from wave functions satisfying a modified Sternheimer equation (simulating a statistical ensemble of determinental wave functions).[1] The formal solution is

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

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

$$+ P_{c} (H^{(0)} - \varepsilon_{\alpha}^{(0)})^{-1} P_{c} H^{(1)} \left| \psi_{\alpha}^{(0)} \right\rangle$$

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

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

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Strain perturbation for metals

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

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

- $\varepsilon_F^{(1)}$ "corrects" the 1st-order wave function found for constant ε_F ,

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

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

- **k**-sample / Fermi-surface-broadening convergence in metals can be much more demanding for strain derivatives than for other quantities.

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

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Kinetic energy cutoff "smoothing"

- Existing Abinit strategy to smooth energy dependence on lattice parameters in GS calculations
  - Forces wave function coefficients smoothly to zero at cutoff sphere.
- RF strain derivative calculations do accurately reproduce GS numerical derivatives with non-zero `ecutsm`
- Divergence can produce large shifts in elastic tensor if calculation is not **well** converged with respect to `ecut`
  - Remember, we take two derivatives
  - Cutoff function was improved when strain was introduced

ecut = 25
ecutsm = 5

With `ecutsm`

Without

Kinetic energy (Hartree)

$K (a_B^{-1})$
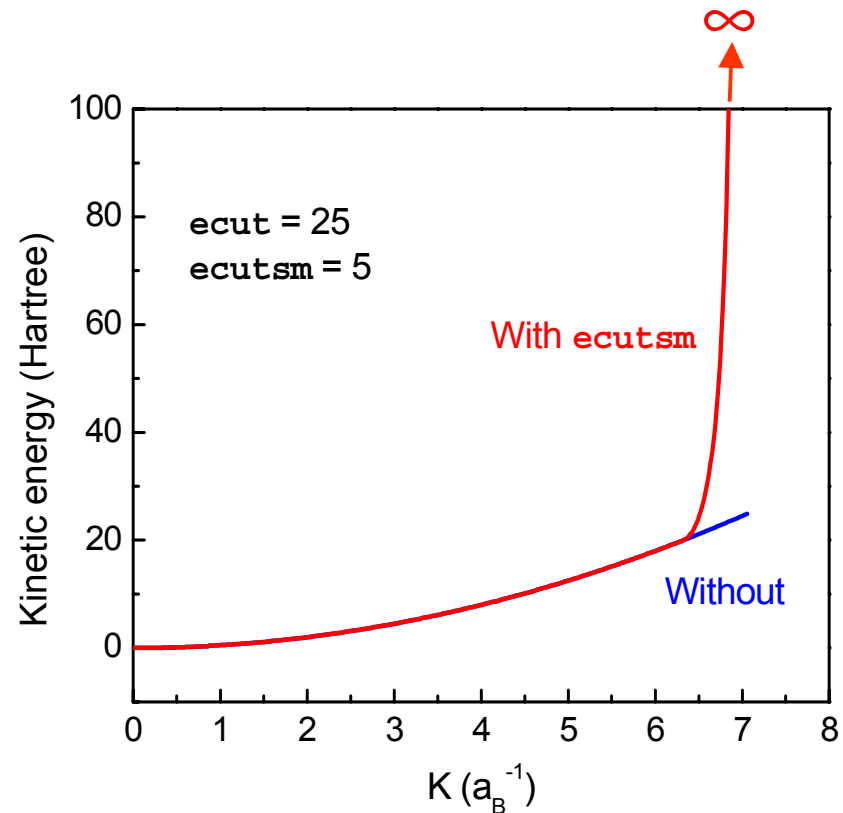
XC non-linear core correction

- On the reduced real-space grid, electron charge depends only on Ω^{-1}

- Model core charge has a detailed dependence on Ξ_{ij}
  - Resulting energy derivatives are rather complicated functions.

- Core charges must be ***extremely smooth*** functions to avoid convergence errors
  - Reason: Strain and atomic position derivatives of the xc self-interaction of a single core don't cancel point-by-point on the grid, but only in the integral
  - 1st and 2nd derivatives of the core model enter these expressions

- Generalized gradient functionals have been implemented for strain as of release 4.4, and are probably even more demanding

Nonlocal pseudopotentials in Abinit

- Most mathematically complex objects for strain derivatives
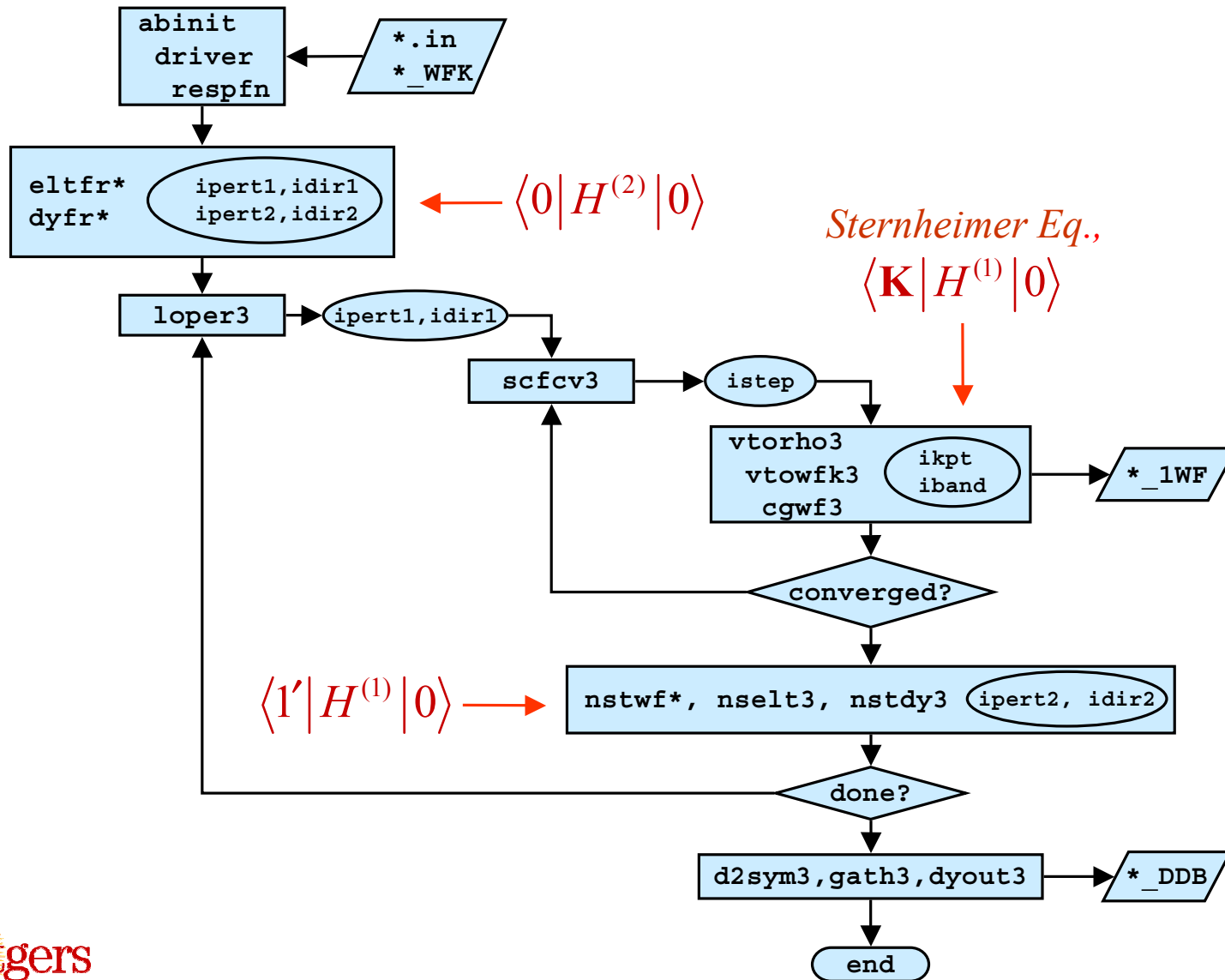
- Reduced-wave-vector matrix elements have the form

$$\langle \tilde{\mathbf{K}}' | V_{NL} | \tilde{\mathbf{K}} \rangle = \frac{1}{\Omega} \sum_{\kappa\ell} e^{2\pi i \tilde{\mathbf{K}}' \cdot \tilde{\tau}_\kappa} f_{\kappa\ell} (\sum_{ij} \Upsilon_{ij} \tilde{K}'_i \tilde{K}'_j) \times$$

$$\wp_\ell (\sum_{ij} \Upsilon_{ij} \tilde{K}'_i \tilde{K}'_j, \sum_{ij} \Upsilon_{ij} \tilde{K}'_i \tilde{K}_j, \sum_{ij} \Upsilon_{ij} \tilde{K}_i \tilde{K}_j) e^{-2\pi i \tilde{\mathbf{K}} \cdot \tilde{\tau}_\kappa} f_{\kappa\ell} (\sum_{ij} \Upsilon_{ij} \tilde{K}_i \tilde{K}_j)$$

  - $\wp_\ell$ modified Legendre polynomials, $f_{\kappa\ell}$ psp form factors, $\tilde{\tau}_\kappa$ reduced atom coordinates
  - All arguments are dot products expressed with metric tensors

- Psp's act on wave functions by summing wave function coefficients times a set of tensor products of reduced $\tilde{\mathbf{K}}$ components ($\sim Y_{\ell m}$).

- Code for the 1st and 2nd strain derivatives was created using Mathematica. (If you can't sleep, read `cont*str*.F90, metstr.F90`.)

- Despite this complexity, the computational cost of psp derivatives acting on wf's is comparable to that of the psp's themselves.

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Response function code organization

Use of symmetry with the strain perturbation

- The reduced-zone **k** sample determined for (space group / strain) is used for $\langle \mathbf{K} | H^{(1)} | 0 \rangle$, *Sternheimer*, and $\langle 1' | H^{(1)} | 0 \rangle$
  - The full-zone sample specified by the input data must have the full space group symmetry (enforced by test).
- Loop on (`ipert1, idir1`) for 1st-order wave functions restricted by input variables (`rfstrs, rfdir`) but not by symmetry
  - This could be improved, but would have limited impact on performance
- Inner loop on (`ipert2, idir2`) in $\langle 1' | H^{(1)} | 0 \rangle$ calculations is carried over all strain and atomic displacement terms
  - piezoelectric contribution is computed if d/dk wf's are avaialble
- All $\langle 0 | H^{(2)} | 0 \rangle$ strain and internal-strain tensor elements are computed, using the full zone **k** sample
  - It is more efficient here to keep loops on strains and displacements inside routines like `nonlop.F90`
  - The reduced zone for pairs of perturbations would seldom be reduced much anyway

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Verification using numerical derivatives - caveats

- RF 2nd strain derivatives do not correspond to strain derivatives of stress

$$C^*_{\alpha\beta,\gamma\delta} \equiv \frac{1}{\Omega}\frac{\partial^2 E_{el}}{\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta}}, \quad C_{\alpha\beta,\gamma\delta} \equiv \frac{\partial\sigma_{\gamma\delta}}{\partial\eta_{\alpha\beta}} = \frac{\partial}{\partial\eta_{\alpha\beta}}\frac{1}{\Omega}\frac{\partial E_{el}}{\partial\eta_{\gamma\delta}} = C^*_{\alpha\beta\gamma\delta} - \delta_{\alpha\beta}\sigma_{\gamma\delta},$$

  – As of release 4.5, anaddb will calculate this correction to give the conventional elastic tensor in the presence of stress.
  – DDB file from GS calculation must be merged with RF DDB file for this

- The strain derivatives of the polarization give the "improper" piezoelectric tensor. Abinit and anaddb (and correctly-performed experiments) give the "proper" tensor.[1]

$$e_{\alpha\beta\gamma} = \frac{dP_\alpha}{d\eta_{\beta\gamma}}, \quad e^{\mathrm{Proper}}_{\alpha\beta\gamma} = e_{\alpha\beta\gamma} + \delta_{\beta\gamma}P_\alpha - \delta_{\alpha\beta}P_\gamma$$

(1) D. Vanderbilt, J. Phys. Chem. Solids **61**, 147 (2000)

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Comparisons with numerical derivatives

- Zinc-blende AlP with random distortions so all tensor elements are non-zero.
  - Ground state calculations of stress and polarization with **clamped atomic coordinates**
  - Finite-difference d/dk $\psi_\alpha^{(1)}$'s for best consistency with polarization calculations
  - 5-point numerical derivatives with strain increment 2×10^{-5}

Elastic Tensor (GPa)

		Numerical	DFPT	Diff
xx	xx	124.999900	124.999900	2.4E-05
yy	xx	66.990360	66.990360	-3.9E-06
zz	xx	68.396840	68.396840	-1.5E-06
yz	xx	0.088373	0.088374	1.1E-07
xz	xx	-1.117333	-1.117333	-4.3E-07
xy	xx	-0.418922	-0.418922	5.7E-08
xx	yz	0.088374	0.088374	-6.6E-07
yy	yz	5.154470	5.154469	-1.0E-06
zz	yz	-5.578270	-5.578270	-2.9E-07
yz	yz	90.315730	90.315730	4.5E-06
xz	yz	-0.404749	-0.404749	5.0E-08
xy	yz	0.644728	0.644728	6.4E-08

Piezoelectric Tensor (C/m^2 x 10^{-2})

		Numerical	DFPT	Diff
x	xx	2.0211410	2.0211400	-8.7E-07
y	xx	5.2336140	5.2336120	-1.8E-06
z	xx	0.4003179	0.4003186	6.7E-07
x	yy	-8.2697310	-8.2697310	3.0E-08
y	yy	0.2471218	0.2471215	-3.3E-07
z	yy	0.7383708	0.7383704	-4.3E-07
x	yz	-69.2631000	-69.2631000	-3.6E-06
y	yz	-0.1423518	-0.1423530	-1.2E-06
z	yz	-1.3531730	-1.3531760	-2.9E-06

- RMS Errors 5.4×10^{-6} (ELT) and 2.0×10^{-8} (PZT)

Incorporating atomic relaxation

- "Homogeneous strain" produced experimentally is only macroscopically homogeneous.

- For all but the simplest structures, strain will change the reduced atomic coordinates, not just the metric tensors.
  - Diamond, for example, has relaxation corrections.

- Atomic relaxation makes modest changes the the elastic constants for "normal" solids, huge changes for special cases (eg., molecular solids)

- There are large relaxation changes in the piezoelectric constants for most piezoelectric materials.

- For all but very simple cases, accurate results by numerical differentiation incorporating GS relaxation are completely impractical.
  - Atomic forces generated by incremental strains are too small.

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Analytic treatment of 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 $\mathcal{E}_\alpha$

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

- 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		

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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

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

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

  - K^{-1} is the pseudo-inverse of the interatomic force constant matrix (zero eigenvalues suppressed).

Implementation of atomic relaxation

- Incorporated in anaddb program to be used as a post-processor of abinit results
  - All the needed second derivatives must be present in the DDB file from the RF run (or merged from several runs).
  - Results are converted to conventional units rather than atomic or reduced units.

- Various other tensors corresponding to differing boundary conditions such as fixed or zero polarization or stress, etc. can be calculated using the same approach.
  - See reference 3 in the bibliography.
  - See notes on the input variables `elaflag`, `instrflag`, and `piezoflag` in the anaddb help file.
  - The dielectric tensor is also needed for some of these calculations.

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Relaxed results compared to numerical derivatives

- Zinc-blende AlP with random distortions so all tensor elements are non-zero.
  - Ground state calculations of stress and polarization with *exquisitely* relaxed atomic coordinates (but unrelaxed stress)
  - Sample of complete set of tensor elements

Elastic Tensor (GPa)

		Numerical	DFPT	Diff
xx	xx	124.991500	124.991500	-1.1E-05
yy	xx	66.999750	66.999760	8.2E-06
zz	xx	68.359440	68.359440	7.0E-07
yz	xx	0.228447	0.228466	1.9E-05
xz	xx	-1.139838	-1.139828	9.6E-06
xy	xx	-0.015028	-0.015117	-9.0E-05
xx	yz	0.228471	0.228466	-4.4E-06
yy	yz	1.940050	1.940054	3.7E-06
zz	yz	-2.079264	-2.079275	-1.1E-05
yz	yz	66.593340	66.593390	5.2E-05
xz	yz	0.773972	0.773977	5.1E-06
xy	yz	-0.568446	-0.568449	-3.2E-06

Piezoelectric Tensor (C/m^2 x 10^{-2})

		Numerical	DFPT	Diff
x	xx	1.714769	1.714694	-7.5E-05
y	xx	5.107069	5.107080	1.1E-05
z	xx	-0.883962	-0.883676	2.9E-04
x	yy	0.828569	0.828454	-1.2E-04
y	yy	3.716843	3.716812	-3.2E-05
z	yy	-0.810201	-0.810176	2.5E-05
x	yz	-3.871980	-3.872154	-1.7E-04
y	yz	-1.245173	-1.245206	-3.3E-05
z	yz	1.902687	1.902693	5.6E-06

- RMS Errors 4.0×10^{-5} (ELT) and 1.7×10^{-6} (PZT)
  - 1-2 orders of magnitude larger than for clamped-atom quantities.

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