Polarization and finite fields

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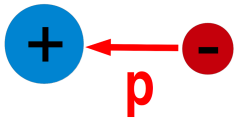
ABINIT school on ground state and linear response properties 2019

Outline

- Polarization in periodic ionic crystals
- Berry phase treatment of polarization
- Finite E-field
- Finite D-field

Polarization in periodic solids

Electric dipole between two charges $+Q$ and $-Q$:



$\mathbf{p} = Q\,\mathbf{d}$

For a collection of charges: $\mathbf{p} = \sum_i Q_i \mathbf{r_i}$

Polarization in periodic solids

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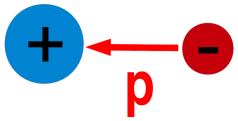

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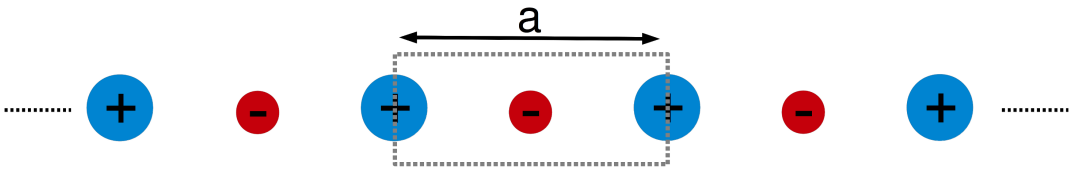
For a non-polar periodic 1-D ionic chain: dipole moment per unit cell

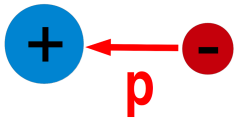


$$\frac{p}{a} = +Q \times 0 - Q \times \frac{1}{2} = -\frac{Q}{2}$$

Non-zero!

Polarization in periodic solids

Electric dipole between two charges $+Q$ and $-Q$:



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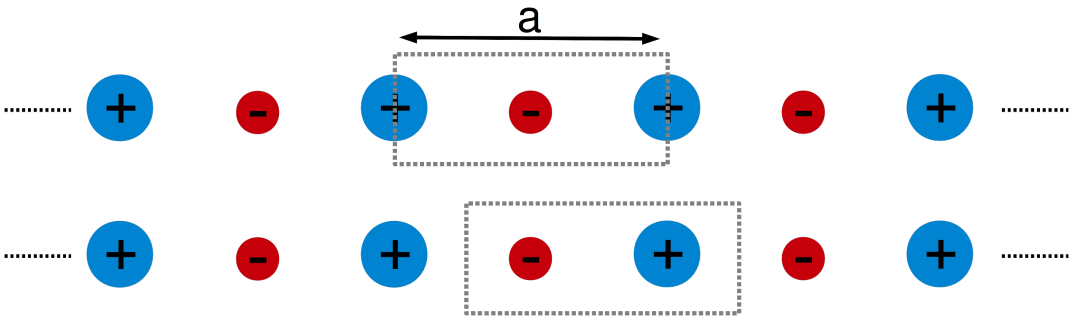

$\frac{p}{a} = +Q \times 0 - Q \times \frac{1}{2} = -\frac{Q}{2}$

$\frac{p}{a} = +Q \times \frac{3}{4} - Q \times \frac{1}{4} = +\frac{Q}{2}$

Polarization in periodic solids

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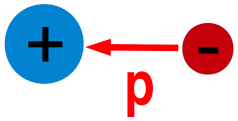

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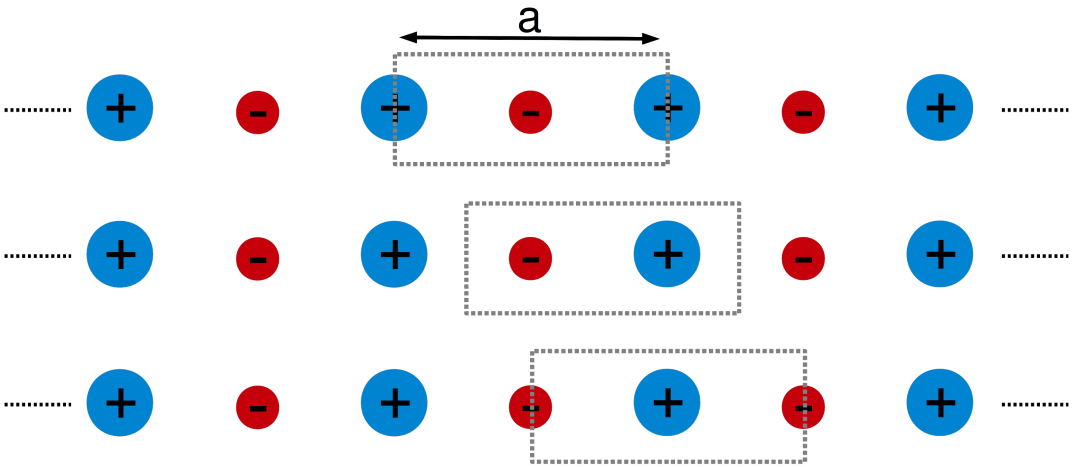

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Polarization in periodic solids

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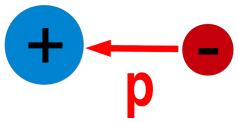

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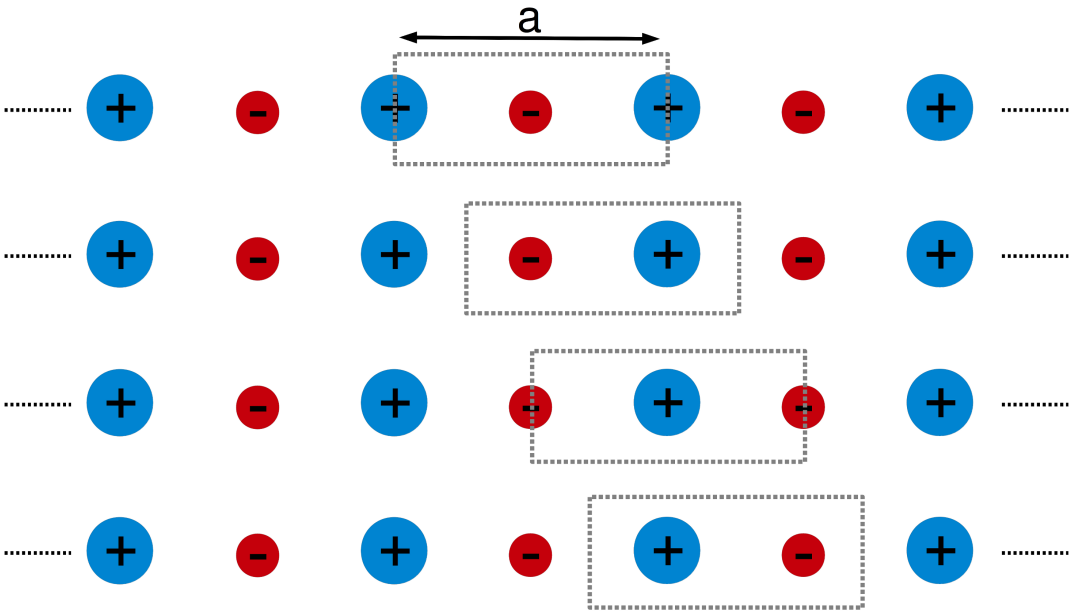

$$\frac{p}{a} = +Q \times 0 - Q \times \frac{1}{2} = -\frac{Q}{2}$$

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Non-zero and origin dependent!

Polarization in periodic solids

Polarization ill defined in periodic solids:

- Non-zero polarization for non-polar crystal!
- Lattice polarization (quantum): . . . , -1/2, 1/2, . . .
- Centrosymmetric around zero (can contain 0)

Polarization in periodic solids

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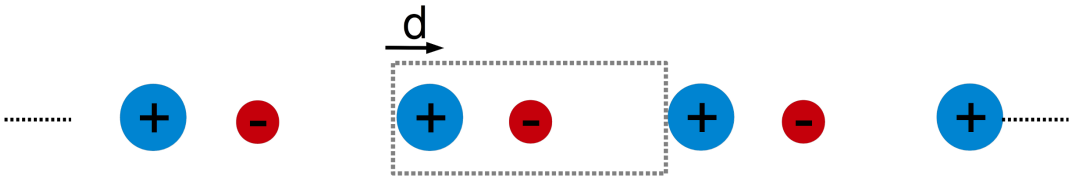
For a polar periodic 1-D chain:



$$\frac{p}{a} = Q \times \frac{(0+d)}{a} - \frac{Q}{2}$$
$$= Q\left(-\frac{1}{2} + \frac{d}{a}\right)$$

Polarization in periodic solids

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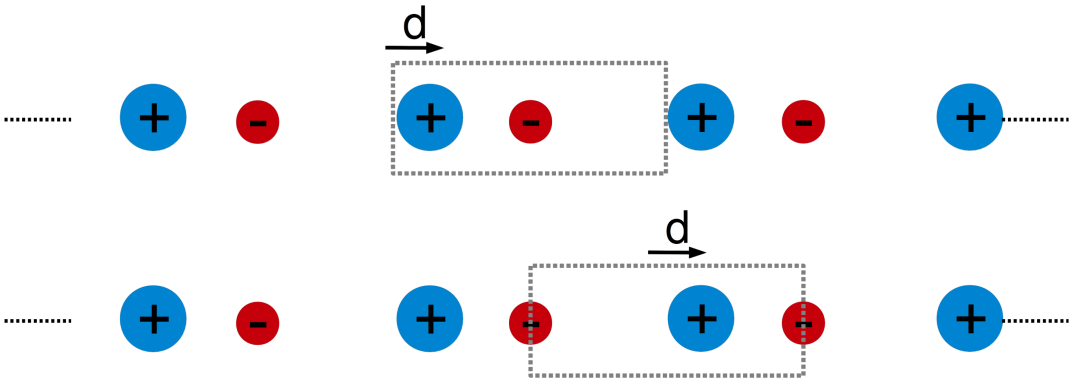


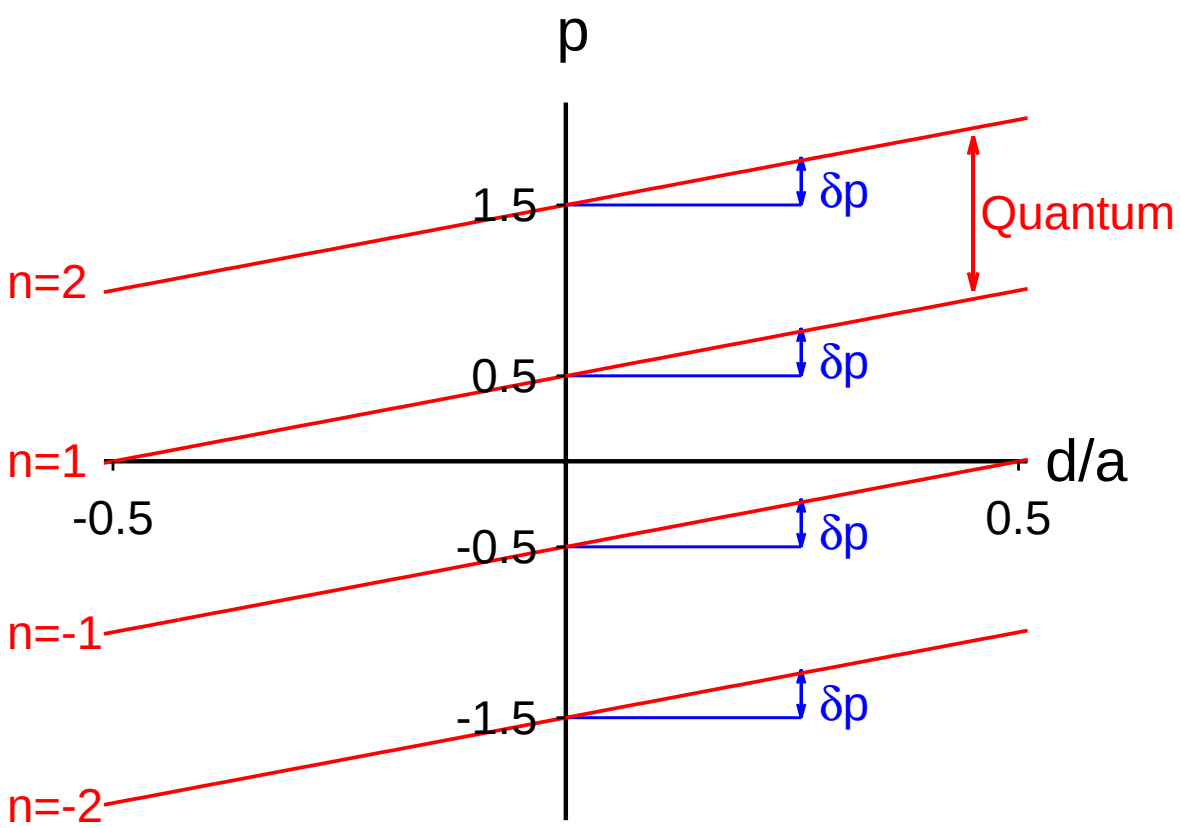
$$\frac{p}{a} = Q \times \frac{(0+d)}{a} - \frac{Q}{2}$$
$$= Q\left(-\frac{1}{2} + \frac{d}{a}\right)$$

$$\frac{p}{a} = Q\left(+\frac{1}{2} + \frac{d}{a}\right)$$

Different values! (differ by a quantum of polarization $\pm\frac{Q}{2}$)

However, the change of polarization is constant: $\delta p = \frac{Qd}{a}$

Polarization in periodic solids

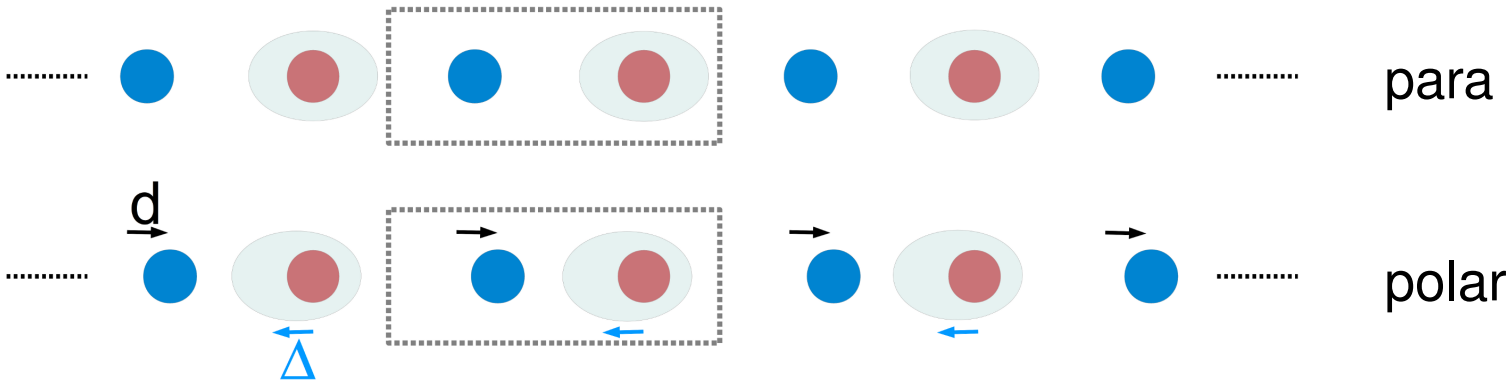


Only the change of polarization is well defined

Idem in 3D: polarization quantum in direction $i = \frac{S.e}{\Omega} a_i$ ($S =$ spin degeneracy, $\Omega =$ unit cell volume)

Polarization in periodic solids

"More realistic" solid: ionic $(+Q \times 2)$ + electronic $(-2Q)$ contributions



$$P(para) = \frac{1}{a}\left(Q\frac{a}{4} + Q\frac{3a}{4} - 2Q\frac{3a}{4}\right) = -\frac{Q}{2}$$

$$P(polar) = \frac{1}{a}\left[Q\left(\frac{a}{4}+d\right) + Q\frac{3a}{4} - 2Q\left(\frac{3a}{4}-\Delta\right)\right] = Q\left(-\frac{1}{2}+\frac{d}{a}+\frac{2\Delta}{a}\right)$$

$$\delta P = Q\left(\frac{d}{a}+\frac{2\Delta}{a}\right)$$

Polarization in periodic solids

How to "localize" the electrons? $\dashrightarrow$ Wannier Functions

They are FT of the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$:

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k}.\mathbf{R}} d^3\mathbf{k}$$

Here it is posible to define the Wannier center ("position"):

$$< \mathbf{r}_n >= \int w_n^*(\mathbf{r})\ \mathbf{r}\ w_n(\mathbf{r}) d^3\mathbf{r}$$

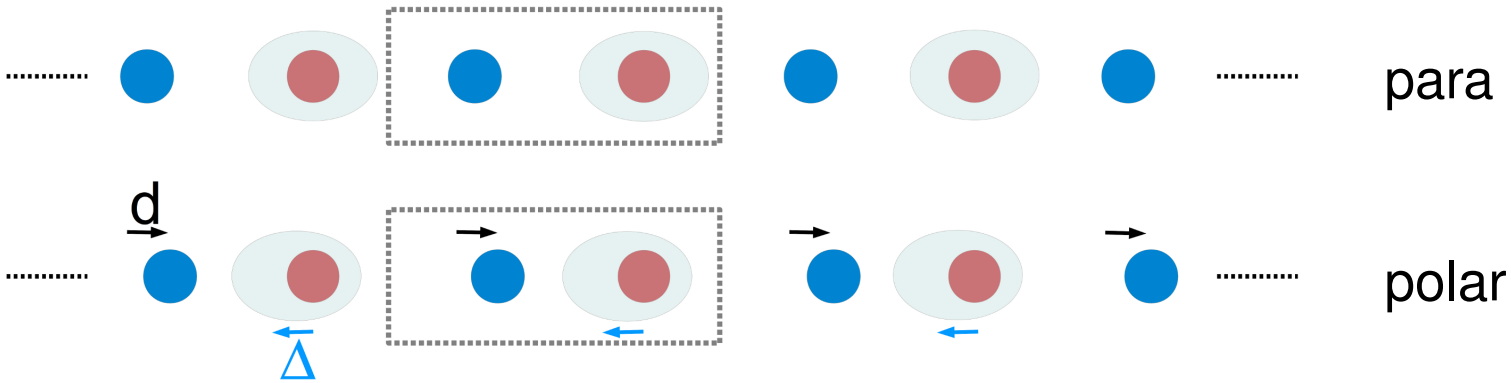
or with $\mathbf{r} = -i\frac{\partial}{\partial \mathbf{k}}$:

$$< \mathbf{r}_n >= i\frac{\Omega}{(2\pi)^3} \int_{BZ} \left\langle u_{n\mathbf{k}} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial \mathbf{k}} \right\rangle e^{-i\mathbf{k}.\mathbf{R}} d^3\mathbf{k}$$

-!- w_n are not uniquely defined (gauge)! $\dashrightarrow$ Maximally-localized w_n

Polarization in periodic solids

Wannier function formulation of P: ionic + electronic (w_n) contributions



$$\mathbf{P} = \frac{1}{\Omega}\left(\sum_i Q_i \mathbf{r}_i + \sum_n Q_n < \mathbf{r}_n >\right)$$

$$\delta\mathbf{P} = \mathbf{P}(polar) - \mathbf{P}(para)$$

$$= \delta\mathbf{P}_{ionic} - \frac{2ie}{(2\pi)^3}\sum_n \int_{BZ} \left\langle u_{n\mathbf{k}}^{polar} \middle| \frac{\partial u_{n\mathbf{k}}^{polar}}{\partial \mathbf{k}} \right\rangle - \left\langle u_{n\mathbf{k}}^{para} \middle| \frac{\partial u_{n\mathbf{k}}^{para}}{\partial \mathbf{k}} \right\rangle e^{-i\mathbf{k}.\mathbf{R}} d^3\mathbf{k}$$

Polarization in periodic solids

To compute polarization one needs to compute (Berry phase)

$$\mathbf{P}^{elec} = -\frac{2ie}{(2\pi)^3}\sum_n \int_{BZ} \left\langle u_{n\mathbf{k}} \left| \frac{\partial u_{n\mathbf{k}}}{\partial \mathbf{k}} \right\rangle e^{-i\mathbf{k}.\mathbf{R}} d^3\mathbf{k}$$

Discretized form (King-Smith & Vanderbilt)

$$\mathbf{P}_{\parallel}^{elec} = -\frac{2ie}{(2\pi)^3}\sum_m \int \sum_{j=1}^{N_k} \mathrm{Im}\left\{ \ln det\left[\left\langle u_{n\mathbf{k}_j} \left| u_{m\mathbf{k}_{j+1}} \right\rangle \right] \right\} e^{-i\mathbf{k}.\mathbf{R}} d^3\mathbf{k}_{\perp}$$

or (Wannier functions)

$$\mathbf{P}^{elec} = -\frac{2e}{\Omega}\sum_n \int \mathbf{r} \left| w_n \right|^2 d\mathbf{r}$$

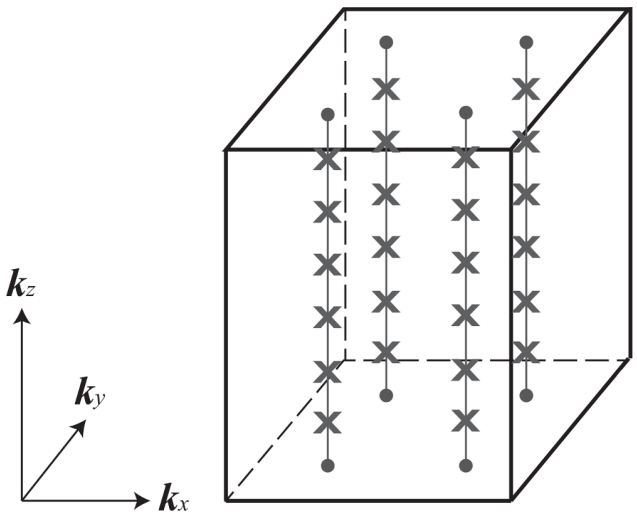
Can be implemented in DFT!

Polarization in periodic solids

King-Smith & Vanderbilt discretized Bery phase of P along a_i ($berryopt = +1$):

$$\mathbf{P}^{elec}.\mathbf{a}_i = -\frac{2e}{\Omega}\frac{1}{N_\perp^{(i)}}\sum_{l=1}^{N_\perp^{(i)}} \mathrm{Im}\ \ln \prod_{j=0}^{N_i-1} det\left[S(\mathbf{k}_j^{(i)}, \mathbf{k}_{j+1}^{(i)})\right]$$

with $S_{nm}(\mathbf{k},\mathbf{k}') = \langle u_{n\mathbf{k}} | u_{m\mathbf{k}'} \rangle$ and $N_\perp^{(i)} = N_k^{(j)} \times N_k^{(h)} =$ # of strings along $\mathbf{a}_i$, each containing N_i points $\mathbf{k}_j^{(i)} = \mathbf{k}_\perp^{(l)} + (j/N_i)\mathbf{a}_i$; Ex:



Calculation for P_z:

- 4 strings

- 6 sampling k-points in the k_z direction

Convergence have to be done on both # of strings and # of sampling points

Sum over all occupied bands n $\dashrightarrow$ Insulating state only

Polarization in periodic solids

Alternative method (input flag *berryopt* $= -1$):

$$\mathbf{P}^{elec}.\mathbf{a}_i = -\frac{2e}{\Omega N_k}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}\mathbf{b}\ \mathrm{Im}\{\ \ln\ det\,[S(\mathbf{k},\mathbf{k}+\mathbf{b})]\}$$

where **b** is a vector connecting a **k** point to one of its nearest neighbors and $w_{\mathbf{b}}$ is a weight factor such that it satisfies:

$$\sum_{\mathbf{b}} w_{\mathbf{b}} b_\alpha b_\beta = \frac{g_{\alpha\beta}}{4\pi^2}$$

with $g_{\alpha\beta}$ is the metric tensor of the real space lattice and b_α the reduced coordinates of **b**.

$\dashrightarrow$ check convergence with the regular k-point grid

$\mathbf{P}^{ion}$ is simply given by $1/\Omega\sum_i Q_i\mathbf{r}_i$

It is recommended to use this method, i.e. *berryopt* $= -1$.

Berry phase polarization calculation in Abinit

Input flags are *berryopt* $= -1$ and *rfdir* $= 111$

Output looks like that:

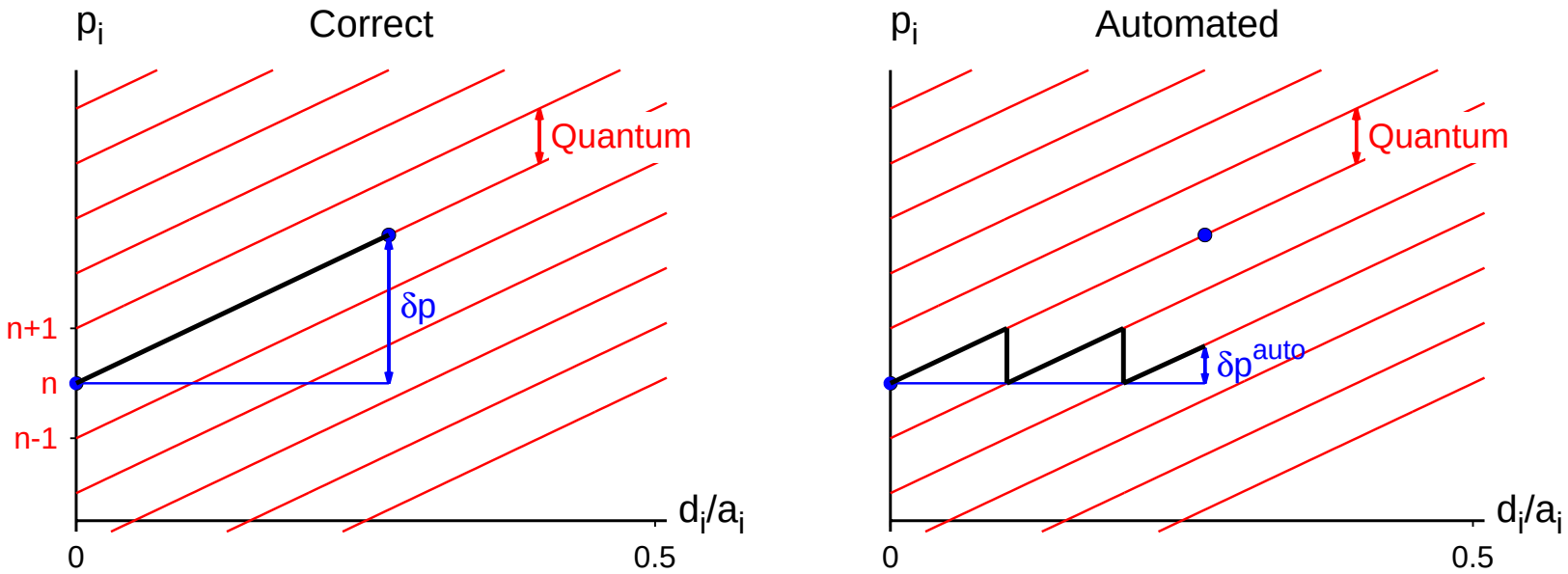
```
Computing the polarization (Berry phase) for reciprocal vector:
 0.00000  0.00000  0.16667 (in reduced coordinates)
 0.00000  0.00000  0.01509 (in cartesian coordinates - atomic units)
Number of strings:    36
Number of k points in string:    6

Summary of the results
Electronic Berry phase     6.741333833E-01
           Ionic phase    -3.744257751E-01
           Total phase     2.997076082E-01
   Remapping in [-1,1]     2.997076082E-01

          Polarization     6.000077073E-03 (a.u. of charge)/bohr^2
          Polarization     3.432929850E-01 C/m^2

Polarization in cartesian coordinates (C/m^2):
(the sum of the electronic and ionic Berry phase has been fold into [-1, 1])
    Electronic:  0.747369006E-13   0.179240839E-13   0.772170126E+00
    Ionic:       0.000000000E+00   0.000000000E+00  -0.428877141E+00
    Total:       0.747369006E-13   0.179240839E-13   0.343292985E+00
```

Polarization in periodic solids

DFT implementation:
Be careful with automatic removal of Quantum (*"remapping"*)!

Quantum of polarization along direction i: $P_i = n\frac{2e}{\Omega}a_i = n\frac{2e}{a_j a_k}$

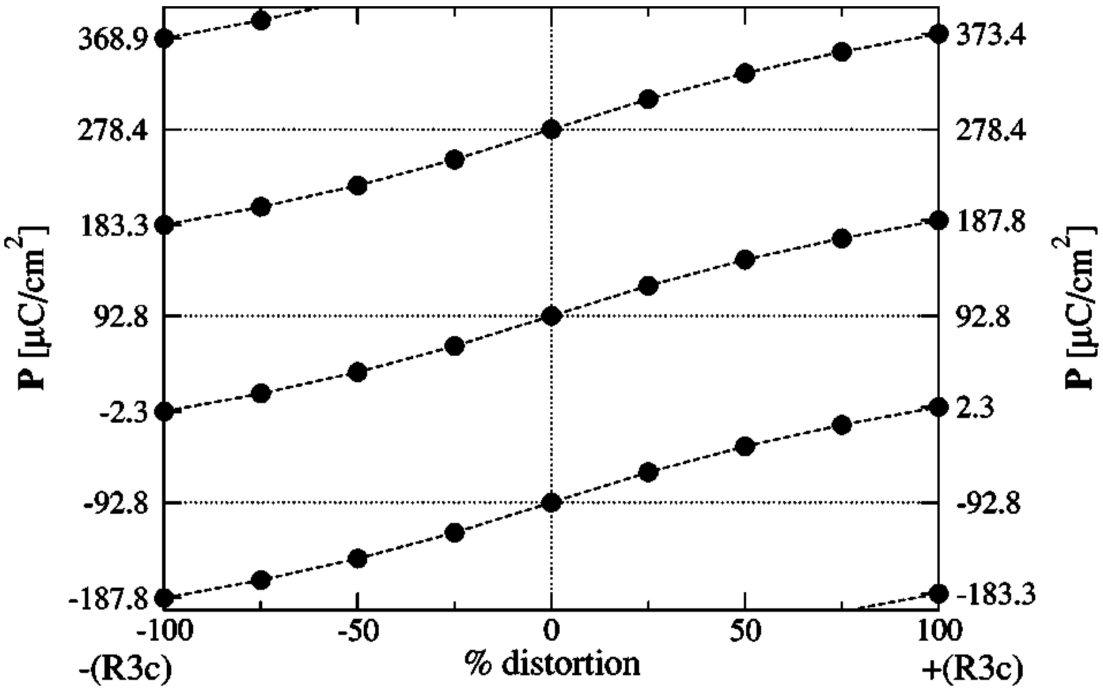
If $\delta P_i > P_i$:



The automatic removal of quantum can incorrectly remove a quantum while it is a real P! ⇢ always check your calculations.

Polarization in periodic solids

Ex: $BiFeO_3$ PRB 71, 014113 (2005)



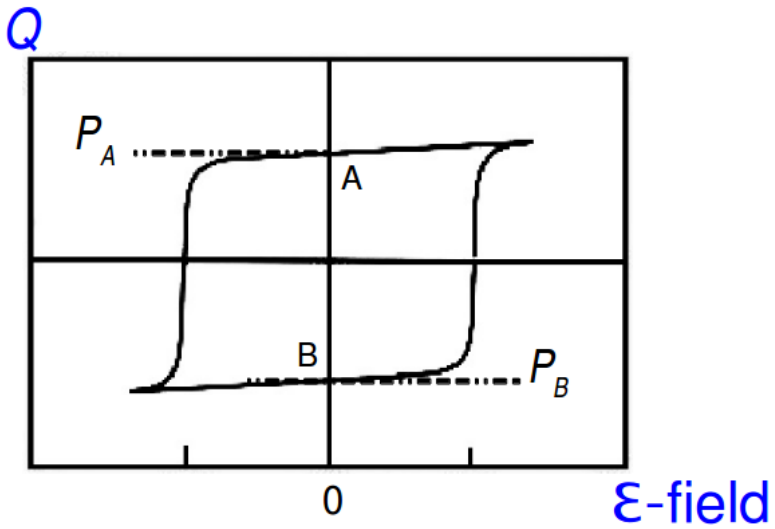
Correct value: 187.8-92.8 = 95.0 μC.cm^{-2}

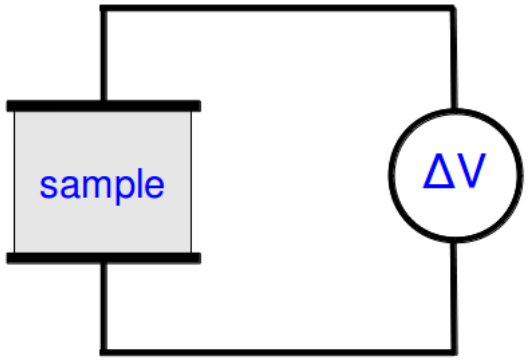
Wrong value: 1/2[2.3-(-2.3)] = 2.3 μC.cm^{-2} and plenty of others!

See also another example in PRB 86, 054107 (2012)

Polarization in periodic solids

How P is measured experimentally?





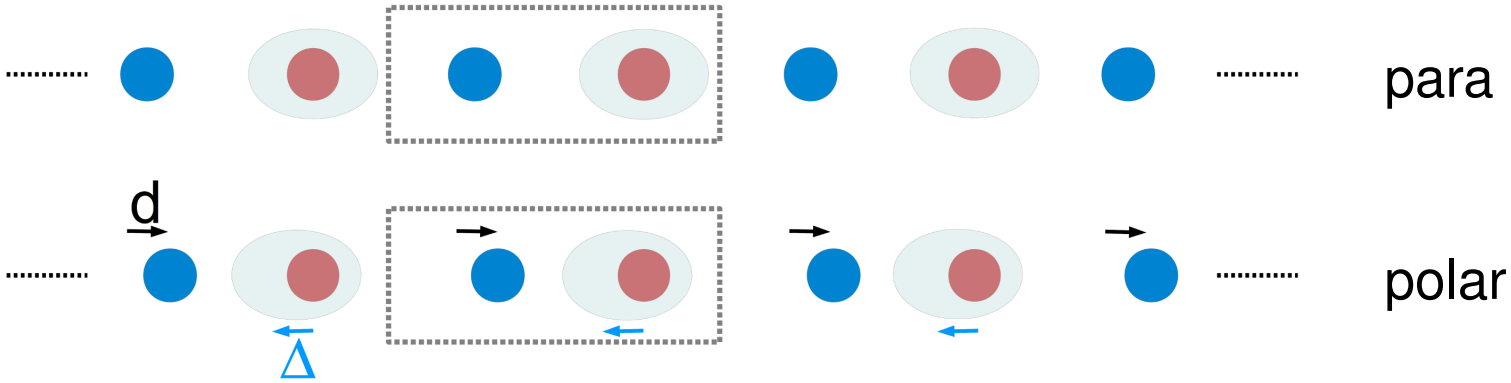
$\Delta P = (P_A - P_B) = 2 \times P$ ⇢ measured through hysteresis!

P is not a direct observable but its integration on a closed loop is.

Berry phase method for P ("modern theory of polarization") does the loop in reciprocal space of periodic crystals.

Application: Born effective charges

Polarization induced by atomic displacement: ionic + electronic



$$\mathbf{P} = \frac{1}{\Omega}\left(\sum_i Q_i \mathbf{r}_i + \sum_n Q_n < \mathbf{r}_n >\right)$$

$$\mathbf{P} \equiv \mathbf{P}^{ion} + \mathbf{P}^{elec}$$

$$\mathbf{P} \equiv \frac{1}{\Omega}\sum_i Q_i^{eff} \mathbf{r}_i$$

P can be seen as induced by a motion of rigid ions of charge Q_i^{eff}

Application: Born effective charges

The change in **P** relative to the displacement $\Delta\mathbf{d}_\kappa$ of an atom κ:

$$\Delta\mathbf{P} = \frac{Q_\kappa^{eff}}{\Omega}\Delta\mathbf{d}_\kappa \dashrightarrow Q_\kappa^{eff} = \Omega\frac{\Delta\mathbf{P}}{\Delta\mathbf{d}}$$

Tensorial notation:

$$Q_{\kappa,ij}^{eff} = \Omega\frac{\Delta P_i}{\Delta d_{\kappa,j}} = Z_{\kappa,ij}^*$$

The Born effective charge Z_{ij}^* can be computed using Berry phase for **P**

Can be large if strong dynamical charge transfer:

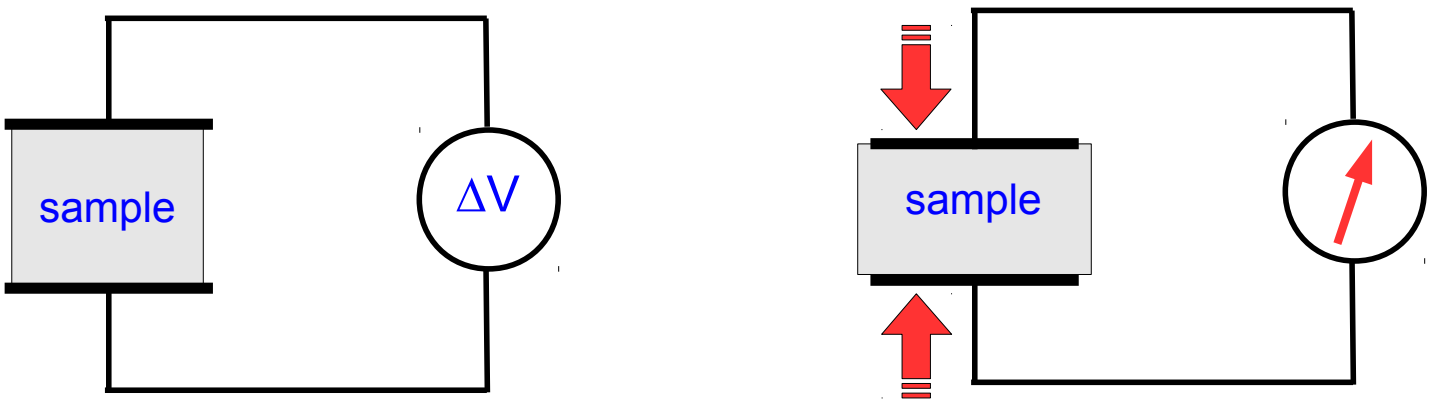
	$\lvert Z^*\rvert$ (e)	nominal (e)		Z^*	nominal
NaCl	1.06	1	GeTe	6.90	2
MgO	1.98	2	$BaTiO_3$ (Ti)	7.00	4
BaO	2.97	2			

(allways check the charge neutrality: $\sum_{\kappa,j} Z_{\kappa,ij}^* = 0$)

Application: Piezoelectric coefficients

The change of **P** relative to a change of strain $\Delta\eta$:

$$\gamma_{\alpha\beta\delta} = \frac{\Delta P_\alpha}{\Delta \eta_{\beta\delta}}$$



Born effective charges and piezoelectric coefficients can thus be calculated from finite differences technique through the calculation of ΔP under small atomic position or strain variations.

Polarization in periodic solids

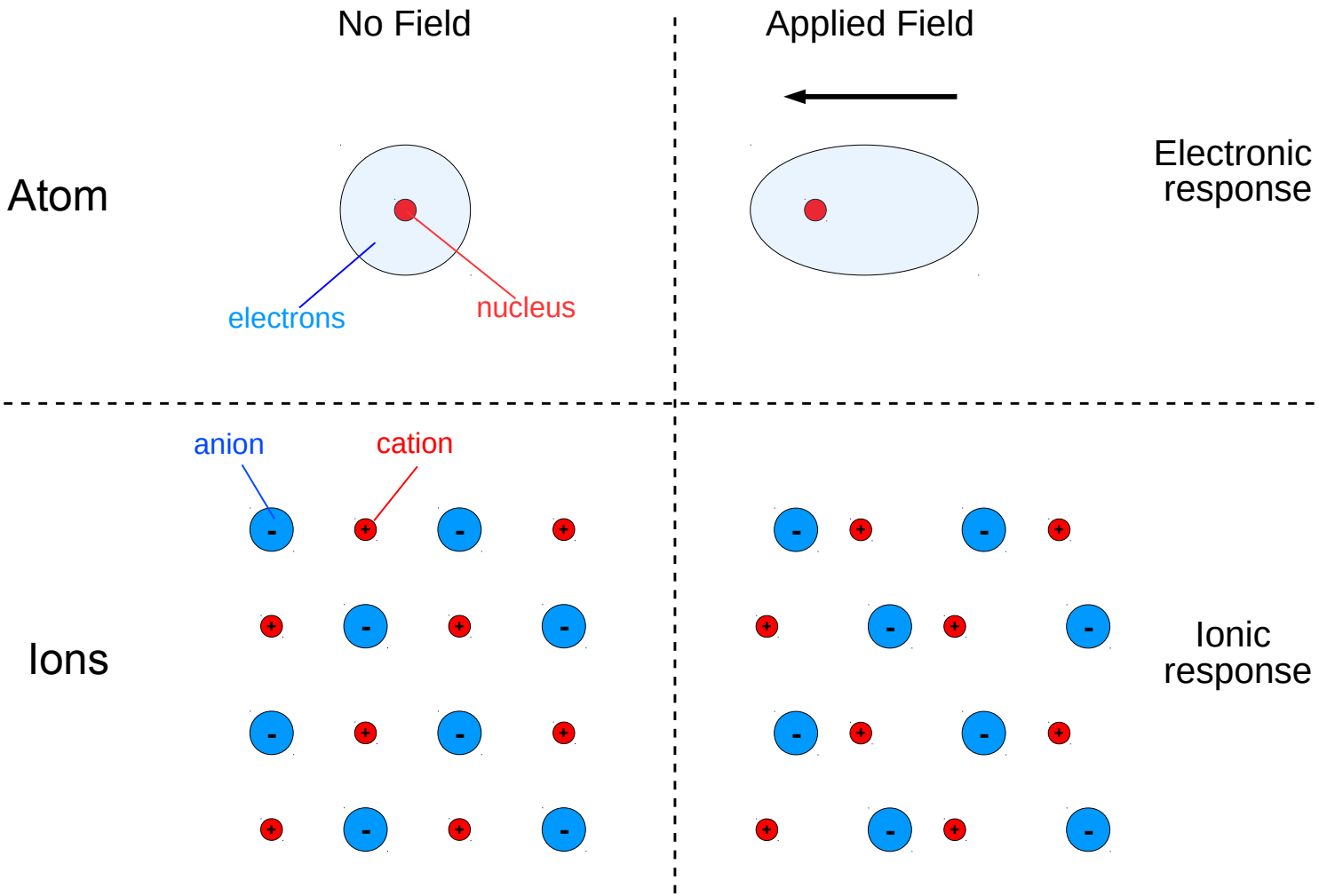
Reference papers:

- King-Smith & Vanderbilt: PRB R47 p.1651 (1993); PRB 48 p.4442 (1993)
- R. Resta: RMP 66 p.899 (1994); Lecture Notes 1999-2000 (see his website)
- N. Spaldin: J. Solid State Chem. 195, 2 (2012)

Wannier functions and P:

- Marzari & Vanderbilt: PRB 56 p.12847 (1997)
- Wu, Diéguez, Rabe & Vanderbilt: PRL 97 p.107602 (2006)
- Stengel & Spaldin: PRB 73 p.075121 (2006)

Ionic crystal under static electric field

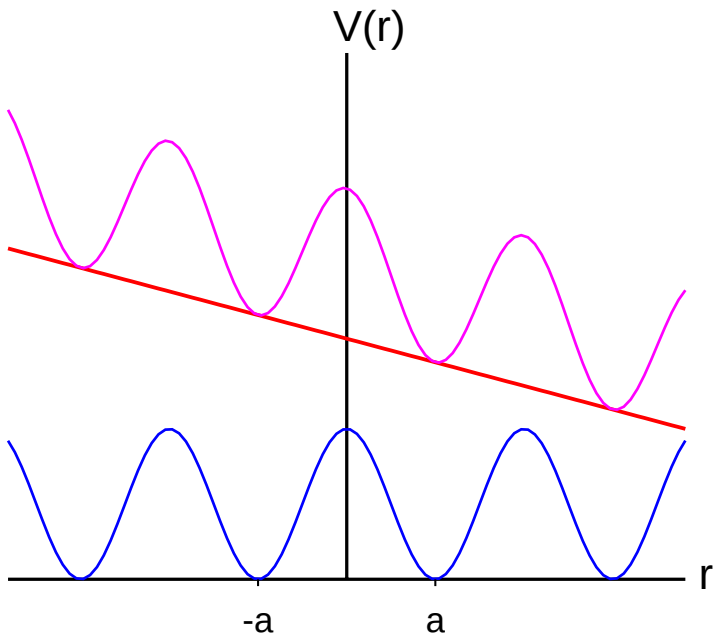


Access to the dielectric responses, field induced phase transition, ...

Treatment of static electric field

How to handle finite electric field in DFT?

Electric potential not periodic: $V(\mathbf{r}) = V_{KS}(\mathbf{r}) - e\mathscr{E}.\mathbf{r}$



$e\mathscr{E}.r$ is not periodic!

Bloch's theorem does not apply!

No ground state!

Potential not bounded from below!

Alternative solution: Electric enthalpy

$$F = E_{KS} - \Omega\mathscr{E}.\mathbf{P}$$

Treatment of static electric field

Minimization of the Electric enthalpy:

$$F = E_0 - \Omega \mathscr{E}.P$$

where E_0 the KS energy and P is computed using the Berry phase formula:

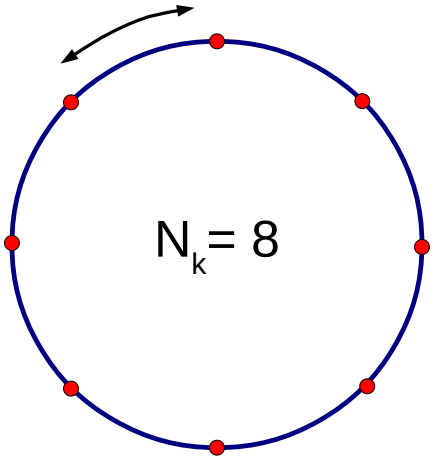
$$-\frac{2e}{\Omega}\frac{1}{N_\perp^{(i)}}\sum_{l=1}^{N_\perp^{(i)}} \mathrm{Im}\ \ln \prod_{j=0}^{N_i-1} det\left[S(\mathbf{k}_j^{(i)}, \mathbf{k}_{j+1}^{(i)})\right]$$

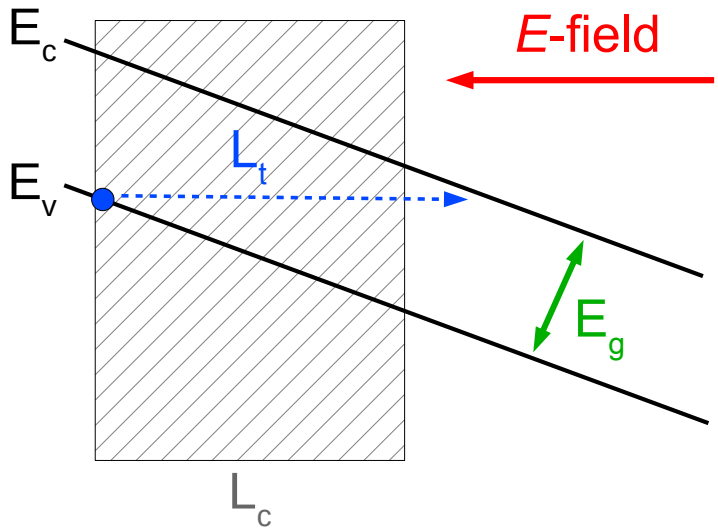
$$\text{or } -\frac{2e}{\Omega N_k}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}\mathbf{b}\ \mathrm{Im}\{\ \ln det\,[S(\mathbf{k}, \mathbf{k}+\mathbf{b})]\}$$

Can be minimized by standrad methods (band by band conjugate-gradient)

Treatment of static electric field

Problem of interband Zener tunneling (breakdown):





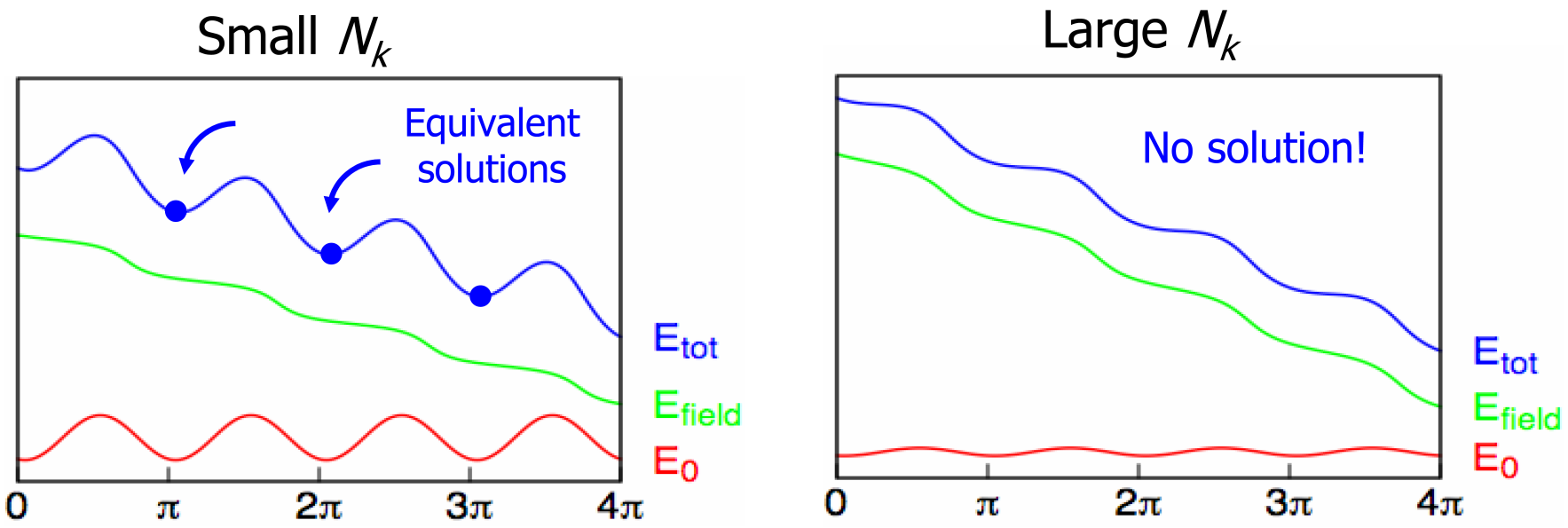
For a given $\mathscr{E}$, there is a limit on N_k point sampling

Length scale $L_c = 2\pi/\Delta k \equiv$ supercell dimension

Keep $L_c < L_t \dashrightarrow N_k a/2\pi > E_g/e\mathscr{E}$

Treatment of static electric field

$$E_{tot} = E_0 - \Omega \mathscr{E} . P$$



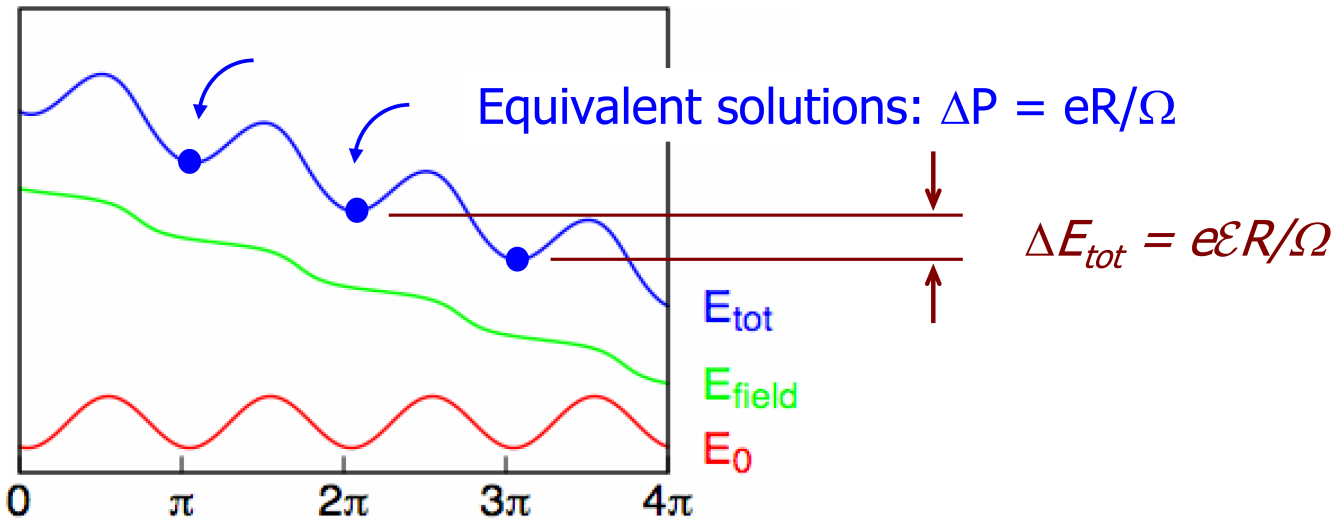
Courtesy of D. Hamann

Not too large N_k / not too large $\mathscr{E}$!

but N_k has to be large enough to have converged results

Treatment of static electric field

$$E_{tot} = E_0 - \Omega \mathscr{E}.P$$



Courtesy of D. Hamann

P defined modulo $e\mathbf{R}/\Omega$ $\dashrightarrow$ E_{tot} defined modulo $e\mathscr{E}\mathbf{R}/\Omega$

Treatment of static electric field

Calculation of forces (Hellmann-Feynman theorem):

$$\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i}\left[E_0 - \Omega\mathscr{E}.\left(\mathbf{P}^{\mathbf{elec}} + \mathbf{P}^{\mathbf{ion}}\right)\right] = -\frac{\partial E_0}{\partial \mathbf{r}_i} + eZ_i^{ion}\mathscr{E}$$

$\frac{\partial E_0}{\partial \mathbf{r}_i}$ already coded!

$\frac{\partial P^{elec}}{\partial \mathbf{r}_i} = 0$, Berry phase only depends on wave function

Idem for stress tensor:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega}\frac{\partial}{\partial \eta_{\alpha\beta}}\left[E_0 - \Omega\mathscr{E}.\mathbf{P}\right]$$

$\frac{\partial P}{\partial \eta_{\alpha\beta}} = 0$ if the potential drop $V = -\mathscr{E}.\mathbf{a}_i$ is fixed across each lattice vector or

$$\sigma_{\alpha\beta}^{(\mathscr{E})} = \sigma_{\alpha\beta}^{(V)} - \sum_{i=1}^{3} \mathscr{E}_\alpha (a_i)_\beta P_i \quad \text{if } \mathscr{E} \text{ is fixed}$$

Treatment of static electric field

In practice in Abinit input just add:

```
berryopt  4  # activate E-field
efield       5.135218E-05  0.0  0.0
```

Output:

```
Constant unreduced E calculation  - final values:
 (a. u.)
      E:   5.135218000E-05   0.000000000E+00   0.000000000E+00
      P:   5.158969927E-05   2.774100906E-09  -3.292033923E-10

[...]

 (S.I.), that is V/m for E, and C/m^2 for P
-     E:   2.640635045E+07   0.000000000E+00   0.000000000E+00
      P:   2.951692338E-03   1.587195217E-07  -1.883529357E-08

  initberry: COMMENT -
   As a rough estimate,
   to be below the critical field, the bandgap of your system
   should be larger than    0.02 eV.
```

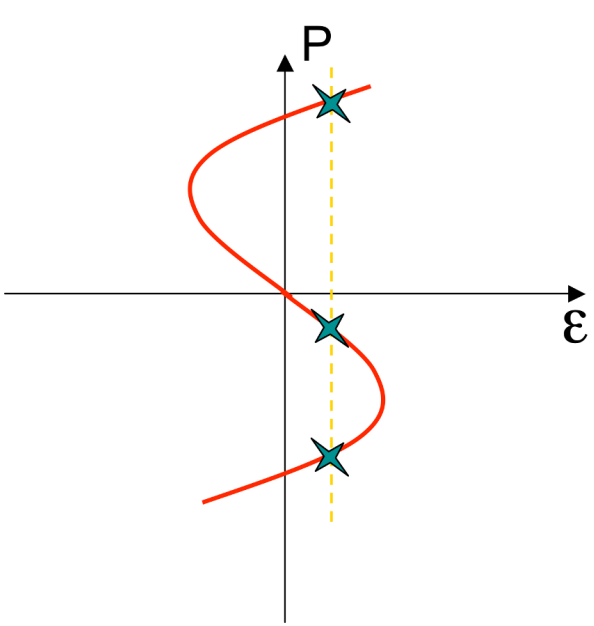
Treatment of static electric field

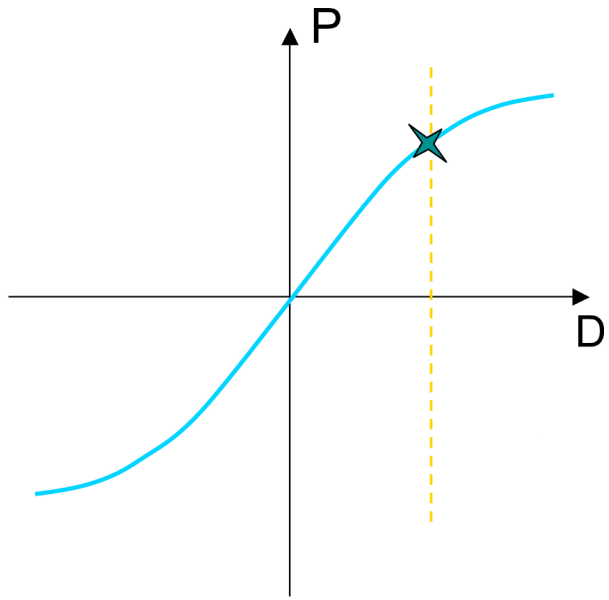
References:

- R.W. Nunes and X. Gonze, PRB 63, 155107 (2001).
- I. Souza, J. Iniguez and D. Vanderbilt, PRL 89, 117602 (2002).
- P. Umari and A. Pasquarello, PRL 89, 157602 (2002).
- N. Sai, K. M. Rabe and D. Vanderbilt, PRB 66, p104108 (2002).
- J. W. Zwanziger *et al.*, Comput. Materials Sci. 58, p113 (2012).

Constrained D calculations

Electric displacement vector: $\mathbf{D} = \mathscr{E} + 4\pi\mathbf{P}$



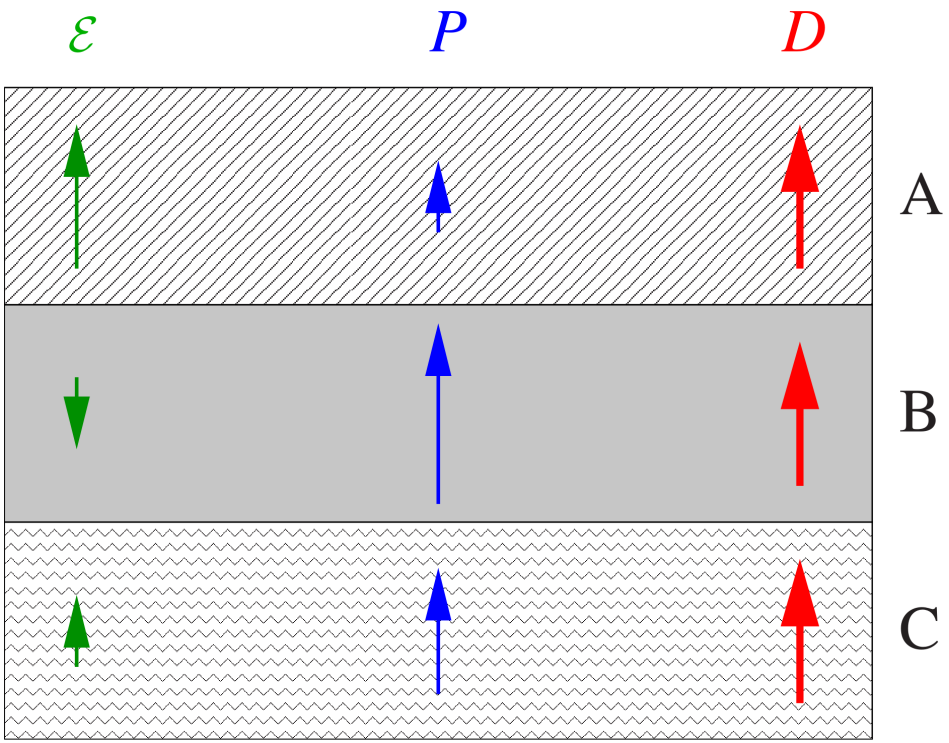


Courtesy of D. Vanderbilt

P(**D**) is monotonic

Constrained D calculations

Electric displacement vector: $\mathbf{D} = \mathscr{E} + 4\pi\mathbf{P}$



In heterostructures, **D** is uniform (continuity at interfaces)

Constrained D calculations

Supposing the functional $U(\mathbf{D}, v) = E_0(v) + \frac{\Omega}{8\pi}\left[\mathbf{D} - 4\pi\mathbf{P}(v)\right]^2$

with $\mathbf{D}$ = external vector parameter and v = internal ionic and electronic degrees of freedom

Minimum of U at $\mathbf{D}$ fixed:

$$\left.\frac{\partial U}{\partial v}\right|_{\mathbf{D}} = \frac{\partial E_0}{\partial v} - \Omega(\mathbf{D} - 4\pi\mathbf{P})\frac{\partial \mathbf{P}}{\partial v} = 0$$

Fixed $\mathbf{D}$, internal energy: $U(\mathbf{D}, v) = E_0(v) + \frac{\Omega}{8\pi}\left[\mathbf{D} - 4\pi\mathbf{P}(v)\right]^2$

Fixed $\mathscr{E}$, electric enthalpy: $E(\mathscr{E}, v) = E_0(v) - \Omega\mathscr{E}\mathbf{P}(v)$

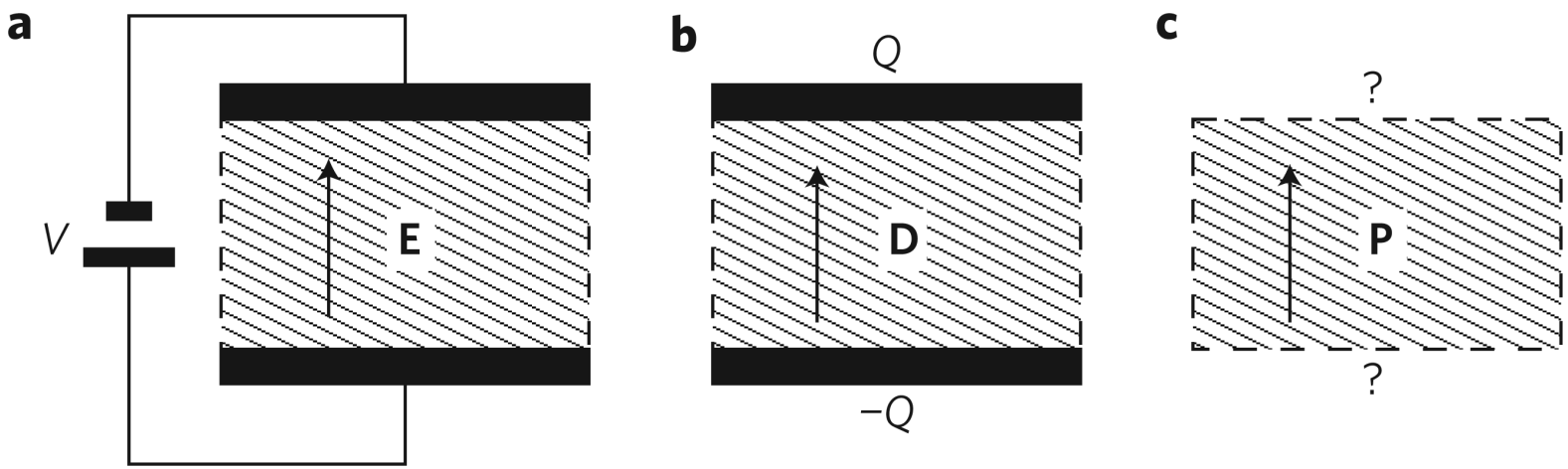
Then:

$$\left.\frac{\partial F}{\partial v}\right|_{\mathscr{E}} = \left.\frac{\partial U}{\partial v}\right|_{\mathbf{D}} \quad \text{if} \quad \mathscr{E} = \mathbf{D} - 4\pi\mathbf{P}$$

$\mathbf{D}$ is then the electric displacement field: $\mathbf{D} = \mathscr{E} + 4\pi\mathbf{P}$

with $U = E_0 + \Omega/8\pi\mathscr{E}^2$ $\dashrightarrow$ correct crystal internal energy under $\mathscr{E}$-field

Constrained D calculations



Fixed-$\mathscr{E}$ = closed-circuit boundary conditions

Fixed-**D** = open-circuit conditions with fixed charge Q

Fixed-**P** = no clear picture

Constrained D calculations

In practice:

Fixed-$\mathscr{E}$, electric enthalpy:

$$F(\mathscr{E}, v) = E_0(v) - \Omega \mathscr{E} \mathbf{P}(v)$$

(already implemented)

Update the $\mathscr{E}$-field after each SCF:

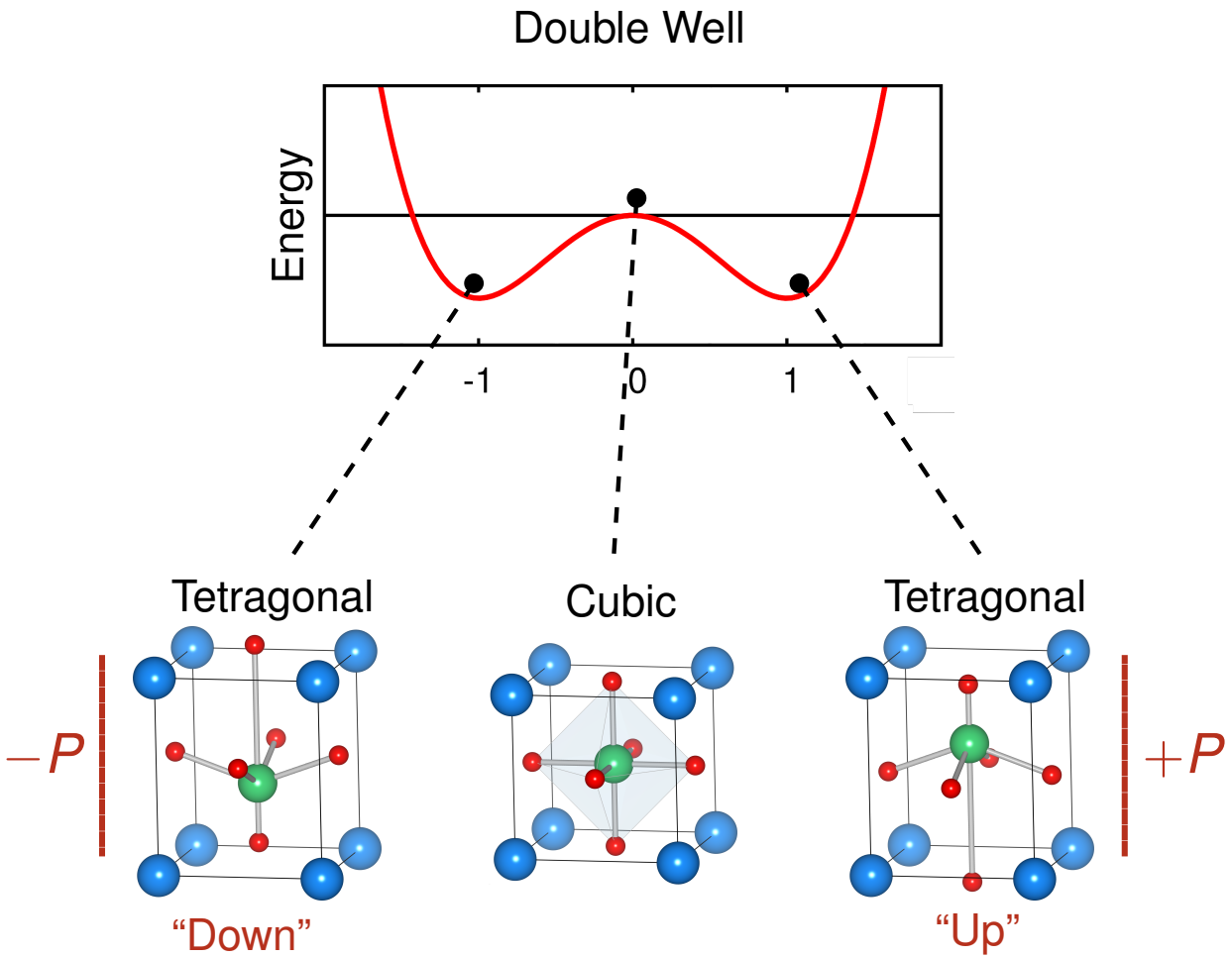
$$\mathscr{E}_{n+1} = \lambda(\mathbf{D} - 4\pi \mathbf{P}_n) + (1-\lambda)\mathscr{E}_n$$

with $\lambda =$ damping parameter to control the convergence

Until criterion on $E(v)$ is reached *and* $|\mathbf{D} - 4\pi \mathbf{P}_n - \mathscr{E}_n| <$ tol

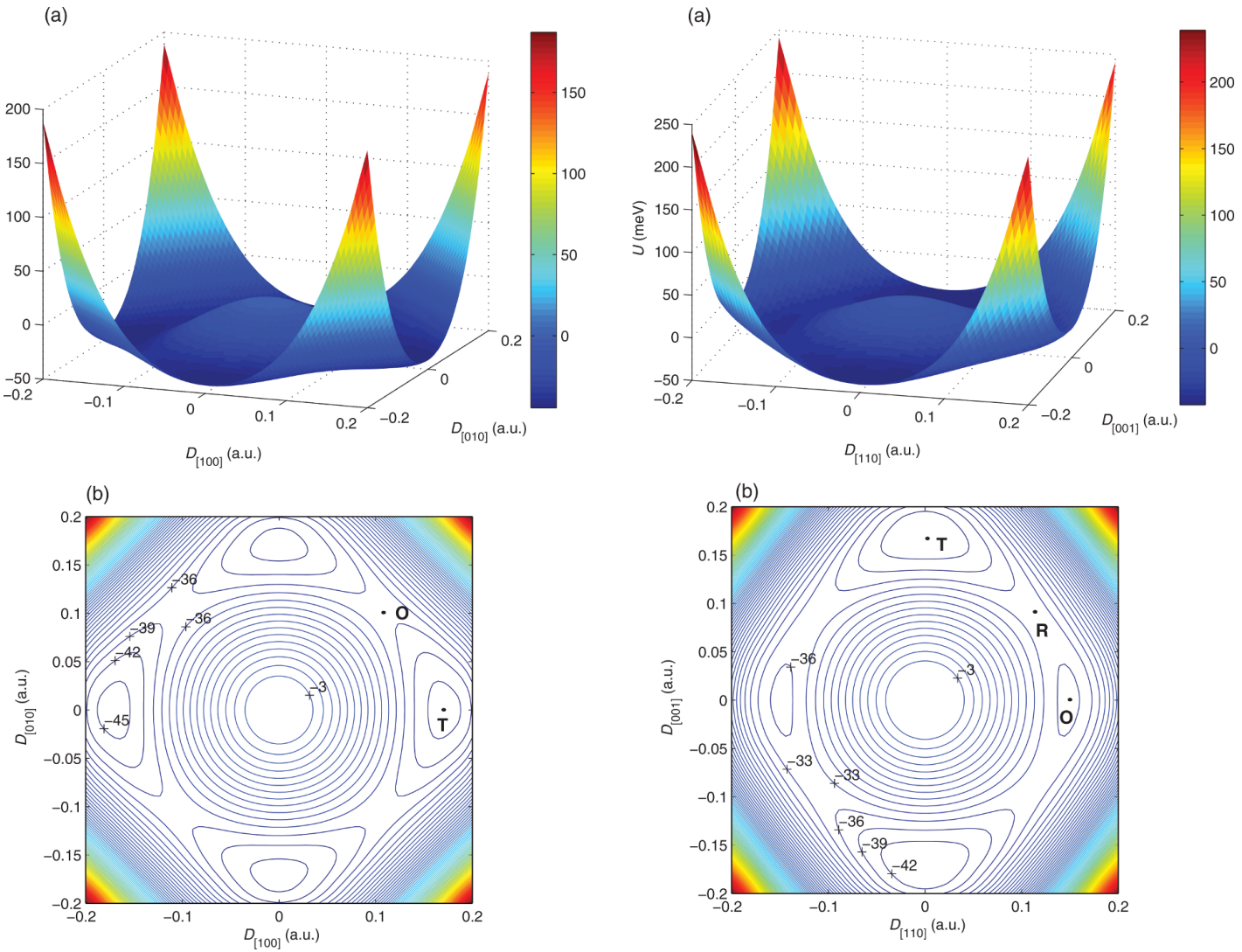
Constrained D calculations

Example: Ferroelectric $PbTiO_3$



Constrained D calculations

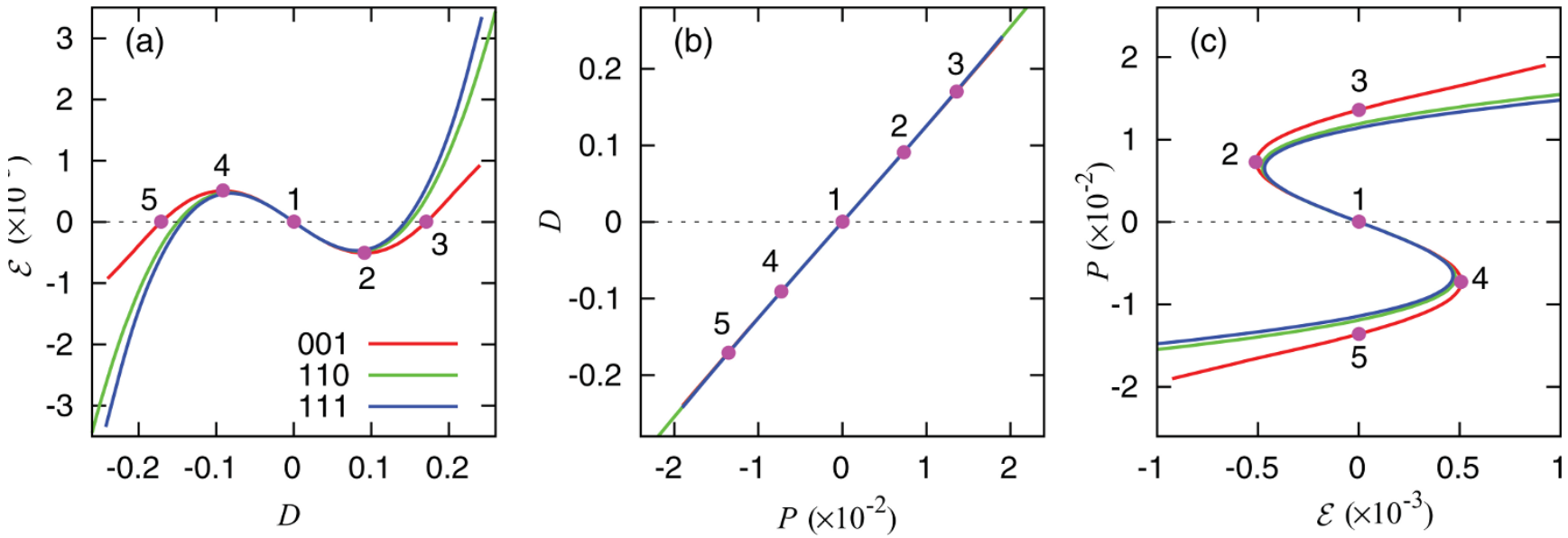
Example: Ferroelectric $PbTiO_3$



Constrained D calculations

Example: Ferroelectric $PbTiO_3$

Electric equation of state: $\mathscr{E}(\mathbf{D})$, $\mathbf{D}(\mathbf{P})$, $\mathbf{P}(\mathscr{E})$



Constrained D calculations

References:

- *Electric displacement as the fundamental variable in electronic-structure calculations*, M. Stengel, N. A. Spaldin and D. Vanderbilt, Nature Physics 5, p304 (2009)

- *First-principles modeling of ferroelectric capacitors via constrained displacement field calculations*, M. Stengel, D. Vanderbilt and N. A. Spaldin, PRB 80, 224110 (2009)

- *Mapping the energy surface of $PbTiO_3$ in multidimensional electric-displacement space*, J. Hong and D. Vanderbilt, PRB 84, 115107 (2011)

Status in Abinit (as of v8.10.3)

Capabilities:

- Berry phase works for both NC and PAW
- Forces and stresses are implemented for applied E-field (NC and PAW)
- Work for *nspden*$= 1, 2, 4$ and SOC

Technical limitations:

- Berry phase calculation parallelized over k-points only (no *parall_kgb*) $\Rightarrow$ idem for E and D field
- Applied D-field might be troublesome to converge (work in progress...)

Other capabilities:

- Calculation of phonons, Born charges and ε^{∞} under applied E-field (works only in sequential mode!), see PRB 74, 054304 (2006) and PRB 75, 115116 (2007).
- Constrained P calculation (https://docs.abinit.org/topics/ConstrainedPol/)