Notes for the implementation of constant electric field and constant electric displacement field methods in ABINIT

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May 21, 2012

1 Introduction

The purpose of these notes is to provide the theoretical and formal background for the implementation of the constant electric field [1] and constant electric displacement field [2] methods in the context of first-principles electronic structure theory, in particular as they are implementated in the ABINIT [3] code package. The full theory can be found in the above two references. Most of the present notes are adopted from the supplementary material of Ref. [2].

2 Energy functionals

2.1 Units

We use Gaussian units so that $\mathbf{D} = \boldsymbol{\mathcal{E}} + 4\pi\mathbf{P}$, etc., where we use $\boldsymbol{\mathcal{E}}$ to denote the electric field. Energies like E, U, $\mathcal{F}$ and $\widetilde{\mathcal{F}}$ are *energies per unit cell* with units of energy.

2.2 Energy functionals for constant field calculation

Internal energy U is introduced for constant displacement field calculation [2]:

$$U(\mathbf{D}, v) = E_{\text{KS}}(v) + \frac{\Omega}{8\pi}[\mathbf{D} - 4\pi\mathbf{P}(v)]^2 \ . \tag{1}$$

$U(\mathbf{D}, v)$ depends directly on an external vector parameter $\mathbf{D}$, and indirectly on the internal (ionic and electronic) coordinates v through the Kohn-Sham energy E_{KS} and the Berry-phase polarization $\mathbf{P}$ [4].

The electric enthalpy $\mathcal{F}$ is introduced for constant $\mathcal{E}$ calculation: [1]

$$\mathcal{F}(\boldsymbol{\mathcal{E}}, v) = E_{\text{KS}}(v) - \Omega\boldsymbol{\mathcal{E}} \cdot \mathbf{P}(v) \ . \tag{2}$$

However, according to Ref. [2], $\widetilde{\mathcal{F}}$ is a more natural functional to be used in constant $\mathcal{E}$ calculation:

$$\tilde{\mathcal{F}} = U - \frac{\Omega}{4\pi}\boldsymbol{\mathcal{E}} \cdot \mathbf{D} = \mathcal{F} - \frac{\Omega}{8\pi}\mathcal{E}^2 \ . \tag{3}$$

(Since $\mathcal{F}$ and $\tilde{\mathcal{F}}$ only differ by a function of $\boldsymbol{\mathcal{E}}$, both of them yield the same equilibrium state at fixed $\boldsymbol{\mathcal{E}}$.)

3 Strains and strain derivatives

3.1 Introducing reduced field variables

For treating variable strain, it is strongly advantageous to change to internal variables. To define internal variables for the fields, we let $\mathbf{a}_j$ be the lattice vectors, and $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$ be the metric. We also let $\mathbf{b}_i$ be dual vectors defined as $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$, in which the conventional factor of 2π is *not included*, so that $\mathbf{b}_i \cdot \mathbf{b}_j = (g^{-1})_{ij}$. There are now two choices of reduced variables. Referencing to the reciprocal vectors, we get reduced variables

$$p_i = \Omega \, \mathbf{b}_i \cdot \mathbf{P} \qquad \Longleftrightarrow \qquad \mathbf{P} = \frac{1}{\Omega} \sum_i p_i \, \mathbf{a}_i \, , \tag{4}$$

$$\varepsilon_i = \frac{\Omega}{4\pi} \, \mathbf{b}_i \cdot \boldsymbol{\mathcal{E}} \qquad \Longleftrightarrow \qquad \boldsymbol{\mathcal{E}} = \frac{4\pi}{\Omega} \sum_i \varepsilon_i \, \mathbf{a}_i \, , \tag{5}$$

$$d_i = \frac{\Omega}{4\pi} \, \mathbf{b}_i \cdot \mathbf{D} \qquad \Longleftrightarrow \qquad \mathbf{D} = \frac{4\pi}{\Omega} \sum_i d_i \, \mathbf{a}_i \, . \tag{6}$$

where the inverse relations are given to the right. The relation $\mathbf{D} = \boldsymbol{\mathcal{E}} + 4\pi\mathbf{P}$ becomes

$$d_i = \varepsilon_i + p_i. \tag{7}$$

The reduced variables d_i, ε_i, and p_i have units of charge, and are related to the free charge, total charge, and bound charge, respectively, found on a surface of orientation $\hat{\mathbf{b}}_i$ if the fields vanish in the vacuum. Note that, aside from a factor of $e/2\pi$, the p_i are nothing other than the Berry phases ϕ_i as given, e.g., in Eq. (23) of Ref. [5].

The other choice is to refer to the real-space lattice vectors, i.e.,

$$\bar{p}_i = 4\pi \, \mathbf{a}_i \cdot \mathbf{P} \qquad \Longleftrightarrow \qquad \mathbf{P} = \frac{1}{4\pi} \sum_i \bar{p}_i \, \mathbf{b}_i \, , \tag{8}$$

$$\bar{\varepsilon}_i = \mathbf{a}_i \cdot \boldsymbol{\mathcal{E}} \qquad \Longleftrightarrow \qquad \boldsymbol{\mathcal{E}} = \sum_i \bar{\varepsilon}_i \, \mathbf{b}_i \, , \tag{9}$$

$$\bar{d}_i = \mathbf{a}_i \cdot \mathbf{D} \qquad \Longleftrightarrow \qquad \mathbf{D} = \sum_i \bar{d}_i \, \mathbf{b}_i \, . \tag{10}$$

The relation $\mathbf{D} = \boldsymbol{\mathcal{E}} + 4\pi\mathbf{P}$ becomes

$$\bar{d}_i = \bar{\varepsilon}_i + \bar{p}_i. \tag{11}$$

The reduced variables $\bar{p}_i$, $\bar{\varepsilon}_i$, and $\bar{d}_i$ have units of electric potential (energy/charge), and are related to the potential drop across the unit cell in direction $\hat{\mathbf{a}}_i$ arising from the displacement field, the total field, and the depolarization field, respectively. They are related to the unbarred quantities by

$$\bar{p}_i = \frac{4\pi}{\Omega} \, g_{ij} \, p_j \, , \qquad \bar{\varepsilon}_i = \frac{4\pi}{\Omega} \, g_{ij} \, \varepsilon_j \, , \qquad \bar{d}_i = \frac{4\pi}{\Omega} \, g_{ij} \, d_j \, , \tag{12}$$

where an implied sum notation is used.

The reduced field variables introduced here are closely related to those discussed in Ref. [1] (see, e.g., Eq. (5) therein) and in Sec. II.C.3 and the Appendix of of Ref. [6]. Eqs. (A4) and (A5) of Ref. [6] introduce field variables that are reminiscent of p_i and $\bar{\varepsilon}_i$ here, but there they were defined in such a way as to coincide with the ordinary $\mathbf{P}$ and $\boldsymbol{\mathcal{E}}$ in the absence of strains or rotations. More closely related are the $\mathbf{P}'$ and ε_μ variables defined in (A13) and (A14) of Ref. [6], which are identical to our p_i and $\bar{\varepsilon}_i$ except for a factor of the charge quantum e.

3.2 Energy functionals in reduced variables

The equation analogous to Eq. (2) is

$$\mathcal{F}(\bar{\varepsilon}) = E(p) - \frac{4\pi}{\Omega} g_{ij}\, \varepsilon_i\, p_j = E(p) - \bar{\varepsilon}_i\, p_i \ . \tag{13}$$

Note that the natural variable of function $\mathcal{F}$ is $\bar{\varepsilon}$, not ε. That is, the variable conjugate to p_i is $(4\pi/\Omega)g_{ij}\varepsilon_j = \bar{\varepsilon}_i$. This is the reason why we recommend to use $\bar{\varepsilon}$ in the constant electric field calculation (as implemented in `ABINIT`). We also have

$$\bar{\varepsilon}_i = \frac{dE}{dp_i} \ , \qquad p_i = -\frac{d\mathcal{F}}{d\bar{\varepsilon}} \ . \tag{14}$$

Then Eq. (3) becomes[1]

$$\widetilde{\mathcal{F}}(\bar{\varepsilon}) = \mathcal{F}(\bar{\varepsilon}) - \frac{\Omega}{8\pi}\, (g^{-1})_{ij}\, \bar{\varepsilon}_i\, \bar{\varepsilon}_j = E(p) - \bar{\varepsilon}_i\, p_i - \frac{\Omega}{8\pi}\, (g^{-1})_{ij}\, \bar{\varepsilon}_i\, \bar{\varepsilon}_j \tag{15}$$

and Eq. (1) becomes

$$U = E + \frac{2\pi}{\Omega}\, g_{ij}\, \varepsilon_i\, \varepsilon_i = E + \frac{1}{2}\, \bar{\varepsilon}_i\, \varepsilon_i = E + \frac{\Omega}{8\pi}\, (g^{-1})_{ij}\, \bar{\varepsilon}_i\, \bar{\varepsilon}_j \ . \tag{16}$$

We also have

$$d_i = -\frac{d\widetilde{\mathcal{F}}}{d\bar{\varepsilon}_i} \ , \qquad \bar{\varepsilon}_i = \frac{dU}{dd_i} \ . \tag{17}$$

For the electric enthalpy function, we can imagine a large number N of crystalline cell layers sandwiched between capacitor electrodes with a voltage V applied across the electrodes. If the cell is strained as a result of the applied voltage or for any other reason, the voltage drop per cell will remain V/N, corresponding to a fixed $\bar{\varepsilon}$. It thus makes sense that this is the natural variable for this kind of problem. On the other hand, the variable ε would change with strain, and so is not an appropriate choice of variable in this context.

On the other hand, instead of a capacitor with fixed voltage across the plates, we can imagine a slab with fixed free charge on the surfaces. More precisely, it would be fixed free charge per surface cell, not per unit area, under general strain deformations. This corresponds to fixed d, and so it is natural that $U(d)$ has natural variable d, not $\bar{d}$.

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[1]The volume Ω was erroneously omitted in Eq.(33) of the supplementary notes of Ref. [2].

3.3 Strain, strain derivatives, and the stress tensor

Let $\eta_{\mu\nu}$ be the strain tensor, and define the stresses $\sigma^E_{\mu\nu} = \Omega^{-1}dE/d\eta_{\mu\nu}$, $\sigma^{\mathcal{F}}_{\mu\nu} = \Omega^{-1}d\mathcal{F}/d\eta_{\mu\nu}$, $\sigma^{\widetilde{\mathcal{F}}}_{\mu\nu} = \Omega^{-1}d\widetilde{\mathcal{F}}/d\eta_{\mu\nu}$, and $\sigma^U_{\mu\nu} = \Omega^{-1}dU/d\eta_{\mu\nu}$. Then

$$\frac{d\Omega}{d\eta_{\mu\nu}} = \Omega\delta_{\mu\nu} \tag{18}$$

and

$$\frac{dg_{ij}}{d\eta_{\mu\nu}} = a_{i\mu}\,a_{j\nu} + a_{j\mu}\,a_{i\nu}\,. \tag{19}$$

The Hellmann-Feynman theorem applied to the electric enthalphy is

$$\left(\frac{d\mathcal{F}(\bar{\varepsilon},\eta;v)}{d\eta_{\mu\nu}}\right)_{\bar{\varepsilon}} = \frac{\partial\mathcal{F}(\bar{\varepsilon},\eta;v)}{\partial\eta_{\mu\nu}} + \frac{\partial\mathcal{F}(\bar{\varepsilon},\eta;v)}{\partial v}\frac{dv}{d\eta_{\mu\nu}} \tag{20}$$

but since $\partial\mathcal{F}/\partial v = 0$ at the equilibrium state of the internal variables $\{v\}$, the second term vanishes. Using $\mathcal{F}(\bar{\varepsilon}) = E(p) - \bar{\varepsilon}_i\,p_i$ we find

$$\frac{d\mathcal{F}(\bar{\varepsilon},\eta)}{d\eta_{\mu\nu}} = \frac{\partial E(p,\eta)}{\partial\eta_{\mu\nu}} - \bar{\varepsilon}_i\frac{\partial p_i}{\partial\eta_{\mu\nu}}\,. \tag{21}$$

But if we assume that the internal variables are atomic coordinates in lattice-vector units and coefficients of plane-wave basis functions in a norm-conserving context, it follows that $\partial p_i/\partial\eta_{\mu\nu} = 0$. Thus

$$\sigma^{\mathcal{F}}_{\mu\nu} = \frac{1}{\Omega}\frac{d\mathcal{F}}{d\eta_{\mu\nu}} = \frac{1}{\Omega}\frac{\partial E}{\partial\eta_{\mu\nu}} = \sigma^E_{\mu\nu} \tag{22}$$

which is just the stress tensor appearing in the usual KS theory. In the case of USPP or PAW approaches, $\partial p_i/\partial\eta_{\mu\nu}$ does not vanish, and augmentation terms need to be included.

For the internal energy, we again use the Hellmann-Feynman argument to write $dU/d\eta_{\mu\nu} = \partial U/\partial d\eta_{\mu\nu}$. Now the natural variable being held fixed is d, and again p is unchanged under a homogeneous strain if the internal variables are chosen properly, and since $d_i = \varepsilon_i + p_i$, this means ε is also fixed (while $\bar{\varepsilon}$ is not). We choose to write Eq. (16) as

$$U(\eta,d) = E + \frac{2\pi}{\Omega}\,g_{ij}\,\varepsilon_i\,\varepsilon_j \tag{23}$$

so that, using Eqs. (18) and (19),

$$\sigma^U_{\mu\nu} = \frac{1}{\Omega}\frac{dU}{d\eta_{\mu\nu}} = \frac{1}{\Omega}\frac{\partial E}{\partial\eta_{\mu\nu}} + \frac{2\pi}{\Omega^2}\left[2\,a_{i\mu}\,a_{j\nu}\,\varepsilon_i\,\varepsilon_j - \delta_{\mu\nu}\,g_{ij}\,\varepsilon_i\,\varepsilon_i\right] \tag{24}$$

or

$$\sigma^U_{\mu\nu} = \sigma^{\mathrm{KS}}_{\mu\nu} + \frac{1}{8\pi}\left[2\,\mathcal{E}_\mu\,\mathcal{E}_\nu - \delta_{\mu\nu}\,\mathcal{E}^2\right] \tag{25}$$

where the second term is just the Maxwell stress tensor arising from the macroscopic electric field. It is straightforward to show that $\sigma^{\widetilde{\mathcal{F}}} = \sigma^U$. Thus, there are basically two stress tensors, one $(\sigma^{\mathcal{F}}_{\mu\nu} = \sigma^E_{\mu\nu})$ that does not include the Maxwell stress, and another $(\sigma^{\widetilde{\mathcal{F}}} = \sigma^U)$ that does.

4 `ABINIT` implementation

In the `ABINIT` implementation, $\widetilde{\mathcal{F}}$ and U have been chosen as the energy functionals for fixed electric field or fixed electric displacement field cases, respectively. The corresponding fields are the reduced variables $\bar{\varepsilon}_i$ or d_i, in units of a.u. Therefore, the stress tensor includes the Maxwell stress. The ion positions and cell parameters can be optimized either under fixed $\bar{\varepsilon}_i$ or fixed d_i boundary conditions. This mode of operation, in which the user inputs target reduced fields for the constrained calculation, is the recommended one when the lattice vectors are going to be relaxed.

When the cell parameters are *not* going to be relaxed, it may be more convenient to work with the unreduced field variables $\boldsymbol{\mathcal{E}}$ or $\mathbf{D}$ instead; `ABINIT` also allows this option, in which the unreduced target field is input directly (in a.u.).

The `ABINIT` implementation does also allow calculations at fixed unreduced $\boldsymbol{\mathcal{E}}$ or $\mathbf{D}$ with relaxation of the cell parameters, but this option should be used with caution. It is important to note that the energy functionals of Eq. (13) and Eq. (16) are still used in these cases. Thus, when working at fixed $\boldsymbol{\mathcal{E}}$ for example, the code searches for a value of $\bar{\varepsilon}_i$ such that the equilibrium structure at fixed $\bar{\varepsilon}_i$ has the unreduced field $\boldsymbol{\mathcal{E}}$ matching the target one. This procedure is not variational in the usual sense. During such a run, the reported forces and stresses that are used to guide the minimization are not, in principle, equal to the numerical derivatives of the energy functional. For these reasons, it is recommended to choose the reduced-field options when relaxing the cell parameters along with the internal coordinates.

Relaxed-cell calculations at fixed $\mathcal{E}$ and D along one dimension were implemented first by M. Stengel in a private code package (`LAUTREC`) as described in Ref. [2] and references therein. Tests of the current `ABINIT` implementation (which supports fixed three-dimensional $\boldsymbol{\mathcal{E}}$ or $\mathbf{D}$) were presented in Ref. [7], showing excellent agreement with the `LAUTREC` implementation.

References

[1] I. Souza, J. Íñiguez, and D. Vanderbilt, Phys. Rev. Lett. **89**, 117602 (2002).

[2] Massimiliano Stengel, Nicola A. Spaldin, and David Vanderbilt, Nat Phys **5**, 304 (2009).

[3] ABINIT is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (http://www.abinit.org). X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D.C. Allan, Comput. Mater. Sci. **25**, 478-492 (2002).

[4] R. D. King-Smith, David Vanderbilt, Phys. Rev. B, **47**,R1651,(1993).

[5] D. Vanderbilt, J. Phys. Chem. Solids **61**, 147 (2000).

[6] X. Wu, D. Vanderbilt, and D.R. Hamann, Phys. Rev. B **72**, 035105 (2005).

[7] Jiawang Hong and David Vanderbilt, Phys. Rev. B **84**, 115107 (2011).