Density functional perturbation theory for electric fields

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Outline

Phenomenological theory - I

The dielectric properties of an insulator are described with the help of three fields: **D** the electric displacement, **E** the electric field inside the solid, and **P** the polarization. The three are linked by the equation

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} \tag{1}$$

(in atomic units). We assume that there is no free charge in the solid, so the fields obey the equations:

$$\text{curl } \mathbf{E} = 0,$$

$$\text{div } \mathbf{D} = 0.$$

Phenomenological theory - II

In the phenomenological theory of the response of a polar insulator to an electric field one introduces two quantities: the dielectric constant $\epsilon_{\alpha\beta}$ and the Born effective charges $Z^*_{s\alpha,\beta}$. Atoms move in the same way in all unit cells (as in a **q=0** phonon). The electric enthalpy per cell is a quadratic function:

$$\begin{aligned} F(\{\mathbf{u}_s\},\mathbf{E}) &= F(\{\mathbf{0}\},\mathbf{0}) + \frac{1}{2}\sum_{s\alpha,s'\beta}\frac{\partial^2 F(\{\mathbf{u}_s\},\mathbf{E})}{\partial \mathbf{u}_{s\alpha}\partial \mathbf{u}_{s'\beta}}\mathbf{u}_{s\alpha}\mathbf{u}_{s'\beta} \\ &+ q\sum_{s\alpha\beta}\mathbf{u}_{s\alpha}Z^*_{s\alpha,\beta}\mathbf{E}_\beta - \frac{\Omega}{8\pi}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}\mathbf{E}_\alpha\mathbf{E}_\beta, \end{aligned}$$

where q is the electron charge (a negative number), Ω is the volume of a unit cell, and s is a sub-lattice index.

Phenomenological theory - III

Derivation of this function with respect to $\mathbf{E}_\beta$ gives:

$$\frac{\partial F(\{\mathbf{u}_s\},\mathbf{E})}{\partial \mathbf{E}_\beta} = q\sum_{s\alpha}\mathbf{u}_{s\alpha}Z^*_{s\alpha,\beta} - \frac{\Omega}{4\pi}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}\mathbf{E}_\alpha,$$

that shows that

$$-\frac{4\pi}{\Omega}\frac{\partial F(\{\mathbf{u}_s\},\mathbf{E})}{\partial \mathbf{E}_\beta} = -\frac{4\pi q}{\Omega}\sum_{s\alpha}\mathbf{u}_{s\alpha}Z^*_{s\alpha,\beta} + \sum_{\alpha,\beta}\epsilon_{\alpha\beta}\mathbf{E}_\alpha = \mathbf{D}_\beta.$$

Comparison with Eq. 1 gives the polarization:

$$\mathbf{P}_\beta = -\frac{q}{\Omega}\sum_{s\alpha}\mathbf{u}_{s\alpha}Z^*_{s\alpha,\beta} + \sum_{\alpha,\beta}\frac{\epsilon_{\alpha\beta}-\delta_{\alpha\beta}}{4\pi}\mathbf{E}_\alpha. \qquad (2)$$

Phenomenological theory - IV

This equation allows to write the dielectric constant and the Born effective charges as derivatives of the polarization:

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \frac{d\mathbf{P}_\beta}{d\mathbf{E}_\alpha}$$

and

$$Z^*_{s\alpha,\beta} = -\frac{\Omega}{q} \frac{d\mathbf{P}_\beta}{d\mathbf{u}_{s\alpha}}.$$

Note that in the first case the derivative of the polarization has to be done at fixed ions, while in the second in zero electric field. The resulting dielectric constant (sometimes indicated with $\epsilon^\infty_{\alpha\beta}$) is the one measured at frequencies sufficiently high that the ions cannot follow and sufficiently small that electrons cannot be excited.

Phenomenological theory - IV

We can use F as the potential energy for the ions and obtain the Hamilton equations of motion:

$$\begin{aligned}
\frac{d\mathbf{u}_{s\alpha}}{dt} &= \frac{\mathbf{p}_{s\alpha}}{M_s} \\
\frac{d\mathbf{p}_{s\alpha}}{dt} &= -\sum_{s'\beta} \frac{\partial^2 F(\{\mathbf{u}_s\}, \mathbf{E})}{\partial \mathbf{u}_{s\alpha} \partial \mathbf{u}_{s'\beta}} \mathbf{u}_{s'\beta} - q \sum_{\beta} Z^*_{s\alpha,\beta} \mathbf{E}_\beta .
\end{aligned}$$

These equations can be solved for a slowly varying electric field described by plane wave with a wave-vector $\mathbf{q}$. We will consider the limit for $\mathbf{q} \to \mathbf{0}$.

Phenomenological theory - V

When $\mathbf{q} \to 0$, $\mathbf{D}$ and $\mathbf{E}$ are almost uniform and we can write them as: [1]

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(\mathbf{q}) e^{i\mathbf{qr}},$$

$$\mathbf{D}(\mathbf{r}) = \mathbf{D}(\mathbf{q}) e^{i\mathbf{qr}}.$$

So the Maxwell equations tell us that:

$$\mathbf{q} \times \mathbf{E} = 0,$$

$$\mathbf{q} \cdot \mathbf{D} = 0.$$

Using the versor of $\mathbf{q}$, $\hat{\mathbf{q}}$, we have

$$\mathbf{E} = \hat{\mathbf{q}}(\hat{\mathbf{q}} \cdot \mathbf{E}).$$

Phenomenological theory - VI

$\hat{\mathbf{q}} \cdot \mathbf{E}$ is obtained from the equation $\hat{\mathbf{q}} \cdot \mathbf{D} = 0$ that becomes:

$$-\frac{4\pi q}{\Omega} \sum_{s\alpha} \mathbf{u}_{s\alpha} Z^*_{s\alpha,\beta} \hat{\mathbf{q}}_\beta + \sum_{\alpha,\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta (\hat{\mathbf{q}} \cdot \mathbf{E}) = 0.$$

This gives

$$\mathbf{E} = \hat{\mathbf{q}} \frac{4\pi q}{\Omega} \sum_{s'\beta} \frac{\sum_\gamma Z^*_{s'\beta,\gamma} \hat{\mathbf{q}}_\gamma}{\sum_{\alpha,\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta} \mathbf{u}_{s'\beta}.$$

Inserting this equation in the equations of motion gives:

$$\begin{aligned} M_s \frac{d^2 \mathbf{u}_{s\alpha}}{dt^2} &= -\sum_{s'\beta} \frac{\partial^2 F(\{\mathbf{u}_s\}, \mathbf{E})}{\partial \mathbf{u}_{s\alpha} \partial \mathbf{u}_{s'\beta}} \mathbf{u}_{s'\beta} \\ &- \frac{4\pi q^2}{\Omega} \sum_{s'\beta} \frac{\sum_\delta Z^*_{s\alpha,\delta} \hat{\mathbf{q}}_\delta \sum_\gamma Z^*_{s'\beta,\gamma} \hat{\mathbf{q}}_\gamma}{\sum_{\alpha,\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta} \mathbf{u}_{s'\beta}. \end{aligned}$$

Phenomenological theory - VII

The phenomenological theory therefore predicts that a non-analytic term, non vanishing only for $\mathbf{q} = 0$, appears in the dynamical matrix of a polar insulator. This term is non analytic since it depends on the direction along which $\mathbf{q} \to 0$. The non analytic term is not computed in this form, but having the Born effective charges and the dielectric constant one can set up the dynamical matrices of a model system which has the same behavior. These dynamical matrices are subtracted to the ab-initio dynamical matrices and only the difference is Fourier interpolated.

Electric field in density functional theory - I

In density functional theory, we can simulate an electric field by adding the potential energy of an electron in an electric field to the local potential:

$$V_{loc}(\mathbf{r}) \rightarrow V_{loc}(\mathbf{r}) - q\mathbf{r} \cdot \mathbf{E}.$$

This term inserted in the total energy, together with a term that accounts for the potential energy of the ions, gives:

$$E^{DFT}(\mathbf{E}) = \tilde{E}^{DFT}(\mathbf{E}) - q \int_V \mathbf{r} \cdot \mathbf{E} n(\mathbf{r}) d^3r - \sum_I Z_s(\mathbf{R}_I + \mathbf{u}_I) \cdot \mathbf{E},$$

where Z_s is ion charge and $\tilde{E}^{DFT}(\mathbf{E})$ is the part of the total energy that does not contain the electric field, but depends upon it through the wavefunctions and the charge density.

Electric field in density functional theory - II

In a finite system we could define the polarization of the system as the total dipole divided by the volume:

$$\mathbf{P} = \frac{q}{V}\int_V \mathbf{r} n(\mathbf{r}) d^3 r + \frac{1}{V}\sum_I Z_s(\mathbf{R}_I + \mathbf{u}_I)$$

and we could write:

$$E^{DFT}(\mathbf{E}) = \tilde{E}^{DFT}(\mathbf{E}) - V\mathbf{P}\cdot\mathbf{E}.$$

In a periodic solid this definition has several problems because it cannot be calculated as written but requires a more sophisticated approach based on the Berry phase. Moreover the electric field potential breaks the translation symmetry of the solid.

Electric field in density functional perturbation theory - I

However we need the derivatives of the polarization and using this expression for **P** the dielectric constants and of the Born effective charges become:

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi q}{V} \int_V \mathbf{r}_\beta \frac{dn(\mathbf{r})}{dE_\alpha} d^3r$$

and

$$Z^*_{s\alpha,\beta} = -\frac{1}{N_c} \int_V \mathbf{r}_\beta \frac{dn(\mathbf{r})}{d\mathbf{u}_{s\alpha}} d^3r - \frac{Z_s}{q}\delta_{\alpha\beta}.$$

We now show that both expressions can be calculated within one unit cell of the crystal using lattice periodic quantities.

Electric field in density functional perturbation theory - II

For small enough electric fields, we can use DFPT to calculate the response of a solid to the field:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \epsilon_{\mathbf{k}v}\right] P_c \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha} = -P_c \frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{E}_\alpha} \psi_{\mathbf{k}v}(\mathbf{r}),$$

where

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{E}_\alpha} = -q\mathbf{r}_\alpha + \frac{\partial V_H}{\partial \mathbf{E}_\alpha} + \frac{\partial V_{xc}}{\partial \mathbf{E}_\alpha}.$$

First we show that:

$$P_c \mathbf{r}_\alpha \psi_{\mathbf{k}v}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \phi^\alpha_{\mathbf{k}v}(\mathbf{r}),$$

where $\phi^\alpha_{\mathbf{k}v}(\mathbf{r})$ is a lattice periodic function.

Electric field in density functional perturbation theory - III

Then we write the linear system as:

$$[H_{\mathbf{k}} - \epsilon_{\mathbf{k}v}]\, P_c^{\mathbf{k}} \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha} = q\phi^\alpha_{\mathbf{k}v}(\mathbf{r}) - P_c^{\mathbf{k}} \frac{\partial V_{Hxc}(\mathbf{r})}{\partial \mathbf{E}_\alpha} u_{\mathbf{k}v}(\mathbf{r}),$$

where

$$H_{\mathbf{k}} = e^{-i\mathbf{k}\mathbf{r}} \left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \right] e^{i\mathbf{k}\mathbf{r}}$$

and

$$P_c^{\mathbf{k}} = e^{-i\mathbf{k}\mathbf{r}} P_c e^{i\mathbf{k}\mathbf{r}}.$$

This linear system contains only lattice periodic functions. Indeed, we have

$$\phi^\alpha_{\mathbf{k}v}(\mathbf{r}) = e^{-i\mathbf{k}\mathbf{r}} P_c \mathbf{r}_\alpha \psi_{\mathbf{k}v}(\mathbf{r}) = \sum_c u_{\mathbf{k}c}(\mathbf{r}) \frac{\langle \psi_{\mathbf{k}c} | \, [H, r_\alpha] \, | \psi_{\mathbf{k}v} \rangle}{\epsilon_{\mathbf{k}c} - \epsilon_{\mathbf{k}v}}.$$

Electric field in density functional perturbation theory - IV

Since

$$\langle \psi_{\mathbf{k}c} | \left[H, r_\alpha \right] | \psi_{\mathbf{k}v} \rangle = -i \langle \psi_{\mathbf{k}c} | \mathbf{p}_\alpha | \psi_{\mathbf{k}v} \rangle = -i \langle u_{\mathbf{k}c} | (\mathbf{k}_\alpha + \mathbf{p}_\alpha) | u_{\mathbf{k}v} \rangle,$$

$\phi^\alpha_{\mathbf{k}v}(\mathbf{r})$ is the solution of the linear system:

$$\left[H_\mathbf{k} - \epsilon_{\mathbf{k}v} \right] \phi^\alpha_{\mathbf{k}v}(\mathbf{r}) = -i P^\mathbf{k}_c (\mathbf{k}_\alpha + \mathbf{p}_\alpha) u_{\mathbf{k}v}(\mathbf{r}),$$

that contains lattice periodic functions only.
With the solution of the linear system $P^\mathbf{k}_c \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha}$ we can write the (lattice periodic) charge density induced by an electric field as:

$$\frac{dn(\mathbf{r})}{dE_\alpha} = 4 \sum_{\mathbf{k}v} u^*_{\mathbf{k}v}(\mathbf{r}) P^\mathbf{k}_c \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha}.$$

Electric field in density functional perturbation theory - V

The dielectric constant becomes:

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{16\pi q}{V} \sum_{\mathbf{k}v} \int_V \psi^*_{\mathbf{k}v}(\mathbf{r}) \mathbf{r}_\beta P_c \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha} d^3r,$$

or

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{16\pi q}{\Omega} \sum_{\mathbf{k}v} \int_\Omega \phi^{*\beta}_{\mathbf{k}v}(\mathbf{r}) P^{\mathbf{k}}_c \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha} d^3r,$$

while the effective charges are:

$$Z^*_{s\alpha,\beta} = -4 \sum_{\mathbf{k}v} \int_\Omega \phi^{*\beta}_{\mathbf{k}v}(\mathbf{r}) P^{\mathbf{k}}_c \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}} d^3r - \frac{Z_s}{q} \delta_{\alpha\beta}.$$

Effective changes: alternative expression

The evaluation of the effective charges requires the response to $3 \times N_{at}$ phonon perturbations at $\mathbf{q} = \mathbf{0}$. We can obtain an alternative expression by observing that the Hellmann-Feynman theorem gives:

$$\frac{dE^{DFT}}{d\mathbf{E}_\beta} = -V\mathbf{P}_\beta.$$

Deriving with respect to $\mathbf{u}_{s\alpha}$ we obtain:

$$qZ^*_{s\alpha,\beta} = -\Omega \frac{d\mathbf{P}_\beta}{d\mathbf{u}_{s\alpha}} = \frac{1}{N_c} \frac{d^2 E^{DFT}(\mathbf{E})}{d\mathbf{u}_{s\alpha} d\mathbf{E}_\beta}.$$

Since the second derivative is symmetric we can first derive with respect to $\mathbf{u}_{s\alpha}$ and then with respect to $\mathbf{E}_\beta$.

Effective charges: alternative expression - II

The first derivative of the energy gives:

$$\frac{1}{N_c}\frac{dE^{DFT}(\mathbf{E})}{d\mathbf{u}_{s\alpha}} = \frac{1}{N_c}\int_V \frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_{s\alpha}} n(\mathbf{r}) d^3r - Z_s \mathbf{E}_\alpha + \frac{1}{N_c}\frac{dU_{II}}{d\mathbf{u}_{s\alpha}},$$

and taking the derivative with respect to the electric field we have:

$$qZ^*_{s\alpha,\beta} = \frac{1}{N_c}\int_V \frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_{s\alpha}}\frac{dn(\mathbf{r})}{d\mathbf{E}_\beta} d^3r - Z_s\delta_{\alpha\beta},$$

or

$$qZ^*_{s\alpha,\beta} = 4\sum_{\mathbf{k}v}\int_\Omega u^*_{\mathbf{k}v}(\mathbf{r})\frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_{s\alpha}} P_c^{\mathbf{k}}\frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\beta} d^3r - Z_s\delta_{\alpha\beta},$$

that can be evaluated from the responses to the 3 components of the electric field.

Relationship with the phenomenological theory

We notice that $E^{DFT}(\mathbf{E})$ does not coincide with the electric enthalpy $F(\mathbf{E})$ of the phenomenological theory. In addition to the fact that the first refers to the volume V while the latter is the energy per cell, the two differ for the free energy of the free electric field. By defining:

$$F^{DFT}(\mathbf{E}) = \frac{1}{N_c} E^{DFT}(\mathbf{E}) - \frac{\Omega}{8\pi}\mathbf{E}^2,$$

we have

$$-\frac{4\pi}{\Omega}\frac{dF^{DFT}(\mathbf{E})}{d\mathbf{E}_\beta} = 4\pi\mathbf{P}_\beta + \mathbf{E}_\beta = \mathbf{D}_\beta.$$

Relationship with the phenomenological theory - II

From the Taylor expansion of the free energy we have:

$$\epsilon_{\alpha,\beta} = -\frac{4\pi}{\Omega}\frac{d^2F^{DFT}(\mathbf{E})}{d\mathbf{E}_\alpha d\mathbf{E}_\beta} = \delta_{\alpha\beta} - \frac{4\pi}{V}\frac{d^2E^{DFT}(\mathbf{E})}{d\mathbf{E}_\alpha d\mathbf{E}_\beta}.$$

Similarly for the effective charges we have:

$$qZ^*_{s\alpha,\beta} = \frac{d^2F^{DFT}(\mathbf{E})}{du_{s\alpha}d\mathbf{E}_\beta} = \frac{1}{N_c}\frac{d^2E^{DFT}(\mathbf{E})}{du_{s\alpha}d\mathbf{E}_\beta}.$$

Note: in the literature the quantity $\phi^\alpha_{\mathbf{k}v}(\mathbf{r})$ is sometimes called $iu^{k_\alpha}_{\mathbf{k}v}(\mathbf{r})$ or $i\frac{\partial u_{\mathbf{k}v}(\mathbf{r})}{\partial k_\alpha}$.

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