Density functional perturbation theory for electric fields

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Outline

Phenomenological theory - I

An insulator in an electric field is 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:

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

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

Phenomenological theory - II

In the classical theory of phonons in polar insulators one introduces two quantities: the dielectric constant $\epsilon_{\alpha\beta}$ that describes the response of the solid to an electric field at fixed ions and the Born effective charges $Z^*_{s\alpha,\beta}$ that describe the coupling between atomic displacements and the electric field. The electric enthalpy is a quadratic function:

$$F(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E}) = F(\{\mathbf{R}_I\}, \mathbf{0}) + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 F(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E})}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta} + q \sum_{I\alpha\beta} \mathbf{u}_{I\alpha} Z^*_{s\alpha,\beta} \mathbf{E}_\beta - \frac{V}{8\pi} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} \mathbf{E}_\alpha \mathbf{E}_\beta,$$

where q is the electron charge (a negative number) and V is the volume of the solid. $I = \{\mu, s\}$ indicates both the Bravais lattice point and the atomic position indeces.

Phenomenological theory - III

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

$$\frac{\partial F(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E})}{\partial \mathbf{E}_\beta} = q \sum_{I\alpha} \mathbf{u}_{I\alpha} Z^*_{s\alpha,\beta} - \frac{V}{4\pi} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} \mathbf{E}_\alpha,$$

that shows that

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

and comparison with Eq. 1 gives the polarization

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

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

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

Since the effective charges do not depend on the unit cell μ this expression is rewritten as:

$$Z^*_{s\alpha,\beta} = -\frac{V}{qN_c}\sum_\mu \frac{d\mathbf{P}_\beta}{d\mathbf{u}_{\mu,s\alpha}} = -\frac{\Omega}{q}\frac{d\mathbf{P}_\beta}{d\mathbf{u}_{s\alpha}(\mathbf{q}=\mathbf{0})}.$$

Phenomenological theory - IV

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

$$\begin{aligned}\frac{d\mathbf{u}_{I\alpha}}{dt} &= \frac{\mathbf{p}_{I\alpha}}{M_I} \\ \frac{d\mathbf{p}_{I\alpha}}{dt} &= -\sum_{J\beta}\frac{\partial^2 F(\{\mathbf{R}_I+\mathbf{u}_I\},\mathbf{E})}{\partial\mathbf{u}_{I\alpha}\partial\mathbf{u}_{J\beta}}\mathbf{u}_{J\beta} - q\sum_{\beta} Z^*_{s\alpha,\beta}\mathbf{E}_\beta.\end{aligned}$$

We can now solve these equations assuming a phonon displacement with wavevector $\mathbf{q}$. The last term will be non vanishing only at $\mathbf{q}=0$ since the interaction term in $F(\{\mathbf{R}_I+\mathbf{u}_I\},\mathbf{E})$ vanishes for finite $\mathbf{q}$, but the value of the electric field will depend on the direction with which we approach $\mathbf{q}=0$.

Phenomenological theory - V

When $\mathbf{q} \to 0$ **D** and **E** become non uniform and their macroscopic value vanishes, but we have [1]

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

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

So the Maxwell equations tell us that:

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

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

Using the versor of **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 taking the scalar product of $\sum_\beta \hat{\mathbf{q}}_\beta \mathbf{D}_\beta = 0$:

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

This gives

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

Inserting this equation in the equations of motion gives:

$$\begin{aligned} M_I \frac{d^2 \mathbf{u}_{I\alpha}}{dt^2} &= -\sum_{J\beta} \frac{\partial^2 F(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E})}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \\ &- \sum_{J\beta} \frac{4\pi q^2}{V} \frac{\sum_\delta Z^*_{s\alpha,\delta} \hat{\mathbf{q}}_\delta \sum_\gamma Z^*_{s'\beta,\gamma} \hat{\mathbf{q}}_\gamma}{\sum_{\alpha,\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta} \mathbf{u}_{J\beta}. \end{aligned}$$

Phenomenological theory - VII

The phenomenological theory therefore predicts that a term, which is non vanishing only for a phonon at $\mathbf{q} = 0$, appears in the dynamical matrix. This term is non analytic since it depends on the direction along which $\mathbf{q} \rightarrow 0$. 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 non analyticity. 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 to the local potential, the potential energy of the electron in the electric field:

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

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:

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

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 using this polarization in the expression of the dielectric constants and of the Born effective charges we get

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

and

$$Z^*_{s\alpha,\beta} = -\frac{1}{N_c} \int_V \mathbf{r}_\beta \frac{dn(\mathbf{r})}{d\mathbf{u}_{s\alpha}(\mathbf{q}=\mathbf{0})} d^3r - \frac{Z_s}{q}\delta_{\alpha\beta}.$$

and both expressions can be calculated within one unit cell of the crystal using the periodic parts of the Bloch functions and of their responses.

Electric field in density functional perturbation theory - II

The electric field potential can be used as a perturbing potential in DFPT:

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

where

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

Demonstrating that the function

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

is lattice periodic, one can write the linear system as:

Electric field in density functional perturbation theory - III

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

where

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

and

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

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

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

Electric field in density functional perturbation theory - IV

Since

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

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

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

that contains only lattice periodic functions.

With the solution of the linear system $P_c^\mathbf{k}\frac{\partial\tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial\mathbf{E}_\alpha}$ we can write the charge density induced by an electric field which is lattice periodic:

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

Electric field in density functional perturbation theory - V

Inserting this expression in the dielectric constant we have

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

or

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

while the effective charges become:

$$Z^*_{s\alpha,\beta} = -4 \sum_{\mathbf{k}v} \int_\Omega \phi^{*\alpha}_{\mathbf{k}v}(\mathbf{r}) P^{\mathbf{k}}_c \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q}=\mathbf{0})} d^3r - \frac{Z_s}{q} \delta_{\alpha\beta}.$$

Electric field in density functional perturbation theory - VI

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

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

and then deriving with respect to $\mathbf{u}_{s\alpha}(\mathbf{q} = \mathbf{0})$

$$qZ^*_{s\alpha,\beta} = \frac{1}{N_c} \frac{d^2 E^{DFT}(\mathbf{E})}{d\mathbf{u}_\alpha(\mathbf{q} = \mathbf{0}) d\mathbf{E}_\beta}$$

Since the second derivative is symmetric we can first derive with respect to $\mathbf{u}_{s\alpha}(\mathbf{q} = \mathbf{0})$ using the Hellmann-Feynman theorem and then with respect to $\mathbf{E}_\beta$.

Electric field in density functional perturbation theory - VII

The first derivative of the energy gives:

$$\frac{1}{N_c}\frac{dE^{DFT}(\mathbf{E})}{d\mathbf{u}_\alpha(\mathbf{q}=\mathbf{0})} = \frac{1}{N_c}\int_V \frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_\alpha(\mathbf{q}=\mathbf{0})} n(\mathbf{r}) d^3r - Z_s \mathbf{E}_\alpha$$

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

$$qZ^*_{s\alpha,\beta} = \frac{1}{N_c}\int_V \frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_\alpha(\mathbf{q}=\mathbf{0})} \frac{dn(\mathbf{r})}{d\mathbf{E}_\beta} d^3r - Z_s \delta_{\alpha\beta}$$

or

$$qZ^*_{s\alpha,\beta} = 4\sum_{\mathbf{k}v}\int_\Omega u^*_{\mathbf{k}v}(\mathbf{r}) \frac{dV_{loc}(\mathbf{r})}{d\mathbf{u}_\alpha(\mathbf{q}=\mathbf{0})} \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{E}_\alpha} d^3r - Z_s \delta_{\alpha\beta}$$

Relationship with the phenomenological theory - I

We notice that $E^{DFT}(\mathbf{E})$ does not coincide with the electric enthalphy $F(\mathbf{E})$ of the phenomenological theory. The two differ for a term quadratic in the electric field. By defining:

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

we have

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

and from the Taylor expansion:

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

Relationship with the phenomenological theory - II

Similarly for the effective charges we have:

$$qZ^*_{s\alpha,\beta} = \frac{1}{N_c} \frac{d^2 F^{DFT}(\mathbf{E})}{du_{s\alpha}(\mathbf{q}=\mathbf{0})d\mathbf{E}_\beta} = \frac{1}{N_c} \frac{d^2 E^{DFT}(\mathbf{E})}{du_{s\alpha}(\mathbf{q}=\mathbf{0})d\mathbf{E}_\beta}.$$

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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