Total energy and polarization integral

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The main idea here is to figure out what the total ground state energy E_{tot} of a system is as a function of where the atoms are located. Specifically, we want to know the total energy E_{tot} as function of the polarization P of a possibly ferroelectric film with electrodes and/or semiconductors on both sides, etc.

Starting from basic principles, we will consider a system of interaction electrons and nuclei. We will also use the standard Born-Oppenheimer approximation and also take the nuclei to be massive and thus classical objects (i.e. no quantum effects for the nuclear degrees of freedom). We label the electron positions r_i and the nuclear positions R_I (these are both 3-vectors). The electron charge is $-e$ and the nuclear charge of ion I is $Z_I e$. The standard non-relativistic Hamiltonian (the standard model of solid state physics) is

$$\begin{aligned} H &= -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{e^2}{|r_i - r_j|} - \sum_i\sum_I \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_I\sum_{J\neq I}\frac{Z_I Z_J e^2}{|R_I - R_J|} \\ &= T + V_{ee} + V_{en} + V_{nn} \end{aligned}$$

where each term has been given a short-hand name in the second line.

In the Born-Oppenheimer picture, we have the electrons in the ground state $|\Psi^0(R)\rangle$ for any given nuclear configuration which has the shorthand R (a collection of 3-vectors). The energy eigenvalue of $T + V_{ee} + V_{en}$ is the electronic ground-state energy $E^0(R)$

$$(T + V_{ee} + V_{en})|\Psi^0(R)\rangle = E^0(R)|\Psi^0(R)\rangle\,.$$

The total electronic ground-state energy for a given nuclear configuration is then

$$E_{tot}(R) = \langle\Psi^0(R)|H|\Psi^0(R)\rangle = E^0(R) + V_{nn}(R)\,.$$

Consider moving nucleus R_I and asking for the change in E_{tot} or more precisely the derivative $\partial E_{tot}/\partial R_I$. The Hellmann-Feynman theorem says that the derivative of the expectation value is the expectation of the derivative of the Hamiltonian (i.e. just first order perturbation theory) so

$$\frac{\partial E_{tot}(R)}{\partial R_I} = \langle\Psi^0(R)|\frac{\partial(T + V_{ee} + V_{en})}{\partial R_I}|\Psi^0(R)\rangle + \frac{\partial V_{nn}}{\partial R_I}\,.$$

The only term in the derivative of the operators that actually depends on R_I is the electron-nuclear attraction V_{en}. The derivative of V_{nn} is also easy to compute. Doing some algebra and noting that V_{en} only involves one electron coordinate at a time so the expectation returns the electron density $n(r)$ in the ground-state, we get

$$\frac{\partial E_{tot}(R)}{\partial R_I} = -Z_I e \mathcal{E}(R_I) \tag{1}$$

where the electric field $\mathcal{E}$ at position of nucleus R_I is

$$\mathcal{E}(R_I) = \int \frac{-en(r)(r - R_I)}{|r - R_I|^3} d^3r + \sum_{J \neq I} \frac{Z_I e (R_J - R_I)}{|R_J - R_I|^3} \,. \tag{2}$$

Equation (2) is just the sum of the electric fields from the electrons and from the nuclei at position R_I, a purely electrostatic calculation. Equation (1) then just says that the derivative of the energy when moving nucleus I (which is the force up to a sign) is just given by the charge of the nucleus times the electric field it feels. This is a purely electrostatic force and the fact that it is so is sometimes called the Feynman electrostatic theorem: the forces from all the complicated quantum many-body effects and whatnot are all piled into the average electrostatic force on a nucleus.

Using the standard definition of the force on nucleus I

$$F_I \equiv -\frac{\partial E_{tot}(R)}{\partial R_I} = Z_I e \mathcal{E}(R_I)$$

along with Equation (1), we arrive at the useful formula for the variation of the total energy

$$\delta E_{tot} = -\sum_I F_I \cdot \delta R_I \,. \tag{3}$$

This already us a good deal of useful information: if a nucleus doesn't move at all, then it doesn't contribute to the energy change no matter how much the electrons in its vicinity polarize, shift about, etc. All we need to worry about is the force on the moving atoms and how much they move: integrating this over the net motion will give us the change in total energy.

The main problem is now to translate this first principles, microscopic result to something useful for Landau theory which is more macroscopic in style. The connection is made in the following way: we look to simplify Eq. (3) in the limit that the atomic motions in adjoining unit cells are the same, any imposed fields on the system are uniform, and any long-range fields developing are quite smooth as well (i.e. the long-wavelength limit). This is the limit of the applicability of traditional Landau theory; gradient corrections incorporating the slow variations in the fields, displacements, polarizations, and so forth are a higher order correction.

For simplicity, assume that each nucleus I labels a unit cell of the material (having multiple ones just makes for more baroque notation but ends in the same place). The macroscopic

averaged electric field in that cell is denoted as $\bar{\mathcal{E}}(R_I)$: this is the average of the electric field over the unit cell (or a few unit cells in that region). The long-wavelength limit means $\bar{\mathcal{E}}(R_I)$ varies very slowly with R_I as we go from unit cell to unit cell. In what follows, I'll omit the I index as all quantities will refer to a particular unit cell. Later, we can sum over all cells.

The first thing to ask is what we can say about the force F. The standard approach is to do a series

$$F = F^0 + Z^* e\bar{\mathcal{E}} + O(\bar{\mathcal{E}}^2)\,.$$

Here F^0 is the force for zero net electric field in the material, namely when the potential on average is periodic. This is the "intrinsic" force coming from the materials properties, and for ferroelectric materials it is the standard Landau free energy function at zero field with a double minimum in the polarization, etc. This is the type of force extracted directly from most *ab initio* calculations. The next term tells us how the presence of the macroscopic field creates a force on the nuclei. The Z^* is the Born effective or dynamical charge (symmetric tensor): it is *defined* by this relation as the coefficient that multiplies the field to give us the force. In general $Z \neq Z^*$ since Z^* includes the effects of the polarization of the electron clouds as well (a renormalization if you like) — the bare nuclear charge Ze and whatever is the force created by the electron distortion in response to $\bar{\mathcal{E}}$ all get lumped into Z^*e. We will ignore the higher order terms so we assume weak macroscopic fields — physically this means weak enough so the materials properties like F^0 and Z^* are not modified.

The next stop is to work in the macroscopic polarization P into this theory. What is the change in polarization in a unit cell δP, due to the motion of the nuclei as well as the presence of the field $\bar{\mathcal{E}}$? For long wavelengths, it is

$$\delta P = \frac{Z^* e}{V}\delta R + \chi_\infty \delta\bar{\mathcal{E}}\,.$$

V is the volume of a unit cell. This is not some ansatz but can be derived from basic relations. The outline of the logic is that for a uniform periodic system, the derivatives of the total free energy G per cell give us the force $F = -\partial G/\partial R$ and the polarization $P = -\partial G/\partial\bar{\mathcal{E}}$. The equality of mixed partials $\partial^2 G/\partial R\partial\bar{\mathcal{E}} = \partial^2 G/\partial\bar{\mathcal{E}}\partial R$ gives us the coefficient of δR_I since $\partial P/\partial R = -\partial^2 G/\partial R\partial\bar{\mathcal{E}} = -\partial^2 G/\partial\bar{\mathcal{E}}\partial R = \partial F/\partial\bar{\mathcal{E}} = Z_I^* e$. The second terms comes from the definition of the optical (clamped-ion) susceptibility $\partial P/\partial\bar{\mathcal{E}} = -\partial^2 G/\partial\bar{\mathcal{E}}^2 = \chi_\infty$.

Physically, the picture from the above equation for δP is simple: if we move the nuclei that have some effective charge, we create polarization since we move charge around. In addition, even if we don't move the nuclei at all — i.e. we *clamp* them — the system can still polarize because the electrons will polarize in response to changes in the macroscopic field, if any.

Using the two above equation, we can do the following manipulations

$$F\cdot\delta R = F^0\cdot\delta R + Z^* e\bar{\mathcal{E}}\cdot\delta R = F^0\cdot\delta R + Z^* e\bar{\mathcal{E}}\cdot\left[\frac{V}{Z^* e}(\delta P - \chi_\infty\delta\bar{\mathcal{E}})\right]$$

so the Z^*e factors cancel to give

$$F\cdot\delta R = F^0\cdot\delta R + V\bar{\mathcal{E}}\cdot(\delta P - \chi_\infty\delta\bar{\mathcal{E}})\,.$$

The quantity in the parenthesis is the "nuclear-only" change in polarization $(Z^*e/V)\delta R$: we subtract out the part coming from the electronic polarization in response to the average field and only want the part due to the nuclear motion itself. This is also the degree of freedom we are interested in as well: it maps linearly onto the motion of the nuclei.

Putting back in the sum over all the nuclei, the total energy variation is

$$\delta E_{tot} = -\sum_I F_I \cdot \delta R_I = \delta E^0_{tot} - V \sum_I (\delta P_I - \chi_\infty \delta \bar{\mathcal{E}}(R_I)) \cdot \bar{\mathcal{E}}(R_I)$$

where the energy E^0_{tot} is that "intrinsic" to the material system when $\bar{\mathcal{E}} = 0$, i.e. $\delta E^0_{tot} = -\sum_I F^0_I \cdot \delta R_I$. This formula says that the energy change is due to the zero field "intrinsic" part E^0_{tot} that is a known quantity plus a term coming from the field times a change in polarization. The change in polarization, however, is only the part coming from the nuclear motion as the part coming from electronic polarization is subtracted out explicitly: this is more clear if we write

$$\delta E_{tot} = \delta E^0_{tot} - \sum_I Z^*_I e \, \delta R_I \cdot \bar{\mathcal{E}}(R_I) \, .$$

So we need to figure out the macroscopic electric field in the system for a given configuration and then figure out how much each atom is moving. This already shows that a standard semiconductor like Si makes no direct contribution to the sum: $Z^* = 0$ for Si atoms (they are net neutral since the material is homopolar). In addition, to lowest order, imposing an electric field on Si just polarizes the electrons and doesn't move the nuclei themselves. In a standard semiconductor-ferroelectric-ideal metal sandwich, the only part contributing to the sum is the ferroelectric.

Therefore, the prescription for computing the energy change can be written as

$$\delta E_{tot} = \delta E^0_{tot} - V \sum_I \delta \tilde{P}_I \cdot \bar{\mathcal{E}}(R_I)$$

where $\tilde{P}_I$ is the part of the polarization coming from the nuclear motions alone

$$\delta \tilde{P}_I = \frac{Z^*_I e \delta R_I}{V} \, .$$

This result already shows that (a) we need only integrate over the ferroelectric region and not the semiconductor or the ideal metal, (b) the correct formula is of the $\bar{\mathcal{E}} dP$ form where $\bar{\mathcal{E}}$ depends on the state of the system and thus on the polarization P, and (c) to get the energy itself one must do the integral of $\bar{\mathcal{E}} dP$. **I think this settles the question of whether $\bar{\mathcal{E}} P$ or integral of $\bar{\mathcal{E}} dP$ is the right energy term.**