



Computational Physics Course

Learn to use software packages

[Home](#)

[More](#)

Modern theory of polarization

Modern theory of polarization

1. Motivation: Intuitive definition of polarization will be

$$\mathbf{P} = \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{r} r \rho(\mathbf{r})$$

but the result depends on the origin under the periodic boundary condition, making this definition inappropriate; the result also depends on how you take the unit cell. This is the well-known problem of the polarization. You may consider that the real sample is finite, so that the polarization should be defined by integrating over the whole sample. Then the integration can be transformed to the surface integration using the Green's theorem. But, there is a way to define it using the unit cell information only.

2. New approach: One can solve the problem by considering "flow of charge" associated with displacement of ions. Phenomenologically, the polarization occurs associated with the displacement, such that the polarization \mathbf{P} is zero at an initial configuration of ions but is nonzero at a displaced configuration. This fact makes it possible to define the polarization by connecting the initial unpolarized state to the final polarized state continuously and integrate the associated flow of charge.

$$\mathbf{P} = \int dt \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{r} \mathbf{j}(\mathbf{r}, t)$$

This "adiabatic" definition has made it possible to modernize the theory of polarization.

3. Formulation: Let us introduce a parameter λ connecting the unpolarized and the polarized states. By applying a first-order perturbation theory, change of the wave function can be written as

$$|\delta\psi_{nk}\rangle = -i\hbar\dot{\lambda} \sum_{m \neq n} \frac{\langle\psi_{mk}|\partial_{\lambda}|\psi_{nl}\rangle}{E_{nk} - E_{mk}} |\psi_{mk}\rangle$$

Corresponding current is

$$\mathbf{j}_n = \frac{d\mathbf{P}_n}{dt} = \frac{i\hbar e \dot{\lambda}}{(2\pi)^3} \sum_{m \neq n} \int d\mathbf{k} \frac{\langle\psi_{nk}|\mathbf{p}|\psi_{ml}\rangle \langle\psi_{mk}|\partial_{\lambda}|\psi_{nl}\rangle}{E_{nk} - E_{mk}} + c.c.$$

When this is rewritten using the periodic part of the Bloch wave function, we get

$$\frac{d\mathbf{P}_n}{dt} = \frac{ie\dot{\lambda}}{(2\pi)^3} \int d\mathbf{k} \langle \nabla_{\mathbf{k}} u_{nk} | \partial_{\lambda} u_{nk} \rangle + c.c.$$

This is appealing in that the contribution from the unoccupied states disappears and that the derivative with respect to k is now accessible with the most localized Wannier orbital method.

When summing over all the occupied states n and integration over t (to connect the initial and final states) we finally arrive at

$$P = \frac{e}{(2\pi)^3} \text{Im} \sum_n \int dk \langle u_{nk} | \nabla_k | u_{nk} \rangle$$

This is equivalent to the Berry phase theory and thus we can regard $i \langle u_{nk} | \nabla_k | u_{nk} \rangle$ as a Berry connection or gauge potential.

4. Quantum of polarization: Suppose we are integrating over a one-dimensional Brillouine zone;

$$P_n = \frac{e}{2\pi} \phi_n = \frac{e}{2\pi} \text{Im} \int_{-\pi/L}^{\pi/L} dk \langle u_{nk} | \partial_k | u_{nk} \rangle$$

The initial and final points are equivalent because of the periodicity. So, we are integrating over a closed loop.

The phase of the wave function can be taken arbitrarily like

$$\tilde{u}_{nk} = e^{-i\beta(k)} u_{nk}$$

except that the difference at the boundary $\beta(\pi/L) - \beta(-\pi/L)$ is a multiple of 2π .

When the polarization is calculated using this new wave function, we get

$$\tilde{\phi}_n = \phi_n + 2\pi m$$

indicating that the polarization can be defined within the modulo of e .

When this discussion is extended to a 3D system, we find that the polarization is well defined within the modulo of

$$eR/\Omega$$

where R is a lattice vector

$$R = \sum_j m_j R_j$$

5. Wannier center: It is possible to show that the polarization is equal to the Wannier center

$$P_n = \frac{e}{\Omega} (r_{nR} - R) = \frac{e}{\Omega} (\langle w_{nR} | r | w_{nR} \rangle - R)$$

where w_{nR} is the Wannier orbital defined as

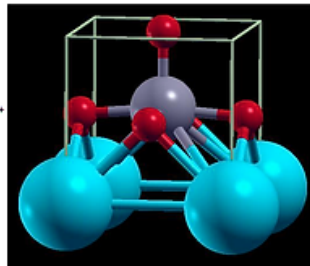
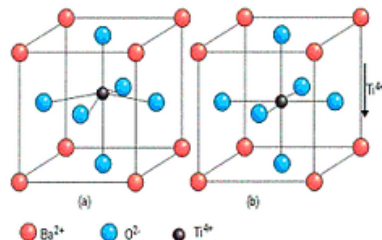


PDF

Slightly modified version available as pdf



$$\langle \psi_{n,\mathbf{k}} | \psi_{m,\mathbf{k}} \rangle = \frac{\Omega}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \psi_{n,\mathbf{k}} | \psi_{m,\mathbf{k}} \rangle$$



Let us study the "modern theory of polarizability" using BaTiO₃ as an example.

Today, we follow the procedures

1. Calculate the Berry's phase
2. Obtain the value for the polarization

Having learned the theory, we come back to the simulation. For this purpose, we follow the tutorial introduced in the portal site of Quantum Espresso (QE), which was prepared by Dr. Sharmila Shirodkar. Let us download the tutorial from http://www.iiserpune.ac.in/~smr2626/hands_on/week2/july10/Hands_on_berry.tar.gz

The next task is to download the pseudopotentials specified in the tutorial. We need the pseudopotentials of Ba, Ti, and O. Let us get them from

<http://www.quantum-espresso.org/pseudopotentials/>

You need to download the PP of Ba, Ti, and O constructed using the PBE functional, ultrasoft PP, and scalar relativistic scheme:

Ba.pbe-nsp-van.UPF

Ti.pbe-sp-van_ak.UPF

O.pbe-rrkjus.UPF

We will then execute the shells shown in exercise-1 and exercise-2.

Exercise-1 is done as a check. Here we calculate the polarization of a symmetric tetragonal BaTiO₃, and confirm that the polarization is zero as it should be. To do the check calculation, make sure that the pseudopotential files are correctly

Deadline of the report is 17-th January 2018.

Important!!

This calculation takes longer time with the new versions of QE. What is worse, the program will be trapped in finalizing the calculation, after writing important results.

A possible solution is to use the older version of QE, such as 5.0 or later. You may run this by building yourselves, or more conveniently, by using a command `#sudo apt-get install quantum-espresso`

In this case, PATH may be troublesome. Possibly the safest way is to make another linux system in your VMware/virtual box to be used only for this older version.

Sorry for this inconvenience.

specified in the input files: sy.scf.in and sy.bsfc.in. The former is used for getting the self-consistent electron density and the latter is used for getting the polarization. Make also sure that executable file pw.x is correctly assigned in the shell file job_sy.sh: The address shown in the original shell file will not be appropriate in your environment. After making the shell file executable by `chmod +x job_sy.sh`, execute it. Then, open the output files to make sure that scf convergence is met and that the polarization is calculated to be zero.

Exercise-2 is done to calculate the polarization of asymmetric tetragonal BTO, which has a finite polarization. We start from a non-distorted BTO and relax the structure using `pw.x < relax.in > relax.out`. You will see from the output file that the atoms are displaced from the initial position and the atomic force is gradually reduced. Then, use the optimized geometry to get the corresponding polarization.



Having learned DFT, let us move to learning program packages. We begin by learning Quantum Espresso

The University of Tokyo

© 2016 by Osamu Sugino

