

1 Ionic and electronic polarizations, ambiguities

For our purposes, “polarization” is what we intuitively consider the electrical dipole moment per unit volume of a sample, P . For any material, we further break this down into the contribution from the nuclei (or ionic cores if we are only considering valence electrons) and from the electrons. Hence,

$$P = P_{ion} + P_e . \quad (1)$$

If we treat the ions as point particles, which is often sufficient for most material problems, we can write P_{ion} in a crystalline environment as

$$P_{ion} = \frac{1}{\Omega} \sum_j Z_j e r_j \quad (2)$$

where Ω is the volume of our unit cell, j ranges over the ions in the unit cell each with charge $Z_j e$ and position vector r_j . Here, the quantum of charge is $e > 0$.

Already at this point, ambiguities appear: depending on how we choose our unit cell and basis, we get different answers for P_{ion} . It turns out that all the different possible results differ by “quanta” of polarization, eR/Ω where R is any lattice vector. The reason is that moving the boundary of the unit cell will cause some ions to exit and their periodic copies to enter from the other side, causing a “jump” of the position by a lattice vector R . Thus this ambiguity, though always present, is not any fundamental problem if we stick with a given unit cell choice, slowly move our atoms and keep track of their motions across boundaries to make sure P doesn’t have any discontinuous jumps.

The real problem is how to deal with the electronic contribution P_e . Electrons are not localized in solids but are distributed in bonds (or itinerant in metals). We can describe their density with continuous field $n(r)$, the density of electrons per unit volume at position r . A naïve formula for P_e would read

$$P_e \stackrel{?}{=} \frac{-e}{N\Omega} \int d^3r n(r) r . \quad (3)$$

Here N is the number of unit cells in the total system. This formula is well defined for a molecular-type system: the electrons are confined to a particular region of space, $N = 1$ since we have only a single unit cell, and the integral makes sense and is convergent. However, in an ideal infinite crystal, $n(r)$ is periodic, the integral is not sensibly defined since r is not bounded, and $N \rightarrow \infty$. A more careful analysis shows that *any* answer is possible depending on how the limit of an infinite crystal is approached.

Another way to state this is that the position operator r is not well-defined in an infinite crystal, so we should not expect an expression of the type in Eq. (3) to give sensible results. However, it is physically obvious that the electrons must have some well defined polarization P_e : after all, one can impose an (AC) electric field on a sample and measure the induced electronic polarization! So the question is really a theoretical one of how one is to define and compute P_e sensibly.

2 First solution: Wannier functions

The most direct approach to the problem is to note that the reason the ionic contribution P_{ion} was so easy to define was because the ions are well localized electric point charges. If we can create a localized description of the electrons, we should be able to define P_e easily. This is possible by using Wannier functions.

In solid state theory, we usually deal with Bloch functions $\psi_{nk}(r)$ which are labeled by a crystal momentum k and band index n ,

$$\psi_{nk}(r) = \frac{1}{\sqrt{N}} e^{ik \cdot r} u_{nk}(r). \quad (4)$$

Here $u_{nk}(r)$ is lattice-periodic, and the $N^{-1/2}$ factor is a convenient choice of normalization in a periodic crystal with N unit cells. Bloch states are eigenstates of the periodic crystalline Hamiltonian. We can trade in Bloch functions for Wannier functions by performing the following Fourier transform:

$$W_n(r - R) = \frac{1}{\sqrt{N}} \sum_k e^{-ik \cdot R} \psi_{nk}(r). \quad (5)$$

Here, there are N values of k being summed over in the first Brillouin zone (Born-von Karman boundary conditions). Each band n has one Wannier function $W_n(r)$ associated with it which can be translated by a lattice vector R to produce identical copies centered in different cells in the entire crystal. Wannier functions, just like the Bloch states, are an orthonormal basis. They are not the eigenstates of the crystal Hamiltonian. Wannier functions have the chief advantage of being well localized.¹ In fact, one can prove or argue that they are exponentially localized: $|W_n(r)| \sim \exp(-\gamma|r|)$ for $\gamma > 0$.

Using Wannier functions we can define a sensible and well-defined electronic polarization:

$$P_e = -\frac{e}{\Omega} \sum_n^{occ} \int d^3r |W_n(r)|^2 r \quad (6)$$

where we sum over the occupied bands. Note that we only use the Wannier functions for a single unit cell ($R = 0$) since we want the dipole moment per unit cell.

Eq. (6) is intuitively sensible, mathematically well-defined, gives the correct answer for the molecular limit or any finite crystal, etc. It is the answer to our problem. The “Modern Theory of Polarization” is concerned about computing this particular definition of P_e . From a theoretical viewpoint, one can claim to have solved the problem: (1) find the Bloch eigenstates ψ_{nk} of the crystalline Hamiltonian, (2) find the number of filled bands based on the number of electrons present, (3) perform the Fourier transform of Eq. (5) to compute the Wannier functions, and (4) use the Wannier functions in Eq. (6) to calculate P_e . In fact, each

¹See, for example, the references in Ismail-Beigi and Arias, *Phys. Rev. Lett.* **82** 2127 (1999).

Wannier function contribution in (Eq. (6) is the “average” position of the electron in that Wannier state: we have written the electronic polarization as a sum over average electronic positions in the same spirit as the ionic polarization.

If the reader is satisfied with this explanation, he or she can stop here since the main physical point has been conveyed. What follows is devoted to a more detailed study of how to calculate P_e in Eq. (6) in the Bloch representation and how P_e turns out to be a “Berry phase”.

3 P_e in the Bloch representation

The only problem with the above program is that Wannier functions are not uniquely defined. This is because we can start with any valid set of eigenstates ψ_{nk} and multiply them by an arbitrary phase and still obtain valid eigenstates:

$$\psi_{nk}(r) \rightarrow e^{i\theta_n(k)}\psi_{nk}(r). \quad (7)$$

(Actually, one can mix different band indices as well using a unitary transform at each k .) The phase $\theta_n(k)$ can be *any* smooth or discontinuous function of k . If we look back at the definition of the Wannier function in Eq. (5), we see that these choices change the Wannier function. This may be bad news because the meaningless and arbitrary choices of phases (called “choice of gauge” in this jargon) should not affect the physical answer for P_e , but it is not at all clear that our definition is unaffected by the phase changes.² Therefore, we may have to end up in the Bloch representation after all.

From a practical standpoint, even without such problems, it would be nice to be able to write P_e in terms of the Bloch functions ψ_{nk} directly so that one could compute P_e without having to create the intermediate Wannier functions. For these two reasons, we would like to write P_e in terms of the Bloch states.

Plugging in the definition of Wannier functions in terms of Bloch ones into Equation (6) yields

$$P_e = -\frac{e}{\Omega} \sum_n^{\text{occ}} \frac{1}{N} \sum_{k,k'} \langle \psi_{nk} | \hat{r} | \psi_{nk'} \rangle \quad \text{where} \quad \langle \psi_{nk} | \hat{r} | \psi_{nk'} \rangle = \int d^3r \psi_{nk}(r)^* \psi_{nk'}(r) r. \quad (8)$$

This expression is not well defined since the expectation $\langle \psi_{nk} | \hat{r} | \psi_{nk'} \rangle$ is not well defined: the integral ranges over the whole crystal and r is unbounded. Again, this shows the unsuitable nature of the the position operator r in an infinite crystal.

There are two ways to solve this problem and they turn out to be equivalent.

²It turns out, in the end, that P_e in terms of Wannier functions can be made “gauge invariant” and well-defined, but the point is not obvious.

3.1 Quick-and-dirty method

The quick-and-dirty method uses a math trick to get rid of r by replacing it with a derivative versus k . In this approach, we note that

$$-i\nabla_k\psi_{nk}(r) = -i\nabla_k \left[e^{ik\cdot r} u_{nk}(r)/\sqrt{N} \right] = r\psi_{nk}(r) - ie^{ik\cdot r} \nabla_k u_{nk}(r)/\sqrt{N}. \quad (9)$$

Here $u_{nk}(r)$ is the lattice periodic part of the Bloch function. So we have the relation defining r acting on a Bloch state in terms of k derivatives:

$$r\psi_{nk}(r) = ie^{ik\cdot r} \nabla_k u_{nk}(r)/\sqrt{N} - i\nabla_k\psi_{nk}(r) \quad (10)$$

Plugging this into Eq. (8), two things happen. First, the second term on the right in Eq. (10) vanishes when we integrate over k' because it is the derivative of $\psi_{nk'}$ integrated over a Brillouin zone and $\psi_{nk'}$ like all physical functions is periodic in the Brillouin zone. Second, $k = k'$ is enforced in the r integral because of the $e^{ik\cdot r}$ phases. We end up with

$$P_e = -\frac{e}{\Omega} \sum_n^{\text{occ}} \frac{1}{N} \sum_k \int_{\Omega} d^3r u_{nk}(r)^* i\nabla_k u_{nk}(r) = -\frac{e}{\Omega} \sum_n^{\text{occ}} \frac{1}{N} \sum_k \langle u_{nk} | i\nabla_k | u_{nk} \rangle. \quad (11)$$

Physically, comparing this to our Wannier function based expression in Eq. (6), we see that we can match all the terms if we identify the following integral as the expectation of r for the states in band n :

$$\langle r \rangle_n = \frac{1}{N} \sum_k \langle u_{nk} | i\nabla_k | u_{nk} \rangle. \quad (12)$$

The above expression is simple looking and well-defined but not very illuminating. We can justify it by saying that position and momentum are conjugate variables so that having a derivative versus k makes sense since we are trying to compute the expectation of r . But it is still unclear what is going on. This brings us to the second method.

3.2 More formal method

All our problems stem from the unboundedness of the r operator in a infinite crystal. A mathematical solution to the problem is to trade in r for a bounded but periodic operator. This is best illustrated in one dimension with periodic length L . We trade in x for the operator η

$$\eta = \exp(-2\pi ix/L).$$

So the η operator is just the position operator modulo L . That is, each position x modulo L is identified with a unique phase (or angle). In the infinite crystal limit, we send $L \rightarrow \infty$ and can label all x uniquely. For finite L , we are just working with periodic Born-von Karman boundary conditions, i.e. with a crystal made up of $L = Na$ unit cells (a is the unit cell length). Clearly, physical results are obtained for large L . The operator η is also bounded since it is just a unit phase with length 1.

Using η we now *define* the expectation of x or its matrix elements to be given by

$$\langle x \rangle \equiv \frac{iL}{2\pi} \ln \langle \eta \rangle. \quad (13)$$

This is a good definition because: (1) formally, for large L it matches the Taylor expansion of η in x ; (2) $\langle \eta \rangle$ is always well-defined since η is bounded; (3) for an electronic state that is localized about some point x_0 (e.g. a narrow Gaussian around x_0), $\langle x \rangle \approx x_0$ and $\langle \eta \rangle \approx \exp(-2\pi i x_0 / L)$ so again the definition works.

We can compute the expectation of η between a pair of Bloch states:

$$\begin{aligned} \langle \psi_{nk} | \hat{\eta} | \psi_{nk'} \rangle &= \frac{1}{N} \int_0^{Na} dx u_{nk}^*(x) e^{-ikx} e^{-2\pi i x / L} e^{ik'x} u_{nk'}(x) \\ &= \frac{1}{N} \int_0^{Na} dx u_{nk}(x)^* u_{nk'}(x) e^{i(k' - 2\pi/L - k)x} \\ &= \delta_{k', k+2\pi/L} \int_0^a dx u_{nk}(x)^* u_{n, k+2\pi/L}(x) \\ &= \delta_{k', k+2\pi/L} \langle u_{nk} | u_{n, k+2\pi/L} \rangle. \end{aligned}$$

The appearance of the delta function enforcing $k' = k + 2\pi/L$ is not a surprise since η is just a plane wave with wave vector $-2\pi/L$ so we get a selection rule relating k and k' . For large L , we can perform a Taylor expansion of the inner product $\langle u_{nk} | u_{n, k+2\pi/L} \rangle$,

$$\langle \psi_{nk} | \hat{\eta} | \psi_{n, k+2\pi/L} \rangle = 1 + \frac{2\pi}{L} \langle u_{nk} | \nabla_k u_{nk} \rangle + O(L^{-2}).$$

Plugging into Eq. (13), we find after a little algebra that

$$\langle \psi_{nk} | \hat{x} | \psi_{n, k+2\pi/L} \rangle = i \langle u_{nk} | \nabla_k u_{nk} \rangle + O(L^{-1}).$$

To leading order, we can ignore the difference between k and $k + 2\pi/L$ and just write

$$\langle \psi_{nk} | \hat{x} | \psi_{nk} \rangle = i \langle u_{nk} | \nabla_k u_{nk} \rangle + O(L^{-1}). \quad (14)$$

Looking back at Eq. (11), we see that we have just derived and justified the key definition of Eq. (12) in one dimension (for $L \rightarrow \infty$).

The generalization to three dimensions is very easy. We define

$$\eta = \exp(-i\epsilon \cdot r). \quad (15)$$

The vector ϵ is supposed to be very small (infinitesimal in the limit of an infinite crystal). We have made our system periodic in all three directions α with $\epsilon_\alpha = 2\pi/L_\alpha$. We define matrix elements of r via

$$\epsilon \cdot \langle r \rangle \equiv i \ln \langle \eta \rangle. \quad (16)$$

All the derivations follow through, and we end with the final result that

$$\epsilon \cdot \langle \psi_{nk} | \hat{r} | \psi_{nk} \rangle = i\epsilon \cdot \langle u_{nk} | \nabla_k u_{nk} \rangle. \quad (17)$$

Since ϵ is small but arbitrary, we have again justified the key definition Eq. (12) and thus the definition of P_e in Eq. (11).

3.3 Alternate interpretation: phase changes

The previous section may have helped clarify where the derivative in k is coming from. However, there is a nice physical interpretation of what is going on without the derivatives. Looking back, we see that the key relation we used was that

$$\langle \psi_{nk} | \eta | \psi_{n,k+\epsilon} \rangle = \langle \psi_{nk} | \exp(-i\epsilon \cdot r) | \psi_{n,k+\epsilon} \rangle = \langle u_{nk} | u_{n,k+\epsilon} \rangle. \quad (18)$$

That is, we are computing the overlap of u_{nk} with the same state but displaced by a small amount ϵ in k -space. Since both vectors are normalized and must become identical for $\epsilon = 0$, the overlap is just measuring the relative phase between the two states. More precisely,

$$\langle u_{nk} | u_{n,k+\epsilon} \rangle \cong e^{-i\delta\phi_{nk}} \quad (19)$$

where $\delta\phi_{nk}$ is a small phase proportional to ϵ . The expectation of r in state ψ_{nk} is thus just this very phase change:

$$\epsilon \cdot \langle \psi_{nk} | \hat{r} | \psi_{nk} \rangle = \delta\phi_{nk}. \quad (20)$$

Using this expression, we see that the expectation of r in band n of Eq. (12) is given by the average over all the phase changes:

$$\epsilon \cdot \langle r \rangle_n = \frac{1}{N} \sum_k \delta\phi_{nk}. \quad (21)$$

Thus we can say that the expectation of r (or the polarization) in a given direction is given by adding up the relative phase changes of the periodic functions in that direction across the Brillouin zone.

4 Berry phases

The statement ending the previous section is equivalent to saying the the polarization is given by a Berry phase. As a quick reminder, I give a simple sketch of how Berry phases come around.³

4.1 Review of Berry phases

Berry phases are best motivated by considering what happens to a quantum system when we change an external parameter adiabatically. To be concrete, imagine we have a spin-1/2 system in an external magnetic field. The ground state for a static field has the spin

³The following section is lifted pretty much verbatim from one of Sakurai's appendices: J. J. Sakurai, Modern Quantum Mechanics (Addison Wesley).

aligned with the field. If we then adiabatically change the direction of the field, we intuitively expect the spin to stay in the eigenstate polarized along the field at all times: it adiabatically “follows” the magnetic field. The math shows this to be true but with an extra phase factor.

The Hamiltonian depends on the field B parameterically, so we will write $H(B)$ for the Hamiltonian. For a given B , write the eigenstates of $H(B)$ as $|\phi_n(B)\rangle$ with energies $E_n(B)$,

$$\hat{H}(B)|\phi_n(B)\rangle = E_n(B)|\phi_n(B)\rangle. \quad (22)$$

What we want to do is to solve the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(B(t))|\psi(t)\rangle. \quad (23)$$

We have written $B(t)$ since the magnetic field will slowly change in time. Let’s write our state $|\psi(t)\rangle$ in terms of the instantaneous eigenstates $|\phi_n(B(t))\rangle$ in the following way:

$$|\psi(t)\rangle = \sum_n a_n(t)|\phi_n(B(t))\rangle e^{-\frac{i}{\hbar}\int_0^t dt' E_n(B(t'))}. \quad (24)$$

We start the system at time $t = 0$ in the ground state $n = 0$: $a_n(0) = \delta_{n,0}$. If the adiabatic hypothesis is true, then as a function of time, we expect only $a_0(t)$ to be sizable and for the rest of the $a_n(t)$ to be small. And the expansion is designed so that in such a case, our state $|\psi(t)\rangle$ is just in the eigenstate for the current value of $B(t)$ (so it will “follow” the field). The extra phase factor is needed to make things work nicely.

Using the Schrödinger equation and the orthonormality of the ϕ_n , it is easy to derive the equation of motion for the $a_n(t)$:

$$\begin{aligned} \frac{da_n(t)}{dt} &= -a_n(t)\langle\phi_n(B(t))|\frac{d}{dt}\phi_n(B(t))\rangle \\ &\quad - \sum_{m \neq n} a_m(t)\langle\phi_n(B(t))|\frac{d}{dt}\phi_m(B(t))\rangle e^{-\frac{i}{\hbar}\int_0^t dt' [E_m(B(t')) - E_n(B(t'))]}. \end{aligned} \quad (25)$$

So far everything has been exact. Now we note that in the above equation, the terms with $m \neq n$ are oscillatory in time because of the phase factor, so their contribution to $a_n(t)$ will be quite small: this is especially true since $B(t)$ is varying slowly so we are averaging over very many oscillations. Thus we can drop the second term. What this means is that if we start in state n at $t = 0$, the “leakage” to the other states is very small and oscillatory and vanishes in the adiabatic limit.

Using the chain rule we get

$$\frac{da_n(t)}{dt} \cong -a_n(t)\langle\phi_n(B(t))|\nabla_B\phi_n(B(t))\rangle \cdot \dot{B}(t). \quad (26)$$

This equation is easy to integrate. We get

$$a_n(t) \cong a_n(0) \exp\left(-\int_0^t dt' \langle\phi_n(B(t'))|\nabla_B\phi_n(B(t'))\rangle \cdot \dot{B}(t')\right). \quad (27)$$

We now introduce a few factors of i and also change the integral to be over the magnetic field ($dB = dt' \dot{B}(t')$):

$$a_n(t) \cong a_n(0) \exp \left(i \int_{B(0)}^{B(t)} dB \cdot \langle \phi_n(B) | i \nabla_B | \phi_n(B) \rangle \right). \quad (28)$$

What does this mean? If we start in a particular state n at time $t = 0$, i.e. $|\psi_n(t = 0)\rangle = |\phi_n(B(0))\rangle$, then we stay in the same n -state adiabatically. This is what we expected. The new thing is the extra phase factor in Eq. (28), the *Berry phase*. It is a dynamic phase accumulated by the system as it evolves adiabatically. The phase depends only on the path we have taken in the parameter space (here $B(t)$). The phase is not an artifact and has physical consequences. For example, in our spin-1/2 problem we can take the magnetic field and slowly rotate it through 360° which brings us back where we started. Calculation of the integral shows that the quantum state of the spin-1/2, however, picks up a phase of exactly -1 . But this is as it should be: spin-1/2 objects must be rotated 720° degrees to become themselves again.

4.2 Polarization as a Berry phase

Looking at Eq. (28), we see that the Berry phase is given by the integral of i times the derivative of the overlap of the state versus the parameter being changed. Comparing this to our equation for P_e in terms of Bloch states Eq. (11), we see that we have exactly the same structure. Here the parameter being “changed” is the crystal momentum k .

To be more precise, we choose some particular axial direction, say x , and write the expression for P_e along this direction after changing the sums over k into integrals:

$$(P_e)_x \propto -\frac{e}{\Omega} \sum_n^{occ} \int dk_y \int dk_z \left(\int dk_x \langle u_{nk} | i \frac{\partial}{\partial k_x} | u_{nk} \rangle \right). \quad (29)$$

The object in the parenthesis is a Berry phase for adiabatically changing our periodic Bloch state along the k_x direction across the Brillouin zone. Staring at this formula for a few moments and comparing it to the other things we have derived shows that we can phrase it in the following way: the polarization along x is given by the average in the (k_y, k_z) plane of the Berry phase for adiabatic transport of the Bloch states along k_x .

While this result regarding the relation of the Berry phase and polarization is interesting from a theoretical point of view and helps make connections to other theoretical realms, it is not clear to me that it is very useful practically or it really helps advance things forward in doing research in the pragmatic sense.

4.3 Using the formalism

Clearly, being able to calculate the polarization will allow one to see ferroelectric transitions and the ferroelectric dipole. One can also compute other quantities depending on the development of dipoles. For example, when we move an ion in an insulator in its electronic ground state, we cause charge to be transferred about and dipoles to be formed (or changed). To be quantitative, we can write the linear response of P to the motion of the ions as

$$\delta P = \frac{e}{\Omega} \sum_j [Z_j^*] \cdot \delta r_j. \quad (30)$$

The quantity $[Z_j^*]$ is called the Born effective or dynamical charge. It is the charge that the ion acts like it has when moved by a small amount (generally a tensorial quantity). It differs from the bare scalar charge Z_j because when we move the ion, the electrons redistribute as well. It is the total charge motion that is the effective charge. In many materials, Z^* and Z have the same sign but different magnitudes and the differences can be large. In addition, the Z^* also can be quite different than formal ionic charges one assumes from basic chemistry. Z^* is useful for many reasons one is which is because it tells us how the ions respond to external fields: the force on ion j due to an electric field \mathcal{E} is $[Z_j^*]e \cdot \mathcal{E}$.

Once we can define P , we can include a uniform external electric field into a total-energy density functional type formalism directly. The total energy as a function of the electron wave functions, ionic positions, and external field is

$$E_{tot}(\{\psi_{nk}\}, \{r_j\}, \mathcal{E}) = E_{KS}(\{\psi_{nk}\}, \{r_j\}) - \Omega \mathcal{E} \cdot P(\{\psi_{nk}\}) \quad (31)$$

where E_{KS} is the standard expression for the Kohn-Sham total energy of an electron system (kinetic+ionic+Hartree+exchange correlation energies) per unit cell and the additional term is the term due to the external field coupling to the polarization in a unit cell. At the self-consistent minimum, E_{tot} is variationally optimized versus ψ_{nk} so that the change in E_{tot} versus electric field and ionic motions is

$$\delta E_{tot} = \sum_j \left(\frac{\partial E_{KS}}{\partial r_j} - Z_j e \mathcal{E} \right) \cdot \delta r_j - \Omega P \cdot \delta \mathcal{E} = - \sum_j F_j \cdot \delta r_j - \Omega P \cdot \delta \mathcal{E}. \quad (32)$$

(Note that for non-zero \mathcal{E} , the electronic states ψ_{nk} and density $n(r)$ are perturbed so that the term $\partial E_{KS}/\partial r_j$ implicitly includes terms of linear and higher order in \mathcal{E} .) The term multiplying δr_j is just the force F_j on ion j . The first observation is that

$$\frac{\partial E_{tot}}{\partial \mathcal{E}} = -\Omega P$$

as it should since \mathcal{E} and P are conjugate variables. Second, when $\mathcal{E} = 0$, the equilibrium condition of zero forces is the usual one. As another example, when we look for variations of P versus r_j at $\mathcal{E} = 0$, we get

$$\frac{e[Z_j^*]}{\Omega} = \left. \frac{\partial P}{\partial r_j} \right|_{\mathcal{E}=0} = -\frac{1}{\Omega} \frac{\partial^2 E_{tot}}{\partial r_j \partial \mathcal{E}} = -\frac{1}{\Omega} \frac{\partial^2 E_{tot}}{\partial \mathcal{E} \partial r_j} = \frac{1}{\Omega} \frac{\partial F_j}{\partial \mathcal{E}}$$

so that in fact, as asserted above, the Born effective charge gives the linear response force that develops on atom j when a weak field is applied.

At any rate, having a computational framework that can solve the density functional problem at finite \mathcal{E} means we can compute arbitrary responses to electric fields \mathcal{E} by simply increasing its strength or changing its direction and computing various observables like total energies, ionic forces, polarization, etc.

One important quantity is the linear dielectric response tensor. If we allow only the electrons to respond and fix the ions at the $\mathcal{E} = 0$ equilibrium position, we are considering electric fields that have high enough frequency so that phonon vibrations can not follow them but the electrons follow the fields adiabatically (obviously, we are talking about an insulator). This defines the tensor ϵ^∞

$$\epsilon^\infty = I + 4\pi\chi^\infty = I + 4\pi \left. \frac{\partial P_e}{\partial \mathcal{E}} \right|_{\mathcal{E}=0}. \quad (33)$$

For a system of high symmetry, this is a scalar and is also called the ‘‘optical’’ dielectric constant. If we have a low enough frequency electric field, the ions will also follow adiabatically, and we find the static dielectric tensor ϵ^0

$$\epsilon^0 = I + 4\pi\chi^0 = I + 4\pi \left. \frac{\partial P}{\partial \mathcal{E}} \right|_{\mathcal{E}=0}. \quad (34)$$

From a computational viewpoint, for ϵ^∞ we simply turn on a weak \mathcal{E} , achieve self-consistency, and look at the change in P_e . For ϵ^0 , we must also relax the ionic positions to their new equilibrium as well and then look at the total change in P .

The alternative method to compute the dielectric response is to use linear response theory. This is more general, more complicated, and also more limited in that it can only compute linear response (where as the above scheme can work at any finite \mathcal{E} and thus gives non-linear responses as well). After one has computed ϵ^∞ via linear response, the formula for ϵ_0 is

$$\epsilon_{\alpha\beta}^0 = \epsilon_{\alpha\beta}^\infty + \sum_m \frac{4\pi e^2 \tilde{Z}_{m\alpha}^* \tilde{Z}_{m\beta}}{\Omega \omega_m^2}, \quad \tilde{Z}_{m\alpha}^* = \sum_{j\gamma} \frac{Z_{j,\alpha\beta}^* \xi_m(j\gamma)}{\sqrt{M_j}}$$

where m labels phonons at zero wave vector with frequencies ω_m and atomic displacement vectors $\xi_m(j\gamma)$ (α, β, γ label axis directions). One needs to compute the Born charges as well as phonon properties. The formula is sensible as it says the ionic response depends on the Born charges (since the ions are pushed by the field and also the ions and electrons respond) as well as the frequencies since the softness or hardness of the phonon modes mean that the system responds well or poorly to the external field.

There is one remaining technical point: one can not make the field strength \mathcal{E} arbitrary. In fact, in an infinite system, a constant field \mathcal{E} will cause an infinite potential drop which will force all electrons out of the crystal and into the infinite well. Since we are using periodic boundary conditions, however, the potential drop is not infinite but given by the supercell

size L times \mathcal{E} . Thus $L \cdot |\mathcal{E}|$ should be smaller than the band gap of the system. As we increase the density of k-point sampling, L gets larger which means the maximum allowable field drops! Thus there is a tradeoff in a practical calculation.

In greater detail, the actual calculation corresponds to a spatially varying cosine field with wave vector $2\pi/L$. Namely, our position operator is really $\exp(-2\pi ix/L)$ and a potential oscillating with that wave vector and corresponding to field strength \mathcal{E} is given by $\phi \sim \mathcal{E}L/(2\pi) \cos(2\pi x/L)$. We are just insisting that the maximum and minimum points of the sinusoid at 0 and $L/2$ give a potential difference that is less than the band gap so the electrons are only weakly perturbed by the external field.