

Esercitazione °4: Calculation of the macroscopic susceptibility as long-wave limit of a sinusoidal modulated perturbation

Exercise I :

1. Definitions - uniform electric field

   The electric susceptibility tensor is gives the relation:

$$\Delta \mathbf{P} = \boldsymbol{\chi} \mathbf{E} \tag{1}$$

   where $\Delta \mathbf{P}$ is the macroscopic polarisation (electric dipole per unit volume) linearly induced by $\mathbf{E}$. $\mathbf{E}$ is the macroscopic (uniform) electric field. $\boldsymbol{\chi}$ is a dimensionless 3x3 tensor. In a finite (insulating) solid (with insulating surfaces) of volume V the polarisation is defined as:

$$\mathbf{P} = \frac{-|e|}{V} \int_V d^3 r \mathbf{r} \rho(\mathbf{r}), \tag{2}$$

   and the induced polarisation is define as:

$$\Delta \mathbf{P} = \frac{-|e|}{V} \int_V d^3 r \mathbf{r} \rho^{(1)}(\mathbf{r}) E, \tag{3}$$

   where $\rho^{(1)}(\mathbf{r})$ is the linearly induced charge by the perturbing Hamiltonian[1]:

$$H^{\text{pert}} = |e| \mathbf{E} \cdot \mathbf{r}. \tag{4}$$

   Show that, using the Hellmann-Feynman theorem:

$$\mathbf{P}(\mathbf{E}) = -\frac{d\mathcal{E}(\mathbf{E})}{d\mathbf{E}}, \tag{5}$$

   where $\mathcal{E}$ is the total energy of the solid per unit volume. As a consequence show that:

$$\boldsymbol{\chi} = -\frac{d^2 \mathcal{E}}{d\mathbf{E} d\mathbf{E}}. \tag{6}$$

   Thus the quadratic variation of the electronic energy of the solid with respect to the electric field is

$$\Delta \mathcal{E} = -\frac{1}{2} \mathbf{E} \boldsymbol{\chi} \mathbf{E} \tag{7}$$

   This last two equations are valid (well-defined) also in an infinite (insulating) solid.

[1] To keep the system in an insulating ground state, we suppose that $|e||\mathbf{E}|L \ll \varepsilon_{\text{gap}}$, where L is the dimension of the finite solid in the direction of the field and ε_{gap} is the band-gap of the insulator. To avoid the electrons, pushed by $\mathbf{E}$, to jump in the vacuum, we also suppose to have an infinite barrier for the electrons in the vacuum region

2. Definitions - modulating field

We now consider a modulating electric field in the $\hat{\mathbf{x}}$ direction:

$$\mathbf{E}(\mathbf{r}) = -\sqrt{2}\epsilon \sin(qx)\hat{\mathbf{x}}. \tag{8}$$

The corresponding electron potential is:

$$V(\mathbf{r}) = \frac{\sqrt{2}\epsilon|e|}{q}\cos(qx) = \frac{\sqrt{2}\epsilon|e|}{q}\left(\frac{e^{iqx}+e^{-iqx}}{2}\right). \tag{9}$$

In the long wavelength limit (namely if $1/q$ is much larger than the size of the unit cell of the crystal) we can suppose that in each point of the crystal the field can be considered uniform on the scale of the unit cell. Under this hypothesis we can define a "local macroscopic polarisation" (uniform on the microscopic periodic-cell scale but non uniform on the macroscopic one), $\mathbf{P}^{(1)}(\mathbf{r})$, that has as x component:

$$P_x^{(1)}(\mathbf{r}) = -\sqrt{2}\epsilon \sin(qx)\chi_{xx}. \tag{10}$$

The variation of the energy if the solid per unit volume would be:

$$\Delta\mathcal{E} = -\frac{1}{V}\int_V d^3r \frac{1}{2}\mathbf{E}(\mathbf{r})\boldsymbol{\chi}\mathbf{E}(\mathbf{r}) = -\frac{\chi_{xx}\epsilon^2}{V}\int_V d^3r \sin^2(qx) = -\frac{1}{2}\chi_{xx}\epsilon^2. \tag{11}$$

This equation tell us that we can obtain χ_{xx} from the limit:

$$\chi_{xx} = -\lim_{q\to 0}\mathcal{E}^{(2)}(q) \tag{12}$$

where $\mathcal{E}^{(2)}(q)$ is the second derivative of the total electronic energy of the solid with respect to ϵ considering the finite q perturbation given by the sinusoidal potential of Eq. (9). Notice that $\mathcal{E}^{(2)}(q)$ is defined for every value of q (small or large) and not only in the $q \to 0$ limit. the The goal of this exercise is to use linear response theory to compute $\mathcal{E}^{(2)}(q)$ and then to obtain χ_{xx} by considering the limit $q \to 0$.

3. Calculation of $\mathcal{E}^{(2)}(q)$

Let's consider a periodic insulating solid with Bloch function $|\psi_{\mathbf{k}i}\rangle = \frac{1}{\sqrt{N}}e^{i\mathbf{k}\cdot r}|u_{\mathbf{k}i}\rangle$ eigenvectors with eigenergies $\varepsilon_{\mathbf{k}i}$. Notice that the periodic part of the Bloch functions, $|u_{\mathbf{k}i}\rangle$ is eigenvector of the $\mathbf{k}$-dependent Hamiltonian $H_{\mathbf{k}}$. We will neglect, in the response, the Hartree and Exchange-correlation by setting $K_{Hxc} = 0$.

(a) Demonstrate that

$$\mathcal{E}^{(2)}(q) = 4\frac{e^2}{2q^2}\int \frac{d^3k}{(2\pi)^3}[F_{\mathbf{k}}(q) + F_{\mathbf{k}}(-q)], \tag{13}$$

where

$$F_{\mathbf{k}}(q) = \sum_i^{\text{occupied}}\sum_j^{\text{empty}} \frac{\langle u_{\mathbf{k}i}|u_{(\mathbf{k}+q\hat{\mathbf{x}})j}\rangle\langle u_{(\mathbf{k}+q\hat{\mathbf{x}})j}|u_{\mathbf{k}i}\rangle}{\varepsilon_{\mathbf{k}i} - \varepsilon_{(\mathbf{k}+q\hat{\mathbf{x}})j}} \tag{14}$$

(b) Demonstrate that $F_{\mathbf{k}}(0) = 0$

4. Perform the $q \to 0$ limit

(a) Demonstrate that for a differentiable function $f(x)$,

$$\lim_{x\to 0} \frac{f(x) + f(-x) - 2f(0)}{x^2} = \frac{d^2 f(0)}{dx^2} \tag{15}$$

(b) Write the explicit expression for $H_{\mathbf{k}}$ and compute

$$\frac{dH_{\mathbf{k}}}{d\mathbf{k}} \tag{16}$$

(c) Demonstrate using perturbation theory that if $\varepsilon_{\mathbf{k}i} \neq \varepsilon_{\mathbf{k}j}$

$$\langle u_{\mathbf{k}i}| \frac{d|u_{\mathbf{k}j}\rangle}{d\mathbf{k}} = \frac{\hbar}{m_e} \frac{\langle u_{\mathbf{k}i}|\mathbf{p}|u_{\mathbf{k}j}\rangle}{\varepsilon_{\mathbf{k}j} - \varepsilon_{\mathbf{k}i}} \tag{17}$$

(d) Demonstrate using Eq. (12) that:

$$\chi_{xx} = 4\frac{\hbar^2 e^2}{m_e^2} \int \frac{d^3k}{(2\pi)^3} \sum_i^{\text{occupied}} \sum_j^{\text{empty}} \frac{|\langle u_{\mathbf{k}j}|p_x|u_{\mathbf{k}i}\rangle|^2}{(\varepsilon_{\mathbf{k}j} - \varepsilon_{\mathbf{k}i})^3} \tag{18}$$