Microscopic calculation of the constitutive relations

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Abstract. Homogenization theory is used to calculate the macroscopic dielectric constant from the quantum microscopic dielectric function in a periodic medium. The method can be used to calculate any macroscopic constitutive relation, but it is illustrated here for the case of electrodynamics of matter. The so-called cell problem of homogenization theory is solved and an explicit expression is given for the macroscopic dielectric constant in a form akin to the Clausius-Mossotti or Lorentz-Lorenz relation. The validity of this expression is checked by showing that the standard formula is recovered for cubic materials and that the average of the microscopic energy density is the macroscopic one. Finally, the general expression is applied to Bloch eigenstates.

PACS. 77.22.Ch Permittivity (dielectric function) – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity) – 03.50.De Classical electromagnetism, Maxwell equations

1 Introduction

When light falls onto a crystal, the quantum interaction of light with matter is represented locally by a microscopic dielectric function $\epsilon(\mathbf{r}, \mathbf{r}')$. To calculate the macroscopic (homogeneous) dielectric constant, one considers that the charge distribution created by the light polarizes the crystal which, in turn, reacts by inducing an electric field that modifies the charge distribution.

In quantum chemistry, this reaction field represents the influence of the solvent on the solute [1–3]. Other descriptions use the related concept of local fields [4,5], which has been described, for disordered media, by a cluster expansion [6–9].

For periodic media, the local field effect was evaluated in the early sixties by Adler [10] and Wiser [11]. However, many textbooks in solid-state physics still identify the macroscopic dielectric constant $\bar{\epsilon}$ with $\langle\epsilon\rangle$, the average of the microscopic dielectric function $\epsilon(\mathbf{r}, \mathbf{r}')$ over a unit cell. Even the most cautious authors [12–14] do not go beyond the relation $\bar{\epsilon} = \epsilon_0(\epsilon_0 + 2\langle\epsilon\rangle)/(4\epsilon_0 - \langle\epsilon\rangle)$, that goes by the name of Clausius-Mossotti or Lorentz-Lorenz (see Refs. [15–17] for a history of this relation). Since the local

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field effect can be quite large [18], its neglect can probably be attributed to the numerical burden of the standard local field formula [10,11].

In this paper, homogenization theory will be used to provide various alternative formulas for the calculation of the local field effects. Homogenization theory is tailored to calculate the macroscopic $\bar{\epsilon}$ from the microscopic $\epsilon(\mathbf{r}, \mathbf{r}')$. The major trick of the method is to expand all fields as a series in ascending powers of the ratio of the lattice parameter over the wavelength of the external electromagnetic field. Physicists have sometimes used such an expansion [19], but mathematicians exploited it extensively and turned it into a rigorous tool. Homogenization theory is a branch of applied mathematics that started its expansion in the late seventies [20,21] to understand the macroscopic properties of composite, porous, disordered, bubbly, fibrous or layered materials. It is now a fully fledged theory [22] that has been applied successfully in many areas, such as mechanics, acoustics, electrostatics, fluid dynamics, statistical physics, numerical analysis, materials sciences, electromagnetism [23], petroleum geophysics [24], shape-memory alloys [25] and pile foundation analysis [26].

This paper starts with an introduction to homogenization theory, then the microscopic Maxwell equations are homogenized to yield the macroscopic Maxwell equations

and the constitutive relations. Since homogenization theory is not a usual tool of solid state physics, the calculations in these sections will be given in detail. The rest of the article will follow the elliptic style of normal research papers. Various formulas will be given, corresponding to different physical situations. Then, several desirable properties of the dielectric constant will be derived. It will be shown that the macroscopic dielectric constant gives the expected energy density and Poynting vector. The formalism is adapted to the case of Bloch eigenstates and a band-structure formula for $\bar{\epsilon}$ is given.

2 The point of view of homogenization theory

Ever since the nineteenth century, physicists have homogenized microscopic systems by performing averages over distances very small compared to the macroscopic wavelength and very large compared to the atomic dimensions. Mathematical homogenization started when homogenization was not considered any longer as an averaging operation, but as a limit process. As an example, consider that a microscopic quantity can be represented by the periodic function $f(x) = \sin x + b$. To express the fact that the oscillation is very fast, mathematicians tried to give a meaning to the limit of $f(x/a)$ as $a \to 0$. In other words, what is the limit of a periodic function when its period becomes infinitely small?

The contact with the physical point of view comes from the fact that the limit is the average of $f(x)$ over a period: $f(x/a) \to b$ as $a \to 0$. However, Figure 1 shows that this limit is somewhat unusual. Physicists generally do not bother very much with the various mathematical limits, but in the present case, it is necessary to realize that we do not deal with a strong limit, but with a weak limit. Strong convergence of $f(x)$ to its limit b, which means that, for a fixed L, $\int_0^L dx|f(x/a) - b| \to 0$ as $a \to 0$, is clearly not realized for oscillating functions (for our example, $\int_0^L dx|f(x/a) - b| \to 2L/\pi$). Oscillating functions enjoy only weak convergence, which is defined by the fact that, for any smooth function $g(x)$, $\int_0^L dxg(x)f(x/a) \to b\int_0^L dxg(x)$ as $a \to 0$. In physical terms, the fast oscillations of $f(x/a)$ are smoothed away by measuring $f(x/a)$ with a device having a finite resolution $g(x)$.

Strong convergence enjoys many nice properties, for instance the product of two strongly convergent functions converges to the product of the limits, but no such thing is available for weak convergence. In our example, the weak limit of $f^2(x/a)$ is $b^2 + 1/2$ and not b^2. Since it is clear that the average of the product of two functions is not the product of the averages of the functions, the reader may wonder why it is useful to consider homogenization as a limit instead of an average. The advantage of homogenization as a limit is twofold. On the first hand, it leads naturally to an asymptotic expansion of the functions in terms of a (i.e. $f(x/a) \to b + af^{(1)}(x/a) + \cdots$), so that corrections to the average become available. On the other
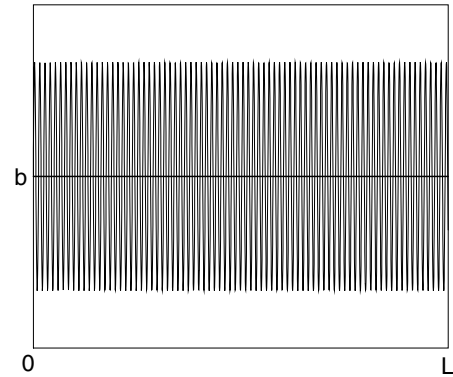

Fig. 1. Limit of $\sin(x/a) + b$ as $a \to 0$.

hand, it enables us to treat not only functions but also differential equations.

The way mathematical homogenization deals with differential equations can be illustrated by a simple example [20]. Consider a wire of length L, uniformly charged with a constant charge density n. A potential V is applied between both ends of the wire, and the wire is assumed to have a periodic structure represented by the periodic dielectric function $\epsilon(x/a)$. Standard electrostatic theory tells us that there is a potential $\phi(x)$ such that the electric field $e(x) = -\phi'(x)$. The microscopic constitutive relation is $d(x) = \epsilon(x/a)e(x)$, and the electrostatic equation $d'(x) = n$ gives us the equation $(\epsilon(x/a)\phi'(x))' = -n$, with the boundary conditions $\phi(0) = 0$, $\phi(L) = V$. For simplicity, we assume that L corresponds to an integer number of periods $2\pi a$. This electrostatic equation has a unique solution $\phi(x)$ for each a

$$\phi(x) = C \int_0^x \frac{dt}{\epsilon(t/a)},$$

where the constant C is determined by the boundary condition $\phi(L) = V$. From the previous discussion, we see that $\phi(x)$ tends weakly to a function $\Phi(x)$ when a tends to zero, such that

$$\Phi(x) = C\frac{1}{\bar{\epsilon}} \int_0^x dt = C\frac{1}{\bar{\epsilon}}x,$$

where $1/\bar{\epsilon}$ is the weak limit of $1/\epsilon(t/a)$. Therefore, $\Phi(x)$ is the solution of $(\bar{\epsilon}\Phi'(x))' = -n$, with $\Phi(0) = 0$, $\Phi(L) = V$ and $\bar{\epsilon}$ is a constant. The surprising fact is that $\bar{\epsilon}$ is not given by the average of $\epsilon(x)$ over a period, but by the inverse of the average of $1/\epsilon(x)$ over a period. Here, the equation for $\Phi(x)$ was deduced from the explicit solution for $\phi(x)$. However, in most problems, no explicit solution is available. This is why homogenization theory was invented.

In general, for a differential equation with rapidly oscillating coefficients, homogenization theory determines whether the solution has a limit when the period tends to zero, and to which equation the limit is a solution, without knowing the solution of the first differential equation. This is precisely the tool we need to derive constitutive relations from a microscopic description of matter. Homogenization

theory has shown that the macroscopic equation can be strongly different from the microscopic one. For instance, instantaneous microscopic equations can turn into equations with memory [27,28], local equations can develop non-local macroscopic terms [29], mixtures of optically inactive materials can become optically active [30,31].

3 Functional transformations

In this section, some functional transformations are introduced.

For the purpose of homogenization, a function $f(\mathbf{r})$ is written as $f(\mathbf{R}, \rho)$, where the dependence of f is slow for the variable $\mathbf{R}$ and periodic for the variable ρ. This so-called two-scale correspondence can be done explicitly as follows. Take a three-dimensional periodic lattice with Brillouin zone BZ. Let C be the Wigner-Seitz cell of the lattice and $|C|$ its volume. The crystal sites will be denoted by $\mathbf{R}_s$, and the reciprocal lattice vectors by $\mathbf{K}$.

Write the function f as a Fourier transform

$$
\begin{aligned}
f(\mathbf{r}) &= \int d\mathbf{q} \exp(i\mathbf{q} \cdot \mathbf{r}) \tilde{f}(\mathbf{q}) \\
&= \sum_{\mathbf{K}} \int_{BZ} d\mathbf{q} \exp[i(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r}] \tilde{f}(\mathbf{q} + \mathbf{K}),
\end{aligned}
$$

where the integral over $\mathbf{q}$ was written as a sum over the reciprocal lattices and an integral over the first Brillouin zone. Define now

$$
\tilde{f}(\mathbf{q}, \rho) = \sum_{\mathbf{K}} \exp(i\mathbf{K} \cdot \rho) \tilde{f}(\mathbf{q} + \mathbf{K}) \quad \text{for} \quad \mathbf{q} \in BZ
$$

$$
\tilde{f}(\mathbf{q}, \rho) = 0 \quad \text{for} \quad \mathbf{q} \notin BZ.
$$

From the fact that $\exp[i\mathbf{K} \cdot \mathbf{R}_s] = 1$, it can be checked that $\tilde{f}(\mathbf{q}, \rho + \mathbf{R}_s) = \tilde{f}(\mathbf{q}, \rho)$, so that $\tilde{f}(\mathbf{q}, \rho)$ has the periodicity of the lattice in ρ. Then it is clear that

$$
f(\mathbf{r}) = \int_{BZ} d\mathbf{q} \exp(i\mathbf{q} \cdot \mathbf{r}) \tilde{f}(\mathbf{q}, \mathbf{r}). \tag{1}
$$

If we define now

$$
f(\mathbf{R}, \rho) = \int_{BZ} d\mathbf{q} \exp[i\mathbf{q} \cdot \mathbf{R}] \tilde{f}(\mathbf{q}, \rho),
$$

it is clear that $f(\mathbf{R}, \rho)$ has the lattice periodicity in ρ and depends more slowly on $\mathbf{R}$ than on ρ. More precisely, homogenization is useful when the function $f(\mathbf{r})$ varies slowly from P to P'' (see Fig. 2), i.e. for two points that differ by a (short) lattice vector and varies arbitrarily from P to P' inside a cell. Then $f(\mathbf{r})$ is transformed into $f(\mathbf{R}, \rho)$, the ρ variable describes the fast variation of the function inside the cell, and the $\mathbf{R}$ variable its smooth variation from cell to cell.

This representation of a function of one variable by a function of a fast periodic variable ρ and a slower variable
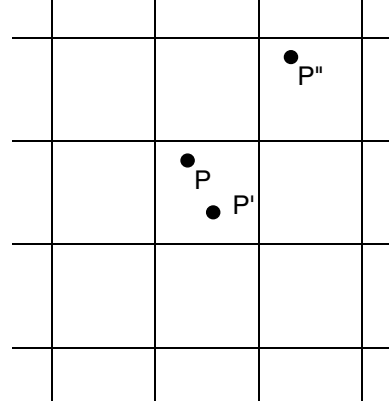
Fig. 2. P and P' are two points in the same cell, P and P'' are separated by a lattice vector.

$\mathbf{R}$ is the essence of the two scale analysis of homogenization theory. Note also that if $f(\mathbf{r})$ is slow, i.e. if the support of the Fourier transform $\tilde{f}(\mathbf{q})$ is contained in the first Brillouin zone, then $\tilde{f}(\mathbf{q}, \rho) = \tilde{f}(\mathbf{q})$ does not depend on ρ.

We shall not homogenize the Maxwell equations with the usual two-scale function $f(\mathbf{R}, \rho)$, but with its Fourier transform with respect to the slow variable $\mathbf{R}$: $\tilde{f}(\mathbf{q}, \rho)$. To establish a direct link between $\tilde{f}(\mathbf{q}, \rho)$ and $f(\mathbf{r})$ and for future reference, we shall make use of the standard relations for infinite Born-von Kármán boundary conditions [32] (which are derived from the Poisson summation formula [33]):

$$
\begin{aligned}
\int_{BZ} d\mathbf{q} \exp(i\mathbf{q} \cdot \mathbf{R}_s) &= \frac{(2\pi)^3}{|C|} \delta_{s,0} \\
\int_C d\rho \exp(i\mathbf{K} \cdot \rho) &= |C| \delta_{\mathbf{K},0} \\
\sum_{\mathbf{K}} \exp(i\mathbf{K} \cdot \rho) &= |C| \sum_s \delta(\rho + \mathbf{R}_s) \\
\sum_s \exp(i\mathbf{q} \cdot \mathbf{R}_s) &= \frac{(2\pi)^3}{|C|} \sum_{\mathbf{K}} \delta(\mathbf{q} - \mathbf{K}). \tag{2}
\end{aligned}
$$

An infinite Born-von Kármán boundary condition avoids the subtle problems linked with the use of a finite Born-von Kármán domain, for instance the question whether or not the other domains contribute to the reaction field.

Using the definition of the Fourier transform we find

$$
\begin{aligned}
\tilde{f}(\mathbf{q}, \rho) &= \sum_{\mathbf{K}} \exp(i\mathbf{K} \cdot \rho) \tilde{f}(\mathbf{q} + \mathbf{K}) \\
&= \frac{1}{(2\pi)^3} \sum_{\mathbf{K}} \exp(i\mathbf{K} \cdot \rho) \int d\mathbf{r} \exp[-i(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r}] f(\mathbf{r}) \\
&= \frac{1}{(2\pi)^3} \int d\mathbf{r} f(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) \sum_{\mathbf{K}} \exp[i\mathbf{K} \cdot (\rho - \mathbf{r})] \\
&= \frac{|C|}{(2\pi)^3} \sum_s \int d\mathbf{r} f(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) \delta(\rho - \mathbf{r} + \mathbf{R}_s) \\
&= \frac{|C|}{(2\pi)^3} \sum_s f(\rho + \mathbf{R}_s) \exp[-i\mathbf{q} \cdot (\rho + \mathbf{R}_s)]. \tag{3}
\end{aligned}
$$

For a function $f(\mathbf{r})$, with two-scale transforms $\tilde{\mathsf{f}}(\mathbf{q}, \rho)$ and $\mathsf{f}(\mathbf{R}, \rho)$, we define the averages over a unit cell by

$$\langle \tilde{\mathsf{f}}(\mathbf{q}, \rho) \rangle = \frac{1}{|C|} \int_C d\rho \tilde{\mathsf{f}}(\mathbf{q}, \rho)$$
$$= \tilde{f}(\mathbf{q}),$$

and

$$\langle f(\mathbf{r}) \rangle = \langle \mathsf{f}(\mathbf{R}, \rho) \rangle = \frac{1}{|C|} \int_C d\rho \, \mathsf{f}(\mathbf{R}, \rho)$$
$$= \int_{BZ} d\mathbf{q} \tilde{f}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}).$$

Since $\mathbf{q}$ is in the first Brillouin zone, the average over a unit cell has the effect of stripping all the high frequency components off the Fourier transform of f. We shall use this average to go from microscopic to macroscopic fields. The macroscopic fields will be microscopic fields averaged over a unit cell, so that all Fourier components of the macroscopic fields are zero when the argument is outside the first Brillouin zone. This definition of macroscopic fields is common in the physical literature [10,11,15,34–36]. Notice also that $\langle \mathsf{f}(\mathbf{R}, \rho) \rangle$ and $\langle \tilde{\mathsf{f}}(\mathbf{q}, \rho) \rangle$ are Fourier transforms of one another. Therefore, the macroscopic fields $\mathbf{E}(\mathbf{R})$ and $\mathbf{E}(\mathbf{q})$ obtained by averaging the corresponding microscopic fields remain Fourier transforms of one another. At first sight, it would seem more natural to define a macroscopic by averaging directly $f(\mathbf{r})$ over a unit cell. In other words, if $\mathbf{R}_s$ is a lattice vector, we could define the macroscopic value of f at $\mathbf{R}_s$ by

$$\overline{f(\mathbf{R}_s)} = \frac{1}{|C|} \int_C d\rho f(\mathbf{R}_s + \rho).$$

However, this definition does not enjoy the nice mathematical properties of our previous average. The difference between the two averages is

$$\overline{f(\mathbf{R}_s)} - \langle f(\mathbf{R}_s) \rangle = \int_{BZ} d\mathbf{q} \exp[i\mathbf{q} \cdot \mathbf{R}_s]$$
$$\frac{1}{|C|} \int_C d\rho \big(\exp(i\mathbf{q} \cdot \rho) - 1 \big) \tilde{\mathsf{f}}(\mathbf{q}, \rho).$$

In practice $\mathbf{q}$ is determined by the wavelength λ of the incident lightbeam and if a is a typical lattice parameter, then the difference is of the order of a/λ, which is small in the optical range. So the two averages agree for a visible or UV lightbeam. This remark is due to Wiser [11].

By direct substitution, it can be shown that the two-scale transforms of the gradient of f are $(\nabla_\mathbf{R} + \nabla_\rho)\mathsf{f}(\mathbf{R}, \rho)$ and $(i\mathbf{q} + \nabla_\rho)\tilde{\mathsf{f}}(\mathbf{q}, \rho)$.

4 The microscopic Maxwell equations

To simplify the presentation, we consider a non magnetic sample and we neglect the effect of spin (see Ref. [5] for the full theory). Moreover, the electromagnetic charges, currents and fields have a time dependence $\exp(-i\omega t)$ which will be implicit for notational convenience.

The random phase approximation of quantum electrodynamics corresponds to the following picture [34]. An external electromagnetic wave $\mathbf{E}^{\text{ext}}(\mathbf{r})$, $\mathbf{B}^{\text{ext}}(\mathbf{r})$ polarizes the dielectric crystal, creating a current density $\mathbf{j}(\mathbf{r})$ and a charge density $n(\mathbf{r})$. These current and charge induce an electric field $\mathbf{e}(\mathbf{r}) - \mathbf{E}^{\text{ext}}(\mathbf{r})$ and a magnetic field $\mathbf{b}(\mathbf{r}) - \mathbf{B}^{\text{ext}}(\mathbf{r})$, that induce additional current and charge, etc. When the medium and the field reach equilibrium, the vacuum (rationalized SI) Maxwell equations describe the connection between the total fields and the induced charge and current densities:

$$\nabla \cdot \mathbf{e}(\mathbf{r}) = n(\mathbf{r})/\epsilon_0$$
$$\nabla \times \mathbf{e}(\mathbf{r}) = i\omega \mathbf{b}(\mathbf{r})$$
$$\nabla \cdot \mathbf{b}(\mathbf{r}) = 0$$
$$\nabla \times \mathbf{b}(\mathbf{r}) + i\omega\epsilon_0\mu_0\mathbf{e}(\mathbf{r}) = \mu_0\mathbf{j}(\mathbf{r}), \quad (4)$$

where charge conservation implies $\nabla \cdot \mathbf{j}(\mathbf{r}) = i\omega n(\mathbf{r})$.

Linear response theory gives us the microscopic relation

$$\mathbf{j}(\mathbf{r}) = -i\omega \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \cdot \mathbf{e}(\mathbf{r}'), \quad (5)$$

where the electric susceptibility χ_{ij} has the well-known expression [5,37–39]

$$\chi_{ij}(\mathbf{r}, \mathbf{r}') = -\frac{e}{m\omega^2} n_0(\mathbf{r})\delta_{ij}\delta(\mathbf{r} - \mathbf{r}')$$
$$+ \frac{e^2}{\omega^2} \sum_{n \neq 0} \left[\frac{V_i^{0n}(\mathbf{r})V_j^{n0}(\mathbf{r}')}{\hbar(\omega_{n0} - \omega)} + \frac{V_i^{n0}(\mathbf{r})V_j^{0n}(\mathbf{r}')}{\hbar(\omega_{n0} + \omega)} \right], \quad (6)$$

where $n_0(\mathbf{r})$ is the charge density in the ground state, e is the (negative) electron charge and m its mass. The velocity matrix elements are

$$\mathbf{V}^{0n}(\mathbf{r}) = -\frac{i\hbar}{2m}[\Psi_0^*(\mathbf{r})\nabla_r\Psi_n(\mathbf{r}) - \Psi_n(\mathbf{r})\nabla_r\Psi_0^*(\mathbf{r})], \quad (7)$$

where $\Psi_0(\mathbf{r})$ and $\Psi_n(\mathbf{r})$ are eigenstates of the crystal. In the one-electron case, the sum is carried out over the occupied (0) and unoccupied (n) states.

In expression (6), the first term, called the diamagnetic term, depends only on the electronic density, and the second (paramagnetic) term is usually much larger than the first in the optical range [5].

Formula (6) for the susceptibility χ holds at zero temperature. The corresponding formula for finite temperature involves a weighted sum over initial states [5]. All the results of the present paper can be straightforwardly adapted to the finite temperature case.

From the microscopic current $\mathbf{j}(\mathbf{r})$ it is customary in dielectric theory to define the polarization $\mathbf{p}(\mathbf{r}) = (i/\omega)\mathbf{j}(\mathbf{r})$ and the displacement field $\mathbf{d}(\mathbf{r}) = \epsilon_0\mathbf{e}(\mathbf{r}) + \mathbf{p}(\mathbf{r})$. In terms of those fields, the microscopic Maxwell equations become

$$\nabla \times \mathbf{e}(\mathbf{r}) = i\omega\mathbf{b}(\mathbf{r})$$
$$\nabla \cdot \mathbf{b}(\mathbf{r}) = 0$$
$$\nabla \cdot \mathbf{d}(\mathbf{r}) = 0$$
$$\nabla \times \mathbf{b}(\mathbf{r}) = -i\omega\mu_0\mathbf{d}(\mathbf{r}), \quad (8)$$

where the microscopic constitutive relation is now

$$d_i(\mathbf{r}) = \epsilon_0 e_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \chi_{ij}(\mathbf{r}, \mathbf{r}') e_j(\mathbf{r}').$$

The microscopic fields $\mathbf{e}(\mathbf{r})$, $\mathbf{b}(\mathbf{r})$ and $\mathbf{p}(\mathbf{r})$ are, as the susceptibility $\chi_{ij}(\mathbf{r}, \mathbf{r}')$, rapidly oscillating functions of $\mathbf{r}$. The macroscopic fields $\mathbf{E}(\mathbf{R})$, $\mathbf{B}(\mathbf{R})$ and $\mathbf{P}(\mathbf{R})$ are averages of the corresponding quantities over a unit cell. The constitutive relations problem is how to go from the relation between $\mathbf{p}(\mathbf{r})$ and $\mathbf{e}(\mathbf{r})$ to a relation between $\mathbf{P}(\mathbf{R})$ and $\mathbf{E}(\mathbf{R})$. Homogenization theory is a very convenient way to solve this problem.

5 Homogenization of the microscopic Maxwell equations

The derivation of the macroscopic Maxwell equations from the microscopic ones is standard [12,15,40]. Hence, the purpose of this section is just to show that homogenization theory gives the known results and to derive equations that will be used in the next sections. The homogenization of the Maxwell equation has been thoroughly studied by applied mathematicians [20–22,27,41–47] and physicists [30,31]. However, the microscopic constitutive relations that they used were always local: $\chi_{ij}(\mathbf{r}, \mathbf{r}') = \chi_{ij}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$. We do not need the full apparatus of homogenization theory of non-local equations [48] and we homogenize the Maxwell equations by a simple adaptation of the method used for local dielectric functions.

In this section, we follow the very clear homogenization procedure of Sanchez-Palencia [21], except that we work with $\tilde{f}(\mathbf{q}, \rho)$ instead of $f(\mathbf{R}, \rho)$.

Using the fact that the two-scale transform of $\nabla f(\mathbf{r})$ is $(i\mathbf{q} + \nabla_\rho)\tilde{f}(\mathbf{q}, \rho)$, we can make the two-scale transform of the Maxwell equations (8) to obtain:

$$i\mathbf{q} \times \mathbf{e}(\mathbf{q}, \rho) + \nabla_\rho \times \mathbf{e}(\mathbf{q}, \rho) = i\omega \mathbf{b}(\mathbf{q}, \rho)$$
$$i\mathbf{q} \cdot \mathbf{b}(\mathbf{q}, \rho) + \nabla_\rho \cdot \mathbf{b}(\mathbf{q}, \rho) = 0$$
$$i\mathbf{q} \cdot \mathbf{d}(\mathbf{q}, \rho) + \nabla_\rho \cdot \mathbf{d}(\mathbf{q}, \rho) = 0$$
$$i\mathbf{q} \times \mathbf{b}(\mathbf{q}, \rho) + \nabla_\rho \times \mathbf{b}(\mathbf{q}, \rho) = -i\omega\mu_0 \mathbf{d}(\mathbf{q}, \rho). \quad (9)$$

For notational convenience, we do not write the fields $\mathbf{e}(\mathbf{q}, \rho)$, etc, with a tilde.

Because they vary slowly, the possible "external" currents and charges would appear as $\mathbf{j}(\mathbf{q})$ and $n(\mathbf{q})$, with no dependence on ρ.

Consider a scattering problem where a plane electromagnetic wave is shined on the dielectric. In equations (9), the order of magnitude of $\mathbf{q}$ will be $2\pi/\lambda$, where λ is the wavelength of the incident wave. The order of magnitude of the unit cell dimensions is $l = |C|^{1/3}$. Let $a = l/\lambda$, the order of magnitude of $\nabla_\rho \cdot \mathbf{e}(\mathbf{q}, \rho)$ is $1/a$ times the order of magnitude of $\mathbf{q} \cdot \mathbf{e}(\mathbf{q}, \rho)$. Now we expand all fields as sums of the type

$$\mathbf{e}(\mathbf{q}, \rho) = \mathbf{e}^{(0)}(\mathbf{q}, \rho) + a\mathbf{e}^{(1)}(\mathbf{q}, \rho) + a^2\mathbf{e}^{(2)}(\mathbf{q}, \rho) + \cdots \quad (10)$$

where all terms of the expansion are periodic in ρ. Since a is small, we keep only the first term of the expansion to define the macroscopic fields as $\mathbf{E}(\mathbf{q}) = \langle \mathbf{e}^{(0)}(\mathbf{q}, \rho) \rangle$, etc. The validity and asymptotic convergence of this expansion is the main technical difficulty that was solved by the mathematicians who homogenized the Maxwell equations (see, for instance, Ref. [44] where the general term of expansion (10) is given). To be complete, we need to know that the order of magnitude of ω is $2\pi c/\lambda$, the order of magnitude of $\mathbf{b}$ is $\mathbf{e}/c$ and the order of magnitude of $\mathbf{d}$ is $\epsilon_0 \mathbf{e}$.

Introducing the expansions (10) into equation (9) and gathering all terms of same power of a we obtain four equations for the a^{-1} term:

$$\nabla_\rho \times \mathbf{e}^{(0)}(\mathbf{q}, \rho) = 0$$
$$\nabla_\rho \cdot \mathbf{b}^{(0)}(\mathbf{q}, \rho) = 0$$
$$\nabla_\rho \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) = 0 \quad (11)$$
$$\nabla_\rho \times \mathbf{b}^{(0)}(\mathbf{q}, \rho) = 0,$$

and four equations for the a^0 term:

$$i\mathbf{q} \times \mathbf{e}^{(0)}(\mathbf{q}, \rho) + a\nabla_\rho \times \mathbf{e}^{(1)}(\mathbf{q}, \rho) = i\omega \mathbf{b}^{(0)}(\mathbf{q}, \rho)$$
$$i\mathbf{q} \cdot \mathbf{b}^{(0)}(\mathbf{q}, \rho) + a\nabla_\rho \cdot \mathbf{b}^{(1)}(\mathbf{q}, \rho) = 0 \quad (12)$$
$$i\mathbf{q} \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) + a\nabla_\rho \cdot \mathbf{d}^{(1)}(\mathbf{q}, \rho) = 0$$
$$i\mathbf{q} \times \mathbf{b}^{(0)}(\mathbf{q}, \rho) + a\nabla_\rho \times \mathbf{b}^{(1)}(\mathbf{q}, \rho) = -i\omega\mu_0 \mathbf{d}^{(0)}(\mathbf{q}, \rho),$$

(recall that $a\nabla_\rho$ has the same order of magnitude as $\mathbf{q}$). These two sets of equations are sufficient to determine the macroscopic Maxwell equations. Further terms would be required if the wavelength were not very large with respect to the unit cell dimensions.

To obtain the macroscopic Maxwell equations, we must eliminate the terms of order one, e.g. $\mathbf{b}^{(1)}(\mathbf{q}, \rho)$. This is achieved by transforming the cell average of the divergence into an integral over the surface ∂C of the unit cell: $\langle \nabla_\rho \cdot \mathbf{b}^{(1)}(\mathbf{q}, \rho) \rangle = 1/|C| \int_{\partial C} \hat{n} \cdot \mathbf{b}^{(1)}(\mathbf{q}, \rho) dS$. On opposite sides of cell C, the outgoing normal $\hat{n}$ is reversed while $\mathbf{b}^{(1)}(\mathbf{q}, \rho)$ is equal (by periodicity). Therefore, the surface integral is zero and $\langle \nabla_\rho \cdot \mathbf{b}^{(1)}(\mathbf{q}, \rho) \rangle = 0$. A similar reasoning leads to $\langle \nabla_\rho \times \mathbf{b}^{(1)}(\mathbf{q}, \rho) \rangle = 0$.

Thus, averaging equation (12) gives $0 = i\mathbf{q} \cdot \langle \mathbf{b}^{(0)}(\mathbf{q}, \rho) \rangle + a\langle \nabla_\rho \cdot \mathbf{b}^{(1)}(\mathbf{q}, \rho) \rangle = i\mathbf{q} \cdot \mathbf{B}(\mathbf{q})$, because the macroscopic field $\mathbf{B}(\mathbf{q})$ was defined as the average of $\mathbf{b}^{(0)}(\mathbf{q}, \rho)$. Carrying out similar calculations for the other microscopic Maxwell equations we obtain the macroscopic Maxwell equations in momentum space:

$$i\mathbf{q} \times \mathbf{E}(\mathbf{q}) = i\omega \mathbf{B}(\mathbf{q})$$
$$i\mathbf{q} \cdot \mathbf{B}(\mathbf{q}) = 0$$
$$i\mathbf{q} \cdot \mathbf{D}(\mathbf{q}) = 0$$
$$i\mathbf{q} \times \mathbf{B}(\mathbf{q}) = -i\omega\mu_0 \mathbf{D}(\mathbf{q}). \quad (13)$$

Fourier transforming back to real space we obtain the usual macroscopic Maxwell equations:

$$\nabla \times \mathbf{E}(\mathbf{R}) = i\omega \mathbf{B}(\mathbf{R})$$
$$\nabla \cdot \mathbf{B}(\mathbf{R}) = 0$$
$$\nabla \cdot \mathbf{D}(\mathbf{R}) = 0$$
$$\nabla \times \mathbf{B}(\mathbf{R}) = -i\omega\mu_0 \mathbf{D}(\mathbf{R}).$$

Notice that this homogenization procedure can be applied directly to equations (9), but the present formulation is required for consistency with the derivation of the constitutive relations.

Homogenization now proceeds classically. We start by homogenizing the magnetic field $\mathbf{b}^{(0)}(\mathbf{q}, \rho)$. From the equation $\nabla_\rho \times \mathbf{b}^{(0)}(\mathbf{q}, \rho) = 0$ we deduce that there is a periodic potential $\phi(\mathbf{q}, \rho)$ and a function of $\mathbf{q}$, denoted by $\mathbf{F}(\mathbf{q})$, such that $\mathbf{b}^{(0)}(\mathbf{q}, \rho) = \mathbf{F}(\mathbf{q}) - \nabla_\rho \phi(\mathbf{q}, \rho)$. Taking the average of both sides, and considering the periodicity of ϕ we obtain $\langle \mathbf{b}^{(0)}(\mathbf{q}, \rho) \rangle = \mathbf{F}(\mathbf{q})$ [49] and, since the left-hand side is defined as the macroscopic magnetic field $\mathbf{B}(\mathbf{q})$, we get $\mathbf{b}^{(0)}(\mathbf{q}, \rho) = \mathbf{B}(\mathbf{q}) - \nabla_\rho \phi(\mathbf{q}, \rho)$. Introducing this equality into $\nabla_\rho \cdot \mathbf{b}^{(0)}(\mathbf{q}, \rho) = 0$ we obtain the equation $\Delta_\rho \phi(\mathbf{q}, \rho) = 0$. The only periodic solution of the Laplace equation is a constant [20], so $\phi(\mathbf{q}, \rho)$ is a constant and $\mathbf{b}^{(0)}(\mathbf{q}, \rho) = \mathbf{B}(\mathbf{q})$. In other words, the magnetic field does not need to be averaged, the zero-th order term of $\mathbf{b}(\mathbf{q}, \rho)$ is smooth and does not depend on ρ. The periodic modulation is only reached at the next and smaller term $a\mathbf{b}^{(1)}(\mathbf{q}, \rho)$.

Such an automatic averaging is not possible for the electric field. Starting from $\nabla_\rho \times \mathbf{e}^{(0)}(\mathbf{q}, \rho) = 0$, the only conclusion that we can reach at this level is that there is a periodic potential $\phi(\mathbf{q}, \rho)$ such that $\mathbf{e}^{(0)}(\mathbf{q}, \rho) = \mathbf{E}(\mathbf{q}) - \nabla_\rho \phi(\mathbf{q}, \rho)$. The determination of ϕ will be the purpose of the next sections, but this result has already an interesting meaning. The zero-th term of the expansion of $\mathbf{e}(\mathbf{q}, \rho)$ is not smooth. In mathematical terms, the limit of $\mathbf{e}(\mathbf{q}, \rho)$ as $a \rightarrow 0$ is still an oscillating function, contrary to our example $f(x/a) = \sin(x/a) + b$. This concept of "oscillating limit" was introduced by the Cameroonese mathematician G. Nguetseng in 1989 [50] and has deeply simplified homogenization theory [51].

6 The constitutive relation

Still, to give a complete description of the macroscopic electromagnetic properties of matter, we have to establish a correspondence between $\mathbf{D}(\mathbf{q})$ and $\mathbf{E}(\mathbf{q})$.

To do this, we use the periodicity of χ: for every lattice vector $\mathbf{R}$, $\chi_{ij}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) = \chi_{ij}(\mathbf{r}, \mathbf{r}')$ [37]. Notice that the same lattice vector must be added to both arguments of χ.

We start from the relation between the polarization and the electric field

$$\mathbf{p}(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \cdot \mathbf{e}(\mathbf{r}').$$

Then, we apply the two-scale transformation equation (3) to find

$$\mathbf{p}(\mathbf{q}, \rho) = \frac{|C|}{(2\pi)^3} \sum_s \exp[-i\mathbf{q} \cdot (\rho + \mathbf{R}_s)]$$
$$\int d\mathbf{r}' \chi(\rho + \mathbf{R}_s, \mathbf{r}') \cdot \mathbf{e}(\mathbf{r}').$$

Now the integral over all space is split into integrals over translated unit cells:

$$\mathbf{p}(\mathbf{q}, \rho) = \frac{|C|}{(2\pi)^3} \sum_{ss'} \exp[-i\mathbf{q} \cdot (\rho + \mathbf{R}_s)]$$
$$\int_C d\rho' \chi(\rho + \mathbf{R}_s, \rho' + \mathbf{R}_{s'}) \cdot \mathbf{e}(\rho' + \mathbf{R}_{s'}).$$

If we introduce the two-scale expression (1) for the electric field $\mathbf{e}(\rho) = \int_{BZ} d\mathbf{q} \exp(i\mathbf{q} \cdot \rho) \mathbf{e}(\mathbf{q}, \rho)$ and use the periodicity of $\mathbf{e}(\mathbf{q}, \rho)$ in ρ we get

$$\mathbf{p}(\mathbf{q}, \rho) = \frac{|C|}{(2\pi)^3} \sum_{ss'} \exp[-i\mathbf{q} \cdot (\rho + \mathbf{R}_s)] \int_{BZ} d\mathbf{q}' \int_C d\rho'$$
$$\exp[i\mathbf{q}' \cdot (\rho' + \mathbf{R}_{s'})] \chi(\rho + \mathbf{R}_s, \rho' + \mathbf{R}_{s'}) \cdot \mathbf{e}(\mathbf{q}', \rho').$$

If we replace $\mathbf{R}_s$ by $\mathbf{R}_t + \mathbf{R}_{s'}$ and use the periodicity of χ we obtain

$$\mathbf{p}(\mathbf{q}, \rho) = \frac{|C|}{(2\pi)^3} \sum_t \exp[-i\mathbf{q} \cdot (\rho + \mathbf{R}_t)] \int_{BZ} d\mathbf{q}'$$
$$\int_C d\rho' \exp(i\mathbf{q}' \cdot \rho') \sum_{s'} \exp[i(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{R}_{s'}]$$
$$\chi(\rho + \mathbf{R}_t, \rho') \cdot \mathbf{e}(\mathbf{q}', \rho').$$

The sum over s' is carried out with equation (2) and, since $\mathbf{q}$ and $\mathbf{q}'$ belong to the first Brillouin zone, only the term $\mathbf{K} = 0$ contributes. We reach finally

$$\mathbf{p}(\mathbf{q}, \rho) = \sum_s \int_C d\rho' \exp[-i\mathbf{q} \cdot (\rho - \rho' + \mathbf{R}_s)]$$
$$\chi(\rho + \mathbf{R}_s, \rho') \cdot \mathbf{e}(\mathbf{q}, \rho')$$
$$= \langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \cdot \mathbf{e}(\mathbf{q}, \rho') \rangle_{\rho'},$$

where the index ρ' designates cell average over variable ρ', and where we have defined the two-scale transform of χ as

$$\tilde{\chi}(\rho, \rho'; \mathbf{q}) = |C| \sum_s \exp[-i\mathbf{q} \cdot (\rho - \rho' + \mathbf{R}_s)] \chi(\rho + \mathbf{R}_s, \rho').$$

$$(14)$$

It can be checked that $\tilde{\chi}(\rho, \rho'; \mathbf{q})$ has the lattice periodicity for each variable ρ and ρ' independently. A related definition was used by Ehrenreich [34].

All quantities are now periodic and diagonal in $\mathbf{q}$: they are in a suitable form for homogenization. From the relation between polarization and electric field, we deduce the

relation between displacement and electric field which will be our starting point:

$$d_i(\mathbf{q}, \rho) = \epsilon_0 e_i(\mathbf{q}, \rho) + \sum_j \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) e_j(\mathbf{q}, \rho') \rangle_{\rho'}. \quad (15)$$

The macroscopic constitutive relation is obtained by restricting all fields to the first term of expansion (10). If we do this in equation (15) and write the electric field as the sum $\mathbf{e}^{(0)}(\mathbf{q}, \rho) = \mathbf{E}(\mathbf{q}) - \nabla_\rho \phi(\mathbf{q}, \rho)$ we obtain

$$d_i^{(0)}(\mathbf{q}, \rho) = \epsilon_0 E_i(\mathbf{q}) + \sum_j \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \rangle_{\rho'} E_j(\mathbf{q})$$
$$- \epsilon_0 \partial_{\rho_i} \phi(\mathbf{q}, \rho) - \sum_j \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \partial_{\rho'_j} \phi(\mathbf{q}, \rho') \rangle_{\rho'}. \quad (16)$$

If equation (16) is averaged over ρ, the fact that $\langle \partial_{\rho_i} \phi(\mathbf{q}, \rho) \rangle = 0$ [49] leads to the first step of the macroscopic constitutive relation:

$$D_i(\mathbf{q}) = \epsilon_0 E_i(\mathbf{q}) + \sum_j \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'} E_j(\mathbf{q})$$
$$- \sum_j \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \partial_{\rho'_j} \phi(\mathbf{q}, \rho') \rangle_{\rho\rho'}. \quad (17)$$

Following Wiser [11], a connexion with the classical approach is possible through the introduction of a macroscopic local field $\mathbf{E}_{\mathrm{loc}}(\mathbf{q})$ defined by

$$\langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'} \cdot \mathbf{E}_{\mathrm{loc}}(\mathbf{q}) = \langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \cdot \mathbf{e}(\mathbf{q}, \rho') \rangle_{\rho\rho'},$$

so that $\mathbf{D}(\mathbf{q}) = \epsilon_0 \mathbf{E}(\mathbf{q}) + \langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'} \cdot \mathbf{E}_{\mathrm{loc}}(\mathbf{q})$.

The next step is the determination of $\phi(\mathbf{q}, \rho')$. We take the microscopic equation $\nabla_\rho \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) = 0$ derived in the previous section (Eq. (11)), and we apply it to equation (16). We obtain an equation for $\phi(\mathbf{q}, \rho)$:

$$\epsilon_0 \Delta_\rho \phi(\mathbf{q}, \rho) + \sum_{ij} \langle \partial_{\rho_i} \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \partial_{\rho'_j} \phi(\mathbf{q}, \rho') \rangle_{\rho'} =$$
$$\sum_{ij} \langle \partial_{\rho_i} \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \rangle_{\rho'} E_j(\mathbf{q}). \quad (18)$$

This so-called cell equation determines a unique periodic solution $\phi(\mathbf{q}, \rho)$ with zero average over a period.

We follow first the standard argument of homogenization theory. Let the three functions $A_k(\mathbf{q}, \rho)$ $(k = x, y, z)$ be the solutions of the cell equation for an electric field $\mathbf{E}$ equal to a unit vector in the direction k. Then, for a general electric field $\mathbf{E}(\mathbf{q})$, the potential is $\phi(\mathbf{q}, \rho) = \mathbf{A}(\mathbf{q}, \rho) \cdot \mathbf{E}(\mathbf{q})$.

If we introduce this expression for $\phi(\mathbf{q}, \rho)$ into equation (17), we obtain the macroscopic constitutive relation $D_i(\mathbf{q}) = \sum_j \epsilon_{ij}(\mathbf{q}) E_j(\mathbf{q})$ where the macroscopic dielectric constant $\epsilon_{ij}(\mathbf{q})$ is given by

$$\epsilon_{ij}(\mathbf{q}) = \epsilon_0 \delta_{ij} + \sum_k \langle \tilde{\chi}_{ik}(\rho, \rho'; \mathbf{q}) [\delta_{kj} - \partial_{\rho'_k} A_j(\mathbf{q}, \rho')] \rangle_{\rho\rho'}.$$

This equation shows that the macroscopic dielectric constant is the average of the microscopic dielectric function plus a correction term. In the case when the dielectric function is a sum of constant factors localized at all sites of a cubic lattice, it is a standard exercise of homogenization theory to show that the macroscopic constitutive relation becomes the Clausius-Mossotti equation (see Ref. [22], p. 45). Therefore, the correction term can be quite large and should not be neglected.

Homogenization usually stops here, and the integro-differential cell equation (18) can only be solved numerically, which seems to be a reasonable task. For instance, the FLAPW approach could be used, where space is cut into non-overlapping spheres plus an interstitial region. $\phi(\mathbf{q}, \rho)$ is then expanded over spherical harmonics (with suitable radial functions) in the spheres and over plane waves $\exp(i\mathbf{K} \cdot \rho)$ in the interstitial region. This reduces the cell equation to a matrix equation.

However, the particular structure of $\chi_{ij}(\mathbf{r}, \mathbf{r}')$ can be used to give an explicit solution for $\phi(\mathbf{q}, \rho)$. This is the purpose of the next section.

7 The cell problem

The cell equation (18) can be interpreted as follows. If a constant electric field $\mathbf{E}(\mathbf{q})$ is applied to the dielectric, linear response theory tells us that it induces a periodic current given by equation (5)

$$\mathbf{j}(\mathbf{q}, \rho) = -i\omega \langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho'} \cdot \mathbf{E}(\mathbf{q})$$

and the corresponding periodic charge is

$$n(\mathbf{q}, \rho) = -(i/\omega) \nabla_\rho \cdot \mathbf{j}(\mathbf{q}, \rho)$$
$$= -\nabla_\rho \cdot \langle \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho'} \cdot \mathbf{E}(\mathbf{q}).$$

The last term is minus the right-hand side of equation (18). This periodic charge induces an additional electric field, that creates an additional polarization, and $\phi(\mathbf{q}, \rho)$ is the periodic potential (with zero average) which represents the local electric field reached at equilibrium under the influence of the external field $\mathbf{E}(\mathbf{q})$. In other words, the cell equation (18) is the electrostatic equation for the potential created in a unit cell of the dielectric by an external field $\mathbf{E}(\mathbf{q})$.

With this picture in mind, we can solve the cell equation iteratively. We need the periodic electrostatic Green function $G^{\#}(\rho)$ which is a solution of $\epsilon_0 \Delta G^{\#}(\rho) = -\delta(\rho)$ in a unit cell. Some properties of $G^{\#}(\rho)$ are discussed in reference [22], p. 121,

$$G^{\#}(\rho) = \sum_{\mathbf{K}} \frac{\exp(i\mathbf{K} \cdot \rho)}{\epsilon_0 |C|(|\mathbf{K}|^2 - i\eta)}$$
$$= \sum_s \frac{1}{4\pi\epsilon_0 |\rho + \mathbf{R}_s|}, \quad (19)$$

where η is an infinitesimal positive real.

If the Green function is applied to both sides of equation (18) we obtain

$$\phi(\mathbf{q}, \rho) = -\frac{1}{|C|} \int d\tau d\rho' G^{\#}(\rho - \tau) \nabla_\tau \cdot \chi(\tau, \rho'; \mathbf{q}) \cdot \mathbf{E}(\mathbf{q})$$
$$+ \frac{1}{|C|} \int d\tau d\rho' G^{\#}(\rho - \tau) \nabla_\tau \cdot \chi(\tau, \rho'; \mathbf{q}) \cdot \nabla_{\rho'} \phi(\mathbf{q}, \rho').$$

An iterative solution of this equation can be written, in simplified notation

$$\phi = -\frac{1}{|C|} G^{\#} \nabla \cdot \tilde{\chi} \cdot \mathbf{E} - \frac{1}{|C|^2} G^{\#} \nabla \cdot \tilde{\chi} \cdot \nabla G^{\#} \nabla \cdot \tilde{\chi} \cdot \mathbf{E} + \cdots$$

If we introduce our iterative solution in equation (17) we obtain

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \langle \tilde{\chi} + \frac{1}{|C|} \tilde{\chi} \cdot \nabla G^{\#} \nabla \cdot \tilde{\chi} + \cdots \rangle \cdot \mathbf{E}. \quad (20)$$

To be more explicit, we introduce the macroscopic susceptibility $\bar{\chi}_{ij}(\mathbf{q})$ and write equation (20) as $\mathbf{D}(\mathbf{q}) = \epsilon_0 \mathbf{E}(\mathbf{q}) + \bar{\chi}(\mathbf{q}) \cdot \mathbf{E}(\mathbf{q})$, where

$$\bar{\chi}_{ij}(\mathbf{q}) = \frac{1}{|C|^2} \int_{C \times C} d\rho d\rho' \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q})$$
$$+ \frac{1}{|C|^3} \sum_{mn} \int_{C^4} d\rho d\rho' d\tau d\tau' \tilde{\chi}_{im}(\rho, \tau; \mathbf{q})$$
$$\partial_{\tau_m} G^{\#}(\tau - \tau') \partial_{\tau'_n} \tilde{\chi}_{nj}(\tau', \rho'; \mathbf{q}) + \cdots \quad (21)$$

or

$$\bar{\chi}(\mathbf{q}) = \left\langle \tilde{\chi}(\mathbf{q}) \cdot \left[1 - \frac{1}{|C|} \nabla G^{\#} \nabla \cdot \tilde{\chi}(\mathbf{q}) \right]^{-1} \right\rangle_{\rho\rho'}.$$

7.1 Using the separable form of $\tilde{\chi}_{ij}$

To sum the right-hand side of equation (20), we need a separable form for $\tilde{\chi}$, akin to work of Cho [52] or the coupled-antenna theory of Keller [5]. If we neglect the diamagnetic component of χ in equation (6), we can write it in the separable form

$$\tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) = \sum_n f_i^n(\rho, \mathbf{q}) g_j^n(\rho', \mathbf{q}). \quad (22)$$

Introducing this representation in equation (20), everything decouples and we obtain $D_i(\mathbf{q}) = \sum_j \epsilon_{ij}(\mathbf{q}) E_j(\mathbf{q})$ where the macroscopic dielectric constant $\epsilon_{ij}(\mathbf{q})$ is now given by

$$\epsilon_{ij}(\mathbf{q}) = \epsilon_0 \delta_{ij} + \sum_{nn'} \langle f_i^n(\rho, \mathbf{q}) \rangle [1 - M(\mathbf{q})]_{nn'}^{-1} \langle g_j^{n'}(\rho, \mathbf{q}) \rangle, \quad (23)$$

and where the reaction field matrix (or screening matrix [53]) is defined as

$$M(\mathbf{q})_{nn'} = |C| \sum_{ij} \langle g_i^n(\rho, \mathbf{q}) \partial_{\rho_i} G^{\#}(\rho - \rho') \partial_{\rho'_j} f_j^{n'}(\rho', \mathbf{q}) \rangle_{\rho\rho'}. \quad (24)$$

Equations (23) and (24), giving an explicit expression for the macroscopic dielectric constant, are the main result of the paper. These equations can be useful when only a few states n contribute to the susceptibility $\chi(\rho, \rho'; \mathbf{q})$

Integrating equation (24) by parts and using the periodicity of all functions involved, we can derive an alternative form for the reaction field matrix $M(\mathbf{q})_{nn'}$, which decreases the singularity of the derivative of $G^{\#}$:

$$M(\mathbf{q})_{nn'} = -|C| \langle G^{\#}(\rho - \rho') \nabla_\rho \cdot \mathbf{g}^n(\rho, \mathbf{q}) \nabla_{\rho'} \cdot \mathbf{f}^{n'}(\rho', \mathbf{q}) \rangle_{\rho\rho'}.$$

An alternative summation of the series (20) can be obtained by separating $G^{\#}(\rho - \rho')$ with equation (19). A calculation similar to the foregoing one leads to

$$\epsilon_{ij}(\mathbf{q}) = \epsilon_0 \delta_{ij} + \langle \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'}$$
$$+ \sum_{\mathbf{K}, \mathbf{K'}}' \frac{1}{\epsilon_0 |\mathbf{K}| |\mathbf{K'}|} \sum_{mn} \langle \exp(i\mathbf{K} \cdot \rho') \partial_{\rho'_m} \tilde{\chi}_{im}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'}$$
$$(1 - N)_{\mathbf{K}\mathbf{K'}}^{-1} \langle \exp(-i\mathbf{K'} \cdot \rho) \partial_{\rho_n} \tilde{\chi}_{nj}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'},$$

where the reaction field matrix is now

$$N_{\mathbf{K}\mathbf{K'}} = \frac{1}{\epsilon_0 |\mathbf{K}| |\mathbf{K'}|} \sum_{ij} \langle \exp(-i\mathbf{K} \cdot \rho) \quad (25)$$
$$[\partial_{\rho_i} \partial_{\rho'_j} \tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q})] \exp(i\mathbf{K'} \cdot \rho') \rangle_{\rho\rho'}. \quad (26)$$

The notation $\sum'$ means that the sum is over all *non-zero* reciprocal lattice vectors. To show that the terms $\mathbf{K} = 0$ or $\mathbf{K'} = 0$ do no contribute, we reintroduce the infinitesimal number $-i\eta$ of equation (19) and, for instance, the $\mathbf{K'} = 0$ term gives us $(i/\eta) \langle \nabla_\rho \cdot \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'} = 0$, because the average of a divergence is zero [49]. Similarly, $N_{\mathbf{K}\mathbf{K'}}$ is zero for $\mathbf{K} = 0$ or $\mathbf{K'} = 0$. The last expression for $\epsilon(\mathbf{q})$ is computationally effective when $\chi(\rho, \rho'; \mathbf{q})$ is smooth and only a few $\mathbf{K}$ contribute.

Notice that equation (26) amounts to using the Fourier transform of the susceptibility $\tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q})$. We do not discuss this approach further, since it has been used by many authors [10,11,19,54,55]. It can be checked that equation (26) is equivalent to their results, in the limit where $a \to 0$.

7.2 Reaction field matrix

It is also possible to integrate equation (24) by parts to apply both gradients to the Green function, but the double gradient of the Green function has a singularity that must be treated with care [56,57]. On the other hand, this form has the advantage of recovering the usual dipole-dipole interaction of classical dielectric theory [15] as will be shown now. In equation (24), an integration by parts transfers the derivative $\partial_{\rho'_j}$ from $f_j^{n'}(\rho', \mathbf{q})$ to $G^{\#}(\rho - \rho')$, then $\partial_{\rho'_j} G^{\#}(\rho - \rho') = -\partial_{\rho_j} G^{\#}(\rho - \rho')$. Therefore, if we define the matrix Green function $\mathbf{G}^{\#}(\rho - \rho')$ by

$$G_{ij}^{\#}(\rho - \rho') = \partial_{\rho_i} \partial_{\rho_j} G^{\#}(\rho - \rho'),$$

the reaction field matrix becomes

$$M(\mathbf{q})_{nn'} = -|C|\langle \mathbf{g}^n(\rho, \mathbf{q}) \cdot \mathbf{G}^{\#}(\rho - \rho') \cdot \mathbf{f}^{n'}(\rho', \mathbf{q})\rangle_{\rho\rho'}.$$

To proceed, we write

$$\mathbf{G}^{\#}(\rho - \rho') = \mathbf{G}^0(\rho - \rho') + \sum_{s \neq 0} \mathbf{G}^0(\rho - \rho' + \mathbf{R}_s).$$

Frahm and Weiglhofer have shown that [56,57]

$$\begin{aligned}
G_{ij}^0(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0}\partial_{r_i}\partial_{r_j}\frac{1}{r} \\
&= -\frac{1}{3\epsilon_0}\delta(\mathbf{r})\delta_{ij} + \frac{1}{4\pi\epsilon_0}\frac{3r_i r_j - r^2\delta_{ij}}{r^5}. \quad (27)
\end{aligned}$$

The first term gives the depolarization term of the classical Lorentz theory [40], the second one is more delicate and is not considered in the classical approach. Finally, we shall need the multiple-scattering expression for $G^0(\rho - \rho' + \mathbf{R}_s)$, valid when $|\rho| + |\rho'| < |\mathbf{R}_s|$ (see Refs. [58,59] for this and the most general cases).

$$\begin{aligned}
G_0(\rho - \rho' + \mathbf{R_s}) &= \sum_{\ell m\ell'm'} Y_\ell^m(\hat{\rho})j_\ell(\rho)H_{\ell m\ell'm'}(\mathbf{R_s}) \\
&\quad Y_{\ell'}^{m'*}(\hat{\rho}')j_{\ell'}(\rho')
\end{aligned}$$

where $j_\ell(\rho) = \rho^\ell/(2\ell+1)!!$ and

$$\begin{aligned}
H_{\ell m\ell'm'}(\mathbf{R_s}) &= -4\pi(-1)^\ell C_{\ell m\ell+\ell'm'-m}^{\ell'm'}Y_{\ell+\ell'}^{m'-m}(\hat{R_s}) \\
&\quad \frac{(2\ell+2\ell'-1)!!}{R_s^{\ell+\ell'+1}}, \quad (28)
\end{aligned}$$

with $(-1)!! = 1$ and where $C_{\ell m\ell+\ell'm'-m}^{\ell'm'}$ is a Gaunt coefficient.

Because of the derivatives in the definition of $\mathbf{G}^{\#}(\rho - \rho')$, the terms $\ell = 0$ or $\ell' = 0$ in equation (28) do not contribute. Therefore, the cell-to-cell electrostatic interaction begins with a $1/R_s^3$. In other words, there is no interaction between the cell total electron charges (that would be in $1/R_s$), although the cells are not neutral. To be more explicit, the cells are neutral if one considers the nuclei, but the nuclei charges did not enter our description, and their contribution to the dielectric function is very small at optical energies. Therefore, there is no $1/R_s$ interaction although only electrons are taken into account.

For an octahedral or a tetrahedral symmetry, group theory tells us that $\sum_s Y_\ell^m(R_s)$ is zero for $\ell = 1$, 2 and 3. Therefore, the electrostatic interaction starts with a $1/R_s^5$ dependence.

8 Discussion

In this section, we would like to compare our results with previous works and to discuss their physical consequences.

As a first difference, our formalism can be used to calculate the index of non-cubic materials, whereas the standard approach deals only with cubic systems [10,11] (see,

however, reference [34] for the general case). Another difference is in the way the two approaches use the fact that a/λ is small. The standard approach uses it to show that the dielectric function is diagonal in $\mathbf{q}$ and at the end of the calculation because only the $\mathbf{K} = 0$ component of the inverse of the reaction field matrix is used. In our approach, we use also the smallness of a/λ when we set up and invert the reaction field matrix in equations (23) and (24). This has a significant computational advantage. Taking local field effects is very time consuming in the standard approach [60] because the reaction field matrix that must be inverted has matrix elements in the whole reciprocal space [11].

In our approach the matrix is much smaller as we now explain. In a band-structure calculation of the dielectric susceptibility tensor, transitions are calculated between occupied and empty states, thus in the quantities f_i^n and g_j^n the index n is a packed form of the indices $\mathbf{k}_o, n_o, \mathbf{k}_e, n_e$ labelling the occupied and empty states (see Sect. 9 for more details). Moreover, if the nonresonant term of equation equation (6) is taken into account, another index is required to distinguish the resonant and nonresonant terms. In contrast to the standard approach, the reciprocal space indices $\mathbf{k}_o$ and $\mathbf{k}_e$ are now in the first Brillouin zone. The influence of the rest of the reciprocal space is taken into account in the ρ dependence but the integral over ρ is carried out *before* the inversion of the matrix M, whereas in the standard procedure one must first invert a large matrix and then take its $\mathbf{K} = 0$ elements. This is why the matrix to be inverted is much smaller. Moreover, the two-scale transform $\tilde{\chi}$ of χ implies that $\mathbf{k}_e = \mathbf{k}_o \pm \mathbf{q} + \mathbf{K}$, where $\mathbf{K}$ is a vector of the reciprocal lattice. In the visible range $\mathbf{q}$ is very small and Umklapp processes can occur only close to the surface of the Brillouin zone. Otherwise we have the relation $\mathbf{k}_e = \mathbf{k}_o \pm \mathbf{q}$, that further limits the size of the matrix M.

8.1 Electric dipole transitions

A further advantage of our formulation appears when we are only interested in the contribution of electric dipole transitions. To have a constitutive relation in the real space, we back Fourier transform the equation $\mathbf{D}(\mathbf{q}) = \epsilon(\mathbf{q}) \cdot \mathbf{E}(\mathbf{q})$ and we obtain

$$D_i(\mathbf{r}) = \sum_j \int d\mathbf{r}'\bar{\epsilon}_{ij}(\mathbf{r} - \mathbf{r}')E_j(\mathbf{r}'), \quad (29)$$

where

$$\bar{\epsilon}_{ij}(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3}\int d\mathbf{q}\exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')]\epsilon_{ij}(\mathbf{q}). \quad (30)$$

Equation (29) is typical of a homogeneous (but generally anisotropic) medium [37]. The fact that equation (29) is non-local corresponds to spatial dispersion, which has been much studied by the Russian school [37], and has received renewed interest recently [61–64]. Besides, the $\mathbf{q}$-dependence of $\epsilon_{ij}(\mathbf{q})$ can be observed experimentally by

inelastic electron, X-ray or neutron scattering [65–67]. In equation (30), it is not necessary to restrict the integral to the first Brillouin zone since, by definition, $\epsilon_{ij}(\mathbf{q})$ is zero outside this zone.

If $\epsilon_{ij}(\mathbf{q})$ is smooth near $\mathbf{q} = 0$, it can be expanded in a Taylor series

$$\epsilon_{ij}(\mathbf{q}) = \epsilon_{ij}(\mathbf{0}) + \sum_k q_k \partial_k \epsilon_{ij}(\mathbf{0}) + \sum_{kl} q_k q_l \partial_k \partial_l \epsilon_{ij}(\mathbf{0}) + \cdots$$

The first term corresponds to the electric dipole approximation, the second term describes optical activity, the following term corresponds to electric quadrupole and magnetic dipole transitions which are small in the optical range [68]. When only the first term is kept, then equation (30) becomes $\bar{\epsilon}_{ij}(\mathbf{r} - \mathbf{r}') = \epsilon_{ij}(\mathbf{0})\delta(\mathbf{r} - \mathbf{r}')$ and the constitutive relation is now local $\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{0}) \cdot \mathbf{E}(\mathbf{r})$.

In most cases we are only interested in the electric dipole contribution. In the standard approach, it is not possible to take $\mathbf{q} = 0$ in the reaction field matrix before the inversion because a non-zero $\mathbf{q}$ is needed to determine the transverse and longitudinal components of the dielectric tensor [10]. This is not necessary here because we do not decompose the dielectric tensor so that the limit $\mathbf{q} = 0$ can be taken in (23) and (24) before the inversion of the matrix M. This further reduces the computation time.

8.2 Connection with classical electrodynamics

For a physical understanding of our results, it is important to see how they are related to classical electrodynamics [40]. We consider the usual case of a cubic system with one atom per unit cell. Firstly, the reaction of the surroundings in classical electrodynamics is local and the system is cubic. Therefore, $\tilde{\chi}_{ij}(\rho, \rho'; \mathbf{q})$ is localized at $\rho = \rho' = 0$ and it is diagonal. To obtain a diagonal dielectric constant $\tilde{\chi}_{ij}(0, 0; \mathbf{q}) = \delta_{ij}\epsilon_0\alpha$ we choose

$$f_i^n = g_i^n = \delta_{in}\sqrt{\epsilon_0\alpha}. \tag{31}$$

In a cubic system, the second term of equation (27) is zero so the reaction field matrix becomes

$$M(\mathbf{q})_{nn'} = \frac{1}{3\epsilon_0} \sum_i g_i^n(0, \mathbf{q}) f_i^{n'}(0, \mathbf{q}) = \frac{1}{3}\delta_{nn'}\alpha,$$

and the macroscopic dielectric constant becomes

$$\epsilon_{ij}(\mathbf{q}) = \epsilon_0\delta_{ij} + \frac{1}{1 - \frac{\alpha}{3}} \sum_n f_i^n(0, \mathbf{q}) g_j^n(0, \mathbf{q})$$

$$= \delta_{ij}\epsilon_0(1 + \frac{\alpha}{1 - \frac{\alpha}{3}}).$$

This is the classical relation between the microscopic and the macroscopic polarizations [40].

On the other hand, one might wonder when the classical approximation is relevant for quantum calculations, i.e. when equation (31) is satisfied. It is clear that this happens when the final states of the dipole transition can be

described with a single index $n = 1, 2$ or 3, without dependence on the Brillouin zone vector $\mathbf{k}$. This is the case for a system that can be described by a tight-binding Hamiltonian with a ground state made of s-orbitals, so that the final state of the absorption process are p-orbitals. A similar conclusion was reached by Wiser [11].

8.3 Energy density

We would like to conclude this section with a discussion of a subtle physical question, which is not addressed in the standard approach. Macroscopic quantities are obtained by averaging microscopic quantities. The energy density is given microscopically by the product of the electric field and the current. Both quantities exhibit fast oscillations over the unit cell, so it is not obvious that the average of the product can be written as a product of averages. We show now that this is indeed the case in our approach.

The microscopic energy balance is [69]:

$$-\int d\mathbf{r} \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{e}(\mathbf{r}, t) = \frac{1}{\mu_0} \int d\mathbf{r} \mathbf{b}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{b}(\mathbf{r}, t)}{\partial t}$$
$$+ \epsilon_0 \int d\mathbf{r} \mathbf{e}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{e}(\mathbf{r}, t)}{\partial t} + \frac{1}{\mu_0} \int_\Sigma \mathbf{e}(\mathbf{r}, t) \times \mathbf{b}(\mathbf{r}, t) \cdot \mathbf{d}\sigma.$$

The definition of $\mathbf{d}(\mathbf{r})$ gives us

$$\epsilon_0 \frac{\partial \mathbf{e}(\mathbf{r}, t)}{\partial t} = \frac{\partial \mathbf{d}(\mathbf{r}, t)}{\partial t} - \mathbf{j}(\mathbf{r}, t),$$

and the energy balance can be written

$$\int d\mathbf{r} u(\mathbf{r}, t) + \int_\Sigma \mathbf{s}(\mathbf{r}, t) \cdot \mathbf{d}\sigma = 0,$$

where the microscopic electromagnetic energy is

$$u(\mathbf{r}, t) = \frac{1}{\mu_0} \int d\mathbf{r} \mathbf{b}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{b}(\mathbf{r}, t)}{\partial t} + \int d\mathbf{r} \mathbf{e}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{d}(\mathbf{r}, t)}{\partial t},$$

and the microscopic Poynting vector is

$$\mathbf{s}(\mathbf{r}, t) = \frac{1}{\mu_0} \mathbf{e}(\mathbf{r}, t) \times \mathbf{b}(\mathbf{r}, t).$$

If we restrict the definition of the macroscopic fields to the average of the first term in expansion (10), we want to determine whether the average of the microscopic Poynting vector is equal to the macroscopic Poynting vector $\mathbf{S}(\mathbf{r}, t) = \frac{1}{\mu_0}\mathbf{E}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)$, and whether the average of the microscopic energy density is equal to the macroscopic energy density. If this were not the case, the energy arguments using the macroscopic Maxwell equations would lack any microscopic basis.

For the Poynting vector, the answer is immediately yes, because we have shown that $\mathbf{b}^{(0)}(\mathbf{q}, \rho) = \mathbf{B}(\mathbf{q})$. Therefore $\mathbf{b}^{(0)}(\mathbf{r}, t) = \mathbf{B}(\mathbf{r}, t)$, the magnetic field does not oscillate rapidly, it is equal to its average and

$$\langle \mathbf{s}(\mathbf{r}, t) \rangle = \frac{1}{\mu_0} \langle \mathbf{e}^{(0)}(\mathbf{r}, t) \times \mathbf{b}^{(0)}(\mathbf{r}, t) \rangle$$
$$= \frac{1}{\mu_0} \langle \mathbf{e}^{(0)}(\mathbf{r}, t) \rangle \times \mathbf{B}(\mathbf{r}, t) = \frac{1}{\mu_0} \mathbf{E}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)$$
$$= \mathbf{S}(\mathbf{r}, t).$$

The proof is similar for the magnetic part of the energy density. However, the problem is more difficult for the electric part, because it is a product of two functions that oscillate very rapidly, and it is not obvious that the average of the product is equal to the product of the averages. We prove now that the average of the microscopic energy density is indeed given by the usual macroscopic formula.

First, we Fourier transform the fields in space and time as

$$\mathbf{e}^{(0)}(\mathbf{r}, t) = \int_{BZ} d\mathbf{q} \int d\omega \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)]\mathbf{e}^{(0)}(\mathbf{q}, \mathbf{r})$$

(the variable ω is still implicit for the fields).

We need to show that $\langle \mathbf{e}^{(0)}(\mathbf{q}', \rho) \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) \rangle$ is equal to the corresponding macroscopic product $\mathbf{E}(\mathbf{q}') \cdot \mathbf{D}(\mathbf{q})$.

The microscopic displacement field $\mathbf{d}^{(0)}(\mathbf{r}, \mathbf{q})$ is given by equation (16) and the electric field by $\mathbf{e}^{(0)}(\mathbf{q}, \rho) = \mathbf{E}(\mathbf{q}) - \nabla_\rho \phi(\mathbf{q}, \rho)$. The macroscopic displacement field is given by equation (17), so that

$$\langle \mathbf{e}^{(0)}(\mathbf{q}', \rho) \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) \rangle = \mathbf{E}(\mathbf{q}') \cdot \mathbf{D}(\mathbf{q})$$
$$- \langle \nabla_\rho \phi(\mathbf{q}', \rho) \cdot \tilde{\chi}(\rho, \rho'; \mathbf{q}) \rangle_{\rho\rho'} \cdot \mathbf{E}(\mathbf{q})$$
$$+ \epsilon_0 \langle \nabla_\rho \phi(\mathbf{q}', \rho) \cdot \nabla_\rho \phi(\mathbf{q}, \rho) \rangle$$
$$+ \langle \nabla_\rho \phi(\mathbf{q}', \rho) \cdot \tilde{\chi}(\rho, \rho'; \mathbf{q}) \cdot \nabla_{\rho'} \phi(\mathbf{q}, \rho') \rangle_{\rho\rho'},$$

where we have used the fact that $\langle \nabla_\rho \phi(\mathbf{q}, \rho) \rangle = 0$. Integrating by parts to eliminate the gradient of $\phi(\mathbf{q}', \rho)$ we obtain

$$\langle \mathbf{e}^{(0)}(\mathbf{q}', \rho) \cdot \mathbf{d}^{(0)}(\mathbf{q}, \rho) \rangle = \mathbf{E}(\mathbf{q}') \cdot \mathbf{D}(\mathbf{q})$$
$$+ \langle \phi(\mathbf{q}', \rho)[\nabla_\rho \cdot \tilde{\chi}(\rho, \rho'; \mathbf{q}) \cdot \mathbf{E}(\mathbf{q})$$
$$- \epsilon_0 \Delta_\rho \phi(\mathbf{q}, \rho) - \nabla_\rho \cdot \tilde{\chi}(\rho, \rho'; \mathbf{q}) \cdot \nabla_{\rho'} \phi(\mathbf{q}, \rho')] \rangle_{\rho\rho'}$$
$$= \mathbf{E}(\mathbf{q}') \cdot \mathbf{D}(\mathbf{q}),$$

where the last step was derived using the cell equation (18).

A mathematical study of the convergence of the energy density was carried out for a local susceptibility by Markowich and Poupaud [45].

9 Bloch wave functions

Many works are devoted to the calculation of the optical response of semiconductors, using a band-structure approach. To deal with this case, we specify now our results to the case of one-electron wavefunctions.

The Bloch theorem tells us that one-electron wavefunctions in a crystal can be written $\exp(i\mathbf{k} \cdot \mathbf{r})u_l(\mathbf{r}; \mathbf{k})$, where the index l runs over the bands. When this equation is introduced into the velocity matrix elements (7), we find

$$\mathbf{V}^{ll'}(\mathbf{r}; \mathbf{k}, \mathbf{k}') = -\frac{i\hbar}{2m} \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}]$$
$$(n_{l', \mathbf{k}'} - n_{l, \mathbf{k}})\mathbf{W}^{ll'}(\mathbf{r}; \mathbf{k}, \mathbf{k}'),$$

where $n_{l, \mathbf{k}}$ is the occupation of the lth band with Bloch vector $\mathbf{k}$ and the periodic functions $\mathbf{W}^{ll'}(\mathbf{r}; \mathbf{k}, \mathbf{k}')$ are

$$\mathbf{W}^{ll'}(\mathbf{r}; \mathbf{k}, \mathbf{k}') = u_l^*(\mathbf{r}; \mathbf{k})\nabla u_{l'}(\mathbf{r}; \mathbf{k}') - u_{l'}(\mathbf{r}; \mathbf{k}')\nabla u_l^*(\mathbf{r}; \mathbf{k})$$
$$+ i(\mathbf{k} + \mathbf{k}')u_l^*(\mathbf{r}; \mathbf{k})u_{l'}(\mathbf{r}; \mathbf{k}').$$

Neglecting the first and the last term in equation (6) we find

$$\chi_{ij}(\mathbf{r}, \mathbf{r}') = -\frac{e^2\hbar^2}{4\omega^2 m^2} \int d\mathbf{k} d\mathbf{k}' \exp[i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{r} - \mathbf{r}')]$$
$$\sum_{ll'} (n_{l', \mathbf{k}'} - n_{l, \mathbf{k}}) \frac{W_i^{ll'}(\mathbf{r}; \mathbf{k}, \mathbf{k}')W_j^{l'l}(\mathbf{r}; \mathbf{k}', \mathbf{k})}{E_{l'}(\mathbf{k}') - E_l(\mathbf{k}) - \hbar\omega}.$$

We treat now the electric dipole case $\mathbf{q} = 0$. From the definition of the two-scale transform of χ and from identity (2) we find

$$\tilde{\chi}_{ij}(\rho, \rho'; \mathbf{0}) = -\frac{(2\pi)^3 e^2 \hbar^2}{4\omega^2 m^2} \int d\mathbf{k} \sum_{ll'} (n_{l', \mathbf{k}} - n_{l, \mathbf{k}}) \quad (32)$$

$$\frac{W_i^{ll'}(\rho; \mathbf{k}, \mathbf{k})W_j^{l'l}(\rho'; \mathbf{k}, \mathbf{k})}{E_{l'}(\mathbf{k}) - E_l(\mathbf{k}) - \hbar\omega}. \quad (33)$$

Therefore, in the electric dipole case, the transitions are vertical. When spatial dispersion is investigated, then the transitions are no longer vertical, they explore a part of the bands around the vertical [62].

We can use the Schrödinger equation for u_l and $u_{l'}$ to show that

$$\nabla_\rho \cdot \mathbf{W}^{ll'}(\rho; \mathbf{k}, \mathbf{k}) = -\frac{2m}{\hbar^2}(E_{l'}(\mathbf{k}) - E_l(\mathbf{k}))u_l^*(\rho; \mathbf{k})u_{l'}(\rho; \mathbf{k}).$$
$$(34)$$

In reference [5], p. 121, Keller has proved that such a relation between $\nabla \cdot \mathbf{V}^{0n}(\mathbf{r})$ and matrix elements of the density operator holds also valid in the many-body case.

To use the macroscopic constitutive relation (23) we must define a separable form (22) for $\tilde{\chi}$ in equation (33). We can choose

$$f_i^{ll'}(\rho; \mathbf{k}) = -\frac{(2\pi)^3 e^2 \hbar^2}{4\omega^2 m^2}(n_{l', \mathbf{k}} - n_{l, \mathbf{k}})$$
$$\frac{W_i^{ll'}(\rho; \mathbf{k}, \mathbf{k})}{E_{l'}(\mathbf{k}) - E_l(\mathbf{k}) - \hbar\omega},$$
$$g_j^{ll'}(\rho'; \underline{\mathbf{k}}) = W_j^{l'l}(\rho'; \underline{\mathbf{k}}, \underline{\mathbf{k}}).$$

Finally, using identity (34) and the alternative definition of the reaction field matrix M we find

$$M_{\mathbf{k}\underline{\mathbf{k}}}^{ll'\underline{l}\underline{l}'} = \frac{|C|(2\pi)^3 e^2}{(\hbar\omega)^2}(n_{l', \mathbf{k}} - n_{l, \mathbf{k}})$$
$$\frac{(E_{l'}(\mathbf{k}) - E_l(\mathbf{k}))(E_{\underline{l}}(\underline{\mathbf{k}}) - E_{\underline{l}'}(\underline{\mathbf{k}}))}{(E_{l'}(\mathbf{k}) - E_l(\mathbf{k}) - \hbar\omega)}$$
$$\langle u_l^*(\rho; \mathbf{k})u_{l'}(\rho; \mathbf{k})G^{\#}(\rho - \rho')u_{\underline{l}'}^*(\rho'; \underline{\mathbf{k}})u_{\underline{l}}(\rho'; \underline{\mathbf{k}}) \rangle_{\rho\rho'}.$$

Because of the presence of the Bloch vector indices $\mathbf{k}$ and $\underline{\mathbf{k}}$, the reaction field matrix is huge and its inversion will be a heavy computation.

All the ingredients are now given for a band-structure calculation of the macroscopic dielectric constant in the electric dipole approximation. The final formula is

$$\bar{\epsilon}_{ij} = \epsilon_0 \delta_{ij} - \frac{(2\pi)^3 e^2 \hbar^2}{4m^2\omega^2} \int d\mathbf{k} d\underline{\mathbf{k}} \sum_{ll'\underline{l}l'} (n_{l',\mathbf{k}} - n_{l,\mathbf{k}})$$

$$\frac{\langle W_i^{ll'}(\rho;\mathbf{k},\mathbf{k})\rangle [(1-M)^{-1}]_{\mathbf{k}\underline{\mathbf{k}}}^{ll'\underline{l}l'} \langle W_j^{l'l}(\rho;\underline{\mathbf{k}},\underline{\mathbf{k}})\rangle}{(E_{l'}(\mathbf{k}) - E_l(\mathbf{k}) - \hbar\omega)}$$

A similar formula can be obtained for spatial dispersion ($\mathbf{q} \neq \mathbf{0}$), adapting the implementation described in reference [70], where the Coulomb singularity and the Umklapp processes are treated in detail.

10 Conclusion

Homogenization theory is usually used to calculate the properties of "real" materials (porous, fibrous, disordered, etc.). It is a somewhat just reward that applied physics can also be useful to basic physics.

Here, homogenization theory was used to calculate the macroscopic dielectric constant from the microscopic dielectric function. Compared to previous works, our approach is not restricted to cubic materials and provides new equations to describe the local field effect in dielectrics. This article does not exhaust the prospects of homogenization theory in solid-state physics. It is rather a detailed presentation of the simplest possible case and the present study can be developed in many directions.

A complete derivation of the macroscopic Maxwell equations should also take magnetism into account. In particular, the mysterious relation between microscopic and macroscopic magnetic properties [71] could be handled with homogenization theory, as well as the question of the general form of the constitutive relations in bianisotropic media [63].

Further terms of the expansion can be calculated [44] to investigate the case when the wavelength of the incident wave is not very large as compared to the unit cell, as in the VUV range and for some near-field optics or inelastic scattering experiments.

We have considered an infinite crystal, but homogenization theory can also treat finite crystals [47,50,51,72]. This is particularly interesting when the medium exhibits spatial dispersion, i.e. $q \neq 0$ in equation (23), because additional boundary conditions can be required to determine the waves inside the dielectric body [37,52,63]. Homogenization theory is well suited to describe the boundary layer that forms at the surface of the dielectric body, and to derive the corresponding boundary conditions. To do this, one adds to the bulk (periodic) functions a boundary function that decreases exponentially out of the dielectric [41,73]. Besides, the Bloch decomposition of the electromagnetic field seems to be a promising alternative for that purpose [46,72,74].

The present work was carried out within the linear response approximation. Homogenization theory is fully developed to deal with non-linear equations [22,47,75].

We have considered periodic media, but homogenization theory applies also when the periodic structure varies slowly [20] or in disordered or polycrystalline media [22]. This field is developing rapidly nowadays [76,77].

Finally, the method is not restricted to electrodynamics and can be used to calculate any constitutive relation corresponding to a microscopic non-local equation.

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