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I. POLARIZATION, MAGNETIZATION, AND THE MACROSCOPIC MAXWELL'S EQUATIONS

A. Introduction

To obtain the electric and magnetic fields from Maxwell's equations we must know the microscopic charge and current densities ρ and \mathbf{J} . However, these are impossible to describe exactly, since a macroscopic amount of matter contains a very large number of electrons and nuclei in motion. Large spatial variations of the densities and corresponding fields occur over distances of the order of angstroms or less, while temporal fluctuations occur with periods of the order of femtoseconds. On the other hand, macroscopic measuring devices average over space and time intervals such as the above. All microscopic fluctuations average out, which allows us to introduce relatively smooth and slowly varying macroscopic quantities. As we discussed earlier, to first approximation we can replace the densities at each point in space by their average values within an appropriately small volume around that point. Here we discuss corrections to this approximation, which are most important in the case of *bound* electrons restricted to move within molecules. Furthermore, when we apply an external electric or magnetic field, ρ and \mathbf{J} change as compared to their values in the absence of fields and can no longer be described simply by the charge average. Such field-induced changes in the charge and current distributions must be included in Maxwell's equations: they change the fields, which in turn change the densities etc.

An external field leads to tiny redistributions of the charge within a neutral atom or molecule, whose average charge is zero. For example, an external electric field pulls the positively charged nucleus in one direction and the negatively charged electrons in the opposite direction. For very large fields, the electrons can separate enough to escape from the pull of the nucleus and become free, thus ionizing the atom. However, for typical values of the available external fields, the electrons remain bound and the competition between the pull

of the nucleus and the push of the external field result in slightly separated positive and negative charge, i.e. to a *polarized* neutral atom. Such tiny distortions in the charge density, on the order of a small fraction of the diameter of the atom, add up in a solid consisting of a macroscopically large number of atoms and result in observable changes in the electric field. We must thus describe the correction to the charge density as compared to its value in the absence of external field. Furthermore, in the case of some polar molecules such as e.g. water, the electrons and nuclei are separated by a significant amount even in the absence of external field (e.g. the electrons accumulate close to the oxygen and are thus separated from the positively charged hydrogen atoms). Such molecules cannot be described by assuming an average charge density (zero within a volume that contains the entire molecule). For example, the application of an external electric field will rotate the molecule due to the separation of positive and negative charge, while a non-homogeneous field will exert a finite force. For describing such effects, we must obtain an adequate description of the deviations of the charge and current densities from their average values.

B. Multipole Expansion: charges

Let us consider an arbitrary charge density $\rho(\mathbf{r})$ restricted within a finite region in space of characteristic dimension a . We want to calculate the electric potential at a point displaced by \mathbf{r} with respect to the chosen origin O , at a distance $r \gg a$ from O . For example, in the case of a molecule, the microscopic density ρ is nonzero only within tiny distances r of the order of the molecule size, i.e. within Angstroms. If we are interested in the electric fields at a macroscopic distance r from O , we can safely assume $r \gg a$.

From the superposition principle, the electrostatic potential is obtained by adding up the contributions from each infinitesimal charge $\rho(\mathbf{r}')d\mathbf{r}'$ displaced by \mathbf{r}' from O :

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0 r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{\sqrt{1 + \left(\frac{r'}{r}\right)^2 - 2\left(\frac{r'}{r}\right) \cos \theta}} \quad (1)$$

where θ is the angle between the vectors \mathbf{r} and \mathbf{r}' and $d\mathbf{r}' = dx'dy'dz'$ denotes the infinitesimal volume. At any point very far from O as compared to the typical extent of the charge distribution, $r'/r \ll 1$ and we can simplify the above expression by using the Taylor expansion of $1/\sqrt{1 + \epsilon}$ for $\epsilon \ll 1$:

$$\frac{1}{\sqrt{1 + \epsilon}} = 1 - \frac{1}{2}\epsilon + \frac{3}{8}\epsilon^2 - \frac{5}{16}\epsilon^3 + \dots \quad (2)$$

Using this expansion for $\epsilon = \left(\frac{r'}{r}\right)^2 - 2\left(\frac{r'}{r}\right)\cos\theta \ll 1$ we obtain that

$$\frac{1}{\sqrt{1+\epsilon}} = 1 + \left(\frac{r'}{r}\right)\cos\theta - \frac{1}{2}\left(\frac{r'}{r}\right)^2 + \frac{3}{2}\left(\frac{r'}{r}\right)^2\cos^2\theta + O\left(\frac{r'}{r}\right)^3 = \sum_{n=0}^{\infty}\left(\frac{r'}{r}\right)^n P_n(\cos\theta), \quad (3)$$

where P_n are polynomials obtained by collecting all terms to given order in r'/r in the above expansion. The $n=0$ term gives, after substituting into Eq.(1), the *monopole contribution* to the potential:

$$V_0(\mathbf{r}) = \frac{\int d\mathbf{r}'\rho(\mathbf{r}')}{4\pi\epsilon_0 r} = \frac{Q_{tot}}{4\pi\epsilon_0 r} \quad (4)$$

which corresponds to the potential produced by the total charge as if it were a point charge. This proves the physically intuitive result that, at sufficiently large distances $r \gg a$ from the region where the charge is confined, the details and finite dimension of the charge distribution do not matter.

What happens however for a neutral object with $Q_{tot}=0$? The monopole term V_0 vanishes and the asymptotic behavior of the potential at large distances is determined by the next contribution in the above expansion, called the *dipole contribution*. Denoting by \hat{r} the unit vector along \mathbf{r} and noting that $\mathbf{r}' \cdot \hat{r} = r' \cos\theta$ we obtain that

$$V_1(\mathbf{r}) = \frac{1}{4\pi\epsilon_0 r^2} \int d\mathbf{r}' r' \cos\theta \rho(\mathbf{r}') = \frac{\mathbf{p} \cdot \hat{r}}{4\pi\epsilon_0 r^2} \quad (5)$$

where the vector quantity

$$\mathbf{p} = \int d\mathbf{r}' \mathbf{r}' \rho(\mathbf{r}') \quad (6)$$

is called the *dipole moment* of the charge distribution ρ . For $Q_{tot}=0$, \mathbf{p} does not depend on our choice of the origin O (prove).

In the case of the microscopic charge density of N point charges q_i moving in trajectories $\mathbf{r}_i(t)$, $\rho(\mathbf{r}, t) = \sum_i q_i \delta[\mathbf{r} - \mathbf{r}_i(t)]$ and we obtain from the above equations that

$$Q_{tot} = \sum_{i=1}^N q_i, \quad \mathbf{p} = \sum_{i=1}^N q_i \mathbf{r}_i. \quad (7)$$

In the case of two charges q and $-q$, the above equation reduces to the well-known dipole moment $\mathbf{p} = qs$, where \mathbf{s} is the vector that points from $-q$ to $+q$. We conclude that, for sufficiently large distances r , the potential due to any charge distribution can be obtained without knowing the full $\rho(\mathbf{r})$, only the total charge and dipole moment of this distribution. We can then replace ρ by a point charge Q_{tot} and a point dipole moment \mathbf{p} defined as above.

C. Polarization

Let us now consider a system that consists, in addition to possible free point charges not associated with a particular nucleus but moving freely in space, charges bound to N individual molecules with non-overlapping charge distributions. The total bound charge density may then be expressed as the sum of the contribution of all individual molecules:

$$\rho_{\text{bound}}(\mathbf{r}t) = \sum_n \rho_n(\mathbf{r}t)$$

where

$$\rho_n(\mathbf{r}t) = \sum_i q_{in} \delta[\mathbf{r} - \mathbf{r}_{in}(t)]$$

is the contribution of all point charges, electrons and nuclei, within the n -th molecule. The coordinates \mathbf{r}_i of the bound point charges may be defined relative to a molecular center of mass (or charge) \mathbf{r}_n :

$$\mathbf{r}_{in} = \mathbf{r}_n + \Delta\mathbf{r}_{in}. \quad (8)$$

We only need fields at distances much larger than the molecular dimensions, so we can describe the total potential as the superposition of the results of the previous section obtained for $\rho = \rho_n$, $n=1 \cdots N$:

$$V(\mathbf{r}) = \sum_{n=1}^N \frac{\mathbf{p}_n \cdot (\hat{\mathbf{r}} - \hat{\mathbf{r}}_n)}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}_n|^2} \quad (9)$$

where

$$\mathbf{p}_n = \sum_i q_i \Delta\mathbf{r}_{in}. \quad (10)$$

Similar to the definition of the charge density ρ in the beginning of the course, we define the density of molecular dipole moments

$$\mathbf{P}(\mathbf{r}t) = \sum_n \mathbf{p}_n \delta[\mathbf{r} - \mathbf{r}_n(t)] \quad (11)$$

and rewrite the above expression of the potential by using the definition of the delta-function as

$$V(\mathbf{r}) = \int d\mathbf{r}' \frac{\mathbf{P}(\mathbf{r}') \cdot (\hat{\mathbf{r}} - \hat{\mathbf{r}}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|^2}. \quad (12)$$

Although the above result gives the desired correction, it is difficult to calculate the integral. Instead, we now transform it into the form of a superposition of Coulomb potentials due to

point charges by using the following mathematical properties:

$$\nabla_{\mathbf{r}'} \frac{1}{|\mathbf{r} - \mathbf{r}'|} = -\nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{(\hat{\mathbf{r}} - \hat{\mathbf{r}}')}{|\mathbf{r} - \mathbf{r}'|^2} \quad (13)$$

and

$$\nabla_{\mathbf{r}'} \frac{\mathbf{P}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \frac{\nabla_{\mathbf{r}'} \mathbf{P}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mathbf{P}(\mathbf{r}') \cdot \nabla_{\mathbf{r}'} \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (14)$$

Substituting in the above equation for the potential and using Gauss's theorem we obtain for any volume V surrounded by a closed surface S that

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int_V d\mathbf{r}' \frac{-\nabla_{\mathbf{r}'} \mathbf{P}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{4\pi\epsilon_0} \int_S \frac{\mathbf{P}(\mathbf{r}') \cdot d\mathbf{S}}{|\mathbf{r} - \mathbf{r}'|}. \quad (15)$$

The first term in the above equation describes the potential due to a charge density

$$\rho_p(\mathbf{r}t) = -\nabla \mathbf{P}(\mathbf{r}, t) \quad (16)$$

confined within a volume V . The second term describes the contribution due to a surface charge density

$$\sigma_p = \hat{\mathbf{n}} \cdot \mathbf{P} \quad (17)$$

confined at the surface S that encloses V . So instead of calculating the field as superposition of all the dipole contributions of all individual molecules, we can simply calculate the field created by the volume and surface charge densities ρ_p and σ_p using all the methods that we learned so far!

We now approximate the discontinuous microscopic polarization Eq.(11) by a macroscopic average value that is a continuous function of space, as we are interested in describing aggregates consisting of a very large (macroscopic) number of $N \rightarrow \infty$ elementary dipoles. Similar to the definition of the macroscopic charge density earlier in the course, we first note from the definition of the Dirac delta-function and Eq.(11) that

$$\int_{\Delta V} d\mathbf{r}' \mathbf{P}(\mathbf{r}') = \sum_{n=1}^N \mathbf{p}_n$$

gives the total charge dipole moment located inside any volume ΔV centered at point \mathbf{r} . We take the dimensions of this ΔV to be *much smaller* than the dimensions and characteristic lengths of the physical system we are studying, but at the same time *much larger* than molecular and atomic lengths, so that ΔV contains a macroscopic number, practically $N \rightarrow \infty$, of molecules. If we calculate the field by approximating the microscopic $\mathbf{P}(\mathbf{r})$, Eq.(11),

by its average value within a small volume ΔV around each \mathbf{r} , there will be no observable difference in the fields. We thus define the average polarization

$$\mathbf{P}(\mathbf{r}, t) \rightarrow \frac{1}{\Delta V} \int_{\Delta V} d\mathbf{r}' \mathbf{P}(\mathbf{r}', t) = \frac{\sum_{n=1}^N \mathbf{p}_n}{\Delta V}.$$

In this way, we deal with a continuous polarization distribution in a way analogous to the theory of elasticity and continuum mechanics. The graininess (discreteness) of the individual molecules is ignored in such a macroscopic treatment, an excellent approximation at the right length scales. We average out the microscopic charges within a sufficiently small volume around each position \mathbf{r} of interest that is smaller than the characteristic lengths of the system and large enough to contain a macroscopic number N of molecules.

The above bound charge distributions, Eqs. (16) and (17), describe real charges. To see this, we note that

$$\rho_n(\mathbf{r}) = \sum_i q_{in} \delta[\mathbf{r} - \mathbf{r}_n - \Delta \mathbf{r}_{in}] \approx q_n \delta[\mathbf{r} - \mathbf{r}_n] - \mathbf{p}_n \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n]$$

where $q_n = \sum_i q_{in}$ is the total charge of molecule n . The above Taylor expansion is valid since we consider bound charges and are interested in \mathbf{r} that vary on a scale much larger than the molecular dimensions and $\Delta \mathbf{r}_{in}$. Therefore, the charge density, which includes the contribution of all free and bound point charges, can be approximately described by two continuous distributions:

$$\rho(\mathbf{r}, t) = \bar{\rho}(\mathbf{r}, t) - \nabla \cdot \mathbf{P}(\mathbf{r}, t)$$

where

$$\bar{\rho}(\mathbf{r}, t) = \sum_{i, \text{ free}} q_i \delta[\mathbf{r} - \mathbf{r}_i(t)] + \sum_{n, \text{ molecules}} q_n \delta[\mathbf{r} - \mathbf{r}_n(t)]$$

is the *macroscopic* average density of both free carrier and total molecular charge, if nonzero, while $\mathbf{P}(\mathbf{r}, t)$ is the macroscopic polarization defined above. We conclude that the polarization $\mathbf{P}(\mathbf{r})$ characterizes the deviation of the charge distribution due to the relative displacement of the point charges bound within each molecule.

D. Electric Displacement

Substituting the above expression of the microscopic charge ρ into Gauss's differential equation we obtain that

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} = \frac{\bar{\rho}}{\epsilon_0} - \frac{\nabla \cdot \mathbf{P}}{\epsilon_0},$$

which can be written in the form

$$\nabla \cdot \mathbf{D} = \bar{\rho}(\mathbf{r}, t)$$

where we introduced the electric displacement field vector

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} + \dots$$

and neglected quadrupole and higher contributions. Note that Faraday's law retains its original form since ρ does not enter there:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

where \mathbf{E} is the *electric* field. Note that, in the case of static problems with $\mathbf{B}=0$, $\nabla \times \mathbf{D} = \nabla \times \mathbf{P} \neq 0$, even though $\nabla \times \mathbf{E} = 0$ and we can still introduce the electric potential by $\mathbf{E} = -\nabla\Phi$. The Poisson equation for Φ takes the form

$$\nabla^2 \Phi = -\frac{\bar{\rho} - \nabla \cdot \mathbf{P}}{\epsilon_0}, \quad (18)$$

with boundary conditions

$$\mathbf{n} \cdot (\mathbf{D}_2 - \mathbf{D}_1) = \bar{\sigma}$$

where $\bar{\sigma}$ is the free charge and net molecular surface charge density, while \mathbf{E} (and not \mathbf{D}) is continuous. Finally, the energy density stored in an electrostatic system is

$$\mathcal{E} = \frac{1}{2} \int \mathbf{D} \cdot \mathbf{E}. \quad (19)$$

In many materials we have for *sufficiently weak* electric fields the following *approximate* linear relationship:

$$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$$

where we expressed the proportionality constant in this way so that we introduce a *dimensionless* quantity χ_e that we call electric susceptibility. If the above relation is a good approximation, we talk about a linear material. Note here that \mathbf{E} is the total electric field, due partly to the free charges and partly due to the polarization itself. The electric field causes a polarization, which through Maxwell's equations creates an electric field correction, etc. In the case of linear materials we have that

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \mathbf{E} + \chi_e \epsilon_0 \mathbf{E} = \epsilon \mathbf{E}$$

where the proportionality constant

$$\epsilon = \epsilon_0(1 + \chi_e)$$

is called the *dielectric permeability*. In vacuum, $\chi_e = 0$ and $\epsilon = \epsilon_0$. The dimensionless quantity

$$K = 1 + \chi_e = \frac{\epsilon}{\epsilon_0}$$

is called the *dielectric constant*. Poisson's equation then takes the form

$$\nabla \cdot (\epsilon \nabla \Phi) = -\bar{\rho}. \quad (20)$$

There are many cases however where the external electric fields are sufficiently strong so that the above approximate linear dependence fails, for example in the case of short laser pulses with sufficiently high intensity. In the general case,

$$\mathbf{D} = \mathbf{D}[\mathbf{E}, \mathbf{B}]$$

is a nonlinear function of the two fields, called the *constitutive* relation. Both \mathbf{E} and \mathbf{D} enter in Maxwell's equations, so we need to know this relation, which is determined by the microscopic quantum mechanical properties of the material.

II. MAGNETIZATION

We now turn to the current density \mathbf{j} due to all the point charges:

$$\mathbf{j}(\mathbf{r}t) = \sum_i q_i \mathbf{v}_i \delta[\mathbf{r} - \mathbf{r}_i(t)]$$

where \mathbf{v}_i is the velocity of the i -th charge. As above, we separate the contributions of the free electrons and the charges bound to the N molecules. The latter is given by $\sum_n \mathbf{j}_n$, where

$$\mathbf{j}_n(\mathbf{r}t) = \sum_{i(n)} q_i (\mathbf{v}_n + \Delta \mathbf{v}_{in}) \delta[\mathbf{r} - \mathbf{r}_n(t) - \Delta \mathbf{r}_{in}(t)].$$

In the above we used the property

$$\mathbf{r}_{in} = \mathbf{r}_n + \Delta \mathbf{r}_{in} \rightarrow \mathbf{v}_{in} = \mathbf{v}_n + \Delta \mathbf{v}_{in}$$

where

$$\mathbf{v}_n = \frac{d\mathbf{r}_n}{dt}, \quad \Delta \mathbf{v}_{in} = \frac{d\Delta \mathbf{r}_{in}}{dt}.$$

After some algebra, a Taylor expansion, and using the definition $\Delta \mathbf{v}_{in} = \frac{d\mathbf{r}_{in}}{dt}$ we obtain

$$\begin{aligned} \mathbf{j}_n(\mathbf{r}t) &= \sum_{i(n)} q_i \mathbf{v}_n \delta[\mathbf{r} - \mathbf{r}_n(t) - \Delta \mathbf{r}_{in}(t)] + \sum_{i(n)} q_i \Delta \mathbf{v}_{in} \delta[\mathbf{r} - \mathbf{r}_n(t) - \Delta \mathbf{r}_{in}(t)] \\ &= \sum_{i(n)} q_i \mathbf{v}_n \delta[\mathbf{r} - \mathbf{r}_n(t)] - \sum_{i(n)} q_i \mathbf{v}_n \Delta \mathbf{r}_{in} \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)] + \sum_{i(n)} q_i \frac{d\Delta \mathbf{r}_{in}}{dt} \delta[\mathbf{r} - \mathbf{r}_n(t) - \Delta \mathbf{r}_{in}(t)]. \end{aligned}$$

Recalling the definition of the molecule polarization \mathbf{p}_n and charge q_n we obtain

$$\mathbf{j}_n(\mathbf{r}t) = q_n \mathbf{v}_n \delta[\mathbf{r} - \mathbf{r}_n(t)] - \mathbf{v}_n (\mathbf{p}_n \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)]) + \sum_{i(n)} q_i \frac{d}{dt} \Delta \mathbf{r}_{in} \delta[\mathbf{r} - \mathbf{r}_n(t) - \Delta \mathbf{r}_{in}(t)]$$

After Taylor expansion

$$\begin{aligned} \mathbf{j}_n(\mathbf{r}t) &= q_n \mathbf{v}_n \delta[\mathbf{r} - \mathbf{r}_n(t)] - \mathbf{v}_n (\mathbf{p}_n \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)]) + \sum_{i(n)} q_i \frac{d\Delta \mathbf{r}_{in}(t)}{dt} \delta[\mathbf{r} - \mathbf{r}_n(t)] \\ &\quad - \sum_{i(n)} q_i \frac{d\Delta \mathbf{r}_{in}(t)}{dt} \Delta \mathbf{r}_{in}(t) \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)] \end{aligned}$$

and after algebra and using the definition of \mathbf{p}_n

$$\begin{aligned} \mathbf{j}_n(\mathbf{r}t) &= q_n \mathbf{v}_n \delta[\mathbf{r} - \mathbf{r}_n(t)] - \mathbf{v}_n (\mathbf{p}_n \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)]) + \frac{d\mathbf{p}_n(t)}{dt} \delta[\mathbf{r} - \mathbf{r}_n(t)] \\ &\quad - \sum_{i(n)} q_i \frac{d\Delta \mathbf{r}_{in}(t)}{dt} (\Delta \mathbf{r}_{in}(t) \cdot \nabla \delta[\mathbf{r} - \mathbf{r}_n(t)]) \end{aligned}$$

From now on we do vector manipulations. First we symmetrize:

$$\frac{d\mathbf{A}}{dt} (\mathbf{A} \cdot \nabla) = \frac{1}{2} \frac{d\mathbf{A}}{dt} (\mathbf{A} \cdot \nabla) + \frac{1}{2} \frac{d}{dt} [\mathbf{A} (\mathbf{A} \cdot \nabla)] - \frac{1}{2} \mathbf{A} \left(\frac{d\mathbf{A}}{dt} \cdot \nabla \right)$$

Using the property

$$\nabla \times (\mathbf{A} \times \mathbf{B}) = (\mathbf{B} \cdot \nabla) \mathbf{A} - (\mathbf{A} \cdot \nabla) \mathbf{B} + \mathbf{A} (\nabla \cdot \mathbf{B}) - \mathbf{B} (\nabla \cdot \mathbf{A})$$

for $\mathbf{B} = d\mathbf{A}/dt$ we obtain

$$\frac{d\mathbf{A}}{dt} (\mathbf{A} \cdot \nabla) = \frac{1}{2} \frac{d}{dt} [\mathbf{A} (\mathbf{A} \cdot \nabla)] + \frac{1}{2} \nabla \times \left(\frac{d\mathbf{A}}{dt} \times \mathbf{A} \right)$$

and therefore, for $\mathbf{A} = \Delta \mathbf{r}_{in}(t)$,

$$-\frac{d\Delta \mathbf{r}_{in}(t)}{dt} (\Delta \mathbf{r}_{in}(t) \cdot \nabla) = -\frac{1}{2} \frac{d}{dt} [\Delta \mathbf{r}_{in}(t) (\Delta \mathbf{r}_{in}(t) \cdot \nabla)] + \frac{1}{2} \nabla \times \left(\Delta \mathbf{r}_{in}(t) \times \frac{d\Delta \mathbf{r}_{in}(t)}{dt} \right)$$

We also obtain that

$$\begin{aligned}\frac{d\mathbf{p}_n(t)}{dt}\delta[\mathbf{r} - \mathbf{r}_n(t)] &= \frac{d}{dt}(\mathbf{p}_n(t)\delta[\mathbf{r} - \mathbf{r}_n(t)]) - \mathbf{p}_n(t)\frac{d}{dt}\delta[\mathbf{r} - \mathbf{r}_n(t)] \\ &= \frac{d}{dt}(\mathbf{p}_n(t)\delta[\mathbf{r} - \mathbf{r}_n(t)]) + \mathbf{p}_n(t)\frac{d\mathbf{r}_n(t)}{dt} \cdot \nabla\delta[\mathbf{r} - \mathbf{r}_n(t)]\end{aligned}$$

Therefore

$$\begin{aligned}\mathbf{j}_n(\mathbf{r}t) &= q_n\mathbf{v}_n\delta[\mathbf{r} - \mathbf{r}_n(t)] - \mathbf{v}_n(\mathbf{p}_n \cdot \nabla)\delta[\mathbf{r} - \mathbf{r}_n(t)] + \mathbf{p}_n(\mathbf{v}_n \cdot \nabla)\delta[\mathbf{r} - \mathbf{r}_n(t)] \\ &+ \frac{d}{dt}\left[\mathbf{p}_n(t)\delta[\mathbf{r} - \mathbf{r}_n(t)] - \frac{1}{2}\sum_{i(n)}q_i\Delta\mathbf{r}_{in}(t)(\Delta\mathbf{r}_{in}(t) \cdot \nabla)\delta[\mathbf{r} - \mathbf{r}_n(t)]\right] \\ &+ \nabla \times \sum_{i(n)}\frac{q_i}{2}\Delta\mathbf{r}_{in} \times \mathbf{v}_{in}\delta[\mathbf{r} - \mathbf{r}_n(t)]\end{aligned}$$

We now neglect the terms of order $(\Delta\mathbf{r}_{in})^2$ for consistency and recall the definition of $\mathbf{P}(\mathbf{r}t)$.

We also introduce the vector

$$\mathbf{m}_n = \frac{1}{2}\sum_{i(n)}q_i\Delta\mathbf{r}_{in} \times \mathbf{v}_{in}$$

which we call the molecular magnetic moment,

$$\mathbf{M}(\mathbf{r}t) = \sum_n\mathbf{m}_n\delta[\mathbf{r} - \mathbf{r}_n(t)]$$

which we call the (macroscopic) magnetization and

$$\mathbf{J}(\mathbf{r}t) = \sum_{i(\text{free})}q_i\mathbf{v}_i\delta[\mathbf{r} - \mathbf{r}_i(t)] + \sum_{n(\text{mol})}q_n\mathbf{v}_n\delta[\mathbf{r} - \mathbf{r}_n(t)],$$

the macroscopic current density. We then obtain for the microscopic current that enters on the right hand side of Maxwell's equations

$$\mathbf{j}(\mathbf{r}t) = \mathbf{J}(\mathbf{r}t) + \nabla \times \mathbf{M}(\mathbf{r}t) + \frac{\partial\mathbf{P}(\mathbf{r}t)}{\partial t}$$

where we neglected the molecular velocities that are typically small (typically thermal velocities in a gas or lattice vibrational velocities in a solid). Substituting into the Ampere-Maxwell equation we obtain

$$\nabla \times \mathbf{B} = \mu_0\mathbf{J} + \mu_0\nabla \times \mathbf{M} + \mu_0\frac{\partial\mathbf{P}}{\partial t} + \epsilon_0\mu_0\frac{\partial\mathbf{E}}{\partial t}.$$

Recalling the definition of \mathbf{D} and defining the magnetic field quantity

$$\mathbf{B} = \mu_0\mathbf{H} + \mu_0\mathbf{M}$$

we express the above equation in the form

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}.$$

Note that the above equation is an approximation, which assumes for example the dipole approximation and neglects the molecular velocities.