Chapter 4

General Formulae for Effective Coefficients of Nonlinear Composites

In this chapter, we concern with the definition and physical meaning of the effective coefficients, and the process to determine the general formulae for the effective coefficients up to the ninth order of nonlinear composites for the case of fifth-order nonlinearity of the electric displacement, Eq. (2.2).

4.1 The definition of effective coefficients

In the quasi-static limit case (zero-frequency case), $(\mathbf{D})$ and $(\mathbf{E})$ are related by the nonlinear equation as shown in Eq. (2.2) and note that ε, χ, and η are constants in each region of inclusions and host medium. Let V be the composite volume, and let a uniform external electric field $(\mathbf{E}_0)$ be applied to the system so that the electric potential on the composite surface is $-\mathbf{E}_0 \cdot \mathbf{x}$. Then it can be shown that the space average electric field of the composite is just $\mathbf{E}_0$ (see Appendix B):

$$\langle \mathbf{E} \rangle = \frac{1}{V} \int_V \mathbf{E}(\mathbf{x}) d^3x = \mathbf{E}_0. \tag{4.1}$$

In a sufficiently strong applied electric field, high-order effective nonlinear coefficients are required for the accurate prediction of the dielectric response [11,12]. Then the effective nonlinear coefficients are extended to include up to the ninth-order in this thesis. The effective coefficients of the composite are defined in terms of the space averaged electric displacement $(\langle \mathbf{D} \rangle)$ and the space averaged electric field $(\langle \mathbf{E} \rangle = \mathbf{E}_0)$ as follows [6]:

$$\langle \mathbf{D} \rangle = \int_V \mathbf{D}(\mathbf{x}) d^3x = \varepsilon_e \mathbf{E}_0 + \chi_e {E_0}^2 \mathbf{E}_0 + \eta_e {E_0}^4 \mathbf{E}_0 + \delta_e {E_0}^6 \mathbf{E}_0 + \mu_e {E_0}^8 \mathbf{E}_0, \tag{4.2}$$

where ε_e, χ_e, η_e, δ_e and μ_e are the first, the third, the fifth, the seventh and the ninth-order effective coefficients, respectively. In general, the coefficient ε_e is the effective linear dielectric response and the coefficients χ_e, η_e, δ_e and μ_e are the effective nonlinear dielectric responses. Another possible definition of the effective coefficients is to relate the electrostatic energy of the composite to that of the homogeneous medium with effective coefficients by the equation [8]

$$W = \int_V \mathbf{D}(\mathbf{x}) \cdot \mathbf{E}(\mathbf{x}) d^3x = V\big[\varepsilon_e E_0^2 + \chi_e E_0^4 + \eta_e E_0^6 + \delta_e E_0^8 + \mu_e E_0^{10}\big]. \tag{4.3}$$

It is shown in Appendix B that both definitions (Eqs. (4.2) and (4.3)) are equivalent. We will use the definition of the effective coefficients from Eq. (4.3) to determine their general formulae for effective coefficients and the details will be shown in the next section.

4.2 Process to determine general formulae for the effective coefficients

We first consider the integrand $\mathbf{D}(\mathbf{x}) \cdot \mathbf{E}(\mathbf{x})$ on the left hand side of the Eq. (4.3). Substituting $\mathbf{D}(\mathbf{x})$ from Eq. (2.2), we find that

$$\mathbf{D}(\mathbf{x}) \cdot \mathbf{E}(\mathbf{x}) = \varepsilon(\mathbf{x})(E(\mathbf{x}))^2 + \chi(\mathbf{x})(E(\mathbf{x}))^4 + \eta(\mathbf{x})(E(\mathbf{x}))^6. \tag{4.4}$$

From Eq. (2.10), we write the electric field ($\mathbf{E}(\mathbf{x})$) in terms of expanded electric potentials, so the quantities $(E(\mathbf{x}))^2$, $(E(\mathbf{x}))^4$ and $(E(\mathbf{x}))^6$ can be calculated as follows:

$$\begin{aligned}
(E(\mathbf{x}))^2 &= \mathbf{E}(\mathbf{x}) \cdot \mathbf{E}(\mathbf{x}) \\
&= \big[-\nabla\phi_0(\mathbf{x}) - \lambda\nabla\phi_1(\mathbf{x}) - \lambda^2\nabla\phi_2(\mathbf{x}) - \lambda^3\nabla\phi_3(\mathbf{x})\big] \\
&\quad \cdot\big[-\nabla\phi_0(\mathbf{x}) - \lambda\nabla\phi_1(\mathbf{x}) - \lambda^2\nabla\phi_2(\mathbf{x}) - \lambda^3\nabla\phi_3(\mathbf{x})\big] \\
&= |\nabla\phi_0(\mathbf{x})|^2 + 2\lambda\nabla\phi_0(\mathbf{x}) \cdot \nabla\phi_1(\mathbf{x}) + \lambda^2(2\nabla\phi_0(\mathbf{x}) \cdot \nabla\phi_2(\mathbf{x}) \\
&\quad + |\nabla\phi_1(\mathbf{x})|^2) + \lambda^3(2\nabla\phi_0(\mathbf{x}) \cdot \nabla\phi_3(\mathbf{x}) + 2\nabla\phi_1(\mathbf{x}) \cdot \nabla\phi_2(\mathbf{x})) \\
&\quad + \lambda^4(|\nabla\phi_2(\mathbf{x})|^2) + 2\nabla\phi_1(\mathbf{x}) \cdot \nabla\phi_3(\mathbf{x})) + \ldots,
\end{aligned} \tag{4.5}$$

$$
\begin{aligned}
(E(\mathbf{x}))^4 &= ((E(\mathbf{x}))^2)((E(\mathbf{x}))^2) \\
&= |\nabla\phi_0(\mathbf{x})|^4 + 4\lambda|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}) \\
&+ \lambda^2(4|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) + 2|\nabla\phi_0(\mathbf{x})|^2|\nabla\phi_1(\mathbf{x})|^2 \\
&+ 4(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2) + \lambda^3(4|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_1(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) \\
&+ 4|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x}) + 8(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})) \\
&(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})) + 4|\nabla\phi_1(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})) + \ldots, \quad (4.6)
\end{aligned}
$$

$$
\begin{aligned}
(E(\mathbf{x}))^6 &= ((E(\mathbf{x}))^4)((E(\mathbf{x}))^2) \\
&= |\nabla\phi_0(\mathbf{x})|^6 + 6\lambda|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}) \\
&+ \lambda^2(6|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) + 3|\nabla\phi_0(\mathbf{x})|^4|\nabla\phi_1(\mathbf{x})|^2 \\
&+ 12|\nabla\phi_0(\mathbf{x})|^2\ (\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2) + \ldots\ . \quad (4.7)
\end{aligned}
$$

Substituting Eqs. (4.5)-(4.7) into Eq. (4.4), $\mathbf{D}(\mathbf{x})\cdot\mathbf{E}(\mathbf{x})$ can be calculated and then it is substituted into Eq. (4.3). Comparing the quantities on both sides of Eq. (4.3) with the same power of E_0, the general formulae for effective coefficients are determined. We note that $\phi_0(\mathbf{x})$, $\lambda\phi_1(\mathbf{x})$, $\lambda^2\phi_2(\mathbf{x})$ and $\lambda^3\phi_3(\mathbf{x})$ in Eqs. (4.5)-(4.7) depend on E_0, $\chi_m E_0^3$, $\chi_m^2 E_0^5$ and $\chi_m^3 E_0^7$, respectively and independent of λ. For convenient, we omit λ^n coefficient of $\phi_n(\mathbf{x})$ in the following derivation for effective coefficients.

For E_0 to the second power, we have

$$\varepsilon_e E_0^2 = \frac{1}{V}\int_V \varepsilon(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2 d^3x, \quad (4.8)$$

the first-order coefficient is

$$\varepsilon_e = \frac{1}{VE_0^2}\int_V \varepsilon(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2 d^3x. \quad (4.9)$$

For E_0 to the fourth power, we have

$$\chi_e E_0^4 = \frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})d^3x + \frac{1}{V}\int_V \chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4 d^3x. \quad (4.10)$$

In general, we can show that $\frac{1}{V}\int_V \varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_n(\mathbf{x})d^3x$ $(n = 1, 2, 3\ldots)$ vanishes as seen in Appendix C. Then the first term of Eq. (4.10) is zero.

We get the third-order nonlinear coefficient as

$$\chi_e = \frac{1}{VE_0^4}\int_V \chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4 d^3x. \tag{4.11}$$

We can see that ε_e and χ_e depend only on the zeroth-order electric potential $(\phi_0(\mathbf{x}))$.

For E_0 to the sixth power, we have

$$\begin{aligned}\eta_e E_0^6 &= \frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x + \frac{1}{V}\int_V \varepsilon(\mathbf{x})|\nabla\phi_1(\mathbf{x})|^2 d^3x \\ &+ \frac{1}{V}\int_V 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})d^3x \\ &+ \frac{1}{V}\int_V \eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^6 d^3x. \end{aligned} \tag{4.12}$$

From Appendix C, the term $\frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x$ in Eq. (4.12) is zero. We get the fifth-order nonlinear coefficient as

$$\begin{aligned}\eta_e &= \frac{1}{V{E_0}^6}\int_V \Big[\varepsilon(\mathbf{x})|\nabla\phi_1(\mathbf{x})|^2 + 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}) \\ &\qquad + \eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^6\Big]d^3x. \end{aligned} \tag{4.13}$$

For E_0 to the eighth power, we have

$$\begin{aligned}\delta_e E_0^8 &= \frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x})d^3x \\ &+ \frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_1(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x \\ &+ \frac{1}{V}\int_V 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x \\ &+ \frac{1}{V}\int_V 2\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2|\nabla\phi_1(\mathbf{x})|^2 d^3x \\ &+ \frac{1}{V}\int_V 4\chi(\mathbf{x})(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2 d^3x \\ &+ \frac{1}{V}\int_V 6\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})d^3x. \end{aligned} \tag{4.14}$$

Again, the term $\frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x})d^3x$ is zero as shown in Appendix C. We get the seventh-order nonlinear coefficient as

$$\begin{aligned}\delta_e &= \frac{1}{VE_0{}^8}\int_V \Big[2\varepsilon(\mathbf{x})\nabla\phi_1(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) + 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) \\ &\quad + 2\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2|\nabla\phi_1(\mathbf{x})|^2 + 4\chi(\mathbf{x})(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2 \\ &\quad + 6\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})\Big]d^3x. \end{aligned} \tag{4.15}$$

For E_0 to the tenth power, we have

$$\begin{aligned}\mu_e E_0^{10} &= \frac{1}{V}\int_V \varepsilon(\mathbf{x})|\nabla\phi_2(\mathbf{x})|^2 d^3x + \frac{1}{V}\int_V 2\varepsilon(\mathbf{x})\nabla\phi_1(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x})d^3x \\ &\quad + \frac{1}{V}\int_V 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_1(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x \\ &\quad + \frac{1}{V}\int_V 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x})d^3x \\ &\quad + \frac{1}{V}\int_V 4\chi(\mathbf{x})|\nabla\phi_1(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x})d^3x \\ &\quad + \frac{1}{V}\int_V 8\chi(\mathbf{x})(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}))d^3x \\ &\quad + \frac{1}{V}\int_V 6\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})d^3x \\ &\quad + \frac{1}{V}\int_V 12\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ (\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2 d^3x \\ &\quad + \frac{1}{V}\int_V 3\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4|\nabla\phi_1(\mathbf{x})|^2 d^3x. \end{aligned} \tag{4.16}$$

We get the ninth-order effective nonlinear coefficient as

$$\begin{aligned}\mu_e &= \frac{1}{VE_0{}^{10}}\int_V \Big[\varepsilon(\mathbf{x})|\nabla\phi_2(\mathbf{x})|^2 + 2\varepsilon(\mathbf{x})\nabla\phi_1(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x}) \\ &\quad + 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_1(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) \\ &\quad + 4\chi(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_3(\mathbf{x}) \\ &\quad + 4\chi(\mathbf{x})|\nabla\phi_1(\mathbf{x})|^2\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}) \\ &\quad + 8\chi(\mathbf{x})(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))(\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x})) \\ &\quad + 6\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4\ \nabla\phi_0(\mathbf{x})\cdot\nabla\phi_2(\mathbf{x}) \\ &\quad + 12\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^2\ (\nabla\phi_0(\mathbf{x})\cdot\nabla\phi_1(\mathbf{x}))^2 \\ &\quad + 3\eta(\mathbf{x})|\nabla\phi_0(\mathbf{x})|^4|\nabla\phi_1(\mathbf{x})|^2\Big]d^3x. \end{aligned} \tag{4.17}$$

Eqs. (4.9), (4.11), (4.13), (4.15) and (4.17) are the general formulae of the first, the third, the fifth, the seventh and the ninth-order effective coefficients, respectively. We can say that the coefficient ε_e is the effective linear dielectric response and the coefficients χ_e, η_e, δ_e and μ_e are the effective nonlinear dielectric responses of the composite.

The formulae of ε_e, χ_e and η_e have been reported previously [8]. We obtain more general formulae of the seventh (δ_e) and the ninth-order (μ_e) effective nonlinear coefficients which are new results. The applications and confirmation of these formulae will be shown in the next chapter.