Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Appendix A: Spherical particle within an oscillating electric field

First consider the electric dipole developed by a spherical particle placed within in a uniform, oscillating electric field, and the subsequent electric dipole absorption. Electromagnetic scattering can be neglected if the sphere is electrically small, in which limit the electromagnetic fields are considered to be quasi-static; specifically, this occurs for a particle radius $a << \lambda_0$, where $\lambda_0 = 2\pi c/\omega$ is the free space wavelength and ω the angular frequency of the applied electric field.

Referring to the spherical polar co-ordinate system of Fig. A1, consider a uniform electric field of magnitude E_0 applied parallel to the *z*-axis. The sphere is considered to have isotropic relative permittivity ε and permeability μ, which can be complex quantities to allow for energy absorption.

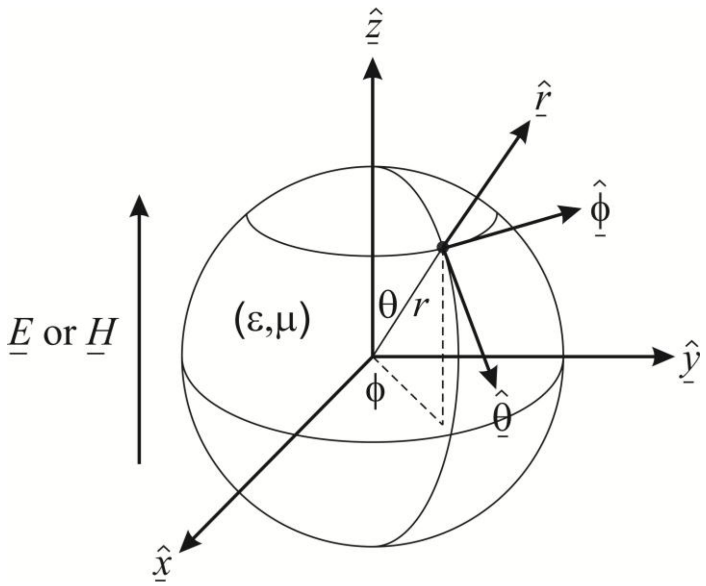

Figure A1: The spherical polar co-ordinate system used to solve the electromagnetic fields in and around a material sphere.

The quasi-static electric and magnetic field fields inside the sphere are of the form $\underline{E} = (E_r \cos\theta, -E_\theta \sin\theta, 0)e^{j\omega t}$ and $\underline{H} = (0, 0, H_\phi \sin\theta)e^{j\omega t}$, where E_r, E_θ and H_ϕ are scalar functions of radial position *r* only, and are proportional to the applied electric field magnitude E_0. This results in an electric dipole moment parallel to the applied electric field. Helmholtz's equation for the induced magnetic field within the sphere is then

$$\nabla^2 (H_\phi \sin\theta) + \left(k^2 - \frac{1}{r^2 \sin^2\theta}\right) H_\phi \sin\theta = 0$$

which reduces to

$$\frac{d}{dx}\left(x^2 \frac{dH_\phi}{dx}\right) + (x^2 - 2)H_\phi = 0 \qquad \text{(A1)}$$

where $x = kr$. The wavenumber *k* is defined (in the usual manner) using $k = \omega\sqrt{\varepsilon\mu}/c$. The unique solution of Eqn.(A1) which remains finite as $x \to 0$ has the Bessel function form

$$H_\phi(x) \propto \frac{J_{3/2}(x)}{\sqrt{x}} = H_1 \frac{\sin x - x\cos x}{x^2}$$

where the magnetic field scaling factor H_1 is independent of radial position *r*. The corresponding electric field components within the sphere can now be calculated from Maxwell's displacement current density, i.e. $\underline{\nabla} \times \underline{H} = j\omega\varepsilon\varepsilon_0 \underline{E}$, resulting in

$$E_r(x) = E_1 \frac{\sin x - x\cos x}{x^3}, \qquad E_\theta(x) = \frac{E_1}{2x}\left(\frac{\cos x}{x} - \frac{\sin x}{x^2} + \sin x\right) \qquad \text{(A2)}$$

where the position-independent electric field scaling factor is $E_1 = 2H_1 k / (j\omega\varepsilon\varepsilon_0)$.

Outside of the sphere, the electric field is that of the original field (of magnitude E_0), perturbed by the dipole field associated with the presence of the sphere. The external electric field is again of the form $\underline{E} = \left(E_r \cos\theta, -E_\theta \sin\theta, 0\right)e^{j\omega t}$, and in terms of the sphere's induced electric dipole moment p

$$E_r = E_0 + \frac{p}{2\pi\varepsilon_0 r^3}, \quad E_\theta = -E_0 + \frac{p}{4\pi\varepsilon_0 r^3} \tag{A3}$$

Applying the electric field boundary conditions at the sphere's surface for the field components of Eqns. (A2) and (A3) allows the electric dipole moment to be found, with the end result being

$$p = 2\pi\varepsilon_0 a^3 E_0 \frac{(2\varepsilon+1)(1-ka\cot ka)-(ka)^2}{(\varepsilon-1)(1-ka\cot ka)+(ka)^2} \tag{A4}$$

In the low frequency limit (i.e. $ka << 1$), Eqn.(A4) reduces to the familiar result of the static electric dipole moment of a uniformly polarised dielectric sphere, namely

$$p_0 = 4\pi\varepsilon_0 a^3 E_0 \left(\frac{\varepsilon-1}{\varepsilon+2}\right)$$

Appendix B: Spherical particle within an oscillating magnetic field

Now consider the magnetic dipole developed by a spherical particle placed within a uniform, oscillating magnetic field, which can be developed in analogy with the treatment of the particle's electric dipole moment discussed in Appendix A. Assume that the sphere is again electrically small (i.e. $a << \lambda_0$) and has complex, isotropic relative permittivity ε and permeability μ. A uniform, oscillating magnetic field of magnitude H_0 applied parallel to the *z*-axis generates a magnetic dipole moment which is also parallel to the *z*-axis. The resulting electric and magnetic fields are then $\underline{H} = (H_r \cos\theta, -H_\theta \sin\theta, 0)e^{j\omega t}$ and $\underline{E} = (0, 0, E_\phi \sin\theta)e^{j\omega t}$, respectively. By the reduction of Helmholtz's equation applied to the azimuthal electric field component, it is found that E_ϕ satisfies

$$\frac{d}{dx}\left(x^2 \frac{dE_\phi}{dx}\right) + (x^2 - 2)E_\phi = 0$$

which has the unique solution

$$E_\phi(x) \propto \frac{J_{3/2}(x)}{\sqrt{x}} = E_2 \frac{\sin x - x\cos x}{x^2}$$

which remains finite as $x \to 0$, where again $x = kr$ and $k = \omega\sqrt{\varepsilon\mu}/c$. The field scaling factor now is E_2, which differs from E_1 encountered in the treatment of the electric dipole moment. The corresponding magnetic field components can be generated using Faraday's law $\underline{\nabla} \times \underline{E} = -j\omega\mu\mu_0 \underline{H}$, resulting in

$$H_r(x) = H_2 \frac{\sin x - x\cos x}{x^3}, \quad H_\theta(x) = \frac{H_2}{2x}\left(\frac{\cos x}{x} - \frac{\sin x}{x^2} + \sin x\right) \qquad \text{(B1)}$$

where the magnetic field scaling factor is defined by $H_2 = 2jE_2 k/\omega\mu\mu_0$.

Outside of the sphere, the magnetic field is that of the original field (of magnitude H_0), perturbed by the dipole field associated with the presence of the sphere. The external magnetic field is again of the form $\underline{H} = (H_r \cos\theta, -H_\theta \sin\theta, 0)e^{j\omega t}$, and in terms of the sphere's induced magnetic dipole moment m

$$H_r = H_0 + \frac{m}{2\pi r^3}, \quad H_\theta = -H_0 + \frac{m}{4\pi r^3} \qquad \text{(B2)}$$

Applying the magnetic field boundary conditions at the sphere's surface for the field components of Eqns. (B1) and (B2) allows the magnetic dipole moment to be found, with the end result being

$$m = 2\pi a^3 H_0 \left(\frac{(2\mu+1)(1-ka\cot ka)-(ka)^2}{(\mu-1)(1-ka\cot ka)+(ka)^2}\right) \qquad \text{(B3)}$$

In the low frequency limit (i.e. $ka \ll 1$), Eqn.(B3) reduces to the familiar result of the static magnetic dipole moment of a uniformly magnetised sphere, namely

$$m_0 = 4\pi a^3 H_0 \left(\frac{\mu-1}{\mu+2}\right)$$