Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Appendix A

The 2^{nd} order ODE describing change variation of current with time in a LCR circuit excited by an AC source (fig 1c of manuscript) is given as

$$L_m \frac{d^2 i}{dt^2} + R_m \frac{di}{dt} + \frac{i}{C_m} = \omega V_o cos \omega_{in} t$$

For solving the ODE, re-arrange

$$\frac{d^2 i}{dt^2} + \frac{R_m}{L_m}\frac{di}{dt} + \frac{1}{L_m C_m} i = \frac{\omega_{in} V_m}{L_m} \cos \omega_{in} t$$

This equation is non-homogeneous and will have two solutions, one the homogeneous part and second a particular part which would depend on the nature of function on the right hand side, The homogeneous solution of the above is found by solving the characteristic equation

$$\lambda^2 + \frac{R_m}{L_m}\lambda + \frac{1}{L_m C_m} = 0$$

and is given as

$$i_h(t) = e^{-\frac{R_m}{2L_m}t}(C_1 sin \omega_o t + C_2 cos \omega_o t)$$

where

$$\omega_o = \sqrt{\frac{1}{L_m C_m} - \frac{R_m^2}{4L_m^2}}$$

The non-homogeneous/ particular solution can be obtained by using the guess solution as

$$i_{nh} = A \sin \omega_{in} t + B \cos \omega_{in} t$$

and substituting back into the original equation. We get a simultaneous equation of A and B as

$$\begin{aligned} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right) B + \frac{R_m \omega_{in}}{L_m} A &= \frac{\omega_{in} V_m}{L_m} \\ -\frac{\omega_{in} R_m}{L_m} B + \left(\frac{1}{L_m C_m} - \omega_{in}^2\right) A &= 0 \end{aligned}$$

Solving for A and B, we have

$$A = \frac{V_m}{R_m} \frac{1}{\left[1 + \frac{L_m^2}{\omega_{in}^2 R_m^2} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)^2\right]}$$

$$B = \frac{V_m}{R_m} \frac{\frac{L_m}{\omega_{in} R_m} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)}{\left[1 + \frac{L_m^2}{\omega_{in}^2 R_m^2} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)^2\right]}$$

Hence, the non-homogeneous solution is

$$i_{nh} = \left[\frac{V_m}{R_m} \times \frac{1}{\sqrt{1 + x^2}}\right] sin(\omega_{in} t + \phi)$$

where

$$\begin{aligned} x &= \frac{L_m}{\omega_{in} R_m} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right) \\ \phi &= tan^{-1}(x) \end{aligned}$$

The complete current expression can be written as

$$i(t) = e^{-\frac{R_m}{2L_m} t}(C_1 sin\omega_o t + C_2 cos\omega_o t) + \frac{V_m}{R_m} \left(\frac{1}{\sqrt{1 + x^2}}\right) sin(\omega_{in} t + \phi)$$

or

$$i(t) = e^{-\frac{R_m}{2L_m} t}(C_1 sin\omega_o t + C_2 cos\omega_o t) + \frac{V_m}{R_m} \left\{\frac{1}{\sqrt{1 + \left[\frac{L_m}{\omega_{in} R_m} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)\right]^2}}\right\} sin(\omega_{in} t + \phi)$$

Since the first term attentuates rapidly (due to the exponential term), the steady state solution would be represented as

$$i_{steady-state}(t) = \frac{V_m}{R_m} \left\{\frac{1}{\sqrt{1 + \left[\frac{L_m}{\omega_{in} R_m} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)\right]^2}}\right\} sin(\omega_{in} t + \phi)$$

The voltage drop across the resistance R_m would hence be given as

$$v_{steady-state}(t) = \left\{\frac{V_m}{\sqrt{1 + \left[\frac{L_m}{\omega_{in} R_m} \left(\frac{1}{L_m C_m} - \omega_{in}^2\right)\right]^2}}\right\} sin(\omega_{in} t + \phi)$$

Appendix B

To obtain an expression for currents in the two loops of the equivalent circuit shown in fig 3a, we essentially have to solve the coupled ordinary differential equation using the operator method

$$
\begin{aligned}
v(t) &= \frac{1}{C_m}\int i_1 dt + L_m\frac{di_1}{dt} + M\frac{d}{dt}(i_1 - i_2) + R_m i_1 \\
0 &= \frac{1}{C_h}\int i_2 dt + L_h\frac{di_2}{dt} + M\frac{d}{dt}(i_2 - i_1) + R_h i_2
\end{aligned}
$$

Removing integral sign, we have

$$
\begin{aligned}
\omega V_o cos\omega t &= \frac{i_1}{C_m} + L_m\frac{d^2 i_1}{dt^2} + M\frac{d^2}{dt^2}(i_1 - i_2) + R_m\frac{di_1}{dt} \\
0 &= \frac{i_2}{C_h} + L_h\frac{d^2 i_2}{dt^2} + M\frac{d^2}{dt^2}(i_2 - i_1) + R_h\frac{di_2}{dt}
\end{aligned}
$$

Solving the coupled differential equation for $\mathrm{i_1}$, we have (for simplification of calculations, we have made a reasonable assumption that $\mathrm{R_m} \sim \mathrm{R_h} \sim 0$ or negligiable compared to the remaining terms. In simulations, we have used $\mathrm{R_m} \sim \mathrm{R_h} = 0.5\Omega$.)

$$
i_1 = \frac{\frac{\omega V_o}{L_m}\left[\frac{1}{L_h C_h} - \left(1 + \frac{M}{L_h}\right)\omega^2\right] cos\omega t}{\left[1 + M\left(\frac{1}{L_m} + \frac{1}{L_h}\right)\right]\omega^4 - \left[\frac{1}{L_h C_h}\left(1 + \frac{M}{L_m}\right) + \frac{1}{L_m C_m}\left(1 + \frac{M}{L_h}\right)\right]\omega^2 + \frac{1}{L_h L_m C_h C_m}} \tag{1}
$$

From this equation, the frequency at which resonance occurs (ω_p) due to culmunated effect of metal nano-particle and surrounding dielectric can be found from

$$
\omega_p = \sqrt{\frac{\left[\frac{1}{L_h C_h}\left(1 + \frac{M}{L_m}\right) + \frac{1}{L_m C_m}\left(1 + \frac{M}{L_h}\right)\right]}{\left[1 + M\left(\frac{1}{L_m} + \frac{1}{L_h}\right)\right]}} \tag{2}
$$

Consider both metal and dielectric materials are non-magnetic, similar permeability would result in $\mathrm{L_m} \approx \mathrm{L_h} = \mathrm{L}$. Hence, above equation would reduce to

$$
\omega_p = \sqrt{\frac{\left[\frac{1}{L}(1 + k)\left(\frac{1}{C_h} + \frac{1}{C_m}\right)\right]}{(1 + 2k)}}
$$

Since the dielectric surrounding medium is EM radiation inactive compared to the metal nano-particle, $\mathrm{C_h} \ll \mathrm{C_m}$. Hence, we write

$$
\omega_p \approx \sqrt{\frac{\left[\frac{1}{LC_h}(1 + k)\right]}{(1 + 2k)}}
$$

$$\omega_p \approx \frac{1}{\sqrt{LC_h}} \left(\sqrt{\frac{1+k}{1+2k}} \right)$$

Since we talk of SPR peak position in terms of wave-lengths

$$\lambda_p \propto \sqrt{LC_h} \left(\sqrt{\frac{1+2k}{1+k}} \right)$$