162(4): Theory of Raman Scattering

As in note 162(3) the problem is to solve the following two equations simultaneously:

$$\hbar\omega + E_i = \hbar\omega' + E_f \quad -(1)$$

$$\hbar\underline{\kappa} + \underline{p}_i = \hbar\underline{\kappa}' + \underline{p}_f \quad -(2)$$

i.e.

$$E_f - E_i = \hbar(\omega - \omega') \quad -(3)$$

$$\underline{p}_f - \underline{p}_i = \hbar(\underline{\kappa} - \underline{\kappa}') \quad -(4)$$

The electron energies and momenta are related by:

$$E_i^2 = c^2 p_i^2 + m^2c^4 \quad -(5)$$

$$E_f^2 = c^2 p_f^2 + m^2c^4. \quad -(6)$$

Theory with Massless Photon

In the first instance assume a massless photon as a first step. Then:

$$\omega = \kappa c, \quad \omega' = \kappa' c. \quad -(7)$$

From eqs. (5) and (6):

$$E_i^2 + E_f^2 = c^2(p_i^2 + p_f^2) + 2m^2c^4 \quad -(8)$$

From eqs. (3) and (4):

$$\hbar^2(\omega^2 + \omega'^2 - 2\omega\omega') = E_f^2 + E_i^2 - 2E_iE_f \quad -(9)$$

$$\hbar^2(\kappa^2 + \kappa'^2 - 2\kappa\kappa'\cos\theta) = p_f^2 + p_i^2 - 2p_ip_f\cos\theta. \quad -(10)$$

Using (7) in (10):

2)

$$\hbar^2(\omega^2+\omega'^2-2\omega\omega'\cos\theta) = c^2(p_f^2+p_i^2)-2c^2p_ip_f\cos\theta \quad -(11)$$

$$= E_i^2+E_f^2-2m^2c^4-2c^2p_ip_f\cos\theta$$

Subtracting (11) from (9):

$$-2\omega\omega'(1-\cos\theta)\hbar^2 = 2m^2c^4+2c^2p_ip_f\cos\theta-2E_iE_f \quad -(12)$$

$$E_iE_f-c^2p_ip_f\cos\theta-m^2c^4 = \hbar^2\omega\omega'(1-\cos\theta) \quad -(13)$$

The experimentally known quantities are the orbital electron energies E_i and E_f. So the momenta p_i and p_f are eliminated using eqs. (5) and (6) to give:

$$-(14)$$

$$(E_i^2-E_0^2)^{1/2}(E_f^2-E_0^2)^{1/2}\cos\theta$$

$$= E_iE_f-m^2c^4-\hbar^2\omega\omega'(1-\cos\theta)$$

where

$$E_0 = mc^2 \quad -(15)$$

is the rest energy of the electron of mass m.

Eq. (14) is:

$$(E_i^2-E_0^2)^{1/2}(E_f^2-E_0^2)^{1/2}\cos\theta+E_0^2 = A \quad -(16)$$

where:

$$A = E_iE_f-\hbar^2\omega\omega'(1-\cos\theta) \quad -(17)$$

is known experimentally.

3) Eq. (16) is a quadratic in E_0^2, so the electron mass m can be found as follows:

$$(E_i^2 - E_0^2)(E_f^2 - E_0^2)\cos^2\theta = (A - E_0^2)^2 \quad -(18)$$

i.e.

$$(E_i^2 E_f^2 - (E_i^2 + E_f^2)E_0^2 + E_0^4)\cos^2\theta = A^2 - 2AE_0^2 + E_0^4 \quad -(19)$$

so:

$$E_0^4(1-\cos^2\theta) + ((E_i^2 + E_f^2)\cos^2\theta - 2A)E_0^2 + A^2 - E_i^2 E_f^2 \cos^2\theta = 0 \quad -(20)$$

$$E_0^2 = \frac{1}{2a}\left(\pm b \pm (b^2 - 4ac')^{1/2}\right) \quad -(21)$$

where:

$$a = 1 - \cos^2\theta,$$
$$b = (E_i^2 + E_f^2)\cos^2\theta - 2A,$$
$$c' = A^2 - E_i^2 E_f^2 \cos^2\theta,$$
$$A = E_i E_f - \hbar^2 \omega\omega'(1 - \cos\theta)$$

Here E_i and E_f are the initial and final energies of the electron in orbitals i and f. The angle θ is the angle of scattering in the Raman experiment. Finally ω and ω' are the initial and final angular frequencies of the e/m radiation.