162(3): Energy and Momentum Conservation in Raman Scattering

a) Stokes Scattering

$$\hbar\omega + E_i = \hbar\omega' + E_f, \quad -(1)$$
$$E_f > E_i, \quad -(2)$$
$$\omega' < \omega \quad -(3)$$

Here ω is the initial angular frequency of the photon, ω' its final angular frequency. In eq (1) E_i is the initial energy of an electron in an atom, and E_f is its final energy. The de Broglie postulates assert:

$$E_i = \hbar\omega_i, \quad E_f = \hbar\omega_f. \quad -(4)$$

Therefore using eq. (4) in eq. (1):

$$\omega + \omega_i = \omega_f + \omega' \quad -(5)$$

i.e. $$(\omega - \omega')(\text{photon}) = (\omega_f - \omega_i)(\text{electron}) \quad -(6)$$

b) Anti-Stokes Scattering

In this case:

$$\hbar\omega + E_i = \hbar\omega' + E_f \quad -(7)$$
$$E_i > E_f \quad -(8)$$
$$\omega' > \omega \quad -(9)$$

$$\omega + \omega_i = \omega_f + \omega' \quad -(10)$$

i.e. $$(\omega' - \omega)(\text{photon}) = (\omega_i - \omega_f)(\text{electron}) \quad -(11)$$

In both cases the equation of conservation of total momentum is:

2)

$$\hbar \underline{k} + \underline{p}_i = \hbar \underline{k}' + \underline{p}_f \quad -(12)$$

where $\hbar \underline{k}$ is the initial photon momentum, $\underline{p}_i$ is the initial electron momentum in orbital i, and where $\hbar \underline{k}'$ is the final photon momentum, and $\underline{p}_f$ the final electron momentum in orbital f.

If orbitals i and f have net non-zero orbital angular momentum $\underline{L}$, each orbital will have net non-zero electronic linear momentum $\underline{p}$. In each orbital:

$$l_z |n, m\rangle = m\hbar |n, m\rangle \quad -(13)$$

$$l^2 |n, m\rangle = \hbar^2 l(l+1) |n, m\rangle \quad -(14)$$

The magnitude of the angular momentum is:

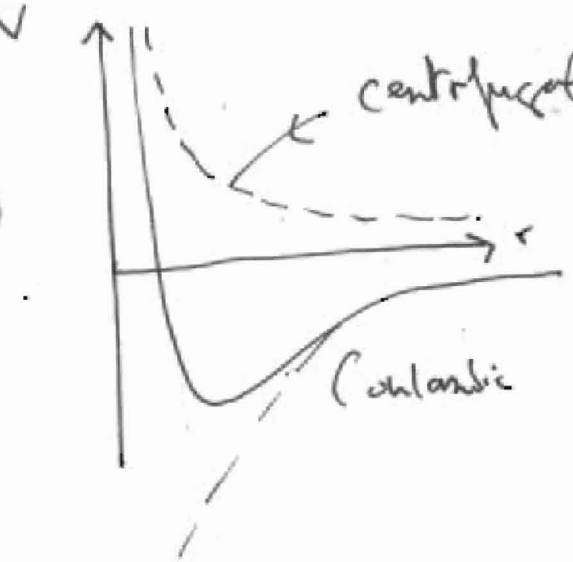
$$L = \hbar l(l+1) \quad -(15)$$

where l is the orbital angular momentum quantum number.

In the H atom for example the potential energy is

$$V = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad -(16)$$

Fig.(1)



3)

The centrifugal part of V is:

$$V\,(\text{centrifugal}) = \frac{L^2}{2\mu r^2} \quad -(17)$$

which is the classical expression. Here:

$$\underline{L} = \underline{r} \times \underline{p} \quad -(18)$$

$$L = rp \quad -(19)$$

so

$$V\,(\text{centrifugal}) = \frac{p^2}{2\mu} \quad -(20)$$

Therefore each orbital has non-zero linear momentum p, QED. There must therefore be conservation of momentum. Therefore eq. (12) must be considered.

In the first instance eq. (12) can be considered by assuming a massless photon. In a more complete theory the other postulates must be used, because the de Broglie postulates alone will fail catastrophically.