84(4): Root Mean Square RFR Chemical Shift

The classical interaction Hamiltonian is calculated from:

$$\underline{p} \rightarrow \underline{p} + \underline{A} + \underline{A}_N \quad -(1)$$

where:

$$\underline{A} = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} - i\underline{j}) e^{i\phi} \quad -(2)$$

$$\underline{A}^* = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} + i\underline{j}) e^{-i\phi} \quad -(3)$$

Thus:

$$H = \frac{-ie^2}{2m} \underline{\sigma} \cdot (\underline{A} + \underline{A}_N) \times (\underline{A}^* + \underline{A}_N) \quad -(4)$$

$$= -i \left(\left(\frac{A^{(0)}}{\sqrt{2}} e^{i\phi} + A_x \right) \left(i \frac{A^{(0)}}{\sqrt{2}} e^{-i\phi} + A_y \right) - \left(-i \frac{A^{(0)}}{\sqrt{2}} e^{i\phi} + A_y \right) \left(\frac{A^{(0)}}{\sqrt{2}} e^{-i\phi} + A_x \right) \right) \underline{k} \quad -(5)$$

$+ \ldots\ldots$

The calculation is simplified if we assume:

$$\underline{A}_N = A_x \underline{i} + A_y \underline{j} \quad -(6)$$

otherwise there are more terms in eqn. (5). Working out the algebra in eqn. (5) give the result along the $\underline{k}$ axis:

$$H = \frac{e^2}{2m}\left(A^{(0)2} + \sqrt{2}\,A^{(0)}(A_x - iA_y)\cos\phi\right)\underline{\sigma} \cdot$$

$$\boxed{H = \frac{e^2}{2m}\left(A^{(0)2} + \sqrt{2}A^{(0)}(A_x - iA_y)\cos\phi\right)\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}} \quad -(7)$$

where we have used:

$$\frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) = \cos\phi. \quad -(8)$$

The root mean square hamiltonian is:

$$\langle H^2 \rangle^{1/2} = \frac{e^2}{2m}\Big\langle A^{(0)4} + 2A^{(0)2}\left(A_x^2 + A_y^2\right)\cos^2\phi + 2\sqrt{2}A^{(0)3}A_x\cos\phi \Big\rangle^{1/2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \cdot \quad -(9)$$

Now we:

$$\langle \cos^2\phi \rangle = \frac{1}{2} \quad -(10)$$

$$\langle \cos\phi \rangle = 0 \quad -(11)$$

to give:

$$\boxed{\langle H^2 \rangle^{1/2} = \frac{e^2 A^{(0)}}{2m}\left(A^{(0)2} + A_x^2 + A_y^2\right)^{1/2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad -(12)}$$

This is chemically shifted by A_x and A_y, which are site specific.

3)

This RMS Hamiltonian can be captured experimentally by using a pump beam of the type:

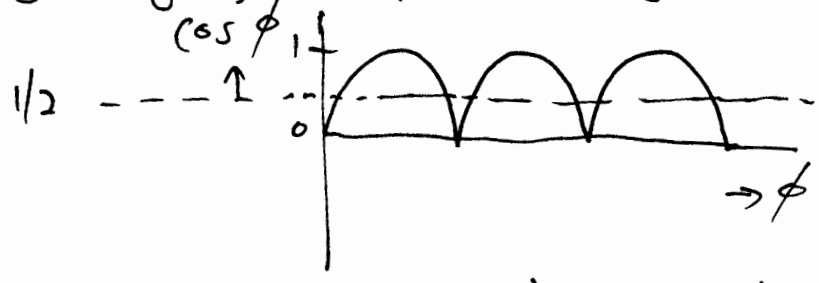

Fig (1)

which can be manipulated electronically. In the absence of A_x and A_y (e.g. in an electron beam):

$$\langle H^2 \rangle^{1/2} = \frac{e^2}{2m} A^{(0)2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad -(13)$$

There are two RMS energy levels in eqn. (12):

$$\langle H^2 \rangle_+^{1/2} = \frac{e^2}{2m} A^{(0)} \left(A^{(0)2} + A_x^2 + A_y^2 \right)^{1/2} \quad -(14)$$

$$\langle H^2 \rangle_-^{1/2} = -\frac{e^2}{2m} A^{(0)} \left(A^{(0)2} + A_x^2 + A_y^2 \right)^{1/2} \quad -(15)$$

The Chemically Shifted Resonance

$$\hbar \omega_{res} = \langle H^2 \rangle_+^{1/2} - \langle H^2 \rangle_-^{1/2} \quad -(16)$$

$$\omega_{res} = \frac{e^2}{\hbar m} A^{(0)} \left(A^{(0)2} + A_x^2 + A_y^2 \right)^{1/2} \quad -(17)$$

4) It is seen from eq. (17) that this is shifted from the resonance frequency of a free fermion:

$$\omega_{res,0} = \frac{e^2 A^{(0)2}}{\hbar m} \quad -(18)$$

Finally we:

$$A^{(0)} = \frac{c}{\omega} B^{(0)} \quad -(19)$$

$$I = \frac{\mu_0}{c} B^{(0)2} \quad -(20)$$

$$= \frac{\mu_0 \omega^2 A^{(0)2}}{c^2}$$

So:

$$\boxed{A^{(0)2} = \mu_0 c^2 \left(\frac{I}{\omega^2}\right)} \quad -(21)$$

where

I = power density of pump beam (watt/m^2)

ω = angular frequency of pump beam $= 2\pi f$.

Eq. (17) is:

$$\boxed{\omega_{res} = \frac{e^2 A^{(0)2}}{\hbar m}\left(1 + \frac{A_x^2 + A_y^2}{A^{(0)2}}\right)^{1/2}} \quad -(22)$$

The final expression for the chemically shifted RFR frequency is, from eqs. (21) and (22):

5)

$$\omega_{res} = \left(\frac{e^2 \mu_0 c^2}{\hbar m}\right) \frac{I}{\omega^2} \left(1 + \frac{(A_x^2 + A_y^2)}{\mu_0 c^2} \frac{\omega^2}{I}\right)^{1/2}$$

— (23)

The RFR shielding constant may be defined as:

$$\sigma_{RFR} = \frac{A_x^2 + A_y^2}{A^{(0)2}} \quad — (24)$$

So:

$$\boxed{\omega_{res} = \left(\frac{e^2 \mu_0 c^2}{\hbar m}\right) \frac{I}{\omega^2} \left(1 + \sigma_{RFR}\right)^{1/2}}$$

— (25)

The main spectral features are that the resolution may be increased by having I/ω^2 and that each RFR line is site-specific through σ_{RFR}. No magnets are needed to produce this spectrum.
