Resonant Inelastic X-ray Scattering (RIXS).

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Introduction

Spectroscopy is a powerful experimental technique to probe electronic structure. X-rays have previously been used for spectroscopic purposes. But with the advent of third generation synchrotron radiation sources it has acquired even greater importance. These synchrotron radiation sources provide highly intense and tunable beams.

X-ray spectroscopy can be broadly classified into two categories. X-ray absorption (XAS) and X-ray Emission spectroscopy (XES). XES can further be subdivided into two categories:

1. Resonant X-ray Emission Spectroscopy (RXES)

2. Normal X-ray Emission Spectroscopy (NXES)

In NXES the energy of the incident photon is large enough to kick an inner shell electron out completely to ionization(final state of photoemission). Relaxation of the excited state then takes place with subsequent emission of x-ray photon. In RXES, the energy of the incident x-ray radiation is sufficient to resonantly knock out an inner shell electron out to a higher, unoccupied excited state of the atom(final state of x-ray absorption).

This leaves behind a hole in the core level and is referred to as the **core-hole**. Relaxation of this core hole state then takes place,with an inner shell electron making a transition,together with an x-ray photon being emitted. This is the physical process behind Resonant Inelastic X-ray Scattering(RIXS).

RIXS provides us with a wealth of information.Unlike the usual X-ray absorption and emission processes which are first order,RIXS is a second order process.

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It incorporates both absorption and subsequent emission.Furthermore,it is a process which is both spatially and temporally coherent.The spatial coherence implies signal from equivalent atoms in the system are obtained,hence RIXS is element specific. There exist a variety of experimental techniques which use these advantages of RIXS to give information on the electronic system symmetry,spin and element specifically.

Theoretical Background

RIXS

X-rays are electromagnetic radiation.The interaction Hamiltonian,$\hat{V}$, describing the interaction of a x-ray photon with matter is given by,

$$\hat{V} = -\frac{e}{m}\vec{p} \cdot \vec{A} + \frac{e^2}{m}\vec{A} \cdot \vec{A} \tag{1}$$

The second term above is quadratic in nature and describes a two photon process. It describes processes such as diffraction and inelastic scattering. The first term which is linear,describes a single-photon process. Processes such as absorption and emission. When considered to second order,i.e.,describing a multiple absorption and emission,this term under suitable conditions give rise to RIXS.
For a typical X-ray inelastic scattering experiment,the scattering cross-section can be derived within the Born approximation. It is referred to as the Kramers-Heisenberg dispersion relation([1],[2])and is given by,

$$\frac{d\sigma}{d\Omega_f} = r_o^2 \frac{\omega_i}{\omega_f} \left[\hat{\epsilon}_f^* \cdot \hat{\epsilon}_i + \frac{1}{m}\sum_I \frac{\langle B|\hat{\epsilon}_f^* \cdot \vec{p}|I\rangle\langle I|\hat{\epsilon}_i \cdot \vec{p}|A\rangle}{E_A^{(o)} + \omega_i - E_I^{(o)} + i\epsilon} \right.$$

$$\left. + \frac{1}{m}\sum_I \frac{\langle B|\hat{\epsilon}_i \cdot \vec{p}|I\rangle\langle I|\hat{\epsilon}_f^* \cdot \vec{p}|A\rangle}{E_A^{(o)} - \omega_i - E_I^{(o)} + i\epsilon} \right]^2 \tag{2}$$

ω_i represents the energy of the incident photons[2].r_o is the classical radius of the electron and is equal to $2.8\times 10^{-13}cm$.

Derivation

The relationship which is central to the understanding of RIXS is the Kramers-Heisenberg dispersion relation. Presented below is a derivation of this dispersion relation.
The Hamiltonian which governs the system is,

$$\hat{H} = \hat{H}_o + \hat{V} \tag{3}$$

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[2]$\hbar$ being set equal to one

where $\hat{H}_o$ is given by,

$$\hat{H}_o \equiv \hat{H}_{RAD} + \hat{H}_{ATOMIC} \tag{4}$$

$\hat{H}_{RAD}$ represents the Hamiltonian for the radiation field. It is simply the sum of independent harmonic oscillators,where the momentum and position have been replaced by the quantum mechanical operators $\hat{P}$ and $\hat{Q}$.
$\hat{H}_{ATOMIC}$ represents the atomic part of the Hamiltonian and is given by,

$$\hat{H}_{ATOMIC} = \frac{\vec{p}^2}{2m} \tag{5}$$

In the total Hamiltonian $\hat{V}$ represents the interaction term of the electromagnetic radiation with matter.Explicitly it is given by,

$$\hat{V} = -\frac{e}{m}\vec{A} \cdot \vec{p} + \frac{e^2}{2m}\vec{A} \cdot \vec{A} \tag{6}$$

Initially let an atom be in a state $|A\rangle$ with a single photon of momentum $\vec{k}_i$ and polarization $\hat{\epsilon}_i$. This state is an eigenstate of $\hat{H}_o$ with eigenvalue $E_A^{(o)} + \omega_i = E_i$. ω_i is the angular frequency of the incident radiation[3]. The eigenvalue equation is,

$$\hat{H}_o|\phi_i\rangle = E_i|\phi_i\rangle \tag{7}$$

Let the final state be that in which the atom is in a state $|B\rangle$ with an outgoing photon of momentum $\vec{k}_f$ and polarization $\hat{\epsilon}_f$. This state is also an eigenstate of $\hat{H}_o$ with eigenvalue $E_f = E_B^{(o)} + \omega_f$. ω_f is the angular frequency of the emitted radiation[4].
In order to obtain an expression for the differential scattering cross section we need to calculate the following transition amplitude,

$$Amp_{fi} = lim_{t \to -\infty \atop t' \to \infty} e^{iE_f t'} \langle \vec{k}_f, \hat{\epsilon}_f | \langle B | \hat{U}(t',t) | A \rangle | \vec{k}_i, \hat{\epsilon}_i \rangle e^{-iE_i t} \tag{8}$$

$\hat{U}(t',t)$ refers to the time development operator.The above amplitude can also be expressed as,

$$Amp_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i) F(E_i) \tag{9}$$

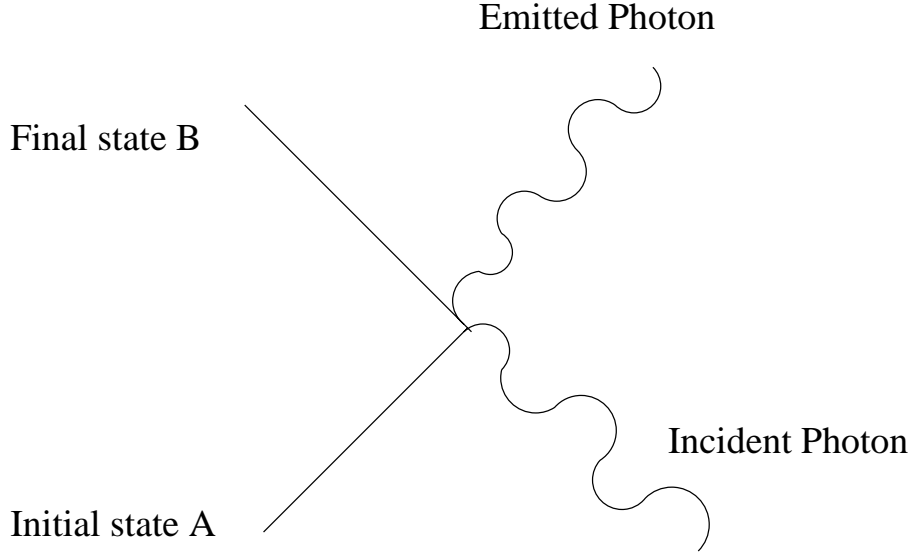[3]$\hbar$ being set equal to one
[4]$\hbar$ being set equal to one

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Figure 1: Seagull Diagram

where $F(E_i)$ is the usual perturbation series in ascending powers of e. It is also referred to as the T or transition matrix.Since $\vec{A}(\vec{x})$ connects states which differ by one in the occupation number of photons,there exists no contribution to $F(E_i)$ of order e.

To second order in e there exists three terms.

There is a single term of first order in the interaction $\hat{V}$. In the long wavelength limit(electric dipole approximation)which becomes,

$$F^{(1)}(E_i) = \langle \phi_f | \hat{V} | \phi_i \rangle$$

$$F^{(1)}(E_i) = \delta_{AB} \frac{e^2}{2m} 2\hat{\epsilon}_f^* \cdot \hat{\epsilon}_i \frac{1}{\sqrt{2\omega_i 2\omega_f}} \tag{10}$$

This corresponds to the Feynmann diagram shown in Fig.1(also referred to as the seagull diagram).

 As mentioned earlier,the second order effect of $\vec{p} \cdot \vec{A}$ gives the remaining two terms.The first of these terms in the electric dipole approximation is,

$$F^{(2)}(E_i) = \sum_I \left(\frac{e}{m}\right)^2 \frac{\langle B | \hat{\epsilon}_f^* \cdot \vec{p} | I \rangle \langle I | \hat{\epsilon}_i \cdot \vec{p} | A \rangle}{E_A^{(o)} + \omega_i - E_I^{(o)} + i\epsilon} \tag{11}$$

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In the intermediate state $|I\rangle$ there is only an atom present with no photons. The factor of $i\epsilon$ in the denominator gets rid of the singularity which occurs at resonance. $E_A^{(o)} + \omega_i$ - $E_I^{(o)} + i\epsilon$ then vanishes. Physically, it corresponds to the mean energy of the core-hole state. If τ be the mean core-hole life time, then from uncertainity principle we have $\epsilon \geq \hbar/\tau$. The Feynmann diagram corresponding to this process is shown in Fig.2.
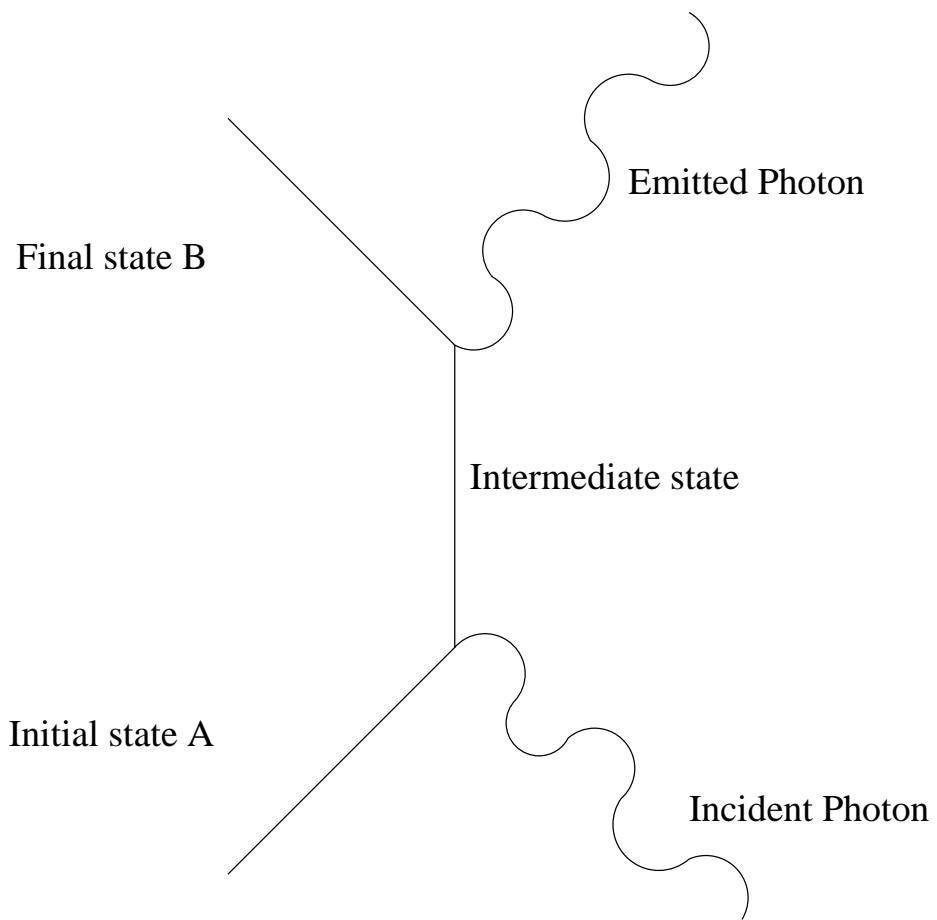
Emitted Photon

Final state B

Intermediate state

Initial state A
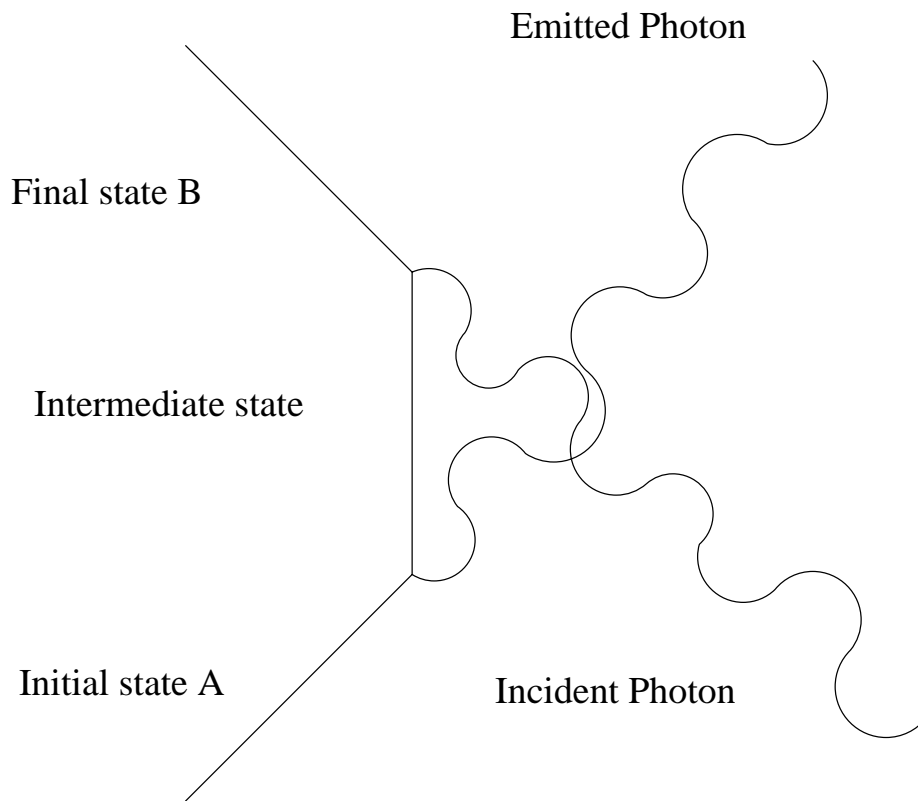
Incident Photon

Figure 2: Second Contribution

Figure 3: Third Contribution

The second term (third contribution to order e^2)in the electric dipole approximation is,

$$F^{(2)}(E_i) = \sum_I \left(\frac{e}{m}\right)^2 \frac{\langle B|\hat{\epsilon}_i \cdot \vec{p}|I\rangle\langle I|\hat{\epsilon}_f^* \cdot \vec{p}|A\rangle}{E_A^{(o)} - \omega_i - E_I^{(o)} + i\epsilon} \tag{12}$$

The above amplitude corresponds to the Feynmann diagram shown in Fig.3. The intermediate state |I⟩ contains both the atom and initial and final photons.

The differential scattering cross-section for RIXS can therefore be written down as follows,

$$\frac{d\sigma}{d\Omega_f} = r_o^2 \frac{\omega_i}{\omega_f} \left[\hat{\epsilon}_f^* \cdot \hat{\epsilon}_i + \frac{1}{m} \sum_I \frac{\langle B|\hat{\epsilon}_f^* \cdot \vec{p}|I\rangle \langle I|\hat{\epsilon}_i \cdot \vec{p}|A\rangle}{E_A^{(o)} + \omega_i - E_I^{(o)} + i\epsilon} \right.$$

$$\left. + \frac{1}{m} \sum_I \frac{\langle B|\hat{\epsilon}_i \cdot \vec{p}|I\rangle \langle I|\hat{\epsilon}_f^* \cdot \vec{p}|A\rangle}{E_A^{(o)} - \omega_i - E_I^{(o)} + i\epsilon} \right]^2 \tag{13}$$

r_o is the classical radius of the electron and is equal to $2.8 \times 10^{-13} cm$.

The first term represents the cross-section for inelastic scattering. The other two terms give the cross-section for anomalous inelastic scattering.

Investigation of the above expression allows us to conclude that when the incident energy is suitably tuned,the denominator in the second term can be made to vanish.This is when RIXS takes place,with a dominant resonant contribution from the second term. Even though the contribution is significant,being a second order process the intensity of the resulting signal is weak.

References

[1]J. J. Sakurai, Advanced Quantum Mechanics (Addison-Wesley, Reading, MA, 1967), Chap. 2.

[2] Yanjun Ma, Phys. Rev. B **49**, 5799 (1994) and references therin.