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Interference of Fluorescence X-rays and Coherent Excitation of Core Levels

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The question of coherence in inelastic x-ray absorption and fluorescence processes among identical interacting atoms is studied using a simple diatomic model. Conditions for the coherence are discussed in terms of energy scales, such as the core hole life-time, instrument energy resolutions, and the splitting of the electronic levels. As in the classical Young double-slit experiment, the primary requirement is that it be impossible to determine which atom has undergone the excitation-decay process.

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Because of the localized nature of core electrons involved in x-ray transitions, x-ray absorption and emission processes are normally regarded as atomic events. In this paper we discuss the coherence between these inelastic scattering processes on identical interacting atoms in a molecule or solid. The coherence has been shown both theoretically [1,2] and experimentally [3-5] to give rise to interference effects in x-ray fluorescence excited by monochromatic photons. We discuss here the conditions for such coherence using a simple homonuclear diatomic model shown in Fig. 1, where the incident x-rays excite a core electron from one of the atoms, and a fluorescence photon is emitted when the core hole is filled with a valence electron. We will explore the interference between the fluorescence photons taking paths 1 and 2 in that figure.

Despite the fact that it involves an inelastic process, this model system is similar to the classical Young double-slit experiment. Because of the uncertainty principle, the criterion for the observation of an interference pattern is that one cannot determine which slit the light wave passed through.[6] This basic principle has important consequences for the inelastic scattering process as well. As long as the photons taking the two paths in Fig. 1 leave the sample in the same final state, they should interfere. Since the inelastic process leaves the sample in an electronically excited state, this means that the excited state has to be delocalized over the two atoms for interference to occur.

For simplicity we assume that the electronic structure of the model system is as shown in Fig. 2, and composed of three levels: a core level (e.g., 1s) ϕ_1 , an occupied valence level ϕ_2 , and an unoccupied valence level ϕ_3 . In the absence of any interactions between the two atoms, these states are localized near the individual atoms. Due to interaction, the valence states are replaced, in a "tight binding" approximation, by symmetric and antisymmetric molecular orbitals, $\chi_2^\pm = \frac{1}{\sqrt{2}}(\phi_2(1) \pm \phi_2(2))$, and $\chi_3^\pm = \frac{1}{\sqrt{2}}(\phi_3(1) \pm \phi_3(2))$. We define the energy splittings between the bonding and

antibonding levels to be $2\Delta_2$, $2\Delta_3$, respectively; a measure of the interaction between the two atoms. We assume that the core level is sufficiently localized so that the energy splitting of the core level is negligible. For the core level then, we may use either a localized or delocalized representation for the wavefunctions. In this simple model we have also neglected the electron-electron and electron-phonon interactions, as well as the effects of the core holes on the electronic orbitals in the intermediate states.

We consider a process where the absorption of the incident photon causes an excitation of an electron from the core level to the χ_3 states. An electron from the χ_2 states subsequently fills the core hole with the emission of a second x-ray photon. Assuming that the energy distributions of the incident and emitted photons are infinitely sharp, the two-photon process is described by the Kramers-Heisenberg formula:[7]

$$\frac{d\sigma}{d\omega_2 d\Omega} = r_0^2 \frac{\omega_2}{m_e \omega_1} \sum_f \left| \sum_m \frac{\langle f | \mathbf{p} \cdot \mathbf{A}_e | m \rangle \langle m | \mathbf{p} \cdot \mathbf{A}_a | i \rangle}{E_m - E_i - \hbar\omega_1 - i\gamma/2} \right|^2 \delta(\hbar\omega_2 - \hbar\omega_1 - \hbar\omega_f), \quad (1)$$

where $\hbar\omega_f = E_f - E_i$, γ is the lifetime width of the intermediate state, and $\mathbf{A}_a \propto e^{i\mathbf{q}_1 \cdot \mathbf{r}}$, $\mathbf{A}_e \propto e^{-i\mathbf{q}_2 \cdot \mathbf{r}}$. In Eq. (1) the first sum is over the four possible final electronic states of the system, $|\bar{\chi}_2^+ \chi_3^+\rangle, |\bar{\chi}_2^- \chi_3^+\rangle, |\bar{\chi}_2^+ \chi_3^-\rangle, |\bar{\chi}_2^- \chi_3^-\rangle$, where the bar above the wavefunction indicates a hole state. The sum over m ranges over all intermediate states, which correspond to states with a core hole located on one of the two atoms and an electron in the χ_3 states.

Using the atomic and molecular wavefunctions, Eq. (1) can be evaluated to give:

$$\begin{aligned}
\frac{m_e \omega_2}{r_0^2 \omega_1} \frac{d\sigma}{d\omega_2 d\Omega} = & \frac{M_{21} M_{13}}{4(\epsilon_3 - \epsilon_1 - \hbar\omega_1 - \Delta_3)^2 + \gamma^2} (2 + 2 \cos(\mathbf{Q} \cdot \mathbf{R})) \delta(\hbar\omega - \Delta_2 - \Delta_3) \\
& + \frac{M_{21} M_{13}}{4(\epsilon_3 - \epsilon_1 - \hbar\omega_1 - \Delta_3)^2 + \gamma^2} (2 - 2 \cos(\mathbf{Q} \cdot \mathbf{R})) \delta(\hbar\omega + \Delta_2 - \Delta_3) \\
& + \frac{M_{21} M_{13}}{4(\epsilon_3 - \epsilon_1 - \hbar\omega_1 + \Delta_3)^2 + \gamma^2} (2 - 2 \cos(\mathbf{Q} \cdot \mathbf{R})) \delta(\hbar\omega - \Delta_2 + \Delta_3) \\
& + \frac{M_{21} M_{13}}{4(\epsilon_3 - \epsilon_1 - \hbar\omega_1 + \Delta_3)^2 + \gamma^2} (2 + 2 \cos(\mathbf{Q} \cdot \mathbf{R})) \delta(\hbar\omega + \Delta_2 + \Delta_3)
\end{aligned} \tag{2}$$

where $\mathbf{Q} = \mathbf{q}_2 - \mathbf{q}_1$, is the scattering vector, and $\hbar\omega = \hbar\omega_2 - \hbar\omega_1 + \epsilon_3 - \epsilon_2$, and M_{21}, M_{13} are the dipole transition matrix elements between the core and valence levels. In the derivation we have assumed that the core electron is localized and that there is no interatomic transitions, i.e., $\int d\mathbf{r} \phi_1(\mathbf{r}) \mathbf{p} \cdot \mathbf{e} \phi_{2 \text{ or } 3}(\mathbf{r} - \mathbf{R}) \approx 0$.

In real experiments, the widths of the incident and emitted x-ray energies are finite, corresponding to the energy resolution, Γ_1 , of the monochromator, and the resolution of the x-ray spectrometer, Γ_2 , respectively. Eq. (2) has to be convoluted with the spectral functions of these instruments.

The $\cos(\mathbf{Q} \cdot \mathbf{R})$ terms come from the interference between the absorption-fluorescence processes on the two atoms. As can be clearly seen from Eq. (2), the interference effect will be maximum if one can experimentally resolve the four possible final states. The condition for this is $\gamma < 2\Delta_3$, and $\Gamma_{1,2} < \Delta_2, \Delta_3$. Even for $\gamma > 2\Delta_3$ when the photoelectron is excited into mixed symmetric and antisymmetric χ_3 states, one can still observe the interference provided that $\Gamma_{1,2} < \Delta_2, \Delta_3$. Physically it is easy to see why this is the condition for the coherence. The photoelectron and the valence hole are initially created in the region of the localized core hole. By the end of the interaction with photons (time $\hbar/\Gamma_{1,2}$), they have to be delocalized over the whole molecule (time $\hbar/\Delta_{2,3}$) so that one

cannot determine from the final state which path that the fluorescence photon has taken. Only then can the interference effects be observed.

On the other hand, when energy resolution is poor, i.e., when $\Gamma_2 > 2\Delta_2$, the interference $\cos(\mathbf{Q} \cdot \mathbf{R})$ terms in Eq. (2) will be smaller by a factor of approximately $(2\Delta_2/\Gamma_2)^2$ than the non-interference term. In the limit $\Delta/\Gamma \rightarrow 0$, there is no interference term present and we recover the normal emission spectra where the fluorescence can be regarded as emitted from the individual atoms. This means that within the interaction time between the photon and the system, the valence hole is in a mixed χ_2^+ and χ_2^- state localized in the neighborhood of the excited atom. Therefore one can in principle determine which atom is excited right after the outgoing photon wave train leaves the system. The size of the interference term is a measure of the delocalization of the final states.

Finally we comment on recent experiments on carbon and silicon[3-5]. For solids the bandwidths of the conduction and valence bands, i.e., $2\Delta_2$ and $2\Delta_3$, are the measure of the interaction strength. Since the C1s and S1s lifetime widths are about 0.1 and 0.3 eV, respectively, and much less than the bandwidths (10 eV), the coherence condition discussed above is clearly satisfied. Indeed interference effects have been observed in the valence band emission spectra in the form of excitation energy dependence[2-5] and anisotropy in emission[2,5].

In summary, interference effects in x-ray fluorescence are a commonly occurring phenomenon. We have illustrated in this paper that the most important requirement for observing the interference effects in x-ray fluorescence using monochromatic photon excitation is that the resolution of the instrument be greater than the interaction energies of the electronic states.

Reference

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- [1] F. Gel'mukhanov, L.N. Mazalov, and N.A. Shklyaeva, Sov. Phys. JETP 42, 1001 (1976).
- [2] Y. Ma, Phys. Rev. B49, 5799 (1994).
- [3] Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P.D. Johnson, J.E. Rubensson, T. Boske, W. Eberhardt, S. Kevan, Phys. Rev. Lett. 69, 2598 (1992).
- [4] J-E. Rubensson, et al, Phys. Rev. Lett. 64, 1047 (1990); K. Miyano, et al, Phys. Rev. B 48, 1918 (1993).
- [5] Y. Ma, K. Miyano, P.L. Cowan, Y.Aglitzkiy, B.A. Karlin, unpublished.
- [6] See, e.g., R.P. Feynman, R.B. Leighton, M. Sands, *The Feynman Lectures on Physics*, Vol. 3 (Addison-Wesley, Reading, MA, 1965).
- [7] See, e.g., J.J. Sakurai, *Advanced Quantum Mechanics*, (Addison-Wesley, Reading, MA 1967), Chapter 2; M. Blume, J. Appl. Phys. 57, 3615 (1985).

Figure Captions

Fig. 1 X-ray resonant inelastic scattering from a diatomic molecule. ω_1 , and ω_2 , $\mathbf{q}_1$ and $\mathbf{q}_2$ are the energy and momentum of the incident and fluorescence photons, respectively.

Fig. 2 Energy level diagram for the diatomic model shown in Fig. 1. The energy splittings are indicated by 2Δ 's and the energy of unsplit levels by ϵ 's. γ is the lifetime width of the core hole. The arrows indicate the absorption (up arrows) and emission (down arrows) transitions involving the core levels located on the two atoms.

Fig. 1

Fig. 2

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