Theory of Recoil Effect in HAXPES and Its Prospect as a Tool for Material Research

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1. Introduction
   Recoil effect of atoms, molecules and solids
2. Core level X-ray photoemission in graphites
3. Valence band X-ray photoemission
4. Outlook
   Recoil spectroscopy?
Anomalies in HXPES for 1s core-level in graphite

1. Shift of the binding energy
2. Anomalous broadening depend on X-ray energy
3. Asymmetric line shape
Recoil effect is observable!

\[ \vec{P} = -\vec{p} \]

\[ \Delta E = \frac{\vec{P}^2}{2M} = \frac{\vec{p}^2}{2m} \times \frac{m}{M} = \frac{1}{22000} \]  

(carbon atom)

\[ \frac{\vec{p}^2}{2m} \approx 8\text{keV} \quad \Rightarrow \quad \Delta E \approx 0.36\text{eV}! \]
Energy momentum relation

$$p_e = \sqrt{2mE}$$

$$p_x = h\nu / c$$

at $\nu = 10\text{keV}$, $p_x / p_e \approx 0.1$ \quad \therefore \quad \Delta E_x / \Delta E_e \approx 0.01$

Momentum of photon is negligible.

But momentum of photoelectron is NOT.
A guy with weight 70kg dived from a ship of 1500t, and you observed the ship to move!
Doppler Broadening

\[ \vec{P}_i \rightarrow \overrightarrow{M} \]

\[ h \nu \]

\( \vec{P}_i - \vec{p} \)

Energy conservation

\[
\varepsilon_c + h \nu + \frac{\vec{P}_i^2}{2M} = \frac{\vec{p}^2}{2m} + \frac{(\vec{P}_i - \vec{p})^2}{2M}
\]

\[
E_{\text{obs}} = \frac{\vec{p}^2}{2m} = \varepsilon_c + h \nu + \frac{\vec{P}_i^2}{2M} - \frac{(\vec{P}_i - \vec{p})^2}{2M}
\]

\[
= \varepsilon_c + h \nu - \frac{\vec{p}^2}{2M} + \frac{\vec{P}_i \cdot \vec{p}}{M}
\]

\[ \left\langle \left( E_{\text{obs}} - \left\langle E_{\text{obs}} \right\rangle \right)^2 \right\rangle = \left\langle \frac{\vec{P}_i \cdot \vec{p}}{M} \right\rangle^2 = \frac{\left\langle \vec{P}_i^2 \right\rangle}{3M^2} \vec{p}^2 = 2\Delta E \ k_B T
\]

In crystal, \( k_B T \rightarrow \hbar \omega \)
We need quantum mechanics

\[ \hbar \omega \]

\[ \Delta = \frac{p^2}{2M} \]

\[ S = \frac{\Delta E}{\hbar \omega} \quad e^{-s} \]

\[ S >> 1 \quad (\Delta E >> \hbar \omega) \quad \Rightarrow \quad \text{Observed peak shift} = \Delta E \]

\[ S << 1 \quad (\Delta E << \hbar \omega) \quad \Rightarrow \quad \text{Observed peak shift} = 0 \]

Mossbauer Effect

Asymmetric line shape \( \leftarrow \) quantum effect of phonons
Recoil effect comes out from only one assumption.

Initial state

\[ \langle \vec{r} | \psi_c \rangle = \psi_c (\vec{r} - \vec{R}) \]

Adiabatic approximation

Translational symmetry

Momentum conservation

Atomic position \( \vec{R} \) is a dynamic variable.

Final state

\[ \langle \vec{r} | \psi_k \rangle = \frac{1}{\sqrt{V}} \exp(i \vec{k} \cdot \vec{r}) \]

Fermi’s golden rule

\[ I(E) = \frac{\Gamma}{\pi} \left\langle \sum_f \frac{|\langle \Psi_f | H_f | \Psi_i \rangle|^2}{(E + \varepsilon_n - h\nu - \varepsilon_c - \varepsilon_m)^2 + \Gamma^2} \right\rangle \]
\[ I(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-\Gamma|t|/\hbar - iE/\hbar} F(t) \]

\[ F(t) \equiv \left\langle e^{iku(t)} e^{-iku} \right\rangle = \exp[G(t)] \]

\[ G(t) = \sum_{q,\lambda} \alpha_{q,\lambda}^2 \left\{ (2n_{q,\lambda} + 1)(\cos \omega_{q,\lambda} t - 1) - i \sin \omega_{q,\lambda} t \right\} \]

\[ \alpha_{q,\lambda}^2 = \left( \frac{\hbar}{2NM\omega_{q,\lambda}} \right) \left| \vec{k} \cdot \vec{\eta}_{q,\lambda} \right|^2 \]

- Displacement vector of atom
- Atomic mass
- Wave vector of electron
Phonon dispersion of graphite


Anisotropic Debye Model

Equi-frequency surface
Excitation energy dependence (normal emission)

\[ \Gamma = 80\text{meV}(\text{HWHM}) \]

Experimental resolution = 120meV(FWHM)

Emission angle dependence (7940eV, RT)

Why?

\[ S_\lambda = \frac{\Delta E}{\hbar \omega_{\lambda,D}} \] Effective electron-phonon coupling const.

if \( S_\lambda \gg 1 \)

\[
\text{Peak shift} = S_\lambda \hbar \omega_{\lambda,D} = \Delta E
\]

\[
\text{Width} = \sqrt{S_{\lambda,D}} \hbar \omega_{\lambda,D} = \sqrt{\Delta E \hbar \omega_{\lambda,D}} \propto \sqrt{\omega_{\lambda,D}}
\]

Doppler broadening is larger for high \( \omega \)

coordinate space \hspace{1cm} \text{Momentum space}
Recoil effect is universal
  Neutron scatterings
  Electron scatterings
  HX photoelectron emission
  ....etc

But,
the photoelectron carries also information on
the electronic state it has occupied initially.

The recoil effect in valence level XPS will
be much more interesting!
Which atom(s) receives the recoil momentum?

Recoil effect in Bloch electrons?
Striking recoil shift does exist!

Au=197
Al=27

Y. Takata et al.
Even nearly free electrons see lattice structure!

\[
\frac{P_{\text{photoelectron}}}{P_{\text{Fermi}}} = \sqrt{\frac{8 \times 10^3 \text{ eV}}{11 \text{ eV}}} \approx 27
\]

Momentum is not conserved.

existence of HX photoemission \( \rightarrow \) existence of Umklapp process

\( \rightarrow \) electrons see lattice
Recoil Effect of Bloch Electrons

\[ H_e = \sum_{i,j} t(\vec{R}_i - \vec{R}_j) a_i^+ a_j \]

\[ \varphi_i(\vec{r}) \equiv \langle \vec{r} | a_i^+ | 0 \rangle = \varphi(\vec{r} - \vec{R}_i) \]

\[ \vec{R}_i = \vec{R}_i^0 + \vec{u}_i \]

\[ H_L = \sum_j \frac{\vec{P}_j}{2M} + \sum_{i \neq j} V(\vec{R}_i - \vec{R}_j) \quad \rightarrow \quad H_L = \sum_{q, \lambda} \hbar \omega_{q, \lambda} \left( b_{q, \lambda}^+ b_{q, \lambda} + \frac{1}{2} \right) \]

\[ |\psi_k\rangle = \sum_i c_i a_i^+ |0\rangle \]

\[ \psi_k(\vec{r}) = \sum_i e^{i k \vec{R}_i^0} \varphi(\vec{r} - \vec{R}_i) \]

\[ c_i = \frac{1}{\sqrt{N}} e^{i k \vec{R}_i^0} \]
\[ I(\vec{k}, \vec{K}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-\frac{1}{\hbar} i(\vec{K} \cdot \vec{u}(t) - E_{\vec{K}}) t / \hbar} \sum_{j} e^{i(\vec{K} - \vec{k}) \vec{R}^{0}} F_j(t) \]

\[ F_j(t) = \left\langle e^{i\vec{K} \cdot \vec{u}_j(t)} e^{-\vec{K} \cdot \vec{u}_0} \right\rangle \]

dynamical structure factor

Off diagonal terms are negligible.

\[ I(\varepsilon_{\vec{k}}, E_{\vec{k}}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-\frac{1}{\hbar} i(\vec{E} - \varepsilon_{\vec{k}} - \epsilon) t / \hbar} F_0(t) \]

It seems that a single atom receives the recoil momentum.

Shrinkage of the wave function by the measurement?
Recoil effect of photoelectrons in the Fermi edge of simple metals

Origins of broadening
1. Temperature (Fermi distribution)
2. Resolution (Gaussian broadening)
3. Recoil effect (New!)
Next Target

How is it in compounds?

Recoil splitting?
Model 1 diatomic molecule

\[ H = H_e + H_a \]

\[ H_e = \epsilon_1 |1\rangle\langle 1| + \epsilon_2 |2\rangle\langle 2| + \Delta (|1\rangle\langle 2| + |2\rangle\langle 1|) \]

\[ H_a = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V(|X_1 - X_2|) \]

\[ H_I = p(A + A^+) \quad p = -i\hbar \frac{d}{dx} \]

\[ \varphi_1(x) \equiv \langle x | 1 \rangle = \varphi_1(x - X_1) \]

\[ \varphi_2(x) \equiv \langle x | 2 \rangle = \varphi_2(x - X_2) \]
\[ |a\rangle = -\beta |1\rangle + \alpha |2\rangle \]
\[ |b\rangle = \alpha |1\rangle + \beta |2\rangle \]

\[ \varphi_1(x) \equiv \langle x | 1 \rangle = \varphi_1(x - X_1) \]
\[ \varphi_2(x) \equiv \langle x | 2 \rangle = \varphi_2(x - X_2) \]

\[ |\Psi_i\rangle = |hv\rangle \otimes |b\rangle \otimes |g\rangle \otimes |0\rangle \]

\[ |\Psi_f\rangle = |\text{vac}\rangle \otimes |k\rangle \otimes |K\rangle \otimes |m\rangle \]

\[ I(\varepsilon_k) = \sum_m \sum_K \left| \langle m, K, k | p | 0, g, b \rangle \right|^2 \delta (h \nu + \varepsilon_b - \varepsilon_k - E_K - \varepsilon_m) \]
\[ I(\varepsilon_k) = \alpha^2 |\zeta_1|^2 I_1(\varepsilon_k) + \beta^2 |\zeta_2|^2 I_2(\varepsilon_k) + \text{cross terms} \]

\[ \zeta_i = \int dx \, e^{-ikx} \left( -i \frac{d}{dx} \right) \varphi_i(x) \]

\[ \times \alpha^2 |\zeta_1|^2 \]

\[ \times \beta^2 |\zeta_2|^2 \]
Model 2 composite metal

Heavy atom and light atom
In a unit cell

Bloch function

\[ \psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j \left\{ C_A(\vec{k}) w_1 (\vec{r} - \vec{R}_j^A) + C_B(\vec{k}) w_2 (\vec{r} - \vec{R}_j^B) \right\} e^{i\vec{k} \cdot \vec{R}_j^0} \]

Atomic positions are dynamic variables (not parameters).
Local DOS

\[ D(\varepsilon) = D_A(\varepsilon) + D_B(\varepsilon) \]

Contribution from A site

\[ I_A(E, \varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i(E-h\nu-\varepsilon)t/\hbar} F_A(t) \]

\[ F_A(t) = \exp \left[ \sum_{q, \lambda} |\alpha_{q, \lambda}^A|^2 \left\{ 2n_{q, \lambda} + 1 \right\} \left( \cos \omega_{q, \lambda} t - 1 \right) - i \sin \omega_{q, \lambda} t \right] \]

\[ |\alpha_{q, \lambda}^A|^2 = \left( \frac{\hbar}{2NM_A\omega_{q, \lambda}} \right) |\vec{k} \cdot \eta_{q, \lambda}|^2 \]

Contribution from B site \( A \rightarrow B \)

\[ I(E) = \int_{-\infty}^{\infty} d\varepsilon \ f(\varepsilon) \left\{ |\zeta_A|^2 D_A(\varepsilon) I_A(E, \varepsilon) + |\zeta_B|^2 D_B(\varepsilon) I_B(E, \varepsilon) \right\} \]

Valence band PES may split due to recoil effect!
How about amorphous materials?
Which atom(s) receive recoil momentum?
Recoil effect as a probe of local atomic environment

LiCoO$_2$

Yokohama CU, Yamada Lab.

Lithium ion battery
Valence level

Valence band Auger

Valence band X-ray emission
Recoil Spectroscopy of Local Vibration

- Site selective
- Angle selective
- Level selective
Message of this work

1. Recoil effect in x-ray photoemission is a purely kinematic effect. Only the adiabatic approximation is needed theoretically.

2. Line shape in core level recoil spectra carries information of the rigidity of the atomic environment. (Doppler broadening)

3. Even Bloch electrons show recoil effect. (From which atom was it ejected?)

4. Valence spectra may split due to recoil effect.

Recoil Spectroscopy, a new tool?