Energy versus time in x-ray scattering

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Momentum- and energy-resolved scattering

Measures a correlation function, $S(q,\omega)$

(See talk yesterday by Toby Perring)
A new approach: Free Electron Lasers

Can—for the first time—study ultrafast dynamics with a momentum-resolved probe

Questions for today:
• How is this different from inelastic scattering techniques, which are also said to measure dynamics? That is, how are time and frequency related?
• Where does scattering come from, and how does it measure dynamics anyway?
Example of $\omega$ vs. $t$: the dielectric function, $\varepsilon(\omega)$

$$
\varepsilon(\omega) = 1 + 4\pi \chi_e(\omega)
$$

$$
\chi_e(\omega) = \frac{\varepsilon(\omega) - 1}{4\pi}
$$

$$
P(\omega) = \chi_e(\omega) E(\omega)
$$

Time relationship is nonlocal:

$$
\chi_e(t) = \int_{-\infty}^{\infty} d\omega \frac{\chi_e(\omega)}{2\pi} e^{-i\omega t}
$$

$$
P(t) = \int_{-\infty}^{\infty} dt' \chi_e(t - t') E(t')
$$

$\chi_e$ is a Green's function

$\omega$ dependence $\leftrightarrow$ retardation
Electron in an EM field (classical)

Can define the fields in terms of potentials:

\[ B = \nabla \times A \quad E = -\nabla \varphi - \frac{1}{c} \frac{\partial A}{\partial t} \]

Classical motion described by the Lagrangian

\[ L = K - V = \frac{1}{2} m \dot{x}^2 + e \varphi - \frac{e}{c} \dot{x} \cdot A \]

The canonical momentum is

\[ p^c = \frac{\partial L}{\partial \dot{x}} = m \dot{x} - \frac{e}{c} A \]

This allows one to define the classical Hamiltonian

\[ H = \sum_i p^c_i \dot{r}_i - L = \frac{1}{2m} \left( p^c + \frac{e}{c} A \right)^2 - e\varphi \]

Hamilton’s equations give the equations of motion:

\[ \dot{x}_i = \frac{\partial H}{\partial p^c_i} \quad \dot{p}_i = -\frac{\partial H}{\partial x_i} \]

Result is the Lorentz force law:

\[ m \ddot{x} = -e \left( E + \frac{1}{c} \dot{x} \times B \right) \]

* Gaussian units
The Hamiltonian is now an operator. Photons are massless so we have to use second quantization:

\[ \hat{H} = \hat{H}_{EM} + \hat{H}_{\text{electron}} + \hat{H}_{\text{interaction}} \]

\[ \hat{H}_{EM} = \int dx \left( \frac{\hat{E}^2}{2} + \frac{\hat{B}^2}{2} \right) \quad \hat{H}_{\text{electron}} = \int d^3x \hat{\psi}^\dagger(x, t) \left[ \frac{\mathbf{p}^2}{2m} + V(x) \right] \hat{\psi}(x, t) \]

Where \( \hat{\psi}(x, t) \) annihilates an electron at position \( x \) and time \( t \).

The vector potential is an operator that creates or annihilates photons:

\[ \hat{\mathbf{A}}(x, t) = \sum_{k, \lambda} c \sqrt{\frac{\hbar}{2\omega_k}} \left[ a_{k, \lambda} e^{i(k \cdot \mathbf{r} - \omega t)} + a^\dagger_{k, \lambda} e^{-i(k \cdot \mathbf{r} - \omega t)} \right] \]

Multiplying everything out gives fundamental interactions between electrons and photons:

\[ H = H_0 + H_1 + H_2 \]

\[ H_2(t) = -\frac{e^2}{2mc^2} \int d^3x \hat{\psi}^\dagger(x, t) \hat{\mathbf{A}}^2(x, t) \hat{\psi}(x, t) = -\frac{e^2}{mc^2} \int d^3x \hat{\mathbf{A}}^2(x, t) \hat{n}(x, t) \]

\[ H_1(t) = -\frac{e}{mc} \int d^3x \hat{\psi}^\dagger(x, t) \left[ \mathbf{p} \cdot \hat{\mathbf{A}}(x, t) \right] \hat{\psi}(x, t) \]
Scattering

Scattering takes place when these interactions evolve a photon from an initial state to a final state, with a corresponding change in the electronic subsystem:

\[ |i\rangle = a_{k_i,\lambda_i}^\dagger |m\rangle \quad \rightarrow \quad |f\rangle = a_{k_f,\lambda_f}^\dagger |n\rangle \]

What does this is the time-evolution operator:

\[ U_I(\infty, -\infty) = \exp \left[ -i \int_{-\infty}^{\infty} dt \ H_I(t) \ e^{-\eta |t|} \right] \]

\[ M = \langle i | U_I(\infty, -\infty) | f \rangle \]

"Nonresonant" x-ray scattering

\[ w_{f \leftarrow i} = r_0^2 (\epsilon_f^* \cdot \epsilon_i)^2 \sum_{n, m} |< n | \hat{n}(k) | m >|^2 P_m \delta(\omega - \omega_n + \omega_m) \]

"Resonant" inelastic x-ray scattering (RIXS)

\[ w_{f \leftarrow i} = \left| \frac{e^2}{mc^2 \hbar^2} \sum_m \frac{< f | p \cdot A | m > < m | p \cdot A | 0 >}{\omega - \omega_m + i\gamma} \right|^2 \delta(\omega - \omega_f + \omega_0) \]

(J. van den Brink, after the coffee break)
Cross section for x-ray scattering

The differential scattering cross section comes from Fermi’s golden rule

\[ \frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{1}{\Phi} \cdot \frac{\partial^2 N}{\partial \Omega \partial E} \]

where counting states in a box of volume V provides the density of final states:

\[ \frac{\partial^2 N}{\partial \Omega \partial E} = \frac{\omega_f V}{8 \pi^3 \hbar c^3} \]

\[ \Phi = \frac{c}{V} \quad \text{(for one incident photon)} \]

Cross section for nonresonant x-ray scattering

\[ \frac{\partial^2 \sigma(q, \omega)}{\partial \Omega \partial E} = r_0^2 \frac{\omega_f}{\omega_i} \left( \varepsilon_f^* \cdot \varepsilon_i \right)^2 S(q, \omega) \]

\[ k = k_f - k_i \quad \omega = \omega_f - \omega_i \]

dynamic structure factor – what is it?
**S(q, ω) and the Van Hove function**

**Cross section:**

\[
\frac{\partial^2 \sigma(q, \omega)}{\partial \Omega \partial E} = n_0^2 \frac{\omega_2}{\omega_1} \left( \mathbf{\epsilon}_2^* \cdot \mathbf{\epsilon}_1 \right)^2 S(q, \omega)
\]

Assuming we are in thermodynamic equilibrium, S has the form

\[
S(q, \omega) = \frac{1}{\hbar} \sum_{m,n} P_m \left| \langle n | \hat{n}(q) | m \rangle \right|^2 \delta(\omega - \omega_n + \omega_m)
\]

\[
P_m = \frac{e^{-\hbar \omega_m / kT}}{Z}
\]

This is the so-called “dynamic structure factor.”

S(q, ω) is the Fourier transform of the Van Hove function, G(x,t), which is the space-time correlation function for the electron density:

\[
S(q, \omega) = \int dx \, dt \, G(x, t) e^{-i(q \cdot x - \omega t)}
\]

where

\[
G(x,t) = \int dx' \, dt' \langle \hat{n}(x', t') \hat{n}(x + x, t + t) \rangle
\]

The brackets denote a QM thermal average:

\[
\langle \hat{O} \rangle = \sum_m P_m \langle m | \hat{O} | m \rangle
\]

What does this have to do with dynamics?
Fluctuation-Dissipation Theorem

\[ S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\hbar\omega/kT}} \text{Im}\left[ \chi(q, \omega) \right] \]

\[ \chi(x_1, x_2, t_1 - t_2) = -\frac{i}{\hbar} \langle [\hat{\rho}(x_2, t_2), \hat{\rho}(x_1, t_1)] \rangle \theta(t_1 - t_2) \]

Describes how charge propagates in a system:
- Phonons
- Plasmons
- Excitons
- Electron-hole pairs
- Etc.
Green’s functions or “Propagators”

Dynamics is described by a propagator

\[ K(x, t; x', t') \]

Electrons:
\[ G(x, t; x', t') = i / \hbar \langle 0 \left| \{ \hat{\psi}(x, t), \hat{\psi}^\dagger(x', t') \} \right| 0 \rangle \theta(t - t') \]

Density:
\[ \chi(x, t; x', t') = i / \hbar \langle 0 \left| [ \hat{\rho}(x, t), \hat{\rho}(x', t') ] \right| 0 \rangle \theta(t - t') \]

Some translational symmetry:
Frequency / momentum representation is more illuminating.

• Best way—in a many-body system—to define what is a “particle”
View propagator in real time?

Crazy idea: Can we Fourier Transform IXS data and make real time movies?

Why? Should be incredibly easy to get attosecond time resolution:

$$\Delta E \cdot \Delta t \sim \frac{\hbar}{2} \quad \Delta t \sim 100 \text{ as} \quad \Rightarrow \quad \Delta E \sim 7 \text{ eV}$$

Can we FT to observe a propagator directly?

Answer: No

$$S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\hbar \omega / kT}} \text{Im} \left[ \chi(q, \omega) \right]$$

Our information is incomplete. Cannot Fourier transform with only the imaginary part.*

*This is what Fermi called the “inverse scattering” problem.
The phase problem reexamined

Central Dogma of x-ray crystallography:

\[ I(q) \propto |\rho(q)|^2 \]

Periodic system (i.e., a crystal):

\[ \rho(r) = \sum_G \rho_G e^{-iG \cdot r} \quad I_G \propto |\rho_G|^2 \]

- Phase problem is solved by incorporating *constraints* (Hg or Se atoms)
- This is the basis for the field of *structural genomics*
- Based on *classical scattering* theory. All scattering is *elastic*.


KcsA channel
R. MacKinnon
Chem. Nobel Prize, 2003
The phase problem reexamined

Van Hove function:

\[ S(q, \omega) = \frac{1}{\hbar} \sum_n |\langle n | \hat{\rho}(q) | 0 \rangle|^2 \delta(\omega - \omega_0 + \omega_m) \quad (T = 0) \]

What we think we measure:

\[ S(q, \omega)|_{\omega = 0} = \frac{1}{\hbar} |\langle 0 | \hat{\rho}(q) | 0 \rangle|^2 = \frac{1}{\hbar} |\langle \hat{\rho}(q) \rangle|^2 \]

What we actually measure:

\[ \int d\omega S(q, \omega) = \frac{1}{\hbar} \sum_n |\langle n | \hat{\rho}(q) | 0 \rangle|^2 = \frac{1}{\hbar} \langle 0 | \hat{\rho}(-q) \hat{\rho}(q) | 0 \rangle = \frac{1}{\hbar} \langle |\hat{\rho}(q)|^2 \rangle \]

More general formulation of the phase problem:

\[ S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\hbar \omega/kT}} \text{Im}[\chi(q, \omega)] \quad \text{Re}[\chi(k, \omega)] = \frac{2}{\pi} P \int_0^\infty \frac{\text{Im}[\chi(k, \omega')] d\omega'}{\omega'^2 - \omega^2} \]

- \( \chi(x, t) = 0 \) for \( t < 0 \)
- Raw spectra do not really describe dynamics – no causal information
- Causality is the constraint. Must assign an arrow of time to the problem.
- Rise of entropy \( \Leftrightarrow \) arrow of time
What if the system is inhomogeneous?

Assume it’s periodic:

\[
\chi(x_1, x_2, t_1 - t_2) = -\frac{i}{\hbar} \left\langle \left[ \hat{\rho}(x_2, t_2), \hat{\rho}(x_1, t_1) \right] \right\rangle \theta(t_2 - t_1)
\]

\[
\chi(k_1, k_2, \omega) = \chi(k_1, G - k_1, \omega)
\]

In regular scattering, we only measure the diagonal (G=0) components of this matrix:

\[
S(k, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\hbar \omega / kT}} \text{Im} [ \chi(k, -k, \omega) ]
\]

Naïvely Fourier transform and you get a spatial average:

\[
\chi(r, t) = \int d r' \chi(r', r + r', t).
\]


If the system is homogeneous, this is OK. If not, things get even better… but let’s start with the homogeneous case.
Plasma oscillations in water

- 8 valence electrons / molecule
- \( \rho = 1 \text{ g/cm}^3 \Rightarrow n = 0.20 \text{ e/Å}^3 \)
- \( \omega_p = \sqrt{4\pi ne^2/m} = 16.6 \text{ eV} \)
Problem #1:

\( \text{Im}[\chi(k, \omega)] \) must be defined on infinite \( \omega \) interval for continuous time interval

Solution:

Extrapolate.

Side effects:

- \( \chi(x, t) \) defined on continuous (infinitely narrow) time intervals.
- Time “resolution” \( \Delta t_N = \pi/\Omega_{\text{max}} \)
- \( \Omega_{\text{max}} \) plays role of pulse width.
More Problems

Problem #2:

*Discrete points violate causality*

\( \text{Im}[\chi(k,\omega)] \) must be defined on *continuous* \( \omega \) interval. Periodicity incompatible with causality.

**Solution:**

Interpolation (i.e., add data)

\[
\chi(k, t) = \int_0^\infty \frac{d\omega}{\pi} \left[ \sin(\omega t) \text{Im}\chi(k, \omega) + \cos(\omega t) \text{Re}\chi(k, \omega) \right]
\]

\[
\chi(k, t) = \frac{2}{\pi} \int_0^\infty d\omega \sin(\omega t) \text{Im}\chi(k, \omega)
\]

**Side effects:**

- \( \chi(x,t) \) defined forever. Vanishes for \( t < 0 \).
- Repeats with period \( T = 2\pi/\Delta\omega \)
- \( \Delta\omega \) plays role of rep rate
Disturbance from a point source in water

Units Å⁻⁶ clipped at 1 Å⁻⁶

Δt_N = 20.7 as
Δx_N = 0.635 Å

Frame-by-frame

- Events transpire in 350 as – *light travels 100 nm in vacuum*
- Causality ↔ Analytic properties ↔ Rise of entropy ↔ Arrow of time

Units Å\(^{-6}\) clipped at 1 Å\(^{-6}\)

\(\Delta t_N = 20.7 \text{ as} \)
\(\Delta x_N = 0.635 \text{ Å} \)
Attosecond imaging with IXS

Ion solvation dynamics ($\Delta t = 26$ fs)
R. Coridan, et al., PRL 103, 237402 (2009)

“Birth” of an exciton in LiF ($\Delta t = 20.6$ as)
P. A. et al., PNAS 105, 12159 (2008)
Effective fine structure constant of graphene

\[ \alpha_g^*(k, \omega) = \alpha_g \left[ 1 + V(k) \chi(k, \omega) \right] \]

Charge propagator. Gives screening correction to \( \alpha_g \).

\( \Delta t = 10.3 \text{ attoseconds (}10^{-17} \text{ sec)}, \Delta r = 0.2 \text{ Å} \)
Effective fine structure constant, $\alpha_g^*(k, \omega)$

\[
\begin{align*}
|\alpha_g^*(k, \omega)| \\
\text{arg}\left[\alpha_g^*(k, \omega)\right]
\end{align*}
\]

\[\alpha_g^* = 2.6 \ (\varepsilon < 1)\]

\[\alpha_g^*(0^+, 0) \equiv \lim_{k \to 0} \alpha_g^*(k, 0) = 0.14 \pm 0.092 \approx \frac{1}{7}\]

New results

Measured and calculated $|\alpha^*|$
We need the off-diagonal terms. Can we measure them?

\[ \chi(x_1, x_2, t_1 - t_2) = -\frac{i}{\hbar} \langle [\hat{\rho}(x_2, t_2), \hat{\rho}(x_1, t_1)] \rangle \theta(t_2 - t_1) \]

\[ \chi(k_1, k_2, \omega) = \chi(k_1, G - k_1, \omega) \quad \text{(periodic case)} \]

Yes ... X-ray standing waves:

X-Ray Scattering, Finally Done “Correctly”

“Incident” photon is in a superposition of momenta:

\[ |i\rangle = (g_1 a_{k_1\alpha_1}^\dagger + g_2 a_{k_2\alpha_2}^\dagger e^{i\gamma}) |m\rangle, \quad |f\rangle = a_{k_3\alpha_3}^\dagger |n\rangle \]

Now do scattering:

\[ \hat{H} = \hat{H}_0 + \frac{e}{2mc} \int \psi^\dagger \hat{A} \cdot \mathbf{p} \psi \, d\mathbf{x} + \frac{e^2}{2mc^2} \int \hat{\rho} \hat{A}^2 \, d\mathbf{x} \]

The cross section contains interference terms:

\[ \frac{d^2\sigma}{dE'd\Omega} = \left( \frac{e^2}{mc^2} \right)^2 \frac{\omega_3}{\omega_1} \left[ g_1^2 |\hat{\epsilon}_3^* \cdot \hat{\epsilon}_1|^2 S(q_1, \omega) + g_2^2 |\hat{\epsilon}_3^* \cdot \hat{\epsilon}_2|^2 S(q_2, \omega) \right. \\
+ g_1 g_2 e^{i\gamma} (\hat{\epsilon}_3^* \cdot \hat{\epsilon}_1)(\hat{\epsilon}_3^* \cdot \hat{\epsilon}_2) S(q_1, q_2, \omega) \left. \right] \\
+ g_1 g_2 e^{-i\gamma} (\hat{\epsilon}_3^* \cdot \hat{\epsilon}_1)(\hat{\epsilon}_3^* \cdot \hat{\epsilon}_2^*) S(q_2, q_1, \omega) \]

Interference terms are off-diagonal dynamic structure factor

\[ S(q_1, q_2, \omega) = \sum_{n,m} b_m \langle m | \rho(q_1) | n \rangle \langle n | \rho(-q_2) | m \rangle \delta(\hbar \omega - E_n + E_m) \]

Generalized fluctuation-dissipation theorem:

\[ S(q_1, q_2, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \hbar \omega}} \text{Im} \chi(q_1, -q_2, \omega). \]

“Crystallography for the collective excitations”

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- Complete reconstruction of $\chi(r_1, r_2, t)$
- Angstrom spatial resolution
- Attosecond time resolution

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