# 1 Development

**Geometry:** Consider an ultrafast time-resolved optical pump and elastic X-ray scattering probe experiment in a perpendicular arrangement, as shown in Figure 1. Initially, the samples are all oriented randomly, but the optical pump preferentially excites chromophores with transition dipoles $\mu$ oriented along $\hat{z}$, with probability $P(\hat{\mu}) \equiv \hat{\mu}_z^2 = \cos^2(\zeta_\mu)$, where $\zeta_\mu$ is the polar angle from $\hat{z}$. This anisotropic absorption will induce anisotropy in the subsequent X-ray scattering signal.

In the independent atom model (IAM), the X-ray scattering signal is,

$$I(\vec{q},t) \equiv \frac{1}{N_I} \sum_I \left| \sum_A f_A(q) e^{i\vec{q}\cdot\vec{r}_A^I(t)} \right|^2$$

Here $\vec{r}_A^I(t)$ are the nuclear coordinates of atom $A$ as a function of delay time $t$, for trajectory $I$ [from molecular dynamics trajectories on the relevant electronic state(s)]). By averaging over many trajectories, and by weighting to account for the $\cos^2(\zeta_\mu)$ anisotropy of the initial conditions, the time-resolved X-ray scattering signal can be obtained on a one-to-one footing with the experiment. The $f_A(q)$ are atom- and X-ray-beam-specific scattering cross sections, and have been tabulated online in a standard Gaussian form.

The X-ray scattering signal is best written in spherical coordinates as $I(\vec{q},t) \equiv I(q,\zeta,\phi,t)$. Here $q$ is the scattering amplitude, $\zeta$ is the polar angle from $\hat{z}$, and $\phi$ is the azimuthal angle in $\hat{x}$-$\hat{y}$. Note that we expect the signal to be isotropic in $\phi$, but not in $\zeta$.

**Spherical Harmonic Transformation:** A useful transformation of the X-ray scattering signal involves the (complete) projection onto spherical harmonics,

$$I(\vec{q},t) = \sum_{lm} Y_{lm}(\zeta,\phi) I_{lm}(q,t)$$

where,

$$I_{lm}(q,t) \equiv \int_\Omega \mathrm{d}\Omega \; Y_{lm}^*(\Omega) I(q,\Omega,t)$$

The solid angle $\Omega$ is shorthand for the set of $< \zeta, \phi >$ coordinates. Here the spherical harmonics are defined to be fully orthonormal on the unit sphere,

$$\int_\Omega \mathrm{d}\Omega \; Y_{lm}^*(\Omega) Y_{l'm'}(\Omega) = \delta_{ll'}\delta_{mm'}$$

Due to parity, the odd-$l$ spherical harmonic contributions must be zero. Due to isotropy in $\phi$, the $m \neq 0$ spherical harmonic contributions must be zero. Thus, the only surviving contributions are the even zonal spherical harmonics $Y_{l0}$ where $l$ is even.

The normalized zonal spherical harmonics are,

$$Y_{l0}(\zeta,\phi) \equiv N_l P_l(\cos\zeta)$$

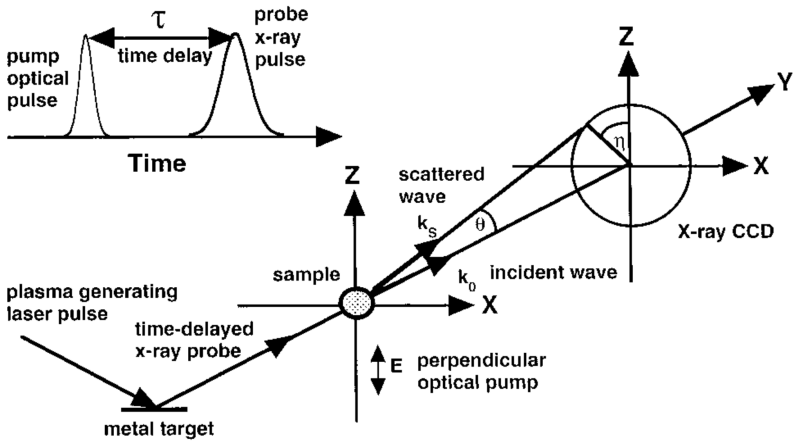


Figure 1: An illustration of ultrafast X-ray diffraction. The X-ray probe arrives a delay of $t$ with respect to the optical pump. In the perpendicular experimental arrangement (shown here), the polarization vector $\vec{E} \propto \hat{z}$ of the optical pump pulse is perpendicular to the incident wave vector $\vec{k}_0 \equiv k\hat{y}$ of the X-ray probe pulse. The incident X-ray photons scatter at angle $\theta$ with respect to $\vec{k}_0$, and azimuthal angle $\eta$ with respect to $\vec{E}$. These two angles fully describe the scattering in the elastic regime, as $|\vec{k}_0| = |\vec{k}_s|$. The scattering vector $\vec{q}$ is the difference between the incident and scattered wave vectors $\vec{q} \equiv \vec{k}_0 - \vec{k}_s$. The amplitude of the scattering vector is $q \equiv |\vec{q}| = 2k \sin\theta/2$. Figure adapted to our notation from Kent Wilson's excellent 1998 ultrafast scattering paper in JPCA [Jianshu Cao and Kent R. Wilson, *J. Phys. Chem. A* **102**, 9523 (1998)].

The Legendre polynomials are,

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_{l+1}(x) = \frac{1}{l+1}\left[(2l+1)xP_l(x) - lP_{l-1}(x)\right]$$

The normalization factors are,

$$N_l \equiv \sqrt{\frac{2l+1}{4\pi}}$$

**Tasking:** For a set of trajectories $r_A^I(t)$ aligned so that $\vec{\mu}(t=0) = \mu\hat{z}$, we must compute,

$$I_{l0}(q,t) \equiv \frac{1}{N_I}\sum_I \int_{\mathrm{SO(3)}} \mathrm{d}\hat{R}\ \hat{R}_z^2 \int_\Omega \mathrm{d}\Omega\ Y_{l0}^*(\Omega) \left|\sum_A f_A(q) e^{i\vec{q}\cdot[\hat{R}\vec{r}_A^I(t)]}\right|^2$$

Colloquially, this says "rotate each trajectory through the full set of rotations $\hat{R}$, and weight these by the square of the projection of the rotation on $\hat{z}$ ($\hat{R}_z^2 \Leftrightarrow \cos^2[\zeta(\hat{R})]$) to account for

the excitational anisotropy. For each trajectory and rotation, compute the diffraction signal in $\vec{q}$, and project onto spherical harmonic contributions $I_{l0}^{I,\hat{R}}(q,t)$. Average these over all rotations and all trajectories."

A key observation is that one can apply the rotations to the diffraction patterns, rather than to the trajectories, which allows for interchange of summation,

$$\left|\sum_A f_A(q) e^{i\vec{q}\cdot[\hat{R}\vec{r}_A^I(t)]}\right|^2 = \left|\sum_A f_A(q) e^{i[\hat{R}^\dagger\vec{q}]\cdot\vec{r}_A^I(t)}\right|^2$$

This amounts to switching working variable from $\vec{q} =< q, \Omega >$ to $\vec{q}' =< q, \hat{R}^\dagger\Omega >$ and leaving the trajectories in $\hat{z}$ frame. The observable may now be written as,

$$I_{l0}(q,t) \equiv \int_\Omega \mathrm{d}\Omega \int_{\mathrm{SO}(3)} \mathrm{d}\hat{R}\ \hat{R}_z^2 Y_{l0}^*(\hat{R}^\dagger\Omega) \underbrace{\frac{1}{N_I}\sum_I \left|\sum_A f_A(q) e^{i\vec{q}'\cdot\vec{r}_A^I(t)}\right|^2}_{I^{\hat{z}}(\vec{q}',t)}$$

**Computational Procedure:**

1. Compute $N_I$ trajectories $r_A^I(t)$ and align these so that $\vec{\mu}(t=0) = \mu\hat{z}$.

2. Lay out a regular grid $q_P$ and a Lebedev grid $< \Omega_Q, w_Q >$ to form a 3D spherical grid $\vec{q}_R \equiv q_P \otimes \Omega_Q$.

3. Evaluate,

$$I^{\hat{z}}(\vec{q}_R,t) \equiv \frac{1}{N_I}\sum_I \left|\sum_A f_A(q_R) e^{i\vec{q}_R\cdot r_A(t)}\right|^2$$

4. Generate a covering sequence of rotation matrices and affiliated weights $< \hat{R}_M, w_M >$ to integrate SO(3). A particularly nice way to do this is to exploit the "rotate around $\hat{z}$ by angle $\omega$, then rotate down to a uniform spherical angle $\Omega$" method for generating uniform random rotation matrices, but adapting this to the appropriate regular quadrature grids for $\omega$ and $\Omega$ (Fourier and Lebedev). That is, lay out uniform Fourier grid $\omega_T \equiv 2\pi T/(N_T+1)$ and $w_T = 1/N_T$ and a Lebedev grid $< \Omega_U, w_U >$. Then form the direct product grid $\Phi_M \equiv \omega_T \otimes \Omega_U$ and $w_M \equiv (w_T \otimes w_U)/4\pi$. For each $M$ point, start with the identity matrix, rotate about $\hat{z}$ by $\omega_T$ (a simple Given's rotation), and then rotate directly down from $\hat{z}$ to $\Omega_M$ (a Householder reflection + parity inversion) to obtain the rotation matrix $\hat{R}_M$.

5. Form the observable,

$$I_{l0}(q_P,t) = \sum_Q w_Q \sum_M w_M (\hat{R}_M^z)^2 Y_{l0}(\hat{R}_M^\dagger\Omega_Q) I^{\hat{z}}(q_P,\Omega_Q,t)$$

**X-Ray Scattering vs. Electron Diffraction:** For ultrafast x-ray scattering, the form factors $f_A(q)$ are the Fourier transform of the electronic density of a spherical atom (possibly selected to reflect the density of the local chemical environment in the true molecule),

$$f_A(q) \equiv \int_{\mathbb{R}^3} \mathrm{d}r_1 \; \rho_A^{\mathrm{e}}(\vec{r}_1) e^{i\vec{q}\cdot\vec{r}_1}$$

These form factors are tabulated for many common atoms at

`http://lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php`

(accessed 01/18/2018). The specific parametrization is,

$$f_A(q) \equiv \sum_{i=1}^{4} a_i \exp\left(-b_i \left(\frac{q}{4\pi}\right)^2\right) + c$$

With 9 parameters $a_{1-4}$ $b_{1-4}$, and $c$ per atom type. Units are $\mathring{A}^{-1}$.

To switch to ultrafast electron diffraction, one must also account for scattering off of the nucleus and for a modified Jacobian element,

$$f_A^{\mathrm{UED}}(q) \equiv \frac{1}{q^2}\left[Z_A - f_A^{\mathrm{XRAY}}(q)\right]$$

See M. Ben-Nunn, J. Cao, and K. Wilson, JPCA, 101, 8744 (1997) for details.