

# 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,

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

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

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

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,

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

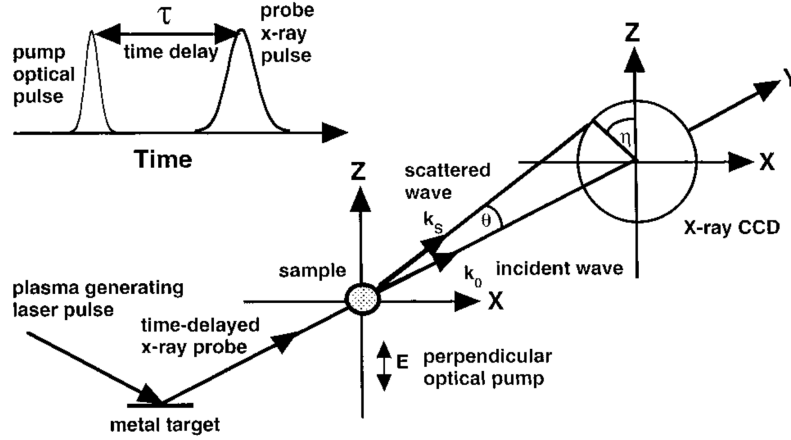


Figure 1: An illustration of ultrafast X-ray diffraction. The X-ray probe arrives a delay of  $t$  with respect to the optical pump. In the perpendicular experimental arrangement (shown here), the polarization vector  $\vec{E} \propto \hat{z}$  of the optical pump pulse is perpendicular to the incident 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,

$$P_0(x) = 1$$

$$P_1(x) = x$$

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

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,

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

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  $\vec{q} = \langle q, \Omega \rangle$  to  $\vec{q}' = \langle q, \hat{R}^\dagger \Omega \rangle$  and leaving the trajectories in  $\hat{z}$  frame. The observable may now be written as,

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

### Computational Procedure:

1. Compute  $N_I$  trajectories  $\vec{r}_A^I(t)$  and align these so that  $\vec{\mu}(t=0) = \mu \hat{z}$ .
2. Lay out a regular grid  $q_P$  and a Lebedev grid  $\langle \Omega_Q, w_Q \rangle$  to form a 3D spherical grid  $\vec{q}_R \equiv q_P \otimes \Omega_Q$ .
3. Evaluate,

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

4. Generate a covering sequence of rotation matrices and affiliated weights  $\langle \hat{R}_M, w_M \rangle$  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  $\langle \Omega_U, w_U \rangle$ . 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,

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