Chapter 2.

A Brief Review of Electron Diffraction Theory

The theory of gas phase electron diffraction is hardly a new topic. It is well established for decades and has been thoroughly described in the literature (see, for example, Ref. 1). Consequently, it will not be dealt with in such depth here. The purpose of this chapter is to serve as a primer such that the subsequent descriptions of the ultrafast gas-phase electron diffraction experimental and theoretical methodology may be understood in the context of the much more familiar field of conventional gas-phase electron diffraction. The following sections will attempt to portray its important aspects in a simple and physically intuitive way.

2.1 Momentum transfer

In electron diffraction, a beam of electrons travels an axis *z* and intersects with a beam of molecules. Although most electrons pass through the beam unperturbed, some are scattered by the atomic and molecular electrostatic potentials. If the molecules in the molecular beam are randomly oriented, and the electron beam is judged to be collimated, the electrons scatter in a radial symmetric pattern about *z*. The resulting patterns may then be described by an intensity measure at an angle θ from the center position. Typically, these scattering intensity features are expressed in terms of the momentum transfer parameter, s, the magnitude of the change in the momentum vectors between the incident and scattered electron. For elastic scattering, the s value (with units of Å^{-1}) at each point from the center position is given by

$$\begin{aligned} s &= \left|\overrightarrow{k_0} - \vec{k}\right| \\ &= 2\left|\overrightarrow{k_0}\right|\sin(\theta/2) \\ &= \frac{4\pi}{\lambda}\sin(\theta/2), \end{aligned} \tag{2-1}$$

where $\overrightarrow{k_0}$ and $\vec{k}$ are the momentum vectors for the initial and scattered electron (for a plane wave of the form Ae^{ik_0z}), respectively. λ is the de Broglie wavelength of the electron. θ, the scattering angle between $\overrightarrow{k_0}$ and $\vec{k}$, is defined by simple trigonometry:

$$\theta = \arctan(d/L), \tag{2-2}$$

where d is the distance on the detector from the center position and L is the distance from the beam interaction region to the center position on the detector, known as "camera length". For a given kinetic energy, T, the relativistically corrected de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{T(T + 2m_0c^2)}}, \tag{2-3}$$

where h is Planck's constant, m_0 is the rest mass of the particle (here, an electron), and c is the speed of light. The relativistic velocity of a particle at a given kinetic energy is given by

$$v = c\sqrt{1 - \left(\frac{m_0c^2}{T + m_0c^2}\right)^2}. \tag{2-4}$$

With T at 30 keV for an electron experiencing a 30 kV acceleration voltage, λ is 0.06979 Å and v is 9.84×10^7 m/s. Comparison between the relativistic and non-relativistic wavelengths and velocities of an electron are shown in Fig. 2-1. It's clear that relativistic corrections, although not without influence in the energetic regime of UED, become much more critical at the higher electron acceleration potentials used in some electron microscopes.

2.2 Atomic scattering

In a molecule, interactions between the valence electrons of nearby atoms hold the positively charged nuclei at the bonding distance. Electrons in the beam of an electron diffraction experiment, as charged particles, scatter from the electrostatic potentials of both the nuclei and the electron distribution (compare this with the much weaker scattering of x-rays which only interact with the electron distribution). Isolated atoms, themselves a roughly spherical positive nucleus surrounded by a roughly spherical shell of electrons, become perturbed once implicated with other atoms in valence electron bonding to form a molecule. As a standard practice in electron diffraction, matters are simplified by assuming that an atom is actually just a spherical potential and that a molecule is simply a collection of these unperturbed atoms at the appropriate internuclear distances. This approximation is known as the independent atomic model (IAM) and it holds remarkably well across gas-phase electron diffraction. This is in great part due to the fact that scattering from the nuclear potential is so much more intense than the scattering from the bonding electron density; even in a molecule, atoms still are roughly spherical. Interactions between the electron beam and the bonding electron density are relatively weak causing the IAM to suffer some inadequacy only at small scattering angles (s < 5 Å^{-1}).[2]

Using the IAM, electron scattering from a molecule is separated into the purely atomic contribution and the interatomic molecular interference contribution. The total scattering intensity, $I(s)$, then can be written as

$$I(s) = I_A(s) + I_M(s). \tag{2-5}$$

The atomic scattering, $I_A(s)$, is a sum of elastic and inelastic components for each atom;

$$I_A(s) = \sum_i \left(f_i^2 + 4\frac{S_i}{a_0^2 s^4} \right), \tag{2-6}$$

where f_i and S_i are the elastic and the inelastic scattering amplitudes, respectively, for the *i*th nucleus, and a_0 is the Bohr radius. The f_i for a particular scattering center (atom) is derived using a simplified expression for a wave scattering from a spherical potential (the first Born approximation). The elastic scattering event may be thought of as

$\left\langle \varphi_m \middle| e^{i\vec{k_0}\cdot\vec{z}} \middle| \varphi_m \right\rangle$ since the no energy is transferred.[3] The f_i are proportional to s^{-2} and have a linear dependency on Z_i (see Fig. 2-2). The inelastic S_i factors take into account excitations of the electrons within each atom caused by the scattering event and are essentially a sum of cross terms of the form $\left\langle \varphi_m \middle| e^{i\vec{k_0}\cdot\vec{z}} \middle| \varphi_n \right\rangle$ to evaluate all possible transitions. Both elastic and inelastic scattering drop off sharply with increasing *s*, with inelastic events important at small scattering angles (see Fig. 2-3). Accurate theoretical values of scattering factors are calculated using the method of partial waves and are available in the literature.[4]

2.3 Molecular scattering

The other main contribution to the total scattered intensity (Eq. 2-5) is the molecular term, $I_M(s)$ – the interferences formed as coherent electron waves scatter off pairs of nuclei in a molecule. The spherical wave interference introduces weak sinusoidal oscillations into the diffraction signal (see Fig. 2-3). These oscillations are the familiar rings visible in a gas electron diffraction pattern. For an isotropic spatial distribution of molecules the diffraction pattern is radially symmetric about the center positions and $I_M(s)$ is defined as

$$I_M(s) = \sum_{i,j} f_i f_j \cos(\eta_i - \eta_j) \left\langle \frac{\sin(sr_{ij})}{sr_{ij}} \right\rangle_{vib}, \qquad (2\text{-}7)$$

where η_i is the phase factor for the *i*th nucleus, r_{ij} is the distance between *i*th and *j*th nuclei, and the bracket denotes an average over all vibrational motion of the nuclei. The η_i terms, added to the molecular scattering formula by the second Born approximation (see Ref. 2) take into account the non-zero phase shift of a wave scattered off two nuclei of different *Z*.[2] The difference, $\eta_i - \eta_j$, is essentially negligible except when the *Z* are very different (see Fig. 2-4). The integral average over all vibrational motion in Eq. (2-7) can be evaluated using the harmonic approximation, by which it becomes

$$I_M(s) = \sum_{i,j} f_i f_j \cos(\eta_i - \eta_j) \exp\left(-\tfrac{1}{2} l_h{}^2 s^2\right) \frac{\sin(s r_{a,ij})}{s r_{e,ij}}, \tag{2-8}$$

where $r_{e,ij}$ and $r_{a,ij}$ are the equilibrium and the effective internuclear distances between *i*th and *j*th nuclei, respectively, and l_h is the harmonic mean vibrational amplitude. The damping term models the reduction of signal when vibrations are intense. By expanding on the harmonic approximation to model the anharmonicity of a Morse potential, the effective distance can be expressed by

$$r_a = r_g - \frac{l_h{}^2}{r_e}, \tag{2-9}$$

$$r_g = r_e + \tfrac{3}{2} a l_h{}^2, \tag{2-10}$$

where a is the anharmonicity constant. r_g corresponds to the distance between centers of gravity at temperature *T*. Although there are some tabulated values for a,[5] it is often simply set at 2 for direct bonds and at 0 for non-bonded distances. r_a is the electron diffraction operational internuclear distance, which must be converted to r_e for comparison with other methods (distances reported in subsequent chapters are r_e values).

To visualize the molecular scattering intensity and emphasize the damped oscillatory behavior, the modified molecular scattering function, $sM(s)$, is created:

$$sM(s) = s\frac{I_M(s)}{f_I f_J}, \tag{2-11}$$

where f_I and f_J are atomic elastic scattering factors of two selected atoms (the scaling atoms). The $sM(s)$ is the standard form in which diffraction data are presented and on which the theoretical model is refined and molecular structures extracted. Chapter 4 will describe the process by which the $sM(s)$ and the molecular structures are obtained from the diffraction pattern.

2.4 The radial distribution curve

In the real space of diffraction data, the signal is represented by the sum of probabilities of two nuclei being separated by distance *r*. Plotted versus *r*, this is known as the radial distribution curve, $D(r)$, often used by diffractionists to show the molecular scattering in a more intuitive way. The conversion from $sM(s)$ in reciprocal space to the $D(r)$ in real space is made through sine transform:

$$D(r) = \int_0^\infty sM(s)\sin(sr)ds \tag{2-12}$$

However, due to the finite *s* range of data detectors, the integral to infinity is not possible and $f(r)$, a modified radial distribution, is needed. In order to account for this cut-off of signal and to stem the spurious ringing that it introduces, a Gaussian window function, $\exp\left(-ks^2\right)$, is included and the integral performed to $s_{\max}$.

$$\begin{aligned}
f(r) &\approx D(r) \\
f(r) &= \int_0^{s_{\max}} sM(s)\sin(sr)\exp\left(-ks^2\right)ds \\
&\approx \sum^{s_{\max}} sM(s)\sin(sr)\exp\left(-ks^2\right)\Delta s,
\end{aligned} \tag{2-13}$$

Typically, k = 0.005 Å^2 in UED. In addition to the cut-off of the data at high *s*, there is also a cut-off at low *s* where the signal from multiple scattering and inelastic effects is greatest – the region of breakdown of the IAM and often the region covered by a beam stop in electron diffraction experiments. Here, a piece of theoretically derived $sM(s)$ is appended such that the integration is continuous from 0.

It is to be noted that for a pair of nuclei *i* and *j*, the area under its corresponding peak in the $f(r)$ is proportional to $\frac{n_{ij}Z_iZ_j}{r_{ij}}$ where n_{ij} is the multiplicity of the distance r_{ij} in the molecule. This can be seen by combining Eqs. (2-8), (2-11), and (2-13) and performing the integration.

$$\begin{aligned}
f(r) &\approx \int_0^{\infty} \frac{s}{f_I f_J}\sum\nolimits_{i,j} f_i f_j \cos(\Delta\eta_{ij})\exp(-\tfrac{1}{2}l_{ij}{}^2 s^2)\frac{\sin(sr_{aij})}{sr_{eij}}\sin(sr)\exp\left(-ks^2\right)ds \\
&= \sum_{i,j}\frac{1}{r_{eij}}\int_0^{\infty}\left[\frac{f_i f_j}{f_I f_J}\cos(\Delta\eta_{ij})\right]\exp[-\tfrac{1}{2}s^2(l_{ij}{}^2+2k)]\sin(sr_{aij})\sin(sr)ds \\
&\approx \sum_{i,j}\frac{1}{r_{eij}}\int_0^{\infty}\left[\frac{Z_iZ_j}{Z_IZ_J}\right]\exp[-\tfrac{1}{2}s^2(l_{ij}{}^2+2k)]\sin(sr_{aij})\sin(sr)ds \\
&= \sum_{i,j}\frac{1}{r_{eij}}\left[\frac{Z_iZ_j}{Z_IZ_J}\right]\left\{\sqrt{\frac{\pi}{8(2k+l_{ij}{}^2)}}\exp\left[-\frac{(r-r_{aij})^2}{2(2k+l_{ij}{}^2)}\right]\right\} \\
&\propto \sum_{i,j}\frac{Z_iZ_j}{r_{e,ij}}\exp\left[-\frac{(r-r_{a,ij})^2}{2(2k+l_{ij}{}^2)}\right],
\end{aligned} \tag{2-14}$$

where the Gaussian function contains the convolution of both the *k*-damping and *l*-

vibrational amplitude.

It is to be noted that although the above treatment is for an isotropic distribution, it has been shown elsewhere[6] that orientational effects in diffraction can be quantitatively expressed.

2.5 References

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[3] R. A. Bonham and M. Fink, *High Energy Electron Scattering*. (Van Nostrand Reinhold Co., New York, 1974); G. F. Drukarev, *Collisions of Electrons with Atoms and Molecules*. (Plenum, New York, 1987).

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