

# Appendix A

## Using Rotational Averaging to Calculate the Response of Isotropic and Anisotropic Samples

For submission to:

*J. Chem. Ed.*

*'I have been spinning around and around the wheel like a squirrel. It is so dark I can't tell which way she is swinging till she is coming around like a whirligig.'*

— Mark Twain

*Life on the Mississippi*

### Abstract

Since most physical chemistry experiments use bulk samples, it is often necessary to calculate experimental responses from molecular parameters, summed over a range of molecular orientations. This paper explains the method of rotational averaging for both isotropically oriented samples and partially oriented samples. Its use is demonstrated with several examples, including calculations of the energy of molecules in an electric field and absorption and fluorescence spectroscopy. A table of commonly used averages allows the method to be generalized to more complex experiments.

### Introduction

Part of the art of experimental chemistry is in determining the behavior of individual molecules from measurements of bulk samples. Conversely, it is often desirable to know how a bulk sample will behave, given a known set of parameters for individual molecules. In both cases, we need to be able to add up individual molecule responses in an experimental situation to derive the bulk response, an ensemble sum which may also be expressed as an average over orientations for a single molecule. Rotational averaging is commonly used for single- or multi-photon spectroscopy<sup>1</sup>, where the latter includes fluorescence<sup>2</sup>, Raman<sup>3</sup>, photoselection<sup>4</sup>, dichroism<sup>5</sup>, pump-probe, and other conventional and laser spectroscopy methods. It is also useful for Stark effect spectroscopy<sup>6-8</sup> and, potentially, for a wide range of other physical chemistry experiments using isotropic or partially oriented samples. Despite its utility, rotational averaging is rarely discussed in textbooks.

This paper explains the math behind rotational averaging by means of several examples, including calculations of the energy of molecules in electric fields and quantitative absorption and fluorescence intensities. In the process, most of the commonly used equations for rotational averaging are derived and it is shown how to derive others using the equations given in Table 1. The method presented here follows notation used in Mathies's doctoral thesis<sup>6</sup>, which he likely borrowed from elsewhere,

but its origin is not known to the author. The math can be carried out in a much more general manner<sup>9,10</sup>, but the results are complicated and rarely required.

### Definitions of Terms

Following the normal convention,  $X$ ,  $Y$ , and  $Z$  are the Cartesian axes in the lab reference frame, used for defining orientations of polarizers, molecular beams, and other lab apparatus. For a molecule, the Cartesian axes are  $x$ ,  $y$ , and  $z$ , which are used for dipole moments, polarizabilities, transition dipoles, symmetry axes, and other molecular properties. The molecule's orientation is given with Euler angles,  $\alpha$ ,  $\beta$ , and  $\gamma$ , where these angles express the rotation of the molecular axes with respect to the lab coordinate system<sup>2,11</sup>.  $\beta$  and  $\gamma$  are the familiar angles from spherical coordinates, giving the direction of the molecule's  $z$  axis in the lab frame:  $\beta$  is the angle between  $Z$  and  $z$ , and  $\gamma$  is the angle between  $X$  and the projection of  $z$  on the  $XY$  plane.  $\alpha$  is an azimuthal angle that expresses the rotation of the molecule about its  $z$  axis.

In a bulk sample, the fraction of molecules with orientations within  $d\alpha$ ,  $d\beta$ , and  $d\gamma$  of the exact orientation  $\alpha$ ,  $\beta$ , and  $\gamma$  is given by  $\rho(\alpha, \beta, \gamma) \sin\beta d\alpha d\beta d\gamma$ ;  $\rho(\alpha, \beta, \gamma)$  is the orientational density and the rest of the expression is a differential element. Since  $\rho(\alpha, \beta, \gamma)$  represents a fraction of the sample, it is non-negative for all values of  $\alpha$ ,  $\beta$ , and  $\gamma$ , and it integrates to 1. For an isotropic sample, which is covered in depth in the next section,  $\rho(\alpha, \beta, \gamma)$  is a constant and is found to be equal to  $(8\pi^2)^{-1}$ . When a molecule interacts with the experimental system, the result (*e.g.* an absorption cross-section) depends upon the molecule's orientation and is given by  $f(\alpha, \beta, \gamma)$ . The bulk response is the average value of  $f(\alpha, \beta, \gamma)$ , properly weighted with the orientational density, and is

$$\text{average value} = 8\pi^2 \langle f(\alpha, \beta, \gamma) \rho(\alpha, \beta, \gamma) \rangle. \quad (1)$$

The brackets indicate an average over the ensemble of molecules. The factor of  $8\pi^2$  accounts for the total "volume" of possible Euler angles and is present because of the way the brackets are normalized: defining  $g(\alpha, \beta, \gamma)$  as an arbitrary function of Euler angles, the brackets are defined by

$$\langle g(\alpha, \beta, \gamma) \rangle = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} g(\alpha, \beta, \gamma) \sin\beta d\alpha d\beta d\gamma. \quad (2)$$

This definition is normalized so that  $\langle f \rangle = 1$ , which is easily confirmed. The constraint that  $\langle f(\theta, \phi, \chi) \rangle$  integrates to 1 can be restated using the bracket notation as  $\langle f(\theta, \phi, \chi) \rangle = (8\pi^2)^{-1}$ . From these equations, rotational averaging is seen to be a linear operation yielding, for example,

$$\langle c_1 g_1(\theta, \phi, \chi) + c_2 g_2(\theta, \phi, \chi) \rangle = c_1 \langle g_1(\theta, \phi, \chi) \rangle + c_2 \langle g_2(\theta, \phi, \chi) \rangle. \quad (3)$$

In principle, all rotational averaging can be carried out with a suitable choice of  $\langle f(\theta, \phi, \chi) \rangle$ ,  $f(\theta, \phi, \chi)$ , and eqs. 1, 2, and 3. However, the problem is vastly simplified by solving it for the general case, which can then be applied to a wide range of standard problems.

### Isotropic Averages

For the case of an isotropically oriented sample,  $\langle f(\theta, \phi, \chi) \rangle$  is independent of  $\theta$ ,  $\phi$ , and  $\chi$ , and is equal to the constant  $(8\pi^2)^{-1}$ , allowing eq. 1 to be simplified to

$$\text{average value} = \langle f \rangle. \quad (4)$$

**Energy of immobilized dipoles in a field.** Suppose we want to calculate the energy of a sample of molecules in a uniform electric field, where each molecule has a dipole moment  $\mathbf{p}$  and is immobilized so it cannot rotate (such as molecules suspended in a polymer matrix). This dipole moment is expressed in the molecule coordinate system; in the lab coordinate system, the same dipole moment vector is given as  $\mathbf{p}_L$ . The two representations are related by a coordinate transformation using the direction cosine matrix,  $\mathbf{L}$ , where  $\mathbf{p}_L = \mathbf{p} \mathbf{L}$ . In terms of the Euler angles that define the relative rotation of the two coordinate systems, the direction cosine matrix is<sup>2</sup>

$$\mathbf{L} = \begin{pmatrix} c\alpha c\beta c\gamma - s\alpha s\beta c\gamma & s\alpha c\beta c\gamma + c\alpha s\beta c\gamma & s\alpha s\beta c\gamma \\ c\alpha c\beta s\gamma + s\alpha s\beta s\gamma & s\alpha c\beta s\gamma - c\alpha s\beta s\gamma & s\alpha s\beta s\gamma \\ c\alpha s\beta & s\alpha s\beta & c\beta \end{pmatrix} = \begin{pmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{pmatrix}. \quad (5)$$

In the matrix, c is used for cosine and s is used for sine. The  $l_i^j$  coefficients, using  $i$  as an index for x, y, or z, are nothing more than a convenient shorthand notation for elements of the  $\mathbf{L}$  matrix. Thus, each  $l_i^j$  term is a function of  $\alpha$ ,  $\beta$  and  $\gamma$ . As  $\mathbf{L}$  is a real unitary matrix,  $\mathbf{L}^T \mathbf{L}$  is the identity matrix ( $^T$  denotes the matrix transpose).

The electric field,  $\mathbf{E}$ , is in a fixed direction for the entire sample. For convenience, the lab coordinate system is defined so that  $\mathbf{E}$  is parallel to the  $Z$  axis, allowing it to be written as the scalar  $E$  times a unit vector on the  $Z$  axis,  $\mathbf{Z}$ . The average energy from electric field interactions is<sup>12</sup>

$$U_{\text{av.}} = \langle \mathbf{p}_L \cdot \mathbf{E} \rangle = E \langle \mathbf{p}_L \cdot \mathbf{Z} \rangle. \quad (6)$$

The brackets are solved using the shorthand form of eq. 5,

$$\langle \mathbf{p}_L \cdot \mathbf{Z} \rangle = \langle \mathbf{p} \cdot \mathbf{Z} \rangle = \langle p_x l_x + p_y l_y + p_z l_z \rangle = p_i \langle l_i \rangle = 0. \quad (7)$$

The second to last equality uses the Einstein summation convention, in which summation is implied over all repeated indices. The final equality follows by either direct integration of the relevant  $\square$  coefficients using eqs. 2 and 5, by an analysis of their symmetry, or by looking up the result in Table 1. It is seen that the total energy of randomly oriented dipoles in a uniform field is zero (which could have been deduced from symmetry).

**Absorption of light.** Molecules absorb light by the interaction of electronic fluctuations in the molecule, along the transition dipole moment  $\mathbf{m}$ , with the oscillating electric field of a light wave<sup>13</sup>, which is in the direction  $\hat{\mathbf{e}}$ . The molar extinction coefficient for a single molecule, integrated over an electronic transition, is<sup>11,14</sup>

$$\int \epsilon(\omega) d\omega = \frac{2\pi^2 N_A \epsilon_0}{hc \ln 10} (\hat{\mathbf{e}} \cdot \mathbf{m})^2. \quad (8)$$

It can be seen that absorption is maximal for molecules oriented with  $\mathbf{m}$  parallel to  $\hat{\mathbf{e}}$ , and is zero for those with  $\mathbf{m}$  perpendicular to  $\hat{\mathbf{e}}$ . For a bulk sample, the vector product needs to be averaged over all molecular orientations, as before. However, since the vector product is squared before averaging, the result will be non-zero this time. Orienting the  $Z$  axis to be parallel to the light polarization, the required rotational average is

$$\begin{aligned} \langle (\mathbf{m}_L \cdot \mathbf{Z})^2 \rangle &= \langle (\mathbf{m} \cdot \mathbf{Z})^2 \rangle = \langle (m_x l_x + m_y l_y + m_z l_z)^2 \rangle = \langle (m_i l_i)^2 \rangle = m_i m_j \langle l_i l_j \rangle \\ &= m_i m_j \frac{\langle l_i^2 \rangle}{3} = \frac{m_i m_i}{3} = \frac{|\mathbf{m}|^2}{3}. \end{aligned} \quad (9)$$

As before, the  $\langle l_i l_j \rangle$  factor can be solved by integration of the sines and cosines in eq. 5 or the solution can be looked up in Table 1. The result shows that an isotropic bulk sample absorbs 1/3 as much light as a sample of molecules that are aligned parallel to the light polarization.

**Fluorescence.** Fluorescence is a two photon process in which a molecule absorbs incident light with its absorption transition dipole,  $\mathbf{m}_a$ , and subsequently emits a photon from the transition dipole,  $\mathbf{m}_e$ . To determine the angle between the two transition dipoles,  $\square$  an experiment excites an isotropic sample with light polarized along  $\mathbf{Z}$  and detects emitted light using a polarizer which transmits light polarized along  $\hat{\mathbf{e}}$ . The lab frame is defined so  $\hat{\mathbf{e}}$  is in the  $X$ - $Z$  plane at angle  $\square$  away from  $Z$ . The absolute fluorescence intensity is essentially just eq. 8 written twice, once for absorption and once for emission, with the product multiplied by the fluorescence quantum yield. The rotational average part of the equation is

$$\begin{aligned} \langle (\mathbf{m}_{e,L} \cdot \hat{\mathbf{e}})^2 (\mathbf{m}_{a,L} \cdot \mathbf{Z})^2 \rangle &= \langle [\mathbf{m}_{e,L} \cdot (\mathbf{Z} \cos \square + \mathbf{X} \sin \square)]^2 (\mathbf{m}_{a,L} \cdot \mathbf{Z})^2 \rangle \\ &= \langle (\mathbf{m}_{e,L} \cdot \mathbf{Z})^2 (\mathbf{m}_{a,L} \cdot \mathbf{Z})^2 \rangle \cos^2 \square + \langle (\mathbf{m}_{e,L} \cdot \mathbf{X}) (\mathbf{m}_{e,L} \cdot \mathbf{Z}) (\mathbf{m}_{a,L} \cdot \mathbf{Z})^2 \rangle \cos \square \sin \square \\ &\quad + \langle (\mathbf{m}_{e,L} \cdot \mathbf{X})^2 (\mathbf{m}_{a,L} \cdot \mathbf{Z})^2 \rangle \sin^2 \square \end{aligned} \quad (10)$$

The three averages are solved independently, using slightly simplified notation and the results in Table 1:

$$\langle (\mathbf{r}_L \cdot \mathbf{Z})^2 (\mathbf{s}_L \cdot \mathbf{Z})^2 \rangle = r_i r_j s_k s_l \langle l_i l_j l_k l_l \rangle = \frac{|\mathbf{r}|^2 |\mathbf{s}|^2 + 2(\mathbf{r} \cdot \mathbf{s})^2}{15} \quad (11)$$

$$\langle (\mathbf{r}_L \cdot \mathbf{X}) (\mathbf{r}_L \cdot \mathbf{Z}) (\mathbf{s}_L \cdot \mathbf{Z})^2 \rangle = r_i r_j s_k s_l \langle l_i l_j l_k l_l \rangle = 0 \quad (12)$$

$$\langle (\mathbf{r}_L \cdot \mathbf{X})^2 (\mathbf{s}_L \cdot \mathbf{Z})^2 \rangle = r_i r_j s_k s_l \langle l_i l_j l_k l_l \rangle = \frac{2|\mathbf{r}|^2 |\mathbf{s}|^2 \square (\mathbf{r} \cdot \mathbf{s})^2}{15}. \quad (13)$$

The cross-term in eq. 10 drops out, leaving terms for the fluorescence intensity parallel,  $I_{\parallel}$  (eq. 11), and perpendicular,  $I_{\perp}$  (eq. 13), to the excitation. Using  $A$  as a proportionality constant, the fluorescence intensity is

$$I = A \frac{|\mathbf{m}_e|^2 |\mathbf{m}_a|^2 + 2(\mathbf{m}_e \cdot \mathbf{m}_a)^2}{15} \cos^2 \theta + A \frac{2|\mathbf{m}_e|^2 |\mathbf{m}_a|^2 - (\mathbf{m}_e \cdot \mathbf{m}_a)^2}{15} \sin^2 \theta. \quad (14)$$

This result can be simplified by confining the  $\theta$  dependence to only one of the terms using the trigonometric identity

$$I_{\parallel} \cos^2 \theta + I_{\perp} \sin^2 \theta = \frac{I_{\parallel} + 2I_{\perp}}{3} + \frac{I_{\parallel} - I_{\perp}}{3} (3 \cos^2 \theta - 1). \quad (15)$$

This, along with the replacement of dot products with  $\cos \theta$  terms, simplifies eq. 14 to yield

$$I = A \frac{|\mathbf{m}_e|^2 |\mathbf{m}_a|^2}{9} + A \frac{|\mathbf{m}_e|^2 |\mathbf{m}_a|^2 (3 \cos^2 \theta - 1)}{45} (3 \cos^2 \theta - 1). \quad (16)$$

The fluorescence anisotropy is defined as  $(I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$  and is found to be equal to  $(3 \cos^2 \theta - 1) / 5$ , allowing a measurement of the internal angle  $\theta$  from parallel and perpendicular fluorescence intensities.

Rather than re-arranging the result after rotational averaging, as was done using eq. 15, it is generally more convenient to do so beforehand. In that case, averages such as  $\langle (l_i l_j + 2l_i' l_j') / 3 \rangle$  and  $\langle (l_i l_j - l_i' l_j') / 3 \rangle$  are needed for the respective terms. These averages are quite simple and are given in Table 1, along with the others.

**Energy of polarizable molecules in a field.** Molecular polarizabilities are matrix quantities that give rise to induced dipole moments when a molecule is in an electric field, as well as Raman scattering and multi-photon absorption. Rotational averages with matrices are similar to the previous examples.  $\alpha$  is taken as a molecule's polarizability matrix and  $\alpha_L$  is the same matrix expressed in the lab coordinate system, terms which are related with the coordinate transformation  $\alpha_L = \alpha \mathbf{Q} \mathbf{Q}^T$ . As in the first example, the sample is assumed to be immobilized and there is a static electric field along the Z axis. The average energy is<sup>12</sup>

$$U_{av} = \frac{1}{2} \langle \mathbf{E} \alpha_L \mathbf{E} \rangle = \frac{|\mathbf{E}|^2}{2} \langle \mathbf{Z} \alpha_L \mathbf{Z} \rangle. \quad (15)$$

The rotational average is

$$\langle \mathbf{Z} \square_{\perp} \mathbf{Z} \rangle = \langle \mathbf{Z} \square^T \square \mathbf{Z} \rangle = \square_{ij} \langle I_i I_j \rangle = \frac{\square_{ij} \square_{ij}}{3} = \frac{\text{Tr} \square}{3}, \quad (16)$$

where the notation ‘‘Tr’’ denotes the trace of a matrix. Thus, the energy decreases with increasing polarizability and is proportional to the sum of the polarizability eigenvalues. Higher rank tensors, such as hyperpolarizabilities, are averaged in an analogous manner to the examples shown for vectors and matrices.

### Anisotropic Averages

Many samples are at least partially oriented, which may arise from photoselection, external electric fields, flow gradients, or other sources. As described above, orientational information is given with the orientational density  $\square(\square, \square, \square)$ , where the only constraints are that it integrates to 1 and is positive everywhere. A useful method is to expand  $\square(\square, \square, \square)$  in terms of the elements of the direction cosine matrix, which then combine easily with the rotational averaging analysis.

**Energy of mobile dipoles in an electric field.** A previous example showed that an electric field does not affect the total energy of isotropically oriented immobilized dipoles. This example considers a similar experiment except that the dipoles are mobile this time, as in a gas or liquid, so they will become partially oriented in a field. As before, the lab frame axes are defined so the electric field is  $E\mathbf{Z}$  and dipole moments in the molecule frame are  $\mathbf{p}$ . The equilibrium orientational density is given by the Boltzmann distribution, where  $\square$  is the Boltzmann factor ( $1/k_B T$ ),

$$\square(\square, \square, \square) \propto \exp(-\square U) = \exp(\square \mathbf{p}_{\perp} \cdot \mathbf{E}) \square 1 + \square E \mathbf{p}_{\perp} \cdot \mathbf{Z}, \quad (17)$$

which is normalized to give

$$\square(\square, \square, \square) \square \frac{1}{8\square^2} (1 + \square E \mathbf{p}_{\perp} \cdot \mathbf{Z}). \quad (18)$$

Using this density, the average  $Z$  component of  $\mathbf{p}$  is non-zero:

$$8\square^2 \langle (\mathbf{p}_{\perp} \cdot \mathbf{Z}) \square \rangle = \langle (\mathbf{p}_{\perp} \cdot \mathbf{Z}) (1 + \square E \mathbf{p}_{\perp} \cdot \mathbf{Z}) \rangle = p_i \langle I_i \rangle + \square E p_i p_j \langle I_i I_j \rangle = \square E \frac{|\mathbf{p}|^2}{3}. \quad (19)$$

Combining this result with eq. 6 yields the average energy of this system, which is  $-\square E^2 |\mathbf{p}|^2 / 3$ . In the infinite temperature limit, the sample approaches isotropy and the

average energy goes to zero, in agreement with eq. 7. The low temperature limit cannot be evaluated with this expression because of the approximation made in eq. 17, although lower temperatures can be evaluated by including more terms in eq. 17.

### **Conclusions**

Rotational averaging is an essential element to a great deal of physical chemistry. While the averaging can be considered separately for each experiment, it is generally preferable to separate this portion of the math from the rest of the analysis. This paper shows that rotational averaging is not difficult and is readily extendable to more complex experiments. Many of the vector and matrix averages presented here are directly useful elsewhere and many more can be easily derived from Table 1.

**Table 1. Useful direction cosine averages**

Note that  $n!! = n(n-2)(n-4)\dots(2 \text{ or } 1)$ .

$$\langle l_i \rangle = \langle l_i l_j l_k \rangle = \langle l_i l_j l_k l_l l_m \rangle = \dots = 0$$

$$\langle 1 \rangle = 1$$

$$\langle l_i l_j \rangle = \frac{\delta_{ij}}{3}$$

$$\langle l_i l_j l_k l_l \rangle = \frac{\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}}{3 \cdot 5}$$

$$\langle l_i l_j l_k l_l l_m l_n \rangle = \frac{\delta_{ij}\delta_{kl}\delta_{mn} + \delta_{ij}\delta_{km}\delta_{ln} + \dots}{3 \cdot 5 \cdot 7} \quad \text{15 terms}$$

$$\langle l_{i_1} l_{i_2} \dots l_{i_n} \rangle = \frac{\delta_{i_1 i_2} \delta_{i_3 i_4} \dots \delta_{i_{n-1} i_n} + \dots}{(n+1)!!} \quad \begin{matrix} n \text{ odd} \\ n \text{ even} \end{matrix} \quad (n-1)!! \text{ terms}$$

$$\langle l_{[ij]} \rangle = \langle l_{[ij]} l_k \rangle = \langle l_{[ij]} l_k l_l \rangle = \dots = 0$$

$$\langle l_{[ij]} l_k l_l \rangle = \frac{4\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}}{2 \cdot 3 \cdot 5}$$

$$\langle l_{[ij]} l_k l_l l_m l_n \rangle = \frac{6\delta_{ij}\delta_{kl}\delta_{mn} + 6\delta_{ij}\delta_{km}\delta_{ln} + 6\delta_{ij}\delta_{kn}\delta_{lm} - \delta_{ik}\delta_{jl}\delta_{mn} - \dots}{2 \cdot 3 \cdot 5 \cdot 7} \quad \text{15 terms}$$

$$\langle l_{[ij]} l_{[kl]} l_{i_3} l_{i_4} \dots l_{i_n} \rangle = \frac{\delta_{i_1 i_2} \langle l_{i_3} l_{i_4} \dots l_{i_n} \rangle - \delta_{i_1 i_2} \langle l_{i_3} l_{i_4} \dots l_{i_n} \rangle}{2} \quad \begin{matrix} n \text{ odd} \\ n \text{ even} \end{matrix}$$

$$\left\langle \frac{l_{i_1} l_{i_2} + 2l_{[ij]} l_{i_3} l_{i_4} \dots l_{i_n}}{3} \right\rangle = \frac{\delta_{i_1 i_2} \langle l_{i_3} l_{i_4} \dots l_{i_n} \rangle}{3}$$

$$\left\langle \frac{l_{i_1} l_{i_2} - l_{[ij]} l_{i_3} l_{i_4} \dots l_{i_n}}{3} \right\rangle = \frac{\langle l_{i_3} l_{i_4} \dots l_{i_n} \rangle}{2} - \frac{\delta_{i_1 i_2} \langle l_{i_3} l_{i_4} \dots l_{i_n} \rangle}{6}$$

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