14.4: The "Long-Wavelength" Approximation

To make progress in further analyzing the first-order results obtained above, it is useful to consider the wavelength λ of the light used in most visible/ultraviolet, infrared, or microwave spectroscopic experiments. Even the shortest such wavelengths (ultraviolet) are considerably longer than the spatial extent of all, but the largest molecules (i.e., polymers and biomolecules for which the approximations we introduce next are not appropriate).

In the definition of the essential coupling matrix element $\alpha_{f,i}$

$$\alpha_{f,i} = \langle \Phi_f | \sum_j \left(\frac{e}{m_e c} \right) e^{-i\mathbf{k}\cdot\mathbf{r}_j} \mathbf{A}_0 \cdot \nabla_j + \sum_a \left(\frac{Z_a e}{m_a c} \right) e^{-i\mathbf{k}\cdot\mathbf{R}_a} \mathbf{A}_0 \cdot \nabla_a | \Phi_i \rangle,$$

the factors $e^{-i\mathbf{k}\cdot\mathbf{r}_j}$ and $e^{-i\mathbf{k}\cdot\mathbf{R}_a}$ can be expanded as:

$$e^{-i\mathbf{k}\cdot\mathbf{r}_j} = 1 + (-i\mathbf{k}\cdot\mathbf{r}_j) + \frac{1}{2}(-i\mathbf{k}\cdot\mathbf{r}_j)^2 + \ldots$$

$$e^{-i\mathbf{k}\cdot\mathbf{R}_a} = 1 + (-i\mathbf{k}\cdot\mathbf{R}_a) + \frac{1}{2}(-i\mathbf{k}\cdot\mathbf{R}_a)^2 + \ldots$$

Because $|\mathbf{k}| = 2\pi/\lambda$, and the scales of $\mathbf{r}_j$ and $\mathbf{R}_a$ are of the dimension of the molecule, $\mathbf{k}\cdot\mathbf{r}_j$ and $\mathbf{k}\cdot\mathbf{R}_a$ are less than unity in magnitude, within this so-called "long-wavelength" approximation.

Electric Dipole Transitions

Introducing these expansions into the expression for af,i gives rise to terms of various powers in $1/\lambda$. The lowest order terms are:

$$\alpha_{f,i}(E1) = \langle \Phi_f | \sum_j \left(\frac{e}{m_e c} \right) \mathbf{A}_0 \cdot \nabla_j + \sum_a \left(\frac{Z_a e}{m_a c} \right) \mathbf{A}_0 \cdot \nabla_a | \Phi_i \rangle$$

and are called "electric dipole" terms, and are denoted E1. To see why these matrix elements are termed E1, we use the following identity (see Chapter 1) between the momentum operator $-i\hbar\nabla$ and the corresponding position operator $\mathbf{r}$:

$$\nabla_j = -\left(\frac{m_e}{\hbar^2} \right) [H, \mathbf{r}_j]$$

$$\nabla_a = -\left(\frac{m_a}{\hbar^2} \right) [H, \mathbf{R}_a]$$

This derives from the fact that H contains ∇_j and ∇_a in its kinetic energy operators (as ∇_a^2 and ∇_j^2). Substituting these expressions into the above $\alpha_{f,i}(E1)$ equation and using $\mathrm{H}\Phi_{\mathrm{i\,or\,f}} = E^0_{\mathrm{i\,or\,f}}\Phi_{\mathrm{i\,or\,f}}$, one obtains:

$$\alpha_{f,i}(E1) = (E_f^0 - E_i^0)\mathbf{A}_0 \cdot \langle \Phi_f | \sum_j \left(\frac{e}{\hbar^2 c} \right) \mathbf{r}_j + \sum_a \left(\frac{Z_a e}{\hbar^2 c} \mathbf{R}_a | \Phi_i \rangle \right)$$

$$= \omega_{f,i} \mathbf{A}_0 \cdot \langle \Phi_f | \sum_j \left(\frac{e}{\hbar c} \right) \mathbf{r}_j + \sum_a \left(\frac{Z_a e}{\hbar c} \right) \mathbf{R}_a | \Phi_i \rangle$$

$$= \left(\frac{\omega_{f,i}}{\hbar c} \right) \mathbf{A}_0 \cdot \langle \Phi_f | \mu | \Phi_i \rangle,$$

where μ is the electric dipole moment operator for the electrons and nuclei:

$$\mu = \sum_j e\mathbf{r}_j + \sum_a Z_a e \mathbf{R}_a.$$

The fact that the E1 approximation to $\alpha_{f,i}$ contains matrix elements of the electric dipole operator between the initial and final states makes it clear why this is called the **electric dipole contribution** to $\alpha_{f,i}$; within the E1 notation, the E stands for electric moment and the 1 stands for the first such moment (i.e., the dipole moment).

Within this approximation, the overall rate of transitions is given by:

$$R_{i,f} = 2\pi g(\omega_{f,i}) |\alpha_{f,i}|^2$$

$$2\pi g(\omega_{f,i})\left(\frac{\omega_{f,i}}{\hbar c}\right)^2 |\mathbf{A}_0 \cdot \langle \Phi_f|\mu|\Phi_i\rangle|^2.$$

Recalling that $\mathbf{E}(\mathbf{r},t) = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = \frac{\omega}{c}\mathbf{A}_0 \sin(\omega t - \mathbf{k}\cdot\mathbf{r})$,

the magnitude of $\mathbf{A}_0$ can be replaced by that of $\mathbf{E}$, and this rate expression becomes

$$R_{i,f} = \left(\frac{2\pi}{\hbar^2}\right) g(\omega_{f,i}) |\mathbf{E}_0 \cdot \langle \Phi_f|\mu|\Phi_i\rangle|^2.$$

This expresses the widely used E1 approximation to the Fermi-Wentzel golden rule.

Magnetic Dipole and Electric Quadrupole Transitions

When E1 predictions for the rates of transitions between states vanish (e.g., for symmetry reasons as discussed below), it is essential to examine higher order contributions to $\alpha_{f,i}$. The next terms in the above long-wavelength expansion vary as $\frac{1}{\lambda}$ and have the form:

$$\alpha_{f,i}(E2+M1) = \langle \Phi_f| \sum_j \left(\frac{e}{m_e c}\right)[-i\mathbf{k}\cdot\mathbf{r}_j]\mathbf{A}_0\cdot\nabla_j + \sum_a \left(\frac{Z_a e}{m_a c}\right)[-i\mathbf{k}\cdot\mathbf{R}_a]\mathbf{A}_0\cdot\nabla_a|\Phi_i\rangle.$$

For reasons soon to be shown, they are called electric quadrupole (E2) and magnetic dipole (M1) terms. Clearly, higher and higher order terms can be so generated. Within the longwavelength regime, however, successive terms should decrease in magnitude because of the successively higher powers of $\frac{1}{\lambda}$ that they contain.

To further analyze the above E2 + M1 factors, let us label the propagation direction of the light as the z-axis (the axis along which **k** lies) and the direction of $\mathbf{A}_0$ as the x-axis. These axes are so-called "lab-fixed" axes because their orientation is determined by the direction of the light source and the direction of polarization of the light source's **E** field, both of which are specified by laboratory conditions. The molecule being subjected to this light can be oriented at arbitrary angles relative to these lab axes. With the x, y, and z axes so defined, the above expression for $\alpha_{f,i}$ (E2+M1) becomes

$$\alpha_{f,i}(E2+M1) = -i\left(\frac{A_0 2\pi}{\lambda}\right)\langle \Phi_f| \sum_j \left(\frac{e}{m_e c}\right) z_j \frac{\partial}{\partial x_j} + \sum_a \left(\frac{Z_a e}{m_a c}\right) z_a \frac{\partial}{\partial x_a}|\Phi_i\rangle.$$

Now writing (for both z_j and z_a)

$$z\frac{\partial}{\partial x} = \frac{1}{2}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} + z\frac{\partial}{\partial x} + x\frac{\partial}{\partial z}\right),$$

and using

$$\nabla_j = -\left(\frac{m_e}{\hbar^2}\right)[H, \mathbf{r}_j]$$

$$\nabla_a = -\left(\frac{m_a}{\hbar^2}\right)[H, \mathbf{R}_a],$$

the contributions of $\frac{1}{2}\left(z\frac{\partial}{\partial x} + x\frac{\partial}{\partial z}\right)$ (E2+M1) can be rewritten as

$$\alpha_{f,i}(E2) = -i\frac{(A_0 e 2\pi\omega_{f,i})}{c\lambda\hbar}\langle \Phi_f| \sum_j z_j x_j + \sum_a Z_a z_a x_a|\Phi_i\rangle.$$

The operator $\sum_i z_i x_j + \sum_a Z_a z_a x_a$ that appears above is the z,x element of the electric quadrupole moment operator $Q_{z,x}$; it is for this reason that this particular component is labeled E2 and denoted the electric quadrupole contribution.

The remaining $\frac{1}{2}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ contribution to $\alpha_{f,i}$ (E2+M1) can be rewritten in a form that makes its content more clear by first noting that

$$\frac{1}{2}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = \left(\frac{i}{2\hbar}\right)(zp_x - xp_z) = \left(\frac{i}{2\hbar}\right)L_y$$

contains the y-component of the angular momentum operator. Hence, the following contribution to $\alpha_{f,i}$ (E2+M1) arises:

$$\alpha_{f,i}(MI) = \frac{A_0 2\pi e}{2\lambda c\hbar}\langle\Phi_f|\sum_j \frac{L_{y_j}}{m_e} + \sum_a Z_a \frac{L_{y_a}}{m_a}|\Phi_i\rangle.$$

The magnetic dipole moment of the electrons about the y axis is

$$\mu_{\text{y, electrons}} = \sum_j \left(\frac{e}{2m_e c}\right) L_{y_j};$$

that of the nuclei is

$$\mu_{\text{y, nuclei}} = \sum_a \left(\frac{Z_a e}{2m_a c}\right) L_{y_a}.$$

The $\alpha_{f,i}$ (M1) term thus describes the interaction of the magnetic dipole moments of the electrons and nuclei with the magnetic field (of strength |H| = A_0 k) of the light (which lies along the y axis):

$$\alpha_{f,i}(M1) = \frac{|H|}{\hbar}\langle\Phi_f|\mu_{\text{y, electrons}} + \mu_{\text{y, nuclei}}|\Phi_i\rangle.$$

The total rate of transitions from Φ_i to Φ_f is given, through first-order in perturbation theory, by

$$R_{i,f} = 2\pi g(\omega_{f,i})|\alpha_{f,i}|^2,$$

where $\alpha_{f,i}$ is a sum of its E1, E2, M1, etc. pieces. In the next chapter, molecular symmetry will be shown to be of use in analyzing these various pieces. It should be kept in mind that the contributions caused by E1 terms will dominate, within the long-wavelength approximation, unless symmetry causes these terms to vanish. It is primarily under such circumstances that consideration of M1 and E2 transitions is needed.
