4.5: The Transition Dipole Moment and Spectroscopic Selection Rules

Once we know what energy a given transition would have, we can ask, "Which transitions between energy levels or states are possible?" In answering this question, we also will learn why the longer cyanine dye molecules have stronger absorptions, or larger absorption coefficients.

Clearly the transitions cannot violate the Pauli Exclusion Principle; that is, they cannot produce an electron configuration with three electrons in the same orbital. Besides the Pauli Exclusion Principle, there are additional restrictions that result from the nature of the interaction between electromagnetic radiation and matter. These restrictions are summarized by spectroscopic selection rules. These rules tell whether or not a transition from one state to another state is possible.

To obtain these selection rules, we consider light as consisting of perpendicular oscillating electric and magnetic fields. The magnetic field interacts with magnetic moments and causes transitions seen in electron spin resonance and nuclear magnetic resonance spectroscopies. The oscillating electric field interacts with electrical charges, i.e. the positive nuclei and negative electrons that comprise an atom or molecule, and cause the transitions seen in UV-Visible, atomic absorption, and fluorescence spectroscopies.

The energy of interaction, E, between a system of charged particles and an electric field ϵ is given by the scalar product of the electric field and the dipole moment, μ, for the system. Both of these quantities are vectors.

$$E = -\mu \cdot \epsilon \tag{4.5.1}$$

The dipole moment is defined as the summation of the product of the charge q_j times the position vector r_j for all charged particles j.

$$\mu = \sum_j q_j r_j \tag{4.5.2}$$

> ### Example 4.5.1
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> Calculate the dipole moment of HCl from the following information. The position vectors below use Cartesian coordinates (x, y, z), and the units are pm. What fraction of an electronic charge has been transferred from the chlorine atom to the hydrogen atom in this molecule? $r_H = (124.0, 0, 0)$, $r_{Cl} = (-3.5, 0, 0)$, $q_H = 2.70x10^{-20}C$, $q_{Cl} = -2.70x10^{-20}C$.

> ### Example 4.5.2
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> Sketch a diagram for Exercise 4.5.1 showing the coordinate system, the HCl molecule and the dipole moment.

To calculate an expectation value for this interaction energy, we need to evaluate the expectation value integral.

$$\langle E \rangle = \int \psi_n^*(-\hat{\mu} \cdot \hat{\epsilon})\psi_n d\tau \tag{4.5.3}$$

The $\int d\tau$ symbol simply means integrate over all coordinates. The operators $\hat{\mu}$ and $\hat{\epsilon}$ are vectors and are the same as the classical quantities, μ and ε.

Usually the wavelength of light used in electronic spectroscopy is very long compared to the length of a molecule. For example, the wavelength of green light is 550 nm, which is much larger than molecules, which are closer to 1 nm in size. The magnitude of electric field then is essentially constant over the length of the molecule, and ϵ can be removed from the integration since it is constant wherever ψ is not zero. In other words, ψ is finite only over the volume of the molecule, and the electric field is constant over the volume of the molecule. What remains for the integral is the expectation value for the permanent dipole moment of the molecule in state n, namely,

$$\langle \mu \rangle = \int \psi_n^* \hat{\mu} \psi_n d\tau \tag{4.5.4}$$

so

$$E = -\langle \mu \rangle \cdot \epsilon \tag{4.5.5}$$

Example 4.5.3

Verify that the vectors in the scalar product in Equation 4.5.5 commute by expanding $\mu \cdot \epsilon$ and $\epsilon \cdot \mu$. Use particle-in-a-box wave functions with HCl charges and coordinates.

Equation 4.5.5 shows that the strength or energy of the interaction between a charge distribution and an electric field depends on the dipole moment of the charge distribution.

To obtain the strength of the interaction that causes transitions between states, the transition dipole moment is used rather than the dipole moment. The transition dipole moment integral is very similar to the dipole moment integral in Equation 4.5.4 except the two wavefunctions are different, one for each of the states involved in the transition. Two different states are involved in the integral because the transition dipole moment integral has to do with the magnitude of the interaction with the electric field that causes a transition between the two states. For a transition where the state changes from ψi to ψf, the transition dipole moment integral is

$$\langle \mu \rangle_T = \int \psi_f^* \hat{\mu} \psi_i d\tau = \mu_T \tag{4.5.6}$$

Just like the probability density is given by the absolute square of the wavefunction, the probability for a transition as measured by the absorption coefficient is proportional to the absolute square $\mu_T^* \mu_T$ of the transition dipole moment, which is calculated using Equation 4.5.6. Since taking the absolute square always produces a positive quantity, it does not matter whether the transition moment itself is positive, negative, or imaginary. The transition dipole moment integral and its relationship to the absorption coefficient and transition probability can be derived from the time-dependent Schrödinger equation. Here we only want to introduce the concept of the transition dipole moment and use it to obtain selection rules and relative transition probabilities for the particle-in-a-box. Later it will be applied to other systems that we will be considering.

If $\mu_T = 0$ then the interaction energy is zero and no transition occurs or is possible between states characterized by ψ_i and ψ_f. Such a transition is said to be forbidden, or more precisely, electric-dipole forbidden. In fact, the electric-dipole electric-field interaction is only the leading term in a multipole expansion of the interaction energy, but the higher order terms in this expansion usually are not significant. If μ_T is large, then the probability for a transition and the absorption coefficient are large.

It is very useful to be able to tell whether a transition is possible, $\mu_T \neq 0$, or not possible, $\mu_T = 0$, without having to evaluate integrals. Properties of the wavefunctions such as symmetry or angular momentum can be used to determine the conditions that must exist for the transition dipole moment to be finite, i.e. not zero. Statements called spectroscopic selection rules summarize these conditions. Selection rules do not tell us how probable or intense a transition is. They only tell us whether a transition is possible or not possible.

For the particle-in-a-box model, as applied to dye molecules and other appropriate molecular systems, we need to consider the transition moment integral for one electron. According to Equation 4.5.2, the dipole moment operator for an electron in one dimension is –ex since the charge is –e and the electron is located at x.

$$\mu_T = -e \int_0^L \psi_f^*(x) x \psi_i(x) dx \tag{4.5.7}$$

This is the integral that must be evaluated for various particle-in-a-box wavefunctions to see which transitions are allowed (i.e. $\mu_T \neq 0$) and forbidden ($\mu_T = 0$) and to determine the relative strengths of the allowed transitions.