A PRACTICAL GUIDE TO MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY

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A PRACTICAL GUIDE
to magnetic
circular dichroism
spectroscopy
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This practical guide is intended to present a concise description of magnetic circular dichroism (MCD) spectroscopy and to illustrate how it can be applied to the interpretation of molecular electronic spectra. The presentation here is intended to be descriptive and thereby to help the reader visualize the optical spectroscopic effects presented by MCD measurements. An important purpose of this text is to call attention to the added dimension that experimental MCD spectra contribute to conventional absorption spectroscopy: The sign of the differential absorption \( \Delta A \), which, together with its magnitude, has the capability in many cases of supporting specific transition assignments and eliminating other hypothetical possibilities, often based upon simple, elegant symmetry arguments. The wave description of polarized light and the development of MCD theory assumes that the reader has familiarity with wave properties of light, quantum chemistry, electronic states, and molecular electronic structure. Advanced symmetry arguments are described which are based on the irreducible tensor methods outlined by S. B. Piepho and P. N. Schatz in their book *Group Theory and Spectroscopy with Applications to Magnetic Circular Dichroism* (Wiley-Interscience, New York, 1983). This book, including its symmetry tables (Appendixes) and precise specification of standard conventions, is invaluable for interpretive MCD spectroscopy, and all investigators in the field owe the authors a great debt of gratitude.

Some practical considerations for experimental MCD measurements based on the present author’s experience are included, but the discussion here is perhaps more general than any specific case may require. The illustrative examples discussed in the case studies were chosen to show the breadth of application of MCD measurements to the interpretation of electronic spectra in the vis–UV region and to the formulation of electronic structure models; the case studies included here are not intended to represent an exhaustive review of MCD spectroscopy. Furthermore, some of the details of the interpretive arguments in the examples are, for reasons of complexity, left for the reader to consult the original literature. The text concludes with a descriptive chapter on vibrational and rotation–vibrational MCD in the IR or near-IR region (MVCD) and on MCD in the X-ray region (XMCD), followed by a chapter that introduces magnetic linear dichroism (MLD).
spectroscopy, a related and complementary magneto-optical technique. Although every effort has been made to eliminate errors in the text, the author takes sole responsibility for any that remain.

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1 Introduction

Magnetic circular dichroism (MCD) spectroscopy is based upon the measurement of the difference in absorption between left circularly polarized (lcp) light and right circularly polarized (rcp) light, induced in a sample by a strong magnetic field oriented parallel to the direction of light propagation. The difference absorption, or dichroism, is defined by convention as \( \Delta A = A_- - A_+ \), where \( A_- \) is lcp absorption and \( A_+ \) is rcp absorption. The measured \( \Delta A \) is the same quantity measured for natural circular dichroism (CD) which is observed for chiral (optically active) molecules in regions of absorption. However, the origin of CD and MCD is quite different. Natural CD requires a molecular environment where molecular structure features distribute electric charge in a spatial array that has helical “handedness.” In contrast, MCD is due to electromagnetic interaction of the external field with electronic charge within the sample, no matter how it is distributed, and is a universal property of light absorption for all matter when placed in a magnetic field. A chiral molecular structure is not a requirement for MCD. In either case, however, the quantity \( \Delta A \) is analogous to conventional light absorption, where \( A = (A_- + A_+)/2 \), in that it obeys the Beer–Lambert law and thus is proportional to the molar concentration of the absorbing species, \( c \), and the path length through the sample, \( \ell \) (in centimeters); in addition, magnetically induced \( \Delta A \) for MCD is proportional to the magnetic field \( B \) Eq. (1.1), where

\[
\Delta A = A_- - A_+ = \Delta \varepsilon_M c \ell B
\]  

(1.1)

\( \Delta \varepsilon_M \) is the differential molar absorptivity per Tesla of field, analogous to \( \varepsilon \), the molar absorptivity. It should be apparent that \( \Delta A \) differs from conventional absorption in that the measured quantity has a sign associated with it that is dependent upon whether \( A_- \) or \( A_+ \) is larger. The positive or negative sign of \( \Delta A \) for MCD adds another dimension to absorption spectra, which present only positive values of \( A \) versus energy or wavelength.

The \( \Delta A \) for MCD results from a magnetic perturbation (the Zeeman effect) of the states involved in optical transition(s) responsible for light absorption. The phenomenon is related to the Faraday effect, discovered by Michael Faraday in the 1840s when it was observed that the plane of polarized light passing through a sample placed in a magnetic field was rotated in transparent regions of the spectrum (magnetic optical rotation or MOR). The optical rotation results from
magnetically induced refractive index differences (birefringence) for plane polarized light in different directions. In regions of absorption, a magnetic field can induce not only differences in index of refraction but also differences in absorption of LCP and RCP light, which differences give rise to elliptically polarized light emerging from the sample. The optical rotation is related to the rotation of the major axis of the ellipse, while \( \Delta A \) is related to the ratio of the minor and major axes of the ellipse as will be explained in Chapter 2. The wavelength dependence of MOR (magnetic optical rotatory dispersion or MORD) and MCD are related to each other. In principle, one can be calculated from the other by means of integral transforms (Kramers–Kronig type) over all wavelengths. However, MCD is almost exclusively used today because of experimental considerations. Perhaps one of the most important is that \( \Delta A \), like \( A \), is \( \approx 0 \) in transparent regions of the spectrum and is not strongly affected by birefringent imperfections in optical elements (windows, lenses, cells, etc.) that are part of spectrometers. In contrast, optical rotation can have significant magnitude in transparent regions of the spectrum and can be strongly affected by birefringence due to strains or other imperfections in optical elements.

The development of MCD really began in the 1930s when a quantum mechanical theory of MOR in regions outside absorption bands was formulated. The expansion of the theory to include MCD and MOR effects in the region of absorptions, which were referred to as “anomalous dispersions,” was developed soon thereafter. There was, however, little effort made to refine MCD as a modern spectroscopic technique until the early 1960s. The publication of important reviews by Buckingham and Stephens [review 1] in 1966 and Schatz and McCaffery [review 2] in 1969 called attention to the potential of MCD, with the added dimension of the sign of \( \Delta A \), as an interpretative tool for electronic spectra. The ability of MCD to interrogate and characterize electronic excited states in a way that was unavailable from other spectroscopic methods at the time was one of the exciting aspects noted by these reviews. Since that time there have been numerous studies of MCD spectra for a very large variety of samples, including stable molecules in solutions, in isotropic solids, and in the gas phase, as well as unstable molecules entrapped in noble gas matrices. More recently, MCD has found useful application in the study of biologically important systems including metalloenzymes and proteins containing metal centers. The application of MCD spectroscopy has been broad and diverse; a single volume cannot hope to touch on all aspects, but the goal here is to concisely describe the technique and then present some examples that illustrate not only the breadth of application, but also some of the more subtle aspects of electronic structure that can be experimentally characterized. MCD is an experimental spectroscopic tool that can help support or reject various proposed models for bonding and electronic structure that are the stock and trade of the chemical scientist.

The phenomenon of polarized light is first described in Chapter 2, followed by the theoretical framework for MCD spectroscopy in Chapter 3, which includes the Rigid Shift model and the definition and properties of MCD \( A, B, \) and \( C \) terms. The presentation follows closely the important book by S. B. Piepho and P. N.
Schatz [ref. 1], which describes the origin of MCD in considerable detail and then uses MCD as the basis for the application of advanced symmetry methods which employ powerful irreducible tensor techniques. The symbolism, definitions, and standard basis conventions of Piepho and Schatz are used here, for the most part, so that if further elaboration of the mathematical development is required, the reader can easily consult the relevant sections of their book. Chapter 4 presents a brief description of practical MCD spectral measurements, which is followed in Chapter 5 by a discussion of how MCD spectra are interpreted. In Chapters 6 and 7 a number of case studies are presented in order to illustrate the utility and breadth of MCD spectroscopy as applied to the study of the properties of electronic states and their electronic transitions in the vis–UV region. Chapter 6 is concerned with diamagnetic systems and $A$ and $B$ terms, while Chapter 7 discusses examples of paramagnetic systems and $C$ terms. Chapter 8 presents brief descriptions of MCD for vibrations and rotation–vibrations in the IR or near-IR region (MVCD), and it also discusses MCD in the X-ray region (XMCD). Chapter 9 introduces magnetic linear dichroism (MLD) spectroscopy, a related and complementary magneto-optical technique involving an external field that is transverse to the light propagation direction.

A list of reviews of MCD spectroscopy is included at the end, which may provide useful historical perspectives on the development of the technique and standard practice used today. It should be noted that the MCD term definitions, which feature so prominently in the interpretation of MCD spectra, originally differed from the standard conventions based on the Stephens definitions of 1976 [review 3] in common use today. The differences between the older definitions and those in standard use today are noted in Appendix A of Piepho and Schatz [ref. 1]. Also some earlier literature report MCD spectra in terms of molar ellipticity angles per Gauss $[\theta]_M$ rather than $\Delta A$ or molar absorptivities per Tesla, $\Delta \varepsilon_M$. The relationships between these older quantities and those in use today are also described in the Appendix A of ref. 1. It should be noted that the shape of the MCD spectra will appear the same because of the proportionality of $[\theta]_M$ and $\Delta \varepsilon_M$, but the quantitative magnitudes will certainly be different due to field and path unit differences.
2 Polarized Light

An understanding of the nature of polarized light and the transitions it can induce in atoms and molecules in the presence of a magnetic field will provide useful background for an understanding of MCD. In this chapter a wave model description of polarized light and its interaction with matter will be given. The description here is brief; for further clarification of the electromagnetic wave properties of light, standard reference works such as Born and Wolf [ref. 2, especially Section 1.4 on vector waves] can be consulted.

2.1. LINEAR POLARIZATION AND PLANE POLARIZED WAVES

A linearly or plane polarized light wave can be conveniently described by the real part (Re) of the time-dependent vector potential \( A = A^0 \exp(i2\pi\nu(t - nz/c)) \), Eq. (2.1), where \( A^0 \) is the vector amplitude, \( \nu \) is the wave frequency, \( n \) is the index of refraction which is inversely related to the wave velocity in the medium, \( t \) is time, \( z \) is the propagation direction, and \( c \) is the speed of light.

\[
\text{Re} A = \text{Re} A^0 \exp(i2\pi\nu(t - nz/c)) = A^0 \cos 2\pi\nu(t - nz/c) \quad (2.1)
\]

The electric \( E \) and magnetic \( B \) field vectors of such a wave are perpendicular to each other, and they each oscillate in a single plane containing the direction of propagation. The oscillating fields can each be described by vectors perpendicular to the propagation direction. Thus if we take the propagation to be in the positive \( z \) direction in a right-handed coordinate system, the electric and magnetic fields will be in the \( xy \) plane. The electric and magnetic field vectors in Gaussian units (electrostatic units for \( E \) and electromagnetic units for \( B \)) are given by

\[
E = -(1/c)\partial A/\partial t = -(i2\pi\nu/c)A \quad (2.2)
\]

\[
B = \nabla \times A = \mu H \approx H \quad (2.3)
\]

within the Coulomb gauge (the so-called “transverse” or “radiation” gauge) defined by the relation \( \nabla \cdot A = 0 \) and where the magnetic permeability \( \mu \approx \mu_0 = 1 \) (the permeability in a vacuum) for nonmagnetic environments (the usual case). It may be remarked here that \( H \) is the magnetic field strength and \( B \) is the...
magnetic field flux density (magnetic induction) within a sample but \( \mathbf{B} = \mathbf{H} \) is assumed here for samples in common nonmagnetic solution or matrix environments. Furthermore, \( \nabla \cdot \mathbf{A} = 0 \) because \( \mathbf{E} \) and \( \mathbf{B} \) are both perpendicular to the direction of propagation; they are also perpendicular to each other. The vector amplitude \( \mathbf{A}^0 \) contains polarization information and can be written as \( \mathbf{A}^0 = \pi \mathbf{A}^0 \), where \( \pi \) is a unit polarization vector. Thus, for the electric field vector amplitude from Eq. (2.2) we have

\[
\mathbf{E}^0 = -(i2\pi v/c)\mathbf{A}^0 = -(i2\pi v/c)\pi \mathbf{A}^0 = \pi \mathbf{E}^0 \quad (2.4)
\]

The unit vectors in the coordinate directions are symbolized by \( \mathbf{e}_x, \mathbf{e}_y, \) and \( \mathbf{e}_z \). Thus a plane-polarized wave in the \( xz \) plane would be represented by

\[
\mathbf{E}_x = \text{Re} \ e_x E^0 \exp (i2\pi v(t - nz/c)) = e_x E^0 \cos 2\pi v(t - nz/c) \quad (2.5)
\]

The \( \mathbf{E}_x \) vector would always point in the \( x \) direction as it is propagated along the \( z \) direction. Such a wave is said to be linearly polarized in the \( x \) direction. Such a wave is illustrated in Figure 2.1. The \( \mathbf{B} \) vector for this wave would, of course, point in the \( y \) direction, \( \mathbf{B}_y \).

2.2. CIRCULAR POLARIZATION AND CIRCULARLY POLARIZED WAVES

A circularly polarized wave can be visualized as the sum of two plane-polarized waves \( \mathbf{E}_x \) and \( \mathbf{E}_y \) that differ in phase by \( \pi/2 \), or one-quarter of a wavelength. Thus circularly polarized waves are given by

\[
\mathbf{E}_\pm = \text{Re}[(i2\pi v A^0/c)(1/\sqrt{2})(\mathbf{e}_x \pm i\mathbf{e}_y) \exp (i2\pi v(t - n \pm z/c))]
\]

\[
= (E^0/\sqrt{2})[\mathbf{e}_x \cos 2\pi v(t - n \pm z/c) \mp \mathbf{e}_y \sin 2\pi v(t - n \pm z/c)] \quad (2.6)
\]

**Figure 2.1.** A plane-polarized wave in the \( x \) direction with propagation in the \( z \) direction.
where the \(+\) subscript indicates a rcp wave and the \(-\) subscript indicates an lcp wave, respectively, and the phase difference between the two plane waves is \(\pm \pi/2\) [the term \(\pm i\varepsilon\) in Eq. (2.6) results from the phase difference \(\exp(\pm i\pi/2)\) for \(E_x\) relative to \(E_y\)]. The resultant vector executes a clockwise (+) or counterclockwise (−) helical motion when viewed face-on or looking toward the source (−z direction) as they precess about the propagation direction (+z direction). Now if an rcp and an lcp wave are both affected by the medium in exactly the same way (an isotropic medium), then they will have equal index of refraction \((n_+ = n_-)\) and we have for \(n = (n_+ + n_-)/2\)

\[
E_x = (1/\sqrt{2})(E_+ + E_-) = e_x E_0 \cos 2\pi v(t - nz/c) \tag{2.7}
\]

which is a plane-polarized wave in the \(x\) direction (see Figure 2.2). Thus two plane-polarized waves with \(\pm \pi/2\) phase difference can be combined to give an lcp or an rcp circularly polarized wave [by Eq. (2.6)]; likewise, two circularly polarized waves, one lcp and the other rcp, traveling through the medium with the same velocity \((n_+ = n_-)\) can be combined to give a plane-polarized wave [by Eq. (2.7)].

For an anisotropic (birefringent) medium where \(n_\pm \neq n_\mp\), the two circularly polarized components of Eq. (2.6) will travel through the medium with different

![Figure 2.2](image-url)
velocities and will differ in phase such that $\psi_{\pm} = 2\pi \nu (t - n_{\pm} z/c)$. If we write 
$\psi = (\psi_{+} + \psi_{-})/2 = 2\pi \nu (t - nz/c)$, where $n = (n_{+} + n_{-})/2$, the mean index of refractive, and write $\delta = (\psi_{+} - \psi_{-})/2 = 2\pi \nu z (n_{-} - n_{+})/2c = \pi \nu z \Delta n/c$, where $\Delta n$ is the index of refraction difference between lcp and rcp waves, then the $E$ vector from Eq. (2.6) is given by [ref. 3]

$$E = (1/\sqrt{2})(E_{+} + E_{-}) = (E^{0}/2)[e_{x} \cos \psi_{+} - e_{y} \sin \psi_{+} + e_{x} \cos \psi_{-} + e_{y} \sin \psi_{-}]$$

$$= (E^{0}/2)[e_{x}(\cos \psi_{+} + \cos \psi_{-}) - e_{y}(\sin \psi_{+} - \sin \psi_{-})]$$

$$= (E^{0}/2)[2e_{x} \cos \psi \cos \delta - 2e_{y} \sin \delta \cos \psi]$$

$$= E^{0} \cos \psi [e_{x} \cos \delta - e_{y} \sin \delta]$$

(2.8)

which describes a plane-polarized wave propagating in the $z$ direction, but rotated by an angle of $\delta$ relative to the $x$ direction. As shown in Figure 2.3, a birefringent medium causes the two circularly polarized components of a plane polarized wave to travel at different velocities, and the emergent plane polarized wave will be rotated about $z$ relative to the incident plane of polarization (assumed here to be the $xz$ plane). Anisotropic or birefringent media thus cause rotation of polarized light which is proportional to the distance traveled through the medium and to the difference in index of refraction for the two circularly polarized components $\Delta n$. The angle of rotation, conventionally symbolized by $\phi$, for a wave

![Figure 2.3. The combination of two circularly polarized waves that travel at differing velocities through the medium ($n_{-} > n_{+}$) gives rise to a linearly polarized wave that is rotated relative to the $x$ axis. Viewed in the $-z$ direction (looking toward the source).](image-url)
that has traveled a distance \( \ell \) along the \( z \) direction is given by

\[
\phi = \arctan\left(-\frac{E_y}{E_x}\right) = \arctan\left[-E^0 e_y \sin(\pi \nu \ell \Delta n/c)/(E^0 e_x \cos(\pi \nu \ell \Delta n/c))\right]
\]  
\(2.9\)

The above description of light passing through a medium holds for transparent regions of the spectrum. If the medium is not transparent but absorbs light with a frequency dependence, then not only will plane-polarized light be rotated on passage through the anisotropic absorbing medium, but also the vector amplitude of the circularly polarized components may no longer be the same. In this case, eliptically polarized light will emerge from the medium. The intensity in the \( z \) direction for a distance \( \ell \) through the medium is given by

\[
e_z I(\nu) = e_z I_0 \exp(-4\pi k \nu \ell/c)
\]  
\(2.10\)

where \( k \) is an absorption coefficient. If \( k_+ = k_- \), then the circularly polarized vectors have the same absorption coefficients in the medium, but if \( k_+ \neq k_- \), then the medium is said to be dichroic. The total absorption can be expressed by the sum of the mean absorption of the circularly polarized vectors and their difference: \( k \pm k' \), where \( k = (k_+ + k_-)/2 \) and \( k' = (k_+ - k_-)/2 = \Delta k/2 \). At this point it is useful to define the complex index of refraction:

\[
n_\pm = n_\pm - ik_\pm
\]  
\(2.11\)

Then upon substitution into Eq. (2.6) we have

\[
E_\pm = \text{Re}\left[(E^0/\sqrt{2})(e_x \pm ie_y) \exp(2\pi \nu(t-n_\pm \ell/c))\right]
\]
\[
= \text{Re}\left[(E^0/\sqrt{2})(e_x \pm ie_y) \exp(2\pi \nu k_\pm \ell/c) \exp(2i\pi \nu(t-n_\pm \ell/c))\right]
\]  
\(2.12\)

The \( E \) vector of the emergent light from the medium can then be written in terms of \( k, \Delta k, \psi = 2\pi \nu(t-n\ell/c), \) (where \( n = (n_+ + n_-)/2 \), \( \Delta n \), and \( \phi = \pi \nu \ell \Delta n/c \) (\( \delta \) in Eq. (2.8) for \( z = \ell \):

\[
E = (1/\sqrt{2})(E_+ + E_-)
\]
\[
= \text{Re}\left[(E^0/2)[(e_x + ie_y) \exp(-(k - \Delta k/2)2\pi \nu \ell/c) \exp(2i\pi \nu(t-n_+ \ell/c)) + (e_x - ie_y) \exp(-(k + \Delta k/2)2\pi \nu \ell/c) \exp(2i\pi \nu(t-n_- \ell/c))\right]
\]
\[
= \text{Re}\left[(E^0/2) \exp(-2\pi \nu \ell k/c) \exp(i\psi)[(e_x + ie_y) \exp(\Delta k \pi \nu \ell/c) \exp(i\phi) + (e_x - ie_y) \exp(-\Delta k \pi \nu \ell/c) \exp(-i\phi)]\right]
\]  
\(2.13\)

Thus the rcp and lcp vectors are both subjected to the mean absorption and mean index of refraction by the common factors \( \exp(-2\pi \nu \ell k/c) \) and \( \exp(i\psi) \), respectively, in Eq. (2.13), but the rcp and lcp vectors are further modified by the absorption difference factors \( \exp(+\Delta k \pi \nu \ell/c) \) and \( \exp(-\Delta k \pi \nu \ell/c) \), respectively. It can be shown that the expansion of the \( \exp(\pm i\phi) \) terms can be described by unit
vectors $e_x'$ and $e_y'$ that have been rotated through an angle $\phi$ with respect to the $x$ axis, which, with some rearrangement, gives Eq. (2.14) [ref. 3]:

$$
E = \text{Re}\left\{\left(\frac{E_0}{2}\right) \exp(-2\pi n \ell / c) \exp(i\psi) \left[e_x'[\exp(\Delta k \pi n \ell / c) + \exp(-\Delta k \pi n \ell / c)]
+ ie_y'[\exp(\Delta k \pi n \ell / c) - \exp(-\Delta k \pi n \ell / c)]\right]\right\}
= \text{Re}\left\{\left(\frac{E_0}{2}\right) \exp(-2\pi n \ell / c) \exp(i\psi) [e_x' \cosh(\Delta k \pi n \ell / c) + ie_y' \sinh(\Delta k \pi n \ell / c)]\right\}
$$

(2.14)

The emergent electric field vector $E$ is elliptically polarized and traces out an ellipse as shown in Figure 2.4. The ellipticity, conventionally symbolized as $\Psi$, for a wave that has traveled a distance $\ell$ along the $z$ direction represents the eccentricity of the ellipse, and the tangent of $\Psi$ is the ratio of the minor axis $(b)$ to major axis $(a)$ of the ellipse:

$$
\tan \Psi = b/a = (|E_-| - |E_+|)/(|E_-| + |E_+|)
= \tanh(\Delta k \pi n \ell / c) = \sinh(\Delta k \pi n \ell / c)/(\cosh(\Delta k \pi n \ell / c))
\approx \Delta k \pi n \ell c \quad \text{for } \Delta k \pi n \ell / c \leq 0.1 \quad \text{(the usual case)}
$$

(2.15)

Figure 2.4. Elliptical polarization of the $E$ vector which emerges from a medium in which $k_- > k_+$ and $n_- > n_+$. Viewed in the $-z$ direction (looking toward the source).
The important point here is that as light passes through the medium, a differential index of refraction $\Delta n$ for two circularly polarized waves leads to optical rotation, while differential absorption $\Delta k$ causes dichroism. It is the latter phenomenon, the differential absorption of circularly polarized light by matter, caused by the presence of an external magnetic field oriented along the propagation direction, that provides the origin of MCD.

2.3. ABSORPTION PROBABILITIES

The absorption of light passing through a distance $\ell$ in the medium is given by

$$\frac{dl}{I} = -\kappa d\ell$$

(2.16)

where $I$ is the light intensity, $\ell$ is the path through the absorbing medium, and $\kappa$ is the Lambert’s law absorption coefficient. From Eq. (2.10) we note that $\kappa$ is related to the absorption coefficient $k$ by $\kappa = 4\pi\nu k/c$. Therefore

$$\kappa = -\frac{dl}{Id\ell} = \frac{4\pi\nu k}{c}$$

(2.17)

In terms of transition probabilities for a transition from state $a$ to state $j$, the differential $-\frac{dl/\ell}{I}$ becomes

$$-\frac{dl}{d\ell} = h\nu(N_a P_{a\rightarrow j} - N_j P_{j\rightarrow a})$$

(2.18)

It is assumed that $P_{a\rightarrow j} = P_{j\rightarrow a}$, and therefore $\kappa(\nu)$ can be written as

$$\kappa(\nu) = [h\nu/I(\nu)](N_a - N_j)P_{a\rightarrow j}$$

(2.19)

From electromagnetic theory, the radiation intensity $I(\nu)$ is the time average ($\langle \rangle$) of the Poynting vector [ref. 2] and is given by

$$I(\nu) = \langle (c/4\pi)(\text{Re} \ E(\nu) \times \text{Re} \ B(\nu)) \rangle = (c/4\pi)\langle (-2\pi\nu A^0/c)^2(\cos^2 2\pi\nu(t - nz/c)) \rangle$$

$$= (c/4\pi)|E^0|^2(1/2) = (c/8\pi)|E^0|^2$$

(2.20)

but also since $|i|^2 = 1$ we have

$$I(\nu) = (c/4\pi)(-2\pi|i|\nu A^0/c)^2(1/2) = \pi(A^0)^2\nu^2/2c$$

(2.21)

The transition probability $P_{a\rightarrow j}$ is given by

$$P_{a\rightarrow j} = \left(\frac{\pi^2}{\hbar^2}\right) \left| \sum q_k/m_k c A^{0*} \cdot P_k \exp(i2\pi\nu z_k/c) \right|^2 \rho_{aj}(\nu)$$

(2.22)

where $\rho_{aj}(\nu)$ is the absorption lineshape function such that $\int \rho_{aj}(\nu) \, d\nu = 1$ and the sum is over $k$ charges $q_k$ with masses $m_k$ and momenta $P_k$; the $*$ for $A^{0*}$ indicates...