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Theoretical studies in photoelectron spectroscopy. Molecular optical activity in the region of continuous absorption and its characterization by the angular distribution of photoelectrons

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The phenomenon of molecular optical activity is examined in the region of continuous absorption. When the "excited" state of the molecule describes an infinite (ionized) system, then the angular distribution of photoelectrons is the sum of coherent contributions corresponding to different magnitudes and interferences of $\hbar\vec{l}$, the angular momentum of the photoelectron. The amplitude for such a process is the sum of terms for each l; thus, since both even and odd values of l can coexist at a single energy in the continuous spectrum, the electric and magnetic dipole matrix elements can *coexist* in this amplitude, making possible the existence of electric-dipole—magnetic-dipole interference in the angular distribution even for a molecule with a center or plane of symmetry. For discrete absorption, in which the intensity is the sum of incoherent contributions corresponding to the intensities for populating the fine-structure levels of a given excited state, the coexistence of the electric and magnetic dipole matrix elements in the amplitude is possible only for a molecule with a site which is asymmetric with respect to inversion or reflection; otherwise both even and odd values of l could not coexist at a single energy in the discrete spectrum. The signs of the electric-dipole—magnetic-dipole interference terms are opposite for left and right circularly polarized light; thus there exists a signal for the angular distribution difference for absorption of left and right circularly polarized light of order α relative to the angular distribution for absorption of light of either polarization. This is just the phenomenon of "circular dichroism" which characterizes molecular "optical activity" in the region of absorption. It exists for the angular distribution of photoelectrons ejected from an *oriented* molecule with a center or plane of symmetry, but vanishes for isotropic systems (atoms) owing to the independence of the radial wave functions from the magnetic quantum number. This ensures the orthogonality of atomic radial wave functions belonging to states of different m and is responsible for the selection rule in atomic spectroscopy that magnetic-dipole transitions are possible only between the fine-structure levels of a given multiplet. Measurement of the angular distribution characteristic for this process would provide a sensitive probe of the parameters of the initial molecular orbital. The existence of even-odd-type interferences of the partial waves of the photoelectron would provide a test of the time-reversal invariance of the wave function for the ionized system, since these interferences depend on the sine rather than the cosine of the phase-shift difference and hence on the normalization of the wave function to satisfy incoming boundary conditions. Calculations are carried out to illustrate these and other points.

I. INTRODUCTION

In a series of three papers[1-3] we have analyzed angular distributions for molecular photoelectrons from the point of view of inverting angular distribution data to determine the parameters of the initial molecular orbital. In this paper we want to examine the characteristics of the angular distribution on the inclusion of terms of higher order in the multipole expansion of the radiation field. In particular we want to present an analysis of the angular distribution expected on measurement of the differential cross-section (angular distribution) difference for left and right circularly polarized light. In this experiment the leading terms due to the electric dipole interaction cancel since each is identical for left or right circular polarization. This cancellation leaves a remainder, the electric-dipole—magnetic-dipole interference term. This term has resulted from the *addition*, rather than the *cancellation*, of the electric-dipole—magnetic-dipole interference terms of the angular distributions for light of either polarization because the signs of these terms are *opposite* for either polarization. This is just the term responsible for the phenomenon of molecular circular dichroism, i.e. the molecular optical activity in the region of absorption.

In the region of continuous absorption, resulting in the ionization of the molecule, this phenomenon can be characterized by measurement of the angular distribution of photoelectrons, or more precisely the angular distribution *difference* for absorption of left and right circularly polarized light. These measurements would provide a new "window" into the molecular process of circular dichroism. In addition, they would bring together a very old field of molecular spectroscopy (the study of molecular optical activity for discrete absorption[4,5]) and a field relatively new to atomic physics, that of molecular photoelectron spectroscopy.

There exists recent experimental work which provides evidence that measurement of what we will henceforth call the "circular dichroic angular distribution" is possible given present-day instrumental means. Among others, these experiments include the development of techniques[6] to produce circularly polarized light in the ultraviolet region of the spectrum of wavelengths short enough to provide energy above the first ionization potential of many molecules. Also, they include measurements of relative differential cross sections[7] for keV photoelectrons. Cross sections at these energies show significant deviations from those expected from electric dipole radiation alone. The leading higher-order correction is the electric-dipole–electric-quadrupole interference term, of order ω/c relative to the electric dipole term, where ω is the frequency and c the velocity of light. The factor ω/c is of order unity for keV radiation, and significant deviations from the angular distribution for electric dipole radiation alone have been observed by Wuilleumier and Krause.[7] The ability to measure this effect suggests very strongly that the circular dichroism in the region of continuous absorption can be measured using these or similar experimental apparatus and techniques. In Sec. II we will show that the circular dichroic angular distribution is of order $(\alpha a_0)^2$, where α is the fine-structure constant and a_0 is the Bohr radius. This cross section close to threshold is on the order of about 10^{-20} cm^2, or about 1% of the cross section for direct electric dipole photoionization. The magnitude of the cross section in the keV region, as measured by Wuilleumier and Krause,[7] is likewise about 1% or less of the cross section *at threshold*. Thus, we can use the measurability of keV angular distributions, replete with electric-dipole–electric-quadrupole interference, as a crude guide for the measurability of the circular dichroic angular distribution near threshold, since each cross section is about 1% of the largest possible cross section in either energy regime. The ability to measure a cross-section difference accurately by substracting the cross sections measured separately for light of either polarization is questionable; however it may be possible to design instrumentation for use in the region of continuous absorption, analogous to that for discrete absorption, by which the cross-section difference is measured *directly*. In discrete absorption, this difference is measured directly by measuring the ellipticity of the absorbed light, where this ellipticity has resulted from unequal absorptions of the left and right circularly polarized components of a plane-polarized beam.

II. THEORY

A. Basic considerations

In this section we will present formulas for the differential cross section for photoionization using left or right circularly polarized light, where we retain terms through order α^2 in the multipole expansion for the radiation field. Formally these terms are closely related to terms already presented by Tully, Berry, and Dalton (TBD),[8] using linearly polarized light. In the present work we want to stress the dependence of the angular distribution on the polarization of the light,[9] and in particular we want to present a detailed study of the angular distribution difference for left or right circularly polarized light. As we have stated previously, a remainder exists because of the addition rather than the cancellation of the electric-dipole–magnetic-dipole interference terms for left or right circular polarization. The angular distribution for absorption of left or right circularly polarized light is given by

$$\frac{d\sigma_{L,R}}{d\Omega}=\frac{\alpha a_0^2}{2\pi}E_p k|\langle\psi_{\vec{k}}^{(-)}|\hat{\rho}_{L,R}\cdot\vec{r}|\psi_i\rangle|^2+\mathrm{Im}\left(\frac{\alpha^2a_0^2}{2\pi}E_p k\langle\psi_{\vec{k}}^{(-)}|\hat{\rho}_{L,R}\cdot\vec{r}|\psi_i\rangle^*\langle\psi_{\vec{k}}^{(-)}|\vec{l}\cdot i(\hat{k}_p\times\hat{\rho}_{L,R})|\psi_i\rangle\right.$$
$$\left.-\frac{\alpha^2a_0^2E_p^2k}{2\pi}\langle\psi_{\vec{k}}^{(-)}|\hat{\rho}_{L,R}\cdot\vec{r}|\psi_i\rangle^*\langle\psi_{\vec{k}}^{(-)}|(\hat{\rho}_{L,R}\cdot\vec{r})(\hat{k}_p\cdot\vec{r})|\psi_i\rangle\right)+O(\alpha^3a_0^2)\,. \qquad (1)$$

The quantities are defined as follows: α is the fine-structure constant, a_0 the Bohr radius, E_p the energy of the photon in atomic units, k the velocity of the ejected electron in atomic units, $\psi_{\vec{k}}^{(-)}$ the wave function for the ionized system normalized to satisfy incoming boundary conditions, ψ_i the wave function for the neutral system, $\vec{r}$ the summation over the positions of all of the electrons in the system, $\vec{l}$ the summation over the angular momenta of all of the electrons in the system, $\hat{k}_p$ the unit vector in the direction of propagation of the photon, whose magnitude is ω/c, and $\hat{\rho}_{L,R}$ is the unit vector in the direction of polarization of the photon. Explicitly,

$$\hat{\rho}_{L,R}=(1/\sqrt{2})(\vec{i}\pm i\vec{j}) \qquad (2)$$

where $\vec{i}$ and $\vec{j}$ are unit vectors along x and y, respectively, and the normalization factor $1/\sqrt{2}$ ensures that the average energy density in the random-phase approximation[10] is normalized to the value $F\hbar\omega/c$, where F is the flux.

All matrix elements in Eq. (1) are evaluated in atomic units. Figure 1 illustrates the geometry of the experiment. $\hat{\rho}_{L,R}$ lies in the x-y plane, and $\hat{k}_p$ is normal to this plane along z. The molecule is assumed to be oriented such that its axis of quantization is along z. The vector $\hbar\vec{k}$ is the momentum of the ejected electron, and the angle between $\hat{k}_p$ and $\hbar\vec{k}$ is the angle of ejection. In an experiment in which the principal axis of quantization of the molecule does not lie along the polar axis in the laboratory frame, the set of Euler angles would define the position of the molecule-fixed frame relative to the laboratory frame, and this set would simply be a constant set of parameters in an experiment involving oriented molecules. In an experiment involving randomly oriented gas-phase molecules, the angular distribution must be averaged over this set of angles.[1-3,8]

B. Choice of phase for the magnetic dipole matrix element

We will focus our attention on the second term of Eq. (1). The magnetic dipole operator is of the form $\vec{l}\cdot\hat{H}$, where $\hat{H}=i(\hat{k}_p\times\hat{\rho}_{L,R})$ is the unit vector in the direction of the magnetic field associated with the radiation. Explicitly,

$$\vec{\mathrm{H}}=i[\vec{\mathrm{k}}_p\times\vec{\mathrm{A}}(\vec{\mathrm{r}})]_0=[\vec{\nabla}\times\vec{\mathrm{A}}(\vec{\mathrm{r}})]_0, \tag{3}$$

where the subscript 0 means that the curl is evaluated in the $r=0$ limit and where $\vec{\mathrm{A}}(\vec{\mathrm{r}})$ is the part of the vector potential depending only on $\vec{\mathrm{r}}$. Explicitly,

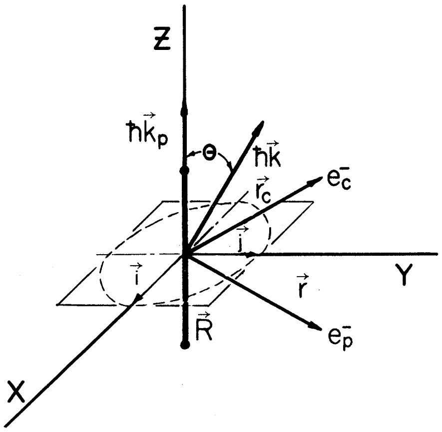

FIG. 1. Coordinate system. $\hbar\vec{k}$ and $\hbar\vec{k}_p$ are the momenta of the ejected electron and incident photon, respectively. $\vec{i}$ and $\vec{j}$ are unit vectors in the direction of the polarization of the light. $\vec{R}$ is the relative position of the nuclei, $\vec{r}$ the position of the photoelectron, and $\vec{r}_c$ the position of the core electron.

$$\vec{\mathrm{H}}=\left(\frac{2\pi F}{\alpha\omega}\right)^{1/2}e(\vec{\nabla}\times\hat{\rho}_{L,R}e^{i\vec{\mathrm{k}}_p\cdot\vec{\mathrm{r}}})_0, \tag{4}$$

where e is the charge of the electron and the other quantities have been previously defined. Evaluating the curl and taking the dot product, we obtain

$$\vec{l}\cdot\hat{H}=\pm(1/\sqrt{2})(l_x\pm i\,l_y)=\pm(1/\sqrt{2})l_\pm\,, \tag{5}$$

for the operator. Matrix elements of the raising and lowering operators are given by[11]

$$(j\,m\pm 1|\,l_\pm|j\,m)=e^{\pm in\pi/2}[(j\pm m+1)(j\mp m)]^{1/2}\,, \tag{6}$$

where $n=0,+1,+2,\ldots,+\infty$. That is, these elements are arbitrary to within a phase. The existence of the electric-dipole–magnetic-dipole interference depends on the choice of this phase. For example, if the light were linearly polarized along z with $\vec{\mathrm{k}}_p$ along x, as in TBD,[8] then the magnetic field $\vec{\mathrm{H}}$ would be along y. The magnetic dipole operator would then be of the form $i\,l_y$. According to Eq. (1), the interference is proportional to the imaginary part of the complex conjugate of the electric dipole matrix element times the magnetic dipole matrix element. Now, below the ionization threshold (case for bound-bound transitions) and for linear polarization along z, the electric dipole element is real; therefore, recognizing that $l_y=(1/2i)(l_+-l_-)$, the interference exists only for n in Eq. (6) equal to the set of odd integers. On the other hand, for a choice of linear polarization along z but $\vec{\mathrm{k}}_p$ along y, such that the magnetic field is directed along x and the operator is of the form $i\,l_x$, then, recognizing that $l_x=\frac{1}{2}(l_++l_-)$, the interference exists only for n equal to zero or the set of even integers. Going through an analogous argument for circular polarization show that the interference term does not exist unless n is chosen to be the set of odd integers. Still, the interference is arbitrary with respect to sign. This ambiguity of sign is a consequence of the condition, as discussed by Condon,[4] that the interference is a pseudoscalar and not a true invariant. A pseudoscalar is the product of a vector (the electric dipole operator) and a pseudovector (the magnetic dipole operator) called by Condon[4] "polar" and "axial" vectors, respectively. The sign of the pseudoscalar changes on transformation of coordinate frames from left to right handed or vice versa. As a consequence, "optical isomers" or molecules one of which is the mirror image of another rotate the plane of polarization in opposite directions, and the absolute value of the sign of the rotation for either direction must be fixed by convention.

The above analysis holds for "polarized" discrete absorption—that is, when the molecule can be oriented such that its principal axis of quantization is directed either along the axis of polarization of the light, if linearly polarized, or along the axis of propagation of the light, if circularly polarized in a plane normal to this axis. Choice of phase for the case of bound-bound transitions puts us in a position to extend the analysis above the ionization threshold to bound-free transitions. Physically we must have an analytic continuation through the threshold region. Had we begun the analysis in the continuum, we would have discovered that the second term contained both real and imaginary parts *for any choice of phase* of the Eq. (6), because of the complex factor multiplying the radial partial waves chosen to ensure normalization to incoming boundary conditions. This factor has the well-known form $(i)^l e^{\mp i\eta_l}$ for incoming-outgoing boundary conditions in the central-field problem (its generalization to molecular fields has been given in Ref. 1 and references therein). Further, circular polarization of the light entails the selection rule, $m_j = m_0 \pm 1$ for both electric dipole and magnetic dipole amplitudes, where m_j and m_0 are the azimuthal quantum numbers of the continuum and bound radial waves, respectively. Provided the bound molecular orbital can be characterized by a single m_0 value, then the angular part of the product of matrix elements in Eq. (1) is real. This means that choice of n equal to zero or the even set of integers leads to a $\cos\Delta\eta$ dependence and choice of n equal to the odd set of integers leads to a $\sin\Delta\eta$ dependence of the angular distribution, where $\Delta\eta$ is the phase-shift difference for two partial waves occurring in the interference. This ambiguity is removed by choice of the phase of Eq. (6) to ensure the existence of bound-bound interference, and then analytically continuing this result above the ionization threshold. For a molecule whose symmetry is high enough so that its molecular orbitals have only a single m_0 value, the angular distribution shows a pure $\sin\Delta\eta$ dependence. This sine dependence, whose sign depends on the sign of the phase angle $\Delta\eta$, provides a test of the normalization of the wave function for the ionized system to obey incoming boundary conditions and hence provides a test of time-reversal invariance. For molecules of lower symmetry, whose molecular orbitals have several m_0 values, the angular distribution can exhibit a mixture of dependences on both $\cos\Delta\eta$ and $\sin\Delta\eta$ and a dependence on the azimuthal angle φ.

C. Partial-wave analysis

In this section we will expand the bound and continuum orbitals in a series of partial waves about the molecular ionic center of mass. We assume molecules with a center or plane of symmetry. This analysis has been presented and discussed in detail in Refs. 1–3. The initial wave function is expanded as follows:

$$\psi_i = \sum_{l_0}{}' \varphi_{l_0 m_0}(r) Y_{l_0 m_0}(\theta_r, \varphi_r)\,, \tag{7}$$

where the prime on the summation means that only all even or all odd terms occur. For symmetry this high, only a single m_0 value is required to specify a given molecular orbital. Terms are retained in this expansion until convergence is reached. The final wave function is expanded

$$\psi_{\vec{k}}^{(-)} = 4\pi \sum_{l_i l_j m_i} \varphi^{(-)}_{l_i l_j m_j} Y_{l_i m_j}(\theta_r, \varphi_r) Y^*_{l_j m_j}(\theta_k, \varphi_k)\,. \tag{8}$$

We can write for the electric dipole interaction,

$$\hat{\rho}_{L,R} \cdot \vec{r} = \mp(\tfrac{4}{3}\pi)^{1/2} r Y_{1\pm1}(\theta_r, \varphi_r)\,. \tag{9}$$

The subscripts on the angles indicate whether these are angles belonging to $\vec{r}$ or $\vec{k}$. In Eq. (8) two sets of quantum numbers $\{l_i, m_i\}$ and $\{l_j, m_j\}$ are required to specify the directions of $\vec{r}$ and $\vec{k}$. For molecules of sufficiently high symmetry, $m_i = m_j$. Please note that from inspection of the operators given by Eqs. (5) and (9), the following selection rules can be deduced:

$$m_j = m_0 \pm 1 \quad \text{for left or right circular polarization,} \tag{10a}$$

$$l_i = l_0 \quad \text{for a magnetic-dipole transition,} \tag{10b}$$

$$l_i = |l_0 \pm 1| \quad \text{for an electric-dipole transition.} \tag{10c}$$

For a two-electron molecule, whose ground state is a singlet, the angular distribution difference or "circular dichroic angular distribution" is given by

$$\begin{aligned}\frac{d\sigma_L}{d\Omega} - \frac{d\sigma_R}{d\Omega} = \frac{-2^3(\alpha a_0)^2 E_p k}{\sqrt{2}} \sum (2\lambda_0+1)^{1/2}(2\lambda_i+1)^{1/2}(2\lambda_j+1)^{1/2}(2l_j+1)^{1/2}(2L+1) \\ \times \begin{pmatrix}\lambda_0 & 1 & \lambda_i\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\lambda_0 & 1 & \lambda_i\\ m_0 & 1 & -m_j\end{pmatrix}\begin{pmatrix}l_j & \lambda_j & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_j & \lambda_j & L\\ m_j & -m_j & 0\end{pmatrix} \\ \times[(l_0+m_0+1)(l_0-m_0)]^{1/2}\,\mathrm{Re}[(\beta^{m_0 m_j}_{\lambda_0\lambda_i\lambda_j})^* \gamma^{m_0 m_j}_{l_0 l_j}] P_L(\cos\theta)\,,\end{aligned} \tag{11a}$$

$$\beta^{m_0 m_j}_{l_0 l_i l_j} = \int_0^\infty dr\, r^2 \varphi^{(-)*}_{l_i l_j m_j} r \varphi_{l_0 m_0}, \tag{11b}$$

$$\gamma^{m_0 m_j}_{l_0 l_j} = \int_0^\infty dr\, r^2 \varphi^{(-)*}_{l_0 l_j m_j} \varphi_{l_0 m_0}, \tag{11c}$$

where we have ignored the vibrational degree of freedom and the overlap between ionic and neutral bound states [these terms can be easily included in a given case; see Eqs. (7a) and (7c) of Ref. 2], and where we have explicitly summed the two terms for left and right circular polarization. According to the selection rules given by Eqs. (10b) and (10c), l_j and λ_j of Eq. (11a) must be of different parity; therefore $L > 0$ and is of odd parity by the rule that for the 3-j symbol with $m_1 = m_2 = m_3 = 0$ to exist, $l_j + \lambda_j + L$ must be even. The condition that $L > 0$ means that the effect vanishes on integration over the solid angle. Also, the radial overlap given by Eq. (11c) vanishes for isotropic system (atoms), owing to the independence of the radial functions from azimuthal quantum number, m, and thus the radial orthogonality for wave functions of different m. It is this condition which is responsible for the selection rule in atomic spectroscopy that magnetic dipole transitions can occur only between states of the same principal quantum number.

The effect vanishes in rotationally averaged angular distributions. This disappearance for the angular distribution for a sample of randomly oriented molecules can be understood from the consideration that use of circularly polarized light causes population of a single fine-structure level of the excited state (or for ionization of a single m wave of the photoelectron), according to the selection rule $m_j = m_0 \pm 1$ for left or right circular polarization, respectively. The distinction between which level (or wave) is populated depends on the condition that each level be a component of a multiplet defined by use of a molecular axis of quantization. In rotationally averaged systems, the angular distribution cannot contain information (or "memory") about an axis of quantization in the molecule fixed frame. This same condition obtains in discrete absorption. The difference between absorption coefficients for left and right circularly polarized light disappears for a sample of randomly oriented molecules in both discrete and continuous absorption unless the molecule has chirality or "handedness." A molecule is chiral if $V(r, \theta, \phi) \neq V(r, \theta, -\phi)$, where V is an effective potential in which an electron moves. The most familiar example of a chiral molecule is a molecule having an "asymmetric carbon" atom or carbon atom bonded tetrahedrally to four distinct groups and existing in the form of a pair of "enantiomers" or "optical isomers."

This means that measurements should be carried out on molcules oriented either in a solid substrate or by use of polarizing fields in beam experiments. The theory would then have to include the details of background effects on the angular distribution in a given case. This could constitute a practical limitation; however recently there has appeared a large interest in the angular distributions of molecules adsorbed on surfaces, and work is being carried out on the background effects on such distributions.[12,13] Oriented molecule beam work has been performed by Beuhler and Bernstein[14] and other workers, and provided a sufficient number of oriented molecules were present to overcome intensity difficulties, this technique could offer the more desirable alternative, from the point of view of the simplicity expected for the experimental and theoretical analysis of the background effects on the angular distribution produced by the orienting electric field.

III. TEST OF TIME-REVERSAL INVARIANCE

We want to outline in more detail how the circular dichroic angular distribution could be used as a test of time-reversal invariance of the wave function for the ionized molecule. Quite generally, interference terms in angular distributions which arise from the cross product of radial amplitudes belonging to partial waves of *opposite parity* will take a sign which is determined by the normalization appropriate for the process—normalization to satisfy *outgoing* boundary conditions for waves involved in scattering processes and *incoming* boundary conditions for waves which occur as final states in transition amplitudes. Yang[15] has derived several general theorems applicable to unpolarized systems undergoing collision by which the forms of the angular distributions of products occurring in both nonradiative and radiative processes in nuclear reactions can be deduced. Table I of his paper provides a summary of his findings. He discusses the occurrence of all even or a combination of even and odd powers of $\cos\theta$ [see our Eq. (11a) in which only odd powers of $\cos\theta$ occur]. Even or odd powers of $\cos\theta$ will be multiplied by coefficients formed by use of partial waves of the same or of opposite parity, respectively. For the radiative processes considered, he finds the occurrence of only even powers of $\cos\theta$ (interference of partial waves of the same parity), stating that the odd powers do not occur because the photon wave has definite parity. In general, this parity will depend on the order of the multipole expansion of the radiation field; the electromagnetic interaction is odd for the electric dipole term and even for the magnetic dipole or electric quadrupole term.

We can gain a physical interpretation of time-reversal invariance by reference to the general argument of Breit and Bethe.[16] Their use of the forms for the wave functions outside of the region of the center of force,

$$\Psi = \int d\vec{k}\, C_{\vec{k}} \psi_{\vec{k}} e^{-iEt/\hbar} , \qquad (12a)$$

$$\psi_{\vec{k}}^{(\pm)} \sim e^{i\vec{k}\cdot\vec{r}} + f^{(\pm)}(\theta) \frac{e^{\pm ikr}}{r} , \qquad (12b)$$

provides the means of arriving at a mathematical statement and a physically transparent analysis of the normalization appropriate for a given process. Equation (12a) gives the time-dependent wave function written quite generally as the superposition of the continuum time-independent wave functions, $\psi_k^{(\pm)}$, calculated at an infinite distance from the center of force and normalized to satisfy outgoing or incoming boundary conditions (±) respectively. $f^{(\pm)}(\theta)$ are the scattering amplitudes for either normalization. Substitution of Eq. (12b) into Eq. (12a) and recognition that $E = k^2$ in rydberg units leads to choice of the normalization condition correct for a given physical process by use of stationary phase analysis. In summary, for a scattering process, at $t = -\infty$, the beam approaches along $z = -\infty$. Choice of the (+) boundary condition then leads to the disappearance of all terms containing e^{+ikr}, since for $t = -\infty$, $kz = -kr$, and cancellation (destructive interference) occurs in the integration over k. On the other hand, at $t = +\infty$, the unscattered beam departs along $z = +\infty$, and choice of the (+) boundary condition leads to the existence of all terms containing e^{+ikr}, since for $t = +\infty$, $kz = kr$, and no cancellation (constructive interference) occurs in the integration over k. Thus, the scattered waves represented by the second term of Eq. (12b), produced in the region of the potential, exist at $t = +\infty$ but do not exist at $t = -\infty$. Choice of the (−) boundary condition would produce the inverse of the above situation and hence result in an incorrect description of the process. If the incorrect normalization were used, then the scattering amplitudes (extracted from the asymptotic forms of the radial equations) would be

$$\alpha_l = [(-1)^l/2i](e^{-2i\eta_l} - 1) , \qquad (13)$$

and even-odd interference terms in the angular distribution would have the wrong sign. Use of incoming boundary conditions for particles created in the region of the potential is necessary because time-reversal invariance requires that on letting $t \to -t$ and $\vec{k} \to -\vec{k}$ the emerging particles must become the particles of an incident beam in a scattering experiment, and as such scattered waves at $t = +\infty$ cannot exist. Thus, the test of the normalization to satisfy incoming or outgoing boundary conditions is a test of time-reversal invariance, since the wave functions for either normalization are related to each other by the transformation, $\psi^{(+)} = \tau_r \psi^{(-)}$, where τ_r is the symmetry operation for time reversal (meaning take the complex conjugate of $\psi^{(-)}$ and let $\vec{k}$ go into $-\vec{k}$).

Although the concept of time reversal which we have briefly reviewed above has a venerable history in quantum mechanics, it does not appear to have had important experimental consequences, particularly in the study of radiative processes in atomic physics, probably for the reason suggested in our brief review of the cases studied by Yang[15] for radiative processes in nuclear physics, namely that interference phenomena involving partial waves of opposite parity, which provide a probe of the boundary conditions of the wave function, evidently were not important in the context of his studies. In the present work, the importance is especially striking because the circular dichroic angular distribution provides a direct measurement of the electric-dipole–magnetic-dipole interference term, whose sign is determined by the appropriate normalization. This is the first such test of time-reversal invariance by a molecular radiative process that we are aware of, and we hope that the present analysis will stimulate experimental interest.

IV. CALCULATIONS AND DISCUSSION

A. Use of Coulombic waves for the photoelectron

In this section we will present calculations. We assume that the molecular orbitals can be put in the form,

$$\psi_g \sim \varphi_0(\zeta_0 r) + \lambda_2 \varphi_2(\zeta_2 r) P_2(\cos\theta) + \cdots , \qquad (14a)$$

$$\psi_u \sim \varphi_1(\zeta_1 r) P_1(\cos\theta) + \lambda_3 \varphi_3(\zeta_3 r) P_3(\cos\theta) + \cdots , \qquad (14b)$$

for a σ_g- or σ_u-type molecular orbital, respectively. Accurate multicenter molecular orbitals can be reexpanded about the molecular center of mass and put in this form. We will assume Slater-type forms for the radial components in Eqs. (14). This assumption frees us to study angular distributions as a function of the sets of anisotropy and effective charge parameters, $\{\lambda_j\}$ and $\{\zeta_j\}$, respectively.[3] For simplicity, we further set all of the effective charge parameters equal to a single parameter ζ. This restriction implies that a given multicenter molecular orbital can be represented less accurately by a single center; however, it is reasonable since we would expect each radial component of a given molecular orbital to have roughly the same "size."

We further simplify the calculation by use of Coulombic waves for the photoelectron. This will give a crude, but reasonably correct, description of the process, especially at low energies where, for waves of order $l > 0$, the centrifugal barrier will cause a given radial wave to be pushed outward such that (i) the photoelectron is found principally outside of the sphere swept out by the nuclei of the molecule and (ii) its motion is determined in large part by the Coulombic tail of the potential, namely by $-1/r$. However, photoelectric current is generated from the region of space occupied by the initial state, and hence the amplitudes for photoionization depend on the continuum wave function in the same region. Thus the phase shifts required for calculating the angular distribution should be fairly accurate, while the radial matrix elements should contain a greater source of error. The calculations could be made systematically more accurate by use of methods recently developed for calculating the wave function for an ionized molecule.[17]

Use of these approximations now allows us to write down the matrix elements of Eqs. (11) in analytic form.[3,18] The first several elements are given by

$$\beta_{01} = -ie^{i\sigma_1}\frac{2^3\zeta^{3/2}C_1(k)}{(\zeta^2+k^2)^3}k(2\zeta-1)e^{-a}\,, \tag{15a}$$

$$\beta_{10} = e^{i\sigma_0}\frac{2^4\zeta^{5/2}C_0(k)}{\sqrt{3}(\zeta^2+k^2)^4}[(3\zeta^3-9\zeta^2+6\zeta-1) - (3\zeta-2)k^2]e^{-a}\,, \tag{15a}$$

$$\beta_{12} = -e^{i\sigma_2}\frac{2^4\zeta^{5/2}C_2(k)}{\sqrt{3}(\zeta^2+k^2)^4}k^2(3\zeta-1)e^{-a}\,, \tag{15c}$$

$$\gamma_{11} = \frac{(2\zeta)}{\sqrt{12}}\beta_{01}\,, \tag{15d}$$

$$\gamma_{22} = \frac{(2\zeta)}{\sqrt{30}}\beta_{12}\,, \tag{15e}$$

$$C_j(k) = \left(\frac{2\pi/k}{1-e^{-2\pi/k}}\right)^{1/2}\prod_{s=1}^{j}[s^2+(1/k)^2]^{1/2}\,, \tag{15f}$$

$$a = \frac{2}{k}\arctan\left(\frac{k}{\zeta}\right), \tag{15g}$$

$$\sigma_j = \arg\Gamma(j+1-i/k)\,. \tag{15h}$$

We note that γ_{11} and γ_{22} vanish at $\zeta = \frac{1}{2}$ and $\zeta = \frac{1}{3}$, respectively, as a result of $2p$, kp and $3d$, kd radial orthogonality for hydrogenic states. By the selection rules given by Eqs. (10), the initial and final waves belong to *different* m; therefore, as stated in Sec. II, the radial overlap is nonzero provided the radial waves depend on m. The hydrogenic functions used above do not depend on m; however, we can mimic m dependence and therefore nonzero overlap by having ζ at our disposal as an adjustable parameter.

We perform the calculations taking $k = 0.1$ a.u. and assuming that the molecule has an ionization potential of 0.5 a.u.

B. Results and discussion

We present our results in Figs. 2 and 3 for the circular dichroic angular distribution for ionization from a σ_g or σ_u molecular orbital, respectively. The most interesting factor of the results for the σ_g orbital is the condition that the leading term in the molecular orbital, namely the $l_0 = 0$ component, has a zero magnetic dipole contribution. The dominant term in the angular distribution is the $\lambda_0 = 0$, $l_0 = 2$ (l_0, λ_0 are angular momenta of the initial molecular orbital) electric-dipole–magnetic-dipole cross term, whose strength is linear in λ_2. Clearly then, this measurement would provide a very sensitive probe of the leading anisotropy parameter of this molecular orbital. Figure 2 shows results for $\lambda_2 = 1$, $\zeta = 1$; $\lambda_2 = \frac{1}{2}$, $\zeta = 1$; and $\lambda_2 = \frac{1}{2}$, $\zeta = \frac{1}{2}$. The latter case is interesting in that the $\lambda_0 = 0 \rightarrow \lambda_i = 1$ (λ_i is the angular momentum of the photoelectron) electric dipole matrix element vanishes [see Eq. (15a)] for this value of ζ, and the leading term is that for $\lambda_0 = 2$, $l_0 = 2$, which is quadratic in λ_2. Accentuation of the terms coming from higher-order l_i values increases the oscillatory nature of the angular distribution, since $|l_i - \lambda_i| \leq L \leq (l_i + \lambda_i)$ (l_i, λ_i are angular momenta for the photoelectron), and contributions from Legendre polynomials P_L of higher order become increasingly important, making possible L number of nodes in the distribution.

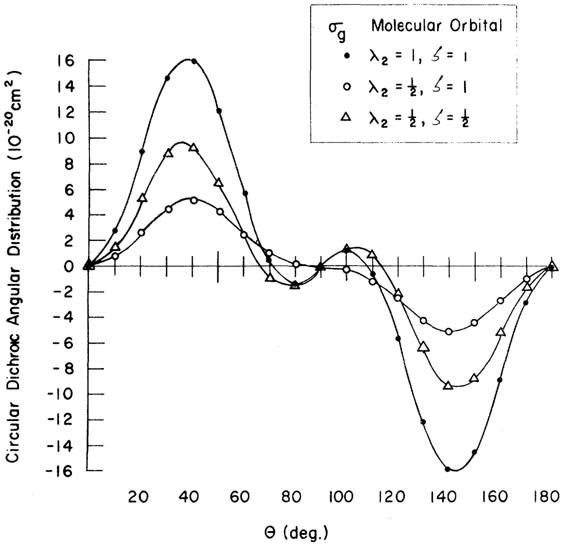

FIG. 2. Circular dichroic angular distribution for a molecular orbital of σ_g symmetry.

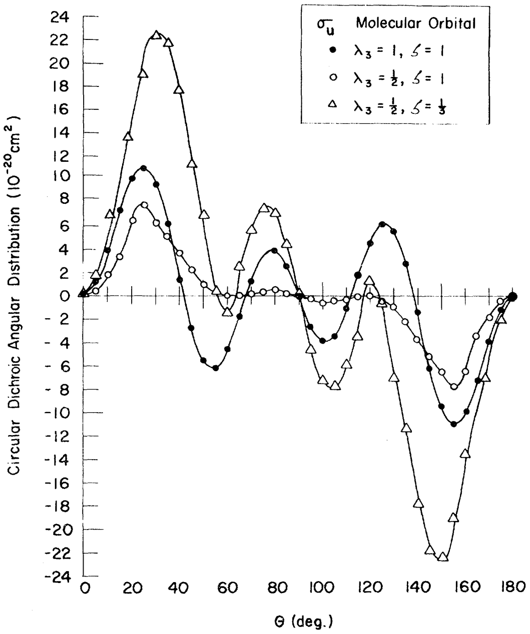

FIG. 3. Circular dichroic angular distribution for a molecular orbital of σ_u symmetry.

Figure 3 is a similar plot for the σ_u molecular orbital. There is greater nodal structure owing to contributions of higher L. Here, however, the leading term of the molecular orbital, namely that for $l_0 = 1$, has a nonzero magnetic dipole contribution, so that the leading term in the angular distribution is not linear in λ_3, providing a less sensitive dependence on anisotropy parameter than in the σ_g case. However, the nodal points in the matrix elements [in Eqs. (15)], if they could be found experimentally, would provide an enhancement of effects due to molecular anisotropy. The first such point occurs at $\zeta = \frac{1}{2}$, where the $l_0 = 1$ magnetic dipole term vanishes, giving an angular distribution whose leading contribution is linear in λ_3. The second occurs at $\zeta = \frac{1}{3}$, where the $\lambda_0 = 1 \rightarrow \lambda_i = 2$ electric dipole term vanishes. This also leads to an angular distribution whose leading contribution is linear in λ_3, since the $\lambda_0 = 1 \rightarrow \lambda_i = 0$ term is zero by the $m_j = m_0 \pm 1$ selection rule.

V. CONCLUSIONS

We have presented formulas for the angular distribution difference for left or right circularly polarized light. We have emphasized that these measurements provide a probe of molecular structure, which can be under certain circumstances more sensitive than that provided by the ordinary angular distribution for the electric dipole process. Also we have stressed another new feature of the measurement, namely that the electric-dipole-magnetic-dipole interference provides a test of time-reversal invariance of the wave function for the ionized system. To our knowledge, no such test by a *molecular* process has been investigated. We hope that this theoretical analysis will stimulate experimental work and further theoretical work.

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