Calculation of a Mirror Asymmetric Effect in Electron Scattering from Chiral Targets

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It is calculated that an unpolarized electron beam elastically scattered from a chiral molecule will acquire a net helicity of $H(s) \sim \eta(\alpha Z)^2$, where $\alpha = e^2/\hbar c$, Z is the atomic number of the heaviest atom in an asymmetric environment in the molecule, and η is a molecular asymmetry factor. For a carbon center ($Z = 6$), η is estimated to be 10^{-2} so that $H(s) \sim 10^{-5}$, which would account for its lack of observation in a recent experiment sensitive to $H(s) > 5\times10^{-3}$. The calculation of other asymmetric electron (and positron)–chiral molecule interactions is discussed.

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The passage of light through a medium composed of an excess of chiral molecules of definite handedness gives rise to a number of well-known chiro-optical effects such as optical rotation and circular dichroism. More recently the induction of a circular polarization in light that has undergone Rayleigh and Raman scattering from chiral substances, and preferential scattering of left- versus right-circularly polarized light from such substances, have been calculated and/or observed.[1] The electromagnetic interaction is parity conserving, and consequently all of the above asymmetric effects are due to the lack of inversion symmetry of the target.

On the basis of symmetry we expect the same effects when any particle with spin interacts with a chiral molecule. Calculations of such effects in the interaction of polarized neutrons with both the nuclei[2] and the electrons[3] of optically active materials [called chiral neutron scattering (CNS) in the literature] have recently been made. Unfortunately the predicted effects were found to be too small to be observed by current techniques. The importance of this initial work lies in its exploration of a new method for investigation of the details of the electronic and nuclear structure of chiral molecules. Similar mirror-asymmetric effects also occur because of parity nonconserving neutron-nucleon and neutron-electron terms in the Hamiltonian and in fact neutron spin rotation in achiral media (^{117}Sn and natural Sn) has recently been observed.[4]

In our article we present a dynamical calculation of the counterpart for electrons of a chiro-optical process [we call such processes, in general, chiral electron scattering (CES)]. Specifically, we calculate the helicity induced in an initially unpolarized electron beam after elastic scattering from an optically active medium. If one assumes that the parity nonconserving electron-nucleon weak interaction may be neglected, this process would be forbidden if the target molecules were in a parity eigenstate since the electromagnetic interaction conserves parity. It is the counterpart for electrons of the circular polarization that is induced when unpolarized light undergoes Rayleigh scattering from chiral targets.

This calculation and similar CES calculations which can now be made based on this work are of current interest for the following reasons. (1) As with CNS, CES will provide a new tool for studying the electronic structure of chiral molecules. It should, in fact, prove to be more useful than CNS since the predicted effects are larger, as will be discussed. (2) An experiment has recently been performed to search for the helicity [$H(s)$] of a 25-eV electron beam scattered at angles of 40°–70° from the L and D isomers of camphor and the limit $H(s) < 5\times10^{-3}$ has been reported.[5] This experiment was suggested by an analysis of Farago[6] which predicted the existence of $H(s)$ from symmetry arguments, but which could not predict the size of $H(s)$ since dynamics were not considered. We show in this article that for the conditions reported in Ref. 5, $H(s)$ is expected to be of order 10^{-5}! (3) New CES experiments are now underway[7] to search for the electron counterparts of optical rotation (electron-spin rotation on scattering from chiral molecules) and circular dichroism (preferential absorption of longitudinally polarized electrons by chiral systems). Farago[7] has expanded his formalism to include these effects, but again without an actual determination of their size, and consequently quantitative calculations are again necessary. We are now extending our work to provide calculations of these and other CES processes. (4) An understanding of the detailed structure of CES in chiral molecules is crucial in attempts to arrive at a nonstochastic causal mechanism for the origin of optical activity in living organisms.[8,9] This application will be discussed further in the last section of the article.

The dynamical model of a chiral molecule used to calculate $H(s)$ is called the bound helical electron model.[10] According to this model the predominant contribution to $H(s)$ comes from the perturbation of the electron bound state by the spin-orbit interaction of the bound electrons moving in the electric field of the molecular core. The same perturbation also creates a helicity density (i.e., helicity per unit volume) in a chiral molecule and gives the model features which are reminiscent of the qualitative "helical electron gas model."[11] Further details may be found in Ref. 10.

The major result of the bound helical electron model used here is that a molecular spin oribtal, given by $|\psi_s{}^0\rangle = \varphi_0 |m_s\rangle$ in the absence of spin-orbit coupling, is perturbed by the spin-orbit coupling operator [$V^{SO} = (\frac{1}{4})\alpha^2(\vec{E}\times\vec{p})\cdot\vec{\sigma} = \vec{\Lambda}\cdot\vec{\sigma}$ where $\vec{E}$ and $\vec{p}$ are the molecular electric field and electron momentum, respectively, and atomic units $e = \hbar = c = 1$ are used] to give the result

$$|\psi_s\rangle = (\varphi_0 + s\textstyle\sum_n \epsilon_n{}^0 \varphi_n)|m_s\rangle + \sum_n \epsilon_n{}^s \varphi_n |\overline{m}_s\rangle. \quad (1)$$

Here m_s is the spin projection quantum number, $s \equiv 2m_s$, $\overline{m}_s \equiv -m_s$, and $\epsilon_n{}^0$, $\epsilon_n{}^s$ are defined by the relations $\vec{\epsilon}_n = (E_0 - E_n)^{-1}\langle\varphi_n|\vec{\Lambda}|\varphi_0\rangle$, $\epsilon_n{}^0 = \vec{\epsilon}_n \cdot \hat{e}_3$, and $\epsilon_n{}^{\pm 1} = \vec{\epsilon}_n \cdot (\hat{e}_1 \pm i\hat{e}_2)$ with orthogonal unit vectors $\hat{e}_i$. The spin is quantized along $\hat{e}_3$. The φ_n are the excited orbitals mixed into the occupied orbital φ_0 by V^{SO}. The ϵ's are seen to depend on the spin-orbit coupling in the electronic bound state and are known to be roughly of order $(\alpha Z)^2$ a.u. where α is the fine-structure constant and Z is the nuclear charge of a dominant heavy atom.[10] For chiral molecules, the unequal perturbation of the spin orbitals in Eq. (1) combined with the asymmetry of the molecular orbitals φ_0 and φ_n give rise to both the net helicity density for the molecular electrons and the CES phenomena.

Using Eq. (1) we can calculate an expression for the 2×2 scattering matrix for the case of elastic scattering of an electron from a closed-shell chiral molecule and then estimate $H(s)$. In order to obtain an order-of-magnitude estimate, it is sufficient to approximate the molecular ground-state wave function by a two-electron state which is a closed-shell singlet in the absence of spin-orbit coupling. In the independent-particle approximation the unperturbed state is given by

$$\begin{aligned} |\Psi^0(1,2)\rangle &= \frac{1}{\sqrt{2}}|\psi_+{}^0(1)\psi_-{}^0(2) - \psi_-{}^0(1)\psi_+{}^0\rangle \\ &= \varphi_0(1)\varphi_0(2)\frac{|\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle}{\sqrt{2}}, \end{aligned} \quad (2)$$

where α and β denote the $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ spin states, respectively. If V^{SO} is now turned on, the $|\psi_s{}^0\rangle$ in Eq. (2) change into the perturbed orbitals $|\psi_s\rangle$ of Eq. (1). This procedure is equivalent to mixing into the two-electron singlet ground state (2) all excited triplet states which can be obtained by single excitations from the occupied molecular orbital φ_0. If we denote the perturbed two-electron state by $\Psi(1,2)$, the transition matrix elements are given by

$$\hat{t}_{s'}{}^s = t_{s'}{}^s(d) - 2t_{s'}{}^s(\mathrm{ex}), \quad (3)$$

where the direct and exchange terms are given by

$$t_{s'}{}^s(d) = \langle\theta_{k_2 m_s'}{}^{(-)}(0)\Psi^{(-)}(1,2)|V^\alpha|\theta_{k_1 m_s}(0)\Psi(1,2)\rangle, \quad (4a)$$

$$t_{s'}{}^s(\mathrm{ex}) = \langle\theta_{k_2 m_s'}{}^{(-)}(1)\Psi^{(-)}(0,2)|V^\alpha|\theta_{k_1 m_s}(0)\Psi(1,2)\rangle. \quad (4b)$$

Here the (−) refers to the "prior" form,[12] the electron label 0 refers to the incident electron and the labels 1 and 2 refer to the bound molecular electrons in the initial state. In the asymptotic limit the functions $\theta_{k_1 m_s}$ and $\theta_{k_2 m_s'}{}^{(-)}$ describe the incident electron with momentum $\vec{k}_1$ and spin m_s and the scattered electron with momentum $\vec{k}_2$ and spin m_s', respectively. The potential energy V^α gives the interaction between the incident electron and the molecule; in the bound helical electron model it is entirely Coulombic. The spins are quantized along $\hat{k}_1$, the direction of the incident beam. It should be pointed out that the existence of the exchange terms in Eqs. (3) and (4) is essential for nonvanishing $H(s)$ in first order; the induced helicity in a beam of incident *positrons* vanishes in first order because of the absence of these exchange terms. Similarly, neutron optical activity has been found[2,3] to be at least a second-order effect, and as a consequence is much smaller than the corresponding electron case.

The order of magnitude of the scattering matrix elements can be estimated by means of the Born approximation in which the functions $\theta_{k_2 m_s'}^{(-)}$ are approximated by plane waves and the distortion of the molecular bound state Ψ by the scattered electron is neglected. With this approximation, the on-shell T matrix may be written to first order in V^{SO} as

$$T=\begin{pmatrix} f+h_3 & h_1-ih_2 \\ h_1+ih_2 & f-h_3 \end{pmatrix}, \tag{5}$$

where

$$f=\langle \vec{k}_2\varphi_0\varphi_0|V^{\alpha}|\vec{k}_1\varphi_0\varphi_0\rangle-\langle\varphi_0\vec{k}_2\varphi_0|V^{\alpha}|\vec{k}_1\varphi_0\varphi_0\rangle \tag{6a}$$

$$h_i=\sum_n \epsilon_{ni}\{\langle\varphi_n\vec{k}_2\varphi_0|V^{\alpha}|\vec{k}_1\varphi_0\varphi_0\rangle-\langle\varphi_0\vec{k}_2\varphi_0|V^{\alpha}|\vec{k}_1\varphi_n\varphi_0\rangle\}, \tag{6b}$$

where $\epsilon_{ni}=\vec{\epsilon}_n\cdot\hat{e}_i$, with $\hat{e}_3=\hat{k}_1$. The sequence of electron labels in the bras and kets is understood to be always 0, 1, 2 and from left to right, i.e., $|\vec{k}_1\varphi_0\varphi_0\rangle\equiv|\vec{k}_1(0)\varphi_0(1)\varphi_0(2)\rangle$, etc. The vectors $\vec{k}_1$ and $\vec{k}_2$ denote pure momentum states. It is evident that f is of the order of magnitude of the Coulomb interaction between the incident electron and the target molecule, i.e., the size of an atomic unit, whereas the h_i's are first order in V^{SO} ($[\alpha Z]^2$ a.u.). In a description which also accurately treats the component of the induced polarization perpendicular to the scattering plane the off-diagonal T-matrix elements $h_1\pm ih_2$ must include the spin-orbit interaction between the incident electron and the target. This interaction is not explicity included here because it does not contribute to $H(s)$ in first order.

We can now calculate $H(s)$ by noting that the cross sections for the scattering of an initially unpolarized electron into a state with final polarization $\vec{P}$ parallel or antiparallel to $\vec{k}_2$ are proportional to $(|\hat{t}_+{}^+|^2+|\hat{t}_+{}^-|^2)$ or $(|\hat{t}_-{}^-|^2+|\hat{t}_-{}^+|^2)$, respectively. Neglecting $|\hat{t}_+{}^-|^2$ and $|\hat{t}_-{}^+|^2$, which are second order in V^{SO} $[|\hat{t}_+{}^-|^2/|\hat{t}_+{}^+|^2\sim(\alpha Z)^4$, etc.$]$ we then obtain (correct to order h_i/f)

$$\begin{aligned} H(s)&=(|\hat{t}_+{}^+|^2-|\hat{t}_-{}^-|^2)/(|\hat{t}_+{}^+|^2+|\hat{t}_-{}^-|^2)\\ &=2\,\mathrm{Re}(h_3/f). \end{aligned} \tag{7}$$

For a collection of randomly oriented molecules, the absolute squares of the T-matrix elements appearing above should be averaged over all molecular orientations. For *achiral* (symmetric) molecules it can be easily shown from conservation of parity and angular momentum that the resulting averages satisfy the equality $|\hat{t}_{s'}{}^{s}|_{\mathrm{av}}{}^2=|\hat{t}_{-s'}{}^{-s}|_{\mathrm{av}}{}^2$ and hence that $H(s)=0$ as expected.

Substituting h_3 and f [Eq. (6)] into Eq. (7) gives the result that for chiral molecules $H(s)$ is formally of order $|\epsilon_n{}^0|\sim(\alpha Z)^2\simeq 2\times10^{-3}$ ($Z=6$). We expect, however, that the actual value of $H(s)$ will be reduced by an asymmetry factor (η) which depends on the degree of dissymmetry in the structure of the molecule. An approximate calculation of η for twisted ethylene,[10,13] the simplest dissymmetric molecule for which a wave function has been published, suggests that $\eta\sim10^{-2}$ to 10^{-3}, which may be typical, although values outside this range cannot be ruled out until more extensive calculations have been performed. Taking $\eta\sim10^{-2}$ in the present case gives a nominal estimate of $H(s)$ for a carbon center;

$$H(s)\simeq\eta(\alpha Z)^2\sim10^{-5}. \tag{8}$$

This result in all likelihood accounts for the lack of observation of $H(s)$ noted in Ref. 5 where a camphor ($C_{10}H_{16}O$) target was used and the minimum detectable value of $H(s)$ was 5×10^{-3}. We suggest the use of target molecules with higher Z chiral centers. Such targets exploit the Z^2 increase in $H(s)$ [Eq. (8)] and should also show maxima in $H(s)$ near minima in f (variation in scattering angle and incident electron energy is implied) as occurs in the well-known transverse polarization effects in low-energy electron scattering. In fact, the possible presence of such transverse polarization complicates the problem of determining $H(s)$ experimentally,[5] so that an optimization procedure is indicated.

We note finally that the dynamical model of a chiral molecule developed in this article may also be used to investigate asymmetric inelastic electron and positron interactions with such molecules. In fact, we have already calculated[10,14] that the asymmetry in triplet positronium formation in L versus D isomers for positrons of unit helicity which form positronium is of order $\eta(\alpha Z)^2$. Experiments to detect this asymmetry are in progress.[14-16] In addition we have shown theoretically[10] that the difference in the electron ionization rates for L versus D isomers and incident electrons of unit helicity and energy about equal to the molecular ionization potential is $\eta(\alpha Z)^2$. The difference is of order $10^{-5}\eta(\alpha Z)^2$

$\simeq 2\times 10^{-8}\eta$ for the 100-keV electrons typical of β decay. This last result is directly relevant to the question of the origin of optical activity in living organisms since, if β-decay electrons are the cause of optical activity (the Vester-Ulbricht hypothesis),[17,18] the specific mechanism involved is most likely a slight asymmetric ionization or excitation of the D isomer with respect to the L isomer, followed by chemical and biological amplification. The small value of the difference indicated above is discussed by Gidley *et al.*[14] in the context of recent experiments to detect such effects.

In summary we have made a quantitative calculation of a CES process and we are now extending this initial work to other CES phenomena. Features of inelastic electron and positron interactions with chiral targets can also be investigated by the techniques described in this article.

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Experimental Detection of HOC$^+$ by Microwave Spectroscopy

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Microwave spectroscopy has been employed to make the first definite experimental observation of the ionic metastable isomer HOC$^+$. Its $J=0\rightarrow 1$ transition and those of its ^{18}O and ^{13}C isotopic variants have been detected in laboratory dc glow discharges. Extensive chemical, spectroscopic, and theoretical evidence permits conclusive identification of these spectra. Comparison of the substitution bond lengths [r_s (CO) = 1.1595 Å and r_s (OH) = 0.9342 Å] to *ab initio* structures strongly supports a large-amplitude (low-frequency) bending vibration.

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While HCN, HNC, HN$_2$$^+$, and HCO$^+$ have been extensively studied by molecular radioastronomy[1,2] and laboratory high-resolution spectroscopy,[2-5] the obvious missing member of this isoelectronic series of molecules, HOC$^+$, has never been detected with certainty in either space or laboratory experiments. The first four molecules have been shown to be widely distributed in the interstellar medium and extremely important as participants in its chemistry and useful as radioastronomical probes of its physical conditions.[1] Furthermore, their molecular structures and other properties as determined from high-resolution spectroscopy have provided very satisfying tests