Atomic and Molecular Parity Nonconservation and Sum Frequency Generation Solutions to the Ozma Problem†

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Two Ozma problems are defined. Parity nonconservation is necessary for their solutions. Both problems may be solved by β decay or atomic optical activity. Atomic and molecular sum frequency generation is chosen, as it supplies rich methods of effecting "gedanken" solutions to the Ozma problems. A new method of measuring a parameter manifesting molecular parity violations is advanced.

I. Introduction

Martin Gardner coined the phrase "Ozma problem" in order to describe how two advanced civilizations could agree on a definition of "left" and "right" without the ability to transmit chiral information.[1] They cannot in the absence of parity nonconservation. Gardner and Feynman showed how the Ozma problem could be solved using parity violating aspects of β decay.[1,2] One of the authors used atomic optical rotation as a method of solution to the problem.[3]

In this paper, we shall define and solve two Ozma problems. To reduce imagery to a minimum, we imagine the following scenario, which is taken from *The Wizard of Oz*.[4] A map of Oz reveals that it is surrounded by the "Deadly Desert". This desert is assumed to be chirally opaque. In The Emerald City of Oz, the Wizard of Oz may be seen placing a heart into the chest of the Tin Woodman (see Figure 1). The Wizard also has a laboratory which analyzes amino acids. We assume the Wizard of Oz is not from Omaha, Nebraska but from Oz. In addition, Dorothy and Toto are not present. Clearly, the presence of creatures from earth would violate the chiral opacity condition. On the earth side of the Deadly Desert, an earthly wizard is performing the same experiments.

Given the above scenario, the Ozma problems are the following:

(a) Can the two wizards communicate such that the tin woodmen will have their hearts placed on the same (earth left) side?

(b) Suppose both wizards have amino acids which are chemically identical and, of course, chiral. How can the wizards unambiguously transmit the handedness of their amino acid to each other?

The microdevice built by Skelley et al. is our inspiration for the second Ozma problem.[5] This apparatus is designed to fit on a Martian rover. Its purpose is to measure the net amino acid chirality on Mars. It is a simple leap of the imagination to go from Mars to Oz!

It is obvious that the solution to Ozma problem (a) using β decay or atomic optical activity provides the solution to Ozma problem (b). We shall, however, answer these questions using sum frequency generation (SFG) and parity nonconservation (PNC). SFG provides a new way of exhibiting the interplay of symmetry and parity nonconservation. Indeed, the solution to Ozma problem (b) points the way to obtaining, linearly, a parameter which is a manifestation of parity violations in a chiral molecule.

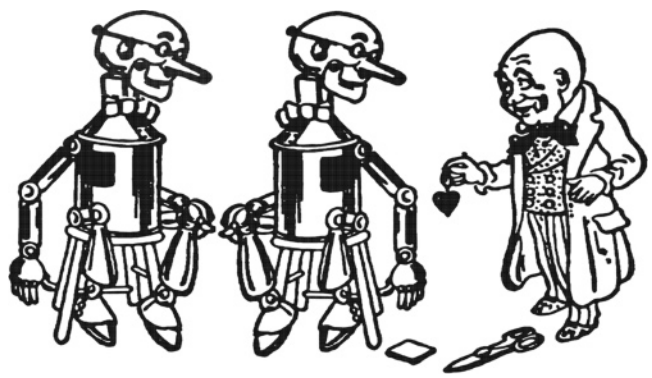

Figure 1. The Wizard of Oz needs to decide in which side of the Tin Woodman's chest to put the heart. Image adapted from the original drawing by W. W. Denslow in *The Wizard of Oz*.

We begin by presenting a brief review of SFG. We then describe how PNC modifies SFG and use PNC-modified SFG to answer questions (a) and (b). In an appendix, we exhibit another way PNC-modified SFG can measure both chirality and handedness and provide a positive solution to question (a). We end the paper with a "pedagogical" Feynman joke.

II. A Brief Introduction to Sum Frequency Generation (SFG)

That sum frequency generation in three-dimensional isotropic chiral media is not zero was proposed by Giordmaine in 1965.[6] The process may be described as follows: In an isotropic, homogeneous medium consisting of N identical atoms or molecules, two impinging linearly polarized beams of wave vectors and polarizations, $\vec{k}_1,\vec{\epsilon}_1$ and $\vec{k}_2,\vec{\epsilon}_2$, result in an outgoing beam, $\vec{k}_3,\vec{\epsilon}_3$.

In the absence of external fields, and neglecting higher multipoles, the intensity of the outgoing beam for a coherent experiment takes the form

$$I(\omega_3) \propto (\vec{\epsilon}_3\cdot\vec{\epsilon}_2 \times \vec{\epsilon}_1)^2|\chi^{(2)}_{\rm chiral}(\omega_1,\omega_2)|^2 \qquad (1)$$

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$\chi^{(2)}_{\text{chiral}}(\omega_1,\omega_2)$ is a (complex) pseudoscalar. In Appendix A, we show that $\chi^{(2)}_{\text{chiral}}(\omega_1,\omega_2)$ has the following properties:

$$\chi^{(2)}_{\text{chiral}}(\omega_1,\omega_2) = -\chi^{(2)}_{\text{chiral}}(\omega_2,\omega_1) \tag{2}$$

and dropping the frequency dependence,

$$\chi^{(2)}_{\text{chiral}}(\text{L}) = -\chi^{(2)}_{\text{chiral}}(\text{R}) \tag{3}$$

where L and R correspond to left-handed (L) and right-handed (R) molecules. $\chi^{(2)}_{\text{chiral}}$ vanishes for achiral molecules, atoms, and racemic mixtures. It was not until 2000 that Giordmaine's prediction was experimentally realized.[7]

The profound thing to notice is that SFG, as described, measures the chirality of a molecule but not whether the molecule is L or R. Hence, unlike linear measures of chirality, SFG a priori appears useless as a way to answer Ozma problems. There are a number of ways to measure the sign of $\chi^{(2)}_{\text{chiral}}$. The knowledge of the sign is a necessary but not sufficient condition for the determination of handedness. We assume that the additional considerations which relate the sign of $\chi^{(2)}_{\text{chiral}}$ to handedness are available.

We now describe three experiments which obtain the sign of $\chi^{(2)}_{\text{chiral}}$. All of them have been carried out. All are germane to the solutions of the Ozma problems. Two of the experiments involve adding an achiral response to the chiral susceptibility. One method introduces an external electric field.[8] The other uses polarization interferometry in order to add susceptibilities linear in magnetic dipole and electric quadrupole matrix elements.[7] The third method introduces a nonlinear, noncentrosymmetric crystal as a "local oscillator".[9]

III. PNC and SFG

The manifestations of PNC in atoms and chiral molecules have been reviewed many times with the exception of SFG.[10−12] Exactly like atomic optical rotation, there is atomic SFG. Even on resonance, the $\chi^{(2)}$ of an atom is tiny and has never been measured. In the absence of interferometry, SFG would measure, for example, thallium (Tl)

$$I_{\text{Tl}} \sim |\chi^{(2)}_{\text{Tl}}|^2 \tag{4}$$

$\chi^{(2)}_{\text{Tl}}$ is the SFG response of Tl, whose explicit form is irrelevant to what follows. The important point is that $\chi^{(2)}_{\text{Tl}}$, for each pair of input frequencies, has a given sign. This is just like the optical rotation, θ_{Tl}. Because these quantities are manifestations of PNC, the opposite signs do not exist. However, like θ_{Tl}, different pairs of frequencies may give rise to a $\chi^{(2)}_{\text{Tl}}$ value which is opposite (or the same) in sign to any other pair of frequencies. $\chi^{(2)}_{\text{Tl}}$ is universal in sign, for any pair of frequencies. We shall use this point to solve the Ozma problems. We now turn to chiral molecules.

It is readily seen that $\chi^{(2)}_{\text{chiral}}$ is a pseudoscalar. The presence of PNC is, crudely, akin to adding a static electric field whose sign is fixed. As mentioned in the last section, a weak electric field generates an achiral response which is added to $\chi^{(2)}_{\text{chiral}}$. PNC is manifested in SFG in the same way. An achiral, or scalar, susceptibility is added to $\chi^{(2)}_{\text{chiral}}$. The response is universal. To be precise, we define $\chi^{(2)}(\text{L})$ and $\chi^{(2)}(\text{R})$ as

$$\chi^{(2)}(\text{L}) \equiv \chi^{(2)}_{\text{chiral}} + \Delta \tag{5}$$

$$\chi^{(2)}(\text{R}) \equiv -\chi^{(2)}_{\text{chiral}} + \Delta \tag{6}$$

where Δ is the scalar response and is the same on earth and Oz.

We now answer the second Ozma problem in two ways. The first way uses $\chi^{(2)}_{\text{Tl}}$. The second method uses Δ. That is, one way uses Tl as the source of PNC, the other uses the PNC correction to the $\chi^{(2)}_{\text{chiral}}$ of an amino acid. In both experiments, the three polarizations are mutually perpendicular,

$$\vec{\epsilon}_3 \cdot \vec{\epsilon}_2 \times \vec{\epsilon}_1 = \pm 1 \tag{7}$$

In this configuration, achiral and external field contributions to SFG vanish to first order. In the first experiment, we have a gas of Tl atoms that plays the role of a chiral crystal. On earth, we carry out the experiment with $\chi^{(2)}(\text{L})$, say, and subtract out the amino acid SFG in the absence of $\chi^{(2)}_{\text{Tl}}$. The result is

$$I_{\text{L+Tl}} - I_{\text{L}} \sim 2\text{Re}\chi^{(2)}_{\text{Tl}}\chi^{(2)*}_{\text{chiral}} \tag{8}$$

Suppose $\chi^{(2)}_{\text{Tl}} > 0$ and Re $\chi^{(2)*}_{\text{chiral}} > 0$. We send Oz the result of our experiment which is that the net intensity is greater than 0. If Oz's net intensity is greater than zero, then their amino acid is the same as ours, even if they call it R. If the net intensity is less than zero, then their amino acid is equivalent to our R, even if they call it L. Hence, we have determined the handedness of their amino acid and they have determined ours.

Perhaps there is no Tl available; then both amino acid enantiomers must be used. On earth, assuming $N_{\text{L}} = N_{\text{R}}$, we obtain for SFG intensities

$$I_{\text{L}} \sim |\chi^{(2)}_{\text{chiral}}|^2 + 2\ \text{Re}\ \chi^{(2)*}_{\text{chiral}}\Delta + \text{O}(\Delta^2) \tag{9}$$

$$I_{\text{R}} \sim |\chi^{(2)}_{\text{chiral}}|^2 - 2\ \text{Re}\ \chi^{(2)*}_{\text{chiral}}\Delta + \text{O}(\Delta^2) \tag{10}$$

Depending on the relative signs of Δ and $\chi^{(2)}_{\text{chiral}}$, I_{L} will either be greater or less than I_{R}. The same obtains on Oz, though what is defined as L and R may be reversed. The second Ozma problem is solved.

Interestingly, SFG provides a linear measure of Δ multiplied by a larger quantity, Re $\chi^{(2)}_{\text{chiral}}$. This result is unlike other proposed measurements of PNC which are linear in the parity violating potential.[11−14] Quantitatively, we see that

$$I_{\text{L}} - I_{\text{R}} \propto 4\ \text{Re}\ \chi^{(2)*}_{\text{chiral}}\Delta \tag{11}$$

We now solve the first Ozma problem. In the absence of Tl, we will use one of the now agreed upon amino acid enantiomers. We assume that the Wizard of Oz is to place the Tin Woodman of Oz's heart on earth's definition of the left side using $\chi^{(2)}(\text{L})$. Once both wizards agree on the handedness of an amino acid, many methods are available to solve the first Ozma problem. One is using optical activity, another is to build a model. We, however, measure all aspects of chirality using SFG. With that caveat in mind, we use SFG to solve the first Ozma problem.

Both wizards construct apparatus which we describe using the usual terminology of SFG. The polarizations are defined relative to the plane of the wave vectors $\vec{k}_1$ and $\vec{k}_2$ (and $\vec{k}_3$ by phase matching). Electric field vectors parallel to the plane are defined as $\vec{P}$, and those perpendicular to the plane are defined as $\vec{S}$. We shall use an external $\vec{E}$ field to supply an extra vector which adds an achiral response to the SFG amplitude.

The plane of wave vectors is taken to be perpendicular to the standing bodies of wizards and tin woodmen. $\vec{k}_3$ is in the direction of the tin woodmen. The polarizations are $\vec{S}_1$, $\vec{P}_2$, and

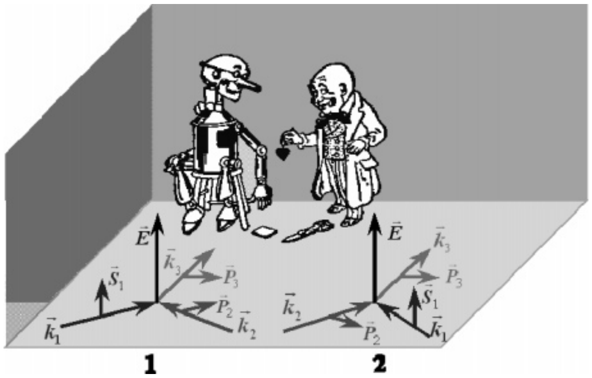

Figure 2. Experimental configurations 1 and 2. The electric field, $\vec{E}$, is normal to the incident plane defined by the wave vectors $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$. The polarizations for the three waves are $\vec{S}_1$, $\vec{P}_2$, and $\vec{P}_3$, respectively, as defined in each configuration. Image adapted from the original drawing by W. W. Denslow in *The Wizard of Oz*.

$\vec{P}_3$ with $\vec{E}$ perpendicular to the plane of the wave vectors and parallel to $\vec{S}_1$. We shall consider two configurations on earth, as shown in Figure 2.

Under each experimental configuration, sum frequency intensity is[8]

$$I \propto |\vec{S}_1 \cdot \vec{P}_2 \times \vec{P}_3 \chi^{(2)}(\mathrm{L}) + (\vec{S}_1 \cdot \vec{E})\vec{P}_2 \cdot \vec{P}_3 \chi^{(3)}|^2 \qquad (12)$$

where we have assumed the amino acid is L and $\chi^{(3)}$ is the achiral response to the $\vec{E}$ field. The two configurations reflect the flipping of wave vectors $\vec{k}_1$ and $\vec{k}_2$. Note that $\vec{P}_2$ and $\vec{P}_3$, as defined in Figure 2, have different directions in configurations 1 and 2. We may write I_1 and I_2 in terms of the angle, θ, between $\vec{P}_2$ and $\vec{P}_3$:

$$I_1 \propto |\sin\theta \chi^{(2)}(\mathrm{L}) + E\cos\theta \chi^{(3)}|^2 \qquad (13)$$

$$I_2 \propto |-\sin\theta \chi^{(2)}(\mathrm{L}) + E\cos\theta \chi^{(3)}|^2 \qquad (14)$$

Depending on the signs of $\chi^{(2)}(\mathrm{L})$ and $\chi^{(3)}$, I_1 will be greater or less than I_2. Since the amino acid used by the Wizard of Oz has been determined to be L, then the wizards can carry out the same two experiments. Because the wave vectors have different frequencies, there will be an unambiguous positioning of left and right. Hence, the Wizard of Oz will be able to place a heart in the Tin Woodman's left side—the same side as the Tin Woodman on earth. The first Ozma problem is solved using SFG. We note that the same result obtains with Tl, rather than the L-amino acid.

Earlier, we described three methods for obtaining the sign of $\chi^{(2)}$. We showed how one of the methods, the inclusion of an external electric field, allowed the first Ozma problem to be solved. In Appendix B, we carry out a complete analysis of a second method that provides an unambiguous solution to the first Ozma problem.

IV. Conclusions

In this paper, we have proposed two Ozma problems using imagery from *The Wizard of Oz*. We emphasize that there are many ways to solve the Ozma problems. We have solved both using SFG. The second Ozma problem is, of course, meaningless in the case of atoms. There are two ways of solving the second Ozma problem. A byproduct is a new way of measuring, linearly, a PNC parameter times a larger quantity.

Our discussions, at least partly, depend on equivalent, up to a mirror image, laboratory configurations. We can well imagine experiments taking place in a spaceship. The results will be the same as long as all relative positions are unchanged.

Our goal is to provide new "gedanken" solutions to the Ozma problems. We believe that we have succeeded. We have not supplied orders of magnitude of the various responses. They are certainly tiny. As far as we know, there have been no calculations of atomic SFG, or the PNC contribution to the SFG of chiral molecules.

Everything in our analysis depends on Oz being made of matter rather than antimatter. Our scenario fails in the latter case, as described by a pedagogical version of a Feynman joke:[2]

Suppose two tin woodmen meet. One is the mirror image of the other.

(i) If P (parity) is conserved and they attempt to shake hands, allow them to do it. Nothing will happen.

(ii) If P is not conserved, the two tin woodmen will not be strict mirror images.

(iii) If P and C (charge conjugation) are not conserved but PC is conserved and one tin woodman puts out his left hand, run!

Acknowledgment. R.A.H. wishes to dedicate this "gedanken" science to his great friend of almost 40 years, Bob Silbey. We thank Prof. D. Budker and Dr. V. Ostroverkhov for many insightful conversations. We thank Prof. J. Cina for helpful suggestions as to how the manuscript may be improved. We thank Dr. P. Fischer for exposing a flaw in one of our arguments. N.J. thanks Prof. Y. R. Shen for helpful discussions and support (U.S. Department of Energy Contract No. DE-AC03-76SF00098). R.A.H. thanks Christine Harris for her imagery.

Appendix A

(i) The amplitude of chiral molecules is

$$A = \vec{\epsilon}_3 \cdot \vec{\epsilon}_2 \times \vec{\epsilon}_1 \chi^{(2)}_{\mathrm{chiral}}(\omega_1,\omega_2) \qquad (\text{a-1})$$

We may just as well interchange labels 1 and 2. A is now

$$A' = \vec{\epsilon}_3 \cdot \vec{\epsilon}_1 \times \vec{\epsilon}_2 \chi^{(2)}_{\mathrm{chiral}}(\omega_2,\omega_1) \qquad (\text{a-2})$$

However, $A = A'$; hence,

$$-\vec{\epsilon}_3 \cdot \vec{\epsilon}_2 \times \vec{\epsilon}_1 \chi^{(2)}_{\mathrm{chiral}}(\omega_2,\omega_1) = \vec{\epsilon}_3 \cdot \vec{\epsilon}_2 \times \vec{\epsilon}_1 \chi^{(2)}_{\mathrm{chiral}}(\omega_1,\omega_2) \qquad (\text{a-3})$$

Thus,

$$\chi^{(2)}_{\mathrm{chiral}}(\omega_1,\omega_2) = -\chi^{(2)}_{\mathrm{chiral}}(\omega_2,\omega_1) \qquad (\text{a-4})$$

(ii) We now drop "chiral" and the frequency labels and put in, for example, L

$$A_{\mathrm{L}} = (\vec{\epsilon}_3 \cdot \vec{\epsilon}_1 \times \vec{\epsilon}_2)\chi^{(2)}(\mathrm{L}) \qquad (\text{a-5})$$

Now, under parity,

$$A_{\mathrm{L}} \xrightarrow{P} -(\vec{\epsilon}_3 \cdot \vec{\epsilon}_1 \times \vec{\epsilon}_2)\chi^{(2)}(\mathrm{R}) \equiv A^P_{\mathrm{L}} \qquad (\text{a-6})$$

However, conservation of parity states that

$$A^P_{\mathrm{L}} \equiv A_{\mathrm{L}} \qquad (\text{a-7})$$

Thus,

$$\chi^{(2)}(\mathrm{L}) = -\chi^{(2)}(\mathrm{R}) \qquad (\text{a-8})$$

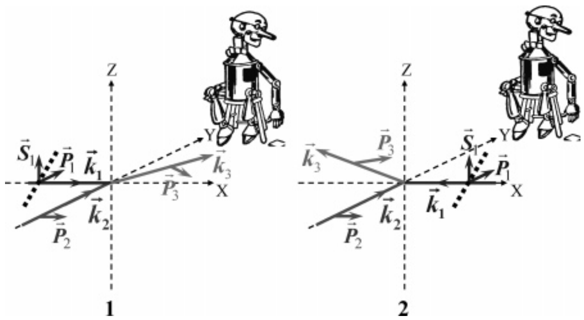

Figure 3. Two experimental configurations (1 and 2) for wave vectors $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$, with the latter two waves having P polarizations ($\vec{P}_2$ and $\vec{P}_3$). The polarization for $\vec{k}_1$ (thick dotted lines) is set to be 45° away from $\vec{S}_1$, with its upper part closer to the Tin Woodman than its bottom part.

Appendix B

One of the ways to distinguish L and R molecules in SFG is to interfere with the achiral response due to the electric quadrupole matrix, which we call $\chi_Q^{(2)}$, with the chiral response $\chi_{\text{chiral}}^{(2)}$. Here, one of the input beams, say $\vec{k}_1$, has an electric field, $\vec{E}_1$, with both $\vec{S}$ and $\vec{P}$ polarization components, which result in chiral and achiral responses simultaneously. Similar to the external electric field method, for L molecules, sum frequency intensity is

$$I_{\mathrm{L}} \propto |\vec{S}_1 \cdot \vec{P}_2 \times \vec{P}_3 \chi^{(2)}(\mathrm{L}) + \sum_{i,j,k,l} (\vec{P}_i \cdot \vec{k}_j)(\vec{P}_k \cdot \vec{P}_l) \chi_{Q,ijkl}^{(2)}|^2 \quad \text{(b-1)}$$

As shown in Figure 2, there are two possible experimental configurations with one of the input beams to the left of the other. With the electric field method, the two different intensities (I_1 and I_2 in the paper) are used to communicate what we mean by "left" to the Wizard of Oz. Similarly, we can use the polarization interferometry method to solve the first Ozma problem.

Figure 3 shows the experimental geometry that can achieve this goal. Here, the Tin Woodman stands along the $\hat{Z}$ direction and perpendicular to the $\hat{X}-\hat{Y}$ plane, which is chosen to be the incidence plane. $\vec{k}_2$ is directed along $\hat{Y}$ toward the Tin Woodman. $\vec{k}_1$ is set to be perpendicular to $\vec{k}_2$, and can be along either $\hat{X}$ (configuration 1) or $-\hat{X}$ (configuration 2). The resulting sum frequency, $\vec{k}_3 = \vec{k}_1 + \vec{k}_2$, is in the $\hat{X}-\hat{Y}$ plane. The polarization of $\vec{k}_2$ and $\vec{k}_3$ is set to be P. The polarizer for $\vec{k}_1$ is oriented so that the polarization axis has a 45° angle with $\hat{Z}$, and the upper part of the axis is closer to the Tin Woodman than the lower part, as shown by the thick dotted lines in Figure 3. With angle θ between $\vec{P}_2$ and $\vec{P}_3$, the sum frequency intensities of configurations 1 and 2 are

$$I_1 \propto |\sin\theta\chi^{(2)}(\mathrm{L}) + \sum_{i,j,k,l} C_{ijkl}\chi_{Q,ijkl}^{(2)}|^2 \quad \text{(b-2)}$$

$$I_2 \propto |-\sin\theta\chi^{(2)}(\mathrm{L}) + \sum_{i,j,k,l} C_{ijkl}\chi_{Q,ijkl}^{(2)}|^2 \quad \text{(b-3)}$$

Here, I_1 is not equal to I_2, and the relationship between them is the same on earth and in Oz. This is true even for general cases where $\vec{k}_1$ is not perpendicular to $\vec{k}_2$, as long as the polarizer for $\vec{k}_1$ is set at the same angle with the upper part closer to the Tin Woodman in two configurations. As shown in the paper, because these two configurations can be distinguished by their differing sum frequency intensities, the earth wizard can use this polarization interferometry scheme to tell the Wizard of Oz our definition of "left".

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