Limitations of a Superchiral Field [1]

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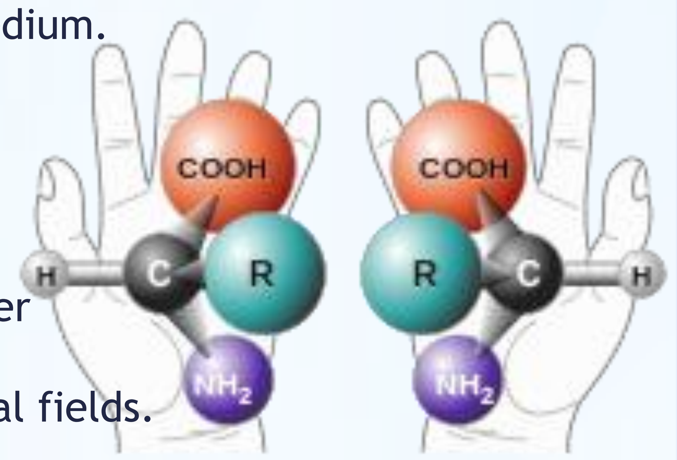
Abstract

- Tang and Cohen [2,3] proposed and demonstrated "superchiral" electromagnetic fields to enhance optical enantioselectivity, typically a very small signal.
- We explicitly show the limitations of such enhancement by including the magnetic susceptibility term.
- We also generalize the dissymmetry factor and Lipkin's "Z^{000} zilch" (or "optical chirality") to that for a linear medium.

Definitions



- **Optical Enantioselectivity** =

  Ability to selectively excite one form, over the other, of a "chiral" molecule (having left- and right-handed forms) using optical fields.

- **Dissymmetry Factor** :

$$g = \frac{A^+ - A^-}{(A^+ + A^-)/2} \le 2, \qquad (1)$$

  where $A^{\pm}$ is Absorption Rate for left(+)- or right(-)- handed fields. This is a good measure of optical enantioselectivity.

- **Circular Dichroism** =

  Numerator of g $(A^L - A^R)$, when Left- and Right-Circularly Polarized Light (LCPL, RCPL) used (aside from some constants).

  When CPL used, we denote $g \to g_{\mathrm{CPL}}$.

- **Optical Chirality** :

$$C \equiv \frac{\epsilon_0}{2}\mathbf{E}\cdot\nabla\times\mathbf{E} + \frac{1}{2\mu_0}\mathbf{B}\cdot\nabla\times\mathbf{B}. \qquad (2)$$

  - Defined originally by Lipkin (Z^{000} "zilch") in 1964, this and other zilches are conserved quantities in vacuum, but were dismissed as physically irrelevant [4].
  - Tang and Cohen related this to the chiral asymmetry of the exciting fields, and termed it "Optical Chirality" [3].
  - Others have since interpreted Lipkin's zilches to represent the "angular momentum" of the curl of the electromagnetic (E&M) field [5]. A "helicity density," not optical chirality, has dimensions of angular momentum per unit volume. For monochromatic fields, helicity densities and zilches are proportional by square of the angular frequency.

- **We generalize this vacuum C with $\epsilon_0 \to \epsilon$ and $\mu_0 \to \mu$ for chiral linear media** [1].
  This implies that **C is no longer a purely E&M field property**.
  Also, despite the chiral nature of the new C, **$|g|$ is symmetric with respect to left- or right-handed forms.**

Background

- Tang and Cohen's theory for enhancement in dissymmetry factor [2,3]:

$$g/g_{\mathrm{CPL}} = \frac{c\,C}{2\,U_e\,\omega}, \qquad (3)$$

  c = speed of light, U_e = electric field energy density, ω = frequency.
  - Enhancement is field-dependent only.
  - Material property in g_{CPL} only.
  - For a standing wave chiral field (called "superchiral" field), at electric field node (Fig. 1):

$$g/g_{\mathrm{CPL}} = \frac{1+\sqrt{R}}{1-\sqrt{R}}, \qquad (4)$$

    R= reflectivity of mirror used.
  - As R→1, enhancement → Infinity! Authors state magnetic field limits this, but claim 400-fold enhancement w/ large R.
  - Experimental demonstration of ~11x enhancement w/ R=0.72 (Fig. 2).

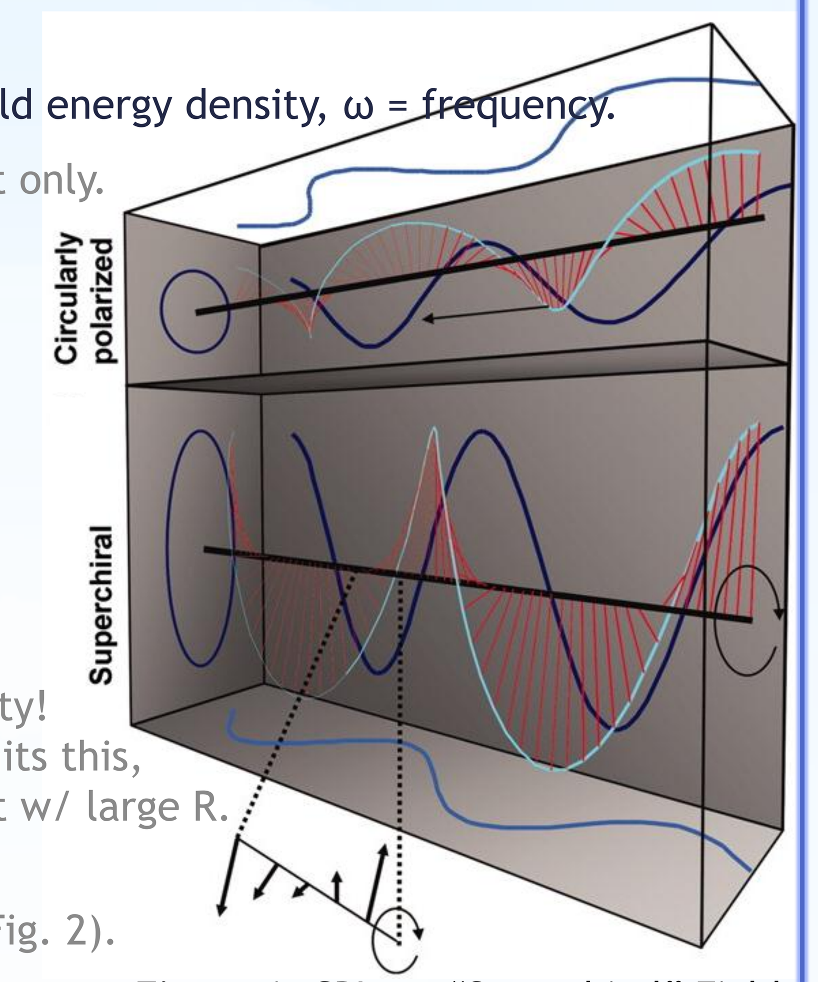
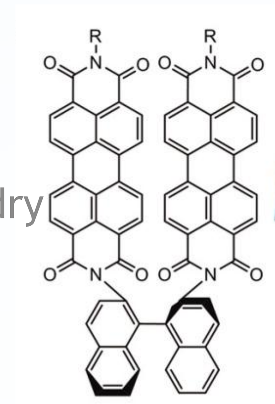


Figure 1: CPL vs. "Superchiral" Field (From [2])

- 10^6 Enhancement w/ 2D Nano-Crosses
  - Independently by Hendry et al, shortly after [6].



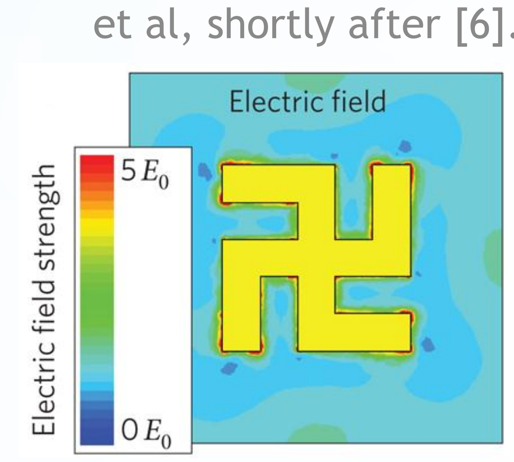


Figure 3: Nano-cross (From [6])

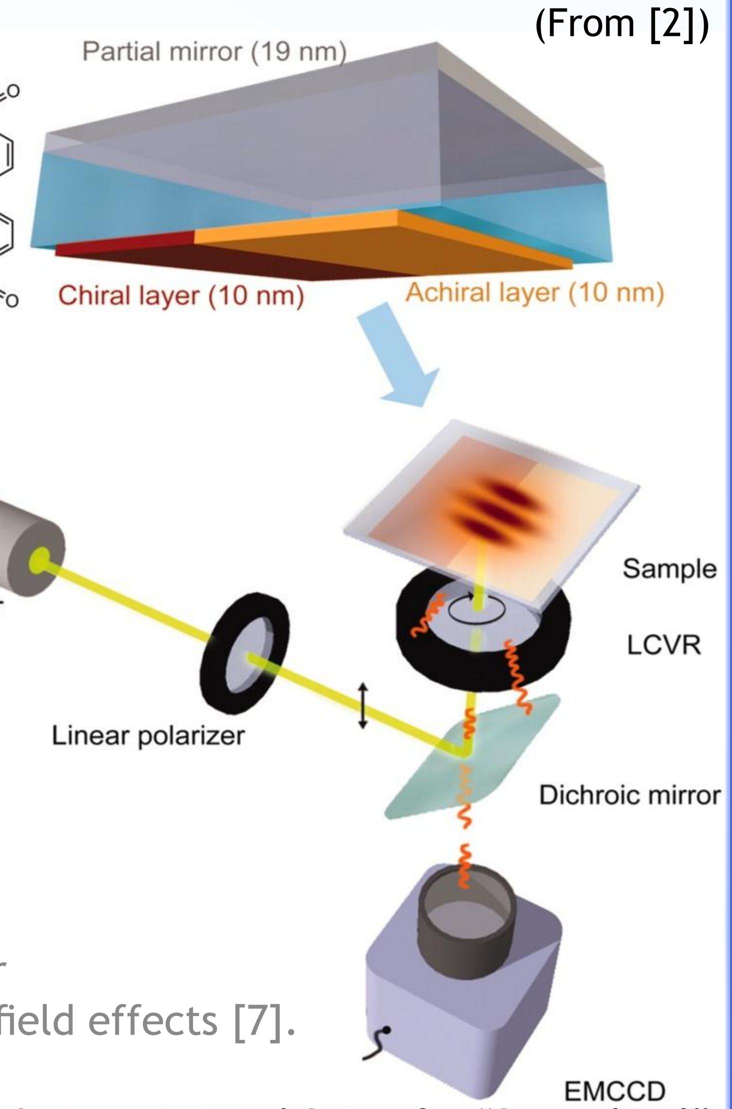


Figure 2: Experimental Setup for "Superchiral" Enhancement (From [2])

  - Enhancement in chiral optical rotation. Used Optical Chirality to explain 10^2 enhancement, but other 10^4 appears to be evanescent near-field effects [7].

- Significance [8]
  - Seemingly arbitrarily large enhancements in small chiral optical signals ($g_{CPL} \approx 10^{-3}\sim10^{-2}$) [1].
  - Possible by engineering E&M fields, independent of chiral molecules.
  - Renewed interest in, now physically significant, Lipkin's zilches.

Assumptions

- **Since enhancement at electric field node of standing wave, magnetic field is maximum, due to conservation of energy. Though usually small, magnetic susceptibility can no longer be ignored**, as was done in Refs [2,3]. This provides correction and limitation of g/g_{CPL}.
- Multipole moment approximation with electric polarizability, magnetic susceptibility, and mixed electric-magnetic dipole polarizability. Absorption rate approximation with electric and magnetic dipoles only.

Dissymmetry Factor Corrections

- Corrected enhancement factor:

$$g/g_{\mathrm{CPL}} = \frac{c\,C}{2\,\omega(U_e + \gamma U_b)}, \qquad (3')$$

  where U_b = magnetic field energy density,
  $\gamma \propto$ (magnetic susceptibility) / (electric polarizability).
- Correction at electric field node:

$$g/g_{\mathrm{CPL}} = \frac{1-R}{(1-\sqrt{R})^2 + \gamma(1+\sqrt{R})^2}, \qquad (4')$$

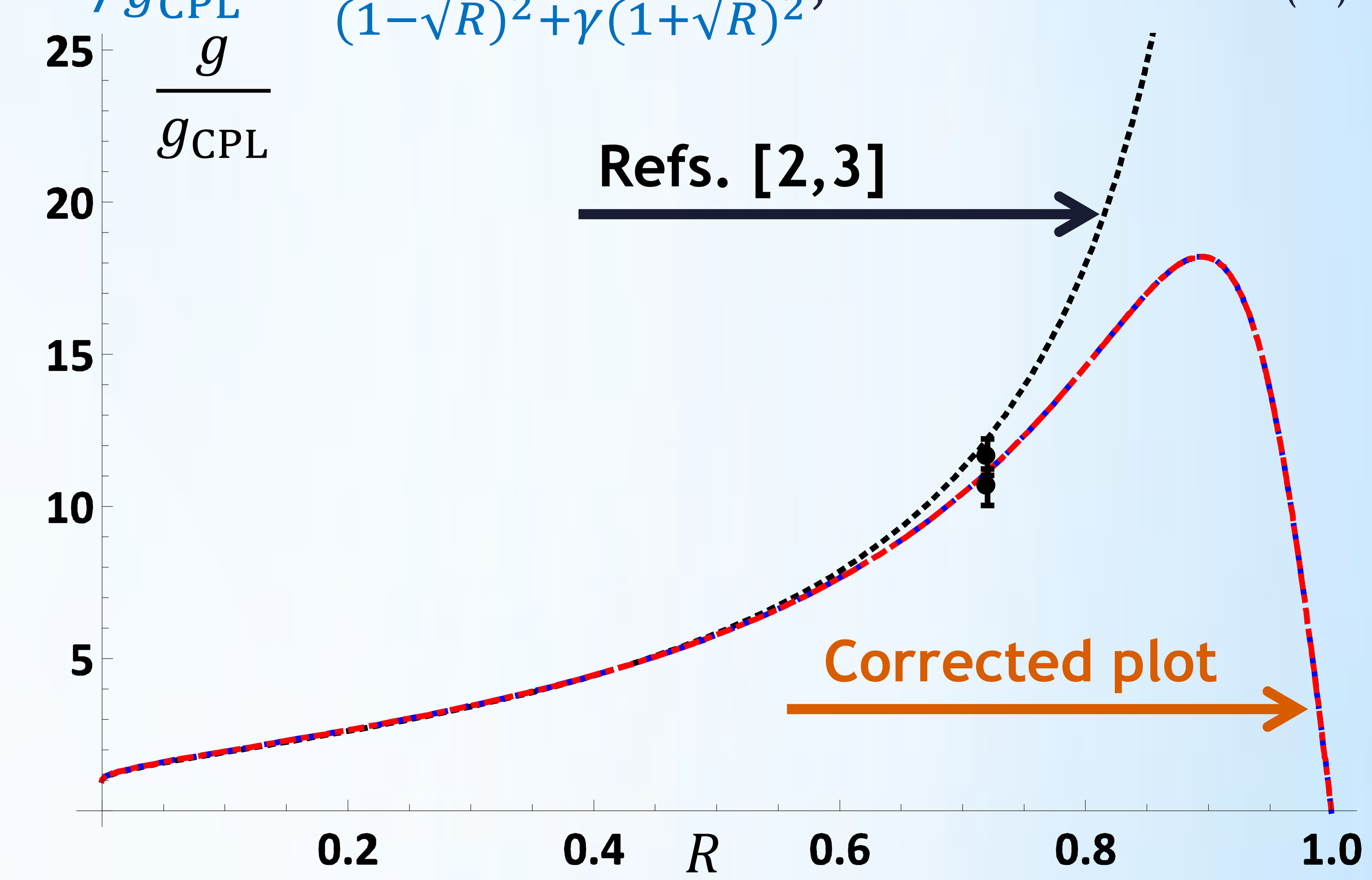


Figure 4: Enhancement in dissymmetry factor vs. reflectivity, for material used in Ref. [2]. Dots w/ error bars obtained experimentally in Ref. [2]. (From [1])

Limitations

- **Enhancement is finite; < 20x for Ref. [2]; goes to 0 for R = 1** (Fig. 4).
- For a given material, **maximum enhancement is fixed at $\sim 1/(2\sqrt{\gamma})$**; for realistic values, the maximum is ~ 500x.
- **Finding material with small $\sqrt{\gamma}$ is not practical since signal goes as γ (so signal decreases faster than enhancement factor increase).**

Conclusions

- Cauchy-Schwarz inequality holds for dissymmetry factor when magnetic susceptibility retained.
- Corrected dissymmetry equation (Eqn. (3')) can be helpful for ongoing research and dialogue in nodal enhancement of optical enantioselectivity.

References

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