Discriminate Chiral Molecule with Linear Pulse

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Sep., 25, 2021.

延吉，第二十届全国基础光学与光物理学术研讨会

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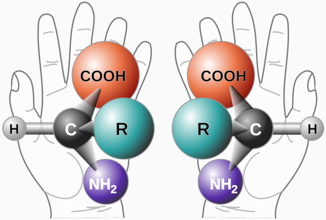
A system S is called **chiral** if the center inversion O on it cannot be replaced by any of rotations R.

$$OS \neq (\text{any of } R)S$$



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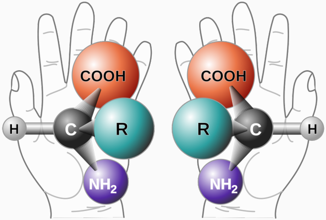

Chirality

Since inversion twice of any system backs to its origin $O^2 = I$, there exists two types of chiral system: left- and right-handed.

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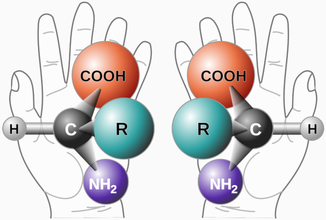

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For a **rotational isotropic chiral ensemble**: unchanged under any of rotations but shows Z_2 symmetry under inversion. Thus one can use a pseudo-scalar ε to describe it.

Discriminate Chiral System: from pseudo-scalar to scalar

Chemical reaction

- Consider a reaction A + B $\longrightarrow$ C.
- Both A(R) + B(R) $\longrightarrow$ C and A(L) + B(L) $\longrightarrow$ C are possible.
- But A(R) + B(L) $\longrightarrow$ C and A(L) + B(R) $\longrightarrow$ C can hardly happens.
- Production of two pseudo-scalars (molecular chirality) is a scalar (reaction rate).

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Optical Discrimination

There exists a pseudo-scalar (helicity) for circular polarized light

$$k \cdot (E \times \partial_t E)$$

Thus chiral light and chiral molecules shows observed effects:

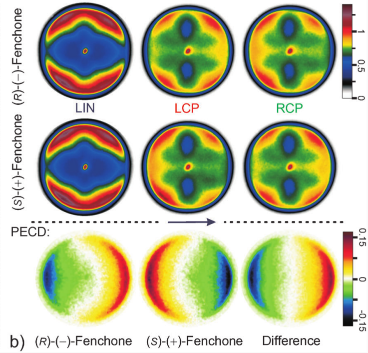
- Reflection index and absorption rate (Optical rotation, 1800s)
- Ionization cross-section (PECD, *Phys. Rev. A* **12**, 567 (1975))
- HHG yield (*Nat. Phys.* **11**, 654 (2015))

Optical Discrimination without k

- The above mentioned effects are generally weak (1st order nondipole correlation), since the chirality of light is directly connected with its wave-vector.
- To observe a larger chiral effect, one may replace k by photoelectron momentum p_e

$$\Pr(p_e) \sim \varepsilon p_e \cdot (E \times \partial_t E)$$

Ritchie, B. *Phys. Rev. A* **14**, 359 (1976)
Lux, C. *et al. Angew. Chem.* **51**, 5001 (2012)



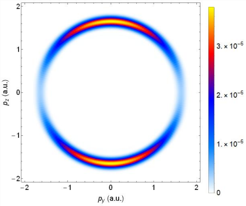
Optical Discrimination without Circular Polarization

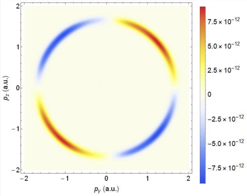
- All of the optical discrimination methods require circular polarization to construct a non-zero pseudo vector.
- For linear polarized light, one can also construct a pseudo tensor

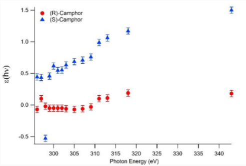
$$\Pr(p_e) \sim \varepsilon (p_e \cdot E)[p_e \cdot (k \times E)]$$

- Such effect has been discussed in one-photon region

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{tot}}}{4\pi}\left[1 + \beta P_2(\cos\theta) + (\delta + \gamma \cos^2\theta)\sin\theta\cos\phi + \varepsilon \sin 2\theta \sin\phi\right]$$



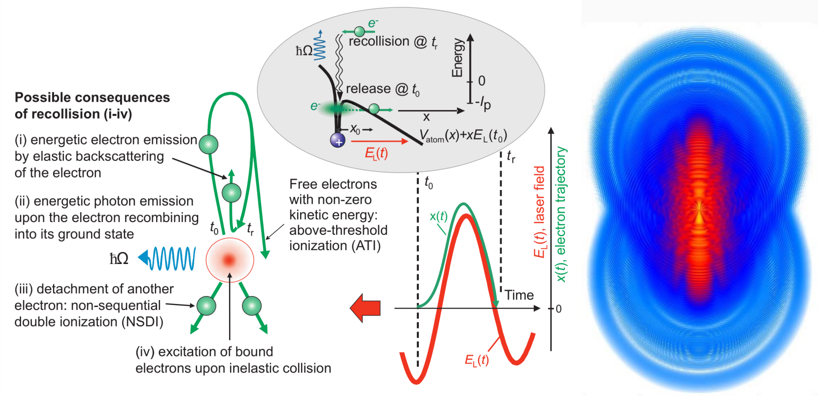




Grum-Grzhimailo, A. N. *J. Phys. B: At. Mol. Opt. Phys.* **36**, 2385 (2003)
K. P. Bowen *et al.* *J. Phys.: Conf. Ser.* **635**, 112053 (2015)

Question

What about the linear discrimination for tunneling ionization?



Krausz F. & Ivanov M., *Rev. Mod. Phys.* **81**, 1 (2009)

Towards Tunneling Region

Question
What about the linear discrimination for tunneling ionization?

Model & Method

- Single-center multi-pole potential

$$V(r,\Omega) = \sum_{l,m} v_{lm} \frac{1 - e^{-(r/a_l)^{2l+1}}}{r^{l+1}} Y_l^m(\Omega)$$

- $l = 0, 1, 2$ is enough to describe a chiral system.
- Multi-center zero range potential

$$\lim_{r \to r_i} \left[\frac{d}{dr} |r - r_i| \psi(r) - \alpha_i |r - r_i| \psi(r) \right] = 0$$

- Four points are enough to describe a chiral system.

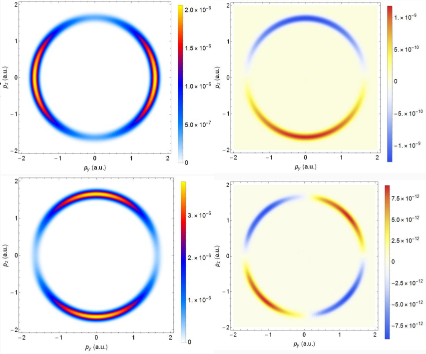
Calculation for One-Photon Region

To evaluate lab-frame photon electron distribution, one has to average over all the molecular orientations (α, β, γ)

$$\overline{P(p_e)} = \frac{1}{8\pi^2} \int d\alpha\, d\cos\beta\, d\gamma\, P(p_e; \alpha, \beta, \gamma)$$
$$\approx \sum_{i,j,k} w_{ijk} P(p_e; \alpha_i, \beta_j, \gamma_k)$$

Circular polarization
Forward backward asymmetry in k direction

Linear polarization
Four-fold asymmetry in polarization plane



Partial Calculation for Tunneling Region

Average over all the orientations is far beyond our computational ability, thus we only consider the aligned case

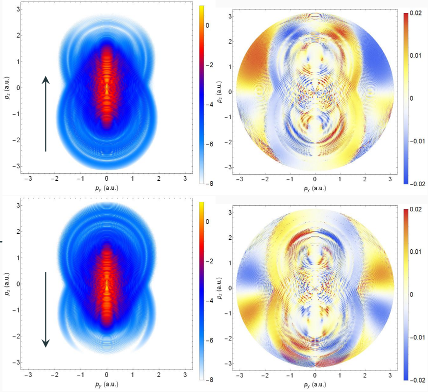
$$\frac{1}{8\pi^2}\int d\alpha\, d\cos\beta\, d\gamma \rightarrow \frac{1}{4\pi}\sum_{\beta=0,\pi}\int d\alpha$$

8-cycle 800 nm linear polarized pulse with $I = 2 \times 10^{14}\,\mathrm{W/cm^2}$

Left: PMD in polarization plane

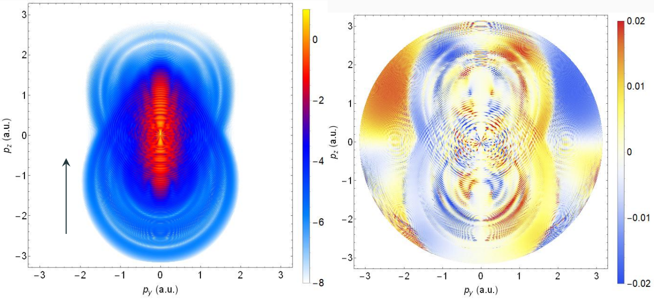
Right: Relative difference for each pixies

$$\mathrm{Asy} \equiv \frac{\Pr_R(p_e) - \Pr_L(p_e)}{\Pr_R(p_e) + \Pr_L(p_e)}$$



Sum over both Orientations

- For molecular dipole ***d*** oriented upward (downward), the yield of upward (downward) re-scattering electron is suppressed; and the re-scattering electron prefers to emitted left (right) side.



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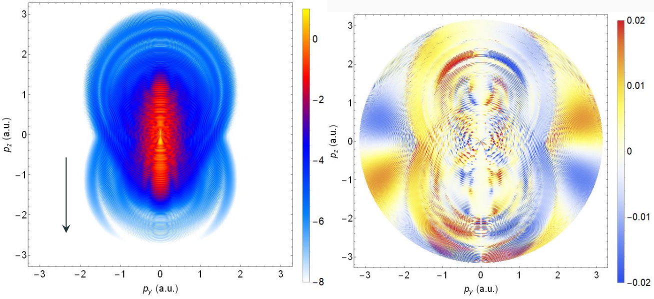
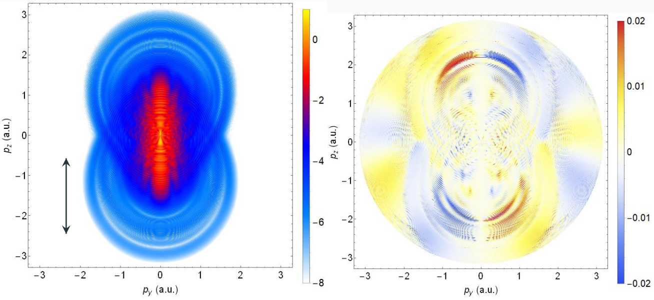


Sum over both Orientations

- For molecular dipole $\boldsymbol{d}$ oriented upward (downward), the yield of upward (downward) re-scattering electron is suppressed; and the re-scattering electron prefers to emitted left (right) side.
- By sum over both orientations, one finds Asy $\propto p_z p_y$



Three Step Model

1. Electron tunnels through the potential barrier. If the molecular dipole is anti-parallel to electric field, the tunneling probability will be largely enhanced.
2. Electron accelerates in laser field

$$\ddot{z} = -E(t), \quad \ddot{x} = -\dot{z}E(t)/c$$

$$\dot{z} = A(t) - A(t_0), \dot{x} = \frac{1}{2c}[A(t) - A(t_0)]^2$$

   Thus when electron returns to the parent ion, it gains a finite x-component velocity.
3. Electron scattered by the parent ion. TDSE results suggest the scattering cross section include terms like

$$P(p_f) \sim p_f \cdot (d \times p_r)\varepsilon$$

Re-Examination on 3rd Step

To have a verification on 3rd step, we study the scattering process with a semi-analytically model: multi-center zero-range potentials.

The scattering state is governing by

$$\alpha_i c_i + \sum_{i \neq j} \frac{\cos kr_{ij}}{r_{ij}} c_j + \cot \eta \left(kc_i + \sum_{i \neq j} \frac{\sin kr_{ij}}{r_{ij}} c_j \right) = 0,$$

and

$$A_\lambda(\hat{n}) = \sum_i c_i^{(\lambda)} e^{ik\hat{n}\cdot r_i}.$$

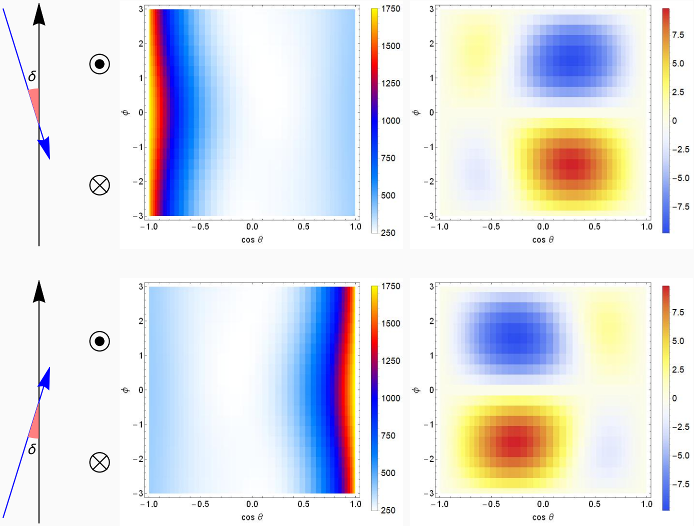
The differential cross section is given by

$$\sigma(\hat{n}, \hat{\nu}) = \frac{4\pi}{k} \left| \sum_\lambda \sin \eta_\lambda A_\lambda^*(\hat{n}) A_\lambda(\hat{\nu}) \right|^2.$$

Demkov, Y. M. & Rudakov, V. S., *JETP*, **32**, 1103 (1971)

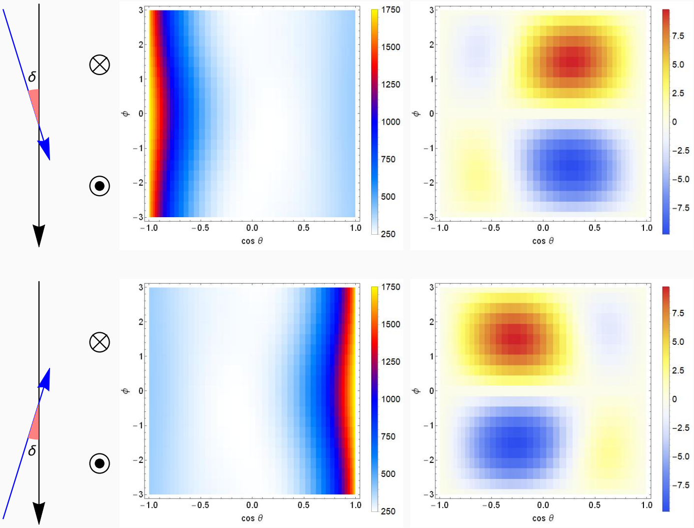
Results on Scattering - Orient Upward

With incident angle $\delta = 0.05$ and oriented molecule, back-scattering electron shows outward/inward asymmetry.



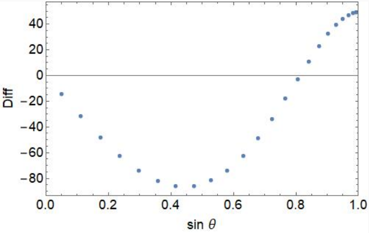
Results on Scattering - Orient Downward

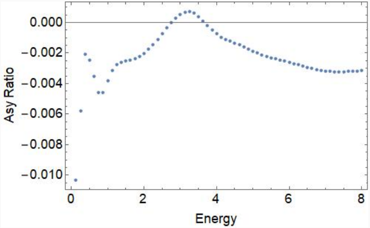
By reverse the orientation, the outward/inward asymmetry also reverse, which coincide with TDSE results.



Angular & Energy Dependent Scattering

- The asymmetry increase linearly as incident angle θ increase (at least when $\theta \ll 1$)
- And it varying slowly as returning energy increase.





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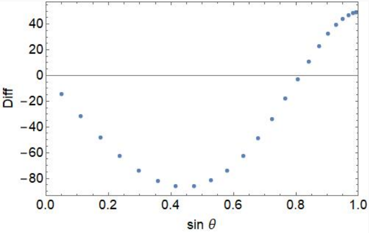
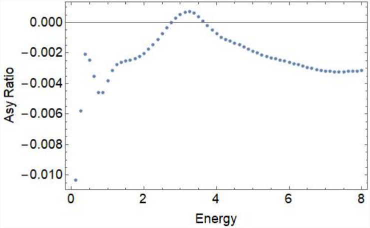


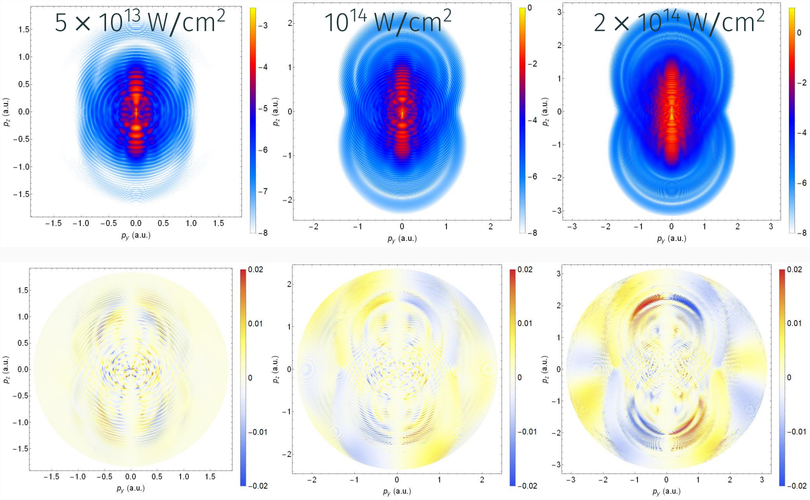


- For strong field ionization: let returning velocity to be v_r, the $\hat{k}$-component of velocity is $v_k \approx v_r^2/2c$, so

$$\theta \approx \frac{v_r}{2c}.$$

thus we predict that the chiral effect increase linearly with vector potential.

TDSE results for different intensities



Brief Summary

- Two model systems are developed to investigate chiral effect.
- From TDSE calculation, we find that for tunneling ionization from chiral system induced by linear polarization pulse, distribution of rescattering electron shows the chirality in polarization plane

$$\Pr(p_e) \sim \varepsilon(p_e \cdot E)[p_e \cdot (k \times E)]$$

- Based on three-step model, the physical mechanism behind the chiral effect is given.
- An individual calculation on third step: scattering, is given, to confirm one of the conjecture proposed in previous mechanism.
- Scatter calculation predicts that chiral effect is more obvious for larger intensities, which is confirmed by TDSE calculation.

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Thanks for Listening!

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- For $l = 1, 2$ and dipole lays on the plane spanned by two of the major axis of quadrupole, inversion is equivalent to the rotation of π respect to the other major axis of quadrupole.
- Finally, one may construct the pseudo-scalar

$$\varepsilon = (F(Q)d, G(Q)d, H(Q)d)\,,$$

  in which F, G, H are three linear independent functions.

DCS for one-photon ionization

For a given channel I, the transition amplitude is

$$\begin{aligned} M_{\boldsymbol{p}}^{I} &= \langle \boldsymbol{p} | \varepsilon_m Y_l^m(\Omega_{\mathrm{lab}}) | g \rangle \\ &= \varepsilon_m D_{mm'}^{lR} \langle \boldsymbol{p} | Y_l^{m'}(\Omega_{\mathrm{mol}}) | g \rangle \\ &= \varepsilon_m D_{mm'}^{lR} (b_{lm'}^{I})_{LM} Y_L^M(\Omega_{\mathrm{mol}}^p) \\ &= \varepsilon_m D_{mm'}^{lR} (b_{lm'}^{I})_{LM} D_{MM'}^{L} Y_L^{M'}(\Omega_{\mathrm{lab}}^p) \end{aligned}$$

where ε_n is determined by the field in lab frame. Considering the interference term among channel I and J

$$\sigma^{IJ} \equiv \frac{1}{8\pi^2} \int M_{\boldsymbol{p}}^{I} (M_{\boldsymbol{p}}^{I})^* \,\mathrm{d}\alpha \mathrm{d}\cos\beta \mathrm{d}\gamma$$

Orientation Average

One reaches

$$\sigma^{IJ} = \frac{1}{8\pi^2}\int \varepsilon_{m_1} D^{l_1 *}_{m'_1 m_1} (b^I_{l_1 m'_1})_{L_1 M_1} D^{L_1}_{M_1 M'_1} Y^{M'_1}_{L_1}$$

$$\varepsilon^*_{m_2} D^{l_2}_{m'_2 m_2} (b^I_{l_2 m'_2})^*_{L_2 M_2} D^{L_2 *}_{M_2 M'_2} Y^{M'_2 *}_{L_2} \,\mathrm{d}\alpha \,\mathrm{d}\cos\beta \,\mathrm{d}\gamma$$

$$= \frac{1}{8\pi^2}\int \mathrm{d}\alpha \,\mathrm{d}\cos\beta \,\mathrm{d}\gamma \; \varepsilon_{m_1}\varepsilon^*_{m_2} (b^I_{l_1 m'_1})_{L_1 M_1} (b^J_{l_2 m'_2})^*_{L_2 M_2} Y^{M'_1}_{L_1} Y^{M'_2 *}_{L_2}$$

$$(-)^{m'_1 - m_1} C^{l_3 (m'_2 - m'_1)}_{l_1 - m'_1 l_2 m'_2} C^{l_3 (m_2 - m_1)}_{l_1 - m_1 l_2 m_2} D^{l_3}_{(m'_2 - m'_1)(m_2 - m_1)}$$

$$(-)^{M'_2 - M_2} C^{L_3 (M_1 - M_2)}_{L_1 M_1 L_2 - M_2} C^{L_3 (M'_1 - M'_2)}_{L_1 M'_1 L_2 - M'_2} D^{L_3}_{(M_1 - M_2)(M'_1 - M'_2)}$$

$$= \frac{1}{2l_3 + 1}\sqrt{\frac{(2L_1+1)(2L_2+1)}{4\pi(2l_3+1)}} \varepsilon_{m_1}\varepsilon^*_{m_2} (b^I_{l_1 m'_1})_{L_1 M_1} (b^J_{l_2 m'_2})^*_{L_2 M_2} Y^{M'_1 - M'_2}_{l_3}$$

$$(-)^{m'_1 - m_1 + M'_1 - M_1 + M'_2} \delta_{m'_2 - m'_1 + M_1 - M_2} \delta_{M'_1 - M'_2 + m_2 - m_1}$$

$$C^{l_3 (m'_2 - m'_1)}_{l_1 - m'_1 l_2 m'_2} C^{l_3 (m_2 - m_1)}_{l_1 - m_1 l_2 m_2} C^{l_3 (M_1 - M_2)}_{L_1 M_1 L_2 - M_2} C^{l_3 0}_{L_1 0 L_2 0}$$

Formula in Y_L^M

With induced notations

$$\begin{aligned}
Q^l_{l_1 l_2} =& \frac{1}{2l+1}\sqrt{\frac{(2L_1+1)(2L_2+1)}{4\pi(2l+1)}}(b^I_{l_1(m'_2+M)})_{L_1(M_2+M)}(b^J_{l_2 m'_2})^*_{L_2 M_2} \\
& (-)^{m'_2-M_2} C^{lM}_{l_1(m'_2+M)l_2-m'_2} C^{lM}_{L_1(M_2+M)L_2-M_2} C^{l0}_{L_1 0 L_2 0} \\
=& (-)^{m'_2-M_2+l_1-l_2}\sqrt{\frac{(2L_1+1)(2L_2+1)}{4\pi}}(b^I_{l_1(m'_2+M)})_{L_1(M_2+M)}(b^J_{l_2 m'_2})^*_{L_2 M_2} \\
& \begin{pmatrix} l_1 & l_2 & l \\ m'_2+M & -m'_2 & -M \end{pmatrix}\begin{pmatrix} L_1 & L_2 & l \\ M_2+M & -M_2 & -M \end{pmatrix}\begin{pmatrix} L_1 & L_2 & l \\ 0 & 0 & 0 \end{pmatrix}
\end{aligned}$$

we have the simplified results

$$\sigma_{IJ} = (-)^{m_2}\varepsilon_{m_2+m}\varepsilon^*_{m_2} Y^m_l C^{l-m}_{l_1-(m_2+m)l_2 m_2} Q^l_{l_1 l_2}$$

One can further analyze it with the symmetries of system and field.