Negative Refraction Induced by Möbius Topology

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We theoretically show the negative refraction existing in Möbius molecules. The negative refractive index is induced by the non-trivial topology of the molecules. With the Möbius boundary condition, the effective electromagnetic fields felt by the electron in a Möbius ring is spatially inhomogeneous. In this regard, the $D_N$ symmetry is broken in Möbius molecules and thus the magnetic response is induced through the effective magnetic field. Our findings open up a new architecture for negative refractive index materials based on the non-trivial topology of Möbius molecules.

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Introduction. It is recognized that materials with simultaneously negative permittivity and permeability also support the coherent propagation of electromagnetic fields [1], like the usual case where both permittivity and permeability are positive. Due to a reversed phase velocity with respect to the group velocity [2], the boundary condition makes the light to bend in an unexpected direction as if the refractive index appears negative according to the Snell’s law. Hence, the effect is termed as negative refraction. Negative refractive index materials is very promising, e.g., in achieving the electromagnetic field cloaking [3,4] as well as facilitating the sub-wavelength imaging [5]. However, such materials do not naturally exist for the absence of magnetic response at the same frequency as electric response. To overcome this difficulty, delicately designed metamaterials have been proposed and tested. Metamaterials rely on structural designing of the sub-wavelength unit cells to tune the electromagnetic resonant characteristic [6]. A key element commonly involved in such artificial architectures is the configuration of split-ring resonator [7,8]. This structure is analogous to an LC resonator with characteristic frequency $\omega_0 \sim 1/\sqrt{LC}$, which is tunable by engineering. A metamaterial with split-ring resonators can negatively respond to the magnetic field when $\omega \gtrsim \omega_0$ [8]. Although the negative refraction has been demonstrated at the visible wavelength, manufacturing of microstructure at the size of 30-100 nm is required [9]. Such technically requesting fabrication, as well as the metallic loss due to absorption at the electromagnetic resonance [11], make it still an open challenge to scale the materials to 3D bulk.

Instead of fabricating those delicately designed structures from the conventional “top-down” approach, an attractive alternative is to generate the dielectric mediums with self-assembled functional atoms or molecules [12–14]. This “bottom up” approach is particularly interesting due to the small size of molecules and their associated quantum effects. For example, by utilizing the quantum interference among multi-level atoms, it is possible to suppress the absorption meanwhile keep reasonable optical response [15]. We notice that the molecular ring can not effectively response to the magnetic field, because there does not exist any split to make the symmetry breaking [14,16]. It is also difficult to realize the necessary structure of split ring resonator in the natural molecules in the “bottom up” fashion.

In this Letter, instead of relying on the split-ring configuration, we describe a potential negative-refracting dielectric medium with the Möbius molecules. Such molecules were theoretically proposed [17] and had been fabricated [18–20] in several experiments. Because of its specific configuration, the $D_N$ symmetry is broken to $C_2$. The motion of an electron in the Möbius ring is subject to an effective spatially-inhomogeneous field even though it is exposed to a physically uniform electromagnetic field. Both electric and magnetic responses can be induced at the same transition and thus both negative permittivity and permeability can be observed at the same frequency. In this sense, the negative refraction in Möbius molecules is intrinsically caused by the non-trivial topology of the molecules. Motivated by this discovery, we propose realizing a new kind of metamaterials based on the Möbius molecules.

The Möbius molecular ring.-The Möbius molecular ring has several physical realizations, e.g., through graphene [21] and the non-conjugated molecules [22]. For a general double-ring system (see Fig. 1(a)) with $2N$ atoms, the Hückel Hamiltonian for a single electron reads as [23,24]

$$H = \sum_{j=0}^{N-1} |A_j| M A_j - \xi (A_j | A_{j+1} + h.c. |),$$  

\[1\)
The transition selection rules for electric dipole operators can be inferred from the matrix elements of \( H' \) between the eigenstates of \( H \), which are the linear combinations of the atomic \( \pi \)-orbitals. In the following we ignore the overlapping integrals at different nuclear sites and assume \( \sum_{j} \langle \phi_j | \phi_i \rangle = \delta_{ji} \langle R_j | \phi_j \rangle \), where \( R_j \) denotes the position vector of the \( j \)th nuclear site. For the Möbius molecular ring with radius \( R \) and width \( w \) (see Fig. 1), the nuclear positions are explicitly written in the molecular coordinate system \( [24] \) as

\[
\tilde{R}_{j\pm} = (R \pm w \sin \frac{\varphi_j}{2}) \cos \varphi_j \hat{e}_x + (R \pm w \sin \frac{\varphi_j}{2}) \sin \varphi_j \hat{e}_y \pm w \cos \frac{\varphi_j}{2} \hat{e}_z,
\]

where the extra plus and minus subscripts correspond to nuclear sites in the \( A \)- and \( B \)-rings respectively, and \( \varphi_j = j\delta \). The non-vanishing matrix elements of \( H'_{E} \) are explicitly given in the Supplemental Material.

The transition selection rules for the electric dipole operator are briefly summarized as

\[
|k, \downarrow \rangle \equiv |k, \downarrow \rangle, |k, \uparrow \rangle \equiv |k + 2\delta, \uparrow \rangle, |k, \sigma \rangle \equiv |k \pm \delta, \sigma' \rangle, |k, \downarrow \rangle \equiv |k + \delta, \uparrow \rangle.
\]

where the energy spectra (see Fig. 2(b)):

\[
E_{k\uparrow} = V - 2\xi \cos(k - \delta \frac{\pi}{2}), \quad E_{k\downarrow} = -V - 2\xi \cos k,
\]

which are obtained by performing the Fourier transform on \( B_j \) with the resulting transformed operator denoted as \( C_k \) and \( k = j\delta (j = 0, 1, \cdots N - 1) \). Compared with the spectrum of a topologically trivial annulenes, the effective magnetic flux results in a shift of the \( E_{k\uparrow} \) band such that the lowest two states become degenerate. Similar shifting behavior has also been suggested for a cyclic polyene under a real magnetic field \([23]\).

\[
\begin{cases}
A_j = \left[ \begin{array}{c}
a_j \\
b_j
\end{array} \right], & \quad M = \left[ \begin{array}{cc}
\epsilon & -V \\
-V & -\epsilon
\end{array} \right].
\end{cases}
\]

Here, the Fermionic operators \( a_j^\dagger \) and \( b_j^\dagger \) create a localized \( \pi \)-orbital \( \phi_j \) at the \( j \)th nuclear site of the \( A \)- and \( B \)-rings respectively; \( 2\epsilon \) describes the on-site energy difference between atoms of two rings; The inter- (intra-) ring resonance integral is denoted by \( V (\xi) \). Hereafter, we consider a special case where all atoms are of the same species, i.e. \( \epsilon = 0 \) \([23]\), as indicated in Fig. 1(a).

The difference between the Möbius molecular ring and the common chemical annulenes lies in the boundary condition. Here, the \( N \)th nucleus in the \( A \)-ring is exactly the \( 0 \)th nucleus of the \( B \)-ring. Therefore, \( a_0 = b_N \) and \( b_0 = a_N \) imply that the operators do not obey the periodical boundary condition.

With a local unitary transformation \( U_j \) \([23]\) (see Supplemental Material), the Hamiltonian becomes

\[
H = \sum_{j=0}^{N-1} \left[ B_j^\dagger V \sigma_x B_j - \xi (B_j^\dagger Q B_{j+1} + \text{h.c.}) \right],
\]

where

\[
B_j = U_j A_j \equiv \left[ \begin{array}{c}
c_j^\dagger \\
c_j^\downarrow
\end{array} \right], \quad Q = \left[ \begin{array}{cc}
e^{i\delta/2} & 0 \\
0 & 1
\end{array} \right].
\]
Here, $|k, \sigma\rangle$ denotes an eigenstate of $H$ with energy $E_{k\sigma}$. The superscripts $x, y, z$ indicate the electric field polarizations. Those allowed inter-band transitions are schematically shown in Fig. 1(b).

Since the negative refraction depends on the simultaneously negative permittivity and permeability, we further investigate the transition selection rules for the magnetic dipole $\vec{m}$. For molecular systems the current is restricted to the chemical bond, thus $\vec{m}$ is written as \[\vec{m} = \sum_{i,j} \beta_{ij} \vec{S}_{ij},\] where $\vec{S}_{ij}$ is an effective area specified below. The bond current $J_{ij}$ flows from the $i$th atom to the $j$th atom, and by the tight-binding approximation the summation only runs over bonded-atoms pairs. The operator corresponding to the bond current is given by $J_{ij} = \epsilon \beta_{ij} a_i^\dagger a_j^/ + h.c.$ [25], where $\beta_{ij}$ is the resonance integral. For the Möbius molecular ring, $\beta_{ij}$ is either $\xi$ or $\nu$, depending on the specific pair of atoms. Consequently, the magnetic dipole operator is explicitly given as

$$\vec{m} = -e \sum_j [A_j^/ (V \vec{S}_{j,j}^{+} \sigma_y) A_j + \xi (i A_j \vec{N}_j A_{j+1} + h.c.)]$$

with the effective area $\tilde{S}_{ij}^{\alpha\beta} \equiv \vec{R}_{i\alpha} \times \vec{R}_{j\beta}/2$ ($\alpha, \beta = \pm$) and the vectorial matrix

$$\vec{N}_j = \begin{bmatrix} \tilde{S}_{j,j+1}^{++} & 0 \\ 0 & \tilde{S}_{j,j+1}^{--} \end{bmatrix}.$$  \hspace{1cm} (10)

Under the dipole approximation, the interaction Hamiltonian describing the coupling of the Möbius molecular ring to an external oscillating magnetic field with amplitude $\vec{B}_0$ and frequency $\omega$ is similar to Eq. 3:

$$H_{D} = -\vec{m} \cdot \vec{B}_0 \cos \omega t.$$  \hspace{1cm} (11)

The explicit expressions of the matrix elements are complicated in the case of magnetic perturbation and thus we do not list them here (see Supplemental Material). Through straightforward calculations, we find the following transition selection rules (see Fig. 1(b)):

$$|k, \downarrow\rangle \overset{xy}{\leftrightarrow} |k, \uparrow\rangle, \quad |k, \downarrow\rangle \overset{xy}{\leftrightarrow} |k + 2\delta, \uparrow\rangle, \quad |k, \uparrow\rangle \overset{xy}{\leftrightarrow} |k + \delta, \downarrow\rangle, \quad |k, \downarrow\rangle \overset{xy}{\leftrightarrow} |k + \delta, \uparrow\rangle.$$  \hspace{1cm} (12)

where only the inter-band transitions are shown since in the limit of large $N$, the spectra $E_{k\sigma}$'s become continuous with respect to $k$ and thus the inter-band transitions are more relevant to the response at high frequency. A comparison between Eq. 12 and Eq. 8 indicates that the selection rules for the inter-band transitions are almost the same for both electric and magnetic couplings.

**Permittivity and permeability.** In this Letter, we propose a medium consisting of multi-layers of Möbius molecules. In each layer, Möbius molecules are densely arranged one by one with translational symmetry. In order to realize the negative refraction, the simultaneous negative permittivity $\varepsilon_r$ and permeability $\mu_r$ are required [1]. Generally speaking, for anisotropic media the relative permittivity $\varepsilon_r$ and permeability $\mu_r$ are dimensionless second order tensors, which depend on the frequency $\omega$ of external fields $\vec{E}$ and $\vec{H}$. $\varepsilon_r$ and $\mu_r$ are calculated by considering that $\vec{D}$ and $\vec{B}$ are related to the polarization $\vec{P}$ as well as the magnetization $\vec{M}$ of the medium [14]: \[\vec{D} = \varepsilon_0 \vec{\varepsilon}_r \vec{E} = \varepsilon_0 \vec{E} + \vec{P}/\varepsilon_0,\] \[\vec{B} = \mu_0 \vec{\mu}_r \vec{H} = \mu_0 \vec{H} + \mu_0 \vec{M}/\mu_0.\] Here, $\varepsilon_0$ and $\mu_0$ is the volume occupied by a Möbius molecule in the material. $\vec{P}$ and $\vec{M}$ are quantum mechanical averaging of the electric polarization and magnetization in the perturbed molecular ground state. In the linear response regime, applying the Green-Kubo formula [27] yields (see Supplemental Material)

$$\vec{P} = -\frac{1}{\hbar} \text{Re} \sum_{k,\sigma} \delta g_{k,\sigma} \langle \frac{\delta \varepsilon_{k,\sigma} \cdot \vec{E}}{\omega - \Delta_{k,\sigma}^\prime + i\gamma} \rangle,$$  \hspace{1cm} (13)

$$\vec{M} = -\frac{\mu_0}{\hbar} \text{Re} \sum_{k,\sigma} \delta g_{k,\sigma} \langle \frac{\delta \mu_{k,\sigma} \cdot \vec{H}}{\omega - \Delta_{k,\sigma}^\prime + i\gamma} \rangle.$$  \hspace{1cm} (14)

Here, $\Delta_{k,\sigma} = E_{k\sigma} - E_g$ is the energy gap between the excited and ground states of $H$. The ground state is excluded in the summation, as indicated by the prime. The lifetimes of the excited states are assumed to be homogeneously $1/\gamma$.

Because $\varepsilon_{\alpha r}^\prime \simeq 1 - O(|\vec{P}/|\vec{E}|])$ and $\mu_{\alpha r}^\prime \simeq 1 - O(|\vec{M}/|\vec{H}|])$, Eqs. 13 and 14 then imply that the negative values of $\varepsilon_r$ and $\mu_r$ occur necessarily around the molecular resonant transition frequencies $\Delta_{k,\sigma}$. Furthermore, the responses exist only if the corresponding transitions are allowed by both electric and magnetic dipole interactions with fields. As for the Möbius ring, it is particularly interesting that the inter-band transition $|k, \underline{\downarrow}\rangle \rightarrow |k', \underline{\uparrow}\rangle$ is allowed both electrically and magnetically by the dipole couplings. The typical value for resonance integral is around the order of a few $eV$ [14], already in the region of visible wavelength. Therefore, it suggests $\varepsilon_r < 0$ and $\mu_r < 0$ might probably be realizable for a medium containing molecules with the Möbius topology in the visible frequency regime.

To quantitatively investigate this possibility, $\varepsilon_r^\prime$ is explicitly calculated for the Möbius ring by using the matrix elements $\delta g_{k,\sigma,\sigma'}$. For positive $V$ and $\xi$, the ground state of $H$ is $|0, \downarrow\rangle$ and thus $E_g = E_{0\downarrow}$. When $\omega$ is near the inter-band transition frequency $\Delta_{0\uparrow}$, $\varepsilon_r^\prime$ is simplified as

$$\varepsilon_r^\prime (\omega) = \begin{bmatrix} 1 - \eta(\omega) & 0 \\ 0 & 1 - \eta(\omega) - 2\eta(\omega) \\ 0 & -2\eta(\omega) - 1 - \eta(\omega) \end{bmatrix}.$$  \hspace{1cm} (15)

in the molecular coordinate system, where

$$\eta(\omega) = \frac{e^2}{8\varepsilon_0 \varepsilon_0} \frac{u^2 [\omega - 2V - 2\xi (1 - \cos \frac{\omega}{2})]}{[\omega - 2V - 2\xi (1 - \cos \frac{\omega}{2})]^2 + \gamma^2}.$$  \hspace{1cm} (16)
The permittivity tensor is not diagonal because of the non-zero off-diagonal term $\varepsilon^{\beta\gamma}$. Since the tensor is real-symmetric, $\varepsilon^{\alpha\beta}$ can be diagonalized by a rotation (in the $yz$ plane) to the principle-axis coordinate system. This yields $1 - \eta$, $1 - 5\eta$ and $1$ for relative permeability along three principal axes (see Fig. 2(a)), respectively. Therefore, the minimal requirement for $\varepsilon_r < 0$ is that $\eta > 1/5$, i.e.,

$$5\varepsilon_0 c^2 \omega^2 > 16\gamma \varepsilon_0 \omega_0. \quad (17)$$

On the other hand, the tensor of the relative permeability $\mu_r^{\alpha\beta}$ is represented by

$$\mu_r^{\alpha\beta}(\omega) = \begin{bmatrix} 1 - \alpha^2 \eta(\omega) & 0 & 0 \\ 0 & 1 - \alpha^2 \eta(\omega) & -2\alpha\beta\eta(\omega) \\ 0 & -2\alpha\beta\eta(\omega) & 1 - 4\beta^2 \eta(\omega) \end{bmatrix}, \quad (18)$$

where

$$\alpha = \frac{R}{c} \left[ V + \xi (\cos \delta - \cos \frac{\delta}{2}) \right], \quad (19)$$

$$\beta = 2 \frac{R\varepsilon_0}{c} \sin^2 \frac{\delta}{2} \cos \frac{\delta}{2} \quad (20)$$

Figure 2: (color online) Relative permittivity $\varepsilon_r$ and permeability $\mu_r^{\alpha\beta}$ as a function of the detuning $\Delta \omega = \omega - \omega_0$, between the frequencies of incident field and transition $|0, \uparrow \rangle = |0, \uparrow \rangle$. Only negative diagonal elements of $\varepsilon_r$ and $\mu_r$ in their corresponding principle axis coordinate systems are shown.

The limitation on the lifetime of the excited state for achieving negative refraction is estimated from Eq. (21). It is possible to synthesize a Möbius ring of carbon atoms with $N = 12$ and radius $0.29\,\text{nm}$ [13, 20]. By taking the value $3.6\,\text{eV}$ for $V$ and $\xi$ [14], one finds that an excited state lifetime of $1.1\,\text{ns}$ is enough for $\mu_r^{\alpha\beta} < 0$. Since the usual excited-state relaxation time of molecular systems is about $3 \sim 4\,\text{ns}$ [28], it is reasonable to expect a medium with Möbius molecules as a potential material to show the negative refraction.

Although in our calculation only one electron is considered, our result is consistent with the more realistic case when all $\pi$ electrons from all atoms in the Möbius molecule are taken into account. In that case, when the spin degree of freedom is considered, two electrons with different spin states can stay in the same energy eigen state $|k, \sigma \rangle$. For the ground state of the entire system including all electrons, all the states of the lower energy band will be filled. The interband transition in our calculation is just the special case of all possible transitions. In this sense, our simplified calculation clearly illustrates the key factors for demonstrating negative refraction in Möbius molecules.

Unlike other proposals utilizing atom gas [15], the electromagnetic response of medium containing the Möbius molecules is anisotropic. For electric response this is inferred from the relative permittivity in the principle axis coordinate, where one of the components is always 1. This indicates the absence of negative refraction if incident electric field had been polarized in that direction. While for the relative permeability, by performing a proper rotation transformation on $\mu_r^{\alpha\beta}$, three diagonal elements are respectively $1 - \eta\alpha^2$, $1 - \eta(\alpha^2 + 4\beta^2)$, and $1$ (see Fig. 2(b)). This also demonstrates the absence of negative refraction for a particular magnetic field polarization (such that $\mu_r = 1$). Nevertheless, by appropriately arranging electromagnetic fields incident in specific directions with electric and magnetic fields polarized in the perpendicular directions, the light will be expected to bend in the direction which shows negative refraction.

**Conclusion.**—We have explored the Möbius molecular ring as a potential candidate for “molecular coordinate” negative refraction. The previous investigations with the functional atoms or molecules rely on the conceptual analogy of the split-ring resonator for magnetic response [14], while for Möbius ring this is induced by its non-trivial boundary condition. Our results demonstrate that engineering on the topology is beneficial in realizing the high frequency magnetic response at the molecular level. This finding opens up an alternative approach to design molecular negative index materials, which is promising in achieving 3D bulk negative refraction at the visible wavelength. We further remark that our proposal is a complementary for the previous experimental investigation [9], where the negative refracting metamaterial was fabricated with Möbius topology in a “top down” fashion.
In order to induce the magnetic response, their element is still based on the configuration of the split-ring resonator. Moreover, due to quantum effect, our architecture is two orders smaller in size than theirs.

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