

Optical Activity of Chiral Nanoscrolls

Anvar S. Baimuratov, Yurii K. Gun'ko,* Alexey G. Shalkovskiy, Alexander V. Baranov, Anatoly V. Fedorov, and Ivan D. Rukhlenko*

A first quantum-mechanical theory of chiral semiconductor nanoscrolls is presented. The theory allows one to analytically calculate the rotatory strengths and dissymmetry factors of optical transitions inside monodisperse ensembles of randomly oriented nanoscrolls, as well as to model the circular dichroism spectra of the ensembles. The theory predicts strong optical activity of semiconductor nanoscrolls upon both intraband and interband transitions, which makes them useful for various biochemical, biophysical, and nanophotonics applications. Specifically, the rotatory strengths of intraband and interband transitions were shown to reach values as high as 10^{-35} erg cm³, which is three to four orders of magnitude larger than the typical rotatory strengths of small chiral molecules.

advantage of such nanocrystals over small chiral molecules is their much stronger dissymmetry in the interaction with circularly polarized light due to the larger number of atoms.

Chiral semiconductor nanocrystals come in all possible shapes and with various sources of chirality.^[9] One of the pioneering experimental works demonstrated that surface layers of CdS quantum dots can acquire chiral structure from enantiopure penicillamine ligands attached to the quantum dot surface.^[10] It was then followed by a number of theoretical and experimental papers, which improved this fabrication technique and theoretically

1. Introduction

The past decade has seen a tremendous growth in the number of studies focused on chiral inorganic nanocrystals of various shapes and compositions.^[1–3] These studies were stimulated by the recent progress in nanofabrication techniques and the great interest in chiral nanoparticles caused by their prospective uses in bio- and chemosensors, as well as by their potential applications as detectors and separators of enantiomeric drug molecules.^[4–6] Chiral semiconductor nanocrystals are especially attractive for these applications owing to their tunable photoluminescence signatures, resistance to photobleaching, and the highly selective affinity to chiral species.^[7,8] The main

addressed the most common origins of nanocrystal chirality. It has become apparent that semiconductor nanocrystals can become chiral and optically active in the presence of all sorts of surface and bulk defects that naturally develop during their fabrication.^[11,12] These include screw dislocations,^[13,14] irregularities of shapes,^[15,16] distortions of the crystal lattice caused by uncompensated torques,^[17] as well as asymmetrically positioned inclusions and impurities.^[18] All these chirality sources were shown to be capable of making semiconductor nanocrystals 100–1000 more optically active than small chiral molecules, which is the factor that roughly shows the increase in the density of atoms.

One particularly important kind of chiral semiconductor nanocrystals that has not been theoretically addressed so far is chiral nanoscrolls.^[19] Chiral nanoscrolls are more or less contorted and rolled nanoflakes or nanoplatelets, which are often produced through the ultrasound exfoliation of semiconductor materials in the presence of chiral ligands. The pronounced optical activity of the so produced MoS₂ nanoscrolls has been recently observed in their circular dichroism spectra. This paper provides a first theory of optical activity of chiral nanoscroll ensembles needed to interpret this and similar experiments. Our theory leads to analytical expressions for the rotatory strengths of intraband and interband optical transitions, which may prove especially useful for qualitative analysis of the nanoscrolls' spectra.

Dr. A. S. Baimuratov, Prof. Yu. K. Gun'ko,
Prof. A. V. Baranov, Prof. A. V. Fedorov,
Dr. I. D. Rukhlenko
ITMO University
49 Kronverksky Pr., St. Petersburg 197101, Russia
E-mail: igounko@tcd.ie; rukhlenko.ivan@gmail.com



Prof. Yu. K. Gun'ko
School of Chemistry and CRANN Institute
Trinity College Dublin
Dublin 2, Ireland

Dr. A. G. Shalkovskiy
Saint Petersburg State University
7-9 University Embankment, St Petersburg 199034, Russia

Dr. A. G. Shalkovskiy
Institute for Design Problems in Microelectronics
of Russian Academy of Sciences
Moscow 124365, Russia

Dr. I. D. Rukhlenko
Faculty of Engineering
Monash University
Victoria 3800, Australia

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2. Perturbative Description of the Electronic Subsystem of Chiral Nanoscrolls

In order to analytically treat the electronic subsystem of a chiral nanoscroll, we employ our recently developed approach of coordinate transformation.^[15] This approach relies on the

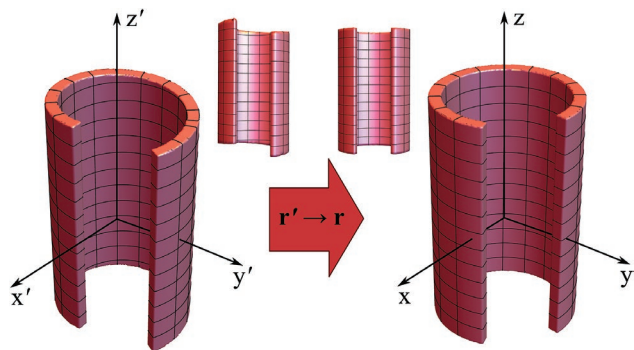


Figure 1. Transformation of a chiral nanoscroll (left) into an achiral one (right) upon the coordinate transformation $\mathbf{r}' \rightarrow \mathbf{r}$. Insets show side views of the two nanoscrolls.

assumption that the surface of a chiral nanocrystal is relatively close to the surface of some regular achiral body, and requires the existence of a linear transformation between the two surfaces. If these two conditions are met, then one can replace the eigenvalue problem $\nabla_{\mathbf{r}'}^2 \psi(\mathbf{r}') = -\epsilon \psi(\mathbf{r}')$ for the nanocrystal with a chiral surface in old coordinates \mathbf{r}' by a much simpler problem $(\nabla_{\mathbf{r}}^2 + \delta V)\psi(\mathbf{r}) = -\epsilon \psi(\mathbf{r})$ for the achiral nanocrystal in new coordinates \mathbf{r} , in which potential δV — produced by coordinate transformation $\mathbf{r}' \rightarrow \mathbf{r}$ — can be treated as a small perturbation of the electronic subsystem.

Consider a chiral nanoscroll shown on the left of **Figure 1** and occupying in cylindrical coordinates (ρ', φ', z') the region of space

$$\rho_1 \leq \rho' \leq \rho_2 \quad (1)$$

$$0 \leq \varphi' \leq \varphi_0 \quad (2)$$

$$-\frac{L}{2} \leq z' + \beta \varphi' \leq \frac{L}{2} \quad (3)$$

where ρ_1 and ρ_2 are the inner and outer radii of the nanoscroll, φ_0 and L its angular and vertical dimensions, and $|\beta| \ll L$ is the small chirality parameter. This chiral nanoscroll of volume $\varphi_0(\rho_2^2 - \rho_1^2)L$ turns into an achiral nanoscroll of the same volume shown on the right of **Figure 1** upon the linear transformation of coordinates

$$\rho = \rho' \quad (4)$$

$$\varphi = \varphi' \quad (5)$$

$$z = z' + \beta \varphi' \quad (6)$$

The transformation modifies the Laplace operator, $\nabla_{\rho' \varphi' z'}^2 = \nabla_{\rho \varphi z}^2 + \delta V$, resulting in the chiral perturbation potential of the form

$$\delta V \approx \frac{2\beta}{\rho^2} \frac{\partial^2}{\partial z \partial \varphi} \quad (7)$$

The considered nanoscroll has a constant radius. This may not always be the case in practice, as it was experimentally demonstrated by the example of a rolled up monolayer MoS₂ sheet.^[19] The effect of the nonuniform nanoscroll rolling can be described by the linear coordinate transformation

$$\rho = \rho' + \alpha \varphi' \quad (8)$$

$$\varphi = \varphi' \quad (9)$$

$$z = z' + \beta \varphi' \quad (10)$$

which leads to the perturbation potential of the form

$$\delta V \approx \frac{\alpha \varphi}{\rho^2} \frac{\partial}{\partial \rho} + \frac{2\alpha \varphi}{\rho^3} \frac{\partial^2}{\partial \varphi^2} + \frac{2\alpha}{\rho^2} \frac{\partial^2}{\partial \rho \partial \varphi} + \frac{2\beta}{\rho^2} \frac{\partial^2}{\partial z \partial \varphi} \quad (11)$$

where we have ignored the term proportional to the product $\alpha\beta$ due to its smallness. **Figure 2** shows how a chiral rolled nanoscroll, characterized by nonzero parameters α and β , can be obtained from an ordinary chiral nanoscroll with $\alpha = 0$. Note that the three additional terms arising in the perturbation potential due to the nonuniform rolling of the nanoscroll do not change sign upon the inversion of coordinates $(\rho, \varphi, z) \rightarrow (\rho, \varphi + \pi, -z)$. This implies that the nonuniform rolling of a chiral nanoscroll does not change its optical activity in the first order with respect to parameters α and β .

Using a simple two-band model of semiconductor^[14] makes it possible to analytically calculate the envelope wave functions and energy spectra of electrons and holes confined by a chiral nanoscroll with impenetrable boundaries from the Schrodinger equation

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \psi}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2\beta}{\rho^2} \frac{\partial^2 \psi}{\partial z \partial \varphi} = -\epsilon \psi \quad (12)$$

where $\epsilon = 2mE/\hbar^2$ and the chiral term is a small perturbation of the otherwise achiral system. The solution to this equation without the chiral potential is given by

$$\psi_{nlp}(\rho, \varphi, z) = \frac{2}{\rho_1 \sqrt{\varphi_0 L}} r_{nl}(\rho/\rho_1) \sin(\lambda_l \varphi) H_p(k_p z) \quad (13)$$

$$\epsilon_{nlp} = \left(\frac{\zeta_{nl}}{\rho_1} \right)^2 + k_p^2 \quad (14)$$

where $\lambda_l = \pi l/\varphi_0$, $l = \pm 1, \pm 2, \pm 3, \dots$, $k_p = \pi p/L$, $p = 1, 2, 3, \dots$, $H_p(u) = \cos u$ for odd p and $H_p(u) = \sin u$ for even p ,

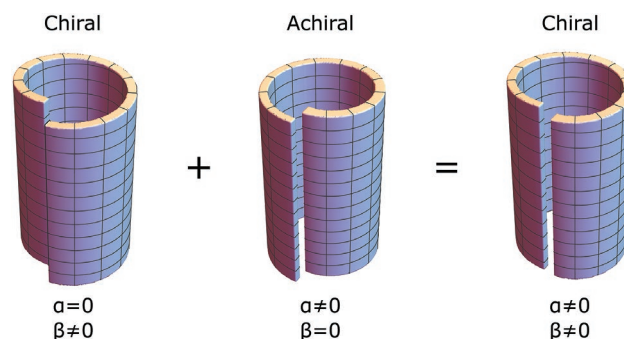


Figure 2. If a chiral nanoscroll of a constant radius is bent inward, it turns into a chiral nanoscroll of variable radius, which exhibits the same optical activity as the unbent one. The three nanoscrolls are plotted for $\varphi_0 = 2\pi$.

$$r_{nl}(x) = a_{nl}[J_\lambda(\zeta_{nl}x) + b_{nl}Y_\lambda(\zeta_{nl}x)] \quad (15)$$

$$a_{nl} = 2\sqrt{2}(\kappa^2\{J_{\lambda-1}(\zeta_{nl}\kappa) - J_{\lambda+1}(\zeta_{nl}\kappa) + b_{nl}[Y_{\lambda-1}(\zeta_{nl}\kappa) - Y_{\lambda+1}(\zeta_{nl}\kappa)]\}^2 - \{J_{\lambda-1}(\zeta_{nl}) - J_{\lambda+1}(\zeta_{nl}) + b_{nl}[Y_{\lambda-1}(\zeta_{nl}) - Y_{\lambda+1}(\zeta_{nl})]\}^2)^{-1/2} \quad (16)$$

$$b_{nl} = -\frac{J_\lambda(\zeta_{nl})}{Y_\lambda(\zeta_{nl})} \quad (17)$$

$J_\lambda(x)$ and $Y_\lambda(x)$ are the cylindrical Bessel functions of the first and second kinds, $\lambda = \lambda_j$, $\kappa = \rho_2/\rho_1$, and where ζ_{nl} is the n th root of the dispersion equation

$$J_\lambda(\zeta_{nl})Y_\lambda(\kappa\zeta_{nl}) = J_\lambda(\kappa\zeta_{nl})Y_\lambda(\zeta_{nl}) \quad (18)$$

It should be noted that the system of envelopes ψ_{nlp} is orthonormal

$$\int_{\rho_1}^{\rho_2} \rho d\rho \int_0^{\varphi_0} d\varphi \int_{-L/2}^{L/2} dz \psi_{nlp} \psi_{n'l'p'} = \delta_{nn'} \delta_{ll'} \delta_{pp'} \quad (19)$$

and that all the quantum states are doubly degenerate with respect to the sign of the angular momentum l .

Nanoscrolls obtained through the ultrasound exfoliation of bulk semiconductors in the presence of chiral ligands are often just a few monolayers thick but have a relatively large surface. The thickness of such nanoscrolls is much smaller than their radius

$$\delta\kappa = \kappa - 1 = \frac{\rho_2 - \rho_1}{\rho_1} = \frac{\delta\rho}{\rho_1} \ll 1 \quad (20)$$

in which case the dispersion equation for small l can be reduced using the asymptotic expansions of Bessel functions at large arguments^[20] to a simple form $\sin(\delta\kappa\zeta_{nl}) = 0$. The roots of this equation are $\zeta_{nl} = \pi n / \delta\kappa$, with $n = 1, 2, 3, \dots$, so that the energy spectrum of the confined charge carriers takes the form

$$\varepsilon_{nlp} = \pi^2 \left(\frac{n^2}{\delta\rho^2} + \frac{p^2}{L^2} \right) \quad (21)$$

and the lowest-order electronic states are degenerate with respect to l .

Using the obtained envelopes, we find the matrix element of the perturbation potential defined in Equation (7) to be given by

$$V_{\mathbf{m}\mathbf{n}} \equiv \langle \psi_{\mathbf{n}} | \delta V | \psi_{\mathbf{m}} \rangle = \frac{2\beta}{\rho_1^2 L} R_{n'l'nl}^{(-1)} B_{l'l} A_{p'p} \quad (22)$$

where $\mathbf{m} = (n, l, p)$ and $\mathbf{n} = (n', l', p')$ are the sets of quantum numbers describing the states of the confined charge carriers

$$R_{n'l'nl}^{(k)} = \int_1^\kappa r_{n'l'}(x) r_{nl}(x) x^k dx \quad (23)$$

$$B_{l'l} = \frac{1}{\varphi_0} \frac{4l'l}{l'^2 - l^2} \frac{1 + (-1)^{l'+l+1}}{2} \quad (24)$$

$$A_{p'p} = \frac{4p'p}{p'^2 - p^2} \text{Re}(i^{p'+p+1}) \quad (25)$$

One can see that coefficients $A_{p'p} = -A_{pp'}$ and $B_{l'l} = -B_{ll'}$ are nonzero only when the quantum numbers p' and p and l' and l are of opposite parities. This implies that the diagonal matrix elements of the perturbation potential vanish and the perturbation does not change the energy spectrum of the nanoscrolls.

3. Rotatory Strengths of Intraband Transitions

Using the stationary perturbation theory and the Rosenfeld approximation, we have recently shown that the modification of electronic wave functions of a semiconductor nanocrystal induced by an arbitrary chiral potential makes the nanocrystal optically active and results in two kinds of rotatory strengths, which to the first order of δV are given by the expressions^[16]

$$R_{\mathbf{m}\mathbf{n}}^{\text{ED}} = \gamma \text{Im} \sum_s \left(\frac{V_{\text{sm}} \Pi_{\mathbf{m}\mathbf{n}}^{\text{sn}}}{\varepsilon_{\mathbf{m}} - \varepsilon_{\mathbf{s}}} + \frac{V_{\text{sn}} \Pi_{\mathbf{m}\mathbf{n}}^{\text{ms}}}{\varepsilon_{\mathbf{n}} - \varepsilon_{\mathbf{s}}} \right) \quad (26)$$

$$R_{\mathbf{m}\mathbf{n}}^{\text{MD}} = \gamma \text{Im} \sum_s \left(\frac{V_{\text{sn}} \Pi_{\mathbf{m}\mathbf{n}}^{\text{mn}}}{\varepsilon_{\mathbf{n}} - \varepsilon_{\mathbf{s}}} + \frac{V_{\text{sm}} \Pi_{\mathbf{m}\mathbf{n}}^{\text{ms}}}{\varepsilon_{\mathbf{m}} - \varepsilon_{\mathbf{s}}} \right) \quad (27)$$

where $\gamma = e^2 \sqrt{\varepsilon_\infty} / (2mc)$, $-e$ and m are the charge and effective mass of an electron, ε_∞ is the high-frequency permittivity of the nanoscroll, c is the speed of light in a vacuum, $\varepsilon_{\mathbf{m}}$ and V_{sm} are given by Equations (14) and (22), respectively, and $\Pi_{\mathbf{m}\mathbf{n}}^{\text{sm}} = \langle \psi_{\mathbf{u}} | \mathbf{r} | \psi_{\mathbf{m}} \rangle \langle \psi_{\mathbf{s}} | \mathbf{L} | \psi_{\mathbf{n}} \rangle$ is the scalar product of the matrix elements of radius vector \mathbf{r} and angular momentum operator $\mathbf{L} = -i\hbar \mathbf{r} \times \nabla$. Rotatory strength $R_{\mathbf{m}\mathbf{n}}^{\text{ED}}$ corresponds to electric dipole (ED) allowed transitions between the unperturbed quantum states of the nanocrystal, for which $\langle \psi_{\mathbf{n}} | \mathbf{r} | \psi_{\mathbf{m}} \rangle \neq 0$, whereas rotatory strength $R_{\mathbf{m}\mathbf{n}}^{\text{MD}}$ describes magnetic dipole (MD) allowed transitions, for which $\langle \psi_{\mathbf{m}} | \mathbf{L} | \psi_{\mathbf{n}} \rangle \neq 0$.

The symmetry of the problem suggests calculating $\Pi_{\mathbf{m}\mathbf{n}}^{\text{sm}}$ using cyclic coordinates (r_{+1}, r_0, r_{-1}) , which are related to the cylindrical ones as $r_{+1} = -r_{-1}^* = -(\rho/\sqrt{2})e^{i\varphi}$ and $r_0 = z$. Taking into account that the cyclic components of angular momentum are given by $L_0 = -i\hbar \partial/\partial\varphi$ and

$$L_{+1} = L_{-1}^* = \frac{\hbar}{\sqrt{2}} e^{i\varphi} \left(\rho \partial_z - z \partial_\rho - i \frac{z \partial_\varphi}{\rho} \right) \quad (28)$$

and introducing two additional sets of quantum numbers $\mathbf{s} = (n'', l'', p'')$ and $\mathbf{u} = (n''', l''', p''')$, after some simple algebra we obtain

$$\begin{aligned} \Pi_{\mathbf{m}\mathbf{n}}^{\text{sm}} &= \sum_{\mu=0,\pm 1} (-1)^\mu \langle \psi_{\mathbf{u}} | r_\mu | \psi_{\mathbf{m}} \rangle \langle \psi_{\mathbf{s}} | L_{-\mu} | \psi_{\mathbf{n}} \rangle \\ &= i\hbar L \left[-\delta_{n''n} \delta_{l''l} D_{p''p} R_{n''l''n'l'}^{(1)} B_{l''l'} \delta_{p''p'} \right. \\ &\quad \left. + R_{n''l''n'l'}^{(2)} \delta_{p''p} M_{n''l''n'l'}^{p''p'} \text{Im}(C_{l''l'} C_{l'l'}^*) \right] \end{aligned} \quad (29)$$

where

$$D_{p'p} = \frac{8p'p}{\pi^2(p'^2 - p^2)^2} \text{Re}(i^{p'+p+1}) \quad (30)$$

$$M_{n'n'l'n'l'}^{p'p} = \sigma^2 R_{n'n'l'n'l'}^{(2)} A_{p'p} - Q_{n'n'l'n'l'} D_{p'p} - \frac{1}{2} \left[1 + (l'^2 - l''^2) \left(\frac{\pi}{\varphi_0} \right)^2 \right] R_{n'n'l'n'l'}^{(0)} D_{p'p} \quad (31)$$

$$Q_{n'l'n'l} = \frac{1}{2} \zeta_{nl} a_{nl} \int_1^k r_{n'l'}(x) \{ J_{\lambda-1}(\zeta_{nl}x) - J_{\lambda+1}(\zeta_{nl}x) \} + b_{nl} [Y_{\lambda-1}(\zeta_{nl}x) - Y_{\lambda+1}(\zeta_{nl}x)] x dx \quad (32)$$

$$C_{l'l} = \frac{4i\pi^2 l' l \varphi_0}{[\varphi_0 + (l+l')\pi][\varphi_0 + (l-l')\pi]} \times \frac{(-1)^{l+l'} e^{i\varphi_0} - 1}{[\varphi_0 - (l+l')\pi][\varphi_0 - (l-l')\pi]} \quad (33)$$

and $\sigma = \rho_1/L$. Coefficients $D_{p'p} = D_{pp'}$ are nonzero provided that p' and p have opposite parities, and coefficients $C_{l'l} = C_{l'l'}$ are nonzero regardless of the parities of l' and l when $\varphi_0 \neq \pi$ or 2π .

By substituting Equations (22) and (29) into (26) and (27) and evaluating the sums in the resulting equations, we obtain the following final expressions for the two kinds of rotatory strengths upon interband transitions inside the nanoscrolls

$$R_{n'l'p'nlp}^{\text{ED}} = -\vartheta \delta_{n'n} \delta_{l'l'} A_{p'p} D_{p'p} \sum_{n''} \left(\frac{1}{\epsilon_{nlp} - \epsilon_{n''l'p'}} + \frac{1}{\epsilon_{nlp'} - \epsilon_{n''l'p}} \right) \times R_{n'n'l'n'l'}^{(-1)} R_{n'n'l'n'l'}^{(1)} B_{l'l}^2 \sum_{n''} \delta_{p'p} \times \left(\frac{R_{n'n'l'n'l'}^{(-1)} M_{n'n'l'n'l'}^{p'p} D_{l'l'}}{\epsilon_{nlp} - \epsilon_{n''l'p'}} + \frac{R_{n'n'l'n'l'}^{(1)} M_{n'n'l'n'l'}^{p'p} D_{l'l'}}{\epsilon_{nlp'} - \epsilon_{n''l'p}} \right) A_{p'p} \quad (34)$$

and

$$R_{n'l'p'nlp}^{\text{MD}} = -\vartheta \delta_{pp'} R_{n'n'l'n'l'}^{(-1)} R_{n'n'l'n'l'}^{(1)} B_{l'l}^2 B_{l'l}^2 \sum_{p''} \left(\frac{1}{\epsilon_{n'l'p} - \epsilon_{n''l'p'}} - \frac{1}{\epsilon_{nlp} - \epsilon_{n''l'p}} \right) \times A_{p'p} D_{p'p} - \vartheta M_{n'n'l'n'l'}^{p'p} A_{p'p} \times \sum_{n''} \left(\frac{R_{n'n'l'n'l'}^{(-1)} R_{n'n'l'n'l'}^{(2)} D_{l'l'}}{\epsilon_{n'l'p} - \epsilon_{n''l'p}} - \frac{R_{n'n'l'n'l'}^{(1)} R_{n'n'l'n'l'}^{(2)} D_{l'l'}}{\epsilon_{nlp} - \epsilon_{n''l'p}} \right) \quad (35)$$

where $\vartheta = 2\beta\hbar\tilde{n}$, $\epsilon_{nlp} = \zeta_{nl}^2 + (\pi p\sigma)^2$ is the dimensionless energy, and we have introduced new coefficients

$$D_{l'l'} = B_{l'l'} \text{Im}(C_{l'l} C_{l'l}^*) = \frac{4\pi^2 l' l \varphi_0}{[\varphi_0 + (l+l')\pi][\varphi_0 + (l-l')\pi]} \times \frac{1}{[\varphi_0 - (l+l')\pi][\varphi_0 - (l-l')\pi]} \times \frac{4\pi^2 l' l \varphi_0}{[\varphi_0 + (l+l'')\pi][\varphi_0 + (l-l'')\pi]} \times \frac{1}{[\varphi_0 - (l+l'')\pi][\varphi_0 - (l-l'')\pi]} \times (-1)^l \frac{2l'l'}{l''^2 - l'^2} \frac{(-1)^{l'} - (-1)^{l'}}{2} \frac{\sin \varphi_0}{\varphi_0} \quad (36)$$

One can see that the rotatory strengths are determined by the scaling factor $\vartheta = 2\beta\hbar e^2 \sqrt{\epsilon_\infty} / (2mc)$. By taking $\beta = 2$ nm, $\sqrt{\epsilon_\infty} = 3$, and $m = 0.1m_0$, where m_0 is the free-electron mass, we get $\vartheta \approx 5 \times 10^{-35}$ erg cm³. This value exceeds the rotatory strengths of chiral molecules by three to four orders of magnitude. The obtained expressions also show that each kind of rotatory strength is a sum of two contributions, with different selection rules. The electric-dipole rotatory strengths are nonzero for transitions

$$(nlp) \rightarrow (nlp') \quad (37)$$

$$(nlp) \rightarrow (n'l'p) \quad (38)$$

without any limitations on quantum numbers $n' \neq n$ and $l' \neq l$, provided the parities of p' and p are different. The magnetic-dipole rotatory strengths are nonzero for transitions

$$(nlp) \rightarrow (n'l'p) \quad (39)$$

$$(nlp) \rightarrow (nlp') \quad (40)$$

without any limitations on quantum numbers $n' \neq n$, provided the parities of l' and l and of p' and p are different.

4. Rotatory Strengths of Interband Transitions

Let us now consider the optical activity upon interband transitions inside semiconductor nanoscrolls. For the sake of simplicity, we restrict ourselves to a two-band model of semiconductor and consider transitions of electrons from a valence band (v) state with a set of quantum numbers \mathbf{m} into a conduction band (c) state with a set of quantum numbers \mathbf{n} . We shall assume that the matrix element of momentum operator, $\mathbf{P}_{\mathbf{nm},\mu}^{(cv)}$, calculated using the rapidly oscillating amplitudes $u_{c,\mathbf{n}}(\mathbf{r})$ and $u_{v,\mathbf{m}}(\mathbf{r})$ over the volume V_μ of the μ th unit cell of an achiral nanoscroll, is independent of \mathbf{m} and \mathbf{n} , but is a function of the location of the unit cell^[21]

$$\mathbf{P}_{\mathbf{nm},\mu}^{(cv)} = \langle u_{c,\mathbf{n}} | \mathbf{p} | u_{v,\mathbf{m}} \rangle_{V_\mu} = \mathbf{P}_\mu \quad (41)$$

Owing to the specific shape of the achiral nanoscroll, we shall also assume that the formal transition to the continuous medium $\mathbf{P}_\mu \rightarrow \mathbf{P}(\mathbf{r})$ leads to a continuous vector field $\mathbf{P}(\mathbf{r}) = (P_\rho, P_\phi, P_z)$ with constant components in cylindrical coordinates. This assumption is justified for nanoscrolls of large radii formed from relatively thin nanoplatelets $\rho_2 - \rho_1 \ll \rho_1$, which is often the case for a few monolayer-thick (quasi-1D) folded nanoplatelets.

We next take into account the dislocation-induced perturbation of the electronic subsystem of nanoscrolls by calculating the full matrix elements of interband transitions using the nontrivial metrics $g^{ij}(\beta, \mathbf{r})$ of the dislocation-distorted space. This metrics changes the scalar product of vector potential \mathbf{A} and momentum \mathbf{P} , leading to a nontrivial interaction of electrons with light. Using the Einstein summation convention, we make replacement $A_i P^i \rightarrow A_i g^{ij} P_j$, which changes the momentum operator as $P^i(\mathbf{r}) \rightarrow g^{ij}(\beta, \mathbf{r}) P_j(\mathbf{r}) = \tilde{P}^i(\beta, \mathbf{r})$ or, in vector form,

$\mathbf{P}(\mathbf{r}) \rightarrow \tilde{\mathbf{P}}(\beta, \mathbf{r})$,^[13] This replacement changes the matrix elements of the radius vector and angular momentum of interband transitions,^[22] which take the forms

$$\langle \psi_{\mathbf{n}} u_{c,\mathbf{n}} | \mathbf{r} | \psi_{\mathbf{m}} u_{v,\mathbf{m}} \rangle = -\frac{\hbar}{E_{\mathbf{nm}} m_0} \langle \psi_{\mathbf{n}} | \tilde{\mathbf{P}}(\beta, \mathbf{r}) | \psi_{\mathbf{m}} \rangle \quad (42)$$

$$\langle \psi_{\mathbf{n}} u_{c,\mathbf{n}} | \mathbf{L} | \psi_{\mathbf{m}} u_{v,\mathbf{m}} \rangle = \langle \psi_{\mathbf{n}} | \mathbf{r} \times \tilde{\mathbf{P}}(\beta, \mathbf{r}) | \psi_{\mathbf{m}} \rangle \quad (43)$$

where $E_{\mathbf{nm}}$ is the transition energy. In the linear approximation with respect to the chiral parameter β , the metric tensor in cylindrical coordinates is given by

$$g^{ij}(\beta, \mathbf{r}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\rho^2 & \beta/\rho^2 \\ 0 & \beta/\rho^2 & 1 \end{pmatrix} \quad (44)$$

and the transformed operator can be conveniently written as a sum

$$\tilde{\mathbf{P}}(\beta, \mathbf{r}) = \mathbf{P}(\mathbf{r}) + \frac{\beta}{\rho} \mathcal{P}(\mathbf{r}) \quad (45)$$

where $\mathcal{P}(\mathbf{r}) = (0, P_z, P_\phi)$.

Using Equations (42)–(45) and dropping the terms proportional to β^2 , one can calculate the rotatory strengths of interband transitions. Much like in the case of intraband transitions, the resulting rotatory strengths have two components

$$R_{\mathbf{cn},\mathbf{vm}}^{\text{ED}} = \frac{\beta \hbar e^2 \sqrt{\epsilon_\infty}}{2cm_0^2 E_{\mathbf{nm}}} \text{Re} \left(\langle \psi_{\mathbf{m}} | \mathbf{P}^* | \psi_{\mathbf{n}} \rangle \langle \psi_{\mathbf{n}} | \rho^{-1} \mathbf{L}^{(P)} | \psi_{\mathbf{m}} \rangle \right) \quad (46)$$

$$R_{\mathbf{cn},\mathbf{vm}}^{\text{MD}} = \frac{\beta \hbar e^2 \sqrt{\epsilon_\infty}}{2cm_0^2 E_{\mathbf{nm}}} \text{Re} \left(\langle \psi_{\mathbf{m}} | \rho^{-1} \mathcal{P}^* | \psi_{\mathbf{n}} \rangle \langle \psi_{\mathbf{n}} | \mathbf{L}^{(P)} | \psi_{\mathbf{m}} \rangle \right) \quad (47)$$

where $\mathbf{L}^{(X)} = \mathbf{r} \times \mathbf{X}$. The matrix elements here are convenient to evaluate using cyclic coordinates, in which the momentum components are given by

$$P_0^* = P_z^*, \quad P_{+1}^* = -\frac{e^{i\phi}}{\sqrt{2}} (P_\rho^* + iP_\phi^*), \quad P_{-1}^* = \frac{e^{-i\phi}}{\sqrt{2}} (P_\rho^* - iP_\phi^*) \quad (48)$$

$$\mathcal{P}_0^* = P_\phi^*, \quad \mathcal{P}_{+1}^* = -i \frac{e^{i\phi}}{\sqrt{2}} P_z^*, \quad \mathcal{P}_{-1}^* = -i \frac{e^{-i\phi}}{\sqrt{2}} P_z^* \quad (49)$$

The components of angular momentum in cyclic coordinates are of the form

$$L_0^{(P)} = \rho P_\phi, \quad L_{+1}^{(P)} = \frac{e^{i\phi}}{\sqrt{2}} (i\rho P_z - izP_\rho + zP_\phi), \quad (50)$$

$$L_{-1}^{(P)} = \frac{e^{-i\phi}}{\sqrt{2}} (i\rho P_z - izP_\rho - zP_\phi)$$

$$L_0^{(P)} = \rho P_z, \quad L_{+1}^{(P)} = \frac{e^{i\phi}}{\sqrt{2}} (i\rho P_\phi + zP_z), \quad (51)$$

$$L_{-1}^{(P)} = \frac{e^{-i\phi}}{\sqrt{2}} (i\rho P_\phi - zP_z)$$

The substitution of Equations (48)–(51) into the scalar products of Equations (46) and (47), yields the interband rotatory strengths

$$R_{\mathbf{cn},\mathbf{vm}}^{\text{ED}} = \frac{\eta}{E_{\mathbf{nm}}} \text{Re} \left(\langle \psi_{\mathbf{m}} | \mathbf{P}^* | \psi_{\mathbf{n}} \rangle \langle \psi_{\mathbf{n}} | \rho^{-1} \mathbf{L}^{(P)} | \psi_{\mathbf{m}} \rangle \right) \quad (52)$$

$$= \frac{\eta}{E_{\mathbf{nm}}} \delta_{pp'} \left[\delta_{nn'} \delta_{ll'} |P_z|^2 - (R_{n'l'nl}^{(1)})^2 |C_{l'l}|^2 |P_\phi|^2 \right],$$

$$R_{\mathbf{cn},\mathbf{vm}}^{\text{MD}} = \frac{\eta}{E_{\mathbf{nm}}} \text{Re} \left(\langle \psi_{\mathbf{m}} | \rho^{-1} \mathcal{P}^* | \psi_{\mathbf{n}} \rangle \langle \psi_{\mathbf{n}} | \mathbf{L}^{(P)} | \psi_{\mathbf{m}} \rangle \right) \quad (53)$$

$$= \frac{\eta}{E_{\mathbf{nm}}} R_{n'l'nl}^{(0)} R_{n'l'nl}^{(2)} \delta_{pp'} \left(\delta_{ll'} |P_\phi|^2 - |C_{l'l}|^2 |P_z|^2 \right).$$

where $\eta = \beta \hbar e^2 \sqrt{\epsilon_\infty} / (2cm_0^2)$ and we have assumed that $\mathbf{m} = (n, l, p)$ and $\mathbf{n} = (n', l', p')$.

One can see all the optically active interband transitions preserve quantum number p . The electric-dipole rotatory strengths are seen to be nonzero for two kinds of transitions

$$(nlp) \rightarrow (nlp) \quad (54)$$

$$(nlp) \rightarrow (n'l'p) \quad (55)$$

without any limitations on quantum numbers $n' \neq n$ and $l' \neq l$. Similarly, the magnetic-dipole rotatory strengths are nonzero for transitions of two kinds

$$(nlp) \rightarrow (n'l'p) \quad (56)$$

$$(nlp) \rightarrow (n'l'p) \quad (57)$$

without any limitations on quantum numbers $n' \neq n$ and $l' \neq l$.

It is instructive to estimate the typical values of the obtained rotatory strengths. By assuming that $E_{\mathbf{nm}} \sim E_g$ and $|P_z|^2 \approx |P_\phi|^2 \sim m_0 E_p / 2$, where E_g is the bandgap of bulk semiconductor and E_p is the Kane energy, it is easy to show that the scaling factor of interband rotatory strengths is given by

$$\vartheta^{(cv)} = \frac{\eta |P_z|^2}{E_{\mathbf{nm}}} \approx \frac{\beta \hbar e^2 \sqrt{\epsilon_\infty} E_p}{4cm_0 E_g} \quad (58)$$

Table 1 shows the material parameters entering this equation for five bulk semiconductors. Despite the dispersion of the parameter values, one can see that $E_p/E_g \approx 10$ and $\sqrt{\epsilon_\infty} \approx 3$. Using these material parameters and taking, as before, $\beta = 2$ nm, we get $\vartheta^{(cv)} \approx 10^{-35}$ erg cm³. Since $m_0/m \sim E_p/E_g$ for electrons from a typical conduction band, we see that the scaling factors of intraband and interband transitions are roughly related as $\vartheta = 4\vartheta^{(cv)}$.

The obtained theoretical results show that chiral nanoscrolls should exhibit strong dissymmetry of their interaction with circularly polarized light. This dissymmetry can be observed in visible and near-infrared circular dichroism spectra of nanoscroll

Table 1. Material parameters of five zincblende-type semiconductors.^[23,24]

| Material | E_g | E_p | E_p/E_g | ϵ_∞ | $\sqrt{\epsilon_\infty} E_p/E_g$ |
|----------|-------|-------|-----------|-------------------|----------------------------------|
| ZnTe | 2.26 | 19.1 | 8.45 | 7.28 | 22.8 |
| ZnSe | 2.67 | 24.2 | 9.06 | 6.20 | 22.6 |
| ZnS | 3.66 | 20.4 | 5.57 | 5.13 | 12.6 |
| CdTe | 1.44 | 20.7 | 14.38 | 7.21 | 38.6 |
| GaAs | 1.42 | 25.7 | 18.10 | 10.88 | 59.7 |

ensembles enriched with one of the enantiomeric forms. We hope that this study will stimulate new experiments and prove useful in the development of new optically active materials and devices.

5. Conclusion

We have developed a theory of optical activity of monodisperse ensembles of randomly oriented chiral semiconductor nanoscrolls. The theory allows one to analytically calculate the rotatory strengths and dissymmetry factors of optical transitions inside the nanoscrolls and to model the circular dichroism spectra of the ensembles. It was shown that the rotatory strengths of intraband and interband transitions can be as high as 10^{-35} erg cm³, exceeding the typical rotatory strengths of small chiral molecules by three to four orders of magnitude. This makes chiral semiconductor nanoscrolls very promising for various applications in biochemistry, biophysics, and nanophotonics.

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