

Calculate circular dichroism using DFT

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1 Theory

1.1 Quantum Explanation

Here, we give a quantum explanation for circular dichroism (CD).

Maxwell equation

$$\nabla \cdot \mathbf{B} = 0 \quad (1)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (2)$$

$$\nabla \cdot \mathbf{E} = 4\pi\rho \quad (3)$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{j} \quad (4)$$

The vector potential (\mathbf{A}) and scalar potential (ϕ) are defined as

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (5)$$

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi \quad (6)$$

and we have equations⁴

$$\nabla^2 \phi + \frac{1}{c} \frac{\partial}{\partial t} \nabla \cdot \mathbf{A} = -4\pi\rho \quad (7)$$

$$\nabla \times (\nabla \times \mathbf{A}) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{A} + \nabla \frac{\partial}{\partial t} \phi = \frac{4\pi}{c} \mathbf{j} \quad (8)$$

In the Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$), Eq. (7) and Eq. (8) simplify to⁴

$$\nabla^2 \phi = -4\pi\rho \quad (9)$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{A} = -\frac{4\pi}{c} \mathbf{j} + \nabla \frac{\partial \phi}{\partial t} \quad (10)$$

We consider that electromagnetic wave propagates in the free space ($\rho = 0$ and $\mathbf{j} = 0$)

$$\nabla^2 \phi = 0 \quad (11)$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{A} = \nabla \frac{\partial \phi}{\partial t} \quad (12)$$

and one of the solutions is

$$\phi = 0 \quad (13)$$

$$\mathbf{A} = A_0 e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} \quad (14)$$

According to Eq. (5) and Eq. (6), we have

$$\mathbf{B} = -i\mathbf{k} \times \mathbf{A} \quad (15)$$

$$\mathbf{E} = -i\omega \mathbf{A} \quad (16)$$

Suppose electromagnetic wave propagates along the z axis, and \mathbf{E} and \mathbf{B} can be written as

$$\mathbf{B}(\mathbf{r}, t) = \frac{E_0}{2c} e^{-ik_z z} \mathbf{e}_B + c.c. \quad (17)$$

$$\mathbf{E}(\mathbf{r}, t) = \frac{E_0}{2} e^{-ik_z z} \mathbf{e}_E + c.c. \quad (18)$$

where for circularly polarized light

$$\mathbf{e}_B = \mathbf{e}_z \times \mathbf{e}_E = \frac{1}{\sqrt{2}}(\mp i, -1, 0) \quad (19)$$

$$\mathbf{e}_E = \frac{1}{\sqrt{2}}(1, \pm i, 0) \quad (20)$$

Using Eq. (16) and (18), \mathbf{A} can be written as

$$\mathbf{A}(\mathbf{r}, t) = -\frac{E_0}{2i\omega} e^{-ik_z z} \mathbf{e}_E + c.c. \quad (21)$$

The Hamiltonian can be split into unperturbed and perturbed terms

$$H = H_0 + H_I \quad (22)$$

$$H_0 = \frac{1}{2m} \mathbf{p}^2 + V(\mathbf{r}) \quad (23)$$

$$H_I = -\frac{q}{2m} (\mathbf{p} \cdot \mathbf{A}(\mathbf{r}, t) + \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{p}) + q\phi(\mathbf{r}, t) - \frac{q}{m} \mathbf{S} \cdot \mathbf{B}(\mathbf{r}, t) \quad (24)$$

where q is electric charge, m is electric mass and \mathbf{S} is electric spin.

The interaction Hamiltonian can be split into terms with and without time

$$H_I(t) = H' e^{i\omega t} + H'^{\dagger} e^{-i\omega t} \quad (25)$$

Since the electromagnetic wave considered here is transverse ($\mathbf{e}_E \perp \mathbf{e}_z$), using Eq. (17) and Eq. (21), H' can be written as

$$\begin{aligned} H' &= -i \frac{qE_0}{2m\omega} e^{-ik_z z} (\mathbf{p} \cdot \mathbf{e}_E + \frac{\omega}{ic} \mathbf{S} \cdot \mathbf{e}_B) \\ &= -i \frac{qE_0}{2m\omega} [1 + (-ik_z z) + \frac{1}{2!} (-ik_z z)^2 + \dots] (\mathbf{p} \cdot \mathbf{e}_E + \frac{\omega}{ic} \mathbf{S} \cdot \mathbf{e}_B) \\ &= -i \frac{qE_0}{2m\omega} [\mathbf{p} \cdot \mathbf{e}_E + (-ik_z z) \mathbf{p} \cdot \mathbf{e}_E + \frac{\omega}{ic} \mathbf{S} \cdot \mathbf{e}_B + \dots] \end{aligned} \quad (26)$$

where the first term is electric dipole interaction, and for circularly polarized light, the second term can be written as

$$\begin{aligned} z(\mathbf{p} \cdot \mathbf{e}_E^{\pm}) &= \frac{1}{\sqrt{2}} (zp_x \pm izp_y) \\ &= \frac{1}{\sqrt{2}} [\frac{1}{2} (zp_x - ixp_z) \pm i\frac{1}{2} (zp_y - iyp_z)] + \frac{1}{\sqrt{2}} [\frac{1}{2} (zp_x + ixp_z) \pm i\frac{1}{2} (zp_y + iyp_z)] \\ &= -\frac{1}{2} \mathbf{L} \cdot \mathbf{e}_B^{\pm} + \frac{1}{\sqrt{2}} [\frac{1}{2} (zp_x + ixp_z) \pm i\frac{1}{2} (zp_y + iyp_z)] \end{aligned} \quad (27)$$

where \mathbf{L} is orbital angular momentum. Combine the first term in Eq. (27) and the third term in Eq. (26), total magnetic dipole interaction can be obtained

$$-\frac{qE_0 k_z}{4m\omega} (\mathbf{L} \cdot \mathbf{e}_B^{\pm}) - \frac{qE_0}{2mc} (\mathbf{S} \cdot \mathbf{e}_B^{\pm}) = -\frac{qB_0}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{e}_B^{\pm} = -\mathbf{m} \cdot \mathbf{B} \quad (28)$$

The perturbed Hamiltonian can be written as

$$\begin{aligned} H' &= -\mathbf{p} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{B} + \text{Higher order term} \\ &= a(\mathbf{p}_x \pm i\mathbf{p}_y) + b(\mathbf{m}_y \mp i\mathbf{m}_x) + \text{Higher order term} \end{aligned} \quad (29)$$

Fermi golden rule

$$I_{g \rightarrow e} = \frac{2\pi}{\hbar} \sum_{g,e} |\langle e | H' | g \rangle|^2 \delta(E_e - E_g - \hbar\omega) \quad (30)$$

The CD is proportional to

$$\begin{aligned} \Delta\epsilon(\omega) &\propto |\langle e | H'_+ | g \rangle|^2 - |\langle e | H'_- | g \rangle|^2 \\ &= |\langle e | [a(p_x + ip_y) + b(m_y - im_x)] | g \rangle|^2 - |\langle e | [a(p_x - ip_y) + b(m_y + im_x)] | g \rangle|^2 \\ &= 2ia^2(p_x^{ge}p_y^{eg} - p_y^{ge}p_x^{eg}) + 2iab(m_x^{ge}p_x^{eg} - p_x^{ge}m_x^{eg}) \\ &\quad + 2iab(m_y^{ge}p_y^{eg} - p_y^{ge}m_y^{eg}) + 2ib^2(m_x^{ge}m_y^{eg} - m_y^{ge}m_x^{eg}) \end{aligned} \quad (31)$$

where $O^{ge} = \langle g | O | e \rangle$ ($O = p_x, p_y, m_x, m_y$).

For molecule, wave function is real, $\langle g | p_\alpha | e \rangle = \langle e | p_\alpha | g \rangle$ and $\langle g | m_\alpha | e \rangle = -\langle e | m_\alpha | g \rangle$ ($\alpha = x, y, z$), Eq. (31) simplifies to

$$\Delta\epsilon(\omega) \propto 4iab(p_x^{ge}m_x^{eg} + p_y^{ge}m_y^{eg}) \quad (32)$$

From Ref 1, we can get a similar CD result

$$\Delta\epsilon(\omega) = \frac{2k}{c} \text{Im}(\mu_{fi}^Y m_{if}^Y + \mu_{fi}^Z m_{if}^Z) \quad (33)$$

where k is the coefficient in Fermi golden rule

Thus, for a single molecule, or a population of molecules that all have the same orientation, the electric and magnetic dipole moments are the ones along the x - and y -axes, arising from the fact that the light's \mathbf{E} - and \mathbf{B} -fields are also along these axes.

After rotational averaging, the CD result for randomly oriented molecules can be written as¹

$$\Delta\epsilon(\omega) = \frac{4k}{3c} \text{Im}(\boldsymbol{\mu}_{fi} \cdot \mathbf{m}_{if}) \quad (34)$$

1.2 Linear Response

The linear (time domain) response function for observable \hat{B} with respect to a time-dependent⁷ perturbation

$$\hat{H}_I = -\hat{A}f(t) \quad (35)$$

is implicitly defined by

$$\langle \hat{B}(t) \rangle - \langle \hat{B} \rangle_0 = \int_{-\infty}^t dt' \langle \langle \hat{B}(t); \hat{A}(t') \rangle \rangle f(t')$$

where

$$\langle \hat{B}(t) \rangle = \text{Tr}[\rho(t)\hat{B}] \quad (36)$$

and $\rho(t)$ is the time-dependent density matrix. $\langle \hat{B} \rangle_0$ denotes that the density matrix is the stationary one.

The frequency domain representation of the linear response function

$$\langle \langle \hat{B}; \hat{A} \rangle \rangle_\omega = \langle \hat{B}(\hbar\omega) \rangle / f(\hbar\omega) \quad (37)$$

where

$$\langle \hat{B}(\hbar\omega) \rangle = \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{\infty} dt (\langle \hat{B}(t) \rangle - \langle \hat{B} \rangle_0) e^{i(\hbar\omega)/\hbar t} e^{-\epsilon t} \quad (38)$$

and $f(\hbar\omega)$ is the FT of $f(t)$.

In RT-TDDFT, the linear response function is obtained essentially by tracking the time evolution of the desired observable with respect to a perturbation and taking the FT.

In linear response, both a time domain (*Kubo formula*)

$$\langle\langle\hat{B}(t); \hat{A}(t')\rangle\rangle = -\frac{i}{\hbar}\theta(t-t')\langle[\hat{B}(t), \hat{A}(t')]\rangle \quad (39)$$

and a frequency domain representation

$$\langle\langle\hat{B}; \hat{A}\rangle\rangle_\omega = \lim_{\epsilon \rightarrow 0} \sum_n \frac{1}{\hbar} \left[\frac{\langle 0 | \hat{B} | n \rangle \langle n | \hat{A} | 0 \rangle}{\omega - (\omega_n - \omega_0) + i\epsilon} - \frac{\langle 0 | \hat{A} | n \rangle \langle n | \hat{B} | 0 \rangle}{\omega - (\omega_0 - \omega_n) - i\epsilon} \right] \quad (40)$$

The macroscopic CD, given by the difference of the L and R molar extinction of a system of N chiral molecules randomly oriented that are under the action of an external electromagnetic field, is written as^{5,8}

$$\Delta\epsilon(\omega) = \frac{16\pi N_A}{\ln(10)10^3} \frac{2\pi}{\hbar c} \omega R(\omega)^{cgs} \quad (41)$$

where N_A is Avogadro's constant, and $R(\omega)^{cgs}$ is the rotatory strength in cgs units. The relationship between rotatory strength in cgs units and in atomic units is

$$R(\omega)^{cgs} = \frac{q^2 \hbar^2}{m^2 \alpha} 10^6 R(\omega) \quad (42)$$

where α is the fine structure constant.

1.2.1 Time Domain

If the average over the isotropic system of randomly oriented chiral particles is considered, the rotatory strength can be written as⁷

$$R(\omega) = -\frac{1}{\pi} \text{Tr}\{\text{Re}[\langle\langle\hat{m}_\alpha; \hat{r}_\beta\rangle\rangle_\omega]\} \quad (43)$$

where the magnetic dipole moment \hat{m} is defined as

$$\hat{m}_\alpha = -\frac{q}{2m} \epsilon_{\alpha\beta\gamma} \hat{r}_\beta \hat{p}_\gamma \quad (43)$$

where $\epsilon_{\alpha\beta\gamma}$ is the totally antisymmetric (Levi-Civita) tensor.

If non-local potentials are considered, the generalized momentum operator

$$\hat{p}_\alpha^{gen} = \frac{m}{i\hbar} [\hat{r}_\alpha, H] = \hat{p}_\alpha + \frac{m}{i\hbar} [\hat{r}_\alpha, \hat{V}^{nl}] \quad (44)$$

In the implementation, $m_j^k(\omega)$ is calculated by FT of $m_j^k(t)$, which has been obtained through time-propagation⁵

$$m_j^k(\omega) = \int_0^T e^{i\omega t} e^{-\frac{\sigma^2}{2}t^2} m_j^k(t) dt \quad (45)$$

where $k \in \{x, y, z\}$ and σ is the parameter that determines the linewidth of the Gaussian line shape. For a desired value of σ , the propagation time T needs to be large enough so that $e^{-\frac{\sigma^2}{2}t^2} T^2 \approx 0$

The magnetic transition dipole moment is not invariant under a change of the gauge origin \mathbf{O}

$$\begin{aligned} \mathbf{m}_{0n}(\mathbf{R}) &= -\frac{1}{2c} \langle \Psi_n | (\hat{\mathbf{r}} - \mathbf{O}) \times \hat{\mathbf{p}} | \Psi_0 \rangle \\ &= -\frac{1}{2c} (\langle \Psi_n | \hat{\mathbf{r}} \times \hat{\mathbf{p}} | \Psi_0 \rangle - \mathbf{O} \times \langle \Psi_n | \hat{\mathbf{p}} | \Psi_0 \rangle) \\ &= \mathbf{m}_{0n}(0) - \frac{i\Omega_{0n}}{2c} \mathbf{O} \times \boldsymbol{\mu}_{0n}^{(v)} \end{aligned} \quad (46)$$

This spurious gauge-origin dependence can be largely eliminated by using methods and basis sets where $|\boldsymbol{\mu}_{0n}^{(v)} - \boldsymbol{\mu}_{0n}^{(l)}|$ is sufficiently small, or entirely by using gauge-including atomic orbitals⁸.

1.2.2 Frequency Domain

If the average over the isotropic system of randomly oriented chiral particles is considered, the rotatory strength can be written as⁸

$$R(\omega) = \frac{1}{3} \text{Tr}\{\text{Im}[\tilde{G}_{\alpha\beta}(\omega)]\} \quad (47)$$

and the tensor $\tilde{G}_{\alpha\beta}(\omega)$ can be derived from (40) and is expressed as^{2,7}

$$\tilde{G}_{\alpha\beta}(\omega) = \frac{1}{\hbar} \sum_{n \neq 0} \left\{ \frac{\langle 0 | \mu_\alpha | n \rangle \langle n | m_\beta | 0 \rangle}{\omega_{n0} - \omega - i\gamma_{n0}} + \frac{\langle 0 | m_\beta | n \rangle \langle n | \mu_\alpha | 0 \rangle}{\omega_{n0} + \omega + i\gamma_{n0}} \right\} \quad (48)$$

where $\boldsymbol{\mu} = q\mathbf{r}$ and $\mathbf{m} = \frac{q}{2m}\mathbf{r} \times \mathbf{p}$, and the excited state $|n\rangle$ and ground state $|0\rangle$ are the eigenfunctions of the unperturbed Hamiltonian. γ_{n0} is the dephasing rate between eigensates, which is normally taken to be zero on the assumption that the field frequency is far from resonance, while in the resonant region it needs to be taken different from zero.

According to $\lim_{\eta \rightarrow 0} \frac{1}{w + i\eta} = P(\frac{1}{\omega}) \mp i\pi\delta(w)$, the imaginary part of Eq. (48) can be written as

$$\text{Im}[\tilde{G}_{\alpha\beta}(\omega)] = \frac{\pi}{\hbar} \sum_{n \neq 0} X_{\alpha\beta} \delta(\omega_{n0} - \omega) - X'_{\alpha\beta} \delta(\omega_{n0} + \omega) \quad (49)$$

where

$$X_{\alpha\beta} = \langle 0 | \mu_\alpha | n \rangle \langle n | m_\beta | 0 \rangle \quad (50)$$

$$X'_{\alpha\beta} = \langle 0 | m_\beta | n \rangle \langle n | \mu_\alpha | 0 \rangle \quad (51)$$

Since the $|0\rangle$ and $|n\rangle$ are many-body states, we use second quantization to analyze Eq. (49). The excited state $|n\rangle$, electric and magnetic dipole in β ($\beta = x, y, z$) direction can be written as

$$|n\rangle = C_k^+ C_l |0\rangle \quad (52)$$

$$\mu_\beta = \sum_{i,j}^{nbase} \mu_\beta^{ij} C_i^+ C_j \quad (53)$$

$$m_\beta = \sum_{i,j}^{nbase} m_\beta^{ij} C_i^+ C_j \quad (54)$$

where $\mu_\beta^{ij} = \langle i | \mu_\beta | j \rangle$, $m_\beta^{ij} = \langle i | m_\beta | j \rangle$ and k sums all the unoccupied bands, while l sums all the occupied bands. Thus, Eq. (50) and Eq. (51) can be written as

$$X_{\alpha\beta} = \mu_\alpha^{lk} m_\beta^{kl} \quad (55)$$

$$X'_{\alpha\beta} = m_\beta^{lk} \mu_\alpha^{kl} \quad (56)$$

Assuming the completeness of the basis set, $\sum_u |u\rangle \langle u| = 1$ and $|u\rangle$ is single-body state, $m_{\alpha,kl}$ can be written as

$$m_\alpha^{kl} = \frac{q}{2m} \sum_u^{nbase} [r_\beta^{ku} p_\gamma^{ul} - r_\gamma^{ku} p_\beta^{ul}] \quad (57)$$

Thus, the diagonal terms of $X_{\alpha\beta}$ and $X'_{\alpha\beta}$ can be written as

$$X_{\alpha\alpha} = \sum_u^{nbase} \frac{q^2}{2m} r_\alpha^{lk} [r_\beta^{ku} p_\gamma^{ul} - r_\gamma^{ku} p_\beta^{ul}] \quad (58)$$

$$X'_{\alpha\alpha} = \sum_u^{nbase} \frac{q^2}{2m} [r_\beta^{lu} p_\gamma^{uk} - r_\gamma^{lu} p_\beta^{uk}] r_\alpha^{kl} \quad (59)$$

Within the length representation, $im\omega^{lk}r_\alpha^{lk} = p_\alpha^{lk}$ and the diagonal terms in Eq (49) can be written as

$$\text{Im}[\tilde{G}_{\alpha\alpha}(\omega)] = \frac{i\pi q^2}{2\hbar} \sum_k \sum_l \sum_u^{nuocc\ nocc\ nbase} [R_{\alpha\alpha}\omega^{lu}\delta(\omega^{kl} - \omega) - R'_{\alpha\alpha}\omega^{ku}\delta(\omega^{kl} + \omega)] \quad (60)$$

where

$$R_{\alpha\alpha} = r_\alpha^{lk} [r_\beta^{ku} r_\gamma^{ul} - r_\gamma^{ku} r_\beta^{ul}] \quad (61)$$

$$R'_{\alpha\alpha} = [r_\beta^{lu} r_\gamma^{uk} - r_\gamma^{lu} r_\beta^{uk}] r_\alpha^{kl} \quad (62)$$

Within the velocity representation, $r_\alpha^{lk} = \frac{1}{im\omega^{lk}} p_\alpha^{lk}$ and the diagonal terms in Eq (49) can be written as

$$\text{Im}[\tilde{G}_{\alpha\alpha}(\omega)] = \frac{\pi q^2}{2\hbar m^3} \sum_k \sum_l \sum_u^{nuocc\ nocc\ nbase} \frac{1}{\omega^{kl}} [\frac{P_{\alpha\alpha}}{\omega_{uk}} \delta(\omega^{kl} - \omega) - \frac{P'_{\alpha\alpha}}{\omega^{ul}} \delta(\omega^{kl} + \omega)] \quad (63)$$

where

$$P_{\alpha\alpha} = p_\alpha^{lk} [p_\beta^{ku} p_\gamma^{ul} - p_\gamma^{ku} p_\beta^{ul}] \quad (64)$$

$$P'_{\alpha\alpha} = [p_\beta^{lu} p_\gamma^{uk} - p_\gamma^{lu} p_\beta^{uk}] p_\alpha^{kl} \quad (65)$$

In our implementation, we calculate $\text{Tr}\{\text{Im}[\tilde{G}_{\alpha\beta}(\omega)]\}$ directly, i.e.

$$\text{Im}[\tilde{\mathbf{G}}(\omega)] = \text{Tr}\{\text{Im}[\tilde{G}_{\alpha\beta}(\omega)]\} = \sum_k \sum_l^{nuocc\ nocc} [P^{kl}\delta(\omega^{kl} - \omega) - P^{lk}\delta(\omega^{lk} + \omega)] \quad (66)$$

where

$$P^{kl} = \boldsymbol{\mu}^{kl} \cdot \mathbf{m}^{kl} \quad (67)$$

2 Results

2.1 (R)-methyloxirane

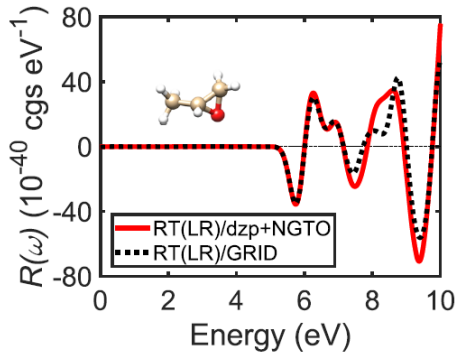
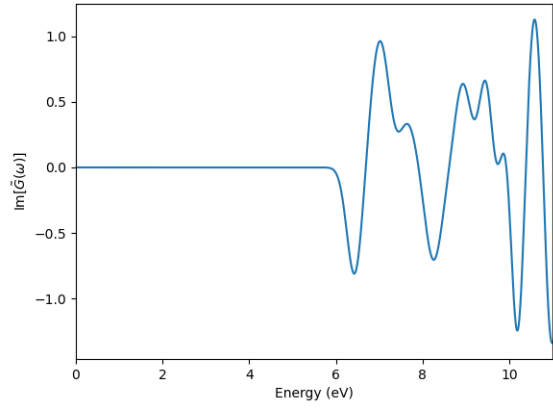
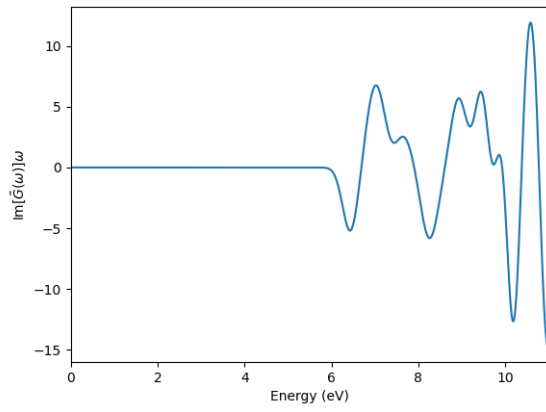


FIG. 1. Rotatory strength of (R)-methyloxirane calculated by RT-TDDFT and LR-TDDFT in both LCAO and real-space grid modes.

(a)



(b)



(c)

Figure 1: (a) GPAW⁶ (b) TZDP results obtained by pyATB and HOMO-LUMO gap obtained from ABACUS is 6.43 eV(c) multiply the ω by the results in Figure 1b

2.2 SWNT

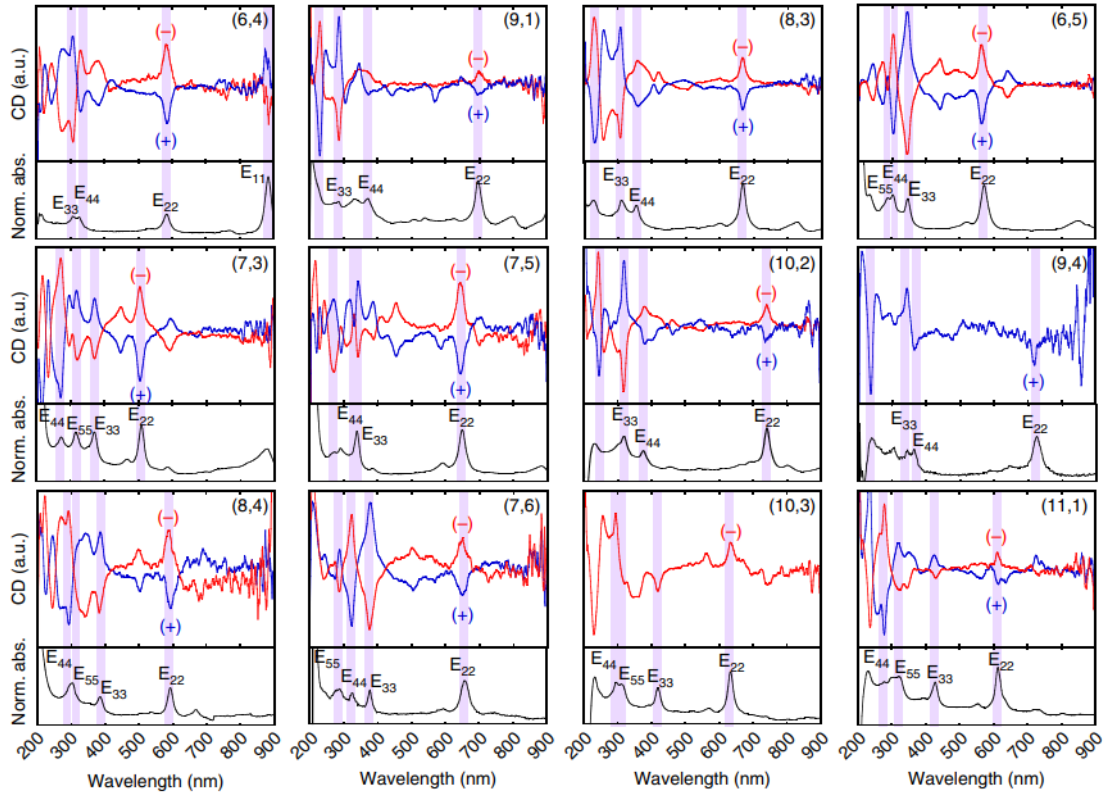
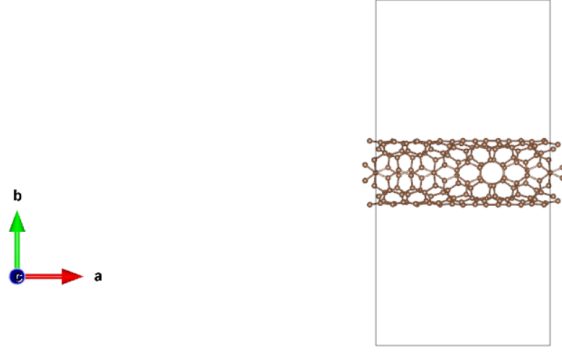


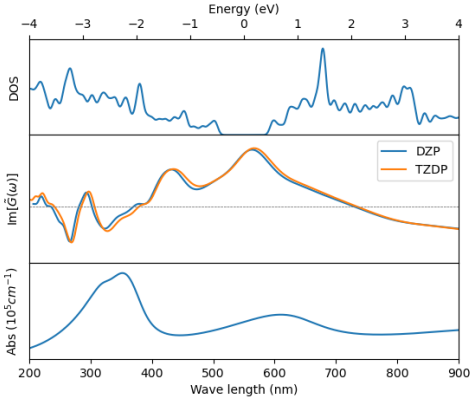
Figure 2 | CD spectra of the separated single-chirality enantiomers. CD spectra and optical absorption spectra of the 12 different (n,m) species. The CD intensities were normalized for all 12 samples.

(a)

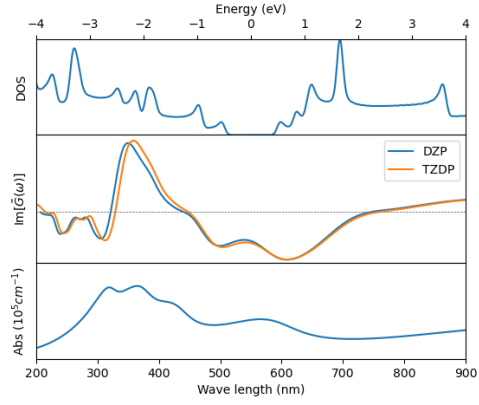
Figure 2: (a) Exp⁹



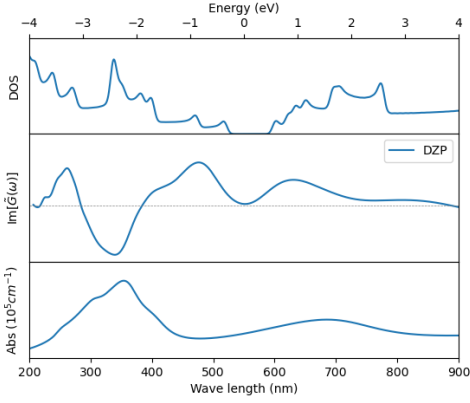
(a)



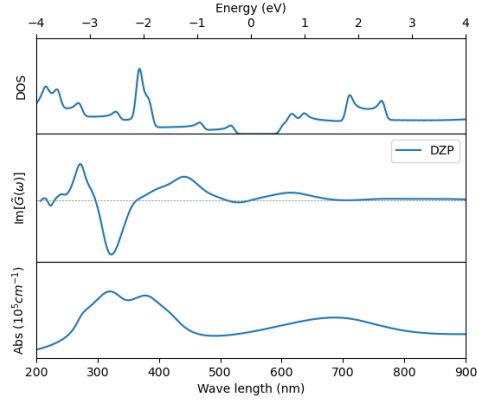
(b)



(c)



(d)



(e)

Figure 3: (a) Structure of SWNT (6, 4). Here we use pyATB to calculate DOS, Eq. (66) and absorption for (-) species: (b) (6, 4) (c) (7, 3) (d) (8, 3) (e) (9, 1). Some positions of peaks do not match with Exp and Abs, especially the first peak.

2.3 NPB

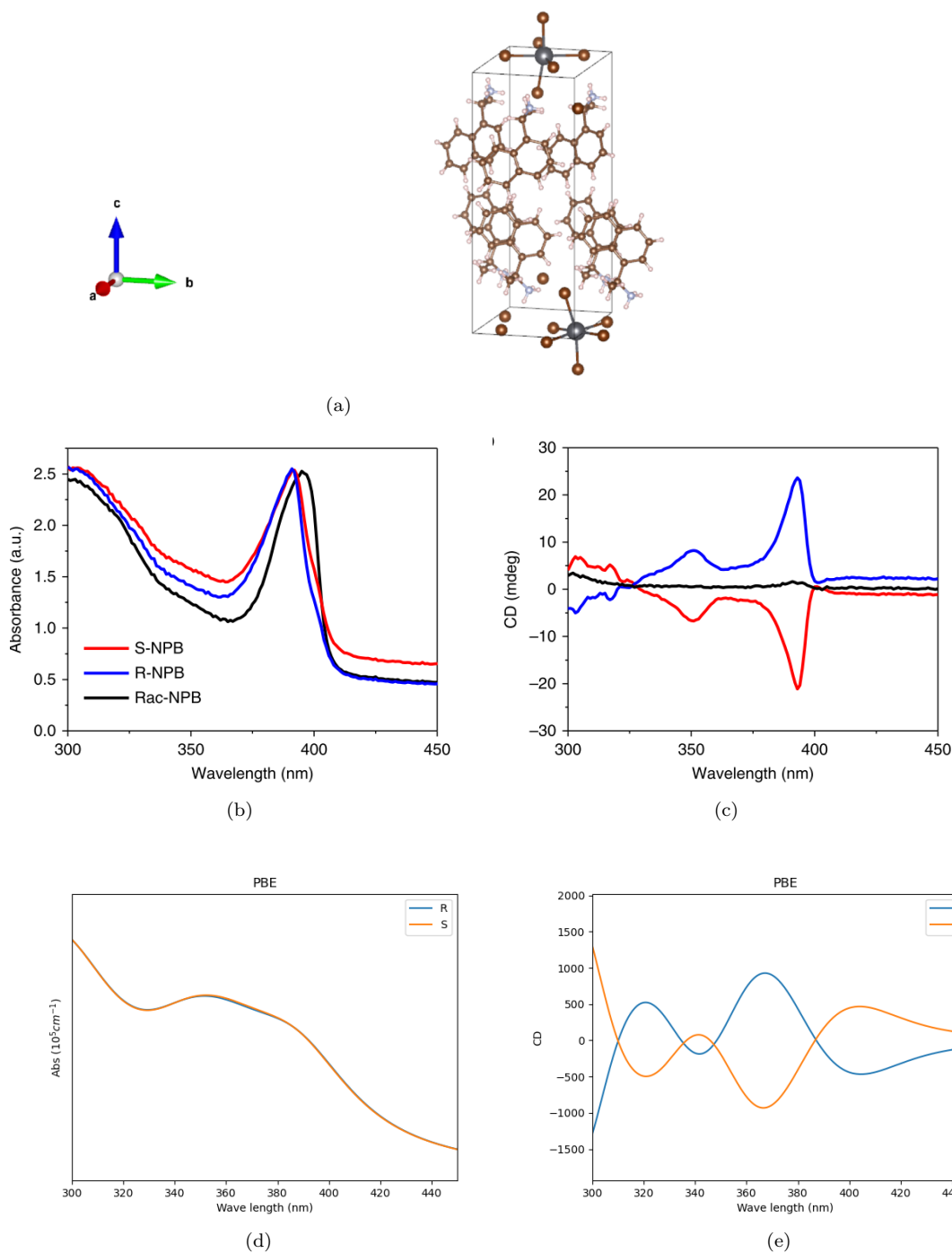


Figure 4: (a) Structure of S-NPB. (b) UV-Vis linear absorption spectra and (c) circular dichroism (CD) spectra recorded at room-temperature for thin films of racemic-, R- and S-NPB³. (d) Absorption spectra and (e) circular dichroism (CD) spectra of R- and S-NPB. calculated by pyATB. Some positions of peaks do not match with Exp and Abs, especially the first peak.

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