Rotational effects on enantioseparation

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Enantioseparation

Existing schemes based on:
- other chiral substances
- optical rotation
Enantioseparation

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- other chiral substances
- optical rotation
Chiral Molecules

Eigenstates of the Hamiltonian

\[ |S\rangle = \frac{1}{\sqrt{2}} (|D\rangle + |L\rangle) \]
\[ |A\rangle = \frac{1}{\sqrt{2}} (|D\rangle - |L\rangle) \]

but one observes

\[ |L\rangle = \frac{1}{\sqrt{2}} (|S\rangle - |A\rangle) \]
\[ |D\rangle = \frac{1}{\sqrt{2}} (|S\rangle + |A\rangle) \]
Basic Idea

\[ |i^\pm\rangle = |S_{i}\rangle \pm |A_{i}\rangle \]
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asymmetric → chiral: \( \Omega_{ij} = \langle i^{\pm} | \mu |A_j\rangle E \]

= \( \langle S_i | \mu |A_j\rangle E \)

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asymmetric → chiral: \( \Omega_{ij} = \langle i^{\pm}|\mu|A_j\rangle E \)
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symmetric → chiral: \( \Omega_{ij} = \langle i^{\pm}|\mu|S_j\rangle E \)
= \( \pm \langle A_i|\mu|S_j\rangle E \)

Basic Idea

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|i^{\pm}\rangle = |S_i\rangle \pm |A_i\rangle
\]

asymmetric \rightarrow \text{chiral}: \quad \Omega_{ij} = \langle i^{\pm}|\mu|A_j\rangle E \\
= \langle S_i|\mu|A_j\rangle E

symmetric \rightarrow \text{chiral}: \quad \Omega_{ij} = \langle i^{\pm}|\mu|S_j\rangle E \\
= \pm\langle A_i|\mu|S_j\rangle E

\text{chiral} \rightarrow \text{chiral}: \quad \Omega_{ij} = \langle i^{\pm}|\mu|j^{\pm}\rangle E \\
= \pm [\langle S_i|\mu|A_j\rangle + \langle A_i|\mu|S_j\rangle] E

Closed Loop Scheme

\[
\begin{align*}
\Omega_{12}^D &= -\Omega_{12}^L \\
\Omega_{13}^D &= -\Omega_{13}^L \\
\Omega_{23}^D &= -\Omega_{23}^L
\end{align*}
\]
Closed Loop Scheme

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we can go to the basis of dressed states \( |\chi_i\rangle \) and obtain effective equations of motion

\[H = \frac{1}{2m} (p - A)^2 + V(x, y) - mGz\]

\[A_i(r) = i\hbar\langle \chi_i(r) | \nabla | \chi_i(r) \rangle\]

\[V_i(r) = \lambda_i(r) + \langle \chi_i(r) | U(r) | \chi_i(r) \rangle\]

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Effects of molecular rotation
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molecule modelled e.g. as symmetric top:

\[ E(J, K, M_J) = \hbar c B J (J + 1) + \hbar c (A - B) K^2 \]

\[ A^{-1}, B^{-1}: \text{moments of inertia} \]

\( J \): rotational quantum number

\( K \): helicity, projection of \( J \) onto molecular axis, \(-J \ldots J\)

\( M \): projection of \( J \) onto space fixed axis, \(-J \ldots J\)
Selection Rules

$$\Omega = \langle \Psi_2 | \mu \cdot E | \Psi_1 \rangle$$
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Transform dipole moment from molecular frame (M) to lab frame (S)

\[ \mu \cdot E = \sum_{\sigma = \{\pm 1, 0\}} \mu^S_\sigma E^S_\sigma \]

\[ \mu^S_\sigma = \sum_{\sigma' = -1}^1 D^{1}_{\sigma', \sigma} (\alpha \beta \gamma) \mu^M_{\sigma'} \]

\[ = \sum_{\sigma' = \{\pm 1, 0\}} \sum_{\sigma = \{\pm 1, 0\}} D^{1}_{\sigma', \sigma} (\alpha \beta \gamma) \mu^M_{\sigma'} E^S_\sigma \]
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\[ \Omega = \langle \Psi_2 | \mu \cdot E | \Psi_1 \rangle \]

\[ |\Psi_1\rangle = |\Psi_{J_1 K_1 M_1}^{1}\rangle \otimes |\nu_1\rangle \]

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\[ = \sum_{\sigma' = \{\pm 1, 0\}} \sum_{\sigma = \{\pm 1, 0\}} D_{\sigma' \sigma}^{1} (\alpha \beta \gamma) \mu_{\sigma'}^M E_{\sigma}^S \]
Selection Rules

\[ \Omega = \langle \Psi_2 | \mu \cdot E | \Psi_1 \rangle \]

\[ = \langle \nu_2 | \otimes \langle \Psi_{K_2 M_2}^{J_2} | \sum_{\sigma'} \sum_{\sigma} D_{\sigma' \sigma}^{1} \mu_{\sigma'}^{M} E_{\sigma}^{S} | \Psi_{K_1 M_1}^{J_1} \rangle \otimes | \nu_1 \rangle \]

\[ = \sum_{\sigma'} \sum_{\sigma} \langle \nu_2 | \mu_{\sigma'}^{M} | \nu_1 \rangle \sum_{\sigma} \langle \Psi_{K_2 M_2}^{J_2} | D_{\sigma' \sigma}^{1} | \Psi_{K_1 M_1}^{J_1} \rangle E_{\sigma}^{S} \]

\[ = \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} D_{K_2 M_2}^{J_2} (\theta \phi \chi) D_{\sigma' , \sigma}^{1} (\theta \phi \chi) D_{K_1 M_1}^{J_1} (\theta \phi \chi) \sin \theta d\theta d\phi d\chi \]
Results

* rotational selection rules do not allow loops involving 3 levels.

* an even number of levels is conceivable:

* But: an even number of levels yields an even number of different \( \Omega \)s in both enantiomers
  ▶ control of chirality is lost
Summary & Outlook

* The potentials from the adiabatic dressed states approach are **not** recovered if molecular rotations are included.

* Transitions other than the electric dipole transition might be applied (multipole transitions, opt. angular momentum, ...).

* Optimal control helps to find
  - Optimal spatial profile $E(x)$
  - Optimal timing $E(t)$

Of laser with the objective to maximize the separation.