Introduction to Molecular Spectroscopy

Fundamental Concepts in Spectroscopy and Electrodynamics

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August 16, 2019

Outline for Today:

1. Course Outline
   - Content and Goals
   - Exercises and Grading
   - Final Project

2. Introduction to Spectroscopy and Electrodynamics
   - What is spectroscopy?
   - What is the Electromagnetic Field?
     - The field as a force map
     - The field as a flow map
     - The field as a propagating wave
   - The interaction of light and matter

Course Outline

Course content and goals

Content: Molecular Spectroscopy

- The field: Electrodynamics
- The matter: Models for molecular systems
- The interaction: Experimental methods and analysis

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Content: Molecular Spectroscopy

- The field: Electrodynamics
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Goals:

- Understand the *fundamental principles* of electrodynamics
- Understand the physical basis of optical and IR spectroscopy
- Uncover the physics behind the "jargon" of nonlinear spectroscopy – response functions, ladder diagrams, coherence, population, etc.
- Learn to use Python for simple simulations and data analysis
- *Have fun.* Learn, engage, ask questions. *Don't focus on grades.*

Exercises and Grading

Grades: Determined by

- 50% Exercises
- 25% Mid-term Exam
- 25% Final Project
- 10% extra credit

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Exercises:

- Significant (guided!) numerical component
- Use Jupyter Notebooks for most calculations
- Some pen/paper calculations ← Watch for exam material
- All Friday Lectures: Calculations and problem-solving

Final Project

Goal: Analyze an experiment from start to finish

- Pick a published paper that uses a method you're interested in
- Consult with me and get approval
- Determine what type of signal is measured *by the detector* in that experiment
- Generate mock-up "raw data"
- Analyze it and make "publication-ready" figures
- Present it to the class (Note: dead week!)

Introduction to Spectroscopy and Electrodynamics

What is Spectroscopy?

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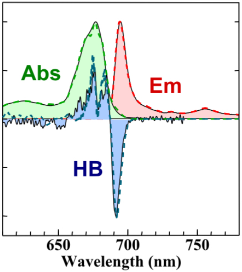
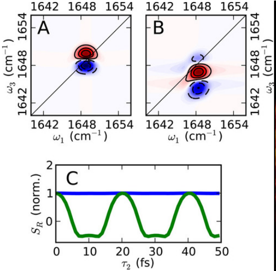
A few examples:

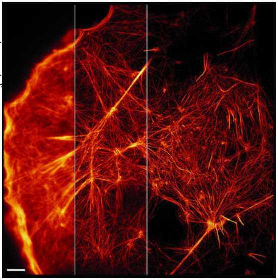
Linear



Multidimensional



Imaging

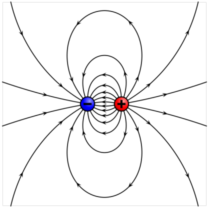


STORM Image Credit:
`www.sciencemag.org/features/2016/05/superresolution-microscopy`

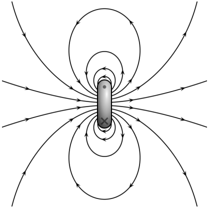
What is the Electromagnetic field?

A Force Map:

The **electric field** $\boldsymbol{e}(\boldsymbol{r})$ describes the hypothetical force experienced by a *stationary* particle with infinitesimal charge at location $\boldsymbol{r}$.



The **magnetic field** $\boldsymbol{b}(\boldsymbol{r})$ describes the *additional* hypothetical force experienced by a *moving* particle with infinitesimal charge at location $\boldsymbol{r}$.



The Lorentz Force Law:

$$\boldsymbol{F}_{EM} = q\left(\boldsymbol{e}(\boldsymbol{r},t) + \boldsymbol{v} \times \boldsymbol{b}(\boldsymbol{r},t)\right).$$

What is the Electromagnetic field?

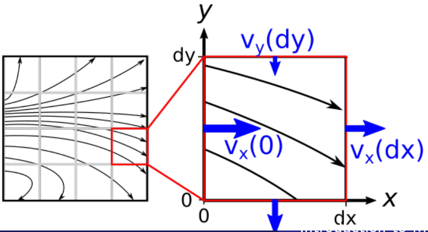
A Flow Map:

Gauss's Law says that the total flow rate of electrical fluid *out of* any closed surface is proportional to the total charge *enclosed by* the surface.

$$\nabla \cdot \boldsymbol{e} \equiv \sum_i \frac{\partial e_i}{\partial x_i} = 4\pi\varrho(\boldsymbol{x}, t)$$

Gauss's Law for Magnetism says that the total flow rate of magnetic fluid out of any closed surface is zero.

$$\nabla \cdot \boldsymbol{e} = 0.$$



In two dimensions:

$$\nabla \cdot \boldsymbol{v} \sim \frac{dv_x}{dx} + \frac{dv_y}{dy}$$

What is the Electromagnetic field?

A Flow Map:

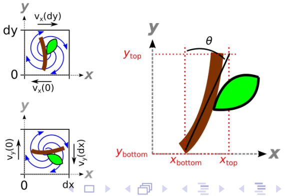
The **Maxwell-Faraday Equation** says that temporal changes in the magnetic field produce "swirls" in the electric field.

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0$$

Ampere's Law says that both flowing currents *and* temporal changes in the electric field produce "swirls" in the magnetic field

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} = \frac{4\pi}{c}\boldsymbol{j}(\boldsymbol{x}, t),$$

$$\nabla \times \boldsymbol{v} = \begin{vmatrix} \hat{\boldsymbol{x}} & \hat{\boldsymbol{y}} & \hat{\boldsymbol{z}} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ v_x & v_y & v_z \end{vmatrix}$$



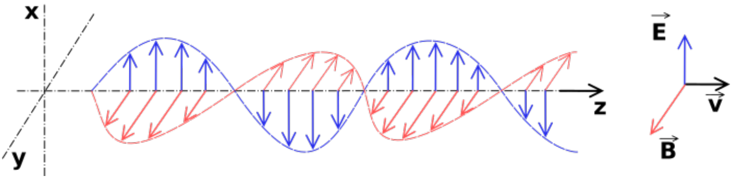
What is the Electromagnetic field?

A Propagating Wave:

According to Maxwell's equations:

- A changing E-field creates a B-field
- A changing B-field creates an E-field...

...self-propagation!



Infinities in Field-Particle Interactions

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The electric field always diverges in the vicinity of point particles

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$$\boldsymbol{F}_{EM} = q\left(\boldsymbol{e}(\boldsymbol{r},t) + \boldsymbol{v} \times \boldsymbol{b}(\boldsymbol{r},t)\right). \leftarrow \text{Not for point particles!}$$

The electric field always diverges in the vicinity of point particles

Okay for point-particles:

$$\boldsymbol{F}_n^{(\mathrm{EM})} = q_n\left(\boldsymbol{e}_n^{(\mathrm{eff})} + \frac{\boldsymbol{v}_n}{c} \times \boldsymbol{b}(\boldsymbol{r}_n)\right),$$

where

$$\boldsymbol{e}_n^{(\mathrm{eff})} = \lim_{\boldsymbol{r}\to\boldsymbol{r}_n}\left(\boldsymbol{e}(\boldsymbol{r}_n) - q_n\frac{\boldsymbol{r}}{|\boldsymbol{r}-\boldsymbol{r}_n|^2}\right)$$