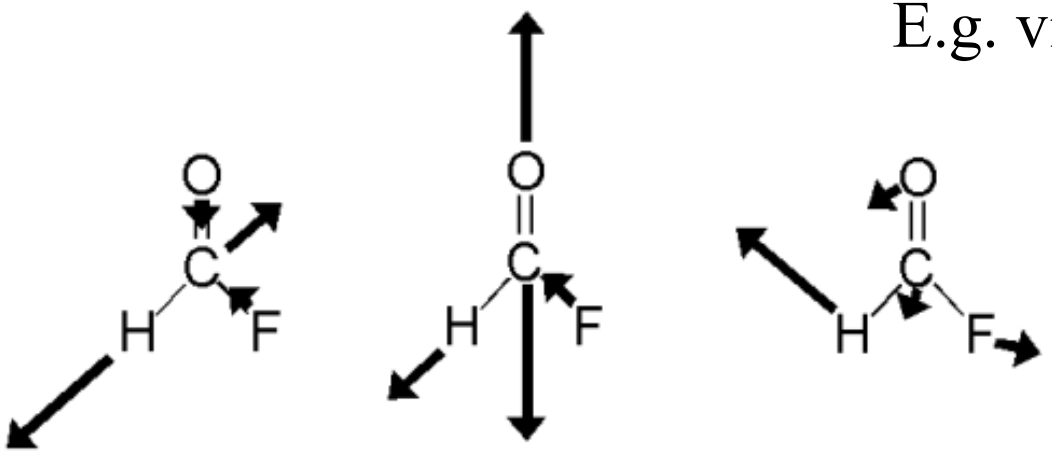
Review:
Quantum mechanics of the harmonic oscillator

Molecular vibrations

Molecular vibrations: may involve complex motions of all atoms

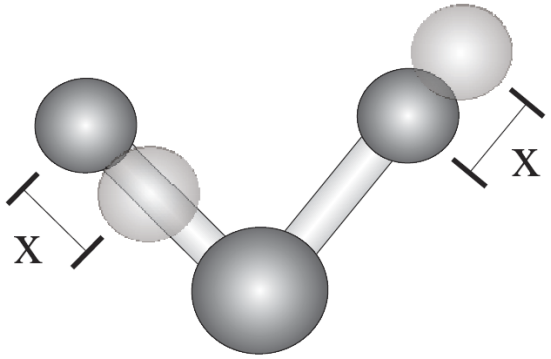
E.g. vibrations of HFCO

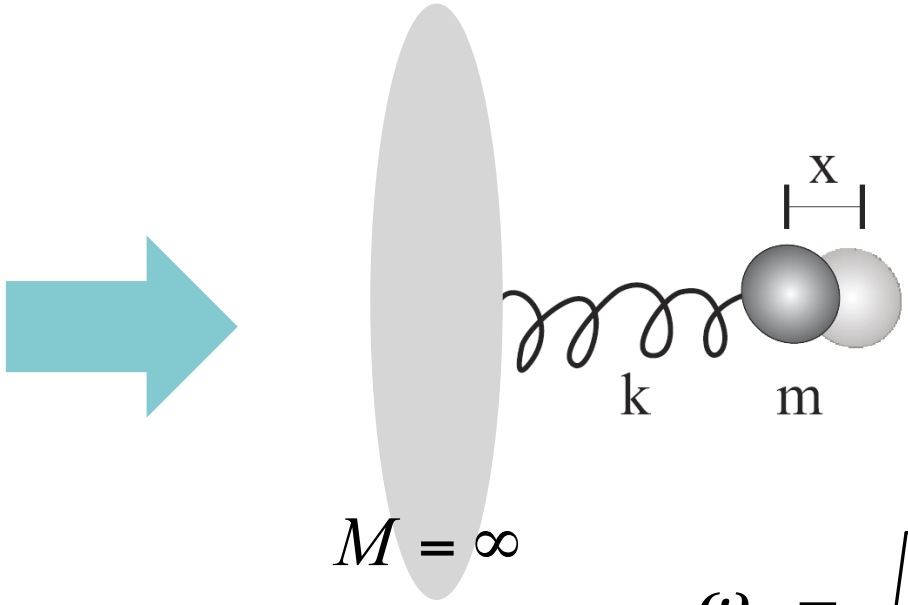


Luckily the equations of motion can be made isomorphic with the equations of motions of a simple harmonic oscillator

Harmonic oscillator

•Normal modes (we will discuss this in detail later)





$M = \infty$

$$\omega_0 = \sqrt{k/m}$$

Harmonic oscillator

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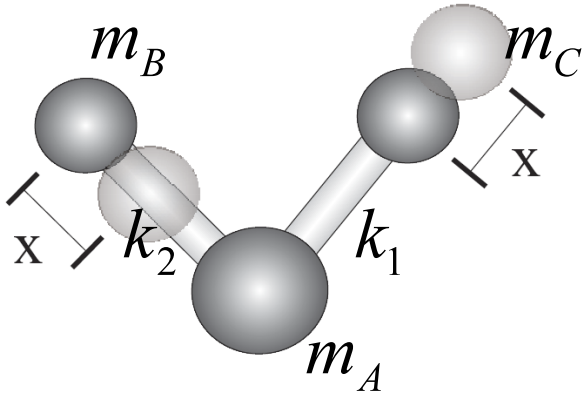

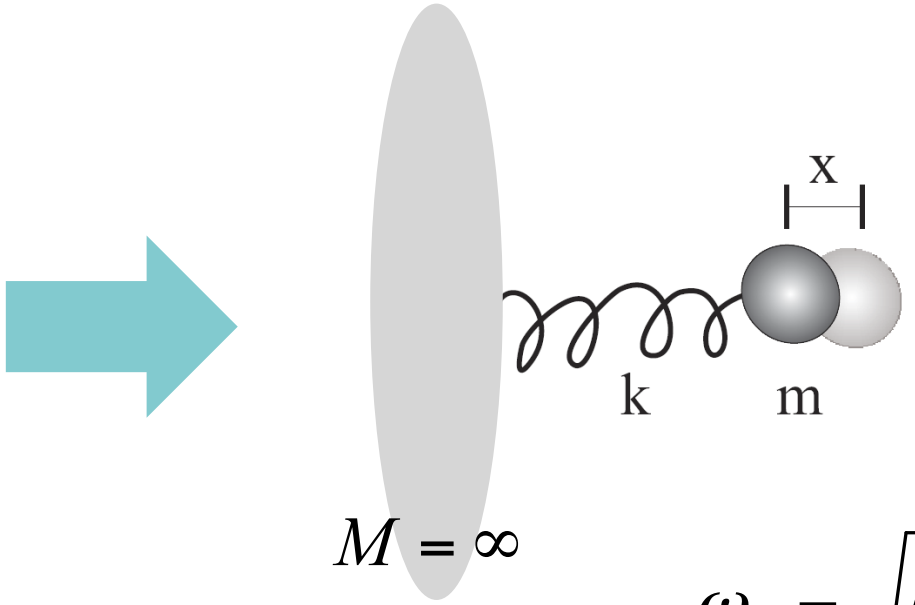

$$\omega_0 = \sqrt{k/m}$$

Harmonic oscillator

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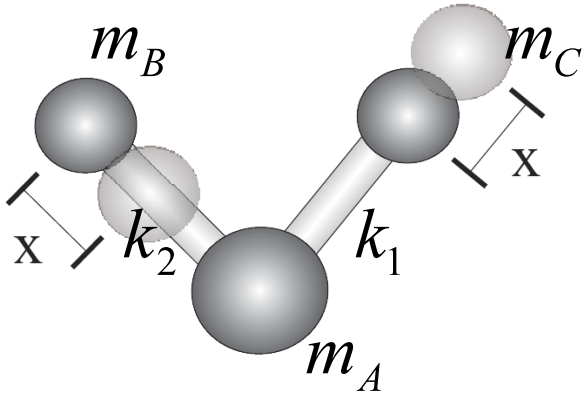
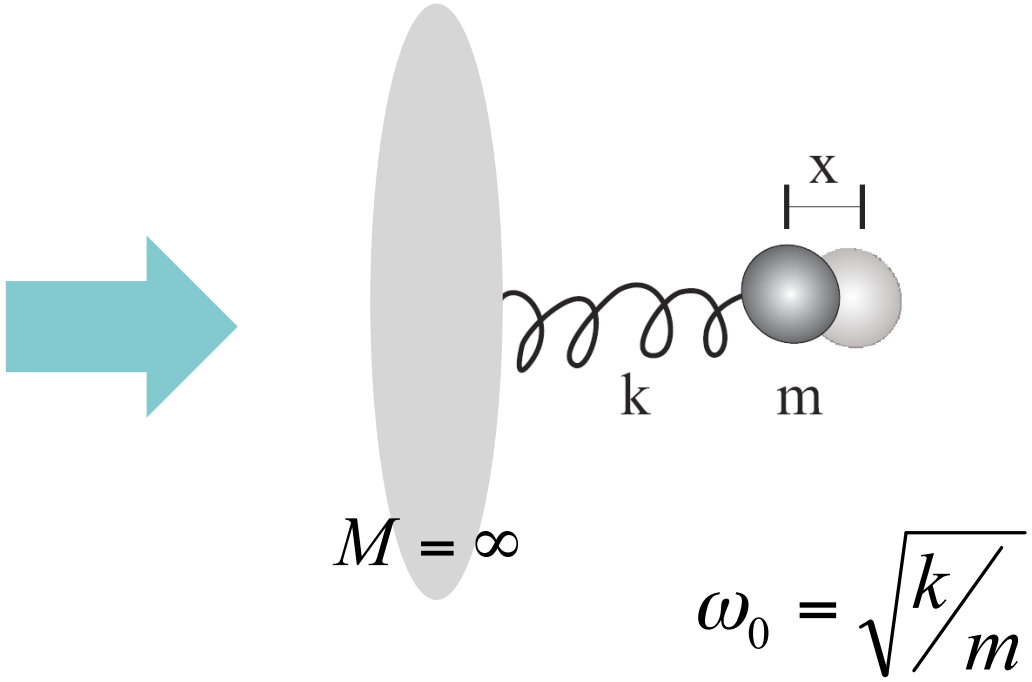
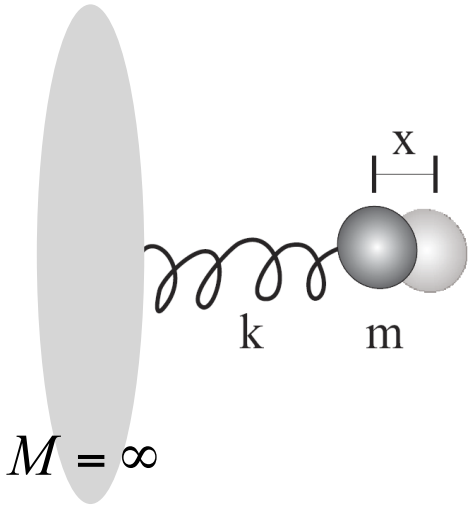




•Classical description

$$\ddot{x} + \omega_0^2 x = 0 \qquad \omega_0 = \omega_0(k_1, k_2, m_A, m_B, m_C)$$

Quantum mechanical description



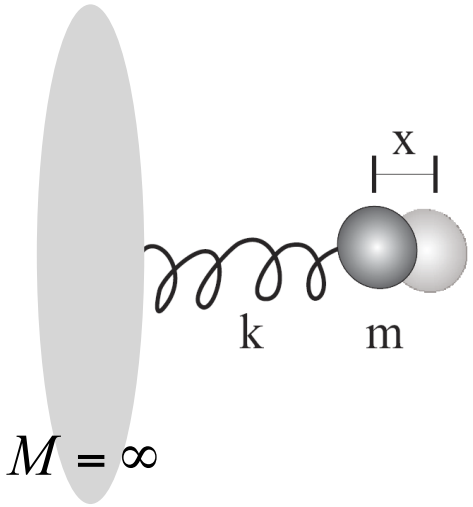
Schrödinger equation

$$\hat{H}_0 \left| \varphi \right\rangle = E \left| \varphi \right\rangle$$

Hamiltonian

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega_0^2 \hat{x}^2$$

Quantum mechanical description



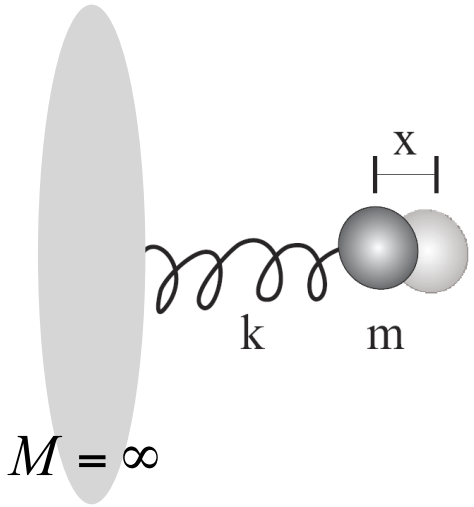
Schrödinger equation

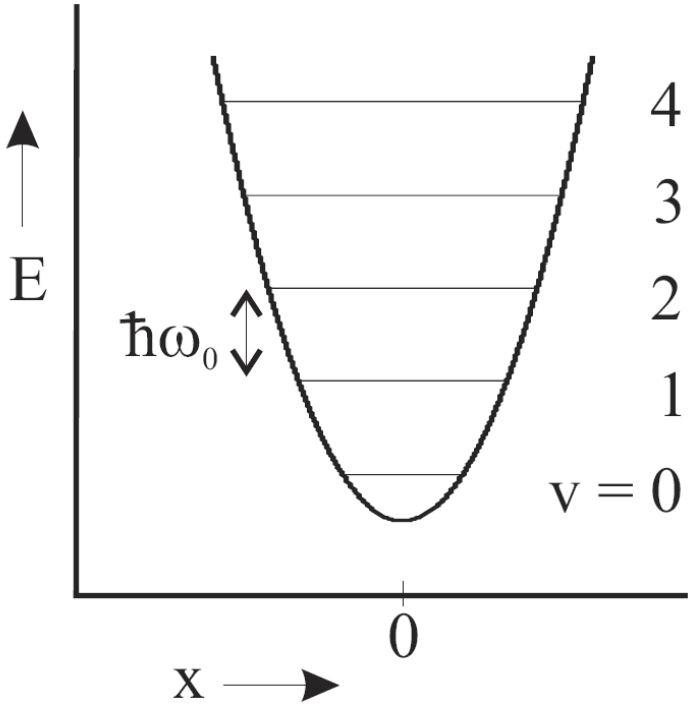
$$\hat{H}_0 \left| \varphi \right\rangle = E \left| \varphi \right\rangle$$

Hamiltonian (explicit operators)

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega_0^2 x^2$$

Solutions

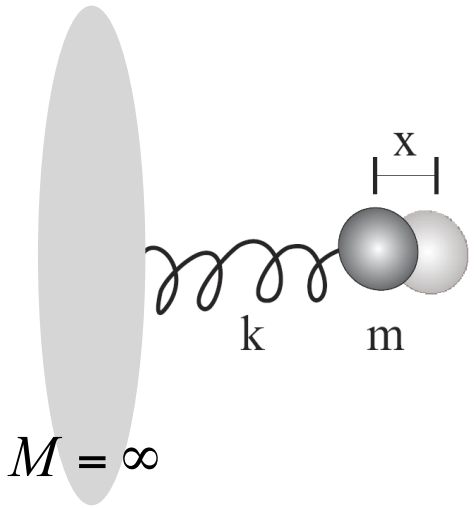


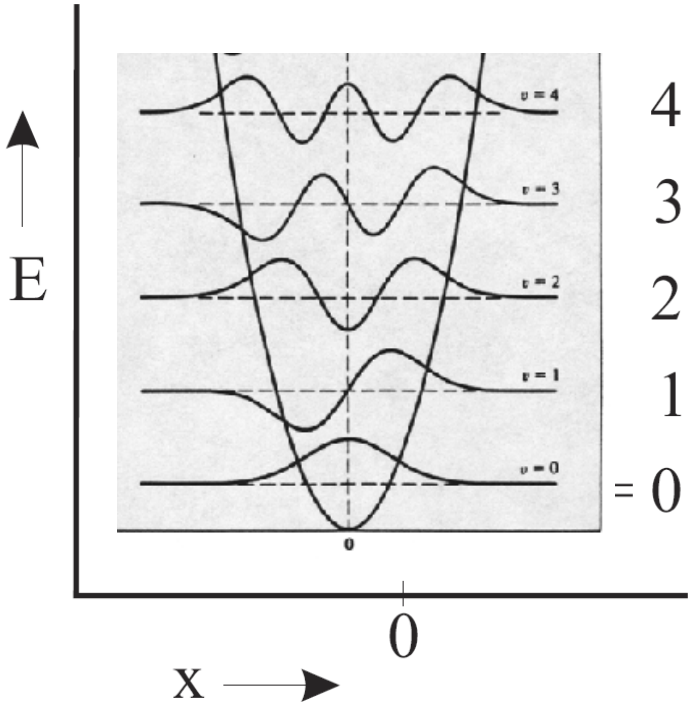


Eigenvalues

$$E_n = \hbar\omega_0\left(n + \frac{1}{2}\right)$$

Solutions





Eigenfunctions (explicit form):

$$\left|\varphi_n(x)\right\rangle = N_n e^{-\alpha^2 x^2/2} H_n(\alpha x) \qquad \alpha = \sqrt{\frac{m\omega_0}{\hbar}}$$

Ladder operator formalism

- We will no longer deal with the explicit solutions

- Instead we use $|\varphi_n\rangle$

- And we define

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega_0}\right)$$

Annihilation (lowering) operator

$$\hat{a}^{\pm} = \sqrt{\frac{m\omega_0}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega_0}\right)$$

Creation (raising) operator

Ladder operator formalism

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega_0}\right)$$

Annihilation (lowering) operator

$$\hat{a}^{\pm} = \sqrt{\frac{m\omega_0}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega_0}\right)$$

Creation (raising) operator

- Work out the following on your own

$$\hat{H}_0 = \hbar\omega_0\left(\hat{a}^{\pm}\hat{a} + \frac{1}{2}\right) \qquad \left[\hat{a}^{\pm}, \hat{a}\right] = 1$$

(use $\left[\hat{x}, \hat{p}\right] = i\hbar$)

Ladder operator formalism

- The following properties are useful

$$\hat{a}^{\pm}\left|\varphi_n\right\rangle = \sqrt{n+1}\left|\varphi_{n+1}\right\rangle \qquad \text{(raising operation)}$$

$$\hat{a}\left|\varphi_n\right\rangle = \sqrt{n}\left|\varphi_{n-1}\right\rangle \qquad \text{(lowering operation)}$$

You can show this by brute force by using the expressions for $\varphi_n(x)$

E.g. see: Brandsen and Joachain,
Introduction to Quantum Mechanics

Why are ladder operators useful?

- We are typically interested in expressions such as

$$\langle \varphi_n | \hat{p}^2 | \varphi_m \rangle \quad \text{or} \quad \langle \varphi_n | \hat{x} | \varphi_m \rangle$$

Plug in

$$\hat{p} = i\sqrt{\frac{m\omega_0\hbar}{2}}\left(\hat{a}^{\pm} - \hat{a}\right)$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega_0}}\left(\hat{a}^{\pm} + \hat{a}\right)$$

$$|n-m| = -2,0,2$$

$$|n-m| = -1,+1$$

Suggested reading

•More elegant solution of the quantum harmonic oscillator (Dirac's method)

All properties of the quantum harmonic oscillator can be derived from:

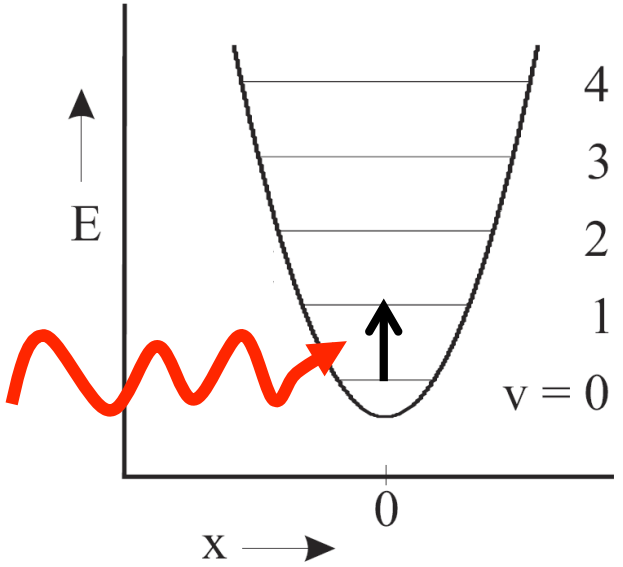
$$\hat{H}_0 = \hbar\omega_0\left(\hat{a}^{\pm}\hat{a} + \frac{1}{2}\right) \qquad \left[\hat{a}^{\pm},\hat{a}\right] = 1$$

E.g. see: Sakurai, ***Modern Quantum Mechanics***

Transitions induced by light

Oscillating electric field induces transitions

- Only single-quantum transitions are allowed ($\Delta n = \pm 1$)



$$i\hbar\frac{\partial}{\partial t}|\phi\rangle = \hat{H}|\phi\rangle$$

$$\hat{H} = \hat{H}_0 + \hat{V}_{\text{int}}$$

$$\hat{V}_{\text{int}} = -\hat{\mu}\cdot E_0\cos(\omega t)$$

Electric dipole Hamiltonian

Transitions induced by light

Oscillating electric field induces transitions

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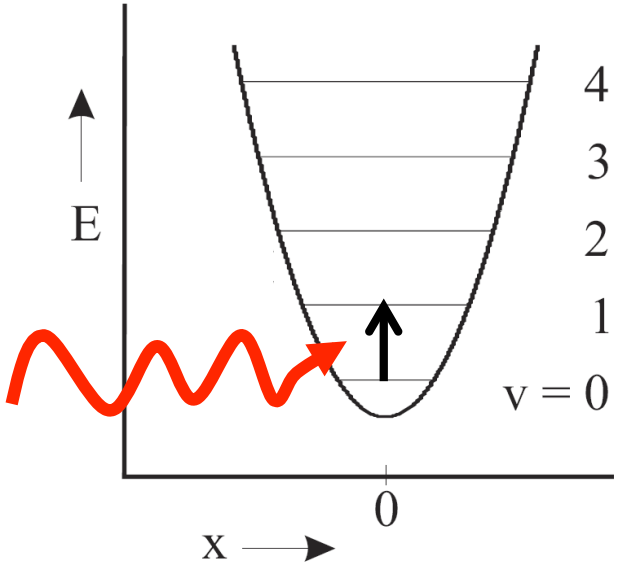


$$i\hbar\frac{\partial}{\partial t}|\phi\rangle = \hat{H}|\phi\rangle$$

$$\hat{H} = \hat{H}_0 + \hat{V}_{\text{int}}(t)$$

$$\hat{V}_{\text{int}}(t) = -\hat{\mu}\cdot E_0\cos(\omega t)$$

Electric-dipole Hamiltonian

Transitions induced by light

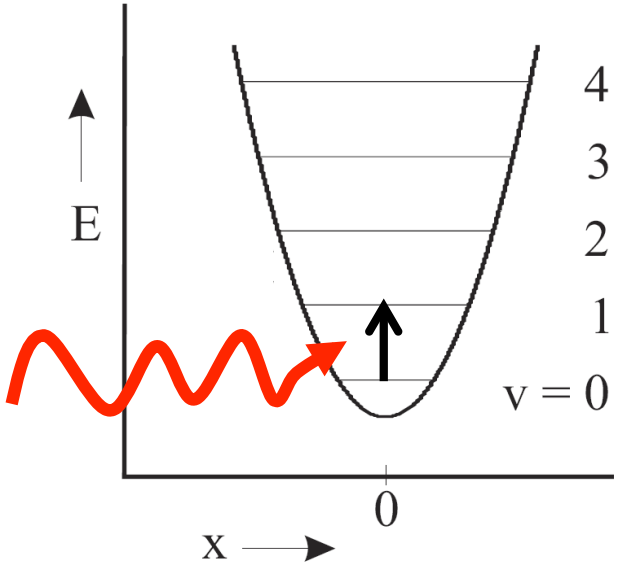
Oscillating electric field induces transitions

- Only single-quantum transitions are allowed ($\Delta n = \pm 1$)

$$\hat{V}_{\text{int}}(t) = -\hat{\mu} \cdot \vec{E}_0 \cos(\omega t)$$

$$= -\frac{1}{2} \hat{\mu} \cdot \vec{E}_0 (e^{i\omega t} + e^{-i\omega t})$$

$$= \hat{V}(e^{i\omega t} + e^{-i\omega t})$$



Transitions induced by light

Oscillating electric field induces transitions

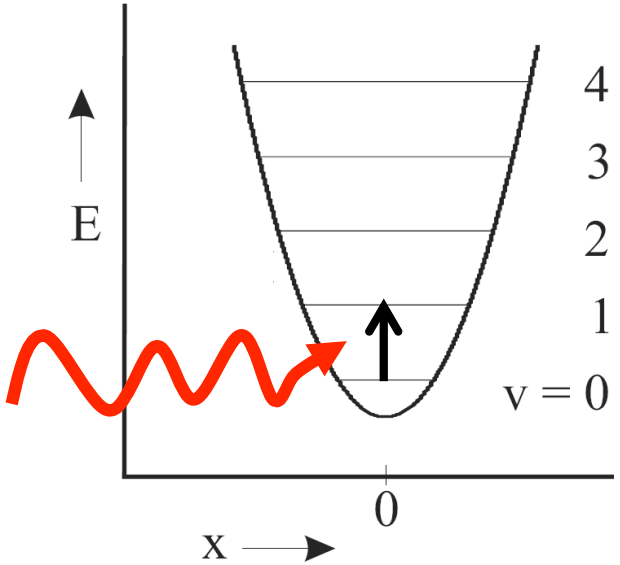
- Only single-quantum transitions are allowed ($\Delta n = \pm 1$)

$$\hat{V}_{\text{int}}(t) = -\hat{\mu} \cdot \vec{E}_0 \cos(\omega t)$$

$$= \hat{V}(e^{i\omega t} + e^{-i\omega t})$$

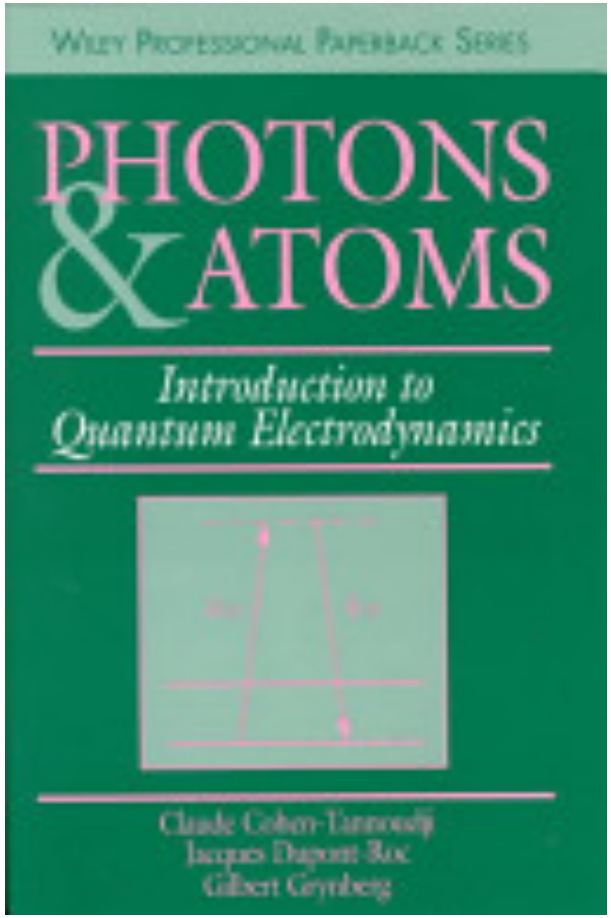
operator time dependence

$$\hat{V} = -\frac{1}{2}\hat{\mu} \cdot \vec{E}_0$$



For those interested

$$\hat{V}_{\text{int}} = -\hat{\mu} \cdot \vec{E}_0 \cos(\omega t)$$



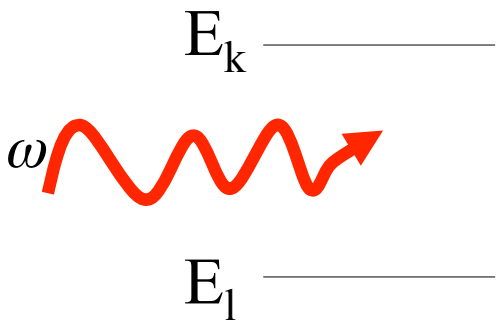
350 page derivation of the
Light-matter Hamiltonian

Cohen-Tannoudji, Dupont-Roc & Grynberg

Effect of perturbation

Solve time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\phi\rangle = \hat{H}|\phi\rangle$$



First order perturbation theory: Fermi's golden rule

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2[\delta(\omega_{kl}-\omega)+\delta(\omega_{kl}+\omega)]$$

Bohr condition: $\Delta E = \hbar\omega$

Effect of perturbation

Solve time-dependent Schrödinger equation

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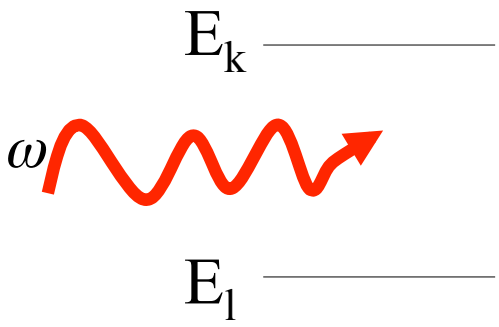


First order perturbation theory: Fermi's golden rule

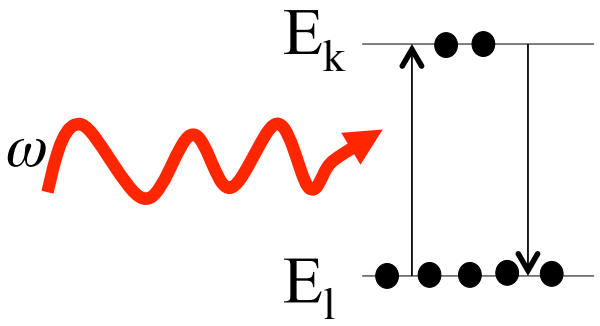
$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$

(on resonance)

Transition probability per second

Effect of perturbation

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$



Absorption probability = stimulated emission probability

$$W_{kl} = W_{lk}$$

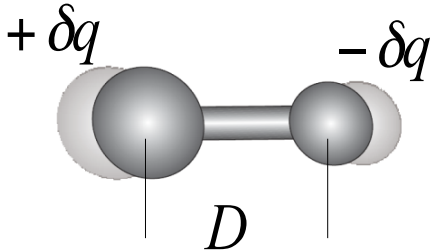
Net energy absorption

$$(N_k - N_l)W_{lk}$$

Selection rules

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$

$$\hat{V} = -\frac{1}{2}\hat{\mu}\cdot\vec{E}_0$$



$$\vec{\mu}_0 = D\delta q$$

Classically

$$\vec{\mu} = \vec{\mu}(x) \approx \vec{\mu}_0 + x\frac{\partial\vec{\mu}}{\partial x}$$

Selection rules

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$

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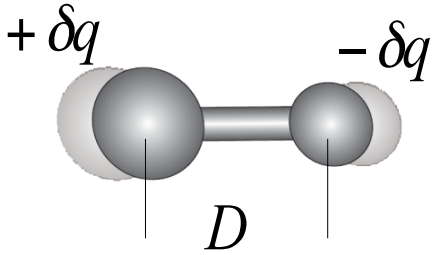


$$\vec{\mu}_0 = D\delta q$$

Quantum

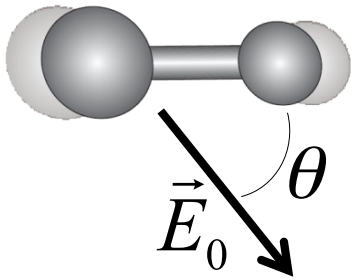
$$\hat{\vec{\mu}} = \vec{\mu}(\hat{x}) \approx \vec{\mu}_0 + \hat{x}\frac{\partial\vec{\mu}}{\partial x}$$

Operator character switches to $\hat{x}$

Selection rules

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$

$$\hat{V} = -\frac{1}{2}\hat{\mu}\cdot\vec{E}_0$$

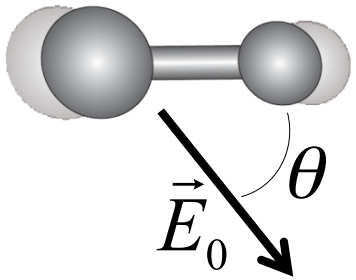


$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2\left|\langle k|\hat{x}|l\rangle\right|^2$$

Selection rules

$$W_{kl} = \frac{2\pi}{\hbar^2}|\langle k|\hat{V}|l\rangle|^2$$

$$\hat{V} = -\frac{1}{2}\hat{\mu}\cdot\vec{E}_0$$



$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta\underbrace{\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2}_{\vec{\mu}_{kl}}\left|\langle k|\hat{x}|l\rangle\right|^2$$

Transition dipole moment

Selection rules

$$W_{kl} = -\frac{\pi E_0}{2\hbar^2}\cos^2\theta\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2\left|\langle k|\hat{x}|l\rangle\right|^2$$

- $W_{kl} \propto \cos^2(\theta)$

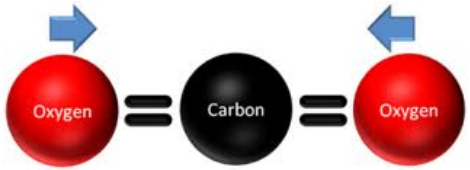
Transition dipole should be parallel to the electric field

Selection rules

$$W_{kl} = -\frac{\pi E_0}{2\hbar^2}\cos^2\theta\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2\left|\langle k|\hat{x}|l\rangle\right|^2$$

- $W_{kl} \propto (\frac{\partial\vec{\mu}}{\partial x})^2$ Dipole moment should change with vibration

E.g. symmetric stretch of CO_2 is not infrared active



Selection rules

$$W_{kl} = -\frac{\pi E_0}{2\hbar^2}\cos^2\theta\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2\left|\langle k|\hat{x}|l\rangle\right|^2$$

- $W_{kl} \propto |\langle k|\hat{x}|l\rangle|^2$

Only single-quantum transitions are allowed $(k-l=\pm 1)$

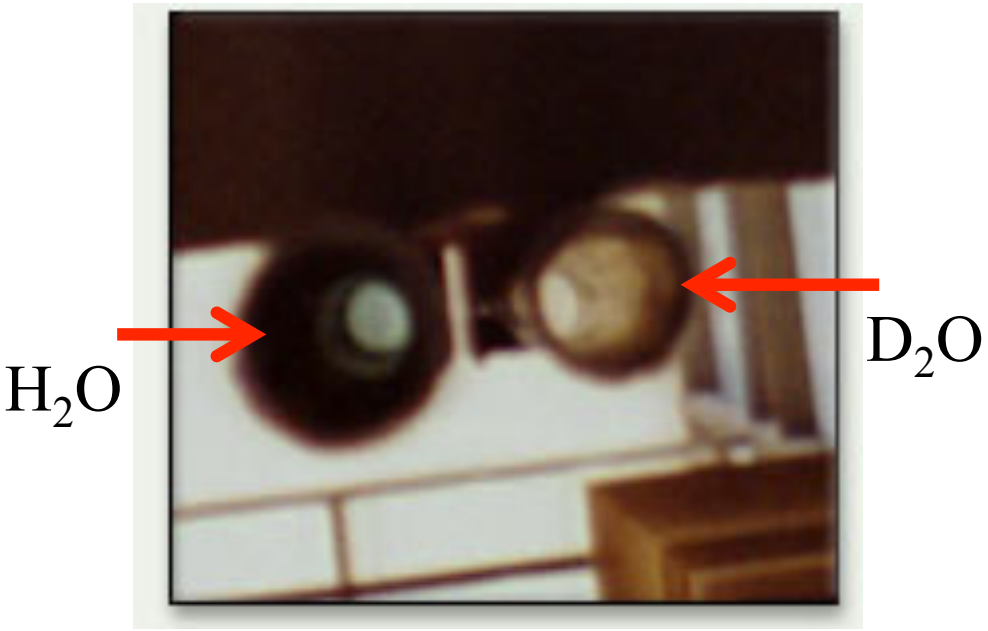
remember $\hat{x} = \sqrt{\frac{\mathrm{h}}{2m\omega_0}}\left(\hat{a}^{\pm}+\hat{a}\right)$

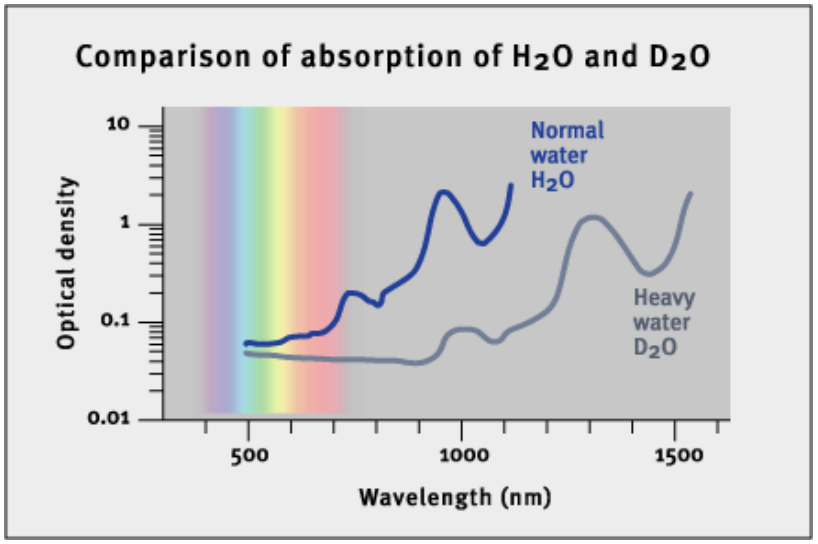
Selection rules

- $W_{kl} \propto |\langle k|\hat{x}|l\rangle|^2$

Only single-quantum transitions are allowed $(k - l = \pm 1)$

If this were true water would not be blue!



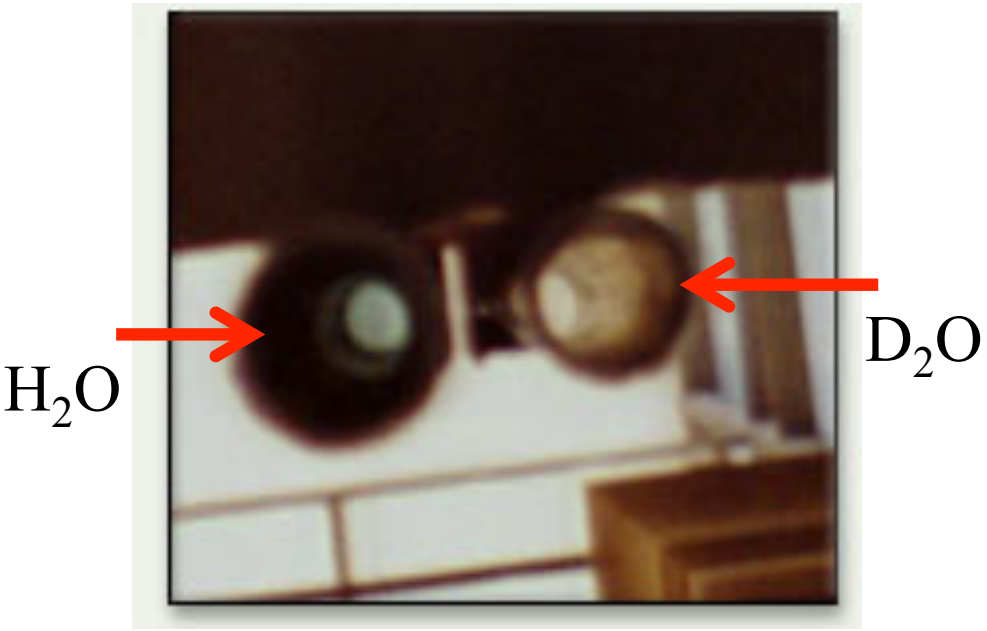


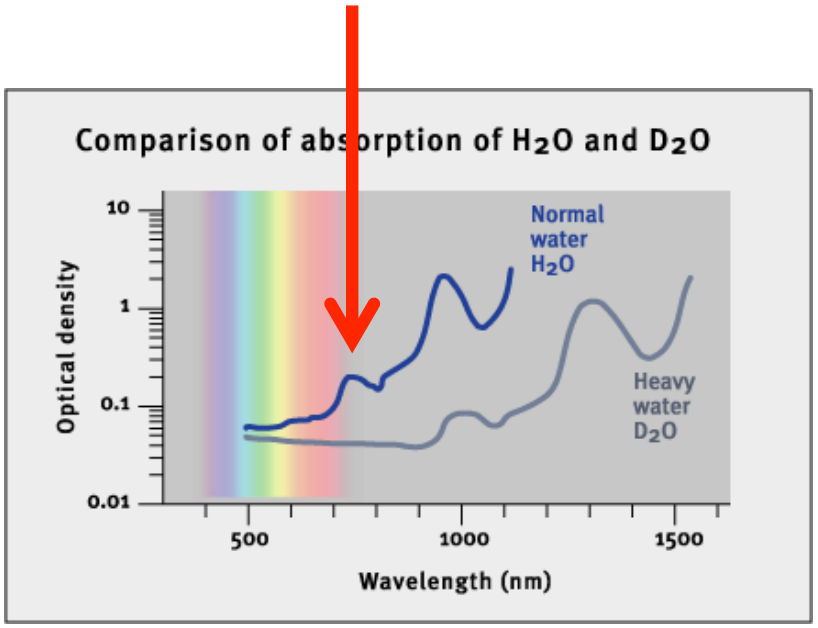
Selection rules

- $W_{kl} \propto |\langle k|\hat{x}|l\rangle|^2$

Only single-quantum transitions are allowed $(k - l = \pm 1)$

4-quantum vibrational transition

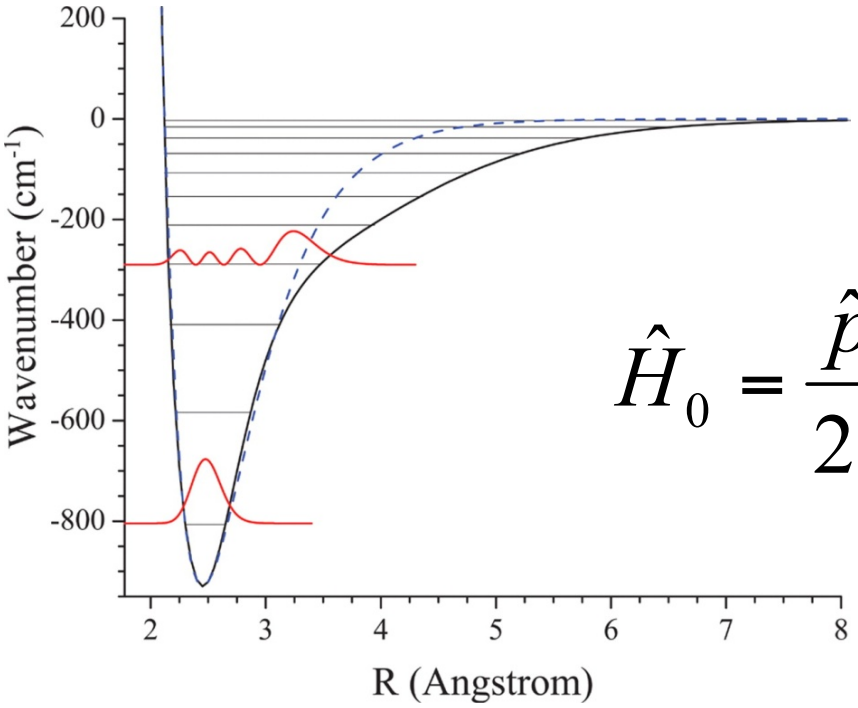




Multiquantum transitions

- $W_{kl} \propto |\langle k|\hat{x}|l\rangle|^2$

1) Anharmonic potential (mechanical anharmonicity)



$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 \hat{x}^2 + a_1 \hat{x}^3 + \ldots$$

Multiquantum transitions

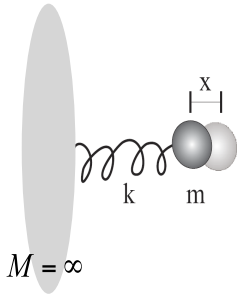
- $W_{kl} \propto |\langle k|\hat{x}|l\rangle|^2$

2) Nonlinear dependence of dipole moment (electrical anharmonicity)

$$\vec{\hat{\mu}} = \vec{\mu}(\hat{x}) \approx \vec{\mu}_0 + \hat{x}\frac{\partial\vec{\mu}}{\partial x} + \frac{1}{2}\hat{x}^2\frac{\partial^2\vec{\mu}}{\partial x^2} + \ldots$$

Summary ‘Quantum Harmonic Oscillator’

- Harmonic oscillator Hamiltonian



$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 \hat{x}^2$$

- Properties of the solutions

$$\hat{a}^{\pm}\left|\varphi_n\right\rangle = \sqrt{n+1}\left|\varphi_{n+1}\right\rangle$$

- Ladder operator formalism

$$\hat{a}\left|\varphi_n\right\rangle = \sqrt{n}\left|\varphi_{n-1}\right\rangle$$

- Transitions induced by light

$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2\left|\left\langle k\left|\hat{x}\right|l\right\rangle\right|^2$$

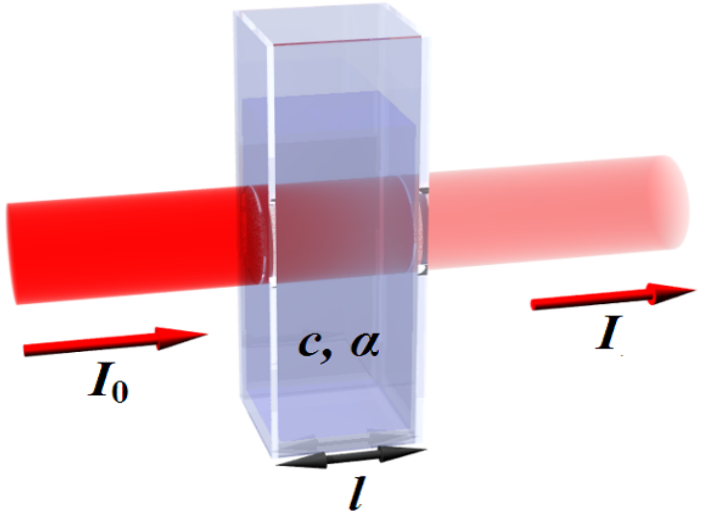
- Selection rules

Lambert-Beer law

Lambert-Beer law

Connects the microscopic to the macroscopic world

$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2}\cos^2\theta \underbrace{\left|\frac{\partial\vec{\mu}}{\partial x}\right|^2}_{\left|\vec{\mu}_{kl}\right|^2} \left|\langle k|\hat{x}|l\rangle\right|^2$$

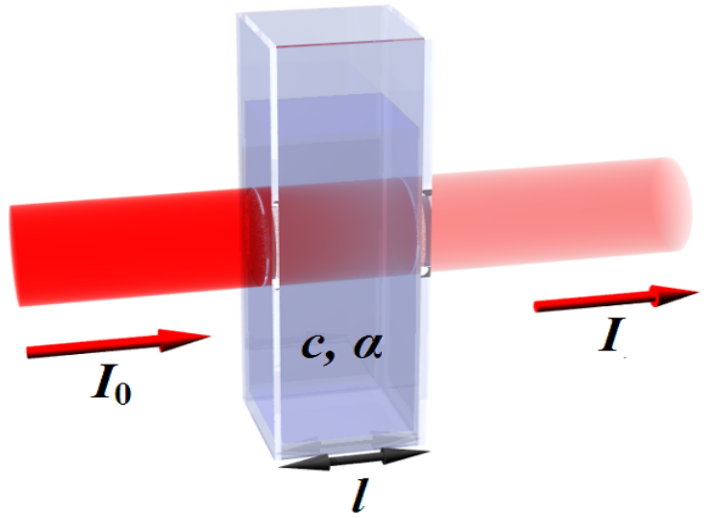


Molecular quantity

Lambert-Beer law

Connects the microscopic to the macroscopic world

$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2} \cos^2\theta \left|\mu_{kl}\right|^2$$

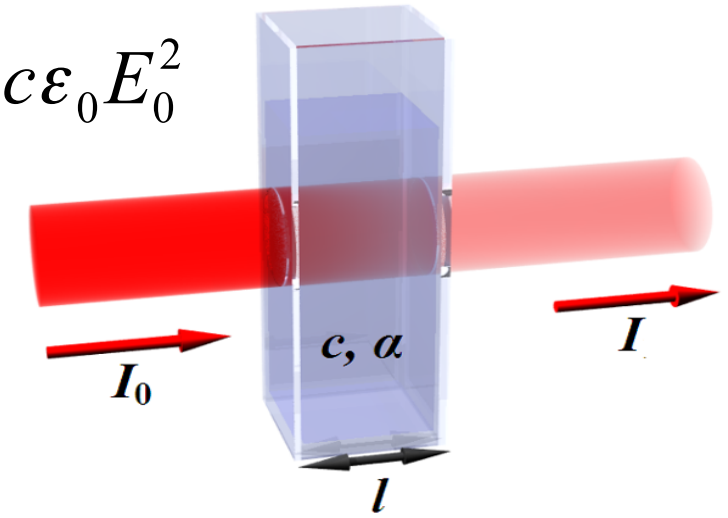


Lambert-Beer law

Connects the microscopic to the macroscopic world

$$I_0 = \frac{1}{2} c \varepsilon_0 E_0^2$$

$$W_{kl} = \frac{\pi E_0^2}{2\hbar^2} \cos^2 \theta \left| \mu_{kl} \right|^2$$



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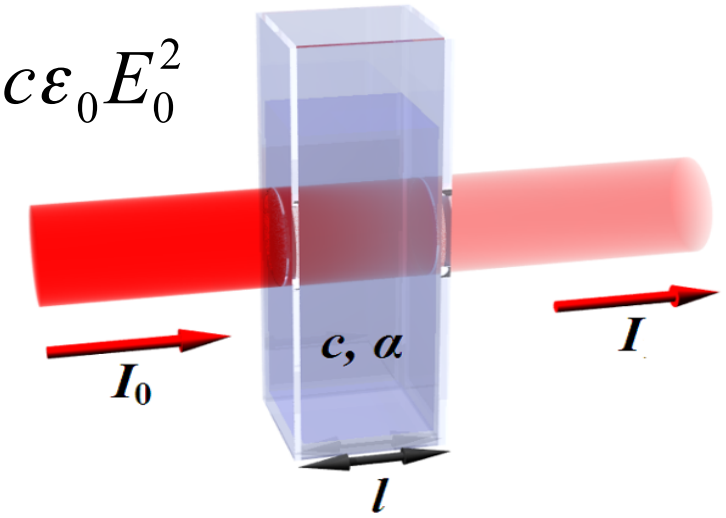
Connects the microscopic to the macroscopic world

$$I_0 = \frac{1}{2} c \varepsilon_0 E_0^2$$

$$W_{kl} = \frac{\pi I_0}{\hbar^2 c \varepsilon_0} \cos^2 \theta \left| \mu_{kl} \right|^2$$



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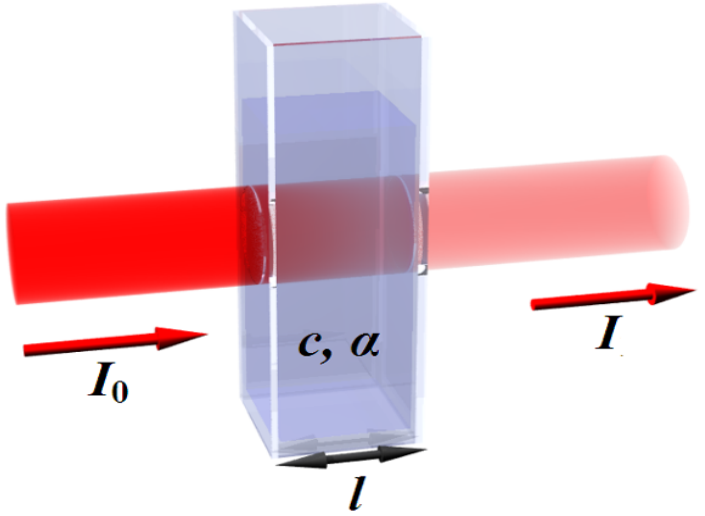
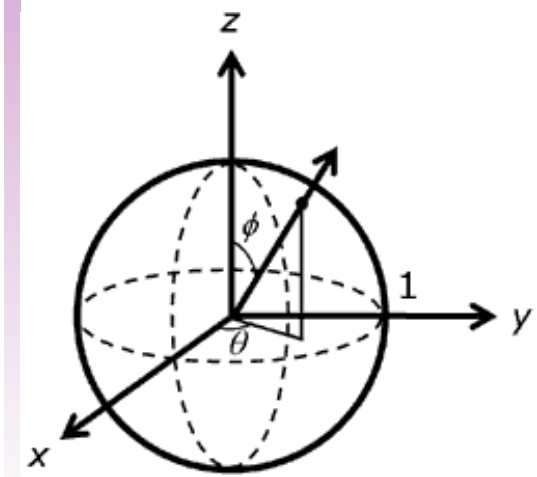




$$\frac{1}{4\pi}\int\int \cos^2\theta \, d\Omega = \frac{1}{3}$$

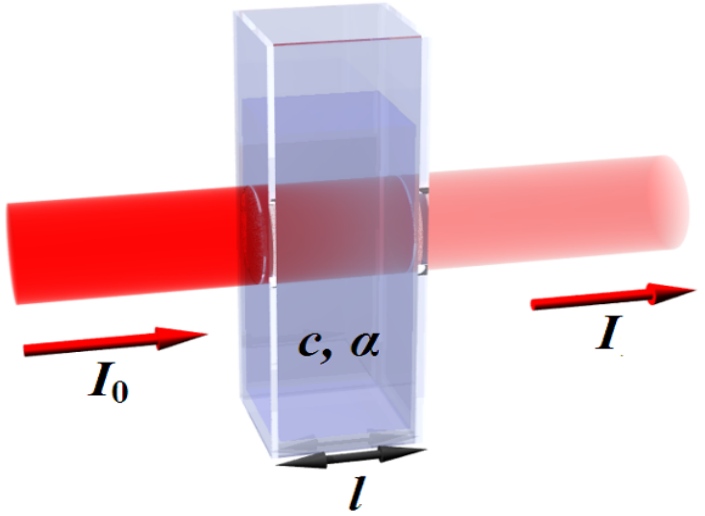
Average over unit sphere

Lambert-Beer law

Connects the microscopic to the macroscopic world

$$W_{kl} = \frac{\pi I_0}{3\hbar^2 c\varepsilon_0}\left|\mu_{kl}\right|^2$$

Transition probability per second



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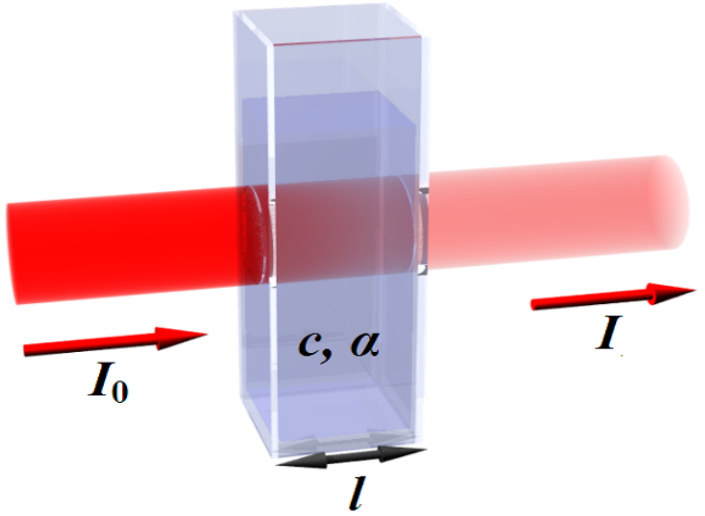


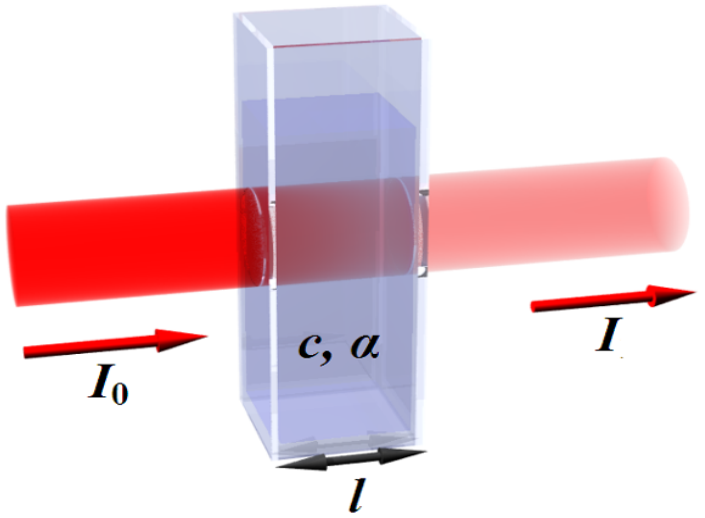
Lambert-Beer law

Connects the microscopic to the macroscopic world

$$W_{kl} = \frac{\pi I_0}{3\hbar^2 c\varepsilon_0}\left|\mu_{kl}\right|^2$$

$$P_{kl} = \hbar\omega_{kl} W_{kl}$$

$$P_{kl} = \frac{\omega_{kl}\pi I_0}{3\hbar c\varepsilon_0}\left|\mu_{kl}\right|^2$$

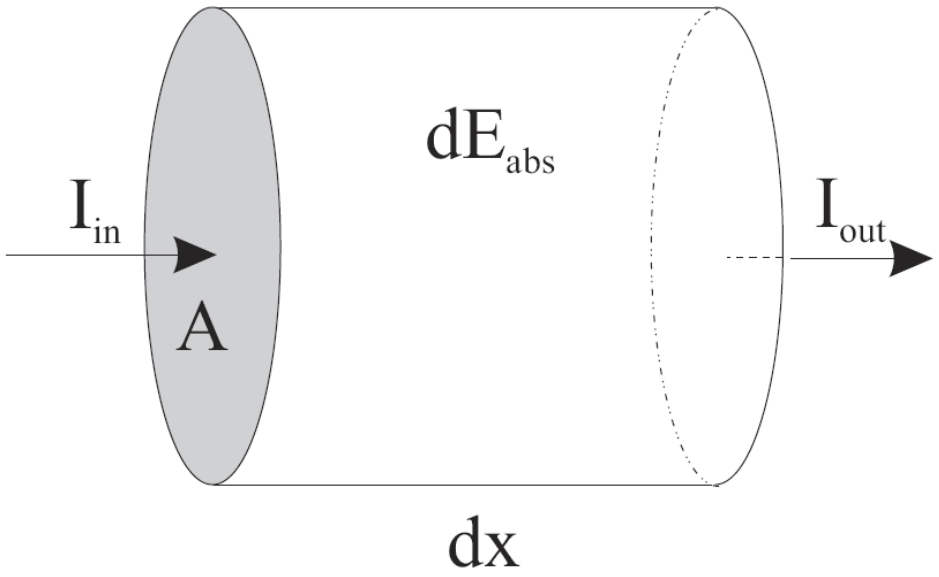


Power absorbed per second by a single molecule

Lambert-Beer law

Connects the microscopic to the macroscopic world

$$P_{kl} = \frac{\omega_{kl}\pi\left|\mu_{kl}\right|^2}{3\hbar c\varepsilon_0} I_0$$



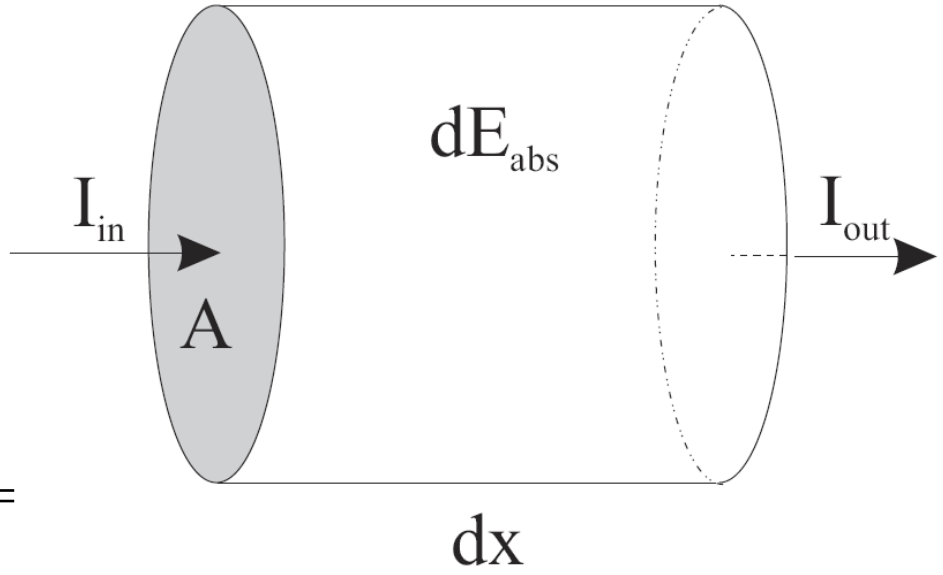
Lambert-Beer law

Connects the microscopic to the macroscopic world

$$P_{kl} = \frac{\omega_{kl}\pi\left|\mu_{kl}\right|^2}{3\hbar c\varepsilon_0} I_0$$

power

light intensity = power/area



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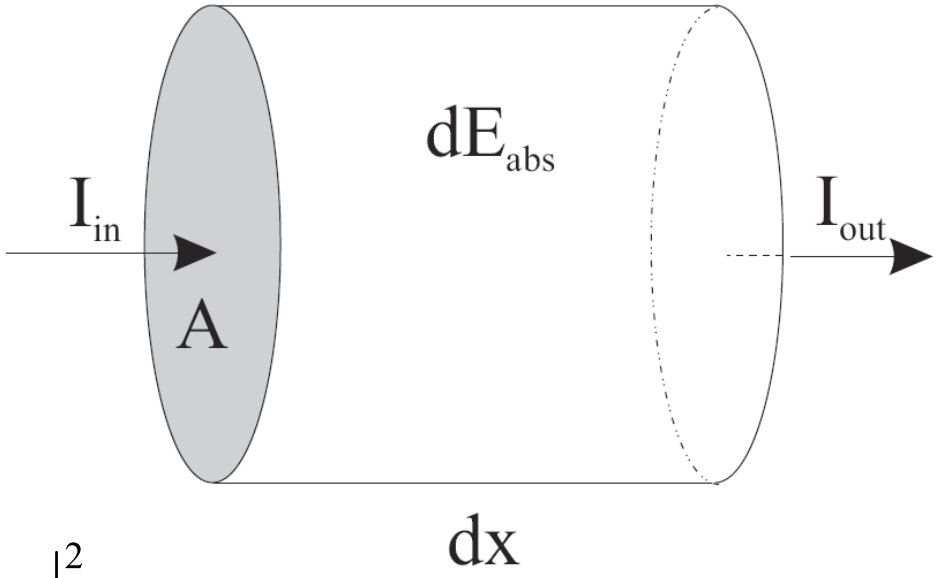


$$P_{kl} = \sigma_{kl} I_0$$

Area
(=cross section)

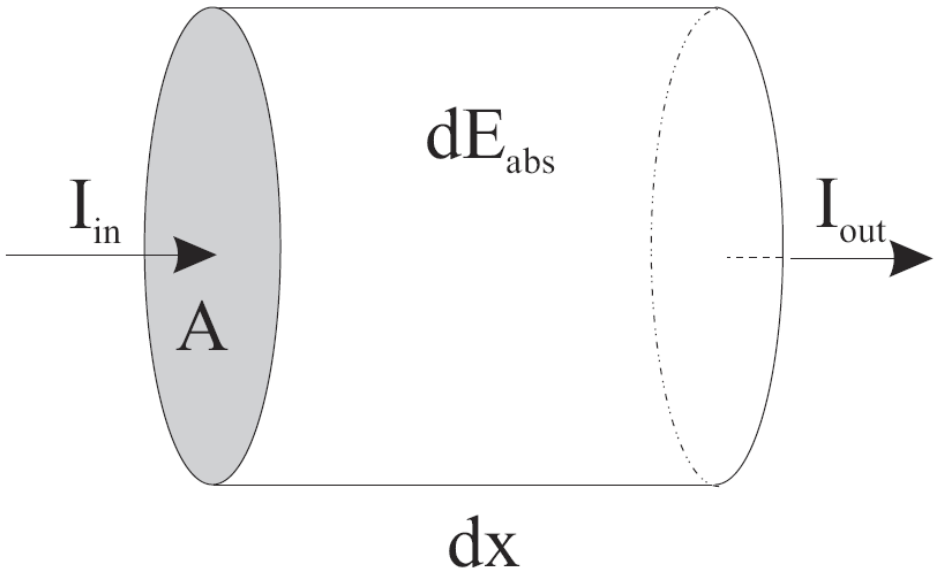
$$\sigma_{kl} = \frac{\omega_{kl}\pi\left|\mu_{kl}\right|^2}{3\hbar c\varepsilon_0}$$

Lambert-Beer law

Connects the microscopic to the macroscopic world

$$P_{kl} = \frac{\omega_{kl}\pi\left|\mu_{kl}\right|^2}{3\hbar c\varepsilon_0} I_0$$

$$P_{kl} = \sigma_{kl} I_0$$



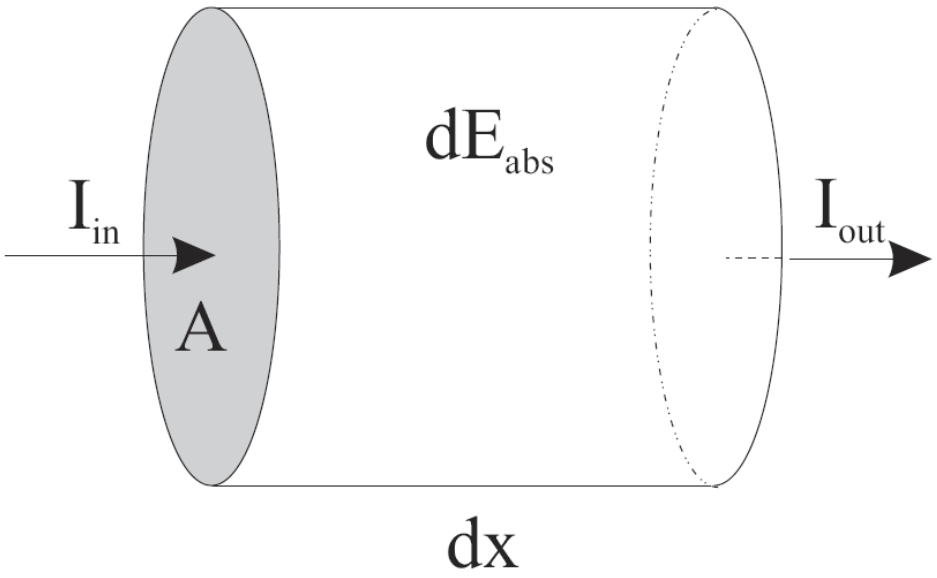
Lambert-Beer law

$$P_{kl} = \sigma_{kl} I_0$$

Relate energy dissipation in the slab to the in- and outgoing intensities

$$\frac{dI}{I} = -\sigma\, C dx$$

$$\frac{I}{I_0} = e^{-\sigma\, Cl}$$

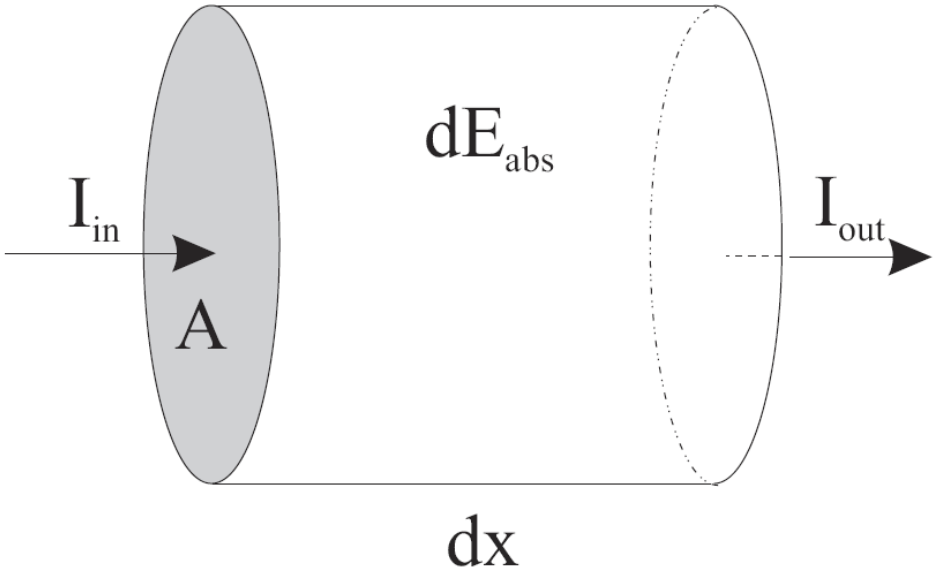


Lambert-Beer law

$$\frac{I}{I_0} = e^{-\sigma Cl}$$

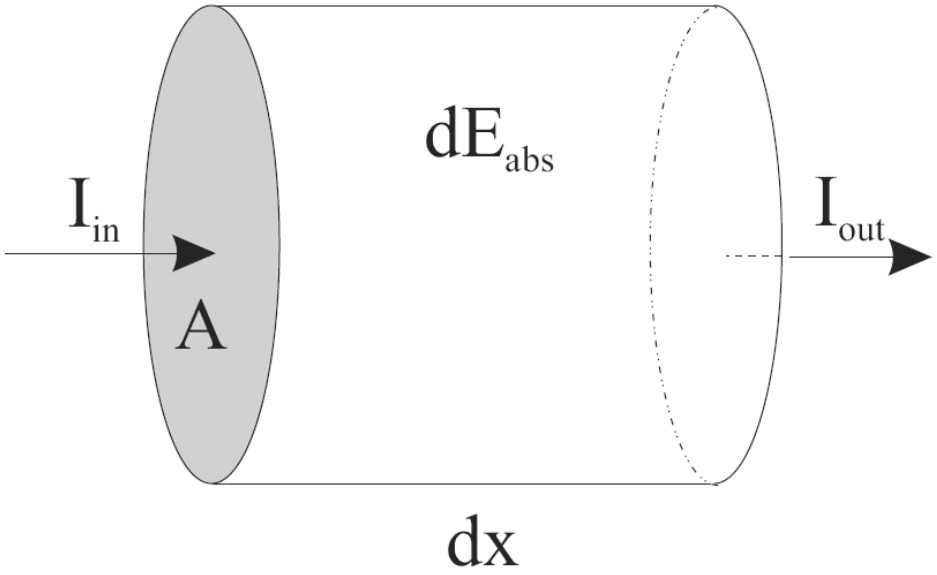
$$\alpha = -\ln\left(\frac{I}{I_0}\right) = \sigma Cl$$

$$\alpha = \sigma N$$



Lambert-Beer law

$$\frac{I}{I_0} = e^{-\sigma Cl}$$



$$\alpha = -\ln\left(\frac{I}{I_0}\right) = \sigma Cl$$

N = concentration per unit area

$$\alpha = \sigma N$$

Lambert-Beer law

$$\frac{I}{I_0} = e^{-\sigma Cl}$$

$$\alpha = -\ln\left(\frac{I}{I_0}\right) = \sigma Cl$$

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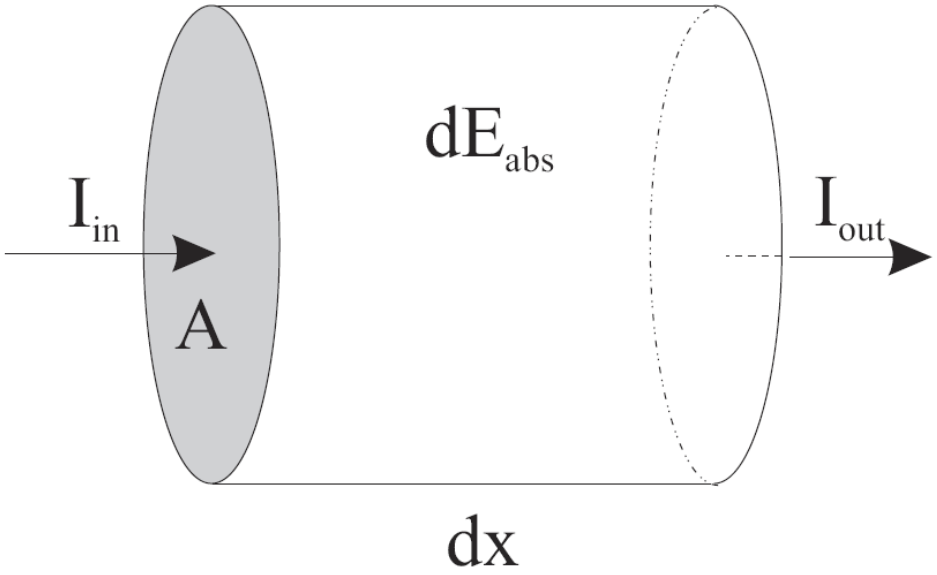
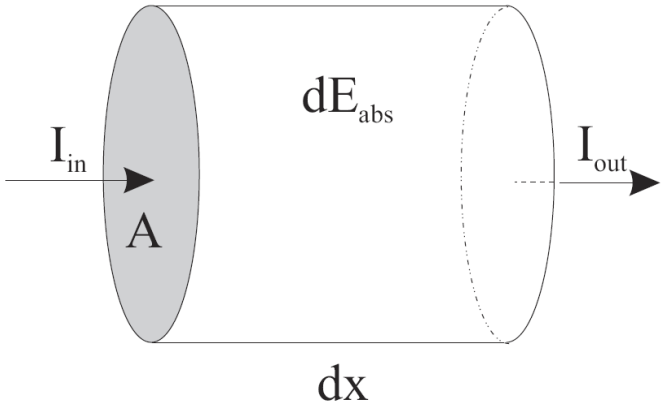


Absorbance is linear with concentration

Lambert-Beer law

Why do we call σ the cross section?

$$\frac{dI}{I} = -\sigma\, C dx$$

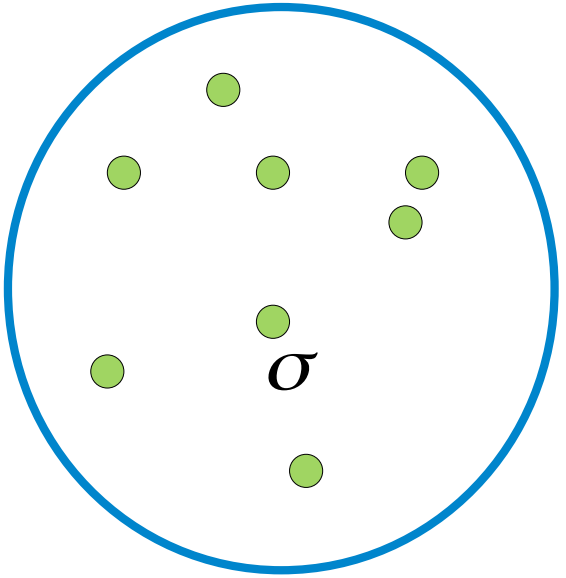


Lambert-Beer law

Why do we call σ the cross section?

$$\frac{dI}{I} = -\sigma C dx$$

Number of molecules per surface area (m^2)



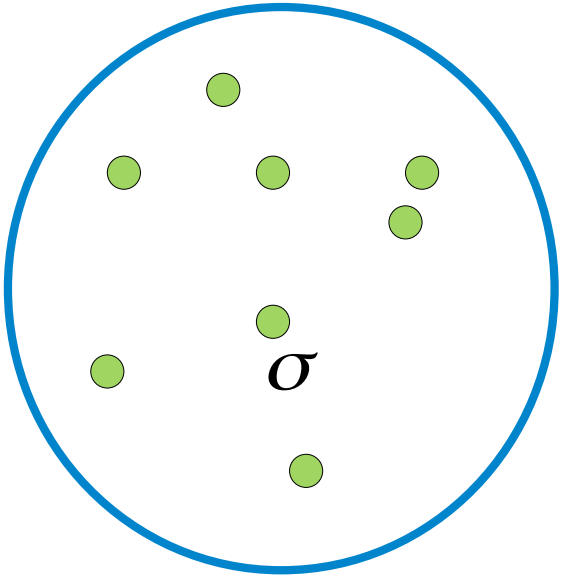
Lambert-Beer law

Why do we call σ the cross section?

$$\frac{dI}{I} = -\sigma\, C dx$$

Number of molecules per surface area (m^2)

Fraction of light blocked in slab of thickness dx



Lambert-Beer law

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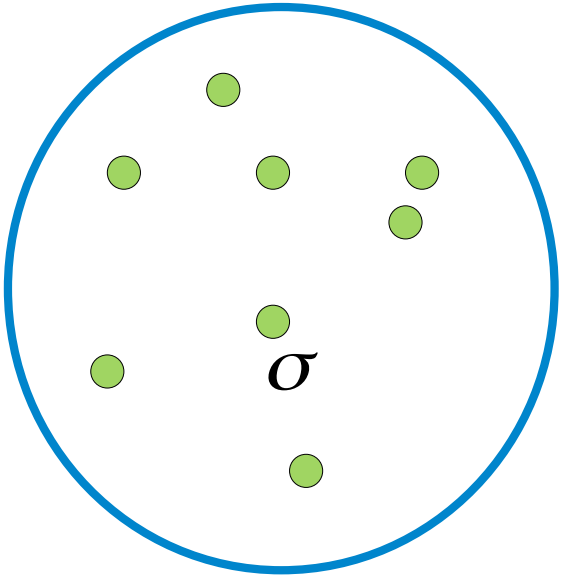
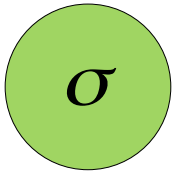


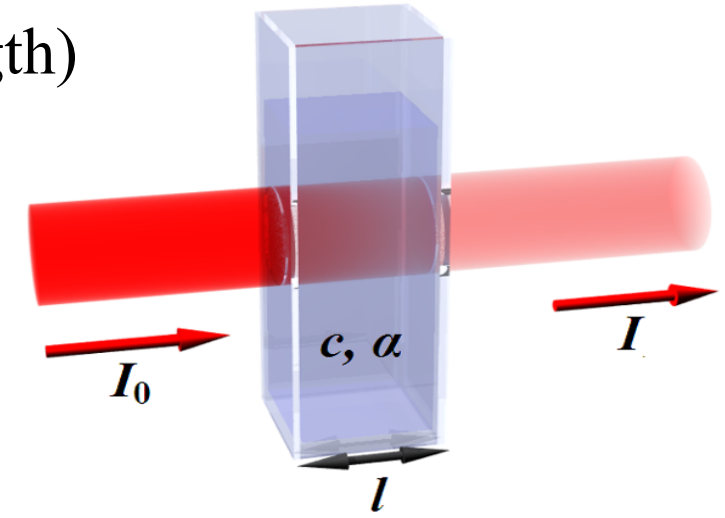
If we represent a molecule by an opaque disk, it should have a surface area σ



Lambert-Beer law

Example

- Dye solution (1 μM, 1 cm pathlength)
- Gives absorbance of 0.1



Transmission

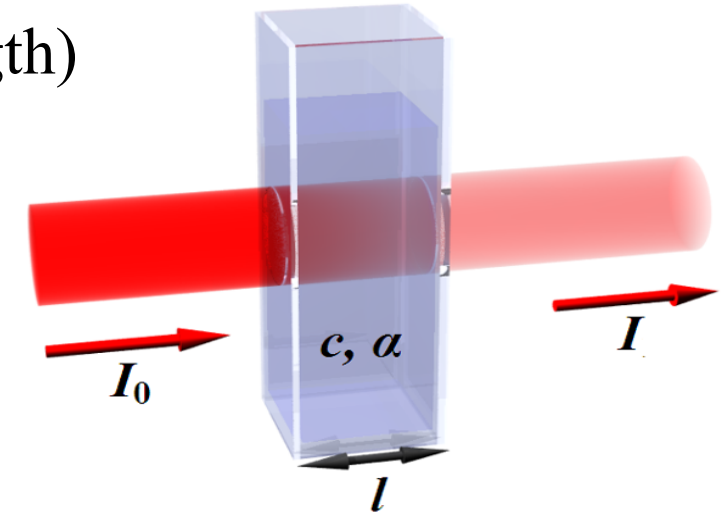
$$\frac{I}{I_0} = e^{-\alpha} \approx 1 - 0.1 = 0.9$$

~10% of light blocked

Lambert-Beer law

Example

- Dye solution (1 μM, 1 cm pathlength)
- Gives absorbance of 0.1



~10% of light blocked

- Number of molecules per cm^2 = 10^{-6} x $6.02 \cdot 10^{23}$ x 10^{-3} = $6 \cdot 10^{14}$
- These molecules apparently cover ~0.1 cm^2

$$\sigma \approx \frac{0.1}{6 \cdot 10^{14}} = 1.6 \cdot 10^{-16} cm^2$$

Summary ‘Lambert Beer’

•Lambert-Beer law: connection between molecular quantity (μ= transition dipole) and macroscopic observable (σ=cross section)

•Absorbance is linear with concentration (per unit area)

$$\alpha = \sigma\ N$$

•Absorption cross section can be interpreted as the physical cross section of the molecule to light