Can we build individual molecules atom by atom?

Mikkel F. Andersen
Jack Dodd Centre for Quantum Technology,
Department of Physics, University of Otago.

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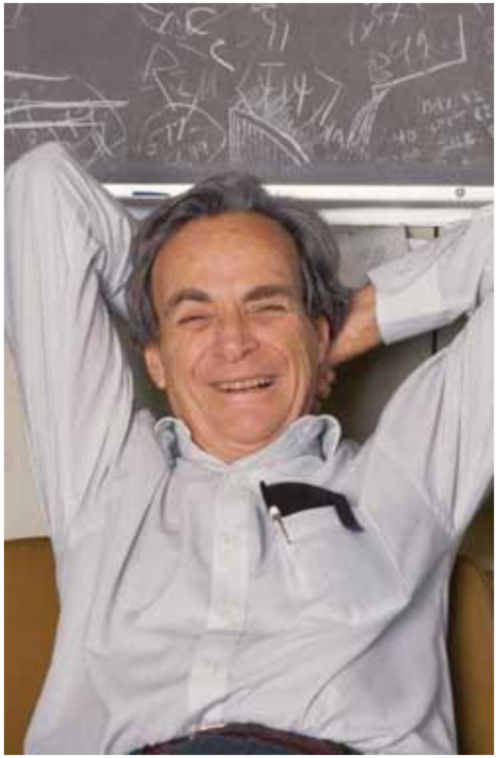


Richard Feynman 1959:
“There's Plenty of Room at the Bottom”

Do we in 2014 have the toolbox required to realize Feynman's dream?

Outline

Lecture 1: Atoms in light

- Two-level atoms in light
- Optical forces on atoms in light
- Cooling atoms with light
- Trapping atoms with light

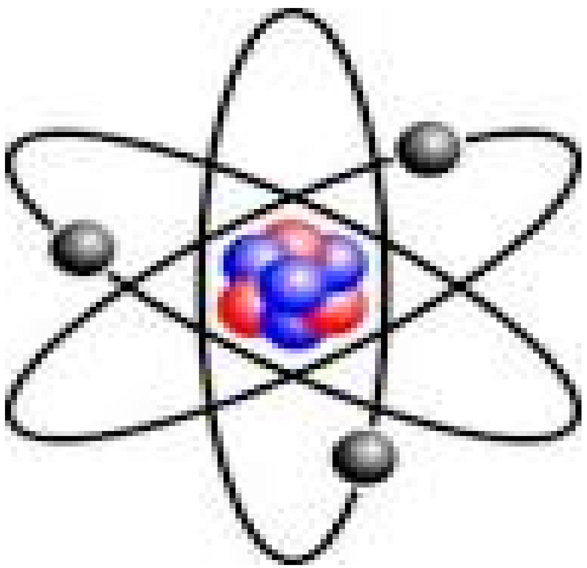
Lecture 2: Basic molecular physics

Lecture 3: Light induced molecule formation processes

Lecture 4: State of the field and how to proceed

An atom in light

$$H = H_A + V_{\text{ext}}\left(\mathbf{r}, \mathbf{R}, t\right)$$



$$H_A = H_{\text{CM}} + H_{\text{Int}} = -\frac{\hbar^2}{2M}\nabla^2_{\text{R}} - \sum \frac{\hbar^2}{2m}\nabla^2_{\text{r}_i} - \frac{Ze^2}{4\pi\epsilon_0}\sum \frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_0}\sum \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + H_{FS} + H_{HF}$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \left(H_A + V_{\text{ext}}\left(\mathbf{r}, \mathbf{R}, t\right)\right)\Psi\left(\mathbf{r}, \mathbf{R}, t\right)$$

The Interaction with the Light

Assume that the atom is much smaller than the wavelength of light:

$$V_{\text{ext}}\left(\mathbf{r},\mathbf{R},t\right)=-e\mathbf{r}\cdot\mathbf{E}\left(\mathbf{R},t\right)$$

$$\mathbf{E}\left(\mathbf{R},t\right)=\frac{1}{2}\hat{\varepsilon}E_0\exp\left(i\left(\mathbf{k}\cdot\mathbf{R}-\omega t\right)\right)+c.c.$$

Two-Level Atom fixed at the origin

Assume **R=0** and only two internal states play a role in the internal Dynamics:

$$|\Psi\rangle = a_1(t)|1\rangle + a_2(t)|2\rangle$$

Plug into Schrödinger equation:

$$i\hbar\dot{a}_1(t)|1\rangle + i\hbar\dot{a}_2(t)|2\rangle = (H_A + V_{\text{ext}})(a_1(t)|1\rangle + a_2(t)|2\rangle)$$

Take inner product with $|1\rangle$ and $|2\rangle$

$$i\hbar\dot{a}_1 = E_1 a_1(t) + \cancel{\langle 1|V_{\text{ext}}|1\rangle} a_1(t) + \langle 1|V_{\text{ext}}|2\rangle a_2(t)$$

$$i\hbar\dot{a}_2 = E_2 a_2(t) + \cancel{\langle 2|V_{\text{ext}}|2\rangle} a_2(t) + \langle 2|V_{\text{ext}}|1\rangle a_1(t)$$

Rewriting:

Recall:

$$\langle 1 |V_{\text{ext}}| 2\rangle = -\frac{1}{2}e\left(\langle 1 |\mathbf{r}| 2\rangle \cdot \hat{\varepsilon}\right) E_0 \exp\left(-i\omega t\right) - \frac{1}{2}e\left(\langle 1 |\mathbf{r}| 2\rangle \cdot \hat{\varepsilon}^*\right) E_0 \exp\left(i\omega t\right)$$

Define:

$$\omega_{21} = \frac{E_2 - E_1}{\hbar}$$

$$\chi_{21} = e\left(\langle 2 |\mathbf{r}| 1\rangle \cdot \hat{\varepsilon}\right) \frac{E_0}{\hbar}$$

And take $E_1 = 0$. The S.E. then becomes:

$$\begin{aligned} i\dot{a}_1 &= -\frac{1}{2}\left(\chi_{12} \exp\left(-i\omega t\right) + \chi_{21}^* \exp\left(-i\omega t\right)\right) a_2 \\ i\dot{a}_2 &= \omega_{21} a_2 - \frac{1}{2}\left(\chi_{21} \exp\left(-i\omega t\right) + \chi_{12}^* \exp\left(-i\omega t\right)\right) a_1 \end{aligned}$$

Rotating wave approximation

Define:
$$a_1(t) = c_1(t)$$
$$a_2(t) = c_2(t)\exp(-i\omega t)$$

For the c-coefficients we obtain:

$$i\dot{c}_1 = -\frac{1}{2}\left(\cancel{\chi_{12}\exp(-i2\omega t)} + \chi_{21}^*\right)c_2$$
$$i\dot{c}_2 = (\omega_{21}-\omega)\,c_2 - \frac{1}{2}\left(\chi_{21} + \cancel{\chi_{12}^*\exp(-i2\omega t)}\right)c_1$$

It is now very simple!

With: $\mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$, $\chi = \chi_{21} = \chi_{12}^*$, and $\Delta = \omega_{12} - \omega$

$$i\hbar\dot{\mathbf{c}} = \hbar \begin{pmatrix} 0 & -\frac{1}{2}\chi \\ -\frac{1}{2}\chi & \Delta \end{pmatrix} \mathbf{c}$$

$$\lambda_{\pm} = \hbar\frac{1}{2}\left(\Delta \pm \sqrt{\Delta^2 + \chi^2}\right) = \hbar\frac{1}{2}\left(\Delta \pm \Omega\right)$$

Solution

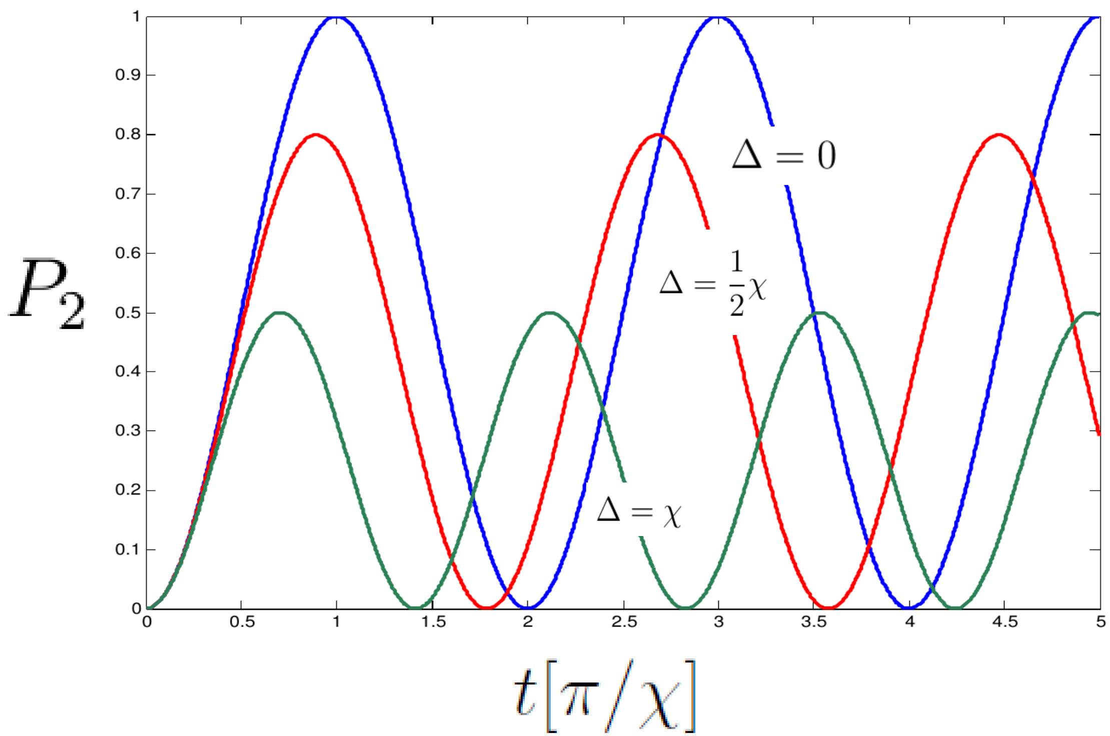
For $\mathbf{c}(0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$
\begin{aligned}
c_1(t) &= \left(\cos\left(\frac{\Omega t}{2}\right) + i\frac{\Delta}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right)\exp\left(-i\frac{\Delta}{2}t\right) \\
c_2(t) &= \left(i\frac{\chi}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right)\exp\left(-i\frac{\Delta}{2}t\right)
\end{aligned}
$$

Rabi-Flopping

$$P_1(t) = \frac{1}{2}\left(1+\left(\frac{\Delta}{\Omega}\right)^2\right)+\frac{1}{2}\left(\frac{\chi}{\Omega}\right)^2\cos(\Omega t)$$

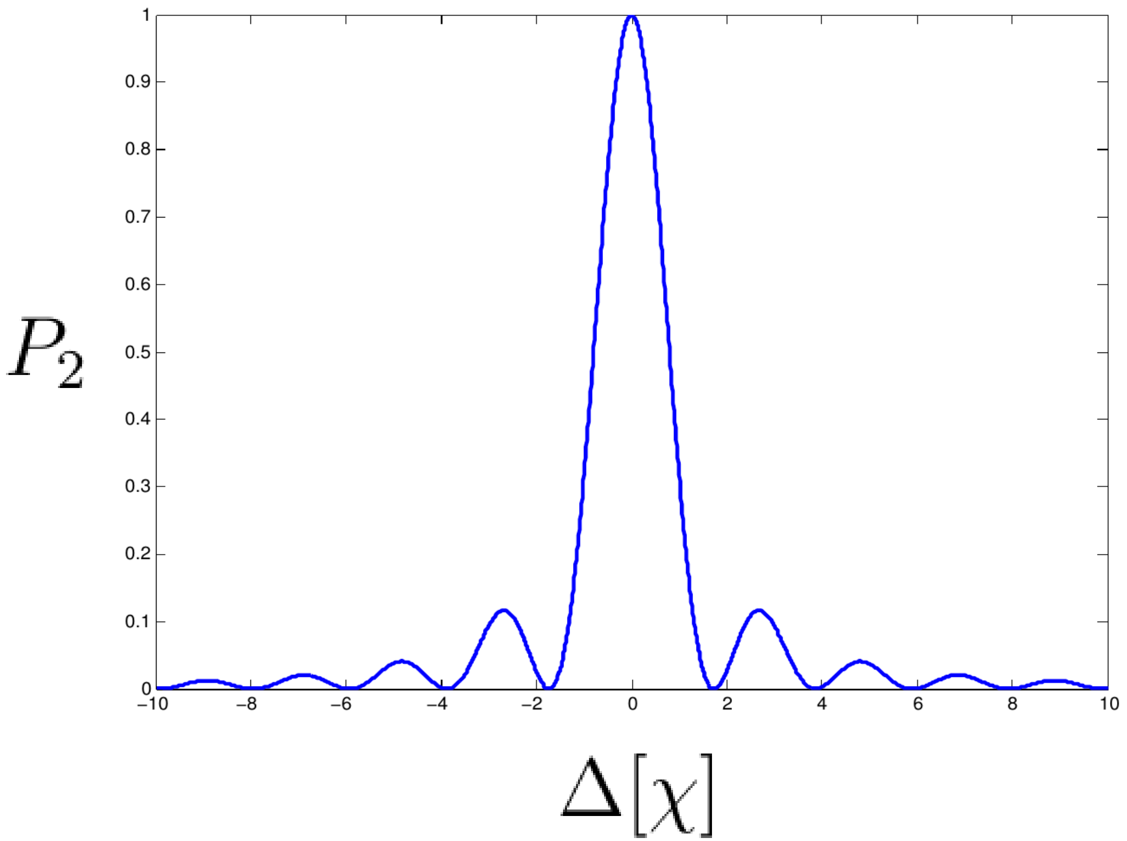
$$P_2(t) = \frac{1}{2}\left(\frac{\chi}{\Omega}\right)^2(1-\cos(\Omega t))$$



Excitation close to resonance

$$P_2(t) \;=\; \frac{1}{2}\left(\frac{\chi}{\Omega}\right)^2 \left(1 - \cos\left(\Omega t\right)\right)$$

For: $t = \pi/\chi$



Spontaneous emission

$$\frac{1}{\tau} = A_{21} = \frac{\omega_{21}^3}{3\pi\epsilon_0\hbar c^3} e^2 \left|\langle 2 \left| \mathbf{r} \right| 1 \rangle\right|^2$$

Include CM motion of atom

1. Expand on eigen-states of $H_A = H_{\text{CM}} + H_{\text{Int}}$

$$\Psi = \left(\frac{1}{\sqrt{2\pi}} \int a_1 (\mathbf{K}, t) \exp (i\mathbf{K} \cdot \mathbf{R})\, d^3\mathbf{K} \right) |1\rangle + \left(\frac{1}{\sqrt{2\pi}} \int a_2 (\mathbf{K}, t) \exp (i\mathbf{K} \cdot \mathbf{R})\, d^3\mathbf{K} \right) |2\rangle$$

2. Plug into time dependent Schrödinger equation
3. Take inner product with eigen-state of H_A to obtain coupled equations for $a_1(\mathbf{K}', t)$ $a_2(\mathbf{K}'', t)$
4. Observe that since the dependence of $V_{\text{ext}}(\mathbf{r}, \mathbf{R}, t)$ on the atoms center of mass coordinate goes like $\exp(\pm i\mathbf{k} \cdot \mathbf{R})$ then the equation for $\dot{a}_1(\mathbf{K}', t)$ only contains $a_2(\mathbf{K}' \pm \mathbf{k}, t)$ and $a_1(\mathbf{K}', t)$
5. Change from *a* to *c* and do rotating wave approximation
6. We now arrive at a problem that is mathematically identical to when we ignored CM motion but with a couple of modifications

Modifications

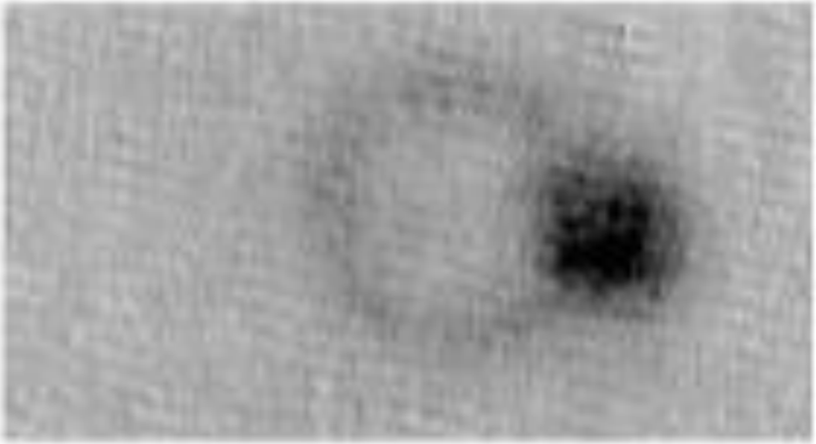
$c_1\left(\mathbf{K}', t\right)$ is only coupled to $c_2\left(\mathbf{K}' + \mathbf{k}, t\right)$ and vice versa. The atom changes center of mass momentum when it absorbs or emits light

$$\mathbf{c}\left(\mathbf{K}', t\right) = \begin{pmatrix} c_1\left(\mathbf{K}', t\right) \\ c_2\left(\mathbf{K}' + \mathbf{k}, t\right) \end{pmatrix} \qquad i\hbar\dot{\mathbf{c}} = \hbar \begin{pmatrix} 0 & -\frac{1}{2}\chi \\ -\frac{1}{2}\chi & \Delta\left(\mathbf{K}'\right) \end{pmatrix} \mathbf{c}$$

Because the atom changes center of mass momentum when it absorbs or emit light its center of mass energy changes as well. This leads to a momentum dependent resonance frequency. The Doppler effect.

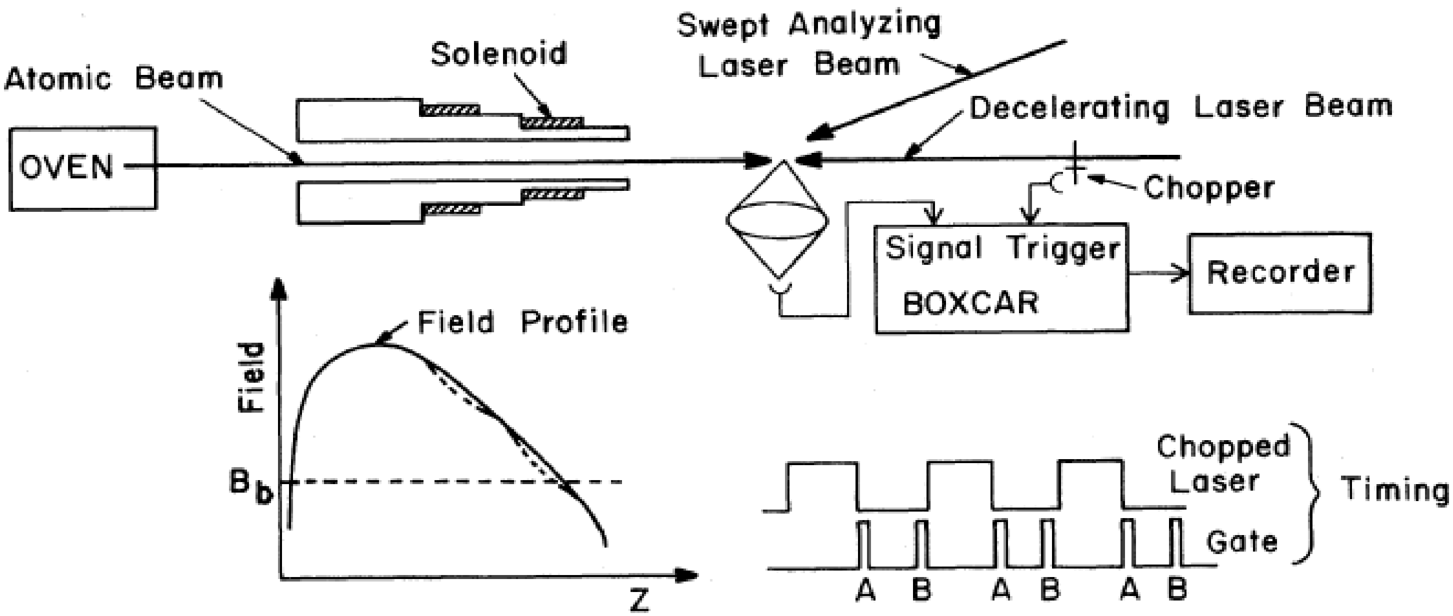
$$\Delta\left(\mathbf{K}'\right) = \frac{E_2 - E_1 + \frac{\hbar^2 k^2}{2M} + \frac{\hbar^2 \mathbf{K}' \cdot \mathbf{k}}{M}}{\hbar} - \omega$$

Radiation Pressure



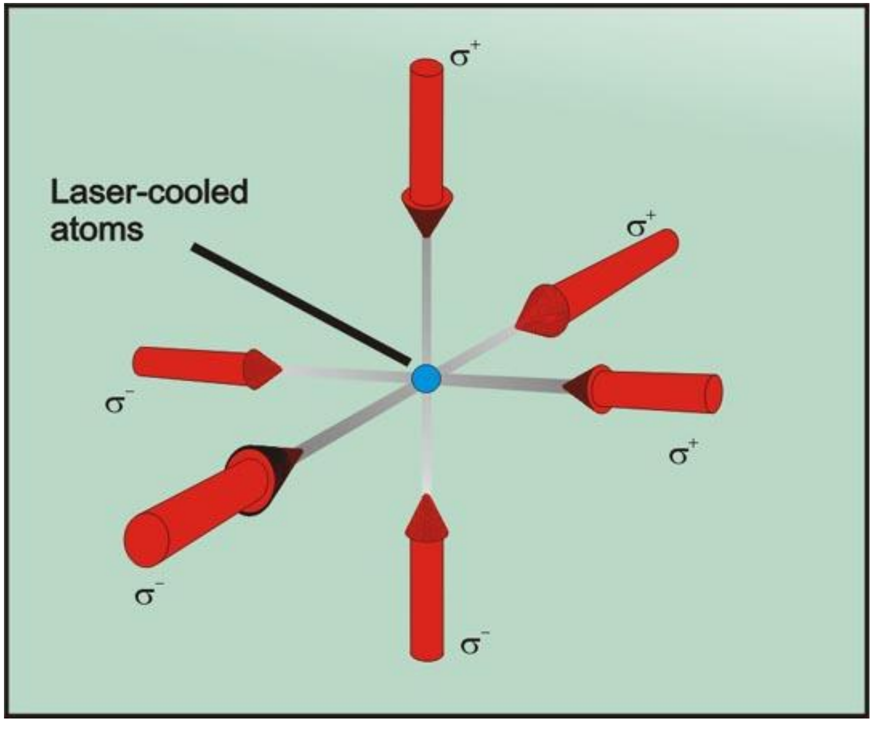
Radiation pressure

Application 1: Slowing of atoms



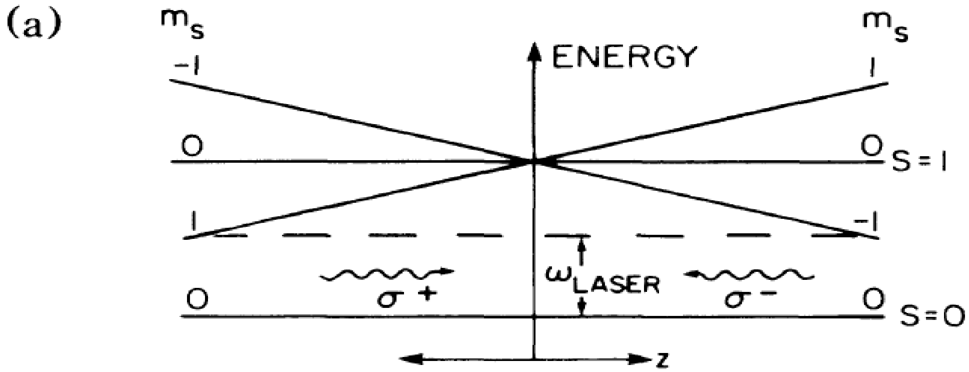
Application 2: Doppler cooling

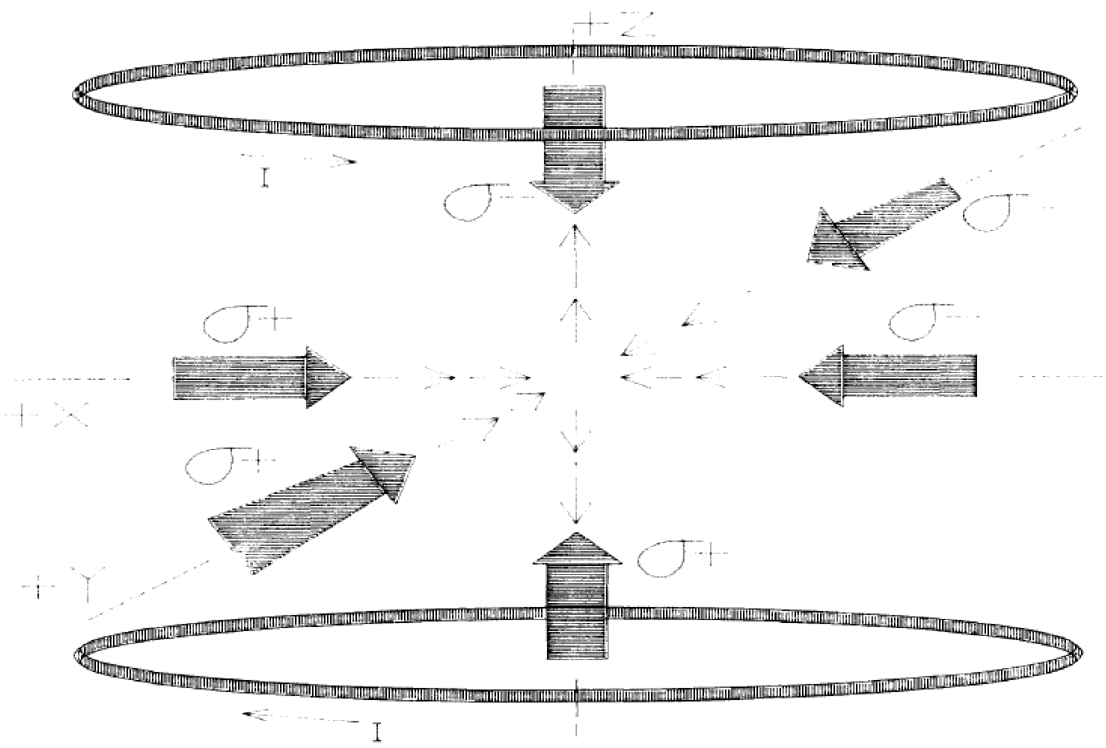
$$\Delta\left(\mathbf{K}'\right) = \frac{E_2 - E_1 + \frac{\hbar^2 k^2}{2M} + \frac{\hbar^2 \mathbf{K}'\cdot\mathbf{k}}{M}}{\hbar} - \omega$$



$$T_D = \frac{h\gamma}{2K_B}$$

Application 3: MOT





Selection rules:

$\Delta m_l = 0, \pm 1$

$\Delta l = \pm 1$

$\Delta j = 0, \pm 1$ ($j = 0 \rightarrow j' = 0$ Forbidden)

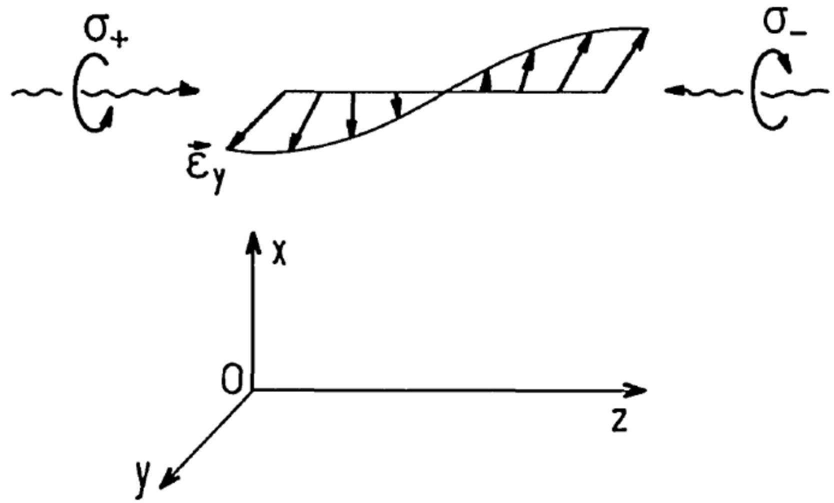
$\Delta m_j = 0, \pm 1$

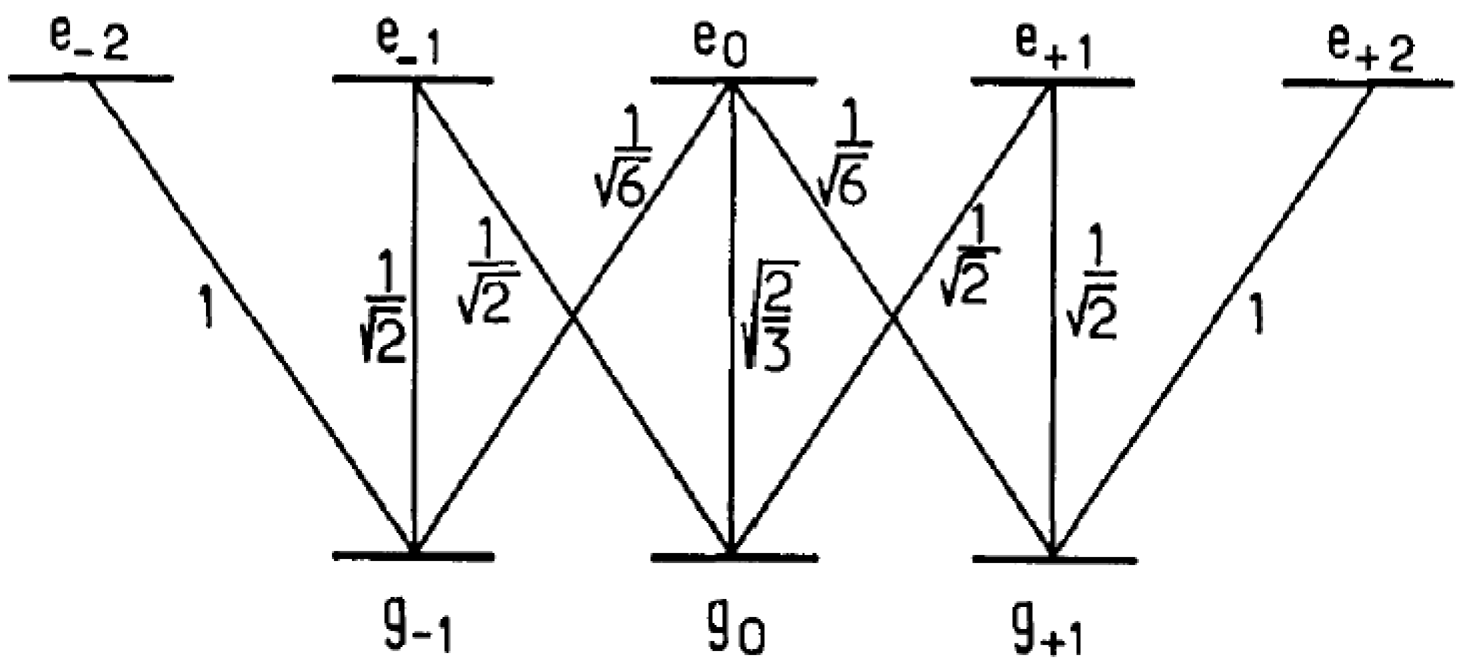
$\Delta s = 0$

$\Delta F = 0, \pm 1$ ($F = 0 \rightarrow F' = 0$ Forbidden)

$\Delta m_F = 0, \pm 1$

Sub-Doppler cooling





Optical dipole force (far off resonance)

$$i\hbar\dot{\mathbf{c}} = \hbar \begin{pmatrix} 0 & -\frac{1}{2}\chi \\ -\frac{1}{2}\chi & \Delta \end{pmatrix} \mathbf{c}$$

$$\lambda_{\pm} = \hbar\frac{1}{2}\left(\Delta \pm \sqrt{\Delta^2 + \chi^2}\right) \simeq \hbar\frac{1}{2}\left(\Delta \pm \left(\Delta + \frac{1}{2}\frac{\chi^2}{\Delta}\right)\right)$$

Summery Lecture 1

- Few-level atoms in light can be treated using rotating wave approximation
- Two-level atoms exposed to near-resonant light undergo Rabi-flopping cycles of absorption an stimulated emission
- Atoms in an excited electronic state can spontaneously emit light and go to a lower energy state
- Cycles of absorption and spontaneous emission result in a directional radiation pressure force
- Radiation pressure can be used to cool and trap atoms
- Far off resonant light interacts with the atoms via the optical dipole force