Atomic response to EM waves

Connections: susceptibility, dielectric constant, refractive index

Complex refractive index, damped propagation

Microscopic to macroscopic material response

Radiation from accelerating charge

Classical oscillator model for dispersion

QM estimation of dipole response

Maxwell's Equations to wave eqn

- The induced polarization, **P**, contains the effect of the medium:

$$\vec{\nabla}\cdot\mathbf{E}=0 \qquad \vec{\nabla}\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t}$$

$$\vec{\nabla}\cdot\mathbf{B}=0 \qquad \vec{\nabla}\times\mathbf{B}=\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}+\mu_0\frac{\partial\mathbf{P}}{\partial t}$$

Take the curl:

$$\vec{\nabla}\times\left(\vec{\nabla}\times\mathbf{E}\right)=-\frac{\partial}{\partial t}\vec{\nabla}\times\mathbf{B}=-\frac{\partial}{\partial t}\left(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}+\mu_0\frac{\partial\mathbf{P}}{\partial t}\right)$$

Use the vector ID:

$$\mathbf{A}\times\left(\mathbf{B}\times\mathbf{C}\right)=\mathbf{B}\left(\mathbf{A}\cdot\mathbf{C}\right)-\mathbf{C}\left(\mathbf{A}\cdot\mathbf{B}\right)$$

$$\vec{\nabla}\times\left(\vec{\nabla}\times\mathbf{E}\right)=\vec{\nabla}\left(\vec{\nabla}\cdot\mathbf{E}\right)-\left(\vec{\nabla}\cdot\vec{\nabla}\right)\mathbf{E}=-\vec{\nabla}^2\mathbf{E}$$

$$\boxed{\vec{\nabla}^2\mathbf{E}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}}$$

"Inhomogeneous Wave Equation"

Maxwell's Equations in a Medium

- The induced polarization, **P**, contains the effect of the medium:

$$\vec{\nabla}^2\mathbf{E} - \frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2} = \mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}$$

- Sinusoidal waves of all frequencies are solutions to the wave equation
- The polarization (**P**) can be thought of as the driving term for the solution to this equation, so the polarization determines which frequencies will occur.
- For linear response, **P** will oscillate at the same frequency as the input.

$$\mathbf{P}(t) = \varepsilon_0\chi\,\mathbf{E}(t)$$

- Then once we know the susceptibility χ, we can calculate the dielectric constant and the refractive index:

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0(1+\chi)\mathbf{E} = \varepsilon_0\varepsilon_r\,\mathbf{E} = \varepsilon_0 n^2\mathbf{E}$$

Complex refractive index

- We will see that when the incident light is near resonance, the atomic response becomes a complex function.
  - What is the meaning of a complex refractive index?
  - Let's separate out the real and imaginary parts:

$$n = n_R + i\,n_I$$

  - then a plane wave propagating in the z direction is:

$$E(z,t) = E_0 e^{i(kz-\omega t)} = E_0 e^{i\left(\frac{\omega}{c}(n_R+in_I)z-\omega t\right)} = E_0 e^{i\left(\frac{\omega}{c}n_R z-\omega t\right)} e^{i\left(\frac{\omega}{c}(in_I)z\right)}$$

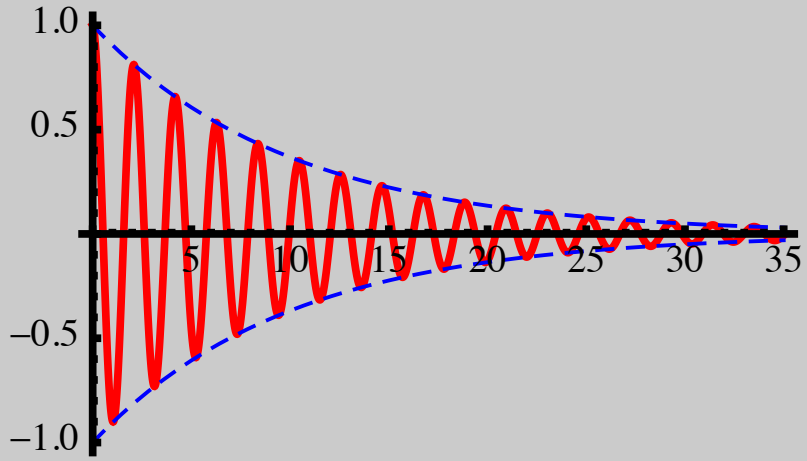
$$E(z,t) = E_0 e^{i(k_R z-\omega t)} e^{-\frac{\omega}{c}n_I z}$$

For $n_I > 0$, absorption coefficient is $\alpha = \frac{\omega n_I}{2c}$

For $n_I < 0$, gain coefficient is $g = \frac{\omega |n_I|}{2c}$

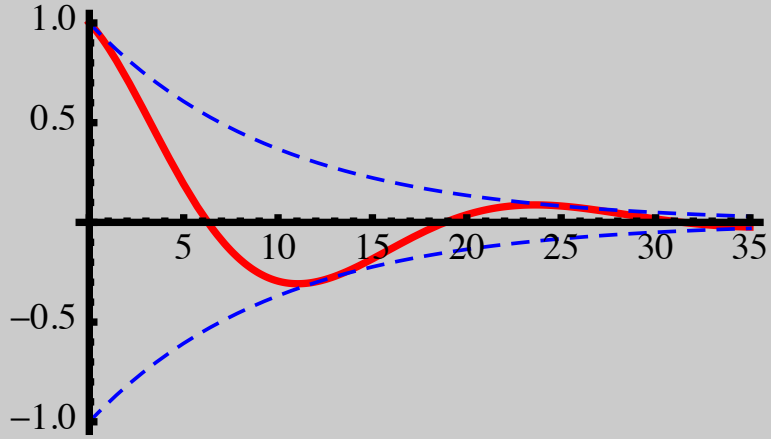
Damped wave propagation

- If absorption length is much larger than the wavelength:



Typical for absorbing dielectric

- Here absorption length is comparable to the wavelength:



Typical for metal:
damping length = “skin depth”

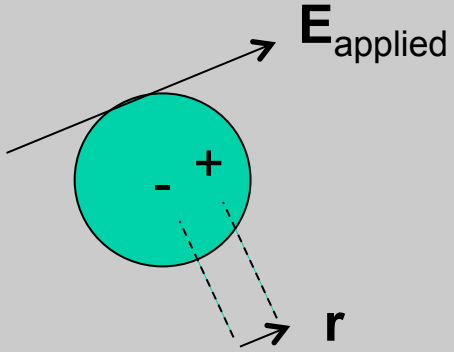
Connecting the macroscopic to the microscopic response

So determining the gain or loss coefficient depends on calculating the macroscopic induced polarization **P** or equivalently the susceptibility χ.

$$\mathbf{P}\left(\mathbf{E}\right) = \varepsilon_0 \chi \mathbf{E} = N_a \mathbf{p}$$

Note that the macrosopic polarization is really a density of dipole moments.

Recall: $\mathbf{p} = q\,\mathbf{r}$



So if the electric field is linearly polarized in the x-direction, then

$$\mathbf{P}\left(t\right) = N_a \mathbf{p}\left(t\right) = -N_a e x\left(t\right)$$

Here we treat x(t) as the position of the *electron*.

Radiation from accelerating charge

- Larmor formula for radiated power: $P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2 a^2}{c^3}$
- An accelerating charge "shakes" the field lines, creating radiating EM waves.

See link to physlet animation of radiation field lines from an oscillating charge:
http://webphysics.davidson.edu/physlet_resources/dav_optics/Examples/oscillate_charge.html

  - If the charge is moving as $x(t) = x_0 \cos\omega t$
  - The dipole is $p(t) = -e\,x_0 \cos\omega t$
  - Then the radiated power is

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2 \ddot{x}^2(t)}{c^3} = -\frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2}{c^3}\omega^4 x_0^2 \cos^2\omega t = -\frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\omega^4}{c^3}p^2(t)$$

  - Power is proportional to E^2, so radiated field is proportional to p(t)

- Applied field induces oscillating dipoles, which re-radiate the field.

Spring model for dipole response

- Assume electron is bound with a spring-like force, with resonant frequency ω_0
- Radiation will effectively damp the motion
- Damped-driven SHO equation of motion

$$m_e\ddot{x}(t) = -eE(t) - m_e\omega_0^2 x(t) - 2m_e\gamma\dot{x}(t)$$

$$m_e\ddot{x}(t) + 2m_e\gamma\dot{x}(t) + m_e\omega_0^2 x(t) = -eE_0 e^{-i\omega t}$$

let $x(t) = x_0 e^{-i\omega t}$ x has to oscillate at driving frequency, not resonance frequency

$$-m_e\omega^2 x_0 - 2i\omega m_e\gamma x_0 + m_e\omega_0^2 x_0 = -eE_0$$ $e^{-i\omega t}$ drops out

$$x_0(\omega) = -\frac{e}{m_e}E_0\frac{1}{\omega_0^2 - 2i\omega\gamma - \omega^2} \equiv -\frac{eE_0}{m_e}\frac{1}{D(\omega)}$$

x is fcn of t, but the amplitude x_0 depends on ω

Spring model for dispersion

- Now we can go from the microscopic response x(t) to the macroscopic χ and n

$$P(t) = -N_a e x(t) = \varepsilon_0 \chi^{(1)} E(t) \rightarrow \chi^{(1)} = -\frac{N_a e x(t)}{\varepsilon_0 E(t)}$$

  - x(t) and E(t) share time dependence, so

$$\chi^{(1)}(\omega) = -\frac{N_a e}{\varepsilon_0}\left(-\frac{e}{m_e}E_0 \frac{e^{-i\omega t}}{D(\omega)}\right)\frac{1}{E_0 e^{-i\omega t}} = \frac{N_a e^2}{\varepsilon_0 m_e}\frac{1}{D(\omega)}$$

$$n^2(\omega) = 1 + \chi^{(1)}(\omega) = 1 + \frac{N_a e^2}{\varepsilon_0 m_e}\frac{1}{D(\omega)} = 1 + \frac{N_a e^2}{\varepsilon_0 m_e}\frac{1}{\omega_0^2 - 2i\omega\gamma - \omega^2}$$

This gives us the complex refractive index.

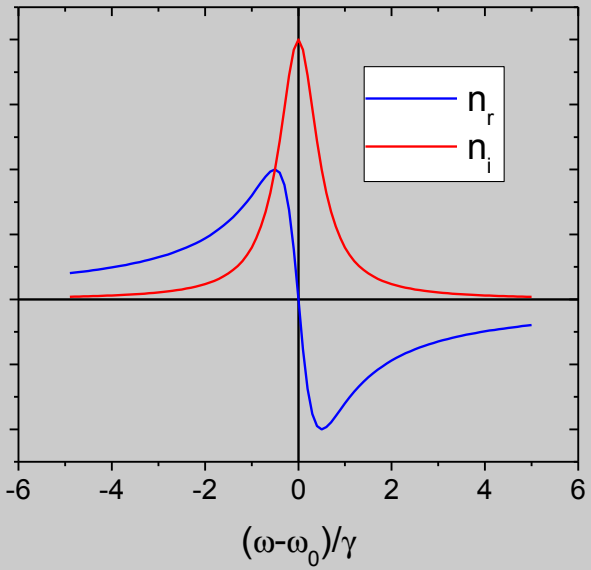
Complex refractive index

- Solve for real and imaginary parts

$$n \to n_r + in_i = 1 + \frac{N_a e^2 (\omega_0{}^2 - \omega^2)}{2\varepsilon_0 m_e [(\omega_0{}^2 - \omega^2)^2 + \omega^2 \gamma^2]} + i \frac{N_a e^2 \gamma \omega}{2\varepsilon_0 m_e [(\omega_0{}^2 - \omega^2)^2 + \omega^2 \gamma^2]}$$

- Near the resonance

$$n_r + in_i = 1 + \frac{N_a e^2 (\omega_0 - \omega)}{4\varepsilon_0 m_e \omega_0 [(\omega_0 - \omega)^2 + (\gamma/2)^2]} + i \frac{N_a e^2 \gamma}{8\varepsilon_0 m_e \omega_0 [(\omega_0 - \omega)^2 + (\gamma/2)^2]}$$



Normalized plot of n-1 and k versus $\omega - \omega_0$

For more than one resonance,

$$n^2 = 1 + \frac{N_a e^2}{\varepsilon_0 m_e} \sum_j \frac{f_j}{(\omega_j^2 - \omega^2 - i\omega\gamma_j)}$$

$\sum_j f_j = Z$ f = oscillator strength

QM atomic transitions

We'll take an approach to understanding transitions from the quantum perspective

- An isolated atom in a pure energy eigenstate is in a *stationary* state: $\psi_n(\mathbf{r},t) = u_n(\mathbf{r})e^{-E_n t/\hbar}$
  - There is time dependence to the phase, but the amplitude remains constant. So, no transitions.
- An applied EM field of the right frequency can induce a mixture of two states:

  $\psi_1(\mathbf{r},t) = u_1(\mathbf{r})e^{-E_1 t/\hbar}$ $\psi_2(\mathbf{r},t) = u_2(\mathbf{r})e^{-E_2 t/\hbar}$

  - Superposition: $\psi(\mathbf{r},t) = a_1(t)\psi_1(\mathbf{r},t) + a_2(t)\psi_2(\mathbf{r},t)$
  - w/ normalization: $|a_1(t)|^2 + |a_2(t)|^2 = 1$

QM charge distribution

- The electron is not localized in QM.
- The *charge* density can be calculated from ψ:

$$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2$$

- For a stationary state:

$$\rho(\mathbf{r},t) = -e\left|\psi_n(\mathbf{r},t)\right|^2 = -e\left|u_n(\mathbf{r})e^{-E_n t/\hbar}\right|^2 = -e\left|u_n(\mathbf{r})\right|^2$$

  - No time dependence, charge is not moving!

- For a superposition state:

$$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2 = -e\left|a_1\psi_1 + a_2\psi_2\right|^2$$

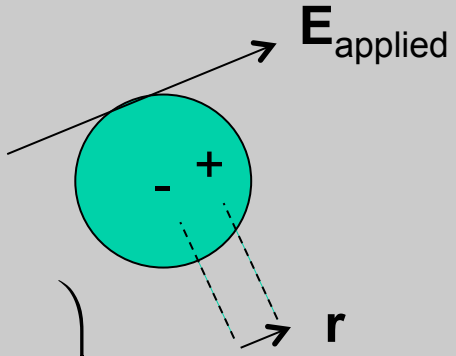
$$= -e\left(\left|a_1\psi_1\right|^2 + \left|a_2\psi_2\right|^2 + a_1 a_2{}^{*}\psi_1\psi_2{}^{*} + a_1{}^{*}a_2\psi_1{}^{*}\psi_2\right)$$

  - Cross terms will lead to time dependence in the charge.

QM dipole moment calculation

- The nucleus is localized, but the electron charge is distributed.
- The effective position is calculated like the center of mass, so dipole moment is:

$$\mu(t) = -e\int \mathbf{r}\,|\psi(\mathbf{r},t)|^2\,dV \qquad \mathbf{p} = q\,\mathbf{r}$$



$$\mu(t) = -e\left(\begin{array}{l}\int \mathbf{r}\,|a_1\psi_1|^2\,dV + \int \mathbf{r}\,|a_2\psi_2|^2\,dV \\ +\int a_1 a_2^{*}\,\mathbf{r}\,\psi_1\psi_2^{*}\,dV + \int a_1^{*} a_2\,\mathbf{r}\,\psi_1^{*}\psi_2\,dV\end{array}\right)$$

  - Terms in red go to zero: parity.

Time dependent dipole moment

- The cross terms (which are like interference terms in optics), lead to time dependent oscillation:

$$\mu_{osc}(t) = -e\left(a_1 a_2^{\,*} \int \mathbf{r}\,\psi_1 \psi_2^{\,*}\, dV + a_1^{\,*} a_2 \int \mathbf{r}\,\psi_1^{\,*} \psi_2\, dV\right)$$

$$= -e\left(a_1 a_2^{\,*} \int \mathbf{r}\, u_1(\mathbf{r}) u_2^{\,*}(\mathbf{r}) e^{+i(E_2-E_1)t/\hbar}\, dV + a_1^{\,*} a_2 \int u_1(\mathbf{r}) u_2^{\,*}(\mathbf{r}) e^{-i(E_2-E_1)t/\hbar}\, dV\right)$$

  - Oscillation frequency: $\omega_{21} = (E_2 - E_1)/\hbar$

$$\mu_{osc}(t) = -e\,\mathrm{Re}\left[2 a_1 a_2^{\,*} \mu_{21} e^{i\omega_{21} t}\right]$$

$$\mu_{21} = \int u_1(\mathbf{r})(-e\mathbf{r}) u_2^{\,*}(\mathbf{r})\, dV$$ Dipole "matrix element"

- μ_{21} is the part that depends on the atomic structure, independent of the populations.
- This is a vector, but the direction of r corresponds to the E-field direction, relative to the atom or molecule.

QM dipole radiation: lifetime

- Estimate the radiated power from this oscillating dipole.

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\ddot{x}^2(t)}{c^3} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{\ddot{\mu}^2(t)}{c^3}$$

Note: μ = p

$$\mu_{osc}(t) = -e\,\mathrm{Re}\left[2a_1a_2^*\mu_{21}e^{i\omega_{21}t}\right]$$

$$\left(z+z^*\right)^2 = |z|^2$$

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{4e^2\omega_{21}^4\mu_{21}^2}{c^3}|a_1|^2|a_2|^2\cos\left[\omega_{21}t\right]$$

Time average over fast oscillation:

$$\bar{P}_{rad} = P'_{rad}|a_1|^2|a_2|^2, \quad P'_{rad} = \frac{e^2\omega_{21}^4\mu_{21}^2}{3\pi\varepsilon_0c^3} \equiv \frac{\hbar\omega_{21}}{\tau_{sp}}$$

$$\tau_{sp} = \frac{1}{A_{21}} = \frac{3\pi\hbar\varepsilon_0c^3}{e^2\omega_{21}^3\mu_{21}^2}$$

Estimate of spontaneous lifetime

Spontaneous decay

- If we assume that the excitation probability of the upper level is small, then $|a_1|^2 = 1 - |a_2|^2 \approx 1$
- We can then deduce the change in upper level population:

$$\frac{dE}{dt} = -\bar{P}_{rad} = \hbar\omega_{21}\frac{d}{dt}|a_2(t)|^2$$

$$\frac{d}{dt}|a_2(t)|^2 \approx -\frac{1}{\tau_{sp}}|a_2(t)|^2 \rightarrow |a_2(t)|^2 \approx |a_2(0)|^2 \exp\left[-t/\tau_{sp}\right]$$

- This connects the spontaneous emission rate to a quantum calculation of the dipole moment.

Selection rules

- In Dirac notation, the dipole matrix element is:

$$\mu_{21} = \langle 2 | -e\mathbf{r} | 1 \rangle = \int u_1(\mathbf{r})(-e\mathbf{r})u_2^*(\mathbf{r})dV$$

- Working with the symmetries of wavefunctions leads to selection rules about which transitions can take place.
  - Parity: r is odd, so u1 must be opposite parity of u2
  - Angular momentum: $\Delta l = \pm 1$. Photon carries 1 unit of ang. mom.

- Exceptions:
  - Transition might take place under other moments:
    - Magnetic dipole, electric quadrupole, etc.
    - Leads to longer lifetimes.
  - States might not be “pure”, mixture of eigenstates
    - External or internal perturbations

HeNe laser transitions

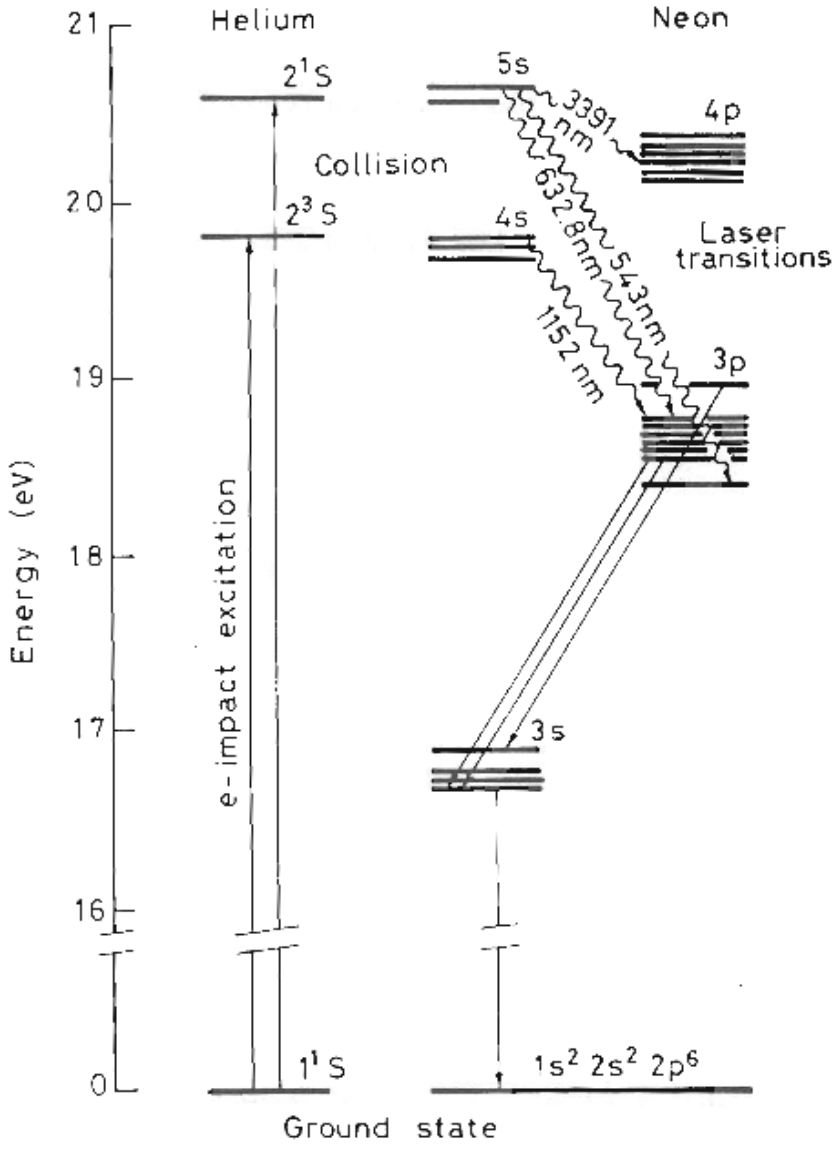


FIG. 10.1. Relevant energy levels of the He-Ne laser.

Transition	Wavelength [nm]	A_{ik} [10^8 s^{-1}]	Gain [%/m]	
3s2→2p1	730.5 ③	0,00255	1,2	
3s2→2p2	640.1 ①	0,0139	4,3	
3s2→2p3	635.2 ①	0,00345	1,0	
3s2→2p4	632.8 ①	0,0339	10,0	→ main red line
3s2→2p5	629.4 ①	0,00639	1,9	
3s2→2p6	611.8 ①	0,00226	1,7	→ orange line
3s2→2p7	604.6	0,00200	0,6	
3s2→2p8	593.9	0,00255	0,5	→ yellow line
3s2→2p9	★			
3s2→2p10	543.3	0,00283	0,52	
2s2→2p1	1523.1 ②			
2s2→2p2	1177.0 ③			
2s2→2p3	1160.5			
2s2→2p4	1152.6 ③			
2s2→2p5	1141.2 ③			
2s2→2p6	1084.7 ③			
2s2→2p7	1062.3			
2s2→2p8	1029.8			
2s2→2p9	★			
2s2→2p10	886.5			
2s3→2p2	1198.8 ③			
2s3→2p5	1161.7 ③			
2s3→2p7	1080.1 ③			

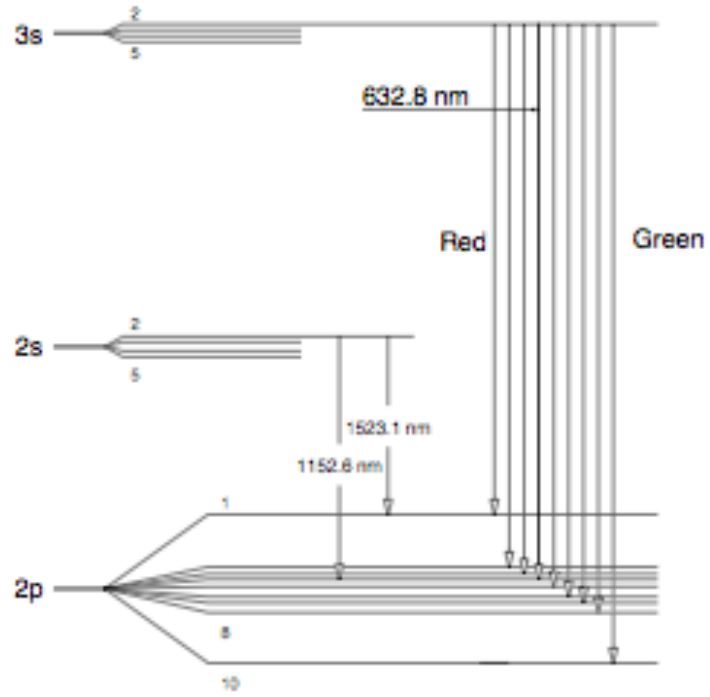


Fig. 3: The most important laser transitions in the neon system