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 u_1 must be opposite parity of u_2
  - Angular momentum: Δl = ±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

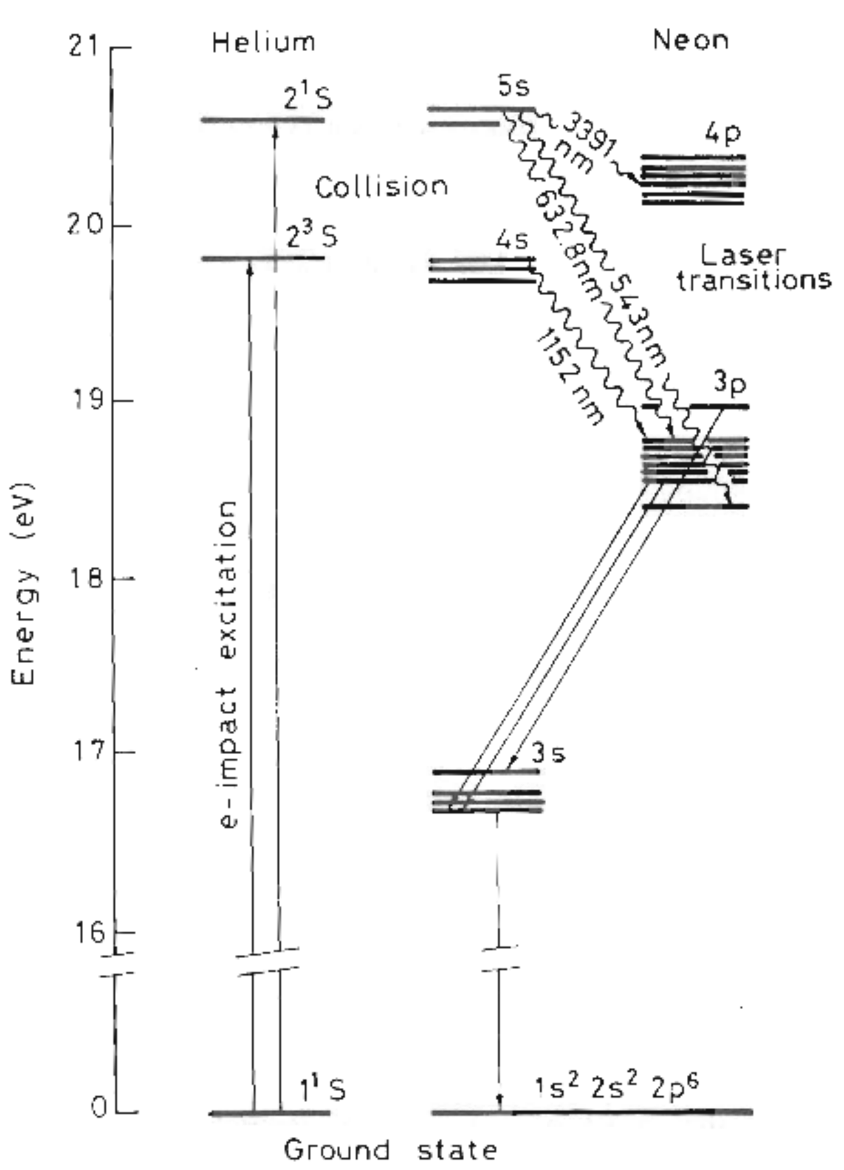

FIG. 10.1. Relevant energy levels of the He-Ne laser.

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
3s2→2p5	629.4 ①	0,00639	1,9
3s2→2p6	611.8 ①	0,00226	1,7
3s2→2p7	604.6	0,00200	0,6
3s2→2p8	593.9	0,00255	0,5
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	1198.8③		
2s3→2p5	1161.7③		
2s3→2p7	1080.1③		

→ main red line (3s2→2p4)

→ orange line (3s2→2p6)

→ yellow line (3s2→2p8)

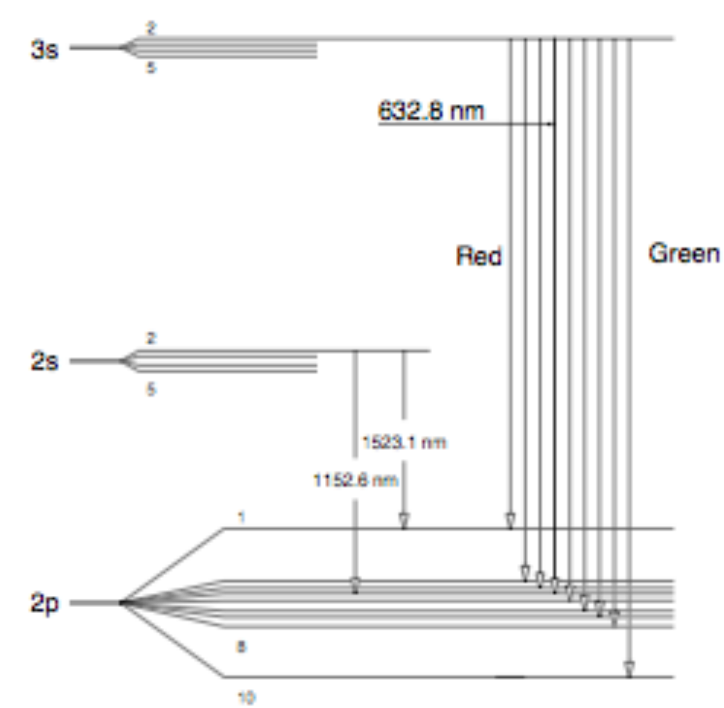

Fig. 3: The most important laser transitions in the neon system

QM approach

- Next level up in accuracy in QM is to approximately solve the Schrodinger equation in the presence of the incident field
  - QM representation of the electron wavefunction $\psi(\mathbf{r},t)$
  - Classical representation of the EM field as a perturbation

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \hat{H} = \hat{H}_0 + \hat{H}'$$

- Without external field: With external field (E-dipole):

$$\hat{H}_0\psi = i\hbar\frac{\partial\psi}{\partial t} \rightarrow \hat{H}_0\psi_n = E_n\psi_n \qquad \hat{H}' = \mu\cdot\mathbf{E} = -e\mathbf{r}\cdot\mathbf{E_0}\sin\omega t$$

- Assume wavefunction *with* field can be written in terms of a linear combination of wavefunctions *without* field

$$\psi(r,t) = \sum_n a_n(t)\psi_n(r,t) \qquad \psi_n(\mathbf{r},t) = u_n(\mathbf{r})e^{-E_n t/\hbar}$$

Time-dependent perturbation theory

- Easiest to concentrate on 2 levels
- Assume close to resonance:

$$\omega \approx \left(E_2 - E_1\right)/\hbar = \omega_{21}$$

- Assume weak probability of excitation:

$$a_1\left(t\right) \approx 1, \quad a_2\left(t\right) \ll 1$$

- Put form of solution into time-dependent SE (with field)
- Transition rate will be

$$W_{12} = \frac{d}{dt}\left|a_2\left(t\right)\right|^2$$

- Result: "Fermi's Golden Rule"

$$W_{12}\left(\nu\right) = \frac{\pi^2}{3h^2}\left|\mu_{21}\right|^2 E_0{}^2 \delta\left(\nu - \nu_0\right)$$

$\delta\left(\nu - \nu_0\right)$ Dirac delta function

$$\int f\left(\nu\right)\delta\left(\nu - \nu_0\right)d\nu = f\left(\nu_0\right)$$

Fermi's golden rule: broadband source

- From previous slide, the transition rate is:

$$W_{12}(\nu) = \frac{\pi^2}{3h^2} |\mu_{21}|^2 E_0{}^2 \delta(\nu - \nu_0)$$

- Express field in terms of (total) energy density:

$$\rho = \tfrac{1}{2} n^2 \varepsilon_0 E_0^2 \qquad \rightarrow W_{12}(\nu) = \frac{2\pi^2}{3n^2 \varepsilon_0 h^2} |\mu_{21}|^2 \rho \delta(\nu - \nu_0)$$

- We need to account for frequency dependence of source.
  - When EM source varies in frequency, energy density btw v' and v'+dv' is $d\rho = \rho_{\nu'} d\nu'$
  - Total energy density is $\rho = \int \rho_{\nu'} \, d\nu'$
  - So the contribution to the rate at v' is

$$dW_{12}(\nu') = \frac{2\pi^2}{3n^2 \varepsilon_0 h^2} |\mu_{21}|^2 \delta(\nu' - \nu_0) \rho_{\nu'} d\nu'$$

Fermi's golden rule: blackbody source

- Using $\rho = \int \rho_{\nu'}\, d\nu'$
- We convert the total rate into an integral over all frequencies:

$$W_{12}(\nu) = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho\,\delta(\nu-\nu_0) \rightarrow \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_{\nu'}\,\delta(\nu'-\nu_0)\,d\nu'$$

- Using the properties of the delta function,

$$W_{12} = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_{\nu_0}$$

- Example: if the source is a blackbody,

$$\rho(\nu)d\nu = \rho_\nu d\nu = 8\pi \frac{\nu^2}{c^3}\frac{h\nu}{e^{h\nu/k_BT}-1}d\nu$$

- the total rate is:

$$W_{12} = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \frac{8\pi}{c^3}\frac{h\nu_0^3}{e^{h\nu_0/k_BT}-1}$$

Fermi's golden rule: general lineshape

- The delta function represents an infinitely narrow linewidth. For a finite linewidth:

For other lineshape:

$$\rightarrow W_{12}(\nu) = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho\,\delta(\nu-\nu_0) \rightarrow \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho\, g(\nu-\nu_0)$$

- For a general input spectral profile:

$$dW_{12}(\nu') = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_{\nu'}\, g(\nu'-\nu_0)\,d\nu'$$

- Integrate to get total rate:

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_{\nu'}\, g(\nu'-\nu_0)\,d\nu'$$

- For a very narrow linewidth laser, the spectral energy density can be approximated by a delta function.

Approaches to more practical calculations

- For laser input the calculation is involved

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2} |\mu_{21}|^2 \rho_{\nu L} \delta(\nu' - \nu_L) g(\nu' - \nu_0) d\nu'$$

$$= \frac{2\pi^2}{3n^2\varepsilon_0 h^2} |\mu_{21}|^2 g(\nu_L - \nu_0) \rho_{\nu L}$$

  – Convert energy density to intensity
  – Put dipole moment in terms of quantities that are measured

- Approaches:
  – Cross-sections for absorption, stimulated emission
  – Einstein A and B coefficients: measure lifetime