Line broadening

QM estimation of dipole radiation and lifetime

Summary of time-dependent perturbation theory approach

Fourier transforms and natural broadening

Reading: Svelto 2.4-2.5

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:

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

  – Superposition:

$$\psi(\mathbf{r},t) = a_1(t)\psi_1(\mathbf{r},t) + a_2(t)\psi_2(\mathbf{r},t)$$

  – w/ normalization: $\left|a_1(t)\right|^2 + \left|a_2(t)\right|^2 = 1$

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:

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

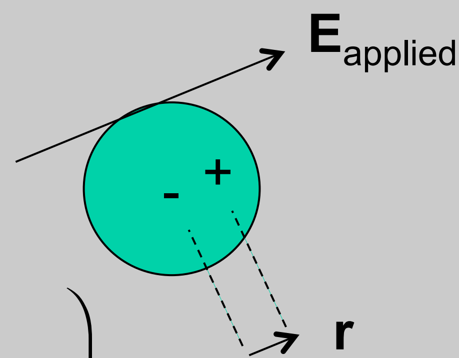
$$= -e\left(\left|a_1\psi_1\right|^2 + \left|a_2\psi_2\right|^2 + a_1 a_2^* \psi_1 \psi_2^* + a_1^* a_2 \psi_1^* \psi_2\right)$$

  – 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:

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



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

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

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

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

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

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

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

Time average over fast oscillation:

$$\bar{P}_{rad} = P'_{rad}|a_1|^2|a_2|^2, \quad P'_{rad} = \frac{e^2\omega_{21}^{\ 4}\mu_{21}^{\ 2}}{3\pi\varepsilon_0 c^3} \equiv \frac{\hbar\omega_{21}}{\tau_{sp}}$$

$$\tau_{sp} = \frac{1}{A_{21}} = \frac{3\pi\hbar\varepsilon_0 c^3}{e^2\omega_{21}^{\ 3}\mu_{21}^{\ 2}}$$

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 u_1 must be opposite parity of u_2
  - 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

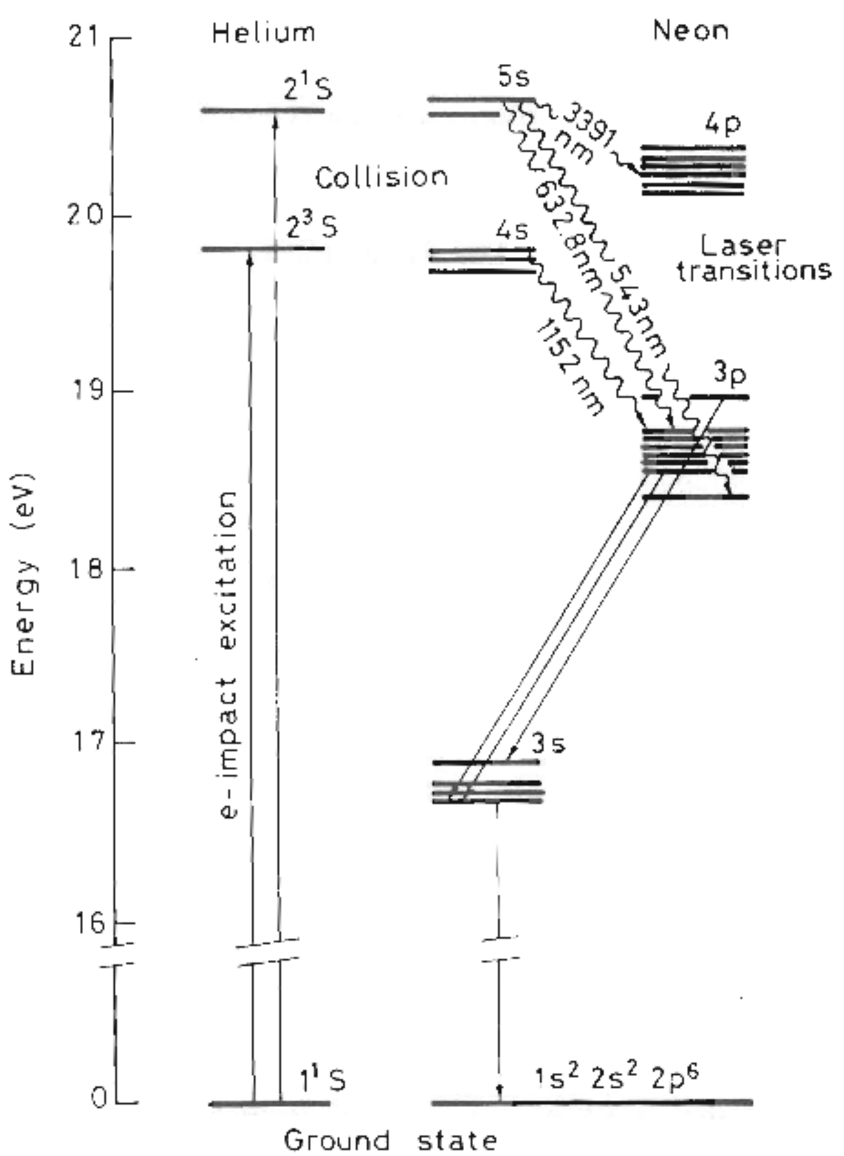


FIG. 10.1. Relevant energy levels of the He-Ne laser.

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
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	1198.8 ③		
2s3→2p5	1161.7 ③		
2s3→2p7	1080.1 ③		

→ main red line (3s2→2p4)

→ orange line (3s2→2p6)

→ yellow line (3s2→2p8)

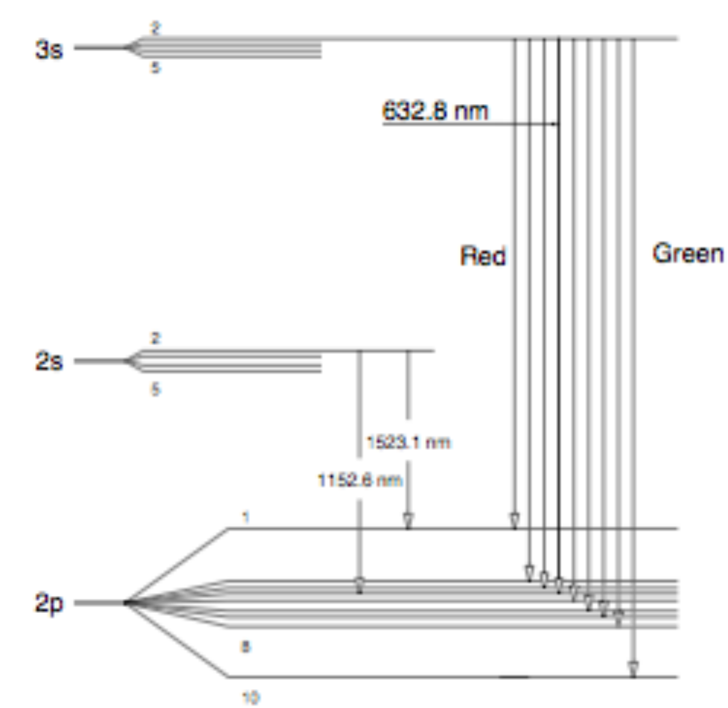


Fig. 3: The most important laser transitions in the neon system

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

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

$$\rho = \tfrac{1}{2} n^2 \varepsilon_0 E_0^2$$

For other lineshape:

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

- When EM source varies in frequency, energy density btw v' and v'+dv' is $d\rho = \rho_{\nu'} d\nu'$
- So the contribution to the rate at v' is

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

- Total rate is:

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

Working with spectral lineshapes

- For atomic system, replace Dirac delta with transition lineshape

$$\int g(\nu-\nu_0)\,d\nu = 1$$

- Lorentzian lineshape (radiative, collisional broadening)

$$\delta(\nu-\nu_0) \rightarrow g_L(\nu-\nu_0) = \frac{2}{\pi\,\Delta\nu_0}\frac{1}{1+\left(\frac{2(\nu-\nu_0)}{\Delta\nu_0}\right)^2}$$

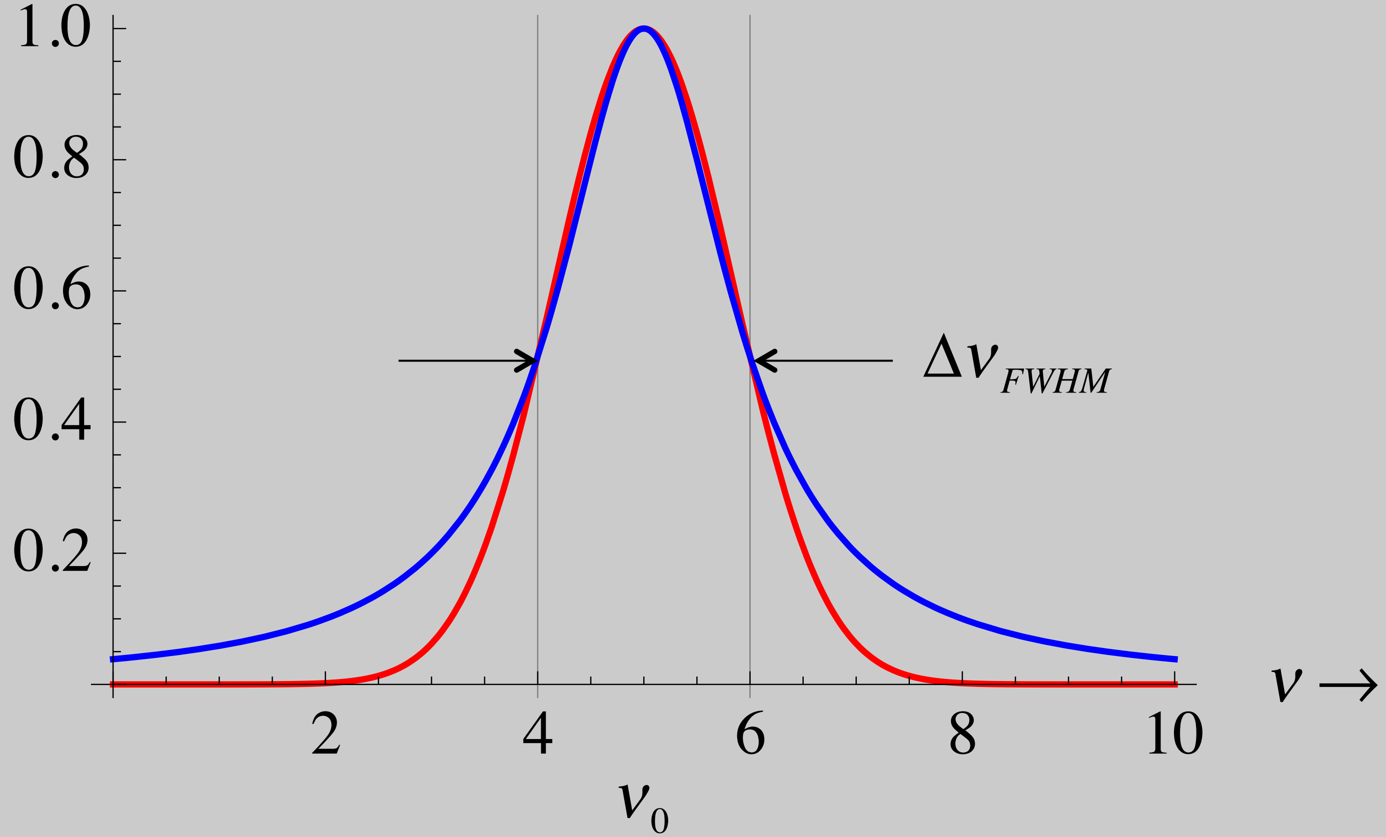
$\Delta\nu_0$ FWHM

- Doppler broadened (Gaussian) lineshape

$$\delta(\nu-\nu_0) \rightarrow g_G{}^*(\nu-\nu_0) = \frac{2}{\Delta\nu_0{}^*}\sqrt{\frac{\ln 2}{\pi}}\exp\left\{-4\ln 2\frac{(\nu-\nu_0)^2}{\Delta\nu_0{}^{*2}}\right\}$$

Lorentzian vs Gaussian lineshapes

- Lorentzian is much broader in spectral wings



Natural broadening

- Radiative broadening results directly from the spontaneous emission lifetime of the state
- Fourier transforms
  - Forward: FT $$F(\omega)=\int_{-\infty}^{\infty} f(t)e^{i\omega t}\,dt$$
  - Inverse: FT^{-1} $$f(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{-i\omega t}\,d\omega$$
- Suppose exponential, oscillating decay in time domain

$$f(t)=\begin{matrix} e^{-\gamma t}e^{-i\omega_0 t} & \text{for } t\geq 0 \\ 0 & \text{for } t<0 \end{matrix}$$

$$F(\omega)=\int_0^{\infty} e^{-\gamma t-i\omega_0 t}e^{i\omega t}\,dt=\left.\frac{e^{\left(-\gamma+i(\omega-\omega_0)\right)t}}{-\gamma+i(\omega-\omega_0)}\right|_0^{\infty}=\frac{1}{\gamma-i(\omega-\omega_0)}$$

Complex Lorentzian

Lorentzian lineshape

- Complex Lorentzian separated into Re and Im

$$\frac{1}{\gamma - i(\omega-\omega_0)} = \frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} + i\frac{(\omega-\omega_0)}{(\omega-\omega_0)^2+\gamma^2}$$

  – Real part corresponds to absorption effects

- Normalize

$$c\int \frac{\gamma}{(\omega-\omega_0)^2+\gamma^2}\,d\omega = c\gamma\frac{\pi}{\gamma} = 1 \quad \to g_L(\omega-\omega_0) = \frac{\gamma/\pi}{(\omega-\omega_0)^2+\gamma^2}$$

- Convert ω to v

$$c\int \frac{\gamma}{4\pi^2(\nu-\nu_0)^2+\gamma^2}\,d\nu = c\gamma\frac{1}{2\gamma} = 1$$

$$\to g_L(\nu-\nu_0) = \frac{2}{\gamma}\left[1+\left(\frac{2(\nu-\nu_0)}{\gamma/\pi}\right)^2\right]^{-1} = \frac{2}{\pi\,\Delta\nu_0}\left[1+\left(\frac{2(\nu-\nu_0)}{\Delta\nu_0}\right)^2\right]^{-1}$$

Collisional broadening

- Elastic collisions don't cause transition, but interrupt the phase
- Timescales:
  - Period of EM cycle much less than radiative lifetime $\dfrac{2\pi}{\omega_0} \ll \tau$
  - Avg time btw collisions < lifetime $\tau_c < \tau$
  - Duration of a collision << time btw coll, lifetime $\Delta\tau_c \ll \tau_c, \tau$
- Calculation:
  - FT over time 0 to τ_1 to get lineshape for a specific oscillation length
  - Average over probability of a given time between collisions:

$$P(\tau_1)\,d\tau_1 = \frac{1}{\tau_c} e^{-\tau_1/\tau_c}\,d\tau_1$$

Result:

Lorentzian shape with new width

$$\Delta\nu = \gamma / 2\pi + 1/\pi\,\tau_c$$

Doppler broadening

- From relative velocity of atom to input beam, Doppler shift:

$$\nu_0' = \frac{\nu_0}{1 - \mathrm{v}_z / c}$$

Beam propagating in *z* direction

  - Each atom in distribution is shifted according to its velocity
- Boltzmann distribution

$$P(\mathrm{v}_z) \sim \exp\left[-\tfrac{1}{2} M v_z^2 / k_B T\right]$$

- Average over distribution to get effective lineshape:

$$g^*(\nu - \nu_0) = \frac{1}{\nu_0}\left(\frac{Mc^2}{2\pi k_B T}\right)^{1/2} \exp\left\{\frac{Mc^2}{2k_B T}\frac{(\nu - \nu_0)^2}{\nu_0{}^2}\right\}$$

FWHM:

$$\Delta\nu_0{}^* = 2\nu_0\left[\frac{2k_B T \ln 2}{Mc^2}\right]^{1/2}$$

Doppler broadening in HeNe lasers

$$\Delta\nu_0^{\;*} = 2\nu_0\left[\frac{2k_B T\ln 2}{Mc^2}\right]^{1/2}$$

$$\lambda_0 = 632.8\text{nm}$$

$$\nu_0 = 4.74\times 10^{14}\,\text{s}^{-1}$$

$$M = 20.12\text{ amu}=3.34\times 10^{-26}\text{kg}$$ For Neon

$$k_B T = 1/40 eV = 4\times 10^{-21} J$$

$$\Delta\nu_0^{\;*} = 1.55 GHz$$

Inhomogeneous vs homogeneous broadening

- Homogeneous broadening: every atom is broadened by same shape
  - Radiative, collisional, phonon
  - All atoms participate in absorption or gain
- Inhomogeneous broadening:
  - Doppler broadening
  - Absorption or gain only by atoms in resonance
  - Leads to “spectral hole burning”