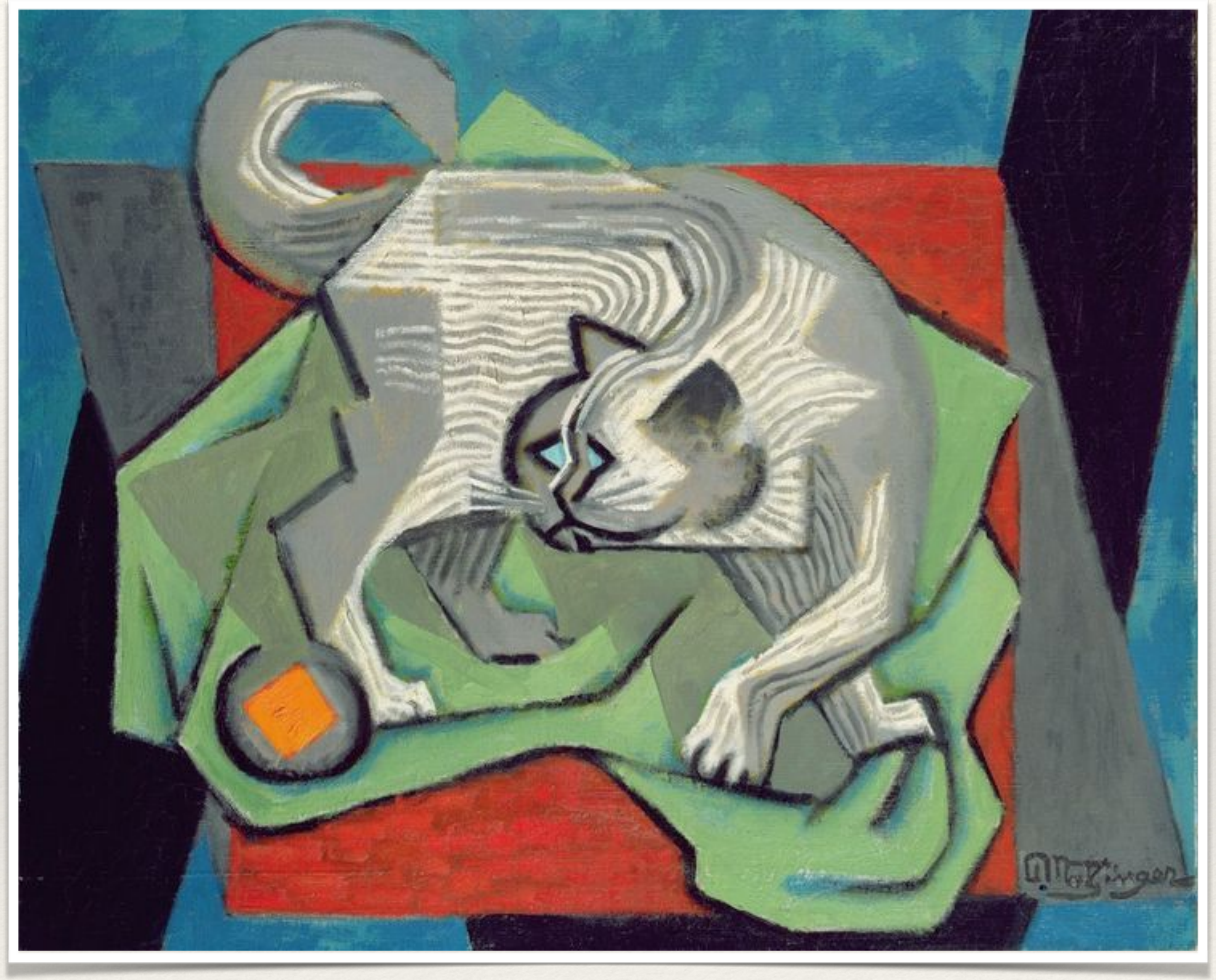
Prof. Steven Flammia

Quantum Mechanics

Lecture 17

Electric dipole approximation;
Einstein A and B coefficients;
Spontaneous Emission;
Selection Rules.



A quick recap

Fermi's golden rule tells us how to compute the rate of a transition from $i \to f$.
For a harmonic perturbation with drive frequency ω, we find:

$$H(t) = H_0 + 2V(\hat{\mathrm{r}})\,\cos(\omega t)$$

$$\omega_{fi} = (E_f - E_i)/\hbar$$

$$R_{i\to f} = \frac{2\pi}{\hbar^2}\,|\langle f\,|\,V(\hat{\mathbf{r}})\,|\,i\rangle\,|^2\,\delta(\omega_{fi} - \omega)$$

If we integrate this over a density of final states $g(E)$, then we find that

$$R_{i\to f} = \frac{2\pi}{\hbar}\,|\langle f\,|\,V(\hat{\mathbf{r}})\,|\,i\rangle\,|^2\,g(E_f)\Big|_{E_f \simeq E_i + \hbar\omega}$$

More complicated driving terms can be handled by expanding the drive as a Fourier series and following the same steps in the argument.

Electric dipole interaction

Consider coupling to an electric dipole, with perturbing term given by

We neglect the **k·x** term that is normally there and treat the field as spatially homogeneous. This is the **electric dipole approximation**.

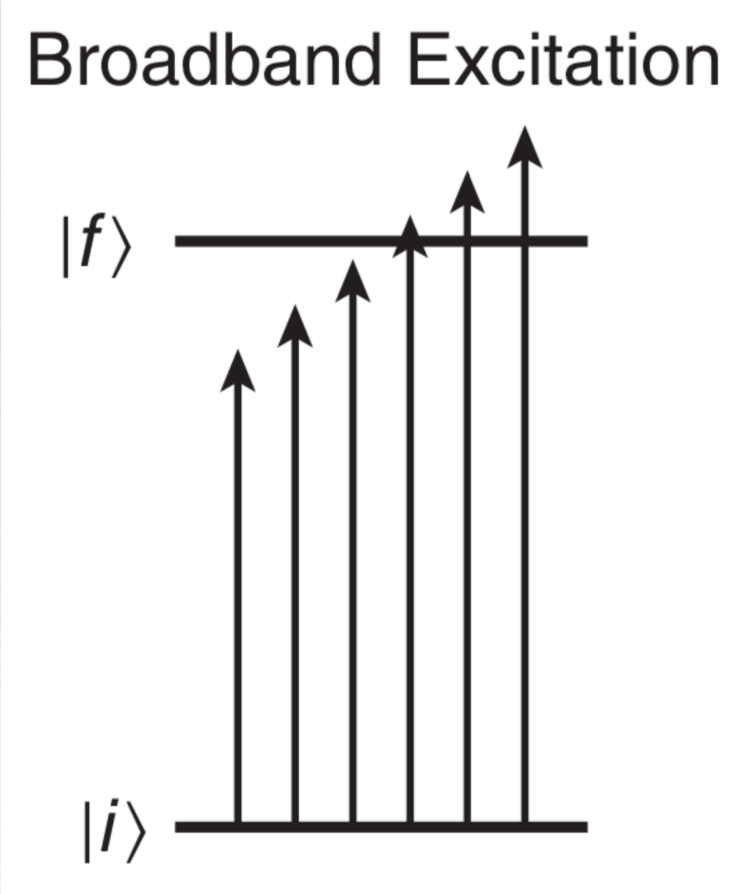
From Fermi's golden rule and the dipole moment, the transition rate is given by

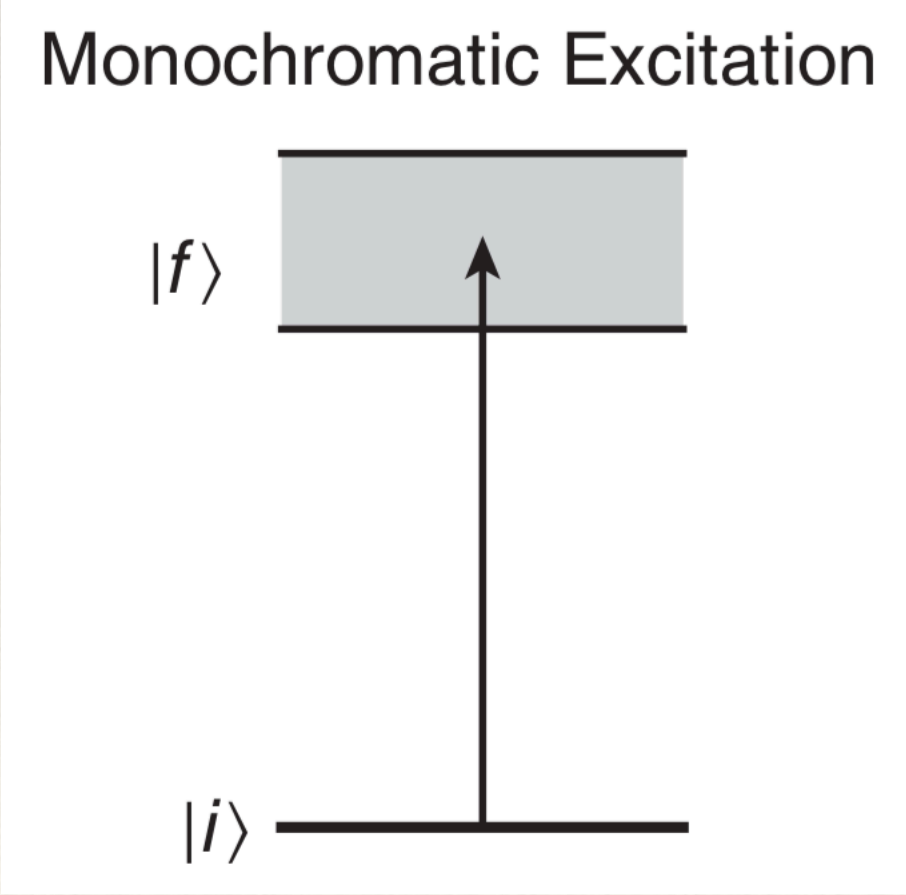
Dealing with multiple frequencies

With more than one frequency in the problem, we have two extreme cases:

Broadband:
If the light is incoherent across many wavelengths, then sum over the *rates for each frequency* in the drive to get the total transition rate.

Monochromatic:
If the target state isn't a well-defined final state (an entire *band* of resonant frequencies), then we integrate over all the *final states* (including a density of states) .





Einstein model of broadband excitation

Consider a gas of non-interacting two-level atoms in thermal equilibrium with blackbody radiation at temperature T. The radiation creates electric dipole transitions between the two states via broadband excitation.

To apply Fermi's golden rule, we need the density of states.

Planck distribution blackbody spectrum in frequency space:

Spatial average over random polarization direction:

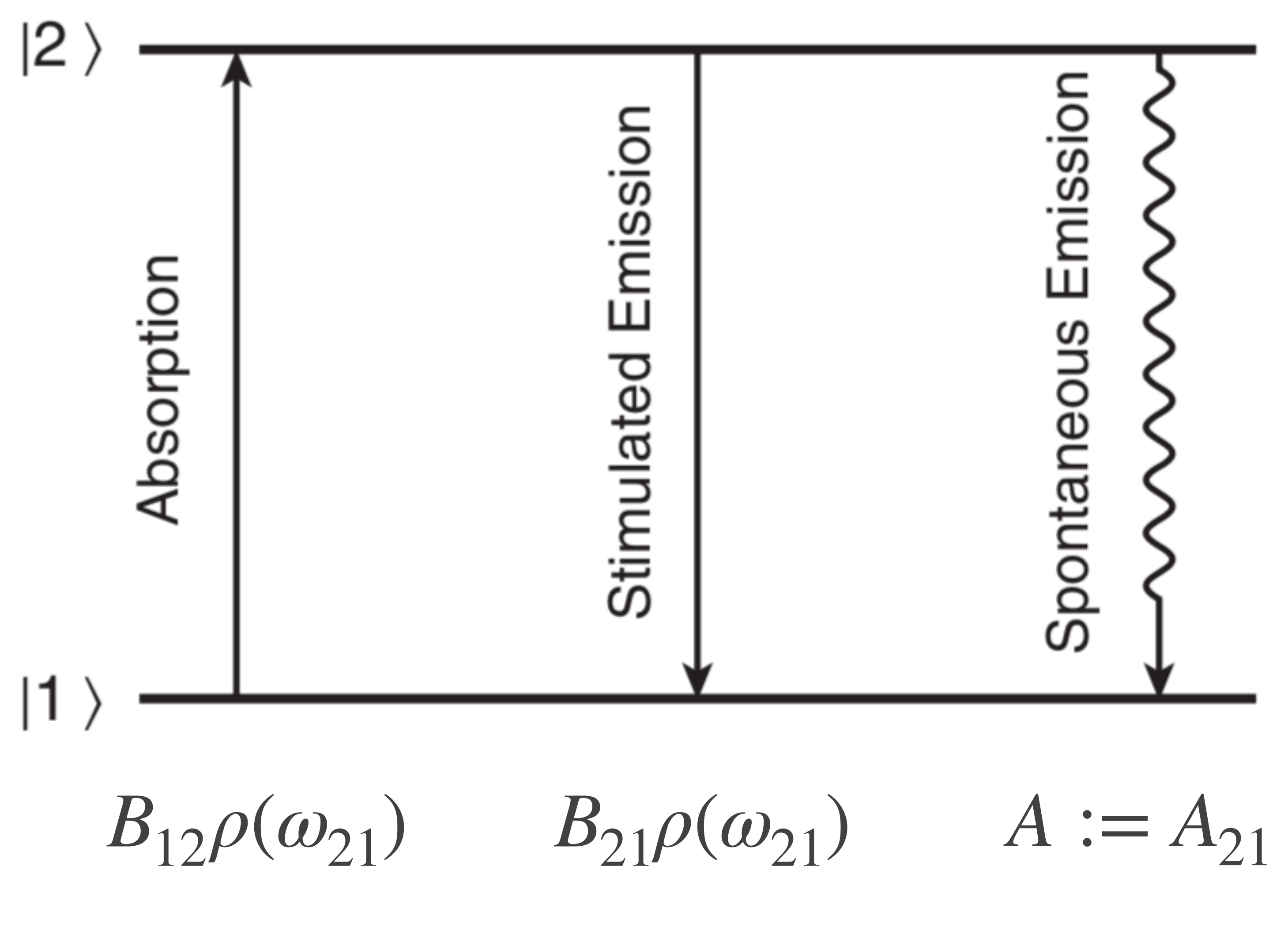
Time-average the electromagnetic energy density (Poynting vec):

Transition rates

Einstein B coefficient

Spontaneous emission

Notice that stimulated emission and absorption occur at the same rate:



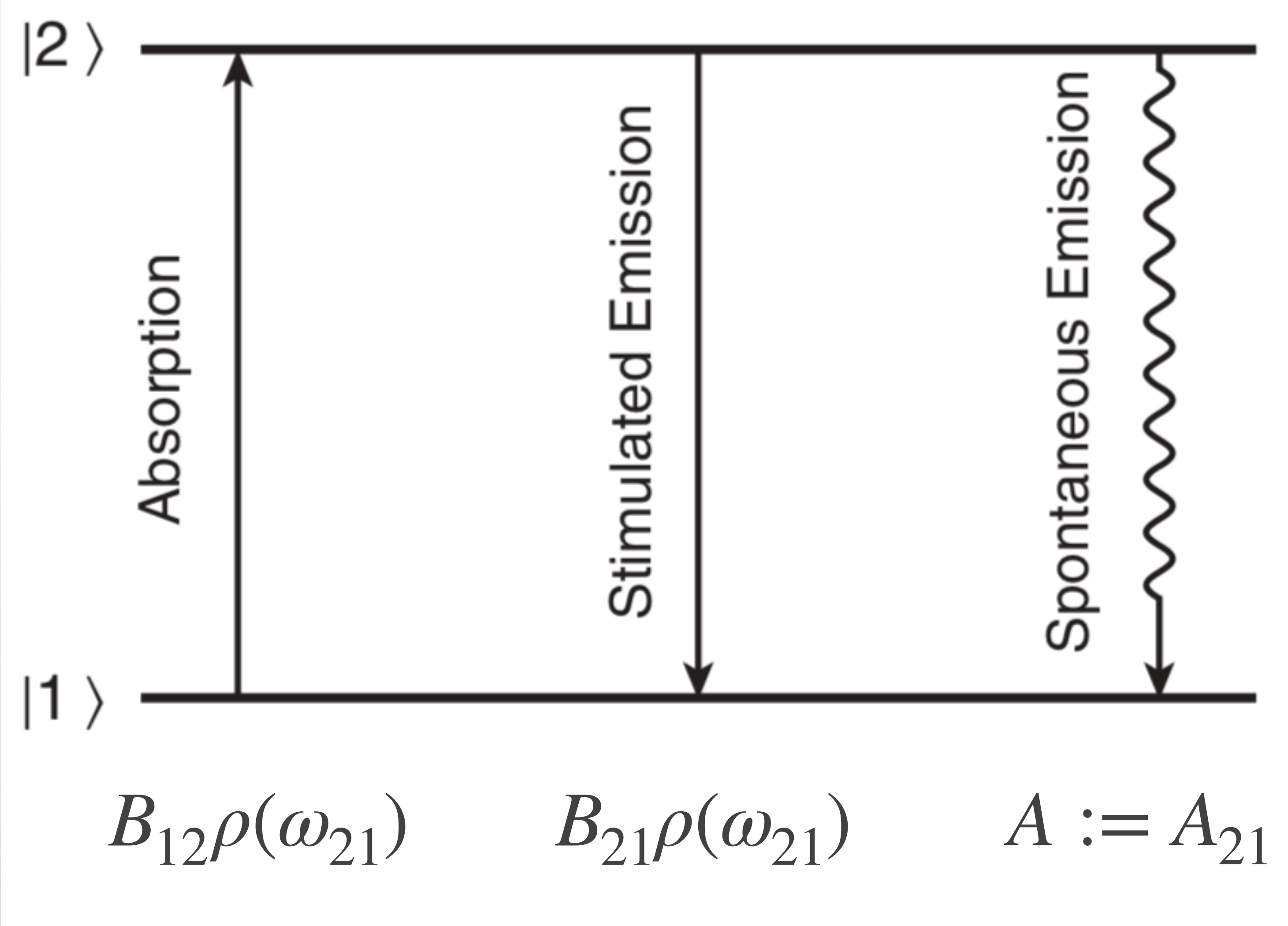
Is this incompatible with Boltzmann's distribution?
In thermal equilibrium, we must have

To preserve equilibrium, we need a third process: **spontaneous emission**.

Spontaneous emission

What is the spontaneous emission rate?

In thermal equilibrium, we have stationary population:



Lifetime of excited states is limited by A, so that $\tau \sim 1/A$ is a fundamental time scale for decay.

Monochromatic light

When the light is monochromatic and not broadband, we cannot just average over the polarization of the light, and the rates will generally depend on it.

For general atomic wave functions, this splits into radial and angular integrals:

The polarization and position unit vector become:

Forbidden transitions

The transition matrix element is now constrained by the angular integrals, which are all of the form:

What does this remind us of? …Clebsch-Gordan coefficients! After some math:

Thus if the associated Clebsch-Gordan coefficient is zero, there can be no transition (from an electric dipole coupling). Such a **forbidden transition** might still have a nonzero transition probability arising from magnetic dipole or electric quadruple transitions, though.

Selection rules

The transition matrix element is now constrained by the angular integrals, which are all of the form:

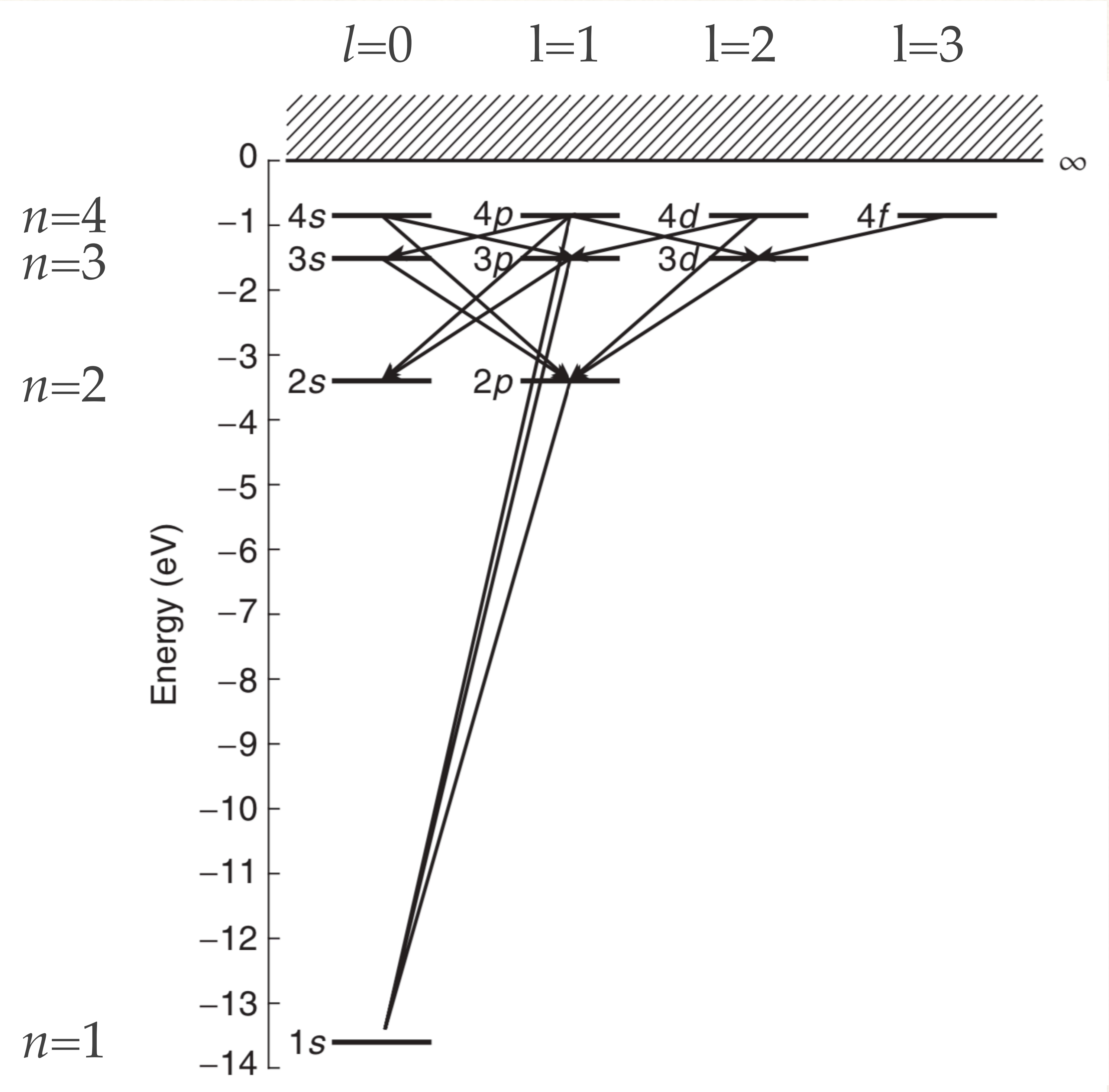
Clebsch-Gordan coefficients are themselves constrained by AM conservation:

A parity argument furthermore shows that the $l_f = l_i$ term vanishes, so we have:

Electric dipole selection rules:

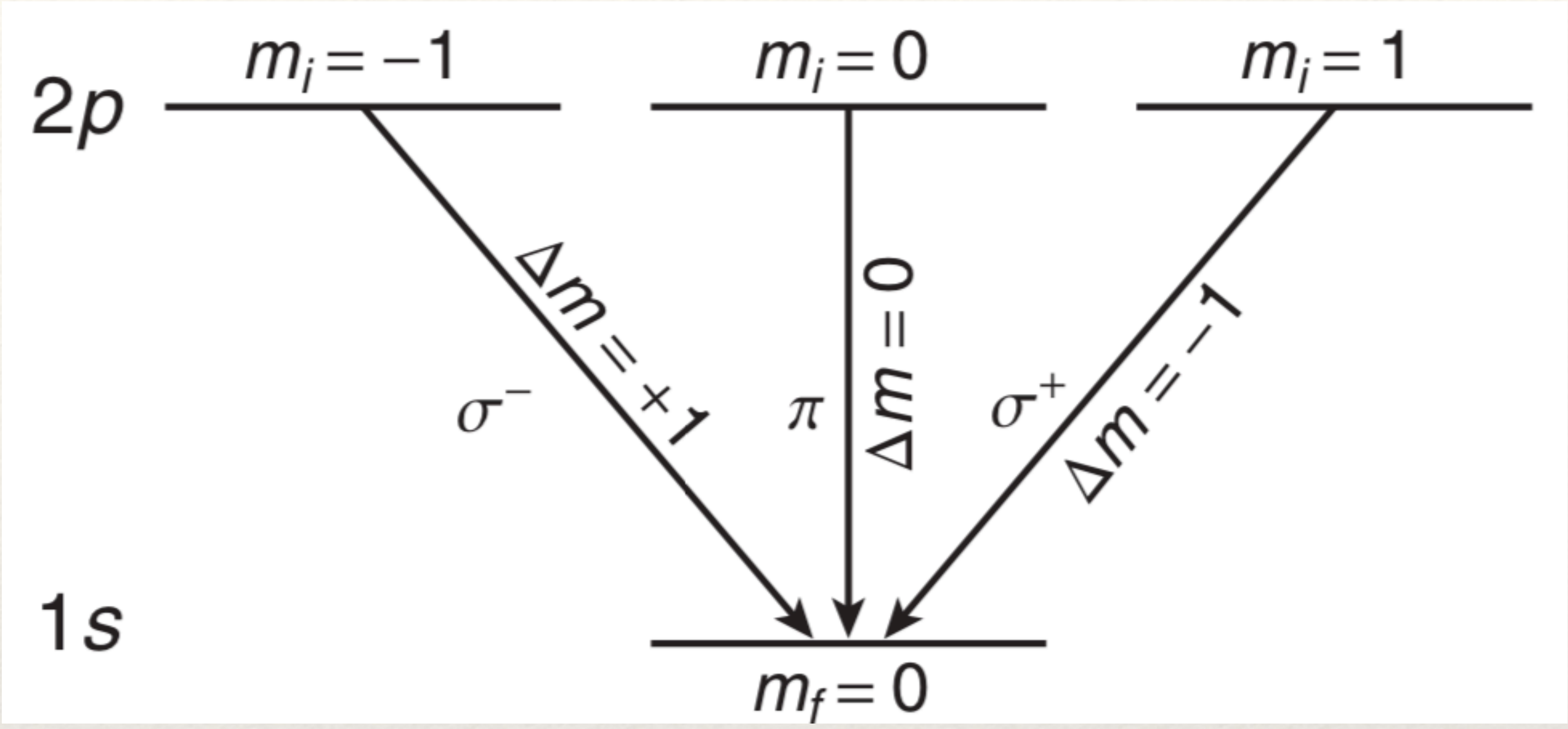
Electric dipole selection rules

For hydrogen, the allowed electric dipole transitions look as follows:



Hydrogen level diagram, ignoring fine structure

$$\Delta l = \pm 1$$
$$\Delta m = 0, \pm 1$$



The $m = \pm 1$ transitions give circularly polarized light to conserve AM. The $m = 0$ transition gives linearly polarized light along the quantization axis.