

Photon–Atom Coupling

From the Dipole Interaction to Cavity QED and the Optical Response of Solids

Photonics Engineering - Lecture course

Abstract

This course develops the physics of the coupling between light and matter along a single conceptual thread: the electric-dipole interaction $-\mathbf{d} \cdot \mathbf{E}$, treated with increasing sophistication. We start from the classical Lorentz oscillator and distil it into the *two-level atom*; we follow its *coherent* dynamics (Rabi oscillations, the Bloch sphere), then add *dissipation* through the density matrix (optical Bloch equations); we recover transition rates as the incoherent limit (*Fermi's golden rule*, Einstein coefficients), *quantize* the field to obtain spontaneous emission, let the field *propagate* (Maxwell–Bloch), engineer the vacuum in a cavity (*Purcell effect*, Jaynes–Cummings), and finally pass from a single atom to the *optical response of solids*. The deliberate ordering; coherent dynamics *before* the rate picture; splits the difficulty into two gentle steps. Main results and full step-by-step demonstrations are highlighted in colored boxes; each chapter closes with concrete numerical applications.

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How to read these notes

A word before we begin. These notes are written to be *read*, not merely consulted: each chapter tells one part of a single story, and the story is the point. To keep the narrative readable while still giving you everything you need for the exam (and, more importantly, for your future work in photonics), the material is organised into colored boxes. Here is what each colour means, and how I suggest you use it.

Why do we need a new theory? (teal)

Every chapter opens with one of these. Physics does not progress by piling up formulas; it progresses when a good theory *fails* and we are forced to build a better one. The teal box tells you what breaks, and why you should care, before any algebra starts. If you read nothing else before a lecture, read this box.

Key result (blue)

The results to remember. There are not many of them, and they are the skeleton of the subject: if you know what each blue box *says* and *when it applies*, you know the course. In the exam you may quote them freely.

Demonstration (orange)

The derivations, written out in full, with the reasoning between the lines made explicit. These are meant to be worked through with pen and paper, not skimmed: the aim of this course is that you understand where every formula comes from, so that you never need to memorise one. About half a dozen of these carry the whole logical chain; the exam will ask you to reproduce one.

Application, numerical example (green)

Real numbers for real systems: a sodium atom, a quantum dot, a micropillar cavity. Physics without orders of magnitude is philosophy; these boxes are where the formulas touch the ground. Redo them with a calculator at least once; the exam will contain an estimate of this kind.

Physical insight (grey)

The interpretation: what a result *means*, the picture to keep in your head, the limits of validity. This is often the hardest part to get from a formula alone, and the part that distinguishes understanding from recall.

Why it matters (violet)

Where this physics lives outside the classroom: in the blue of the sky, in an MRI scanner, in the GPS constellation, in the quantum processors now being built. Not examinable as such, but these boxes are the answer to the question “why am I learning this?”

Check yourself (yellow)

A few plain-language questions at the end of each chapter. If you can answer them out loud, without notes, in one or two sentences each, you have understood the chapter. If not, you know exactly what to reread.

One deliberate choice deserves a word: the two-level atom is introduced at the end of Chapter 1, its *coherent* dynamics is treated in Chapter 2, and *dissipation* is added only in Chapter 3, so that

the density matrix and relaxation do not land on you all at once. Trust the ordering; each chapter uses only what came before.

Prerequisites. Quantum mechanics of two-level systems, time-dependent perturbation theory, classical electromagnetism (Maxwell equations, Poynting flux), harmonic oscillator, density of states. Throughout we use SI units and quote orders of magnitude for real systems (alkali atoms, semiconductor quantum dots, optical microcavities).

Notation. $|g\rangle, |e\rangle$ ground/excited states, transition frequency $\omega_0 = (E_e - E_g)/\hbar$; field frequency ω ; detuning $\delta = \omega - \omega_0$; dipole matrix element $\mathbf{d} = \langle e | \hat{\mathbf{d}} | g \rangle$; Rabi frequency Ω ; spontaneous decay rate Γ .

Learning outcomes

By the end of the course the student should be able to:

- write the dipole interaction Hamiltonian, reduce a real atom to a two-level system, and justify the dipole and rotating-wave approximations from first principles (L1–L2);
- solve the *coherent* two-level dynamics: Rabi oscillations, the Bloch sphere as rotations, π -pulses, Ramsey interferometry and the light shift (L2);
- add *dissipation* via the density matrix, write and interpret the optical Bloch equations, and explain saturation, power broadening and the photon echo (L3);
- derive Fermi’s golden rule; as the incoherent limit of the Bloch equations; and apply it to absorption, photoionization and interband transitions, identifying the density of states in each case (L4, L8);
- explain why spontaneous emission requires field quantization, and compute decay rates, natural linewidths and lifetimes for real transitions (L5);
- connect the microscopic dipole to the macroscopic susceptibility and explain absorption, dispersion and slow light via the Maxwell–Bloch equations (L6);
- distinguish weak and strong coupling, derive the Purcell factor and cooperativity, and size a cavity for a single-photon source (L7);
- build the dielectric function of a solid from Drude and Lorentz oscillators, use the Kramers–Kronig relations, and interpret bands, the absorption edge, excitons and polaritons (L8).

Assessment. A short problem set after each block (worked solutions in the final section), plus a written exam combining one derivation with an order-of-magnitude estimate; that is, one orange box and one green box, chosen from the notes.

0 Light and matter: where we stand

This opening chapter contains no calculations. Its purpose is to place the whole course inside a larger question (how do light and matter exchange energy?) and to sketch how the answer has reshaped our picture of the physical world, from classical waves to quantum field theory. It is also, deliberately, a chapter about *how physics thinks*: what a model is, what it means for a theory to fail well, and why the strange objects you will meet (the photon, the vacuum that is not empty, the atom that is also a wave) earned their place in our description of nature. Read it once for orientation; the working machinery begins in Lecture 1.

0.1 Two ingredients, one question

The physical world of this course has only two characters: the electromagnetic field (light) and electric charges (matter). In the 19th century Maxwell showed that electricity, magnetism and optics are one subject, and that light is a travelling wave of the electromagnetic field. Matter, meanwhile, was resolved into atoms and (later) electrons. The single question that organises everything below is then: by what mechanism, and at what rate, do these two exchange energy?

For a while the classical answer seemed enough: a wave of continuous energy shakes the charges, which radiate. But three experiments broke this picture. The thermal (blackbody) spectrum could not be explained by classical waves (the energy diverged at high frequency); the photoelectric effect showed that light delivers energy in discrete packets proportional to its frequency; and atomic spectra came not as continuous bands but as sharp, discrete lines, a unique fingerprint for each element.

0.2 The quantum turn

The resolution came in two waves. First, energy exchange is quantised: Planck and Einstein established that light of frequency ω is exchanged in packets (photons) of energy $\hbar\omega$. Second, the atom itself has discrete energy levels (Bohr), so a spectral line is the signature of a jump between two of them. Both partners in the dialogue are therefore *lumpy*: discrete atomic levels on one side, photons on the other, and a spectral line is literally a photon whose energy matches a level spacing.

There is a subtlety that drives much of this course. In the simplest quantum treatment we quantise the *atom* (discrete levels) but keep the *field* classical (a prescribed wave). This semiclassical description is remarkably successful for processes *driven* by an applied field. Yet it has a glaring hole: an isolated excited atom, sitting in the dark with no applied field at all, still decays and emits a photon. Nothing in a classical field can cause this. Spontaneous emission forces us to quantise the field as well.

0.3 Crisis as method: how physics actually advances

Pause on how that happened, because the pattern will repeat inside this course. Physics rarely advances by someone simply having a good idea in the abstract. It advances when an excellent theory is pushed into a corner where it *visibly fails*, and the failure is taken seriously. Classical electrodynamics was arguably the most successful theory of the 19th century; applied to the glow of a hot oven it predicted infinite energy at high frequencies. Planck resolved the contradiction in 1900 with a hypothesis he himself distrusted for years, energy exchanged in packets $\hbar\omega$, introduced, in his own later words, as an act of desperation. Einstein in 1905 took the packets more literally than Planck ever wished; Bohr in 1913 quantised the atom with rules he could not justify; and each of these “temporary scaffoldings” held long enough for a real building, quantum mechanics (1925–26), to be built under it.

Notice what did *not* happen: classical electrodynamics was not discarded. It was *bounded*. We learned the domain in which it is excellent (fields with many photons, scales far above atomic) and

the domain in which it must hand over to a deeper description. That is the general fate of good theories, and it is worth internalising as a working epistemology: in physics, an old theory that worked never becomes wrong; it becomes a *limiting case*. You will watch this happen three times in miniature here: the Lorentz oscillator of Chapter 1 survives inside the quantum susceptibility of Chapter 6; the rate equations of Chapter 4 survive as the strong-damping limit of the Bloch equations; and the semiclassical theory survives inside QED wherever the field is bright.

0.4 Models, not mirrors

A second habit of thought matters even more for a physicist or an engineer, and this course practises it constantly: our theories are *models*, not mirrors of nature. The “two-level atom” that stars in these notes does not exist; every real atom has infinitely many levels. The classical “electron on a spring” exists even less. Yet both models are spectacularly predictive within their stated limits, and a large part of professional skill is knowing what a model may be trusted for, and what it silently ignores. When we truncate sodium to two levels, we do not claim sodium *is* a two-level system; we claim that, for light tuned near one specific line, nature *answers as if* it were, to within corrections we can estimate. A model, in short, is judged not by its realism but by the questions it answers correctly, and the honest statement of its domain of validity is part of the model itself.

Even the photon deserves this scepticism. It is tempting to picture a small ball of light, and for bookkeeping (energy $\hbar\omega$, momentum $\hbar k$, one click per detector event) the picture serves. But the photon of QED is an excitation of a field mode, delocalised over the whole mode; it has no position operator, and a famous 1995 polemic by Willis Lamb (of Lamb-shift fame) argued, only half in jest, that the word “photon” does more harm than good. What is beyond dispute is the *structure*: a quantised field whose exchanges with matter are discrete. Whether the vacuum fluctuations of Lecture 5 are “really there” or are an exceptionally convenient way of speaking, nature answers questions posed to that structure (the Lamb shift, the Casimir force between two mirrors, spontaneous emission itself) with measurable, and measured, numbers. In this course we adopt the physicist’s pragmatism: we use the picture that makes the calculation transparent, and we let experiment arbitrate the rest.

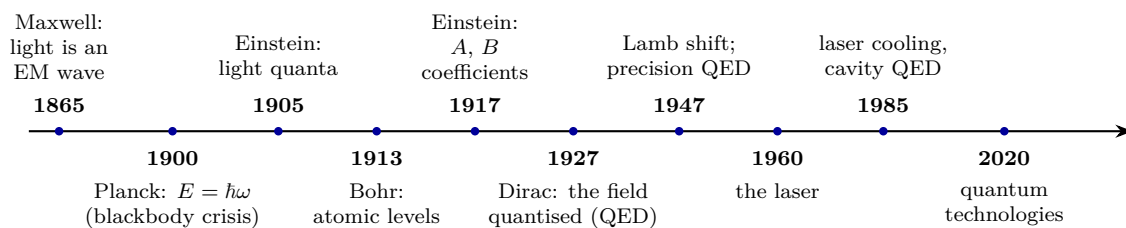


Figure 1: A century and a half in one line. Each date marks a place where the previous theory failed productively or a new tool changed what could be asked. Everything in this course sits on this axis: the Lorentz oscillator belongs to the Maxwell era, Fermi’s golden rule and the Einstein coefficients to 1917–1927, spontaneous emission and the Lamb shift to the 1940s, and the cavities, tweezers and qubits of the closing chapters to the ongoing quantum-technology period.

0.5 Quantising the field: toward quantum electrodynamics

Quantising the electromagnetic field turns each of its modes into a quantum harmonic oscillator whose excitations are photons. A startling consequence is that the lowest state (the vacuum) is not empty: it carries irreducible zero-point fluctuations. These vacuum fluctuations are not a mathematical artefact; they are what knocks the excited atom down (spontaneous emission) and what shifts its levels by a tiny, measurable amount (the Lamb shift). The complete theory of charges and the quantised field is *quantum electrodynamics* (QED).

0.6 One elementary process

QED is built from a single elementary event: a charge emits or absorbs one photon. Everything else (absorption, stimulated and spontaneous emission, scattering of light, the forces between charges) is assembled from repetitions of this one vertex. Feynman diagrams are the bookkeeping for such assemblies: straight lines stand for electrons, wavy lines for photons, and a point where they meet is one interaction event. Figure 2 shows the building blocks.



Figure 2: The building blocks of quantum electrodynamics (straight lines: electrons; wavy lines: photons; dots: interaction vertices). From left to right: the fundamental vertex (a charge emits or absorbs one photon); absorption of a photon, raising the electron; emission of a photon, lowering it; and a self-energy loop, in which the electron emits and reabsorbs a virtual photon (the origin of the Lamb shift). Every process in this course is some assembly of the first vertex.

The strength of the vertex is set by one dimensionless number, the fine-structure constant $\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$. Because it is small, each extra vertex adds only a small correction, so we may compute by counting vertices (this is the deep reason perturbation theory works so well for light and matter; see Lecture 4 and Appendix D).

0.7 Where we stand today

QED is the most accurately tested theory in all of physics: the prediction for the electron’s magnetic moment agrees with experiment to about twelve significant figures. It became the template for the entire Standard Model of particle physics, in which the same vertex idea (matter fields exchanging force-carrier fields) describes the other interactions. In that sense the humble question of how an atom absorbs light sits at the root of our deepest picture of nature.

And yet, for atoms, molecules and solids at optical frequencies, we almost never need the full apparatus. The dipole coupling $-\mathbf{d} \cdot \mathbf{E}$ that runs through this entire course is simply the low-energy face of the QED vertex. The chapters ahead climb gradually from the classical charged oscillator up to the quantised vacuum and the engineered cavity, meeting the field-theoretic ideas (vacuum fluctuations, the photon, the vertex) exactly where the physics demands them, and not before.

One last philosophical remark, which the final chapter will make concrete. Knowing the fundamental interaction is not the same as understanding what matter does. A solid is 10^{23} atoms, every one obeying the same $-\mathbf{d} \cdot \mathbf{E}$; yet nothing at the level of one atom announces the existence of bands, of excitons, of a metal’s plasma edge, or of a polariton. These are *emergent* objects: perfectly derivable in hindsight, essentially unforeseeable in advance, and each one demanding new concepts of its own. “More is different,” as the condensed-matter physicist P. W. Anderson famously put it: the reductionist ladder can be climbed down, but science mostly lives on its upper rungs. This course walks the ladder in both directions, from one atom to a technology and from a crystal back to one atom, and part of what you should take from it is a feel for which rung a given question belongs to. This chapter is the map; the rest of the course is the territory.

0.8 What is assumed, and where to find it

The reader is assumed to know basic quantum mechanics (the Schrödinger equation, stationary states, elementary perturbation theory) and classical electromagnetism. So that the course is self-contained, the indispensable quantum-mechanical tools are recalled in the appendices:

Appendix C (the Schrödinger equation and stationary states), Appendix D (perturbation theory, both stationary and time-dependent), and Appendix E (the harmonic oscillator and second quantisation, the language in which the field is quantised in Lecture 5).

1 Foundations of the atom–field interaction

Why start with a classical oscillator?

Because it is free intuition before we pay the quantum price. A charge on a spring, pushed by a light wave, already reproduces *absorption*, *refraction* and the coloured sky, and it hands us the right orders of magnitude. We keep it as a benchmark until it visibly fails (it cannot saturate, and it has no discrete levels), and that very failure is what forces us into the two-level atom at the end of this chapter. Starting classical is the shortest road to understanding what is genuinely quantum later.

Roadmap, and the symbols introduced here

Progress: **(you are here)** classical oscillator → two-level atom.

New symbols: ω_0 (resonance / transition frequency), γ_c (classical damping rate), $\alpha(\omega)$ (polarizability of one oscillator), $\chi(\omega)$ (susceptibility of the medium), $\mathbf{d}$ (dipole matrix element), $H_{\text{int}} = -\mathbf{d} \cdot \mathbf{E}$ (the coupling that runs through the whole course).

1.1 The classical benchmark: the Lorentz oscillator

Before any quantum treatment, a single classical picture already captures absorption, dispersion and radiative damping. An electron of charge $-e$ and mass m_e bound to a nucleus is modeled as a damped harmonic oscillator of resonance frequency ω_0 , driven by a monochromatic field $\mathbf{E}(t) = \mathbf{E}_0 \cos \omega t$:

$$m_e \ddot{\mathbf{r}} + m_e \gamma_c \dot{\mathbf{r}} + m_e \omega_0^2 \mathbf{r} = -e \mathbf{E}_0 \cos \omega t. \quad (1)$$

In steady state the dipole $\mathbf{p} = -e\mathbf{r}$ oscillates with a complex amplitude, and the medium acquires a polarization $\mathbf{P} = N\mathbf{p} = \varepsilon_0 \chi(\omega) \mathbf{E}$.

Solving the driven oscillator

Seek a steady-state solution $\mathbf{r}(t) = \text{Re}[\mathbf{r}_0 e^{-i\omega t}]$ with $\mathbf{E}(t) = \text{Re}[\mathbf{E}_0 e^{-i\omega t}]$. Substituting into the equation of motion turns the differential equation into an algebraic one:

$$(-\omega^2 - i\gamma_c \omega + \omega_0^2) \mathbf{r}_0 = -\frac{e}{m_e} \mathbf{E}_0 \Rightarrow \mathbf{r}_0 = \frac{-e/m_e}{\omega_0^2 - \omega^2 - i\gamma_c \omega} \mathbf{E}_0.$$

The induced dipole is $\mathbf{p}_0 = -e\mathbf{r}_0 = \alpha(\omega) \mathbf{E}_0$, and the polarization of N dipoles per unit volume is $\mathbf{P} = N\mathbf{p} = \varepsilon_0 \chi \mathbf{E}$, giving the results boxed below. The complex denominator is the origin of the 90° phase lag at resonance, i.e. of absorption.

Lorentz polarizability and susceptibility

$$\alpha(\omega) = \frac{e^2/m_e}{\omega_0^2 - \omega^2 - i\gamma_c \omega}, \quad \chi(\omega) = \frac{Ne^2/(m_e \varepsilon_0)}{\omega_0^2 - \omega^2 - i\gamma_c \omega}. \quad (2)$$

The real part of χ governs *dispersion* (refractive index), the imaginary part governs *absorption*. Near resonance ($\omega \simeq \omega_0$) the imaginary part is a Lorentzian of full width γ_c .

This structure; a resonant denominator with real (dispersive) and imaginary (absorptive) parts; reappears in every later chapter, from the quantum susceptibility of Sec. 6 to the dielectric function of solids in Sec. 8. It is worth memorising Fig. 3: absorption peaks where dispersion crosses zero, and the steepest dispersion (largest group index) occurs exactly at line centre.

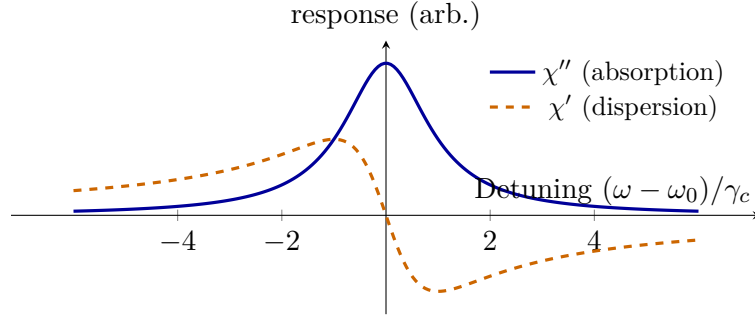


Figure 3: The universal resonant lineshape. The absorptive part χ'' is a Lorentzian peaked on resonance; the dispersive part χ' is its antisymmetric partner. The same pair governs atomic vapours (Sec. 6) and solids (Sec. 8), linked by the Kramers–Kronig relations.

Scattering that grows as ω^4 : the colour of the sky

Why is the sky blue? You already hold every ingredient of the answer; two facts combine. (i) *Radiation*. An oscillating dipole is an *accelerating* charge, and an accelerating charge radiates; the radiated power scales as the square of the acceleration. If the dipole swings as $p_0 \cos \omega t$, its acceleration is $\ddot{p} \propto \omega^2 p_0$, so

$$P_{\text{scatt}} \propto (\ddot{p})^2 \propto \omega^4 p_0^2.$$

(ii) *The Lorentz model*. For light far below the resonance ($\omega \ll \omega_0$, the case of transparent air whose resonances are in the ultraviolet), $\alpha \approx e^2/m_e \omega_0^2$ is *constant*, so the dipole amplitude p_0 is the same for every visible colour. The colour dependence is therefore *entirely* the ω^4 :

$$\frac{P_{\text{blue}}}{P_{\text{red}}} = \left(\frac{\omega_{\text{blue}}}{\omega_{\text{red}}}\right)^4 = \left(\frac{\lambda_{\text{red}}}{\lambda_{\text{blue}}}\right)^4 \approx \left(\frac{650}{450}\right)^4 \approx 4.4.$$

Blue is scattered out of a sunbeam a few times more strongly than red. That single factor is the essential reason the scattered sky is blue and the low sun red (the full story adds the geometry of the atmospheric path, but the physics that decides the colour is the ω^4).

The real part does the complementary job

The argument above used the imaginary (dissipative / scattering) side of the response. The real part χ' does the complementary job: it fixes the refractive index $n \simeq 1 + \chi'/2$, and its slow growth with ω makes blue bend a little more than red, which is dispersion, the origin of prisms and chromatic aberration. Absorption and refraction are simply the imaginary and real halves of the one resonant denominator of Fig. 3.

1.2 The atom–field Hamiltonian

Where does the coupling between light and a charge come from in quantum mechanics? We cannot guess it; we inherit it from classical electrodynamics. There, the force on a charge in a field described by potentials $(\phi, \mathbf{A})$ follows from the Lagrangian by the standard *minimal-coupling* substitution $\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A}$ (this is the unique prescription that reproduces the Lorentz force; it is derived in any mechanics course). Quantum mechanics takes over the same Hamiltonian, now with operators:

$$H = \frac{1}{2m_e}(\mathbf{p} + e\mathbf{A}(\mathbf{r}, t))^2 - e\phi(\mathbf{r}, t) + V(\mathbf{r}), \quad (3)$$

where V is the binding potential.

From minimal coupling to $\mathbf{A} \cdot \mathbf{p}$

Step 1: expand the square.

$$\frac{1}{2m_e}(\mathbf{p} + e\mathbf{A})^2 = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic}} + \underbrace{\frac{e}{2m_e}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})}_{\text{linear in } A} + \underbrace{\frac{e^2}{2m_e}A^2}_{\text{quadratic}}.$$

In Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$, and $\phi = 0$ for a pure radiation field) the operators $\mathbf{p}$ and $\mathbf{A}$ commute, since $\mathbf{p} \cdot \mathbf{A} \psi = \mathbf{A} \cdot \mathbf{p} \psi - i\hbar(\nabla \cdot \mathbf{A})\psi = \mathbf{A} \cdot \mathbf{p} \psi$. Hence

$$H_{\text{int}} = \frac{e}{m_e} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m_e} A^2.$$

Step 2: why the A^2 term may be dropped. Compare the two interaction terms for a field of amplitude E_0 at frequency ω (so $A_0 \sim E_0/\omega$). Using the atomic momentum scale $p \sim m_e v \sim m_e \alpha c$,

$$\frac{e^2 A^2 / 2m_e}{(e/m_e) A p} \sim \frac{e A_0}{2p} \sim \frac{e E_0}{2\omega m_e \alpha c}.$$

For the laser of the next subsection ($E_0 \sim 275$ V/m, optical ω) this ratio is $\sim 10^{-9}$: utterly negligible. The two terms only become comparable at extreme intensities ($\sim 10^{14}$ – 10^{15} W/cm², the regime of high-harmonic generation and strong-field optics); everywhere in this course the A^2 term can be dropped.

Dipole approximation. Optical wavelengths ($\lambda \sim 500$ nm) are huge compared with atomic sizes ($a_0 \sim 0.05$ nm), so $\mathbf{A}(\mathbf{r}, t) \approx \mathbf{A}(\mathbf{r}_0, t)$ across the atom: $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$ since $ka_0 \sim 10^{-3}$. The atom is a point compared with the wave; it samples the field at one position and feels no spatial gradient (Fig. 4).

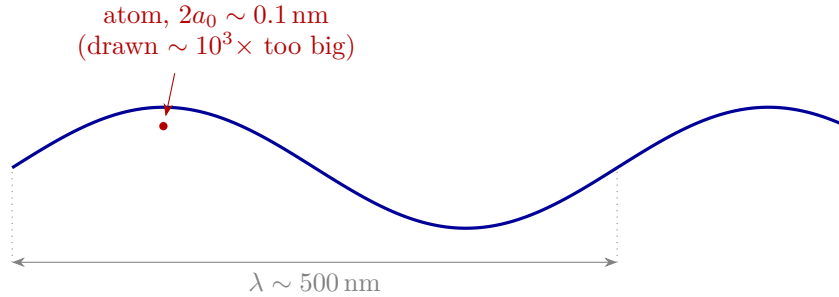


Figure 4: The scale hierarchy behind the dipole approximation. An optical wavelength is ~ 5000 times the size of an atom, so the field is spatially uniform on the atomic scale: the atom feels $\mathbf{E}(t)$, not $\mathbf{E}(\mathbf{r}, t)$. The expansion parameter is $ka_0 \sim 10^{-3}$; magnetic-dipole and quadrupole effects enter only at this order, which is why “forbidden” lines are $\sim 10^6$ times weaker in rate.

From $\mathbf{A} \cdot \mathbf{p}$ to $-\mathbf{d} \cdot \mathbf{E}$

The $\mathbf{A} \cdot \mathbf{p}$ form is correct but opaque: $\mathbf{A}$ is not measurable, and the momentum operator hides the physics. Two routes lead to the transparent *length gauge*; we give the elementary one, which works at the level of matrix elements (the systematic route is the Power–Zienau–Woolley unitary transformation $U = \exp(-ie \mathbf{r} \cdot \mathbf{A}/\hbar)$, which yields the same result exactly).

Step 1: a commutator identity. For any binding potential $V(\mathbf{r})$, the position operator obeys $[\mathbf{r}, H_0] = [\mathbf{r}, p^2/2m_e] = i\hbar \mathbf{p}/m_e$. Taking matrix elements between atomic eigenstates

$$H_0 |i\rangle = E_i |i\rangle,$$

$$\langle f | [\mathbf{r}, H_0] | i \rangle = (E_i - E_f) \langle f | \mathbf{r} | i \rangle \implies \langle f | \mathbf{p} | i \rangle = im_e \omega_{fi} \langle f | \mathbf{r} | i \rangle, \quad \omega_{fi} = \frac{E_f - E_i}{\hbar}.$$

The momentum matrix element is just the position one times $im_e \omega_{fi}$; this is the quantum version of $p = m\dot{x}$ for an oscillation at frequency ω_{fi} .

Step 2: substitute into the coupling. For a near-resonant field ($\omega \simeq \omega_{fi}$), using $\mathbf{E} = -\partial_t \mathbf{A}$, i.e. $E_0 = \omega A_0$ for a monochromatic wave:

$$\left| \frac{e}{m_e} A_0 \langle f | \mathbf{p} | i \rangle \right| = \frac{e}{m_e} \frac{E_0}{\omega} m_e \omega_{fi} |\langle f | \mathbf{r} | i \rangle| \simeq e E_0 |\langle f | \mathbf{r} | i \rangle| = |\langle f | (-\hat{\mathbf{d}} \cdot \mathbf{E}_0) | i \rangle|.$$

On resonance the two forms give *identical* matrix elements, hence identical transition rates and Rabi frequencies. Every observable in this course can therefore be computed with the simple, gauge-transparent form boxed below, where only the measurable field $\mathbf{E}$ appears.

Electric-dipole interaction

$$H_{\text{int}} = -\hat{\mathbf{d}} \cdot \mathbf{E}(\mathbf{r}_0, t), \quad \hat{\mathbf{d}} = -e \hat{\mathbf{r}}. \quad (4)$$

This is the workhorse of the whole course. Its matrix element between atomic states, $\mathbf{d} = \langle e | \hat{\mathbf{d}} | g \rangle$, sets the strength of every light-matter process.

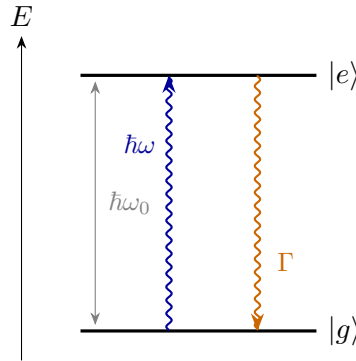


Figure 5: The two-level atom. Lower line: ground state $|g\rangle$; upper line: excited state $|e\rangle$; the vertical direction is energy. The upward (blue) arrow is absorption of a photon $\hbar\omega$, which together with stimulated emission scales with the applied field; the downward (orange) arrow is spontaneous emission at the rate Γ , which requires the quantized vacuum. These are the three Einstein processes.

When does the dipole approximation fail?

It breaks down when (i) the wavelength becomes comparable to the system size (X-rays, or large Rydberg atoms / quantum dots), or (ii) the dipole matrix element vanishes by symmetry, so that magnetic-dipole or electric-quadrupole terms (of relative order $ka_0 \sim 10^{-3}$) dominate; these give the very weak “forbidden” lines.

1.3 Orders of magnitude

Dipole moment and Rabi scale of sodium

The Na D₂ line ($3s \rightarrow 3p$) has $\lambda_0 = 589 \text{ nm}$, i.e. $\omega_0 = 2\pi c/\lambda_0 = 3.2 \times 10^{15} \text{ rad/s}$. The dipole matrix element is $d \simeq 2.5 ea_0$:

$$d \simeq 2.5 \times (1.6 \times 10^{-19}) \times (5.3 \times 10^{-11}) \approx 2.1 \times 10^{-29} \text{ C m} (\approx 6.3 \text{ Debye}).$$

For a modest laser intensity $I = 10 \text{ mW/cm}^2 = 100 \text{ W/m}^2$ we need the field amplitude. Where does the conversion come from? The intensity is the time-averaged Poynting flux $I = \langle |\mathbf{E} \times \mathbf{H}| \rangle = \varepsilon_0 c \langle E^2 \rangle$, and for a sinusoid $\langle E^2 \rangle = E_0^2/2$, so $I = \frac{1}{2} \varepsilon_0 c E_0^2$, i.e.

$$E_0 = \sqrt{\frac{2I}{\varepsilon_0 c}} = \sqrt{\frac{2 \times 100}{8.85 \times 10^{-12} \times 3 \times 10^8}} \approx 275 \text{ V/m}.$$

(For calibration: bright sunlight, $I \approx 1 \text{ kW/m}^2$, has $E_0 \approx 870 \text{ V/m}$; a 1 mW laser pointer focused to a $1 \mu\text{m}$ spot reaches $7e5 \text{ V/m}$. All are tiny compared with the atom's internal field $e/4\pi\varepsilon_0 a_0^2 \approx 5e11 \text{ V/m}$, which is why the field can be treated as a weak perturbation.) The resulting Rabi frequency (defined in Sec. 2) is

$$\Omega = \frac{dE_0}{\hbar} \approx \frac{2.1 \times 10^{-29} \times 275}{1.05 \times 10^{-34}} \approx 5.5 \times 10^7 \text{ rad/s} \Rightarrow \Omega/2\pi \approx 8.7 \text{ MHz}.$$

The number itself is what matters here: Ω is a *control speed*. At this intensity the field can drive the atom from the ground state up to the excited state in a time

$$t_\pi = \frac{\pi}{\Omega} \approx 60 \text{ ns}.$$

Keep this figure in mind. We will find later that the excited state also *decays* on its own, in a comparable time (the natural lifetime is $\tau \approx 16 \text{ ns}$ for this line). The central drama of the next chapters is precisely this race: a *control* time t_π against a *decay* time τ . When $t_\pi \ll \tau$ the atom completes many clean oscillations; when $t_\pi \gtrsim \tau$, as here, the decay wins and we cross over into a rate description. We are not equipped to make that comparison yet, which is exactly why the next two chapters exist.

1.4 From the Lorentz oscillator to the two-level atom

The Lorentz model captures dispersion and absorption, but it has a fatal flaw: a classical oscillator responds *linearly* to any field, however strong, and its energy spectrum is *continuous*. A real atom has *discrete* levels and (as we will prove in Sec. 3) it *saturates*: it cannot absorb without limit. Quantum mechanics fixes both defects at once. Since the laser is near-resonant with a single transition $|g\rangle \rightarrow |e\rangle$, we keep only those two levels (all others are far off-resonance and adiabatically eliminated). This *two-level atom* is the object of the next three lectures.

The bare two-level atom

$$H_0 = E_g |g\rangle\langle g| + E_e |e\rangle\langle e| \xrightarrow{\text{shift origin}} H_0 = \hbar\omega_0 |e\rangle\langle e|, \quad \omega_0 = \frac{E_e - E_g}{\hbar} \quad (5)$$

The single classical frequency ω_0 of the Lorentz oscillator survives as the transition frequency, but the response is now bounded: at most one quantum can be stored. The chapters that follow switch on the coupling $-\mathbf{d} \cdot \mathbf{E}$ and study this object in stages, first its reversible coherent motion, then relaxation, and only afterwards the familiar rate picture, which appears as the

limit in which coherence is rapidly lost.

The two-level atom is the hub of the course

The same object reappears in every later setting: driven by a classical field, coupled to the quantized vacuum (which produces spontaneous emission), placed inside a cavity (where atom and photon exchange a single quantum), or replicated 10^{23} times into the electronic bands of a solid. Mastering its coherent and dissipative dynamics now pays off throughout.

The thread of this course: one chain, six demonstrations

This is not a catalogue of formulas. The whole course is a single logical chain, and only about half a dozen *demonstrations* (the orange boxes) carry it. If you can reproduce these six, you own the subject; everything else is application or enrichment.

1. **Rabi (this idea, next chapter).** Solve the two-level atom under a field with the Schrödinger equation. Out comes the Rabi oscillation. (*clean 2×2 algebra*)
2. **Bloch.** Add collisions through T_1, T_2 , take the steady state, and read off the Lorentzian line shape and saturation. (*same 2×2 , now damped*)
3. **Fermi's golden rule.** Weak field plus a continuum of final states; the sinc^2 becomes a Dirac δ and a constant *rate* appears.
4. **Spontaneous emission.** Apply Fermi's rule to the empty modes of the vacuum, admitting only the single-photon field $\mathcal{E}_{\text{vac}}$. Out comes the decay rate Γ .
5. **Purcell.** Put the emitter in a cavity; recount the optical density of states with classical wave modes; Fermi's rule then gives the Purcell factor.
6. **Solids.** Let the emitter itself have a width (an exciton, a band): the response is a product of the emitter and the medium line shapes.

Steps 3 and 4 use the *same* golden rule; steps 4 and 5 use the *same* density of states. The story closes on itself; watch for these recurrences as we go.

Can you now answer these? (Chapter 1)

- Why does the classical oscillator scatter blue light much more than red?
- What do the real and imaginary parts of $\chi(\omega)$ each describe physically?
- Why is the dipole approximation ($e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$) so good at optical wavelengths?
- In one line: why must we eventually abandon the Lorentz oscillator for a two-level atom?

2 Coherent dynamics of the two-level atom

Why is a rate equation not enough?

The Einstein picture of “the atom absorbs a photon, then emits one” assigns a *probability per second* to each jump. That is fine for a light bulb, but it can only ever say how *full* the excited state is. It cannot describe an atom that is driven coherently *back and forth*, nor a superposition of ground and excited, nor the phase that makes two paths interfere. Yet those are precisely the ingredients of a laser pulse acting on an atom, and of every quantum bit. To capture them we must stop tracking probabilities and start tracking the *amplitudes* c_g, c_e themselves, with the full Schrödinger equation. That is the whole job of this chapter.

Roadmap, and the symbols introduced here

Progress: ✓ classical oscillator ✓ two-level atom → **(you are here)** coherent dynamics.
 New symbols: Ω (Rabi frequency, the coupling strength $dE_0/\hbar$), $\delta = \omega - \omega_0$ (detuning), $\Omega_R = \sqrt{\Omega^2 + \delta^2}$ (generalised Rabi frequency), the Bloch vector (u, v, w) , and U_{dip} (light-shift potential).

We now switch on the dipole coupling and follow the two-level atom under the *Schrödinger equation alone*, with no relaxation. The result is a fully reversible, coherent dynamics: under a resonant field the atom does not simply “absorb” but cycles smoothly back and forth between its ground and excited states.

This may look academic, but it is the single most important idea in modern quantum technology. The ability to drive an atom from $|g\rangle$ to $|e\rangle$ and back *on demand*, with a phase we control, is exactly what it means to operate a quantum bit. Everything in this chapter is the working principle of trapped-ion and superconducting quantum computers, of the atomic clocks inside GPS, and of the optical tweezers that hold single atoms in place. We will meet each of these as we go. Relaxation, the enemy of all of them, is the subject of the following chapter.

2.1 Rabi oscillations and the rotating-wave approximation

Take the bare atom $H_0 = \hbar\omega_0 |e\rangle\langle e|$ of Sec. 1.4 and add the classical drive $H_{\text{int}} = -\hat{\mathbf{d}} \cdot \mathbf{E}_0 \cos \omega t$. With the state $|\psi\rangle = c_g |g\rangle + c_e |e\rangle$, define the *Rabi frequency*

$$\Omega = \frac{\mathbf{d} \cdot \mathbf{E}_0}{\hbar}. \quad (6)$$

Rotating-wave approximation and Rabi oscillations

Step 1: coupled amplitudes. With $H_{\text{int}} = -dE_0 \cos \omega t (|e\rangle\langle g| + |g\rangle\langle e|)$, the Schrödinger equation gives (factoring the free phase $c_e \rightarrow c_e e^{-i\omega_0 t}$)

$$i\dot{c}_e = -\frac{dE_0}{2\hbar} (e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}) c_g.$$

Step 2: the RWA. The first exponential oscillates slowly at the detuning $\delta = \omega - \omega_0$; the second oscillates at $\omega + \omega_0 \sim 2\omega_0$ and averages to zero over an optical cycle. Dropping it is the *rotating-wave approximation*.

Why the next move? Even after the RWA the equations still contain an explicit $e^{i\delta t}$, and time-dependent Hamiltonians are awkward to solve. We therefore look for a viewpoint in which that oscillation disappears: a reference frame co-rotating with the laser, at frequency ω . (This is the same idea as watching a spinning carousel from a seat on the carousel: the horses stop moving.) Defining $\Omega = dE_0/\hbar$ and passing to that frame, the Hamiltonian becomes *time*

independent:

$$\tilde{H} = -\hbar\delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(|e\rangle\langle g| + |g\rangle\langle e|).$$

Step 3: diagonalise. In the $\{|g\rangle, |e\rangle\}$ basis, $\tilde{H} = \frac{\hbar}{2} \begin{pmatrix} 0 & \Omega \\ \Omega & -2\delta \end{pmatrix}$, whose eigenvalue splitting is the *generalised Rabi frequency* $\Omega_R = \sqrt{\Omega^2 + \delta^2}$.

Step 4: time evolution. Starting in $|g\rangle$, let us solve the 2×2 dynamics explicitly. The coupled equations from $\tilde{H}$ read

$$i\dot{c}_g = \frac{\Omega}{2}c_e, \quad i\dot{c}_e = \frac{\Omega}{2}c_g - \delta c_e.$$

Differentiate the first and substitute the second to close an equation on c_e alone. The cleanest route: take resonance first ($\delta = 0$). Then $\ddot{c}_e = -\frac{i\Omega}{2}\dot{c}_g = -\left(\frac{\Omega}{2}\right)^2 c_e$: a harmonic oscillator at frequency $\Omega/2$. With the initial conditions $c_g(0) = 1$, $c_e(0) = 0$ (hence $\dot{c}_e(0) = -i\Omega/2$),

$$c_e(t) = -i \sin\left(\frac{\Omega t}{2}\right) \implies P_e(t) = |c_e|^2 = \sin^2\left(\frac{\Omega t}{2}\right).$$

Off resonance we follow exactly the same route, keeping every term. Differentiating $i\dot{c}_e = \frac{\Omega}{2}c_g - \delta c_e$ and using $i\dot{c}_g = \frac{\Omega}{2}c_e$ to eliminate c_g :

$$\ddot{c}_e - i\delta\dot{c}_e + \left(\frac{\Omega}{2}\right)^2 c_e = 0.$$

Try $c_e \propto e^{i\lambda t}$; the characteristic equation $-\lambda^2 + \delta\lambda + (\Omega/2)^2 = 0$ has the two roots $\lambda_{\pm} = \frac{1}{2}(\delta \pm \Omega_R)$ with $\Omega_R = \sqrt{\Omega^2 + \delta^2}$, so the general solution is

$$c_e(t) = e^{i\delta t/2} \left(A e^{i\Omega_R t/2} + B e^{-i\Omega_R t/2} \right).$$

Now impose the initial conditions. $c_e(0) = 0$ forces $B = -A$, turning the bracket into $2iA \sin(\Omega_R t/2)$. And $\dot{c}_e(0) = -i\Omega/2$ (read off the equation of motion at $t = 0$, where $c_g = 1$) fixes $A = -\Omega/2\Omega_R$. Hence

$$c_e(t) = -i \frac{\Omega}{\Omega_R} e^{i\delta t/2} \sin\left(\frac{\Omega_R t}{2}\right) \implies P_e(t) = |c_e|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2\left(\frac{1}{2}\sqrt{\Omega^2 + \delta^2} t\right),$$

the boxed result. The prefactor Ω^2/Ω_R^2 is the maximum reachable population: only on resonance does it equal unity. (Physically: a detuned drive rotates the Bloch vector about a tilted axis, so the vector traces a cone that never reaches the north pole.)

Generalized Rabi oscillations

$$P_e(t) = \frac{\Omega^2}{\Omega_R^2} \sin^2\left(\frac{\Omega_R t}{2}\right), \quad \Omega_R = \sqrt{\Omega^2 + \delta^2} \quad (7)$$

On resonance ($\delta = 0$) the population fully cycles between $|g\rangle$ and $|e\rangle$ at the Rabi frequency Ω : a π -pulse ($\Omega t = \pi$) inverts the atom, a $\pi/2$ -pulse creates an equal superposition. This coherent, reversible cycling is something a simple absorption/emission rate cannot capture; it requires following the full quantum amplitudes.

A Rabi pulse is a quantum logic gate

Read the two special pulses again, but think of $|g\rangle$ and $|e\rangle$ as the “0” and “1” of a quantum bit. A π -pulse takes $|0\rangle \rightarrow |1\rangle$ and $|1\rangle \rightarrow |0\rangle$: this is the quantum NOT gate. A $\pi/2$ -pulse takes

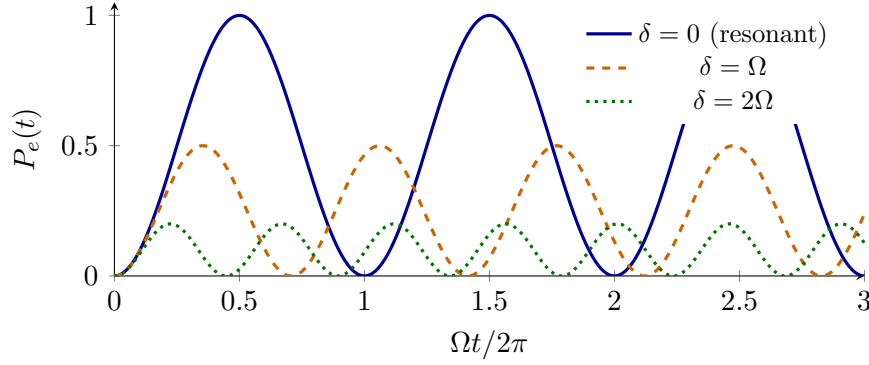


Figure 6: Rabi oscillations of the excited-state population. On resonance the population fully inverts ($P_e = 1$ at the π -pulse, $\Omega t = \pi$). With detuning the oscillation is faster ($\Omega_R = \sqrt{\Omega^2 + \delta^2}$) but shallower (amplitude Ω^2/Ω_R^2).

$|0\rangle \rightarrow (|0\rangle + |1\rangle)/\sqrt{2}$: it creates the superposition that has no classical analogue and that gives quantum computers their power. A trapped-ion or superconducting quantum processor does *nothing else* at the hardware level: it fires precisely timed Rabi pulses (microwave or laser) at each qubit. The whole game is to make the pulse area Ωt exactly right and to finish before relaxation (next chapter) scrambles the phase. The equation you just derived is, quite literally, the instruction set of a quantum computer.

2.2 The Bloch sphere: coherent rotations

The pure state of a two-level atom is fully described by three real numbers, the *Bloch vector* $\mathbf{S} = (u, v, w)$ with $u = 2 \operatorname{Re} c_e c_g^*$, $v = 2 \operatorname{Im} c_e c_g^*$ and the inversion $w = |c_e|^2 - |c_g|^2$. Why exactly three, and why a *unit* sphere? A normalised pair (c_g, c_e) has four real parameters, minus one for normalisation and one for the irrelevant global phase: two remain, the two angles on a sphere. And a one-line computation shows the radius is fixed:

$$u^2 + v^2 + w^2 = 4|c_e|^2|c_g|^2 + (|c_e|^2 - |c_g|^2)^2 = (|c_e|^2 + |c_g|^2)^2 = 1.$$

Every pure state is a point *on* the sphere; the interior, reachable only when the ensemble averaging of the next chapter shrinks the vector, is the territory of mixed states. Under $\hat{H}$ the Schrödinger equation becomes a pure *rotation* of $\mathbf{S}$ on the unit sphere; every coherent operation is a rotation. Relaxation (treated in the next chapter) later contracts the vector toward the centre.

Ramsey interferometry. Two $\pi/2$ -pulses separated by a free evolution T map the accumulated phase δT onto a population (Problem 7), giving fringes $P_e = \cos^2(\delta T/2)$. The longer T , the finer the fringes; the heart of atomic clocks.

This is how GPS knows where you are

The definition of the second, and the atomic clocks that realise it, are Ramsey's two-pulse sequence run on a chosen atomic transition. Because the fringe spacing is $2\pi/T$, a longer interrogation time T pins the laser to the atomic frequency ever more tightly; modern optical clocks reach a fractional accuracy near 10^{-18} (they would lose less than a second over the age of the Universe). Every GPS satellite carries atomic clocks, and your position is computed from the tiny differences in their tick times: an error of a few nanoseconds is an error of a metre on the ground. The humble $\cos^2(\delta T/2)$ fringe is the reason a phone can locate itself at all.

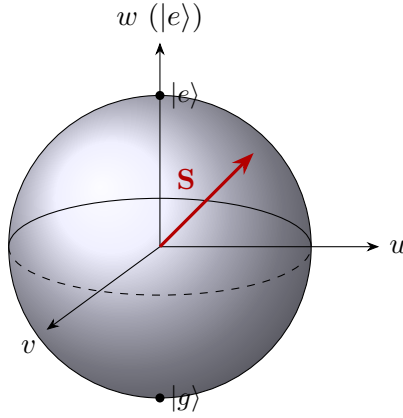


Figure 7: The Bloch sphere. A pure two-level state is the unit vector $\mathbf{S} = (u, v, w)$; coherent driving rotates it; a resonant pulse of area $\theta = \Omega t$ rotates $\mathbf{S}$ by θ about an equatorial axis fixed by the laser phase. A π -pulse carries $|g\rangle$ (south pole) to $|e\rangle$ (north pole); a $\pi/2$ -pulse lands on the equator. Dissipation, added in the next chapter, contracts the vector inward.

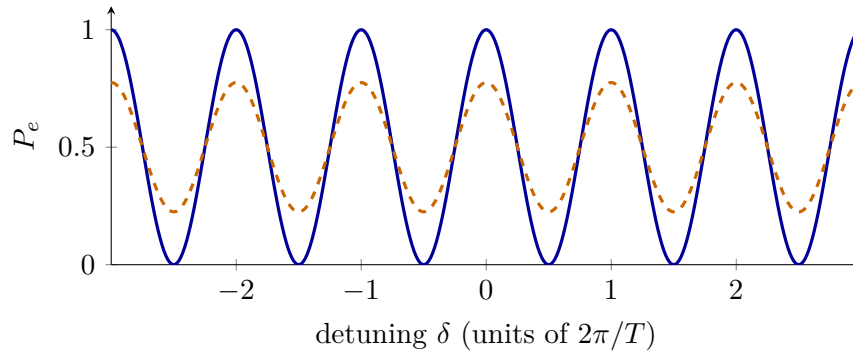


Figure 8: Ramsey fringes $P_e(\delta) = \cos^2(\delta T/2)$ from two $\pi/2$ -pulses separated by a free evolution T (Problem 7). Solid: the ideal case; dashed: with decoherence. The fringe spacing $2\pi/T$ narrows with longer interrogation time (the basis of atomic-clock precision), while decoherence reduces the fringe contrast by e^{-T/T_2} .

2.3 Dressed states of a driven atom: the light shift

Diagonalising the time-independent RWA Hamiltonian $\tilde{H}$ not only gives the Rabi frequency but also *shifts* the levels; still a purely coherent (Hamiltonian) effect, and the foundation of optical dipole traps and the AC Stark effect.

Light shift from the dressed-state energies

Step 1: eigenvalues. In the $\{|g\rangle, |e\rangle\}$ basis, $\tilde{H} = -\hbar\delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(|e\rangle\langle g| + \text{h.c.})$ is the matrix $\frac{\hbar}{2} \begin{pmatrix} 0 & \Omega \\ \Omega & -2\delta \end{pmatrix}$. Its characteristic equation $\lambda^2 + \hbar\delta\lambda - (\hbar\Omega/2)^2 = 0$ has roots

$$E_{\pm} = -\frac{\hbar\delta}{2} \pm \frac{\hbar}{2}\sqrt{\Omega^2 + \delta^2}.$$

Step 2: expand for large detuning. For $|\delta| \gg \Omega$, factor $|\delta|$ out of the square root and use $\sqrt{1+x} \simeq 1 + x/2$:

$$\sqrt{\Omega^2 + \delta^2} = |\delta|\sqrt{1 + \Omega^2/\delta^2} \simeq |\delta| + \frac{\Omega^2}{2|\delta|}.$$

The branch that connects continuously to the *bare ground state* (energy 0 when $\Omega \rightarrow 0$) is then shifted by

$$\Delta E_g \simeq + \frac{\hbar \Omega^2}{4\delta},$$

while the excited state moves by the opposite amount: the two levels *repel*, by the same second-order mechanism as stationary perturbation theory (Appendix D), with $\hbar\delta$ playing the role of the energy denominator.

Step 3: express with laboratory quantities. Using the resonant saturation parameter of Lecture 3, $I/I_{\text{sat}} = 2\Omega^2/\Gamma^2$, i.e. $\Omega^2 = \Gamma^2 I/2I_{\text{sat}}$:

$$\Delta E_g = \frac{\hbar \Gamma^2}{8\delta} \frac{I}{I_{\text{sat}}}.$$

Alternatively, writing $\Omega^2 = d^2 E_0^2/\hbar^2 = 2d^2 I/(\varepsilon_0 c \hbar^2)$ and eliminating the dipole with the spontaneous-emission formula of Lecture 5 ($d^2 = 3\pi\varepsilon_0 \hbar c^3 \Gamma/\omega_0^3$) gives the widely used form of the box below, $U_{\text{dip}} = \frac{3\pi c^2 \Gamma}{2\omega_0^3} \frac{I}{\delta}$; nothing new, just the same shift dressed in measurable parameters (Γ , I , δ).

Step 4: the sign. The sign of δ matters: a *red-detuned* beam ($\delta < 0$) lowers the ground-state energy where the intensity is highest, creating an attractive potential well; a *blue-detuned* beam repels the atom from the bright regions (used to make hollow “box” traps and atom mirrors).

Optical dipole potential

$$U_{\text{dip}}(\mathbf{r}) = \frac{\hbar \Omega^2(\mathbf{r})}{4\delta} = \frac{3\pi c^2 \Gamma}{2\omega_0^3} \frac{I(\mathbf{r})}{\delta} \quad (8)$$

This conservative potential (scaling as I/δ) traps atoms in a focused red-detuned laser, while photon scattering (scaling as I/δ^2) is suppressed at large detuning; the principle of far-off-resonance optical tweezers. (Here Γ is the natural linewidth of the transition and I_{sat} its saturation intensity.)

A far-detuned optical tweezer

A 1064 nm trap on the Na D line ($\lambda_0 = 589$ nm) has a detuning of order $\delta/2\pi \sim -2e14$ Hz. For a focused beam of 10 mW into a 1 μm waist, the peak intensity is $I = 2P/\pi w^2 \approx 6e9$ W/m², giving a trap depth $U_{\text{dip}}/k_B \sim 0.3$ mK while the scattering rate is only a few photons per second; deep enough to hold a laser-cooled atom (at ~ 10 μK after sub-Doppler cooling) for many seconds.

Holding single atoms with light: tweezers and atom arrays

The light shift you just computed is a real, usable force. Arthur Ashkin shared the 2018 Nobel Prize for turning it into “optical tweezers”, which grip everything from single atoms to living cells with nothing but a focused laser. Today this is the backbone of a leading approach to quantum computing: a laser is split into hundreds of microscopic traps, each holding exactly one neutral atom, arranged into programmable two-dimensional patterns. A complementary use of the same physics, laser cooling (1997 Nobel Prize), slows atoms from supersonic speeds to a near standstill so they can be loaded into these traps. None of it works without the simple $U_{\text{dip}} \propto I/\delta$ derived above, together with the suppression of scattering at large detuning that keeps the trapped atom coherent.

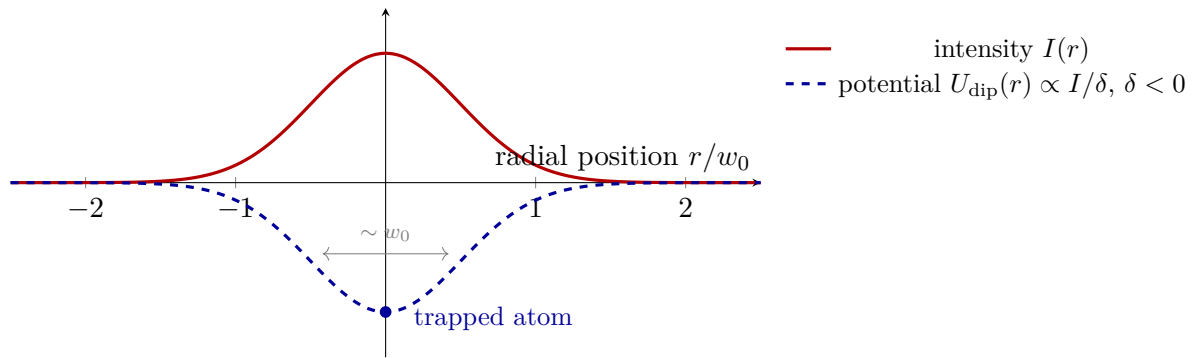


Figure 9: An optical tweezer, drawn directly from the light shift. A focused red-detuned beam has a Gaussian intensity profile (red); since $U_{\text{dip}} \propto I/\delta$ with $\delta < 0$, the intensity maximum becomes a potential *minimum* (blue dashed), a well typically ~ 1 mK deep for milliwatts of light, in which a single laser-cooled atom sits like a marble in a bowl. Blue detuning would flip the potential and expel the atom.

Can you now answer these? (Chapter 2)

- What is the physical meaning of the Rabi frequency Ω ?
- Why do we move to a frame rotating at the laser frequency before solving?
- What does a π -pulse do to the atom, and a $\pi/2$ -pulse?
- Why can a simple absorption/emission rate never reproduce Rabi flopping?

3 Dissipation: the density matrix and optical Bloch equations

Why is the Schrödinger equation no longer enough?

The Schrödinger equation describes an *isolated* system, evolving forever without loss. But a real atom is never isolated. It

- emits photons spontaneously into the surrounding vacuum,
- collides with other atoms or with phonons in a solid,
- sees a laser whose phase and intensity fluctuate,
- feels stray fields that jitter its levels.

After any of these random events we no longer know the exact wavefunction, only its statistics. A single wavefunction $|\psi\rangle = c_g |g\rangle + c_e |e\rangle$ can no longer describe the atom. We therefore need a new object, one that can hold “populations we know” together with “coherences that are being scrambled”. That object is the density matrix.

Roadmap, and the symbols introduced here

Progress: ✓ classical oscillator ✓ two-level atom ✓ coherent dynamics → **(you are here)** dissipation.

New symbols: ρ (density matrix), T_1 (population / energy relaxation time), T_2 (coherence / phase relaxation time), T_2^* (pure dephasing time), s (saturation parameter).

The clean coherent dynamics of the previous chapter is an idealisation: the Schrödinger equation describes a closed system and conserves coherence forever. Real atoms *relax*; they decay back to the ground state and they lose the phase of any superposition. This is not a minor correction to be ignored: it is simultaneously the great enemy (it limits every quantum computer and every clock) and a powerful tool (it is what makes laser cooling work and what generates the contrast in every hospital MRI scan). Capturing relaxation requires one new object, the *density matrix*, which plays the role of the friction we added by hand to the classical Lorentz oscillator. The two timescales it introduces, T_1 and T_2 , are among the most-quoted numbers in all of physics and medicine.

3.1 The density matrix as a practical tool

We do not need the full formal theory of statistical mixtures here; we need one practical piece of bookkeeping. When an atom suffers random collisions we can no longer write a single clean wavefunction $|\psi\rangle = c_g |g\rangle + c_e |e\rangle$, because the phase between c_g and c_e is being kicked at random. The fix is to track, instead of the amplitudes, the products of amplitudes, arranged in a small 2×2 table, the *density matrix*

$$\rho = \begin{pmatrix} \rho_{ee} & \rho_{eg} \\ \rho_{ge} & \rho_{gg} \end{pmatrix}, \quad \rho_{ee} = \overline{|c_e|^2}, \quad \rho_{eg} = \overline{c_e c_g^*},$$

where the bar is an average over the random kicks. Read it simply: the *diagonal* entries ρ_{gg}, ρ_{ee} are the *populations* (the chance of being in each level), and the *off-diagonal* entry ρ_{eg} is the *coherence* (the surviving phase relationship that makes interference, and hence Rabi oscillations, possible). Collisions leave the populations alone but scramble the coherence, so they drive $\rho_{eg} \rightarrow 0$ while keeping the diagonal; that single sentence is the whole physics of this chapter.

From an ensemble of wavefunctions to the density matrix

Let us make the averaging completely explicit, because this is where the new concept really enters. Picture the actual experimental situation: not one atom, but a dilute vapour of N atoms (or, equivalently, the same single atom measured over N repetitions of the experiment).

Each atom k is in a perfectly ordinary pure state,

$$|\psi_k\rangle = c_g |g\rangle + c_e e^{i\varphi_k} |e\rangle,$$

with the *same* moduli $|c_g|, |c_e|$ (they were all prepared identically) but its *own* phase φ_k , because each atom has suffered its own random history of collisions.

Step 1: what does a measurement see? Any measured signal (the fluorescence, the absorbed power, the radiated field) is a sum over the atoms, so it involves the *average* of the quantum expectation values. For the populations,

$$\overline{|c_e|^2} = \frac{1}{N} \sum_k |c_e|^2 = |c_e|^2 :$$

the phases φ_k drop out entirely; the average changes nothing. Populations are *robust* against dephasing.

Step 2: the coherence is not so lucky. The off-diagonal product picks up the phase:

$$\overline{c_e c_g^*} = c_e c_g^* \frac{1}{N} \sum_k e^{i\varphi_k} = c_e c_g^* \overline{e^{i\varphi}}.$$

If the phases are completely random over $[0, 2\pi]$, the sum of N unit vectors with random directions is $\sim \sqrt{N}$, so $\overline{e^{i\varphi}} \sim 1/\sqrt{N} \rightarrow 0$: the coherence of the ensemble is destroyed even though every individual atom is still in a pure superposition. Nothing happened to any single atom's quantum state; what died is the *agreement between atoms*.

Step 3: dephasing in time. Now let the phases random-walk: each collision, occurring at the rate $1/\tau_c$, kicks φ by a random amount. For Poissonian kicks that fully scramble the phase, the probability of having suffered *no* kick up to time t is e^{-t/τ_c} , and only those unknicked atoms still contribute to the average:

$$\overline{e^{i\varphi(t)}} = e^{-t/\tau_c} \implies \rho_{eg}(t) = \rho_{eg}(0) e^{-t/T_2^*}, \quad T_2^* = \tau_c.$$

An exponential decay of the coherence, at a rate set by the collision rate: this is precisely the $-\rho_{eg}/T_2$ term that appears in the Bloch equations below, now with a microscopic face.

Step 4: the bookkeeping object. All the averages we will ever need ($\overline{|c_e|^2}$, $\overline{c_e c_g^*}$, ...) are the entries of one 2×2 matrix, $\rho = |\psi\rangle\langle\psi|$. That is all the density matrix is: the smallest object that carries *both* the surviving populations *and* the dying coherence of an ensemble. For a single, undisturbed atom it contains nothing beyond the wavefunction ($\rho = |\psi\rangle\langle\psi|$); its power appears exactly when statistics enter.

For a two-level atom we repackage these into the same Bloch vector as in Lecture 2: $u = 2 \operatorname{Re} \rho_{eg}$, $v = 2 \operatorname{Im} \rho_{eg}$ (the coherence) and $w = \rho_{ee} - \rho_{gg}$ (the inversion). Coherent driving rotates $\mathbf{S}$; dissipation now shrinks it, and it does so along two independent directions, with two characteristic times. (The general definition $\rho = \sum_k p_k |\psi_k\rangle\langle\psi_k|$ and the Lindblad master equation from which all this follows rigorously are recalled in Appendix A, for those who want them.)

What T_1 and T_2 mean, in words

T_1 is the *energy* (population) lifetime: left alone, an excited atom returns to equilibrium in a time T_1 , so $1/T_1$ is the decay *rate* in s^{-1} . For an atom whose only loss is spontaneous emission, $T_1 = 1/\Gamma$ (the radiative lifetime of Lecture 5).

T_2 is the *phase* (coherence) lifetime: it measures how long the superposition of $|g\rangle$ and $|e\rangle$ keeps a well-defined phase. Two things destroy that phase: the population decay itself (which ends the superposition, contributing $1/2T_1$) and “pure dephasing” $1/T_2^*$ from random frequency

jitter (collisions, moving atoms), so

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}.$$

The key consequence, used repeatedly below: *a coherence that lives for a time T_2 produces a spectral line of width $1/T_2$ in angular frequency*. A short coherence time means a broad line; a long one means a sharp line. This is just the Fourier relation between a decay time and a linewidth.

T_1 and T_2 are what an MRI scanner measures

These equations are not new to medicine; Felix Bloch wrote them in 1946 for nuclear spins and won the 1952 Nobel Prize. A magnetic-resonance imaging (MRI) scanner is, at heart, a machine that applies $\pi/2$ and π pulses (here radio-frequency, on the proton spins of water) and then reads out exactly the T_1 and T_2 of those spins, voxel by voxel. Different tissues have different T_1 and T_2 (fat, grey matter, tumours, cerebrospinal fluid all relax differently), and the machine turns those numbers into the greyscale of the image. A “ T_1 -weighted” and a “ T_2 -weighted” scan of the same patient look completely different because they map the two relaxation times you have just defined. The Bloch vector is literally spinning inside every hospital.

Where the optical Bloch equations come from

Step 1: the coherent part is just Schrödinger rewritten. Take the rotating-frame amplitudes of Lecture 2, $\dot{c}_g = \frac{\Omega}{2}c_e$ and $\dot{c}_e = \frac{\Omega}{2}c_g - \delta c_e$, and differentiate the Bloch components. For the inversion, for instance,

$$\dot{w} = \frac{d}{dt}(|c_e|^2 - |c_g|^2) = 2 \operatorname{Re}(\dot{c}_e c_e^*) - 2 \operatorname{Re}(\dot{c}_g c_g^*) = -2\Omega \operatorname{Im}(c_e c_g^*) = -\Omega v,$$

and the same one-line manipulations on $\rho_{eg} = c_e c_g^*$ give $\dot{u} = \delta v$ and $\dot{v} = -\delta u + \Omega w$ (the signs of the δ and Ω terms depend on the phase conventions chosen for the field and for $|e\rangle$; we adopt the standard form, and no observable depends on the choice). Compactly, $\dot{\mathbf{S}} = \mathbf{\Omega}_{\text{eff}} \times \mathbf{S}$ with $\mathbf{\Omega}_{\text{eff}} = (-\Omega, 0, -\delta)$: coherent driving is a pure *rotation* of the Bloch vector about a fixed axis, at angular speed $\Omega_R = \sqrt{\Omega^2 + \delta^2}$. This is the geometric content of Lecture 2, and it conserves the length $|\mathbf{S}|$: nothing decays yet.

Step 2: add the damping, one term per physical process. Relaxation cannot be obtained from the Schrödinger equation (which is reversible); it must be imported from the coupling to the environment. Two experimental facts fix its form. (i) Left alone ($\Omega = 0$), the populations relax exponentially to their thermal equilibrium value $w_{\text{eq}} (= -1$ at optical frequencies, where $\hbar\omega_0 \gg k_B T)$: this adds $-(w - w_{\text{eq}})/T_1$ to $\dot{w}$. (ii) The coherence, being a *phase* relationship, is destroyed both by the population decay and by pure dephasing; it relaxes to zero at the total rate $1/T_2$: this adds $-u/T_2$ and $-v/T_2$. Linearity in ρ and the requirement that ρ remain a valid density matrix allow nothing else for a two-level system; the rigorous route (the Lindblad master equation, Appendix A) confirms exactly these terms and, for purely radiative damping, delivers the bonus relation $T_1 = 1/\Gamma$, $T_2 = 2/\Gamma$.

Optical Bloch equations

$$\begin{aligned}
\dot{u} &= \delta v - \frac{u}{T_2}, \\
\dot{v} &= -\delta u + \Omega w - \frac{v}{T_2}, \\
\dot{w} &= -\Omega v - \frac{w - w_{\text{eq}}}{T_1}.
\end{aligned} \tag{9}$$

These couple coherent driving (Ω, δ) to dissipation (T_1, T_2) and interpolate between coherent Rabi oscillations (short times, $T_{1,2} \rightarrow \infty$) and a *rate-equation limit* (long times or strong damping), in which the coherences follow the populations adiabatically and one recovers simple transition rates. The microscopic derivation from a Lindblad master equation is given in Appendix A.

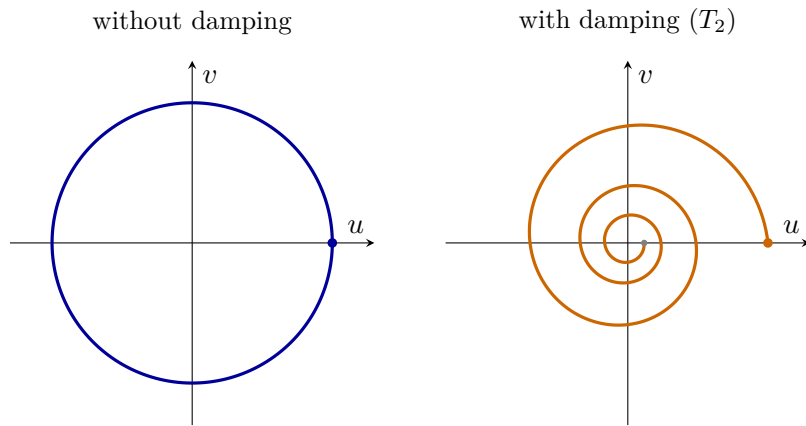


Figure 10: What dissipation does to the Bloch vector, seen in the equatorial (u - v) plane. Left: under coherent evolution alone the coherence precesses at the detuning δ and its magnitude is conserved; the trajectory is a circle. Right: with relaxation the same precession spirals inward, the coherence dying at the rate $1/T_2$; the memory of the initial phase is progressively lost. On the full sphere the vector meanwhile drifts toward the thermal equilibrium point near the south pole at the rate $1/T_1$.

3.2 Steady state, saturation and power broadening

Under continuous illumination the transients die out after a few T_1, T_2 and the Bloch vector freezes: driving (which pumps the atom up) and relaxation (which pulls it down) balance. Setting $\dot{u} = \dot{v} = \dot{w} = 0$ with $w_{\text{eq}} = -1$ turns the three differential equations into three algebraic ones, and finally proves the saturation claimed in Sec. 1.4.

Solving for the steady state

Step 1: eliminate u . From $\dot{u} = 0$: $u = \delta T_2 v$. The in-phase quadrature is slaved to the in-quadrature one.

Step 2: eliminate v . Insert into $\dot{v} = 0$:

$$0 = -\delta(\delta T_2 v) + \Omega w - \frac{v}{T_2} \implies v = \frac{\Omega T_2}{1 + \delta^2 T_2^2} w.$$

The coherence is proportional to the inversion, with a Lorentzian factor in the detuning: the atom responds only within $\sim 1/T_2$ of resonance.

Step 3: close on w . Insert into $\dot{w} = 0$:

$$0 = -\frac{\Omega^2 T_2}{1 + \delta^2 T_2^2} w - \frac{w + 1}{T_1} \implies w = -\frac{1 + \delta^2 T_2^2}{1 + \delta^2 T_2^2 + \Omega^2 T_1 T_2}.$$

Step 4: read off the population. With $\rho_{ee} = (1 + w)/2$,

$$\rho_{ee}^{\text{ss}} = \frac{1}{2} \frac{\Omega^2 T_1 T_2}{1 + \delta^2 T_2^2 + \Omega^2 T_1 T_2},$$

the boxed result. Note the structure: the drive term $\Omega^2 T_1 T_2$ competes in the denominator with the detuning term $\delta^2 T_2^2$; whichever is larger wins.

Step 5: power broadening for free. Read the same formula as a function of δ at fixed drive. It is a Lorentzian whose half-width is set by where the denominator doubles: $\delta^2 T_2^2 = 1 + \Omega^2 T_1 T_2$, i.e. a full width

$$\Delta\omega = \frac{2}{T_2} \sqrt{1 + \Omega^2 T_1 T_2} = \frac{2}{T_2} \sqrt{1 + s_0},$$

with $s_0 = \Omega^2 T_1 T_2$ the on-resonance saturation parameter. A strong drive does not just saturate the peak; it *widens* the line, because near resonance the response is already maxed out while the wings can still grow. This is why precision spectroscopy is always done at $s_0 \ll 1$: turning up the laser power to “get more signal” quietly degrades the resolution.

Steady-state excited population

$$\rho_{ee}^{\text{ss}} = \frac{1}{2} \frac{\Omega^2 T_1 T_2}{1 + \delta^2 T_2^2 + \Omega^2 T_1 T_2} = \frac{1}{2} \frac{s}{1 + s}, \quad s = \frac{\Omega^2 T_1 T_2}{1 + \delta^2 T_2^2}. \quad (10)$$

s is the *saturation parameter*. As $\Omega \rightarrow \infty$, $\rho_{ee} \rightarrow 1/2$: a strongly driven two-level atom can at most be half-excited; the bound the classical Lorentz oscillator lacked. The on-resonance linewidth broadens as $\Delta\omega = \frac{2}{T_2} \sqrt{1 + s_0}$ (*power broadening*).

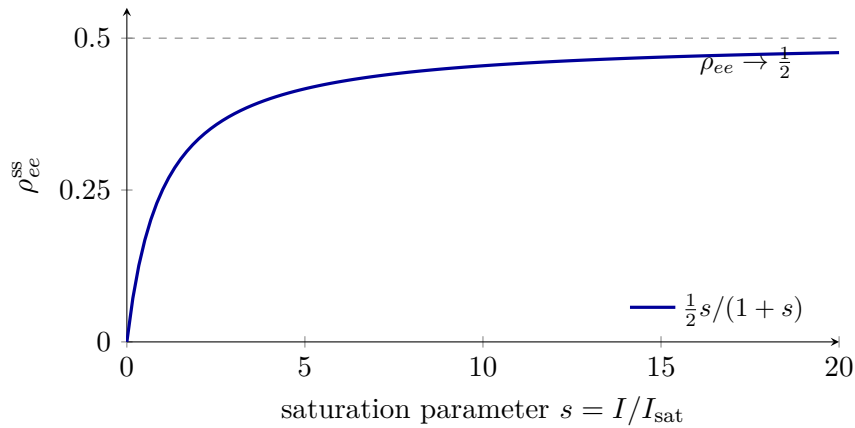


Figure 11: Saturation of a driven two-level atom. The excited population rises linearly with intensity at low drive and saturates at $\frac{1}{2}$: a two-level atom cannot be more than half-excited in steady state, capping its photon-scattering rate at $\Gamma/2$.

Where the saturation intensity comes from

For a closed, purely radiative transition, $T_1 = 1/\Gamma$ and $T_2 = 2/\Gamma$, so the resonant saturation parameter is $s_0 = \Omega^2 T_1 T_2 = 2\Omega^2/\Gamma^2$. To convert to intensity, use $\Omega^2 = d^2 E_0^2/\hbar^2$ and $I = \frac{1}{2}\varepsilon_0 c E_0^2$ (Chapter 1):

$$s_0 = \frac{4d^2}{\varepsilon_0 c \hbar^2 \Gamma^2} I \equiv \frac{I}{I_{\text{sat}}} \implies I_{\text{sat}} = \frac{\varepsilon_0 c \hbar^2 \Gamma^2}{4d^2}.$$

This still contains the dipole d , hard to measure directly. Eliminate it with the spontaneous-emission formula of Lecture 5, $d^2 = 3\pi\varepsilon_0 \hbar c^3 \Gamma/\omega_0^3$:

$$I_{\text{sat}} = \frac{\varepsilon_0 c \hbar^2 \Gamma^2 \omega_0^3}{12\pi\varepsilon_0 \hbar c^3 \Gamma} = \frac{\hbar \omega_0^3 \Gamma}{12\pi c^2} = \frac{\pi \hbar c}{3\lambda_0^3} \Gamma \quad (\text{using } \omega_0 = 2\pi c/\lambda_0, \hbar = h/2\pi).$$

Everything atom-specific has collapsed into two measured numbers, λ_0 and $\tau = 1/\Gamma$. Physically, I_{sat} is the intensity at which the atom is asked to absorb about one photon per lifetime through its resonant cross section $\sigma_0 \sim \lambda_0^2$: indeed $I_{\text{sat}} \sigma_0 \sim \hbar \omega_0 \Gamma$, one photon energy per decay time. More light than that cannot be processed; the transition clogs.

Saturation intensity of the sodium D₂ line

For a closed transition with $T_1 = 1/\Gamma$, $T_2 = 2/\Gamma$, the resonant saturation parameter is $s_0 = 2\Omega^2/\Gamma^2 = I/I_{\text{sat}}$, with

$$I_{\text{sat}} = \frac{\pi \hbar c}{3\lambda_0^3 \tau}.$$

For Na ($\lambda_0 = 589 \text{ nm}$, $\tau = 16.2 \text{ ns}$):

$$I_{\text{sat}} = \frac{\pi(6.63 \times 10^{-34})(3 \times 10^8)}{3(589 \times 10^{-9})^3(16.2 \times 10^{-9})} \approx 62 \text{ W/m}^2 = 6.2 \text{ mW/cm}^2.$$

This is the canonical scale for laser cooling: below I_{sat} the atom is unsaturated and scatters proportionally to intensity; far above it the scattering rate saturates at $\Gamma/2 \approx 3 \times 10^7$ photons/s.

Promise kept: the sodium number from Chapter 1

We can now finish the sodium calculation we deliberately left open in Chapter 1. There the laser had intensity $I = 10 \text{ mW/cm}^2$ and gave a Rabi frequency $\Omega/2\pi \approx 8.7 \text{ MHz}$, with $\Gamma/2\pi \approx 9.8 \text{ MHz}$. Two routes give the same answer. Directly, $s = I/I_{\text{sat}} = 10/6.2 \approx 1.6$. Or from the Rabi frequency, $s = \Omega^2 T_1 T_2 = 2\Omega^2/\Gamma^2 = 2(8.7/9.8)^2 \approx 1.6$. So $s \approx 1.6$, of order unity: that modest laser drives the atom *close to saturation*, and equivalently the control time $t_\pi \approx 60 \text{ ns}$ and the decay time $\tau \approx 16 \text{ ns}$ are comparable, so clean Rabi oscillations are only marginally resolved. This is the comparison we were not yet able to make in Chapter 1; now it means something.

Saturation is the engine of laser cooling

Each of those $\sim 10^7$ scattered photons per second gives the atom a tiny momentum kick. Aimed against an atomic beam, the kicks add up to a deceleration of order 10^5 times gravity, braking atoms from hundreds of metres per second to a crawl in milliseconds. Because the scattering rate *saturates* at $\Gamma/2$, there is a hard ceiling on this force, which sets how strongly one can cool; the same saturation is why an atom cannot be made to fluoresce arbitrarily brightly. Laser cooling and trapping (1997 Nobel Prize) is the gateway to almost all of modern atomic physics, including Bose–Einstein condensation and the atom arrays of the previous

chapter, and it rests on the simple $s/(1+s)$ curve you just derived.

3.3 Reversible vs irreversible dephasing: the photon echo

Pulses as rotations, and the photon echo

On the Bloch sphere every coherent operation is a rotation. In an inhomogeneous ensemble the dipoles precess at slightly different rates and fan out (T_2^* *dephasing*), so the macroscopic coherence appears to decay. A π -pulse inserted at time τ flips the fan; the faster dipoles now lag and the slower ones lead, so at 2τ they *rephase* and re-emit a burst; the *photon echo*. Crucially the echo amplitude decays only with the *true* T_2 , separating reversible dephasing (T_2^*) from irreversible decoherence. This is the optical analogue of the Hahn spin echo and a workhorse of coherent spectroscopy.

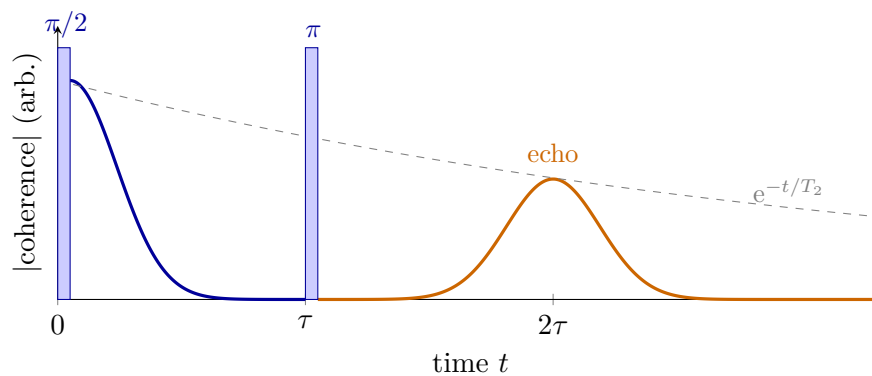


Figure 12: The photon-echo sequence. A $\pi/2$ -pulse creates the coherence, which appears to vanish rapidly by inhomogeneous (T_2^*) dephasing as the dipoles fan out. A π -pulse at $t = \tau$ flips the fan; the dipoles rephase and spontaneously re-emit a burst at $t = 2\tau$. The echo amplitude follows the *irreversible* envelope e^{-t/T_2} (grey dashed): scanning τ and recording the echo height measures the true T_2 , with the reversible inhomogeneous broadening removed.

Fighting decoherence, and building a quantum memory

T_2 is the clock that every quantum computer races against: once the phase is lost, the quantum information is gone. The echo trick generalises into *dynamical decoupling*, a train of π -pulses that repeatedly reverses the slow noise and can extend usable coherence by orders of magnitude; it is standard practice on real qubits today. The same rephasing, applied to a dense ensemble of atoms, lets one store a pulse of light as a collective coherence and then re-emit it on command: a *quantum memory*, a key component of future quantum networks and the quantum internet. Reversible versus irreversible dephasing, the distinction this section is built on, is therefore the dividing line between information you can recover and information you have truly lost.

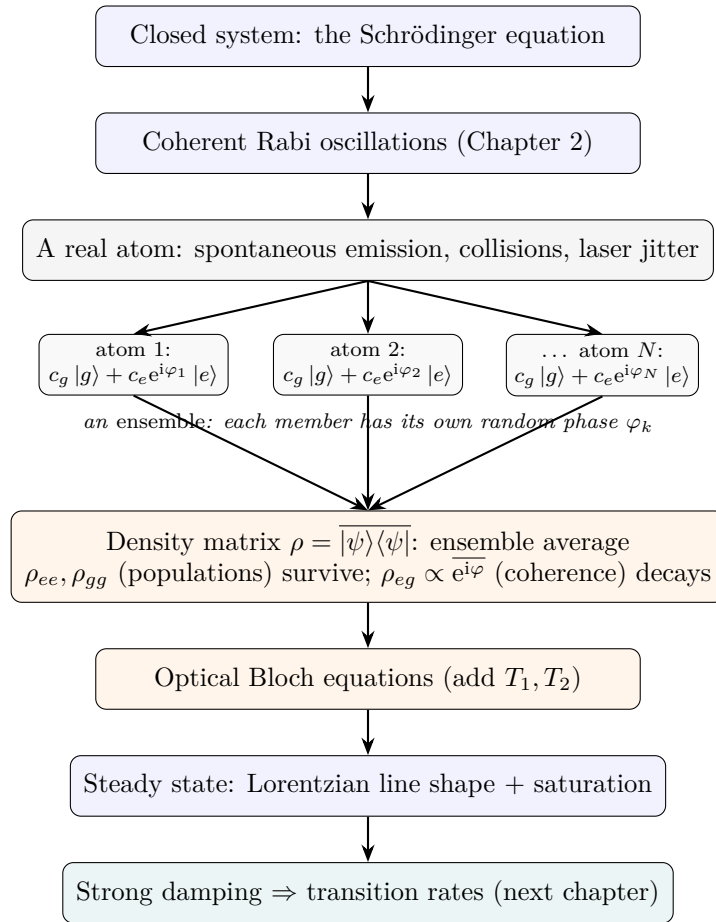


Figure 13: Concept map of Chapter 3. The coherent motion of Chapter 2 (top) is disturbed by the real world (grey). The key conceptual step is statistical: we describe not one wavefunction but an *ensemble*, many atoms (or many repetitions of the same experiment), each with its own randomly kicked phase φ_k . Averaging over the ensemble defines the density matrix ρ : the populations, which do not depend on φ , survive the average, while the coherence, which carries $e^{i\varphi}$, is washed out at the rate $1/T_2$. The equations of motion of ρ are the optical Bloch equations; their steady state gives the line shape and saturation, and their strong-damping limit is the rate picture of the next chapter.

The story of this chapter, in one picture

Can you now answer these? (Chapter 3)

- Why is a single wavefunction no longer enough to describe a real atom?
- What is the physical difference between T_1 and T_2 ?
- Why can a strongly driven two-level atom never be more than half excited?
- Why does a coherence that lives for a time T_2 produce a line of width $1/T_2$?

4 Fermi’s golden rule

Why do coherent oscillations turn into transition rates?

In Lecture 2 a driven atom *oscillated* between two levels; nothing decayed, and there was no “rate”. Yet a spectroscopist measures exactly rates: an absorption coefficient, a number of fluorescence photons per second. How can the same atom show reversible oscillation in one experiment and a steady rate in another? The answer is that a rate appears when the atom couples not to *one* final state but to a whole *continuum* of them (many photon directions, many final momenta). This chapter shows precisely when and how oscillation becomes rate, and the result, Fermi’s golden rule, is the single most reused formula in the whole course.

Roadmap, and the symbols introduced here

Progress: ✓ coherent dynamics ✓ dissipation → **(you are here)** transition rates.
 New symbols: $W_{i \rightarrow f}$ (transition rate, per second), $\rho(E)$ (density of final states), A, B (Einstein coefficients), σ_0 (resonant absorption cross section), f (oscillator strength).

So far we have followed the two-level atom under a strong, resonant drive (Lectures 2 and 3). We now ask a different and more elementary question: if a *weak* field shines on an atom, at what *rate* does it kick the atom from one state to another? This rate is what a spectroscopist actually measures (an absorption coefficient, a fluorescence intensity), and it is the quantity that, in the limit of strong dephasing, the optical Bloch equations of Lecture 3 reduce to. The tool that delivers it is time-dependent perturbation theory, and its central result is Fermi’s golden rule.

4.1 Time-dependent perturbation theory: the idea

Before any algebra, here is the physical picture. The atom alone has a set of known stationary states $|n\rangle$ with energies E_n (Appendix C). A weak applied field is a small, time varying perturbation $V(t)$ added to the atomic Hamiltonian. It cannot change the states themselves much, but it can slowly *leak* probability from the initially occupied state $|i\rangle$ into other states $|f\rangle$. Perturbation theory is simply the systematic expansion of that leak in powers of the small coupling V ; to lowest order we keep only one power, which is why the answer ends up proportional to $|V_{fi}|^2$.

Reminder: what we assume, and what “rate” means

Three physical assumptions underlie everything in this lecture (the mathematics in Appendix D makes them precise).

1. **Weak coupling.** The field is weak enough that the initial state is barely emptied over the times of interest, so we may set its amplitude to one and keep only first order in V .
2. **Intermediate times.** We watch for a time long compared with an optical period $1/\omega_0$ (so that energy conservation becomes sharp) but short compared with the depletion time (so that assumption 1 holds). For an optical transition this window is enormous (femtoseconds to nanoseconds).
3. **A continuum of final states.** A genuine *rate* (a constant probability per unit time) appears only when the atom can decay into many closely spaced final states; their number per unit energy is the density of states ρ , which is why ρ appears in the final formula. With a single final state one gets oscillations, not a rate (this is exactly the coherent Rabi flopping of Lecture 2).

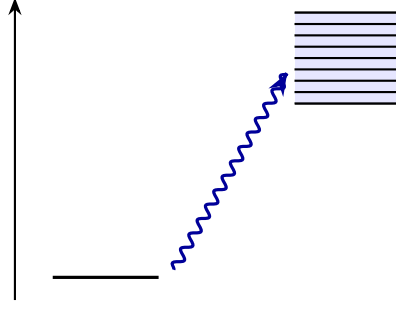


Figure 14: The setting of the golden rule. A single initially occupied state (lower left) is weakly coupled (wavy arrow) to a dense band of final states (upper right, shaded); the vertical direction is energy. The transition rate is proportional to the squared coupling and to the number of final states available per unit energy (the density of states). With only one final state the probability would oscillate instead of growing steadily.

4.2 The first-order amplitude

Write $H = H_0 + V(t)$ with $H_0 |n\rangle = E_n |n\rangle$ and expand $|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$. Inserting into the Schrödinger equation gives the exact coupled equations

$$i\hbar \dot{c}_m(t) = \sum_n V_{mn}(t) e^{i\omega_{mn}t} c_n(t), \quad \omega_{mn} = \frac{E_m - E_n}{\hbar}. \quad (11)$$

For a system prepared in $|i\rangle$ with a weak perturbation switched on at $t = 0$, to first order $c_i \approx 1$ and

$$c_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{fi}(t') e^{i\omega_{fi}t'} dt'. \quad (12)$$

This derivation answers two separate questions

Keep them apart in your head, because they are genuinely different. *First question: why does a steady **rate** appear at all?* That is Steps 1–4 below, and the key event is that the probability builds up in proportion to time. *Second question: why does the **density of states** enter?* That is Step 5, and it comes purely from summing over the continuum of final states. Nothing forces the two ideas to occur together; they just both happen to be needed here.

First idea: why a rate appears (Steps 1–4)

Step 1: the perturbation. Take a harmonic perturbation

$$V(t) = V e^{-i\omega t} + V^\dagger e^{+i\omega t},$$

whose two terms describe respectively the absorption ($E_f > E_i$) and stimulated emission ($E_f < E_i$) of one quantum $\hbar\omega$. We treat absorption and keep only the first term.

Step 2: write down and evaluate the amplitude. Ordinary first-order perturbation theory (Appendix D) gives the amplitude to have leaked from $|i\rangle$ into $|f\rangle$ after a time t as

$$c_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{fi} e^{i\omega_{fi}t'} dt', \quad \omega_{fi} = \frac{E_f - E_i}{\hbar}.$$

All the physics sits in the phase, so it pays to name the *energy mismatch* between the photon and the level spacing, $\Delta \equiv \omega_{fi} - \omega$ (it is zero exactly on resonance). Combining the drive's $e^{-i\omega t'}$ with the level phase $e^{i\omega_{fi}t'}$ leaves $e^{i\Delta t'}$, so

$$c_f^{(1)}(t) = \frac{V_{fi}}{i\hbar} \int_0^t e^{i\Delta t'} dt' = \frac{V_{fi}}{i\hbar} \frac{e^{i\Delta t} - 1}{i\Delta} = -\frac{V_{fi}}{\hbar} \frac{e^{i\Delta t} - 1}{\Delta},$$

where we simply did the elementary integral $\int_0^t e^{i\Delta t'} dt' = (e^{i\Delta t} - 1)/i\Delta$. Already the essential asymmetry is visible: on resonance ($\Delta \rightarrow 0$) the amplitude keeps growing, while off resonance it only wobbles between fixed bounds.

Step 3: turn the amplitude into a probability. What we can measure is the probability $P_{i \rightarrow f} = |c_f^{(1)}|^2$, so we take the modulus squared. The only awkward factor is $|e^{i\Delta t} - 1|^2$; evaluate it by multiplying by its complex conjugate, then use $1 - \cos x = 2 \sin^2(x/2)$:

$$|e^{i\Delta t} - 1|^2 = (e^{i\Delta t} - 1)(e^{-i\Delta t} - 1) = 2 - 2 \cos \Delta t = 4 \sin^2 \frac{\Delta t}{2}.$$

Therefore

$$P_{i \rightarrow f}(t) = \frac{|V_{fi}|^2}{\hbar^2} \frac{4 \sin^2(\Delta t/2)}{\Delta^2} = \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2(\Delta t/2)}{(\Delta/2)^2}.$$

As a function of the mismatch Δ this is peaked at resonance and decays in wiggles away from it (it is the curve plotted in Fig. 16).

Step 4: watch it for a long time. Now ask what this looks like once we have waited a time t long compared with a single optical cycle. Write the lineshape $f_t(\Delta) = \sin^2(\Delta t/2)/(\Delta/2)^2$ and read off three facts, each a one-line calculation:

- *Height.* At $\Delta = 0$, using $\sin x \simeq x$, we get $f_t(0) = t^2$: the peak grows as t^2 .
- *Width.* The first zeros are where $\Delta t/2 = \pm\pi$, i.e. $\Delta = \pm 2\pi/t$: the peak narrows as $1/t$.
- *Area.* With the substitution $u = \Delta t/2$, $\int_{-\infty}^{+\infty} f_t(\Delta) d\Delta = 2t \int_{-\infty}^{+\infty} \frac{\sin^2 u}{u^2} du = 2\pi t$, using the standard integral $\int (\sin^2 u / u^2) du = \pi$.

A spike whose height diverges, whose width vanishes, but whose area is a finite $2\pi t$, is by definition a Dirac delta:

$$f_t(\Delta) \xrightarrow{t \rightarrow \infty} 2\pi t \delta(\Delta).$$

Physically, this δ is just *energy conservation becoming exact*: after enough time, only the final states with $E_f = E_i + \hbar\omega$ get any probability at all. The probability grows in *proportion to time*: that is the whole content of the first idea, and it is what lets us speak of a constant rate rather than an ever-changing probability.

Second idea: why the density of states appears (Step 5)

Step 5: rate and sum over final states. Hence $P_{i \rightarrow f}(t) = \frac{2\pi t}{\hbar^2} |V_{fi}|^2 \delta(\Delta)$ grows *linearly* in t , which defines a time-independent rate $W = P/t$. So far this is for one final state. But a real final state belongs to a continuum; summing over it with density of states $\rho(E_f)$ and converting the frequency δ -function to an energy one via $\delta(\Delta) = \delta((E_f - E_i - \hbar\omega)/\hbar) = \hbar \delta(E_f - E_i - \hbar\omega)$ gives

$$W = \sum_f \frac{2\pi}{\hbar^2} |V_{fi}|^2 \hbar \delta(E_f - E_i - \hbar\omega) = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f) \Big|_{E_f = E_i + \hbar\omega}.$$

Fermi's golden rule

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \rho(E_f) \Big|_{E_f = E_i + \hbar\omega} \quad (13)$$

The rate is constant in time (valid for $1/\omega_0 \ll t \ll$ depletion time), proportional to the squared coupling matrix element and (crucially) to the *density of final states* ρ . The last factor is the lever that the Purcell effect (Sec. 7) will exploit.

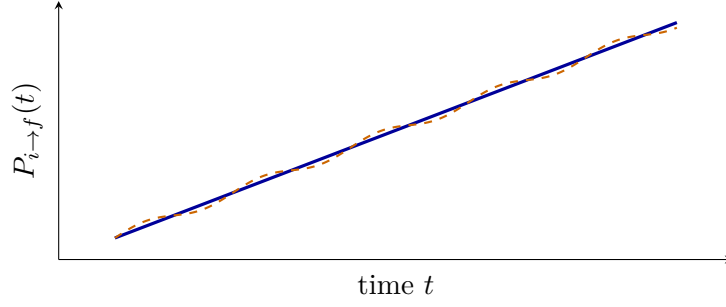


Figure 15: Why a constant rate emerges. Summed over the continuum of final states, the probability of having left the initial state grows in proportion to time (solid line); its slope *is* the transition rate W . The dashed curve recalls that a single final state would merely oscillate; only the continuum turns oscillation into steady decay. The linear law holds in the window where the state is neither freshly prepared nor appreciably depleted.

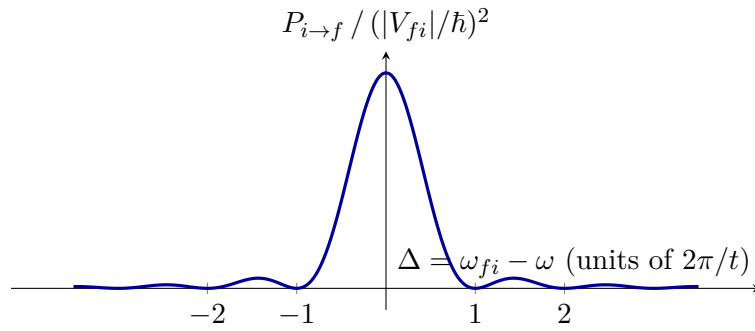


Figure 16: The transition probability $\propto \text{sinc}^2(\Delta t/2)$. Its central peak height grows as t^2 and its width narrows as $1/t$, so the *area* grows as t : this linear-in-time growth is what defines a constant rate and, in the limit, the energy-conserving δ -function.

Exercise 2.1: validity window of the golden rule

The derivation assumes (i) $t \gg 1/\omega_0$ so that the peak in Fig. 16 is narrow on the scale of ω_0 , and (ii) $t \ll 1/W$ so that the initial state is not appreciably depleted ($c_i \approx 1$). For the Na D₂ line ($\omega_0 \sim 10^{15} \text{ s}^{-1}$, $\Gamma \sim 10^8 \text{ s}^{-1}$) this leaves a huge window $10^{-15} \text{ s} \ll t \ll 10^{-8} \text{ s}$ in which the rate picture is exact; justifying its everyday use.

4.3 Selection rules: which transitions are allowed

The golden-rule rate is proportional to $|\mathbf{d}_{fi}|^2 = |\langle f | \hat{\mathbf{d}} | i \rangle|^2$. For most pairs of states this matrix element is exactly zero, and the transition simply does not happen no matter how strong the light. The rules that say when $\mathbf{d}_{fi} \neq 0$ are the *selection rules*, and they are the reason atomic spectra consist of a few sharp lines rather than a featureless smear. Their origin is simple bookkeeping of symmetry and angular momentum.

Physical picture: the photon carries angular momentum

A photon is a spin-1 particle of odd parity. When the atom absorbs or emits one, that unit of angular momentum and that change of parity must be accounted for by the electron. This single fact produces all the rules below: the electron's orbital must change by one unit, and its spatial parity must flip.

Electric-dipole selection rules

A one-electron transition is electric-dipole allowed only if

- parity: initial and final states have *opposite* parity;
- orbital: $\Delta\ell = \pm 1$;
- magnetic: $\Delta m = 0, \pm 1$ ($\Delta m = 0$ for light polarised along z , $\Delta m = \pm 1$ for circular);
- spin: $\Delta s = 0$, $\Delta j = 0, \pm 1$ (but not $j=0 \rightarrow j=0$).

If any rule is violated, $\mathbf{d}_{fi} = 0$ and the line is “forbidden” (it can still appear, far more weakly, through magnetic-dipole or electric-quadrupole coupling).

Why this matters for spectroscopy

The strong sodium D line is $3s \rightarrow 3p$ ($\Delta\ell = +1$): allowed, hence bright. A $3s \rightarrow 3d$ ($\Delta\ell = +2$) or $3s \rightarrow 4s$ ($\Delta\ell = 0$) transition is dipole-forbidden and essentially absent. Because each element has its own ladder of levels and its own allowed jumps, the set of observed lines is a fingerprint that identifies the atom; this is the entire basis of emission and absorption spectroscopy.

The aurora: forbidden lines painted across the sky

The eerie green of the aurora borealis is a *forbidden* line: the 557.7 nm transition of atomic oxygen violates the electric-dipole rules, so its upper state lives for ≈ 0.7 s; ten million times longer than an allowed state. At ground-level densities a collision would carry the energy away long before such a slow photon could be emitted, which is why this light exists only in the rarefied upper atmosphere (~ 100 km up), where seconds pass between collisions. The red auroral curtain higher still comes from an even more forbidden oxygen line ($\tau \approx 110$ s). Nebulae glow with similar “forbidden” lines that were once attributed to a new element (“nebulium”) because no laboratory gas, at laboratory density, could ever show them. Selection rules do not just organise spectra; they decide what parts of the universe are allowed to shine.

How we know what stars are made of

We will never bring back a sample of a star, yet we know their compositions precisely. Starlight passing through a cooler outer layer has exactly the dipole-allowed wavelengths absorbed, leaving dark lines (the Fraunhofer lines) at the positions fixed by each element’s selection rules. Helium was discovered this way, in the spectrum of the Sun, before it was ever found on Earth. The same trick, applied to the faint light filtering through a planet’s atmosphere as it crosses its star, is how we now detect water and other molecules on planets light-years away. Every one of those measurements is the golden rule plus a selection rule: a transition either has $\mathbf{d}_{fi} \neq 0$ and prints a line, or it does not.

4.4 Absorption, stimulated emission and Einstein coefficients

For the dipole coupling in a field of spectral energy density $u(\omega)$, the golden rule yields stimulated rates proportional to $u(\omega_0)$; we first derive that proportionality (and its coefficient B) rather than assume it.

The B coefficient from first-order perturbation theory

Step 1: a broadband field is a continuum in disguise. Thermal light is not monochromatic: it contains a dense spread of frequencies with random phases. The roles are swapped relative to the golden-rule setup above: the *atomic* final state is unique, but the *perturbation*

itself supplies a continuum of frequencies. The same $\text{sinc}^2 \rightarrow \delta$ mechanism will operate, now integrated over the spectrum.

Step 2: one spectral slice. A component of amplitude E_ω in a band $d\omega$ drives the transition with $|V_{fi}| = \frac{1}{2}|\mathbf{d} \cdot \boldsymbol{\epsilon}|E_\omega$, giving (Step 3 of the golden-rule box) $P(t) = \frac{|V_{fi}|^2}{\hbar^2} f_t(\omega - \omega_0)$. For isotropic, unpolarized light the orientation average is $\langle |\mathbf{d} \cdot \boldsymbol{\epsilon}|^2 \rangle = d^2/3$, and the electromagnetic energy density in the slice fixes the amplitude: $u(\omega)d\omega = \frac{1}{2}\varepsilon_0 E_\omega^2$, i.e. $E_\omega^2 = 2u(\omega)d\omega/\varepsilon_0$.

Step 3: add the slices (random phases add probabilities). Because thermal phases are uncorrelated, the contributions add incoherently:

$$P(t) = \int \frac{d^2}{3} \frac{2u(\omega)}{4\hbar^2\varepsilon_0} f_t(\omega - \omega_0) d\omega \simeq \frac{d^2 u(\omega_0)}{6\varepsilon_0\hbar^2} \underbrace{\int f_t(\Delta) d\Delta}_{=2\pi t} = \frac{\pi d^2}{3\varepsilon_0\hbar^2} u(\omega_0) t,$$

where $u(\omega)$ was taken out at ω_0 because f_t is sharply peaked there. Linear in t : a rate. Hence

$$W_{\text{abs}} = B u(\omega_0), \quad B = \frac{\pi d^2}{3\varepsilon_0\hbar^2}$$

The same algebra with $E_f < E_i$ gives the identical coefficient for stimulated emission; the equality $B_{12} = B_{21}$ is automatic, not an assumption.

Step 4: a consistency check to savour. Combine with the thermodynamic relation $A/B = \hbar\omega_0^3/\pi^2c^3$ derived below:

$$A = \frac{\hbar\omega_0^3}{\pi^2c^3} \cdot \frac{\pi d^2}{3\varepsilon_0\hbar^2} = \frac{\omega_0^3 d^2}{3\pi\varepsilon_0\hbar c^3},$$

which is *exactly* the spontaneous rate Γ that Lecture 5 will obtain from field quantization. Einstein's 1917 thermodynamics knew the answer before the theory existed.

Comparing with Einstein's phenomenological rate equations for a two-level atom in thermal radiation,

$$\dot{N}_e = -A N_e - B u(\omega_0) N_e + B u(\omega_0) N_g, \quad (14)$$

fixes the famous relations.

Planck's law, derived (we are about to use it)

The detailed-balance argument below needs the spectral energy density $u(\omega)$ of thermal radiation. Since we have all the ingredients, let us build it rather than quote it; the calculation takes four lines and is one of the most consequential in the history of physics.

Step 1: count the modes. From the mode counting of Appendix A.3, a cavity holds $\rho(\omega) = \omega^2/\pi^2c^3$ modes per unit volume and unit angular frequency. The energy density is then

$$u(\omega) = \rho(\omega) \times \langle E \rangle_{\text{per mode}}.$$

Step 2: the classical answer, and its catastrophe. Classically each mode is an oscillator in equilibrium and equipartition gives $\langle E \rangle = k_B T$, independent of frequency. Then $u \propto \omega^2 k_B T$ grows without bound: integrated over all frequencies the oven contains infinite energy. This is the ultraviolet catastrophe of Chapter 0; the mode counting is impeccable, so the error must lie in $\langle E \rangle$.

Step 3: Planck's mean energy. Let each mode exchange energy only in packets $\hbar\omega$, so its allowed energies are $E_n = n\hbar\omega$ with Boltzmann weights e^{-nx} , $x \equiv \hbar\omega/k_B T$. The partition function is a geometric series, $Z = \sum_{n \geq 0} e^{-nx} = 1/(1 - e^{-x})$, and the mean occupation follows

by the standard trick of differentiating $\ln Z$:

$$\langle n \rangle = -\frac{d \ln Z}{dx} = \frac{e^{-x}}{1 - e^{-x}} = \frac{1}{e^{\hbar\omega/k_B T} - 1}.$$

For $\hbar\omega \ll k_B T$ this returns $\langle E \rangle = \hbar\omega \langle n \rangle \rightarrow k_B T$ (classical limit); for $\hbar\omega \gg k_B T$ it is exponentially cut off, because a mode that can only take a big first step $\hbar\omega$ is frozen out. The quantum of energy is what tames the ultraviolet.

Step 4: assemble.

$$u(\omega) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

This is Planck’s law (1900), the first quantum formula ever written, and the input the detailed-balance argument requires.

Detailed balance fixes A/B

Step 1: equilibrium populations. At thermal equilibrium the rate equation $\dot{N}_e = 0$ holds and the level populations follow Boltzmann statistics (equal degeneracies), $N_e/N_g = e^{-\hbar\omega_0/k_B T}$.

Step 2: balance the rates. Setting $\dot{N}_e = -AN_e - BuN_e + BuN_g = 0$ and dividing by N_g ,

$$A \frac{N_e}{N_g} + Bu \frac{N_e}{N_g} = Bu \Rightarrow A e^{-\hbar\omega_0/k_B T} = Bu(1 - e^{-\hbar\omega_0/k_B T}).$$

Step 3: solve for u . Divide through by $B e^{-\hbar\omega_0/k_B T}$:

$$u(\omega_0) = \frac{A/B}{e^{\hbar\omega_0/k_B T} - 1}.$$

Step 4: match Planck. This must equal the Planck spectral energy density $u(\omega_0) = \frac{\hbar\omega_0^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega_0/k_B T} - 1}$. The temperature-dependent Bose factor $1/(e^{\hbar\omega_0/k_B T} - 1)$ is identical on both sides and cancels, leaving a relation valid at *all* T :

$$\frac{A}{B} = \frac{\hbar\omega_0^3}{\pi^2 c^3}.$$

Step 5: the lesson. Spontaneous emission (A) is *required* by consistency; without it the populations could not reach equilibrium. Yet a purely classical or semiclassical field gives $A = 0$: only quantizing the vacuum (Sec. 5) supplies it. This logical gap is the bridge from L2 to L3.

The resonant cross section $\sigma_0 = 3\lambda^2/2\pi$

First, what is a cross section? It is the effective “target area” the atom presents to the beam: (power removed from the beam) = $\sigma \times$ (incident intensity). A big σ means a strongly absorbing atom. We compute it from resonant *scattering*, the driven dipole re-radiating the light it absorbs, and the striking result will be that σ_0 does *not* depend on how strong the dipole is, only on the wavelength.

Step 1: scattered power. A dipole oscillating as $\mathbf{p}(t) = \text{Re}[\mathbf{p}_0 e^{-i\omega t}]$ radiates the time-averaged (Larmor) power

$$P_{\text{sc}} = \frac{\omega^4 |\mathbf{p}_0|^2}{12\pi\epsilon_0 c^3}.$$

(Where does this come from? Larmor’s formula $P = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}$ for an accelerating charge is derived in electromagnetism courses from the radiation zone of the retarded potentials; its *structure* is forced on us: the power must be even in the charge and in the acceleration, hence $\propto q^2 a^2$, and the only combination of $q^2 a^2, \epsilon_0, c$ with the dimensions of power is $q^2 a^2 / \epsilon_0 c^3$. For our dipole, $qa \rightarrow |\dot{p}| = \omega^2 |p_0|$ and time-averaging the $\cos^2$ brings the extra $\frac{1}{2}$, giving the expression above.)

Step 2: incident flux and definition of σ . The driving plane wave of amplitude E_0 carries intensity $I = \frac{1}{2}\epsilon_0 c E_0^2$. With $\mathbf{p}_0 = \alpha(\omega)\mathbf{E}_0$ (the polarizability of Sec. 1), the cross section is

$$\sigma(\omega) = \frac{P_{\text{sc}}}{I} = \frac{\omega^4 |\alpha|^2 E_0^2 / 12\pi\epsilon_0 c^3}{\frac{1}{2}\epsilon_0 c E_0^2} = \frac{\omega^4 |\alpha(\omega)|^2}{6\pi\epsilon_0^2 c^4}.$$

Step 3: polarizability on resonance. From $\alpha(\omega) = \frac{e^2/m_e}{\omega_0^2 - \omega^2 - i\gamma_c\omega}$, at $\omega = \omega_0$ the real part of the denominator vanishes, leaving $\alpha(\omega_0) = \frac{e^2/m_e}{-i\gamma_c\omega_0}$, hence

$$|\alpha(\omega_0)|^2 = \frac{(e^2/m_e)^2}{\gamma_c^2 \omega_0^2}.$$

Step 4: the radiative damping rate. If radiation is the *only* loss, the damping rate is fixed self-consistently: the oscillator’s energy must decay exactly as fast as it is radiated away. A free oscillation of amplitude x_0 stores $U = \frac{1}{2}m_e\omega_0^2 x_0^2$ and radiates (Step 1, with $p_0 = ex_0$) $P_{\text{rad}} = e^2\omega_0^4 x_0^2 / 12\pi\epsilon_0 c^3$. The energy decay rate, which for a damped oscillator equals γ_c (since $U \propto x_0^2 \propto e^{-\gamma_c t}$), is therefore

$$\gamma_c = \frac{P_{\text{rad}}}{U} = \frac{e^2\omega_0^4 x_0^2 / 12\pi\epsilon_0 c^3}{\frac{1}{2}m_e\omega_0^2 x_0^2} = \frac{e^2\omega_0^2}{6\pi\epsilon_0 m_e c^3} \implies \gamma_c^2 = \frac{e^4\omega_0^4}{36\pi^2\epsilon_0^2 m_e^2 c^6}.$$

(For an optical transition $\gamma_c \sim 10^8 \text{ s}^{-1}$, remarkably close to the true quantum Γ : the classical estimate is off only by the oscillator strength $f \sim 1$.)

Step 5: assemble. Substitute Steps 3–4 into Step 2:

$$\sigma_0 = \frac{\omega_0^4}{6\pi\epsilon_0^2 c^4} \frac{(e^2/m_e)^2}{\gamma_c^2 \omega_0^2} = \frac{\omega_0^2}{6\pi\epsilon_0^2 c^4} \frac{e^4/m_e^2}{e^4\omega_0^4 / (36\pi^2\epsilon_0^2 m_e^2 c^6)} = \frac{\omega_0^2}{6\pi\epsilon_0^2 c^4} \cdot \frac{36\pi^2\epsilon_0^2 c^6}{\omega_0^4} = \frac{6\pi c^2}{\omega_0^2}.$$

Every reference to e , m_e and the dipole has cancelled. Finally, with $k = \omega_0/c = 2\pi/\lambda_0$,

$$\sigma_0 = \frac{6\pi c^2}{\omega_0^2} = \frac{6\pi}{k^2} = \frac{3\lambda_0^2}{2\pi}$$

Step 6: degeneracies. For a real transition this isotropic value is multiplied by $(2J_e + 1)/[3(2J_g + 1)]$ and by a polarization/orientation factor; the order of magnitude $\sim \lambda_0^2$ is universal. The atom’s resonant “size” is set purely by the wavelength: a weaker dipole simply gives a narrower line of the same peak cross section.

Photoionization-style estimate of an absorption cross section

The resonant absorption cross section of a two-level atom is, on resonance, $\sigma_0 = 3\lambda_0^2/2\pi$. For

the Na D₂ line ($\lambda_0 = 589 \text{ nm}$):

$$\sigma_0 = \frac{3(589 \times 10^{-9})^2}{2\pi} \approx 1.66 \times 10^{-13} \text{ m}^2 = 1.66 \times 10^{-9} \text{ cm}^2.$$

This is about 10^5 times the geometric cross section ($\pi a_0^2 \sim 10^{-16} \text{ cm}^2$): on resonance an atom is an enormously efficient absorber. A vapor with density $N = 1 \times 10^{16} \text{ m}^{-3}$ has an absorption coefficient $\alpha = N\sigma_0 \approx 1.7 \times 10^3 \text{ m}^{-1}$, i.e. an e -folding length of $\sim 0.6 \text{ mm}$.

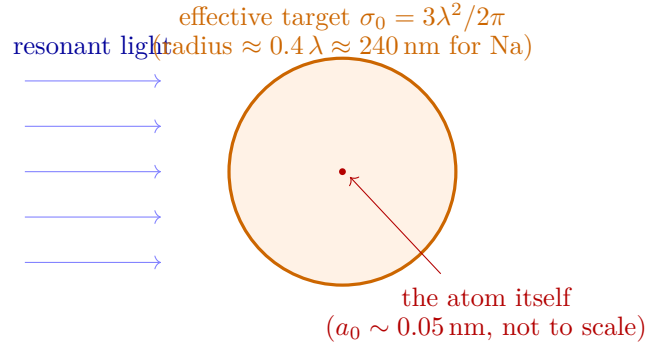


Figure 17: How big is an atom, as seen by resonant light? Not its geometric size. On resonance the sodium atom removes photons from the beam as if it were a disc of area $\sigma_0 = 3\lambda_0^2/2\pi$, about 10^5 times its geometric cross section: the atom “fills” a region set by the *wavelength*, not by its electron cloud. Off resonance this target shrinks by the Lorentzian factor $1/(1 + 4\delta^2/\Gamma^2)$.

4.5 Oscillator strength and the sum rule

It is convenient to compare the quantum result with the classical Lorentz oscillator of Sec. 1 through the dimensionless *oscillator strength*

$$f_{ge} = \frac{2m_e\omega_0}{\hbar e^2} |\mathbf{d}_{ge}|^2, \quad (15)$$

which measures how many “classical electrons” a transition is worth.

Thomas–Reiche–Kuhn sum rule

$$\sum_e f_{ge} = Z \quad (16)$$

The oscillator strengths of all transitions from a given state sum to the number of electrons Z . A strong resonance line ($f \simeq 1$) therefore exhausts most of the available strength, which is why a single transition (the D line for Na) dominates the optical response of an alkali atom. The sum rule is the quantum statement that the medium contains a fixed total amount of polarizability, distributed among its resonances.

Proof of the sum rule in four lines

The proof is a beautiful commutator trick; nothing about light is needed, only $[x, p] = i\hbar$. Work with one electron ($Z = 1$) and one Cartesian component x .

Step 1: a double commutator with a fixed value. With $H = p^2/2m_e + V(\mathbf{r})$, $[H, x] = -i\hbar p/m_e$ (the potential commutes with x), and therefore

$$[x, [H, x]] = \left[x, -\frac{i\hbar}{m_e} p \right] = \frac{\hbar^2}{m_e},$$

a pure number, independent of the potential.

Step 2: the same object as a sum over states. Expand the double commutator and insert a complete set of eigenstates $|e\rangle$ between the operators:

$$\langle g | [x, [H, x]] | g \rangle = 2 \sum_e (E_e - E_g) |\langle e | x | g \rangle|^2.$$

Step 3: equate. With $\hbar\omega_{eg} = E_e - E_g$ and the definition $f_{ge} = 2m_e\omega_{eg}|x_{eg}|^2/\hbar$ (which is the oscillator strength above, since $d = ex$):

$$\frac{\hbar^2}{m_e} = 2 \sum_e \hbar\omega_{eg}|x_{eg}|^2 \implies \sum_e f_{ge} = 1.$$

For Z independent electrons the contributions add, giving $\sum f = Z$. Note that transitions *downward* from an excited state enter with $\omega_{eg} < 0$, i.e. negative oscillator strength: an inverted medium has negative absorption, which is gain, the seed of the laser.

From oscillator strength to the decay rate

Substituting $|\mathbf{d}_{ge}|^2 = \hbar e^2 f_{ge} / (2m_e\omega_0)$ into the spontaneous-emission rate of Sec. 5, $\Gamma = \omega_0^3 d^2 / 3\pi\epsilon_0 \hbar c^3$, gives the compact and widely used form

$$\Gamma = \frac{\omega_0^3}{3\pi\epsilon_0 \hbar c^3} \cdot \frac{\hbar e^2 f_{ge}}{2m_e\omega_0} = \frac{e^2 \omega_0^2}{6\pi\epsilon_0 m_e c^3} f_{ge} = \gamma_c f_{ge}.$$

The quantum decay rate is the *classical* radiative rate γ_c of Sec. 4 times the oscillator strength: f literally measures “what fraction of a classical electron” the transition behaves as. For a fully allowed transition ($f \simeq 1$) at $\lambda_0 = 500 \text{ nm}$ this yields $\Gamma \sim 10^8 \text{ s}^{-1}$ ($\tau \sim$ a few ns), the universal order of magnitude for optical dipole transitions.

Can you now answer these? (Chapter 4)

- Why does a constant transition *rate* appear only when the final states form a continuum?
- Where does the density of states $\rho(E)$ come from in the golden rule?
- Why does a purely classical field predict $A = 0$, and what does that force us to do next?
- Give one dipole-allowed and one dipole-forbidden transition, and say why.

5 Field quantization and spontaneous emission

Why can't a classical field explain spontaneous emission?

Take an excited atom and switch off every lamp and laser. Classically the electric field is now exactly zero, so the force on the atom is zero, so nothing should happen: the atom should stay excited forever. But it does not; it decays, emitting a photon, in nanoseconds. Something must remain in “empty” space to knock it down. That something is the irreducible fluctuation of the *quantized* electromagnetic field: even with zero photons, the field has a non-zero zero-point amplitude. To account for spontaneous emission we are therefore *forced* to quantize the field. This is the one place in the course where the semiclassical picture truly breaks, and it is worth the price.

Roadmap, and the symbols introduced here

Progress: ✓ transition rates (Fermi) → **(you are here)** quantized field → spontaneous emission.

New symbols: $a, a^\dagger$ (photon annihilation / creation operators, Appendix E), $\mathcal{E}_k = \sqrt{\hbar\omega_k/2\varepsilon_0 V}$ (electric field of one photon), Γ (spontaneous-emission rate), $\tau = 1/\Gamma$ (radiative lifetime), LDOS (local density of optical states).

5.1 Quantizing the electromagnetic field

In a cavity of volume V with periodic boundary conditions, the transverse field is expanded over modes $(\mathbf{k}, \lambda)$ of frequency $\omega_k = ck$. Each mode is a harmonic oscillator; canonical quantization promotes its amplitude to operators $\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}\lambda}^\dagger$ with $[\hat{a}, \hat{a}^\dagger] = 1$. The electric-field operator is

$$\hat{\mathbf{E}}(\mathbf{r}) = \sum_{\mathbf{k}\lambda} \mathcal{E}_k \epsilon_{\mathbf{k}\lambda} (\hat{a}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}), \quad \mathcal{E}_k = \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}. \quad (17)$$

Where $\mathcal{E}_k = \sqrt{\hbar\omega_k/2\varepsilon_0 V}$ comes from (energy bookkeeping)

The normalisation constant $\mathcal{E}_k$ is not decreed; it is fixed by requiring that the field energy come out right. The electromagnetic energy in the volume V is

$$H_{\text{field}} = \int_V \left(\frac{\varepsilon_0}{2} E^2 + \frac{B^2}{2\mu_0} \right) d^3r,$$

with electric and magnetic parts contributing equally on average. Insert the mode expansion for one mode: the terms $aa^\dagger$ and $a^\dagger a$ survive the volume integral (the aa and $a^\dagger a^\dagger$ terms oscillate in space and integrate to zero), giving

$$H_{\text{field}} = \varepsilon_0 \mathcal{E}_k^2 V (aa^\dagger + a^\dagger a) = 2\varepsilon_0 \mathcal{E}_k^2 V \left(a^\dagger a + \frac{1}{2} \right).$$

But we *know* what this must equal: each mode is a harmonic oscillator with $H = \hbar\omega_k (a^\dagger a + \frac{1}{2})$ (Appendix E). Matching the two expressions:

$$2\varepsilon_0 \mathcal{E}_k^2 V = \hbar\omega_k \quad \implies \quad \mathcal{E}_k = \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}.$$

In words: the zero-point energy $\frac{1}{2}\hbar\omega_k$, spread over the mode volume V , is the vacuum field squared. A quick sanity check of the scale: for an optical mode confined to $V = 1 \mu\text{m}^3$, $\mathcal{E}_k \approx 1\text{e}5 \text{ V/m}$; within an order of magnitude of the field of a focused mW laser, but present with *zero* photons. This is the field that shakes the excited atom.

Vacuum field per mode

The “electric field of one photon” (the vacuum amplitude of a single mode) is

$$\mathcal{E}_k = \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}. \quad (18)$$

Even in the vacuum $|0\rangle$, $\langle\hat{\mathbf{E}}\rangle = 0$ but $\langle\hat{\mathbf{E}}^2\rangle \neq 0$: these *vacuum fluctuations* drive spontaneous emission. Note $\mathcal{E}_k \propto V^{-1/2}$: shrinking the mode volume increases the coupling, the key to cavity QED.

5.2 Spontaneous emission: Fermi’s golden rule applied to the vacuum

We do not need any new heavy machinery here (in particular, not the full Weisskopf–Wigner treatment with its contour integrals). Spontaneous emission is simply *demonstration 4 of our thread run on the vacuum*: an excited atom is a state weakly coupled to a continuum of empty photon modes, exactly the situation the golden rule was built for. The only quantum-field input we admit is the value of the electric field carried by a single photon, $\mathcal{E}_k = \sqrt{\hbar\omega_k/2\varepsilon_0 V}$ (justified in the previous subsection and Appendix E); everything else is Fermi’s rule and mode counting.

An excited atom can therefore decay into any of the continuum of empty modes. The golden rule with $V = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}$ couples $|e, 0\rangle \rightarrow |g, 1_{\mathbf{k}\lambda}\rangle$ with strength $d\mathcal{E}_k$, and the final-state density is the photon mode density.

Free-space spontaneous emission rate

Step 1: matrix element. The interaction $V = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}$ couples $|e, 0\rangle$ to $|g, 1_{\mathbf{k}\lambda}\rangle$. Only the creation part $\hat{a}^\dagger$ of $\hat{\mathbf{E}}$ contributes (it makes one photon), and $\langle 1_{\mathbf{k}\lambda} | \hat{a}^\dagger | 0 \rangle = 1$, so

$$|\langle g, 1_{\mathbf{k}\lambda} | V | e, 0 \rangle|^2 = \mathcal{E}_k^2 |\mathbf{d} \cdot \boldsymbol{\epsilon}_{\mathbf{k}\lambda}|^2, \quad \mathcal{E}_k^2 = \frac{\hbar\omega_k}{2\varepsilon_0 V}.$$

Step 2: sum over every mode the photon could go into. The excited atom can emit into *any* empty mode, and each mode is one possible final state, so we apply the golden rule to each and add up the rates:

$$\Gamma = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\lambda} \mathcal{E}_k^2 |\mathbf{d} \cdot \boldsymbol{\epsilon}_{\mathbf{k}\lambda}|^2 \delta(\hbar\omega_k - \hbar\omega_0).$$

The modes are labelled by their wavevector $\mathbf{k}$ (direction and wavelength) and polarization λ . There are so many of them, packed so densely, that the sum is really an integral. The standard “box” counting (allowed $\mathbf{k}$ form a grid of spacing $2\pi/L$, see Appendix E) turns the sum into

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int \underbrace{k^2 dk}_{\text{magnitude}} \underbrace{d\Omega}_{\text{direction}}.$$

We now do the direction part (Step 3) and the magnitude part (Step 4) separately.

Step 3: the direction part, and why a dipole does not radiate along its own axis.

Point the dipole along $\hat{z}$. A photon going in direction $\mathbf{k}$ can only carry the *transverse* part of the dipole; adding the two polarizations gives $\sum_{\lambda} |\mathbf{d} \cdot \boldsymbol{\epsilon}_{\mathbf{k}\lambda}|^2 = d^2 \sin^2 \theta$, where θ is the angle from the dipole axis. This is the familiar doughnut radiation pattern: zero emission along $\hat{z}$ ($\theta = 0$), maximum in the equatorial plane ($\theta = \pi/2$). Its integral over all directions is

$$\int d^2 \sin^2 \theta d\Omega = d^2 \int_0^{2\pi} d\phi \int_0^\pi \sin^2 \theta \underbrace{\sin \theta d\theta}_{d\Omega = \sin \theta d\theta d\phi} = d^2 (2\pi) \underbrace{\int_0^\pi \sin^3 \theta d\theta}_{=4/3} = \frac{8\pi}{3} d^2.$$

Step 4: the magnitude part, killed by the δ -function. Collect everything, and trade k for frequency via $\omega_k = ck$ (so $k^2 dk = \omega_k^2 d\omega_k / c^3$):

$$\Gamma = \frac{2\pi}{\hbar} \frac{V}{(2\pi)^3} \frac{8\pi}{3} d^2 \int \underbrace{\frac{\hbar\omega_k}{2\varepsilon_0 V}}_{\varepsilon_k^2} \underbrace{\frac{\omega_k^2}{c^3}}_{\text{from } k^2 dk} \delta(\hbar\omega_k - \hbar\omega_0) d\omega_k.$$

Two things happen at once. The mode volume V cancels (in *free* space the answer cannot depend on the size of an imaginary box). And the δ -function, rewritten as $\delta(\hbar\omega_k - \hbar\omega_0) = \delta(\omega_k - \omega_0)/\hbar$, does the integral for us by simply setting $\omega_k = \omega_0$ everywhere:

$$\Gamma = \frac{2\pi}{\hbar} \cdot \frac{1}{(2\pi)^3} \cdot \frac{8\pi}{3} d^2 \cdot \frac{\hbar\omega_0}{2\varepsilon_0} \cdot \frac{\omega_0^2}{c^3} \cdot \frac{1}{\hbar}.$$

Step 5: collect the numbers. Gathering the numerical factors, $\frac{2\pi}{(2\pi)^3} \cdot \frac{8\pi}{3} \cdot \frac{1}{2} = \frac{2\pi \cdot 8\pi}{8\pi^3 \cdot 3 \cdot 2} = \frac{1}{3\pi}$, giving the boxed result

$$\Gamma = \frac{\omega_0^3 d^2}{3\pi\varepsilon_0 \hbar c^3}.$$

The cavity volume V cancelled (free space); it reappears the moment the mode density is modified, which is exactly the Purcell effect of Sec. 7.

Spontaneous emission rate and natural linewidth

$$\Gamma = \frac{\omega_0^3 d^2}{3\pi\varepsilon_0 \hbar c^3} = A_{21} \quad (19)$$

The excited-state population decays as $e^{-\Gamma t}$ (Weisskopf–Wigner), the emitted line is a Lorentzian of full width Γ (the *natural linewidth*), and the radiative lifetime is $\tau = 1/\Gamma$. Writing Γ via the local density of optical states (LDOS) makes the Purcell effect transparent (Sec. 7).

From a constant rate to $e^{-\Gamma t}$ and to the Lorentzian line

Two short arguments finish the picture; both are used constantly in practice.

(a) Why exponential decay? The golden rule gives a probability *per unit time* Γ that is independent of how long the atom has already survived (the photon continuum keeps no memory: once emitted, the photon flies off and never returns). For a memoryless process the population obeys

$$\dot{\rho}_{ee} = -\Gamma\rho_{ee} \implies \rho_{ee}(t) = e^{-\Gamma t}.$$

The full Weisskopf–Wigner treatment solves the atom+field dynamics without perturbation theory and confirms this exponential to excellent accuracy (tiny deviations exist at ultra-short and ultra-long times, but they have never mattered for an optical transition).

(b) Why a Lorentzian of width Γ ? The emitted field is the decaying oscillation $E(t) \propto e^{-i\omega_0 t} e^{-\Gamma t/2}$ (amplitude decays at $\Gamma/2$ so that the *intensity* decays at Γ). Its spectrum is the Fourier transform,

$$E(\omega) \propto \int_0^\infty e^{i(\omega-\omega_0)t} e^{-\Gamma t/2} dt = \frac{1}{\Gamma/2 - i(\omega - \omega_0)}, \quad |E(\omega)|^2 \propto \frac{1}{(\omega - \omega_0)^2 + (\Gamma/2)^2},$$

a Lorentzian of full width at half maximum Γ . A finite lifetime *is* a finite linewidth; this Fourier pair (decay time $\leftrightarrow$ width) is the same statement as the T_2 -linewidth relation of Lecture 3, and it sets the ultimate resolution of any spectroscopy on that transition.

The rate Γ runs the lit world, and limits qubits

Spontaneous emission is how almost everything glows: the LED bulbs overhead, the OLED pixels in a phone screen, a firefly, the phosphors in a fluorescent tube. The rate Γ you just derived sets how fast each emitter can produce a photon, and engineering it is a billion-dollar business. The flip side appears in quantum computing: for any qubit encoded in an optical transition, this same Γ is the fundamental T_1 , the unavoidable decay that erases the stored information. This is why such qubits are often built on *nearly forbidden* transitions (recall the selection rules): a tiny $\mathbf{d}_{fi}$ means a tiny Γ , hence a very long-lived “clock state”, at the price of being harder to drive. Atomic clocks and optical-qubit designers spend their lives trading off exactly this Γ .

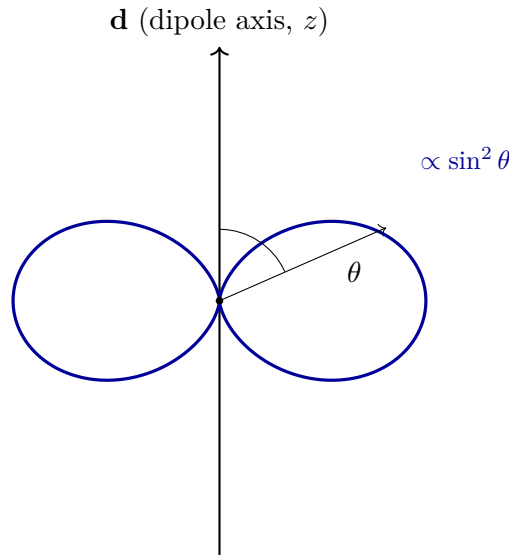


Figure 18: The dipole radiation pattern $\propto \sin^2 \theta$ that emerges from the polarization sum in Step 3. No power is emitted along the dipole axis; emission is maximal in the equatorial plane. Integrating this pattern over 4π gave the factor $8\pi/3$.

Lifetime of the sodium 3p state

With $\omega_0 = 3.2 \times 10^{15}$ rad/s and $d = 2.1 \times 10^{-29}$ C m:

$$\Gamma = \frac{(3.2 \times 10^{15})^3 (2.1 \times 10^{-29})^2}{3\pi (8.85 \times 10^{-12}) (1.05 \times 10^{-34}) (3 \times 10^8)^3} \approx 6.0 \times 10^7 \text{ s}^{-1}.$$

Hence $\tau = 1/\Gamma \approx 17$ ns and $\Gamma/2\pi \approx 9.5$ MHz, in good agreement with the measured Na D₂ lifetime (16.2 ns). The small discrepancy comes from our rounded dipole element; the scaling $\Gamma \propto \omega_0^3 d^2$ is exact.

Why $\Gamma \propto \omega_0^3$?

One power of ω_0 comes from the photon energy in $\mathcal{E}_k^2$, and two from the mode density $\rho \propto \omega^2$. This steep frequency scaling explains why X-ray transitions are fast (femtoseconds) while radio-frequency / hyperfine transitions are extraordinarily slow (the 21 cm line of hydrogen has $\tau \sim 10^7$ years).

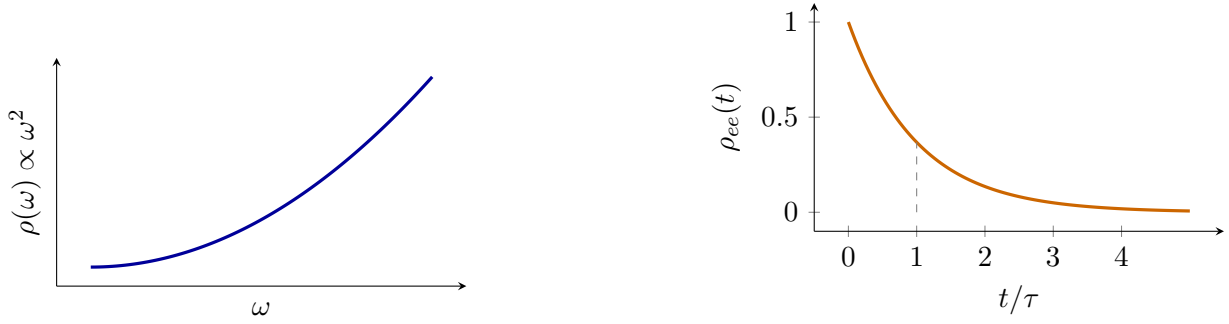


Figure 19: Left: the free-space photon density of states $\rho \propto \omega^2$ that, together with the ω from the per-photon energy, gives $\Gamma \propto \omega_0^3$. Right: the Weisskopf–Wigner exponential decay $\rho_{ee} = e^{-\Gamma t}$ (reaching $1/e$ at $t = \tau$, grey dashed), whose Fourier transform is the Lorentzian natural line of width Γ .

The Lamb shift: the other face of the vacuum

The same coupling to vacuum modes that *damps* the excited state also *shifts* the levels. The real part of the self-energy (which we dropped in deriving Γ from the imaginary part) produces the *Lamb shift*: in hydrogen the $2s_{1/2}$ and $2p_{1/2}$ levels, degenerate in the Dirac theory, are split by ≈ 1 GHz. Physically, the fluctuating vacuum field jitters the electron position, smearing its sampling of the Coulomb potential. Decay rate and energy shift are thus the imaginary and real parts of one complex self-energy; a recurring theme: dissipation and dispersion are inseparable.

Can you now answer these? (Chapter 5)

- Why can a classical field never produce spontaneous emission?
- What is $\mathcal{E}_{\text{vac}}$, and where did we admit it?
- Why does the spontaneous-emission rate scale as $\Gamma \propto \omega_0^3$?
- What sets the natural linewidth of a spectral line?

6 Maxwell–Bloch equations and macroscopic response

How does one atom become a material?

Until now the field was a given, imposed from outside, and we asked how a single atom responds. But a real optical material is N atoms (or defects, or dots) that all radiate, and the light each one feels is the incoming wave *plus* what all the others have re-emitted. Field and matter are no longer independent: the field drives the atoms, and the atoms reshape the field. Solving the two together is what turns a single emitter into a *medium* with an index, an absorption coefficient and a colour. The coupled set is the Maxwell–Bloch equations.

Roadmap, and the symbols introduced here

Progress: ✓ single-atom response → **(you are here)** many atoms = a medium.
 New symbols: $\mathbf{P}$ (macroscopic polarization), $\chi(\omega)$ (susceptibility), n (refractive index), α (absorption coefficient), n_g (group index).

So far the field was externally imposed. In a medium the atomic dipoles *radiate*, so the field and the atoms must be solved self-consistently: the Bloch equations supply the polarization, Maxwell’s equations propagate the field.

6.1 Closing the loop

The macroscopic polarization of N atoms per unit volume is $\mathbf{P} = N \text{Tr}(\rho \hat{\mathbf{d}}) = Nd(u \cos \omega t - v \sin \omega t)$. Inserting this into the wave equation

$$\partial_z^2 E - \frac{1}{c^2} \partial_t^2 E = \mu_0 \partial_t^2 P \quad (20)$$

and using the slowly-varying-envelope approximation (SVEA) couples the field amplitude $\mathcal{E}(z, t)$ to the coherences u, v .

The SVEA reduction

Step 1: factor out the carrier. Optical fields oscillate $\sim 10^{15}$ times per second, but pulses and coherences evolve on nanoseconds: the interesting dynamics is a slow *envelope* on a fast *carrier*. Write

$$E(z, t) = \frac{1}{2} \mathcal{E}(z, t) e^{i(kz - \omega t)} + \text{c.c.}, \quad P(z, t) = \frac{1}{2} \mathcal{P}(z, t) e^{i(kz - \omega t)} + \text{c.c.},$$

with $k = \omega/c$ and $\mathcal{E}, \mathcal{P}$ slowly varying: $|\partial_z \mathcal{E}| \ll k|\mathcal{E}|$, $|\partial_t \mathcal{E}| \ll \omega|\mathcal{E}|$.

Step 2: substitute and discard the small second derivatives.

$$\partial_z^2 E \rightarrow \frac{1}{2} (-k^2 \mathcal{E} + 2ik \partial_z \mathcal{E}) e^{i\phi}, \quad \frac{1}{c^2} \partial_t^2 E \rightarrow \frac{1}{2} \left(-\frac{\omega^2}{c^2} \mathcal{E} - \frac{2i\omega}{c^2} \partial_t \mathcal{E} \right) e^{i\phi},$$

and on the right, $\mu_0 \partial_t^2 P \rightarrow -\frac{1}{2} \mu_0 \omega^2 \mathcal{P} e^{i\phi}$ (the envelope derivatives of P are negligible against $\omega^2 \mathcal{P}$).

Step 3: watch the cancellation. Because $k = \omega/c$, the big terms $-k^2 \mathcal{E}$ and $+\omega^2 \mathcal{E}/c^2$ cancel *exactly*; this is the whole point of expanding around the free-space carrier. What survives is first order:

$$ik \left(\partial_z + \frac{1}{c} \partial_t \right) \mathcal{E} = -\frac{\mu_0 \omega^2}{2} \mathcal{P} \implies \left(\partial_z + \frac{1}{c} \partial_t \right) \mathcal{E} = \frac{i\mu_0 \omega c}{2} \mathcal{P}.$$

A second-order wave equation has become *first order*: the envelope simply advects at c while the polarization source reshapes it.

Step 4: insert the atomic source. From the Bloch vector, $\mathcal{P} = Nd(u + iv)$; multiplying through by $d/\hbar$ to convert the field envelope into a Rabi frequency $\Omega = d\mathcal{E}/\hbar$ gives the boxed equation.

Maxwell–Bloch equations (SVEA, plane wave along z)

$$\left(\partial_z + \frac{1}{c}\partial_t\right)\Omega = i\frac{\mu_0 c \omega N d^2}{2\hbar}(u + iv), \quad (21)$$

together with the optical Bloch equations for (u, v, w) driven by $\Omega(z, t)$. The medium shapes the pulse; the pulse drives the medium.

6.2 The simplest case: a dilute set of two-level emitters

The Maxwell–Bloch equations above are nonlinear (the field drives the emitter, whose state then changes the field) and in general must be solved numerically; their rich consequences (pulses, gain, solitons) are previewed at the end of this lecture. But there is one limit that is both solvable by hand and enormously useful, and it is the right place to start: a *weak* field on a *dilute* collection of identical two-level emitters. “Weak” means each emitter stays almost entirely in the ground state ($w \approx -1$), so the response is *linear* in the field; “dilute” means the emitters do not see each other, so we may treat one and multiply by the number density N . In this limit the whole medium is summarised by a single function, the susceptibility $\chi(\omega)$, which already contains the refractive index, the absorption coefficient and Beer’s law. It is the quantum version of the classical Lorentz result of Lecture 1, with a real dipole matrix element and the coherence linewidth $1/T_2$ in place of the ad hoc classical damping.

A “two-level emitter” is usually a piece of solid

Do not picture only a gas. The most important hosts of this physics are *solids*: a nitrogen-vacancy (NV) colour centre in diamond, a rare-earth ion (erbium, europium) doped into a crystal, or a semiconductor quantum dot all behave, optically, as a two-level system with a dipole d and a coherence time T_2 . The susceptibility we are about to derive is exactly what describes their absorption and refraction, which is why this chapter is the natural bridge from single atoms to engineered solid-state photonics. Throughout this lecture, read “ N emitters” as “ N defects or dots in a crystal” rather than “ N atoms in a vapour”.

Susceptibility from the steady-state coherence

Step 1: use that the field is weak. A weak probe barely disturbs the atom, so it stays almost entirely in the ground state: the inversion $w = \rho_{ee} - \rho_{gg} \simeq -1$. We therefore only need the *coherence* $\tilde{\rho}_{eg}$, and its equation of motion is one of the optical Bloch equations of the previous chapter (written here in the rotating frame). Freezing $w = -1$ in it linearises the problem:

$$\dot{\tilde{\rho}}_{eg} = -\left(\frac{1}{T_2} - i\delta\right)\tilde{\rho}_{eg} - \frac{i\Omega}{2}w \xrightarrow{w=-1} \dot{\tilde{\rho}}_{eg} = -\left(\frac{1}{T_2} - i\delta\right)\tilde{\rho}_{eg} + \frac{i\Omega}{2}.$$

The two terms on the right have a clear meaning: the first is the decay of the coherence at rate $1/T_2$ (with a rotation at the detuning δ), the second is the drive that keeps creating it.

Step 2: wait for the steady state. Shine the probe continuously and the transients die out; the coherence then settles to a constant value, $\dot{\tilde{\rho}}_{eg} = 0$. That turns the differential equation into a one-line algebra problem:

$$0 = -\left(\frac{1}{T_2} - i\delta\right)\tilde{\rho}_{eg}^{\text{ss}} + \frac{i\Omega}{2} \implies \tilde{\rho}_{eg}^{\text{ss}} = \frac{i\Omega/2}{1/T_2 - i\delta} = -\frac{\Omega/2}{\delta + i/T_2},$$

where the last step multiplied numerator and denominator by i (recall $i \cdot (-i\delta) = \delta$, and $i \cdot i\Omega/2 = -\Omega/2$).

Step 3: go from one atom to the medium. The polarization of the material is simply the number of emitters per unit volume times the dipole each one now carries, $P = 2Nd\tilde{\rho}_{eg}^{\text{ss}}$.

On the other hand the susceptibility is *defined* by $P = \varepsilon_0 \chi E$. Setting the two equal and using $\Omega = dE/\hbar$:

$$\varepsilon_0 \chi E = -2Nd \frac{dE/2\hbar}{\delta + i/T_2} = -\frac{Nd^2 E/\hbar}{\delta + i/T_2}.$$

Step 4: read off absorption and dispersion. Cancel the common E , then split into real and imaginary parts by multiplying top and bottom by the conjugate $(\delta - i/T_2)$:

$$\chi(\omega) = -\frac{Nd^2}{\varepsilon_0 \hbar} \frac{1}{\delta + i/T_2} = -\frac{Nd^2}{\varepsilon_0 \hbar} \frac{\delta - i/T_2}{\delta^2 + 1/T_2^2}.$$

The real part is the dispersion χ' , the imaginary part the absorption χ'' (boxed below). With the $e^{-i\omega t}$ convention used throughout, $\chi'' > 0$ is precisely what absorption requires, and it comes out automatically, as it must. Notice that this is exactly the classical Lorentz χ of Chapter 1, with the ad hoc damping γ_c replaced by the physically meaningful coherence rate $1/T_2$: the *same resonant denominator*, now with a quantum pedigree.

Absorption and dispersion of N two-level emitters

$$\chi'(\omega) = -\frac{Nd^2}{\varepsilon_0 \hbar} \frac{\delta}{\delta^2 + 1/T_2^2}, \quad \chi''(\omega) = \frac{Nd^2}{\varepsilon_0 \hbar} \frac{1/T_2}{\delta^2 + 1/T_2^2}. \quad (22)$$

The imaginary part χ'' governs *absorption* and the real part χ' governs *refraction* (the index is $n \simeq 1 + \chi'/2$). χ'' is a Lorentzian centred on resonance whose half-width is exactly $1/T_2$, the coherence linewidth introduced above: a longer-lived coherence gives a sharper line. The intensity then obeys Beer's law $I(z) = I_0 e^{-\alpha z}$ with absorption coefficient $\alpha = \omega \chi''/c$, while the steep slope of χ' at line centre is what slows light (next subsection). Absorption and refraction are not independent; they are tied together by the Kramers–Kronig relations (Lecture 8).

Storing light in a crystal: solid-state quantum memories

Apply this to rare-earth ions (europium, erbium) frozen into a crystal. Their optical coherence time T_2 can reach milliseconds, giving spectacularly narrow lines ($1/T_2$ down to kilohertz) even though the ions sit in a solid. A weak light pulse drives the collective coherence described by the susceptibility above; with a clever sequence of control pulses that coherence can be frozen, stored, and read back out on demand. This is a *quantum memory*: a device that holds a photonic qubit and re-emits it later, the storage element a quantum network (and a quantum computer's communication bus) needs. Erbium is especially prized because its transition sits at the $1.5 \mu\text{m}$ telecom wavelength, so it can plug directly into existing optical fibre. The same $\chi(\omega)$ you just derived sets how much light the crystal absorbs and therefore how efficiently it can catch and hold a photon.

Order of magnitude: why the world's data travels at $1.55 \mu\text{m}$

The global fibre network operates at $\lambda = 1.55 \mu\text{m}$ because silica's $\chi''(\omega)$ has a deep minimum there, pinched between two mechanisms met in this course: Rayleigh scattering off density fluctuations, falling as ω^4 (Chapter 1), and the infrared wing of the Si–O vibrational resonances (a phonon Lorentz oscillator, Chapter 8), rising steeply beyond $1.6 \mu\text{m}$. At the bottom of this valley the attenuation is $\approx 0.2 \text{ dB/km}$: light still retains 1% of its power after 100 km. For comparison, window glass at visible wavelengths loses that much in metres. It is also why erbium ($1.53\text{--}1.56 \mu\text{m}$ transition) became the amplifier ion of the internet: its two-level physics sits exactly in the transparency window.

Beyond linear: famous Maxwell–Bloch phenomena

Keeping the full nonlinearity, the Maxwell–Bloch equations predict *self-induced transparency* (a 2π “soliton” pulse propagates loss-free through a resonant absorber), *photon echoes*, and (for a collection of inverted atoms) *superradiance*, where N atoms in a sub-wavelength volume emit cooperatively with peak intensity $\propto N^2$ and rate $\propto N\Gamma$.

Why superradiance scales as N^2 : amplitudes, not probabilities

No heavy formalism is needed for the key scaling; only the distinction between adding *fields* and adding *intensities*.

Step 1: independent atoms. If N excited atoms radiate with random relative phases, the emitted fields add with random signs; the mean intensity is the sum of the individual intensities, $I \propto N$, and the sample empties in the single-atom time $1/\Gamma$. This is an ordinary fluorescent lamp.

Step 2: phased atoms. If the N dipoles sit within $\ll \lambda^3$ (so a detector cannot tell them apart) and oscillate in phase, their *field amplitudes* add: $E_{\text{tot}} \propto Nd$, hence

$$I_{\text{max}} \propto |E_{\text{tot}}|^2 \propto N^2.$$

Step 3: energy conservation fixes the time scale. The sample holds only N quanta, $U = N\hbar\omega_0$. If it radiates at a peak power $\propto N^2\hbar\omega_0\Gamma$, it can only sustain it for

$$t_{\text{burst}} \sim \frac{U}{I_{\text{max}}} \sim \frac{1}{N\Gamma} :$$

the emission is a *flash*, N times faster than a lone atom. Enhanced rate and enhanced peak intensity are two faces of the same constructive interference. (The full Dicke treatment adds one subtlety: starting from perfect inversion the dipoles have no phase yet, so the burst builds up from noise after a delay $\sim \ln N/N\Gamma$; the phasing is spontaneous.)

Dicke superradiance

N identical atoms within a volume $\ll \lambda^3$ share a single radiating dipole. The collective state with all dipoles in phase radiates at the enhanced rate $\Gamma_N = N\Gamma$, and the burst from a fully inverted sample peaks at

$$I_{\text{max}} \propto N^2 \hbar\omega_0 \Gamma, \quad t_{\text{delay}} \sim \frac{\ln N}{N\Gamma}. \quad (23)$$

The N^2 scaling (versus N for independent emitters) is the hallmark of constructive interference of the emitted fields; the many-atom analogue of the single-atom coherence captured by the Bloch vector.

Superradiant burst

For $N = 10^4$ atoms with single-atom $\Gamma = 6e7 \text{ s}^{-1}$, the collective rate is $\Gamma_N = N\Gamma \approx 6e11 \text{ s}^{-1}$ (lifetime $\sim 1.7 \text{ ps}$), and the peak intensity is enhanced by $N = 10^4$ over the incoherent sum. Such bursts are routinely seen in dense atomic and molecular gases and in arrays of solid-state emitters.

Resonant absorption length and slow light

Take a rubidium vapor, $N = 1 \times 10^{17} \text{ m}^{-3}$, $d = 2.5 \times 10^{-29} \text{ C m}$, $1/T_2 = \Gamma/2$ with $\Gamma/2\pi = 6 \text{ MHz}$. On resonance ($\delta = 0$):

$$\chi'' = \frac{Nd^2}{\varepsilon_0 \hbar} T_2 = \frac{10^{17}(2.5 \times 10^{-29})^2}{(8.85 \times 10^{-12})(1.05 \times 10^{-34})} \times \frac{2}{2\pi \cdot 6 \times 10^6} \approx 3.6 \times 10^{-3}.$$

The absorption coefficient is $\alpha = \omega \chi''/c \approx (2.4 \times 10^{15})(3.6 \times 10^{-3})/(3 \times 10^8) \approx 2.9 \times 10^4 \text{ m}^{-1}$, giving an absorption length of only $\sim 35 \mu\text{m}$. The steep dispersion $d\chi'/d\omega$ at line center implies a group index $n_g \gg 1$: the same resonance that absorbs strongly also slows light dramatically, the basis of EIT-based slow-light experiments.

6.3 Group velocity and slow light

The refractive index is $n(\omega) = \sqrt{1 + \chi'} \approx 1 + \frac{1}{2}\chi'(\omega)$ for a dilute medium. Because χ' varies steeply near resonance (Fig. 3), the *group* velocity can differ enormously from c .

Group index in three lines

A pulse is a superposition of neighbouring frequencies; its envelope travels at the speed at which those components stay in step, $v_g = d\omega/dk$ (the stationary-phase velocity of the beat pattern). In a medium the dispersion relation is $k(\omega) = n(\omega)\omega/c$, so

$$\frac{dk}{d\omega} = \frac{1}{c} \left(n + \omega \frac{dn}{d\omega} \right) \implies v_g = \frac{d\omega}{dk} = \frac{c}{n + \omega \frac{dn}{d\omega}} \equiv \frac{c}{n_g}.$$

The index n itself stays close to 1 in a dilute vapour; it is the *slope* $dn/d\omega$, multiplied by the enormous optical frequency $\omega \sim 10^{15} \text{ rad/s}$, that can make n_g huge. Steep dispersion, not a large index, is what slows light.

Group index near resonance

$$v_g = \frac{c}{n_g}, \quad n_g = n + \omega \frac{dn}{d\omega}. \quad (24)$$

On the steep, low-absorption slope between the Lorentzian wings (or at the transparency window of EIT), $dn/d\omega > 0$ is large and positive, so $n_g \gg 1$ and light is *slowed*. On anomalous-dispersion regions ($dn/d\omega < 0$, inside the absorption line) the group index can even be negative.

How slow is slow light?

A normal-dispersion slope of $dn/d\omega \sim 10^{-7} \text{ s}$ near a sharp resonance at $\omega_0 \sim 2.4 \times 10^{15} \text{ rad/s}$ gives $n_g = 1 + \omega_0 dn/d\omega \sim 2 \times 10^8$, i.e. $v_g \sim c/(2 \times 10^8) \approx 1.5 \text{ m/s}$; walking pace. The headline demonstration that light can be slowed to a few m/s, and even stopped and revived, was first done in cold atoms, but the same steep dispersion is now routinely engineered in *solids*: rare-earth doped crystals and semiconductor structures.

Slow light: optical buffers and the quantum internet

A pulse that crawls through a crystal at a few m/s is delayed by microseconds in a few millimetres of material; it has been *stored*. Two payoffs follow. Classically, such “optical buffers” would let photonic routers hold and reorder data packets without converting light into electronics and back, a long-standing goal for high-speed networks. Quantum mechanically,

stopping light in a rare-earth crystal is precisely how the quantum memories of the previous box catch and release a photonic qubit. Slow light is therefore the same physics viewed dynamically: the steep $\chi'(\omega)$ that the susceptibility predicts is what makes a solid hold onto light long enough to be useful.

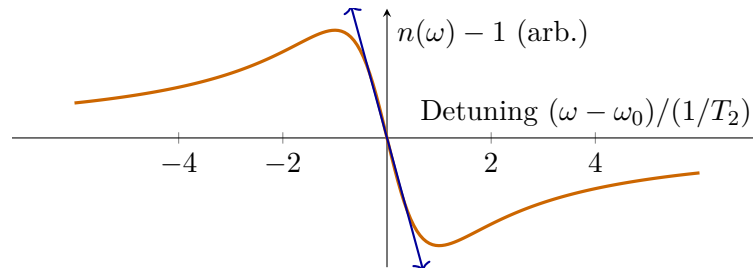


Figure 20: Refractive index near an atomic resonance. The steep positive slope at line centre (marked by the blue double arrow) is normal dispersion; it yields a large group index and hence slow light. The negative-slope wings inside the absorption profile give anomalous (fast or negative) group velocity.

Can you now answer these? (Chapter 6)

- Why must the field and the atoms be solved self-consistently in a medium?
- What does χ' control, and what does χ'' control?
- Why does a sharp resonance slow light down?
- Why is the width of the absorption line equal to $1/T_2$?

7 Cavity QED and the Purcell effect

Can we modify spontaneous emission?

Spontaneous emission at the rate Γ looked like a fixed property of the atom, almost a constant of nature. But look again at how we obtained it: Γ was Fermi’s rule times the *density of available photon modes*. The atom’s dipole is fixed, but the mode density is not; it depends on the atom’s *surroundings*. So if we change the surroundings, by putting the atom in a mirror box (a cavity), we should be able to change Γ itself, speeding emission up or shutting it off. Can we really? Yes, and the result (the Purcell effect) is one of the most useful knobs in all of photonics.

Roadmap, and the symbols introduced here

Progress: ✓ free-space spontaneous emission → **(you are here)** emission engineered by a cavity.

New symbols: Q (cavity quality factor), V (mode volume), g (single-photon / vacuum Rabi coupling), κ (cavity loss rate), γ (atomic loss into other modes), F_P (Purcell factor), $C = g^2/\kappa\gamma$ (cooperativity).

In free space the atom decays at the fixed rate Γ set by the free-space mode density. Place it inside a cavity and the mode density, hence Γ , can be enhanced or suppressed. This is the Purcell effect.

What you actually need from this chapter

The core result is the *Purcell factor*, and it is demonstration 6 of our thread: it needs *nothing more* than the spontaneous-emission rate of Lecture 5 (Fermi’s rule times a density of states) with the free-space density of states replaced by the cavity one. That is a short classical mode-counting calculation, done in Sec. 7.3. Everything between here and there, the single-mode Jaynes–Cummings model and its dressed states, is *enrichment*: it describes the opposite, ultra-strong-coupling regime and builds intuition, but it is not required for Purcell. A reader short on time may jump straight to Sec. 7.3.

7.1 The Jaynes–Cummings model (enrichment)

As a warm-up and for physical intuition (not as a prerequisite for Purcell), consider the simplest model of one atom talking to one light mode. We will not postulate its Hamiltonian; we will *assemble* it from three pieces we have already met, each one a quantity the reader already knows.

Two pieces of notation

For the two-level atom (Lecture 2) it is convenient to use the *atomic lowering and raising operators*

$$\sigma = |g\rangle\langle e| \quad (\text{de-excites: } |e\rangle \rightarrow |g\rangle), \quad \sigma^\dagger = |e\rangle\langle g| \quad (\text{excites: } |g\rangle \rightarrow |e\rangle),$$

so that $\sigma^\dagger\sigma = |e\rangle\langle e|$ counts whether the atom is excited. For the cavity mode we use the photon annihilation/creation operators $a, a^\dagger$ of the harmonic oscillator (Appendix E), with $a^\dagger a$ counting photons. These are the only two ingredients.

Building the Jaynes–Cummings Hamiltonian

Step 1: the atom on its own. From Lecture 2 the bare two-level atom has energy $\hbar\omega_0$ when excited and zero when not:

$$H_{\text{atom}} = \hbar\omega_0 |e\rangle\langle e| = \hbar\omega_0 \sigma^\dagger \sigma.$$

Step 2: the light mode on its own. A single cavity mode is one harmonic oscillator (Appendix E); its energy is $\hbar\omega_c$ per photon (dropping the constant zero-point term):

$$H_{\text{field}} = \hbar\omega_c a^\dagger a.$$

Step 3: how they talk to each other. The coupling is the same dipole interaction $-\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}$ as everywhere else in the course, with two changes. First, the *atomic dipole* has no diagonal part (an atom in a definite level has no permanent dipole on this transition); it only connects $|g\rangle$ and $|e\rangle$, so $\hat{\mathbf{d}} = \mathbf{d}(\sigma + \sigma^\dagger)$. Second, the *field* is now the quantized mode operator (Appendix E), $\hat{\mathbf{E}} \propto (a + a^\dagger)$. Multiplying,

$$\begin{aligned} -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}} \propto (\sigma + \sigma^\dagger)(a + a^\dagger) = & \underbrace{\sigma^\dagger a}_{\text{absorb photon, excite}} + \underbrace{\sigma a^\dagger}_{\text{emit photon, de-excite}} \\ & + \underbrace{\sigma^\dagger a^\dagger}_{\text{excite \& create}} + \underbrace{\sigma a}_{\text{de-excite \& destroy}}. \end{aligned}$$

Step 4: keep only what conserves energy (the RWA). The last two terms would create or destroy *two* quanta at once (an excited atom plus an extra photon, or neither); they oscillate fast and average away, exactly the rotating-wave approximation of Lecture 2. Dropping them leaves the two energy-conserving terms. Collecting Steps 1–3 gives the boxed result.

The Jaynes–Cummings Hamiltonian

$$H_{\text{JC}} = \underbrace{\hbar\omega_0 \sigma^\dagger \sigma}_{\text{atom}} + \underbrace{\hbar\omega_c a^\dagger a}_{\text{light}} + \underbrace{\hbar g(\sigma^\dagger a + \sigma a^\dagger)}_{\text{exchange}} \quad g = \frac{d\mathcal{E}_c}{\hbar} = d\sqrt{\frac{\omega_c}{2\hbar\epsilon_0 V}}. \quad (25)$$

The coupling g is the *vacuum Rabi frequency*: it is the dipole d times the electric field of a *single* photon, $\mathcal{E}_c = \sqrt{\hbar\omega_c/2\epsilon_0 V}$ (Lecture 5). Because $g \propto 1/\sqrt{V}$, squeezing the mode into a smaller volume makes the atom and the single photon talk to each other more strongly, which is the whole idea behind cavity QED.

Dressed states and vacuum Rabi splitting

Step 1: conserved excitation number. The operator $\hat{N} = \sigma^\dagger \sigma + a^\dagger a$ commutes with H_{JC} (each term either creates a photon and de-excites the atom, or vice versa). The Hilbert space therefore splits into 2×2 blocks of fixed N , spanned by $\{|e, n\rangle, |g, n+1\rangle\}$.

Step 2: the one-excitation block. Take $N = 1$: $\{|e, 0\rangle, |g, 1\rangle\}$. The coupling acts as $\hbar g(\sigma^\dagger a + \sigma a^\dagger)$: $\sigma a^\dagger |e, 0\rangle = 0 + \dots$, precisely $\sigma a^\dagger |e, 0\rangle = |g, 1\rangle$ and $\sigma^\dagger a |g, 1\rangle = |e, 0\rangle$. At resonance ($\omega_0 = \omega_c$) both diagonal energies equal $\hbar\omega_c$; dropping this common offset,

$$H = \hbar \begin{pmatrix} 0 & g \\ g & 0 \end{pmatrix}.$$

Step 3: diagonalise. The eigenvalues solve $\det(H - \lambda \mathbb{K}) = \lambda^2 - (\hbar g)^2 = 0$, i.e. $\lambda = \pm \hbar g$. The eigenvectors of a symmetric off-diagonal 2×2 matrix are the symmetric/antisymmetric

combinations

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|e, 0\rangle \pm |g, 1\rangle), \quad E_{\pm} = \hbar\omega_c \pm \hbar g.$$

Step 4: dynamics. Expanding the initial state $|e, 0\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$ and propagating each eigenstate with its phase $e^{-iE_{\pm}t/\hbar}$ gives

$$P_e(t) = |\langle e, 0 | \psi(t) \rangle|^2 = \cos^2(gt), \quad P_{g,1}(t) = \sin^2(gt).$$

The quantum is exchanged back and forth with the empty cavity at frequency $2g$: these are the *vacuum Rabi oscillations*, and $2\hbar g$ is the level splitting.

Vacuum Rabi splitting

$$E_{\pm} = \hbar\omega_c \pm \hbar g, \quad \text{splitting} = 2\hbar g = 2\hbar d \sqrt{\frac{\omega_c}{2\hbar\epsilon_0 V}} \quad (26)$$

Observing this doublet is the signature of *strong coupling*: coherent exchange faster than any loss.

Your superconducting quantum computer is a cavity-QED experiment

The leading quantum computers today (the machines built by IBM, Google and others) are, almost exactly, the model on this page. The “atom” is a superconducting circuit, a *transmon*, engineered to have two usable levels; the “cavity” is a microwave resonator on the same chip. They are coupled by precisely the Jaynes–Cummings Hamiltonian, in a field called *circuit QED*, and the vacuum Rabi splitting $2g$ is measured routinely. Two of its features run the whole machine: in strong coupling, a control photon swaps quantum information between qubit and resonator (and, via the resonator, between distant qubits); in the dispersive (far-detuned) limit, the qubit’s state pulls the resonator frequency by a tiny amount, and detecting that pull is how the qubit is *read out*. The doublet you just diagonalised is the beating heart of a quantum processor.

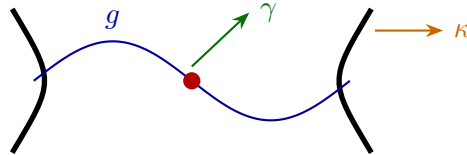


Figure 21: Cavity QED. A single atom (red dot) sits in the standing-wave mode (blue) between two mirrors, of mode volume V and frequency ω_c , coupling to it at the vacuum Rabi rate g . Two loss channels compete: photons leak through the mirrors at rate κ (orange arrow), and the atom emits into free-space modes at rate γ (green arrow). Strong coupling requires $g \gg \kappa, \gamma$.

The unequal rung spacing $2g\sqrt{n+1}$ means that driving the $|g, 0\rangle \rightarrow |\pm, 1\rangle$ transition detunes the next step: one photon “blocks” the absorption of a second (*photon blockade*), turning the cavity into a single-photon turnstile. With a coherent input (a spread of photon numbers), the many incommensurate Rabi frequencies dephase and then rephase, producing the celebrated *collapse and revival* of the atomic inversion; direct evidence of field quantization.

7.2 Weak vs strong coupling (enrichment)

Two loss rates compete with g : the cavity decay κ (photon escapes) and the atomic decay γ into non-cavity modes.

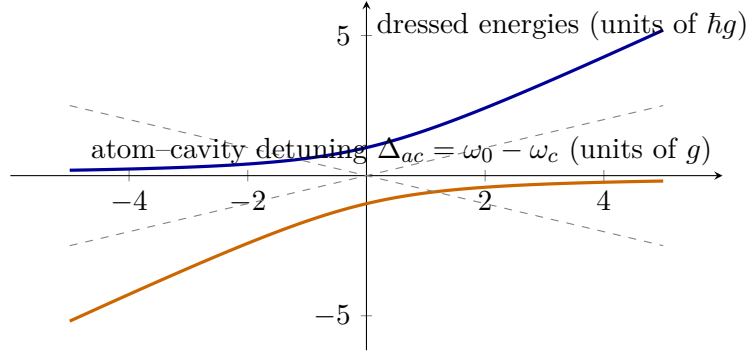


Figure 22: Avoided crossing of the dressed states $|\pm\rangle$ (solid) versus the bare atom/photon levels (dashed). At resonance ($\Delta_{ac} = 0$) the gap is the vacuum Rabi splitting $2\hbar g$; a single atom and an empty cavity repel like two coupled oscillators.

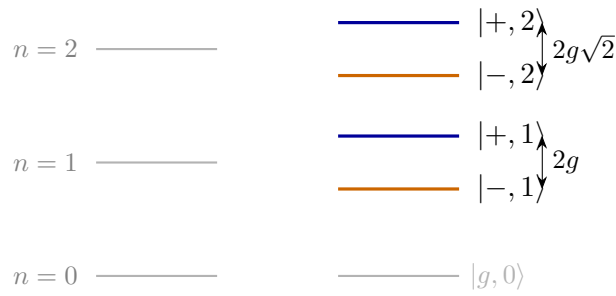


Figure 23: The Jaynes–Cummings ladder (bare uncoupled rungs on the left, dressed states on the right). Each n -excitation manifold splits into a doublet $|\pm, n\rangle$ separated by $2g\sqrt{n+1}$. The $\sqrt{n+1}$ anharmonicity is genuinely quantum (a classical field would give equally spaced rungs) and underlies photon blockade and the collapse–revival of Rabi oscillations in a coherent field.

- **Strong coupling** $g \gg (\kappa, \gamma)$: reversible energy exchange, vacuum Rabi doublet, dressed states. The atom–photon system is a new quantum object.
- **Weak coupling** $g \ll \kappa$: the cavity is essentially a modified continuum; emission stays irreversible but its *rate* is changed; the Purcell regime.

7.3 The Purcell factor: the core result

This is demonstration 6 of the thread, and it stands on its own: we take the spontaneous-emission rate of Lecture 5 (Fermi’s rule times the density of optical states) and simply swap the free-space density of states for the cavity’s. No Jaynes–Cummings, no dressed states, no matrix diagonalisation are needed; only the classical counting of cavity modes.

In weak coupling the golden rule applies with the cavity mode density replacing the free one. A cavity of quality factor $Q = \omega_c/\kappa$ concentrates the mode density into a bandwidth κ around ω_c .

Deriving the Purcell factor

The strategy is to apply the golden rule $\Gamma = \frac{2\pi}{\hbar} |d\mathcal{E}|^2 \rho(\omega_c)$ twice; once with the cavity density of states, once with free space; and take the ratio.

Step 1: cavity mode density. In free space the atom saw a broad continuum of modes; in a cavity it sees essentially *one* mode, but that mode is not infinitely sharp: it has a Lorentzian profile of width $\kappa = \omega_c/Q$ in frequency (a better cavity, higher Q , gives a narrower mode). The “density of states” is the number of modes per unit frequency. There is *one* mode in

total, so its Lorentzian must be normalised to $\int \rho d\omega = 1$:

$$\rho_{\text{cav}}(\omega) = \frac{1}{\pi} \frac{\kappa/2}{(\omega - \omega_c)^2 + (\kappa/2)^2},$$

(the standard normalised Lorentzian), whose peak value at line centre $\omega = \omega_c$ is

$$\rho_{\text{cav}}(\omega_c) = \frac{1}{\pi} \frac{2}{\kappa} = \frac{2}{\pi \kappa} = \frac{2Q}{\pi \omega_c}.$$

The physics to hold onto: a higher Q squeezes that one mode into a narrower band, so the density of states *on resonance* is larger, and the emission it stimulates is faster.

Step 2: cavity vacuum field. The matrix element uses $\mathcal{E}_c^2 = \frac{\hbar \omega_c}{2\varepsilon_0 V}$. Assuming the emitter sits at the field antinode with its dipole aligned, the cavity rate is

$$\Gamma_{\text{cav}} = \frac{2\pi}{\hbar} d^2 \frac{\hbar \omega_c}{2\varepsilon_0 V} \frac{2Q}{\pi \omega_c} = \frac{2d^2 Q}{\hbar \varepsilon_0 V}.$$

Step 3: free-space rate. From Sec. 5, $\Gamma_{\text{free}} = \frac{\omega_c^3 d^2}{3\pi \varepsilon_0 \hbar c^3}$ (with $c \rightarrow c/n$ in a medium of index n).

Step 4: take the ratio. The d^2 , ε_0 and $\hbar$ cancel:

$$F_P = \frac{\Gamma_{\text{cav}}}{\Gamma_{\text{free}}} = \frac{2Q/V}{\omega_c^3/3\pi(c/n)^3} = \frac{6\pi Q}{V} \left(\frac{c/n}{\omega_c}\right)^3 = \frac{6\pi Q}{V} \left(\frac{\lambda_c/n}{2\pi}\right)^3.$$

Step 5: simplify. With $\omega_c = 2\pi c/\lambda_c$ so that $(c/n)/\omega_c = \lambda_c/(2\pi n)$, the $(2\pi)^3$ in the denominator combines with the 6π :

$$F_P = \frac{6\pi}{(2\pi)^3} \left(\frac{\lambda_c}{n}\right)^3 \frac{Q}{V} = \frac{3}{4\pi^2} \left(\frac{\lambda_c}{n}\right)^3 \frac{Q}{V}$$

Purcell factor

$$F_P = \frac{3}{4\pi^2} \left(\frac{\lambda_c}{n}\right)^3 \frac{Q}{V} \quad (27)$$

The spontaneous-emission rate of a matched emitter is enhanced by F_P (large Q , small mode volume V). Off resonance, or in a photonic band gap, emission is instead *inhibited* ($F_P < 1$). The same LDOS that gave Γ in free space is now an engineering parameter.

Purcell enhancement in a semiconductor micropillar

A typical micropillar cavity for a single quantum dot has $Q = 10000$ and a mode volume $V \simeq 10 (\lambda/n)^3$ (a pillar about a micrometre across) at $\lambda_c = 950 \text{ nm}$, $n = 3.5$. Then

$$F_P = \frac{3}{4\pi^2} \frac{Q}{V/(\lambda/n)^3} = \frac{3}{4\pi^2} \times \frac{10000}{10} \approx 76.$$

A quantum dot with free-space lifetime $\tau_0 = 1 \text{ ns}$ thus emits in $\tau_{\text{cav}} = \tau_0/F_P \approx 13 \text{ ps}$, and funnels a fraction $\beta = F_P/(F_P + 1) \approx 0.99$ of its photons into the single cavity mode; the principle of bright, on-demand single-photon sources. With the *smallest conceivable* mode volume, $V = (\lambda/n)^3$, the same Q would give $F_P \approx 760$; real devices sit an order of magnitude below this diffraction-limited optimum.

Purcell-engineered light: single photons and faster LEDs

Controlling Γ on demand has two big payoffs. First, a quantum dot in a microcavity becomes a near-perfect *single-photon source*: press a button, get exactly one photon, emitted into one mode. These are the light bulbs of quantum communication and photonic quantum computing, where information is carried by individual photons and security relies on there being no second copy. Second, the same Purcell speed-up makes ordinary emitters *faster*: it is used to build LEDs and nanolasers that can be modulated at higher data rates, and conversely a photonic band gap can *suppress* emission to make a light source more efficient. The single knob $F_P = \frac{3}{4\pi^2}(\lambda/n)^3 Q/V$ is what photonics engineers turn to design all of these.

Strong-coupling threshold

For the same dot–cavity system, $g/2\pi \sim 20$ GHz is achievable, while $\kappa/2\pi = \nu_c/Q \approx (3.2 \times 10^{14} \text{ Hz})/10000 \approx 32$ GHz and $\gamma/2\pi \sim 0.2$ GHz. Since $g \gtrsim \kappa, \gamma$, the system sits at the onset of strong coupling: increasing Q to $\sim 10^5$ pushes κ below g and reveals the vacuum Rabi doublet; realized experimentally in pillar and photonic-crystal cavities.

7.4 Purcell rate from the cavity parameters

In the weak-coupling (“bad-cavity”) limit the atom never re-absorbs the photon, and the emission into the cavity mode is an irreversible decay whose rate follows from second-order perturbation theory in g .

Adiabatic elimination of the cavity field

Step 1: the coupled amplitudes. In the one-excitation sector, write the state as $c_e |e, 0\rangle + c_c |g, 1\rangle$. The Jaynes–Cummings coupling plus the cavity loss give

$$\dot{c}_e = -ig c_c, \quad \dot{c}_c = -ig c_e - \left(\frac{\kappa}{2} + i\Delta_{ac}\right)c_c,$$

where $\Delta_{ac} = \omega_0 - \omega_c$ and $\kappa/2$ damps the *amplitude* (the photon number decays at κ).

Step 2: the fast variable follows the slow one. With $\kappa \gg g$ the photon amplitude relaxes in a time $2/\kappa$, far shorter than the time $1/g$ on which c_e moves. On the slow time scale we may set $\dot{c}_c \approx 0$ (the cavity field is *slaved* to the atomic dipole):

$$c_c \simeq \frac{-ig}{\kappa/2 + i\Delta_{ac}} c_e.$$

Step 3: substitute back. The atom then obeys a closed equation,

$$\dot{c}_e = -\frac{g^2}{\kappa/2 + i\Delta_{ac}} c_e,$$

whose real part is an exponential decay of $|c_e|^2$ at the rate

$$\Gamma_{\text{cav}} = 2 \text{Re} \left[\frac{g^2}{\kappa/2 + i\Delta_{ac}} \right] = \frac{4g^2}{\kappa} \frac{1}{1 + (2\Delta_{ac}/\kappa)^2}$$

(and whose imaginary part is a cavity-induced level shift, the dispersive shift used to read out superconducting qubits). On resonance ($\Delta_{ac} = 0$), $\Gamma_{\text{cav}} = 4g^2/\kappa$. Forming the ratio to the free-space rate γ and using $g^2 \propto 1/V$, $\kappa = \omega_c/Q$ reproduces exactly the Purcell factor $F_P = \frac{3}{4\pi^2}(\lambda/n)^3 Q/V$ of the LDOS derivation; the two viewpoints agree.

The cooperativity

$$C = \frac{g^2}{\kappa\gamma} \quad (28)$$

The single-atom cooperativity sets the figure of merit of cavity QED: $C \simeq F_P$ in weak coupling, and $C \gg 1$ is required for efficient single-photon devices, atom–photon gates and spin–photon entanglement, even when $g < \kappa$ (so that the system is not strongly coupled).

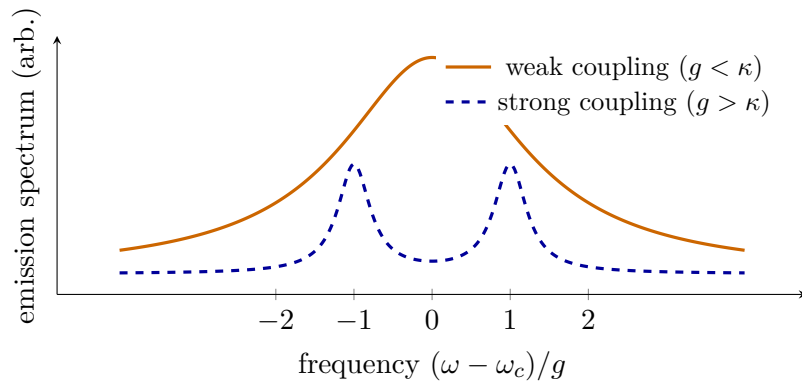


Figure 24: Cavity emission spectrum. In weak coupling a single (Purcell-broadened) line; in strong coupling the vacuum Rabi doublet split by $2g$. Crossing from one to the other as Q increases is the experimental signature of reaching strong coupling.

Can you now answer these? (Chapter 7)

- Why is the spontaneous-emission rate Γ *not* a fixed constant of nature?
- In one sentence, how does a cavity change Γ ?
- What roles do the quality factor Q and the mode volume V play in the Purcell factor?
- Why do we *not* need the dressed states to obtain the Purcell factor?

8 Optical response of solids

What changes when one atom becomes 10^{23} ?

Everything so far concerned one emitter with a few sharp levels. A solid is $\sim 10^{23}$ atoms bonded together, so close that their discrete levels overlap and broaden into continuous *bands*. The dipole coupling $-\mathbf{d} \cdot \mathbf{E}$ is unchanged, but “initial and final state” now means valence band and conduction band, and the sum over final states becomes an integral over a continuum. The question of the chapter is simply: what does our two-level machinery become when the two levels smear into bands, and the single emitter acquires its own width (an exciton line)? The answer is the optical response of every semiconductor device you own.

Roadmap, and the symbols introduced here

Progress: $\checkmark$ one emitter $\rightarrow$ (**you are here**) 10^{23} emitters = a solid.
 New symbols: E_g (band gap), $J(\hbar\omega)$ (joint density of states), $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ (dielectric function), Ry^* (exciton Rydberg), ω_p (plasma frequency), ω_T, ω_L (transverse / longitudinal phonon frequencies).

Finally we pass from one atom to $\sim 10^{23}$. The coupling is unchanged, but the continuum of electronic states in a solid reshapes the response into the *dielectric function* $\varepsilon(\omega)$, the central quantity of solid-state optics. This is the longest lecture: we build the solid’s optical response from the ground up, starting from how discrete atomic levels broaden into bands.

8.1 From atomic levels to energy bands

When N atoms are brought together, each atomic level $|n\rangle$ splits into N closely spaced levels; a *band*. The tight-binding model makes this quantitative and shows where the continuum of final states used by the golden rule comes from.

Tight-binding band from a chain of atoms

Step 1: ansatz. Place one orbital $|n\rangle$ on each site n of a 1D lattice of spacing a . By Bloch’s theorem the eigenstates are

$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikna} |n\rangle.$$

Step 2: Hamiltonian. Keep the on-site energy $\langle n|H|n\rangle = E_0$ and the nearest-neighbour hopping $\langle n|H|n \pm 1\rangle = -t$. Acting with H ,

$$H|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikna} (E_0 |n\rangle - t |n+1\rangle - t |n-1\rangle).$$

Step 3: shift the dummy index in the hopping terms ($n \pm 1 \rightarrow m$) to factor $|\psi_k\rangle$ back out:

$$H|\psi_k\rangle = (E_0 - t e^{-ika} - t e^{+ika}) |\psi_k\rangle.$$

Step 4: dispersion. Using $e^{ika} + e^{-ika} = 2 \cos ka$,

$$E(k) = E_0 - 2t \cos(ka)$$

The single atomic level E_0 has spread into a band of width $4t$ as k runs over the Brillouin zone $[-\pi/a, \pi/a]$. Near the band bottom, $\cos ka \approx 1 - (ka)^2/2$, so $E(k) \approx E_0 - 2t + ta^2 k^2$, i.e. a *parabolic* band with effective mass $m^* = \hbar^2/(2ta^2)$.

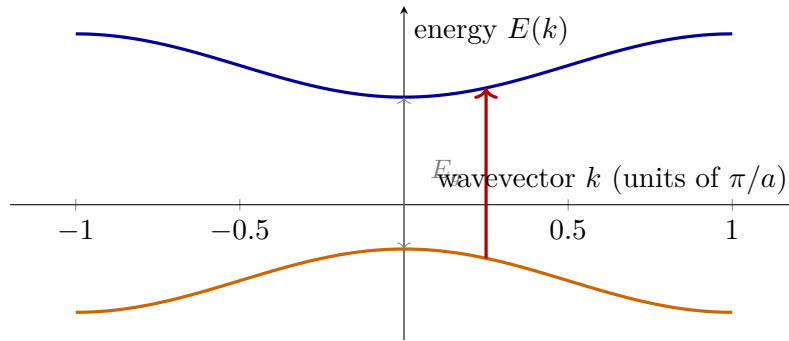


Figure 25: Two tight-binding bands (upper blue: conduction band; lower orange: valence band; horizontal axis k in units of π/a , vertical axis energy). The red arrow is an optical transition, essentially *vertical* on this scale because the photon momentum $\hbar\omega/c$ is negligible compared with the zone size π/a (the solid-state version of the dipole approximation). The minimum vertical gap E_g sets the absorption threshold.

Why optical transitions are vertical

A visible photon carries momentum $\hbar\omega/c \sim e - 27 \text{ kg m/s}$, whereas an electron at the zone boundary has $\hbar\pi/a \sim e - 24 \text{ kg m/s}$, a thousand times larger. Momentum conservation thus forces $\mathbf{k}_c \approx \mathbf{k}_v$: transitions are vertical in the band diagram. This is precisely the dipole approximation of L1 ($e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$), now phrased in crystal momentum.

8.2 From microscopic dipoles to the dielectric function

The complex dielectric function $\varepsilon(\omega) = 1 + \chi(\omega) = \varepsilon_1 + i\varepsilon_2$ relates $\mathbf{D} = \varepsilon_0\varepsilon\mathbf{E}$. Its real part fixes the refractive index and dispersion; its imaginary part ε_2 fixes absorption. The Drude and Lorentz contributions of Sec. 1 reappear: free carriers give the Drude term, bound interband transitions give Lorentz oscillators. Notice the recurrence: the *same* resonant Lorentzian denominator $\omega_0^2 - \omega^2 - i\gamma\omega$ that we first wrote for the classical oscillator in Chapter 1, then met again as the quantum susceptibility $1/(\delta + i/T_2)$ of a two-level emitter in Chapter 6, now returns a third time as the building block of the dielectric function of a solid. One denominator, three chapters: that is the red thread of the whole course made visible.

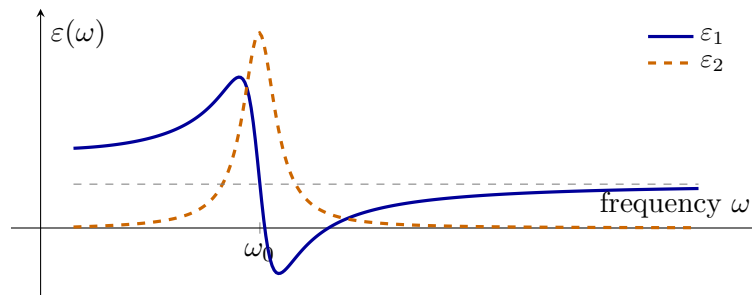


Figure 26: A single Lorentz oscillator contribution to the dielectric function. ε_2 (absorption) is a Lorentzian at ω_0 ; ε_1 (dispersion) shows normal dispersion away from resonance and anomalous dispersion across it. Summing many such oscillators (one per interband transition) plus a Drude term ($\omega_0 \rightarrow 0$) builds the full optical response of any solid.

Microscopic ε_2 from the golden rule

Step 1: power absorbed. The energy absorbed per unit volume and time from a field $\mathbf{E} = \text{Re}[\mathbf{E}_0 e^{-i\omega t}]$ is the work done on the bound charges, $\langle \mathbf{J}_{\text{pol}} \cdot \mathbf{E} \rangle$ with the polarization current $\mathbf{J}_{\text{pol}} = \partial_t \mathbf{P}$. With $\mathbf{P} = \text{Re}[\varepsilon_0 \chi \mathbf{E}_0 e^{-i\omega t}]$ and the average of a product of two real oscillations, $\langle \text{Re}[A e^{-i\omega t}] \text{Re}[B e^{-i\omega t}] \rangle = \frac{1}{2} \text{Re}[AB^*]$:

$$\langle P_{\text{abs}} \rangle = \frac{1}{2} \text{Re}[(-i\omega) \varepsilon_0 \chi |\mathbf{E}_0|^2] = \frac{1}{2} \varepsilon_0 \omega \text{Im} \chi |\mathbf{E}_0|^2 = \frac{1}{2} \varepsilon_0 \omega \varepsilon_2(\omega) |\mathbf{E}_0|^2.$$

Only the *imaginary* part survives the time average: the in-phase response (χ') borrows and returns energy each cycle, while the quadrature response (χ'') works against the field continuously. This relates ε_2 to a *rate*.

Step 2: same power from the golden rule. Each upward transition $v \rightarrow c$ removes one quantum $\hbar\omega$ at the golden-rule rate W_{vc} . With the dipole coupling $V = -\frac{1}{2} e \mathbf{E}_0 \cdot \mathbf{r}$ (the factor $\frac{1}{2}$ from the cosine), summed over the occupied valence and empty conduction states,

$$\langle P_{\text{abs}} \rangle = \hbar\omega \sum_{v,c} W_{vc} = \hbar\omega \frac{2\pi}{\hbar} \sum_{v,c} \left| \frac{1}{2} e \mathbf{E}_0 \cdot \mathbf{r}_{cv} \right|^2 \delta(E_c - E_v - \hbar\omega).$$

Step 3: equate and read off ε_2 . Dividing the two expressions for $\langle P_{\text{abs}} \rangle$ and writing the volume density of pairs as the joint density of states J ,

$$\varepsilon_2(\omega) = \frac{\pi e^2}{\varepsilon_0 m_e^2 \omega^2} \sum_{v,c} |\mathbf{e} \cdot \mathbf{p}_{cv}|^2 \delta(E_c - E_v - \hbar\omega)$$

(using $\mathbf{r}_{cv} = \mathbf{p}_{cv}/im_e\omega$ to switch to the momentum matrix element $\mathbf{p}_{cv}$, the standard band-structure quantity). Absorption is thus the golden rule dressed as a dielectric function: *matrix element* $\times$ *joint density of states*. The real part ε_1 then follows for free from causality (next box).

Kramers–Kronig from causality

The claim is astonishing: the refractive index and the absorption of *any* material are not independent; measure one at all frequencies and you can compute the other. The only assumption is causality, and here is why it is enough.

Step 1: cause before effect. Think of $\chi(t)$ as the medium's response to a sharp kick of field at time 0; $P(t) = \varepsilon_0 \int \chi(t-t') E(t') dt'$. The medium cannot polarise *before* it is kicked, so $\chi(t) = 0$ for $t < 0$. This single, almost trivial fact carries everything.

Step 2: one-sided in time $\Rightarrow$ analytic in frequency. Fourier transform, $\chi(\omega) = \int_0^\infty \chi(t) e^{i\omega t} dt$ (the lower limit is 0, not $-\infty$, precisely because of Step 1). If we now let ω have a positive imaginary part, the factor $e^{-\text{Im} \omega t}$ only *improves* the convergence, so $\chi(\omega)$ is well behaved (analytic, no poles) throughout the upper half of the complex- ω plane. Causality in time has become smoothness in frequency.

Step 3: analyticity ties ω to all other frequencies. For an analytic function Cauchy's theorem expresses its value at one point as an integral over a surrounding contour,

$$\chi(\omega) = \frac{1}{2\pi i} \oint \frac{\chi(\omega')}{\omega' - \omega} d\omega'.$$

Close the contour along the real axis and a big semicircle in the upper half plane (where $\chi \rightarrow 0$), and indent around the point $\omega' = \omega$; the standard Sokhotski manipulation gives the

principal-value relation

$$\chi(\omega) = \frac{1}{i\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega')}{\omega' - \omega} d\omega'.$$

The value at ω is now welded to the values at *all* other frequencies.

Step 4: split into the two halves. Write $\chi = \chi' + i\chi''$ and equate real and imaginary parts. Because of the i in front, the real part of the left side is fixed by the *imaginary* part of the integrand and vice versa: $\chi'(\omega) = \frac{1}{\pi} \mathcal{P} \int \frac{\chi''(\omega')}{\omega' - \omega} d\omega'$, and its partner. Folding the integral onto $[0, \infty)$ with $\chi(-\omega) = \chi^*(\omega)$ gives the boxed form. The upshot, used daily in optics: absorption and refraction are two faces of one causal function, so an ellipsometer measures the absorption spectrum and *computes* the index without ever measuring it.

Kramers–Kronig relations

Causality alone (response cannot precede excitation) forces ε_1 and ε_2 to be Hilbert transforms of each other:

$$\varepsilon_1(\omega) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad \varepsilon_2(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^{\infty} \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'. \quad (29)$$

Measuring absorption over all frequencies determines the dispersion, and vice versa; an exact, model-independent constraint used throughout optical spectroscopy.

8.3 Interband absorption via the golden rule

The absorption edge of a semiconductor is Fermi's golden rule applied to the continuum of valence→conduction transitions.

Joint density of states and the $\sqrt{\cdot}$ edge

Step 1: what a vertical transition costs. A photon lifts an electron straight up from the valence band to the conduction band (vertical, because the photon carries no momentum on this scale). Near their extrema both bands are parabolic, $E_c = E_g + \hbar^2 k^2 / 2m_c$ and $E_v = -\hbar^2 k^2 / 2m_v$, so the energy the photon must supply at wavevector $\mathbf{k}$ is

$$\hbar\omega = E_c(\mathbf{k}) - E_v(\mathbf{k}) = E_g + \frac{\hbar^2 k^2}{2m_c} + \frac{\hbar^2 k^2}{2m_v} = E_g + \frac{\hbar^2 k^2}{2\mu}, \quad \frac{1}{\mu} = \frac{1}{m_c} + \frac{1}{m_v}.$$

The two masses combine into a single reduced mass μ , exactly as for the relative motion of two bodies. At the band edge ($k = 0$) the cost is just E_g ; deeper in the bands it grows.

Step 2: which k is resonant with a given colour? Invert the relation:

$$k(\omega) = \frac{1}{\hbar} \sqrt{2\mu(\hbar\omega - E_g)}, \quad (\hbar\omega > E_g).$$

A photon of energy $\hbar\omega$ can only be absorbed by electrons at this particular $|\mathbf{k}|$.

Step 3: how many electrons are at that k ? That number is the joint density of states, the count of $\mathbf{k}$ per unit volume and unit energy that satisfy the resonance condition:

$$J(\hbar\omega) = 2 \int \frac{d^3 k}{(2\pi)^3} \delta\left(\hbar\omega - E_g - \frac{\hbar^2 k^2}{2\mu}\right).$$

The factor 2 is for spin. The δ -function restricts the integral to a thin spherical shell in $\mathbf{k}$ -space of radius k ; its area is $4\pi k^2$, and converting the energy δ -function to a k -shell brings a Jacobian $(d(\hbar\omega)/dk)^{-1}$:

$$J = \frac{2}{(2\pi)^3} 4\pi k^2 \left(\frac{d(\hbar\omega)}{dk} \right)^{-1}.$$

With $d(\hbar\omega)/dk = \hbar^2 k/\mu$ one power of k cancels:

$$J(\hbar\omega) = \frac{1}{\pi^2} k^2 \frac{\mu}{\hbar^2 k} = \frac{\mu k}{\pi^2 \hbar^2}.$$

Step 4: put in $k(\omega)$ and read the edge. Insert Step 2:

$$J(\hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2\mu}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

Since the absorption coefficient is $\alpha = \frac{\omega}{c} \varepsilon_2 \propto |\mathbf{p}_{cv}|^2 J(\hbar\omega)/\omega$, a slowly varying matrix element gives

$$\alpha(\omega) \propto (\hbar\omega - E_g)^{1/2}.$$

The physical picture: right at the gap there are almost no resonant electrons, so absorption switches on gently as $\sqrt{\hbar\omega - E_g}$; the further above the gap, the more $\mathbf{k}$ -states are available. This square-root edge is the fingerprint of a direct-gap semiconductor. Squeeze the crystal into a thin sheet (a 2D quantum well) and the same counting gives a *staircase* of constant steps instead; in a 1D wire it gives $1/\sqrt{\cdot}$ spikes.

Direct-gap absorption edge

$$\alpha(\omega) \propto (\hbar\omega - E_g)^{1/2} \quad (\text{direct allowed transitions}) \quad (30)$$

Indirect gaps (Si, Ge) require phonon assistance and give a weaker $(\hbar\omega - E_g \pm \hbar\omega_{\text{ph}})^2$ edge. Below E_g the crystal is transparent.

The band gap that lights your room and powers your roof

This one number E_g decides the colour and the job of a semiconductor. Choose E_g in the visible and you get a light-emitting diode; the long quest for a *blue* LED (a wide-gap material, gallium nitride) was solved only in the 1990s and won the 2014 Nobel Prize, because blue was the missing colour needed to make white LED lighting and full-colour displays. Run the process backwards, absorbing sunlight to create electron-hole pairs, and the same edge is a *solar cell*; the gap sets which part of the solar spectrum is harvested. And the *direct* versus *indirect* distinction in this box is decisive in practice: gallium arsenide (direct) emits light efficiently and makes the lasers in every fibre-optic link, while silicon (indirect) barely emits, which is exactly why your computer is silicon but its data travels as GaAs-laser light.

8.4 Excitons: the hydrogen atom inside a crystal

The single-particle picture misses the Coulomb attraction between the photo-excited electron and the hole it leaves behind. This bound pair is the *exciton*, and its spectrum is hydrogen-like; a direct callback to the atomic physics of Lectures 1–5.

The Wannier exciton Rydberg series

Step 1: the effective two-body problem. An electron (mass m_c) and a hole (mass m_v) attract through a Coulomb potential screened by the host dielectric constant ε_r . Their relative motion obeys a hydrogen-like equation

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \right] \phi(\mathbf{r}) = E_b \phi(\mathbf{r}), \quad \frac{1}{\mu} = \frac{1}{m_c} + \frac{1}{m_v}.$$

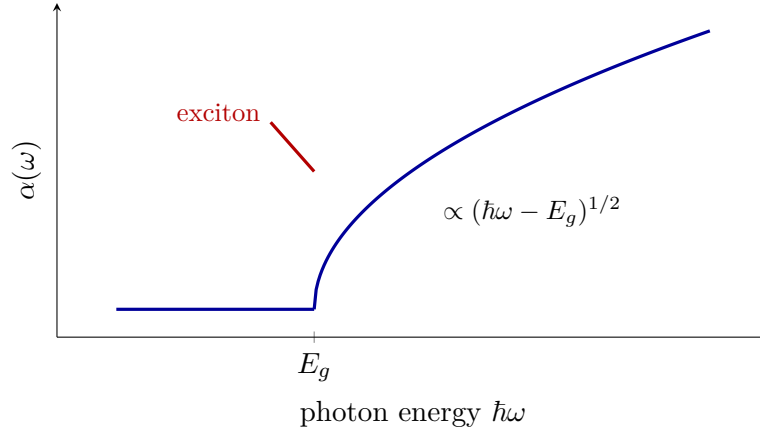


Figure 27: Direct-gap absorption edge. The continuum rises as $(\hbar\omega - E_g)^{1/2}$ from the joint density of states; bound excitons add a sharp line just below E_g (red).

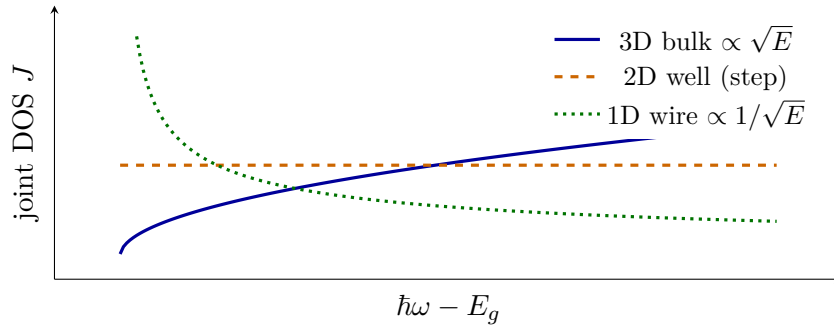


Figure 28: The joint density of states depends on dimensionality: a square-root edge in 3D bulk, a staircase of constant steps in a 2D quantum well, and inverse-square-root (van Hove) singularities in a 1D wire. Quantum confinement thus reshapes the absorption spectrum; the basis of band-gap engineering in heterostructures.

Step 2: map onto hydrogen. This is exactly the hydrogen problem with two replacements: $m_e \rightarrow \mu$ and $e^2 \rightarrow e^2/\epsilon_r$. The hydrogen binding energy $\text{Ry} = m_e e^4 / (2(4\pi\epsilon_0)^2 \hbar^2) = 13.6 \text{ eV}$ therefore rescales as

$$E_n = -\frac{\mu e^4}{2(4\pi\epsilon_0\epsilon_r)^2 \hbar^2} \frac{1}{n^2} = -\frac{\mu/m_e}{\epsilon_r^2} \frac{\text{Ry}}{n^2}, \quad n = 1, 2, 3, \dots$$

Step 3: the exciton Rydberg and Bohr radius. Define the exciton Rydberg $\text{Ry}^* = (\mu/m_e)\epsilon_r^{-2} \text{Ry}$ and Bohr radius

$$a_X = \frac{\epsilon_r m_e}{\mu} a_0, \quad E_n = E_g - \frac{\text{Ry}^*}{n^2}$$

The absorption lines sit at $E_g - \text{Ry}^*/n^2$, converging onto the band edge E_g as $n \rightarrow \infty$, where they merge into the continuum derived above.

Step 4: why ϵ_r and μ make excitons giant and weak. In a typical semiconductor $\epsilon_r \sim 10$ and $\mu \sim 0.1 m_e$, so $\text{Ry}^* \sim (0.1/100) \times 13.6 \text{ eV} \sim 10 \text{ meV}$ (vs 13.6 eV for hydrogen) and $a_X \sim 100 a_0 \sim 5 \text{ nm}$, spanning many unit cells. This justifies the continuum-screening (*Wannier*) picture; in molecular crystals with $\epsilon_r \sim 1$ the exciton is instead tightly bound (*Frenkel*).

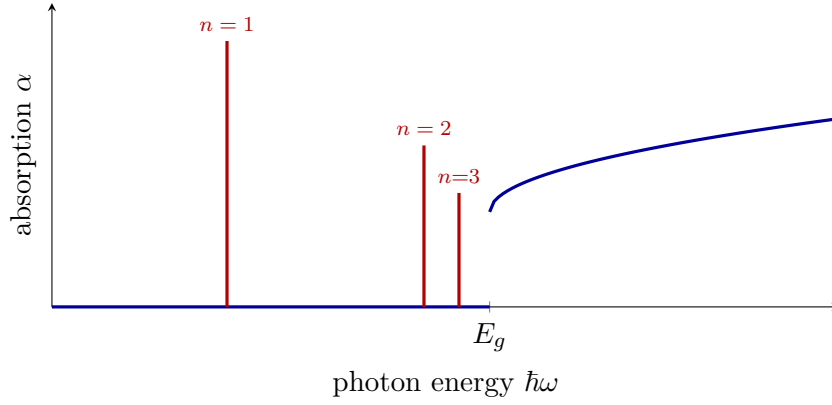


Figure 29: Excitonic absorption (Elliott spectrum). The red lines below the gap are the hydrogen-like exciton Rydberg series at $E_g - \text{Ry}^*/n^2$ ($n = 1, 2, 3, \dots$), accumulating at the gap E_g . The blue curve above the gap is the band-to-band continuum, which rises as $\sqrt{\hbar\omega - E_g}$ and is further enhanced by the Coulomb interaction (Sommerfeld factor), so the edge does not simply vanish. The lines are resolved only when $k_B T \lesssim \text{Ry}^*$.

GaAs vs ZnO excitons

For GaAs, $\mu = 0.059 m_e$, $\varepsilon_r = 12.9$: $\text{Ry}^* = (0.059/12.9^2) \times 13.6 \text{ eV} \approx 4.8 \text{ meV}$ and $a_X = (12.9/0.059)a_0 \approx 12 \text{ nm}$; observable only below $\sim 50 \text{ K}$. For ZnO, $\mu \approx 0.18 m_e$, $\varepsilon_r \approx 7.8$: $\text{Ry}^* \approx (0.18/60.8) \times 13.6 \approx 40 \text{ meV}$ (often quoted $\sim 60 \text{ meV}$ with anisotropy), *larger* than $k_B T$ at room temperature; which is why ZnO and other wide-gap materials show excitonic effects and lasing even at 300 K .

Qubits made of crystal: quantum dots and colour centres

The two-level emitters of Lecture 6 live inside these solids. A semiconductor *quantum dot*, a nanoscale box that traps a single electron-hole pair, behaves like an artificial atom with a tunable gap; engineered in a cavity (previous lecture) it is today's brightest single-photon source. A nitrogen-vacancy *colour centre* in diamond holds an electronic spin that can be initialised, rotated and read out optically at room temperature, and is used both as a qubit and as a nanoscale magnetic-field sensor sensitive enough to image the currents in a single neuron. Silicon itself, the substrate of all electronics, can host single-electron *spin qubits* that piggyback on the trillion-dollar chip industry. In every case the solid-state band physics of this lecture sets where the levels sit, and the coupling physics of the earlier lectures says how to talk to them with light.

8.5 Polaritons: light–matter hybrids in bulk

When a dipole-active resonance (a phonon, or the exciton just derived) couples to light, the two cannot be treated separately: the propagating mode is a mixture, a *polariton*. This is the bulk-crystal analogue of the vacuum Rabi splitting of Sec. 7.

Polariton dispersion and the LST relation

Step 1: the dielectric function of one resonance. A transverse optical phonon at ω_T contributes a Lorentz oscillator (undamped):

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_{\text{st}} - \varepsilon_\infty)\omega_T^2}{\omega_T^2 - \omega^2},$$

where $\varepsilon_{\text{st}} = \varepsilon(0)$ and $\varepsilon_\infty = \varepsilon(\infty)$.

Step 2: transverse modes: the polariton branches. A transverse EM wave obeys $k^2 c^2 = \omega^2 \varepsilon(\omega)$. Substituting Step 1 gives a quadratic in ω^2 for each k , hence *two* solutions: the lower and upper polariton branches. As $k \rightarrow \infty$ the lower branch saturates at ω_T (where $\varepsilon \rightarrow \infty$); as $k \rightarrow 0$ the upper branch starts at the frequency where $\varepsilon = 0$.

Step 3: longitudinal mode and ω_L . A longitudinal mode requires $\varepsilon(\omega_L) = 0$. Setting Step 1 to zero,

$$\varepsilon_\infty(\omega_T^2 - \omega_L^2) + (\varepsilon_{\text{st}} - \varepsilon_\infty)\omega_T^2 = 0 \Rightarrow \omega_L^2 = \omega_T^2 \frac{\varepsilon_{\text{st}}}{\varepsilon_\infty}.$$

Step 4: the Lyddane–Sachs–Teller relation.

$$\frac{\omega_L^2}{\omega_T^2} = \frac{\varepsilon_{\text{st}}}{\varepsilon_\infty}$$

Between ω_T and ω_L one has $\varepsilon(\omega) < 0$: k is imaginary, no wave propagates, and the crystal reflects totally. This is the *reststrahlen* band, and its width is fixed by the LST ratio; a purely macroscopic measurement of the ionicity of the bond.

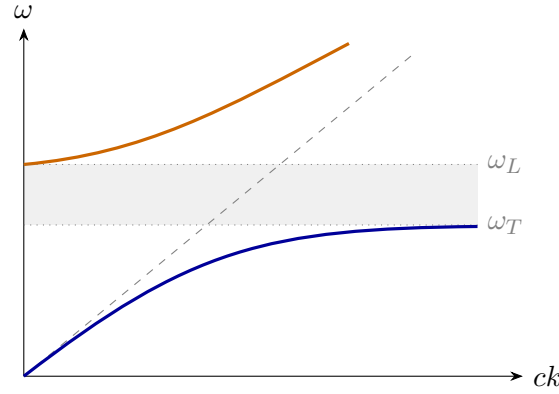


Figure 30: Polariton dispersion for a single dipole-active resonance (horizontal axis ck , vertical axis ω). The lower branch (blue) starts photon-like and bends over to saturate at ω_T ; the upper branch (orange) starts at ω_L and becomes photon-like at large ck ; the grey dashed line is the bare light line. No propagating mode exists in the shaded reststrahlen gap $\omega_T < \omega < \omega_L$ (total reflection). This is the bulk-matter counterpart of the vacuum Rabi splitting of Fig. 22.

8.6 Free carriers: the Drude model and metallic reflection

Setting the restoring force to zero ($\omega_0 \rightarrow 0$) turns the Lorentz oscillator into the *Drude* model of free electrons, which governs metals and doped semiconductors.

Drude dielectric function and plasma frequency

Step 1: equation of motion. A free electron with phenomenological collision rate γ obeys $m_e(\ddot{\mathbf{r}} + \gamma\dot{\mathbf{r}}) = -e\mathbf{E}$. For $\mathbf{E} \propto e^{-i\omega t}$ the steady-state displacement is

$$\mathbf{r}_0 = \frac{e/m_e}{\omega^2 + i\gamma\omega} \mathbf{E}_0.$$

Step 2: polarization and ε . With N electrons per unit volume the polarization is $\mathbf{P} = -Ner_0 = \varepsilon_0\chi\mathbf{E}$, so

$$\varepsilon(\omega) = 1 + \chi = 1 - \frac{Ne^2/\varepsilon_0 m_e}{\omega^2 + i\gamma\omega} = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega},$$

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m_e}$$

Step 3: the two regimes. Neglecting damping, $\varepsilon = 1 - \omega_p^2/\omega^2$. For $\omega < \omega_p$, $\varepsilon < 0$: $n = \sqrt{\varepsilon}$ is imaginary, the wave is evanescent and $R \rightarrow 1$ (perfect mirror). For $\omega > \omega_p$, $\varepsilon > 0$: the metal is transparent and $n < 1$. The plasma frequency is the watershed between metallic reflection and dielectric transparency.

Step 4: low frequency (Hagen–Rubens). For $\omega \ll \gamma$ the dielectric function is dominated by its imaginary part, $\varepsilon \approx i\omega_p^2/\gamma\omega = i\sigma_0/\varepsilon_0\omega$ with the DC conductivity $\sigma_0 = Ne^2/m_e\gamma$, recovering Ohmic absorption and the skin effect.

Plasma frequency and reflectivity of a metal

Free electrons (Drude, $\omega_0 \rightarrow 0$, neglecting damping) give $\varepsilon(\omega) = 1 - \omega_p^2/\omega^2$ with the plasma frequency $\omega_p = \sqrt{Ne^2/\varepsilon_0 m_e}$. For aluminium, $N = 1.8 \times 10^{29} \text{ m}^{-3}$:

$$\omega_p = \sqrt{\frac{(1.8 \times 10^{29})(1.6 \times 10^{-19})^2}{(8.85 \times 10^{-12})(9.1 \times 10^{-31})}} \approx 2.4 \times 10^{16} \text{ rad/s},$$

i.e. $\hbar\omega_p \approx 15 \text{ eV}$ (ultraviolet). For $\omega < \omega_p$, $\varepsilon < 0$: the wave is evanescent and the metal is highly reflecting; why aluminium mirrors are excellent across the whole visible range, turning transparent only in the far UV.

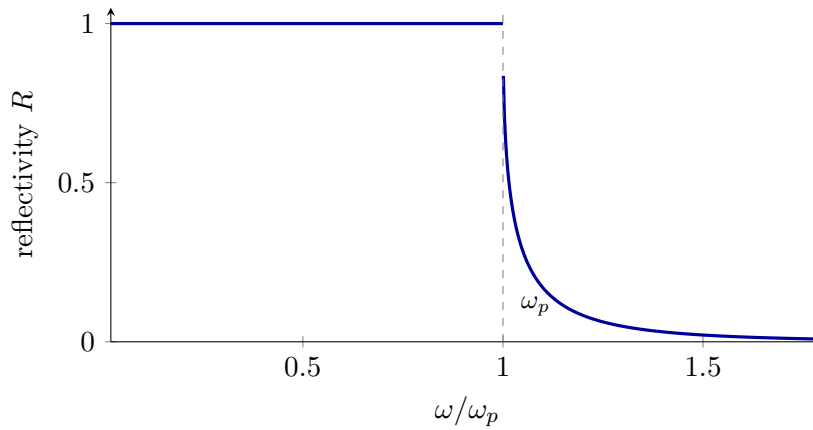


Figure 31: Drude reflectivity of an ideal metal. Below the plasma frequency ω_p the dielectric function is negative, the wave is evanescent and $R = 1$ (perfect mirror); above ω_p the metal becomes transparent. For Al, $\hbar\omega_p \approx 15 \text{ eV}$ keeps the whole visible band ($\hbar\omega \lesssim 3 \text{ eV}$) in the reflecting region.

Why gold is yellow, silver is white, and glass is transparent

The dielectric function just assembled explains the look of everyday materials. *Silver* is the pure Drude story: its interband transitions lie in the UV ($\gtrsim 3.9 \text{ eV}$), so across the whole visible range ε is dominated by free electrons, $R \approx 1$ at all colours: a neutral, white mirror. *Gold* adds a Lorentz term inside the visible: transitions from its filled $5d$ band to the Fermi level start near $\hbar\omega \approx 2.4 \text{ eV}$ ($\approx 520 \text{ nm}$, green). Blue and green light is therefore *absorbed* rather than reflected, and the reflected remainder (red + green – blue) is the familiar yellow. Copper’s interband edge sits lower still ($\sim 2 \text{ eV}$), hence its redder hue. *Window glass* is the opposite limit: no free carriers (no Drude term) and a band gap of $\sim 9 \text{ eV}$ (deep UV), so in the visible $\varepsilon_2 \approx 0$; there is nothing to absorb, only the real $\varepsilon_1 \approx 2.25$ ($n \approx 1.5$) that refracts. The colour of every object around you is a statement about where its oscillators sit.

Exercise 7.1: a Kramers–Kronig check

A narrow absorption line modeled as $\varepsilon_2(\omega) = A \delta(\omega - \omega_1)$ gives, by the first Kramers–Kronig relation, $\varepsilon_1(\omega) - 1 = \frac{2A\omega_1}{\pi(\omega_1^2 - \omega^2)}$; precisely the dispersive Lorentz shape of Fig. 3. Causality alone thus dictates that any absorption peak is accompanied by anomalous dispersion across it: absorption and dispersion are never independent.

Exciton absorption line in GaAs

GaAs has $E_g = 1.42$ eV and exciton binding energy $E_b = 4.2$ meV, so the $n = 1$ exciton absorbs at $\hbar\omega = E_g - E_b = 1.4158$ eV ($\lambda = 876$ nm). The exciton Bohr radius $a_X = \frac{4\pi\varepsilon_0\varepsilon_r\hbar^2}{\mu e^2}$ with $\varepsilon_r = 12.9$, $\mu = 0.06 m_e$ gives

$$a_X = \frac{\varepsilon_r}{\mu/m_e} a_0 = \frac{12.9}{0.06} \times 0.053 \text{ nm} \approx 11 \text{ nm},$$

spanning ~ 20 unit cells; a giant, weakly bound exciton, observable as a sharp line only at low temperature ($k_B T \lesssim E_b$ requires $T \lesssim 50$ K).

8.7 Microcavity exciton-polaritons: closing the loop with Lecture 7

Place an exciton-bearing quantum well at the antinode of a planar microcavity and the bulk polariton of Sec. 8 becomes a *cavity* polariton; the exact solid-state realisation of the Jaynes–Cummings physics of Lecture 7, now with a collective exciton playing the role of the two-level atom.

Cavity-polariton anticrossing

Step 1: two coupled modes. Near resonance keep one cavity photon mode (energy $E_c(k)$, tunable by the in-plane wavevector k or the incidence angle) and one exciton mode (energy E_X , nearly flat). The coupled Hamiltonian is the same 2×2 as the dressed atom:

$$H = \begin{pmatrix} E_c(k) & \hbar\Omega_R/2 \\ \hbar\Omega_R/2 & E_X \end{pmatrix},$$

where $\hbar\Omega_R$ is the (collective, $\propto \sqrt{N}$) light–matter coupling.

Step 2: eigenvalues. Diagonalising,

$$E_{\pm}(k) = \frac{E_c + E_X}{2} \pm \frac{1}{2} \sqrt{(E_c(k) - E_X)^2 + (\hbar\Omega_R)^2}.$$

Step 3: the anticrossing. At resonance $E_c(k_0) = E_X$ the branches are split by $\hbar\Omega_R$ (the *vacuum Rabi splitting*, here *normal-mode splitting*) and the eigenstates are the half-light/half-matter *upper* and *lower polaritons*. Away from resonance each branch returns smoothly to a pure photon or pure exciton; an avoided crossing identical in form to Fig. 22.

Numbers for a GaAs microcavity

A high-quality GaAs/AlAs microcavity reaches a normal-mode splitting $\hbar\Omega_R \approx 4$ meV for a single quantum well (and ~ 15 meV for several wells), far exceeding the cavity and exciton linewidths (~ 0.5 meV): the system is firmly in strong coupling. The lower-polariton effective mass is $\sim 10^{-4}$ of the bare electron mass, set by the photon component; which is why polariton condensation occurs at tens of kelvin rather than nanokelvin. Wide-gap materials (GaN, ZnO, organics) push $\hbar\Omega_R$ to ~ 0.1 eV and strong coupling to room temperature.

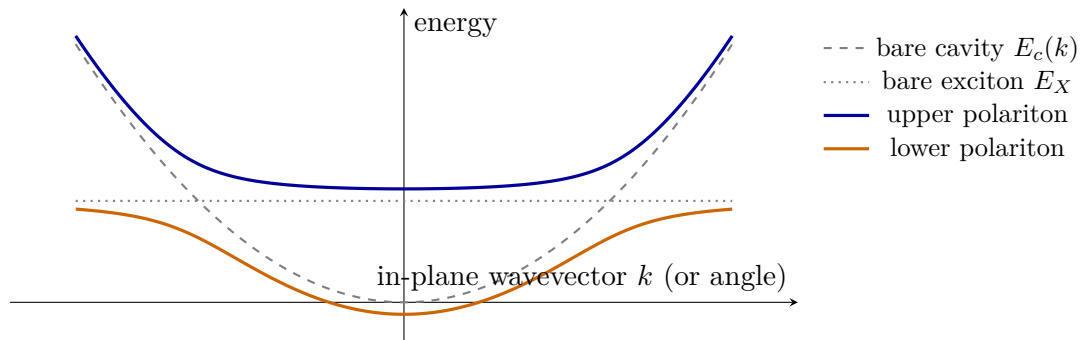


Figure 32: Microcavity exciton-polariton dispersion. The parabolic cavity photon and the flat exciton (dashed/dotted) anticross; the gap at resonance is the normal-mode (vacuum Rabi) splitting $\hbar\Omega_R$. The very light lower-polariton mass enables polariton Bose–Einstein condensation and low-threshold “polariton lasing”; strong-coupling cavity QED in a chip.

Can you now answer these? (Chapter 8)

- In a solid, what plays the role of the “initial” and “final” states of the golden rule?
- Why does a direct-gap absorption edge rise as $\sqrt{\hbar\omega - E_g}$?
- Why is silicon a poor light emitter but a fine solar cell?
- What is an exciton, and why is it “hydrogen inside a crystal”?

Synthesis: one coupling, five tools

Tool	Keeps / adds	Answers the question
Fermi golden rule	rates, density of states	How fast does the atom absorb / emit?
Optical Bloch eqs.	coherence, T_1, T_2	How does a driven atom evolve in time?
Maxwell–Bloch	field propagation	How does light traverse a resonant medium?
Purcell / cavity QED	engineered mode density	How does the environment reshape emission?
Solid-state response	continuum of states	How does bulk matter respond optically?

All five rest on the single interaction $-\mathbf{d} \cdot \mathbf{E}$ and on one recurring idea: the response is a resonant denominator whose imaginary part is absorption and whose strength is set by a density of states; of final atomic levels (Fermi), of photon modes (spontaneous emission, Purcell), or of electronic states (solids).

Problems with worked solutions

Problem 1 (Fermi golden rule; two-photon vs one-photon). Show that the ratio of two-photon to one-photon transition rates at intensity I scales as I , and estimate the intensity at which they become comparable for an optical transition.

Solution 1

A one-photon rate is first order in the perturbation, $W^{(1)} \propto |V|^2 \propto I$. A two-photon rate is second order in V through a virtual state, $W^{(2)} \propto |V|^4 \propto I^2$, with an extra energy denominator $\sim (\hbar\Delta)^2$ where Δ is the detuning from the virtual level. Hence $W^{(2)}/W^{(1)} \sim I d^2 / (\varepsilon_0 c \hbar^2 \Delta^2)$. Putting $d \sim ea_0$, $\hbar\Delta \sim 1 \text{ eV}$, the two rates equalize at $I \sim 10^{15} \text{ W/m}^2$ (10^{11} W/cm^2); only reachable with pulsed lasers, which is why multiphoton processes are a nonlinear-optics phenomenon.

Problem 2 (Spontaneous emission of hydrogen $2p \rightarrow 1s$). Given $d_{2p,1s} = 0.74 ea_0$ and $\lambda_0 = 121.6 \text{ nm}$ (Lyman- α), compute the lifetime.

Solution 2

With $\omega_0 = 2\pi c/\lambda_0 = 1.55e16 \text{ rad/s}$ and $d = 0.74 \times 1.6 \times 10^{-19} \times 5.3 \times 10^{-11} = 6.3e-30 \text{ C m}$,

$$\Gamma = \frac{\omega_0^3 d^2}{3\pi\varepsilon_0 \hbar c^3} \approx \frac{(1.55 \times 10^{16})^3 (6.3 \times 10^{-30})^2}{3\pi(8.85 \times 10^{-12})(1.05 \times 10^{-34})(3 \times 10^8)^3} \approx 6.3e8 \text{ s}^{-1},$$

so $\tau \approx 1.6 \text{ ns}$, matching the textbook value. The shorter wavelength (vs Na) raises Γ through the ω_0^3 factor despite the smaller dipole.

Problem 3 (Optical Bloch; steady-state fluorescence). Find the photon-scattering rate $R_{\text{sc}} = \Gamma \rho_{ee}^{\text{ss}}$ as a function of detuning and intensity, and its maximum.

Solution 3

Using $\rho_{ee}^{\text{ss}} = \frac{1}{2}s/(1+s)$ with $s = (I/I_{\text{sat}})/(1 + (2\delta/\Gamma)^2)$,

$$R_{\text{sc}} = \frac{\Gamma}{2} \frac{I/I_{\text{sat}}}{1 + I/I_{\text{sat}} + (2\delta/\Gamma)^2}.$$

At fixed I this is a power-broadened Lorentzian in δ , peaked on resonance; as $I \rightarrow \infty$ it saturates at $R_{\text{sc}} \rightarrow \Gamma/2$. For Na this caps the fluorescence at $\approx 3e7$ photons/s per atom; the maximum force available for laser cooling is $F_{\text{max}} = \hbar k \Gamma/2$.

Problem 4 (Purcell engineering for a single-photon source). What cavity Q/V is needed so that a quantum dot ($\tau_0 = 1 \text{ ns}$, $\lambda = 900 \text{ nm}$, $n = 3.5$) funnels $\beta = 0.95$ of its photons into the cavity mode?

Solution 4

$\beta = F_P/(F_P + 1) = 0.95 \Rightarrow F_P = 19$. From $F_P = \frac{3}{4\pi^2}(\lambda/n)^3 Q/V$, taking the smallest possible mode volume $V = (\lambda/n)^3$ gives $Q = 4\pi^2 F_P/3 \approx 250$; very modest. A more realistic $V = 5(\lambda/n)^3$ needs $Q \approx 1250$. The lesson: high collection efficiency does not require ultrahigh Q ; small mode volume does most of the work.

Problem 5 (Solids; plasma edge of a doped semiconductor). Doped InSb has carrier density $N = 1e24 \text{ m}^{-3}$ and effective mass $m^* = 0.014 m_e$. Find the plasma wavelength.

Solution 5

$\omega_p = \sqrt{Ne^2/\varepsilon_0\varepsilon_\infty m^*}$ with $\varepsilon_\infty \approx 16$:

$$\omega_p = \sqrt{\frac{10^{24}(1.6 \times 10^{-19})^2}{(8.85 \times 10^{-12})(16)(0.014 \times 9.1 \times 10^{-31})}} \approx 1.2e14 \text{ rad/s},$$

i.e. $\lambda_p = 2\pi c/\omega_p \approx 16 \mu\text{m}$ (mid-infrared). The small effective mass and low density push the plasma edge from the UV (metals) deep into the infrared, making doped semiconductors tunable infrared mirrors and plasmonic materials.

Problem 6 (Lorentz $\rightarrow$ quantum: oscillator strength of Na). Estimate the oscillator strength of the Na D line from its measured lifetime $\tau = 16 \text{ ns}$ and wavelength $\lambda_0 = 589 \text{ nm}$.

Solution 6

Step 1. Invert the relation $\Gamma = \frac{e^2\omega_0^2}{6\pi\varepsilon_0 m_e c^3} f$ of Sec. 4.5 for f :

$$f = \frac{6\pi\varepsilon_0 m_e c^3}{e^2\omega_0^2} \Gamma.$$

Step 2. Numbers: $\omega_0 = 2\pi c/\lambda_0 = 3.2e15 \text{ rad/s}$, $\Gamma = 1/\tau = 6.25e7 \text{ s}^{-1}$. Then

$$f = \frac{6\pi(8.85 \times 10^{-12})(9.11 \times 10^{-31})(3 \times 10^8)^3}{(1.6 \times 10^{-19})^2(3.2 \times 10^{15})^2} \times 6.25 \times 10^7 \approx 0.98.$$

Step 3: interpret. $f \approx 1$: the D line exhausts almost the entire Thomas–Reiche–Kuhn strength of the single valence electron, consistent with the sum rule $\sum f = Z_{\text{valence}} = 1$. This is why a two-level model of sodium is so accurate.

Problem 7 (Ramsey fringes from the Bloch equations). Two short resonant $\pi/2$ -pulses are separated by a free-evolution time T at detuning δ . Find the excited-state probability versus δ .

Solution 7

Step 1: first $\pi/2$ -pulse. Starting at the south pole $|g\rangle$, a $\pi/2$ rotation puts the Bloch vector on the equator: a coherence ρ_{eg} of unit magnitude.

Step 2: free precession. During T the coherence precesses at the detuning, acquiring a phase δT : $\rho_{eg} \rightarrow \rho_{eg} e^{i\delta T}$ (no driving, so the Bloch vector simply rotates about the vertical axis).

Step 3: second $\pi/2$ -pulse. The final inversion is the projection of the precessed vector onto the new pulse axis. Adding the two amplitude paths coherently,

$$P_e(\delta) = \frac{1}{2}[1 + \cos(\delta T)] = \cos^2\left(\frac{\delta T}{2}\right).$$

Step 4: interpret. These are *Ramsey fringes* of period $2\pi/T$ in δ : the longer the free evolution T , the finer the fringes and the more precise the resulting frequency measurement; the principle of the atomic clock. Decoherence damps the fringe contrast as e^{-T/T_2} .

Problem 8 (Optical-trap depth from the light shift). A red-detuned Gaussian beam of power P , waist w_0 , detuning δ traps an atom. Derive the trap depth and evaluate it.

Solution 8

Step 1: peak intensity. A Gaussian beam has $I_0 = 2P/\pi w_0^2$ at the focus.

Step 2: dipole potential. From Sec. 2.3, $U_{\text{dip}} = \frac{3\pi c^2 \Gamma}{2\omega_0^3 \delta} I_0$. For red detuning ($\delta < 0$) this is negative (attractive); the depth is $|U_{\text{dip}}|$.

Step 3: numbers. For Na ($\omega_0 = 3.2e15 \text{ rad/s}$, $\Gamma = 6e7 \text{ s}^{-1}$) with $P = 10 \text{ mW}$, $w_0 = 1 \mu\text{m}$, $\delta/2\pi = -1e13 \text{ Hz}$: $I_0 = 2(0.01)/\pi(10^{-6})^2 \approx 6.4e9 \text{ W/m}^2$, and

$$|U_{\text{dip}}| = \frac{3\pi(3 \times 10^8)^2}{2(3.2 \times 10^{15})^3} \frac{6 \times 10^7}{2\pi \times 10^{13}} (6.4 \times 10^9) k_B^{-1} \approx 6 \text{ mK}.$$

Step 4: scattering. The photon-scattering rate scales as I/δ^2 , suppressed relative to the trap ($\propto I/\delta$) by $1/\delta$: deep trap, few scattered photons; the optical tweezer principle.

Problem 9 (Reststrahlen width from LST). Given GaAs $\omega_T/2\pi = 8.0 \text{ THz}$, $\varepsilon_{\text{st}} = 12.9$, $\varepsilon_\infty = 10.9$, find ω_L and the reststrahlen bandwidth.

Solution 9

Step 1: LST. From Sec. 8.5, $\omega_L = \omega_T \sqrt{\varepsilon_{\text{st}}/\varepsilon_\infty} = 8.0 \text{ THz} \times \sqrt{12.9/10.9} = 8.0 \text{ THz} \times 1.087 = 8.7 \text{ THz}$.

Step 2: band. Total reflection occurs for $\omega_T < \omega < \omega_L$, a band of width $\Delta = 0.7 \text{ THz}$ ($\approx 3 \text{ meV}$, $\lambda \approx 35 \mu\text{m}$, mid-IR).

Step 3: interpret. A purely macroscopic reflectivity measurement of the band edges ω_T, ω_L yields the ratio $\varepsilon_{\text{st}}/\varepsilon_\infty$ and hence the ionicity of the Ga–As bond; microscopic information from a far-IR mirror.

Problem 10 (Quantum-well absorption step). Show that a 2D quantum well has a constant (step-like) joint density of states, and hence a staircase absorption spectrum.

Solution 10

Step 1: 2D counting. In 2D the number of states up to k is $\mathcal{N} = 2 \cdot \frac{\pi k^2}{(2\pi)^2} = \frac{k^2}{2\pi}$ per unit area. With $\hbar\omega - E_g = \hbar^2 k^2 / 2\mu$,

$$J_{2D} = \frac{d\mathcal{N}}{d(\hbar\omega)} = \frac{1}{2\pi} \frac{dk^2}{d(\hbar\omega)} = \frac{\mu}{\pi\hbar^2} = \text{const.}$$

Step 2: subbands. Each confined subband n turns on at its own threshold $E_g + E_n^{\text{conf}}$, adding a constant $\mu/\pi\hbar^2$ to the absorption: the spectrum is a *staircase* (Fig. 28).

Step 3: consequence. The sharp, temperature-robust 2D edge (plus enhanced exciton binding, up to $4\times$ the 3D value) is exactly why quantum-well lasers and modulators outperform bulk: confinement engineers the density of states the golden rule integrates over.

Problem 11 (Strong-coupling condition for a quantum dot). A dot has dipole $d = 1e - 28 \text{ C m}$ in a cavity of mode volume $V = (\lambda/n)^3$, $\lambda = 950 \text{ nm}$, $n = 3.5$. Find g and compare with a cavity decay $\kappa/2\pi = 10 \text{ GHz}$.

Solution 11

Step 1: mode volume. $\lambda/n = 271 \text{ nm}$, so $V = (2.71 \times 10^{-7})^3 \approx 2.0e - 20 \text{ m}^3$.

Step 2: coupling. Use $g = d\sqrt{\frac{\omega_c}{2\hbar\epsilon_0 V}}$ with $\omega_c = 2\pi c/\lambda = 2.0e15$ rad/s. Evaluate the denominator first:

$$2\hbar\epsilon_0 V = 2(1.05 \times 10^{-34})(8.85 \times 10^{-12})(2.0 \times 10^{-20}) = 3.7e-65.$$

Then $\omega_c/(2\hbar\epsilon_0 V) = 5.4e79$, whose square root is $7.3e39$, so

$$g = d \times 7.3e39 = (10^{-28})(7.3 \times 10^{39}) \approx 7.3e11 \text{ rad/s}, \quad \frac{g}{2\pi} \approx 120 \text{ GHz}.$$

Step 3: compare. Since $g/2\pi = 120 \text{ GHz} \gg \kappa/2\pi = 10 \text{ GHz}$, the dot is deep in strong coupling: the spectrum shows a vacuum Rabi doublet split by $2g$.

Further exercises (no solution given).

1. Derive Einstein's A/B ratio directly from the quantized-field golden rule and compare with the thermodynamic derivation of Sec. 4.
2. Integrate the optical Bloch equations numerically for a finite- T_2 π -pulse and quantify the gate infidelity versus ΩT_2 .
3. Show, from the Jaynes–Cummings ladder, that the n -photon Rabi frequency is $2g\sqrt{n+1}$, and discuss the resulting collapse and revival of Rabi oscillations.
4. From a measured $\epsilon_2(\omega)$ of a thin film, reconstruct ϵ_1 by Kramers–Kronig and locate the interband and plasma features.

Appendix A: Mathematical toolbox

A.1 Interaction picture and the rotating frame

The transformation to the frame rotating at the drive frequency ω is generated by $U = \exp(i\omega t |e\rangle\langle e|)$. A state $|\psi\rangle \rightarrow |\tilde{\psi}\rangle = U |\psi\rangle$ obeys $i\hbar \partial_t |\tilde{\psi}\rangle = \tilde{H} |\tilde{\psi}\rangle$ with

$$\tilde{H} = U H U^\dagger - \hbar\omega |e\rangle\langle e|. \quad (31)$$

Why the RWA removes the time dependence

Writing the drive $-dE_0 \cos \omega t = -\frac{dE_0}{2}(e^{i\omega t} + e^{-i\omega t})$ and applying U , each coupling term acquires a factor $e^{\pm i\omega t}$. The atomic raising operator $|e\rangle\langle g|$ picks up $e^{+i\omega t}$ from U ; combined with the $e^{-i\omega t}$ of the drive it becomes *static*, while the pairing with $e^{+i\omega t}$ oscillates at 2ω and averages to zero over an optical cycle. Dropping the latter is the RWA, valid when $\Omega, \delta \ll \omega_0$; essentially always in the optical domain. The result is the time-independent $\tilde{H} = -\hbar\delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(|e\rangle\langle g| + \text{h.c.})$ used in Secs. 2 and 7.

A.2 Density matrix and the master equation

A statistical mixture or an open system is described by $\rho = \sum_k p_k |\psi_k\rangle\langle\psi_k|$, with $\text{Tr } \rho = 1$ and observables $\langle O \rangle = \text{Tr}(\rho O)$. Coherences ρ_{eg} encode the phase relations that the golden rule discards.

Lindblad master equation

$$\dot{\rho} = -\frac{i}{\hbar}[\tilde{H}, \rho] + \Gamma\left(\sigma\rho\sigma^\dagger - \frac{1}{2}\{\sigma^\dagger\sigma, \rho\}\right), \quad \sigma = |g\rangle\langle e|. \quad (32)$$

The commutator gives coherent (Hamiltonian) evolution; the dissipator describes spontaneous emission at rate Γ . Reading off the matrix elements of this equation reproduces the optical

Bloch equations of Sec. 3, with $T_1 = 1/\Gamma$ and $T_2 = 2/\Gamma$ for purely radiative relaxation; adding a pure-dephasing Lindblad operator $\propto \sigma_z$ shortens T_2 without affecting T_1 .

Optical Bloch equations from the master equation

With $\tilde{H}$ above and $\rho = \begin{pmatrix} \rho_{ee} & \rho_{eg} \\ \rho_{ge} & \rho_{gg} \end{pmatrix}$, the master equation gives

$$\dot{\rho}_{ee} = -\Gamma\rho_{ee} - \frac{i\Omega}{2}(\rho_{ge} - \rho_{eg}), \quad \dot{\rho}_{eg} = -\left(\frac{\Gamma}{2} - i\delta\right)\rho_{eg} - \frac{i\Omega}{2}(\rho_{ee} - \rho_{gg}).$$

Substituting $u = 2\operatorname{Re}\rho_{eg}$, $v = 2\operatorname{Im}\rho_{eg}$, $w = \rho_{ee} - \rho_{gg}$ yields precisely the Bloch equations quoted earlier; the bridge between the abstract master equation and the geometric Bloch-vector picture.

A.3 Counting field modes

The density of states used throughout follows from counting plane-wave modes in a box of side L with periodic boundary conditions: allowed wavevectors form a lattice of spacing $2\pi/L$, so the number of modes with $|\mathbf{k}| < k$ (two polarizations) is $\mathcal{N} = 2 \cdot \frac{4}{3}\pi k^3 / (2\pi/L)^3$. Differentiating and using $\omega = ck$,

$$\rho(\omega) d\omega = \frac{d\mathcal{N}}{V} = \frac{\omega^2}{\pi^2 c^3} d\omega, \quad (33)$$

the result quoted in Sec. 5. The identical counting, with the electronic dispersion $E(\mathbf{k})$ in place of $\omega = ck$, gives the joint density of states of Sec. 8; one technique, two chapters.

Appendix B: Constants and useful relations

Quantity	Symbol	Value
Reduced Planck constant	$\hbar$	$1.055 \times 10^{-34} \text{ J s}$
Speed of light	c	$2.998 \times 10^8 \text{ m/s}$
Vacuum permittivity	ε_0	$8.854 \times 10^{-12} \text{ F/m}$
Electron charge	e	$1.602 \times 10^{-19} \text{ C}$
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Bohr radius	a_0	$5.29 \times 10^{-11} \text{ m}$
Atomic dipole unit	ea_0	$8.48 \times 10^{-30} \text{ C m} (= 2.54 \text{ D})$
Fine-structure constant	α	$1/137.04$
Boltzmann constant	k_B	$1.381 \times 10^{-23} \text{ J/K}$

Handy conversions. $1 \text{ eV} \leftrightarrow 1240 \text{ nm} \leftrightarrow 2.42 \times 10^{14} \text{ Hz} \leftrightarrow 8066 \text{ cm}^{-1}$; field amplitude $E_0 = \sqrt{2I/\varepsilon_0 c}$; intensity of 1 mW in a $1 \mu\text{m}$ waist $\approx 6 \times 10^8 \text{ W/m}^2$; thermal energy at 300 K is $k_B T \approx 25 \text{ meV}$.

Appendix C: The Schrödinger equation and stationary states

This appendix recalls, without proof, the minimum of quantum mechanics used in the main text.

The time-dependent Schrödinger equation. The state of a system is a vector $|\psi(t)\rangle$ in a Hilbert space, evolving as

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle, \quad (34)$$

where H is the Hamiltonian (the energy operator). Probabilities are squared amplitudes: the chance of finding the system in a state $|\phi\rangle$ is $|\langle\phi|\psi\rangle|^2$.

Stationary states. The special states that do not change in shape are the eigenstates of H :

$$H |n\rangle = E_n |n\rangle \implies |\psi(t)\rangle = |n\rangle e^{-iE_n t/\hbar}. \quad (35)$$

A stationary state carries only a rotating phase; all measurable quantities are constant in time (hence “stationary”). The energies E_n are exactly the discrete atomic levels whose differences give spectral lines.

Superposition and time evolution. Because the $|n\rangle$ form a complete basis, any state can be expanded as $|\psi\rangle = \sum_n c_n |n\rangle$, and each component simply acquires its own phase:

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle. \quad (36)$$

Interference between these phases is the origin of every dynamical effect in the course, from Rabi oscillations (a two-component superposition) to the spreading of a wave packet.

The two-level atom in this language

Keeping only $|g\rangle$ and $|e\rangle$, a general state is $|\psi\rangle = c_g |g\rangle + c_e |e\rangle$ with $|c_g|^2 + |c_e|^2 = 1$. The pair (c_g, c_e) is what the Bloch vector of Lecture 2 represents geometrically; an applied field makes c_g and c_e exchange amplitude, which is absorption and emission seen at the level of amplitudes rather than rates.

Appendix D: Perturbation theory

Most problems have no exact solution; perturbation theory builds an approximate one when the Hamiltonian is a solvable part H_0 plus a small extra piece V .

Stationary (time-independent) perturbation theory. If $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$ and V is small and constant, the corrected energies and states are, to leading orders,

$$E_n = E_n^{(0)} + \langle n^{(0)} | V | n^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle m^{(0)} | V | n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} + \dots \quad (37)$$

The first correction is the average of V in the unperturbed state; the second describes how states “repel” through their mutual coupling. The light shift of Lecture 2 and the Lamb shift mentioned in Chapter 0 are physical instances of such energy corrections.

Time-dependent perturbation theory. If instead $V = V(t)$ is switched on, we expand the amplitudes $c_n(t)$ in powers of V . Writing $|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$ and keeping first order for a system starting in $|i\rangle$,

$$c_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \langle f | V(t') | i \rangle e^{i\omega_{fi} t'} dt', \quad \omega_{fi} = \frac{E_f - E_i}{\hbar}. \quad (38)$$

The probability $|c_f^{(1)}|^2$, summed over a continuum of final states, is what Lecture 4 turns into Fermi’s golden rule. The expansion is trustworthy precisely when the transferred probability stays small, i.e. when the field is weak or the observation time short.

When perturbation theory fails

If the drive is strong and resonant, probability sloshes fully back and forth between two states and the first-order expansion (which assumes the initial state stays nearly full) breaks down. That regime is not a failure of physics but a different question, and it is exactly the non-perturbative Rabi problem solved exactly in Lecture 2.

Appendix E: Harmonic oscillator and second quantisation

The quantisation of the electromagnetic field (Lecture 5) rests entirely on one solved problem: the quantum harmonic oscillator.

Ladder operators. For $H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2x^2$, define the lowering and raising operators

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{i}{m\omega}p\right), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{i}{m\omega}p\right), \quad [a, a^\dagger] = 1. \quad (39)$$

They step between equally spaced levels: $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$, $a|n\rangle = \sqrt{n}|n-1\rangle$, and the energies are

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right), \quad E_n = \hbar\omega\left(n + \frac{1}{2}\right). \quad (40)$$

The half-quantum $\frac{1}{2}\hbar\omega$ that remains in the ground state ($n=0$) is the zero-point energy; for the field it becomes the vacuum fluctuation responsible for spontaneous emission.

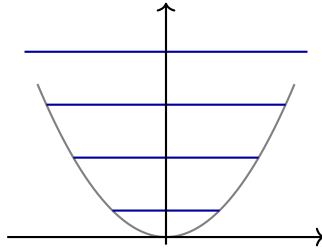


Figure 33: The quantum harmonic oscillator: a parabolic potential with equally spaced energy levels (spacing $\hbar\omega$). The lowest level sits above the bottom of the well by the zero-point energy $\frac{1}{2}\hbar\omega$. Each mode of the electromagnetic field is one such oscillator, and its excitation number counts photons.

Second quantisation of the field. The free electromagnetic field is a collection of independent oscillators, one per mode $(\mathbf{k}, \lambda)$. Quantising each gives creation and annihilation operators $a_{\mathbf{k}\lambda}^\dagger, a_{\mathbf{k}\lambda}$ whose quanta are *photons*: $a^\dagger$ adds a photon to a mode, a removes one, and the vacuum $|0\rangle$ is the state with no photons in any mode (yet with non-zero $\langle E^2 \rangle$). The field operator is a sum over modes of a and $a^\dagger$, and the interaction $-\mathbf{d} \cdot \mathbf{E}$ then connects $|e, n \text{ photons}\rangle$ to $|g, n+1 \text{ photons}\rangle$, which is emission, and to $|g, n-1\rangle$, which is absorption. This is the machinery used in Lecture 5 to obtain spontaneous emission and in Lecture 7 for the Jaynes–Cummings model.

References

- C. Cohen-Tannoudji, J. Dupont-Roc, G. Grynberg, *Atom–Photon Interactions* ; the authoritative reference for the dipole coupling, dressed atom and master equation (L1–L3, appendix).
- R. Loudon, *The Quantum Theory of Light*, 3rd ed.; the optical Bloch equations, field quantization and spontaneous emission (L3–L5).

- M. Fox, *Quantum Optics: An Introduction and Optical Properties of Solids* ; accessible at M1 level; the second volume is the main source for L8.
- S. Haroche, J.-M. Raimond, *Exploring the Quantum: Atoms, Cavities and Photons* ; the definitive cavity-QED text (L7), including Purcell, Jaynes–Cummings and collapse–revival.
- G. Grynberg, A. Aspect, C. Fabre, *Introduction to Quantum Optics*; balanced semiclassical/quantum treatment, good problem sets.
- For solids specifically: C. Kittel, *Introduction to Solid State Physics*, and P. Yu & M. Cardona, *Fundamentals of Semiconductors* (excitons, polaritons).

How to use this document. Read each lecture once for the narrative, then a second time reproducing every orange demonstration box with pen and paper and redoing every green numerical application with the constants of Appendix B. The blue boxes and the summary sheet of Appendix F are the minimum set of results to commit to memory.

Appendix F: Formula summary sheet

The course on one page

Dipole interaction	$H_{\text{int}} = -\mathbf{d} \cdot \mathbf{E}$
Lorentz susceptibility	$\chi = \frac{Ne^2/m_e\epsilon_0}{\omega_0^2 - \omega^2 - i\gamma_c\omega}$
Fermi golden rule	$W = \frac{2\pi}{\hbar} V_{fi} ^2 \rho(E_f)$
Einstein relation	$A/B = \hbar\omega_0^3/\pi^2c^3$
Vacuum field per mode	$\mathcal{E}_k = \sqrt{\hbar\omega_k/2\epsilon_0V}$
Spontaneous emission	$\Gamma = \frac{\omega_0^3 d^2}{3\pi\epsilon_0\hbar c^3}$
Resonant cross section	$\sigma_0 = 3\lambda_0^2/2\pi$
Rabi oscillation	$P_e = \frac{\Omega^2}{\Omega_R^2} \sin^2(\Omega_R t/2), \Omega_R = \sqrt{\Omega^2 + \delta^2}$
Saturation	$\rho_{ee} = \frac{1}{2}s/(1+s), s = I/I_{\text{sat}}$
Light shift	$U_{\text{dip}} = \hbar\Omega^2/4\delta$
Susceptibility (gas)	$\chi'' \propto \frac{1/T_2}{\delta^2 + 1/T_2^2}$
Jaynes–Cummings coupling	$g = d\sqrt{\omega_c/2\hbar\epsilon_0V}$
Vacuum Rabi splitting	$2\hbar g$ (rung n : $2\hbar g\sqrt{n+1}$)
Purcell factor	$F_P = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \frac{Q}{V}$
Cooperativity	$C = g^2/\kappa\gamma$
Kramers–Kronig	$\epsilon_1 - 1 = \frac{2}{\pi} \mathcal{P} \int \frac{\omega'\epsilon_2}{\omega'^2 - \omega^2} d\omega'$
Direct-gap edge	$\alpha \propto (\hbar\omega - E_g)^{1/2}$
Plasma frequency	$\omega_p = \sqrt{Ne^2/\epsilon_0 m^*}$