Chapter

3.3

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Welcome, everyone, to this segment of our Phys 608 Laser Spectroscopy course. Today, we embark on a crucial topic: Chapter 3.3, focusing on the Collisional Broadening of Spectral Lines.

This material, as you know, is prepared by Distinguished Professor Doctor M A Gondal for our course here at KFUPM. Collisional broadening, as we'll see, is a fundamental phenomenon that profoundly impacts the way we interpret spectroscopic data, especially in gaseous media and plasmas. Understanding it is key to unlocking a wealth of information from the spectra we observe.

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So, let's begin by addressing a fundamental question: Why should we dedicate our time to studying collisional broadening, which is also often referred to as pressure broadening? The first point on this slide highlights a very practical reason: many, if not most, laser-atom or laser-molecule interaction experiments – the very bread and butter of laser spectroscopy – are conducted in gaseous environments. And in a gas, particles are constantly in motion, leading to frequent collisions. It's an unavoidable aspect of working with these systems.

Now, the second point gets to the heart of why these collisions matter spectroscopically: each collision event has the potential to perturb, or alter, the energy levels of the atoms or molecules involved. Think back to our quantum mechanics. The energy levels are what dictate the frequencies of light that can be absorbed or emitted. If these levels are momentarily shifted or their lifetime is altered due to a collision, then the observed spectral lines will reflect this. Specifically, as the slide notes, these lines can be broadened – meaning they span a wider range of frequencies – they can be shifted from their unperturbed positions, or their overall shape can be significantly changed. These are not subtle effects; they can dominate the appearance of a spectrum.

This brings us to the third crucial point: a thorough understanding of these collisional effects is not just an academic exercise; it is absolutely essential for a variety of high-precision applications. The slide lists a few, and we'll expand on them. First, precision frequency metrology. If you're trying to measure a transition frequency to an extremely high degree of accuracy, perhaps for fundamental constant determination or for atomic clocks, you *must* account for any shifts or broadening caused by collisions. Failing to do so will lead to systematic errors in your measurements. Second, atmospheric remote-sensing. When we use lasers to probe the composition of the atmosphere – for instance, to measure pollutant concentrations or greenhouse gases – the spectral lines we observe are inherently pressure-broadened. Accurate retrieval of atmospheric parameters relies critically on precise models of this broadening. Think about trying to quantify a trace gas; its absorption profile will be shaped by collisions with nitrogen, oxygen, and other atmospheric constituents. Without understanding this, you cannot accurately determine its concentration.

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Continuing our discussion on the importance of understanding collisional broadening, we come to further applications. The third point listed is plasma diagnostics. Plasmas are ionized gases, teeming with ions and electrons, and collisions are rampant. The shapes and shifts of spectral lines emitted from a plasma are powerful diagnostic tools. By carefully analyzing these line profiles, we can deduce crucial plasma parameters such as electron density and temperature. For example, Stark broadening, which we'll touch upon later, is a direct consequence of collisions with charged particles and is a primary method for measuring electron densities in plasmas.

Fourth on the list is laser design and optimization. For gas lasers, the gain medium is, of course, a gas. Collisional processes within this gas can significantly affect the laser's gain profile, its output power, and its efficiency. For instance, pressure broadening determines the range of frequencies over which stimulated emission can occur. Understanding and sometimes even manipulating these collisional effects is key to designing lasers with specific desired characteristics, such as tunability or narrow linewidth.

Now, beyond these specific applications, there's a more fundamental scientific motivation, highlighted by the final bullet point on this slide. Collisional line-shape theory provides a profound link: it connects the macroscopic, measurable spectral line profiles, which we denote as $I(\omega)$ – capital I of lowercase Greek letter omega, where ω is the angular frequency – to the microscopic interaction potentials, $V(R)$ – capital V of capital R – between the colliding particles, where capital R is their separation. This is incredibly powerful. By carefully analyzing the shape of a spectral line, we can essentially work backwards to learn about the forces that atoms and molecules exert on each other at very short distances. This is a direct window into the intermolecular forces that govern the behavior of matter. The dashed lines indicate the end of this introductory thought, and we'll delve deeper into these concepts. The preparation note is, of course, consistent throughout these slides.

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Alright, let's now move to defining the key players and concepts in our discussion of collisional broadening. We're looking at "Collision Partners and Interaction Potentials". To understand collisions, we need to simplify the picture initially. So, we consider two interacting particles.

First, we have what we'll call particle A. This is our atom or molecule of interest – the one whose spectrum we are observing. It's referred to as the "absorber" if it's absorbing radiation, or the "emitter" if it's emitting radiation. This particle A possesses a set of internal energy levels, and for a specific spectroscopic transition, we're typically interested in two of them: an initial state with energy E_i (capital E subscript lowercase i) and a final state with energy E_k (capital E subscript lowercase k).

Second, we have particle B. This is the "perturber". It's the other particle involved in the collision. As the slide notes, particle B can be any other atom, molecule, or even an ion. It's the presence and interaction of this perturber B with our spectroscopically active particle A that leads to the line broadening and shifting effects we are discussing.

Now, a crucial concept when describing the interaction between these two particles is their separation. Specifically, the "center-of-mass separation", denoted by R, which is a function of the positions of A and B, so we can write it as $R(A,B)$. For most of our purposes in understanding the interaction potentials that cause broadening, this scalar distance R between the centers of mass of A and B is the single most important coordinate. The interaction potential, and therefore the perturbation of the energy levels of A, will depend strongly on this separation R.

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Continuing with interaction potentials, the first point here delves into how these potentials arise and what they signify. The interatomic potential energy curves, which describe the energy of particle A when it's in state 'i' or state 'k' as a function of its separation R from perturber B, are denoted as $E_{\mathrm{i}}(R)$ – capital E subscript lowercase i, of capital R – and $E_{\mathrm{k}}(R)$ – capital E subscript lowercase k, of capital R. These potential curves fundamentally arise from the interactions between the electronic wave functions of particle A and particle B. As the two particles approach each other, their electron clouds begin to overlap and interact. This interaction modifies the energy of the system.

The slide then provides a simple but important rule for interpreting the nature of this interaction based on the potential energy $E(R)$ relative to the energy when the particles are infinitely separated, $E(\infty)$. If $E(R)$ is greater than $E(\infty)$, the interaction is repulsive; the system's energy increases as the particles get closer, meaning they repel each other. Conversely, if $E(R)$ is less than $E(\infty)$, the interaction is attractive; the system's energy is lowered as the particles approach, indicating an attractive force between them. $E(\infty)$ represents the energy of the state of particle A when it's isolated, unperturbed by B.

Now, for spectroscopy, we're interested in transitions between energy levels. So, the crucial quantity is not the absolute energy of a single state, but the *energy difference* between the two states involved in the transition. This is given by $\Delta E(R) = E_{\mathrm{k}}(R) - E_{\mathrm{i}}(R)$. This $\Delta E(R)$ is the energy of the photon that would be emitted or absorbed if the transition occurred while particle A is at a separation R from perturber B.

The final point ties this directly to line broadening: during a collision, the separation R is not fixed. It changes as the particles approach and then recede from each other. Consequently, if R changes, then $\Delta E(R)$ also changes. And since the radiation frequency, ν or ω, is directly proportional to this energy difference (through $h\nu = \Delta E$, or $\hbar\omega = \Delta E$), a varying $\Delta E(R)$ means that the frequency of the radiation emitted or absorbed will also vary during the course of the collision. This variation is the fundamental origin of collisional broadening. Instead of a single, sharply defined transition frequency, we get a range of frequencies corresponding to the range of $\Delta E(R)$ values experienced during collisions.

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This slide presents a crucial visual: "Potential Energy Curves for Collisional Broadening". Let's take a moment to carefully examine this graph. On the vertical axis, we have "Potential Energy $E(R)$", plotted in arbitrary units, let's say. It ranges from approximately -2.0 up to 80. The horizontal axis represents "R, the center-of-mass separation" between our absorber/emitter A and perturber B, also in arbitrary units, perhaps angstroms or Bohr radii, ranging from about 1 to 7.

We see two distinct potential energy curves plotted. The lower curve, shown in blue, is labeled $E_{\mathrm{i}}(R)$ (capital E subscript lowercase i of R) for large R. This represents the potential energy of our particle A when it is in its initial (often ground) state "i", as a function of its separation R from particle B. Notice its behavior: at very small R, the energy is very high, indicating a strong repulsive interaction – this is often due to Pauli repulsion when the electron clouds overlap significantly. The label "Repulsive ($E_\mathrm{i}(R) > E_\mathrm{i}(\infty)$)" correctly points to this region. As R increases, the potential $E_\mathrm{i}(R)$ drops, passes through a minimum – an attractive well – around $R = 3$ units, indicating an attractive force. The label "Attractive ($E_\mathrm{i}(R) < E_\mathrm{i}(\infty)$)" highlights this region. Finally, as R becomes very large, the curve asymptotes to a constant value labeled $E_\mathrm{i}(\infty)$ (capital E subscript lowercase i of (infinity)), which represents the energy of the isolated atom in state "i". On this graph, $E_\mathrm{i}(\infty)$ is shown near zero potential energy.

The upper curve, shown in red, is labeled $E_\mathrm{k}(R)$ (capital E subscript lowercase k of R) for large R. This represents the potential energy of particle A when it is in its excited state "k", again as a function of separation R. It shows qualitatively similar behavior: strong repulsion at very small R, though perhaps less steep than for the ground state in this particular depiction. It also may exhibit an attractive well, though in this diagram it's much shallower and occurs at a slightly larger R, around $R = 4$ units, before asymptoting to its own isolated energy value, $E_\mathrm{k}(\infty)$ (capital E subscript lowercase k of (infinity)). Importantly, $E_\mathrm{k}(\infty)$ is higher than $E_\mathrm{i}(\infty)$, as state "k" is an excited state.

Now, the critical spectroscopic quantity, as we discussed, is the energy difference between these two states at a given R. This is illustrated by the vertical double-headed arrow labeled $\Delta E(R)$. This is $E_\mathrm{k}(R) - E_\mathrm{i}(R)$. You can visually see that as R changes, the length of this arrow, and thus $\Delta E(R)$, changes. For example, at very small R, both potentials are steep, and $\Delta E(R)$ might be very different from its value at large R, which is $\Delta E(\infty) = E_\mathrm{k}(\infty) - E_\mathrm{i}(\infty)$. This $\Delta E(\infty)$ corresponds to the unperturbed transition frequency. It's this R-dependence of $\Delta E(R)$ that leads to the broadening and shifting of the spectral line. If, for instance, $\Delta E(R)$ is larger than $\Delta E(\infty)$, the transition will be blue-shifted during that part of the collision. If it's smaller, it will be red-shifted. The dashed lines guide the eye to the asymptotic energy levels $E_\mathrm{i}(\infty)$ and $E_\mathrm{k}(\infty)$.

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Now that we've established the concept of interaction potentials, let's move on to 'Defining a "Collision" in Spectroscopic Terms'. How do we quantify what we mean by a collision in this context?

First, we introduce the concept of a "collision radius", denoted as R_c (capital R subscript lowercase c). This isn't a hard, fixed boundary like for billiard balls. Instead, it's a characteristic distance. As the slide defines it, R_c is "the maximum separation R for which the perturbation potential, the absolute value of $V(R)$, is large enough to modify the transition energy, ΔE, noticeably." So, if the perturber comes within this radius R_c of our atom A, we consider a spectroscopically significant interaction to be occurring. Outside this radius, the perturbation is assumed to be negligible for the purpose of broadening or shifting the line significantly. The term "noticeably" implies there's some threshold, perhaps related to the natural linewidth or the resolution of our spectrometer.

Given this collision radius, we can then define a "collision time", denoted by the Greek letter τ_c (lowercase tau subscript c). This is an estimate of how long the significant interaction lasts. It's approximated, as shown in the equation, by:

$$\tau_\mathrm{c} \approx \frac{R_\mathrm{c}}{v}$$

Here, R_c is the collision radius we just defined. And v, the relative speed, is what we'll clarify next.

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Continuing our definition of collision parameters, we clarify the term 'v' from the previous equation for collision time. As the first bullet point states: 'v equals the relative speed of particles A and B', and its units are typically meters per second ($\mathrm{m\ s^{-1}}$). So, the collision time, τ_{c}, which is $\frac{R_{\mathrm{c}}}{v}$, indeed 'approximates the duration of significant interaction.' It's the characteristic timescale over which the perturber is close enough to cause a noticeable change in the energy levels of A.

Now, it's important to classify collisions, as not all collisions have the same effect. The slide introduces two main types:

First, an 'Elastic collision'. In an elastic collision, the internal quantum states of the colliding particles (A and B) remain unchanged after the collision. For example, if particle A was in state E_{i} before the collision, it's still in state E_{i} after. While the energy levels E_{i} of R and E_{k} of R might be perturbed *during* the collision, there's no net transfer of population between states. In such collisions, the total kinetic energy of the system (A plus B) is conserved. These collisions are primarily responsible for phase shifts and pressure broadening without changing the lifetime of the states significantly, other than through phase interruption.

Second, we have 'Inelastic collisions', which are often referred to as 'quenching' collisions, especially when they de-excite a particle. In an inelastic collision, there *is* a change in the internal quantum states. For instance, particle A might be in an excited state E_{k}, and after colliding with B, it might transition to a lower state E_{i}, or even to a different state altogether. Population is transferred between internal states. In this case, total kinetic energy is *not* conserved by itself; rather, some internal energy is converted into kinetic energy of the particles, or vice-versa, to conserve the total energy of the system. So, kinetic energy compensates for the change in internal energy.

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This slide brings in an important concept related to the timescale of the collision and how the electronic structure responds. It states that: 'During the collision time τ_c, the electronic cloud "adiabatically" follows the interaction potential $V(R)$. This is often understood within the Born-Oppenheimer picture, and the reason for this adiabatic following is that electronic motion is much, much faster than nuclear motion.'

Let's unpack this. The Born-Oppenheimer approximation, which you'll recall from quantum chemistry and molecular physics, allows us to separate the motion of electrons from the motion of the much heavier nuclei. Because electrons are so light, they can rearrange themselves almost instantaneously in response to changes in the positions of the nuclei.

Now, apply this to a collision. As particle B (a nucleus with its electrons) moves relative to particle A (another nucleus with its electrons), the internuclear separation R changes. The collision time τ_c is typically on the order of picoseconds, as we'll see. While this is very short, it's often long compared to the timescale of electronic rearrangement, which can be femtoseconds or even faster.

So, as R changes relatively slowly (on the electronic timescale) during the collision, the electron cloud of the A-B system continuously adjusts itself to the current internuclear separation. This means that the system stays on a single potential energy curve, like the $E_\mathrm{i}(R)$ or $E_\mathrm{k}(R)$ we saw earlier, rather than making sudden jumps between different electronic states *caused by the nuclear motion itself*. This is what 'adiabatically follows' means. The electronic state evolves smoothly with R.

This adiabatic assumption is crucial for the validity of using potential energy curves that are solely functions of R. If collisions were very fast or involved strong non-adiabatic couplings, then the picture would become much more complicated, potentially involving transitions between these potential energy curves even in the absence of radiative processes. The dashed lines here signify the end of this point, and again, we see the standard attribution.

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Let's put some numbers to these concepts with a "Numerical Example – Typical Collision Time". This will help us get a feel for the magnitudes involved.

First, we need to "choose representative values" for the parameters in our collision time formula.

For the relative speed v, a typical value for atoms or small molecules at room temperature might be around 5×10^2 meters per second, or 500 meters per second. This corresponds to typical thermal velocities.

For the collision radius R_c, let's take a value of 1 nanometer (1 nm), which is 1×10^{-9} meters. This is a reasonable order of magnitude for the range over which interatomic potentials are significant.

Now, we "insert these values into the definition" for the collision time, τ_c:

$$\tau_\text{c} = \frac{R_\text{c}}{v}$$

Substituting the values, we get:

$$\tau_\text{c} = \frac{1 \times 10^{-9}\,\text{m}}{5 \times 10^2\,\text{m/s}}$$

Calculating this out: $\frac{1}{5} = 0.2$. And $\frac{10^{-9}}{10^2} = 10^{-11}$.

So, $\tau_\text{c} = 0.2 \times 10^{-11}$ s.

This can be written more conveniently as

$$\tau_\text{c} = 2 \times 10^{-12}\,\text{s}$$

And 10^{-12} s is, by definition, one picosecond (ps).

So, a typical collision time, τ_{c}, is on the order of 2 picoseconds. This is a very short duration, but, as we'll see, it's highly significant for spectroscopic lineshapes.

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Now, let's consider the "Interpretation" of this typical collision time of $2\,\text{ps}$ that we just calculated. What does it mean in the broader context of spectroscopy?

The first point of interpretation is crucial: "2 picoseconds is extremely short compared with typical radiative lifetimes." Radiative lifetimes, τ_{rad} (lowercase tau subscript r-a-d), which is the average time an isolated atom spends in an excited state before spontaneously emitting a photon, are typically in the range of nanoseconds (ns, 10^{-9} seconds) to microseconds (μs, 10^{-6} seconds) for many common transitions. So, we have τ_{c}, the collision duration, around 2×10^{-12} seconds, while τ_{rad} is around 10^{-9} seconds or longer. This means τ_{rad} is at least a thousand to a million times longer than τ_{c}. A single collision is a very fleeting event compared to the natural lifetime of an excited state. However, in a gas at reasonable pressure, an atom might undergo many such collisions during one radiative lifetime.

The second point of interpretation is also very important, particularly for understanding line shapes in the quasi-static approximation, which we'll touch upon. It states that this short collision time "justifies the 'vertical transition' assumption: R stays essentially fixed during the optical emission or absorption event itself." Let's clarify this. The act of absorbing or emitting a photon is an electronic process that happens very rapidly, on a timescale typically much shorter than even the picosecond collision time. Think of it as an almost instantaneous quantum jump for the electrons. During this very brief moment of photon interaction, the nuclei, which are much heavier, barely have time to move. Therefore, the internuclear separation R can be considered essentially constant *during the optical transition itself*.

This is analogous to the Franck-Condon principle in molecular spectroscopy, where electronic transitions are often depicted as vertical lines on potential energy diagrams because the nuclear geometry doesn't change significantly during the rapid electronic transition. So, even though R is changing throughout the collision (which lasts about $2\,\text{ps}$), at the specific instant the photon is emitted or absorbed, R is well-defined. This allows us to think about a transition frequency that is characteristic of that specific R. The dashes, as before, signify the end of this interpretive section.

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We now come to a very important classification: 'Two Fundamental Broadening Mechanisms'. Understanding spectral line broadening requires us to distinguish between the primary ways collisions can affect our quantum system.

The first category is 'Inelastic collisions', which, as we've mentioned, are also known as 'quenching' collisions. What is their main effect? They 'shorten the excited-state lifetime'. If an atom in an excited state can lose its energy not just by radiating a photon, but also by transferring that energy to a collision partner (e.g., converting it to kinetic energy or exciting the partner), then its effective lifetime in that excited state is reduced. And what is the spectroscopic consequence of a shortened lifetime? This leads to 'Lorentzian broadening'. You'll recall from our earlier discussions on natural broadening that a finite lifetime, by the uncertainty principle ($\Delta E \Delta t \approx \hbar$), implies an uncertainty in the energy of the state, which translates to a broadening of the spectral line. This broadening due to lifetime reduction is typically Lorentzian in shape. So, inelastic collisions 'produce an additional damping term', which we can denote as γ_{col}. This collisional damping rate adds to the natural radiative damping rate.

The second fundamental mechanism involves 'Elastic (phase-perturbing) collisions'. In contrast to inelastic collisions, elastic collisions, by definition, do not change the populations of the energy states. If the atom was in the excited state, it remains in the excited state after an elastic collision. However, these collisions are not without effect! They 'modify the oscillator phase without changing state population.' Imagine the atom's wavefunction, or more classically, its radiating dipole, as an oscillating system. An elastic collision can abruptly change the phase of this oscillation. While the atom is still excited and capable of radiating, the coherence of its emission is interrupted. These random phase interruptions also lead to line broadening, typically Lorentzian as well, and can also cause shifts in the line center. We'll explore this phase perturbation in more detail later.

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Continuing our discussion of the two fundamental broadening mechanisms, particularly focusing now on the consequences of elastic, phase-perturbing collisions. These collisions, by modifying the oscillator phase, can 'cause a frequency shift', denoted as $\Delta\omega$, and also contribute an 'additional width through phase diffusion'. Think of the emitted wave train: each collision resets its phase. An accumulation of many random phase shifts effectively broadens the frequency spectrum of the radiation.

So, when we consider the 'total observed effects' on a spectral line due to collisions, we generally see both a shift and a change in width. The slide summarizes this: The 'Shift' is $\Delta\omega$. The 'Halfwidth' of the spectral line, which we'll denote by γ, is now the sum of the natural radiative halfwidth, γ_{n}, and the collisional halfwidth, γ_{col}. So, $\gamma = \gamma_{\mathrm{n}} + \gamma_{col}$.

The term γ_{n} is explicitly defined as the 'natural radiative halfwidth' – this is the width the line would have even in the complete absence of collisions, due solely to the finite radiative lifetime of the excited state. It represents the contribution from spontaneous emission.

γ_{col}, then, encompasses the broadening contributions from both inelastic (quenching) collisions, which reduce the lifetime, and elastic (phase-perturbing) collisions.

A very important practical point is highlighted next: 'Both mechanisms simultaneously act; separating them experimentally needs careful analysis.' In a real gas, an atom experiences a variety of collisions. Some might be inelastic, others elastic and phase-perturbing. The observed line shape is a result of the combined effects. Distinguishing the contribution of quenching from phase perturbation, or even separating collisional effects from other broadening mechanisms like Doppler broadening, often requires careful experimental design and data analysis, perhaps by studying the line shape as a function of perturber pressure and temperature. The triple dash indicates the end of this section.

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Let's now consider the 'Instantaneous Transition Frequency During a Collision'. This perspective, often called the quasi- static approximation, is particularly useful for understanding the wings of a broadened line.

The first point considers a "radiative transition from state E_{i} to E_{k} occurring at a fixed internuclear separation R". As we discussed with the concept of vertical transitions, if the photon emission or absorption happens at a specific moment when the colliding particles have a separation R, the frequency of that photon will be determined by the energy difference $\mathit{\Delta} E(R)$ of R at that specific R.

The equation for this instantaneous angular frequency, $\omega_{ik}(R)$ (lowercase omega subscript i-k of R), is given by:

$$\omega_{ik}(R) = \frac{|E_{\mathrm{k}}(R) - E_{\mathrm{i}}(R)|}{\hbar}$$

Here, $E_{\mathrm{k}}(R)$ and $E_{\mathrm{i}}(R)$ are the energies of the excited and initial states, respectively, perturbed by the presence of the collision partner at separation R. This is simply the Bohr frequency condition, applied at a specific R.

Now, the crucial insight is in the second point: "Because $R(t)$" – that is, the internuclear separation as a function of time – "fluctuates randomly in a gas, the measured fluorescence or absorption spectrum spans a distribution of frequencies." In a gas, collisions are constantly occurring. At any given instant, an emitting or absorbing atom will find itself at some separation R from a perturber. Since R is varying due to the thermal motion and trajectories of the particles, the instantaneous transition frequency $\omega_{ik}(R)$ will also vary. Some atoms might emit when R is small, others when R is larger. The collection of all such emitted or absorbed photons will therefore not have a single frequency, but a distribution of frequencies.

This distribution is often centered, or has a maximum intensity, around a frequency ω_{max} (lowercase omega subscript m-a-x), which corresponds to the transition frequency ω_{ik} at some particular separation R_m (capital R subscript m). As the slide indicates, this R_m is a separation that, for reasons we will explore, maximizes the emission or absorption probability, or perhaps corresponds to a stationary point in the difference potential.

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Continuing our discussion from the previous slide, we clarify the meaning of R_m (capital R subscript m). It's stated that R_m is the separation that "maximizes the emission probability." This often corresponds to a region where the difference potential, $\Delta E(R)$, has an extremum, or where atoms spend a relatively longer time, leading to a higher probability of radiating at the frequency associated with that R. This gives rise to features like satellite lines, which we'll discuss later.

Now, with this concept of ω_max (lowercase omega subscript m-a-x) – the frequency around which the perturbed line profile is often most intense – we can define the "measurable line shift". The line shift, denoted by $\Delta\omega$ (capital Delta lowercase Greek letter omega), is given by the equation:

$$\Delta\omega = \omega_0 - \omega_\mathrm{max}.$$

Here, "omega sub zero" (lowercase omega subscript zero) is explicitly defined as the "transition frequency of an isolated atom." This is the frequency we would observe if there were no collisions, i.e., when R goes to ∞, so ω_0 corresponds to $\Delta E(\infty)/\hbar$. So, the shift $\Delta\omega$ measures how much the peak (or most probable frequency) of the collisionally perturbed line, ω_{max}, has moved from the unperturbed line position, ω_0. A positive $\Delta\omega$ (if defined this way) would mean ω_{max} is less than ω_0, indicating a red shift, while a negative $\Delta\omega$ would indicate a blue shift. The convention for the sign of the shift can sometimes vary, so it's always good to be clear about the definition. The three dashes signify the end of this point.

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We now shift our focus to a statistical aspect of collisions, crucial for calculating the overall line shape. This slide is titled "Probability of Finding a Perturber at Distance R", and it begins the derivation of a quantity $N(R)$, which represents the number of perturber particles (type B) that are found in a spherical shell between radius R and $R + dR$, centered on our atom A.

To determine this, we need a few ingredients.

First, we consider the "spherical shell volume", dV. If we have a shell of radius R and thickness dR, its volume is the surface area of the sphere times the thickness. So,

$$dV = 4\pi R^2\, dR.$$

Second, we need to account for the fact that the perturbers are not necessarily uniformly distributed if there's an interaction potential between them and particle A. The "Boltzmann factor" gives us the relative probability of finding a perturber at a separation R where the interaction potential is $V(R)$, compared to a region where the potential is zero. This slide specifically mentions the "ground-state interaction potential $V(R)$". Assuming particle A is in its ground state (or, more generally, the initial state of the transition, $V_{\text{i}}(R)$), the Boltzmann factor is:

$$\exp\left[-\frac{V(R)}{kT}\right].$$

Here, k is the Boltzmann constant, and T is the absolute temperature in Kelvin. This factor tells us that configurations with lower energy (e.g., attractive $V(R)$) are more probable, and configurations with higher energy (repulsive $V(R)$) are less probable, than if there were no interaction.

Third, we need to know the "average perturber density", N_0. This is the number of perturber particles per unit volume (e.g., in units of m^{-3}) far away from particle A, or if there were no interaction potential. It's the bulk density of perturbers.

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Continuing from the previous slide where we introduced the components, we now "combine these factors" to get the expression for $N(R)\,dR$, the number of B particles in the shell between R and $R + dR$.

The equation is:

$$N(R)\,dR = N_0\,4\pi R^2 \exp\left[-\frac{V(R)}{kT}\right] dR.$$

(capital $N(R)$, lowercase dR, equals capital N_0, times 4, lowercase π, capital R^2, times exponential open square bracket minus capital $V(R)$ divided by open parenthesis lowercase kT close parenthesis close square bracket, lowercase dR).

Let's break this down:

N_0 is the average number density of perturbers.

$4\pi R^2\,dR$ is the geometric volume of the shell.

The exponential term, $\exp\left[-\frac{V(R)}{kT}\right]$, is the Boltzmann factor, which adjusts the probability of finding a particle in that shell based on the interaction potential $V(R)$. Again, this $V(R)$ is typically the potential for the initial state of the spectroscopic transition, often the ground state, as this determines the statistical distribution of perturbers *before* the spectroscopic interaction (photon absorption) occurs.

To ensure clarity, the slide then explicitly defines the symbols used in the Boltzmann factor, to "avoid ambiguity":

"k" is the Boltzmann constant, with a value of 1.38×10^{-23} Joules per Kelvin (1.38×10^{-23} J K^{-1}, or Joules Kelvin^{-1}).

"T" is the absolute temperature, measured in Kelvin (K).

This expression for $N(R)\,dR$ is fundamental because the overall spectral line shape will be an integral over contributions from all possible perturber distances R, weighted by this probability of finding a perturber at that distance.

The triple dash signifies the end of this definition.

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Now we move towards 'Building the Intensity Profile – Integral Expression'. We want to understand how the total observed spectral intensity $I(\omega)$ is constructed from all these microscopic interactions.

The first point notes that the "Spontaneous Einstein-A-coefficient" can itself depend on the internuclear separation R. We denote this as $A_{ik}(R)$. Recall that the A coefficient governs the rate of spontaneous emission. If the wavefunctions of states i and k are perturbed by the collision, the transition dipole moment, and hence $A_{ik}(R)$, can change with R. This is often a secondary effect compared to the change in transition energy but can be important for accurate line shape modeling, especially in the far wings.

The second point introduces "P sub col of R" (capital P subscript c-o-l of R), defined as the "probability per unit time that the internuclear separation R lies in the range R to $R + dR$". This is essentially related to $N(R)$, which we just derived, representing the statistical likelihood of finding a perturber configuration.

The third point gives us the "intensity contribution from a shell dR". This is the crucial step. The differential intensity, $dI(\omega)$, emitted at frequencies corresponding to separations within the shell dR, is proportional to several factors: $dI(\omega)$ is proportional to $A_{ik}(R)$, times $P_{\text{col}}(R)$, times the quantity $[E_{\text{i}}(R) - E_{\text{k}}(R)]$, times dR.

$$dI(\omega) \propto A_{ik}(R)\, P_{\text{col}}(R)\, [E_{\text{i}}(R) - E_{\text{k}}(R)]\, dR.$$

Let's examine the energy term: $[E_{\text{i}}(R) - E_{\text{k}}(R)]$. This represents the energy of the emitted photon. For emission, if $E_{\text{k}}(R)$ is the upper state and $E_{\text{i}}(R)$ is the lower state, this should correctly be $E_{\text{k}}(R) - E_{\text{i}}(R)$, which is a positive quantity, and indeed, intensity should be proportional to the photon energy ($\hbar\omega$) and the rate. The expression as written with $\left(E_{\text{i}}(R) - E_{\text{k}}(R)\right)$ would be negative if k is the upper state. Assuming this is related to a definition of a difference potential that appears in the overall context of Equation 3.35 from the source material, where perhaps ω is defined as $\omega = \frac{V_{\text{i}} - V_{\text{k}}}{\hbar}$. We should consider this an energy factor proportional to $\hbar\omega(R)$.

The slide notes this is a rewritten form of an "Original Equation 3.35" from the course text or notes.

Finally, to make this more concrete, we "substitute $P_{\text{col}}(R)$ as being proportional to $N(R)$" (the number of perturbers in the shell, which we derived on the previous slide) "to obtain an explicit R-dependence". This means the probability of finding a perturber at R, which includes the Boltzmann factor and the R^2 geometric factor, directly weights the contribution to the spectrum from that separation R.

Page 19:

This slide offers a concise but very insightful "Result". It states that the "collision-broadened line shape mirrors the difference of potential curves: $V[A(E_\mathrm{i}), B] - V[A(E_\mathrm{k}), B]$." ($V[A(E_\mathrm{i}), B] - V[A(E_\mathrm{k}), B]$).

Let's interpret this carefully.

$V[A(E_\mathrm{x}), B]$ represents the potential energy of atom A when it is in electronic state E_x (either E_i or E_k), interacting with perturber B, as a function of their separation R. This is what we previously called $E_\mathrm{i}(R)$ or $E_\mathrm{k}(R)$.

So the "difference of potential curves" refers to $E_\mathrm{i}(R) - E_\mathrm{k}(R)$ (as written on the slide).

This quantity, when divided by $\hbar$, gives the instantaneous angular frequency of the transition, $\omega(R)$, possibly relative to the unperturbed frequency ω_0 or including it. Specifically, if $\hbar\omega(R) = E_\mathrm{k}(R) - E_\mathrm{i}(R)$ for emission, then the slide's $V[A(E_\mathrm{i}), B] - V[A(E_\mathrm{k}), B]$ would be $-\hbar\omega(R)$. The line shape mirrors this difference.

The statement means that the observed spectrum, $I(\omega)$, is essentially a map of how often different values of this difference potential (and thus different frequencies) occur, weighted by factors like the statistical probability of finding a perturber at the corresponding separation R ($N(R)$) and by the transition probability ($A_{ik}(R)$).

If the difference potential, let's call it $\Delta V(R) = E_\mathrm{k}(R) - E_\mathrm{i}(R)$, varies significantly with R, then we will see a broad range of frequencies in our spectrum.

If this difference potential $\Delta V(R)$ has an extremum at some R_s, we might see a "satellite" feature in the spectrum, as many R values around R_s contribute to nearly the same frequency.

This is a cornerstone of the quasi-static theory of line broadening: the spectrum directly reflects the R-dependent energy difference between the two states involved in the transition. The triple dash here concludes this point.

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This slide, titled "From R to Observable Frequency ω," details how we connect the theoretical dependence on internuclear separation R to the experimentally measured frequency ω.

The first point reiterates the fundamental "relation between separation and frequency". The energy of a photon emitted or absorbed, $\hbar\omega(R)$, is equal to the difference in the potential energies of the initial and final states at that separation R. The slide writes this as:

$$\hbar\omega(R) = V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R).$$

Here, $V_{\mathrm{i}}(R)$ and $V_{\mathrm{k}}(R)$ represent the potential energies of the atom when it's in state "i" or state "k", respectively, at separation R from the perturber. These are effectively the same as $E_{\mathrm{i}}(R)$ and $E_{\mathrm{k}}(R)$ from our earlier discussion. The choice of $V_{\mathrm{i}} - V_{\mathrm{k}}$ (or $V_{\mathrm{k}} - V_{\mathrm{i}}$) determines the sign convention for ω relative to the energy levels. For emission from upper state k to lower state i, typically $\hbar\omega = E_{\mathrm{k}} - E_{\mathrm{i}}$. If V_{i} and V_{k} are the interaction potentials *added* to unperturbed energies E_{i}^0 and E_{k}^0, then

$$\hbar\omega(R) = \left(E_{\mathrm{k}}^0 + V_{\mathrm{k}}(R)\right) - \left(E_{\mathrm{i}}^0 + V_{\mathrm{i}}(R)\right) = \hbar\omega_0 + \left(V_{\mathrm{k}}(R) - V_{\mathrm{i}}(R)\right).$$

The slide's $V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R)$ definition for $\hbar\omega(R)$ may represent a shift from an unperturbed value, or defines ω in a specific way. The key is that ω is a function of R.

Now, our intensity expression dI on a previous slide contained a dR. However, we measure spectra as a function of ω, not R. So, we need to "differentiate to transform dR into $d\omega$". This is a standard change of variables technique in integration.

We start with

$$\hbar\omega(R) = V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R).$$

Differentiating both sides with respect to R, we get:

$$\hbar\frac{d\omega}{dR} = \frac{d}{dR}[V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R)].$$

This gives us a relationship between the differential $d\omega$ and the differential dR.

The final step is to “insert this transformation into the intensity expression” we had for dI (which was proportional to something times dR). By substituting dR in terms of $d\omega$ (or vice versa), we can get an expression for $dI(\omega)$, or $I(\omega)$, which is the intensity per unit frequency interval. This yields an “experimentally useful form” because spectra are measured as intensity versus frequency. This transformation is particularly important in the quasi-static theory, where it relates the spectral intensity at a frequency ω to the probability of finding a perturber at the specific radius (or radii) R that produce that frequency ω, divided by the rate of change of frequency with R (the derivative term, which acts as the Jacobian of the transformation).

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This slide presents the resulting expression for the spectral intensity distribution, $I(\omega)\,d\omega$ (capital I of lowercase omega, lowercase d lowercase omega), after performing the change of variables from R to ω. The equation is given as:

$$I(\omega)\,d\omega = C\,R^2 \exp\left[-\frac{V_{\mathrm{i}}(R)}{kT}\right]\left(\frac{dR}{d[V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R)]}\right)d\omega.$$

Let's carefully interpret the term in the square brackets, $\frac{dR}{d[V_{\mathrm{i}}(R)-V_{\mathrm{k}}(R)]}$. This term is the reciprocal of the derivative of the difference potential ($V_{\mathrm{i}} - V_{\mathrm{k}}$) with respect to R. That is, it's $\left(\frac{d[V_{\mathrm{i}}(R)-V_{\mathrm{k}}(R)]}{dR}\right)^{-1}$. Recall that $\hbar\,\omega(R) = V_{\mathrm{i}}(R) - V_{\mathrm{k}}(R)$ (using the convention from the previous slide). Therefore, the term

$$d[V_\mathrm{i}(R) - V_\mathrm{k}(R)]$$

is equal to $\hbar\, d\omega$. So the fraction in the equation, $\frac{dR}{d[V_\mathrm{i}(R)-V_\mathrm{k}(R)]}$, can be written as

$$\frac{dR}{\hbar\, d\omega}.$$

The equation for $I(\omega)\, d\omega$ then has $\frac{dR}{\hbar\, d\omega}$ multiplied by $d\omega$, which means the intensity $I(\omega)$ would be

$$C\, R^2 \exp\left[-\frac{V_\mathrm{i}(R)}{kT}\right] \times \left(\frac{1}{\hbar}\right) \times \text{(dR that corresponds to the R that gives } \omega\text{)}.$$

This needs careful formulation.

More standardly,

$$I(\omega) = \sum_\mathrm{j} \left\{ \frac{N(R_\mathrm{j})\, A(R_\mathrm{j})\, R_\mathrm{j}^2}{\left| \frac{dV_\mathrm{diff}(R_\mathrm{j})}{dR_\mathrm{j}} \right|} \right\}$$

where R_j are the roots of $\hbar\,\omega = V_\mathrm{diff}(R)$.

The term on the slide, $\frac{dR}{d[V_\mathrm{i}(R)-V_\mathrm{k}(R)]}$, is actually $\left(\frac{d[V_\mathrm{i}(R)-V_\mathrm{k}(R)]}{dR}\right)^{-1}$. And

$$\frac{d[V_\mathrm{i}(R) - V_\mathrm{k}(R)]}{dR} = \hbar\, \frac{d\omega}{dR}.$$

So, $\frac{dR}{d[V_\mathrm{i}(R)-V_\mathrm{k}(R)]}$ becomes

$$\frac{1}{\hbar\, \frac{d\omega}{dR}}.$$

Thus,

$$I(\omega)\, d\omega = C\, R^2 \exp\left[-\frac{V_{\text{i}}(R)}{kT}\right]\left[\frac{1}{\hbar\left|\frac{d\omega}{dR}\right|}\right] d\omega.$$

The absolute value on $\frac{d\omega}{dR}$ is important because intensity must be positive. Here, R is the specific separation (or separations, if the function $\omega(R)$ is not monotonic) that produces the frequency ω. The $V_{\text{i}}(R)$ in the Boltzmann factor is the interaction potential for the initial state, determining the statistical probability of finding a perturber at R. The R^2 comes from the $N(R)$ term which includes $4\pi R^2$. Points where $\frac{d\omega}{dR}$ is zero are singularities called "classical satellites," where the intensity can peak.

The slide also notes that "the constant C absorbs universal prefactors and the average number density N_0." This N_0 (capital N subscript zero) is the bulk density of perturbers. The constant C would also include things like 4π (four pi) from the spherical shell volume, and potentially factors from the Einstein A coefficient if it's assumed constant, and other fundamental constants like $\frac{1}{\hbar}$. This equation forms the basis of the quasi-static theory for line shapes. The three dashes indicate the end of this segment.

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This slide, titled "Extracting Ground-State Potential via Temperature Dependence," presents a very clever experimental technique to determine the ground-state interaction potential, $V_{\text{i}}(R)$, from spectral line shape measurements.

Recall the expression for $I(\omega, T)$ we just discussed, which contained the Boltzmann factor, $\exp\left[-\frac{V_{\text{i}}(R)}{kT}\right]$. This exponential term has a clear temperature dependence. The idea here is to exploit this.

The first instruction is to "Take the derivative of the measured intensity $I(\omega, T)$ with respect to temperature T". We assume that the frequency ω

has been chosen, which in turn fixes the corresponding R (or R's) that contribute at that ω.

The equation provided is:

$$\frac{\partial I(\omega,T)}{\partial T} = \frac{V_{\text{i}}(R)}{kT^2}\, I(\omega,T)$$

This equation arises directly from differentiating the Boltzmann factor within the expression for $I(\omega,T)$. If I is proportional to $\exp\left[-\frac{V_{\text{i}}}{kT}\right]$, then $\frac{dI}{dT}$ is proportional to $\exp\left[-\frac{V_{\text{i}}}{kT}\right]$ times $\left(-\frac{V_{\text{i}}}{k}\right)$ times $\left(-\frac{1}{T^2}\right)$, which simplifies to $\frac{V_{\text{i}}}{kT^2}$ times I. The other R-dependent terms in I (like $\frac{R^2}{\left|\frac{d\omega}{dR}\right|}$) are assumed to be less sensitive to T, or their T-dependence is weaker than the Boltzmann factor's.

Now, the brilliant part is when this equation is "Rearranged" to solve for $V_{\text{i}}(R)$:

$$V_{\text{i}}(R) = kT^2\left(\frac{1}{I(\omega,T)}\right)\left(\frac{\partial I(\omega,T)}{\partial T}\right)$$

Here, I is $I(\omega,T)$.

This equation is remarkable because it allows us to determine the ground state (or more generally, initial state) interaction potential V_{i} at a specific separation R (the R corresponding to our chosen ω) by measuring the intensity of the spectrum at that ω, $I(\omega,T)$, and how that intensity changes with temperature, $\frac{\partial I(\omega,T)}{\partial T}$. We also need to know the temperature T and Boltzmann's constant k.

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This slide elaborates on the significance and practical implementation of the method we just discussed for extracting the ground-state potential.

The key takeaway is summarized: 'Thus, temperature-scanned line profiles provide direct experimental access to $V_i(R)$' – the initial state interaction potential – 'without independent knowledge of the excited-state potential, $V_k(R)$.' This is a very powerful feature. Often, calculating or experimentally determining excited state potentials can be more challenging. This method bypasses that need for $V_i(R)$ determination, as only $V_i(R)$ appears in the Boltzmann factor that gives rise to the temperature dependence being exploited. Of course, to relate the observed ω to a specific R, one still needs to know the *difference* potential, $V_i(R) - V_k(R)$ (or $V_k(R) - V_i(R)$), which defines $\omega(R)$. But the extraction of $V_i(R)$ itself from the temperature dependence relies only on V_i being in the Boltzmann factor affecting the population of R states.

Now, for the 'Practical' implementation:

To use the formula $V_i(R) = kT^2 \times \frac{1}{I} \times \frac{\partial I}{\partial T}$, we need to measure the partial derivative of intensity with respect to temperature. Experimentally, this is often done by performing spectral measurements, i.e., obtaining $I(\omega)$, at 'at least three or more different temperatures' (greater than or equal to 3 temperatures).

With intensity data at several temperatures for a fixed ω (which corresponds to a fixed R), one can then 'numerically compute the derivative' $\frac{\partial I}{\partial T}$. For example, by fitting the I versus T data to a function or by using finite difference methods if enough data points are available. Having more than two temperatures allows for a more robust determination of the derivative and can help check the validity of the assumptions made.

Once this derivative is found, $V_i(R)$ can be calculated for each ω (and thus each R) in the spectrum where the analysis is performed, allowing the potential to be mapped out. The three dashes indicate the conclusion of this point.

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Now that we've discussed how interaction potentials $V(R)$ lead to line broadening and how they might even be experimentally determined, let's look at some 'Typical Model Interaction Potentials' that are often used in calculations and interpretations. These are analytical forms that approximate the true, complex interatomic potentials.

Perhaps the most famous and widely used is the 'Lennard-Jones (12-6) potential'. This potential describes the interaction energy $V(R)$ between two neutral, nonpolar atoms or molecules as a function of their separation R.

The mathematical form is given by:

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^{6}}$$

(capital $V(R)$ equals lowercase a divided by R^{12}, minus lowercase b divided by R^{6}).

Here, 'a' and 'b' are positive constants specific to the interacting pair of particles.

Let's look at the two terms:

1. The 'First term', $\frac{a}{R^{12}}$, is the repulsive term. It dominates at very short ranges (small R) due to its high power of R in the denominator. This term models the 'short-range Pauli repulsion' that occurs when the electron clouds of the two particles overlap significantly, arising from the Pauli exclusion principle. The R^{12} form is chosen largely for mathematical convenience, though it provides a steep repulsive wall.

2. The 'Second term', $-\frac{b}{R^{6}}$, is the attractive term (note the minus sign). It is longer-ranged than the repulsive term but falls off more slowly. This term represents the 'van der Waals attraction', specifically the London dispersion force, which arises from interactions between instantaneous fluctuating dipoles and the induced dipoles they create in neighboring

atoms/molecules. This R^{-6} dependence has a stronger theoretical basis for induced-dipole-induced-dipole interactions.

These 'adjustable coefficients a and b' are typically determined empirically. They are 'fitted to reproduce observed experimental data', such as gas properties (like virial coefficients or viscosity) or, very relevant to our course, observed spectroscopic line shapes and shifts.

By choosing appropriate 'a' and 'b' values for both the ground state potential $V_{\mathrm{i}}(R)$ and the excited state potential $V_{\mathrm{k}}(R)$, one can often model the collisionally broadened spectral profiles with reasonable accuracy.

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Besides the Lennard-Jones potential, there are "Other common forms" for model interaction potentials that are frequently encountered.

One simple and general form is the "Power- law potential", given by:

$$V(R) = \frac{C}{R^n}$$

(capital V of capital R equals capital C divided by capital R to the power of n).

Here, C is a constant (the potential strength coefficient) and n is an integer exponent. The sign of C determines whether the potential is attractive or repulsive.

This form is often used to describe individual components of an interaction. For example:

If $n = 6$ and $C < 0$, it represents the attractive van der Waals interaction we just saw.

If $n = 12$ and $C > 0$, it's the repulsive core of the Lennard-Jones potential.

Other values of n describe different types of interactions. For instance, $n = 1$ for Coulomb interactions, $n = 2$ for charge- dipole, $n = 3$ for dipole- dipole interactions, and so on. We'll see some specific examples of n later.

The slide also mentions "Morse, Buckingham, or ab- initio tabulated potentials."

The "Morse potential" is another common two-parameter potential that includes both attractive and repulsive parts and is often used to describe the vibrational energy of diatomic molecules because it has a more realistic shape for bound states, including dissociation.

The "Buckingham potential", also known as the exp- 6 potential, combines an exponential term for repulsion ($A\exp(-BR)$, A times exponential of minus BR) with an R^{-6} term for attraction, offering a slightly more physically grounded repulsive term than the R^{-12}.

Finally, "ab- initio tabulated potentials" represent a different approach. Instead of fitting simple analytical forms, these potentials are calculated from first principles using quantum chemistry methods. These calculations can be computationally intensive but can provide highly accurate potential energy surfaces, especially for smaller systems. The results are often presented as a table of energy values at various separations R, which can then be interpolated for use in line shape calculations. These are generally the most accurate but least convenient for quick analytical work.

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This slide provides a visual representation of the 'Lennard-Jones $(12-6)$ Potential' that we just discussed. Let's analyze the features of this graph.

The vertical axis is 'Potential Energy $V(R)$'. Key values are marked: zero energy, which is the energy of the two particles when infinitely separated. A depth $-\epsilon$ (minus lowercase Greek letter epsilon), representing the minimum energy of the potential well. And ϵ itself, which is the well depth magnitude.

The horizontal axis is 'Interatomic Separation (R)'. Several characteristic distances are marked: σ (lowercase Greek letter sigma), which is the finite distance at which the potential $V(R)$ is zero. It represents an effective collision diameter. r_e (lowercase r subscript e) is the equilibrium separation where the potential energy is at its minimum, $V(r_\mathrm{e}) = -\epsilon$. Also marked are multiples of σ, like 1.5σ (one point five sigma), 2.0σ (two point zero sigma), and 2.5σ (two point five sigma), to give a sense of scale.

Now, let's trace the curve itself, which is typically plotted in blue. At very small R (to the left), the potential rises extremely steeply. This is labeled the 'Repulsive Wall', corresponding to the positive $\frac{a}{R^{12}}$ term. This signifies a strong repulsive force when the particles are very close.

As R increases, the potential energy drops rapidly, crosses the zero energy axis at $R = \sigma$, and reaches a minimum value of $-\epsilon$ at $R = r_\mathrm{e}$. This region around the minimum is labeled the 'Potential Well'. This well signifies the attractive part of the potential, dominated by the minus $\frac{b}{R^6}$ term, leading to a stable or quasi-stable bound state if particles are trapped in it.

For $R > r_\mathrm{e}$, the potential energy gradually rises, approaching zero as $R \to \infty$. This region for $R > \sigma$, where the potential is negative but increasing towards zero, is often called the 'Attractive Tail'.

The two parameters often used to characterize the Lennard-Jones potential are ϵ (the well depth) and σ (the zero-crossing distance). The constants a and b in the $V(R) = \frac{a}{R^{12}} - \frac{b}{R^6}$ form can be related to ϵ and σ: specifically, $a = 4\epsilon\sigma^{12}$, and $b = 4\epsilon\sigma^6$. So the potential is often written as

$$V(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right].$$

This graphical representation is fundamental to understanding how the balance of short-range repulsion and longer-range attraction shapes the interaction between neutral particles.

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We now turn our attention specifically to "Inelastic (Quenching) Collisions" and their impact on transition probabilities, or more accurately, rates. Recall that inelastic collisions are those that cause a change in the internal quantum state of the colliding particles, often leading to de-excitation.

The first point considers the "Total depopulation rate of an excited level", let's say level "i". If "i" is an excited state, its population can decrease through two main channels: radiative decay and collisional quenching. The total depopulation rate, denoted as A_i, is therefore the sum of the radiative decay rate and the collisional decay rate:

$$A_\mathrm{i} = A_\mathrm{i}^\mathrm{rad} + A_\mathrm{i}^\mathrm{coll}$$

Here, $A_\mathrm{i}^\mathrm{rad}$ is the Einstein A coefficient for spontaneous emission from state "i" (summed over all possible lower states if "i" can decay to multiple levels). It's the rate of radiative decay in the absence of collisions. $A_\mathrm{i}^\mathrm{coll}$ is the rate of depopulation of state "i" due to inelastic collisions.

The second point gives an expression for this "Collision contribution", $A_\mathrm{i}^\mathrm{coll}$:

$$A_\mathrm{i}^\mathrm{coll} = N_\mathrm{B}\,\bar{v}\,\sigma_\mathrm{i}$$

Let's define these terms, which will be detailed on the next slide but we can anticipate them: N_B is the number density of the perturber particles B. The more perturbers there are, the higher the collision rate. $\bar{v}$ (v with a bar) is the mean relative speed between our particle A (in state i) and the perturber particles B. Faster speeds mean more frequent encounters. σ_i (lowercase sigma subscript i) is the "inelastic (quenching) cross section" for state "i". This cross section is a crucial parameter. It represents an effective area presented by particle A to particle B for an inelastic collision to occur. If B passes within this area around A, quenching happens. It has units of area (e.g., meters squared) and encapsulates the quantum mechanical probability of the quenching process occurring during a typical encounter. The "where" indicates that the definitions will follow.

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This slide continues by defining the terms in the expression for the collisional quenching rate, $A_{\mathrm{i}}^{\mathrm{coll}}$.

First, N_{B} is the "perturber number density", with typical units of particles per cubic meter (m^{-3}). This is simply how many perturber particles B are present per unit volume.

Second, $\bar{v}$ is the "mean relative speed" between the particle of interest A and the perturbers B. The rate of collisions will naturally depend on how fast, on average, they are approaching each other.

Third, σ_{i} is the "inelastic (quenching) cross section" for the state "i" that is being depopulated. Its units are area, for example, meters squared (m^2). This cross section effectively measures the "size" of the target for a quenching collision. It’s a critically important parameter that depends on the specific states involved and the nature of the interaction potential.

Next, the slide provides an expression for the "Mean speed for a Maxwellian gas of reduced mass μ". If the gas particles (A and B) are in thermal equilibrium, their speeds follow a Maxwell-Boltzmann distribution. The mean relative speed, $\bar{v}$, between particles A and B is given by:

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}}$$

Here, k is the Boltzmann constant, T is the absolute temperature, and π is the mathematical constant pi.

The "reduced mass", μ, of the colliding pair A and B is given by:

$$\mu = \frac{m_{\mathrm{A}} m_{\mathrm{B}}}{m_{\mathrm{A}} + m_{\mathrm{B}}}$$

(lowercase μ equals open parenthesis lowercase m_{A} times lowercase m_{B} close parenthesis divided by open parenthesis lowercase m_{A} plus lowercase m_{B} close parenthesis), where m_{A} and m_{B} are the masses of particles A and B, respectively.

Finally, the slide points towards establishing a "Pressure-rate relation using the ideal gas law for the perturbers, $p_{\mathrm{B}} = N_{\mathrm{B}} kT$". Here, p_{B} is the partial pressure of the perturber gas B. Since N_{B} appears in the expression for $A_{\mathrm{i}}^{\mathrm{coll}}$, and N_{B} is directly proportional to p_{B} at a given T, it means the collisional quenching rate will be directly proportional to the perturber pressure. This is a key experimental signature of pressure broadening and quenching.

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This slide combines the relationships we've just discussed to express the total depopulation rate A_{i} in a very useful form, often encountered in experimental analysis.

Recall that the total depopulation rate A_{i} is A_{i}^{rad} plus A_{i}^{coll}. A_{i}^{rad}, the radiative rate, is simply the reciprocal of the natural radiative lifetime of state 'i', which we can denote as τ_{p} (lowercase tau subscript p, perhaps 'p' for "proper" lifetime or "purely radiative" lifetime). So, $A_{\mathrm{i}}^{rad} = \frac{1}{\tau_{\mathrm{p}}}$. And $A_{\mathrm{i}}^{coll} = N_{\mathrm{B}}\, \bar{v}\, \sigma_{\mathrm{i}}$.

Using the ideal gas law, $N_{\mathrm{B}} = \frac{p_{\mathrm{B}}}{kT}$, where p_{B} is the perturber pressure. And $\bar{v} = \sqrt{\frac{8\,kT}{\pi\mu}}$. Substituting these into A_{i}^{coll}, we get: $A_{\mathrm{i}}^{coll} = \frac{p_{\mathrm{B}}}{kT}\, \sigma_{\mathrm{i}} \sqrt{\frac{8\,kT}{\pi\mu}}$.

This can be simplified. The total depopulation rate A_{i} is expressed as:

$$A_{\mathrm{i}} = \frac{1}{\tau_{\mathrm{p}}} + a p_{\mathrm{B}}$$

(capital A_{i} equals $\frac{1}{\tau_{\mathrm{p}}}$, plus lowercase a times lowercase p_{B}).

Here, the coefficient a groups together several terms: $a = \sigma_{\mathrm{i}}\sqrt{\frac{8}{\pi\mu kT}}$ (lowercase a equals lowercase σ_{i} times square root of open parenthesis 8 divided by open parenthesis lowercase π lowercase μ lowercase k capital T close parenthesis close parenthesis).

This form, $A_{\mathrm{i}} = \frac{1}{\tau_{\mathrm{p}}} + ap_{\mathrm{B}}$, is very convenient. It shows that the total depopulation rate (which is also the observed linewidth, γ, in angular frequency units, if this is the dominant broadening mechanism and $\gamma = A_{\mathrm{i}}$) is a linear function of the perturber pressure p_{B}. The intercept of a plot of A_{i} versus p_{B} gives $\frac{1}{\tau_{\mathrm{p}}}$ (the natural radiative rate), and the slope gives the coefficient a. From this slope a, and knowing T and μ, one can then extract the inelastic quenching cross section, σ_{i}. This is a standard method for measuring quenching cross sections. The triple dash indicates the end of this development.

Page 30:

Now we connect the concept of lifetime shortening due to collisions directly to the observed spectral line shape. This slide is titled "Lorentzian Profile from Lifetime Shortening".

We start by considering the "time-dependent dipole of a damped oscillator". In the classical picture, an emitting atom can be thought of as an oscillating dipole, $d(t)$ (lowercase $d(t)$). If this oscillation is damped, meaning its amplitude decays over time, then the emitted radiation will not be perfectly monochromatic.

The damping can come from natural radiative decay (rate γ_{n}, lowercase γ_{n}) and from collisional quenching (rate γ_{col}, lowercase γ_{col}). These rates add up. The amplitude of the dipole moment $d(t)$ is proportional to the exponential of minus $(\gamma_{\mathrm{n}} + \gamma_{col})t$ divided by 2, i.e.,

$$d(t) \propto e^{-\frac{(\gamma_{\text{n}}+\gamma_{col})t}{2}}.$$

The factor of $\frac{1}{2}$ in the exponent arises because the intensity (which is proportional to $d^2(t)$) decays at a rate $\gamma_{\text{n}} + \gamma_{col}$. So the amplitude $d(t)$ decays at half that rate. Here, γ_{n} and γ_{col} are total decay rates (inverse of lifetime), which are FWHM values in angular frequency units.

The fundamental connection between the time-domain behavior of the dipole and the frequency-domain spectrum is the "Fourier transform". Taking the Fourier transform of this exponentially decaying oscillating dipole (which would also have an $e^{i\omega_0 t}$ term for the oscillation frequency if we wrote it fully) yields the spectral line shape.

The result is a "Lorentzian line shape" for the intensity $I(\omega)$ (capital I of lowercase omega):

$$I(\omega) = \frac{C}{(\omega - \omega_0)^2 + \left(\frac{\gamma_{\text{n}} + \gamma_{col}}{2}\right)^2}.$$

Let's analyze this Lorentzian function: "C" is a constant related to the overall strength of the line. ω_0 (lowercase omega subscript zero) is the resonant angular frequency of the transition, i.e., the center frequency of the line if there are no collisional shifts (we are only considering lifetime shortening here). The term $\gamma_{\text{n}} + \gamma_{col}$ is the total decay rate of the excited state population, or equivalently, the total homogeneous Full Width at Half Maximum (FWHM) in angular frequency units. Let's call this total rate $\Gamma = \gamma_{\text{n}} + \gamma_{col}$. Then the denominator is

$$(\omega - \omega_0)^2 + \left(\frac{\Gamma}{2}\right)^2.$$

This function peaks at $\omega = \omega_0$. The FWHM of this Lorentzian profile is exactly Γ, or $\gamma_{\text{n}} + \gamma_{col}$.

So, inelastic collisions, by adding to γ_{col} and thus increasing Γ, directly broaden the spectral line, and this broadening is Lorentzian in shape.

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This slide summarizes the 'Halfwidth parameters' that appear in the Lorentzian line shape arising from lifetime shortening, and clarifies some terminology.

We just saw that the total Full Width at Half Maximum (FWHM) in angular frequency units is γ, where $\gamma = \gamma_{\text{n}} + \gamma_{\text{col}}$.

Let's look at the components: 'γ_{col}' (lowercase gamma subscript c-o-l), the collisional contribution to the FWHM, is directly proportional to the perturber pressure p_{B}. We can write:

$$\gamma_{\text{col}} = a\, p_{\text{B}}$$

(lowercase gamma subscript c-o-l equals lowercase a times lowercase p_{B}). This a is the same pressure broadening coefficient we encountered on page 29, which contains the quenching cross section σ_{i} and factors dependent on temperature and reduced mass. This explicitly shows the linear dependence of the collisional width on pressure.

'γ_{n}' (lowercase gamma subscript n), the natural radiative contribution to the FWHM, is simply the radiative decay rate:

$$\gamma_{\text{n}} = \frac{1}{\tau_{\text{p}}}$$

(lowercase gamma subscript n equals $\frac{1}{\tau_{\text{p}}}$), where τ_{p} is the natural radiative lifetime.

This leads to the important 'Terminology': The term "pressure broadening" often refers specifically to this 'linear growth of the total linewidth γ with the perturber pressure p_{B}'. So, if you measure the linewidth γ (FWHM) as a function of pressure p_{B}, you should expect to see a relationship like

$$\gamma(p_\mathrm{B}) = \gamma_\mathrm{n} + a\, p_\mathrm{B}$$

Plotting γ versus p_B yields a straight line. The y-intercept (at $p_\mathrm{B} = 0$) gives the natural linewidth γ_n. The slope of this line is the pressure broadening coefficient a. This linear relationship is a hallmark of collisional broadening dominated by lifetime reduction (quenching) or phase-perturbing collisions, as we'll see. The triple dash ends this explanation.

Page 32:

We now turn our attention to the second fundamental broadening mechanism: 'Elastic Collisions – Phase Perturbations'. Unlike inelastic collisions that change the state population and shorten the lifetime, elastic collisions preserve the population of the state but can still significantly affect the spectral line.

The key idea is stated first: 'Collisions change phase, not the amplitude of the dipole oscillator.' This means the atom remains in the excited state, but the phase of its radiating wavefunction (or classical dipole oscillation) is suddenly and randomly altered by each elastic collision. An accumulation of these random phase shifts over time leads to a dephasing of the ensemble of radiators, which results in line broadening. Furthermore, these phase shifts can also lead to a net 'frequency shift' of the line center.

The slide then presents an 'Empirical Lorentzian with shift' that describes the line shape when both phase-perturbing elastic collisions and lifetime-limiting effects (natural and inelastic) are present. The intensity $I(\omega)$ is given by:

$$I(\omega) = \frac{C^*}{\left[(\omega - \omega_0 - \Delta\omega)^2 + \left(\frac{\gamma}{2}\right)^2\right]}.$$

Let's break this down: 'C star' is an overall strength constant. 'omega sub zero' (ω_0) is the unperturbed resonant frequency. 'Capital Delta omega' ($\Delta\omega$) is the 'collisional shift' of the line center, caused by the phase-perturbing collisions. The line is now centered at $\omega_0 + \Delta\omega$. 'gamma' (γ) is the total full width at half maximum (FWHM) of the Lorentzian profile, in angular frequency units.

The next part shows how these 'Quantities are expressed through cross sections', similar to how we did for quenching: The collisional shift, capital Delta omega, is given by:

$$\Delta\omega = N_\mathrm{B}\,\bar{v}\,\sigma_\mathrm{s}.$$

Here, N_B is the perturber density, $\bar{v}$ is the mean relative speed, and 'sigma sub s' (σ_s) is the 'cross section for line shifting'. It's an effective area for collisions that cause a phase shift leading to a net frequency shift.

The total linewidth, gamma, is given by:

$$\gamma = \gamma_\mathrm{n} + N_\mathrm{B}\,\bar{v}\,\sigma_\mathrm{b}.$$

Here, γ_n is the natural radiative width. The collisional contribution to the width is $N_\mathrm{B}\,\bar{v}\,\sigma_\mathrm{b}$, where 'sigma sub b' ($\sigma_\mathrm{b}$) is the 'cross section for line broadening' due to phase-perturbing elastic collisions (and can also include inelastic contributions if they are lumped together). Notice that both the shift $\Delta\omega$ and the collisional part of the width are proportional to the perturber density N_B (and thus to pressure), and they involve distinct cross sections, σ_s for shift and σ_b for broadening.

Page 33:

This slide elaborates on the 'Distinct sigmas', or cross sections, that we just introduced for elastic phase-perturbing collisions: σ_s for shifts and σ_b for broadening. It's important to recognize that these are generally not the same.

First, let's consider σ_s (lowercase sigma subscript s), the cross section associated with 'shifts'. The slide notes that shifting collisions can be 'efficient even at large impact parameters'. The impact parameter, you'll recall, is the perpendicular distance between the path of the perturber and the target atom if they were to undergo no interaction. A large impact parameter means a distant, or "soft," collision. Even these distant encounters can cause small, cumulative phase shifts that result in an overall shift of the line center. This is because the long-range part of the interaction potential (like the R^{-6} van der Waals term) can still exert an influence at larger distances, perturbing the energy levels slightly and for a longer duration during the glancing fly-by.

Next, consider σ_b (lowercase sigma subscript b), the cross section associated with 'broadening' due to phase interruption. This type of broadening is often 'dominated by close encounters', or collisions with small impact parameters. These are the "harder" collisions where the phase of the atomic oscillator is significantly disrupted, often by a large amount (e.g., a radian or more). While distant collisions also contribute to phase changes, strong phase interruptions that effectively terminate the coherence of the emitted wave train and thus lead to significant broadening typically require the perturber to come closer to the radiating atom.

So, the key message is that the physical processes and the range of impact parameters that contribute most effectively to line shifting can be different from those that contribute most to line broadening. This is why σ_s and σ_b are distinct quantities. Their relative magnitudes will depend on the specific interaction potential $V(R)$ and the states involved. For example, for some potentials (like R^{-6}), the ratio of broadening to shift cross section can be theoretically calculated. The triple dash marks the end of this point.

Page 34:

We now encounter an important reality check: 'Real-World Line Profiles Are Rarely Perfect Lorentzians'. While the Lorentzian profile is a good starting point and often provides a reasonable approximation, especially near the line center, actual experimental line shapes can exhibit significant deviations, particularly in the wings.

Why is this so? The first point gives a crucial reason: 'The Einstein $A_{ik}(R)$ coefficient, and the transition energy difference, $\Delta E(R)$, both depend non-linearly on the internuclear separation R.' We've mostly assumed A_{ik} is constant and focused on $\Delta E(R)$. However, if $A_{ik}(R)$ also varies, and especially if both vary in complex ways, the simple assumptions leading to a symmetric Lorentzian break down. This non-linear dependence often leads to an 'asymmetry between the red and blue wings' of the spectral line. The red wing (frequencies lower than line center) might have a different shape or extent than the blue wing (frequencies higher than line center). This asymmetry is a direct reflection of the details of the interaction potentials $E_i(R)$ and $E_k(R)$.

The second point highlights another fascinating feature: 'A non-monotonic $V(R)$ (or more accurately, a non-monotonic *difference potential* $\Delta E(R)$) can produce "satellite" features far in the wings.'

Consider the Lennard-Jones potential we saw earlier. It has a well. The difference potential, $\Delta E(R) = E_k(R) - E_i(R)$, can also be non-monotonic, meaning it might have a local maximum or minimum at some separation R_s (R subscript s). At such an extremum, $\frac{d\Delta E}{dR}$ is zero, which means $\frac{d\omega}{dR}$ is zero. In our quasi-static intensity formula, $I(\omega)$ was proportional to $\frac{1}{\left|\frac{d\omega}{dR}\right|}$. So, if $\frac{d\omega}{dR}$ goes to zero, the intensity formula blows up! This singularity indicates a "classical satellite" – a peak or enhanced intensity in the wing of the line at the frequency ω_s corresponding to this R_s. Many different collision trajectories passing through R values near R_s will all radiate at nearly the same frequency ω_s, causing a pile-up of intensity there. These satellites are often seen in the far wings of pressure-broadened lines and are extremely sensitive probes of the shape of the difference potential.

The concluding statement emphasizes the opportunity here: 'Analysis of these asymmetric profiles and satellite features can retrieve detailed information about intermolecular potentials.' While more complex to analyze than simple Lorentzians, these details in the line shape are not just nuisances; they are rich sources of information about the forces between atoms and molecules.

Page 35:

This slide offers a crucial piece of advice for experimentalists, flowing directly from our previous discussion about non-Lorentzian line shapes. It states: "Practical spectroscopy must fit experimental data with sophisticated (often numerical) models rather than simple Lorentzians," especially if one is interested in the details of the line wings or in extracting accurate information about collision dynamics and intermolecular potentials.

While a simple Lorentzian fit might be adequate for determining the approximate line center and width in some cases, it will fail to capture asymmetries, satellite features, and the true behavior in the far wings. Using more sophisticated line shape models, which often require numerical computation, is necessary to accurately represent these complex profiles. These models might incorporate:

1. The detailed R-dependence of both the difference potential $\Delta E(R)$ and the transition probability $A_{ik}(R)$. 2. Statistical averaging over different collision trajectories, impact parameters, and velocities. 3. Consideration of both quasi-static effects (for the wings) and impact or phase-shift effects (for the core). 4. Sometimes, quantum mechanical scattering calculations are needed for the most accurate models, going beyond semi-classical approximations.

Fitting experimental data with such models, while more challenging, allows for a much deeper understanding of the underlying physics and can yield quantitative information about the interaction potentials, cross sections for various collisional processes, and other microscopic parameters. Ignoring these complexities by just fitting a Lorentzian can lead to a loss of valuable information or even erroneous conclusions about the system under study.

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This slide beautifully illustrates the points made on the previous two slides about 'Real-World Line Profiles'. It displays a graph titled 'Measured Line with Asymmetric Wings and Fitted Theoretical Curve'.

Let's examine the plot. The vertical axis represents 'Intensity I, in arbitrary units', ranging from 0.0 to 1.1. The horizontal axis is 'Frequency ω (lowercase Greek letter omega), also in arbitrary units', spanning from 55 to 145.

The solid blue line represents 'Measured Data'. Observe its features carefully. There is a main, strong peak centered roughly around $\omega = 100$. However, the line is far from being a simple, symmetric Lorentzian.

Notice the distinct asymmetry: the intensity drops off differently on the low-frequency side (the "red wing," to the left of the main peak) compared to the high-frequency side (the "blue wing," to the right).

More strikingly, there are clear 'satellite' features. An arrow points to a secondary peak in the red wing, around $\omega = 80$, explicitly labeled 'Satellite (Red Wing)'. This indicates an extremum in the difference potential at a separation R that produces this frequency.

Similarly, on the blue wing, around $\omega = 115$, another arrow points to a feature, possibly a shoulder or a less resolved satellite, labeled 'Satellite (Blue Wing)'.

The red dashed line shows a 'Fitted Theoretical Curve'. Crucially, this theoretical curve is *not* a simple Lorentzian. It's clearly a more sophisticated model that has been tailored to reproduce the observed features, including the overall asymmetry and, importantly, the satellite peaks in both the red and blue wings. This demonstrates that with appropriate theoretical models, one can indeed account for these complex line shapes. The excellent agreement between the measured data and the fitted curve suggests that the model is capturing the essential physics of the interatomic interactions responsible for these features. This is a prime example of how detailed line shape analysis goes beyond simple peak fitting to probe fundamental molecular physics.

Page 37:

We now revisit a specific type of model potential: "Power-Law Potentials", which take the general form

$$V(R) = \frac{C}{R^n}$$

(capital V of capital R equals capital C divided by capital R to the power of n). This form is very useful for understanding how different types of interactions influence line shapes.

First, let's consider the "Ground and excited state potentials". We can assume that both the interaction potential for the initial state (let's call it $V_\mathrm{i}(R)$) and for the final state ($V_\mathrm{k}(R)$) can be approximated by a power law. The slide writes them as:

$$V_\mathrm{i}(R) = \frac{C_\mathrm{i}}{R^{n'}}$$

(capital $V_\mathrm{i}(R) = \frac{C_\mathrm{i}}{R^{n'}}$).

And

$$V_\mathrm{k}(R) = \frac{C_\mathrm{k}}{R^n}$$

(capital $V_\mathrm{k}(R) = \frac{C_\mathrm{k}}{R^n}$).

For simplicity, let's assume $n' = n$, meaning both potentials have the same R-dependence type. So,

$$V_\mathrm{i}(R) = \frac{C_\mathrm{i}}{R^n} \quad \text{and} \quad V_\mathrm{k}(R) = \frac{C_\mathrm{k}}{R^n}$$

. Here, C_{i} and C_{k} are the potential coefficients for the initial and final states, respectively. These are *interaction* potentials, representing the energy shift of the respective levels due to the perturber, relative to their unperturbed energies.

The "Corresponding instantaneous frequency shift" from the unperturbed line center, $\Delta\omega(R)$ (capital Delta lowercase omega of R), is then given by the difference in these interaction potentials, divided by $\hbar$. The slide presents it as:

$$\hbar\,\Delta\omega(R) = \frac{(C_{\mathrm{i}} - C_{\mathrm{k}})}{R^n}$$

(capital Delta lowercase omega of R equals $\frac{(C_{\mathrm{i}} - C_{\mathrm{k}})}{R^n}$).

If we define ΔC as $(C_{\mathrm{i}} - C_{\mathrm{k}})$, this equation tells us how the frequency of the emitted/absorbed photon is shifted from its unperturbed value when the colliding particles are at a separation R. If the transition is from state i to k, and

$$\hbar\,\omega(R) = \left(E_{\mathrm{k}}^0 + V_{\mathrm{k}}(R)\right) - \left(E_{\mathrm{i}}^0 + V_{\mathrm{i}}(R)\right) = \hbar\,\omega_0 + \left(V_{\mathrm{k}}(R) - V_{\mathrm{i}}(R)\right),$$

then the frequency shift from ω_0 is

$$\frac{V_{\mathrm{k}}(R) - V_{\mathrm{i}}(R)}{\hbar} = \frac{C_{\mathrm{k}} - C_{\mathrm{i}}}{\hbar\,R^n}.$$

So the slide's definition of $\Delta\omega(R)$ is effectively $-$(shift from ω_0). The magnitude and R-dependence are key.

This power-law form particularly "highlights the influence of the exponent n". The value of n dictates how rapidly the frequency shift changes with internuclear separation, which in turn strongly influences the shape of the collisionally broadened line, especially its wings, and also determines the temperature dependence of the broadening and shifting coefficients.

Page 38:

This slide provides concrete examples of the exponent n in the power-law potential, $\hbar\Delta\omega(R) = \frac{\Delta C}{R^n}$, for different types of physical interactions. Understanding these specific values of n is crucial as they lead to distinct line shape characteristics.

First, for "Van der Waals (dispersion) interaction", the exponent $n = 6$.

This is the interaction between instantaneous induced dipoles in two neutral atoms or nonpolar molecules. The interaction potential for each state (ground and excited) typically goes as $\frac{1}{R^6}$. Therefore, the difference potential, $\frac{\Delta C}{R^6}$, also follows this R^{-6} dependence. This is a very common interaction responsible for broadening in neutral atom/molecule collisions. It leads to what's often called "van der Waals broadening."

Second, for "Dipole-dipole resonant interaction", the exponent $n = 3$.

This occurs when two identical atoms or molecules interact, and one is in an excited state that can make an allowed dipole transition to the ground state, while the other is in the ground state. There's a resonant exchange of excitation energy, leading to an interaction potential that falls off as $\frac{1}{R^3}$. This R^{-3} dependence is much longer-ranged than the van der Waals R^{-6}. This type of interaction often leads to very large broadening cross sections and is important in "self-broadening" where an atom is perturbed by other atoms of the same kind.

Third, for "Coulomb (ion-electron) interaction", the exponent $n = 1$.

The fundamental Coulomb potential itself goes as $\frac{1}{R}$. This is the longest-range interaction. Broadening due to collisions with charged particles is known as Stark broadening. If the perturbers are electrons or ions creating an electric field E, the energy shift can be linear in E (linear Stark effect) or quadratic in E (quadratic Stark effect). For an ion perturber, E itself scales as $\frac{1}{R^2}$, so linear Stark gives energy shift $\sim \frac{1}{R^2}$ ($n = 2$ for $\frac{\Delta C}{R^n}$ type potential), and quadratic Stark gives energy shift $\sim \frac{1}{R^4}$ ($n = 4$). The $n = 1$ here perhaps refers to the potential energy $V(R) \sim \frac{1}{R}$ itself, from which the field is derived, or a specific case like a hydrogenic ion interacting with an electron where the overall interaction scales this way. It underscores the long-range nature.

These values of n (6, 3, 1, and others like 4 for quadratic Stark by ions, or 2 for charge-permanent dipole interactions) are critical inputs for theories that predict line shapes, widths, and shifts, and their temperature dependencies.

Page 39:

We now transition to a different theoretical approach for understanding collisional effects, focusing on the 'Phase Shift for a Single Collision'. This is central to the "impact approximation" or "phase shift theory" of line broadening, which is particularly useful for describing the core of the spectral line. We'll be using the 'Straight Path Approximation' for simplicity.

First, let's define the 'Geometry' of the collision under this approximation.

We have an 'Impact parameter, R_0' (capital R_0). This is defined as the 'distance of closest approach' between the perturber and the radiating atom *if there were no interaction potential* to deflect their paths. A diagram on a subsequent slide will illustrate this. So, R_0 characterizes how "head-on" or "glancing" a collision is.

A key simplifying assumption is that the 'Relative velocity v' (lowercase v) between the two particles is 'assumed constant' throughout the collision, both in magnitude and direction. This means we are ignoring any acceleration or deceleration due to the interaction potential. Furthermore, the 'trajectory' of the perturber relative to the radiator is 'assumed to be a straight line'. This is a reasonable approximation for distant collisions or for high-velocity collisions where the deflection is minimal.

Under these conditions, we want to calculate the total accumulated phase shift of the atomic oscillator during one complete collision event. This phase shift, let's call it $\mathit{\Delta}\phi$ (capital Delta, lowercase phi), is obtained by integrating the instantaneous frequency shift, $\mathit{\Delta}\omega(R,t)$, over the entire duration of the collision, from $t = -\infty$ to $t = +\infty$.

The slide indicates 'Integral', implying we will set up this integral next.

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Here, we see the integral for the total phase shift, $\mathit{\Delta}\phi$ (capital Delta lowercase phi), accumulated during a single collision characterized by an impact parameter R_0 (capital R subscript zero). The phase shift $\mathit{\Delta}\phi(R_0)$ is given by the integral of the instantaneous angular frequency shift, $\mathit{\Delta}\omega(R)$, with respect to time t, from $t = -\infty$ to $t = +\infty$:

$$\mathit{\Delta}\phi(R_0) = \int_{-\infty}^{+\infty} \mathit{\Delta}\,\omega\big(R(t)\big)\,dt.$$

(capital Delta lowercase phi of capital R subscript zero equals integral from minus infinity to plus infinity of capital Delta lowercase omega of R of t, dt).

Now, if we use the power-law form for the frequency shift from slide 37, where

$$\hbar\,\mathit{\Delta}\omega(R) = \frac{C_{\mathrm{i}} - C_{\mathrm{k}}}{R^n},$$

then

$$\mathit{\Delta}\omega(R) = \frac{C_{\mathrm{i}} - C_{\mathrm{k}}}{\hbar\,R^n}.$$

Substituting this into the integral gives:

$$\mathit{\Delta}\phi(R_0) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} \frac{C_{\mathrm{i}} - C_{\mathrm{k}}}{[R(t)]^n}\,dt.$$

(equals one over aitch-bar, integral from minus infinity to plus infinity, of, open square bracket, open parenthesis capital C subscript i minus capital C subscript k close parenthesis, divided by, R of t to the power of n, close square bracket, dt).

Here, $C_{\mathrm{i}} - C_{\mathrm{k}}$ is the difference potential coefficient, let's call it $\Delta C'$. So

$$\Delta\omega(R) = \frac{\Delta C'}{\hbar\, R^n}.$$

Now, we need to "Evaluate integral".

First, for a straight-line trajectory with impact parameter R_0 and constant relative speed v, the separation $R(t)$ at time t is given by the Pythagorean theorem:

$$R(t) = \sqrt{R_0^2 + (vt)^2}.$$

(R of t equals square root of open parenthesis capital R subscript zero squared plus open parenthesis lowercase v lowercase t close parenthesis squared close parenthesis).

Here, $t = 0$ is defined as the time of closest approach, when $R(t) = R_0$.

Substituting this $R(t)$ into the integral and performing the integration yields a "Standard result" for the phase shift:

$$\Delta\phi(R_0) = \alpha_{\mathrm{n}}\, \frac{C_{\mathrm{i}} - C_{\mathrm{k}}}{v\, R_0^{n-1}}.$$

(capital Delta lowercase phi of capital R subscript zero equals lowercase alpha subscript n, times, open parenthesis capital C subscript i minus capital C subscript k close parenthesis, divided by, open parenthesis lowercase v times capital R subscript zero to the power of open parenthesis n minus 1 close parenthesis close parenthesis).

The $C_{\mathrm{i}} - C_{\mathrm{k}}$ here is the same coefficient from

$$\hbar\,\Delta\omega(R) = \frac{C_{\mathrm{i}} - C_{\mathrm{k}}}{R^n}.$$

So if we denote

$$C_{\mathrm{diff}} = (C_{\mathrm{i}} - C_{\mathrm{k}}),$$

then

$$\Delta\phi(R_0) = \frac{\alpha_{\mathrm{n}}\,C_{\mathrm{diff}}}{\hbar\,v\,R_0^{n-1}},$$

because $\Delta\omega$ was $\frac{C_{\mathrm{diff}}}{\hbar\,R^n}$. The $\hbar$ should be in the denominator of the phase shift if C_{diff} is an energy coefficient. The slide's expression for $\Delta\phi(R_0)$ seems to absorb $\hbar$ into C_{i} and C_{k} or α_{n} if C_{i}, C_{k} are energy coefficients. Let's assume C_{i} and C_{k} now implicitly contain the $1/\hbar$ factor for simplicity, or that α_{n} does. So

$$\Delta\phi(R_0) = \frac{\alpha_{\mathrm{n}}\,\Delta C_{\mathrm{effective}}}{v\,R_0^{n-1}}.$$

Let's break down this result:

"alpha sub n" (lowercase Greek letter alpha subscript n) is a "numerical factor that depends only on the exponent n" of the power-law potential. It arises from the specific mathematical form of the integral over time. For example, as the slide notes, for $n = 6$ (which corresponds to the van der Waals interaction),

$$\alpha_6 = \frac{\pi}{8}$$

(lowercase alpha subscript 6 equals lowercase pi divided by 8). Each value of "n" will have a different, calculable α_{n}. For $n = 3$, $\alpha_3 = \frac{\pi}{2}$; for $n = 4$, $\alpha_4 = \frac{\pi}{2}$.

$C_\mathrm{i} - C_\mathrm{k}$ is the effective difference in the potential strength coefficients. v is the relative speed of the collision. R_0 is the impact parameter. So, for a given type of interaction (fixed n), the phase shift is proportional to the strength of the difference potential, inversely proportional to the velocity (v) – slower collisions produce larger phase shifts because the interaction lasts longer – and inversely proportional to R_0 raised to the power of $(n-1)$ – closer collisions produce much larger phase shifts. This dependence on R_0^{n-1} is very strong.

This expression for $\Delta\phi(R_0)$ is fundamental in the impact theory of line broadening, as the broadening and shifting cross sections are derived by averaging effects related to this phase shift over all impact parameters.

Page 41:

This slide provides the promised 'Collision Trajectory Diagram (Straight Path Approximation)' to help visualize the geometry we've been discussing.

Let's examine the diagram carefully. We see two particles. 'Stationary Particle A' is depicted as a blue circle at the origin of our coordinate system. This is our radiating atom. 'Moving Particle B' is depicted as a red circle. This is the perturber. It moves with a constant velocity v (lowercase v), indicated by a green arrow, along a straight line. The 'Path of Particle B' is shown as a horizontal dashed line. The 'Impact parameter R_0' is clearly marked. It's the perpendicular distance from Particle A to the straight-line path of Particle B. It's shown as a vertical purple line segment from A to the path of B.

The point on the trajectory directly above A, where the separation is R_0, is marked as $t = 0$ (t equals zero), representing the time of closest approach. At some arbitrary time t, Particle B has moved a horizontal distance vt (lowercase v times lowercase t) from the $t = 0$ position. This distance is labeled. The instantaneous separation between A and B at this time t is

$R(t)$ (capital R of t), shown as a magenta line segment connecting A and B.

From the diagram, we can see a right-angled triangle formed by R_0, vt, and $R(t)$ (with $R(t)$ as the hypotenuse). This visually confirms the relationship we used on the previous slide:

$$R(t)^2 = R_0^2 + (vt)^2 \quad \text{or} \quad R(t) = \sqrt{R_0^2 + v^2 t^2}$$

This diagram is a simple but powerful illustration of the idealized collision geometry assumed in the straight-path approximation. It allows us to calculate the time-dependent separation $R(t)$ and, from that, the phase shift accumulated during the collision as a function of the impact parameter R_0 and relative velocity v.

Page 42:

Now that we have an expression for the phase shift $\Delta\phi(R_0)$ for a single collision, this slide, titled "Connecting Phase Shifts to Cross Sections," shows how these phase shifts are used to calculate the macroscopic cross sections for line shifting (σ_s) and broadening (σ_b). These are the cross sections that appeared in our Lorentzian line shape formula when discussing elastic phase-perturbing collisions.

The slide presents two integrals.

First, the "Line-shift cross section", σ_s (lowercase sigma subscript s):

$$\sigma_\text{s} = 2\pi \int_0^\infty \left[1 - \cos\big(\Delta\phi(R_0)\big)\right] R_0 \, dR_0.$$

$$\sigma_\text{s} = 2\pi \int_0^\infty \left[1 - \cos\big(\Delta\phi(R_0)\big)\right] R_0 \, dR_0.$$

This form is one standard definition for a *broadening* cross section, often denoted σ' in texts like Griem or Sobelman, or sometimes as the

"Weisskopf cross section" if the integral is cut off when $\Delta\phi$ reaches 1 radian. It's unusual to see $1-\cos(\Delta\phi)$ associated with the shift cross section, which typically involves $\sin(\Delta\phi)$.

Second, the "Broadening (phase-diffusion) cross section", σ_{b} (lowercase sigma subscript b):

$$\sigma_{\mathrm{b}} = 2\pi \int_0^\infty \left[1 - \frac{\cos\big(\Delta\phi(R_0)\big)}{2}\right] R_0\, dR_0.$$

$$\sigma_{\mathrm{b}} = 2\pi \int_0^\infty \left[1 - \frac{\cos\big(\Delta\phi(R_0)\big)}{2}\right] R_0\, dR_0.$$

This expression simplifies to

$$\sigma_{\mathrm{b}} = \pi \int_0^\infty \big[1 - \cos\big(\Delta\phi(R_0)\big)\big]\, R_0\, dR_0.$$

Thus, according to the explicit formulae on this slide, σ_{b} equals one half of σ_{s}.

This fixed ratio of 2:1 between the shift cross section and the broadening cross section, if these definitions are taken literally, is specific and not generally true for all potentials. More commonly, as mentioned, σ_{s} involves an integral of $\sin(\Delta\phi)$ and σ_{b} involves an integral of $1-\cos(\Delta\phi)$ or $\sin^2\left(\frac{\Delta\phi}{2}\right)$. These lead to different functional dependencies on the potential parameters and thus different values for σ_{s} and σ_{b}.

However, adhering strictly to what is presented, the impact parameter R_0 is integrated from 0 (head-on collision) to infinity (very distant collision). The term $R_0\, dR_0$ is an element of area $(d(\pi R_0^2) = 2\pi R_0\, dR_0)$. The term involving the cosine of the phase shift acts as a weighting factor, determining how much collisions at a given R_0 contribute. For example, in the expression for σ_{s}, if $\Delta\phi(R_0)$ is a multiple of 2π, $\cos(\Delta\phi)$ is 1, and that R_0 contributes nothing to the integral. If $\Delta\phi(R_0)$ is an odd multiple of π, $\cos(\Delta\phi)$ is -1, and the term $\big(1-\cos(\Delta\phi)\big)$ becomes 2, contributing maximally.

Once these cross sections are calculated by performing the integration (often numerically, or analytically for simple power laws and certain approximations), they can be used in the expressions:

$$\Delta\omega = N_{\mathrm{B}}\,\bar{v}\,\sigma_{\mathrm{s}}$$

$$\gamma_{\text{collisional}} = N_{\mathrm{B}}\,\bar{v}\,\sigma_{\mathrm{b}}.$$

Page 43:

This slide provides an important insight into the behavior of these cross sections, particularly for distant collisions.

It states: "For small capital $\Delta\phi$" (small phase shifts), which typically occur in "far-off collisions" (collisions with large impact parameters R_0), the following approximations can be made:

The term $1-\cos(\Delta\phi)$ becomes approximately $\frac{(\Delta\phi)^2}{2}$ for small $\Delta\phi$.

So, based on the definitions from the previous slide:

The integrand for σ_{s}, $[1-\cos(\Delta\phi)]R_0$, behaves like $\frac{(\Delta\phi)^2 R_0}{2}$.

The integrand for σ_{b}, $\frac{[1-\cos(\Delta\phi)]R_0}{2}$, behaves like $\frac{(\Delta\phi)^2 R_0}{4}$.

Since $\Delta\phi$ of R_0 falls off as $\frac{1}{R_0^{n-1}}$, then $(\Delta\phi)^2$ falls off as $\frac{1}{R_0^{2(n-1)}}$.

So, the integrand for both σ_{s} and σ_{b} effectively behaves as R_0 times $\frac{1}{R_0^{2(n-1)}}$, which is $\frac{1}{R_0^{2n-3}}$.

For this integral (from some $R_{\min}$ to infinity) to converge, the exponent $2n-3$ must be greater than 1, meaning $2n > 4$, or $n > 2$.

For $n = 3$ (resonant dipole-dipole), the exponent is $2 \times 3 - 3 = 3$, so the integral of $\frac{1}{R_0^3}$ converges.

For $n = 6$ (van der Waals), the exponent is $2 \times 6 - 3 = 9$, so the integral of $\frac{1}{R_0^9}$ converges very rapidly.

The slide says that "σ_s remains finite". This is true if $n > 2$.

It then states that "whereas σ_b converges faster". Given the formulae on the previous page, σ_b is simply $\frac{\sigma_\mathrm{s}}{2}$, so they converge in exactly the same way. This statement "converges faster" strongly suggests that the intended underlying formulae for σ_s and σ_b are the more standard ones where σ_s involves $\sin(\Delta\phi) \sim \Delta\phi$ and σ_b involves $1 - \cos(\Delta\phi) \sim \frac{\Delta\phi^2}{2}$.

If we use those standard forms:

$\sigma_\mathrm{s} \sim \int (\Delta\phi\, R_0)\, dR_0 \sim \int \frac{1}{R_0^{n-2}}\, dR_0$. Converges if $n - 2 > 1$, i.e., $n > 3$.

$\sigma_\mathrm{b} \sim \int (\Delta\phi)^2 R_0\, dR_0 \sim \int \frac{1}{R_0^{2n-3}}\, dR_0$. Converges if $2n - 3 > 1$, i.e., $n > 2$.

In this standard case, for $n = 3$, the σ_s integral is $\sim \frac{1}{R_0}$ (diverges or needs cutoff), and the σ_b integral is $\sim \frac{1}{R_0^3}$ (converges). For $n = 6$, the σ_s integral is $\sim \frac{1}{R_0^4}$ (converges), and the σ_b integral is $\sim \frac{1}{R_0^9}$ (converges much faster).

The concluding remark on the slide is: "demonstrates why distant collisions shift but scarcely broaden" the line.

Page 44:

This slide takes us back to the fascinating topic of 'Satellites and Non-Monotonic Potentials', which we touched upon earlier when discussing real-world line shapes.

The first point explains the origin of satellite peaks: "If the difference potential, $\mathit{\Delta} E(R)$, has an extremum (a local maximum or minimum) at some internuclear separation $R = R_{\mathrm{s}}$" (capital R_{s}), then "many collisions accumulate the same ω (angular frequency), leading to a satellite peak at ω_{s}" (lowercase ω_{s}).

The frequency of this satellite peak is given by:

$$\omega_{\mathrm{s}} = \frac{\mathit{\Delta} E(R_{\mathrm{s}})}{\hbar}$$

(lowercase ω_{s} equals $\mathit{\Delta} E(R_{\mathrm{s}})$ divided by $\hbar$). At an extremum of $\mathit{\Delta} E(R)$, the derivative $\frac{d\mathit{\Delta} E(R)}{dR}$ is zero. Since $\omega(R)$ is proportional to $\mathit{\Delta} E(R)$, this means $\frac{d\omega}{dR}$ is also zero at $R = R_{\mathrm{s}}$. In the quasi-static theory of line broadening, the intensity $I(\omega)$ of ω is inversely proportional to the absolute value of $\frac{d\omega}{dR}$. So, when $\frac{d\omega}{dR}$ approaches zero, the intensity $I(\omega)$ of ω tends to infinity, creating a "classical satellite" peak. Quantum mechanically, this singularity is smoothed out, but a distinct peak or shoulder in the line wing often remains at ω_{s}. The idea is that a range of R values around R_{s} all contribute to frequencies very close to ω_{s}, causing an enhancement of intensity there.

The second point notes that the "Satellite intensity is sensitive to the slope $\frac{d^2\mathit{\Delta} E(R)}{dR^2}$ at R_{s}" (the second derivative of the difference potential with respect to R, evaluated at R_{s}). This second derivative determines how quickly $\mathit{\Delta} E(R)$ curves away from its extremum value. A smaller second derivative (a flatter extremum) means more R values contribute to the satellite frequency, leading to a more intense satellite.

Therefore, as the third point concludes, "Observing satellites in a spectral line profile therefore pinpoints potential minima or maxima" in the difference potential curve, $\mathit{\Delta} E(R)$. This makes satellite spectroscopy an incredibly powerful tool for probing the details of intermolecular interaction potentials, especially the shape of $V_{\mathrm{k}}(R) - V_{\mathrm{i}}(R)$, at specific internuclear separations.

Page 45:

This slide provides a concrete "Example" of where such satellite features are observed. It states: "Cesium-Xenon (Cs-Xe) collisions show satellites in the far red wing of the Cesium $6\,s$ to $9\,p_{3/2}$ transition."

Let's break this down:

The radiating atom is Cesium (Cs). The perturber atom is Xenon (Xe), a heavy noble gas. The specific spectroscopic transition in Cesium being observed is from the $6\,s$ ground state (or an initial state related to it) to the highly excited $9\,p_{3/2}$ state. (That's $6\,S \rightarrow 9\,P_{3/2}$.)

When Cesium atoms are in a Xenon gas environment, collisions between Cs and Xe perturb the Cesium energy levels. The difference potential, $\Delta E(R)$, between the (Cs in $9\,p$ state + Xe) system and the (Cs in $6\,s$ state + Xe) system must have an extremum at some Cs-Xe separation R_{s}.

This extremum leads to the appearance of satellite peaks. In this specific case, the satellites are observed in the "far red wing" of the main spectral line. A red wing means frequencies lower than the unperturbed transition frequency. This implies that at the separation R_{s} which causes the satellite, the energy difference $\Delta E(R_{\mathrm{s}})$ $(9\,p - 6\,s)$ is *smaller* than the unperturbed energy difference.

Such observations are invaluable for testing and refining theoretical models of the Cs-Xe interaction potentials for both the ground and, especially, the highly excited states.

Page 46

This slide presents a graph illustrating the 'Wing of Cs-Xe Line Profile with Annotated Satellite' that was mentioned as an example on the previous slide. It's described as an 'Illustrative example based on Cs-Xe 6s to 9p three-halves transition'.

Let's look at the graph:

The vertical axis is 'Intensity (arb. units)', ranging from 0 to 110. The horizontal axis is '$\Delta\omega$ (Frequency Detuning from ω_0)', also in arbitrary units. ω_0, the unperturbed line center, is marked at $\Delta\omega = 0$. The detuning ranges from minus 100 (red wing) to about plus 15 (blue wing). Since it's the "wing" of the line, the main peak at ω_0 is not fully shown, or this plot focuses only on the red wing features.

The blue curve shows the spectral line profile. We are looking at the red wing (negative $\Delta\omega$).

There is a prominent feature, a distinct peak, in this wing. An arrow points directly to this peak, which is labeled 'Satellite Peak'. This peak occurs at a specific detuning, labeled ω_s (lowercase omega subscript s) on the horizontal axis, which is at a negative value of $\Delta\omega$ (e.g., around -30 to -40 in these arbitrary units, judging by the arrow position).

This visually confirms what we discussed: an extremum in the difference potential ΔE of R for the Cs(9p)-Xe and Cs(6s)-Xe interaction leads to a pile-up of intensity at the corresponding satellite frequency ω_s in the red wing of the line.

The shape is non-Lorentzian; it shows a clear bump or separate peak away from the main line center. Such data is precisely what experimentalists use to map out features of the interaction potentials.

Page 47:

We now shift our focus to a specific environment where collisional broadening is extremely important: 'Broadening & Shift in Plasmas'. The dominant mechanism here is often the 'Stark Effect'. The first point notes that in plasmas, we have 'Charged perturbers' – primarily ions and electrons. These charged particles interact with the radiating atom or ion via the 'Coulomb potential', which, as we saw earlier, has a $V \propto \frac{1}{R}$ dependence ($V \propto \frac{1}{R}$). This corresponds to a power-law potential with $n = 1$

governing the potential energy between charges. This long-range interaction is very effective at perturbing atomic energy levels via the electric fields these charges create.

The perturbation of energy levels by the electric fields produced by these charged perturbers is known as the Stark effect.

The slide distinguishes between two types: First, the 'Linear Stark effect'. This effect, as the asterisk notes, "Splits the m-sublevels symmetrically" around the unperturbed energy. (m refers to the magnetic quantum number, or projection of angular momentum). Degenerate states (like those in Hydrogen or highly excited Rydberg states) are particularly susceptible to the linear Stark effect. Because it causes a symmetric splitting of levels, it "contributes mainly to broadening" of the spectral line, rather than a net shift of the center of gravity of the multiplet, although individual components are shifted. The energy shift for a given m-sublevel is proportional to the electric field strength, E.

Second, the 'Quadratic Stark effect'. This effect is generally more common for non-hydrogenic atoms or for states that are not nearly degenerate. The energy shift in the quadratic Stark effect is proportional to the square of the electric field strength, E^2. As the asterisk notes, it "Shifts the center of gravity of the multiplet – adds line shift." So, the quadratic Stark effect causes an overall shift of the spectral line, and can also contribute to broadening if the shifts are different for different sublevels or if there's a distribution of field strengths.

In plasmas, radiating atoms experience a fluctuating microfield due to the constantly moving ions and electrons. The Stark effect caused by this microfield is the primary cause of line broadening and shifting for many spectral lines emitted from plasmas. The $n = 1$ in the first bullet refers to the underlying $\frac{1}{R}$ nature of the Coulomb potential creating the fields.

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Continuing our discussion of broadening and shift in plasmas (Stark effect), this slide highlights its 'Diagnostic use' and impact on certain types of lasers.

The first point emphasizes the diagnostic power:

From the analysis of Stark-broadened line profiles, one can make 'Inference of n_e (electron density) and T_e (electron temperature)'. (n_e for electron density, and capital T_e for electron temperature). The extent of Stark broadening, particularly the width of the line, is often strongly dependent on the electron density (n_e) because electrons are typically fast-moving and cause rapid fluctuations in the microfield (impact broadening by electrons), while ions, being slower, contribute more to the quasi-static wings. The shape of the line, including asymmetries and shifts, can also provide information about the ion temperature or the nature of plasma turbulence. Thus, careful measurement and modeling of Stark profiles are standard and powerful techniques for diagnosing plasma conditions in astrophysics, fusion research, industrial plasma processing, and more.

The second point notes the relevance to specific lasers:

'Gas-discharge lasers', such as Helium-Neon (HeNe, H-E-N-E) lasers or Argon ion (Ar^+) lasers, are 'strongly influenced' by Stark broadening. The gain medium in these lasers is a plasma (a gas discharge). Collisions with electrons and ions in the discharge can significantly broaden the atomic transitions responsible for laser action. The slide mentions that this 'broadening can reach GHz-level' (Gigahertz-level). A Gigahertz is 10^9 Hertz. This is a very substantial amount of broadening, often much larger than the natural linewidth and, in some cases, comparable to or even larger than Doppler broadening, especially at higher pressures or electron densities. This broadening affects the gain bandwidth, the number of longitudinal modes that can oscillate, and the overall efficiency of the laser. Understanding and accounting for Stark broadening is therefore crucial in the design and optimization of such lasers. The triple dash indicates the end of this point.

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This slide, titled 'Numerical Examples (Based on Demtröder Ex. 3.4),' provides some concrete values for collisional broadening parameters for a few common systems. These numbers help to give a quantitative feel for the magnitude of these effects.

The first example is the 'Sodium D-line broadening by Argon'. The Sodium D-lines (around $\lambda = 589$ nm, lowercase $\lambda = 589$ nm) are very well-studied. When Sodium atoms are in an Argon buffer gas, collisions with Argon atoms cause broadening and shifting.

The slide gives a pressure broadening coefficient:

$$\frac{d\Delta\nu}{dp} = 0.228\,\text{MHz Pa}^{-1}$$

Here, $\Delta\nu$ (lowercase delta nu) is the frequency width (likely FWHM in Hertz), and p is the pressure of Argon in Pascals. This coefficient tells us how much the linewidth increases for each Pascal of Argon pressure added. For example, at 1000 Pa (which is 0.01 bar, or about 7.5 torr), the broadening would be 228 MHz.

Next, it gives an example of 'Self-broadening (Na-Na)' for the Sodium D-line. This is when Sodium atoms are broadened by collisions with other Sodium atoms (e.g., in a pure Sodium vapor). The broadening is given as approximately $150\,\text{MHz torr}^{-1}$. Torr is a unit of pressure, where 1 atmosphere is 760 torr, and 1 torr is about 133.322 Pa.

Let's compare these. For Argon broadening:

$$0.228\,\text{MHz/Pa} \times 133.322\,\text{Pa/torr} \approx 30.4\,\text{MHz/torr}$$

So, self-broadening by Na (150 MHz/torr) is significantly more efficient (by about a factor of 5) than broadening by Argon (30.4 MHz/torr) for the Sodium D-line. This is often because resonant interactions (like dipole-dipole for Na*-Na, with an R^{-3} potential) can occur in self-broadening, leading to much larger cross sections than the van der Waals (R^{-6}) interactions typical for unlike neutral atoms.

The second general case is for 'Mid-IR vibration-rotation lines', with a typical wavelength of $\lambda \approx 5\,\mu$m (lowercase lambda approximately $5\,\mu$m, mu m). These are molecular transitions.

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This slide continues with numerical examples of collisional broadening.

Following up on the 'Mid-IR vibration-rotation lines ($\lambda \approx 5\,\mu$m)', the slide provides a typical pressure broadening coefficient for these molecular transitions: $\frac{d(\delta\nu)}{dp}$ is approximately 2 to $5\,\text{MHz torr}^{-1}$ (approximately 2 to $5\,\text{MHz torr}^{-1}$).

This is the rate at which the linewidth ($\delta\nu$, likely FWHM in frequency units) increases with pressure (p in torr).

This range (2–$5\,\text{MHz torr}^{-1}$) is common for many small molecules broadened by air (Nitrogen or Oxygen) or by themselves.

An important consequence is then stated: "At 1 atmosphere pressure, the pressure width is approximately 1 GHz, which is typically greater than the Doppler width" for these molecules at room temperature.

Let's check this: 1 atmosphere is 760 torr. If the broadening coefficient is, say, an average of $3.5\,\text{MHz torr}^{-1}$, then at 760 torr, the pressure broadening would be $3.5\,\text{MHz torr}^{-1} \times 760$ torr, which equals 2660 MHz, or 2.66 GHz.

So, indeed, the pressure-broadened width is on the order of a Gigahertz or more.

The Doppler width for a molecule with mass around 30 atomic mass units at $5\,\mu$m (which is 60 THz frequency) and room temperature (say 300 K) is typically a few hundred Megahertz.

For example, for CO2 (mass 44 amu) at $4.3\,\mu$m, the Doppler width is about 60 MHz.

For H2O (mass 18 amu) at $5\,\mu$m, it would be larger, perhaps around 150–200 MHz.

Thus, at atmospheric pressure, pressure broadening often dominates over Doppler broadening for these mid-IR transitions.

This is crucial for atmospheric spectroscopy and for the design of mid-IR gas lasers.

The third example is the "Helium-Neon (HeNe) laser red line ($\lambda = 633$ nm) in discharge".

Here, two values are given, possibly representing different contributions or different ways of expressing the broadening:

$\delta\nu = 150$ MHz torr^{-1}.

$\Delta\nu = 20$ MHz torr^{-1}.

The 150 MHz torr^{-1} is a substantial broadening coefficient. In a typical HeNe laser tube operating with a few torr of total gas pressure, this collisional broadening would contribute significantly to the overall gain profile width, which is typically around 1.5 GHz (largely Doppler broadened for Neon at 633 nm).

Finally, for an "Argon-ion laser plasma":

$\delta\nu \approx 1.5$ GHz torr^{-1}.

This is a very large broadening coefficient, reflecting the harsh plasma environment with high electron and ion densities and temperatures within the Argon-ion laser discharge.

Since Argon-ion lasers operate at pressures of a fraction of a torr to a few torr, the total collisional broadening due to Stark effects and other plasma interactions can be many Gigahertz.

This wide gain profile is what allows Argon-ion lasers to lase on multiple longitudinal modes simultaneously or to be mode-locked for short pulse generation.

The triple dash signifies the end of these examples.

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We now encounter a fascinating and somewhat counter-intuitive phenomenon: "Collisional (Dicke) Narrowing – Concept". So far, we've discussed how collisions broaden spectral lines. But under certain conditions, collisions can actually lead to a *narrowing* of the line.

The first point states when this occurs: "Occurs when the mean free path, Λ (capital Greek letter Lambda), of the radiating atom is less than the transition wavelength, λ (lowercase Greek letter lambda)." Or more precisely, when it's less than $\frac{\lambda}{2\pi}$. So, $\Lambda < \frac{\lambda}{2\pi}$. The mean free path Λ is the average distance an atom travels between successive velocity-changing collisions. If this distance is smaller than roughly the wavelength of the radiation it's trying to emit or absorb, something interesting happens.

The italicized statement explains the mechanism: "Frequent velocity-changing collisions randomize Doppler shifts, leading to a net spectral narrowing." Let's unpack this. Doppler broadening arises because atoms moving towards the observer emit/absorb at a higher frequency, and atoms moving away emit/absorb at a lower frequency. If an atom's velocity is constant during the emission/absorption process, it contributes to a specific point in the Doppler profile.

However, if the atom undergoes many velocity-changing collisions *during the time it takes to radiate (or during the coherence time of the radiation-matter interaction)*, and if these collisions occur so frequently that the atom doesn't travel a significant fraction of a wavelength with a constant velocity, then its effective Doppler shift gets averaged out. The atom doesn't have a well-defined, persistent Doppler shift anymore. Instead, it diffuses in space, and its average velocity component along the line of sight might be much smaller than its instantaneous thermal velocity. This "motional averaging" of the Doppler effect results in a narrowing of the Doppler-broadened line. This is Dicke narrowing, named after Robert H. Dicke who first predicted it.

A "Condition" for observing Dicke narrowing is that the "Doppler width must be larger than the collisional (pressure) broadening width". If pressure broadening (from dephasing or quenching) is already dominant, then adding more collisions will just broaden the line further via those mechanisms. Dicke narrowing is a phenomenon that primarily affects the Doppler contribution to the linewidth.

It is "Observed primarily in microwave and IR rotational-vibrational lines". This is because for these transitions, the wavelengths λ are longer (e.g., millimeters to centimeters for microwave, micrometers for IR). Also, Doppler widths can be substantial. The condition $\Lambda < \frac{\lambda}{2\pi}$ is more easily met in these regimes, especially at moderate to high pressures where Λ becomes small. It's less common in the visible or UV where λ is much shorter, making the mean free path requirement more stringent.

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This slide provides a graphical representation of 'Collisional (Dicke) Narrowing – Concept'. The graph is titled 'Linewidth vs. Pressure: Dicke Narrowing & Pressure Broadening'.

Let's analyze the graph: The vertical axis is "Linewidth ($\Delta\nu$) [arb. units]", ranging from 0 to above 83, say 100 arbitrary units. The horizontal axis is "Pressure (P) [arb. units]", ranging from 0 to 10.

The blue curve shows the total observed linewidth as a function of pressure. At very low pressures (P approaching 0), the linewidth is high (around 90 units). This corresponds to the regime where Doppler broadening is dominant, and the mean free path Λ is large. As pressure initially increases, the curve shows the linewidth decreasing. This is the 'Dicke Narrowing' regime, as labeled. An arrow points downwards along this part of the curve, from high linewidth at low pressure to a minimum. As pressure increases, Λ decreases. When Λ becomes comparable to or less than $\lambda/(2\pi)$, the velocity-changing collisions start to average out the Doppler shifts, and the Doppler contribution to the linewidth shrinks.

However, this narrowing doesn't continue indefinitely. As pressure increases further, the contribution from collisional (pressure) broadening, which is proportional to pressure, starts to become significant and eventually dominant. The graph shows that the linewidth reaches a minimum value, labeled "$\Delta\nu_{\text{min}}$" (capital Delta nu subscript m-i-n), which is about 50 units, at a specific pressure labeled "P_{min}" (capital P subscript m-i-n), around 2.5 units. This point is marked with a red dot and labeled as the 'Dicke Minimum'.

For pressures greater than P_{min}, the linewidth starts to increase again, approximately linearly with pressure. This region is labeled "Pressure Broadening", with an arrow pointing upwards along this part of the curve. Here, the usual collisional broadening mechanisms (lifetime reduction, phase perturbation) take over and cause the line to widen.

So, the overall behavior is a competition: at low pressures, increasing collisions leads to Dicke narrowing. At high pressures, increasing collisions leads to pressure broadening. In between, there's a minimum linewidth. The observation of this characteristic "V-shape" or "U-shape" in a plot of linewidth versus pressure is the hallmark of Dicke narrowing. The extent of the initial drop and the position of the minimum depend on the relative magnitudes of the Doppler width, the pressure broadening coefficient, and the velocity-changing collision frequency.

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This slide provides a specific experimental example: "Dicke Narrowing – Water Vapor Example".

The first point identifies the system: "H two O rotational line at $\tilde{\nu} = 1871\,\text{cm}^{-1}$ ($\lambda = 5.34\,\mu\text{m}$)." (H_2O rotational line at $\tilde{\nu} = 1871\,\text{cm}^{-1}$, which corresponds to a wavelength $\lambda = 5.34\,\mu\text{m}$). This is a specific rotational transition in the water molecule, occurring in the mid-infrared region.

The second point describes the "Experimental trend observed with Argon (Ar) and Xenon (Xe) as perturber gases": An asterisk indicates that the "Linewidth decreases up to pressures of $100–150$ torr". This is the direct observation of Dicke narrowing. As the pressure of Ar or Xe is increased from low values up to around $100–150$ torr, the H_2O spectral line gets narrower. Another asterisk states that the "Minimum width" (the Dicke minimum) is observed "when the mean free path Λ is approximately equal to the transition wavelength λ" ($\Lambda \approx \lambda$). Or more precisely, $\frac{\lambda}{2\pi}$. A third asterisk notes: "Beyond that pressure (i.e., beyond $100–150$ torr), normal pressure broadening dominates", and the linewidth starts to increase with pressure, as shown in the general graph on the previous slide.

The final point highlights a subtle but important difference between using Argon and Xenon as perturbers: "The heavier Xenon (Xe) perturber, which has a larger collision cross section σ (lowercase sigma for velocity-changing collisions) and thus leads to a shorter mean free path Λ at a given pressure, shifts the Dicke minimum to lower pressures relative to Argon (Ar)." Let's break this down. Xenon is heavier and generally larger than Argon. This means the collision cross section (σ) for H_2O-Xe velocity-changing collisions is likely larger than for H_2 O-Ar collisions. A larger σ means a shorter mean free path Λ (since Λ is inversely proportional to $N\sigma$, where N is number density, and N is proportional to P). Because Λ becomes small more quickly with pressure for Xe, the condition for optimal Dicke narrowing ($\Lambda \sim \frac{\lambda}{2\pi}$) and the subsequent dominance of pressure broadening will occur at lower total pressures when Xe is the perturber compared to when Ar is the perturber. So, the $P_{\min}$ in the Dicke profile will be at a lower pressure for Xe. This is a nice example of how the identity of the collision partner affects the details of Dicke narrowing.

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We now encounter another type of narrowing phenomenon, distinct from Dicke narrowing, called "Diffusion-Limited Narrowing in Long-Lived States". This is particularly relevant for transitions involving metastable states or ground states.

The first point sets the stage: "For metastable or ground-state transitions:" An asterisk elaborates: "The Natural lifetime of these states can be very long, on the order of milliseconds (ms) or even longer." For a ground state, the lifetime is effectively infinite if not for collisions or other interactions. For metastable states, radiative decay is forbidden or highly suppressed, leading to long lifetimes.

Another asterisk notes that in such cases, if one is doing spectroscopy with a spatially confined laser beam (as is almost always the case), the "Transit-time out of the laser beam becomes a limiting factor" for the observed linewidth. If an atom only interacts with the laser field for the short time it takes to fly through the beam, this finite interaction time leads to broadening, known as transit-time broadening. This can be much larger than the natural linewidth for long-lived states, effectively becoming the dominant homogeneous broadening mechanism at low pressures.

The crucial idea for narrowing is in the second main bullet: "Adding an inert buffer gas slows diffusion of the atoms of interest." The buffer gas atoms collide with the spectroscopically active atoms, and these collisions impede their free flight. Instead of flying straight out of the laser beam, the active atoms undergo a random walk, a diffusive motion. This significantly "increases the effective interaction time" with the laser field, as the atoms are confined to the beam volume for a longer period due to the frequent, randomizing collisions with the buffer gas.

The consequence is that this increased interaction time "reduces the homogeneous width" component that was previously limited by transit time. So, adding a buffer gas can *narrow* the line by reducing transit-time broadening. This is diffusion-limited narrowing or sometimes called "collisionally aided narrowing of transit time broadening."

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This slide continues the discussion on diffusion-limited narrowing.

The first point states: 'A pressure region exists where this narrowing (by diffusion delay) competes with and surpasses pressure broadening.' This sounds similar to the Dicke narrowing scenario where a minimum linewidth is observed, but the mechanisms are different. Here, at very low buffer gas pressures, transit-time broadening (due to atoms quickly leaving the laser beam) might be the dominant contribution to the observed linewidth. As buffer gas pressure is initially increased, the diffusion of atoms slows down, they stay in the beam longer, and transit-time broadening decreases, leading to a net narrowing of the spectral line. However, as the buffer gas pressure is increased further, the conventional pressure broadening (due to dephasing or quenching collisions with the buffer gas itself) will start to increase and eventually become the dominant factor, causing the linewidth to increase again. So, one might again observe a minimum in the linewidth versus buffer gas pressure curve, but the initial narrowing here is due to suppression of transit-time effects, not averaging of Doppler shifts (though

Dicke narrowing could also be present if conditions for it are also met, i.e., if Doppler broadening was initially significant).

The second point highlights a significant application of this technique: 'This technique is exploited in ultra-high-resolution spectroscopy of alkali D-lines in buffer-gas-filled vapor cells.' Alkali atoms (like Sodium, Rubidium, Cesium) have D-lines that are strong and well-studied. Their ground states are, of course, very long-lived. By placing the alkali vapor in a cell filled with an inert buffer gas (like Argon or Neon) at an appropriate pressure, one can significantly reduce transit-time broadening. This allows for much higher spectral resolution than would be achievable with a low-pressure vapor where atoms quickly fly through the laser beam or collide with the cell walls (wall collisions also limit interaction time). This technique has been crucial for many precision measurements and fundamental studies using alkali atoms, such as in atomic clocks or magnetometry. The triple dash ends this section.

Page 56

This slide provides some 'Key Takeaways for Experimentalists' regarding collisional broadening. These are practical points to keep in mind when designing experiments and analyzing spectroscopic data.

1. 'Always separate shift and broadening contributions; their cross sections are different.'

We've seen that collisional line shifts ($\Delta\omega$) are governed by a shift cross section (σ_s), while collisional line broadening (γ_{col}) is governed by a broadening cross section (σ_b). These two cross sections, σ_s and σ_b, arise from different weightings of the phase shift $\Delta\phi(R_0)$ and are generally not equal. Therefore, one must analyze them independently. For example, plotting both the measured shift and the measured broadening as a function of pressure can provide separate information about the interaction potential. Don't assume that if you know the broadening, you also know the shift, or vice-versa, without a specific model connecting them (though for certain potentials, like $n = 6$ van der Waals, there's a theoretical ratio between them).

2. 'Measure at multiple pressures and temperatures to extract microscopic potentials.'

As we discussed with the temperature dependence method for $V_{\mathrm{i}}(R)$ (slide 22-23), and the pressure dependence for determining broadening/shifting coefficients (which relate to cross sections, and thus to potentials), varying both pressure and temperature systematically is key. Pressure dependence helps isolate collisional effects and determine rate coefficients (the slopes of width/shift vs pressure plots). Temperature dependence probes the Boltzmann factor (for quasi-static analysis of wings) or affects the mean relative velocity $\bar{v}$ (which appears in $N_{\mathrm{B}}\bar{v}\sigma$ expressions) and also the population distribution over states. For specific power-law potentials $\frac{C}{R^n}$, the temperature dependence of the broadening/shifting coefficients can also reveal 'n'. Combining these measurements provides much more robust data for fitting to potential models or extracting potential parameters.

3. 'Beware of non-Lorentzian wings and satellites; fitting only the central peak hides essential physics.'

If your experimental line profile clearly shows asymmetry or satellite features in the wings, fitting the entire line with a simple Lorentzian function will be inadequate. While a Lorentzian might approximate the core, it will miss these crucial details. These non-Lorentzian features, as we've seen, contain rich information about the specifics of the interaction potential, particularly its shape at short range or the presence of extrema in the difference potential. Ignoring them means throwing away valuable physical insight. Use more sophisticated line shape models, such as unified theories or quantum calculations, when the data demand it and when information from the wings is important.

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This slide continues with key takeaways for experimentalists, focusing on specific regimes.

4. 'In plasma or high-pressure regimes, Stark broadening can dwarf all other effects – include Coulomb perturbations in models.'

If you are working with plasmas (ionized gases) or even very high-pressure neutral gases where ionization might become non-negligible or interactions become very strong and short-ranged, the Stark effect due to charged particle collisions can become the dominant line broadening mechanism. Its long-range $1/R$ nature of the underlying Coulomb potential makes it very effective. When modeling spectra from such environments, it's crucial to incorporate the effects of Coulomb interactions (i.e., Stark broadening) into your line shape models. Neglecting it can lead to severe misinterpretation of the plasma conditions or the spectral features. Standard Stark broadening theories (like Griem's) and extensive tabulated calculations exist for many atomic lines and a wide range of plasma conditions (electron densities and temperatures).

The triple dash signifies the end of these takeaways.

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To conclude this chapter on collisional broadening, this slide offers 'Suggested Visual Aids and Further Reading' to help deepen your understanding.

For 'Visual Aids':

* 'Potential-curve diagrams for various A-B pairs.' Seeing more examples of ground state $V_{\mathrm{i}}(R)$ and excited state $V_{\mathrm{k}}(R)$ potential curves for different colliding partners (A and B), and especially the resulting difference potential $\Delta E(R)$, can build intuition about how satellites form or why line shapes become asymmetric.

* 'Phase-perturbation animations illustrating $\Delta\phi(t)$' ($\Delta\phi(t)$, meaning the instantaneous phase evolution, or perhaps $\Delta\phi(R_0)$, the total accumulated phase shift). Visualizing how the phase of an atomic oscillator is perturbed during a collision, especially for different impact parameters, can make the concepts of phase shift theory more tangible.

* 'Satellite-bearing experimental spectra (Cs-Xe, Na-H, etc.).' Looking at more real-world examples of spectra that clearly show satellite features, like the Cesium-Xenon example we saw, or perhaps Sodium-Hydrogen (Na-H) or other alkali-rare gas systems, reinforces the reality and importance of these non-Lorentzian features.

For 'Further Reading', several 'Review articles' or books are suggested:

* 'Griem, "Principles of Plasma Spectroscopy"'. This is a classic and authoritative text by Hans Griem on the spectroscopy of plasmas, with extensive coverage of Stark broadening and other line shape phenomena in plasma environments. (Cambridge University Press).

* An asterisk points to 'Hartmann et al., "Collisional Effects on Molecular Spectra"'. This reference by Jean-Michel Hartmann and colleagues would be excellent for a deeper dive into collisional broadening of molecular lines, likely covering both atomic and molecular perturbers, and advanced line shape theories relevant to molecules. (Elsevier or Wiley are common publishers for such monographs).

* Another asterisk lists 'Griem, "Principles of Plasma Spectroscopy"' again, emphasizing its importance for plasma-related aspects. It's possible this was intended to be two different key works by Griem, or to simply underscore its relevance. For instance, Griem also authored the seminal book "Spectral Line Broadening by Plasmas" (Academic Press, 1974), which is a cornerstone in the field.

These resources will provide much more detail and mathematical rigor than can be covered in a lecture format and are highly recommended for those of you specializing in these areas of spectroscopy.

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This page appears to be a note to the user of these slides, likely from the system generating this lecture. It indicates that the full generated answer is extensive and, for practical reasons related to interface limits, the complete output will be provided separately. It also mentions that a preview of the initial slides is included to confirm that formatting and style requirements have been met. It ends with an instruction to request the "FULL SLIDE DECK" if the entire set is needed. The usual course preparation note is also present.

Page 60:

This page continues the note to the user, reiterating the request to ask for the "FULL SLIDE DECK" due to the size of the complete output. It concludes with the triple dash and the course preparation information. This marks the end of the provided slide material for this lecture segment on collisional broadening.

And that brings us to the end of our discussion on Chapter 3.3, Collisional Broadening of Spectral Lines. I trust this has given you a solid foundation in understanding the various mechanisms by which collisions affect spectral lines, the theoretical frameworks used to describe these effects, and their importance in various applications from precision metrology to plasma diagnostics and laser design. Remember to consult the suggested readings for more in-depth treatments. Thank you.