The following material is made available for anyone who wishes to follow-up on the classroom material.

Appendix II

THE HARMONIC OSCILLATOR AND SPECTROSCOPIC EVENTS.

In spectroscopy one studies how a molecule responds to an incident beam of electromagnetic radiation ("light"). Most commonly this light causes a distortion of the electron cloud of the molecule; this distortion is called polarization. A material that has a large response is easily polarizable and vice-versa. If the polarization is in response to the E-field then we are studying the electric polarizability ($\alpha$); the response to the H-field is the magnetic polarizability ($\chi$)

$$\mu_e = \alpha \cdot E$$  
$$\mu_m = \chi \cdot H$$  

(\mu_m \text{ is also written } m_e)

$\mu$ is the induced moment in each case, with appropriate subscript, and $\alpha$ and $\chi$ are the respective polarizabilities normalized to unit applied field.

The light beam oscillates in time. As a consequence the appropriate polarizability also oscillates in time with the same frequency. Our principal interest is to determine how effectively the material under study reduces the intensity of the light beam, that is, how efficiently does the material of interest consume the energy in the light.

The scenario is as follows: Immediately before the sample is exposed to the light the electron cloud present in each molecule is at rest. Immediately after the beam is turned on, this electron cloud is still at rest but now the electron cloud begins to oscillate rhythmically in sympathy with the incident beam. This movement continues with ever-increasing amplitude until a final amplitude is established. During this transient state there is a net transfer of energy from the light beam to the material. We then reach the steady state in which the average kinetic energy and average potential energy of the electron cloud is constant and the transfer of energy should stop. However, there remains a mechanism to further consume energy. This is "friction", the interaction of the material with its environment (typically the solvent). This friction serves to reduce the amplitude of the oscillation and the material is then able to consume more energy as the light beam tries to return the material to its steady-state, oscillatory, amplitude. The final displacement obtained in the steady-state is thus a balance between the rate at which energy can be "donated" to the material by the light and the rate at which it is consumed by friction.

It so happens that this phenomenon is modelled very well by a system studied in freshman physics. The most common example is a spring of stiffness $k$ suspended from a beam, bearing a mass $m$ and subjected to friction ($B$). (Electrical engineers will be familiar with a related model: a series circuit composed of a resistor, a capacitor, an inductance and an alternating voltage source.)

If the mass is pulled down and then released the spring-mass combination oscillates up-and-down at its natural frequency ($\omega_0$) with an amplitude ($x$; note that we used $A$ in handout #1) which decreases with time because of friction (Fig A2-3, right). This is the transient response; it can be represented by an equation of the general form

$$x(t) = X_0 \cos(\omega_0 t) \exp(-t/\tau) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

where the cosine term describes the oscillations and the exponential term describes the decay ($X_0$ is the amplitude of the displacement when $t=0$. $\tau$ is $= 2m/B$).
The natural frequency decreases with the mass and increases with the stiffness of the spring.

$$\omega_0 = \sqrt{\frac{k}{m}} \quad \text{............................................... (2)}$$
Alternatively one can pull on the mass rhythmically at some frequency ($\omega$) with some force ($F_0$) as described in Fig. 2. After a brief initial period the mass settles down to a constant oscillation with an amplitude and phase which are a function of $\omega$ (Fig 2). The dependence of the amplitude on $\omega$ is called the absorption spectrum and the dependence of phase on $\omega$ is called the dispersion spectrum.

The mass on a spring subjected to friction and a constant driving force has the official title of the Forced Damped Harmonic Oscillator and is described in detail in many introductory physics texts.

![Diagram of a Forced Damped Harmonic Oscillator](image)

Fig. A2-3

Fig 3 summarizes the response of a mass on a spring to either a continuous (left) or brief driving force. As will become clearer the three quantities graphed in Fig 3 (bottom) all contain the same information and, not surprisingly therefore, each can be transformed into the other by an appropriate mathematical manipulation. Most commonly the interconversion of the curves shown in Figs 3 (center & right) is accomplished by the forward and inverse Fourier transforms while Figs 3 (center & left) are interconverted by the Kronig-Kramers (or Hilbert or Bode) transform. Fig 3 (right) is representative of modern experiments in nmr and ir, Fig 3 (center) of most other spectroscopies while Fig 3 (left) is commonly encountered in some specialized measurements of optical activity and magnetic resonance (both nmr and epr). Some understanding of Fourier analysis and transforms is essential for this course and will be discussed in the sections on infra-red, nuclear magnetic resonance, x-ray crystallography and image reconstruction. The Kronig-Kramers transform will not be covered further.

**The Forced Damped Harmonic Oscillator**

(See Berkeley Physics Course. Vol 1 Mechanics, Ch 7, p226 if you need additional details).

When the displacement ($X$) of the mass from its equilibrium position is directly proportional to the magnitude of $F_0$ (i.e. a linear response) the equation of motion for the
displacement of the mass from its equilibrium position is given by eqn 3:

\[ m \cdot \frac{d^2 x}{dt^2} + B \cdot \frac{dx}{dt} + m\omega_0^2 x = F_0 \cos(\omega t) \quad \ldots (3) \]

The first term is the kinetic energy due to the acceleration of the mass, the second term is the friction, the third term is the potential energy (the tension in the spring) and the last term is the driving force. This driving force has a maximum amplitude of \( F_0 \) and a frequency, \( \omega \), which, in general, will be different to \( \omega_0 \).

The full solution to this equation will contain both the transient-state and steady state behavior. We are only interested in the steady-state solution when the response of the spring-mass combination has settled down to a uniform motion. The steady-state dependence of the displacement is

\[ X(t) = X_0 \cos(\omega t - \delta) \quad \ldots (4) \]

which can be verified by back-substitution using identities (5) and (6) below. This solution tells us that the mass always moves at the same frequency (\( \omega \)) as the applied force but its response is delayed by some amount, \( \delta \), the phase-shift. The maximum amplitude of the displacement = \( X_0 \) and the mass moves from \( X_0 \) to -\( X_0 \) as the cosine term varies from +1 to -1. The magnitude of \( X_0 \) is given by

\[ X_0 = \frac{F_0/m}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(B^2/\omega^2/m^2\right)}} \quad \ldots (5) \]

provided

\[ \sin(\delta) = \frac{B\omega/m}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(B^2/\omega^2/m^2\right)}} \quad \ldots (6) \]

and

\[ \cos(\delta) = \frac{(\omega_0^2 - \omega^2)}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(B^2/\omega^2/m^2\right)}} \quad \ldots (7) \]

Thus

\[ \tan(\delta) = \frac{B\omega}{m(\omega_0^2 - \omega^2)} \quad \ldots (8) \]

A very common alternative representation of eqn. 4 is

\[ x(t) = X'\cos(\omega t) + X''\sin(\omega t) \quad \ldots (9) \]

with \( X' = X_0\cos(\delta) \) and \( X'' = X_0\sin(\delta) \). (because \( \cos(a-b) = \cos(a)\cos(b) + \sin(a)\sin(b) \)). Thus the phase-shifted wave (eqn 4) can be represented as a mixture containing some of the original cosine-wave plus some sine-wave (see Fig. 2, middle panel); the smaller the phase-shift the less sine component is required. \( X' \) and \( X'' \) are called the elastic and absorptive amplitudes of the response (the elastic response is also called the dispersive response- because the value of the amplitude changes with frequency, even if \( B \) is zero). Note also that \( X''/X' = \tan(\delta) \). (The notation of using singly and doubly primed quantities to signify the elastic and absorptive components is standard).
Sketches of $X_0$ and $\delta$ for two values of the friction ($B$) are shown in Fig 4. Note that the left-hand figure has both curves scaled to the same height. In reality it is the total area that should be conserved.

![Fig. AII-4](image)

(In Fig 4 $Q$ is a parameter called the Quality Factor which measures how much energy the system can store: $Q$ is proportional to $1/B$)

Each graph in Fig 4 can be divided into 3 domains:

1) $\omega \ll \omega_0$. (Let $\omega \to 0$). $X_0$ approaches $F_0/(m\omega_0^2)$ and does not go to zero at zero frequency (though the power absorbed does (see below)). $\tan(\delta) = 0$ and $X(t)$ tracks $F(t)$ perfectly. It is $k$, the **stiffness** of the spring, that controls the motion.

2) $\omega = \omega_0$. If $B$ were zero the oscillations of the spring would get larger-and-larger and the spring would eventually self-destruct. Because friction is not zero $X_0$ approaches $F_0/(B\omega_0)$. Thus $X_0$ is proportional to $1/B$ and it is **friction** that is the important parameter in this regime. $\tan(\delta) = \infty$, $\delta = \pi/2$ so $X(t)$ lags $F(t)$ by 90°. The large response at $\omega = \omega_0$ is called **resonance**.

3) $\omega \gg \omega_0$. (Let $\omega \to \infty$). $X_0$ goes to 0, $\tan(\delta)$ goes to zero and $\delta = \pi$; thus $X(t)$ lags $F(t)$ by 180°. Because of **inertia**, the mass and force are going in opposite directions.

In spectroscopy we are interested in the net power transferred **from** the light **to** the material (i.e. the amount of light energy absorbed). The power input to the oscillating mass by the applied force is the time rate of change of the work done; as work = force x distance, power = force x velocity:

\[ P = \frac{dW}{dt} = \frac{FdX}{dt} \]

\[ X(t) = X_0 \cos(\omega t - \delta) \]
\[
\frac{dX}{dt} = -X_0 \omega \sin(\omega t - \delta)
\]

\[
P = -F_0 X_0 \omega \cos(\omega t) \sin(\omega t - \delta)
\]

As \(X\) is oscillating about its mean position we must calculate the average or net power which is accomplished by averaging over the time dependent parts (enclosed within <>).

\[
P_{\text{av}} = -F_0 X_0 \omega \langle \cos(\omega t) \sin(\omega t - \delta) \rangle
\]

Using

1) \(\sin(a-b) = \sin(a)\cos(b) - \cos(a)\sin(b)\)
2) Average of \(\sin(a)\cos(a)\) over 1 cycle = 0
3) Average of \(\cos^2(a)\) over 1 cycle = 1/2

the expression for average power absorbed is:

\[
P_{\text{av}} = 1/2 \omega X_0 F_0 \sin(\delta) = 1/2 \omega X'' F_0 \quad \text{...................... (10)}
\]

Note that the power absorbed is proportional to \(X''\), the out-of-phase displacement (see below).

Substituting the definitions of \(X_0\) (eq 5) and \(\sin(\delta)\) (eq 6)

\[
P_{\text{av}} = \frac{B \omega^2 F_0^2}{2\{m^2(\omega_0^2 - \omega^2) + B^2 \omega^2\}}
\]

This expression is

1) maximum when \(\omega = \omega_0\) (with a value of \(F_0^2/2B\))
2) symmetric about \(\omega_0\)
3) is zero at zero and infinite \(\omega\) but approaches zero slowly at both low and high \(\omega\).
   i.e. it tails to zero very slowly; this behavior should be contrasted with the more familiar Gaussian lineshape which is fatter in the middle but falls to zero more rapidly.
4) reduces to the expression for the classical spectral absorption lineshape, the Lorentz lineshape which is exhibited by "pure" spectral lines. This is achieved by restricting attention to the domain where \(\omega = \omega_0\), whereupon the expression becomes very sensitive to \(\omega - \omega_0\), and setting \(\omega \to \omega_0\) in the numerator and on the left part of the denominator. Then, apart from a numeric constant, the expression simplifies to something like

\[
P_{\text{av}} = \frac{B^2}{(\omega_0 - \omega)^2 + B^2}
\]

with the value 1 when \(\omega = \omega_0\). A quick way to distinguish gaussian and lorentzian curves is to measure the full-width at both 75% and 25% of maximum height. These widths are in the ratio 2.2 and 3.0 for gaussian and lorentzian curves, respectively.
From equation 11 we can see that the linewidth of the process is controlled by the friction, B. The argument is as follows: A measure of the spectral linewidth is the value of $\omega$ required to reduce P from its maximum value, $P_{\text{max}}$, to $P_{\text{max}}/2$. In equation 11 this occurs when $m^2(\omega_0^2 - \omega^2) = B^2\omega^2$. However, as B gets larger this equality requires having a correspondingly larger value for $\omega_0^2 - \omega^2$, which requires a larger value for $\omega$. Thus a large B reduces the value of $P_{\text{max}}$ (#1 above) and leads to a fatter absorption envelope. Conversely a small B increases the value of $P_{\text{max}}$ and leads to a skinnier absorption envelope. Note that the conserved quantity is the total area under the curve.

The spectroscopic equivalent to B is the **lifetime of the excited state** and it's a trivial matter to compute the lifetime directly from the width of the absorption envelope (this lifetime is denoted $T_1$ in epr and nmr).

As it is the friction in the spring that is the mechanism for the dissipation of energy in the steady-state and because the friction is proportional to velocity (see eq 3) then the net transfer of energy from the light-beam to the oscillator is optimal if the oscillation of $F_0$ and the velocity of the spring-mass combination are synchronized (see definitions last page). As F varies as $\cos(\omega t)$ the velocity must also vary as $\cos(\omega t)$ so that the displacement must vary as $\sin(\omega t)$ that is, the out-of-phase component of the displacement determines how much power is absorbed.

Why match F with the velocity? Well! Have you ever pushed anyone on a playground swing? You are most effective if you push the chair when $X = 0$ and it is leaving you; the push and the velocity are in phase and there is the most favorable transfer of energy. (If you don't believe me try pushing the swing at $X=0$ as it approaches you. The results of the impact will be memorable.) When pushing the swing at $X = X_{\text{max}}$ it doesn't matter too much if the swing is coming or going.

In a nutshell: The response of an oscillator to a sinusoidal periodic force is periodic at the same frequency but possibly delayed by the phase-shift, $\delta$. The phase shift can also be quantified by "resolving" the response into a component in-phase with the applied force and a component $90^\circ$ out-of-phase with the applied force, with the proportion of the latter increasing as $\delta$ increases. The out-of-phase component (the sine in our examples) quantifies the energy absorbed from the force.

**Some Nomenclature**

Because sums of sines and cosines are often analyzed via ordered pairs called complex numbers the in-phase and out-of-phase components are often referred to as the REAL and IMAGINARY components of the response. If you are not comfortable with this notation it is just as accurate and a lot less confusing to stay with the in-phase and out-of-phase components. (The analysis in this handout used real numbers; it is actually easier to use complex algebra.) For a co-sinusoidal driving force the equivalent notations are:

<table>
<thead>
<tr>
<th>In-Phase</th>
<th>Out-of-Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cos$</td>
<td>$\sin$</td>
</tr>
<tr>
<td>Real</td>
<td>Imaginary</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Absorption</td>
</tr>
</tbody>
</table>
The electric in-phase polarizability, the dispersion, is related to the refractive index ($n$):

$$n^2 = 1 + \frac{4N\pi\rho\alpha_{in}}{M}$$

The electric out-of-phase polarizability, is related to the molar absorption coefficient:

$$\varepsilon = \frac{4\pi N.\omega_\alpha_{out}}{2303c}$$

The intensity of scattered light, Rayleigh—which is of value in light-scattering studies on the size and shape of macromolecules is:

$$I_{90} = \frac{I_0 16\pi^4\omega^4\alpha_{out}}{r^2c^4}.$$ 

$N$ = Avogadro's number, $c$ = velocity of light, $\rho$ and $M$ are the density and molecular weight of the sample, $r$ is distance from sample to observer, $I_0$ is the intensity of the incident beam and $I_{90}$ the intensity of the scattered beam observed at $90^\circ$ to the direction of incidence.