



The Quantum Theory of
Atoms and Molecules:

Electrostatics and Vibrations

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Electrostatics – Coulomb's law

A fundamental property of electrons and protons is charge. Charged particles are either positively or negatively charged, and experiments show that like charges repel whilst opposite charges attract. It is these electrostatic interactions that are responsible for the existence of molecules, and their chemical and thermodynamic properties.

Most fundamental particles possess an electrical charge

e.g. proton, q = 1.602189×10^{-19} coulomb = e
 electron, q = $-1.602189 \times 10^{-19}$ coulomb = $-e$
 neutron, q = 0.0 coulomb

Macroscopic particles can also have a charge which must be a multiple of the elementary charge, e .

Two charges interact Ψ force, given quantitatively by Coulomb's law.

$$F = \frac{1}{4\pi\epsilon} \left(\frac{q_1 q_2}{r^2} \right)$$

Coulomb's law continued

The magnitude of the force between the particles is dependent on the medium in which the charges are situated, and this is taken into account by the factor ϵ which is known as the *permittivity* of the medium.

The permittivity of a medium is $\epsilon = \epsilon_r \epsilon_0$ where ϵ_0 is a fundamental constant known as the *vacuum permittivity* and ϵ_r is the relative permittivity of the medium. ϵ_0 has the value $8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$. $\epsilon_r > 1$ and so the interaction potential in the medium is reduced from that in a vacuum.

Molecule	CCl_4	C_6H_6	$\text{C}_2\text{H}_5\text{OH}$	CH_3OH	H_2O
ϵ_r	2.2	2.3	24.3	32.6	78.5

A consequence of the reduced ionic interaction is the wide variation in the rates of ionic reactions in solution with different solvents.

Electric field

The influence of electrostatic forces is described in terms of an *electric field*. The electric field strength, \mathbf{E} , at a particular point in space is defined as the force exerted per unit charge on a positive test charge located at that point. The force experienced by a test charge q is $\mathbf{F} = q\mathbf{E}$, and so the electric field \mathbf{E} is a vector that is parallel to the force \mathbf{F} .

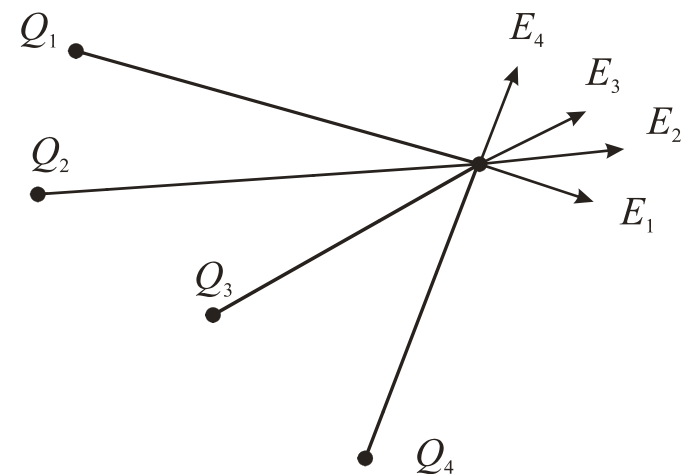
From Coulomb's law, the electric field at a position \mathbf{r} away from an isolated charge q_1 located at the origin is

$$\mathbf{E} = \frac{q_1}{4\pi\epsilon_0 r^2} \frac{\mathbf{r}}{r}$$

For several charges, the fields at a point are additive.

$$\mathbf{E} = \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 + \text{etc}$$

$$\text{Total force } \mathbf{F} = Q\mathbf{E}.$$



Electrostatic energy

Intrinsically linked to the electrostatic force is the electrostatic potential V . The electrostatic potential at a point in an electric field is defined as the work done in bringing a unit positive charge from infinity to that point. Since

$$F = -\left(\frac{\partial V}{\partial r}\right) \quad \Rightarrow \quad V = -\int_{\infty}^r F \cdot d\mathbf{r} = \frac{q_1}{4\pi\epsilon_0 r}$$

and so the interaction potential energy, U , of a charge q_2 with charge q_1 is

$$U = q_2 V = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

U is a *scalar* quantity \Rightarrow the net electrostatic potential due to an array of charges is simply the *algebraic sum* of their individual contributions.

NB: The Coulomb interaction is *long range* and continues to exert its influence at distances that are far beyond those of any other intermolecular force. e.g. r^{-6} for Van der Waals' interaction between atoms.

Applications

(a) Can be used to describe the potential energy of any assembly of static charges

$$V = \sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_0 R_{ij}}$$

(b) Important for describing the energy of ionic compounds, e.g. ionic crystals.

(c) In atoms/molecules - can be used to describe the interactions between nuclei and electrons

$$V = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R_{12}} + \dots\dots\dots(\text{nuclear} - \text{nuclear})$$
$$- \frac{Z_1 e^2}{4\pi\epsilon_0 R_{1i}} + \dots\dots\dots(\text{electron} - \text{nuclear})$$
$$+ \frac{e^2}{4\pi\epsilon_0 R_{ij}} + \dots\dots\dots(\text{electron} - \text{electron})$$

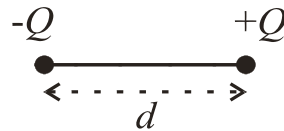
(d) Useful in quantum mechanics when describing the energies of atoms and molecules.

The electric dipole

In molecules, the charge distribution is usually not “uniform”; the centre (of gravity) of positive charge does not coincide with the centre of negative charge.

This charge asymmetry can be represented by an *electric dipole*.

The simplest electric dipole consists of two equal and opposite charges ($\pm Q$) separated by a distance d .



The value of the electric dipole moment is given by $\mu = Qd$.

(The correct SI units are C m. However the dipole moment is frequently quoted in Debye units. 1 Debye (D) = 3.336×10^{-30} C m).

Molecule	H ₂	HF	HCl	CO
μ /Debye	0.00	1.826	1.109	0.112

N.B. the dipole moment is a **vector** quantity because it has magnitude **and** direction (in the direction from negative to positive charge).

Electric dipoles continued

Within larger molecules, to a good approximation, we can consider the overall dipole moment as the *vector sum* of the dipole moments associated with the individual bonds within the molecule.

For example, the dipole moment of benzene is zero (by symmetry). However that of chlorobenzene takes the value of 1.45 Debye (this corresponds to the difference of the C-Cl and C-H moments). We can then estimate the dipole moments of the dichlorobenzenes by straight vector addition of bond moments. Although not quantitative, the results are reasonable.

	Ortho	Meta	Para
μ_{calc}	$2 \mu_{\text{PhCl}} \cos 30^\circ$ = 2.51 Debye	$2 \mu_{\text{PhCl}} \cos 60^\circ$ = 1.45 Debye	$2 \mu_{\text{PhCl}} \cos 90^\circ$ = 0.00 Debye
μ_{obs}	2.27 Debye	1.38 Debye	0.00 Debye

Electric dipole in an electric field

Consider a dipole in a uniform electric field. Each end of the dipole experiences *equal and opposite* force \Rightarrow net force = 0.

Dipole does experience a torque, Γ , which will rotate dipole so that it is aligned with E :

$$\Gamma = \mu \times E$$

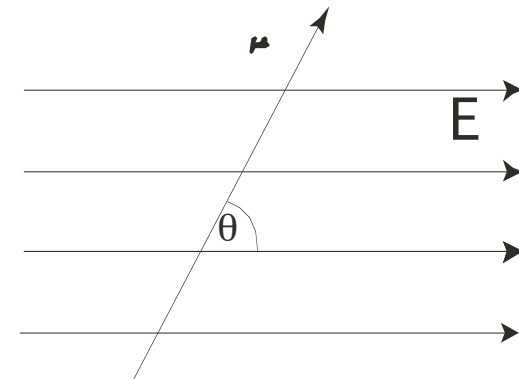
The work done, W , in rotating the dipole from angle θ_1 to θ_2 is:

$$W = - \int_{\theta_1}^{\theta_2} \mu E \sin \theta \, d\theta = \mu E (\cos \theta_2 - \cos \theta_1)$$

The work done is the change in electrical PE of the dipole in the field (i.e. $W = \Delta U = U_2 - U_1$), and so the PE of a dipole in an electric field is given by

$$U = -\mu E \cos \theta = -\mu \cdot E$$

State of lowest PE has $\theta = 0$ and the dipole lies **along** the electric field direction.



Electric field and potential due to a dipole

The total potential at a point A is given by the^(a) sum of the potentials due to each charge in the dipole:

$$V = \frac{q}{4\pi\epsilon_0} \left(\frac{1}{r+d} - \frac{1}{r-d} \right)$$



Assuming that $2d \ll r$ then

$$V \approx \frac{q}{4\pi\epsilon_0} \left(\frac{-2d}{r^2} \right) = - \frac{\mu}{4\pi\epsilon_0 r^2}$$

The interaction PE, U , for an ion of charge Q with a dipole is then

$$U = - \frac{\mu Q}{4\pi\epsilon_0 r^2}$$

Very similar to the Coulomb potential between two ions except that it declines more rapidly with $r \Rightarrow$ as ion moves further away from the dipole the two charges of the dipole 'merge' (from the point of view of the ion) and produce a neutral entity.

An atom in an electric field - polarisability

An electric field \mathbf{E} can induce a dipole moment, $\boldsymbol{\mu}_{ind}$, in an atom or a non-polar molecule by interacting with and distorting the electron distribution in the atom or molecule.

The induced dipole moment is directly proportional to E and the proportionality constant is called the *polarisability* α :

$$\boldsymbol{\mu}_{ind} = \alpha \mathbf{E} \quad \xrightarrow{\mathbf{E}}$$

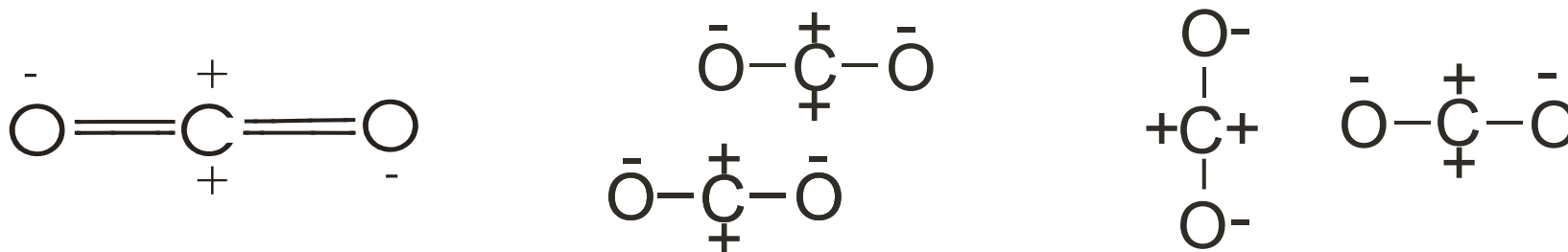

α related to how strongly the nuclear charges interact with the electron distribution as this governs the degree to which the electron distribution can be distorted by an applied field
 \Rightarrow light atoms / molecules with few electrons have low polarisabilities whereas large systems with many electrons, where the electron distribution is more diffuse, show large polarisabilities.

Atom / Molecule	He	Ar	Xe	N ₂ (\parallel)	N ₂ (\perp)
$\alpha' = (\alpha/4\pi\epsilon_0) / 10^{-30} \text{ m}^3$	0.206	1.642	4.02	1.972	1.276

Higher multipole moments

Many molecules with no dipole moments have charge distributions that are not spherically symmetric and as a consequence they create a non-zero electric field e.g. H_2 , N_2 , O_2 , CO_2 and C_2H_2 .

Consider CO_2 : Each $\text{C}=\text{O}$ bond possesses an electric dipole moment, whose values cancel in the overall molecule. However since these dipoles are displaced relative to each other, the fields due to these dipoles do not cancel \Rightarrow charge distribution can be described by a *quadrupole moment*, Θ , and can be represented as two displaced dipoles.



Field due to a quadrupole falls as R^{-4} (compared with R^{-2} for a charge and R^{-3} for a dipole). More symmetric molecules like methane have both a zero dipole moment and a zero quadrupole moment. The first non-zero multipole moment is the *octupole moment* (and its field drops off as R^{-5}) – see **States of Matter course in Trinity Term**.

Molecular charge distribution + spectroscopy

The total charge, dipole moment, quadrupole moment, and the polarisability often provide the best descriptions of the charge distribution* (charges are not static) in a molecule. *(charges are not static points and we must speak of a charge distribution)

For example, in the case of a *linear molecule* the electric potential $\phi(r)$ due to the charge distribution is:

$$\phi(r) = \frac{Aq}{r} + \frac{B\mu}{r^2} + \frac{C\Theta}{r^3} + \dots \quad A, B, C \text{ are constants}$$

It is the interaction between the charge distribution and the electric field associated with electromagnetic radiation that is the physical basis of many spectroscopies.

For example: In Uv/Vis and IR spectroscopies the electric field of the radiation interacts with a *changing dipole moment* in the molecule and causes the electronic or vibrational state (or both) of the molecule to be changes from some initial states to a final state.

Waves and Vibrations

One of the most common forms of mechanical behaviour is that of **periodic motion**; that is to say, an action that is repeated at regular intervals. This includes:

- i. swinging of a pendulum,
- ii. ripples on a pond,
- iii. the vibrational modes of molecules
- iv. the wave-like properties of electromagnetic radiation.

The best illustration of oscillatory characteristics is given by *simple harmonic motion* (**SHM**), which is often used as an idealised model to analyse real-life situations.....

Simple harmonic motion (revision)

An object in stable equilibrium moves back towards its 'resting position' if it is nudged away from it. If restoring force, F , is proportional to the displacement from equilibrium, x , then the resultant motion is said to be *simple harmonic*. i.e.

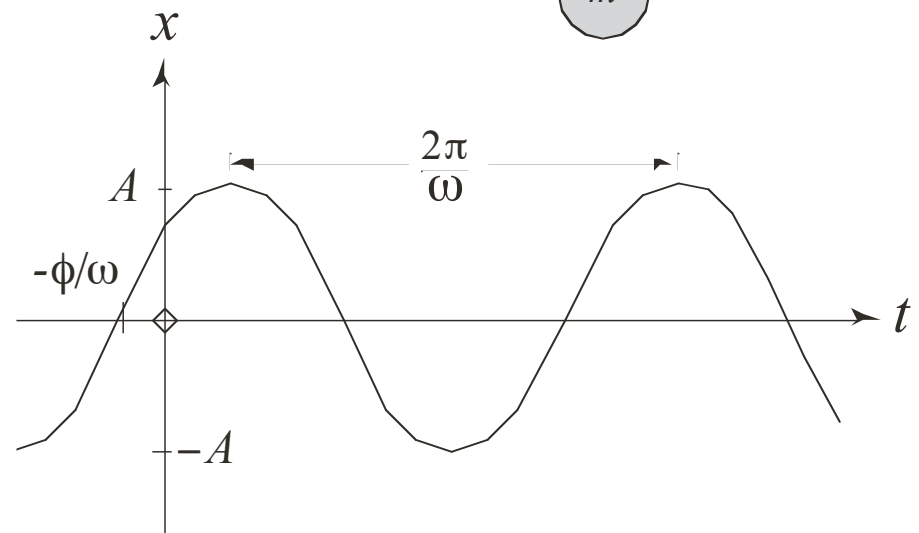
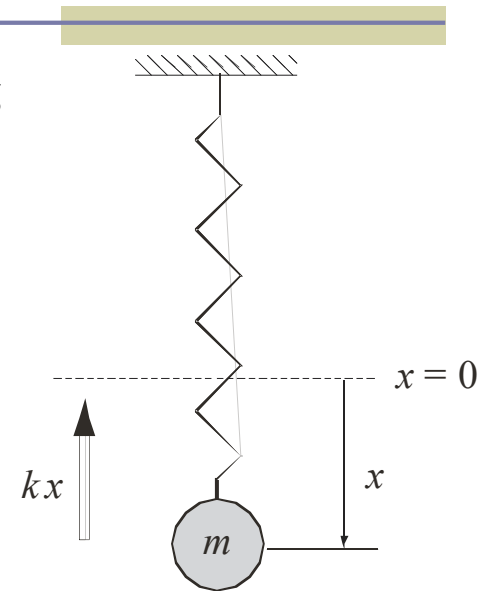
$$F = -k x$$

where k is a (positive) constant having units Nm^{-1} .

Newton's 2nd law:
$$\frac{d^2 x}{dt^2} = -\frac{k}{m} x$$

which has the solution: $x = A \sin(\omega t + \phi)$

where $\omega^2 = k/m$; A and ϕ are constants that are determined by two boundary conditions, such as the values of x and dx/dt at $t = 0$.



SHM continued

- The periodicity of SHM is enshrined in the sine term, which repeats itself every $2\pi/\omega$ seconds (with ω given in rad s^{-1}).
- The maximum displacement from equilibrium is $x = \pm A$, with A referred to as the *amplitude* of the oscillation.
- Any temporal offset with respect to $x = A\sin(\omega t)$, which has x increasing as it passes through the origin ($x = 0, t = 0$), is encapsulated in the *phase* constant ϕ by $x = A\sin(\omega t + \phi)$.
- The total energy (KE+PE) is **conserved**:

$$\frac{1}{2}m\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}kx^2 = \frac{A^2}{2}\left[\omega^2 m \cos^2(\omega t + \phi) + k \sin^2(\omega t + \phi)\right] = \frac{1}{2}A^2\omega^2 m$$

since $\omega^2 = k/m$ and $\sin^2\theta + \cos^2\theta = 1$. While the energy continually interchanges between kinetic and potential their sum is *independent* of time.

Damped oscillations

The oscillations represented by $x(t) = A \sin \omega t$ are executed indefinitely once they are initiated because there is no mechanism for losing energy in the system.

The amplitude of the oscillations in a real (e.g. pendulum-like) system diminishes \Rightarrow modelled by introducing a dissipative term proportional to the speed, dx/dt , into equation on motion:

$$\frac{d^2 x}{dt^2} = -\omega^2 x - 2q \frac{dx}{dt}$$

(factor of 2 is included to simplify the subsequent algebra, and $q > 0$)

With trial solution $x = \alpha e^{pt}$, the *auxiliary equation* becomes $p^2 + 2qp + \omega^2 = 0$ and has the complex roots $p = -q \pm (q^2 - \omega^2)^{1/2}$. Hence, the general solution is:

$$x = e^{-qt} \left[\alpha e^{+t\sqrt{q^2 - \omega^2}} + \beta e^{-t\sqrt{q^2 - \omega^2}} \right]$$

Damped oscillations - solutions

$$x = e^{-qt} \left[\alpha e^{+t\sqrt{q^2 - \omega^2}} + \beta e^{-t\sqrt{q^2 - \omega^2}} \right]$$

1. When $0 < q < \omega$, we obtain *damped* SHM:

$$x = [\alpha e^{i\omega_0 t} + \beta e^{-i\omega_0 t}] e^{-qt} = A e^{-qt} \sin(\omega_0 t + \phi)$$

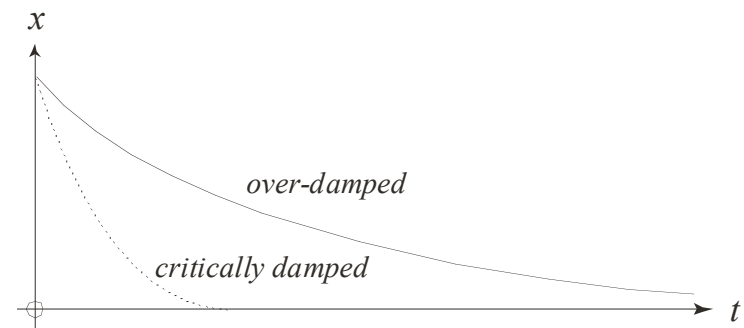
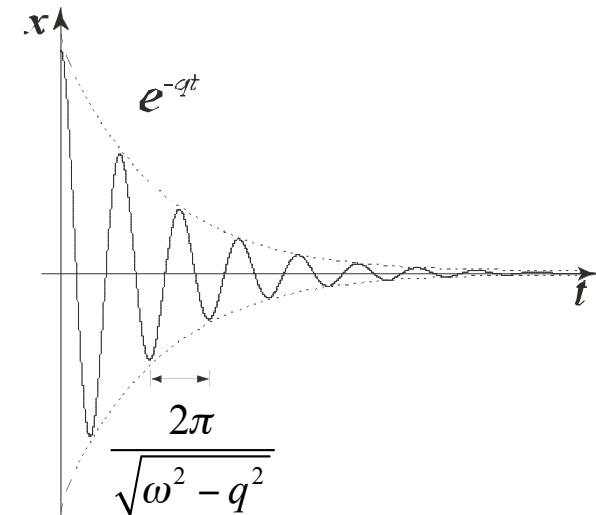
where $\omega_0^2 = \omega^2 - q^2 \Rightarrow$ Oscillation has an angular frequency of $(\omega^2 - q^2)^{1/2}$ but an amplitude that decays exponentially with time.

2. If $q > \omega$, there is only a decay and no oscillations:

$$x = \alpha e^{-(q+q_0)t} + \beta e^{-(q-q_0)t}$$

where $q_0 = (q^2 - \omega^2)^{1/2} < q$.

3. If $q = \omega$ we have *critical damping*: $x = (\alpha + \beta) e^{-qt}$, so that there is a fast decay to $x = 0$.



Forced oscillations

To overcome the loss of amplitude due to friction and air-resistance when, for example, pushing a swing, we often tend to give it periodic jolts \Rightarrow *driven* SHM.

Consider pulling down a mass attached to the ceiling by a spring and letting it go while the fixture is itself made to vibrate at a certain frequency ω . How does the system react?

If ω_0 is the natural frequency of the spring-and-mass system ($\omega_0 = (k/m)^{1/2}$) that is subject to a damping force defined by q , then the equation of motion is:

$$\frac{d^2x}{dt^2} + q \frac{dx}{dt} + \omega_0^2 x = \sin(\omega t)$$

Try $Z = Be^{i\omega t}$ as the solution of $d^2Z/dt^2 + q dZ/dt + \omega_0^2 Z = e^{i\omega t}$; this yields

$$B = (\omega_0^2 - \omega^2 + iq\omega)^{-1}$$

Resonance

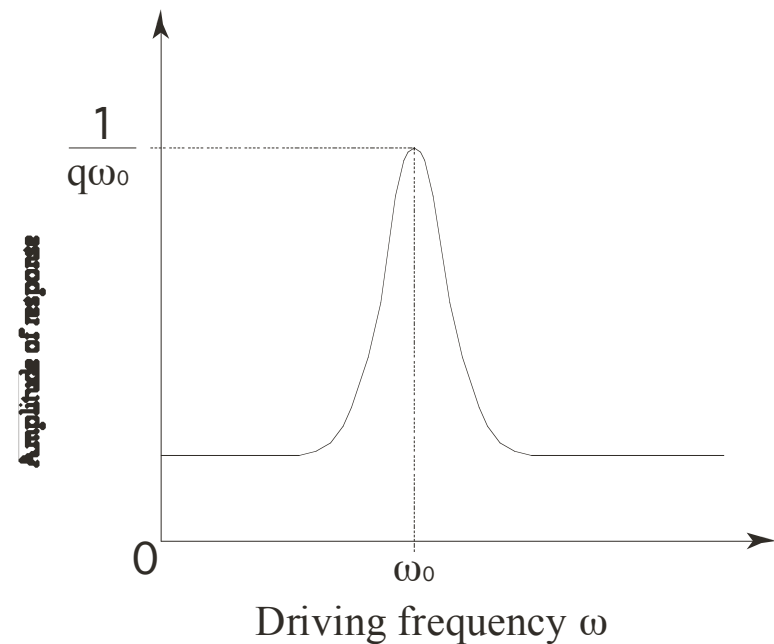
The magnitude of the resultant forced oscillations of frequency ω is then

$$|B| = \sqrt{BB^*} = \left((\omega_0^2 - \omega^2)^2 + \omega^2 q^2 \right)^{1/2}$$

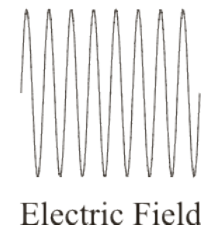
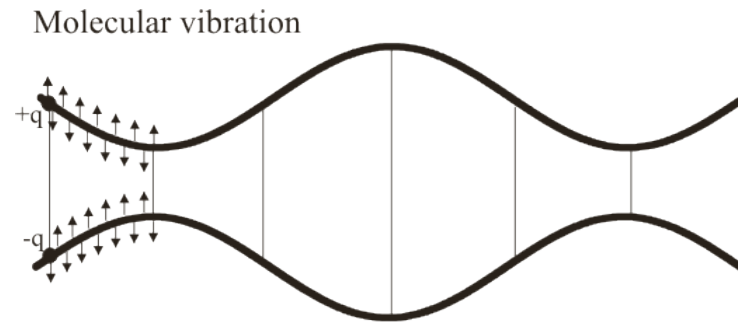
where B^* is the complex conjugate of B .

$|B|$ has the largest value when $\omega = \omega_0$, of $1/(q\omega_0)$, and diminishes as the difference increases.

This **enhancement of response as the driving frequency matches the natural one** is called *resonance* \Rightarrow the physical basis of **absorption spectroscopy**.



A classical picture for IR spectroscopy



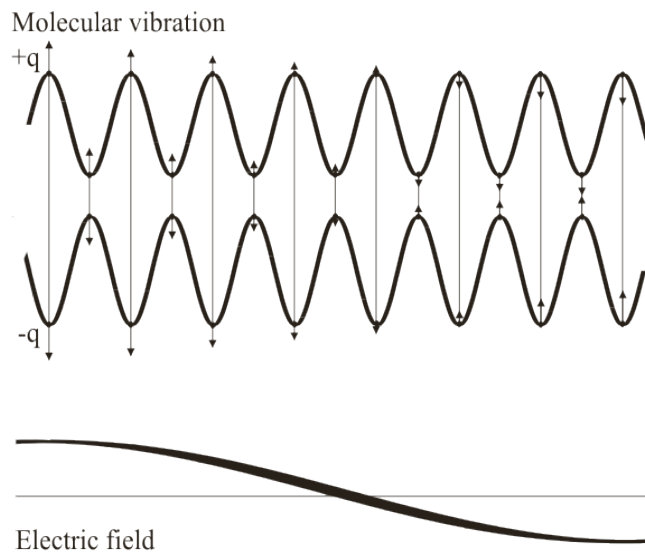
Consider a heteronuclear diatomic molecule \Rightarrow has a *dipole moment*.

Electric field of IR radiation (see later) oscillates in time and exerts an instantaneous force on a dipole that changes bond length.

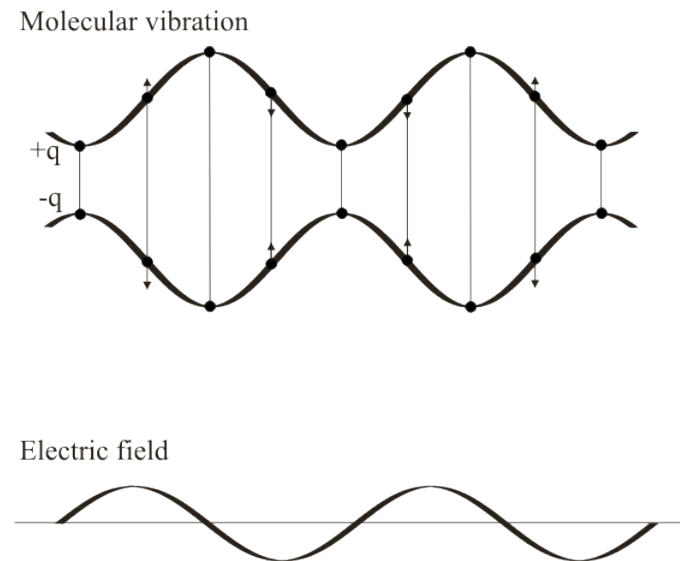
(See Berry, Rice and Ross: *Physical Chemistry*, OUP)

Case 1: If $\omega \gg \omega_0$ then field reverses itself many times during a single vibrational period and motion is only slightly perturbed.

Classical model for IR spectroscopy continued



Case 2: If $\omega \ll \omega_0$ and field can only slightly effect a change in the value of the charge separation and only for some cycles \Rightarrow no uptake of energy from the field.



Case 3: If $\omega = \omega_0$ then field stretches bond when it is expanding and compresses it when it is contracting \Rightarrow maximises energy exchange between molecule and the field.

Such an exchange of energy is called an *electric dipole* transition.