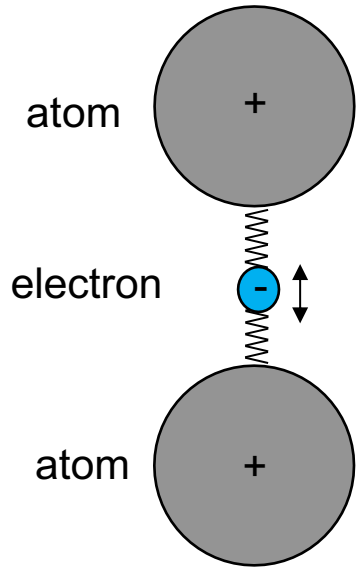


Lecture 3

Nonlinear susceptibility of a classical anharmonic oscillator

Nonlinear Susceptibility of a Classical Anharmonic Oscillator



The Lorentz model of the atom treats the atom (molecule) as a harmonic oscillator

For a monochromatic wave $E = E \cos(\omega t) = \text{Re}\{E e^{i\omega t}\}$

$$m\ddot{x} + b\dot{x} + kx = qE e^{i\omega t} \quad (q = -e)$$

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{qE e^{i\omega t}}{m} \quad (3.1) \quad (\omega_0^2 = \frac{k}{m}, \quad \gamma = b/m)$$

Here q and m are the charge and mass of the electron, ω_0 is the fundamental frequency of the oscillator, and γ is a damping constant associated with the loss of energy by radiation or collisions.

we get $(-\omega^2 + i\omega\gamma + \omega_0^2)x = qE/m$

so that $x = \frac{qE/m}{(\omega_0^2 - \omega^2 + i\omega\gamma)}$ and the induced dipole moment per molecule is $p = qx$

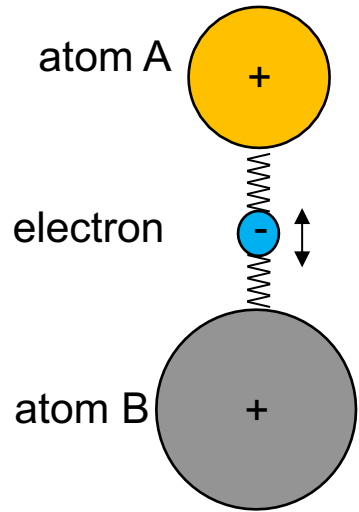
Polarization P of the material = dipole moment per unit volume: $P = qNx = \frac{q^2 N/m}{(\omega_0^2 - \omega^2 + i\omega\gamma)} E$ (N - density of dipoles)

From L2: $D = \epsilon_0(1 + \chi)E$ and $D = \epsilon_0 E + P \rightarrow P = \epsilon_0 \chi E$ and $\boxed{\chi = P/\epsilon_0 E}$

and thus $\boxed{\chi = n^2 - 1 = \frac{q^2 N/\epsilon_0 m}{(\omega_0^2 - \omega^2 + i\omega\gamma)}}$

This formula provides a very good description of the linear optical properties (including refractive index and absorption) of atomic vapors and some solids.

Nonlinear Susceptibility of a Classical Anharmonic Oscillator



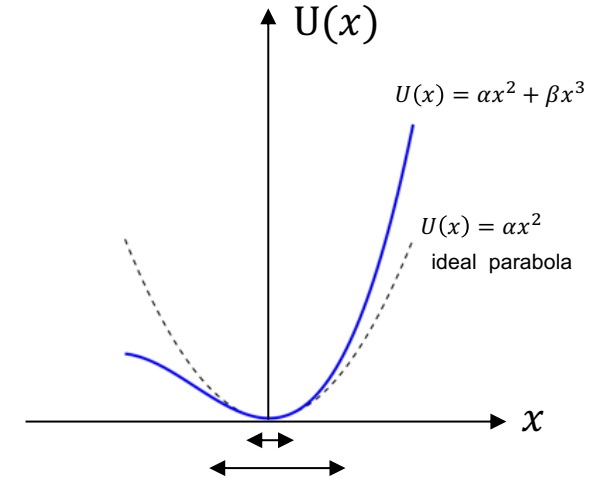
Now imagine that we have a non-symmetric molecule with potential energy function $U(x)$ looking like this :

The restoring force, given by $F = \frac{dU(x)}{dx}$, now acquires components $\sim x^2$

so that eq. (1) becomes:

$$\ddot{x} + \gamma\dot{x} + \omega_0^2x + ax^2 = \frac{qE(t)}{m} \quad (3.2)$$

here a is a parameter that characterizes the strength of the nonlinearity



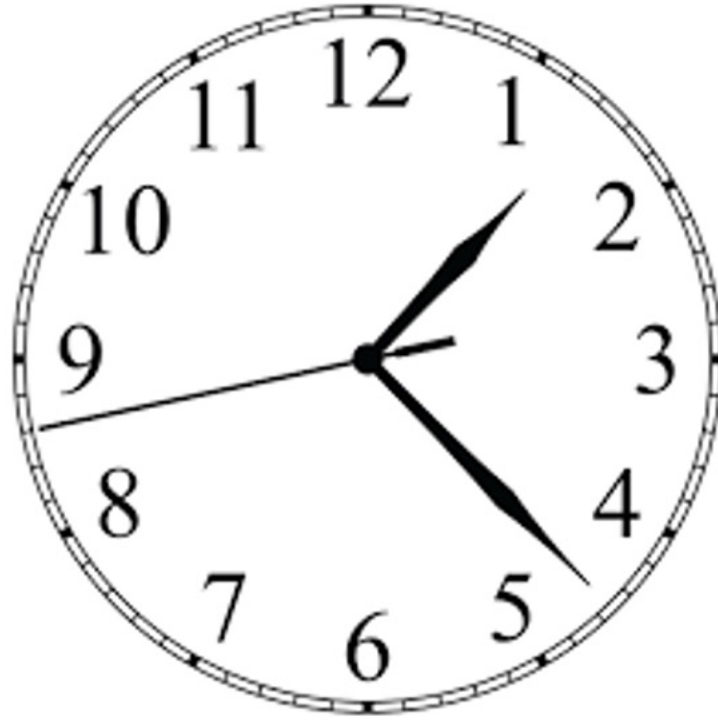
Perturbation technique in mathematics – start from the exact solution of a related, simpler problem and then solve the main problem by adding correction terms.

We replace $E(t)$ in Eq. (2) by $\lambda E(t)$, where λ is a ‘tuning’ parameter that ranges continuously between 0 and 1 and that will be set equal to one at the end of the calculation; λ thus characterizes the strength of the perturbation. Equation (2) then becomes

$$\ddot{x} + \gamma\dot{x} + \omega_0^2x + ax^2 = \lambda \frac{qE(t)}{m} \quad (3.3)$$

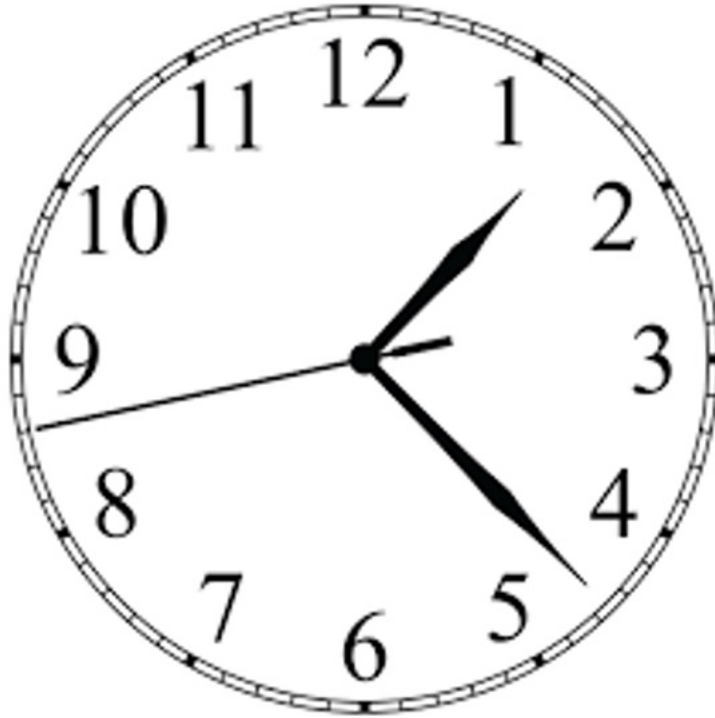
with $E(t) = \text{Re}(E_0 e^{i\omega t}) = \frac{1}{2}(E_0 e^{i\omega t} + c.c.)$

Perturbation technique (one example)



What is the interval (in mins) between the moments when the minute and the hour arms meet?

Perturbation technique



What is the interval (in mins) between the moments when the minute and the hour arms meet?

1st approximation: 60 mins

2nd approximation: $60 (1+1/12)= 65$ mins

3rd approximation: $60 (1+1/12+(1/12)^2)= 65.42$ mins

.....

.....

$60 \times (1+1/12+(1/12)^2+(1/12)^3+....)= 65.4545... \text{ mins}$

Exact answer: $60/(1-1/12) = 65.4545... \text{ mins}$

Nonlinear Susceptibility of a Classical Anharmonic Oscillator

We now seek a solution in the form of a power series expansion in the strength λ of the perturbation:

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \dots$$

Require that the terms in Eq. (3.3) proportional to λ , λ^2 , λ^3 .. each satisfy the equation separately

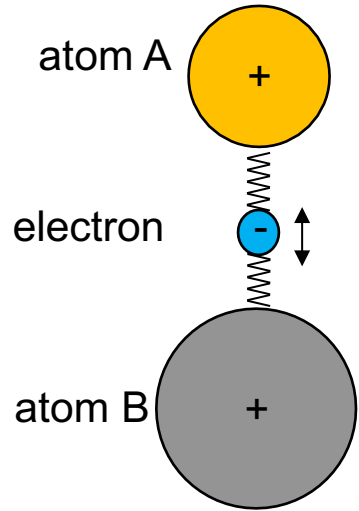
$$\ddot{x}^{(1)} + \gamma \dot{x}^{(1)} + \omega_0^2 x^{(1)} = qE(t)/m \quad (3.3a)$$

$$\ddot{x}^{(2)} + \gamma \dot{x}^{(2)} + \omega_0^2 x^{(2)} + a[x^{(1)}]^2 = 0 \quad (3.3b)$$

$$\ddot{x}^{(3)} + \gamma \dot{x}^{(3)} + \omega_0^2 x^{(3)} + 2ax^{(1)}x^{(2)} = 0 \quad (3.3c)$$

....

plug $E_0 e^{i\omega t}$ (complex) instead of $E(t)$ and seek solution in the form $x^{(1)}(t) = x^{(1)} e^{i\omega t}$ (also complex)



the incoming field is in the form:

$$E(t) = E_0 \cos(\omega t) = \text{Re}(E_0 e^{i\omega t}) = \frac{1}{2}(E_0 e^{i\omega t} + c.c.)$$

Next, express these results in terms of the linear $\chi^{(1)}$ and nonlinear $\chi^{(2)}$ susceptibilities.

1. Linear $\chi^{(1)}$ susceptibility

seek a steady-state solution of (3.3a) the form $x^{(1)}(t) = x^{(1)} e^{i\omega t}$ and get $x^{(1)} = \frac{q/m}{(\omega_0^2 - \omega^2 + i\omega\gamma)} E_0 e^{i\omega t}$ (3.4) linear approximation, complex form

The linear contribution to polarization (dipole moment per unit volume) is:

$$P^{(1)} = qN x^{(1)}, \quad (\text{N is the density of molecules})$$

From the relation $P^{(1)}(t) = \epsilon_0 \chi^{(1)} E(t)$ we get

$$\chi^{(1)} = \frac{1}{\epsilon_0} \frac{P^{(1)}(t)}{E(t)} = \frac{q^2 N/m}{\epsilon_0 (\omega_0^2 - \omega^2 + i\omega\gamma)} \quad (3.3d)$$

please note that we just divided one complex number by another; it is OK, since the dependence is linear

Nonlinear Susceptibility of a Classical Anharmonic Oscillator

2. Nonlinear $\chi^{(2)}$ susceptibility \longrightarrow $\ddot{x}^{(2)} + \gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} + a[x^{(1)}]^2 = 0$ (3.3b)

The expression for $x^{(1)}$ is now squared and substituted into the next equation (3b) to obtain the second-order correction term $x^{(2)}$

Important: because it is squared, $x^{(1)}$ needs to be taken in its real form: $\frac{1}{2} \left(\frac{q/m}{(\omega_0^2 - \omega^2 + i\omega\gamma)} E_0 e^{i\omega t} + c.c. \right) = \frac{1}{2} \left(\frac{q/m}{(\omega_0^2 - \omega^2 + i\omega\gamma)} E_0 e^{i\omega t} + \frac{q/m}{(\omega_0^2 - \omega^2 - i\omega\gamma)} E_0 e^{-i\omega t} \right)$

$$\ddot{x}^{(2)} + \gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} = -a[x^{(1)}]^2 = -a \frac{E_0^2}{4} \left(\frac{q}{m} \right)^2 \left\{ \frac{e^{i2\omega t}}{(\omega_0^2 - \omega^2 + i\omega\gamma)^2} + \frac{e^{-i2\omega t}}{(\omega_0^2 - \omega^2 - i\omega\gamma)^2} + \frac{2}{(\omega_0^2 - \omega^2 + i\omega\gamma)(\omega_0^2 - \omega^2 - i\omega\gamma)} \right\} \quad (3.5)$$

↖ DC component
 $\omega=0$

2.1 Second-harmonic generation

Let us first pick up components at frequency 2ω and seek a steady-state solution of the form

$$x^{(2)}(t) = x^{(2)} e^{i2\omega t}$$

$$\ddot{x}^{(2)} + \gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} = \frac{-a(q/m)^2 E_0^2}{4(\omega_0^2 - \omega^2 + i\omega\gamma)^2} e^{i2\omega t}$$

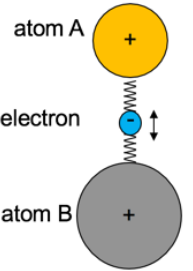
the solution is $x^{(2)} = \frac{-a(q/m)^2 E_0^2}{4(\omega_0^2 - (2\omega)^2 + i2\omega\gamma)(\omega_0^2 - \omega^2 + i\omega\gamma)^2} e^{i2\omega t}$ (3.6)

we can use complex number format again since the equation is linearized

Nonlinear Susceptibility of a Classical Anharmonic Oscillator

The nonlinear polarization oscillating at frequency 2ω is:

$$P^{(2)}(t) = qNx^{(2)} = \frac{-aNq(q/m)^2 E_0^2}{4(\omega_0^2 - (2\omega)^2 + i2\omega\gamma)(\omega_0^2 - \omega^2 + i\omega\gamma)^2} e^{i2\omega t} \quad (3.7)$$



this will be plugged as a source into SVEA equation (2.11)
with $P^{(2)}(t) \rightarrow P$

$$\frac{\partial E(z)}{\partial z} = -\frac{i\omega c}{2n} \mu_0 P$$

it will describe the evolution of the field $E(z)$ at the frequency 2ω

Now, according to the definition of the nonlinear susceptibility $\chi^{(2)}$ describing second-harmonic generation process:

$$P^{(2)}(2\omega) = \frac{1}{2} \epsilon_0 \chi^{(2)} E(\omega)^2 \quad (\text{will come back to that formula in the following lectures})$$

$$\chi^{(2)} = \frac{2 P^{(2)}(2\omega)}{\epsilon_0 E(\omega)^2} = \left(\frac{2}{\epsilon_0} \frac{-aN(q^3/m^2)E_0^2}{4(\omega_0^2 - (2\omega)^2 + i2\omega\gamma)(\omega_0^2 - \omega^2 + i\omega\gamma)^2} \right) / \left(\frac{1}{2} E_0 \right)^2 = \frac{-2aNq^3/m^2}{\epsilon_0(\omega_0^2 - (2\omega)^2 + i2\omega\gamma)(\omega_0^2 - \omega^2 + i\omega\gamma)^2} \quad (3.8)$$

Fourier component (+2 ω)
Fourier component (+ ω) = $E_0/2$

$P^{(2)} \sim E_0^2$ (nonlinear effect)
 $P^{(2)}$ is enhanced if either ω or 2ω is **in resonance** with spring motion

Nonlinear Susceptibility of a Classical Anharmonic Oscillator

2.2 Optical rectification

Now, let us look at the DC component on the right side of (3.5)

$$\cancel{\ddot{x}^{(2)}} + \gamma \cancel{\dot{x}^{(2)}} + \omega_0^2 x^{(2)} = -a \frac{E_0^2}{4} \left(\frac{q}{m}\right)^2 \left\{ \frac{e^{i2\omega t}}{(\omega_0^2 - \omega^2 + i\omega\gamma)^2} + \frac{e^{-i2\omega t}}{(\omega_0^2 - \omega^2 - i\omega\gamma)^2} + \frac{2}{(\omega_0^2 - \omega^2 + i\omega\gamma)(\omega_0^2 - \omega^2 - i\omega\gamma)} \right\}$$

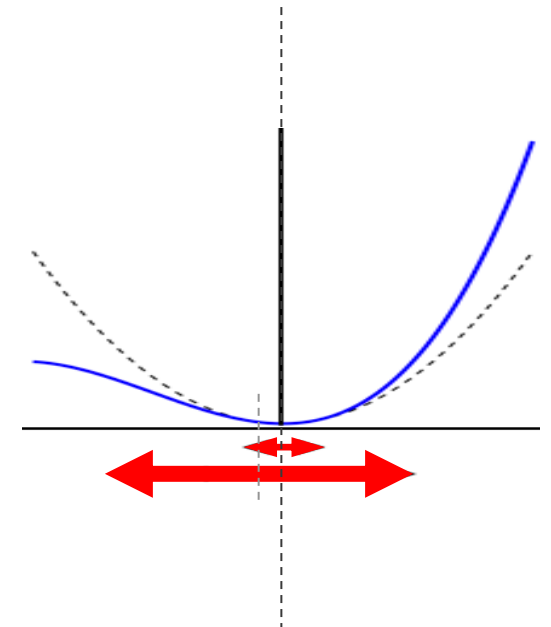
a DC solution ($\omega=0$) is obviously

$$x^{(2)} = -a \frac{E_0^2}{4} \frac{2 \left(\frac{q}{m}\right)^2}{\omega_0^2 (\omega_0^2 - \omega^2 + i\omega\gamma)(\omega_0^2 - \omega^2 - i\omega\gamma)} = \frac{-aE_0^2 \left(\frac{q}{m}\right)^2}{2\omega_0^2 [(\omega_0^2 - \omega^2)^2 + (\omega\gamma)^2]}$$

The DC nonlinear polarization is:

$$P_{DC}^{(2)} = qN x^{(2)} = \frac{-aNq^3/m^2 E_0^2}{2\omega_0^2 [(\omega_0^2 - \omega^2)^2 + (\omega\gamma)^2]} \sim E_0^2 \quad (3.9)$$

This is called **optical rectification**: as a result of applying a harmonic field, the crystal gets a DC dipole moment. In other words, the average position of an electron is shifted from zero at large pump field amplitudes because of the asymmetry of the potential function.



$\chi^{(2)}$ Nonlinear susceptibility

$\chi^{(2)}$ effects (such as second-harmonic generation and optical rectification) can happen only in **noncentrosymmetric crystals**—that is, in crystals that do not display inversion symmetry.

A crystalline material is centrosymmetric if a Cartesian reference system can be chosen such that for each position of one atom in xyz there an equivalent one in position $-x-y-z$.

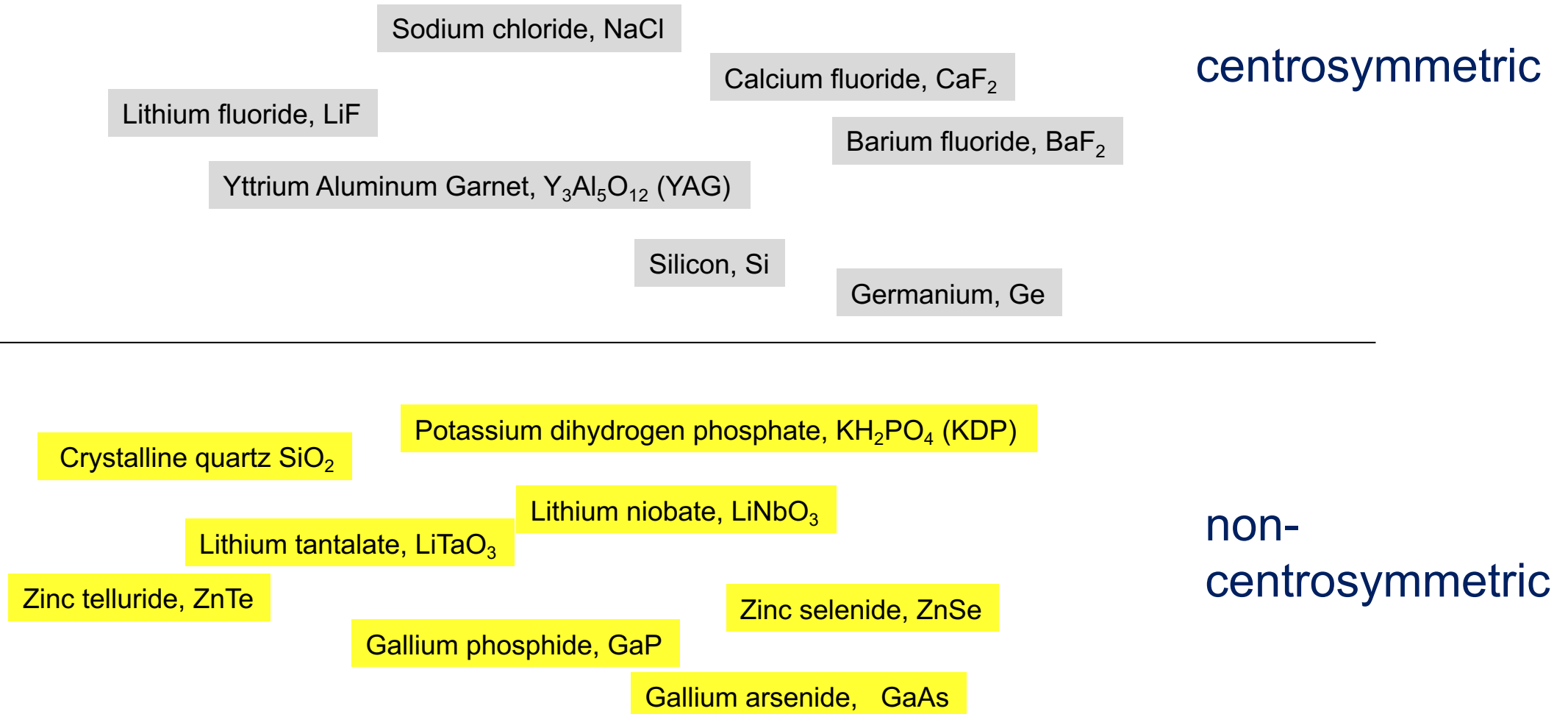
Examples in 2D:

letters **H I N O S X Z** – are centrosymmetric

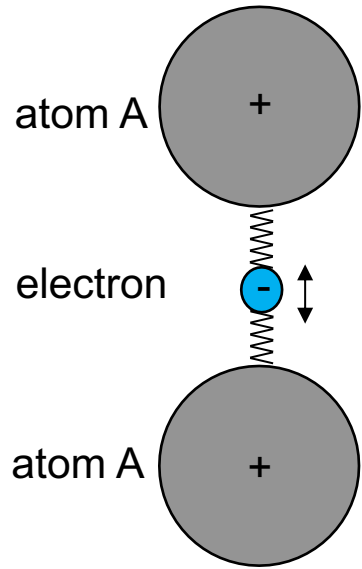
letters **A B C D E F G J K L M Y** – are noncentrosymmetric

$\chi^{(2)}$ Nonlinear susceptibility

3D crystals:



$\chi^{(3)}$ Nonlinear Susceptibility



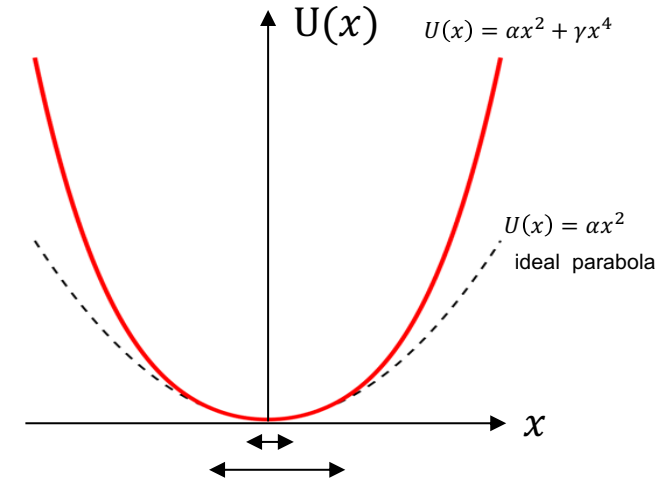
Centrosymmetric Media

– e.g. liquids, gases, amorphous solids (such as glass), and many crystals (such as Si, Ge etc.)

There is no cubic term in $U(x)$:

$$U(x) = \alpha x^2 + \gamma x^4 + ..$$

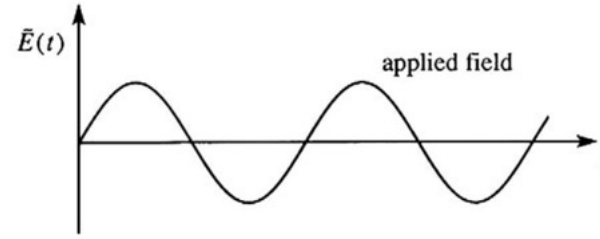
As a consequence, such effects as second-harmonic generation and optical rectification (and also piezoelectric effect) are forbidden.



Third-harmonic generation

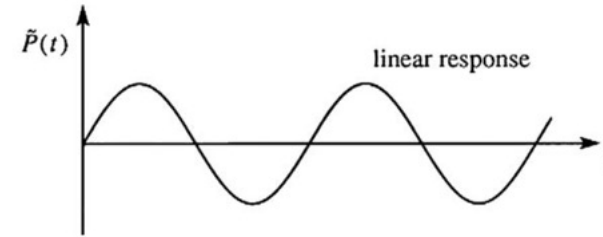
Using similar formalism, one can show that high excitation field produces the nonlinear polarization oscillating at frequency 3ω (in addition to the one oscillating at ω).

Nonlinear Susceptibility



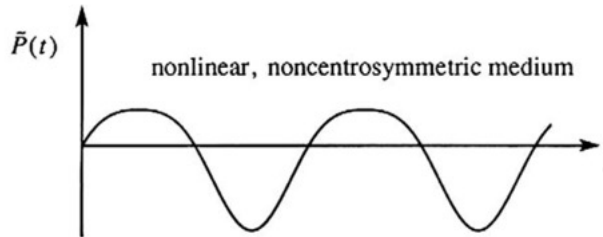
$$E \sim e^{i\omega t}$$

Induced polarization

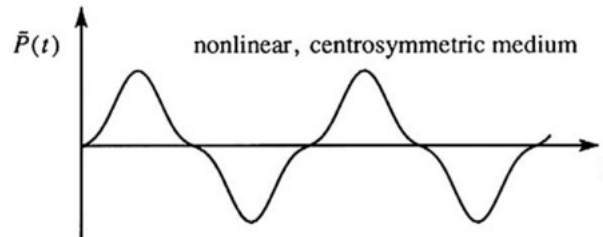


$$\omega$$

Waveforms associated with different atomic responses



$$0, \omega, 2\omega, 4\omega, \dots$$

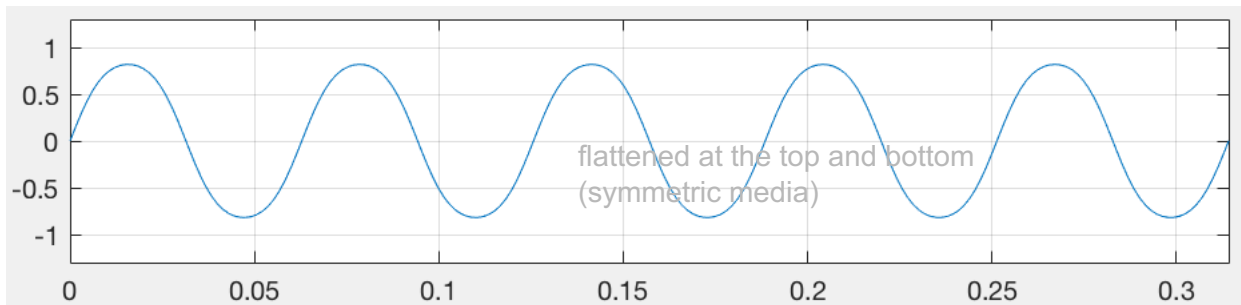
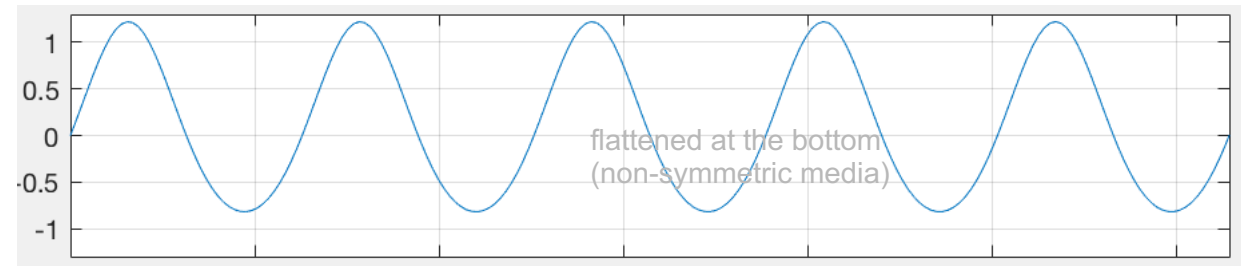
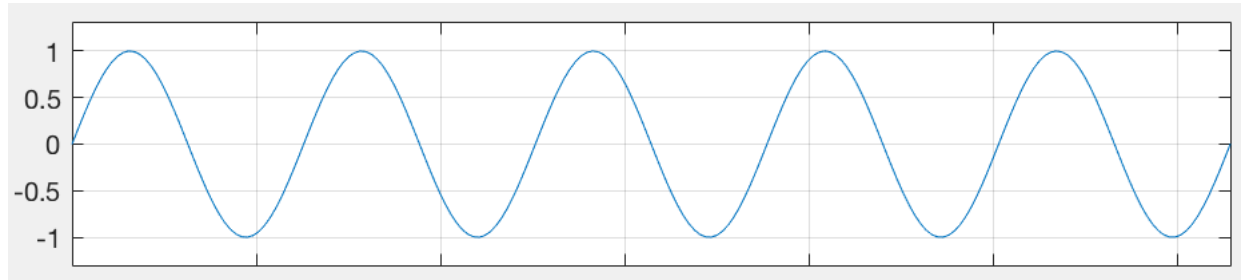


$$\omega, 3\omega, 5\omega, \dots$$

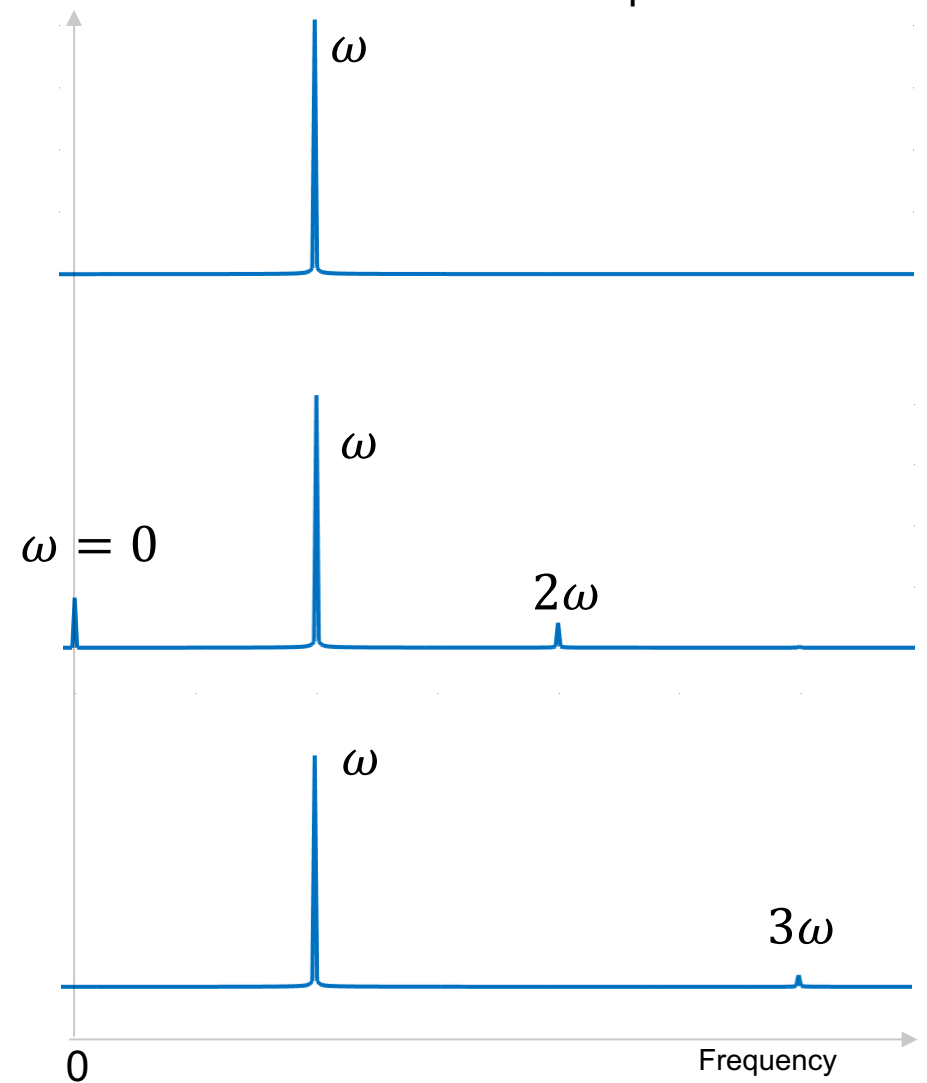
Nonlinear Susceptibility

A simple matlab exercise

Real-time sinusoidal wave



Fourier Spectra



The quantum-mechanical theory of the nonlinear optical susceptibility will be developed in Lecture 4

Please come on time!