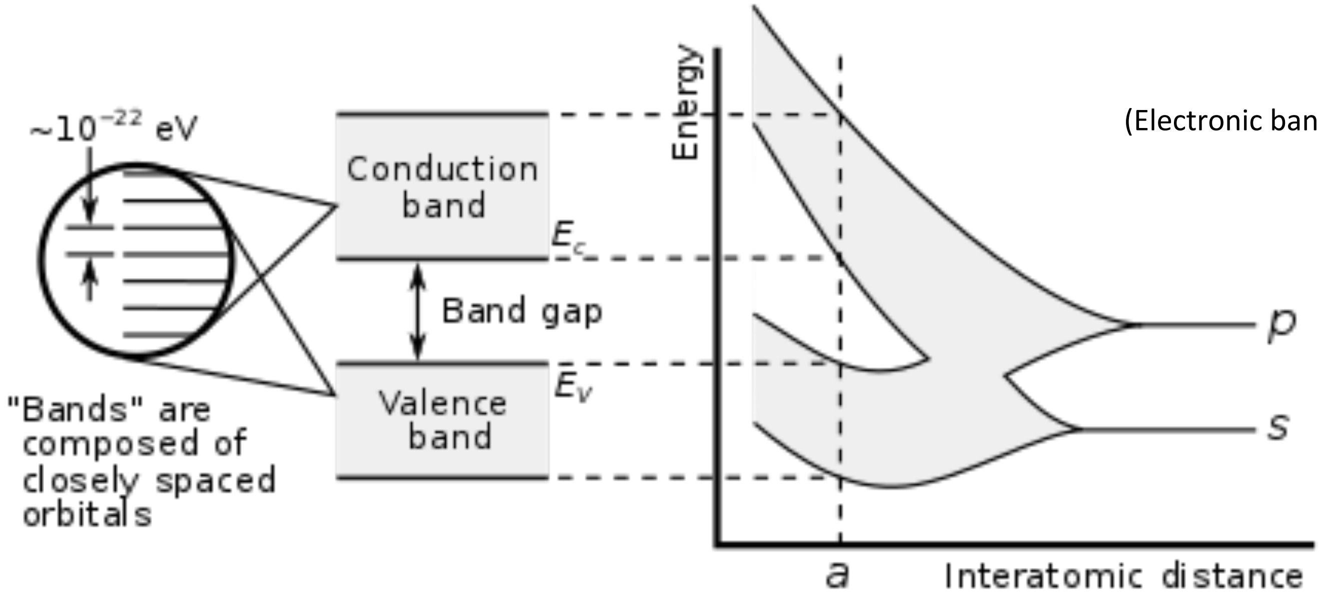
The 1D chain of atoms with s-p hybridization (a model Silicon): see Exercise 19

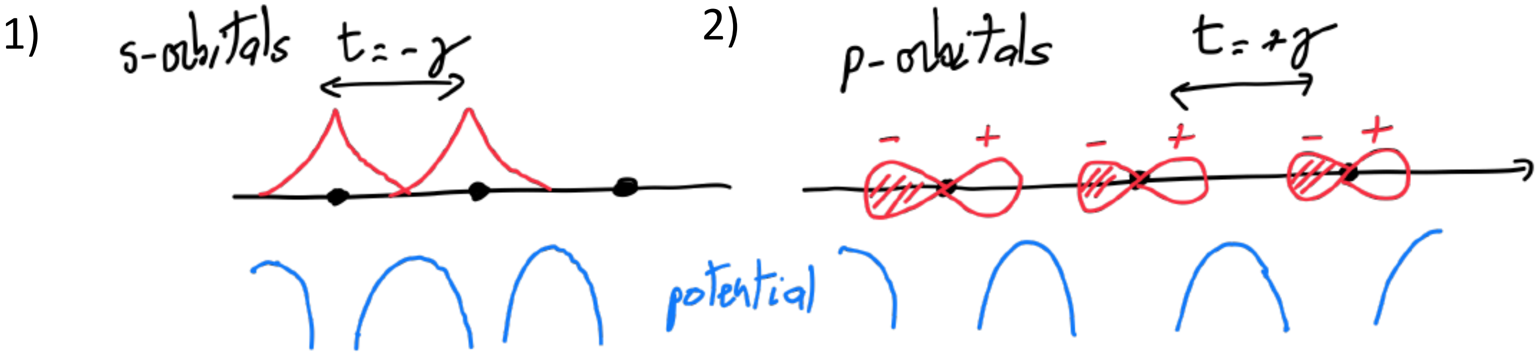


(Electronic band structure, wikipedia)

3*s* and 3*p* bands in silicon as a function of interatomic distance.

In the exercise we vary the hoping energy t : decreasing the distance means increasing the hoping integral !

The 1D chain of atoms with s-p hybridization (a model Silicon): see Exercise 19



First question : chain of atom with one s-orbital per atom (exactly what was done in class)

Bloch theorem: (I) $\psi_k(x+a) = e^{ika}\psi_k(x)$

(II) $\psi_k(x) = e^{ikx}u_k(x) \quad \text{with} \quad u_k(x) \quad \text{periodic}$

With only one type of s-type orbital per atom, the only possible Bloch state for a given k-vector is :

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi_s^{at}(x - na)$$

For a given k-vector, the energy of this state is given by the Schrödinger equation

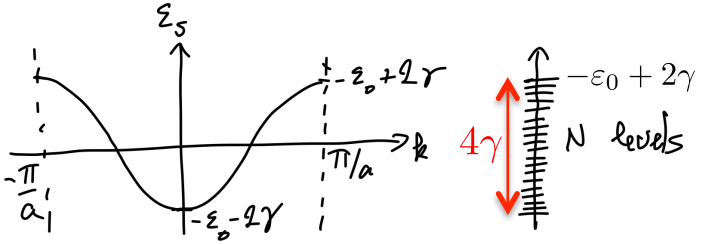
$$\hat{H}|\psi_k\rangle = \varepsilon_k|\psi_k\rangle$$

that we project on $\langle\psi_k|$ to obtain :

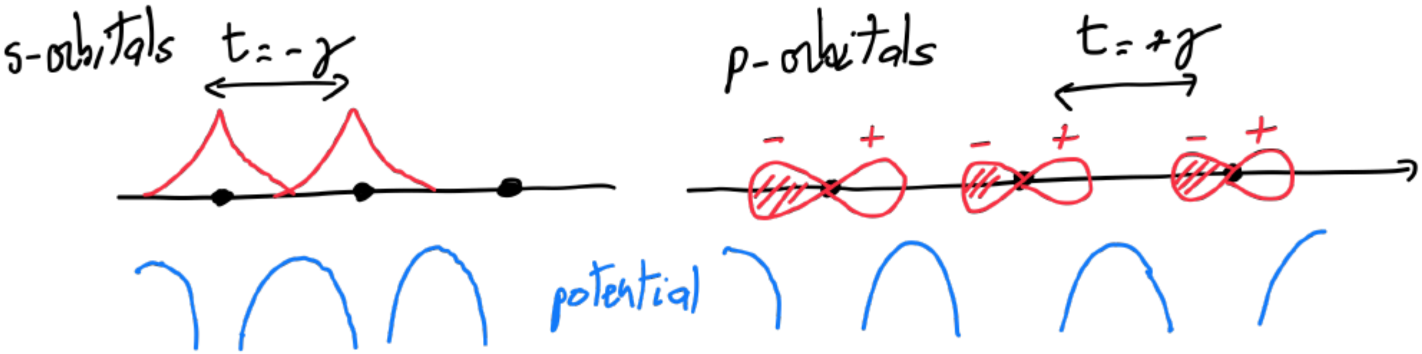
$$\langle\psi_k|\hat{H}|\psi_k\rangle = \varepsilon_k\langle\psi_k|\psi_k\rangle = \varepsilon_k$$

that is :

$$\begin{aligned}\langle\psi_k|\hat{H}|\psi_k\rangle &= \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N} e^{-ikna}e^{ikma}\langle\phi_s^{at}(x-na)|\hat{H}|\phi_s^{at}(x-ma)\rangle \\ &= \frac{1}{N}\sum_{n=1}^{N} \left(e^{ik0a}\varepsilon_0^s + e^{ika}t + e^{-ika}t\right) \\ &= -\varepsilon_0 - 2\gamma\cos(ka)\end{aligned}$$



Second question : chain of atom with one p-orbital per atom



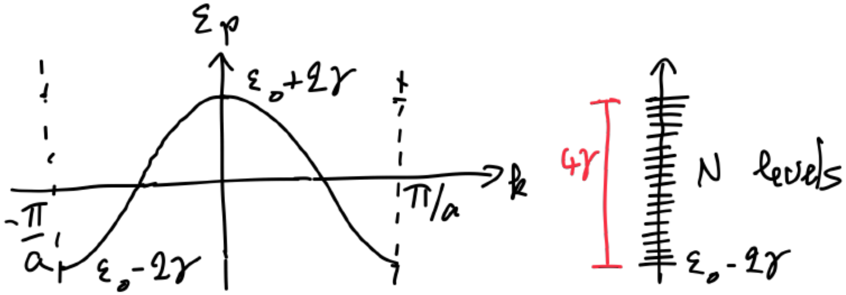
With only one type of p-type orbital per atom, the only possible Bloch state for a given k-vector is :

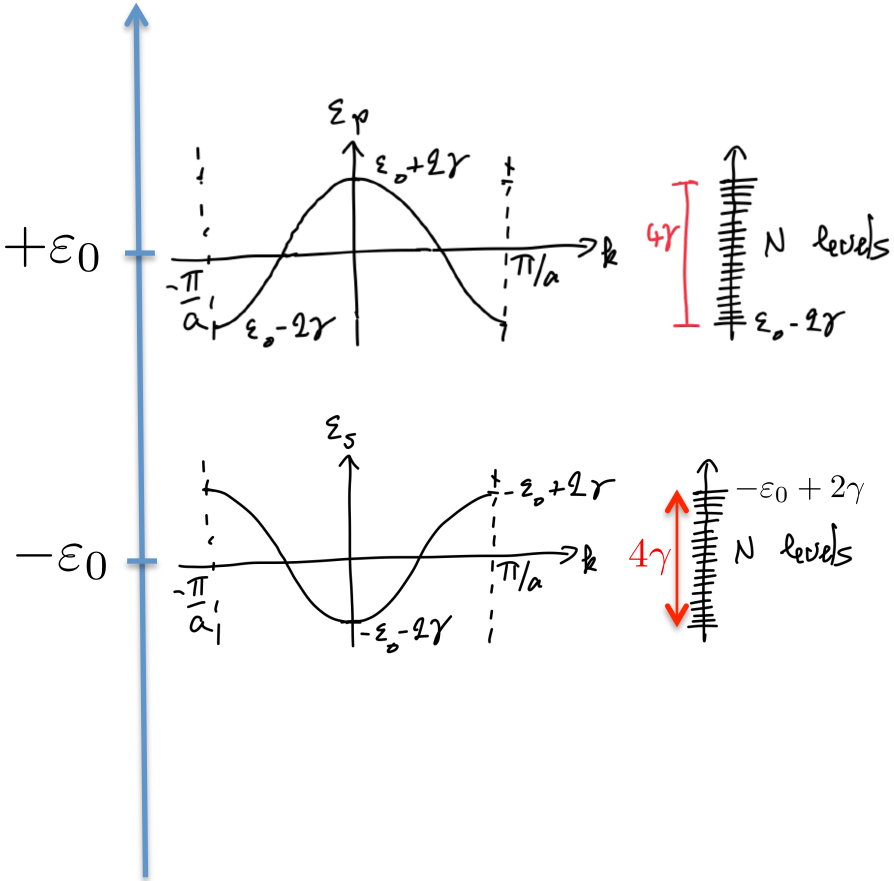
$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi_p^{at}(x - na)$$

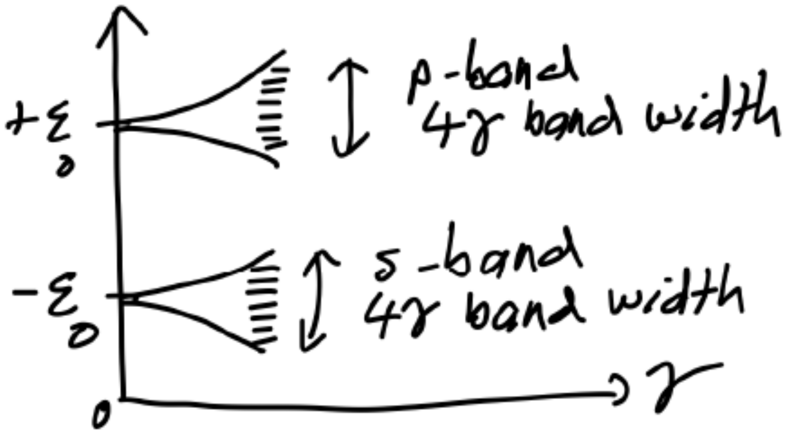
$$\langle \psi_k | \hat{H} | \psi_k \rangle = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} e^{-ikna} e^{ikma} \langle \phi_p^{at}(x-na) | \hat{H} | \phi_p^{at}(x-ma) \rangle$$

$$= \frac{1}{N} \sum_{n=1}^{N} \left(e^{ik0a} \varepsilon_0^p + e^{ika} t_p + e^{-ika} t_p \right)$$

→ $\boxed{\varepsilon_k = +\varepsilon_0 + 2\gamma \cos(ka)}$







Overlap of s- and p-band begins at: $-\varepsilon_0 + 2\gamma = \varepsilon_0 - 2\gamma$

$$\boxed{\gamma = \varepsilon_0/2}$$

Question 3 : Now we put the s and p orbitals all-together => there are 2 atomic orbitals per atom (and per unit cell) => 2 possible basis Bloch state:

$$\psi_s(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi_s^{at}(x - na)$$

$$\psi_p(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi_p^{at}(x - na)$$

Any Bloch state is a linear combination of these 2 basis Bloch states:

$$\psi_k(x) = \alpha\psi_s(x) + \beta\psi_p(x)$$

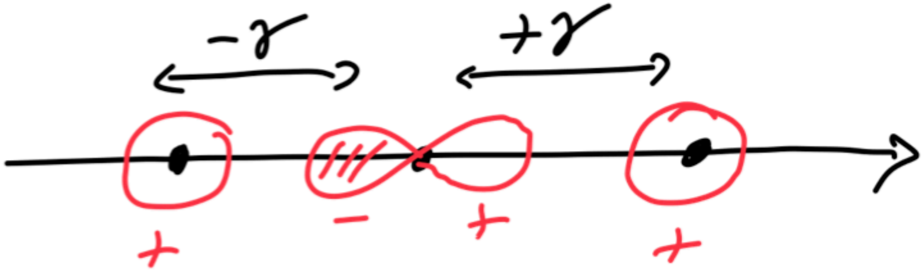
By projection of onto $\hat{H}|\psi_k\rangle = \varepsilon_k|\psi_k\rangle$ onto $\langle\psi_s|$ and $\langle\psi_p|$

$$\boxed{\begin{aligned} \alpha H_{ss} + \beta H_{sp} &= \varepsilon\alpha \\ \alpha H_{ps} + \beta H_{pp} &= \varepsilon\beta \end{aligned}}$$

$$H_{ss} = \langle \psi_s | \hat{H} | \psi_s \rangle = \varepsilon_s(k) = -\varepsilon_0 - 2\gamma \cos(ka) \qquad \text{(first question)}$$

$$H_{pp} = \langle \psi_p | \hat{H} | \psi_p \rangle = \varepsilon_p(k) = +\varepsilon_0 + 2\gamma \cos(ka) \qquad \text{(second question)}$$

s-p coupling



sp coupling : no onsite energy and hoping change sign from right to left :

$$H_{sp} = \langle \psi_s | \hat{H} | \psi_p \rangle = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} e^{-ikna} e^{ikma} \langle \phi_s^{at}(x - na) | \hat{H} | \phi_p^{at}(x - ma) \rangle$$

$$= \frac{1}{N} \sum_{n=1}^{N} \left(e^{ika}\gamma + e^{-ika}(-\gamma) \right) = \gamma 2i \sin(ka)$$

Solve : $(H_{ss} - \varepsilon)(H_{pp} - \varepsilon) - |H_{sp}|^2 = 0$

$$\Rightarrow \quad (\varepsilon - \varepsilon_s(k))(\varepsilon - \varepsilon_p(k)) = 4\gamma^2 \sin^2(ka)$$

Trick : $\varepsilon_{av} = (\varepsilon_s + \varepsilon_p)/2 \quad \text{and} \quad \Delta\varepsilon = \varepsilon_p - \varepsilon_s$

$$\Downarrow$$

$$\begin{aligned}(\varepsilon - \varepsilon_s)(\varepsilon - \varepsilon_p) &= (\varepsilon - \varepsilon_{av} + \Delta\epsilon/2)(\varepsilon - \varepsilon_{av} - \Delta\epsilon/2) \\ &= (\varepsilon - \varepsilon_{av})^2 - (\Delta\epsilon/2)^2\end{aligned}$$

$$\boxed{\varepsilon = \varepsilon_{av} \pm \sqrt{(\Delta\epsilon/2)^2 + 4\gamma^2 \sin^2(ka)}}$$

Note : when *sp* coupling goes to zero, one recovers the original uncoupled *s* and *p* bands.

$$H_{ss} = \langle \psi_s | \hat{H} | \psi_s \rangle = \varepsilon_s(k) = -\varepsilon_0 - 2\gamma\cos(ka) \qquad \text{(first question)}$$

$$H_{pp} = \langle \psi_p | \hat{H} | \psi_p \rangle = \varepsilon_p(k) = +\varepsilon_0 + 2\gamma\cos(ka) \qquad \text{(second question)}$$

$$\Rightarrow \quad \epsilon_{av} = \frac{\epsilon_s + \epsilon_p}{2} = 0 \qquad \frac{\Delta\epsilon}{2} = \frac{\epsilon_p - \epsilon_s}{2} = \varepsilon_0 + 2\gamma\cos(ka)$$

$$\Rightarrow \quad \varepsilon(k) = \pm\sqrt{\varepsilon_0^2 + 4\gamma\varepsilon_0\cos(ka) + 4\gamma^2}$$

Limit

$\gamma/\varepsilon_0 >> 1$

$$\varepsilon(k) = \pm 2\gamma\sqrt{\left(\frac{\varepsilon_0}{2\gamma}\right)^2 + \frac{\varepsilon_0}{\gamma}\cos(ka) + 1}$$

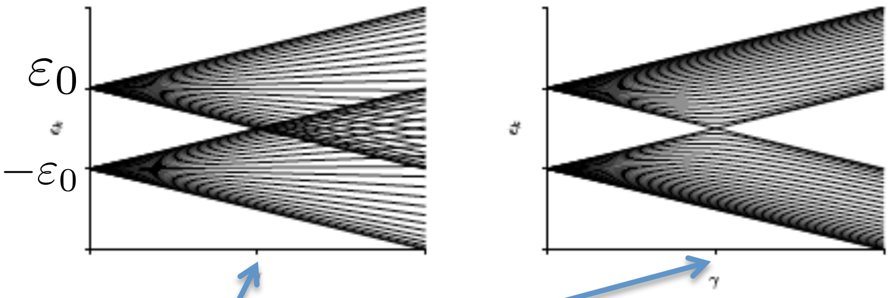
$$= \pm 2\gamma\left(1 + \frac{1}{2}\frac{\varepsilon_0}{\gamma}\cos(ka) + \cdots\right)$$

$$= \pm\left(2\gamma + \varepsilon_0\cos(ka) + \cdots\right)$$

Two bands centered on $\pm\gamma$ with a bandwidth $2\varepsilon_0$ ⇐

No sp-coupling

With sp-coupling



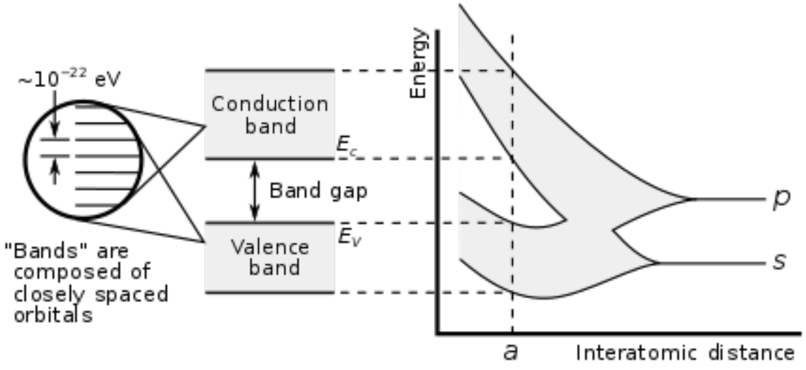
$\gamma = \varepsilon_0/2$

Figure 1: Evolution of energy levels as a function of γ in the case of (Left) no t_{sp} coupling, and (Right) with a $t_{sp} = \pm\gamma$ coupling. For each value of (γ) we plot a few energy levels, that is $\varepsilon(k)$ with 20 k-points equally spaced in the Brillouin zone.

With 2 electrons per atom, the s-band is filled => insulating for $\gamma < \varepsilon_0/2$

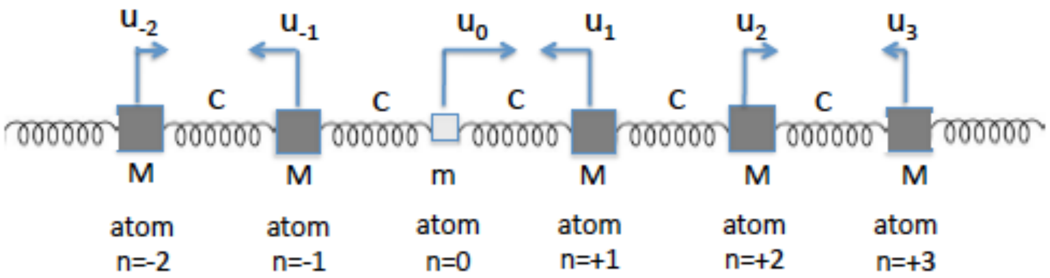
For $\gamma > \varepsilon_0/2$

- metallic in the case of no sp-coupling
- insulating in the case of sp-coupling



Exercise 29 Localized vibrational modes around an impurity

We study the vibrational modes of a 1D chain of atoms. All springs have the same spring constant C. All atoms have the same mass M except the central atom that has a mass m.

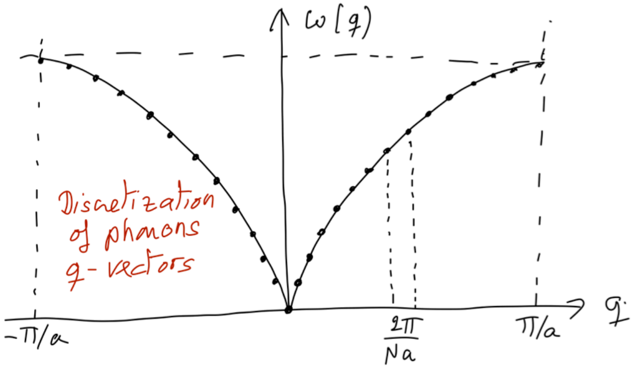


a) In the case of a chain with all identical atoms with mass M and spring constants C, re-derive the equation of motion for any atom with index (n), calling u_n its displacement out of its equilibrium position. Plot the phonon modes energy dispersion relation in the Brillouin zone for the perfect chain (q = phonon momentum).

$$M\frac{d^2u_n}{dt^2} = C(u_{n+1}-u_n) - C(u_n - u_{n-1}) = C(u_{n+1}+u_{n-1}-2u_n)$$

Use : $u_n = u_0 e^{iqna} e^{-i\omega t}$

$$\Rightarrow \quad \omega(q) = \sqrt{\frac{4C}{M}}|\sin(qa/2)|$$



b) In the presence of the impurity, we try vibrational modes that are localized around the impurity of mass m, assuming displacements of the form: $u_n = A(-1)^n e^{-\alpha|n|} e^{-i\omega_0 t}$ where A is a constant and |n| the absolute value of the n-index.

- What is the equation of motion for an atom n with (n > 1) ?
- Show that the "localized" solution satisfies this equation of motion provided that:

$$M\omega_0^2 = C\left(2 + X + \frac{1}{X}\right) \quad \text{with} \quad X = e^{\alpha}$$

$$M\frac{d^2u_n}{dt^2} = C(u_{n+1} + u_{n-1} - 2u_n)$$

Plug in localized mode (with 0 < n-1 < n < n+1) :

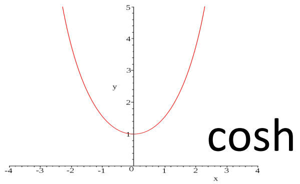
$$-M\omega_0^2(-1)^n e^{-\alpha n} = C\Big((-1)^{n+1}e^{-\alpha(n+1)} + (-1)^{n-1}e^{-\alpha(n-1)} - 2(-1)^n e^{-\alpha n}\Big)$$

➡ $$-M\omega_0^2 = C\Big((-1)^1 e^{-\alpha} + (-1)^{-1}e^{\alpha} - 2\Big)$$

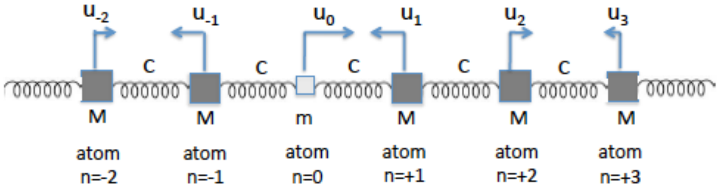
- Deduce that the energy of the localized vibrational mode is necessarily above the band of energy of the phonon modes of the 1D chain without impurities.

Indication: cosh(x) always larger than cosh(0)=1.

$$\omega_0^2 = \frac{2C}{M}\Big(1+\cosh(\alpha)\Big) > \frac{4C}{M}$$



c) What is the equation of motion for the central impurity atom of mass m ? Using this equation of motion, obtain a second equation relating ω_0^2 , m, C and X.



$$m\frac{d^2u_0}{dt^2} = C(u_1+u_{-1}-2u_0)$$

Use $u_n = A(-1)^n e^{-\alpha|n|}e^{-i\omega_0 t}$ (warning absolute value for n=-1 !!)

$$-m\omega_0^2 = C\Big(-e^{-\alpha}-e^{-\alpha}-2\Big) \Longrightarrow m\omega_0^2 = 2C\Big(1+\frac{1}{X}\Big)$$

d) Using the two expressions for ω_0^2 derived in b) and c), calculate (M-m)/m as a function of X and show that the above solution is possible (not diverging) only if (m < M).

$$M\omega_0^2 = C\Big(2 + X + \frac{1}{X}\Big) \quad \text{with} \quad X = e^{\alpha}$$

$$m\omega_0^2 = 2C\Big(1 + \frac{1}{X}\Big)$$

$$\frac{M-m}{m} = \frac{2 + X + 1/X - 2 - 2/X}{2 + 2/X} = \frac{X - 1/X}{2 + 2/X} = \frac{1}{2}\frac{X^2 - 1}{X + 1}$$

$$= \frac{X-1}{2}$$

Localized vibrations around defect

$$u_n = A(-1)^n e^{-\alpha|n|} e^{-i\omega_0 t}$$

$$\alpha > \boxed{0} \implies X = e^{\alpha} > 1 \implies (M - m) > 0$$