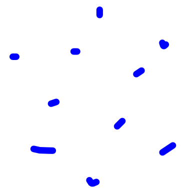
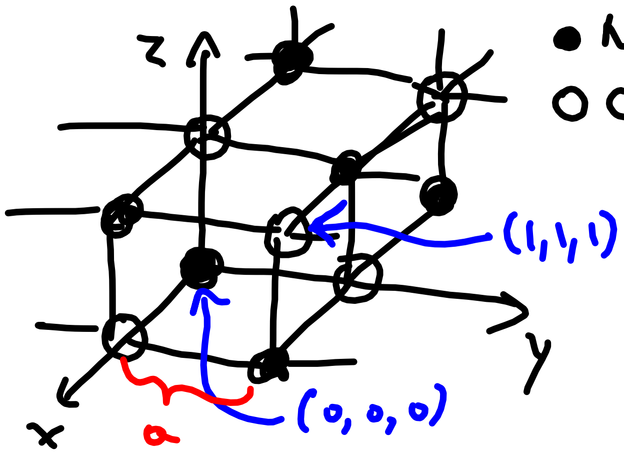
Electrostatic energy



$$W = \frac{1}{8\pi\epsilon_0} \sum_{i=1}^{n} \sum_{\substack{j=1 \\ (i\neq j)}}^{n} \frac{q_i q_j}{|\vec{x}_i - \vec{x}_j|}$$

$$= \frac{1}{8\pi\epsilon_0} \int\int \frac{\rho(\vec{x})\,\rho(\vec{x}')}{|\vec{x}-\vec{x}'|}\, d^3x\, d^3x'$$

Electrostatic energy of ionic crystals



● Na^+

○ Cl^-

$\vec{n}a = (n_x, n_y, n_z)\, a$

$\ldots -2, -1, 0, 1, 2 \ldots$

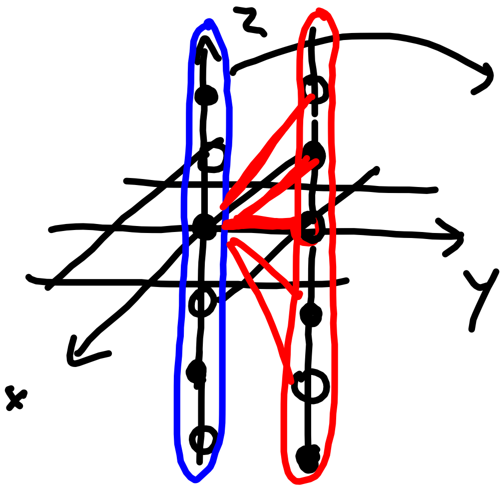
$a \sim 2.8$ Å

$$\underset{\substack{\uparrow \\ \text{electrostatic} \\ \text{energy of ion} \\ \text{at } (0,0,0)}}{U} = \frac{e^2}{4\pi\epsilon_0 a} \sum_{n_x} \sum_{n_y} \sum_{n_z} \frac{(-1)^{n_x+n_y+n_z}}{|\vec{n}|}$$

$\neq (0,0,0)$

analog of $|\vec{x}_i - \vec{x}_j|$

$\int^{\Lambda} \frac{dx}{x} \sim \ln \Lambda$; $\int^{\Lambda} \frac{dx}{x^2}$ converges



$2 \to 0 + 2 \infty$

$$U_0 = \frac{2e^2}{4\pi\epsilon_0 a}\underbrace{\left[-1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \cdots\right]}_{-\ln 2}$$

0 +1 0 +2 +1 0

$$U = U_0 + 4U_{01} + \cdots$$

$$U = -\frac{e^2}{4\pi\epsilon_0 a}\underbrace{(1.7476)}_{\text{Madelung constants}}$$

good agreement with experiments

2.8 Orthogonal functions and expansions

ξ coordinates ; (a,b) domains ; $U_n(\xi)$ $(n=1,2,3,\ldots)$

orthogonal, square integrable

$$\int_a^b U_n^*(\xi)\,U_m(\xi)\,d\xi = \delta_{nm} \; ; \quad \int_a^b |U_n(\xi)|^2\,d\xi = 1$$

Expansion of an arbitrary function $f(\xi)$:

$$f(\xi) = \sum_n a_n U_n(\xi)$$

analog 3-D

$$\vec{x} = \sum_{i=1}^{3} c_i \hat{e}_i$$

$$\sum_n U_n^*(\xi')\,U_n(\xi) = \delta(\xi-\xi')$$

completeness relation

$$\int_a^b U_m^*(\xi) f(\xi)\,d\xi = \sum_n a_n \underbrace{\int_a^b U_m^*(\xi)\,U_n(\xi)\,d\xi}_{\delta_{mn}} = a_m$$

Example: $\sqrt{\frac{2}{a}}\,\sin\left(\frac{2\pi m x}{a}\right), \quad \sqrt{\frac{2}{a}}\,\cos\left(\frac{2\pi m x}{a}\right)$

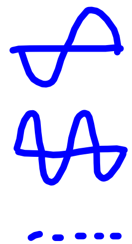
$$f(x) = \frac{A_0}{2} + \sum_{m=1}^{\infty}\left[A_m \cos\left(\frac{2\pi m x}{a}\right) + B_m \sin\left(\frac{2\pi m x}{a}\right)\right]$$

$-a/2 \qquad a/2$

$m = 1, 2, \ldots, \infty$

$$A_m = \frac{2}{a}\int_{-a/2}^{+a/2} f(x)\cos\left(\frac{2\pi m x}{a}\right)dx$$

B_m sin



$$a \to \infty, \quad \frac{2\pi m}{a} = k, \quad \sum_{m=1}^{\infty} \to \frac{a}{2\pi}\int_{-\infty}^{+\infty} dk$$

Fourier integrals

$\sin, \cos$

$\hookrightarrow e^{\pm ikx}$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} A(k)\, e^{ikx}\, dk$$

$\hookrightarrow$ analog of "a_n"

symmetric

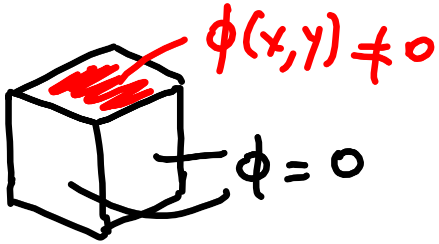
$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x)\, e^{-ikx}\, dx$$

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i(k-k')x}\, dx = \delta(k-k')$$ orthogonality

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ik(x-x')}\, dk = \delta(x-x')$$ completeness

2.9 Separation of variables

If $\rho = 0$, $\nabla^2 \phi = 0$ Laplace



$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

$$\phi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

and then divide by ϕ

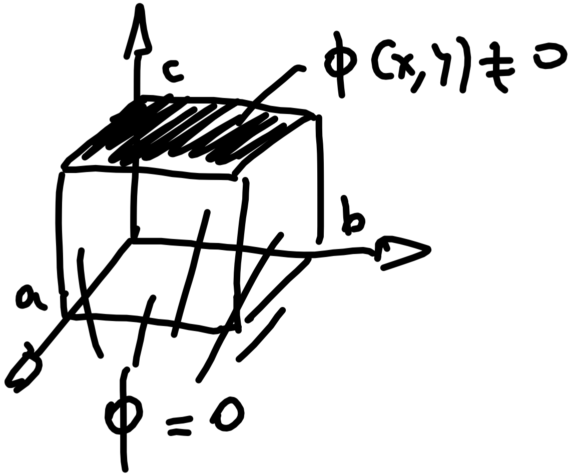
$$\underbrace{\frac{1}{X(x)}\frac{d^2X}{dx^2}}_{-\alpha^2} + \underbrace{\frac{1}{Y(y)}\frac{d^2Y}{dy^2}}_{-\beta^2} + \underbrace{\frac{1}{Z(z)}\frac{d^2Z}{dz^2}}_{\alpha^2+\beta^2} = 0$$

$-\alpha^2$ $\quad$ $\alpha^2+\beta^2$ $\quad$ $-\beta^2$

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\alpha^2 \; ; \quad X(x) = e^{\pm i\alpha x} \longrightarrow \sin(\alpha x),\ \cos(\alpha x)$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -\beta^2 \; ; \quad Y(y) = e^{\pm i\beta y} \longrightarrow \sin(\beta y),\ \cos(\beta y)$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = \alpha^2+\beta^2 \; ; \quad Z(z) = e^{\pm\sqrt{\alpha^2+\beta^2}\,z} \longrightarrow \sinh\left(\sqrt{\alpha^2+\beta^2}\,z\right),\ \cosh\left(\sqrt{\alpha^2+\beta^2}\,z\right)$$

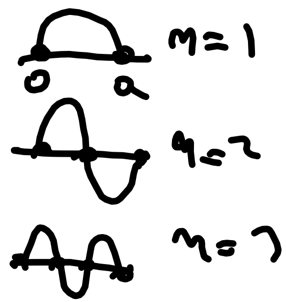


$\sin(\alpha x)$

$\sin(\alpha 0) = 0$ ✓

$\sin(\alpha a) = 0 \rightarrow \boxed{\alpha_n = \frac{n\pi}{a}}$

$\sin(\beta y)$; $\boxed{\beta_m = \frac{m\pi}{b}}$



$$\phi(x,y,z) = \sum_{n,m} A_{n,m} \sin(\alpha_n x)\sin(\beta_m y)\underbrace{\sinh\left(\sqrt{\alpha_n^2+\beta_m^2}\, z\right)}_{}$$

$Z(z)$

if $z=0$
then $\sinh = 0$