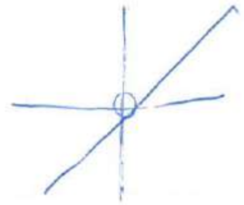
- Current approach in DFT + use in real world.
- Broyden – Fletcher – Goldfarb – Shanno scheme.
- Problems of DFT and in DMC.
- $E = \frac{\int \psi H \psi}{\int \psi \psi}$, $\hat{H} = \nabla^2 + V_{i-i} + V_{e-i} + V_{e-e}$
- Derive $H'' = H' = 0$ term
- $\frac{d^2 E}{dR_I \, dR_J} = \left\langle \frac{d^2 V_{ii}}{dR_I \, dR_J} + \frac{d^2 V_{ei}}{dR_I \, dR_J} + \frac{1}{2}\left(\frac{dV_{ei}}{dR_I}\frac{d\ln\psi}{dR_J} + \frac{dV_{ei}}{dR_J}\frac{d\ln\psi}{dR_I} \right) \right\rangle$

- Results from DMC / Full story
- Springs in crystals, quadratic modes → phonons
- Crystals (draw lattice)

First order term:



$$V = \frac{1}{\sqrt{(x-X)^2+Y^2+Z^2}} + \frac{1}{\sqrt{(x+X)^2+Y^2+Z^2}} + \frac{1}{\sqrt{X^2+(y-Y)^2+Z^2}} + \frac{1}{\sqrt{X^2+(y+Y)^2+Z^2}} + \frac{1}{\sqrt{X^2+Y^2+(z-Z)^2}} + \frac{1}{\sqrt{X^2+Y^2+(z+Z)^2}}$$

check $\frac{dV}{dX} = 0$ by symmetry

$$\frac{dV}{dX} = -\left(\frac{(X-x)}{((x-X)^2+Y^2+Z^2)^{3/2}} + \frac{X+x}{((x+X)^2+Y^2+Z^2)^{3/2}} + 4\frac{X}{(X^2+(Y+y)^2+Z^2)^{3/2}} \right)$$

$$\frac{d^2V}{dX^2} = -\left(1+1+4 - \frac{3}{2}\frac{2X^2}{|\ 1 \quad 1\ |^{5/2}} \cdot 2 \right) = 0 \quad \checkmark.$$

Not a surprise as $\nabla^2 = 0$ so by symmetry

Holds for all radii shells

Holds for cubic, BCC, FCC but not HCP (must have unstable)

Holds for other cubic based structures eg NaCl, diamond

What about other terms: analyze in NFE and tight binding limits

Nearly free electron limit: No change in ψ so $\frac{d\psi}{dz} = 0$

$$V_{ei} = -\int \frac{\cos kx + \cos ky + \cos kz}{3\sqrt{(x-X)^2 + (y-Y)^2 + (z-Z)^2}}\, dx\, dy\, dz$$

$$= -\int \frac{e^{iq_xX + iq_yY + iq_zZ}}{q_x^2 + q_y^2 + q_z^2} \sum_\alpha \frac{\delta(q_\alpha - k) + \delta(q_\alpha + k)}{2}\, dq_x\, dq_y\, dq_z$$

$$= -(\cos kX + \cos kY + \cos kZ)$$

$$= 3. + \frac{3}{2}k^2(X^2 + Y^2 + Z^2)$$

Electron density highest over atoms so naturally atoms pulled back over high density

Metals often have cubic lattices (show on board).

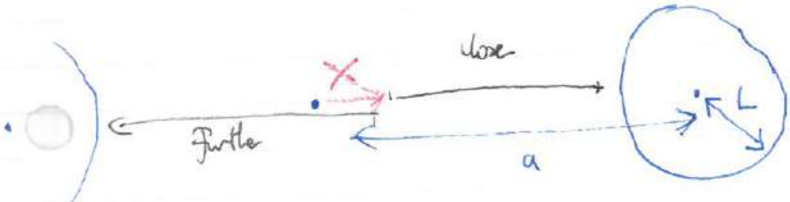
Tight binding:

With 0 radius electrons on top of atoms so no interaction

With finite radius L, $\left[|\psi_i\rangle = |\phi_0\rangle + \sum_i \frac{\langle \phi_i | \hat{V} | \phi_0 \rangle}{\epsilon_i - \epsilon_0} |\phi_i\rangle \right]$ ← exp small.

$d\psi / dR_0$ term small / due to exponentially bound wavefunction

Look at next order terms: d^4V_{ii} / dR^4 and d^2V_{ei} / dR^2:
- Only anharmonic vibrations



- Expand d^2V/dR^2 around electron cloud, similar to d^4V/dR^4.
- Similar term, $\epsilon = |x^2 y^2 z| (V''''_{ii}) \begin{pmatrix} x^2 \\ y^2 \\ z \end{pmatrix} + |xyz| (V''_{ei} L^2) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ opposite sign — write out examples
- looks like
- Is there a single tight-binding system that is stable?
- Looking at more complex crystal structures.
- FCC: 1.36 Fermi sphere contacts BZ boundary
- BCC: 1.48
- HCP: 1.69

What has this got to do with our stability

Qns: — How calculate energetics of these systems:

when can escape?

- Other ways to explain crystal stability
- Drop Born approximation
- Quasicrystals

- Ion trap experiment
- link to Wigner crystal
- $r \to \infty$ issues?