

Current approach in DFT + use in real world,

Broyden - Fletcher - Goldfarb - Shanno scheme.

Problems of DFT and in DMC.

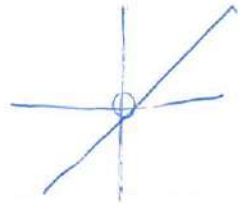
$E = \frac{\int \Psi H \Psi}{\int \Psi \Psi}$ ,  $\hat{H} = \nabla^2 + V_{i-i} + V_{e-i} + V_{e-e}$

Derive  $H'' = H' = 0$  term

$\frac{d^2 E}{dR_i dR_j} = \left\langle \frac{d^2 V_{ii}}{dR_i dR_j} + \frac{d^2 V_{ei}}{dR_i dR_j} + \frac{1}{2} \left( \frac{dV_{ei}}{dR_i} \frac{d^2 \Psi}{dR_j} + \frac{dV_{ei}}{dR_j} \frac{d^2 \Psi}{dR_i} \right) \right\rangle$

Results from DMC / Full string  
 Springs in crystals, quadratic nodes  $\rightarrow$  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

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

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

Not a surprise as  $\sigma^2 = 0$  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 higher

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

$$\begin{aligned}
 V_{ei} &= - \int \frac{\cos k_x x + \cos k_y y + \cos k_z z}{3 \sqrt{(x-X)^2 + (y-Y)^2 + (z-Z)^2}} dx dy dz \\
 &= - \int \frac{e^{iq_x x + iq_y y + iq_z z}}{q_x^2 + q_y^2 + q_z^2} \cdot \frac{\sum_{\alpha} \frac{\delta(q_{\alpha} - k) + \delta(q_{\alpha} + k)}{2}}{\alpha} dq_x dq_y dq_z \\
 &= - (\cosh k_x + \cosh k_y + \cosh k_z) \\
 &= 3 + \frac{3}{2} k^2 (x^2 + y^2 + z^2)
 \end{aligned}$$

Electro-pull back as highest per atoms so naturally strong  
 Metals after here cubic lattices (slow or hard).

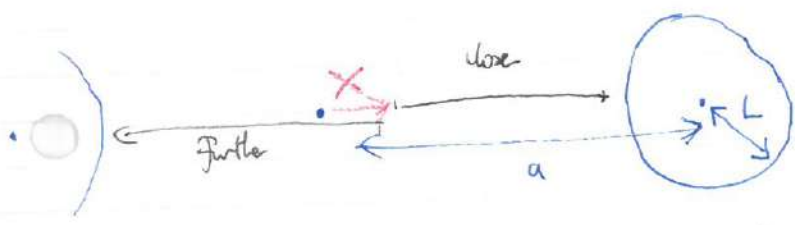
Tight binding:

With  $\infty$  radius electrons on top of atoms so no exp. small.  
 interaction

With finite radius  $L$ ,  
 $d^2V/dR^2$  term small due to exponentially bound wavefunction

$$|\psi_i\rangle = |\phi_0\rangle + \sum_i \frac{\langle \phi_i | V | \phi_0 \rangle}{\epsilon_i - \epsilon_0} |\phi_i\rangle$$

Look at next order terms' anharmonic vibrations  $d^4V/dR^4$  and  $d^2V/dR^2$ :



Expand  $d^2V/dR^2$  around electron cloud, similar to  $d^2V/dR^2$ .

Simple term  $\epsilon = \sum_i (x^2 + y^2 + z^2) |V_{ii}| |\phi_i\rangle + \sum_i (x^2 + y^2 + z^2) |V_{ei}| |\phi_i\rangle$  write out examples  
 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:



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

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