Current approach in DFT + use in real world. 

Problems of DFT and OMC. 

\[ E = \int \frac{1}{2} \left( \frac{\partial^2}{\partial r^2} \right) \right) \]

\[ \frac{\partial^2 E}{\partial r \partial R} = \left( \frac{\partial^2 V_{ii}}{\partial r \partial R} + \frac{\partial^2 V_{ii}}{\partial R \partial r} \right) + \frac{1}{2} \left( \frac{\partial V_{ii}}{\partial R} \right) \frac{\partial^2 V}{\partial R^2} \]

Results for OMC / full shell 

Crystals (draw lattice) 

First order form: 

\[ V = \sqrt{(2-x)^2 + y^2 + z^2} + \sqrt{(2-x)^2 + y^2 + z^2} + \sqrt{x^2 + (y-1)^2 + z^2} + \sqrt{x^2 + y^2 + (z-1)^2} + \sqrt{x^2 + y^2 + (z+1)^2} \]

Check \( \frac{\partial V}{\partial x} = 0 \) by symmetry. 

\[ \frac{\partial^2 V}{\partial x^2} = - \left( \frac{(x-2x)}{(2-x)^2 + y^2 + z^2} \right) + \frac{x-2x}{(x^2 + y^2 + z^2)} + \frac{x}{(x^2 + y^2 + z^2)} \]

Note a surprise or \( \sigma^2 = 0 \) so by symmetry. 

Holds for all radii, shells. 

Holds for cubic, BCC, FCC but not HCP limit has instable. 

Holds for all cubic based structures e.g. NaCl, diamond. 

What about all tense: analyze in NFE and tiny.
Nearly free electron limit: No change in $\mathcal{E}$ so $\frac{\partial \mathcal{E}}{\partial \mathcal{Z}} = 0$

\[
V_e = -\int \frac{\cos h x + \cos h y + \cos h z}{\sqrt{x^2 + y^2 + z^2}} \, dx \, dy \, dz = \int \frac{\cos h x + \cos h y + \cos h z}{\sqrt{x^2 + y^2 + z^2}} \, dx \, dy \, dz
\]

\[
= 3 + \frac{3}{2} \hbar^2 \left( x^2 + y^2 + z^2 \right)
\]

Electrons don't have highest density states so naturally do.

Metals after have cubic lattice (low on bond).
Tight binding:

- Without electron on top of atom so no exp small.
- With finite radius \( R \),
  \[
  \frac{\partial^4 V}{\partial r^4} \text{ term small due to separability localisation.}
  \]
  - Only next order terms \( \frac{\partial^3 V}{\partial r^3} \) and \( \frac{\partial^5 V}{\partial r^5} \):

Expand \( \frac{\partial^3 V}{\partial r^3} \) around electron cloud, similar to \( \frac{\partial^4 V}{\partial r^4} \).

Simple term \( \sim \exp \) opposite sign \( \sim \exp \) - write our examples looks like \( e \sim \exp \) - simple tight-binding system that is stable?

Looking at more complex crystal structures:

- FCC: 1.36
- BCC: 1.28
- HCP: 1.29

What has this got to do with our stability?

\( \text{Ans: - How calculate energies of these systems?} \)

- Wigner-Seitz vs. Lennard-Jones
- DFT, Born approximation
- HSE: GGA
- \( r \to 0 \) issues?