

$$G(\vec{r}, \vec{r}', t, t') = -i \langle N | \hat{\psi}(\vec{r}, t) \hat{\psi}^\dagger(\vec{r}', t') | N \rangle \Theta(t - t') \\ + i \langle N | \hat{\psi}^\dagger(\vec{r}, t) \hat{\psi}(\vec{r}', t') | N \rangle \Theta(t' - t)$$

\uparrow zero if $t - t' < 0$
 $= 1$ otherwise

for $t > t'$ G describes the propagation of an electron from position \vec{r}' at time t' to position \vec{r} at time t .

for $t' > t$: propagation of hole : delete electron (\equiv create a hole) at (\vec{r}, t) and delete the hole (\equiv fill it with an electron) at (\vec{r}', t') .

Insert $\mathbb{1} = \sum_{s=0}^{\infty} |N's\rangle \langle N's|$

$$G(\vec{r}, t, \vec{r}', t') = -i \sum_s \langle N | \hat{\psi}(\vec{r}) | N+1, s \rangle e^{-i(E_{N+1}^s - E_N)(t-t')}$$

$$\langle N+1, s | \hat{\psi}^\dagger(\vec{r}') | N \rangle \Theta(t-t')$$

$$+ i \sum_s \langle N | \hat{\psi}^\dagger(\vec{r}') | N-1, s \rangle e^{-i(E_{N-1}^s - E_N)(t'-t)}$$

$$\langle N-1, s | \hat{\psi}(\vec{r}) | N \rangle \Theta(t'-t)$$

E_N = ground state of N -electron problem
so far it was called E_0

$$E_s = E_{N+1}^s - E_N; \quad \psi_s(\vec{r}) = \langle N | \hat{\psi}(\vec{r}) | N+1, s \rangle \text{ for } E_s > \mu$$

$$E_s = E_N - E_{N-1}^s; \quad \psi_s(\vec{r}) = \langle N-1, s | \hat{\psi}(\vec{r}) | N \rangle \text{ for } E_s < \mu$$

with μ = chemical potential

Fourier transformation of t -dependence

$$G(\vec{r}, \vec{r}', \omega) = \lim_{\eta \rightarrow +0} \sum_s \psi_s(\vec{r}) \psi_s^*(\vec{r}') \left[\frac{\Theta(E_s - \mu)}{\omega - (E_s - i\eta)} + \frac{\Theta(\mu - E_s)}{\omega - (E_s + i\eta)} \right]$$

The poles are the true excitation energies
This is the bandstructure.

non interacting system

$$h_0 \rightarrow \epsilon_n, \psi_n(\vec{r})$$

$$G_0(\vec{r}, \vec{r}', \epsilon) = \lim_{\eta \rightarrow 0} \sum_n \psi_n(\vec{r}) \psi_n^*(\vec{r}')$$

$$\left[\frac{\theta(\epsilon_n - \epsilon)}{\epsilon - (\epsilon_n - i\eta)} + \frac{\theta(\epsilon_n - \epsilon)}{\epsilon - (\epsilon_n + i\eta)} \right]$$

formally:

$$G_0 = (\epsilon - h_0)^{-1}$$

$$\mathbb{1} = \sum_n \psi_n(\vec{r}) \psi_n^*(\vec{r}')$$

formally we $\sum \frac{\psi_n(\vec{r}) \psi_n^*(\vec{r}')}{(\epsilon - \epsilon_n)}$ can get zero

$$h_0 = \frac{-\hbar^2}{2m} + v(\vec{r}) + v^{\text{Hartree}}(\vec{r})$$

we now write

$$G = [\omega - (h_0 + \Sigma)]^{-1}$$

Σ self energy

non local $\Sigma(\vec{r}, \vec{r}')$

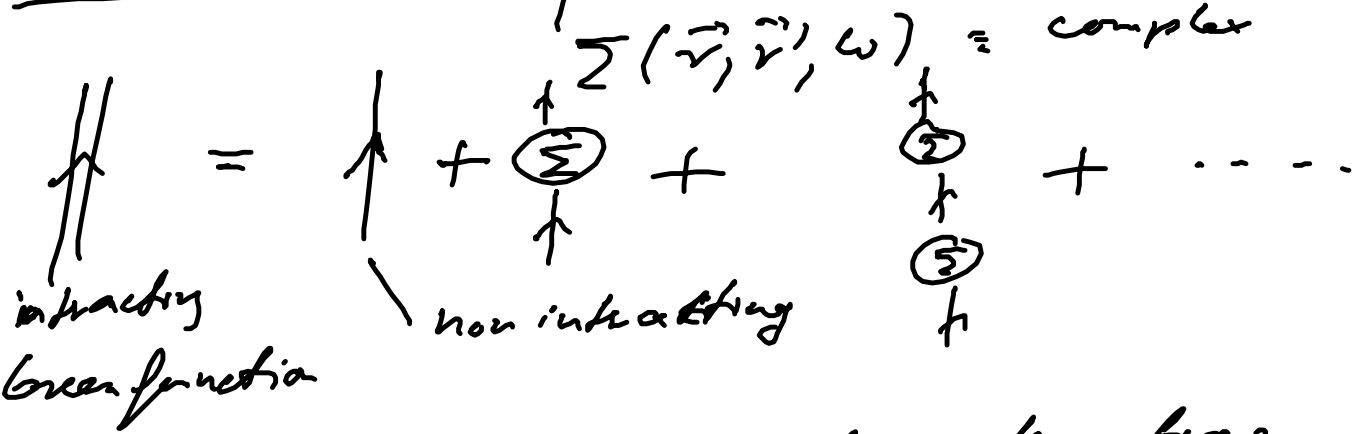
complex

series expansion

$$G = \underbrace{(\omega - h_0)^{-1}}_{G_0} + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots$$

G

$$G = G_0 + G_0 \Sigma G \quad \text{Dyson equ.}$$



$\Sigma \equiv$ describes all q.m. e electron interactions

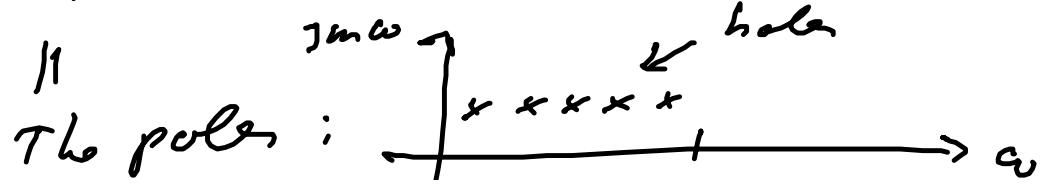
contact with DFT: $h^{KS} = h_0 + v^{xc}$

$$E_s = \langle \psi_s | h_0 + \Sigma | \psi_s \rangle$$

$$\approx \langle \varphi_s^{KS} | h_0 + \Sigma | \varphi_s^{KS} \rangle = \langle \varphi_s^{KS} | h^{KS} - v^{xc} + \Sigma | \varphi_s^{KS} \rangle$$

I find order perturbation theory

$$E_s \approx E_s^{KS} + \langle \varphi_s^{KS} | \Sigma - v^{xc} | \varphi_s^{KS} \rangle$$



only for non interacting particles
 prob. \rightarrow real axis.

$\mu \times \times \times \times \times \leftarrow$ electron,

$\Sigma \equiv$ self-energy \equiv series expansion
 using Feynman diagrams.

L. Hedin: sum a subclass of diagrams

$$\Rightarrow \Sigma \approx G_0 W$$

Screened Coulomb

\uparrow dielectric function
 $\epsilon(\vec{r}, \vec{r}', \omega)$

Will
 be done
 end
 Jan or
 beginning
 of July

6 Cohesion (Bonding) Solids

6.1 Intro

as before: at first: only $T=0K$.
 < At high T : thermal excitation of electrons & vibrations
 had also enter free energy - will be discussed later >

Cohesive energy: $E^{coh} = - \left[\frac{E(\{\vec{R}_0\})}{N} - \frac{E(\{\vec{R}\} \rightarrow \infty)}{N} \right]$

N = number of atoms in the solid

$\{\vec{R}_0\}$ = equilibrium geometry of atoms

$\{\vec{R}\} \rightarrow \infty \equiv$ free, non interacting atoms

Cohesive energy \equiv energy required to separate the solid into its constituents.

$$E_{\text{cohesion}} > 0$$

↑ typically these are neutral atoms, sometimes it may be convenient to use molecules, e.g. N_2 ; or ions, e.g. Na^+ , Cl^- .

important that the reference is stated.

$$E_{\text{cohesion}} \equiv 0.01 \text{ eV} \dots 10 \text{ eV}$$

What can we learn from E_{cohesion} and what not.

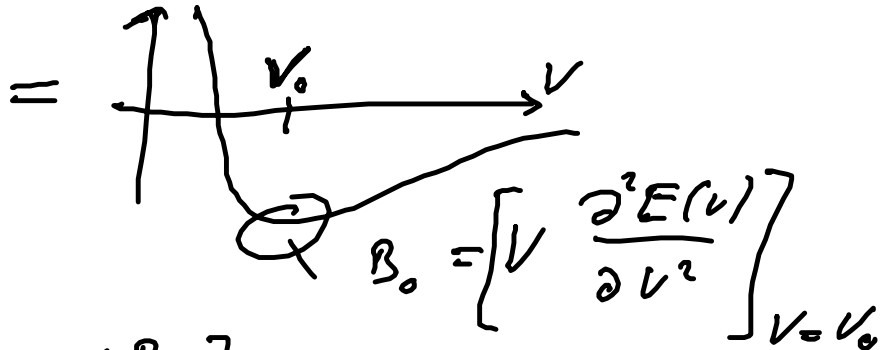
equation of state

$$\frac{E(V)}{N} - \frac{E(V_0)}{N} =$$

equilibrium

Murnaghan equ. of state used to connect DFT at different points — also used by experimentalists to analyze data

$$= \frac{B_0 V}{B_0' (B_0' - 1)} \left[B_0' \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B_0'} - 1 \right]$$



$$B_0' = \left[\frac{dB}{dP} \right]_{V=V_0}$$

$E(V)$ for different crystal structures identifies the stable structure and the equilibrium volume (interatomic distances) via Gibbs construction it tells about phase-transitions.

E^{coh} = how much energy is gained to form a solid.

— stability, hardness, scratch resistance are only indirectly connected to E^{coh} .

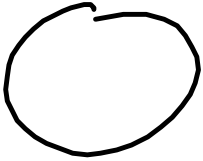
Typically one distinguishes 5 idealized types of bonding

- 1) van der Waals
- 2) ionic
- 3) covalent
- 4) metallic
- 5) hydrogen bonding

no real solid is 100% of one of these types.

Nevertheless ... a useful classification.

6.2. v. d. Waals Bonding



free neutral atom:
average over time \Rightarrow spherical
no long-range electrostatic field

fluctuation give rise
to momentary dipoles.

This induces an
instantaneously a dipole
in a nearby
polarizable system
(e.g. another atom)

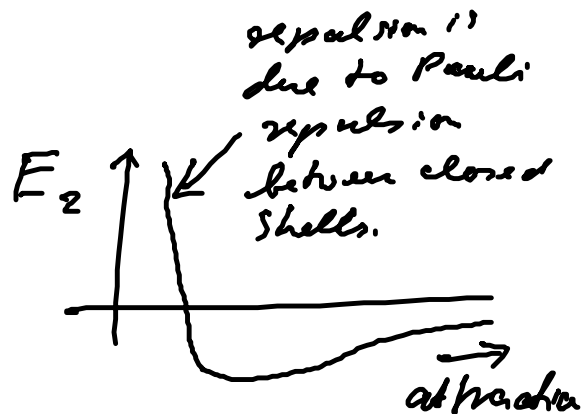
\Rightarrow attraction

DFT with present popular functionals

(that are based on jellium) do not capture these
fluctuations.

Example: Ne, Ar, Kr, Xe

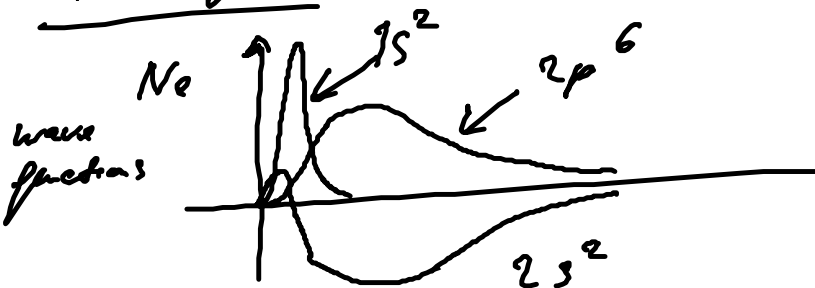
interaction between
two atoms



for all system the long-range attraction
is v. d. Waals

for noble gases this essentially all.

Noble gases: closed shells



$\overbrace{\hspace{10em}}^{\uparrow}$
 half distance to get Ne₂
 \equiv distance when close shell states start to overlap.

attraction: momentary dipole $\vec{P}_1 \rightarrow$ electric field
 $\vec{E} \sim \frac{\vec{P}_1}{r^3}$ this field induces a dipole

\vec{P}_2 in the other atom.

interaction energy $\sim \frac{\vec{P}_1 \cdot \vec{P}_2}{r^3} = \frac{\alpha P_1}{r^6} \sim \frac{1}{r^6}$

$\frac{\alpha P_1}{r^6}$
 polarizability of atom.

repulsive: eqn. \sim exponential
 but not so important
 potential

Lennard-Jones: $E_2^{LJ} = \underbrace{B r^{-12}}_{\text{repulsion}} - \underbrace{A r^{-6}}_{\text{attraction}}$

$= 4 \epsilon \left\{ \left(\frac{\sigma}{r} \right)^{+12} - \left(\frac{\sigma}{r} \right)^{+6} \right\}$

$A = 4 \epsilon \sigma^6$

$B = 4 \epsilon \sigma^{12}$

$\sigma = \left(\frac{A}{B} \right)^{-6}$

$\epsilon = \frac{A^2}{4B}$

ϵ & σ can be obtained from gas phase scattering experiments.

Ne: $\sigma = 2.74 \text{ \AA}$
 $\epsilon = 31 \text{ meV}$

How bad bad DFT-LDA ?

Ne₂

