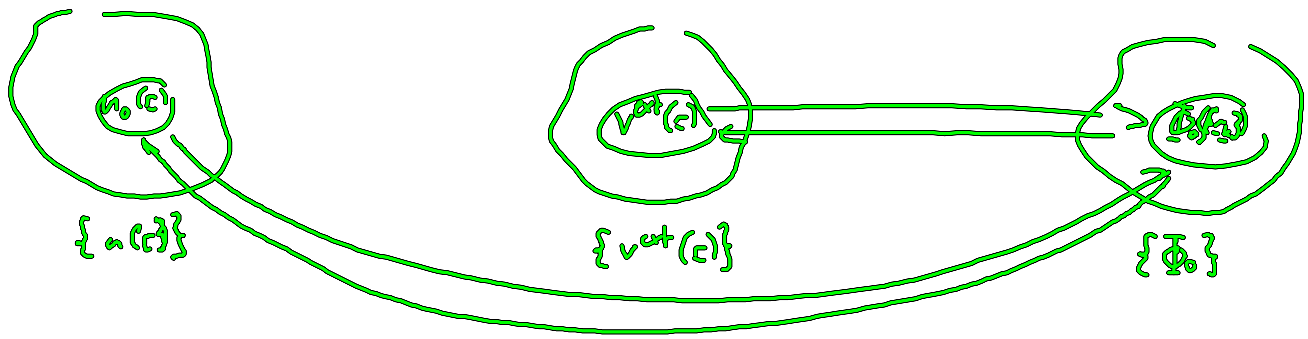
Recap: Hohenberg - Kohn theorem

"Can we get <u>exact</u> physical observables (in principle) without first solving the full $\Phi_0(\{\underline{r}_k\})$?"

A) The ground state density $n_0(\underline{r})$ <u>uniquely</u> determines the ground state w.f. $\Phi[n_0]$, and thus all qm. observables $\langle\hat{O}\rangle = O[n_0(\underline{r})]$



B) Variational principle for densities:

There exists a <u>unique</u> functional $F_{HK}[n]$ such that:

$$E[n] = F_{HK}[n] + \int d^3r\, v^{ext}(\underline{r})\, n(\underline{r})$$

For a <u>given</u> v^{ext}, the g.s. density $n_0(\underline{r})$ minimizes $E[n]$.

Proof of B)

Define $E[n] = \langle \Phi[n] | \hat{T} + \hat{V}^{ext} + \hat{V}^{e-e} | \Phi[n] \rangle$

- $n(\underline{r})$ ground state density of <u>any</u> system
- $\Phi[n]$ corresponds to $n(\underline{r})$, not necessarily to our chosen $v^{ext}(\underline{r})$

Thus $$E[n] = \underbrace{\langle \Phi[n] | \hat{T} + \hat{V}^{e-e} | \Phi[n] \rangle}_{F_{HK}[n]} + \int d^3r\, v^{ext}(\underline{r})\, n(\underline{r})$$

well, it's a <u>functional</u> (not necessarily explicit, but well defined)

Ritz principle :

for our given v^{ext}

$$E[n_0] = \langle \Phi[n_0] | \hat{H}^e | \Phi[n_0] \rangle \overset{\text{Ritz}}{<} \langle \Phi[n] | \hat{H}^e | \Phi[n] \rangle$$

$$= F_{HK}[n] + \int d^3r\, v^{ext}(\underline{r})\, n(\underline{r})$$

indeed variational

4.2 Use of the HK theorem – (i) direct

- HK theorem is exact, but the way to compute $F_{HK}[n]$ right now is to solve for $|\Phi[n]\rangle$ first.
- If we had an explicit formula for $F_{HK}[n]$, we could determine determine $n_0(\underline{r})$ for any given $v^{ext}(\underline{r})$ without ever touching $\Phi_0(\{\underline{r}_i\})$.

Variational principle :

Minimize $E[n]$ with constraint $\int d^3r\, n(\underline{r}) \overset{!}{=} N$

$$\delta \left\{ E[n] - \mu \left[\int d^3r\, n(\underline{r}) - N \right] \right\} = 0 \quad \text{for any variation } \delta n(\underline{r}).$$

Formally $\dfrac{\delta E[n]}{\delta n(\underline{r})} - \mu = 0$

or $v^{ext}(\underline{r}) + \dfrac{\delta F_{HK}[n]}{\delta n(\underline{r})} = \mu$.

... but we need some idea for $F_{HK}[n]$

On the side note:
- the trial $n(\underline{r})$ must somehow be ground state densities of something for this to work
- $F_{HK}[n]$ better be differentiable in that space!

... long formal discussion – Levy, Lieb, many others

4.3 The Homogeneous Electron Gas

Motivation: If we do not wish to compute $\Phi_0(\{\underline{r}_k\})$
for every single $v^{ext}(\underline{r})$, can we approximate
F_{HK} by throwing in $\Phi_0(\{\underline{r}_k\})$ for <u>one</u> particular
system that we know ... and hope that other
$\Phi[n]$ are somehow similar?

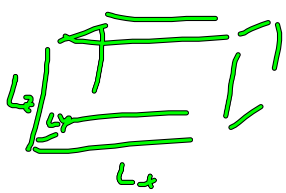
Definition HEG A system where $\langle \Phi_0 | \hat{V}^{ext} + \hat{V}^{e-e} | \Phi_0 \rangle = \text{const.}$

Thus, for g.s. $\hat{H}^e |\Phi_0\rangle = \hat{T} |\Phi_0\rangle = -\sum_{k=1}^{N} \frac{\nabla_k^2}{2} |\Phi_0\rangle$ seperable

N single-particle equations $-\frac{\nabla^2}{2} \varphi_k(\underline{r}) = \epsilon_k \varphi_k(\underline{r})$ – how to solve?

Effective non-interacting particles in infinitely extended const potential:

Assume periodic boundary conditions over a finite volume:



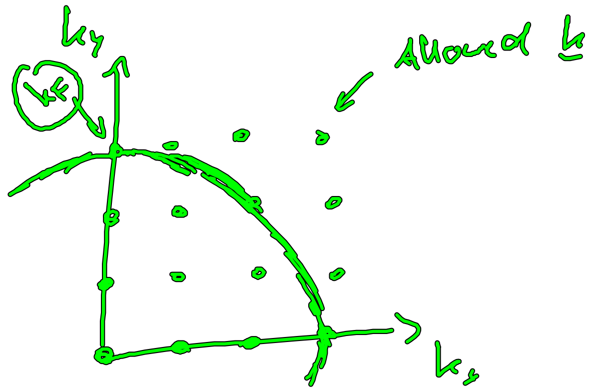
$$\varphi(\underline{r}) = \varphi(\underline{r} + L_x \underline{e}_x)$$
$$L_y \underline{e}_y$$
$$L_z \underline{e}_z$$

$$\varphi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{V_{box}}} e^{i \underline{k} \underline{r}} \quad ; \quad \epsilon(\underline{k}) = \frac{k^2}{2} \qquad V_{box} = L_x \cdot L_y \cdot L_z$$

and $\underline{k}$ quantized: $k = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right)$

n_x, n_y, n_z integer.

In $\underline{k}$ space, the number of allowed $\underline{k}$ points is now <u>countably</u> finite



Effective "volume" per k-point is $\frac{(2\pi)^3}{V_{box}}$

Fill in electrons ($N\ e^-$ in V_{box}):

- Each state can only be filled by 2 electrons (non-spin-polarized HEG)
- $\epsilon(\underline{k}) \equiv \epsilon(|\underline{k}|)$

$\rightarrow$ fill a sphere in $\underline{k}$ space up to some max. radius k_F (Fermi momentum)

Count:
$$N \overset{!}{=} 2 \cdot \frac{4}{3}\pi k_F^3 \Big/ \frac{(2\pi)^3}{V_{box}} = \frac{1}{3\pi^2} k_F V_{box}$$

$$\Rightarrow k_F = \sqrt[3]{3\pi^2 \frac{N}{V_{box}}} = \sqrt[3]{3\pi^2 n}$$

Likewise:
$$\epsilon_F := \epsilon(k_F) = \frac{(3\pi^2 n)^{2/3}}{2}$$

Kinetic energy:
$$T_{HEG}[n] = -\sum_{k=1}^{N} \int d^3r\, \varphi_k^*(\underline{r}) \frac{\nabla^2}{2} \varphi_k(\underline{r})$$

$$= 2 \cdot \int_0^{k_F} d^3k \frac{V_{box}}{(2\pi)^3} \frac{1}{V_{box}} e^{-i\underline{k}\underline{r}} e^{i\underline{k}\underline{r}} \cdot \frac{k^2}{2}$$

$$= \frac{1}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 dk\, k^2$$

$$= \frac{1}{5\pi^2} \cdot \frac{1}{2} k_F^5 = \frac{1}{2} \cdot \frac{1}{5\pi^2} \cdot \underline{(3\pi^2 n)^{5/3}}$$

Original Thomas-Fermi Idea (1927)

1. Use $T_{HEG}[n]$ as an "energy functional" for any system

Rewrite T as an energy density:

$$T[n] \approx \frac{1}{V_{box}} \int d^3r \; n(\underline{r}) \cdot t_{HEG}[n]$$

for any $n(\underline{r})$

kin. energy density of the HEG at any point.

$$\rightarrow t_{HEG}[n] = \frac{1}{2} \cdot \frac{3}{5} \, (3\pi^2)^{2/3} \cdot n^{2/3}$$

(2) Approximate $\langle \Phi[n] | \hat{V}^{e-e} | \Phi[n] \rangle$ by $\frac{1}{2} \int d^3r \, d^3r' \, \frac{n(\underline{r}) \, n(\underline{r}')}{|\underline{r} - \underline{r}'|}$

(Hartree term ~ class. electrostatics)

$\rightarrow$ for a general system $n(\underline{r})$: $T_{TF}[n]$

"local-density approximation" (to T)

Problems: 1) Approximate a large term $T[n]$

2) Electron correlation (incl. exchange, self-interaction) has gone missing.

Nevertheless:

$$\delta \left\{ E_{TF}[n] - \mu \left[\int d^3r \, n(\underline{r}) - N \right] \right\} = 0 \quad \text{for approx. } n_0(\underline{r})$$

$(n_{TF}(\underline{r}))$

Variation: $\delta T[n] = T[n + \delta n(\underline{r})] - T[n(\underline{r})]$ $\qquad [f(n) = n \cdot t_{HEG}[n]]$

$$\overset{TF}{=} \int d^3r \left[f(n(\underline{r}) + \delta n(\underline{r})) - f(n(\underline{r})) \right]$$

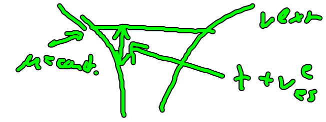
$$\overset{Taylor}{=} \int d^3r \left[f(n(\underline{r})) + \delta n(\underline{r}) \left.\frac{\partial f}{\partial n}\right|_{n(\underline{r})} - f(n(\underline{r})) \right] =$$

$$= \int d^3r \; \delta n(\underline{r}) \left.\frac{\partial f}{\partial n}\right|_{n(\underline{r})}$$

so if $T[n] = \int d^3r \, f(n(\underline{r}))$, then $\frac{\delta T[n]}{\delta n(\underline{r})} = \left.\frac{\partial f}{\partial n}\right|_{n(\underline{r})}$

For TF, $f(n) = \frac{1}{2} \cdot \frac{3}{5} \cdot (3\pi^2)^{2/3} \cdot n^{5/3} \rightarrow \frac{\partial f}{\partial n} = \frac{1}{2} \cdot (3\pi^2)^{2/3} \cdot n^{2/3}$

and $\left[\frac{1}{2} (3\pi^2 n(\underline{r}))^{2/3} + V^e_{es}(\underline{r}) + v^{ext}(\underline{r}) - \mu \right] = 0$



Thomas-Fermi Equation for $n(\underline{r})$ - can solve self-consistently.

- ok for some simple metals
- atoms lose shell structure
- "atoms do not bind"

4.4 The Kohn-Sham Equations - "Exact" effective single particle formalism

Interacting $\hat{H}^e = \hat{T} + \hat{V}^{nuc} + \hat{V}^{e-e}$

Hohenberg-Kohn theorem:

$$E_0 = E[n_0] = \underbrace{T[n_0] + V^{ee}[n_0]}_{F_{HK}[n_0]} + \int d^3r\, v^{nuc}(\underline{r})\, n_0(\underline{r})$$

$$= T[n_0] + \int d^3r\, v^{nuc}(\underline{r})\, n_0(\underline{r}) + \frac{1}{2}\int d^3r\, d^3r' \frac{n_0(\underline{r})\, n_0(\underline{r}')}{|\underline{r} - \underline{r}'|}$$

$$+ \tilde{E}_{xc}[n_0]$$

Problems: $T[n_0] = -\langle \Phi[n_0] | \sum_{k=1}^{N} \frac{\nabla_k^2}{2} | \Phi[n_0] \rangle$ via $\Phi[n_0]$

large term, must know Φ

$$\tilde{E}_{xc}[n_0] = \frac{1}{2} \langle \Phi_0 | \sum_{\substack{k k' \\ k \neq k'}}^{NN} \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} | \Phi_0 \rangle - \frac{1}{2}\int d^3r'\, d^3r \frac{n_0(\underline{r})\, n_0(\underline{r}')}{|\underline{r} - \underline{r}'|}$$

relatively small but unknown.

Kohn-Sham scheme: Construct a non-interacting system of electrons that yields exactly the same ground state density as the real interacting system.

Non-interacting system $\hat{H}_s = \hat{T} + \hat{V}_s$ $\quad$ V_s: local potential $\sum_{k=1}^{N} v_s(\underline{r}_k)$

HK theorem: There exists a unique Energy functional

$$E_s[n] = T_s[n] + \int d^3r\, v_s(\underline{r})\, n(\underline{r})$$

so that $\delta E_s[n]$ yields the exact g.s. density $n_s(\underline{r})$ to $\hat{H}_s$

For non-degenerate ground state, we know $T_s[n]$

- Solution to $\hat{H}_s$ is single SD:

$$\Phi_s(\{\underline{r}_k\}) = SD\{\varphi_{0k\sigma_k}(\underline{r}_1) \cdot \ldots \cdot \varphi_{0N\sigma_N}(\underline{r}_N)\}$$

with $\left(-\frac{\nabla^2}{2} + v_s(\underline{r})\right) \varphi_{0k}(\underline{r}) = \epsilon_{0k}\, \varphi_{0k}(\underline{r})$

$$n_s(\underline{r}) = \underset{\text{spin}}{2} \sum_{k=1}^{N} |\varphi_{0k}(\underline{r})|^2 \quad , \quad T_s[n] = -\sum_{k=1}^{N} \int d^3r\, \varphi^*_{0k\sigma_k}(\underline{r}) \frac{\nabla^2}{2} \varphi_{0k\sigma_k}(\underline{r})$$

For a given interacting system $\hat{H}^e = \hat{T} + \hat{V}^{nuc} + \hat{V}^{e-e}$,

can we find a non-interacting system that has exactly the same g.s. density? $\quad [n_s(\underline{r}) = \underset{\text{interacting}}{n_0(\underline{r})}]$

Must find suitable $v_s(\underline{r})$!

$$\underset{\text{interacting}}{E[n]} = F_{HK}[n] + \int d^3r\, v^{nuc}(\underline{r})\, n(\underline{r})$$

$$\overset{!}{=} T_s[n] + \int d^3r\, v^{nuc}(\underline{r})\, n(\underline{r}) + \frac{1}{2}\int d^3r\, d^3r' \frac{n(\underline{r})\, n(\underline{r}')}{|\underline{r}-\underline{r}'|} + E_{xc}[n]$$

This defines a piece

$$E_{xc}[n] = \underbrace{F_{HK}[n] + \frac{1}{2}\int d^3r\, d^3r' \frac{n(\underline{r}')\,n(\underline{r}'')}{|\underline{r}-\underline{r}'|} - T_s[n]}_{\text{"everything we do not know"}}$$

- rest of kinetic energy
- Exchange
- correlation
- self-interaction

- Formally exact!
- Hopefully small!

Variational principle:

$$\delta E[n] = E[n+\delta n] - E[n]$$

$$= \delta T_s[n] + \int d^3r\, \delta n(\underline{r}) \left[v^{nuc}(\underline{r}) + 2\cdot\frac{1}{2}\int d^3r' \frac{n(\underline{r}')}{|\underline{r}-\underline{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\underline{r})} \right]$$

$$= \delta T_s[n] + \int d^3r\, \delta n(\underline{r})\, v_s(\underline{r})$$

$$v_s(\underline{r}) = v^{nuc}(\underline{r}) + v_{es}^{e}(\underline{r}) + v_{xc}(\underline{r})$$

$$v_{xc}(\underline{r}) = \frac{\delta E_{xc}[n]}{\delta n(\underline{r})}$$

For $\delta T_s[n]$, the usual functional derivative with effective single-particle orbitals $\varphi_{\alpha_k s_k}(\underline{r})$ of non-interacting Hamiltonian yields

$$\left\{ -\frac{\nabla^2}{2} + v_s(\underline{r}) \right\} \varphi_{\alpha_k s_k}(\underline{r}) = \epsilon_{\alpha_k s_k} \varphi_{\alpha_k s_k}(\underline{r}) \quad \Longleftarrow \quad \boxed{\text{Kohn-Sham Equations}}$$

because we requested $n(\underline{r}) \overset{!}{=} \sum_{k=1}^{N} |\varphi_{\alpha_k s_k}(\underline{r})|^2$

with $v_s(\underline{r})$ through v_{nuc}, v_{es}^{e}, v_{xc} as above.

Thus we have - A way to get $n(\underline{r})$ by hiding everything in $v_{xc}(\underline{r})$

- A way to get $E_{H}[n]$

From here on:

- must find good approx. for $E_{xc}[n]$
- rely on the fact that <u>every</u> interacting density <u>can</u> be represented by a non-interacting density of the form above.

HERE BE DRAGONS.

- for any explicit form of $E_{xc}[n]$ (approximate!) the above point might not be a formal problem.