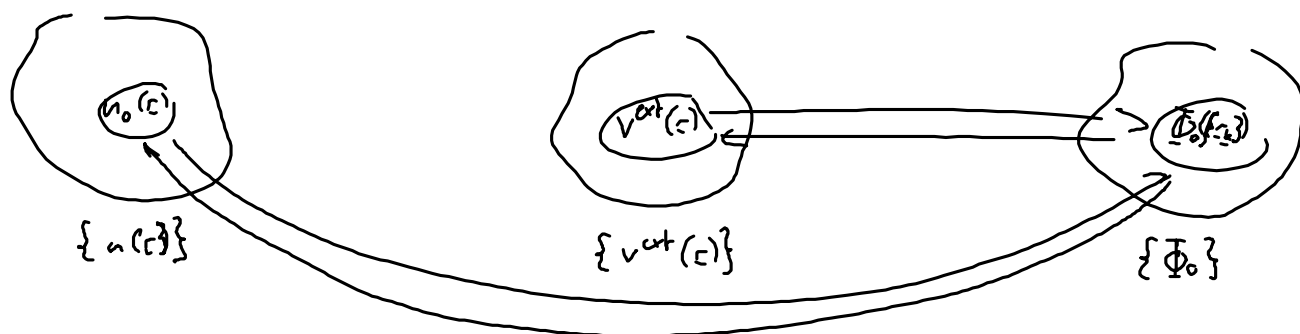


# Recap: Hohenberg-Kohn theorem

"Can we get exact physical observables (in principle) without first solving the full  $\hat{\Phi}_0(\{\epsilon_k\})$ ?"

A) The ground state density  $n_0(\mathbf{r})$  uniquely determines the ground state wf.  $\hat{\Phi}[n_0]$ , and thus all gm. observables  $\langle \hat{O} \rangle = O[n_0(\mathbf{r})]$



B) Variational principle for densities:

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

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

For a given  $v^{\text{ext}}$ , the g.s. density  $n_0(\mathbf{r})$  minimizes  $E[n]$ .

Proof of B)

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

-  $n(\mathbf{r})$  ground state density of any system

-  $\hat{\Phi}[n]$  corresponds to  $n(\mathbf{r})$ , not necessarily to our chosen  $v^{\text{ext}}(\mathbf{r})$

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

well, it's a functional (not necessarily explicit, but well defined)

Ritz principle:

$$E[n_0] \stackrel{\text{for our given } v^{\text{ext}}}{=} \langle \Phi[n_0] | \hat{H}^e | \Phi[n_0] \rangle$$

$$\stackrel{\text{Ritz}}{\downarrow} \langle \Phi[n] | \hat{H}^e | \Phi[n] \rangle$$

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

indeed variational

4.2 Use of the HK theorem - (i) direct

- HK theorem is exact, but the way to compute  $F_{\text{HK}}[n]$  right now is to solve for  $|\Phi[n]\rangle$  first.

- If we had an explicit formula for  $F_{\text{HK}}[n]$ , we could determine  $n_0(\mathbf{r})$  for any given  $v^{\text{ext}}(\mathbf{r})$  without ever touching  $\Phi_0(\{\mathbf{r}_i\})$ .

Variational principle:

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

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

$$\text{Formally } \frac{\delta E[n]}{\delta n(\mathbf{r})} - \mu = 0$$

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

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

On the side note:

- the trial  $n(\mathbf{r})$  must somehow be ground state densities of something for this to work

-  $F_{\text{HK}}[n]$  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  $\Phi_0(\{\epsilon_k\})$  for every single  $v^{\text{ext}}(\underline{r})$ , can we approximate  $F_{HK}$  by throwing in  $\Phi_0(\{\epsilon_k\})$  for one particular system that we know ... and hope that other  $\Phi[\epsilon]$  are somehow similar?

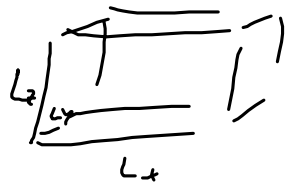
Definition HEG A system where  $\langle \Phi_0 | \hat{V}^{\text{ext}} + \hat{V}^e | \Phi_0 \rangle = \text{const.}$

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

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

Effective non-interacting particles in infinitely extended const potential:

Assume periodic boundary conditions over a finite volume:



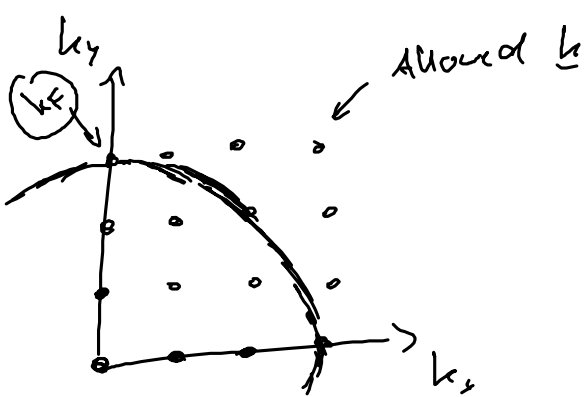
$$\phi(\underline{r}) = \phi(\underline{r} + L_x \underline{e}_x) \\ L_y \underline{e}_y \\ L_z \underline{e}_z$$

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

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

$n_x, n_y, n_z$  integer.

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



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

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

- Each state can only be filled by  
2 electrons, (non-spin-polar HEG)

→ fill a sphere in  $k$  space up to  
some max. radius  $k_F$  (Fermi momentum)

-  $\epsilon(k) \equiv \epsilon(|k|)$

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

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

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

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

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

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

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

Original Thomas-Fermi idea (1927)

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

Rewrite  $T$  as an energy density:

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

↑ for any  $n(\underline{r})$

↑  
Kin. energy density of the HEG  
at any point.

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

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)

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

"local-density approximation" (to  $T$ )

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

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

Nonetheless:

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

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

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

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


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

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

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



Thomas-Fermi Equation for  $n(r)$  - can solve self-consistently.

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

#### 4.4 The Kohn-Shan Equations - "Exact" effective single particle formalism

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

Hohenberg-Kohn theorem:

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

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

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  $\Phi$

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

relatively small but unknown.

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

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

HK theorem: There exists a unique Energy functional

$$E_S[\psi] = T_S[\psi] + \int d^3r V_S(\underline{r}) n(\underline{r})$$

so that  $\delta E_S[\psi]$  yields the exact g.s. density  $n_S(\underline{r})$  to  $\hat{H}_S$

For non-degenerate ground state, we know  $T_S[\psi]$

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

$$\bar{\Phi}_S(\{\underline{r}_k\}) = \text{SD} \{ \phi_{0k\uparrow}(\underline{r}_1) \cdot \dots \cdot \phi_{0N\downarrow}(\underline{r}_N) \}$$

with  $(-\frac{\nabla^2}{2} + V_S(\underline{r})) \phi_{0k}(\underline{r}) = \epsilon_{0k} \phi_{0k}(\underline{r})$

$$n_S(\underline{r}) = 2 \sum_{\substack{k=1 \\ \text{spin}}}^N |\phi_{0k}(\underline{r})|^2, \quad T_S[\psi] = - \sum_{k=1}^N \int d^3r \phi_{0k}^*(\underline{r}) \frac{\nabla^2}{2} \phi_{0k}(\underline{r})$$

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?  $[n_S(\underline{r}) = n_0(\underline{r})]$   
 $\uparrow$   
 1-body

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

✓ interacting

$$E[\psi] = E_{HK}[\psi] + \int d^3r V^{nuc}(\underline{r}) n(\underline{r})$$

$$\stackrel{!}{=} T_S[\psi] + \int d^3r V^{nuc}(\underline{r}) n(\underline{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} + E_{xc}[\psi]$$

This defines a piece

$$E_{xc}[\psi] = F_{HK}[\psi] + \frac{1}{2} \int d^3r d^3r' \frac{h(r)h(r')}{|r-r'|} - T_S[\psi]$$

"everything we do not know"

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

- Formally exact!
- Hopefully small!

Variational principle:

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

$$= \delta T_S[\psi] + \int d^3r \delta\psi(r) \left[ V^{loc}(r) + 2 \cdot \frac{1}{2} \int d^3r' \frac{h(r')}{|r-r'|} + \frac{\delta E_{xc}[\psi]}{\delta h(r)} \right]$$

$$= \delta T_S[\psi] + \int d^3r \delta\psi(r) V_S(r)$$

$$V_S(r) = V^{loc}(r) + V_{es}^e(r) + V_{xc}(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}[\psi]}{\delta h(r)}$$

For  $\delta T_S[\psi]$ , the usual functional derivative with effective single-particle orbitals

$\phi_{\alpha\beta}(r)$  of non-interacting Hamiltonian yields

$$\left\{ -\frac{\nabla^2}{2} + V_S(r) \right\} \phi_{\alpha\beta}(r) = \epsilon_{\alpha\beta} \phi_{\alpha\beta}(r) \quad \Leftarrow \quad \boxed{\text{Kohn-Shan Equations 1}}$$

because we requested  $h(r) \stackrel{!}{=} \sum_{\alpha\beta} |\phi_{\alpha\beta}(r)|^2$

with  $V_S(r)$  through  $V^{loc}$ ,  $V_{es}^e$ ,  $V_{xc}$  as above.

Thus we have - Army to get  $h(r)$  by hiding everything in  $V_{xc}(r)$



- A way to get  $E_{\rho_1}[u]$

From here on:

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

HERE BE DRAGONS.

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