

B. I. Lundqvist, Phys. Kondens. Mat

6, 193 (1967)

6, 206 (1967)

7, 117 (1968)

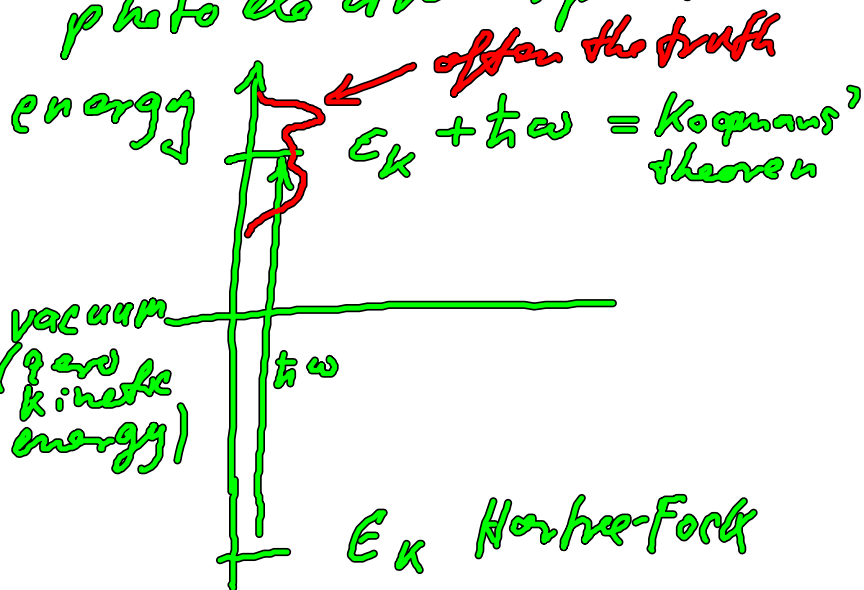
9, 236 (1969)

≈ name?

Botti?

Chem Phys Lett V. 7, (1970)

Sum rule for the total intensity of a photoelectron spectrum:



photoemission spectrum  
 $A(e)$   
 $\int_{-\infty}^{\infty} A(e) e \, de = -E_k$

### 3.6 The $X_\alpha$ - method

see script .. no longer important

### 3.7 Thomas - Fermi Theory

~~... and the concept of screening!~~

significant for understanding and modern concept

Idea  $\left( \frac{-\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(r) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$

$\psi_i =$  needed to build a Slater det.  
 $n(\vec{r}) = \langle \phi | \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) | \phi \rangle = \sum_{i=1}^N |\psi_{i, s_i}(\vec{r})|^2$

Can we simplify the route from

$H^e \rightarrow n(\vec{r})$  ?

jellium  $\psi(\vec{r}) =$  plane waves  
 $\langle \psi_i | \hat{h} | \psi_i \rangle = \frac{\hbar^2}{2m} k^2 + \langle \psi_i | v^{\text{eff}} | \psi_i \rangle = \epsilon_i$

exact for true jellium

$\frac{\hbar^2}{2m} k_i^2 + v^{\text{eff}} = \epsilon_i$

The highest occupied state =  $k_F$

$\frac{\hbar^2}{2m} k_F^2 + v^{\text{eff}} = \epsilon_N = \mu$   
"electron chemical potential"

"nearly jellium"

$k_F(\vec{r}) = \sqrt[3]{3\pi^2 n(\vec{r})}$

$\frac{\hbar^2}{2m} (3\pi^2 n(\vec{r}))^{2/3} + v^{\text{eff}}(\vec{r}) = \mu$   
"const."

Thomas Fermi eqn.

$\Rightarrow$  if we know  $v^{\text{eff}}$  we get  $n(\vec{r})$

$n(\vec{r})$  is a functional of  $v^{\text{eff}}$

$n(\vec{r}) = F_1 [v^{\text{eff}}]$

$$n(\vec{r}) = \frac{1}{3\pi^2} \left( \frac{2m}{\hbar^2} [\mu - v_{eff}] \right)^{3/2}$$

has been useful. However, it's too severe an approx. for realistic materials. Main problem: atoms don't have their shell structure.

### 3.8. Density-Functional Theory

$$H^e \phi = E^e \phi$$

to ease the presentation

1) non magnetic systems

2) non degenerate ground state

what we find is true in general.

spin density

$$n_{\uparrow}(\vec{r}) = \langle \phi_0 | \sum_{i=1}^N \delta_{\uparrow \xi_i} \delta(\vec{r} - \vec{r}_i) | \phi_0$$

$$n_{\downarrow}(\vec{r}) = \dots \delta_{\downarrow \xi_i}$$

$$n_{\uparrow} = n_{\downarrow}$$

$$n(\vec{r}) = n_{\uparrow} + n_{\downarrow}$$

non real yet  
emeritus prof. at  
UC Santa Barbara  
Nobel Prize 1998

### Hohenberg-Kohn Theorem (1965)

$\langle \phi_0 | H^e | \phi_0 \rangle$  is a functional of the electron density

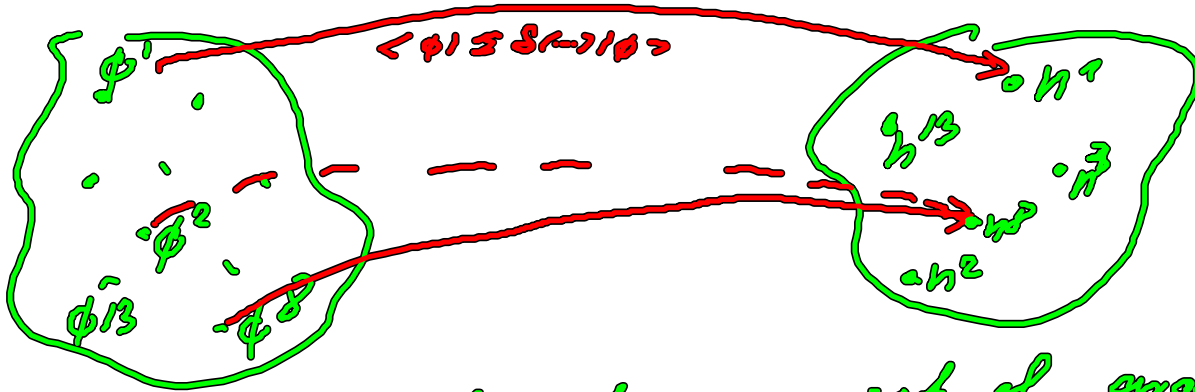
$$E_0^e = E_0[n] = \underbrace{\int v(\vec{r}) n(\vec{r}) d^3\vec{r}}_{\text{interaction of } e \text{ with nuclei}} + F[n]$$

interaction of e with nuclei

↑  
a universal functional =

$$F[n] = \langle \phi_0 | T^e + V^{e-e} | \phi_0 \rangle \quad \text{independent of } v(\vec{r})$$

Proof: obvious  $F$  is functional of  $\phi$   
 $\phi \equiv$  is functional of  $n(\vec{r})$



Set of all non degenerate ground state wave functions.  
 - of all  $N$ -particle hamiltonians  $H^e$

set of ground state densities  $n(\vec{r})$ , with  $\int n(\vec{r}) d^3r = N$

HK: dashed line is not allowed

$\phi \rightarrow n$  function is known

$n \rightarrow \phi$  ?

Proof: "reductio ad absurdum"  
starting point: two different hamiltonians  
 different potentials  $v(\vec{r}) \neq \tilde{v}(\vec{r})$

different:  $v(\vec{r}) - \tilde{v}(\vec{r}) \neq \text{const.}$

Assumption 1:  $H^e$  and  $\tilde{H}^e$  can have the same ground state:  $\phi_0 = \tilde{\phi}_0$

$$\begin{aligned} (\tilde{H}^e - H^e) \phi_0 &= \sum_{i=1}^N [v(\vec{r}_i) - \tilde{v}(\vec{r}_i)] \phi_0 \\ &= (\tilde{E}_0^e - E_0^e) \phi_0 \end{aligned}$$

derived  $\phi_0$

$$\sum_i (v(\vec{r}_i) - \tilde{v}(\vec{r}_i)) = \tilde{E}_0^e - E_0^e$$

$$\underline{v(\vec{r}) - \tilde{v}(\vec{r}) = \text{const.}}$$

not consistent with stat

$\Rightarrow$  Assumption is wrong.

$\Rightarrow$  2 different hamiltonians have different ground state wave functions

Assumption 2  $\phi_0$  and  $\tilde{\phi}_0$  have the same density. definitely  $<$

$$E_0^e = \langle \phi_0 | H^e | \phi_0 \rangle < \langle \tilde{\phi}_0 | H^e | \tilde{\phi}_0 \rangle =$$

$$= \langle \tilde{\phi}_0 | \tilde{H}^e - \sum \tilde{v}(r_i) + v(r_i) | \tilde{\phi}_0 \rangle$$

$$= \tilde{E}_0^e + \langle \tilde{\phi}_0 | \sum v(r_i) - \tilde{v}(r_i) | \tilde{\phi}_0 \rangle$$

$$E_0^e < \tilde{E}_0^e + \int (v(\vec{r}) - \tilde{v}(\vec{r})) n(\vec{r}) d^3\vec{r}$$

do the same for  $\tilde{E}_0^e$

$$\tilde{E}_0^e = \langle \tilde{\phi}_0 | \tilde{H}^e | \tilde{\phi}_0 \rangle < \langle \phi_0 | \tilde{H}_e | \phi_0 \rangle$$

$$\tilde{E}_0^e < E_0^e + \int (\tilde{v}(\vec{r}) - v(\vec{r})) n(\vec{r}) d^3\vec{r}$$

add both equ.

$$\Rightarrow E_0^e + \tilde{E}_0^e < \tilde{E}_0^e + E_0^e$$

↑ wrong!

$\Rightarrow$  Assumption was wrong.

$\Rightarrow$  2 different ground states must have 2 different densities  $\equiv$  the dashed arrow in the figure is never possible.

$$\phi_0 \rightleftharpoons v$$

$$F[v] = \langle \phi_0 | T^e + v^e - e | \phi_0 \rangle$$

is a functional of  $v$

Variational principle for  $\langle \phi | H^e | \phi \rangle$  carries over to

$$E_0 [H]$$

$$E_0^e = \langle \Psi | H | \Psi \rangle_{n(\vec{r})}$$

$$E_0 [H]$$

under constraint is

$$\delta [E_0 [H] - \mu (\int n(\vec{r}) d^3r - N)] = 0$$

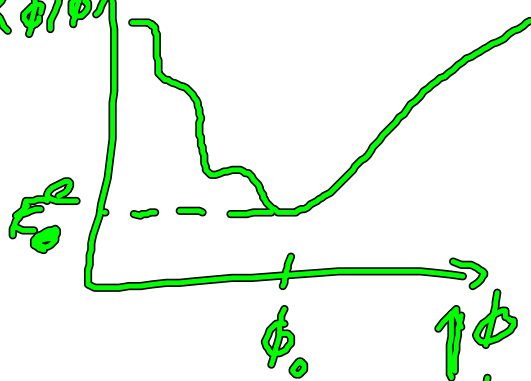
↑ Lagrange parameter

$$\frac{\delta E_0 [H]}{\delta n} = \mu$$

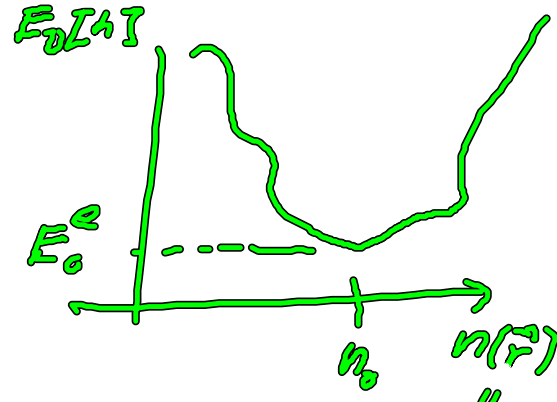
Hohenberg-Kohn equation

we know  $E_0$  is a functional, but don't know how it looks.

$\langle \Psi | H^e | \Psi \rangle$   
 $\langle \Psi | \Psi \rangle$



high-dim.  
 $\phi \approx 10^{23}$   
coordinates



3 coordinates

Kohn & Sham

ref. UC San Diego

$$E_0 [H] = T_s [H] + \int v(\vec{r}) n(\vec{r}) d^3r$$

kinetic energy functional of non interacting electrons

$$+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'$$

$$+ E^{xc}[n]$$

Exchange & correlation

unknown functional

it must correct the self interaction that is contained in  $E_{Hartree}$

+ Pauli correlation

+ Coulomb correlation

$T_S[n] \leftarrow$  we know  $\frac{\delta T_S}{\delta n}$  for jellium (see

Thomas Fermi)  $\sim \sqrt{2\pi n(r)}$

series expansion

$$+ \sim \gamma n$$

$$+ \gamma^2 n$$

$$+ \dots$$

$\leftarrow$  C.F. Weizsäcker

$$\frac{\delta T_S[n]}{\delta n} + v_{eff}(r) = \mu$$

Kohn-Sham equation

looks exactly like Thomas Fermi

$$v_{eff} = \frac{\delta E_{Hartree}}{\delta n} + \frac{\delta E_{xc}}{\delta n}$$



$$= v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + \frac{\delta E^{xc}}{\delta n}$$

equation of non-interacting electrons moving in a potential  $v^{\text{eff}}(\vec{r})$

$$T_s[\underline{n}] \quad n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2$$

solutions of a single particle Schrödinger equ.

$$\Rightarrow \left[ \frac{-\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\vec{r}) \right] \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

Kohn-Sham equ.

so far (essentially) exact

We restricted the allowed densities to those that can be written

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2$$

all physical meaningful density can be approximated with infinitesimal error by

$\Rightarrow$  fine - if  $E^{xc}[n]$  is well behaved.

?

$\frac{\delta E^{xc}}{\delta n}$

For most known approximations

to  $E^{xc}[h]$  there is no problem.

The challenge of DFT is

find a good approximation of  $E^{xc}$  that is practical.

$$T_s[h] = \langle \psi_i | \frac{-\hbar^2 \nabla^2}{2m} | \psi_i \rangle$$

$$\uparrow = \sum_{i=1}^N \epsilon_i - \int \psi^\dagger(r) \psi(r) d^3r.$$

requires  
wave function

problem  $E^{xc}[h]$

if there is another  
Nobel Prize to DFT  
J. Perdew  
A. Becke  
...