

B. I. Lundqvist, Phys. Kondens. Mat

6, 193 (1967)

6, 206 (1967)

7, 117 (1968)

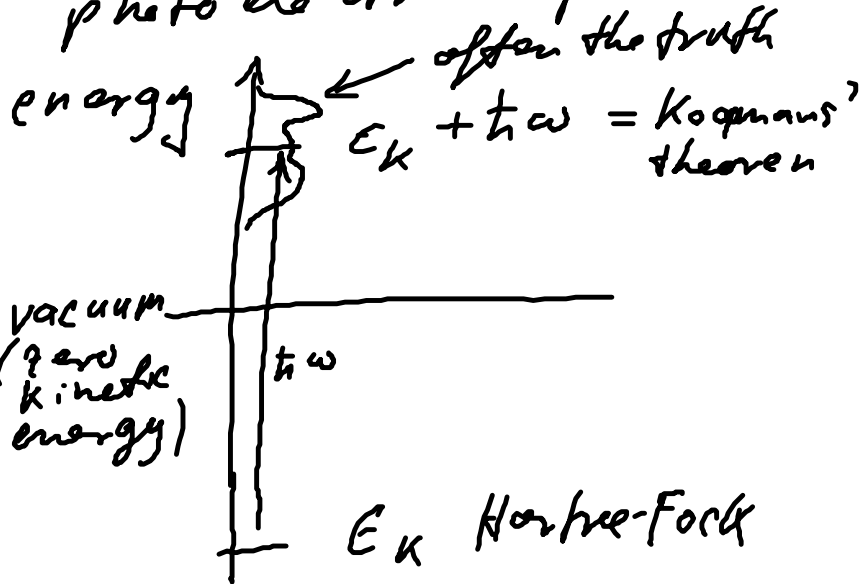
9, 236 (1969)

≈ name?

Botti?

Chem Phys Lett V. 7, (1970)

Sum rule for the total intensity of a photoelectron spectrum:



photoemission spectrum

$A(\epsilon)$

$$\int_{-\infty}^{\infty} A(\epsilon) \epsilon d\epsilon = -\epsilon_K$$

3.6 The X_α - method

see script ... no longer important

3.7 Thomas - Fermi Theory

~~... and the concept of screening~~
significant for understanding and modern concept

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

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

Can we simplify the route from

$\text{He} \rightarrow n(\vec{r})$

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

exact for true jellium

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

The highest occupied state $\equiv k_F$

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

"electron chemical potential"

"nearly jellium"

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

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

Thomas Fermi eqn. "const."

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

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

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

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

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

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

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

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

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

Hohenberg-Kohn Theorem (1965)

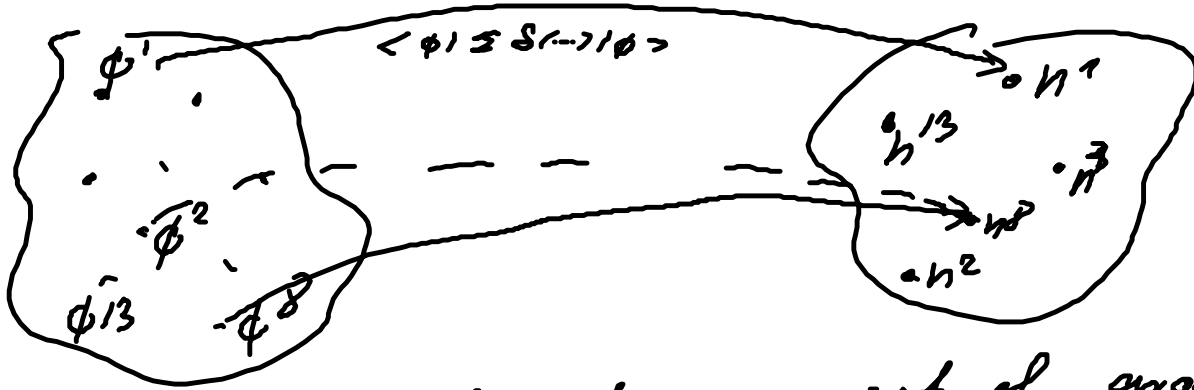
$\langle \phi_0 | H^e | \phi_0 \rangle$ is a functional of the electron density

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

\uparrow
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 ϕ
 $\phi \equiv n$ 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 $\int n(\vec{r}) d^3 = N$

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: $\phi_0 = \tilde{\phi}_0$

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

derived ϕ_0

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

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

not consistent with start

\Rightarrow Assumption is wrong.

\Rightarrow 2 different hamiltonians have different ground state wave functions

Assumption 2 ϕ_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

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

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

add both equ.

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

↑ wrong!

⇒ Assumption was wrong.

⇒ 2 different ground states must have 2 different densities ≡ the dashed arrow in the figure is never possible.

$$\phi_0 \rightleftharpoons n$$

$$F[n] = \langle \phi_0 | T^e + v^{e-e} | \phi_0 \rangle \text{ is a functional of } n$$

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

$$E_0[\psi]$$

$$E_0^e = \min_{\psi(\vec{r})}$$

$$E_0[\psi]$$

under constraint is

$$\delta [E_0[\psi] - \mu (\int \psi(\vec{r})^2 d^3r - N)] = 0$$

↑ Lagrange parameter

$$\frac{\delta E_0[\psi]}{\delta \psi} = \mu$$

Hohenberg-Kohn equation

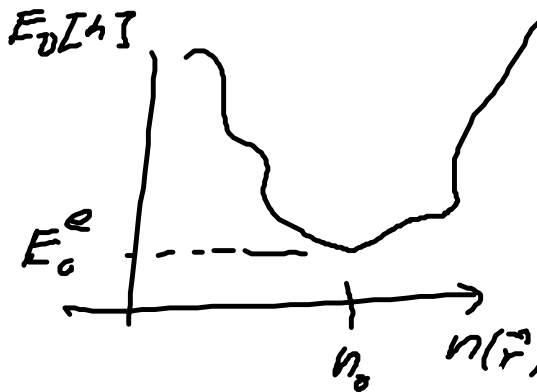
we know E_0 is a functional, but don't know how it looks.

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

$$\langle \psi | \psi \rangle$$



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



||
3 coordinates

Kohn & Sham

prof. UC San Diego

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

kinetic energy functional of non interacting electrons

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

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

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

$$+ n \nabla n$$

$$+ \nabla^2 n$$

$$+ \dots$$

\leftarrow C. F. Weizsäcker

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

Kohn-Sham equation

\uparrow looks exactly like Thomas Fermi

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

$$= v(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + \frac{\delta E^{xc}}{\delta n}$$

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

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

↑ 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

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.

$$T_s[H] = \langle \Psi | \frac{-\hbar^2}{2m} \nabla^2 | \Psi \rangle$$
$$\uparrow = \sum_{i=1}^N \epsilon_i - \int v^{eff}(r) n(r) d^3r.$$

requires
wave function

problem $E^{xc}[H]$

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