

That is all about ψ

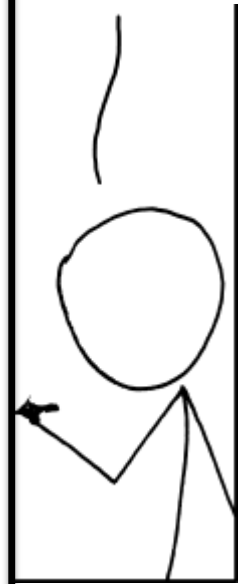
OKAY, ANYONE WHO'S
FEELING LIKE THEY CAN'T
HANDLE THE QUANTUM
HERE SHOULD PROBABLY
JUST THINK NOW



BECAUSE I'M MULTIPLYING
THE WAVEFUNCTION BY ITS
COMPLEX CONJUGATE

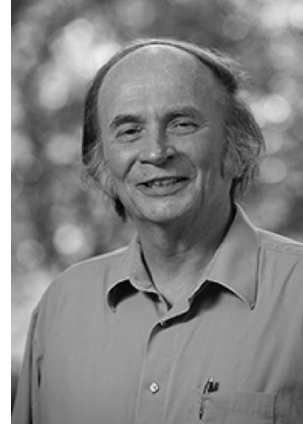
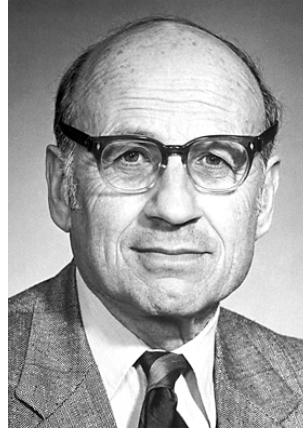
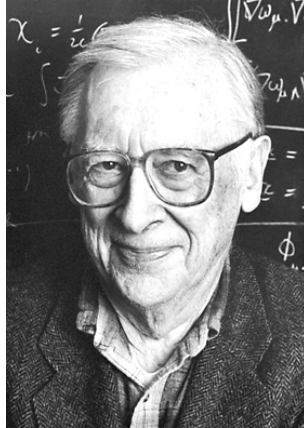


OH! MY GOD
GOT REAL.





Density Functional Theory





Frank Gehry

Radical Inversion

$$\rho = \sum_{i=1}^{n_{occ}} n_i |\psi_i|^2$$

Radical Inversion

$$\rho = \sum_{i=1}^{n_{occ}} n_i |\psi_i|^2$$

Can we formally replace ψ by the observable $\rho(\mathbf{r})$
as the basic variational object?

charge density $\rightarrow \rho(r)$, is an observable quantity
(that is it can be measured)



Alloy Physics

“In the summer of 1963, Kohn arrived in Paris to spend the fall with the research group of Philippe Nozières at the école Normale Supérieure. His plan was to study the effects of the electron–phonon interaction on the optical properties of metals. Instead, he began thinking about how to calculate the total energy of a disordered metal alloy.”

-Physics Today

Inhomogeneous Electron Gas*

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

1. The Density as Basic Variable

We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving

Let's See How

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We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving

Remember \rightarrow the usual wavefunction based approach (the Hartree way) to Schrödinger equation is:

$V_{e-n}(r)$ once defined
 \Downarrow solve Schrödinger equation

we get

$$\psi(r)$$

\Downarrow

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle$$

\Downarrow

properties [observables],
Forces, Force constants, etc.

Contrary to Hartree way, DFT assumes that $\rho(r)$ determines all the ground state properties (which we will see later in theorems).

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Let's define the charge (electron) density which is a function of 3 coordinates

$$\rho(r) = N \int d^3r_2 \int d^3r_3 \dots \int d^3r_N \psi^*(r, r_2, r_3, \dots, r_N) \psi(r, r_2, r_3, \dots, r_N)$$

N = number of electrons

d^3r = volume element

$$\rho(r) = \sum_{i=1}^{n_{occ}} n_i |\psi_i|^2$$

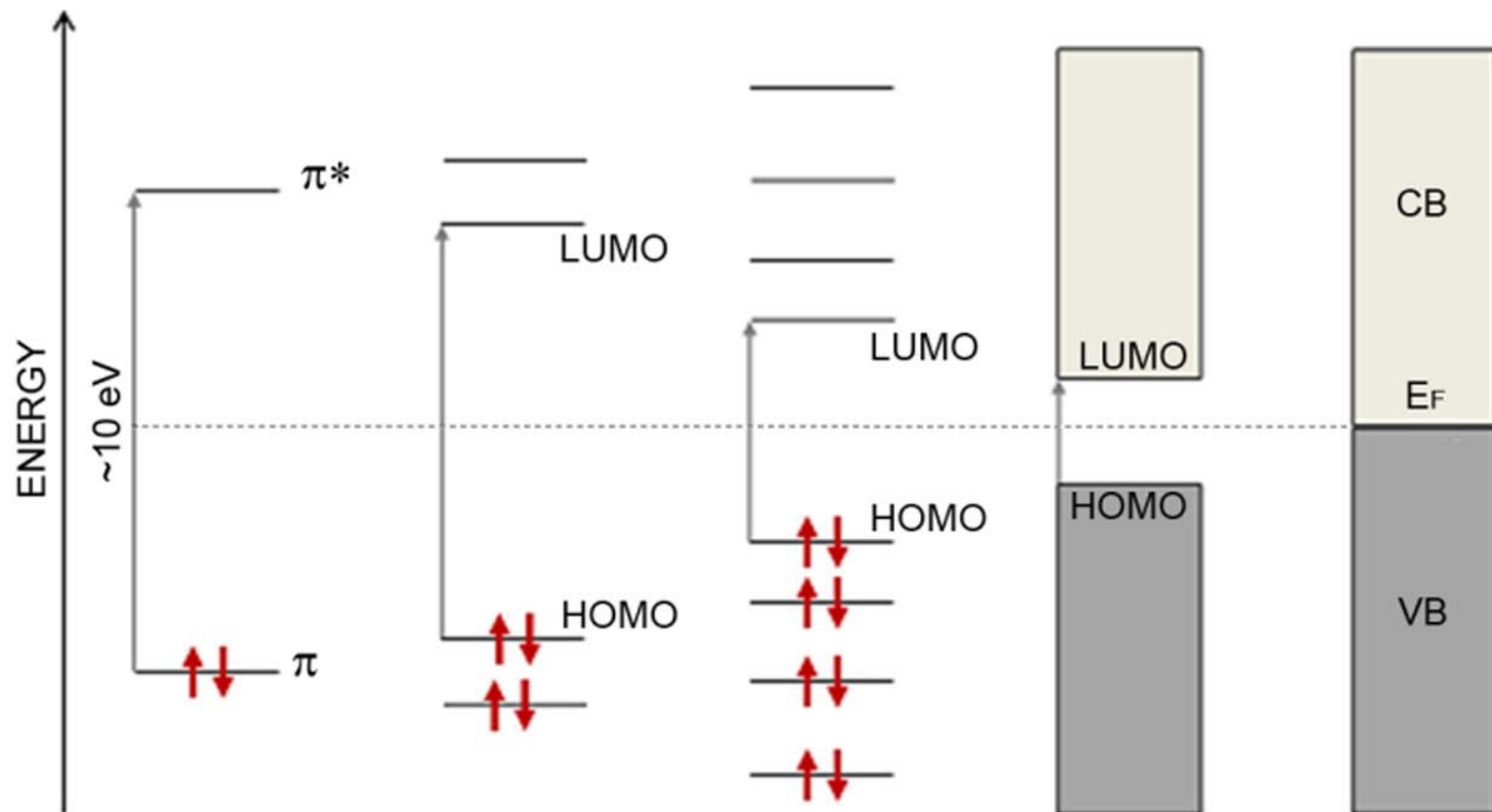
$n_i = 2$ for a total of
 $2n$ electrons; n = occupied
 energy levels.

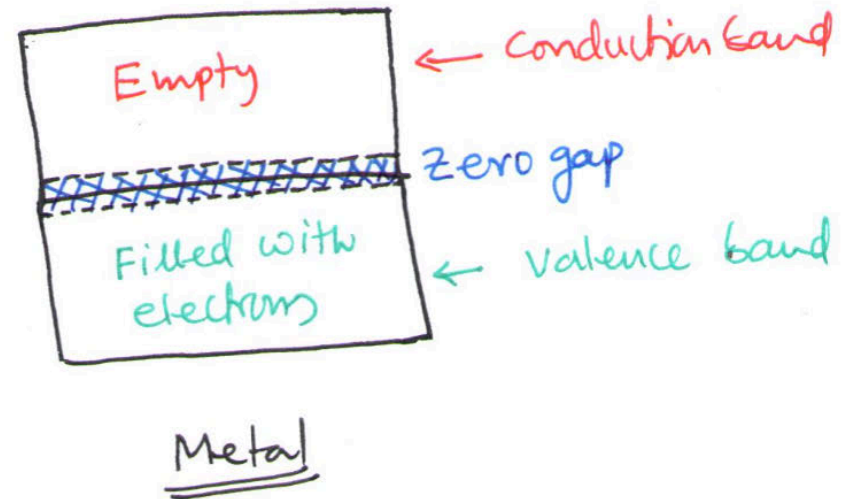
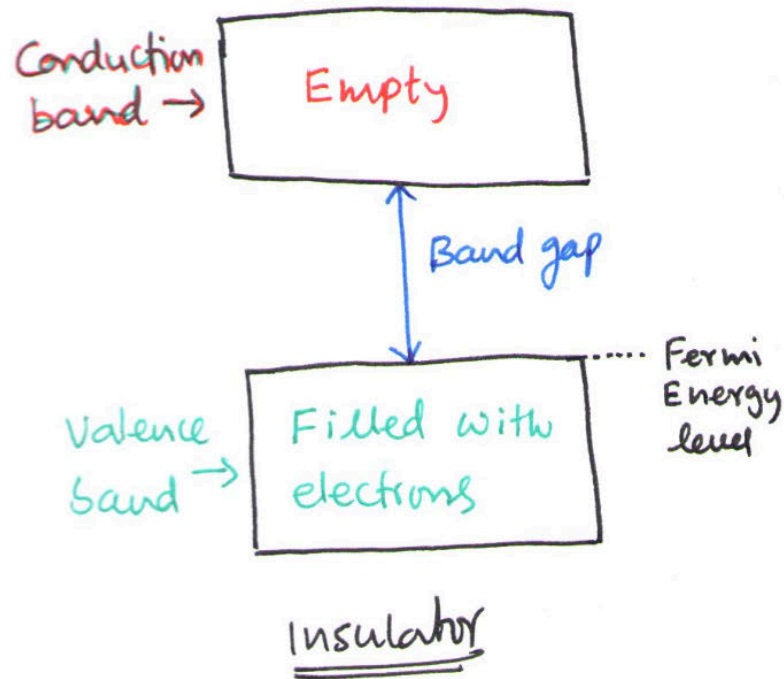
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$\uparrow\downarrow$
 $\uparrow\downarrow$

$2n = 4$
 $2(2) = 4$

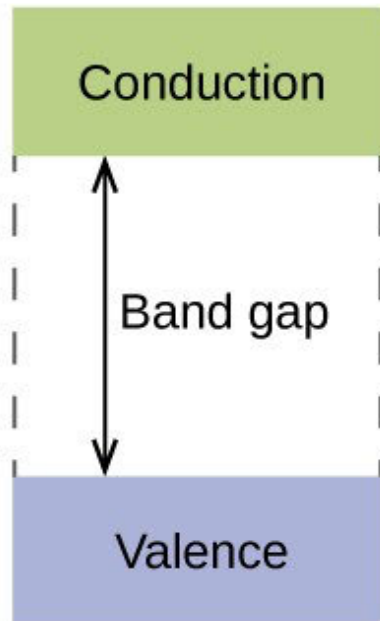
Molecules to Solids.....



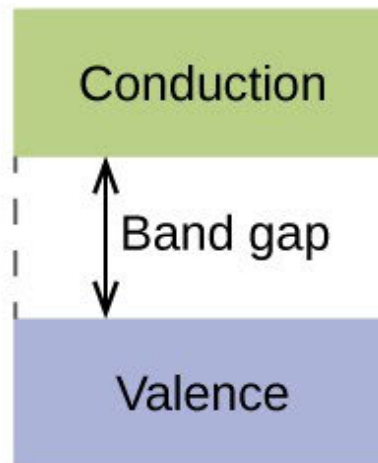


Schematic Band diagram at $T \rightarrow 0\text{K}$

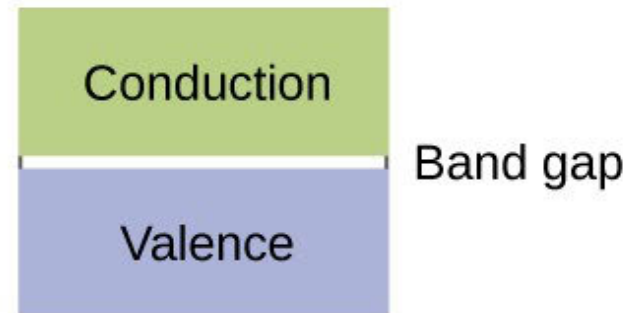
Insulator



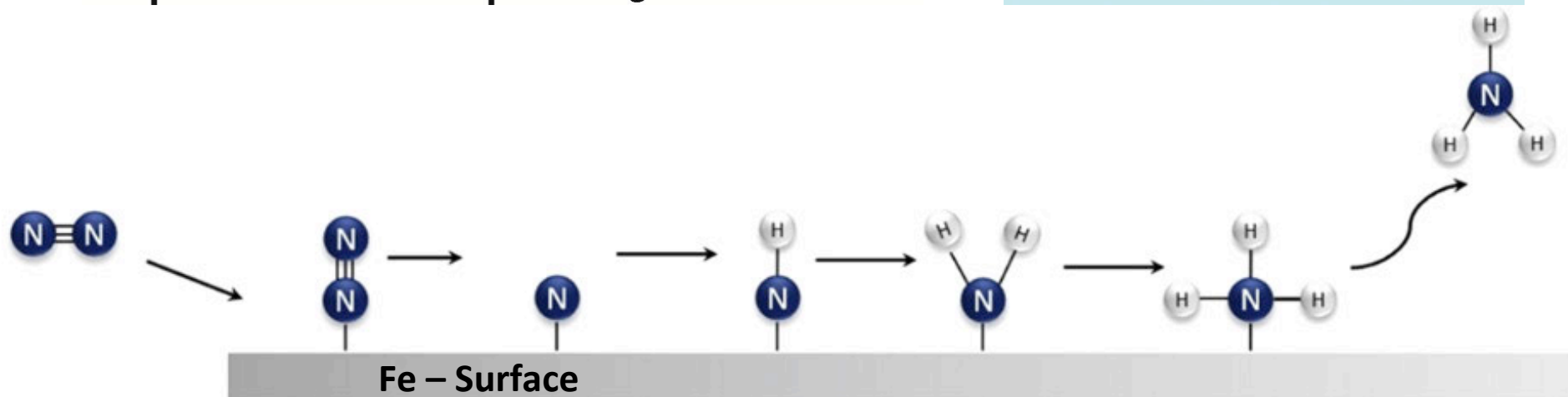
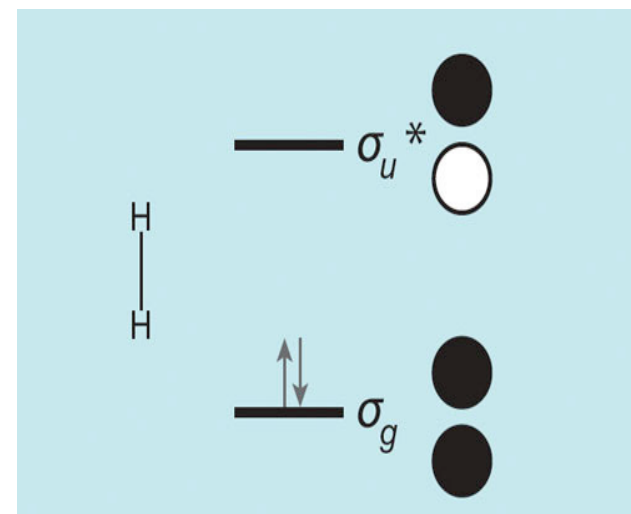
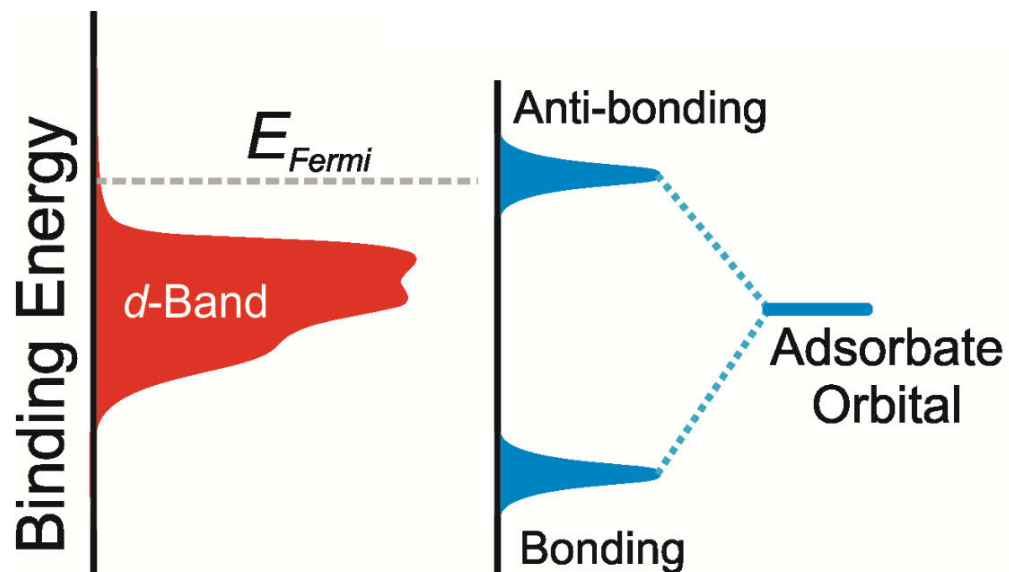
Semiconductor



Conductor



Frontier Orbitals in Chemical Reactions



$$\int \rho(r) d^3r = N$$

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In DFT one begins to understand the many-body matter (the interacting system) by knowing the fact that the ground state energy (E_0) of a system is a unique functional of the charge density $\rho(r)$.

So, what is functional?

Even before functional, Let's see what is a function:

Function: It is a rule which assigns a number $f(x)$ to a number x . In other words it transforms a number to another number.

Let the function $f(x) = x^2$
 $y = f(x)$] for $x = 2$ $\xleftarrow{\text{number to}}$
 $y = f(x) = 4$ $\xleftarrow{\text{another number}}$

Functional: It assigns a number $F[f]$ to a function f .
In other words, a functional is a rule that transforms a function to a number.

For example integral is a function of $f(x)$

$$f(x) = x^2$$

$$\int_0^2 f(x) dx = \int_0^2 x^2 dx = \left. \frac{x^3}{3} \right|_0^2 = \frac{8}{3}$$

function \rightarrow number

Simply functional is a "function of a function"

Now we will see that the ground state energy is a functional of charge density i.e. $E[\rho(r)]$.

Let's Set up a System to get into Density Functional Theory (DFT) and it's notation (Language).

For a single electron moving under nuclear potential (e-n), $V(r)$, the Schrödinger equation can be written as

$$\left[\sum_i^N \left(\frac{-\hbar^2}{2m} \nabla_i^2 + V(r_i) \right) + \sum_{i < j} U(r_i, r_j) \right] \psi(r_1, r_2, \dots, r_N) = E \psi(r_1, r_2, \dots, r_N)$$

old notation \longrightarrow

T_{el}	V_{en}	V_{ee}
\hat{T}	\hat{V}	\hat{U} (only Coulomb part)

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old notation \longrightarrow

\Downarrow	\Downarrow	\Downarrow
T_{el}	V_{en}	V_{ee}
\hat{T}	\hat{V}	\hat{U} (only Coulomb part)

$N \rightarrow$ Number of electrons

$$\hat{U} = \sum_{i < j} U(r_i, r_j) = \sum_{i < j} \frac{q^2}{|r_i - r_j|}$$

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla_i^2$$

$$\hat{V} = \sum_i v(r_i) = \sum_i \frac{Qq}{|r_i - R|}$$

Q is nuclear charge

$Q = Ze$; Z = atomic number

\hat{V} depends on the spatial orientation of the atoms in the system under consideration. That is $v(r)$ distinguishes a system from another system — atom from molecule from solid.

The nuclear position R , is usually fixed as zero of the coordinate system, for single atom.

one may define \hat{V} for a molecule or solid as

$$\hat{V} = \sum_{iK} \frac{Q_K q}{|r_i - R_K|} \quad Q_K = Z_K e$$

K extends over all nuclei in the molecule or solid.

DFT: What it says?

Does it do exactly what it says? i.e. charge density as a basic variational object which determines all the ground state properties of the system.

There are two theorems that talk about what DFT is:

1. Hohenberg-Kohn Theorem-1 [HKT-1]

2. Hohenberg-Kohn Theorem-2 [HKT-2]

And a practical approach towards solving the Schrödinger equation considering the fact that the density as a basic variational object. This practical approach proposed by Kohn and Sham - The Kohn-Sham ansatz.

HKT-1 :

It states that the ground state energy (E_0) of a many-body interacting system is a unique functional of the electron density, $\rho(r)$.

$$E_0 = E[\rho(r)]$$

In simple words the HKT-1 states that the $\rho(r)$ determines $V(r)$ and N . Therefore, knowing $V(r)$ and N , the Hamiltonian can be constructed.

Hamiltonian determines the total energy of the system - by solving Schrödinger equation, $H\psi = E\psi$

And therefore all other ground state properties can be obtained.

HKT-1 workflow:

$\hat{V} = \sum_i v(r_i) = \sum_{i,k} \frac{Q_k q}{|r_i - R_k|}$ $\leftarrow \dots \dots v(r)$ $\dots \dots \rightarrow \int \rho(r) d^3r = N$ (# of electrons)

$\rho(r)$

N

$v(r)$

$$\Downarrow$$
$$\hat{H}$$

$\left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) \right]$ example, for one particle

$$\Downarrow$$

$$H\psi = E\psi$$

$$\Downarrow$$

E and other ground state properties.