

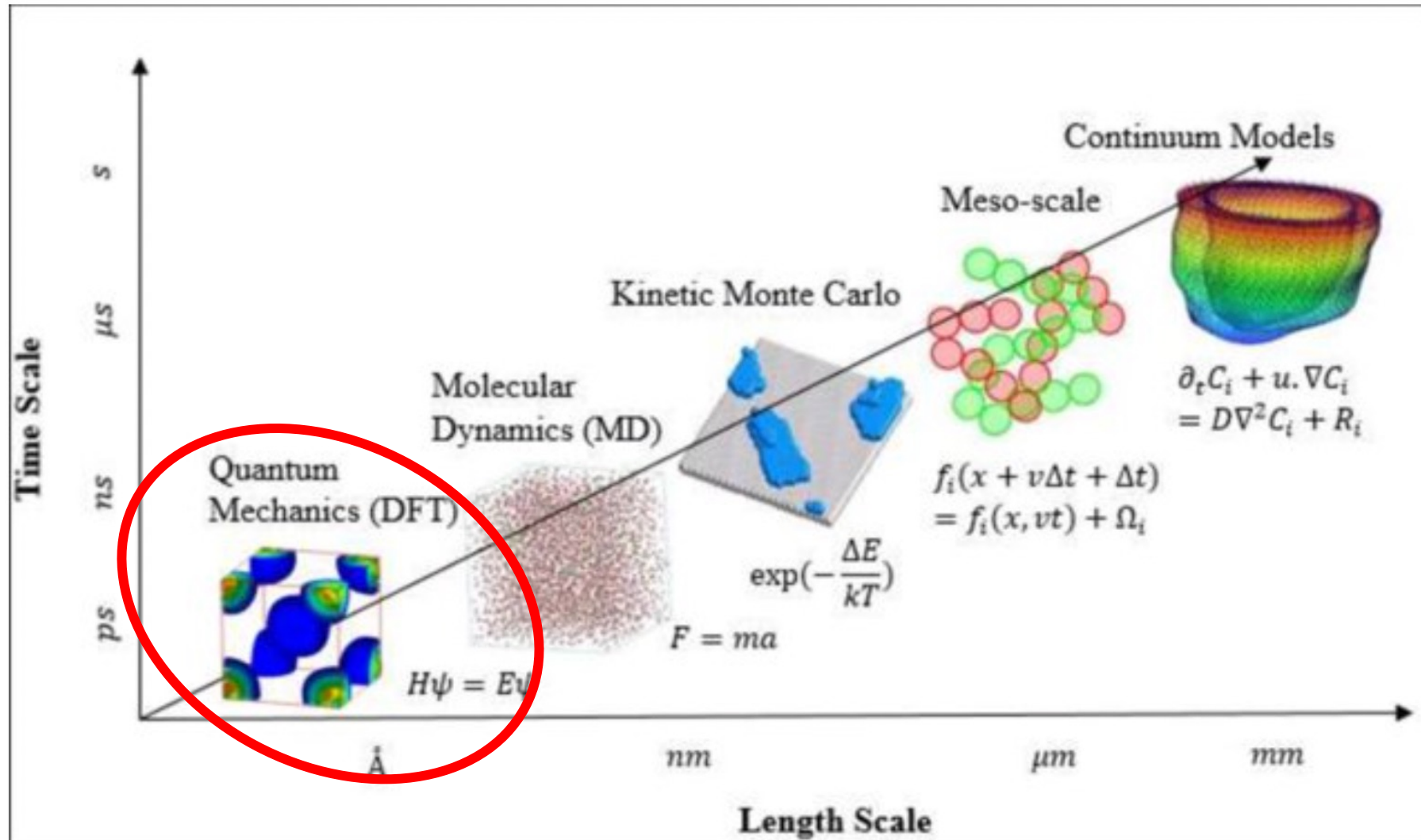
# MT3350 - Materials Modelling

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# DFT based Materials Modelling

- L1- Introduction to DFT
- L2- DFT Based Simulations
- L3- Applications

# Modeling Tools at Different Time and Length Scales



# Comparison of Different Modeling Tools

Computational tool	Maximum sample size (Approximately)	Limitations
DFT	Fit for around 10 nm	Mostly computational resource availability
Molecular Dynamics	Upto several 100 nm	Electron properties cannot be evaluated
Finite Element Methods	Bulk materials	Atomic scale properties cannot be evaluated

# Schrödinger Equation

- In 1926, Erwin Schrödinger published the wave equation, Schrödinger equation.
- Schrödinger equation is heart of quantum mechanics. It helps to models atoms, molecules, solids.
- One simple form of the Schrödinger equation—more precisely, the time-independent, nonrelativistic Schrödinger equation—

$$H(\psi) = E(\psi)$$

- $H$  is the Hamiltonian operator and  $\psi$  is a set of solutions, or eigenstates, of the Hamiltonian. Each of these solutions,  $\psi_n$ , has an associated eigenvalue,  $E_n$ , a real number that satisfies the eigenvalue equation.
- Solving above eigenvalue problem give 2 things;
  1. The quantum states of the system ( eigenfunctions, or wave functions,  $\psi$ )
  2. The energy corresponding to every state ,  $E$

- The detailed definition of the **Hamiltonian** depends on the physical system being described by the Schrödinger equation.
- There are several well-known examples like the particle in a box or a harmonic oscillator where the Hamiltonian has a simple form and the Schrödinger equation can be solved exactly.

- The situation we are interested in where multiple electrons are interacting with multiple nuclei is more complicated. In this case, a more complete description of the Schrödinger is;

$$\hat{H}\Psi = [\hat{T} + \hat{V} + \hat{U}] \Psi = \left[ \underbrace{\sum_{i=1}^N \left( -\frac{\hbar^2}{2m_i} \nabla_i^2 \right)}_{\text{Kinetic energy of each electron}} + \underbrace{\sum_{i=1}^N V(\mathbf{r}_i)}_{\text{Electron-nuclei interaction energy}} + \underbrace{\sum_{i < j}^N U(\mathbf{r}_i, \mathbf{r}_j)}_{\text{Electron-electron interaction energy}} \right] \Psi = E\Psi,$$

$\psi$  is the electronic wave function, which is a function of each of the spatial coordinates of each of the N electrons, so  $\psi(r_1, \dots, r_N)$ , and E is the ground-state energy of the electrons. The ground-state energy is independent of time, so this is the **time-independent Schrödinger equation**.

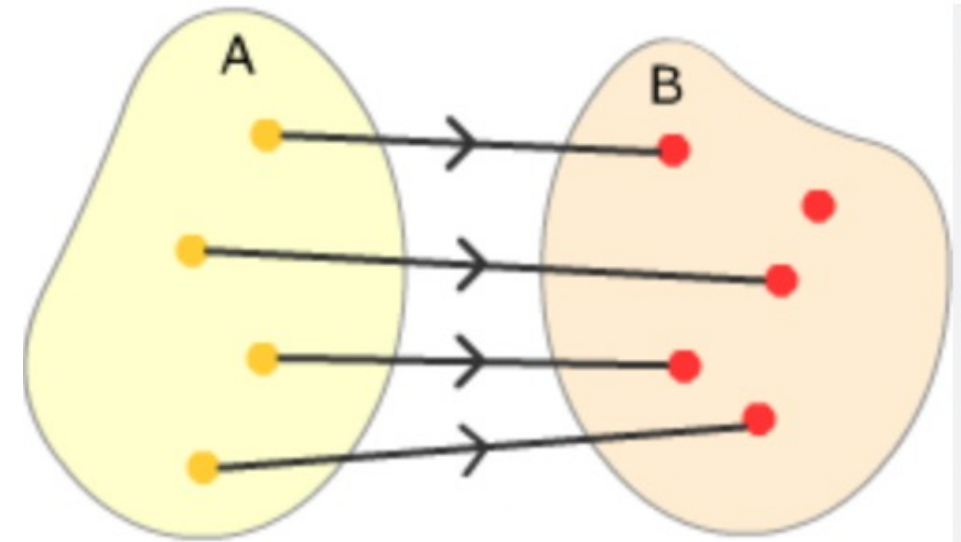
- Although the electron wave function is a function of each of the coordinates of all  $N$  electrons, it is possible to approximate  $\psi$  as a product of individual electron wave functions,  $\psi_1(r) \psi_2(r), \dots, \psi_N(r)$ .
- This expression for the wave function is known as a **Hartree product**, and there are good motivations for approximating the full wave function into a product of individual one-electron wave functions.
- Notice that  $N$ , the number of electrons. If we were interested in a single molecule of  $\text{CO}_2$ , the full wave function is a 66-dimensional function (3 dimensions for each of the 22 electrons ( $6 + (8 \times 2)$ )).
- Before 1960, people knew how to solve Schrödinger equation for H atom. But what about molecules with more atoms? It is too hard to solve.



# Density Functional Theory (DFT)

- DFT is not a theory of nature.
- DFT is a theory to help solve a theory of nature.
- DFT help to solve Schrödinger equation, the theory of nature- help in simplifying Schrödinger equation.
- The entire field of density functional theory rests on **two fundamental mathematical theorems**.

- The **first theorem**, proved by **Hohenberg and Kohn**, is: *The ground-state energy from Schrödinger's equation is a unique functional of the electron density.*
- This theorem states that there exists a one-to-one mapping between the ground-state wave function and the ground-state electron density.



- To appreciate the importance of this result, you first need to know what a “functional” is?
- A functional is closely related to the more familiar concept of a function. A function takes a value of a variable or variables and defines a single number from those variables.
- A simple example of a function dependent on a single variable is;

$$f(x) = x^2 + 1$$

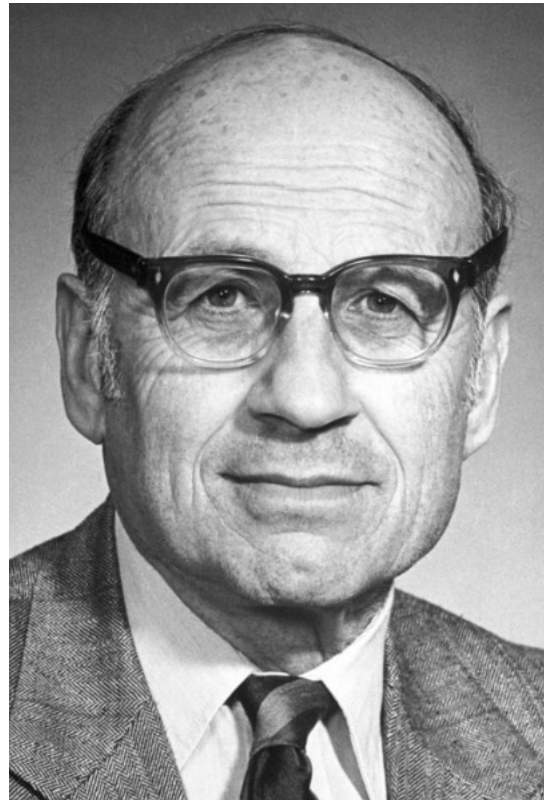
- A functional is similar, but it takes a function and defines a single number from the function. For example,

$$F[f] = \int_{-1}^1 f(x) dx,$$

- $F[f(x)] = 8/3$

- Similarly, we can restate Hohenberg and Kohn's result by saying that the **ground-state energy  $E$  can be expressed as  $E[n(r)]$ , where  $n(r)$  is the electron density.**
- This is why this field is known as **density functional theory**.
- Why is this result important? It means that we can think about solving the Schrödinger equation by finding the electron density, rather than the wave function.
- Here, by “solving the Schrödinger equation” we mean, to say it more precisely, **finding the ground-state energy**. The lowest energy state is known as the **ground state** of the electrons.
- The theorem reduces the problem from all degree of freedoms, DOFs, to a problem with just 3 DOFs.
- Unfortunately, although the first Hohenberg–Kohn theorem rigorously proves that a functional of the electron density exists that can be used to solve the Schrödinger equation, the theorem says nothing about what is the actual functional?

- 1964- Hohenberg- Kohn's Noble price winning theorem : you do not really need to solve the Schrödinger equation in terms of all those DOFs. It's enough to solve in terms of the electron density, which has only THREE DOFs.



Walter Kohn is awarded the Nobel Prize in Chemistry on October 13, 1998 for his development of the density-functional theory.

- The second theorem Hohenberg – Kohn theorem defines an important property of the functional, it is, The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.
- If the “true” functional form were known, then we could vary the electron density until the energy from the functional is minimized, giving us a prescription for finding the relevant electron density.
- This variational principle is used in practice with approximate forms of the functional.

- The Hohenberg–Kohn theorem is in terms of the single-electron wave functions,  $\psi_i(\mathbf{r})$ .

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}],$$

$$E_{\text{known}}[\{\psi_i\}] = \frac{\hbar^2}{2m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{e^2}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{ion}}.$$

$E_{\text{XC}}$ =exchange–correlation functional, and it is defined to include all the quantum mechanical effects that are not included in the “known” terms.

the electron kinetic energies, the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between pairs of electrons, Coulomb interactions between pairs of nuclei

- What is involved in finding minimum energy solutions of the total energy functional?
- This difficulty was solved by **Kohn and Sham**, who showed that the task of finding the right electron density can be expressed in a way that involves solving a set of equations in which each equation only involves **a single electron**.
- The Kohn–Sham equations;

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \overset{\text{Single Electron wave function}}{\psi_i(\mathbf{r})} = \epsilon_i \psi_i(\mathbf{r})$$

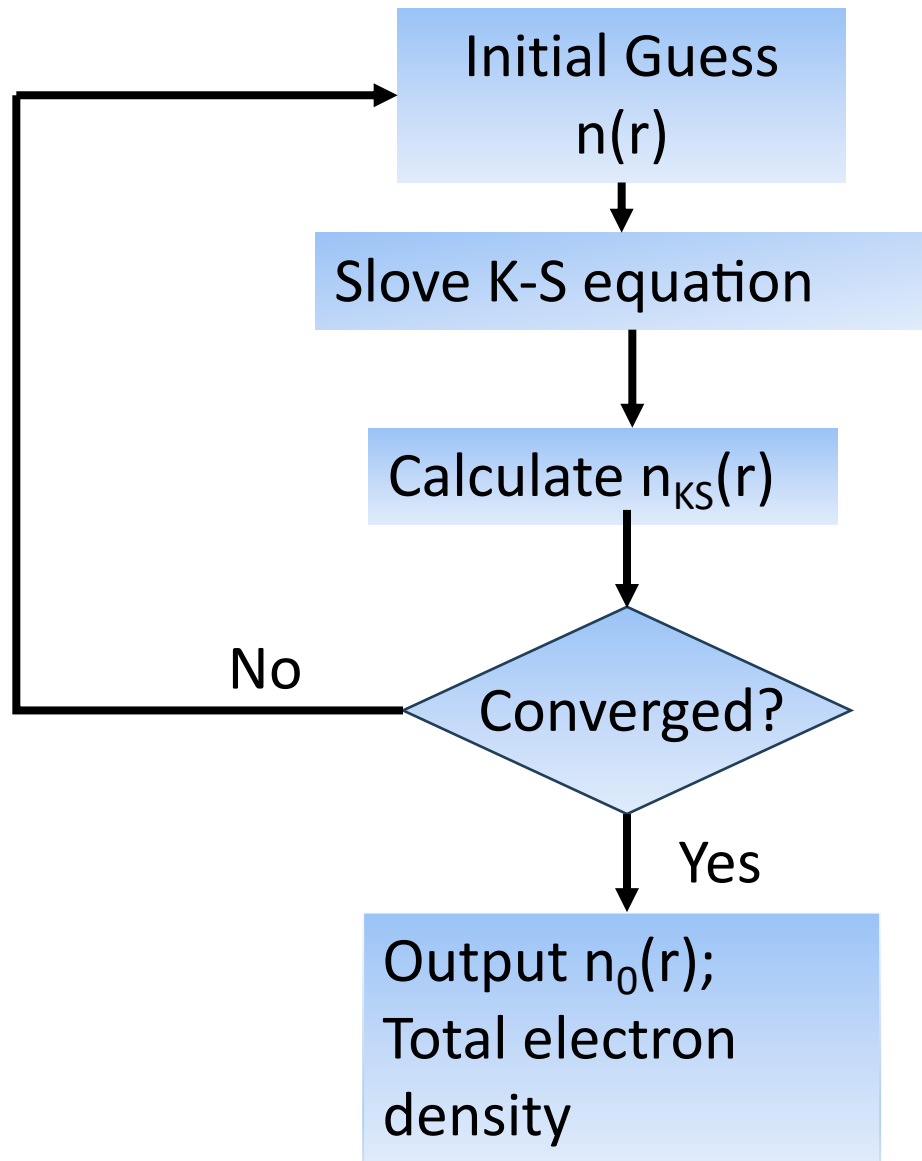
$V_H(\mathbf{r})$  Hartree potential- This potential describes the Coulomb repulsion between the electron being considered in one of the Kohn – Sham equations and the total electron density defined by all electrons in the problem.

$V_{XC}$ = exchange and correlation contributions to the single- electron equations.

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r', \quad V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}.$$



- Do you have a vague sense that there is something circular about our discussion of the Kohn–Sham equations?
  - to solve the Kohn–Sham equations, we need to define the Hartree potential,
  - to define the Hartree potential we need to know the electron density.
  - But, to find the electron density, we must know the single-electron wave functions.
  - to know these wave functions we must solve the Kohn – Sham equations.
- To break this circle, the problem is usually treated in an iterative way.



1. Define an initial, trial electron density,  $n(r)$ .

2. Solve the Kohn-Sham equations defined using the trial electron density to find the single-particle wave functions,  $\psi_i(r)$ .

3. Calculate the electron density defined by the Kohn-Sham single particle wave functions from step 2,  
$$n_{KS}(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

4. Compare the calculated electron density,  $n_{KS}(r)$ , with the electron density used in solving the Kohn-Sham equations,  $n(r)$ . If the two densities are the same, then this is **the ground-state electron density**. If the two densities are different, then the trial electron density must be updated.

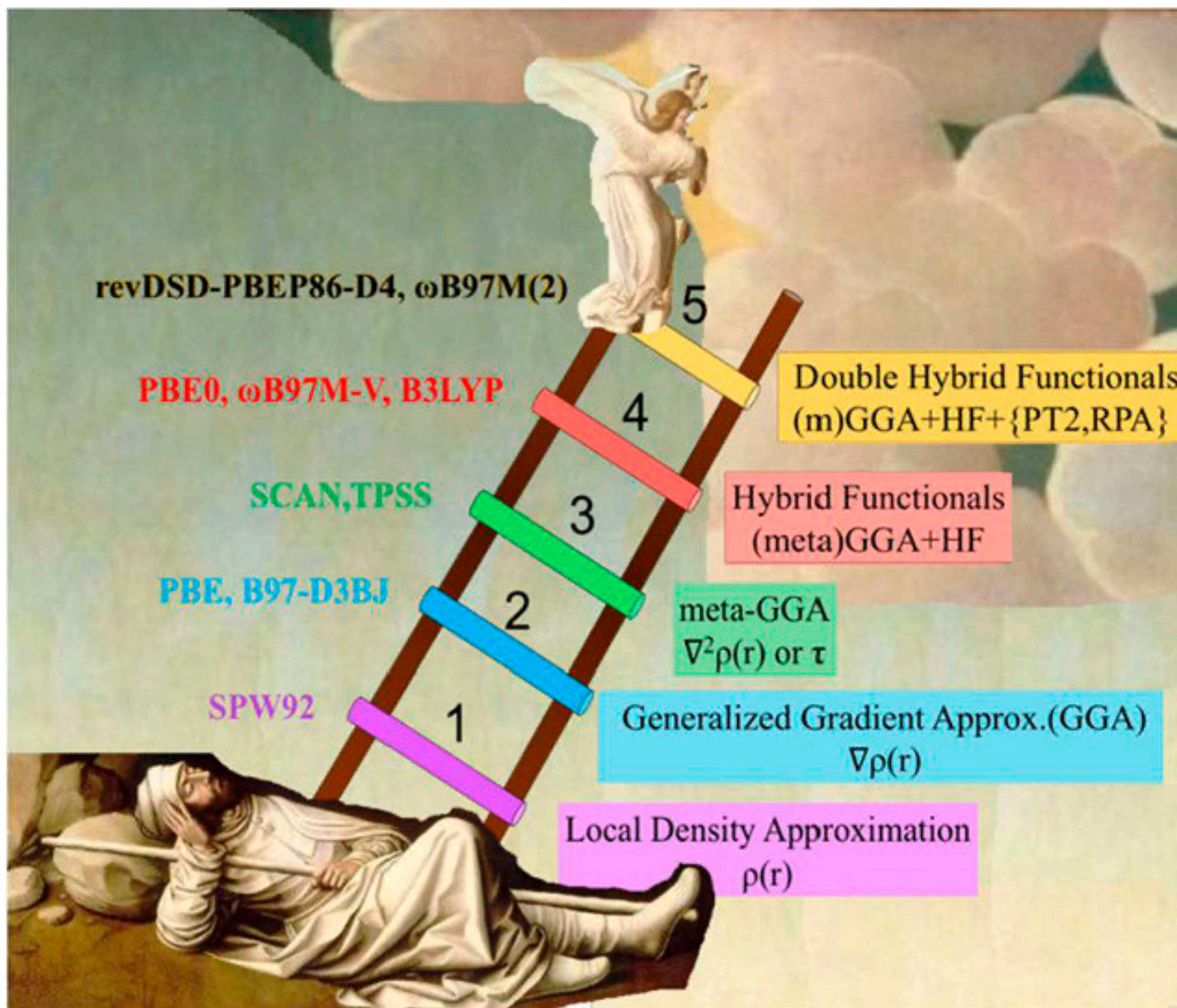
# Exchange – Correlation Functional

- To find the ground-state energy of the Schrödinger equation, is extremely difficult for a many-body problem.
- Although, the results of Kohn, Hohenberg, and Sham showed that the ground state can be found by minimizing the energy of an energy functional, and that this can be achieved by finding a self-consistent solution to **a set of single-particle equations**.
- To solve the Kohn–Sham equations we must specify the exchange–correlation function.

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

*The major problem with DFT is that the exact functionals for exchange and correlation are not known, approximations exist which permit the calculation of certain physical quantities quite accurately.*

– Approximations: LDA, GGA (PW91, PBE)



Jacob's ladder from Hartree world to Chemical accuracy heaven .

Local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA, and hybrid functional can be shown as the well-known