DENSITY FUNCTIONAL THEORY

A brief reminder of what you know already

12 APRIL 2021 I STEFAN BLÜGEL

cecam
Centre Européen de Calcul Atomique et Moléculaire

Mitglied der Helmholtz-Gemeinschaft

MAX DRIVING THE EXASCALE TRANSITION

JÜLICH
Forschungszentrum

QUANTUM MECHANICS

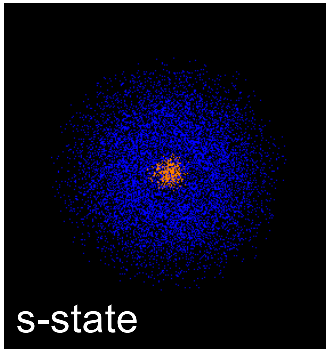
I am sure many of you have solved the Schrödinger equation for 1 electron once analytically

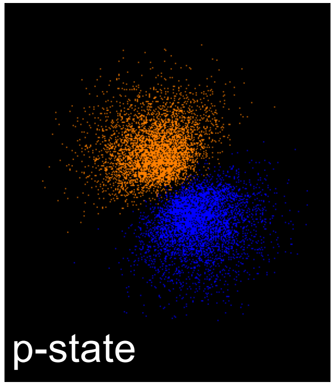
- Schrödinger equation

$$\boxed{\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x)}$$

E. Schrödinger (1926), Annalen der Physik, 361-377

➢ Wavefunction based theory





- First-principles theory

„In physics and other sciences, theoretical work is said to be **from first principles, or *ab-initio***, if it starts directly at the level of established science and **does not make assumptions such as empirical model and parameter fitting**.“

QUANTUM MECHANICS OF MANY ELECTRONS

- 0^{th} Order kinetic approx.
- Adiabatic approximation
- Matter as spatial structure
- Ions at fixed positions

Hamiltonian of many electrons

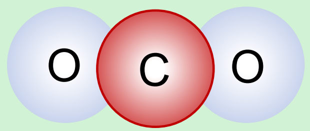
$$H = -\frac{1}{2}\cancel{\sum_{n}^{Ni}\frac{m}{M^n}\Delta^n} - \frac{1}{2}\sum_{j}^{Ne}\Delta_j - \sum_{n,j}^{Ni,Ne}\frac{Z^n}{|\mathbf{R}^n-\mathbf{r}_j|} + \frac{1}{2}\sum_{i\neq j}^{Ne}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \overbrace{\frac{1}{2}\sum_{n\neq n'}^{Ni}\frac{Z^nZ^{n'}}{|\mathbf{R}^n-\mathbf{R}^{n'}|}}^{\text{const.}}$$

Atomic units (Bohr radius $a_0 = \hbar^2/(me^2)$, Hartree energy $= me^4/\hbar^2$)

Solution: Many body wave function

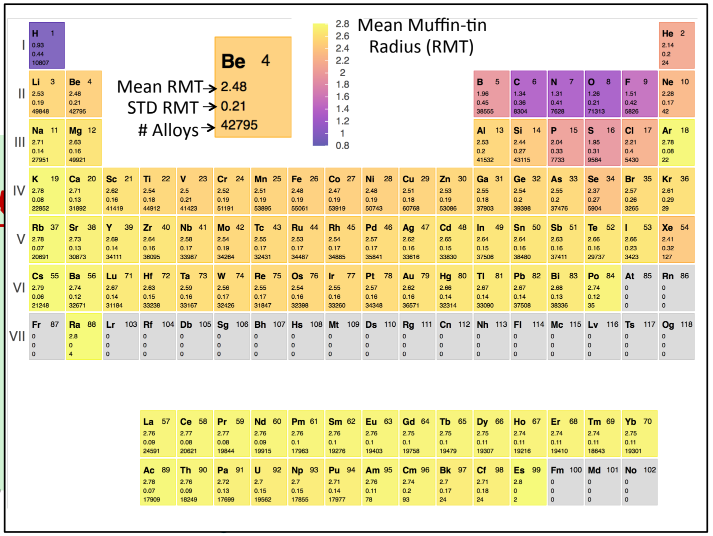
$$\psi(\mathbf{r}_1,\dots,\mathbf{r}_N,\dots) = \psi(\{\mathbf{r}_i\}|\{\mathbf{R}^n\})$$

$\underline{CO_2 \text{ molec}}$



Periodic table of chemical elements

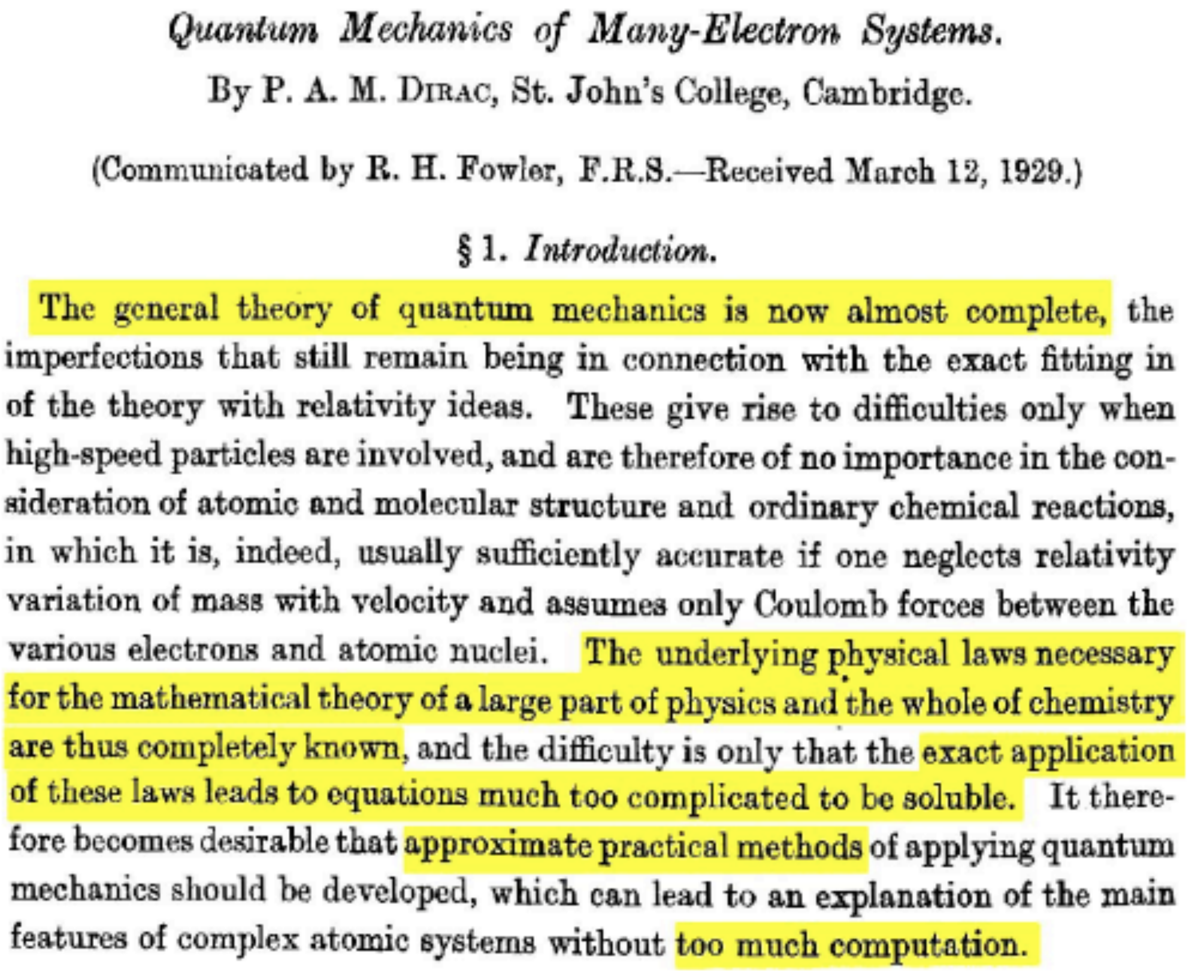
(8 + 6 + 8



MANY-BODY PROBLEM: TOO COMPLICATED TO SOLVE!

Scanned at the American Institute of Physics

P.M.A. Dirac



Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 **(1930)**

APPROXIMATE SOLUTION

Use variational ansatz for unknown wave function

- Rayleigh-Ritz variational principle

$$E = \min_{\psi} \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

Throw in ansatz with strong physical intuition plus flexible functional form and parameters

$$E(\{\vec{R}^n\}) = \min_{\psi} \frac{\langle\psi|H(\{\vec{R}^n\})|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0(\{\vec{R}^n\})$$

- Ansatz: Slater determinant of independent single particle wave function including antisymmetry of many body wave function explicitely

$$\Psi_{\mathrm{Slater}}(\mathbf{x}_1 \ldots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_1(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$\mathbf{x}_i = \mathbf{r}_i \sigma_i$$

$$\psi_i(\mathbf{r}_j \sigma_j) = \phi_{j\sigma}(\mathbf{r}_j)\chi(\sigma_j)$$

J.C. Slater, Phys. Rev. 35, 210 (1930)

John C. Slater

HARTREE-FOCK APPROXIMATION

D.R. Hartree, Proc. Camb. Phil. Soc. 24, 89, 111 (1928)
V. Fock, Z. Physik 61, 126 (1930)

Minimize Energy

$$E = \min_{\psi}\langle\Psi_{\mathrm{Slater}}|H|\Psi_{\mathrm{Slater}}\rangle \quad \text{under constraint that} \quad \langle\psi_i|\psi_i\rangle \quad \forall i \in \mathrm{occ.\ states}$$

$$0 = \frac{\delta}{\delta\psi_i^*(\mathbf{r},\sigma)}\left(\langle\Psi_{\mathrm{Slater}}\,|H|\,\Psi_{\mathrm{Slater}}\rangle - \underbrace{\sum_{i,\sigma}\epsilon_{i,\sigma}\left\{\int dV\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) - 1\right\}}_{\mathrm{Normalisation}}\right)$$

Vladimir Fock

Hartree-Fock Equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{Hartree}}(\mathbf{r}) - V_{\mathrm{ex}}(\mathbf{r}; i\sigma)\right)\phi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\phi_{i\sigma}(\mathbf{r})$$

$$-\sum_{n}^{N_i}\frac{Z^n}{|\mathbf{R}^n - \mathbf{r}|} \qquad \int dV'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \qquad \int dV'\frac{n_2(\mathbf{r}; i\sigma|\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$n_2(\mathbf{r}; i\sigma) = \sum_{i'\sigma'}\frac{\phi^*_{i\sigma}(\mathbf{r})\phi_{i'\sigma'}(\mathbf{r})\phi^*_{i'\sigma'}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')}{\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}$$

- ➢ V_{ex} is a potential that acts only at the state of same spin
- ➢ Solution is a self-consistency problem

THOMAS-FERMI APPROXIMATION

L.H. Thomas, *Proc. Camb. Phil. Soc.* **23** (5), 542 (1927)
Enrico Fermi, *Rend. Accad. Naz. Lincei*. **6,** 602 (1927)
C.F. von Weizsacker, Z. Phys. **96**, 431 (1935)

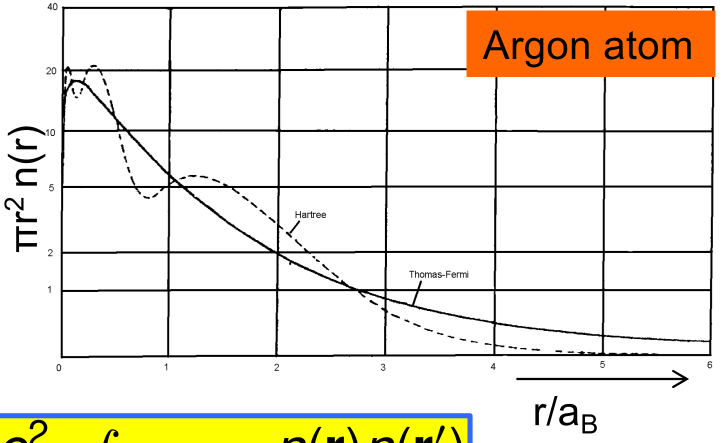
① Interpret total energy as functional of density $E\{n\}$

② Describe kinetic energy in terms of density dependent kinetic energy of homogeneous electron gas. Replace constant density *n* in

$$T = N\frac{3}{5}\frac{\hbar^2 k_F^2}{2m} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}\frac{\hbar^2}{m}V(n)^{\frac{5}{3}}$$

- by slowly varying density *n*(*r*)

$$T\{n(\mathbf{r})\} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}\frac{\hbar^2}{m}\int_{\mathbb{R}^3} d\mathbf{r}\,[n(\mathbf{r})]^{\frac{5}{3}}$$



➢Energy functional

$$E\{n(\mathbf{r})\} = \frac{3}{5}(3\pi^2)^{\frac{2}{3}}\frac{\hbar^2}{2m}\int d\mathbf{r}\,[n(\mathbf{r})]^{\frac{5}{3}} + \int d\mathbf{r}\,V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

DENSITY FUNCTIONAL THEORY

HOHENBERG-KOHN THEOREMS

P. Hohenberg, W. Kohn, *Phys. Rev.* 136, B864 (1964)

Hohenberg und Kohn establish the density as a basic variable in quantum mechanics

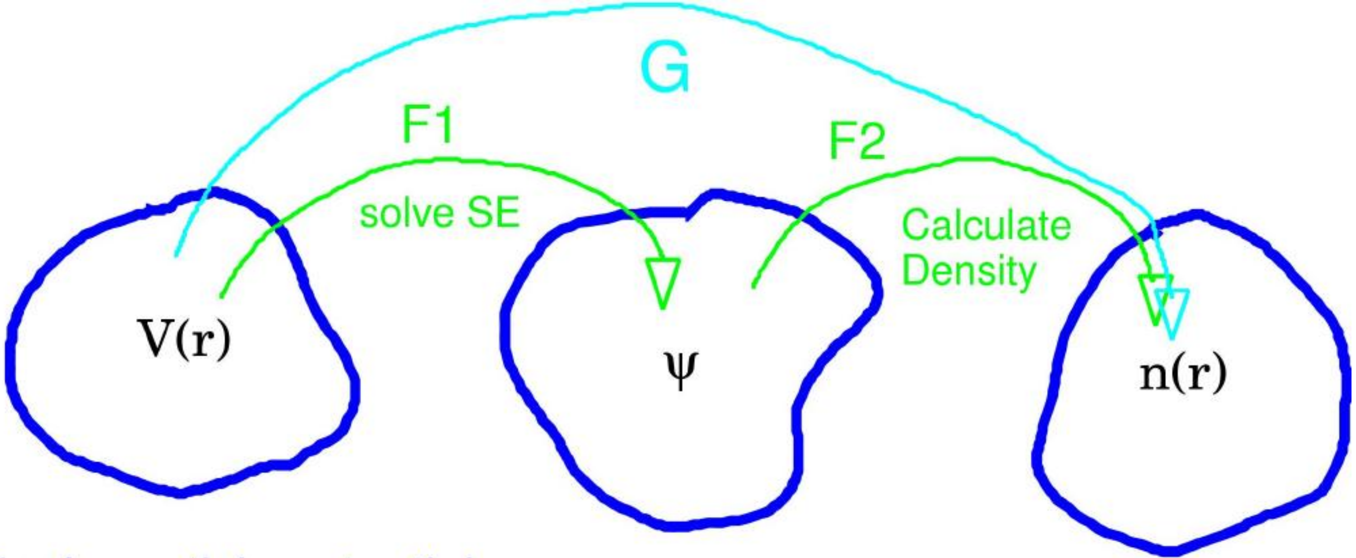
Known: the external potential and the number of electrons determine uniquely the charge density *n*

Theorem 1: *For a given external potential V, the ground-state properties of a system are uniquely determined by the electron density alone, i.e. they are functionals of the density.*

Theorem 2: *The exact ground-state density minimizes the energy functional* $E[n(\mathbf{r})]$

DENSITY FUNCTIONAL THEORY

HOHENBERG-KOHN THEOREMS



Single particle potential of non-degenerate Ground state

GS-Wavefct.

GS-Density

$$\left.\begin{array}{lcl} F_1 & : & V(\mathbf{r}) \longmapsto \psi \\ F_2 & : & \psi \longmapsto n(\mathbf{r}) \end{array}\right\} \text{ per construction surjective}$$

$$F_1 \circ F_2 := G \quad : \quad V(\mathbf{r}) \longmapsto n(\mathbf{r})$$

Hohenberg-Kohn-Theorem 1:
G is invertable

PROOF OF HK-THEOREM 1: V[n]

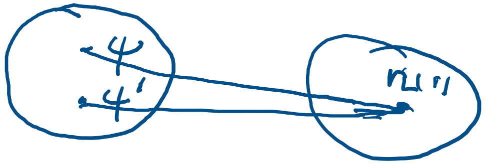
- **Proof:** By *reducis ad adsurdum*

$$(\hat{T} + \hat{V} + \hat{W})\Psi = E\Psi$$

$$(\hat{T} + \hat{V}' + \hat{W})\Psi' = E'\Psi'$$

We have to show

$$\Psi \neq \Psi' \Rightarrow n \neq n'$$



Assume 2 systems with $\Psi \neq \Psi'$ map to the same density n

$$\mathrm{I}\ :\ E = \langle\Psi|H|\Psi\rangle < \langle\Psi'|H|\Psi'\rangle = \langle\Psi'|H' + H - H'|\Psi'\rangle = \langle\Psi'|H' + V - V'|\Psi'\rangle$$

$$= \langle\Psi'|H'|\Psi'\rangle + \langle\Psi'|V - V'|\Psi'\rangle$$

$$= E' + \int \mathrm{d}\mathbf{r}\, n'(\mathbf{r})\ \big(V(\mathbf{r}) - V'(\mathbf{r})\big)$$

$$\mathrm{II}\ :\ E' = \langle\Psi'|H'|\Psi'\rangle < \langle\Psi|H'|\Psi\rangle = \langle\Psi|H + H' - H|\Psi\rangle = \langle\Psi|H + V' - V|\Psi\rangle$$

$$= \langle\Psi|H|\Psi|\rangle + \langle\Psi|V' - V|\Psi|\rangle$$

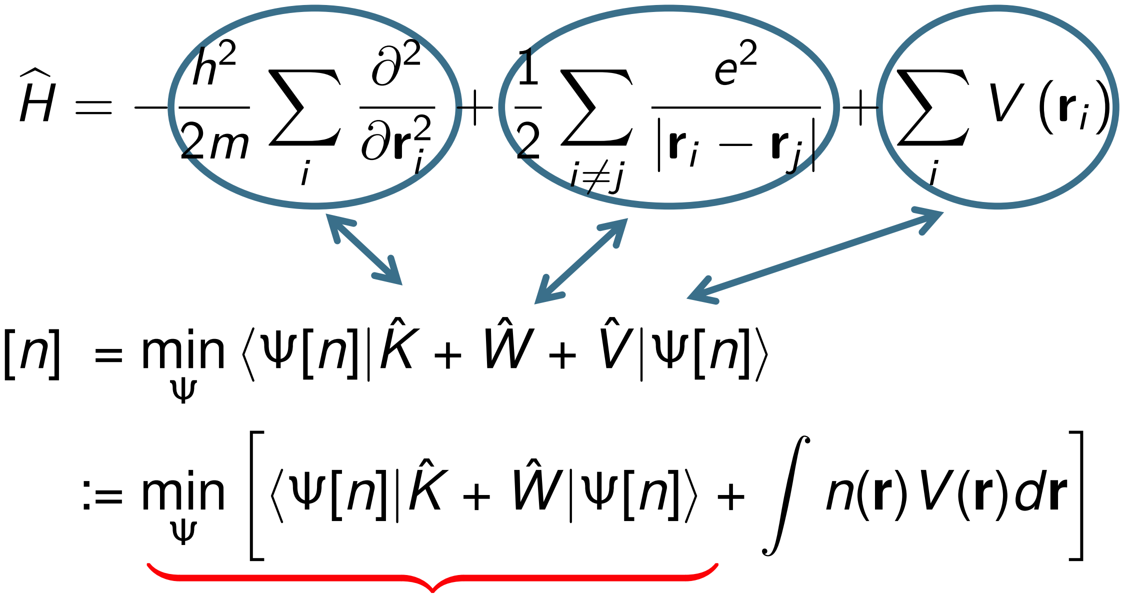
$$= E + \int \mathrm{d}\mathbf{r}\, n(\mathbf{r})\ \big(V'(\mathbf{r}) - V(\mathbf{r})\big)$$

$$\mathrm{I} + \mathrm{II}:\ E + E' < E + E' + 0$$ ↯

UNIVERSAL FUNCTIONAL *F*[*n*(r)]

- **Definition of Energy Functional for a given potential *V*(r)**

  The ground state density $n(\mathbf{r})$ determines the potential of the Schrödinger equation, and thus the wavefunction Ψ



$$\widehat{H} = -\frac{h^2}{2m}\sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V(\mathbf{r}_i)$$

$$E_V[n] = \min_{\Psi}\langle \Psi[n]|\hat{K} + \hat{W} + \hat{V}|\Psi[n]\rangle$$

$$:= \min_{\Psi}\left[\underbrace{\langle \Psi[n]|\hat{K} + \hat{W}|\Psi[n]\rangle}_{F[n(\mathbf{r})]} + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}\right]$$

- **Universal Functional** $F[n(\mathbf{r})]$

  F[*n*(r)] depends only on the density, thus it is universal i.e. it is the same independent of the number of particles and for all systems where the particles interact with each other by the Coulomb interaction *W*

PROOF OF HK-THEOREM 2: $n_{GS}(\mathbf{r})$ MINIMIZES $E[n_{GS}]$

$$E_V[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} \geq E_0 \quad (= \text{sign if } n(\mathbf{r}) = n_{GS}(\mathbf{r}))$$

- **Proof:** By *construction*

  Assume ground state density $n_{GS}(\mathbf{r}) = n_0(\mathbf{r}) \Longleftrightarrow V_0(\mathbf{r})$

  Given arbitrary density $n(\mathbf{r})$: $n(\vec{r}) \xrightarrow{G^{-1}} V(r) = V[n](r) \overset{SE}{\Longrightarrow} \Psi[n]$

$$E_{v_0}[n] := \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle$$

if $n \neq n_{gs} \Rightarrow \Psi \neq \Psi_0 \Rightarrow \langle \Psi | \hat{T} + \hat{V}_0 + \hat{W} | \Psi \rangle > E_0$

↖ Generalized Ritz' principle

if $n = n_0 \Rightarrow \Psi = \Psi_{gs} \Rightarrow \langle \Psi_{gs} | \hat{T} + \hat{V}_0 + \hat{W} | \Psi_{gs} \rangle = E_0$

- **Hence:** E_0 and n_0 can be obtained by minimizing $E[n]$

KOHN-SHAM DENSITY FUNCTIONAL THEORY

Toward a practical scheme

W. Kohn, L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)

- **non-interacting electron system "s"** $\hat{W} = 0$
  - Universal functional $F[n] = \min_{\Psi} \langle \Psi | \widehat{K} | \Psi \rangle = T_s[n] = \langle \Psi_{\mathrm{Slater}} | -\frac{1}{2}\Delta | \Psi_{\mathrm{Slater}} \rangle$
  - *Orbitals* of non-interacting electrons in (external) *potential* V_{s} → one-electron Schrödinger equation: $\left(-\nabla^2/2 + V_{\mathrm{s}}\right)\psi_i = \epsilon_i \psi_i$
  - For N electron states, construct the *electron density* of non-interacting electrons from the lowest-lying *one-particle states that is consistent with* V_{s}*:*

$$n_{\mathrm{s}}(\mathbf{r}) = \sum_{i=1}^{N/2} 2\,|\psi_i(\mathbf{r})|^2$$

  - For small variations around the ground-state density, E is stationary:

$$0 = \delta\left(T_{\mathrm{s}}[n] + \int n V_{\mathrm{s}}\right) = \delta E_{\mathrm{s}} = E_{\mathrm{s}}[n_{\mathrm{s}} + \delta n_{\mathrm{s}}] - E_{\mathrm{s}}[n_{\mathrm{s}}] \Longrightarrow \delta T_{\mathrm{s}}[n] = -\int \delta n V_{\mathrm{s}}$$

yields the exact ground state density corresponding to V_{s}

KOHN-SHAM EQUATIONS

- **interacting electron system**

  - Find ***an effective potential*** V_s such that for non-interacting electrons $n_\mathrm{s}(\mathbf{r}) = n(\mathbf{r})$ where $n(\mathbf{r})$ is the ***ground state density of an interacting system.***

$$E[n(\mathbf{r})] = T_\mathrm{s}[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})\mathrm{d}\mathbf{r} + \underbrace{\frac{1}{2}\int\int \frac{n(\mathbf{r})\cdot n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}')|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'}_{\text{Hartree term } E_\mathrm{H}} + \underbrace{E_\mathrm{xc}[n(\mathbf{r})]}$$

kinetic energy of the non-interacting system

Approximate!

$= T[n] - T_\mathrm{s}[n]$
$+ W[n] - E_\mathrm{H}$

Exchange and correlation; contains the exchange interactions and the corrections to the kinetic energy

  - From $\dfrac{\delta E}{\delta n(\mathbf{r})} = 0 \Rightarrow 0 = \overbrace{\delta T_\mathrm{s}[n]}^{-\int \delta n V_\mathrm{s}} + \displaystyle\int \mathrm{d}\mathbf{r}\, n(\mathbf{r}) \left[V(\mathbf{r}) + \int \frac{\cdot n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}')|}\mathrm{d}\mathbf{r}' + \frac{\delta E_\mathrm{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\right]$

- **Kohn-Sham Potential** $V_\mathrm{s}(\mathbf{r}) = V(\mathbf{r}) + \displaystyle\int \frac{\cdot n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}')|}\mathrm{d}\mathbf{r}' + \frac{\delta E_\mathrm{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$

→ **Kohn-Sham equation** $\left(-\dfrac{\nabla^2}{2} + V_\mathrm{s}\right)\psi_i = \epsilon_i\psi_i$

Equations solved self-consistently:
guess $V_\mathrm{s} \rightarrow \psi_i \rightarrow n$

KOHN-SHAM: CAUTIONARY NOTES

- DFT describes first and foremost ground state densities and ground state-properties.

- Kohn-Sham orbitals have, strictly speaking, **no** physical meaning, except that $n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$ is the exact density of the interacting system. In particular, is $\det(\psi_i(\mathbf{r}))$ not to be taken as an approximation to the many-body wave-function of the system.

- Likewise, the orbital energies ϵ_i have in general **no** physical meaning.

LOCAL DENSITY APPROXIMATION (LDA)

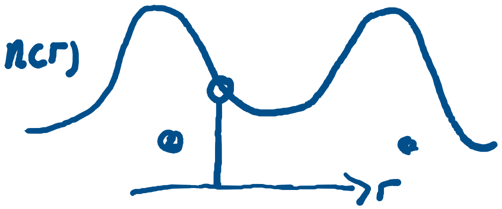
W. Kohn, L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)

- Kohn-Sham equations transfer the problem of ***finding the correct density*** to ***finding the correct exchange-correlation potential***.

- The simplest approximation is LDA, which exploits the nearsightedness of the electronic matter:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n(\mathbf{r})] = \int \varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(n(\mathbf{r}))\; n(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

Local Density
Approximation

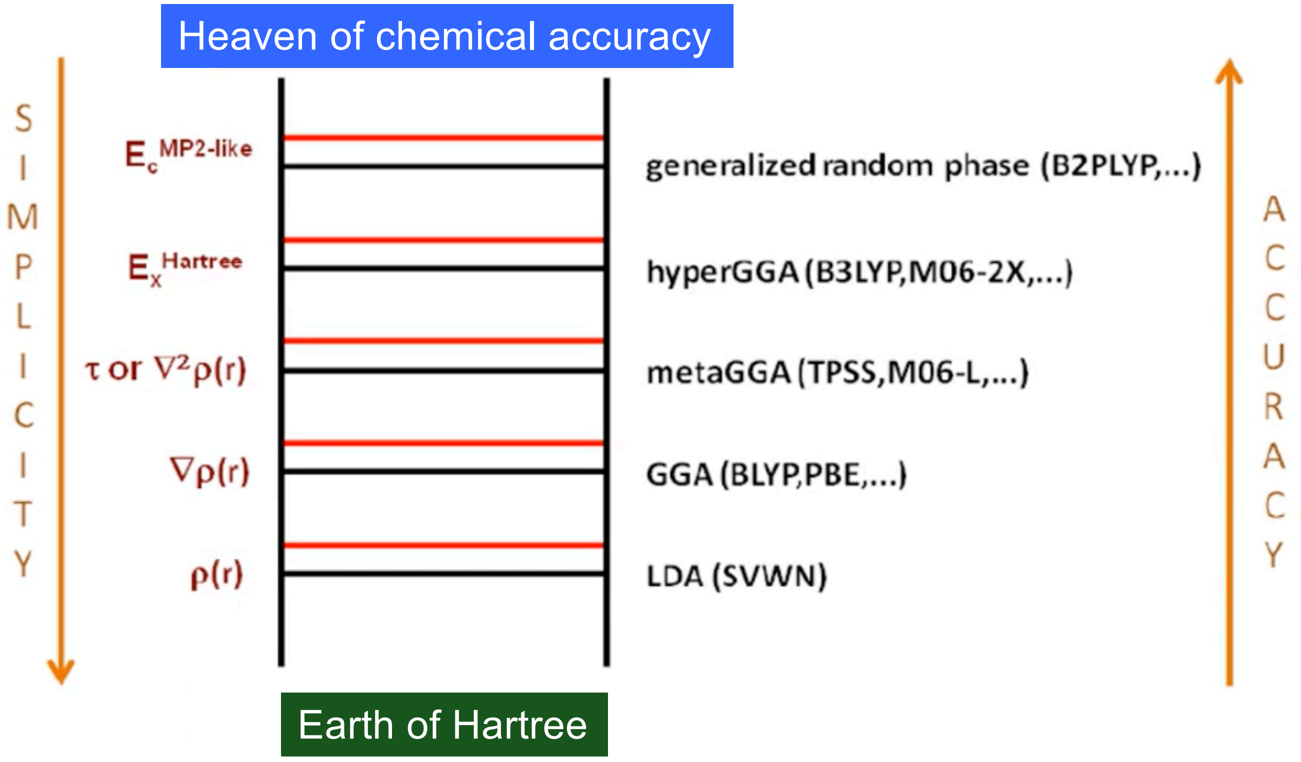


where $\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(n)$ is exchange and correlation energy per particle of a ***homogeneous*** electron gas (HEG).

Kohn & Sham: ***"We do not expect an accurate description of chemical binding"***

“JACOB’S LADDER” OF XC-FUNCTIONALS

(according to J. P. Perdew)



Heaven of chemical accuracy

SIMPLICITY

ACCURACY

$E_c^{\text{MP2-like}}$	generalized random phase (B2PLYP,...)
E_x^{Hartree}	hyperGGA (B3LYP,M06-2X,...)
τ or $\nabla^2\rho(r)$	metaGGA (TPSS,M06-L,...)
$\nabla\rho(r)$	GGA (BLYP,PBE,...)
$\rho(r)$	LDA (SVWN)

Earth of Hartree

“And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.” Genesis 28:12 (King James Version).

More on Thursday: lecture by Gustav Bihlmayer

THE KOHN-SHAM STANDARD MODEL

“**The** Computational Approach”

For: Physics, Chemistry, Nanoscience, Materials Science, Bio-Physics, Minerology, Geology,…

Total Energy: $E = E[n, \{\mathbf{R}_\mathrm{I}\}, a, \ldots]$

Energy is functional of electron density n and external parameters such as lattice constants, atoms positions, magnetization direction…

Secular Equation: $\hat{H}[n]\,\psi_i[n] = \epsilon_i[n]\,\psi_i[n]$

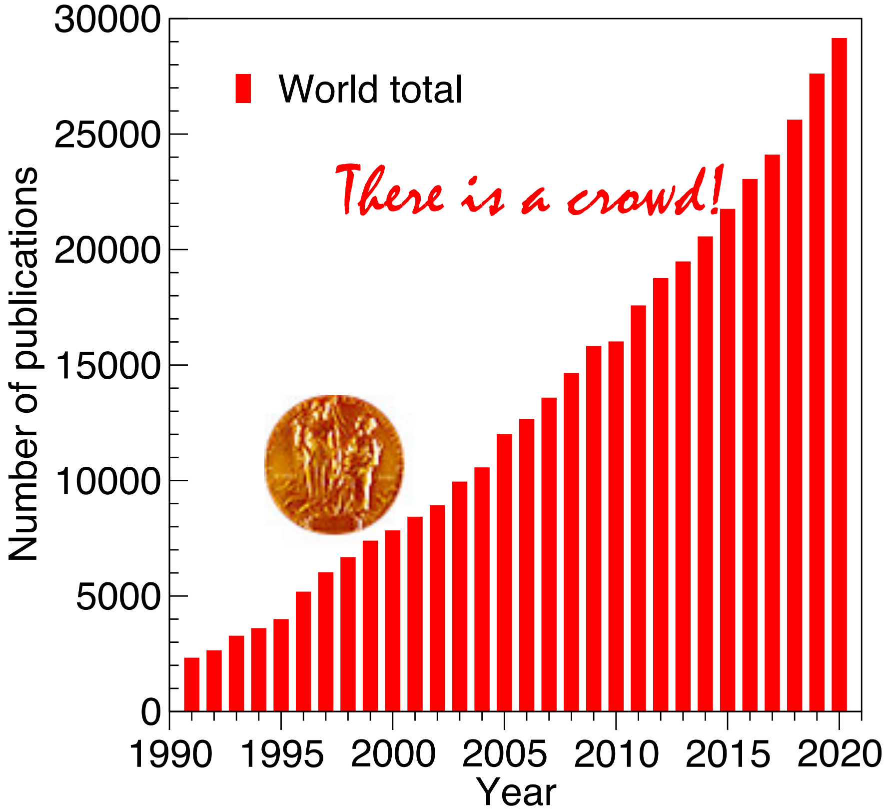
Selfconsistency loop

Density: $$n(\mathbf{r}) = \sum_{i(\mathrm{occ})}^{M} |\,\psi_i(\mathbf{r})\,|^2$$

CPU-Time scaling: $\approx N^3_{\mathrm{atom}} \approx \mathrm{Volume}^3, \approx \mathrm{Precision}^3$

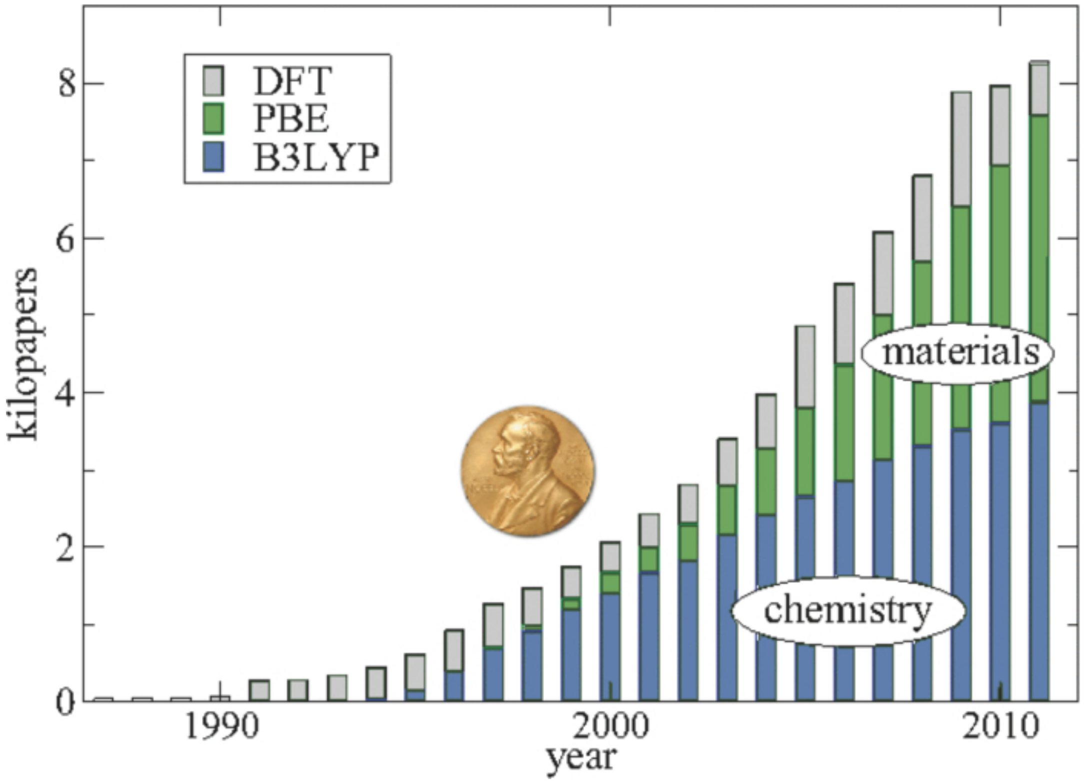
THE CROWD

- DFT-calculations became a huge international Enterprise reaching 30.000 publications a year



Web of Science | Key words: First-principles, Ab initio, Density functional

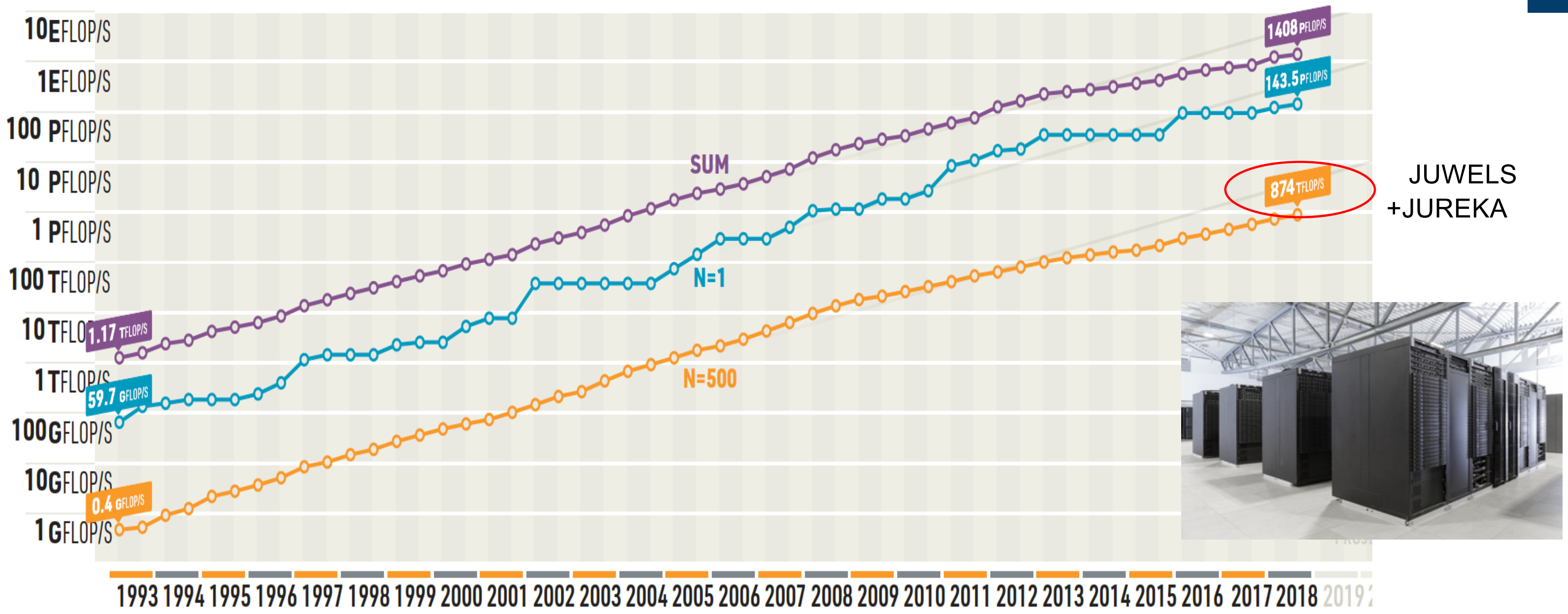
- Number of DFT papers: Materials vs. Chemisty



Web of Science | Key words: B3LYP, PBE DFT

THE DIGITAL SPACE

- **Evolution of peak performance on Top500 list**



top500.org

- A computation that took **one year in 1989** would take **one second in 2018** (30-million-fold increase in 1 generation)

- CPUs AND THROUGHPUT CAPACITY DOUBLE EVERY 14 MONTHS

THE QUANTUM MATERIALS SPACE

- **Quantum Space of electrons** (Hilbert Space)**:**

$$\left[-\frac{\hbar^2}{2m}\Delta + V(x)\right]\Psi(x) = E\Psi(x) \quad \Longleftrightarrow$$

DFT — Static + Dynamik

GW — Excitation

Kubo — Transport

Challenges

- Larger Systems
- More electron correlation
- Longer spin-dynamics simulation

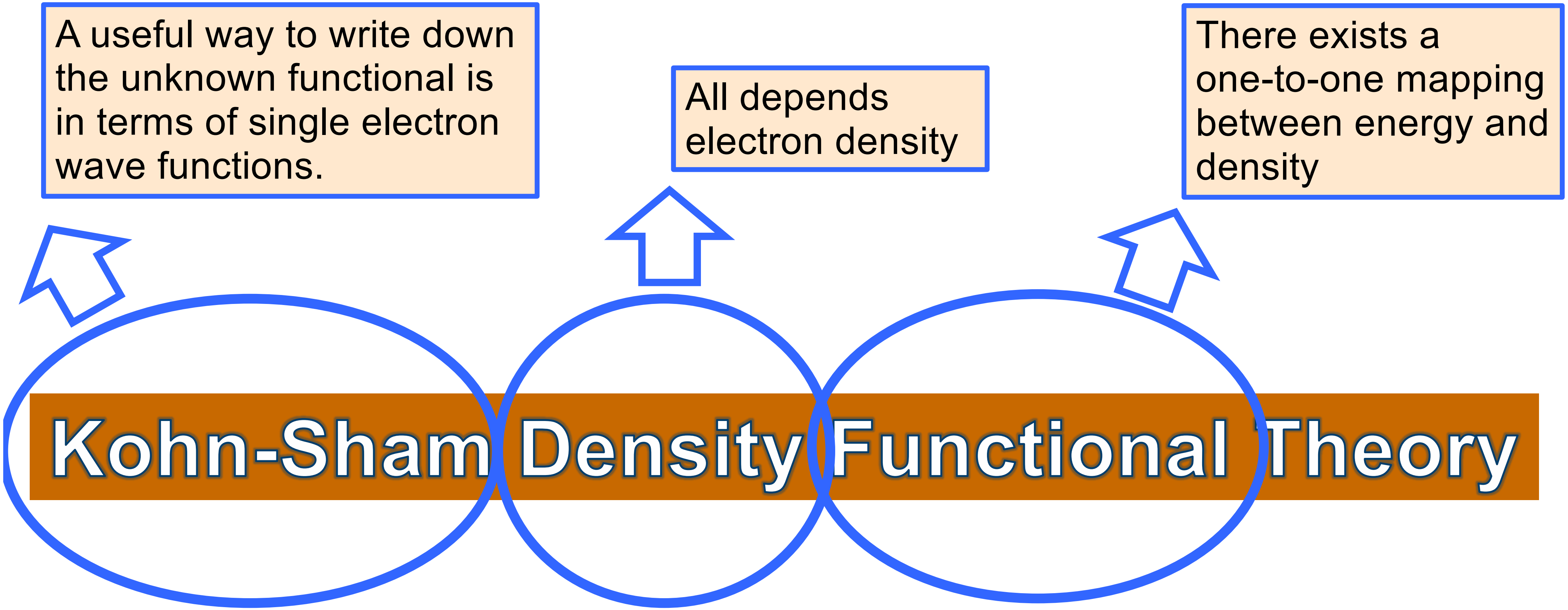
Very different computational challenges

- **Chemical Space** (Configuration Space)**:**

Combining: quantum engine + autonomous high-throughput framework + data informatics

Challenges

- Making quantum engines resilient and robust (Error handling and recovery)
- Writing workflows
- Connecting high-thru'put frameworks with Exascale computer considering security



A useful way to write down the unknown functional is in terms of single electron wave functions.

All depends electron density

There exists a one-to-one mapping between energy and density

Kohn-Sham Density Functional Theory

Thanks !

And enjoy the workshop