

Density Functional Theory: Principles, Self-Consistency, and Practical Implementation

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Why Density Functional Theory ?

✓ The calculation of physical and chemical properties of multi- particle systems (atoms, molecules or solids) require the
exact determination of **electronic structure** and **total energy** of these systems.

✓ Schrödinger equation successfully explains the electronic structure of simple systems and numerically exact solutions are found for small no. of atoms and molecules.

✓ This n-electron problem was solved when Kohn and Sham in 1965 formulated a theory concerning 3-dimensional electron density and energy functionals.

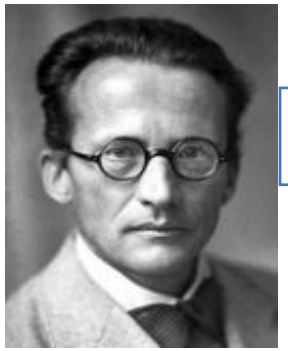
✓**Electron density n(r) plays central role instead of wave function ψ(r)**. The problem of **many-interacting particles** system in static potential is reduced to **non-interacting single particle** system in an effective potential.

Outline

- ✓ The Born-Oppenheimenr approximation
- ✓ Hartree-Fock method
- ✓ Thomas-Fermi model
- ✓ Hohenberg-Kohn Theorems
- ✓ Kohn-Sham equations
- ✓ Results and summary

Many body problem:

- For large interacting system, we first need to consider a many particle wave function.
- Many body Hamiltonian for electron and nucleus is of the form given below



1926

Schrödinger

Innocent look of wave equation → $H\psi(r,R,t) = E\,\psi(r,R,t)$

M nuclear R
m electronic r
e mixed

$$H\psi = \underbrace{-\sum_n \frac{\hbar^2}{2M}\nabla_n^2}_{\hat{T}_R} \underbrace{-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2}_{\hat{T}_r}$$

Kinetic terms

$$+ \underbrace{\frac{1}{2}\sum_{n\neq m}\frac{Z_n Z_m e^2}{|\boldsymbol{R}_n - \boldsymbol{R}_m|}}_{\hat{V}_r} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}}_{\hat{V}_r} \underbrace{-\sum_{i,n}\frac{Z_n e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_n|}}_{\hat{V}_{r,R}}$$

Potential terms

$$H\psi = \hat{T}_r + \hat{T}_R + \hat{V}_r + \hat{V}_{r,R} + \hat{V}_R$$

$$= \underbrace{\hat{T}_R + \hat{V}_R}_{\text{nuclear}} + \underbrace{\hat{T}_r + \hat{V}_r}_{\text{electronic}} + \underbrace{\hat{V}_{r,R}}_{\text{mixed}}$$

Notational convenience:

$$\Psi(r_1, r_2, \ldots, \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; t) = (\{r_i\}, \{\boldsymbol{R}_i\}; t)$$

$$\Psi\ (r, \boldsymbol{R}; t)$$

1. Born-Oppenheimer approximation:

- The nuclei are much heavier than electrons.
- They move much more slowly and hence neglect the nuclear kinetic energy.
- The wave function separated into electronic and nuclear part and determine motion of electrons with nuclei held fixed.



Max Born and Robert Oppenheimer **1927**

Since the total Hamiltonian for electron and nucleus is:

$$[T_R + V_{RR}(\vec{R}) + \varepsilon(\vec{R})]\chi(\vec{R}) = E\chi(\vec{R})$$

$$H = \hat{T}_r + \hat{T}_R + \hat{V}_r + \hat{V}_{r,R} + \hat{V}_R$$

$$= \underbrace{\hat{T}_R + \hat{V}_R}_{\text{nuclear}} + \underbrace{\hat{T}_r + \hat{V}_r}_{\text{electronic}} + \underbrace{\hat{V}_{r,R}}_{\text{mixed}}$$

$\Psi = \psi\chi$

$$V_{\text{ext}}(\mathbf{r}_i) = -\sum_{i,I} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

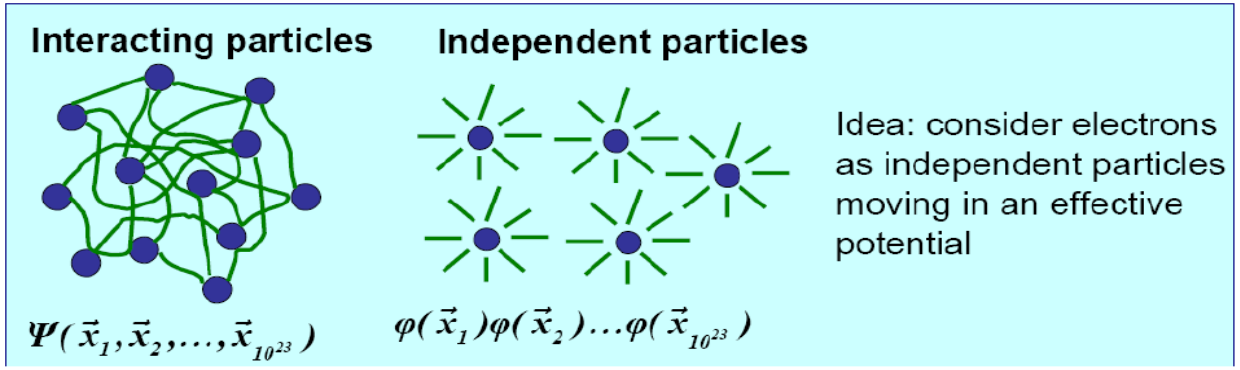
then the hamiltonian for the electronic part will be

$$He = \underbrace{\hat{T}_r + \hat{V}_r}_{\text{electronic}} + \underbrace{\hat{V}_{r,R}}_{\text{mixed}}$$

$$\hat{H}_e = \sum_{i=1}^{N_e} \left[-\frac{1}{2}\nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

2. Hartree approximation: One electron model

- Reduce the complexity of electron-electron interactions.
- Electrons are independent and interacts with others in an averaged way.
- For an n-electron system, each electron does not recognize other as single entities but as a mean field.
- Hence, n-electron system becomes a set of non-interacting one-electron system where each electron moves in the average density of rest electrons.





Hartree 1928

$$E[\{\phi_i\}] = \sum_{i=1}^{N_e} \int \phi_i^*(\mathbf{r}_i) \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i)\, d^3r_i + \frac{1}{2} \sum_{i \neq j} \iint \frac{|\phi_i(\mathbf{r}_i)|^2\, |\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3r_i\, d^3r_j$$

The Variational Principle

- **Objective:** Minimize $E[\{\phi_i\}]$ subject to normalization constraints
- **Introduce Lagrange Multipliers:** ε_i for each orbital
- **Constrained Functional:**

$$\mathcal{L}[\{\phi_i\}] = E[\{\phi_i\}] - \sum_{i=1}^{N_e} \varepsilon_i \left(\int |\phi_i(\mathbf{r})|^2 \, d^3r - 1 \right)$$

- **Requirement:**
  $\delta \mathcal{L} = 0$ for all variations $\delta \phi_i^*(\mathbf{r})$

Deriving the Euler–Lagrange Equation

- Collecting All Variations for Orbital i:

$$\int d^3r_i \, \delta\phi_i^*(\mathbf{r}_i) \left\{ \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) + V_{\text{H}}(\mathbf{r}_i)\phi_i(\mathbf{r}_i) - \varepsilon_i \, \phi_i(\mathbf{r}_i) \right\} = 0$$

- Since $\delta\phi_i^*(\mathbf{r}_i)$ is arbitrary, the term in braces must vanish:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) + V_{\text{H}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) = \varepsilon_i \, \phi_i(\mathbf{r}_i)$$

- This is the Hartree Equation for the ith orbital.

$$V_{\text{ext}}(\mathbf{r}_i) = -\sum_{i,I} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

$$V_{\text{H}}(\mathbf{r}_i) = \sum_{j \neq i} \int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3r_j$$

Interpretation of the Hartree Equation

- **Kinetic & External Potential Terms:**
  $-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{\text{ext}}(\mathbf{r}_i)$
- **Hartree (Mean–Field) Potential:**
  $V_{\text{H}}(\mathbf{r}_i)$ represents the averaged Coulomb repulsion from all other electrons.
- **Eigenvalue ε_i:**
  Serves as a Lagrange multiplier ensuring normalization and is interpreted as the orbital energy.
- **Self–Consistency:**
  Since $V_{\text{H}}(\mathbf{r}_i)$ depends on all orbitals $\{\phi_j\}$, the equations must be solved iteratively.

Hartree method produced crude estimation of energy due to two oversimplifications:

✓. *Hartree method does not follow two basic principles of quantum mechanics: the antisymmetry principle and Pauli's exclusion principle.*

✓ *Does not count the exchange and correlation energies coming from n-electron nature*



Hartree

The Hartree method, therefore, was soon refined into the Hartree-Fock method…...continue…

3. Hartree-Fock method

Based on the one-electron and mean-field approach by Hartree, V.A. Fock enhanced the methods to higher perfection. Fock and J.C. Slater in 1930 generalised the Hartree's theory to take into account the antisymmetry requirement.

❖ In HF method, the n-electron wave function approximated as a linear combination of non-interacting one-electron wave function in the form of Slater determinant.

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

❖Slater determinant



Fock

$$E[\{\phi_i\}] = \sum_{i=1}^{N_e} \int \phi_i^*(\mathbf{r}_i) \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i)\, d^3r_i + \frac{1}{2} \sum_{i,j=1}^{N_e} \Big[J_{ij} - K_{ij} \Big]$$

- **Where:**
  - **Coulomb Integral:**

$$J_{ij} = \iint \frac{|\phi_i(\mathbf{r}_i)|^2 \, |\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3r_i \, d^3r_j$$

  - **Exchange Integral:**

$$K_{ij} = \iint \frac{\phi_i^*(\mathbf{r}_i) \, \phi_j^*(\mathbf{r}_j) \, \phi_j(\mathbf{r}_i) \, \phi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3r_i \, d^3r_j$$

Hartree–Fock Equations:

$$\int d^3r_i \, \delta\phi_i^*(\mathbf{r}_i) \left\{ \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) + \sum_{j=1}^{N_e} \left[\hat{J}_j \phi_i(\mathbf{r}) - \hat{K}_j \phi_i(\mathbf{r}) \right] - \varepsilon_i \, \phi_i(\mathbf{r}_i) \right\} = 0$$

$$\hat{J}_j \phi_i(\mathbf{r}_i) = \left[\int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3r_j \right] \phi_i(\mathbf{r}_i)$$

Coulomb (Direct) Term

$$\hat{K}_j \phi_i(\mathbf{r}_i) = \left[\int \frac{\phi_j^*(\mathbf{r}_j) \, \phi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3r_j \right] \phi_j(\mathbf{r}_i)$$

Exchange Term

Recap:

- Started with the many–electron Hamiltonian and the antisymmetric Slater determinant wavefunction.
- Expressed the energy expectation value in terms of one–electron and two–electron (Coulomb and exchange) integrals, with integration variables explicitly written as $\mathbf{r}_i$ and $\mathbf{r}_j$.
- Set up the variational problem with normalization constraints and introduced Lagrange multipliers ε_i.
- Derived the Euler–Lagrange equations, leading to the definition of the Fock operator.

Difficulties with Hartree-Fock Theory:

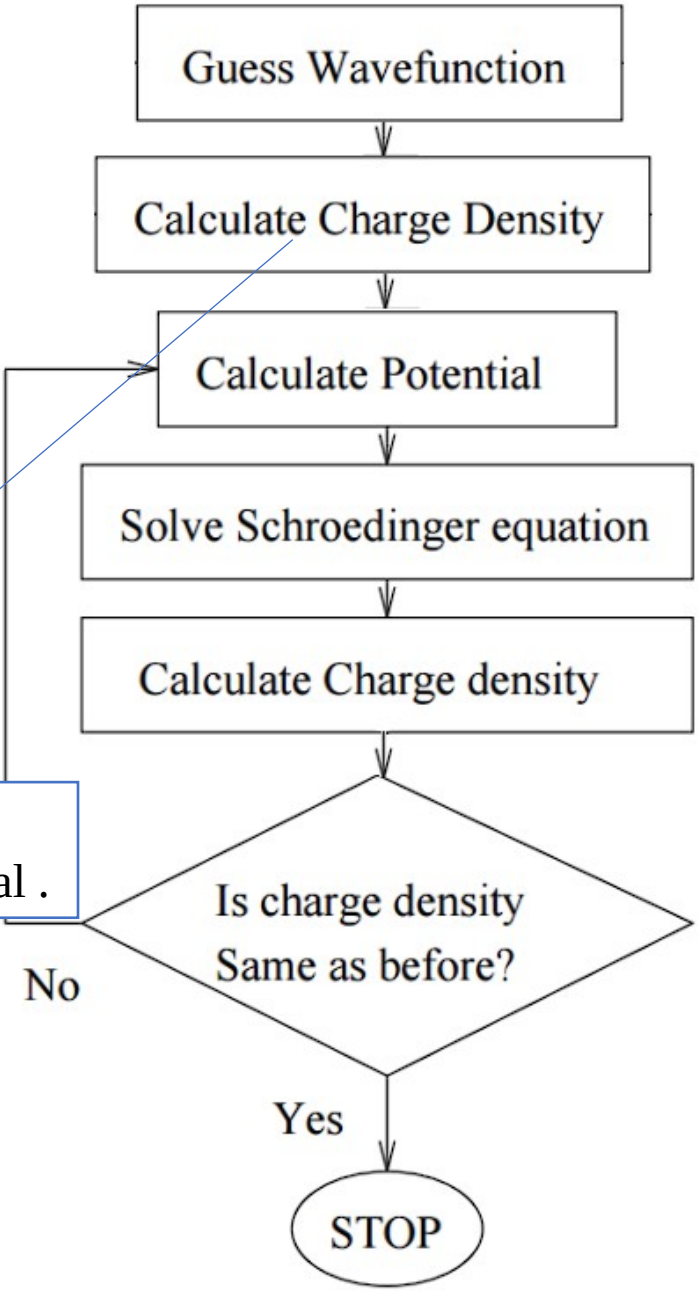
- Correlation energy and
- Problem of dealing 3N dimensional .

- **Electron Density $n(\mathbf{r})$:**

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$$

- Here, $n(\mathbf{r})$ gives the number of electrons per unit volume at point $\mathbf{r}$.

Algorithm for Self-consistent field theory.



Thomas-Fermi Model

Motivation and Background

- For many–electron systems, solving for individual orbitals $\phi_i(\mathbf{r}_i)$ is challenging.
- The Thomas–Fermi model replaces the orbital details with a continuous electron density $n(\mathbf{r})$.
- This semiclassical model is particularly useful for heavy atoms and solids.

Energy Functional in Terms of $n(\mathbf{r})$

The total energy $E[n]$ is approximated by three main contributions:

1. **Kinetic Energy:** Approximated using the local density of a uniform electron gas. (LDA approximation)
2. **External Potential Energy:** Due to the attraction to the nuclei.
3. **Electron–Electron Interaction Energy:** Classical Coulomb repulsion.

In LDA approximation

$$E[n] = T[n] + V_{\text{ext}}[n] + U[n].$$

$$U[n] = \frac{1}{2}\iint \frac{n(\mathbf{r}_i)\, n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_i\, d^3\mathbf{r}_j$$



Llewellyn Thomas
1903-1992



Enrico Fermi
1901-1954

Thomas-Fermi Model

$$T[n] \approx T^{LDA}[n] \approx T_s{}^{LDA}[n] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int n(\mathbf{r}_i)^{5/3}\, d^3\mathbf{r}_i$$

Kinetic energy functional for electrons in motion within an external field

LDA – Local density approximation

External Potential Energy:

$$V_{\text{ext}}[n] = \int V_{\text{ext}}(\mathbf{r}_i)\, n(\mathbf{r}_i)\, d^3\mathbf{r}_i \quad V_{\text{ext}}(\mathbf{r}_i) = -\sum_{i,I} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

Electron–Electron Interaction Energy:

$$U[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r}_i)\, n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_i\, d^3\mathbf{r}_j\,.$$

The $1/2$ prevents double counting of interactions between pairs $(\mathbf{r}_i, \mathbf{r}_j)$.

$$E[n] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int n(\mathbf{r}_i)^{5/3}\, d^3\mathbf{r}_i + \int V_{\text{ext}}(\mathbf{r}_i)\, n(\mathbf{r}_i)\, d^3\mathbf{r}_i + \frac{1}{2}\int\int \frac{n(\mathbf{r}_i)\, n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_i\, d^3\mathbf{r}_j$$

- **Final Thomas–Fermi Equation:**

$$\frac{5}{3}\frac{3}{10}\left(3\pi^2\right)^{2/3} n(\mathbf{r}_i)^{2/3} + V_{\text{ext}}(\mathbf{r}_i) + \int \frac{n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_j = \mu\,.$$

- $\frac{5}{3}\frac{3}{10}\left(3\pi^2\right)^{2/3} n(\mathbf{r}_i)^{2/3}$ is the local kinetic energy per electron.
- $V_{\text{ext}}(\mathbf{r}_i)$ is the external potential (e.g., due to nuclei).
- $\int \frac{n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_j$ represents the classical Coulomb potential from electron–electron repulsion.
- μ is the chemical potential ensuring the total electron number N is fixed.

Physically, this equation tells us that at every point $\mathbf{r}_i$, the sum of the local kinetic energy (per electron), the potential energy due to the nuclei, and the electrostatic repulsion from all other electrons must equal the chemical potential μ. Solving this equation (often numerically) yields the electron density $n(\mathbf{r})$ that minimizes the total energy while keeping the electron number fixed.

The extension of Thomas- Fermi Model

- Thomas–Fermi–Dirac (TFD) Correction

  Accounts for exchange effects (Pauli exclusion) in a uniform electron gas.

- Weizsäcker (W) Gradient Correction

  $T_W[n] = \lambda \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}\, d^3\mathbf{r}$, gradient correction to account for spatial variations in $n(\mathbf{r})$.

- Meaning of TFD1/9W, TFD1/5W, and TFDW

  The specific value of λ may be chosen as 1/9, 1/5, or determined by further refinements.

Methods comparison

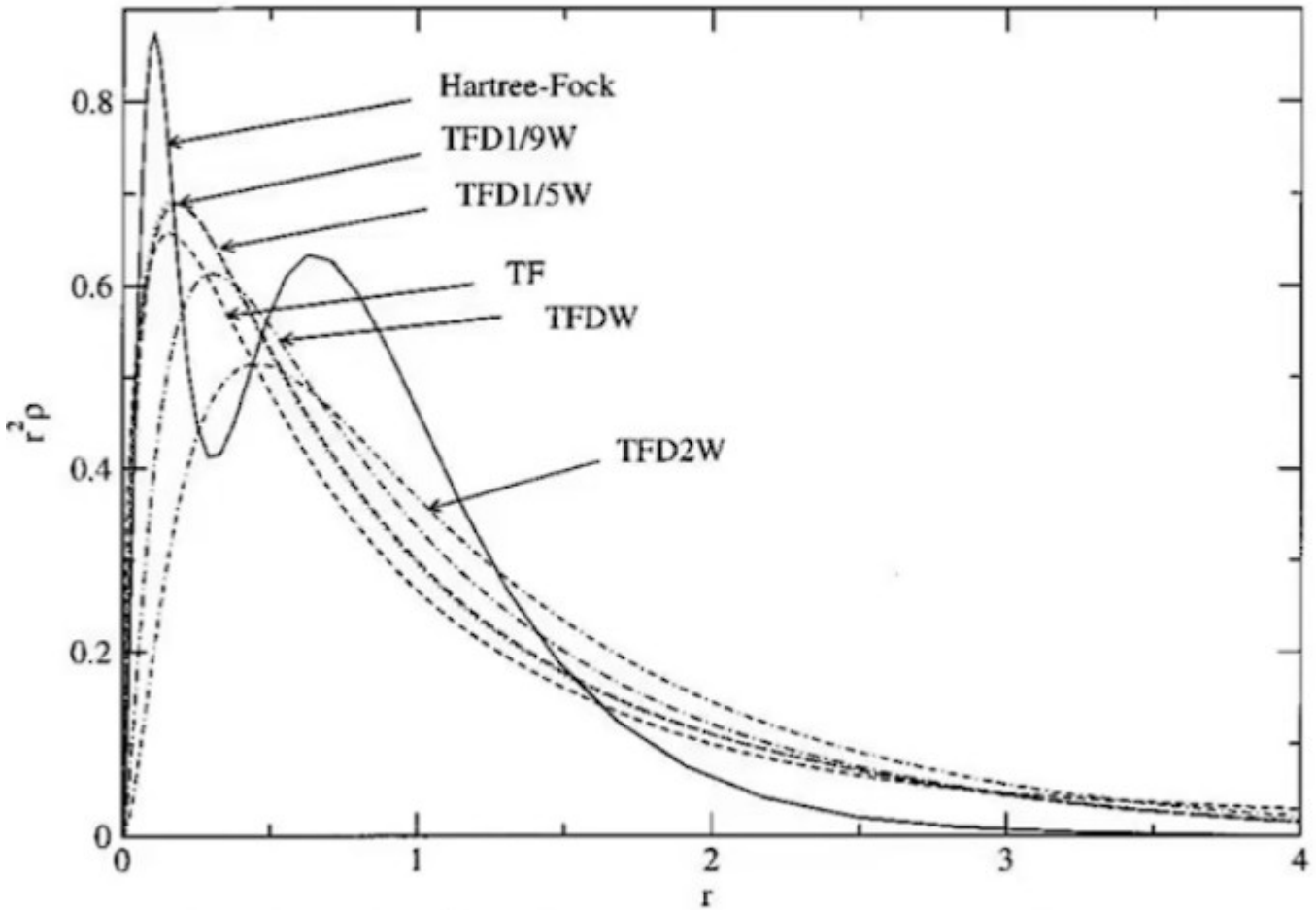
TABLE I. Atomic energies using various Thomas–Fermi-type models, compared with literature and Hartree–Fock results. The literature results for Ne are taken from TF (exact formula), TFD, TFDW, TFDλW and the HF

	TF	TFD	TFD$\frac{1}{9}$W	TFD$\frac{1}{5}$W	TFDW	HF
H	−0.7491	−1.0224	−0.6664	−0.5666	−0.2618	−0.5000
He	−3.8234	−4.6093	−3.2228	−2.8184	−1.4775	−2.8617
Li	−9.8414	−11.3465	−8.2515	−7.3227	−4.1054	−7.4327
Be	−19.2464	−21.6413	−16.1631	−14.4841	−8.4922	−14.5730
B	−32.3865	−35.8191	−27.2876	−24.6284	−14.9258	−24.5291
C	−49.5281	−54.1558	−41.9052	−38.0332	−23.6568	−37.6886
N	−70.9520	−76.8929	−60.2622	−54.9428	−34.9084	−54.4009
O	−96.8564	−104.2472	−82.5798	−75.5765	−48.8831	−74.8094
F	−127.4524	−136.4158	−109.0592	−100.1345	−65.7674	−99.4094
Ne	−162.9263	−173.5801	−139.8865	−128.8014	−85.7343	−128.5471
Ne (lit)	−165.61	−176.3	−139.91	−128.83	−86.43	

J. Chem. Phys., Vol. 114, No. 2, 8 January 2001

Methods comparison

J. Chem. Phys., Vol. 114, No. 2, 8 January 2001



Radial density $r^2\rho$ with various Thomas–Fermi-type models.

Hohenberg-Kohn Theorems

Inhomogeneous Electron Gas

P. Hohenberg and W. Kohn
Phys. Rev. **136**, B864 – Published 9 November 1964

Physics

Article | References | Citing Articles (38,993) | PDF | Export Citation

ABSTRACT

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) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\frac{\tilde{n}}{n_0} \ll 1$, and (2) $n(\mathbf{r}) = \phi\left(\frac{r}{r_0}\right)$ with ϕ arbitrary and $r_0 \to \infty$. 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.

Received 18 June 1964



Pierre Hohenberg
1934-2017



Walter Kohn
1923-2016



Chemistry,1998

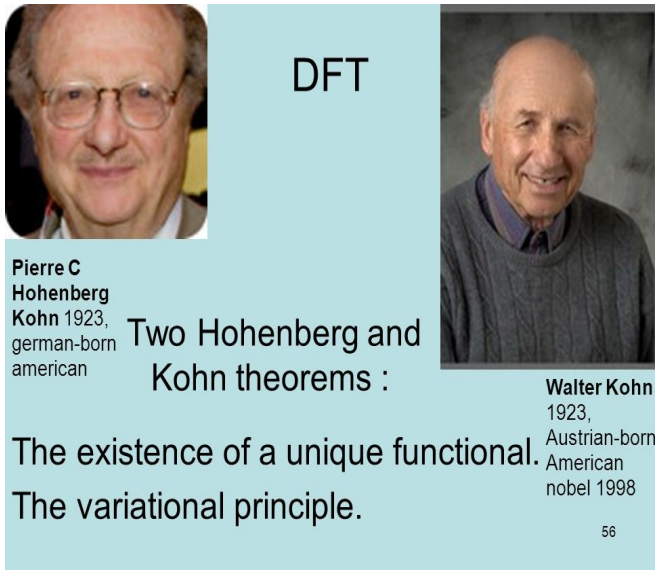
A new approach has been developed known as **Density Functional Theory (DFT).**

- In 1964 Hohenberg and Kohn showed that schrodinger equation (3N dimensional e.g. 10 electrons require 30 dimensions) could be reformulated in terms **of electron density n(r)** with non-interacting n separate 3-dimensional ones.
- The main objective of DFT is to replace **the many-particle electronic wavefunction** with **the electron density** as the basic quantity.
- The electron density n(r), the central player in DFT decides everything in an n-electron quantum state where there is **no individual electron density** but a **3-dimensional density of electrons**.
- The addition of *all the electron densities over the whole space* naturally return to *the total number of electrons* in the system.
- The knowledge of overlapping of atomic electron density, roughly generate the electron density of the solids.
- This theory gives approximate solutions to both **Exchange** and **Correlation** Energies.

The Fundamental Pillars of DFT

First Hohenberg Kohn (HK) theorem: *The ground-state energy is a unique functional of the electron density n(r).*

- This theorem provides one to one mapping between ground state wave function and ground state charge density.
- The ground state charge density can uniquely describe all the ground state properties of system.
- The fundamental concept behind density functional theory is that charge density (3-Dimensional) can correctly describe the ground state of N-particle instead of using a wave function (3N-Dimensional).



Second Hohenberg Kohn (HK) theorem: *The electron density that **minimizes the energy** of the overall functional is the **true electron density.***

- If the true functional form of energy in terms of density gets known, then one could vary the electron density until the energy from the functional is minimized, giving us required **ground state density**.
- This is essentially a **variational principle** and is used in practice with approximate forms of the functional.
- The simplest possible choice of a functional can be a constant electron density all over the space.

Kohn–Sham Energy Partitioning

- The Kohn–Sham total energy functional is written as

$$E[n] = T_s[n] + U[n] + E_{xc}[n] + \int V_{\text{ext}}(\mathbf{r}_i)\, n(\mathbf{r}_i)\, d^3\mathbf{r}_i \,,$$

where:

- $T_s[n]$ is the kinetic energy of non-interacting electrons yielding density $n(\mathbf{r}_i)$.
- $U[n]$ is the classical electron–electron repulsion energy (the Hartree energy).
- $E_{xc}[n]$ contains exchange and correlation effects beyond $T_s[n]$ and $U[n]$.

$$U[n] = \frac{1}{2} \int n(\mathbf{r}_i) \underbrace{\left(\int \frac{n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_j \right)}_{V_H(\mathbf{r}_i)} d^3\mathbf{r}_i \,.$$

We do not know!

Exchange and Correlation

- **Non-Interacting Kinetic Energy $T_s[n]$:**
  - Calculated exactly for the Kohn–Sham non-interacting electrons with density $n(\mathbf{r}_i)$.
- **True Interacting Kinetic Energy $T[n]$:**
  - The exact kinetic energy for the interacting system.
- **Kinetic Correlation Energy:**

$$T_c[n] = T[n] - T_s[n]\,.$$

- $T_c[n]$ captures the change in kinetic energy due to electron–electron interactions (correlation effects).

Exchange and Correlation

Exchange Energy $E_x[n]$ – Dirac Exchange

- For a homogeneous electron gas, Dirac derived the exchange energy per electron:

$$\epsilon_x(n) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}\,.$$

- **Total Exchange Energy:**

$$E_x[n] = \int \epsilon_x\big(n(\mathbf{r}_i)\big)n(\mathbf{r}_i)\,d^3\mathbf{r}_i = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\mathbf{r}_i)^{4/3}\,d^3\mathbf{r}_i\,.$$

- This is the Local Density Approximation (LDA) for exchange.

Exchange and Correlation

Correlation Energy $E_c[n]$

- **Definition:**

$$E_c[n] = E_{xc}[n] - E_x[n]\,,$$

where $E_{xc}[n]$ is the full exchange–correlation energy.

- $E_c[n]$ captures additional many-body effects (dynamic electron–electron correlations) not included in the exchange term.
- Typically, $E_c[n]$ is determined from many-body theory or via parameterizations from Quantum Monte Carlo data.

Exchange and Correlation

Full Exchange–Correlation Energy

- The complete exchange–correlation energy is:

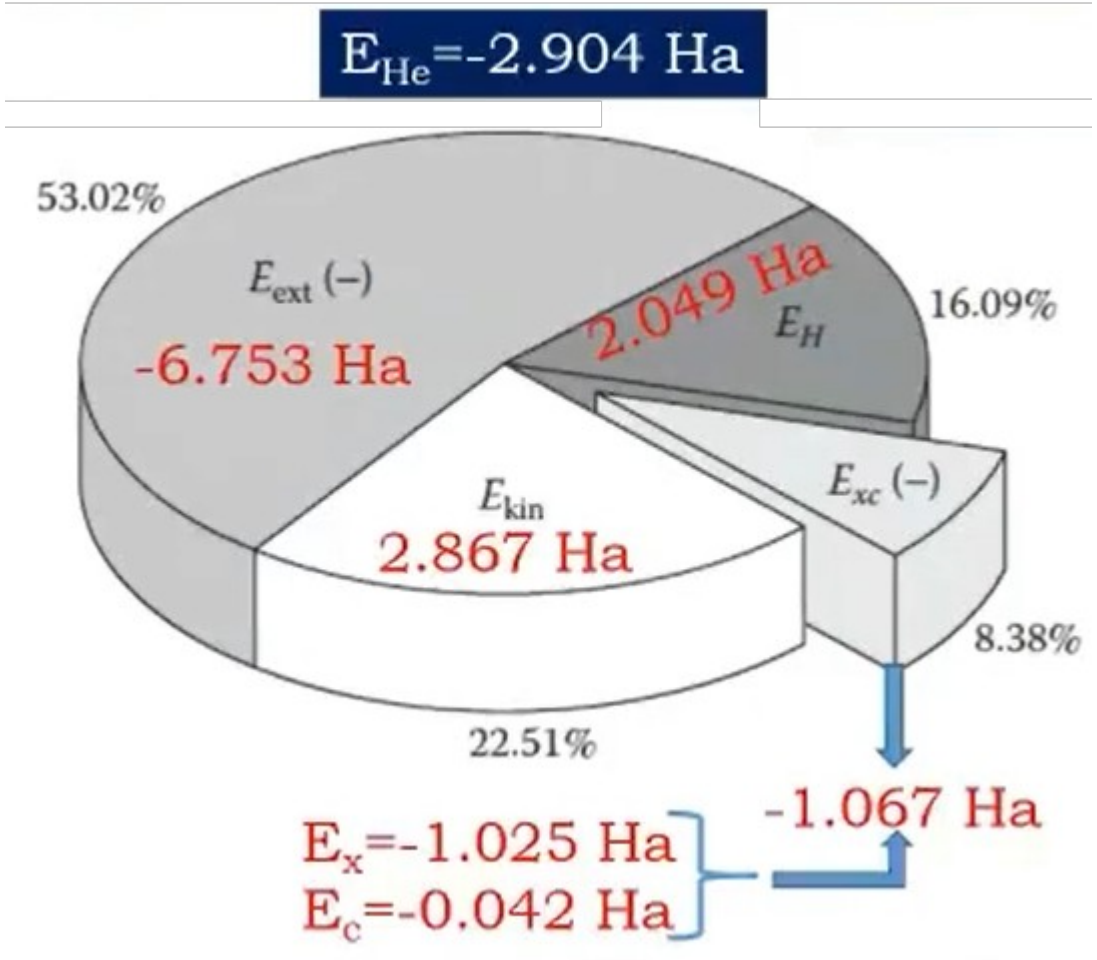
$$E_{xc}[n] = T_c[n] + (V_{ee}[n] - U[n]) \ ,$$

and is often partitioned as:

$$E_{xc}[n] = E_x[n] + E_c[n] \, .$$

- Here, $V_{ee}[n]$ represents the true electron–electron interaction energy.

Energy Contribution in He Atom



Exchange-Correlation Energy

Probabilistic Approach

Correlation energy represents an additional decrease in energy due to the attempts of electrons to 'avoid' each other, thereby lowering the energy of Coulombic repulsion

Strongly correlated system – is one in which the correlation energy is comparable to other energy terms, such as single-particle kinetic energy or Hartree energy

	Total Energy	E_{xc}	Exchange	Correlation	% Exchange	% Correlation
He	-2.9065	-1.0619	-1.0182	-0.0437	35.0316	1.5041
Ne	-128.9577	-12.4733	-12.0902	-0.3830	9.3754	0.2970
Ar	-527.5412	-30.8663	-30.1150	-0.7513	5.7086	0.1424
Kr	-2753.8291	-95.5146	-93.7655	-1.7490	3.4049	0.0635

DFT: XC functionals

DFT is *exact* in principle, *approximated* in practice! there are 400+ XC functionals (from LibXC documentation)



N. Mardirossian, M. Head-Gordon, Mol. Phys. 2017. P. 2315-2372

DFT: XC functionals

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = E_{\mathrm{xc}}^{\mathrm{LDA}}[n(\vec{r})],$$ Local Density Approximation

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = E_{xc}^{\mathrm{GGA}}[n(\vec{r}), \vec{\nabla} n(\vec{r})],$$ Generalized Gradient Approximation

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = E_{\mathrm{xc}}^{\mathrm{mGGA}}[n(\vec{r}), \vec{\nabla} n(\vec{r}), \nabla^2 n(\vec{r}), \tau(\vec{r})].$$ Meta Generalized Gradient Approximation

$$E_{\mathrm{xc}}^{\mathrm{GH}} = c_x E^{\mathrm{EXX}} + E_{\mathrm{xc}}^{\mathrm{DFT}}[n(\vec{r}), \dots],$$ Global Hybrid functional

$$E_{\mathrm{xc}}^{\mathrm{RSH}} = c_{\mathrm{sr}} E_{\mathrm{sr}}^{\mathrm{EXX}} + c_{\mathrm{lr}} E_{\mathrm{lr}}^{\mathrm{EXX}} + E_{\mathrm{xc}}^{\mathrm{DFT}}[n(\vec{r}), \dots].$$ Range Separated Hybrid functional

+ vdW non-local functionals
+ Kinetic Energy functionals (KEDF)

Kohn-Sham Equations

Idea: replace the original system of interacting electrons with a system of equations for non-interacting electrons. A system where the electronic density remains the same as in the multi-particle system

- The Lagrangian to be minimized is:

$$\mathcal{L}[\{\phi_i\}] = T_s[\{\phi_i\}] + U[n] + E_{xc}[n] + \int V_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\, d^3\mathbf{r} - \sum_{i=1}^{N} \varepsilon_i \left(\int |\phi_i(\mathbf{r})|^2\, d^3\mathbf{r} - 1 \right) .$$

- Taking the variation with respect to $\phi_i^*(\mathbf{r})$ yields:

$$-\frac{1}{2}\nabla^2 \phi_i(\mathbf{r}_i) + [V_{\text{ext}}(\mathbf{r}_i) + V_H(\mathbf{r}_i) + V_{xc}(\mathbf{r}_i)]\, \phi_i(\mathbf{r}_i) = \varepsilon_i\, \phi_i(\mathbf{r}_i)\,,$$

for $i = 1, 2, \ldots, N_e$.

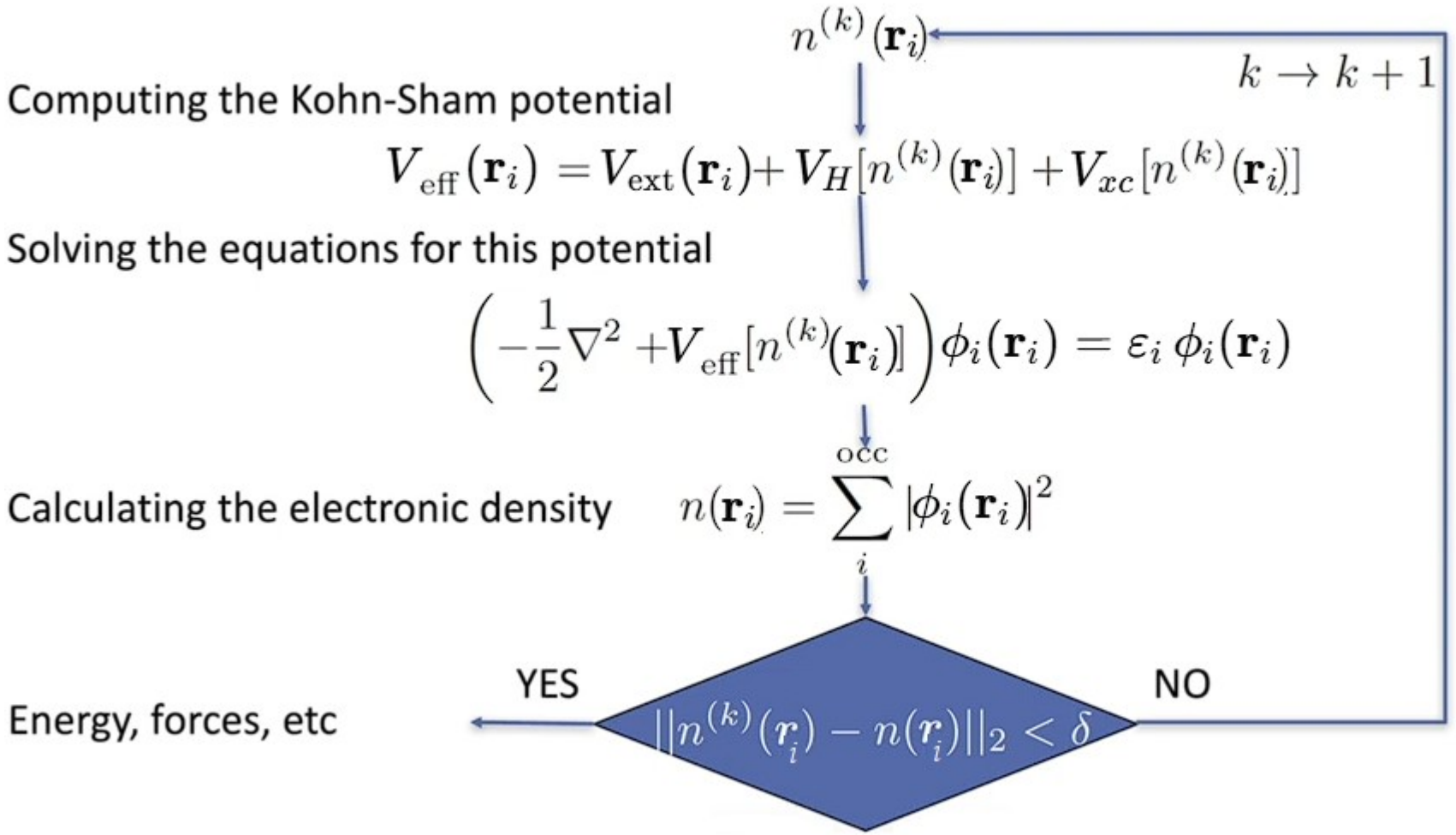
$$V_H(\mathbf{r}_i) = \int \frac{n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}\, d^3\mathbf{r}_j \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

- The electron density is obtained from the orbitals as: $n(\mathbf{r}_i) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r}_i)|^2 .$

$$V_{\text{ext}}(\mathbf{r}_i) = -\sum_{i,I} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

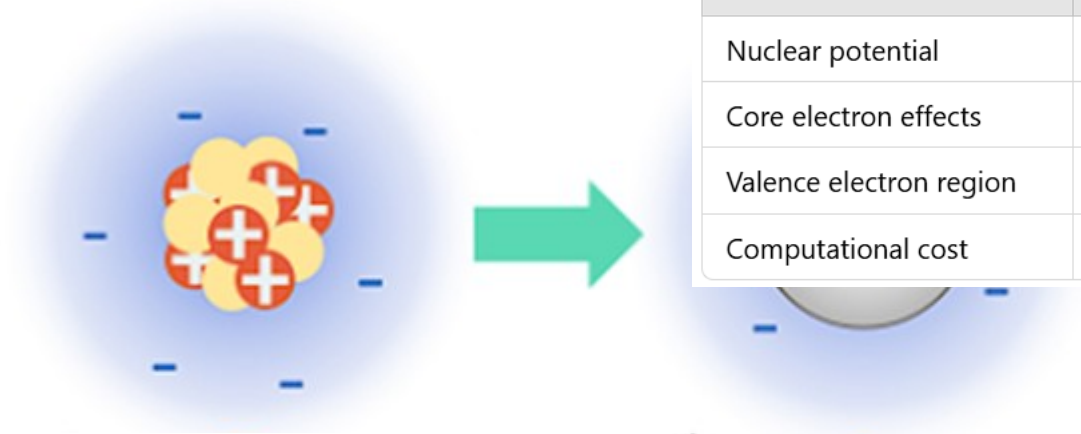
Kohn-Sham Equations: the Algorithm

The first approximation (k=1), for example, is the superposition of electronic densities for atoms





Pseudopotential

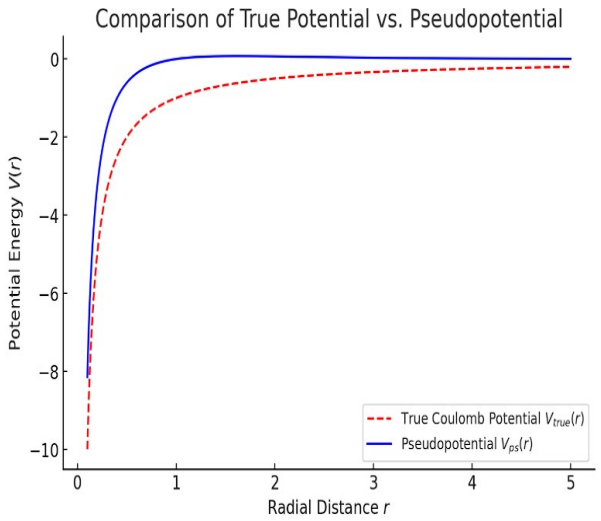


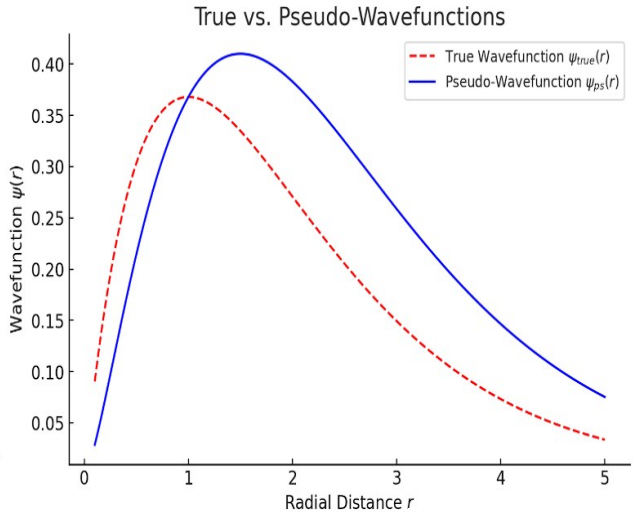
Feature	True Potential & Wavefunction	Pseudopotential & Pseudo-Wavefunction
Nuclear potential	$V_{\text{true}}(r) = -Z/r$	Smooth $V_{\text{ps}}(r)$, no singularity
Core electron effects	Must be computed	Replaced with effective potential
Valence electron region	Physically accurate	Matched to true wavefunction outside r_c
Computational cost	High	Reduced

replace

atoms,

removing the need to explicitly treat tightly bound core electrons.





- **Goal:**
  - Simplify calculations by focusing on valence electrons.
  - Reduce the number of basis functions required due to the smoothness of the pseudo-wavefunctions.

First Level: Local Density Approximation

Based on the approximation of a homogeneous electron gas

$$T[n] \approx T^{LDA}[n] \approx T_s{}^{LDA}[n] = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3}\int d^3r\, n(\mathbf{r})^{5/3}$$

$$E_x[n] = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r n(\mathbf{r})^{4/3}$$ exchange energy functional

The correlation energy functional is unknown; it is approximated using various methods such as quantum Monte Carlo or random phase approximation(RPA, Random Phase Approximation)

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}[n^\alpha, n^\beta] = \int d^3r n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n^\alpha(\mathbf{r}), n^\beta(\mathbf{r}))$$ general form with spins

Second Level: General Gradient Approximation

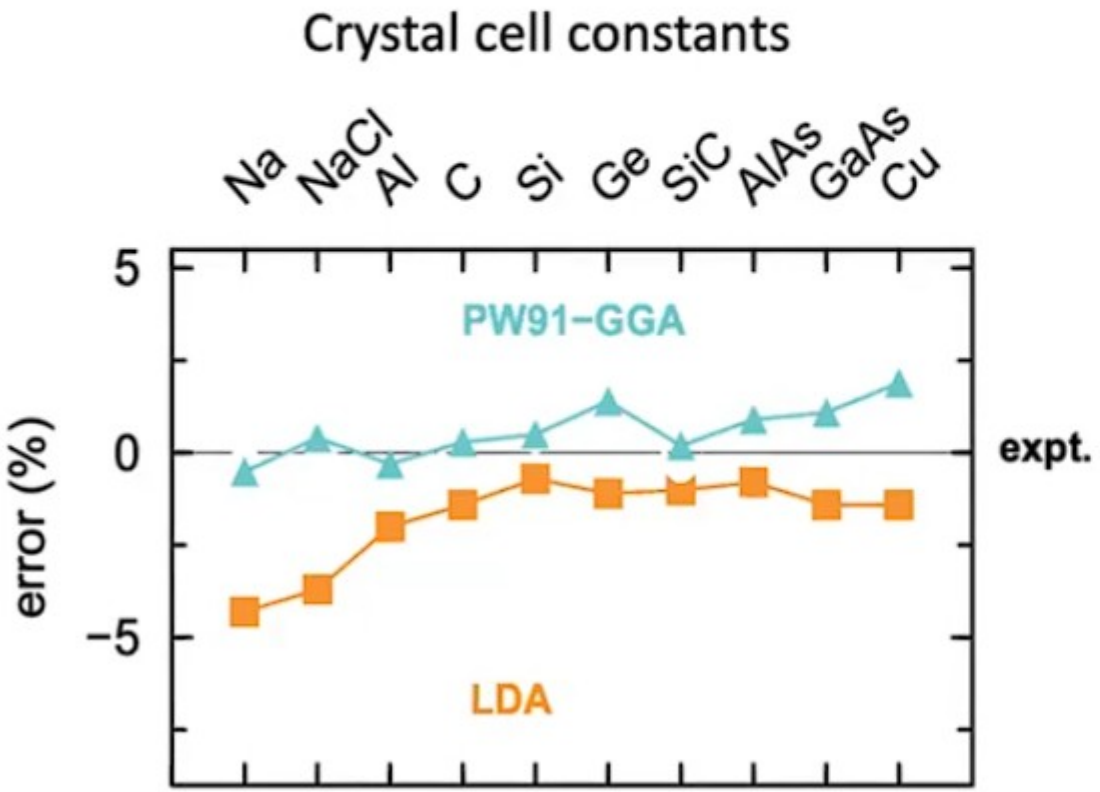
$$T[n] \approx T^{LDA}[n] \approx T_s{}^{LDA}[n] = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3}\int d^3r\, n(\mathbf{r})^{5/3}$$ kinetic energy within LDA

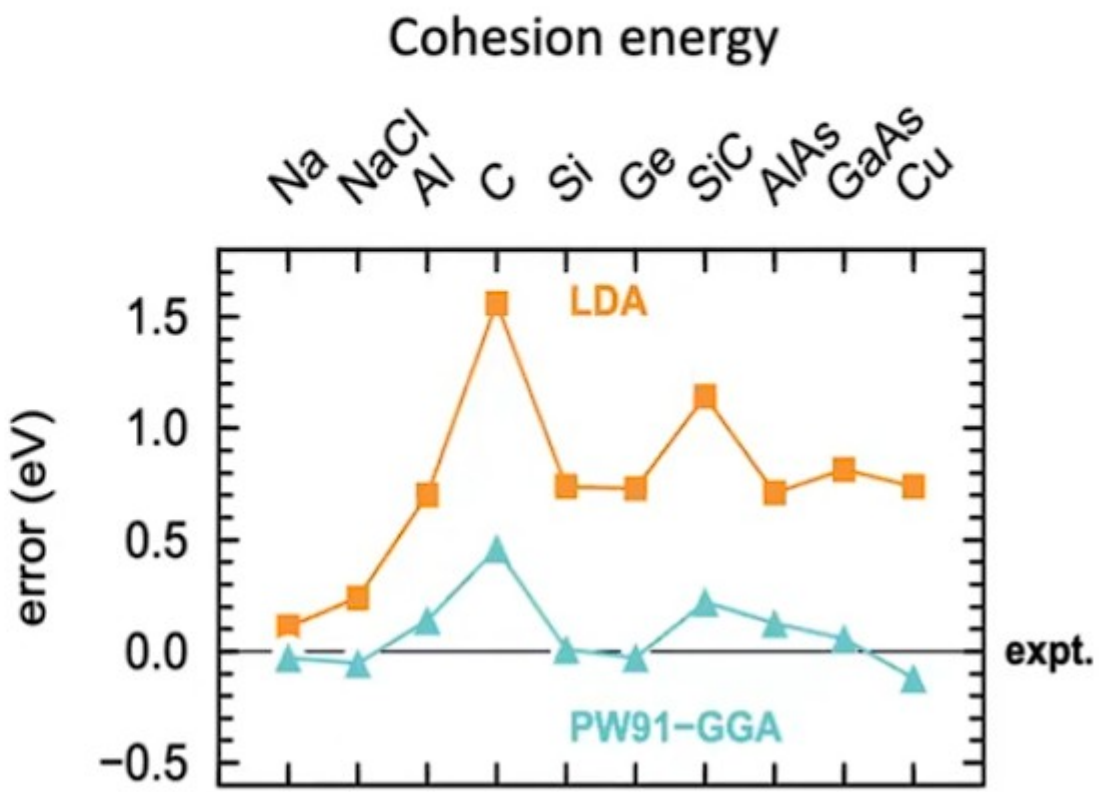
$$T_s[n] \approx T_s^{LDA}[n] + \frac{\hbar^2}{8m}\int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$ kinetic energy within GGA

$$E_x[n] = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r n(\mathbf{r})^{4/3}$$ exchange energy within LDA

$$E_x[n] \approx E_x^{LDA}[n] - \frac{10q^2}{432\pi(3\pi^2)^{1/3}}\int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}}$$ exchange energy within GGA

LDA vs GGA


Crystal cell constants
Na
NaCl
Al
C
Si
Ge
SiC
AlAs
GaAs
Cu
5
0
−5
error (%)
PW91−GGA
LDA
expt.


Cohesion energy
Na
NaCl
Al
C
Si
Ge
SiC
AlAs
GaAs
Cu
1.5
1.0
0.5
0.0
−0.5
error (eV)
LDA
PW91−GGA
expt.

Second Level: General Gradient Approximation

BP86 (Becke, Perdew, 1988) – functional B88 with correlation energy previously proposed by Perdew. It predicts geometry and vibrational frequencies accurately and is fairly good for spectroscopic investigations

BLYP (Becke, Lee, Yang, Parr) – functional B88 with correlation energy proposed by Lee, Yang та Parr. It predicts excessively long interatomic bonds; however, it is popular in chemistry.

Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density

C **Lee**, W **Yang**, RG **Parr** - Physical review B, 1988 - APS

A correlation-energy formula due to Colle and Salvetti [Theor. Chim. Acta 37, 329 (1975)], in which the correlation energy density is expressed in terms of the electron density and a …

PBE (Perdew, Burke, Ernzerhof) – very popular in physics non-empirical GGA-functional

Generalized gradient approximation made simple

JP Perdew, K Burke, M Ernzerhof - Physical review letters, 1996 - APS

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior …

DFT extensions and limitations

- Although standard DFT is a ground-state theory, various extensions (TDDFT, ensemble DFT, constrained methods, and ΔSCF) allow us to study excited states.

- The ΔSCF (delta self-consistent field) approach involves performing separate DFT calculations for the ground and excited states and then taking the energy difference.
- This method can be used for cases where the excited state is well described by a single Slater determinant.
- Ensemble DFT is another framework that can be applied to excited states by considering a statistical ensemble of ground and excited states.
- It provides an alternative way to define a density functional that accounts for multiple states.

- **Limitation:**
- DFT may struggle with systems where electron correlation is strong (e.g., transition metal oxides, Mott insulators)
- **Outcome:**
- Predicts incorrect electronic structure and magnetic properties

Summary

LDA, GGA, meta-GGA, hybrid: practical picture

- LDA uses only the local density and works best when the density varies slowly.
- GGA, especially PBE, adds density gradients and is the usual starting point for solids and materials calculations.
- meta-GGA includes additional semilocal information and can improve equilibrium properties and energetics.
- Hybrid functionals mix in exact exchange and often improve band gaps, but at much higher computational cost.
- DFT+U is often introduced when localized d or f electrons are not described well by semilocal functionals.

How to choose the exchange-correlation functional?

- Match the functional to the physical question, not to a general idea of 'best possible accuracy'.
- For geometry optimization and qualitative trends, GGA/PBE is often sufficient and computationally efficient.
- For band gaps, defect levels, and localized states in oxides, hybrids or beyond-DFT methods are often needed.
- Every result should therefore be interpreted together with the limitations of the chosen functional.
- In that sense, semilocal DFT should be viewed as a reliable baseline, not as a universally exact description.

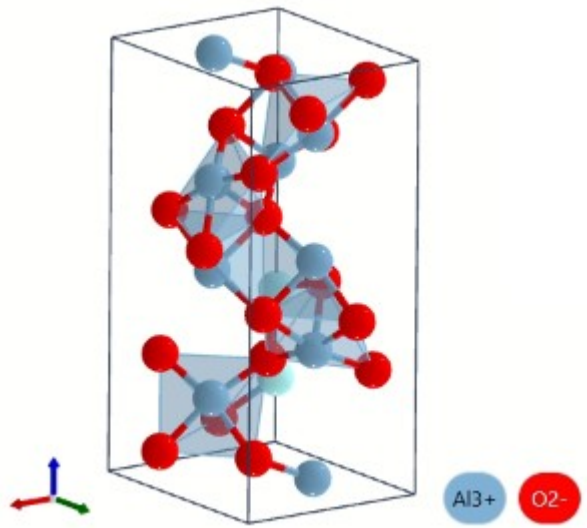
Electronic structure of the band edge formed by Ga doping in the α-Al2O3 unit cell

Motivation

- Ultra-wide bandgap oxides for power electronics
- Ga_2O_3 as active electronic component
- Role of Al_2O_3 host environment
- Need for atomistic electronic structure insight

From Materialsproject website

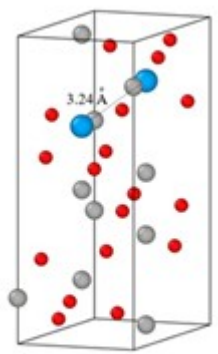
Crystal Structure



Lattice (Conventional)

a	4.81 Å
b	4.81 Å
c	13.12 Å
α	90.00 °
β	90.00 °
γ	120.00 °
Volume	262.26 Å³

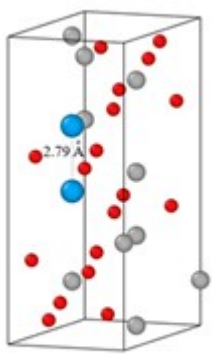
(a) Config A



$d_{Ga\text{-}Ga}$=3.24 Å

ΔE = 114.94 meV/cell

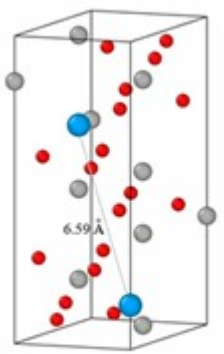
(b) Config B



$d_{Ga\text{-}Ga}$=2.79 Å

ΔE = 0.00 meV/cell

(c) Config C



$d_{Ga\text{-}Ga}$=6.59 Å

ΔE = 18.56 meV/cell

Computational Model

- Ga atoms embedded in Al_2O_3-derived supercell
- Periodic boundary conditions
- Chemically embedded Ga-rich region
- Not a vacuum-isolated nanocrystal

DFT Methodology

- Quantum ESPRESSO v7.4.1
- PBE exchange–correlation functional
- Plane-wave basis and PAW pseudopotentials
- SCF → NSCF → DOS / PDOS → charge density

$$D = \frac{1}{6}\sum_{i=1}^{6}\frac{\left|d_i - \bar{d}\right|}{\bar{d}}$$

$$\sigma = \left[\frac{1}{6}\sum_{i=1}^{6}(d_i - \bar{d})^2\right]^{1/2}$$

$$\lambda = \frac{1}{6}\sum_{i=1}^{6}\left(\frac{d_i}{\bar{d}}\right)^2$$

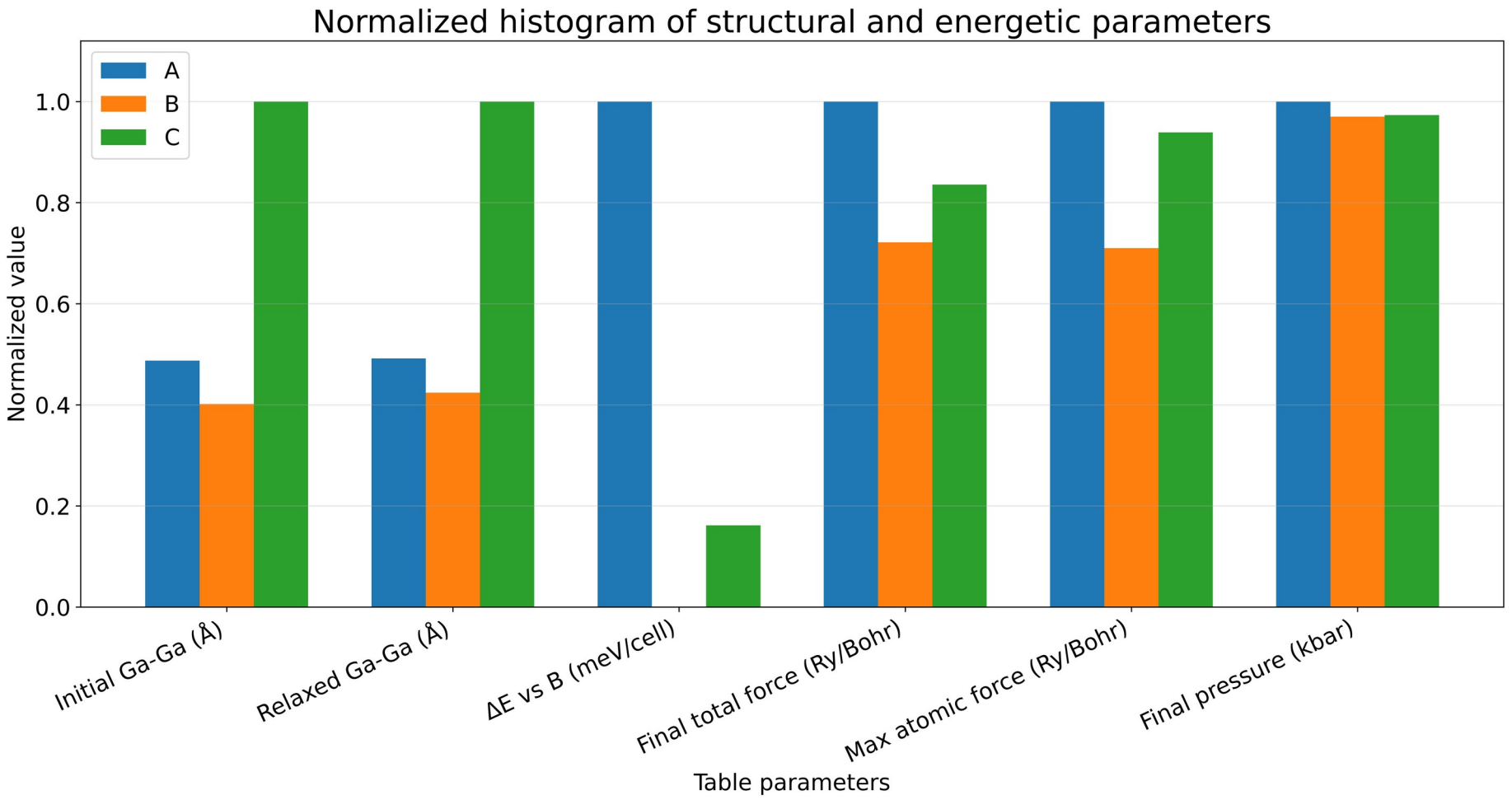
$$\sigma_\theta^2 = \frac{1}{15}\sum_{j=1}^{15}(\theta_j - \bar{\theta})^2$$

Config	Initial Ga–Ga (Å)	Relaxed Ga–Ga (Å)	Final relax energy (Ry)	ΔE vs B (meV/cell)	Final total force (Ry/Bohr)	Max atomic force (Ry/Bohr)	Final pressure (kbar)
A	3.2552	3.2397	-1704.41622669	114.94	0.000280	8.83×10^{-5}	58.66
B	2.6815	2.7918	-1704.42467465	0.00	0.000202	6.27×10^{-5}	56.90
C	6.6785	6.5862	-1704.42331023	18.56	0.000234	8.29×10^{-5}	57.09

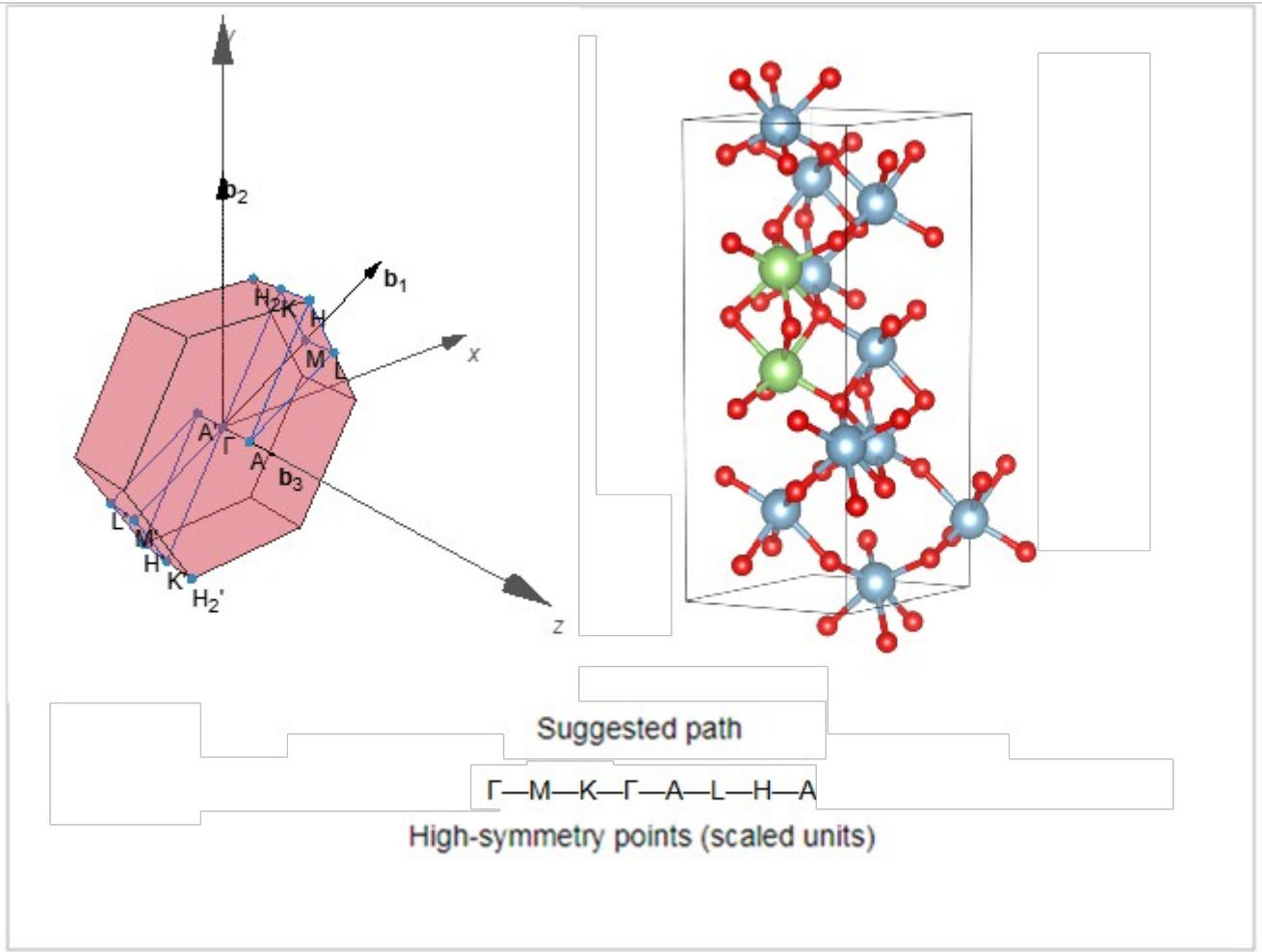
Config	Ga site indices	Average Ga–O (Å)	Min Ga–O (Å)	Max Ga–O (Å)	Host reference average Al–O (Å)	Average expansion vs host (Å)
A	1, 2	1.9811	1.9007	2.0615	1.9340	+0.0471
B	2, 9	1.9956	1.9239	2.0673	1.9340	+0.0616
C	2, 5	1.9930	1.9193	2.0668	1.9340	+0.0590

System	Ga site indices	D	σ (Å)	λ	σ^2_θ (deg)
Host ref.	same sites	0.0299	0.0578	1.000894	98.882
A	1,2	0.0406	0.0804	1.001649	126.953
B	2,9	0.0359	0.0717	1.001291	116.836
C	2,5	0.0370	0.0737	1.001368	141.310

Histogram of the Structural parameters



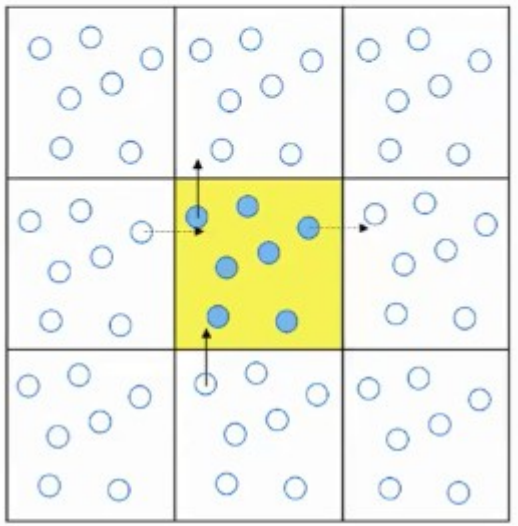
SeeK-path: the *k*-path finder and visualizer



Plane Waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

$$u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

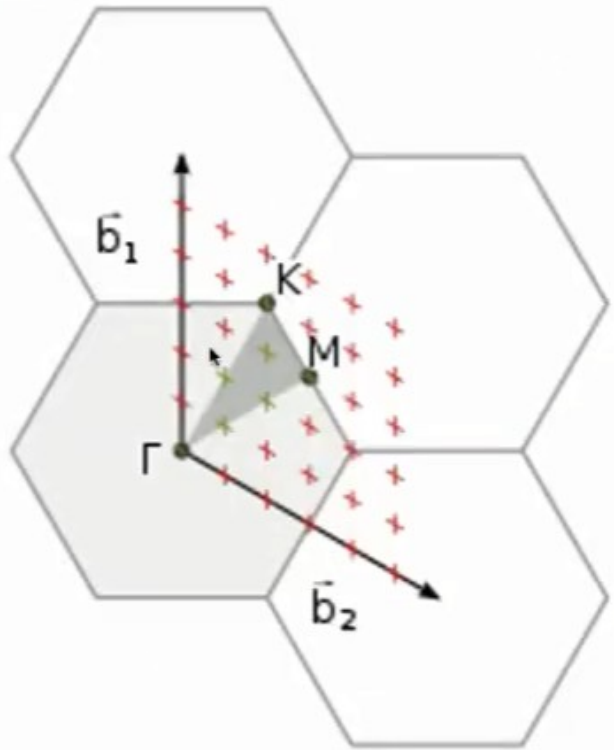


Reciprocal Space

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\mathrm{BZ}}} \sum_n \int_{\mathrm{BZ}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

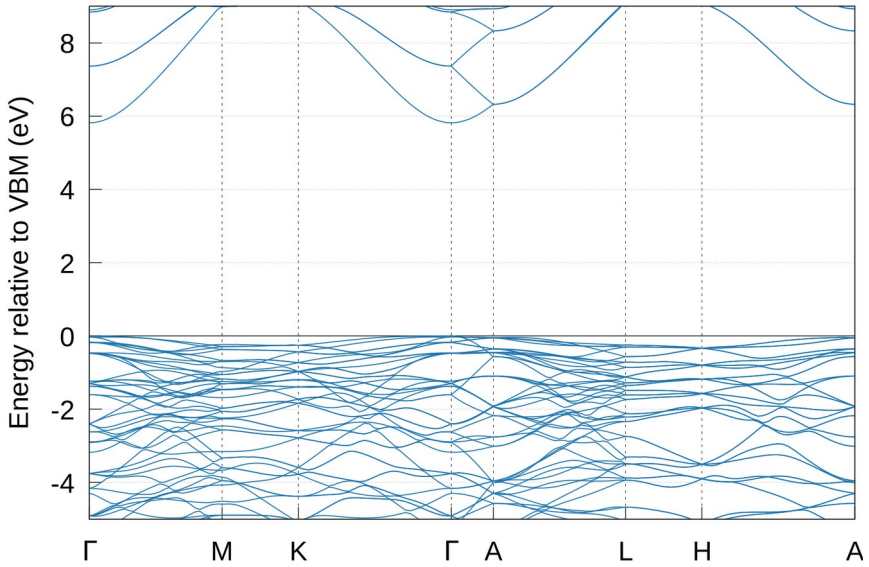
$$\rho(\mathbf{r}) = \sum_{n\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{\mathrm{cutoff}}$$

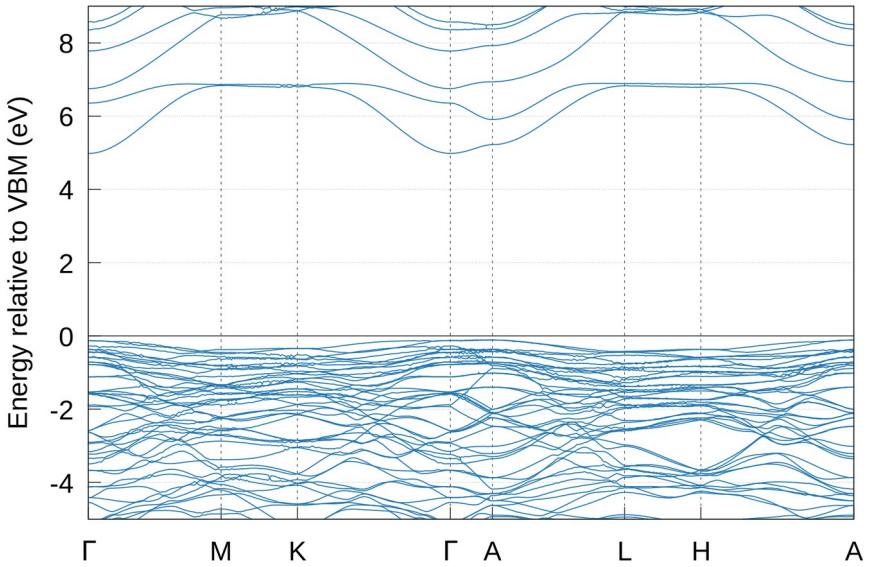


Comparative Band Structure Analysis

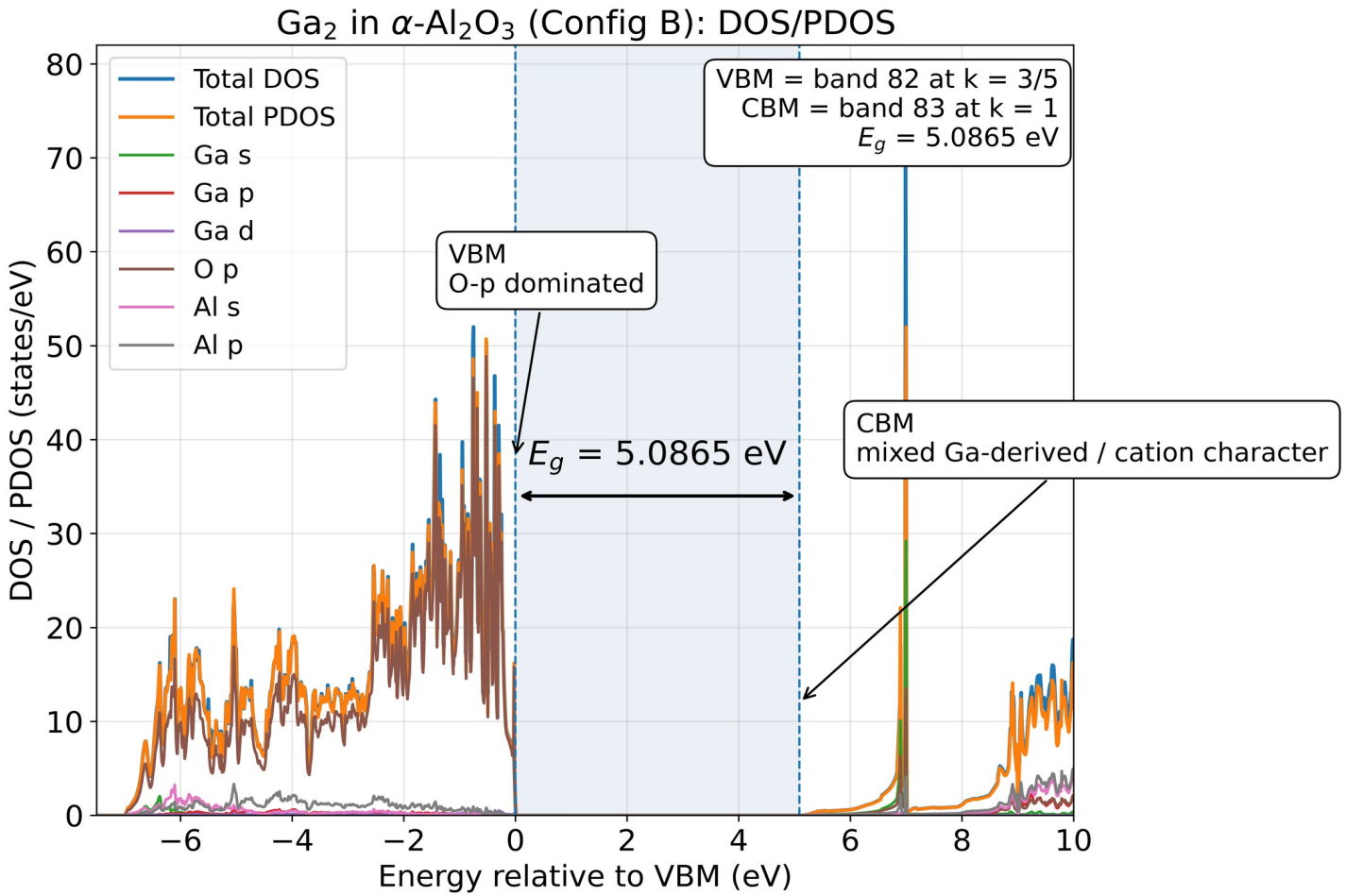
Pristine α - Al_2O_3

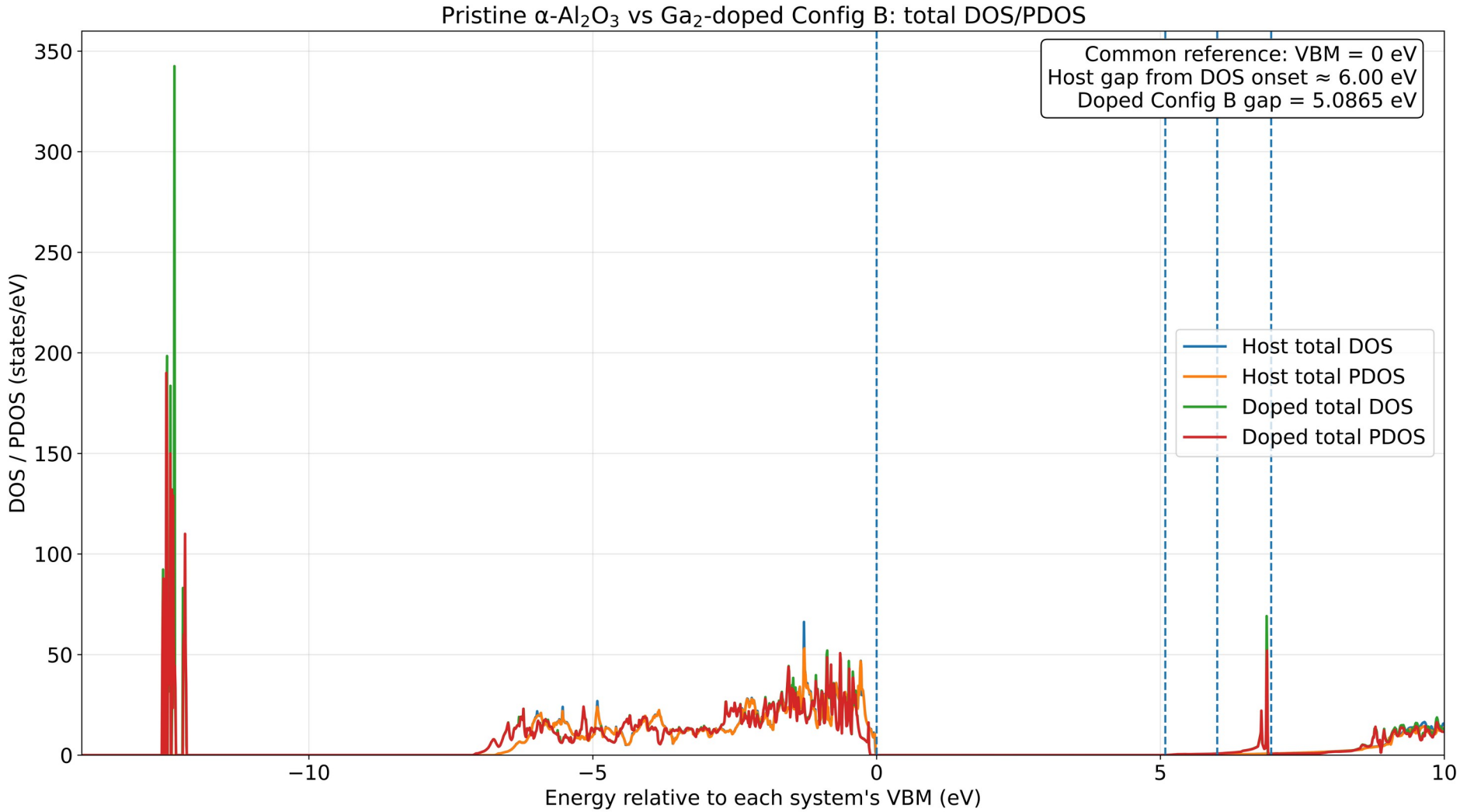


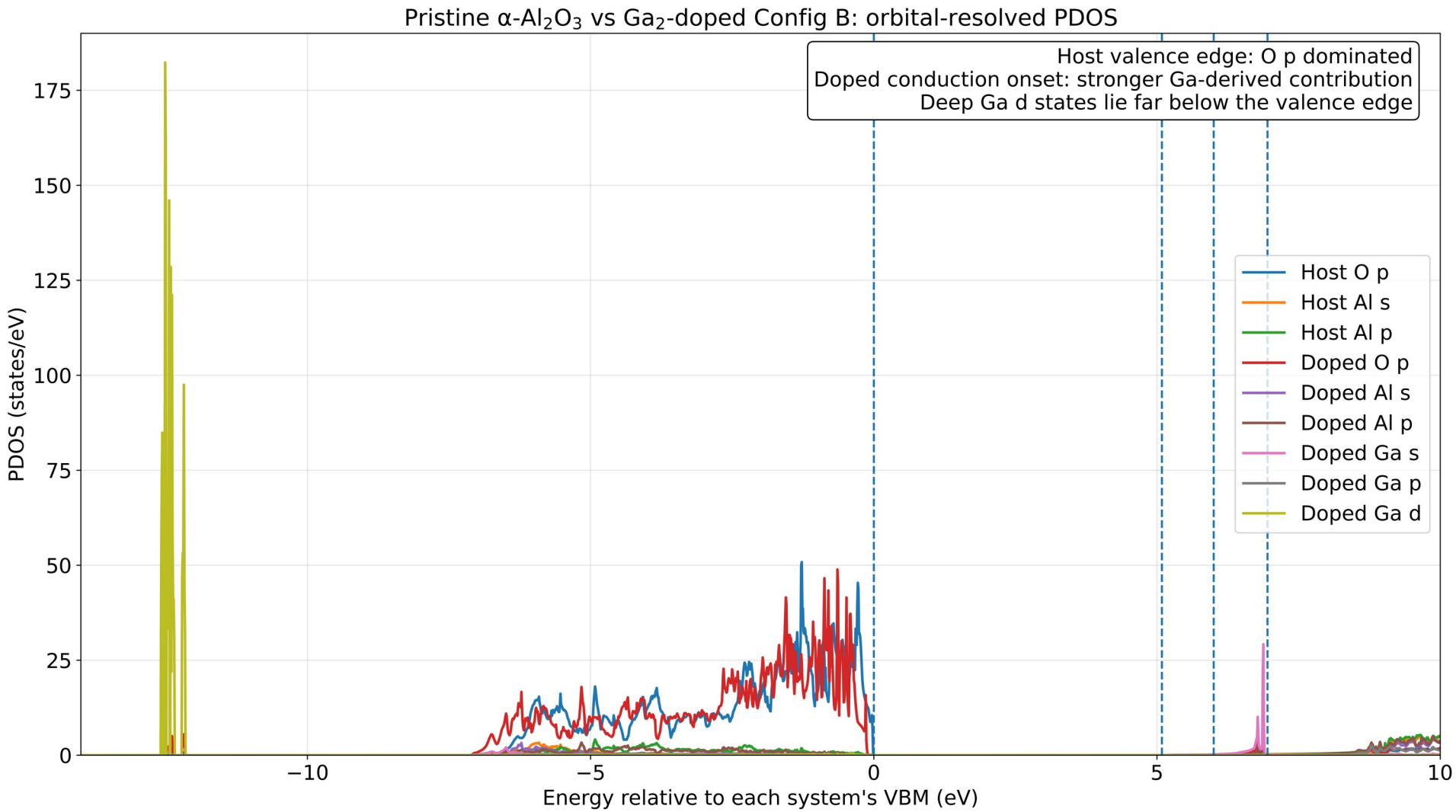
Ga_2 - doped Config B



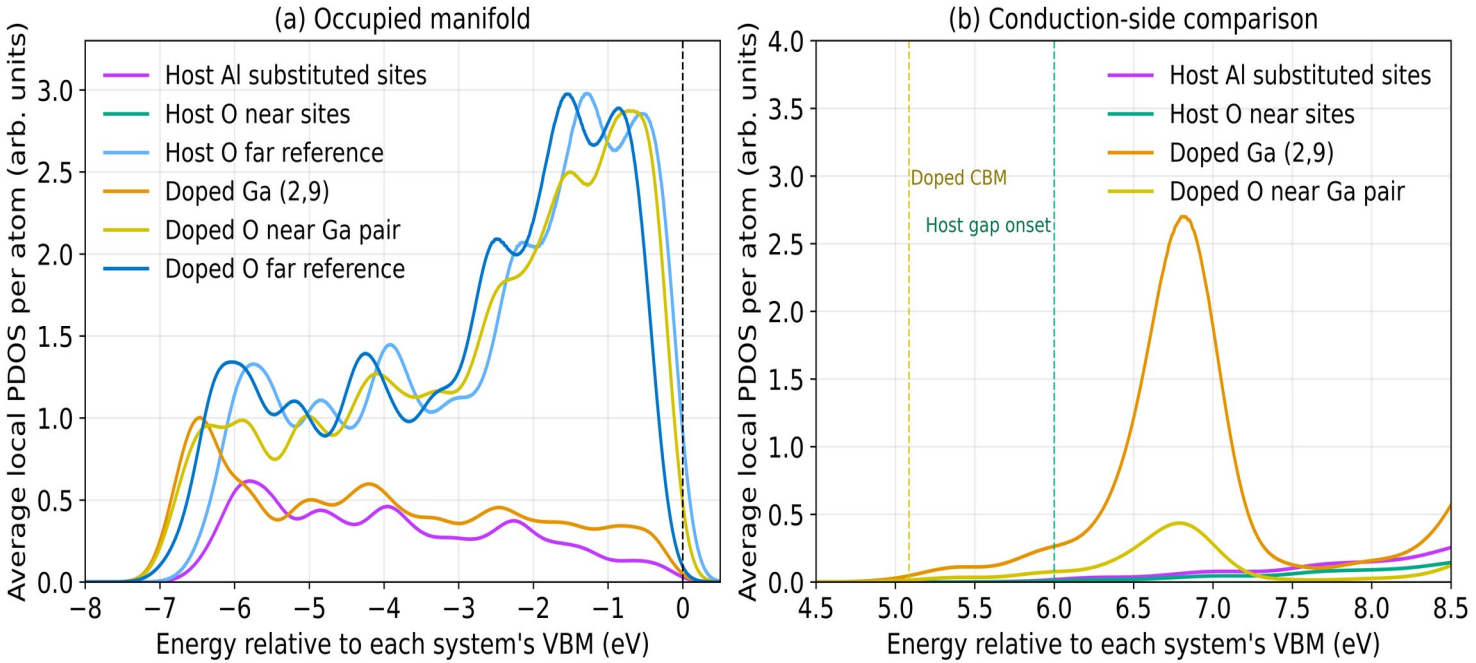
Total and Projected Density of States



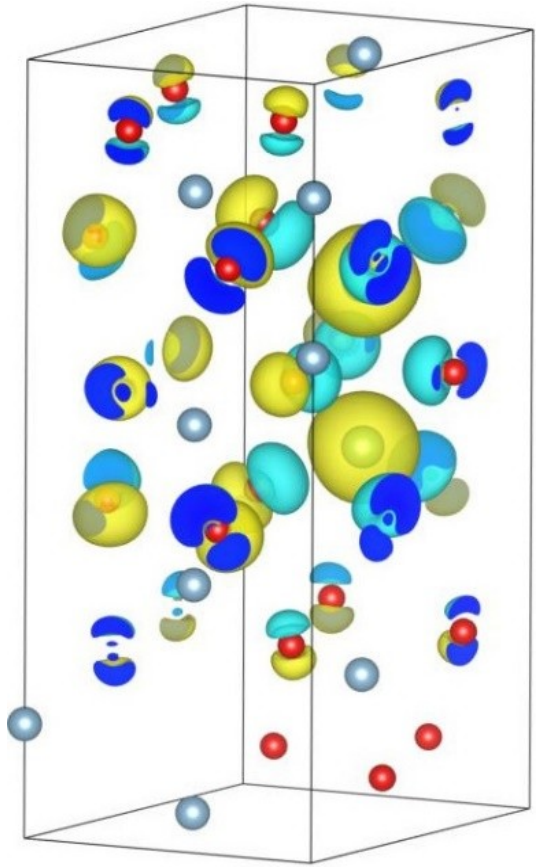

Pristine α-Al2O3 vs Ga2-doped Config B: total DOS/PDOS
Common reference: VBM = 0 eV
Host gap from DOS onset ≈ 6.00 eV
Doped Config B gap = 5.0865 eV
Host total DOS
Host total PDOS
Doped total DOS
Doped total PDOS
DOS / PDOS (states/eV)
Energy relative to each system's VBM (eV)
0
50
100
150
200
250
300
350
−10
−5
0
5
10


Pristine α-Al2O3 vs Ga2-doped Config B: orbital-resolved PDOS
Host valence edge: O p dominated
Doped conduction onset: stronger Ga-derived contribution
Deep Ga d states lie far below the valence edge
Host O p
Host Al s
Host Al p
Doped O p
Doped Al s
Doped Al p
Doped Ga s
Doped Ga p
Doped Ga d
PDOS (states/eV)
Energy relative to each system's VBM (eV)
0
25
50
75
100
125
150
175
−10
−5
0
5
10

Site-Resolved Local PDOS Comparison



Charge-density-difference isosurfaces for configuration B, defined as $\Delta\rho = \rho(B) - \rho(host)$.



The charge-density-difference map shows that the electronic response to Ga substitution is strongly localized in the vicinity of the substituted Ga pair and the surrounding oxygen coordination environment.

Electronic Structure Analysis

- Valence band dominated by O-2p states
- Strong O-p peak deep in valence region
- Conduction band formed by Ga-p and O-p antibonding states
- Weak Al contribution near band edges

Model Limitations

- No explicit vacuum confinement
- Chemical rather than spatial quantum dot
- PBE underestimates band gap
- Finite supercell effects

Conclusions and Outlook

- Clear identification of band-edge character
- Ga–O network controls electronic structure
- Results guide realistic quantum-dot modeling
- Future work: explicit nanoclusters, hybrids, optics

Thank you for attention!

Back slides

Variation – One–Electron Term

- Expression:

$$\int \phi_i^*(\mathbf{r}_i) \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) \, d^3 r_i$$

- Variation:

$$\delta \left[\cdots \right] = \int \delta\phi_i^*(\mathbf{r}_i) \left[-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V_{\text{ext}}(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) \, d^3 r_i$$

Variation – Normalization Constraint

- Normalization Variation for Orbital i:

$$\delta \left[-\varepsilon_i \left(\int |\phi_i(\mathbf{r}_i)|^2 \, d^3 r_i - 1 \right) \right] = -\varepsilon_i \int \delta\phi_i^*(\mathbf{r}_i) \, \phi_i(\mathbf{r}_i) \, d^3 r_i$$

Variation – Electron–Electron Interaction

- **Coulomb Term for Orbital i:**

$$E_{ee}^{(i)} = \sum_{j \neq i} \iint \frac{|\phi_i(\mathbf{r}_i)|^2 \, |\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3 r_i \, d^3 r_j$$

- **Variation with Respect to $\phi_i^*(\mathbf{r}_i)$:**

$$\delta E_{ee}^{(i)} = \sum_{j \neq i} \int d^3 r_i \, \delta\phi_i^*(\mathbf{r}_i) \, \phi_i(\mathbf{r}_i) \left[\int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3 r_j \right]$$

- **Define the Hartree Potential:** $V_{\mathrm{H}}(\mathbf{r}_i) = \sum_{j \neq i} \int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \, d^3 r_j$

Setting Up the Variational Problem

- **Objective:** Minimize E with respect to the orbitals $\{\phi_i\}$ under the constraint

$$\langle \phi_i | \phi_i \rangle = \int |\phi_i(\mathbf{r}_i)|^2 \, d^3 r_i = 1 \quad \text{for each } i.$$

- **Introduce Lagrange Multipliers ε_i:**

$$\mathcal{L}[\{\phi_i\}] = E[\{\phi_i\}] - \sum_{i=1}^{N} \varepsilon_i \left(\langle \phi_i | \phi_i \rangle - 1 \right)$$

- **Variation:** Perform independent variations with respect to $\phi_i^*(\mathbf{r}_i)$

Variation – Coulomb (Direct) Term

- For orbital i:

$$\delta\left(\frac{1}{2}\sum_{j=1}^{N} J_{ij}\right) = \sum_{j=1}^{N}\int \delta\phi_i^*(\mathbf{r}_i)\left[\int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\,d^3r_j\right]\phi_i(\mathbf{r}_i)\,d^3r_i$$

- Define the Coulomb Operator:

$$\hat{J}_j\phi_i(\mathbf{r}_i) = \left[\int \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\,d^3r_j\right]\phi_i(\mathbf{r}_i)$$

Variation – Exchange Term

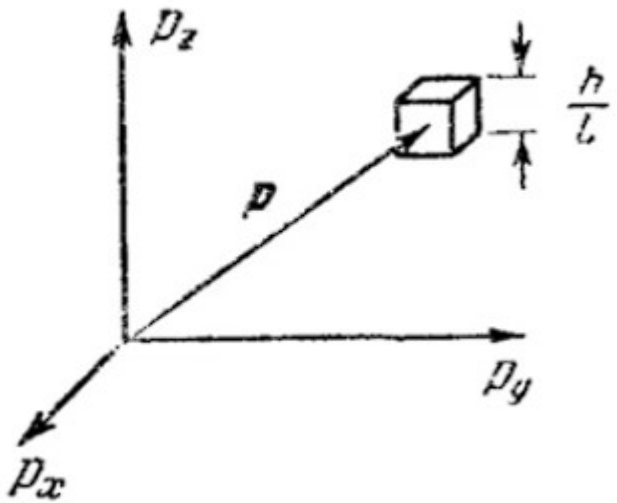
- For orbital i:

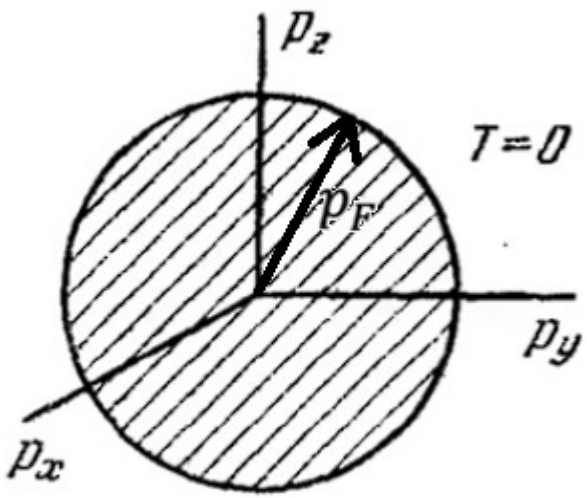
$$\delta\left(-\frac{1}{2}\sum_{j=1}^{N} K_{ij}\right) = -\sum_{j=1}^{N}\int \delta\phi_i^*(\mathbf{r}_i)\left[\int \frac{\phi_j^*(\mathbf{r}_j)\,\phi_i(\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|}\,d^3r_j\right]\phi_j(\mathbf{r}_i)\,d^3r_i$$

- Define the Exchange Operator:

$$\hat{K}_j\phi_i(\mathbf{r}_i) = \left[\int \frac{\phi_j^*(\mathbf{r}_j)\,\phi_i(\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|}\,d^3r_j\right]\phi_j(\mathbf{r}_i)$$

Thomas-Fermi Model: uniform electron gas





All electron states up to a certain momentum p_F are occupied (Fermi-Dirac statistics)

Each state with a volume of $(h/L)^3$ is occupied by 2 electrons

$\Delta p_x = \frac{h}{L}$ - uncertainty of momentum

$\frac{h^3}{L^3} = \frac{h^3}{V}$ $\qquad \frac{4}{3}\pi p_F^3$

$2\frac{\frac{4}{3}\pi p_F^3}{h^3/V} = N$ - number of electrons

Thomas-Fermi Model: uniform electron gas

$$2\frac{\frac{4}{3}\pi p_F^3}{h^3/V} = N$$ - number of electrons

$$n = \frac{N}{V} = \frac{8\pi}{3h^3}p_F^3$$ - electron density

$$p_F = (\frac{3h^3}{8\pi}n)^{1/3} \longrightarrow T_{\max} = \frac{p_F^2(\mathbf{r})}{2m}$$

$$T_{\max} = \frac{1}{2m}(\frac{3h^3}{8\pi})n(\boldsymbol{r})^{2/3}$$

Thomas-Fermi Model: uniform electron gas

kinetic energy density

$T = \int t(\mathbf{r})\,\mathbf{dr}$. - kinetic energy of electrons

$$
\begin{aligned}
t &= \frac{T}{V} = \frac{1}{V}\int \frac{p^2}{2m} dN = \frac{1}{V}\int_0^{p_F} \frac{p^2}{2m} \cdot \frac{4\pi p^2 \cdot V \cdot 2}{h^3}\, dp \\
&= \frac{8\pi}{2mh^3}\int_0^{p_F} p^4 dp = \frac{8\pi}{2mh^3} \cdot \frac{p_F^5}{5}\,.
\end{aligned}
$$

Normalization Constraint

The total number of electrons is fixed:

$$\int n(\mathbf{r}_i)\, d^3\mathbf{r}_i = N\,.$$

To enforce this during minimization, we introduce a Lagrange multiplier μ (the chemical potential) and define

$$\mathcal{L}[n] = E[n] - \mu\left(\int n(\mathbf{r}_i)\, d^3\mathbf{r}_i - N\right)\,.$$

Minimization – Variational Condition

The optimal density satisfies

$$\frac{\delta \mathcal{L}[n]}{\delta n(\mathbf{r}_i)} = 0\,.$$

We now compute the variation for each term with respect to $n(\mathbf{r}_i)$.

Second Level: General Gradient Approximation

$$T[n] \approx T^{LDA}[n] \approx T_s{}^{LDA}[n] = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3}\int d^3r\, n(\mathbf{r})^{5/3}$$ kinetic energy within LDA

$$T_s[n] \approx T_s^{LDA}[n] + \frac{\hbar^2}{8m}\int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$ kinetic energy within GGA

$$E_x[n] = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r n(\mathbf{r})^{4/3}$$ exchange energy within LDA

$$E_x[n] \approx E_x^{LDA}[n] - \frac{10q^2}{432\pi(3\pi^2)^{1/3}}\int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}}$$ exchange energy within GGA

$$E_{xc}^{GGA}[n] = \int d^3r\, f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$ general form for exchange-correlation functional in GGA

First Level: Local Density Approximation

VWN (Vosko, Wilks, Nusair) – one of the first successful LDAs

Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis

SH **Vosko**, L **Wilk**, M **Nusair** - Canadian Journal of physics, 1980 - cdnsciencepub.com

We assess various approximate forms for the correlation energy per particle of the spin-polarized homogeneous electron gas that have frequently been used in applications of the local …

PZ (Perdew, Zunger)

Self-interaction correction to density-functional approximations for many-electron systems

JP **Perdew**, A **Zunger** - Physical Review B, 1981 - APS

The exact density functional for the ground-state energy is strictly self-interaction-free (ie, orbitals demonstrably do not self-interact), but many approximations to it, including the local-…

PW92 (Perdew, Wang, 1992)

Accurate and simple analytic representation of the electron-gas correlation energy

JP **Perdew**, Y Wang - Physical review B, **1992** - APS

We propose a simple analytic representation of the correlation energy ε c for a uniform electron gas, as a function of density parameter rs and relative spin polarization ζ. Within the …

Second Level: General Gradient Approximation

Density-functional exchange-energy approximation with correct asymptotic behavior

AD Becke - Physical review A, 1988 - APS

Current gradient-corrected density-functional approximations for the exchange energies of atomic and molecular systems fail to reproduce the correct 1/r asymptotic behavior of the exchange-energy density. Here we report a gradient-corrected exchange-energy functional with the proper asymptotic limit. Our functional, containing only one parameter, fits the exact Hartree-Fock exchange energies of a wide variety of atomic systems with remarkable accuracy, surpassing the performance of previous functionals containing two parameters or …

$$F^B = \frac{\beta s_\sigma^2}{1 + 6\beta s_\sigma \sinh^{-1} s_\sigma} \qquad s_\sigma(\mathbf{r}) = \frac{|\nabla \rho_\sigma(\mathbf{r})|}{\rho_\sigma^{4/3}(\mathbf{r})}$$

Parameter β=0.0042 was chosen to reproduce the known exchange energy for noble gases

Second Level: General Gradient Approximation

BP86 (Becke, Perdew, 1988) – functional B88 with correlation energy previously proposed by Perdew. It predicts geometry and vibrational frequencies accurately and is fairly good for spectroscopic investigations

BLYP (Becke, Lee, Yang, Parr) – functional B88 with correlation energy proposed by Lee, Yang та Parr. It predicts excessively long interatomic bonds; however, it is popular in chemistry.

Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density

C **Lee**, W **Yang**, RG **Parr** - Physical review B, 1988 - APS

A correlation-energy formula due to Colle and Salvetti [Theor. Chim. Acta 37, 329 (1975)], in which the correlation energy density is expressed in terms of the electron density and a …

PBE (Perdew, Burke, Ernzerhof) – very popular in physics non-empirical GGA-functional

Generalized gradient approximation made simple

JP Perdew, K Burke, M Ernzerhof - Physical review letters, 1996 - APS

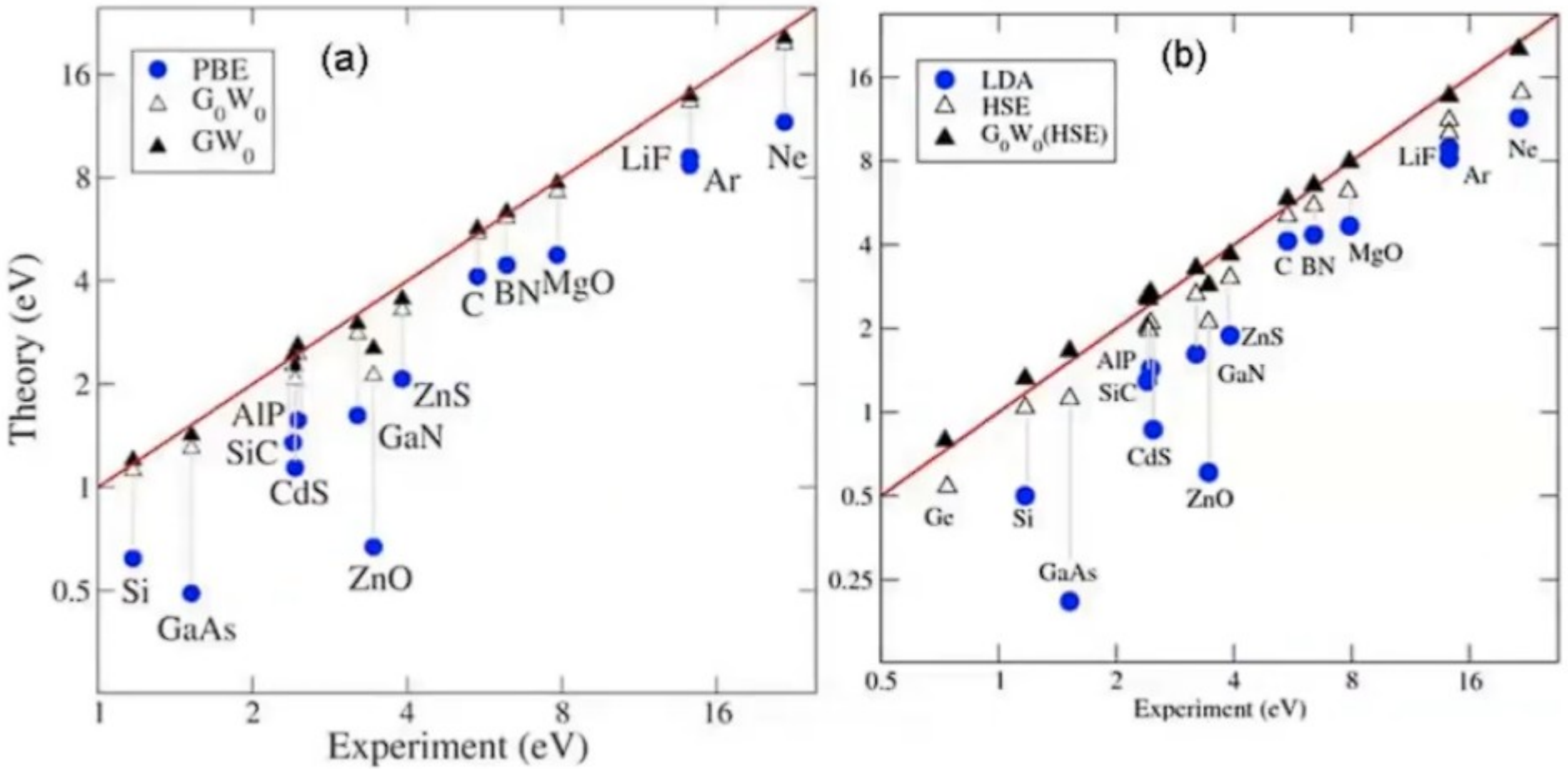
Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior …

Second Level: General Gradient Approximation

TABLE I. Atomization energies of molecules, in kcal/mol (1 eV = 23.06 kcal/mol). E_{XC} has been evaluated on self-consistent densities at experimental geometries [33]. Nonspherical densities and Kohn-Sham potentials have been used for open-shell atoms [34]. The calculations are performed with a modified version of the CADPAC program [35]. The experimental values for ΔE (with zero point vibration removed) are taken from Ref. [36]. PBE is the simplified GGA proposed here. UHF is unrestricted Hartree-Fock, for comparison.

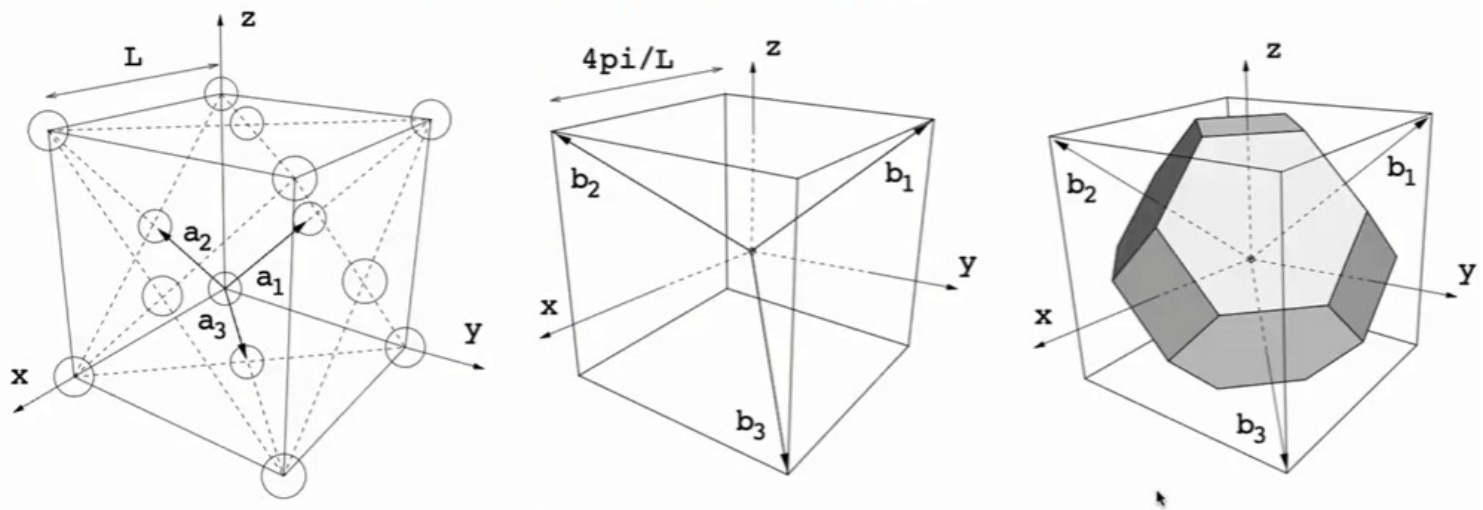
System	ΔE^{UHF}	ΔE^{LSD}	ΔE^{PW91}	ΔE^{PBE}	ΔE^{expt}
H_2	84	113	105	105	109
LiH	33	60	53	52	58
CH_4	328	462	421	420	419
NH_3	201	337	303	302	297
OH	68	124	110	110	107
H_2O	155	267	235	234	232
HF	97	162	143	142	141
Li_2	3	23	20	19	24
LiF	89	153	137	136	139
Be_2	−7	13	10	10	3
C_2H_2	294	460	415	415	405
C_2H_4	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N_2	115	267	242	243	229
NO	53	199	171	172	153
O_2	33	175	143	144	121
F_2	−37	78	54	53	39
P_2	36	142	120	120	117
Cl_2	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	...

LDA vs GGA



Liu, Peitao. "Low scaling GW method: implementation and applications." (2017).

Reciprocal Space



$$\mathbf{b}_1 = \frac{2\pi}{\Omega}\mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega}\mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega}\mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \qquad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$