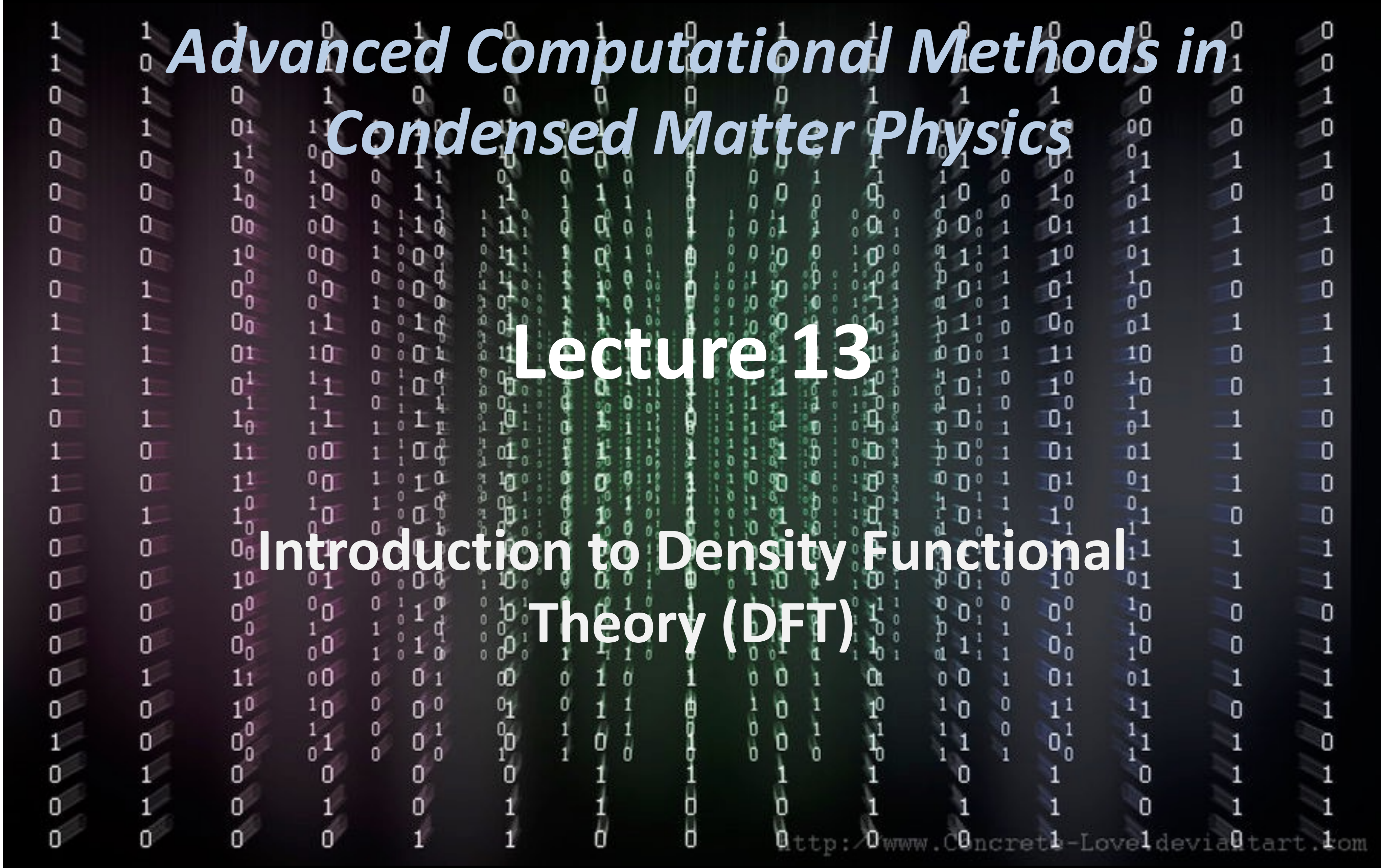


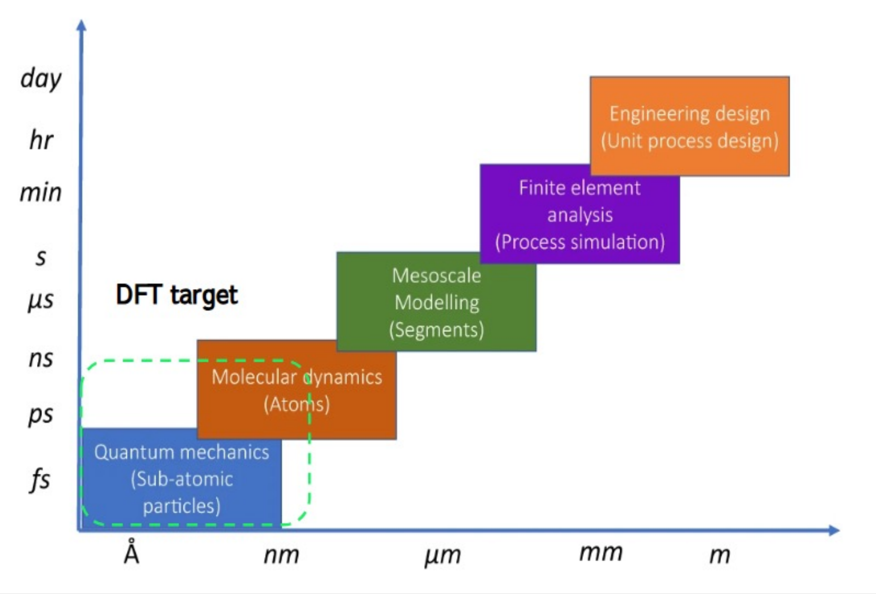
Advanced Computational Methods in Condensed Matter Physics

Lecture 13

Introduction to Density Functional Theory (DFT)

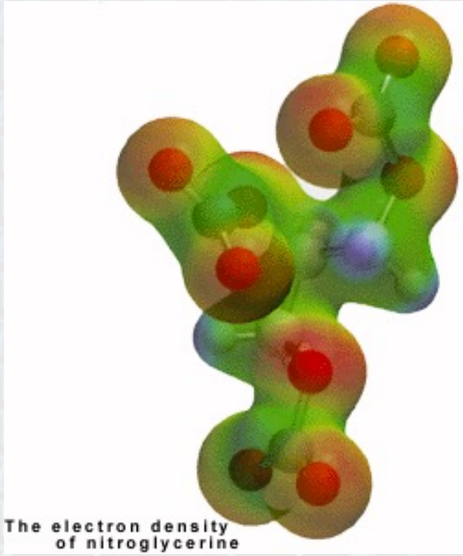
What can DFT do?

- It is the gold standard calculation for material modeling from first principles (quantum mechanical), balancing high accuracy with computational efficiency.
- Solids, surfaces, solution, molecules.
- Ground-state material properties, e.g., lattice constants, phase diagram, phonon structure, band structure, chemical reactions.
- Material discovery, predicting mechanical and electronic properties, ab initio molecular dynamics of biochemical systems



What doe DFT solve for?

The starting point is the full, exact time-independent Schrödinger Equation for interacting electrons and nuclei:



The electron density of nitroglycerine

$$\hat{H}\Psi = E\Psi$$

The full Hamiltonian (H) has 5 terms:

$$\hat{H} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{T}}_{\mathrm{N}} + \hat{\mathrm{U}}_{\mathrm{ee}} + \hat{\mathrm{U}}_{\mathrm{NN}} + \hat{\mathrm{V}}_{eN}$$

- T_e, T_N : Kinetic energies of electrons and nuclei.
- $\mathrm{U}_{ee}, \mathrm{U}_{NN}$: Repulsive Coulomb interactions (electron-electron, nuclei-nuclei).
- V_{eN} : Attractive Coulomb interaction between electrons and nuclei.

Solving this exactly for macroscopic systems is impossible. We must approximate.

The Born-Oppenheimer Approximation

- Goal: Decouple the motion of nuclei and electrons.
- Concept: Nuclei are much heavier than electrons ($\mathrm{M}_{\mathrm{ion}} \gg \mathrm{m}_{\mathrm{e}}$) and move much slower.
- Result: We can set the nuclear kinetic energy (T_N) to zero and treat the nuclei-nuclei repulsion (U_{NN}) as a classical constant.
- Electrons are assumed to move in a static potential generated by these 'frozen' nuclei.
- This reduces our problem to solving for the electronic ground state for a given nuclear configuration.

$$\Psi = \psi_e \chi_{\mathrm{N}}$$

The Electronic Schrödinger Equation

Applying the Born-Oppenheimer approximation yields the N-electron Hamiltonian:

$$\hat{H}_e\psi = [\hat{T}_e + \hat{V}_{ext} + \hat{U}_{ee}]\psi = E\psi(r_1, r_2, \ldots r_N)$$

- $\hat{T}_e = -\frac{1}{2}\sum_i^N \nabla_i^2$ Kinetic energy of electrons
- $\hat{V}_{ext} = -\sum_i^N \sum_I^M \frac{Z_I}{|r_i - R_I|}$ External potential from the fixed nuclei
- $\hat{U}_{ee} = \sum_j^N \sum_i^j \frac{1}{|r_i - r_j|}$ Electron-electron interaction

The Challenge: A system with N electrons still has 3N degrees of freedom. The $\hat{U}_{ee}$ term couples all electrons together, making it intractable for N > a few.

The Hartree-Fock Precursor

- Early attempt to solve the many-body problem using a mean-field approximation.
- Approximates the wavefunction as a Slater determinant to satisfy Pauli exclusion.
- Successfully handles ‘exchange’ (quantum mechanical effect of indistinguishable fermions).
- Fails to capture ‘correlation’ (the tendency of electrons to avoid each other due to Coulomb repulsion).

$$\Psi(1,\ldots,\mathrm{N})=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & \psi_1(2) & \cdots & \psi_1(N)\\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N)\end{vmatrix}$$

Hohenberg-Kohn Theorem I (1964)

- The foundational theorem of DFT.
- Theorem: The ground-state electron density $\mathrm{n}_0(r)$ uniquely determines the external potential $\mathrm{V}_{\mathrm{ext}}(r)$.
- Implication: Since the kinetic and electron-electron interaction energies of the ground state can be expressed as universal functionals of the electron density, $\mathrm{V}_{\mathrm{ext}}(r)$ determines the Hamiltonian, the density $\mathrm{n}_0(r)$ contains all information about the ground state.
- Paradigm Shift: We can use the 3-dimensional density $\mathrm{n}(r)$ instead of the 3N-dimensional wavefunction Ψ.

Hohenberg-Kohn Theorem II

- The Variational Principle for Density.
- Theorem: A universal functional for the energy E[n] exists in terms of the density.

$$E[n] = F[n] + \int V_{ext}\, n(r)\, dr$$

- The global minimum of this functional yields the exact ground-state energy, and the density that minimizes it is the exact ground-state density.
- The Catch: The exact form of the universal functional F[n] is unknown.

The Kohn-Sham Mapping (1965)

- Kohn and Sham provided the practical framework to use the HK theorems.
- Concept: Map the intractable interacting many-body system onto a fictitious non-interacting system.
- Requirement: The fictitious non-interacting system must have the exact same ground-state density n(r) as the real interacting system.
- We construct n(r) by summing the squares of single-particle 'Kohn-Sham orbitals'.

The Kohn-Sham Equations

- The effective single-particle equations:

$$[-\frac{1}{2}\nabla^2 + \mathrm{V_{ks}(r)}]\varphi_\mathrm{i}(\mathrm{r}) = \varepsilon_\mathrm{i}\varphi_\mathrm{i}(\mathrm{r})$$

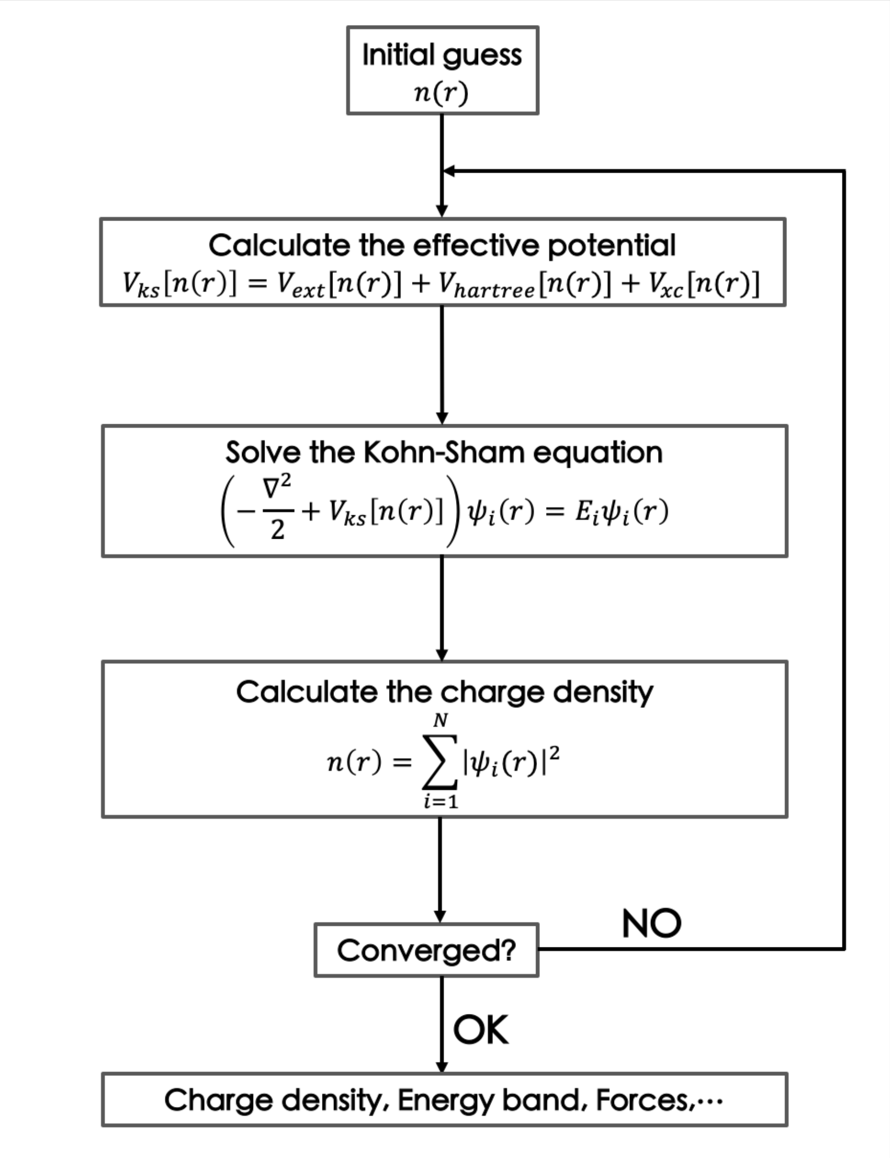
- The total density is: $n(r) = \sum |\varphi_\mathrm{i}(r)|^2$
- The effective potential $\mathrm{V_{ks}(r)}$ is:

$$\mathrm{V_{ks}(r)} = \mathrm{V_{ext}(r)} + \mathrm{V_{Hartree}(r)} + \mathrm{V_{xc}(r)}$$

- These equations are non-linear ($\mathrm{V_{ks}(r)}$ depends on $n(r)$, which depends on $\varphi(r)$) and must be solved iteratively.

The Self-Consistent Field (SCF) Cycle

- Initialize guess for electron density, usually the superposition of atomic orbitals of the valance electrons
- Evaluate the KS Hamiltonian with the current density
- Solve the Hamiltonian for diagonalized orbitals
- Repeat until the solution agrees with the previous loop



Initial guess

$n(r)$

Calculate the effective potential

$V_{ks}[n(r)] = V_{ext}[n(r)] + V_{hartree}[n(r)] + V_{xc}[n(r)]$

Solve the Kohn-Sham equation

$\left(-\frac{\nabla^2}{2} + V_{ks}[n(r)]\right)\psi_i(r) = E_i\psi_i(r)$

Calculate the charge density

$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$

Converged?

Charge density, Energy band, Forces,⋯

The Exchange-Correlation (XC) Potential

$$V_{xc}(r) = \delta E_{xc}[n]/\delta n$$

- This term contains all the complex quantum many-body effects that we don't know exactly.
- It corrects for the self-interaction error in the Hartree term.
- It accounts for Pauli exchange and Coulomb correlation.
- Approximating $E_{xc}[n]$ accurately is the central challenge of modern DFT.

$$E_{xc}[n] = T[n] - T_{ks}[n] + V_{ee}[n] - V_{Hartree}[n]$$

Jacob’s Ladder of Functionals

A classification of XC approximations by John Perdew, climbing towards 'chemical heaven' (exact accuracy).

- 1: LDA (Depends only on local density n)
- 2: GGA (Depends on density and its gradient ∇n)
- 3: Meta-GGA (Adds kinetic energy density or $\nabla^2 n$)
- 4: Hybrid Functionals (Mixes in exact Hartree-Fock exchange, e.g., B3LYP, HSE06, PBE0)
- 5: Fully non-local functionals (RPA)

Rung 1: Local Density Approximation (LDA)

- Assumes the XC energy at a point is that of a Uniform Electron Gas (UEG) with the same local density.
- $E_{xc}^{LDA} = \int n(r)\, \varepsilon_{xc\_UEG}(n(r))\, dr$
- Pros: Simple, computationally cheap, surprisingly good for simple metals and bulk moduli.
- Cons: Over-binds molecules (predicts bond lengths that are too short) and fails for strongly correlated systems.

Rung 2: Generalized Gradient Approximation (GGA)

- Accounts for the fact that real electron density is not uniform by including the density gradient ∇n(r).
- E_xc^GGA = ∫ n(r) ε_xc(n(r), ∇n(r)) dr
- LYP, Becke-LYP: Most popular in quantum chemistry
- PBE (Perdew-Burke-Ernzerhof): The most famous and widely used GGA functional in solid-state physics.
- Improves significantly over LDA for binding energies, bond lengths, and surface energies.

Most cited physics papers are DFT

Rank: **7** Citations: **46,702**

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

Lee, C., Yang, W. & Parr, R. G.

Phys. Rev. B **37**, 785–789 (1988).

Rank: **8** Citations: **46,145**

Density-functional thermochemistry. III. The role of exact exchange.

Becke, A. D.

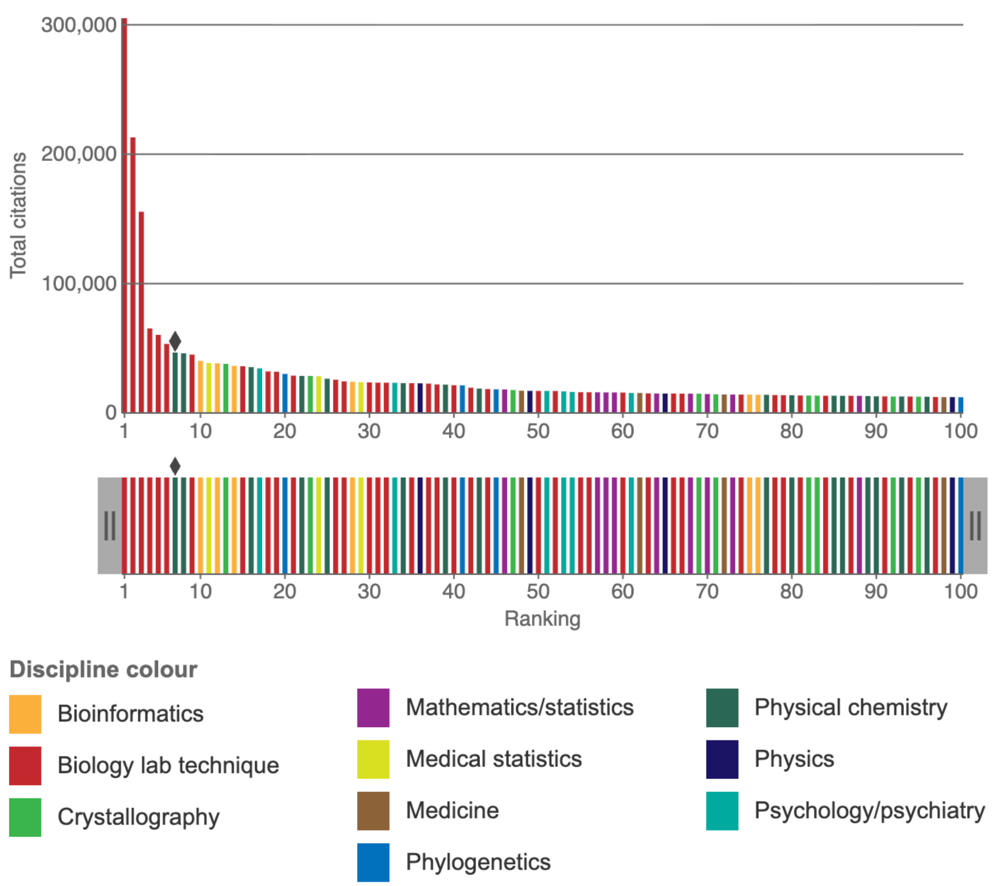
J. Chem. Phys. **98**, 5648–5652 (1993).

Rank: **16** Citations: **35,405**

Generalized gradient approximation made simple.

Perdew, J. P., Burke, K. & Ernzerhof, M.

Phys. Rev. Lett. **77**, 3865–3868 (1996).



Periodic Systems & Plane Waves

- For bulk materials, the external potential is periodic: V(r) = V(r + R).
- Bloch's Theorem: The wavefunction can be written as a plane wave modulated by a periodic function.

$$\varphi_{\mathrm{nk}}(\mathrm{r}) = \mathrm{e}^{\mathrm{ikr}} \mathrm{u}_{\mathrm{nk}}(\mathrm{r})$$

- We expand u_nk(r) in a basis set of plane waves that is part of the reciprocal lattice G:

$$\mathrm{u}_{\mathrm{nk}}(\mathrm{r}) = \sum_{\mathrm{G}} \mathrm{c}_{\mathrm{G}}\, \mathrm{e}^{\mathrm{iGr}}$$

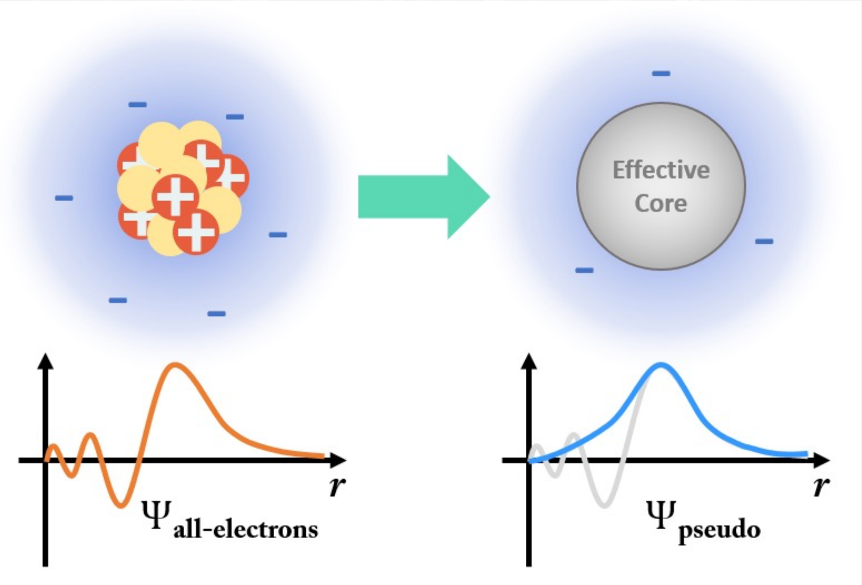
- Cutoff Energy (E_cut): We truncate the infinite sum by only including plane waves with kinetic energy ½|k+G|² < E_cut.

Pseudopotentials

- Problem: Core electrons oscillate wildly near the nucleus, requiring an enormous number of plane waves (high E_cut) to resolve.

- Solution: Core electrons are deeply bound and don't participate in chemical bonding. We replace the strong nuclear potential and the core electrons with a smoother ‘pseudopotential’, reducing computational cost.

- Types: Norm-Conserving (NC), Ultrasoft (USPP), Projector Augmented Wave (PAW).



Brillouin Zone & k-point Sampling

- To calculate macroscopic properties (like total energy or charge density), we must integrate over all valid momenta (k-points) in the first Brillouin Zone.
- $\int_{BZ} f(k)\, dk \approx \sum w_i f(k_i)$
- We use discrete grids of k-points. The standard is the Monkhorst-Pack grid.
- Denser grids (e.g., 8x8x8 vs 2x2x2) provide higher accuracy but cost more compute time.
- Metals require denser grids than insulators due to sudden changes in occupancy at the Fermi level.

Quantum Espresso: Input File Anatomy

- A typical pw.x input file uses Fortran namelists:

```
&CONTROL
 calculation='scf', prefix='silicon', pseudo_dir='./'
&SYSTEM
 ibrav=2, celldm(1)=10.2, nat=2, ntyp=1, ecutwfc=30
&ELECTRONS
 conv_thr=1.0d-8
ATOMIC_SPECIES
 Si  28.086  Si.pbe-n-rrkjus_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
 4 4 4 0 0 0
```

https://www.quantum-espresso.org/Doc/INPUT_PW.html

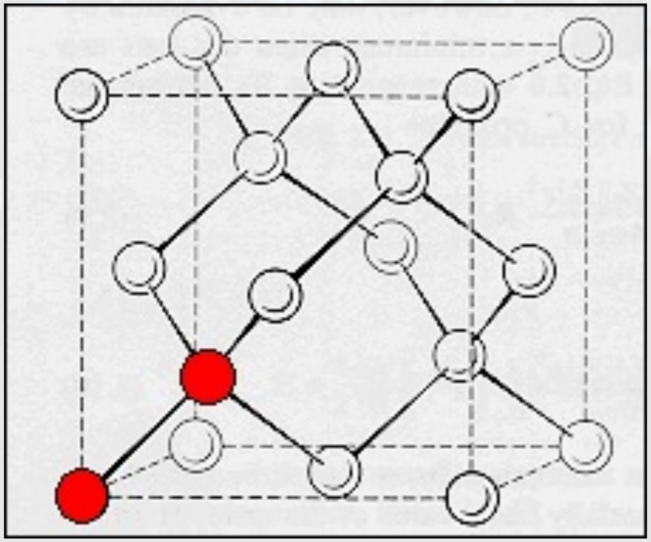
Convergence Testing

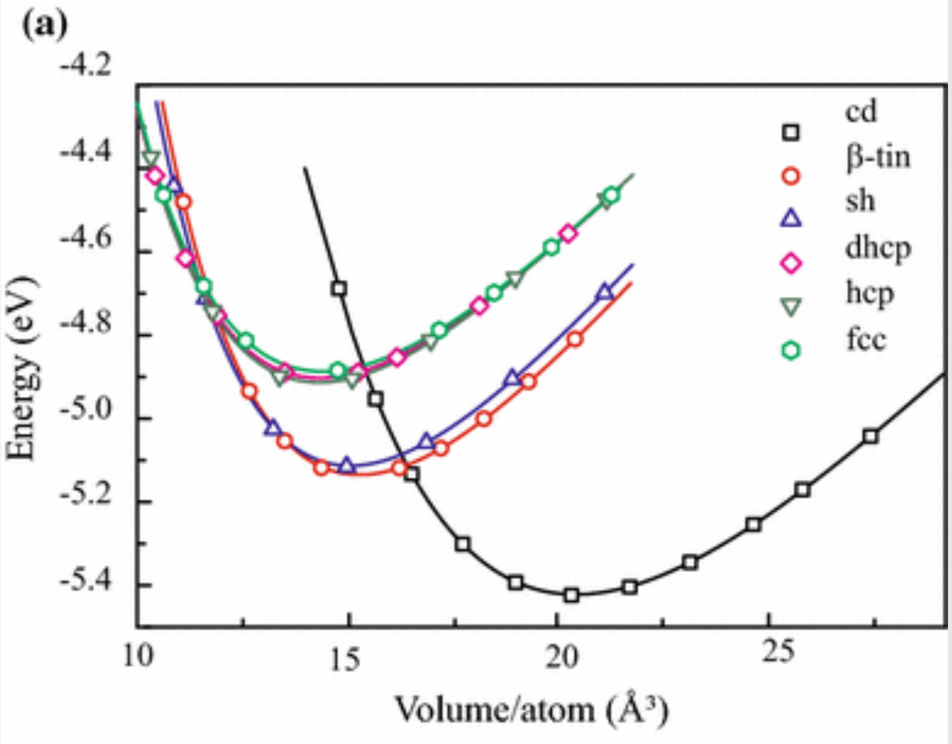
- Before generating data, you MUST ensure your parameters are converged.
- 1. E_cut Convergence: Run SCF at increasing ecutwfc until Total Energy stabilizes (changes by < 1 meV/atom).
- 2. K-point Convergence: Run SCF at increasing grid sizes (2x2x2, 4x4x4, 6x6x6) until Total Energy stabilizes.
- Failure to converge parameters leads to non-physical 'Pulay stress' and unreliable structures.

Example 1: Silicon Lattice Constant

Method: Run SCF calculations at various lattice parameters (a) and plot Total Energy.

The minimum of the Energy vs Volume curve gives the equilibrium lattice constant.





Hands-on 2: Band Structure of Silicon

Step 1: Perform a converged SCF run to get the ground-state density.

Step 2: Perform a 'bands' calculation along a high-symmetry path (L → Γ → X → U).

Observation: You will identify Silicon as an indirect band gap semiconductor (VBM at Γ, CBM near X).

Example 3: Charge Density Visualization

Module: Use `pp.x` (post-processing) to extract the charge density ρ(r) from the SCF output.
Output: A 3D volumetric data file (e.g., .cube or .xsf).
Visualization Tools: Load the file into VESTA or XCrySDen.
Insight: By setting an isosurface level, you will clearly see charge accumulation between the Silicon atoms, visualizing the sp^3 covalent bonds.