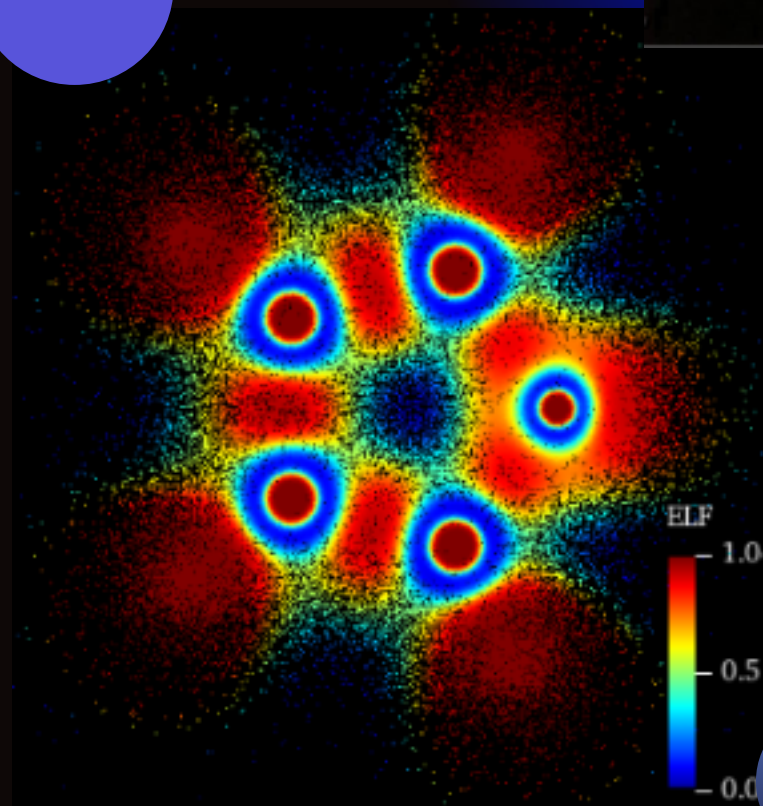
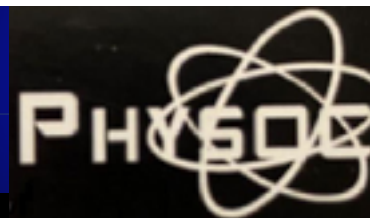




Quantum Chemistry

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QUANTUM CHEMISTRY

The central goal of quantum chemistry is to understand the structure and dynamics of chemical systems by developing computational solutions to the Schrödinger equation.

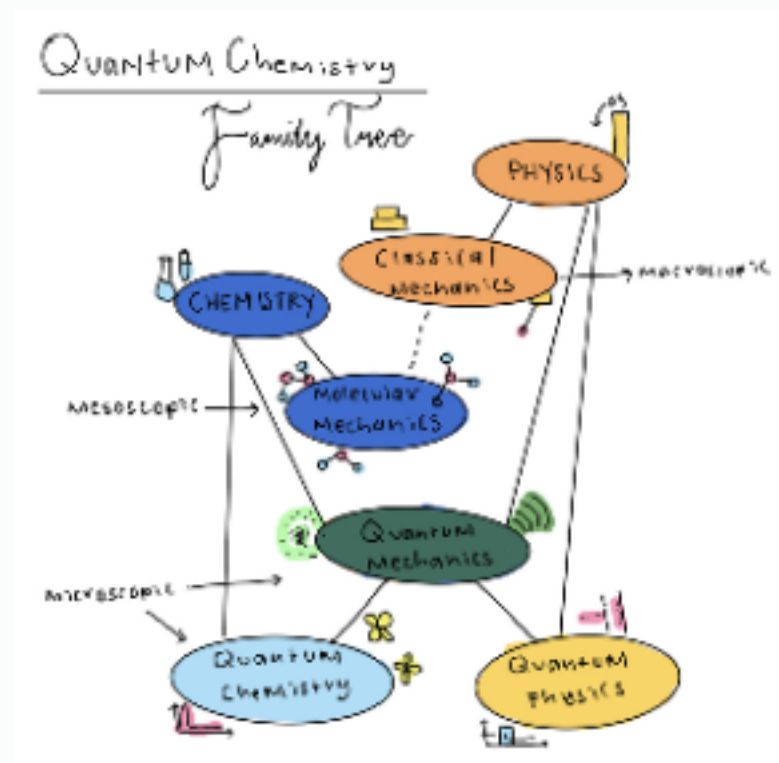
$$\frac{-\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}) + V(\mathbf{r}) \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

Kinetic Energy + *Potential Energy* = *Total Energy*

■ ■ ■

Density Functional Theory (DFT) : A method that investigates the properties of a system through its electronic density rather than explicitly solving the electronic wavefunction. It is widely used due to its balance of accuracy and computational cost.

Wavefunction-Based Methods
WFT methods directly approximate the true wavefunction Ψ of a system. They are generally more systematically improvable than DFT but come with a higher computational cost, which limits their application to smaller systems.



The Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Phi = \hat{H} \Phi$$

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

$$+ \underbrace{\frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n \neq m} \frac{Z_n Z_m e^2}{|\mathbf{R}_n - \mathbf{R}_m|}}_{\hat{V}_r} + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_r}$$

$$+ \underbrace{-\frac{1}{4\pi\epsilon_0} \sum_{i,n} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|}}_{\hat{V}_{r,R}} \quad \text{Potential terms}$$

nuclear	R
electronic	r
mixed	

Born-Oppenheimer Approximation



Born-Oppenheimer Approximation

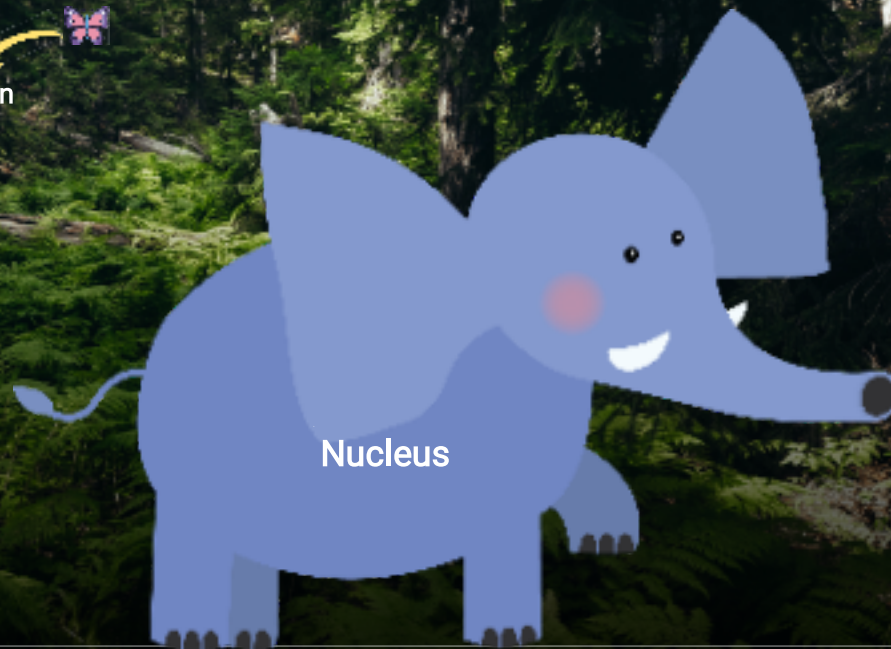
Nuclear Motion

$$\Psi(R, r) = \Psi_n(R) \Psi_e(r, R)$$

Electronic Motion

$$\hat{H}_e \Psi_e(r, R) = E_e \Psi_e(r, R)$$

Complete and Easy Explanation



The Kohn-Sham ansatz

→ Replace the original many-body problem with an auxiliary system of non-interacting particles.

Interacting electrons
+ real potential



Non-interacting
auxiliary
particles in an
effective potential



Assumption:

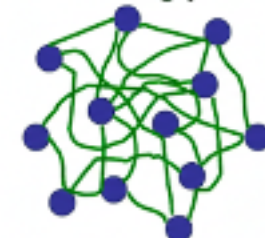
Ground state density of **interacting system** is equal to that of some **non-interacting system** that is exactly soluble, with all the difficult parts (exchange and correlation) included in some **approximate functional of the density**.

Walter Kohn Lu Jeu Sham



1998 (chemistry)

Interacting particles



$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_{10^{23}})$$

Independent particles



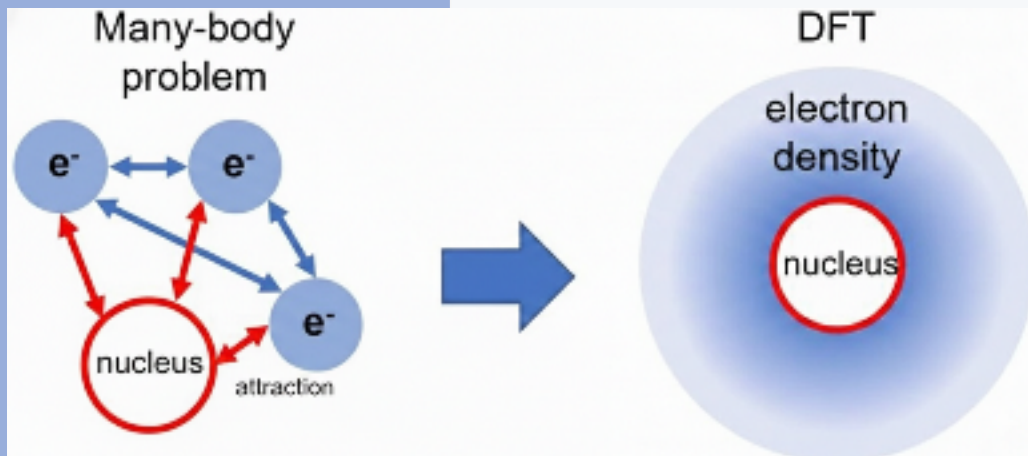
$$\varphi(\vec{x}_1)\varphi(\vec{x}_2)\dots\varphi(\vec{x}_{10^{23}})$$

Idea: consider electrons as independent particles moving in an effective potential

Real interacting electrons are too cumbersome to calculate.

We need to match the density of this fictitious system to the density of the real system.

HOHENBERG-KOHN THEORMS



DFT replaces the $3n$ -dimensional variables with the 3-dimensional electron density.

The ground-state electron density uniquely determines the external potential V (e.g., from nuclei) and thus the entire Hamiltonian.

The ground-state electron density uniquely determines the external potential

Introduction

DFT in practice: The self-consistency loop

Initial guess (usually superposition of atomic densities for $k=1$)

$$n^{(k)}(\mathbf{r})$$

$k \rightarrow k + 1$

Evaluate effective potential

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H[n^{(k)}(\mathbf{r})] + v_{xc}[n^{(k)}(\mathbf{r})]$$

Solve KS equations (for given potential)

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{eff}}[n^{(k)}(\mathbf{r})] \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Evaluate actual density

$$n(\mathbf{r}) = \sum_{\text{occ}} |\psi_i(\mathbf{r})|^2$$

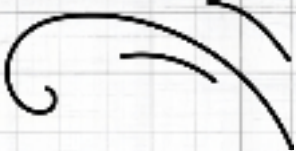
Compute energy,
forces, stresses ...

Yes

Consistent?
 $\|n^{(k)}(\mathbf{r}) - n(\mathbf{r})\|_2 < \delta$

No

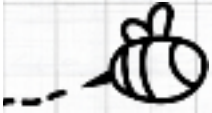




Some

Applications

Density Functional Theory (DFT)

- ... yields total energies, forces, and electronic structure and therefore allows computing e.g., – Structural relaxation and phase stability – Energy differences (input for thermodynamics, kinetics ...) – Phonon dispersions (mechanical stability) – Property prediction and screening – Band structures (a bit more complicated)
 - ... provides a reasonable balance between computational efficiency and accuracy (thousands of electrons, hundreds of atoms)
 - ... has limitations e.g., with respect to – Band gaps and optical properties (excitonic effects) – Strongly correlated systems
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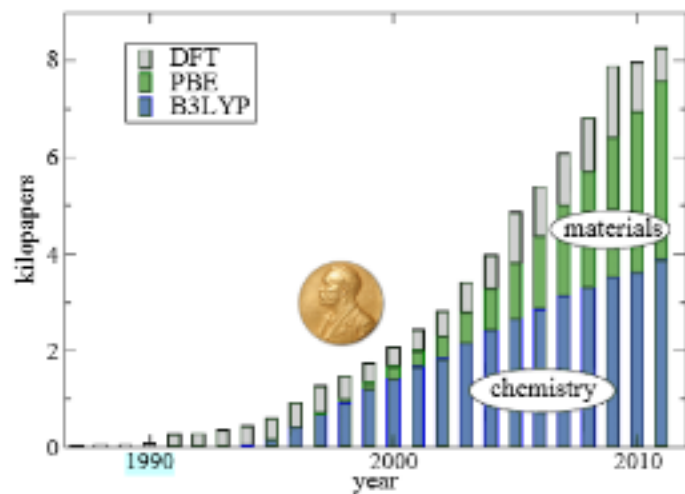
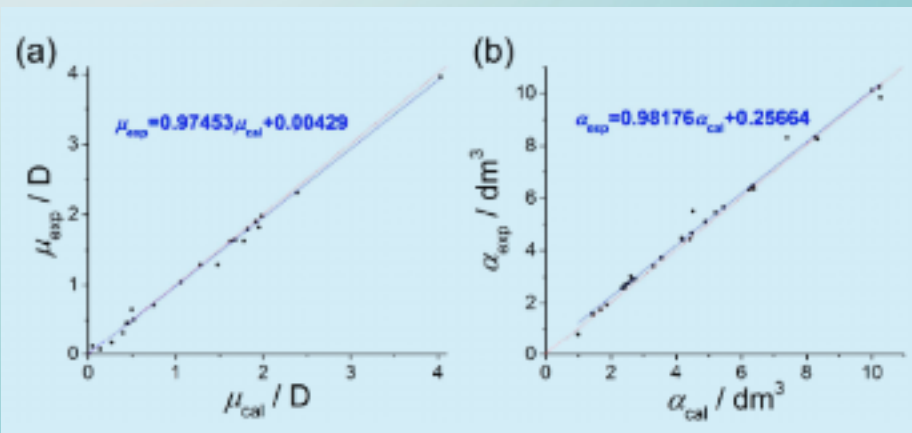
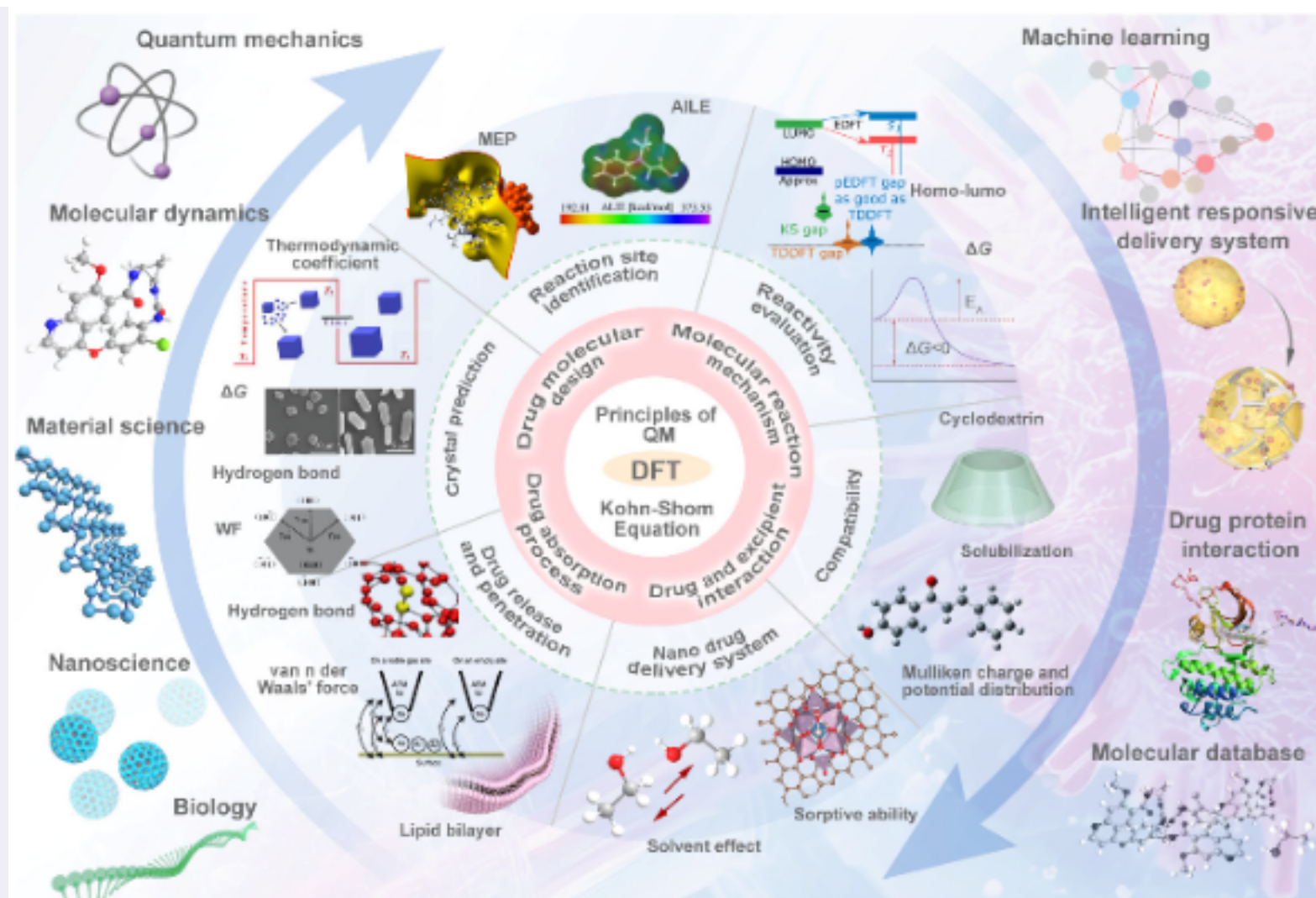


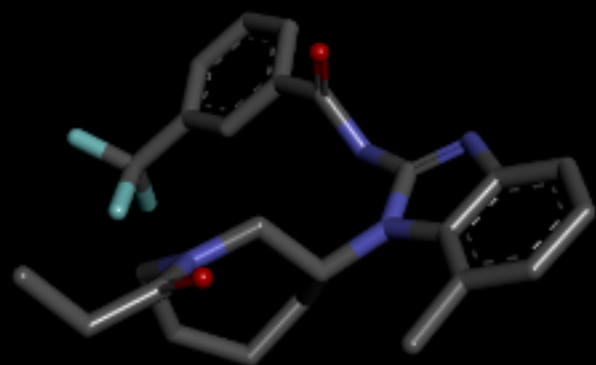
FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).



Comparison between DFT calculated and experimental results for the selected microscopic parameters (red dash line is $y=x$ and blue solid line is fitting line). (a) Comparison of ground state electric dipole moment; (b) Comparison of average electric polarizability.

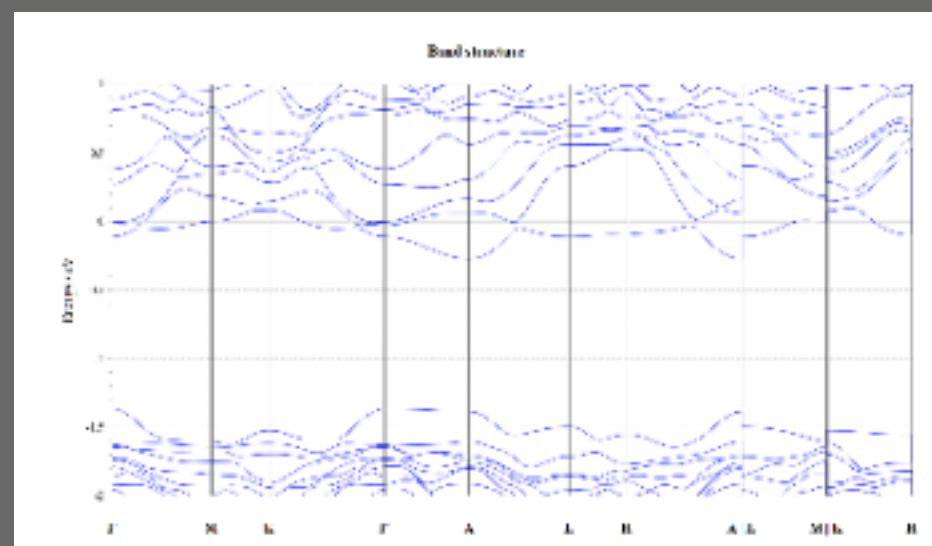
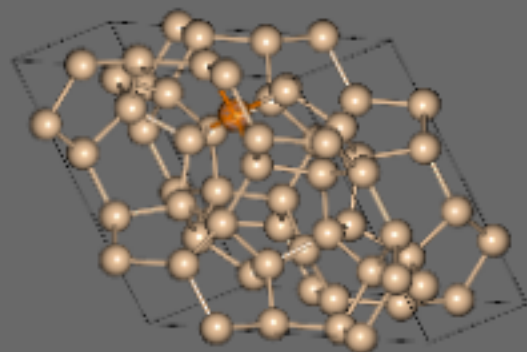
C. Zhang et al.: First Principles based Computational Scheme for Designing New SF6 Replacement





Si

P





THANK YOU