NATIONAL RESEARCH UNIVERSITY

An Introduction about Density Functional Theory (DFT) and its Applications

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SCHRÖDINGER EQUATION

Time-independent SE

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

Born–Oppenheimer Approximation

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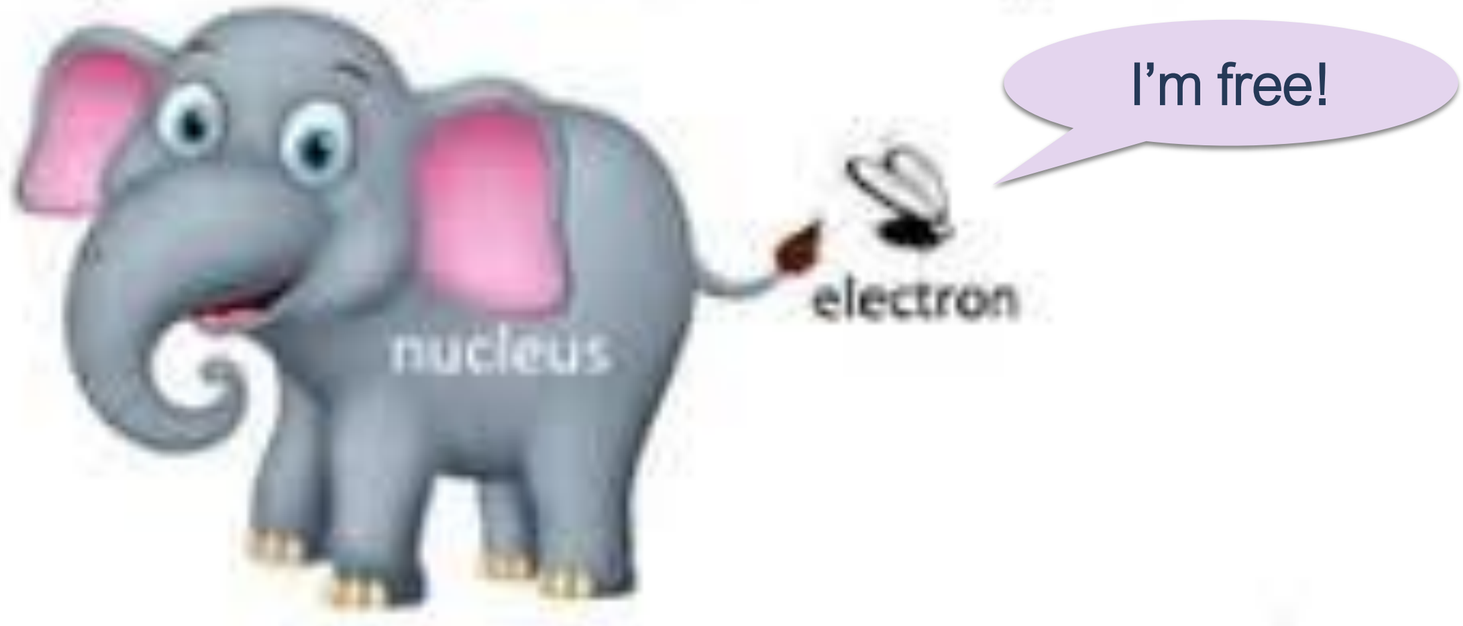
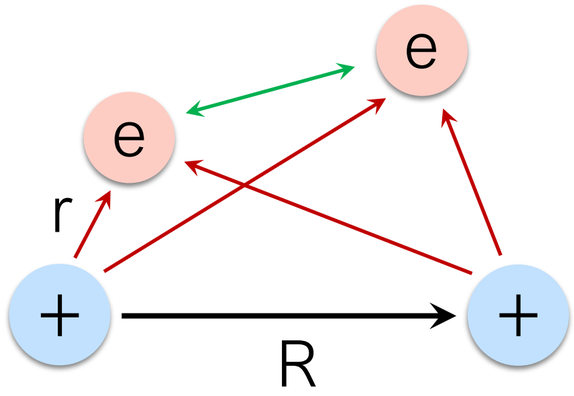


SCHRÖDINGER EQUATION



For real systems (H_2 molecular)

$$\left\{-\frac{1}{2}\sum_{i=1,2}\nabla_i^2+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\sum_{i=1,2}v_{\text{ext}}(\mathbf{r}_i)\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2)=E\Psi(\mathbf{r}_1,\mathbf{r}_2),$$

e kinetic energy **e-e interactions** **e-nucleus interactions**

$$v_{\text{ext}}(\mathbf{r})=-Z/r-Z/|\mathbf{r}-R\hat{\mathbf{z}}|,$$

where $Z=1$ is the charge on each nucleus, $\hat{\mathbf{z}}$ is a unit vector along the bond axis, and R is a chosen internuclear separation. Except where noted, we use atomic units throughout this

SCHRÖDINGER EQUATION

The Many-Body Schrödinger equation

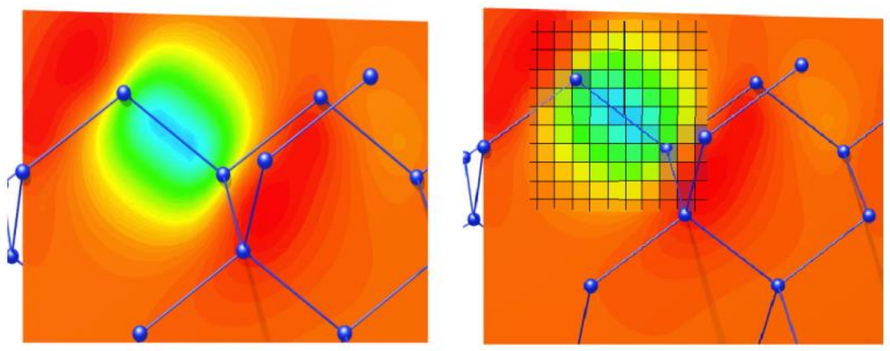
$$\hat{H}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\left(-\frac{1}{2}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

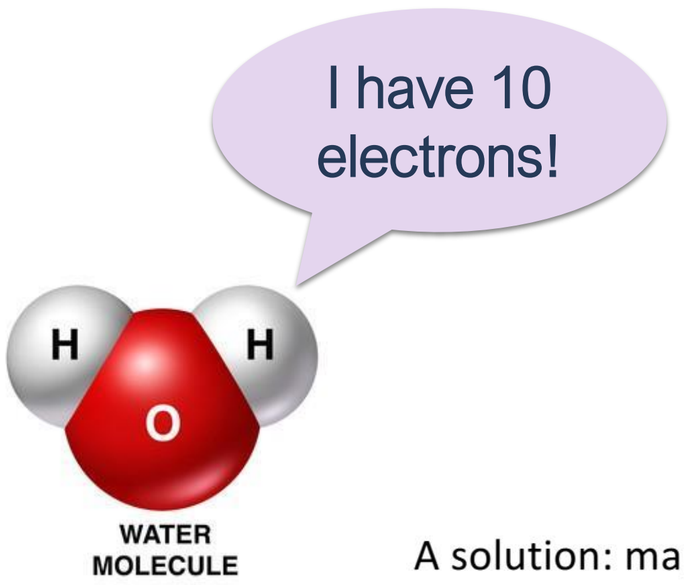
Erwin Schrödinger
Nobel Prize in Physics
(1933)

For instance, many-body WF storage demands are prohibitive:

$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ $(\#\text{grid points})^N$



5 electrons on a 10×10×10 grid ~ 10 PetaBytes !



WATER MOLECULE

A solution: map onto "one-electron" theory:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\}$$

https://www.vasp.at/wiki/images/5/5d/VASP_lecture_Basics.pdf

DENSITY FUNCTIONAL THEORY

The Hohenberg—Kohn theorem

- **The potential for the ground state of a finite system is directly** (up to a trivial constant) **defined by the electron density**

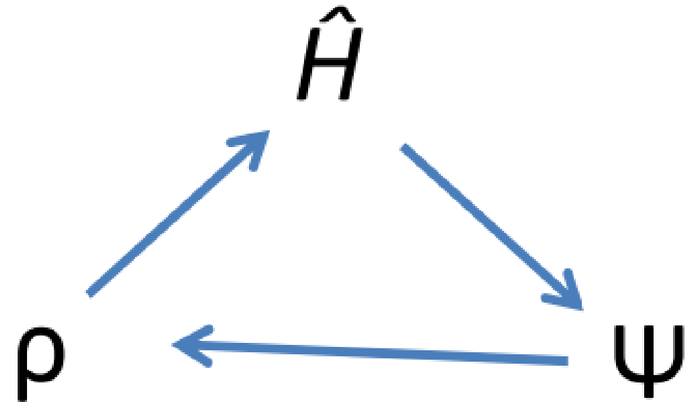
$\hat{T}_{e,}$ electronic kinetic energy

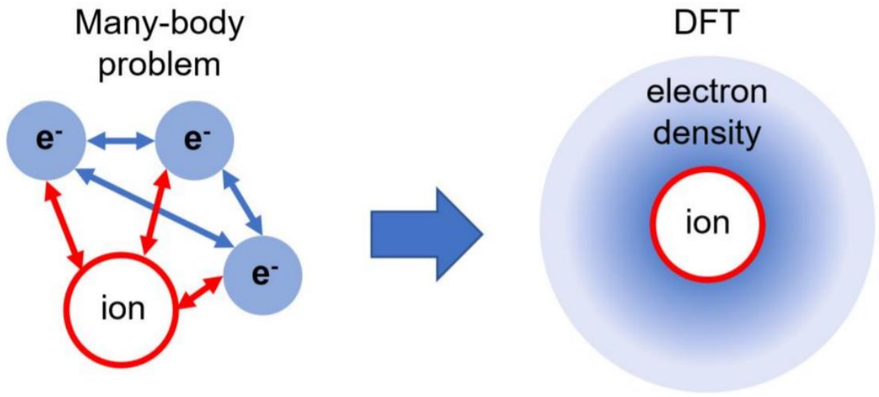
$\hat{V}_{ee,}$ electron-electron repulsion

$$\hat{H} = -\frac{1}{2}\sum_{i}^{n}\nabla_i^2 - \sum_{i}^{n}\sum_{I}^{N}\frac{Z_I}{r_{Ii}} + \sum_{i<j}^{n}\frac{1}{r_{ij}} + V^{\text{nuc}}$$

$\hat{V}_{nn,}$ nucleus-nucleus repulsion

$\hat{V}_{ne,}$ electron-nucleus attraction





DENSITY FUNCTIONAL THEORY

Hohenberg-Kohn-Sham DFT

Map onto “one-electron” theory:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\} \qquad \Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i)$$

Total energy is a functional of the density:

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\mathrm{xc}}[\rho] + E_Z[\rho] + U[Z]$$

The density is computed using the one-electron orbitals:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

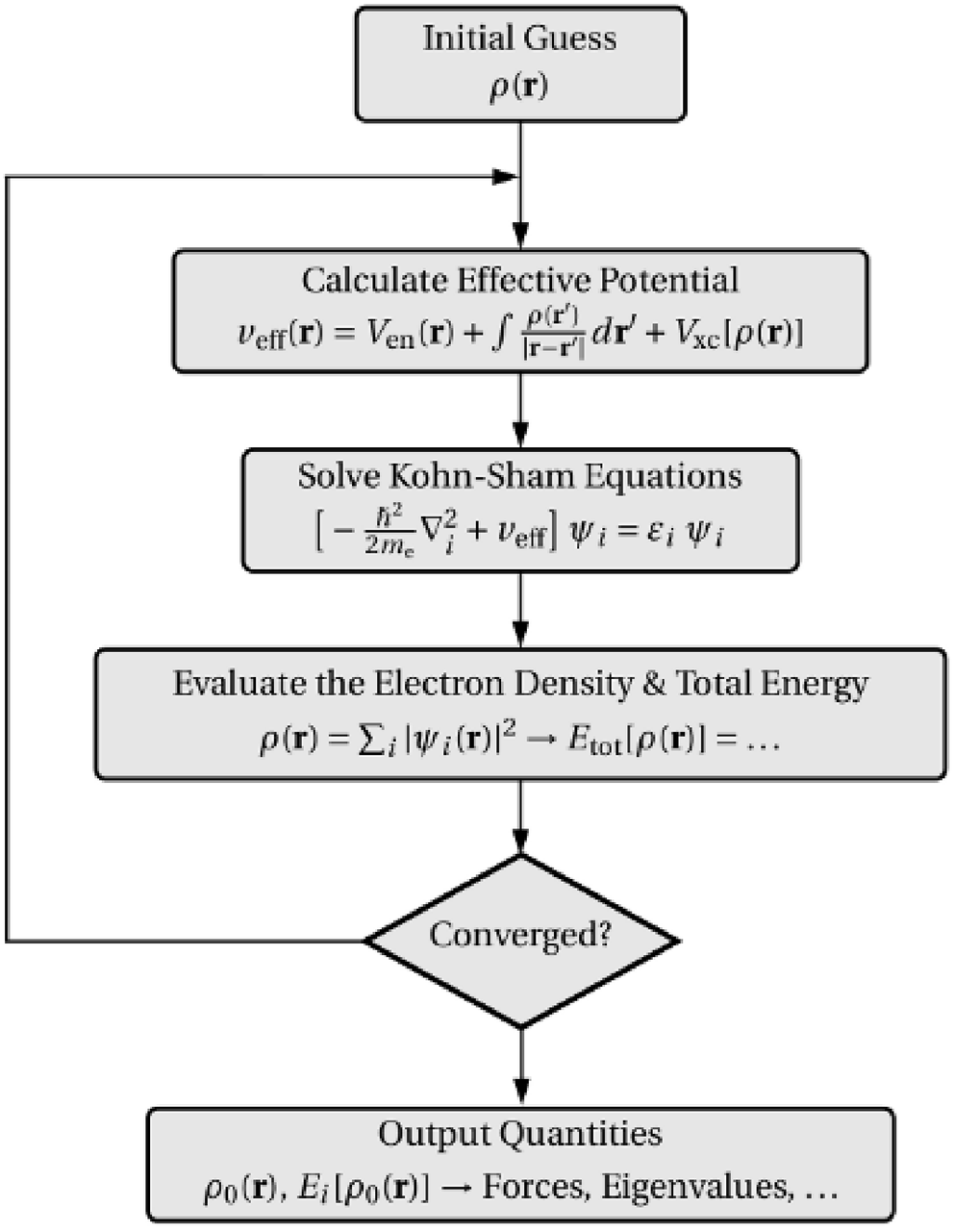
Walter Kohn
Nobel Prize in Chemistry
(1998)

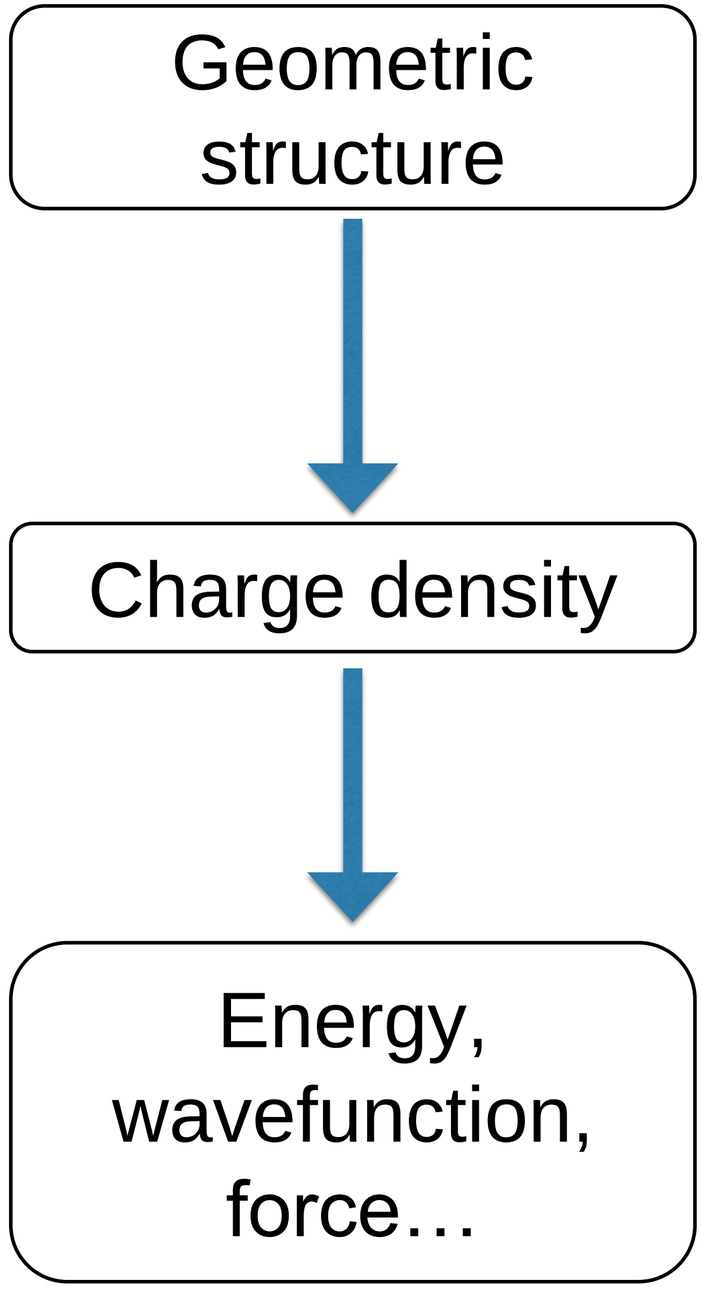
The one-electron orbitals are the solutions of the Kohn-Sham equation:

$$\left(-\frac{1}{2}\Delta + V_Z(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

https://www.vasp.at/wiki/images/5/5d/VASP_lecture_Basics.pdf

DFT CALCULATION PROCEDURE



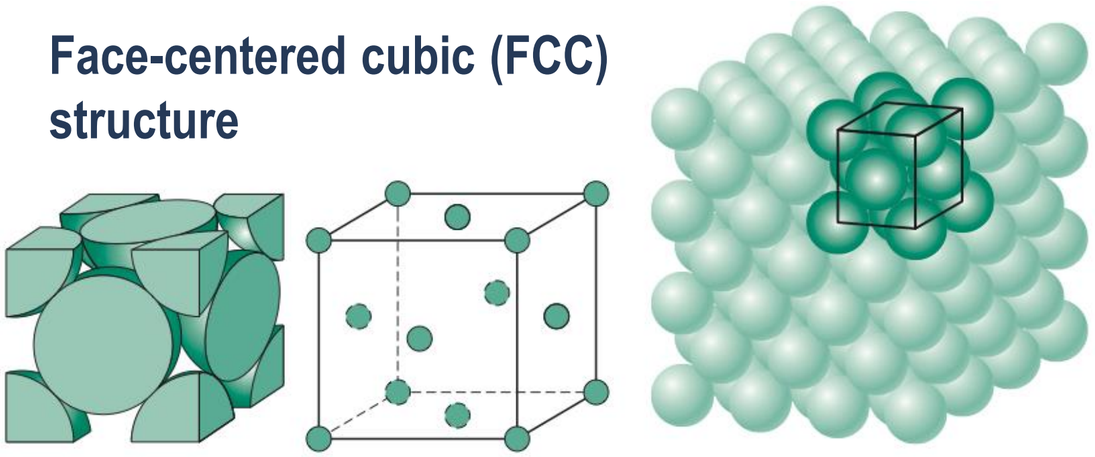


https://www.iue.tuwien.ac.at/phd/goes/dissse14.html

TWO TYPES OF DFT CALCULATIONS

Periodic systems: crystal

Face-centered cubic (FCC) structure



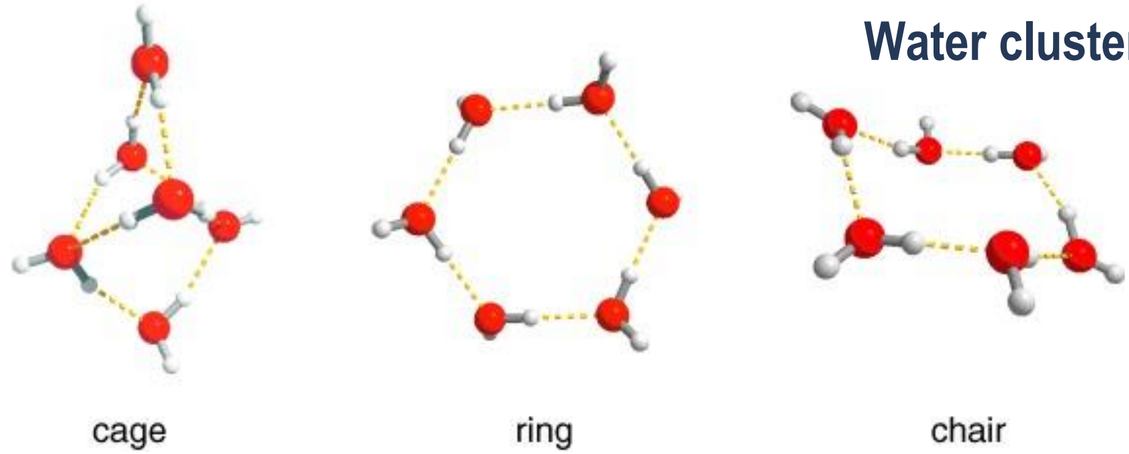
-Basis set: plane wave

-Energy band, phonon spectroscopy, electron-phonon coupling…

-Software: VASP, Quantum Espresso, CP2K…

Nonperiodic systems: molecule

Water cluster



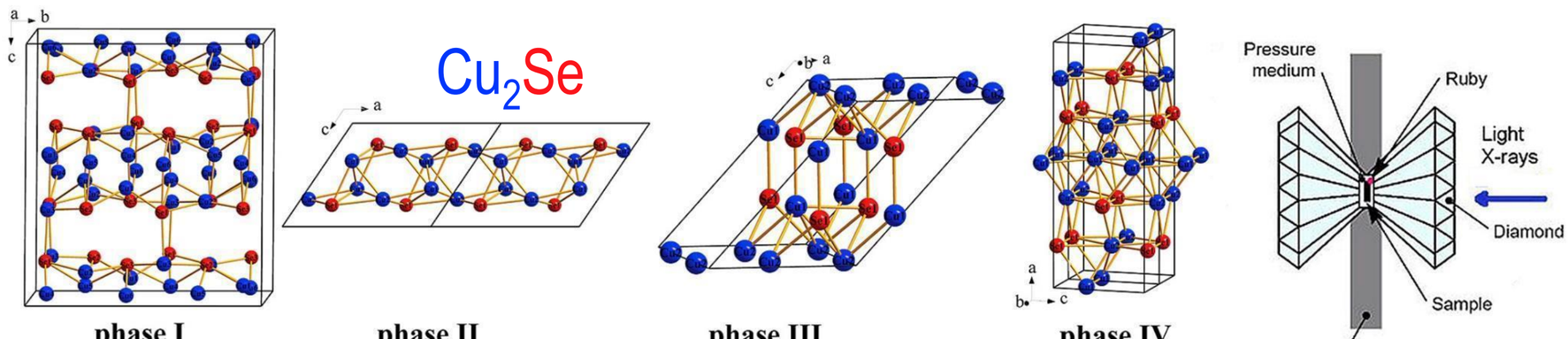
-Basis set: localized basis function

-Molecular orbital, Hessian matrix, vibrationally resolved spectroscopy…

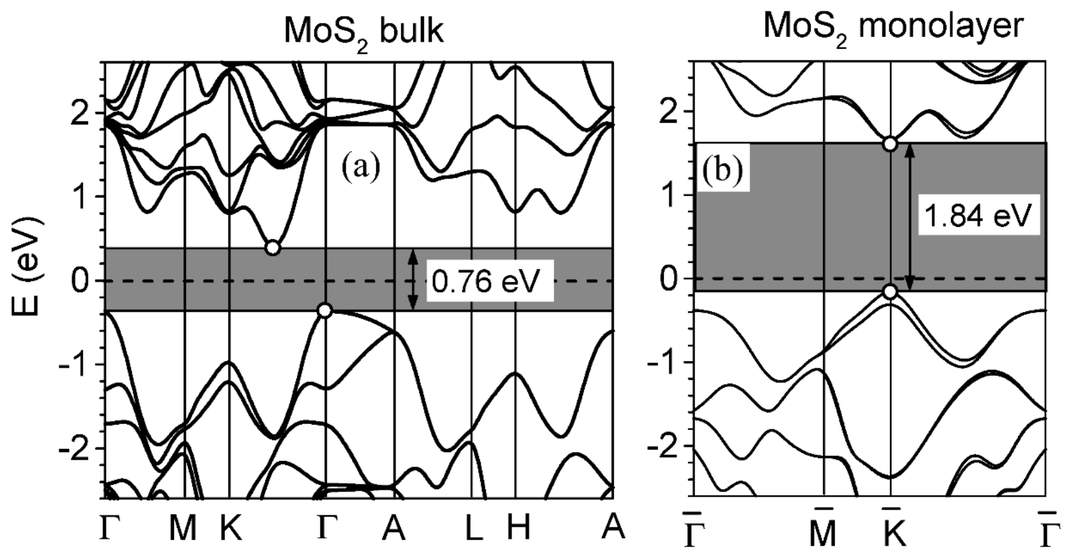
-Software: Gaussian, ORCA…

WHAT CAN DFT DO?

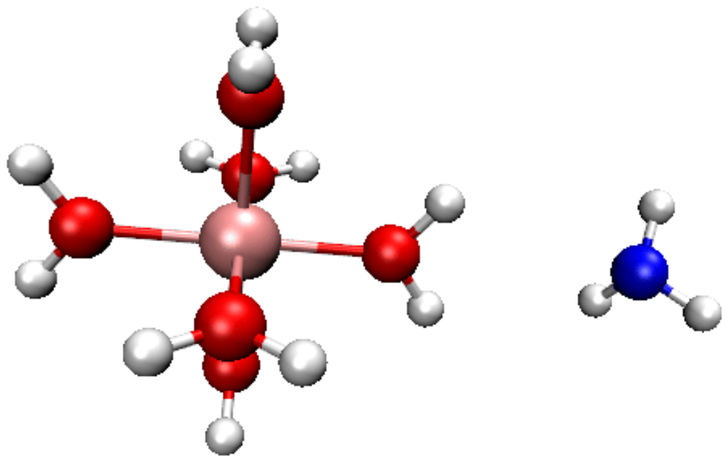
Structure prediction (total energy)



Band structure (energy level)



Molecular dynamics (force)



$[Al(H_2O)_6]^{3+} + NH_3 \rightarrow [Al(H_2O)_5(OH)]^{2+} + NH_4^+$

ADVANCED APPLICATIONS OF DFT

DFT + electron-phonon coupling

$$g_{\mathbf{q}\nu}(\mathbf{k},i,j) = \left(\frac{\hbar}{2M\omega_{\mathbf{q}\nu}}\right)^{1/2} \langle\psi_{i,\mathbf{k}}|\frac{\partial V_{KS}}{\partial U^{(\nu)}(\mathbf{q})}|\psi_{j,\mathbf{k}+\mathbf{q}}\rangle$$

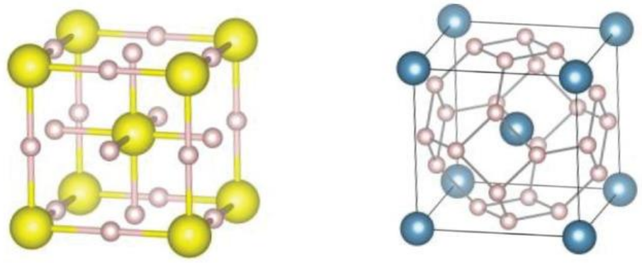
Mc-Millan expression

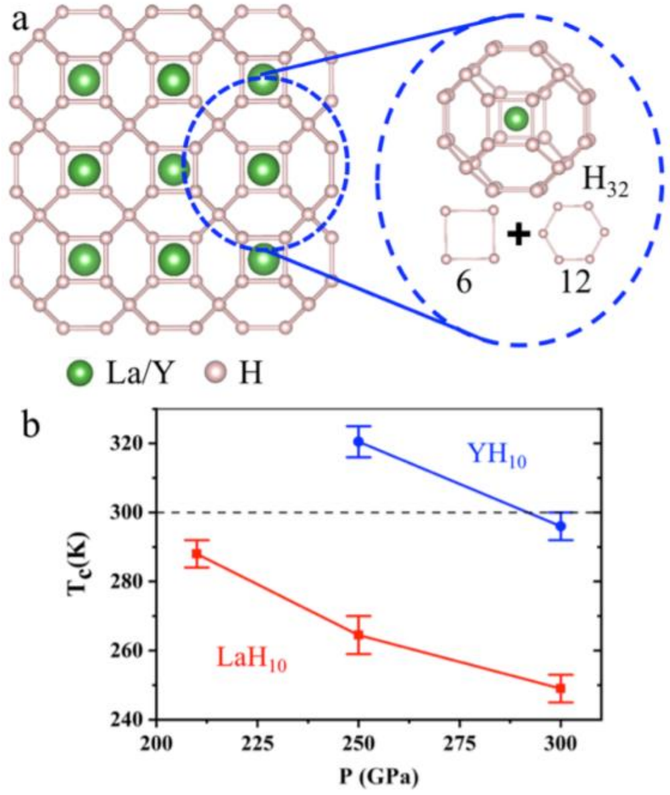
$$T_c = \frac{\omega_{\log}}{1.2k_B}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]$$

λ: e-p coupling constant

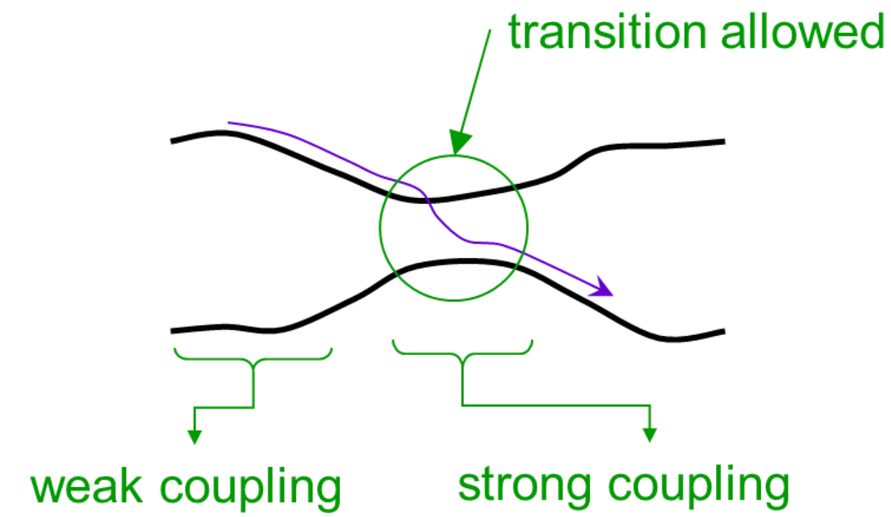
Hydrogen-rich superconductors

Found	T_c	Predicted
H_3S: 203K; 200GPa		YH_6: 264K; 120GPa



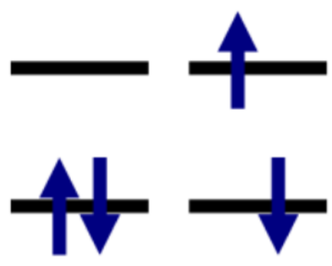


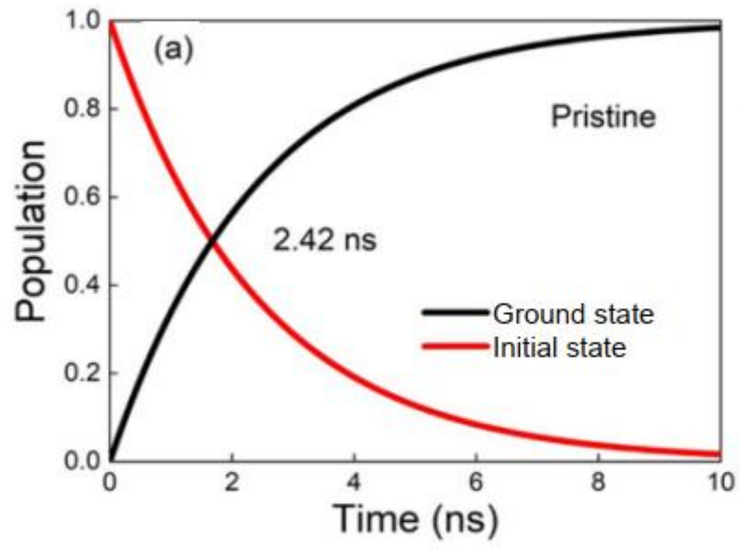
DFT + nonadiabatic molecular dynamics



Non-adiabatic coupling (scalar)

$$\boldsymbol{d_{jk}}\cdot\dot{\boldsymbol{R}} = \langle\psi_j|\nabla_{\boldsymbol{R}}|\psi_k\rangle\cdot\dot{\boldsymbol{R}} = \frac{\left\langle\psi_j\left|\nabla_{\boldsymbol{R}}\hat{H}\right|\psi_k\right\rangle}{\varepsilon_k-\varepsilon_j}\cdot\dot{\boldsymbol{R}}$$





QUANTUM MECHANICS CALCULATIONS

Schrödinger equation

$H\,\Psi = E\,\Psi$

+

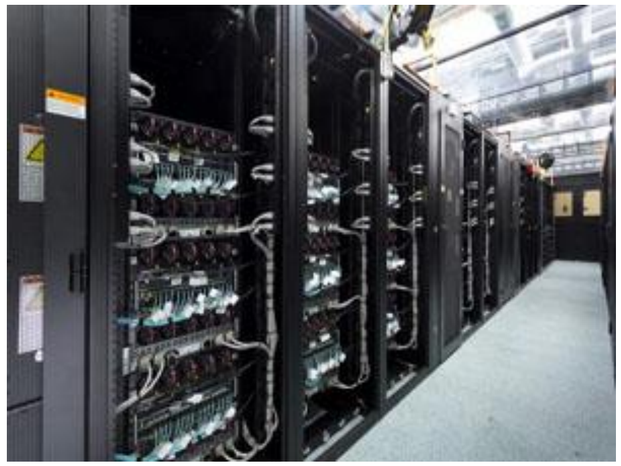
DFT

$E(\boldsymbol{r}) \rightarrow E[\rho(\boldsymbol{r})]$

+

High-performance computer

Multicore parallel



Linux

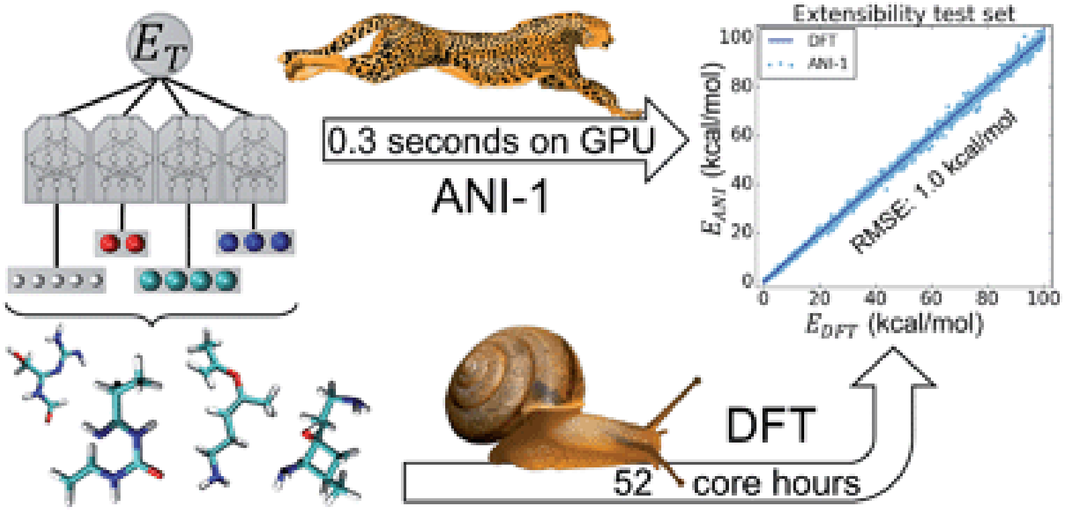
intel oneAPI HPC TOOLKIT

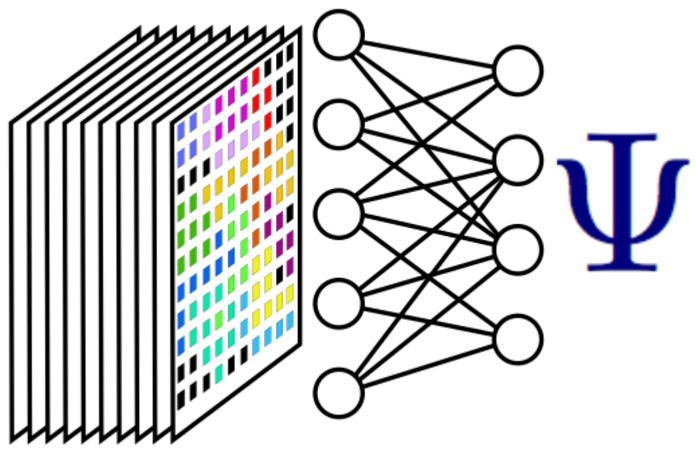
b-initio VASP ienna ackage imulation

ORCA

Machine learning

+





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Any Questions?