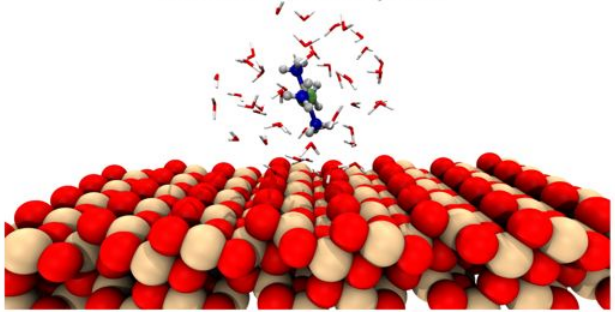
Introduction to electronic structure calculations

QM/MM and ab initio Molecular Dynamics
Summer School
June 23 – June 27, 2025



Solving the single-e^- equation in practical calculations

Mario F. Borunda

– Challenges of Simulation of Materials

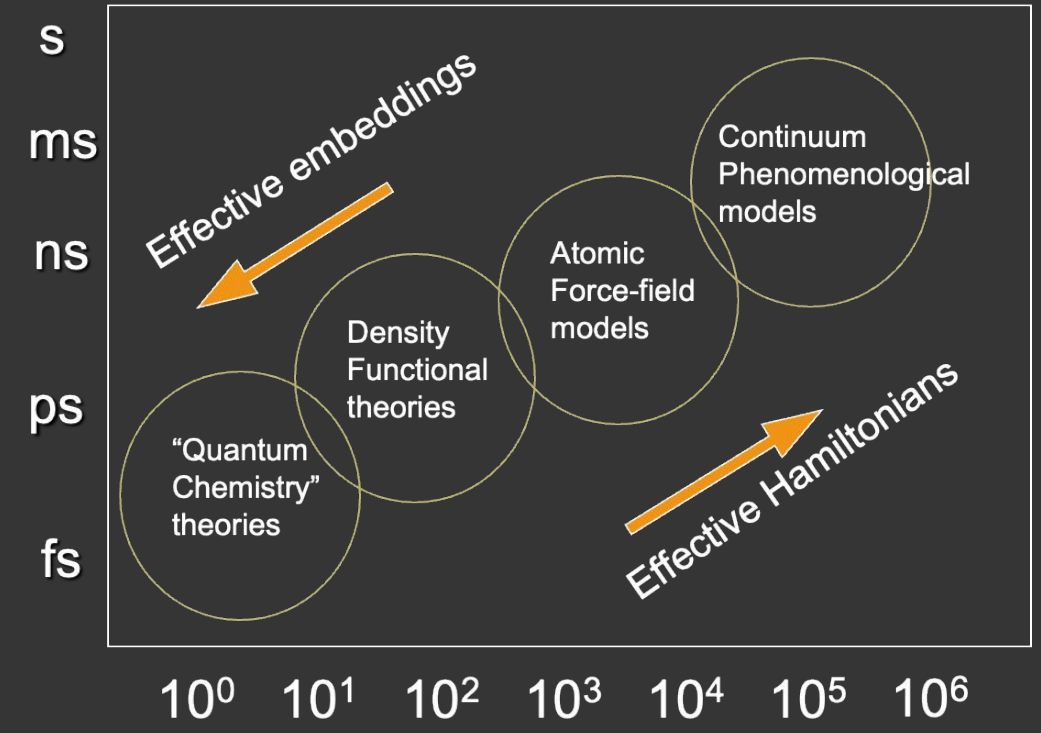
Multiple scales

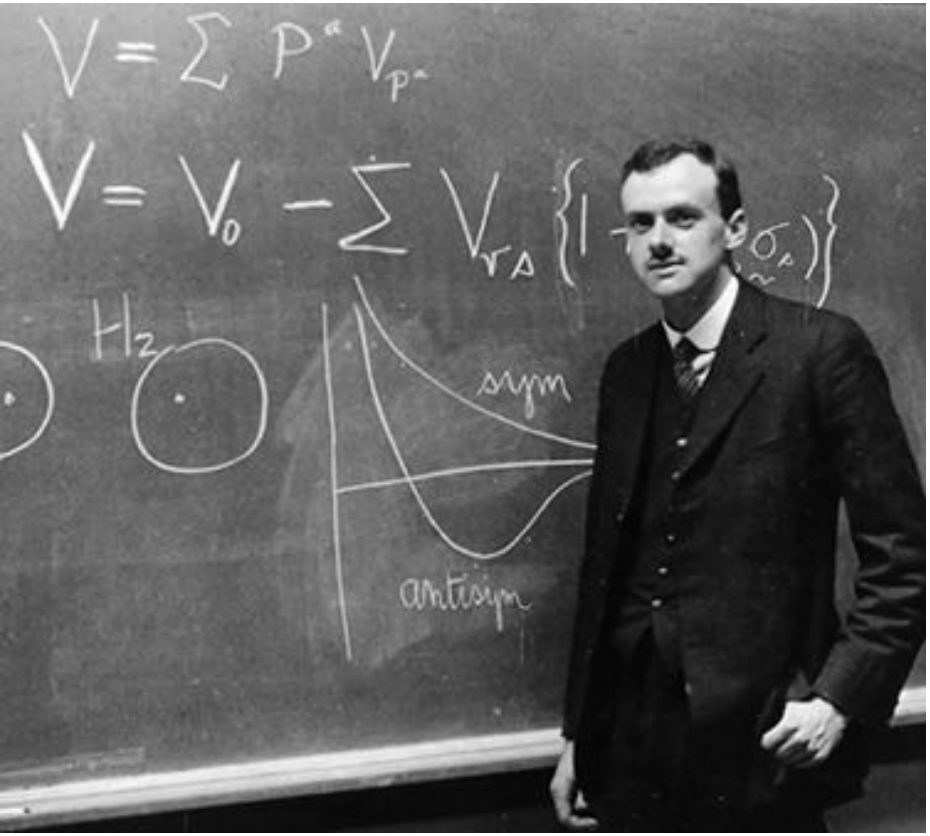
Taken from: Ceperley/Johnson UIUC

Macro – and *mesoscopic* phenomena; Thermodynamics

Atomic structure and dynamics

Electronic states Chemical bonds and reactions, excitations …





“The general theory of quantum mechanics is now almost complete. 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.”

Dirac, 1929

Quantum Mechanics

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2}\sum_{j,j'} \frac{Z_j Z_{j'}}{4\pi\epsilon_0 |R_j - R_{j'}|}$$
$$+\frac{1}{2}\sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 |r_i - r_{i'}|} - \sum_{j,i} \frac{Z_j e}{4\pi\epsilon_0 |r_i - R_j|}$$

Impossible to solve for more than just a few particles

Approximations:

[1] Separate e^- into two groups: core vs valence

[2] Born-Oppenheimer (adiabatic) approximation:

Ions are slow (10^{13} s^{-1}) while e^- are fast (10^{15} s^{-1})

Born-Oppenheimer Approximation

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2}\sum_{j,j'} \frac{Z_j Z_{j'}}{4\pi\epsilon_0 |R_j - R_{j'}|}$$

$$+\frac{1}{2}\sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 |r_i - r_{i'}|} - \sum_{j,i} \frac{Z_j e}{4\pi\epsilon_0 |r_i - R_j|}$$

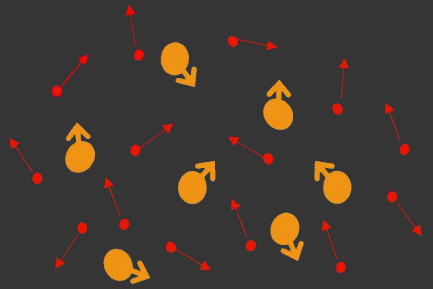
$$\mathcal{H} = \mathcal{H}_{ions}(R_j) + \mathcal{H}_e(r_i, R_{j0}) + \mathcal{H}_{e-ions}(r_i, \delta R_j)$$

Electron-Phonon Interaction

$$\mathcal{H}_e = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 |r_i - r_{i'}|} - \sum_{j,i} \frac{Z_j e}{4\pi\epsilon_0 |r_i - R_j|}$$

10^{23} e$^-$
[3] Mean field

Adiabatic or Born-Oppenheimer approx.



$$\frac{M_\alpha}{m_e} >> 1$$

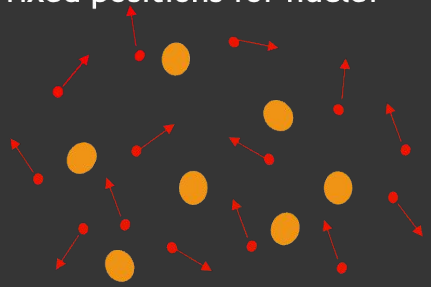
Nuclei much slower than the electrons $\frac{v_{electron}}{v_{nucleus}} >> 1$

$v_{electron} \approx v_F \approx 10^8$ cm/s $\qquad$ $v_{nucleus} \approx 10^5$cm/s

At any moment the electrons will be in their ground state for that particular instantaneous ionic configuration.

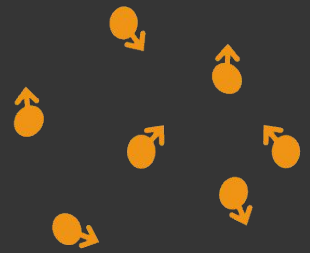
Solve electronic equations assuming fixed positions for nuclei

(1)



Move the nuclei as classical particles in the potential generated by the e-

(2)



Traditional density functional theory

- A many-body wave function

$$\mathcal{H}\Psi = [\mathcal{T} + \mathcal{V} + \mathcal{U}]\,\Psi = \left[\sum_i^N -\frac{\hbar^2\nabla_i^2}{2m_i} + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i,\vec{r}_j)\right]\Psi = E\Psi$$

- We solve instead for the density using the Kohn-Sham equations

$$n(\vec{r}) = N\int d^3r_2 \cdots \int d^3r_N \Psi^*(\vec{r}_1,\ldots\vec{r}_N)\Psi(\vec{r}_1,\ldots\vec{r}_N)$$

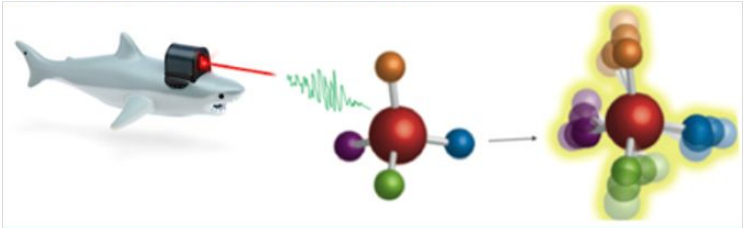
$$\left[-\frac{\hbar^2\nabla_i^2}{2m_i} + V_s(\vec{r})\right]\phi_i = \epsilon_i\phi_i \qquad n(\vec{r}) = n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2$$

$$V_s(\vec{r}) = V(\vec{r}) + \int d^3r' \frac{e^2\; n_s(\vec{r})}{|\vec{r}-\vec{r}'|} + V_{XC}[n_s(\vec{r})]$$

Effective potential

Time-dependent density functional theory

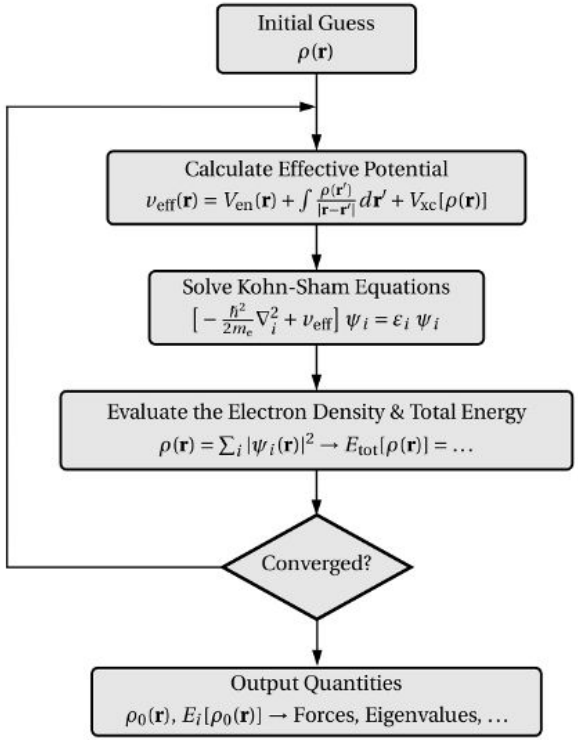
- Time-dependent density: $n(\vec{r},t)=\sum_{i}^{N}\phi_i^*(\vec{r},t)\phi_i(\vec{r},t)$
- We solve now for time-dependent Kohn-Sham equations (Runge-Gross): $i\frac{\partial}{\partial t}\phi_i(\vec{r},t)=-\nabla^2\phi_i(\vec{r},t)+V_{eff}\left[\phi_i(\vec{r},t)\right]\phi_i(\vec{r},t)$
- The initial condition on the potential can give us several properties such as response to laser fields…



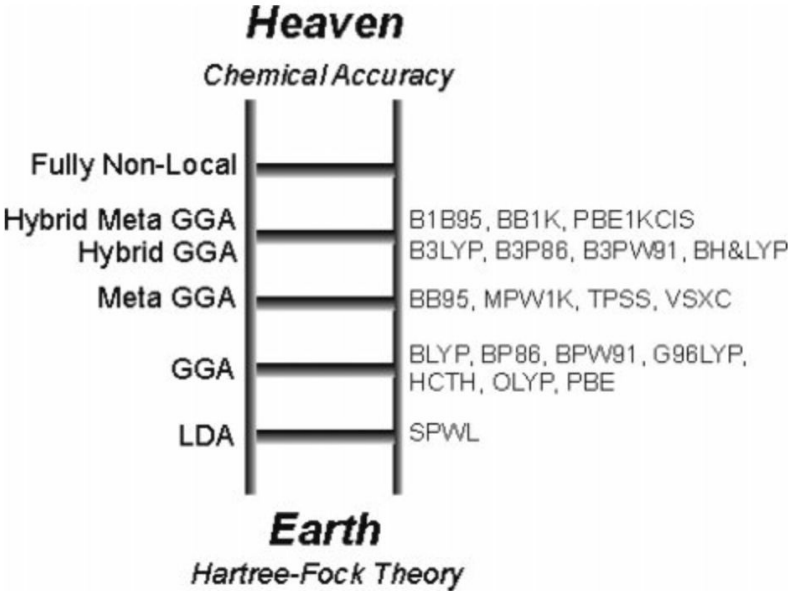
Density Functional Theory

$$\hat{H}_{eff}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}).$$

$$\psi_j(\vec{r}) = \sum_{i=1}^{K} \alpha_{j,i}\phi_i(\vec{r})$$



Accuracy: theory level & basis set



General Performance of Density Functionals
Souza, Fernandez, and Ramos.
J. Phys. Chem. A 2007, 111, 42, 10439–10452

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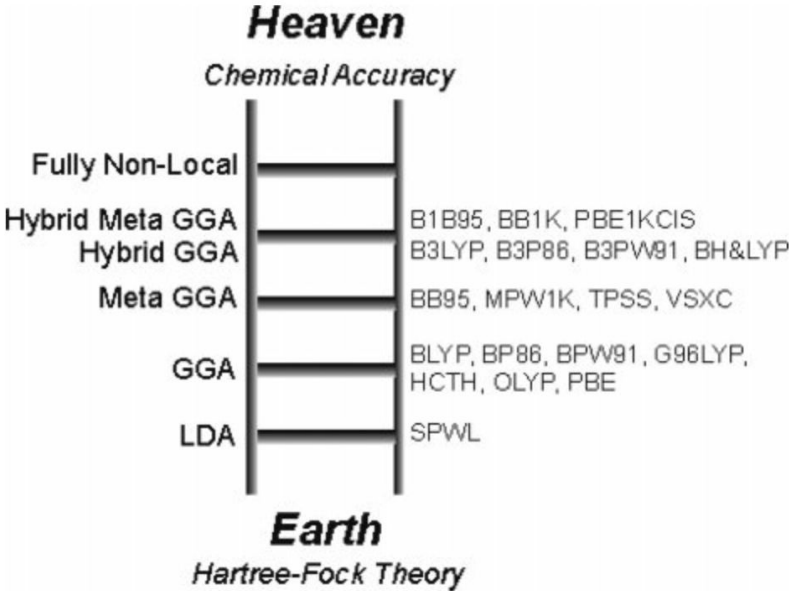

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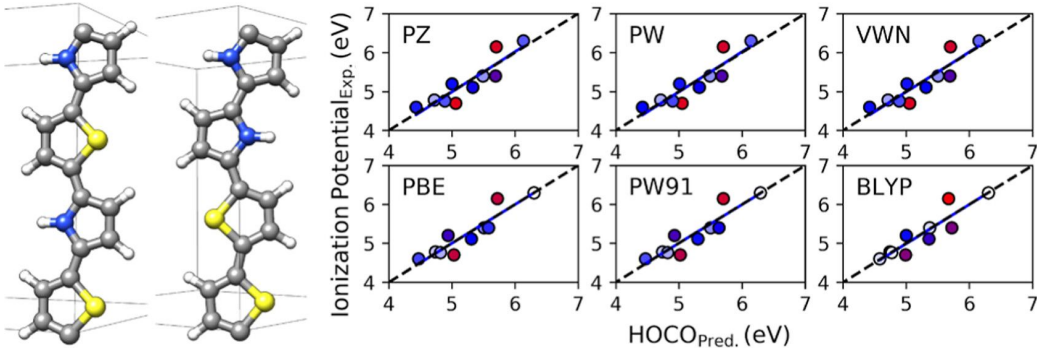
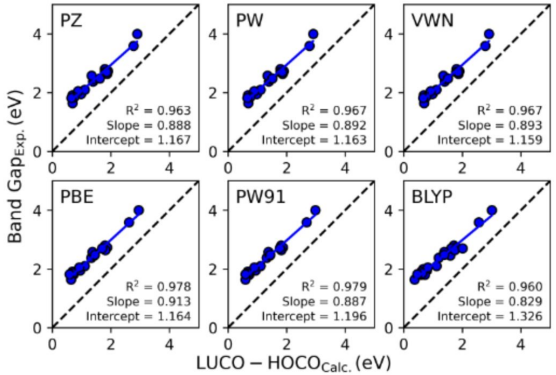
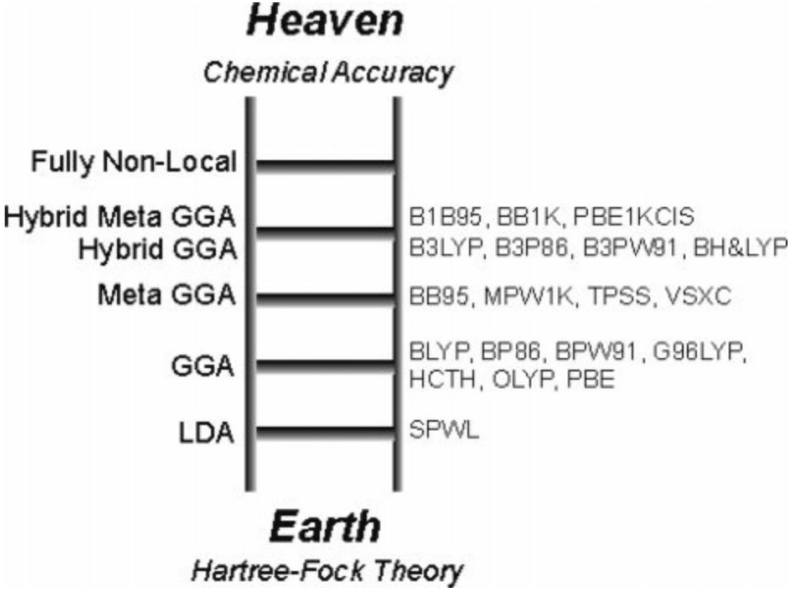




Benchmarking DFT and Supervised Machine Learning: An Organic Semiconducting Polymer Investigation

Stoltz & Borunda.
J. Phys. Chem. A 2024, 128, 4, 709–715

Accuracy: theory level & basis set



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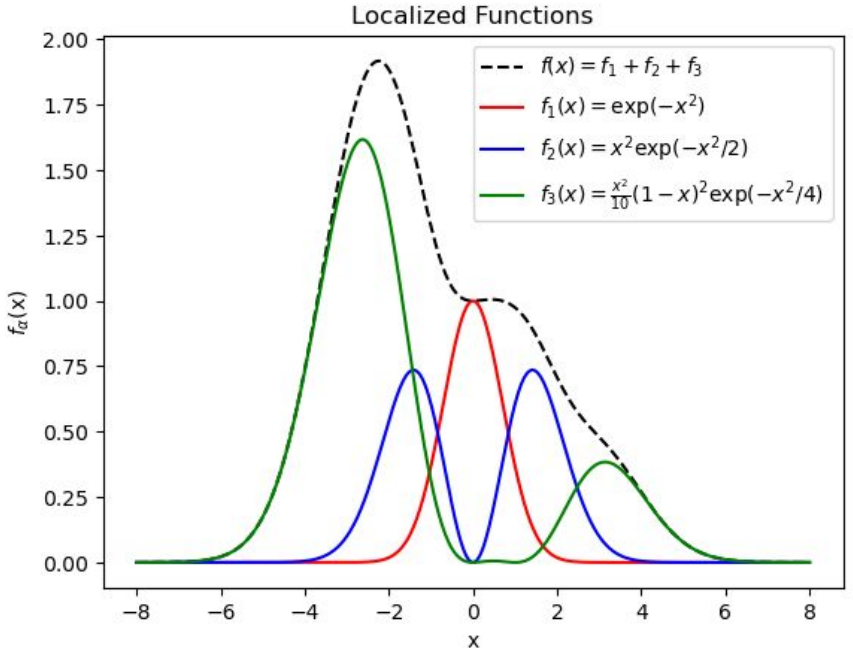
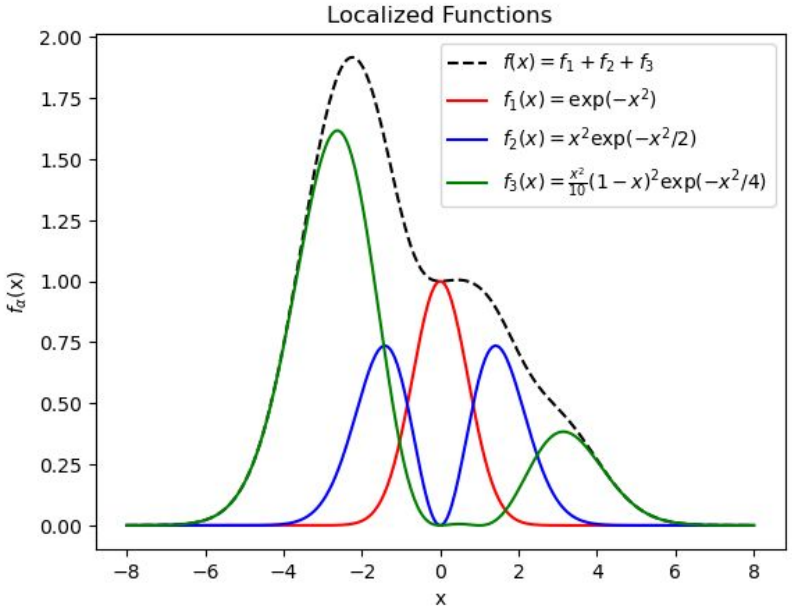
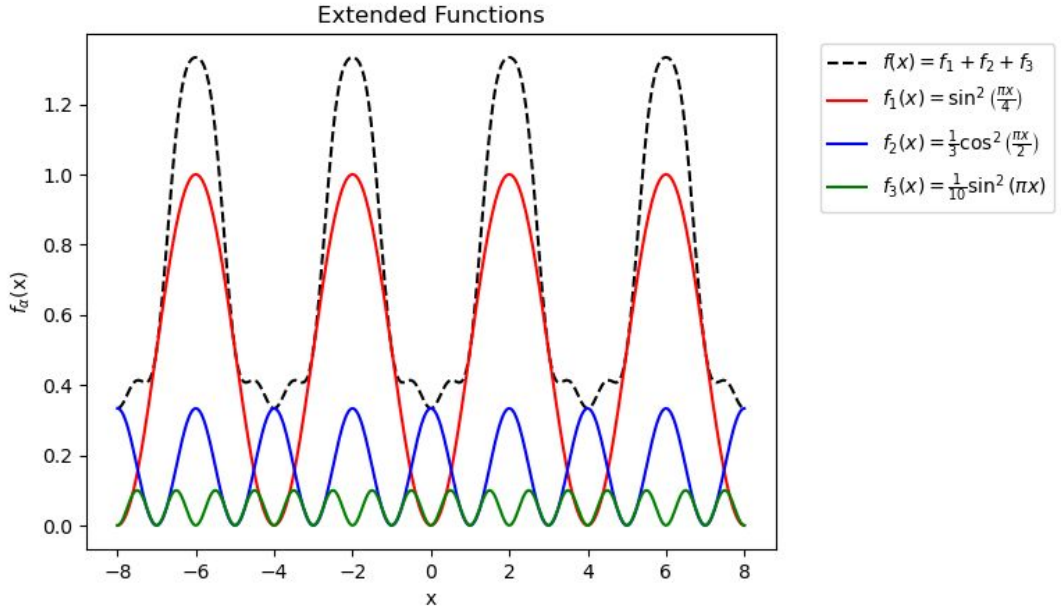


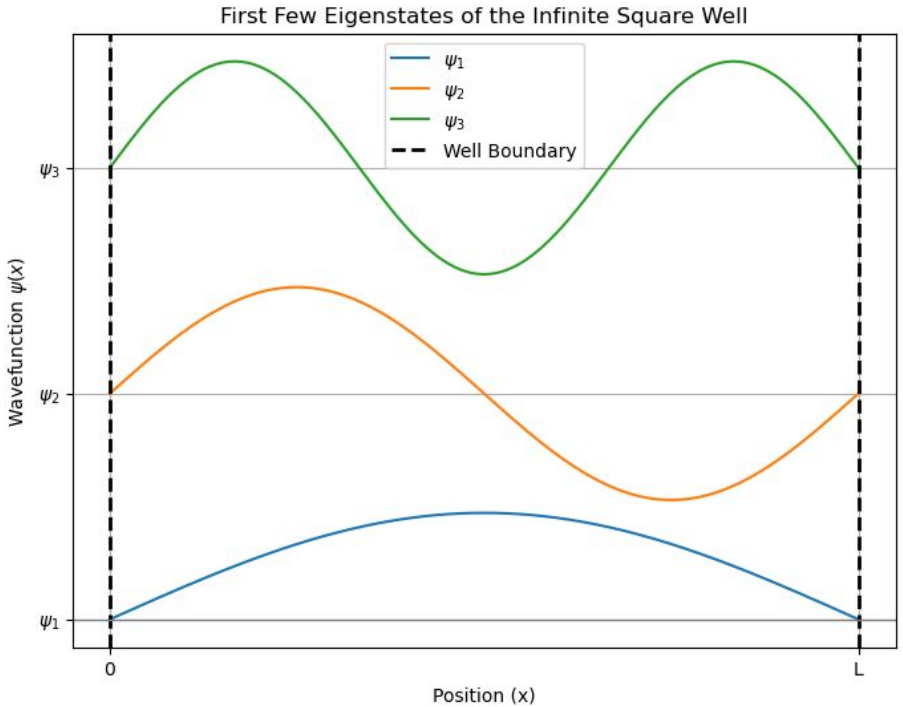
Basis sets for each situation





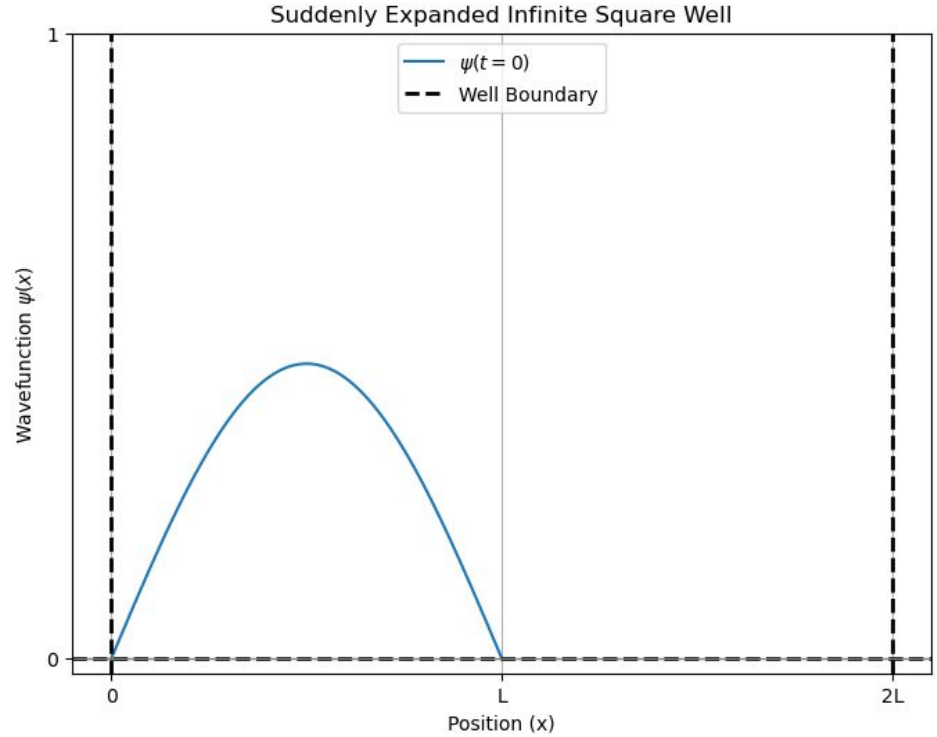
What is the periodicity of this function?

Basis sets for each situation



What is the basis in this situation?

Basis sets for each situation



Using the following functions as basis,

$$\psi_n(x) = \sqrt{\frac{1}{L}} \sin\left(n\frac{\pi x}{2L}\right)$$

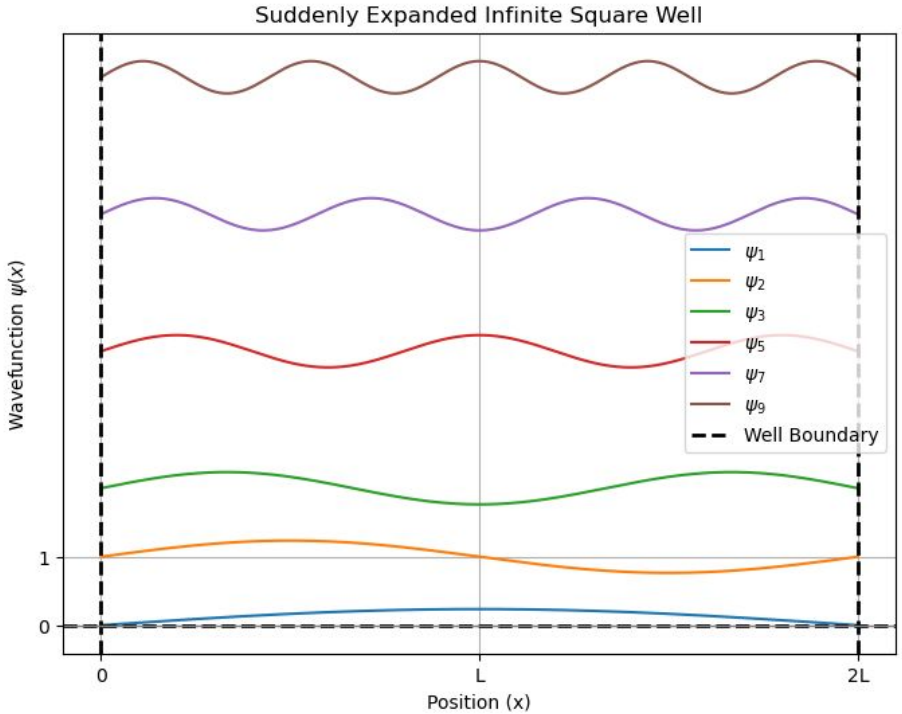
can you build the wavefunction at t=0?

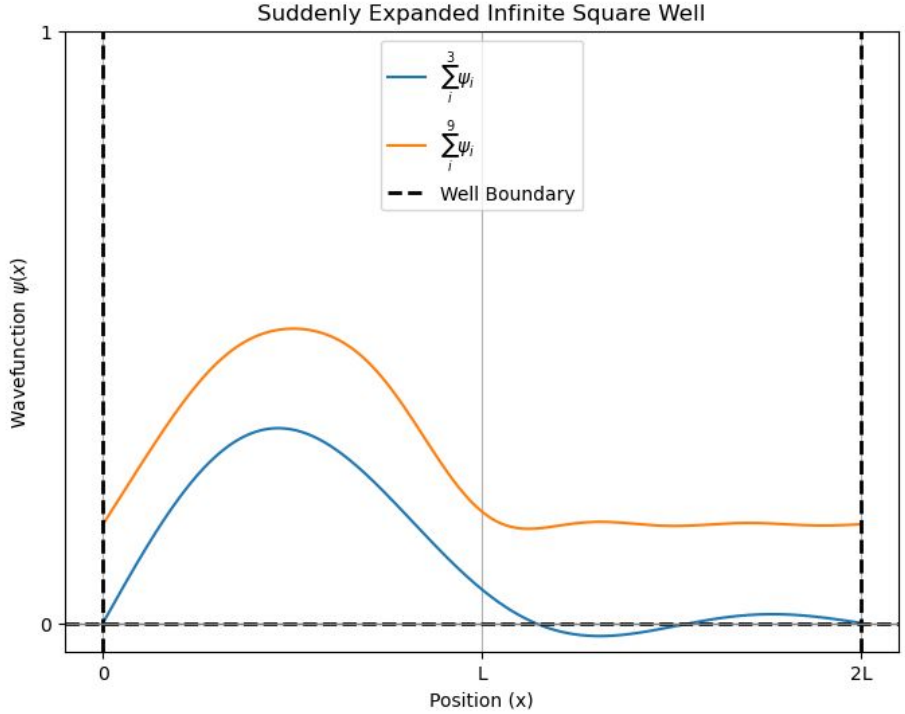
$$\psi(x, t = 0) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

Basis sets for each situation

$$\psi(x) = \sum a_n \psi_n(x);$$

$$a_1 = 0.6, a_2 = 0.707, a_3 = 0.36, a_5 = -0.086, a_7 = 0.04, a_9 = -0.023$$





– Treatment of the boundary conditions

Isolated objects (atoms, molecules, clusters)

open boundary conditions

(defined at infinity)

3D periodic objects (crystals)

periodic boundary conditions

(might be considered as the repetition of a building block, the unit cell)

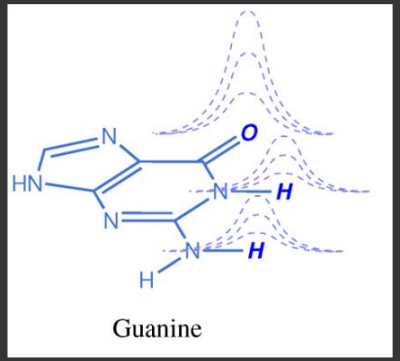
Mixed boundary conditions

1D periodic (chains)

2D periodic (slabs and interfaces)

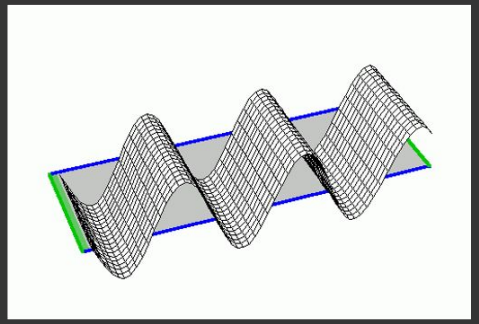
Three main families of methods depending on the basis sets

Gaussian basis methods

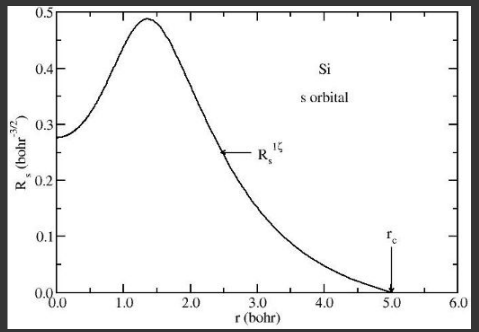


Guanine

Plane wave and grids

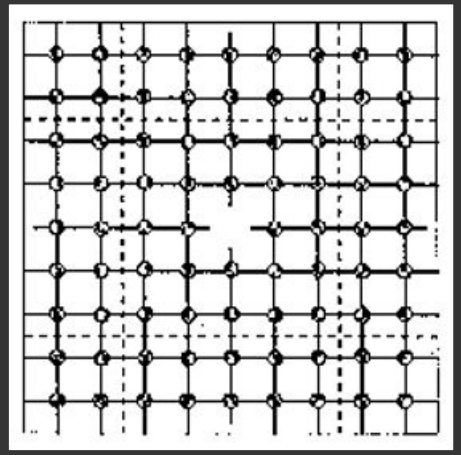


Localized basis sets

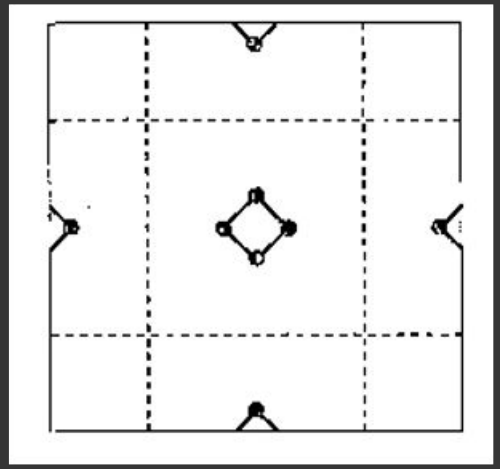


– Periodic boundaries…

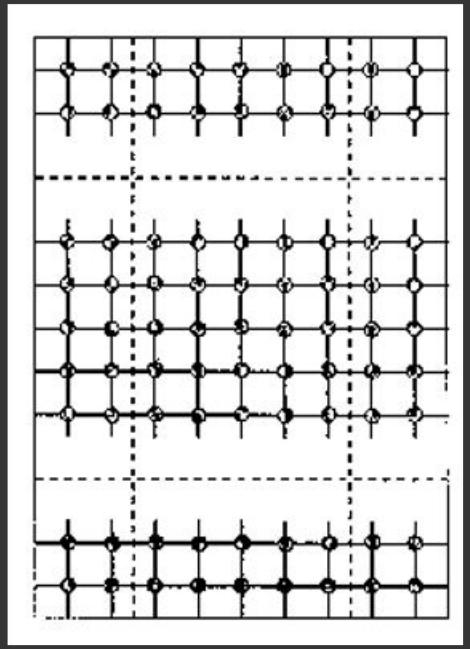
Defects



Molecules



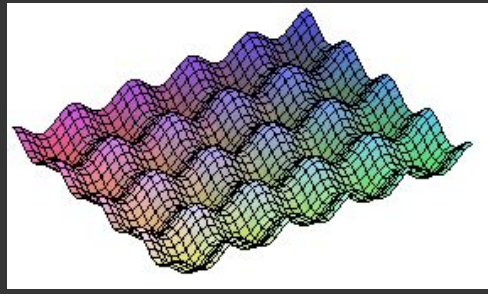
Surfaces

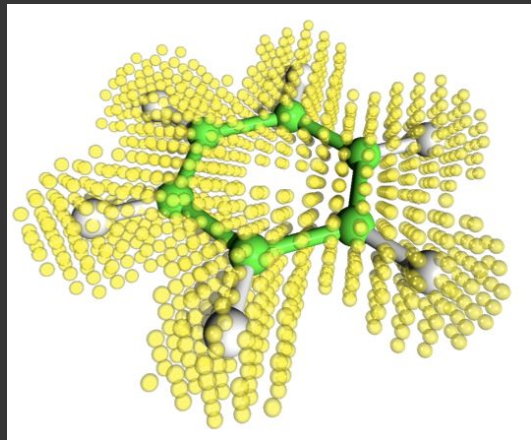


M. C. Payne *et al.*, Rev. Mod. Phys., 64, 1045 (1992)

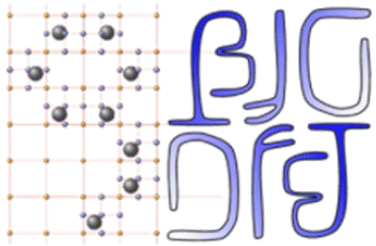
Real-space grid

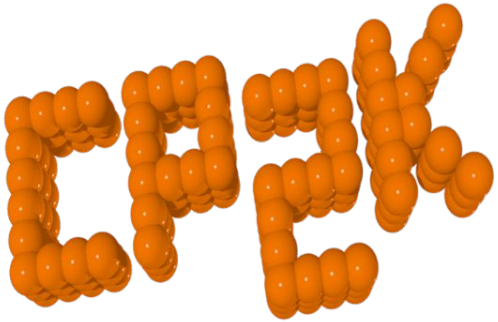
- We are solving the partial differential equation (that has infinite degrees of freedom) using a finite number of degrees of freedom.
- Discretize the functions using values on a set of points.
- The distance between points is the **SPACING**
- Natural boundary conditions for all of our problems:
  - Dirichlet Boundaries for molecules
  - Mix one periodic with two Dirichlet for wires (polymers)
  - Mix two periodic with one Dirichlet for surfaces (or 2D materials)
  - Use periodic for crystals
- Want more accuracy? Decrease the spacing!
- Orthogonal basis set.
- Finite differences, sparse matrices…
- Issues?
  - Breaks translational invariance (egg box effect)
  - Breaks rotational invariance






Abinit


BIGDFT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Simulation Package for Ab-initio Real-space Calculations

7 Contributors · 10 Issues · 78 Stars · 39 Forks