# modeling materials using quantum mechanics and digital computers
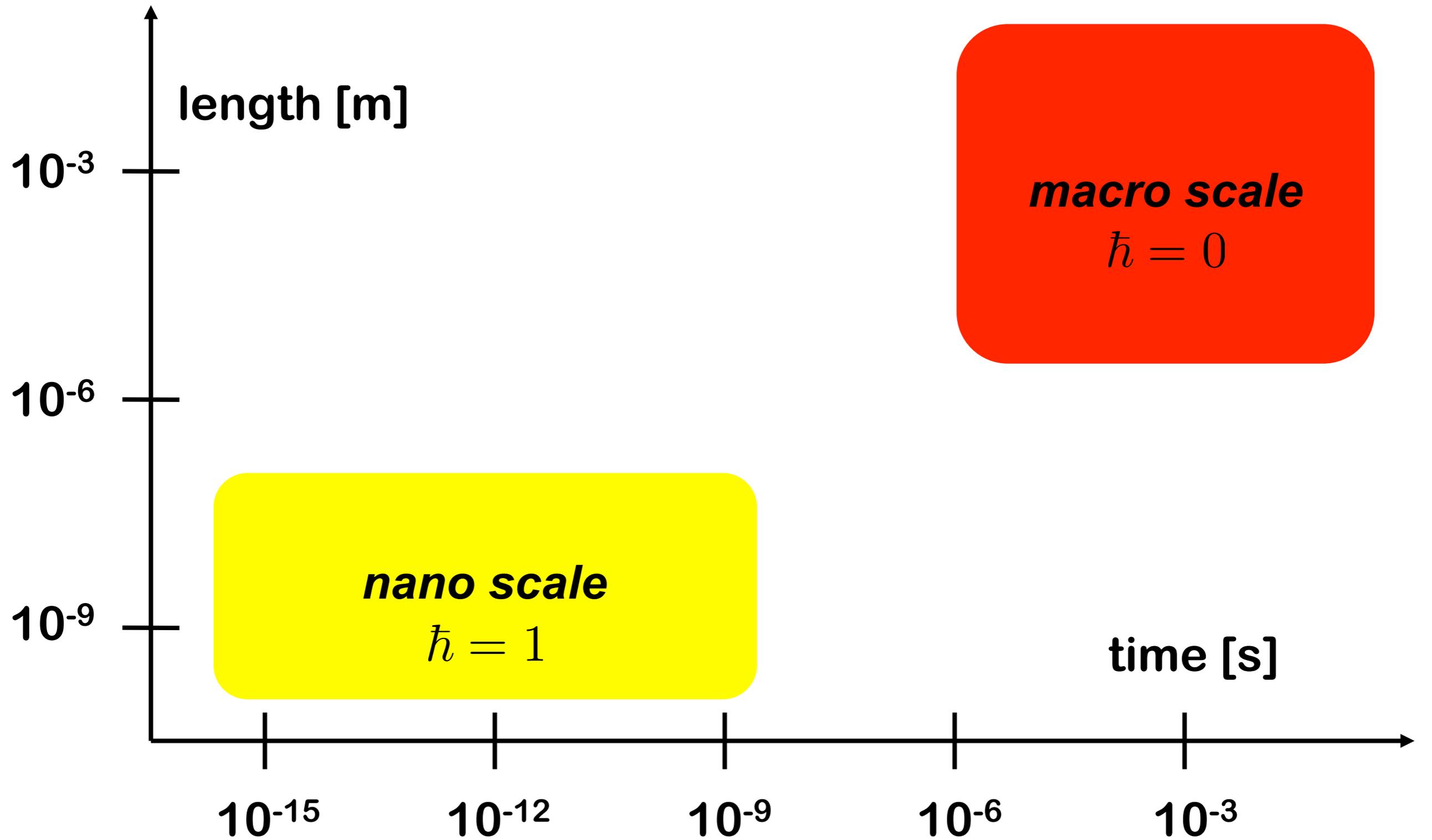## *the plane-wave pseudo potential way*
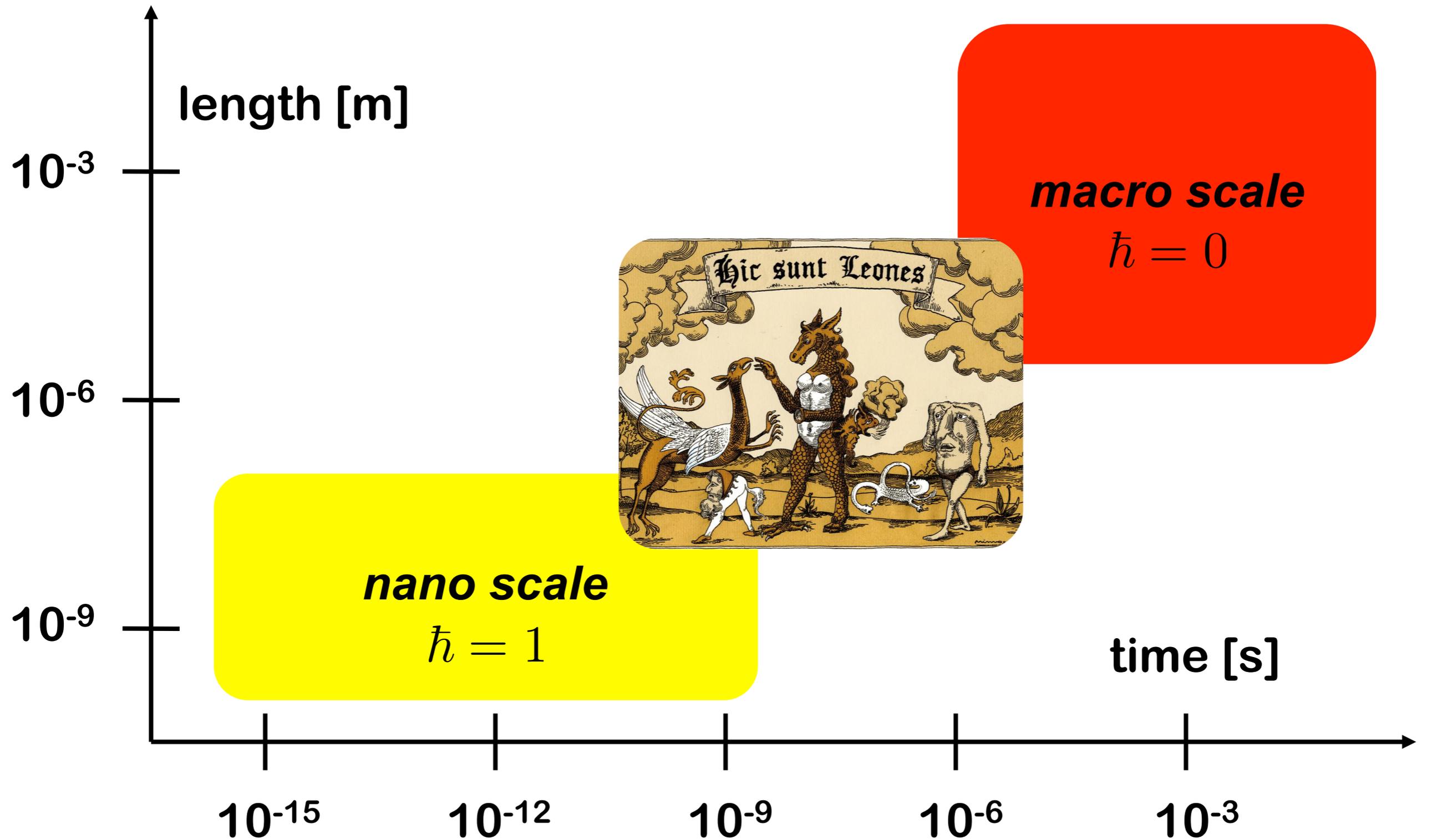
## Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati

Trieste - Italy

# the saga of time and length scales
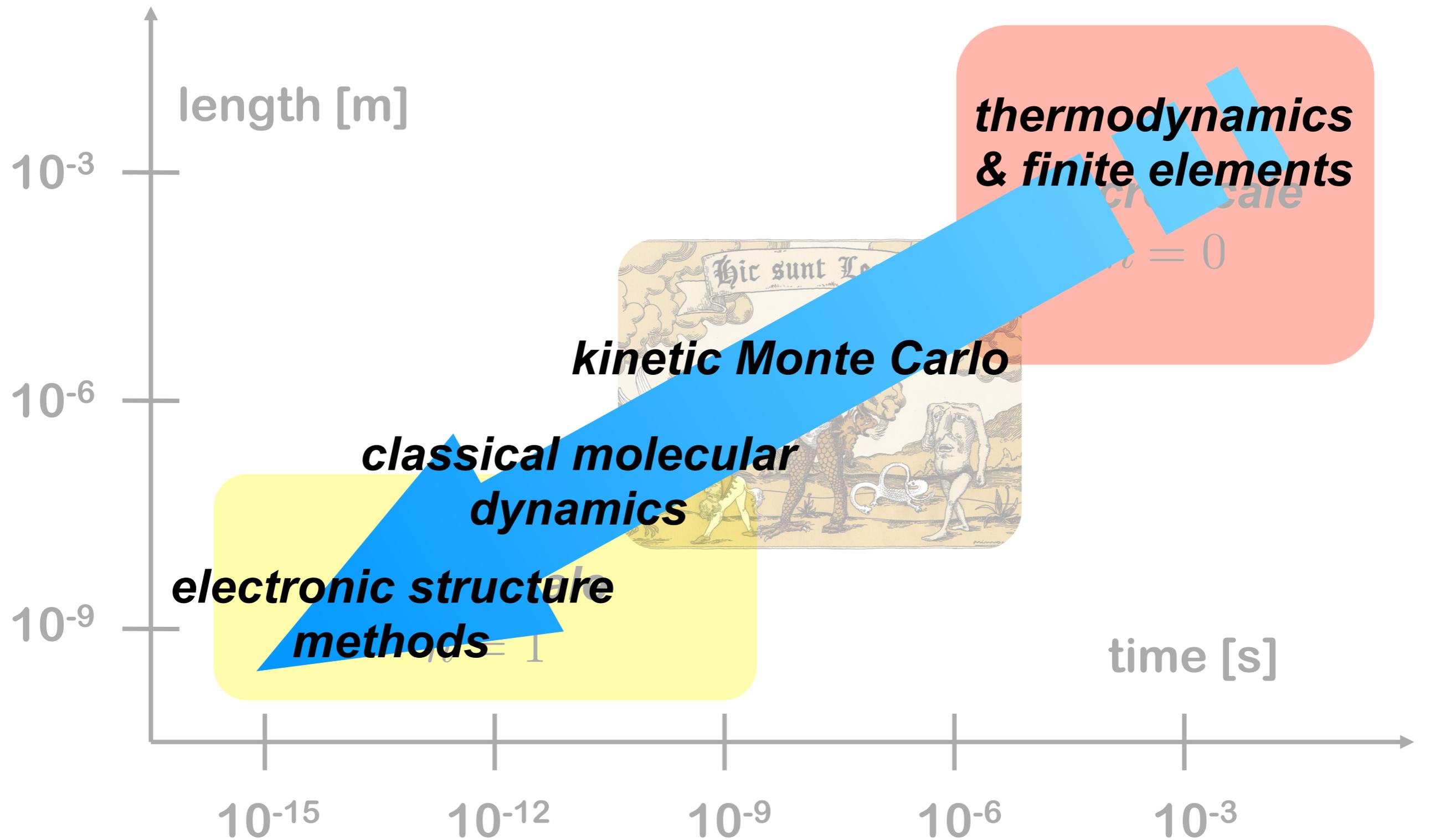
# the saga of time and length scales

**length [m]**

$10^{-3}$

$10^{-6}$

$10^{-9}$

**macro scale**
$\hbar = 0$

Hic sunt Leones

**nano scale**
$\hbar = 1$

**time [s]**

$10^{-15}$   $10^{-12}$   $10^{-9}$   $10^{-6}$   $10^{-3}$

# the saga of time and length scales



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**thermodynamics & finite elements**

**kinetic Monte Carlo**

**classical molecular dynamics**

**electronic structure methods**

time [s]

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# size vs. accuracy

**classical empirical methods**
☞ *pair potentials*
☞ *force fields*
☞ *shell models*

**quantum empirical methods**
☞ *tight-binding*
☞ *embedded atom*

**quantum self-consistent methods**
☞ *density Functional Theory*
☞ *Hartree-Fock*

**quantum many-body methods**
☞ *quantum Monte Carlo*
☞ *MP2, CCSD(T), CI*
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size/duration

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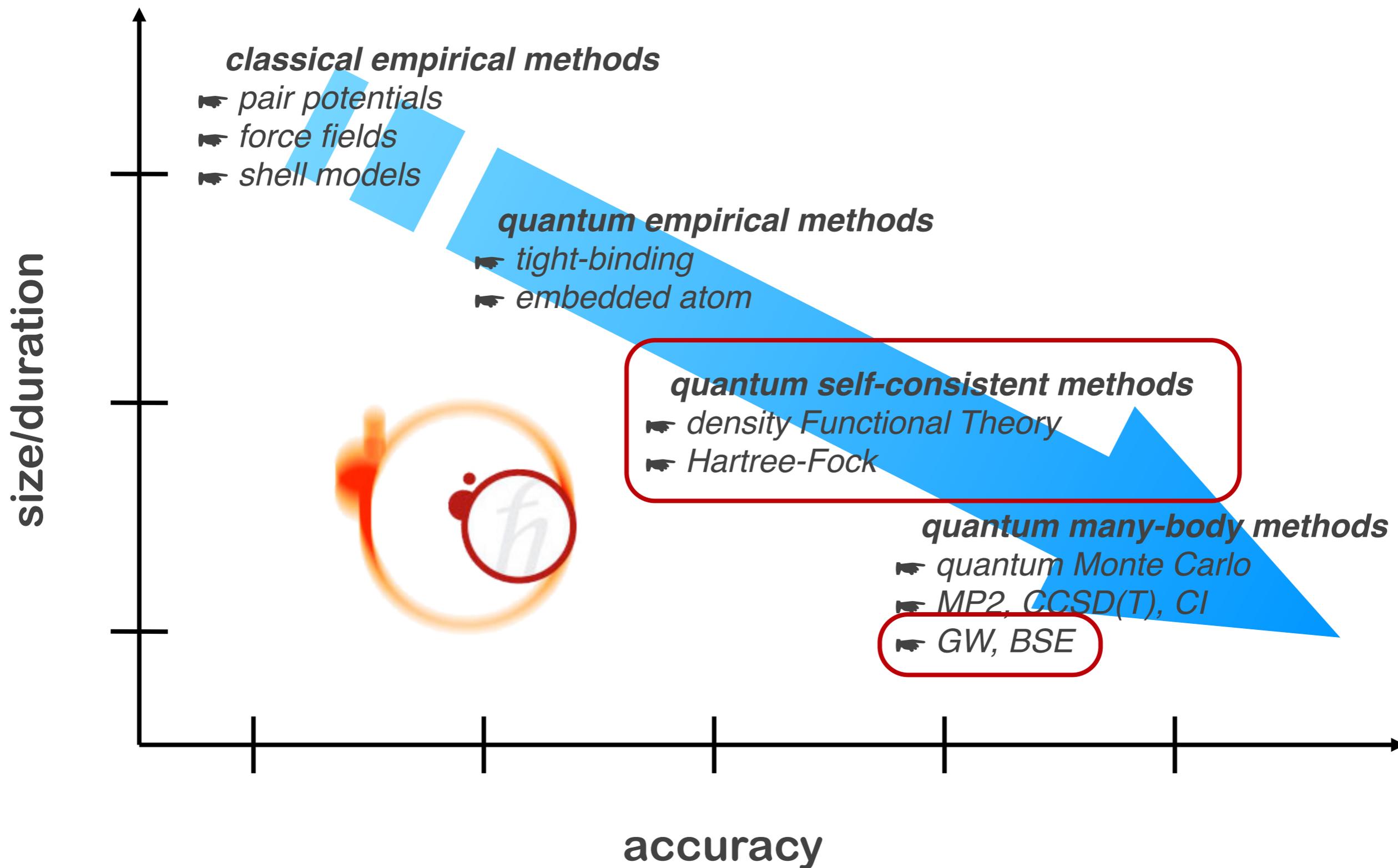
# *ab initio* calculations: what, why, when, how

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# *ab initio* calculations: what, why, when, how

**what:** simulate the properties of materials using Schrödinger and Maxwell equations and chemical composition as the *sole* input ingredients

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**when:** if currently available approximations make the calculations *feasible* and the results *meaningful* (and no meaningful results can be obtained with cheaper methods)

**how:** using digital computers, clever algorithms, common sense, and *scientific rigor*

# ab initio simulations

$$i\hbar\frac{\partial \Phi(\mathbf{r},\mathbf{R};t)}{\partial t} = \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{R}^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r},\mathbf{R})\right)\Phi(\mathbf{r},\mathbf{R};t)$$

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M ≫ m: the Born-Oppenheimer approximation

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r}, \mathbf{R})\right) \Psi(\mathbf{r}|\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}|\mathbf{R})$$

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# density-functional theory

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DFT

$$V(\mathbf{r}, \mathbf{R}) \to \frac{e^2}{2} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + v_{[\rho]}(\mathbf{r})$$

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Kohn-Sham
equations

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$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + v_{[\rho]}(\mathbf{r}) \right) \psi_v(\mathbf{r}) = \epsilon_v \psi_v(\mathbf{r})$$

# functionals

$$G[f] : \{f\} \mapsto \mathbb{R}$$

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examples:

$$G[f] : \{f\} \mapsto \mathbb{R}$$

$$G[f] = f(x_0)$$

$$G[f] = \int_a^b f^2(x)dx$$

$$G[f] = \int_a^b |f'(x)|^2 dx$$

$$\dots$$

# functionals

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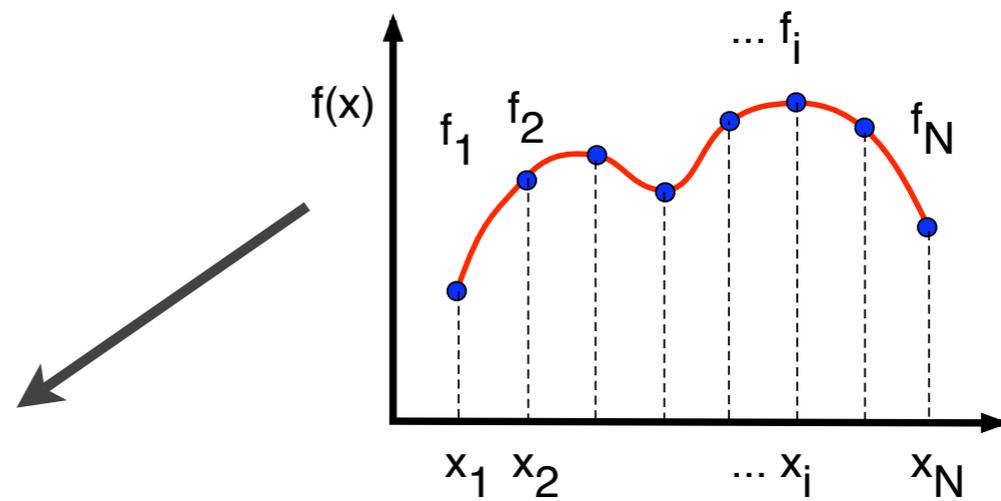$$G[f] : \{f\} \mapsto \mathbb{R}$$

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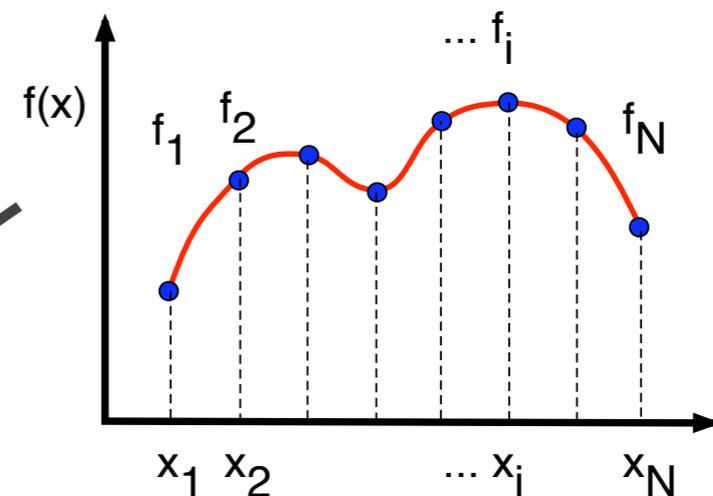
$$f(x) \approx \sum_n c_n \phi_n(x)$$

# functional derivatives

$$G[f_0 + \epsilon f_1] = G[f_0] + \epsilon \int f_1(x) \left.\frac{\delta G}{\delta f(x)}\right|_{f=f_0} dx + \mathcal{O}\left(\epsilon^2\right)$$
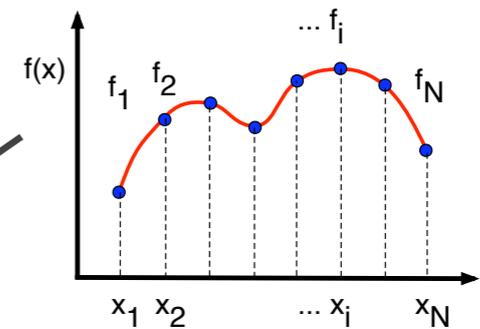
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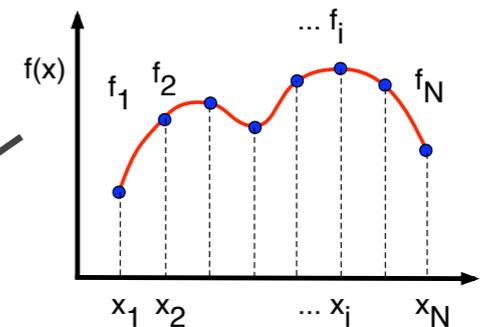
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$$\frac{\delta G}{\delta f(x)} \text{ “ = ” } \lim_{\epsilon \to 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

# the Hellmann-Feynman theorem

$$M\ddot{\mathbf{R}} = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}}$$

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$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$

$$\frac{\partial E_\lambda}{\partial \lambda} = \ ???$$

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&= E_\lambda \big( \langle \Psi_\lambda' | \Psi_\lambda \rangle + \langle \Psi_\lambda | \Psi_\lambda' \rangle \big) + \langle \Psi_\lambda | \hat{H}_\lambda' | \Psi_\lambda \rangle
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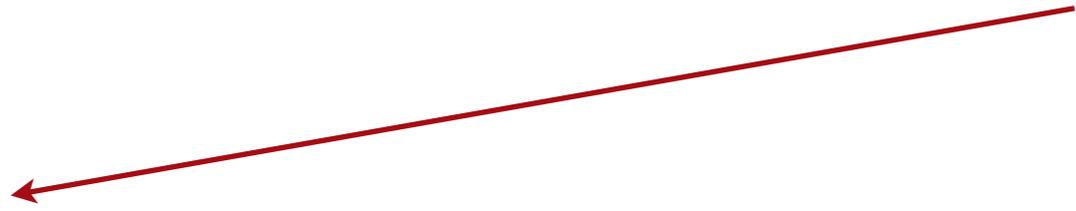$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$

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# Hohenberg-Kohn DFT

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properties:

- $E[V]$ is convex   (requires some work to demonstrate)

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consequences:

- $V(\mathbf{r}) \rightleftarrows \rho(\mathbf{r})$   (1st *HK theorem*)

- $F[\rho] = E - \displaystyle\int V(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$   is the Legendre transform of $E$

- $E[V] = \min_\rho \left[ F[\rho] + \displaystyle\int V(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right]$   (2nd *HK theorem*)

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$$\frac{\delta T_0}{\delta \rho(\mathbf{r})} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + V(\mathbf{r}) = \mu$$

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$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}[\rho](\mathbf{r}) \right) \psi_v(\mathbf{r}) = \epsilon_v \psi_v(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2 \theta(\epsilon_v - \mu)$$

# exchange-correlation energy functionals

▶ LDA (Kohn & Sham, 60's)

$$E_{xc}[\rho] = \int \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$

▶ GGA (Becke, Perdew, *et al.*, 80's)

$$E_{xc} = \int \rho(\mathbf{r})\epsilon_{GGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)\, d\mathbf{r}$$

▶ DFT+U (Anisimov *et al.*, 90's)

$$E_{DFT+U}[\rho] = E_{DFT} + Un(n-1)$$

▶ hybrids (Becke *et al.*, 90's)

$$E_{hybr} = \alpha E_{HF}^x + (1-\alpha)E_{GGA}^x + E^c$$

▶ meta-GGA (Perdew, early 2K's)

$$E_{mGGA} = \int \rho(\mathbf{r}) \times$$

$$\epsilon_{mGGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \tau_s(\mathbf{r}))d\mathbf{r}$$

$$\tau_s(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla^2\psi_i(\mathbf{r})|^2$$

▶ VdW (Langreth & Lundqvist, 2K's)

$$E_{VdW} = \int \rho(\mathbf{r})\rho(\mathbf{r}') \times$$

$$\Phi_{VdW}[\rho](\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

▶ ...

# KS equations from functional minimization

$$E[\{\psi\}, \mathbf{R}] = -\frac{\hbar^2}{2m} \sum_v \int \psi_v^*(\mathbf{r}) \frac{\partial^2 \psi_v(\mathbf{r})}{\partial \mathbf{r}^2} dr + \int V(\mathbf{r}, \mathbf{R}) \rho(\mathbf{r}) d\mathbf{r} +$$

$$\frac{e^2}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho]$$

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$$E(\mathbf{R}) = \min_{\{\psi\}} \big( E[\{\psi\}, \mathbf{R}] \big)$$

$$\int \psi_u^*(\mathbf{r}) \psi_v(\mathbf{r}) d\mathbf{r} = \delta_{uv}$$

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# solving the Kohn-Sham equations

$$\psi_v(\mathbf{r}) = \sum_j c(j,v)\varphi_j(\mathbf{r})$$

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$$\dot{c}(i,v) = -\sum_j h_{KS}[c](i,j)c(j,v)+$$

$$\sum_u \Lambda_{vu} c(i,v)$$

these slides shortly at
http://talks.baroni.me