The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2145-25

Spring College on Computational Nanoscience

17 - 28 May 2010

Variational Principles, the Hellmann-Feynman Theorem, Density Functional Theo

Stefano BARONI

SISSA & CNR-IOM DEMOCRITOS Simulation Center
Trieste
Italy

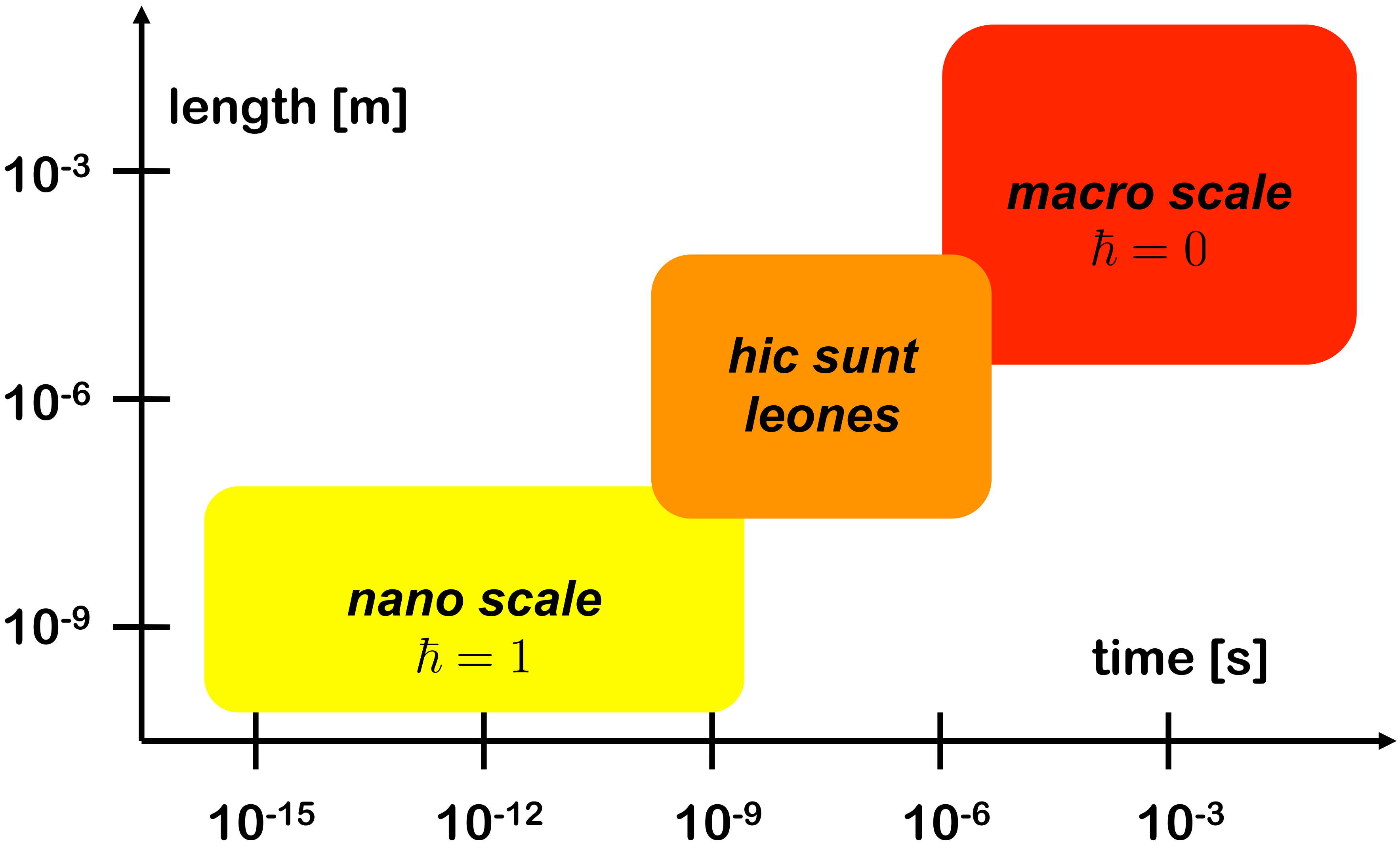
variational principles, the Hellmann-Feynman theorem, density-functional theory

Stefano Baroni

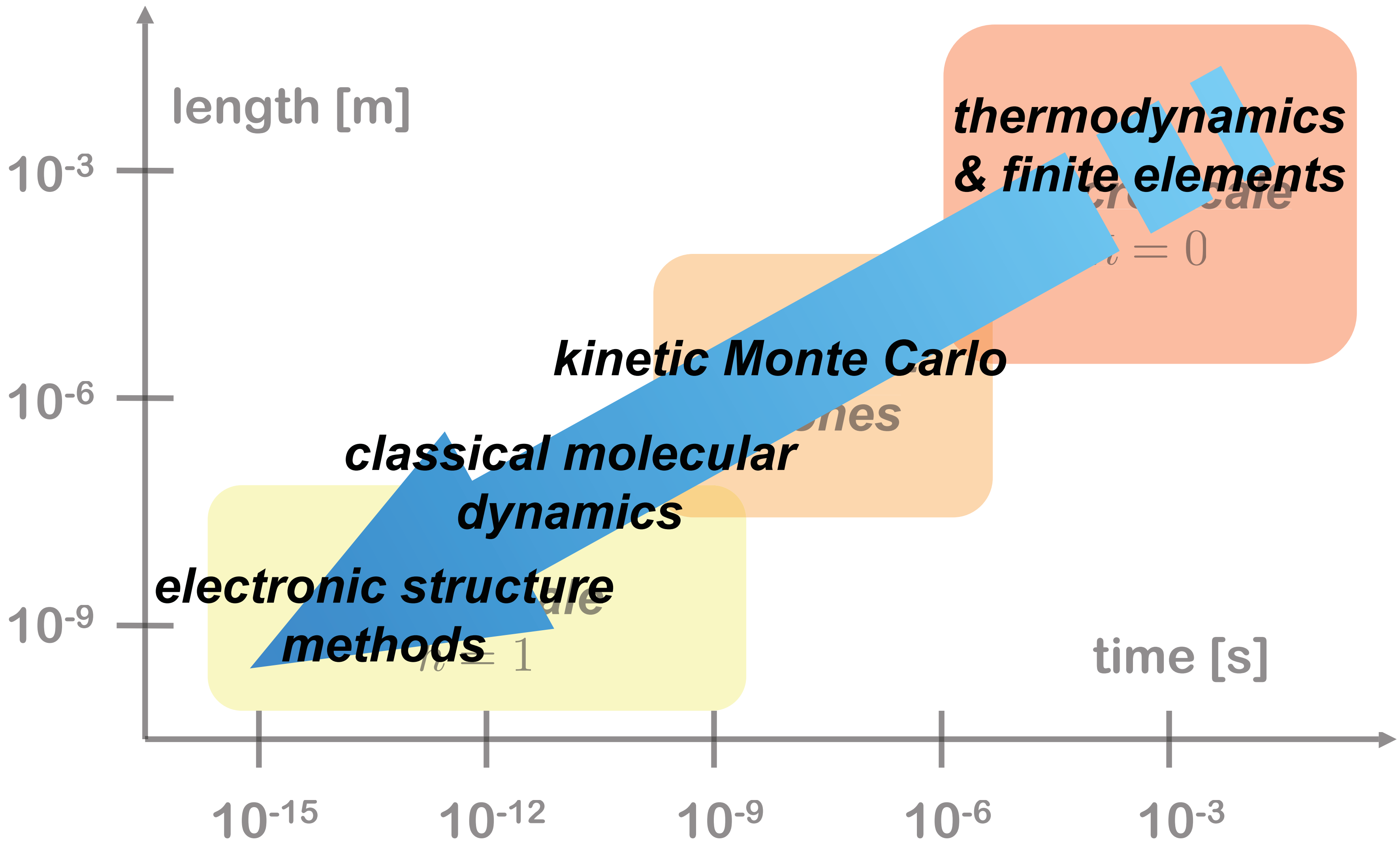
Scuola Internazionale Superiore di Studi Avanzati &
CNR-IOM *DEMOCRITOS* Simulation Center
Trieste - Italy

lecture given at the *Spring College on Computational Nanoscience*
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, May 17-28, 2010

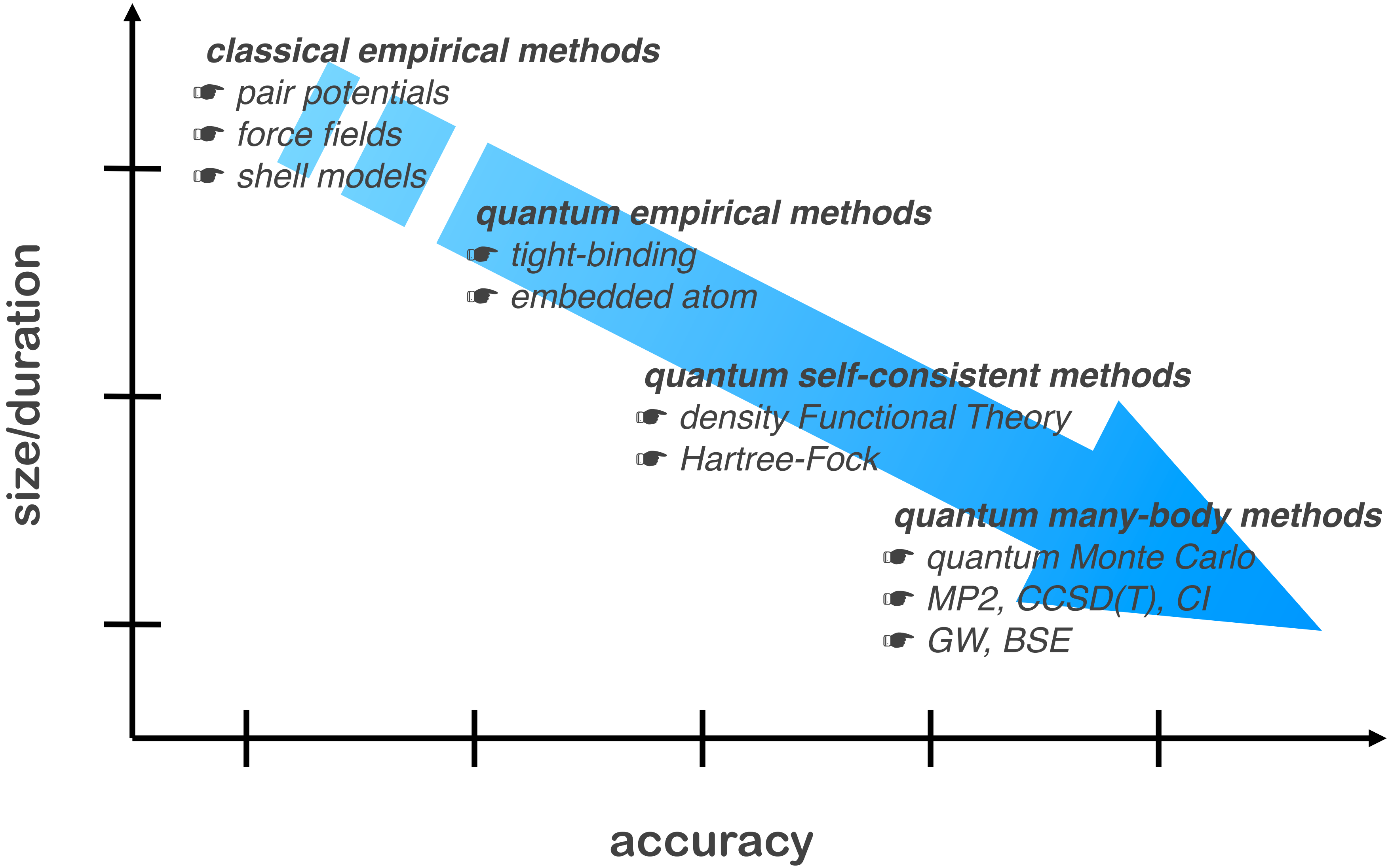
the saga of time and length scales



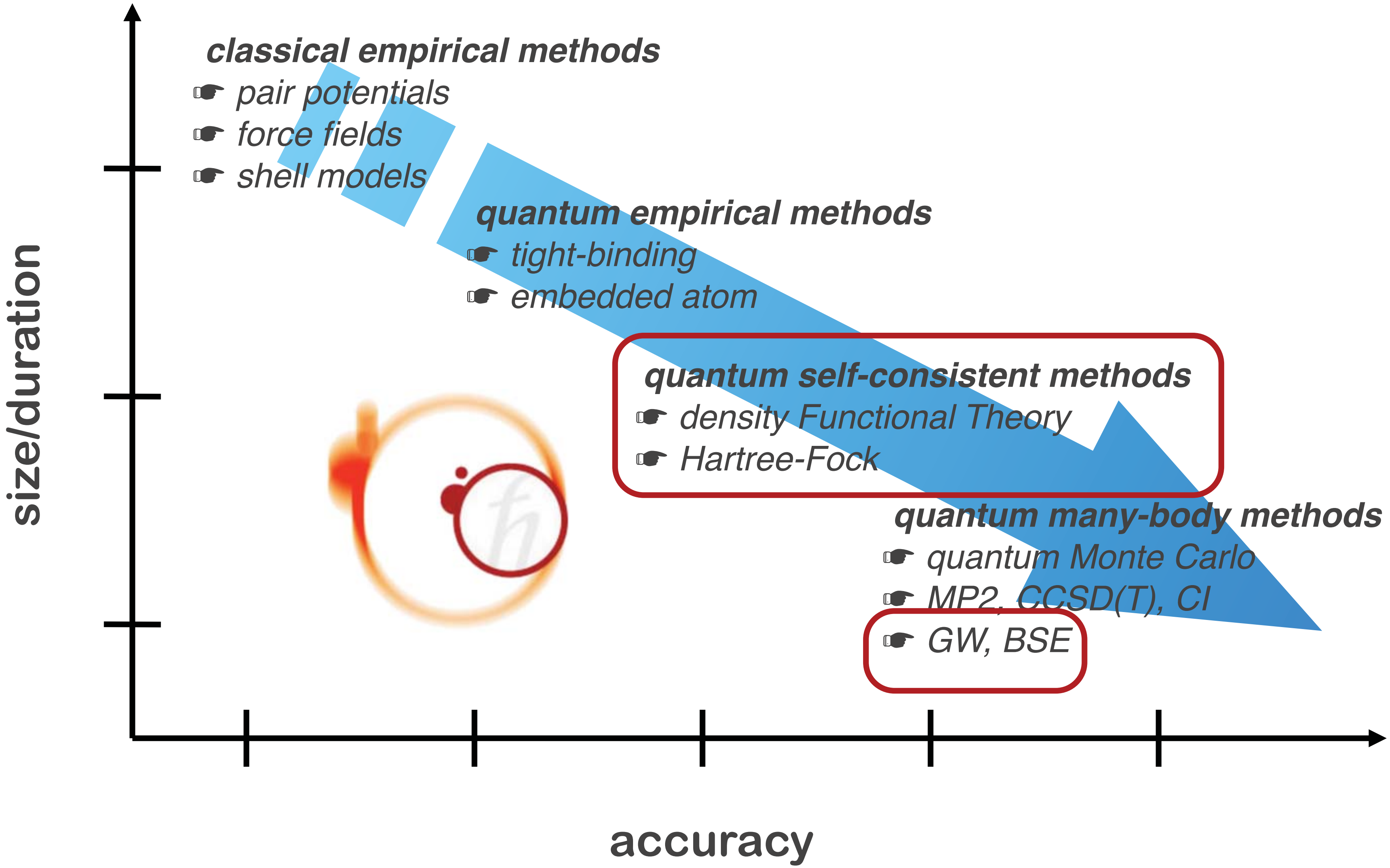
the saga of time and length scales



size vs. accuracy



size vs. accuracy



ab initio simulations

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

The Born-Oppenheimer approximation (M≫m)

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

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

density-functional theory

$$V(\mathbf{r}, \mathbf{R}) = \frac{e^2}{2} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{e^2}{2} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

density-functional theory

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{2}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{e^2}{2}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

↓ DFT

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

Kohn-Sham
Hamiltonian

$$\rho(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2$$

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

functionals

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

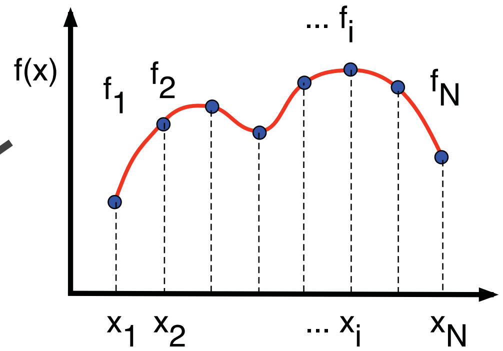
examples:

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

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

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

$$\cdots$$



approximations:

$$G[f] \approx g(f_1, f_2, \cdots, f_N)$$

$$G[f] \approx g(c_1, c_2, \cdots, c_N)$$

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

functional derivatives

$$G[f_0 + \epsilon f_1] = G[f_0] + \epsilon \int f_1(x)\ \frac{\delta G}{\delta f(x)}\bigg|_{f=f_0} dx + \mathcal{O}\left(\epsilon^2\right)$$

$$\frac{\delta G}{\delta f(x)}\bigg|_{f=f_0} \approx \frac{1}{h}\frac{\partial g}{\partial f_i}$$

$$\frac{\delta G}{\delta f(x)} \text{``}=\text{''} \lim_{\epsilon \to 0} \frac{G[f(\bullet) + \epsilon\delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

the Hellmann-Feynman theorem

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

the Hellmann-Feynman theorem

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

$$\begin{aligned} E'_\lambda &= \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle \end{aligned}$$

$$E_\lambda = \min_{\{\Psi:\ \langle \Psi | \Psi \rangle = 1\}} \langle \Psi | \hat{H}_\lambda | \Psi \rangle$$

$$g(\lambda) = \min_x G[x, \lambda] \longrightarrow \left. \frac{\partial G}{\partial x} \right|_{x = x(\lambda)} = 0$$

$$g(\lambda) = G[x(\lambda), \lambda] \longrightarrow g'(\lambda) = x'(\lambda) \left. \frac{\partial G}{\partial x} \right|_{x = x(\lambda)} + \frac{\partial G}{\partial \lambda}$$

the Hellmann-Feynman theorem

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

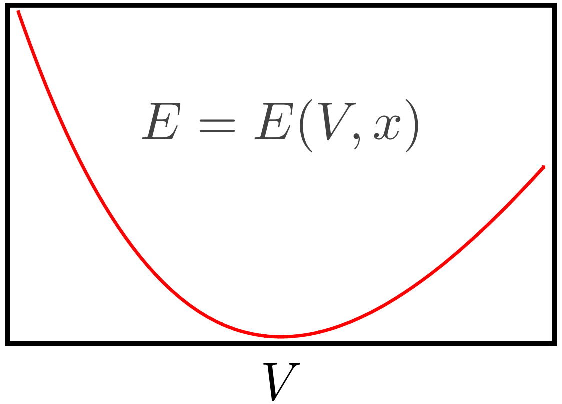
$$\begin{aligned} E'_\lambda &= \frac{\partial}{\partial\lambda}\langle\Psi_\lambda|\hat{H}_\lambda|\Psi_\lambda\rangle \\ &= \langle\Psi_\lambda|\hat{H}'_\lambda|\Psi_\lambda\rangle \end{aligned}$$

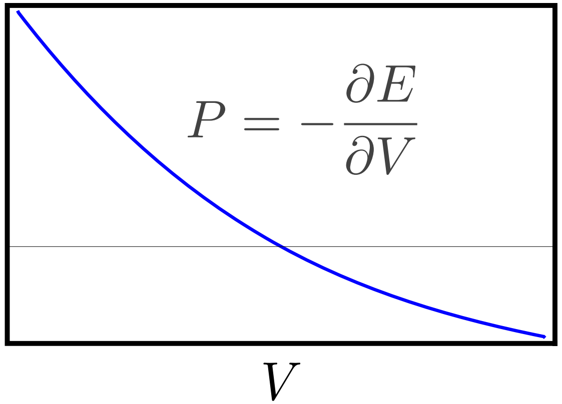
$$E_\lambda = \min_{\{\Psi:\ \langle\Psi|\Psi\rangle=1\}} \langle\Psi|\hat{H}_\lambda|\Psi\rangle$$

$$g(\lambda) = \min_x G[x,\lambda] \longrightarrow \left.\frac{\partial G}{\partial x}\right|_{x=x(\lambda)} = 0$$

$$g(\lambda) = G[x(\lambda),\lambda] \longrightarrow g'(\lambda) = \cancel{x'(\lambda)\left.\frac{\partial G}{\partial x}\right|_{x=x(\lambda)}} + \frac{\partial G}{\partial\lambda}$$

conjugate variables & Legendre transforms





Legendre transform: $H(P, x) = E + PV$

properties:

- E convex $\Rightarrow V \rightleftarrows P$
- $H(P, x) = \max_V \big(E(V, x) + PV\big)$
- Hellmann-Feynman: $\frac{\partial H}{\partial x} = \frac{\partial E}{\partial x}$
- H concave
- $E(V, x) = \min_P \big(H(P, x) - PV\big)$

Hohenberg-Kohn DFT

$$H = -\frac{\hbar^2}{2m}\sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V(\mathbf{r}_i)$$

$$\begin{aligned} E[V] &= \min_{\Psi} \langle \Psi | \hat{K} + \hat{W} + \hat{V} | \Psi \rangle \\ &= \min_{\Psi} \left[\langle \Psi | \hat{K} + \hat{W} | \Psi \rangle + \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \right] \end{aligned}$$

properties:

- $E[V]$ is convex (requires some work to demonstrate)
- $\rho(\mathbf{r}) = \dfrac{\delta E}{\delta V(\mathbf{r})}$ (from Hellmann-Feynman)

consequences:

- $V(\mathbf{r}) \rightleftarrows \rho(\mathbf{r})$ (1st *HK theorem*)
- $F[\rho] = E - \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ is the Legendre transform of E
- $E[V] = \min_{\rho} \left[F[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right]$ (2nd *HK theorem*)

Hohenberg-Kohn DFT

$$E[V] = \min_{\rho} \left[F[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right]$$

exchange-correlation energy functionals

- local-density approximation (LDA, Kohn and Sham, 1965)

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

- generalized-gradient approximation (GGA, Becke, Perdew, and Wang, 1986)

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

- DFT+U (Anisimov and others, early 90's)

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

- meta-GGA (Perdew and others 2003)

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

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

- hybrid functionals (B3Lyp, PBE0, Becke 1993)

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

- ...

KS equations from functional minimization

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

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

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

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

KS equations from functional minimization

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

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

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

$$\longrightarrow \quad \frac{\delta E_{KS}}{\delta \psi_v^*(\mathbf{r})} = \sum_u \Lambda_{vu}\psi_u(\mathbf{r})$$

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

solving the Kohn-Sham equations

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

$$\psi_v(\mathbf{r}) \rightleftarrows c(v,j)$$

$$\frac{\delta E_{KS}}{\delta \psi_v^*(\mathbf{r})} = \sum_{uv} \Lambda_{vu}\psi_u(\mathbf{r})$$

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

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

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