

modeling materials using
density-functional theory
the plane-wave pseudopotential way

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati
Trieste - Italy

lecture given at the *MASTANI Summer School on Materials Simulations: Theory and Numerics*,
Indian Institute of Science, Education, and Research, Pune, India, June 30 - July 11, 2014

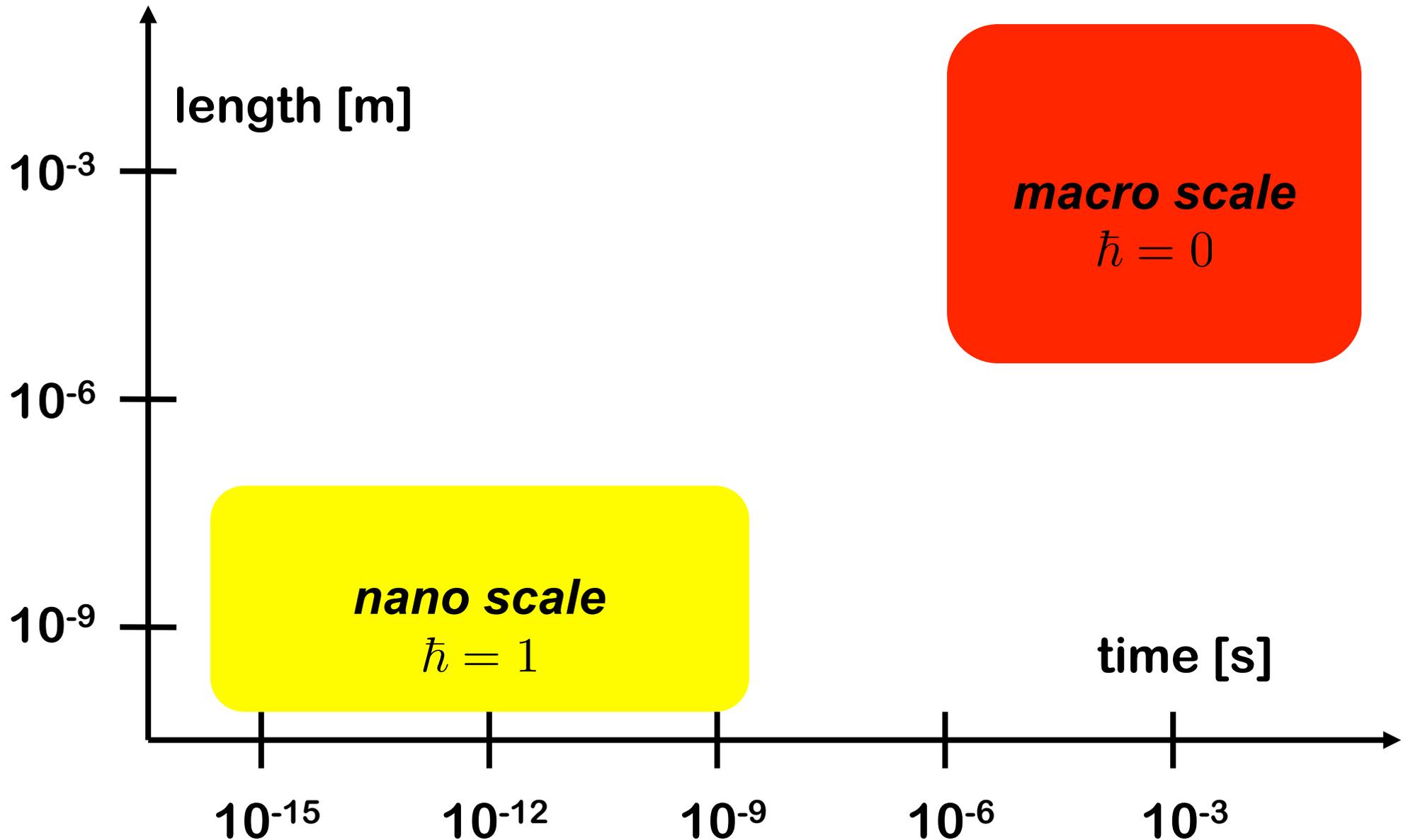
modeling materials using
density-functional theory
the plane-wave pseudopotential way

Stefano Baroni

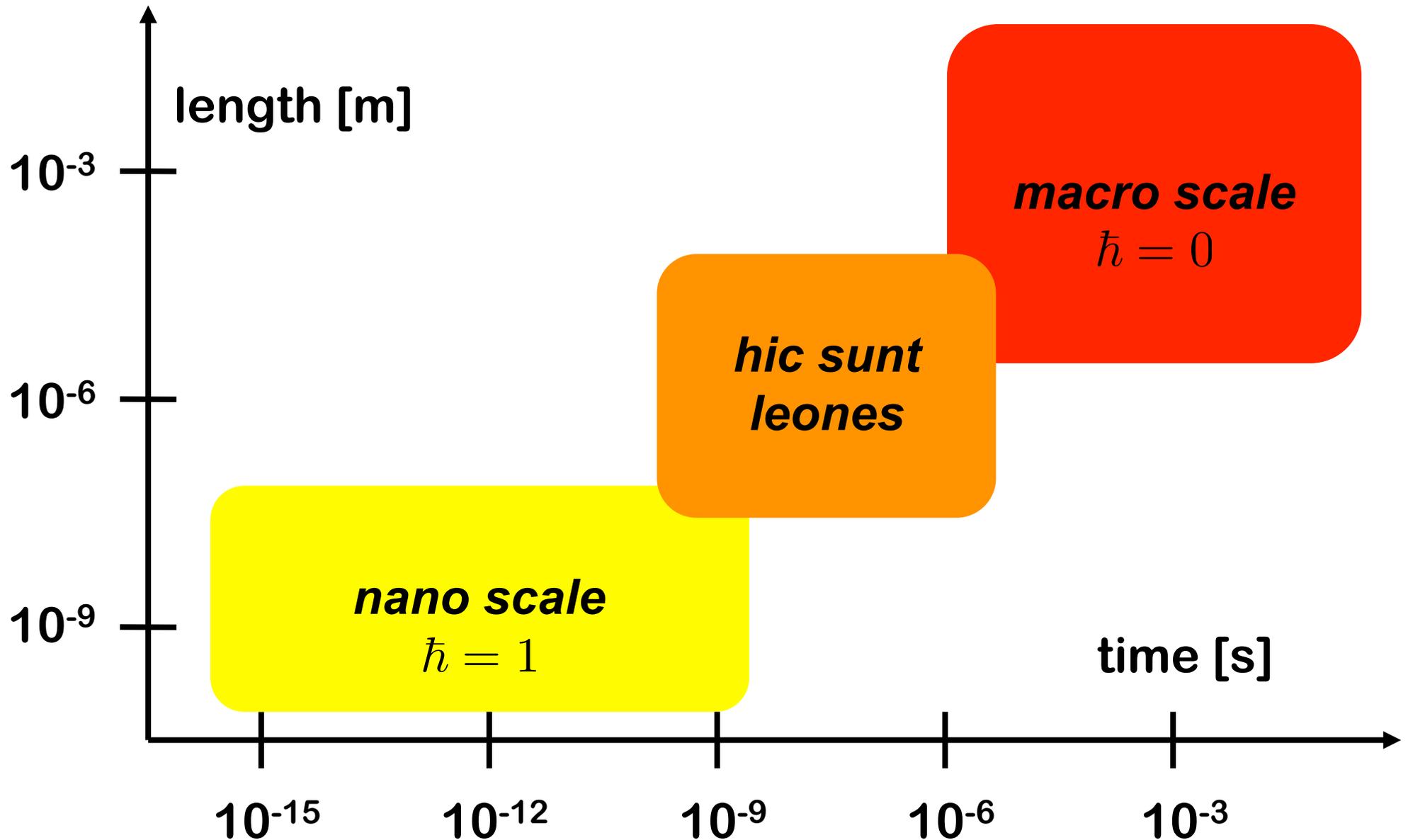
Scuola Internazionale Superiore di Studi Avanzati
Trieste - Italy

lecture given at the *CECAM Summer School on Atomistic Simulation Techniques
for Materials Science, Nanotechnology, and Biophysics*,
SISSA, Trieste, July 7-19, 2014

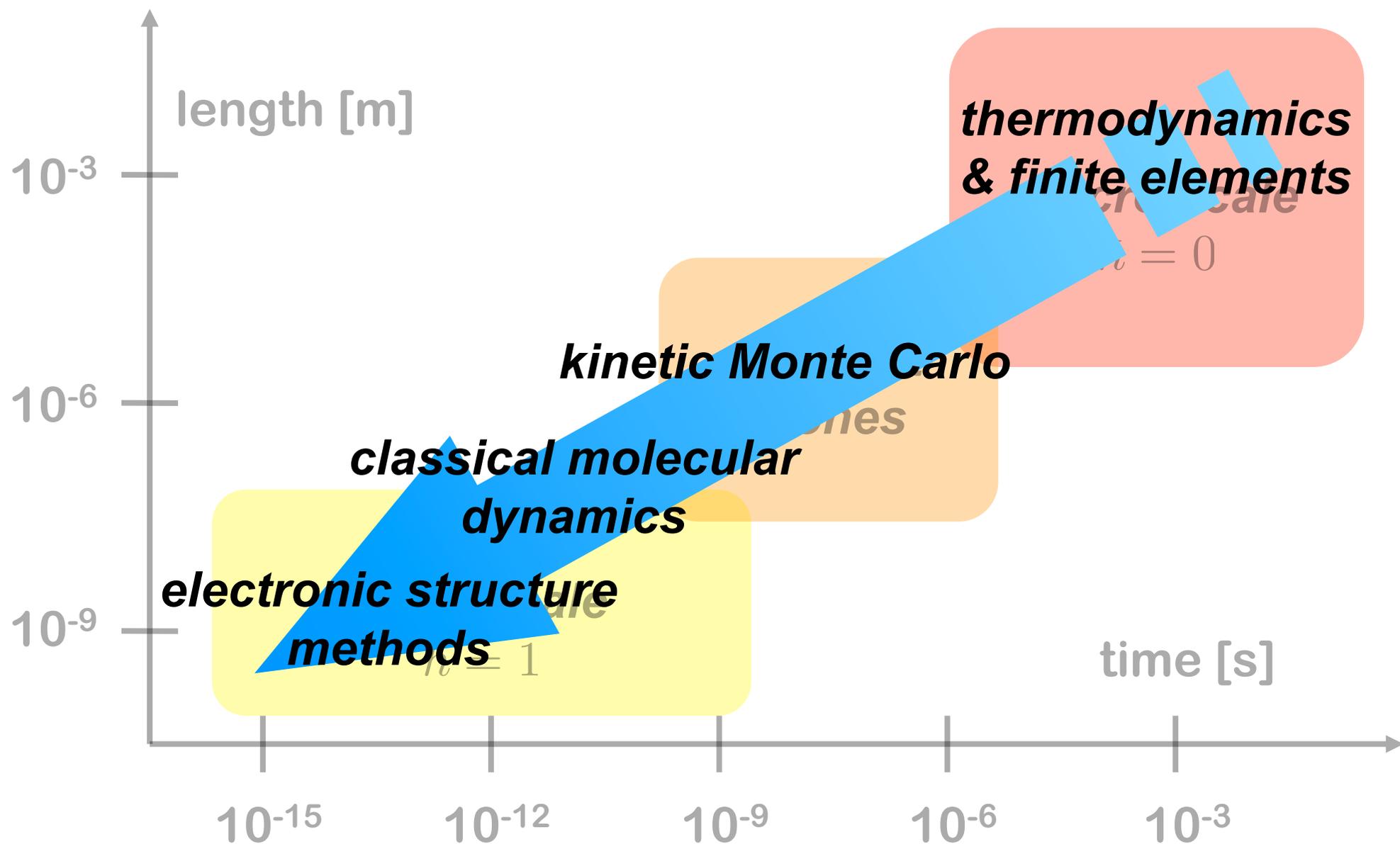
the saga of time and length scales



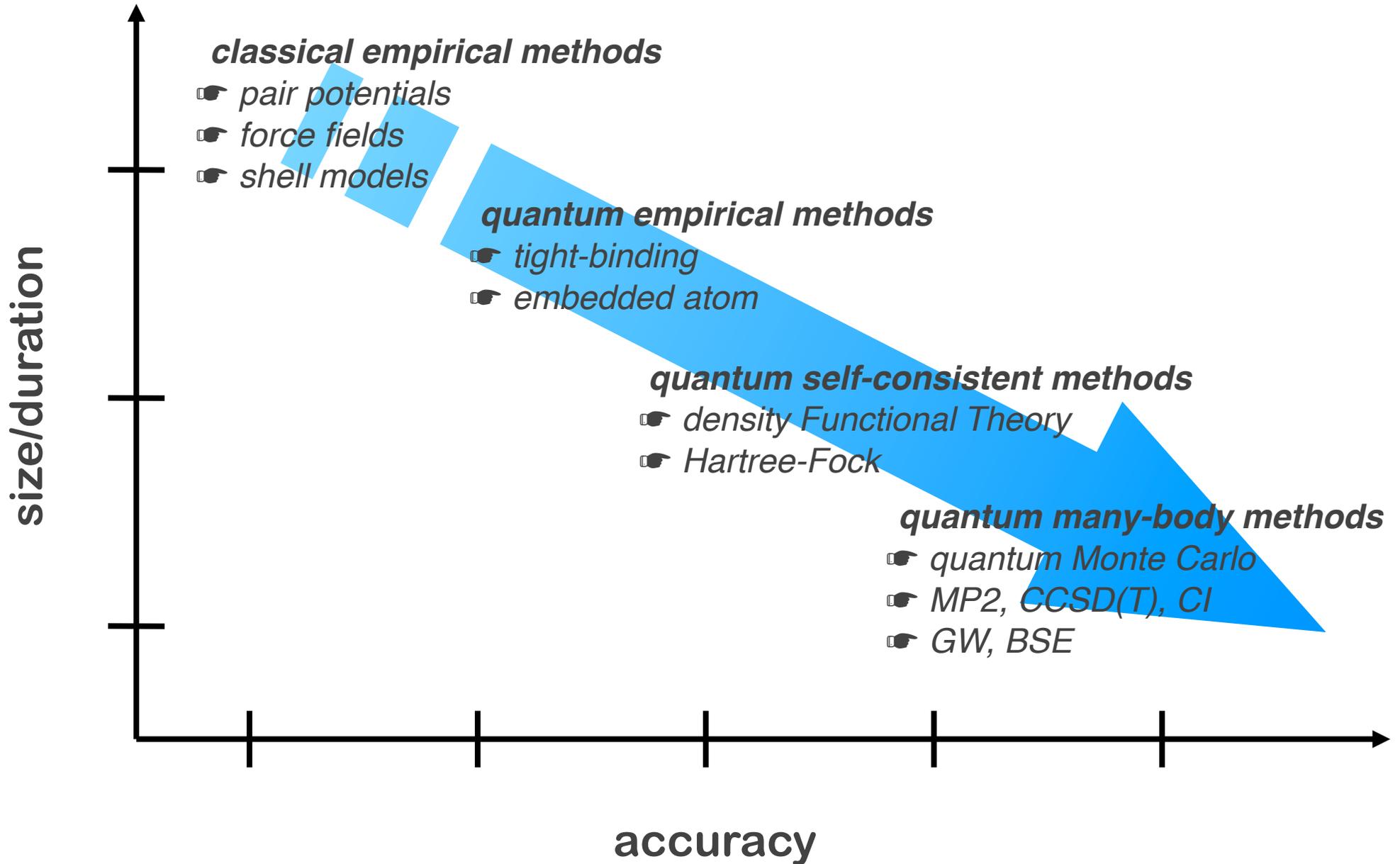
the saga of time and length scales



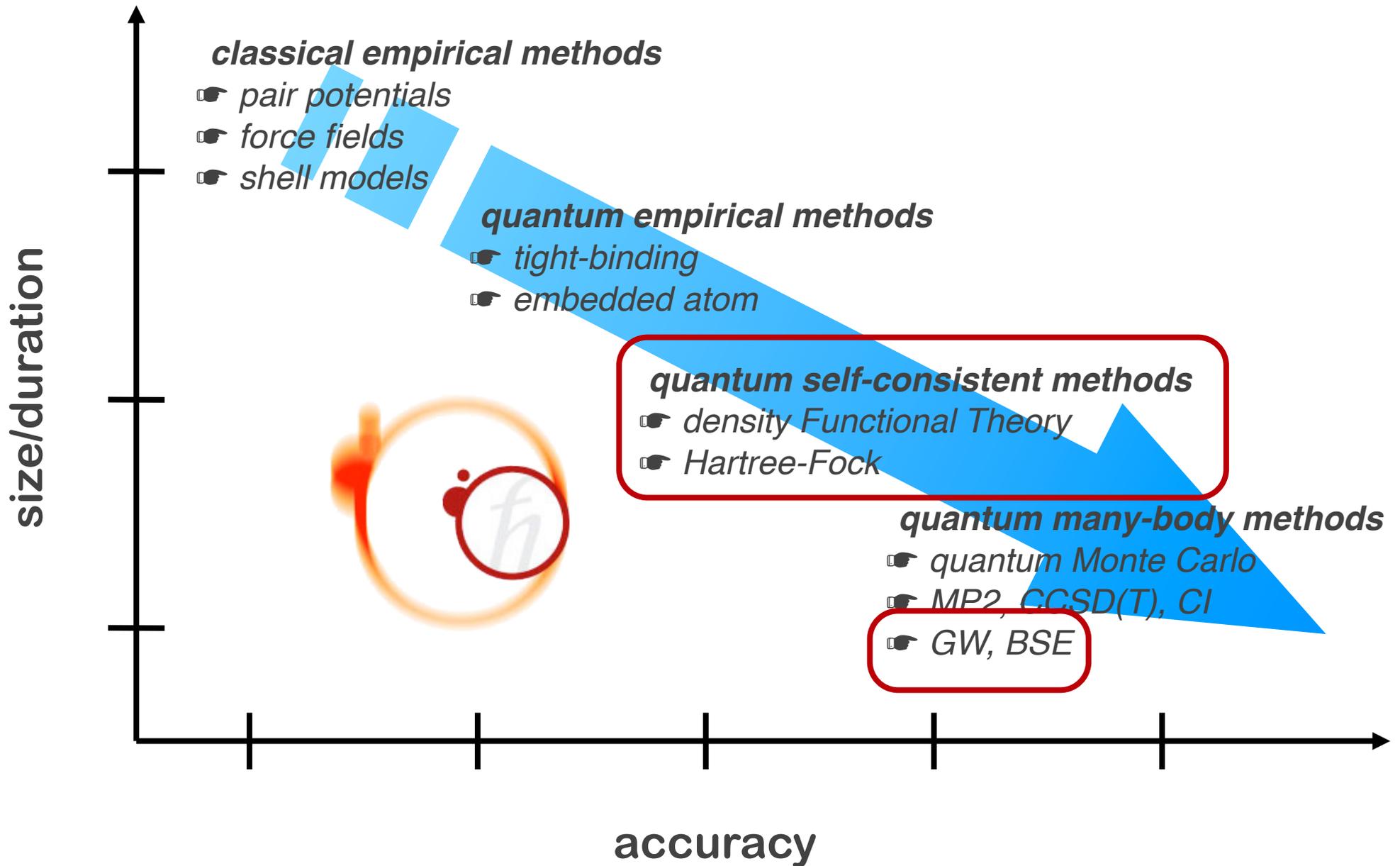
the saga of time and length scales



size vs. accuracy



size vs. accuracy



ab initio calculations: what, why, when, how

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

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

why: they are accurate and *predictive*

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

why: they are accurate and *predictive*

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

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

why: they are accurate and *predictive*

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

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

ab initio simulations

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

$M \gg m$

ab initio simulations

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

$M \gg m$: the Born-Oppenheimer approximation

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

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

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

density-functional theory

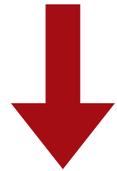
$$V(\mathbf{r}, \mathbf{R}) = \frac{e^2}{2} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{e^2}{2} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

 DFT

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

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**

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

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

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

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

functionals

examples:

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

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

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

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

...

functionals

examples:

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

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

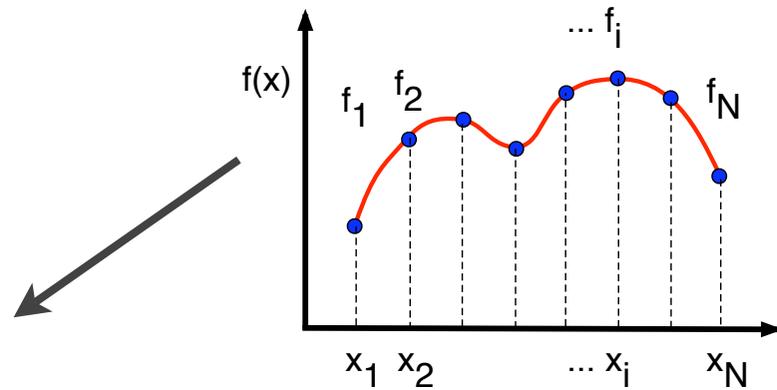
$$G[f] = \int_a^b f^2(x) dx$$

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

...

approximations:

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



functionals

examples:

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

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

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

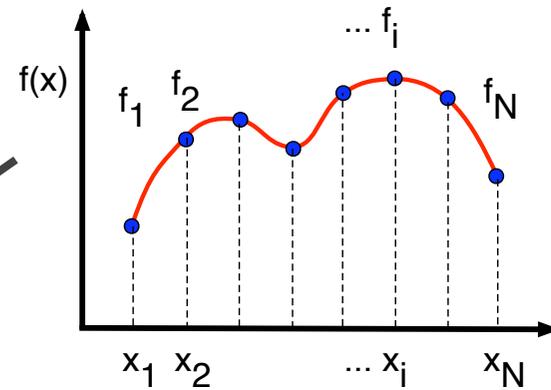
$$G[f] = \int_a^b |f'(x)|^2 dx$$

...

approximations:

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

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

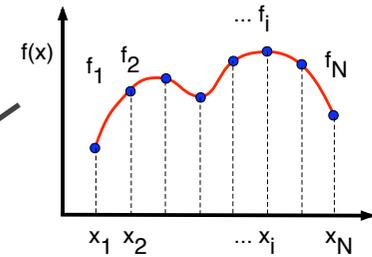


$$f(x) \approx \sum_n c_n \phi_n(x)$$

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

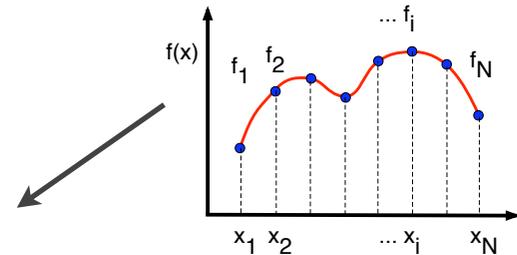
$$G[f_0 + \epsilon f_1] = G[f_0] + \epsilon \int f_1(x) \left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} dx + \mathcal{O}(\epsilon^2)$$

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



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

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



$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \text{ “ = ” } \lim_{\epsilon \rightarrow 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

the Hellmann-Feynman theorem

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

the Hellmann-Feynman theorem

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

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

the Hellmann-Feynman theorem

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

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

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$
$$E'_\lambda = \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle$$
$$= \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle$$

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

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \qquad E'_\lambda = \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle$$
$$\qquad \qquad \qquad = \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle$$

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

$$g(\lambda) = \min_x G[x, \lambda]$$

the Hellmann-Feynman theorem

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \qquad E'_\lambda = \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle$$
$$= \langle \Psi_\lambda | \hat{H}'_\lambda | \Psi_\lambda \rangle$$

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

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

the Hellmann-Feynman theorem

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

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

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

$$g(\lambda) = \min_x G[x, \lambda]$$



$$\left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)} = 0$$



$$g(\lambda) = G[x(\lambda), \lambda]$$

the Hellmann-Feynman theorem

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

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

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

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

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

the Hellmann-Feynman theorem

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

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

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

$$g(\lambda) = \min_x G[x, \lambda]$$



$$\left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)} = 0$$

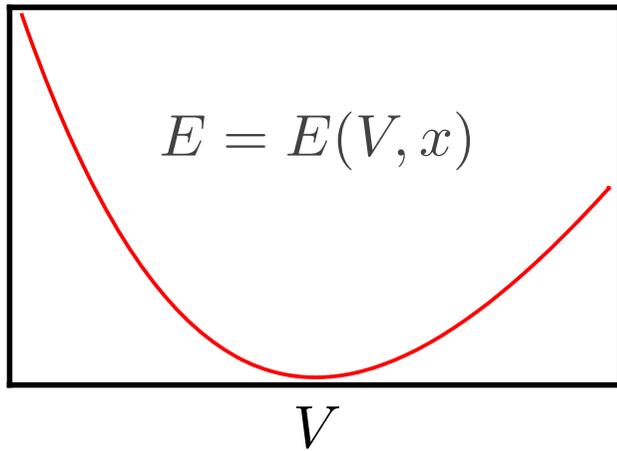


$$g(\lambda) = G[x(\lambda), \lambda]$$

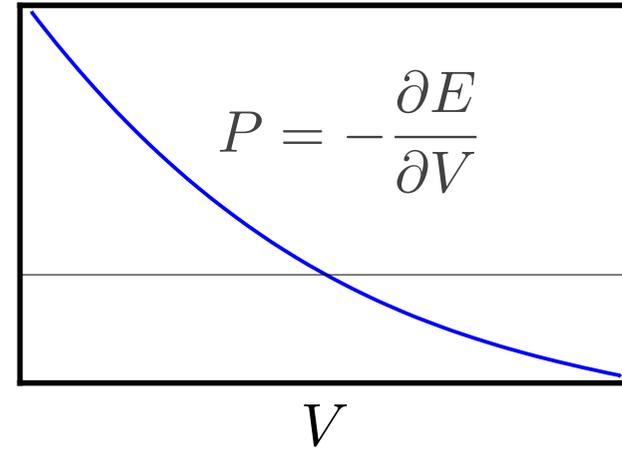
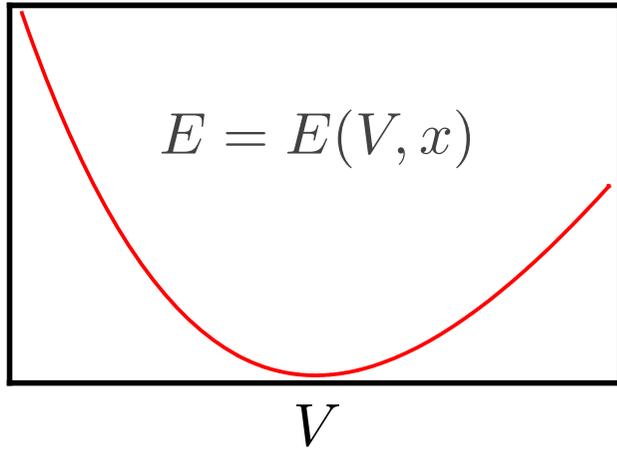


$$g'(\lambda) = x'(\lambda) \cancel{\left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)}} + \frac{\partial G}{\partial \lambda}$$

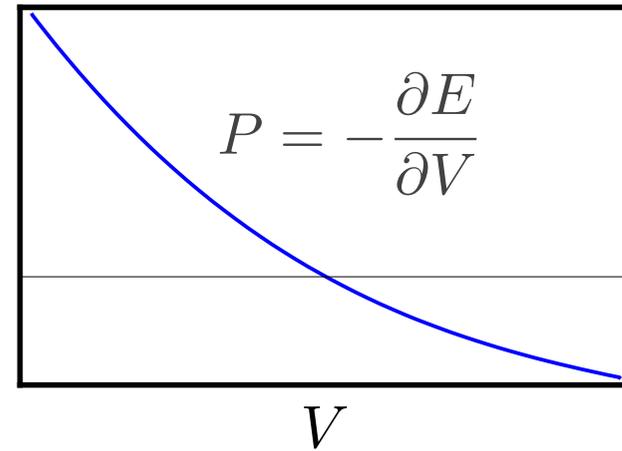
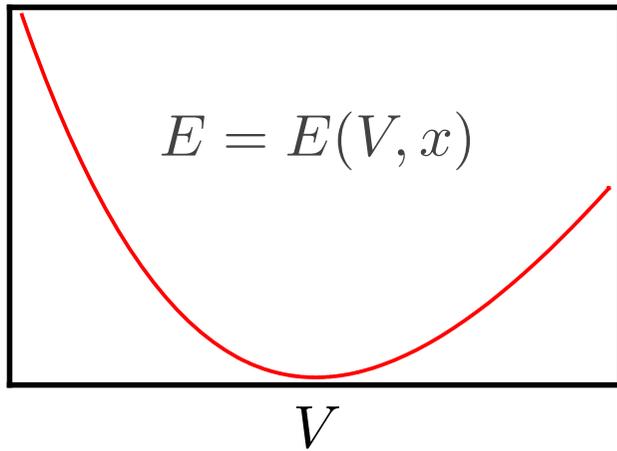
conjugate variables & Legendre transforms



conjugate variables & Legendre transforms

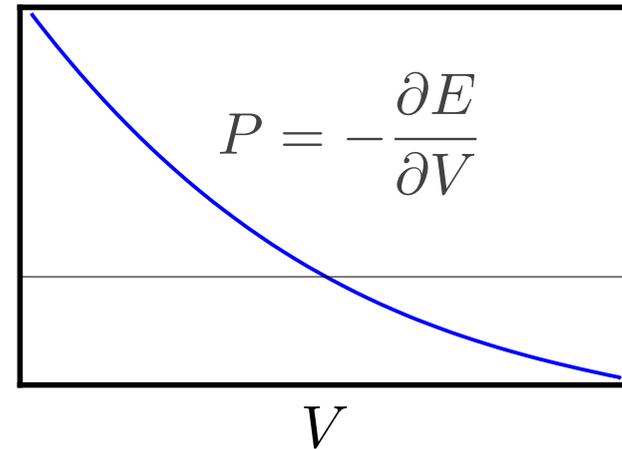
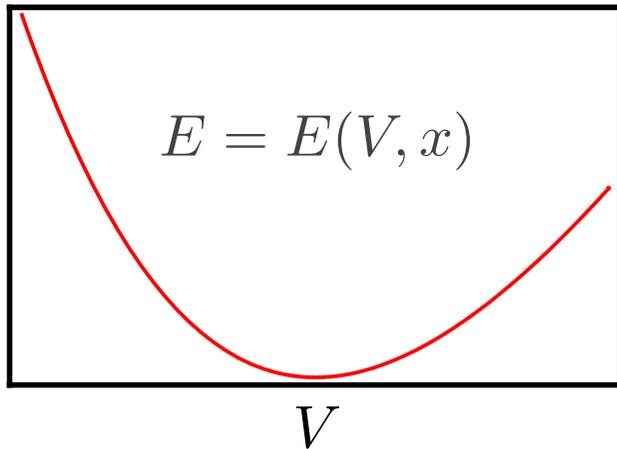


conjugate variables & Legendre transforms



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

conjugate variables & Legendre transforms

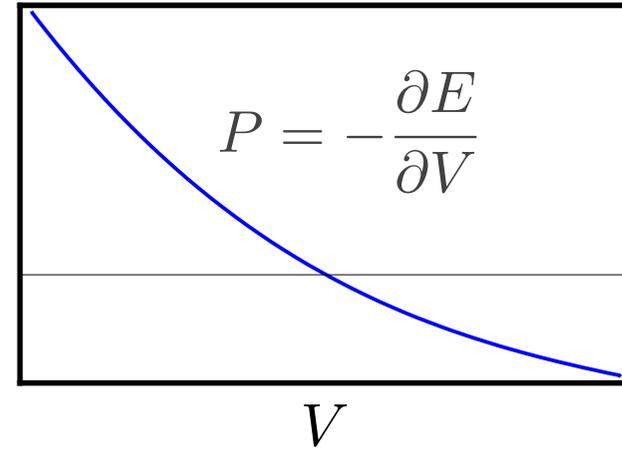
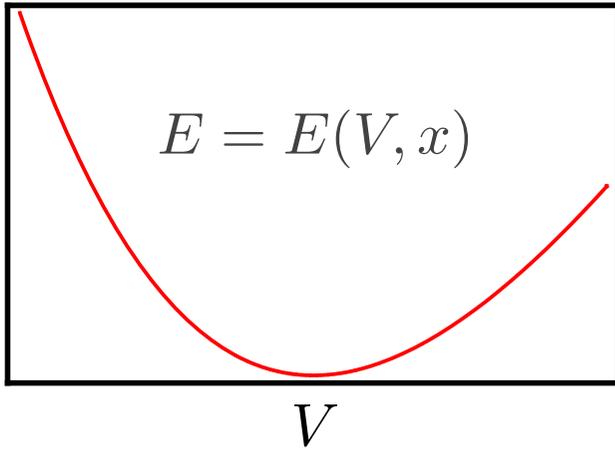


Legendre transform: $H(P, x) = E + PV$

properties:

- E convex $\Rightarrow V \rightleftharpoons P$

conjugate variables & Legendre transforms

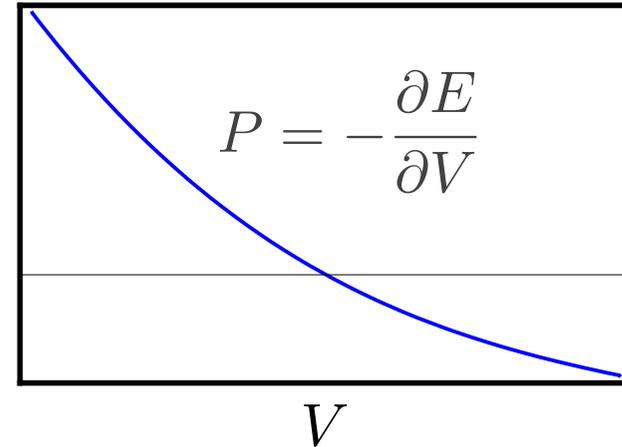
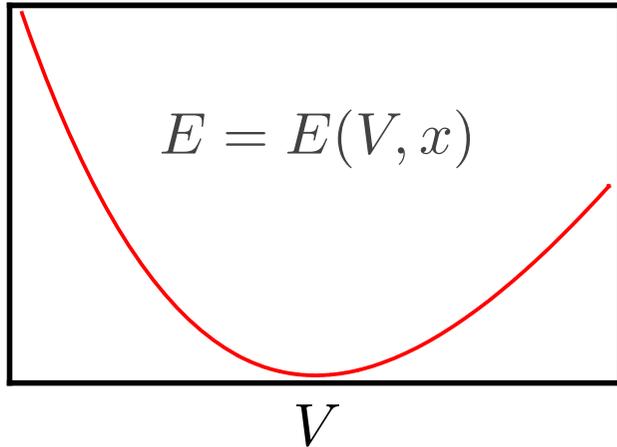


Legendre transform: $H(P, x) = E + PV$

properties:

- E convex $\Rightarrow V \rightleftharpoons P$
- $H(P, x) = \max_V (E(V, x) + PV)$

conjugate variables & Legendre transforms

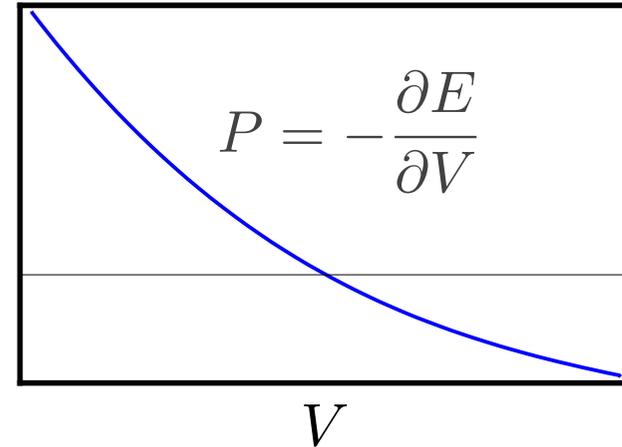
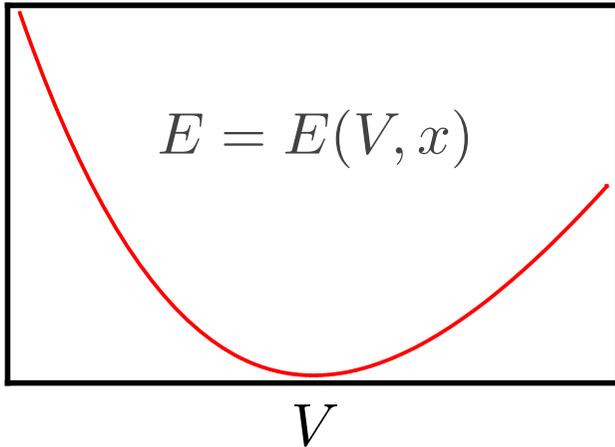


Legendre transform: $H(P, x) = E + PV$

properties:

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

conjugate variables & Legendre transforms

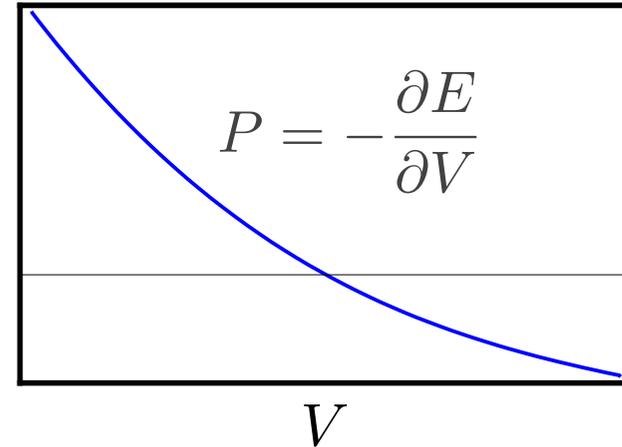
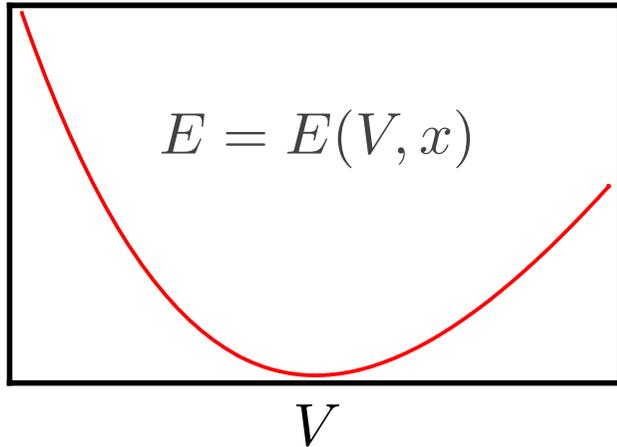


Legendre transform: $H(P, x) = E + PV$

properties:

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

conjugate variables & Legendre transforms



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

properties:

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

Hohenberg-Kohn DFT

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

Hohenberg-Kohn DFT

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

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

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)
- $\rho(\mathbf{r}) = \frac{\delta E}{\delta V(\mathbf{r})}$ (from Hellmann-Feynman)

Hohenberg-Kohn DFT

$$H = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V(\mathbf{r}_i)$$
$$E[V] = \min_{\Psi} \langle \Psi | \hat{K} + \hat{W} + \hat{V} | \Psi \rangle$$
$$= \min_{\Psi} \left[\langle \Psi | \hat{K} + \hat{W} | \Psi \rangle + \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \right]$$

properties:

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

consequences:

- $V(\mathbf{r}) \Leftrightarrow \rho(\mathbf{r})$ (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

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

$$E[V] = \min_{\Psi} \langle \Psi | \hat{K} + \hat{W} + \hat{V} | \Psi \rangle$$

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

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

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

consequences:

- $V(\mathbf{r}) \Leftrightarrow \rho(\mathbf{r})$ (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)

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$

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

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$

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

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$

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

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

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

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \underbrace{V(\mathbf{r}) + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]}_{v_{KS}[\rho](\mathbf{r})}$$

$\rho(\mathbf{r})$

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

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

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

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$

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

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

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

Kohn-Sham DFT

$$F[\rho] = T_0[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]$$
$$\frac{\delta T_0}{\delta \rho(\mathbf{r})} + \underbrace{\frac{e^2}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}}_{v_{KS}[\rho](\mathbf{r})} + V(\mathbf{r}) = \mu$$

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

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

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

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

KS equations from functional minimization

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

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

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

KS equations from functional minimization

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

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

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



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

KS equations from functional minimization

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

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

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



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

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

solving the Kohn-Sham equations

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

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

solving the Kohn-Sham equations

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

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

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

solving the Kohn-Sham equations

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

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

$$\frac{\delta E_{KS}}{\delta \psi_v^*(\mathbf{r})} = \sum_{uv} \Lambda_{vu} \psi_u(\mathbf{r}) \quad \rightarrow \quad \sum_j h_{KS}[c](i, j) c(j, v) = \epsilon_v c(i, v)$$

solving the Kohn-Sham equations

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

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

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

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

requirements

requirements

- ▶ (effective) completeness easily checked and systematically improved

requirements

- ▶ (effective) completeness easily checked and systematically improved
- ▶ matrix elements easy to calculate and/or $H\psi$ products easily computed on the fly

requirements

- ▶ (effective) completeness easily checked and systematically improved
- ▶ matrix elements easy to calculate and/or $H\psi$ products easily computed on the fly
- ▶ Hartree and XC potentials easy to represent and compute

requirements

- ▶ (effective) completeness easily checked and systematically improved
- ▶ matrix elements easy to calculate and/or $H\psi$ products easily computed on the fly
- ▶ Hartree and XC potentials easy to represent and compute
- ▶ orthogonality is a plus

plane-wave basis sets

$$\psi(\mathbf{r}) = \sum_j c(j) \varphi_j(\mathbf{r})$$

$$\varphi_j(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}_j \cdot \mathbf{r}} \quad \frac{\hbar^2}{2m} \mathbf{q}_j^2 \leq E_{cut}$$

plane-wave basis sets

$$\psi(\mathbf{r}) = \sum_j c(j) \varphi_j(\mathbf{r})$$

$$\varphi_j(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}_j \cdot \mathbf{r}} \quad \frac{\hbar^2}{2m} \mathbf{q}_j^2 \leq E_{cut}$$

periodic boundary conditions

$$\varphi(x + \ell) = \varphi(x) \rightarrow q_j = \frac{2\pi}{\ell} j$$

plane-wave basis sets

$$\psi(\mathbf{r}) = \sum_j c(j) \varphi_j(\mathbf{r})$$

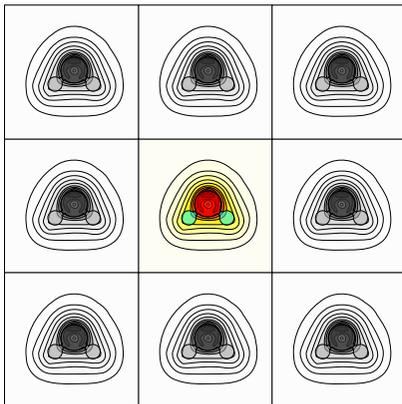
$$\varphi_j(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}_j \cdot \mathbf{r}}$$

$$\frac{\hbar^2}{2m} \mathbf{q}_j^2 \leq E_{cut}$$

periodic boundary conditions

$$\varphi(x + \ell) = \varphi(x) \rightarrow q_j = \frac{2\pi}{\ell} j$$

finite systems ($\ell = a$)



$$\mathbf{q} = \mathbf{G}$$

plane-wave basis sets

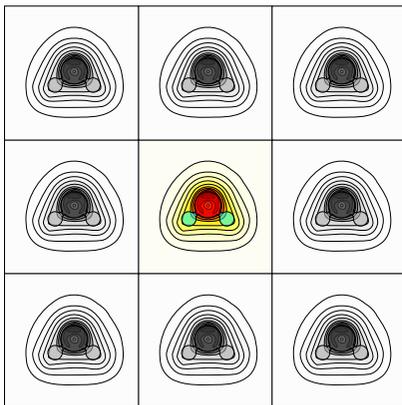
$$\psi(\mathbf{r}) = \sum_j c(j) \varphi_j(\mathbf{r})$$

$$\varphi_j(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}_j \cdot \mathbf{r}} \quad \frac{\hbar^2}{2m} \mathbf{q}_j^2 \leq E_{cut}$$

periodic boundary conditions

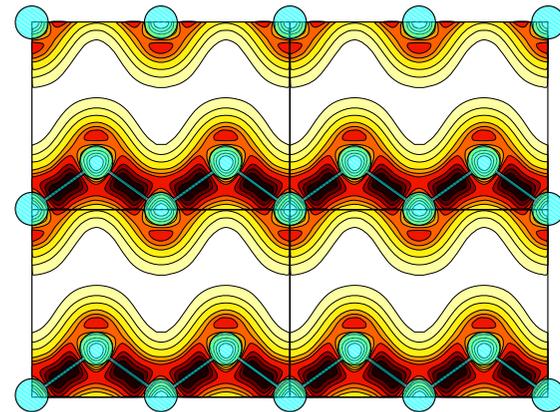
$$\varphi(x + \ell) = \varphi(x) \rightarrow \mathbf{q}_j = \frac{2\pi}{\ell} \mathbf{j}$$

finite systems ($\ell = a$)



$$\mathbf{q} = \mathbf{G}$$

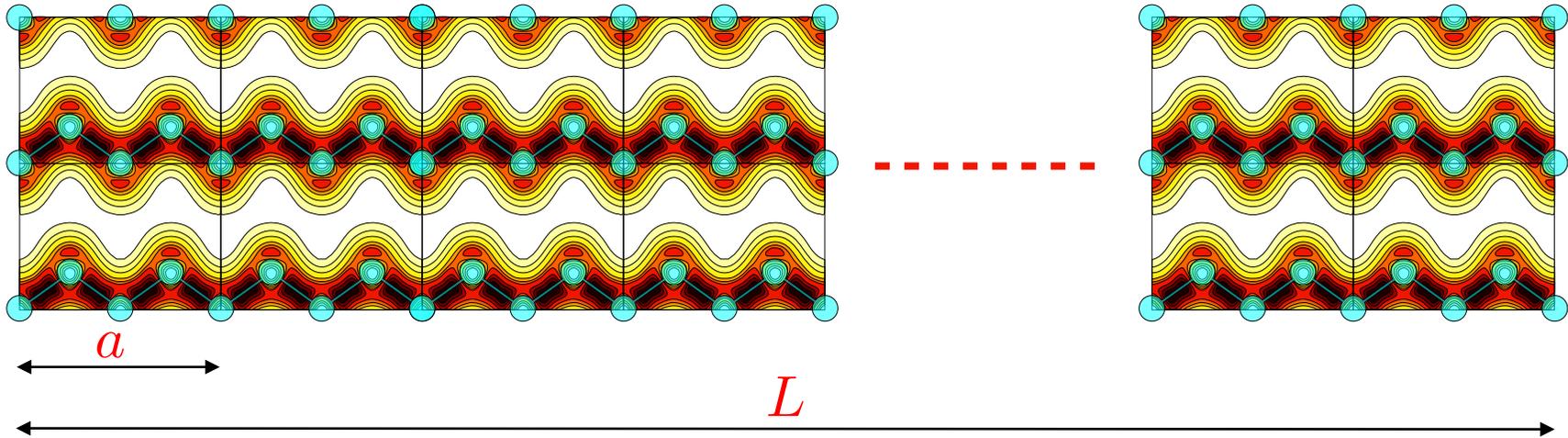
infinite crystals ($\ell = L$)



$$\mathbf{q} = \mathbf{k} + \mathbf{G}; \quad \mathbf{k} \in BZ$$

the Bloch theorem & plane waves

infinite crystals



$$\psi(x + L) = \psi(x)$$

$$\psi_k(x + a) = e^{ika} \psi_k(x)$$

$$\psi_k(x) = e^{ikx} u_k(x)$$

$$u_k(x + a) = u_k(x)$$

$$u_k(x) = \sum_n c_k(n) e^{i \frac{2n\pi}{a} x}$$

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$-\nabla^2 \psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto |\mathbf{k} + \mathbf{G}|^2 c_{n\mathbf{k}}(\mathbf{G})$$

$$V(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$-\nabla^2 \psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto |\mathbf{k} + \mathbf{G}|^2 c_{n\mathbf{k}}(\mathbf{G})$$

$$V(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

$$\rho(\mathbf{r}) = \sum_{v\mathbf{k}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$-\nabla^2 \psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto |\mathbf{k} + \mathbf{G}|^2 c_{n\mathbf{k}}(\mathbf{G})$$

$$V(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

$$\rho(\mathbf{r}) = \sum_{v\mathbf{k}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

$$V_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r}))$$

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$-\nabla^2 \psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto |\mathbf{k} + \mathbf{G}|^2 c_{n\mathbf{k}}(\mathbf{G})$$

$$V(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

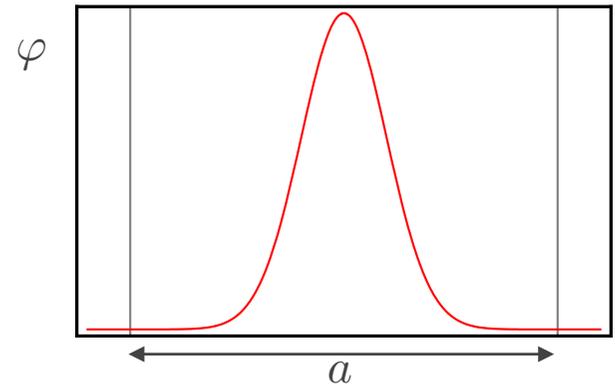
$$\rho(\mathbf{r}) = \sum_{v\mathbf{k}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

$$V_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r}))$$

$$\begin{aligned} V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= e^2 \sum_{\mathbf{G} \neq 0} e^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G}) \end{aligned}$$

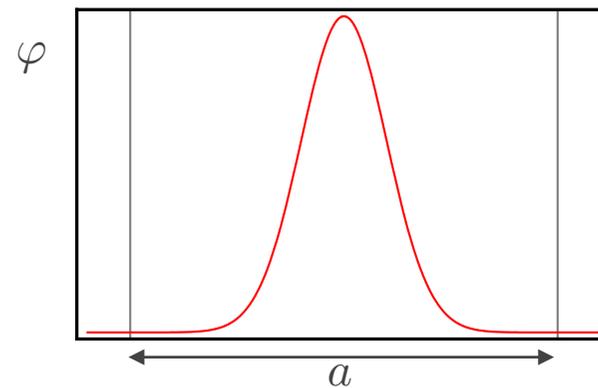
sampling theorem

$$\varphi(x) = 0 \quad \text{for} \quad |x| > \frac{a}{2}$$

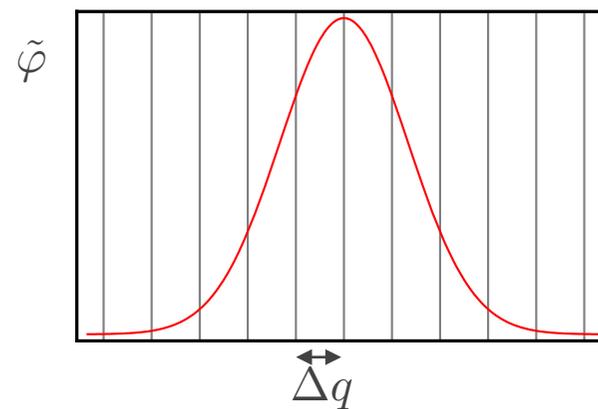


sampling theorem

$$\varphi(x) = 0 \quad \text{for} \quad |x| > \frac{a}{2}$$

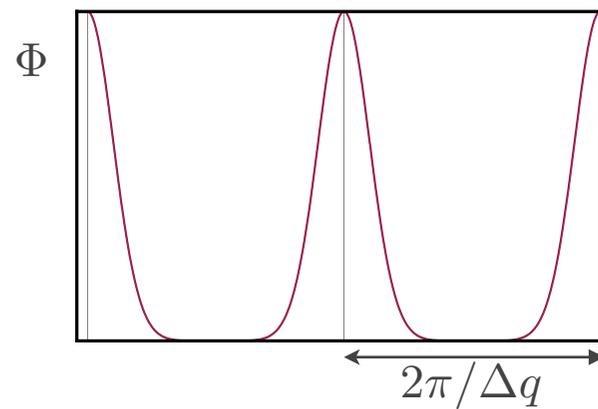
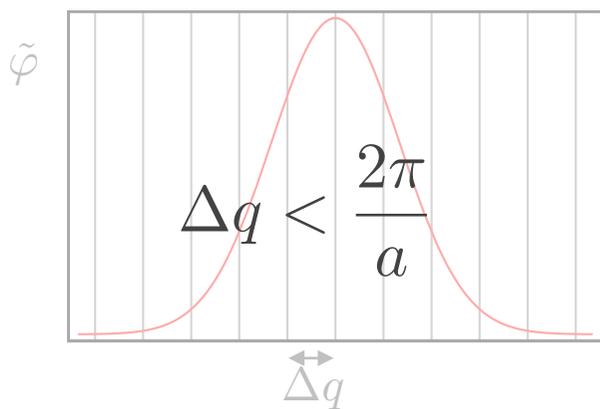
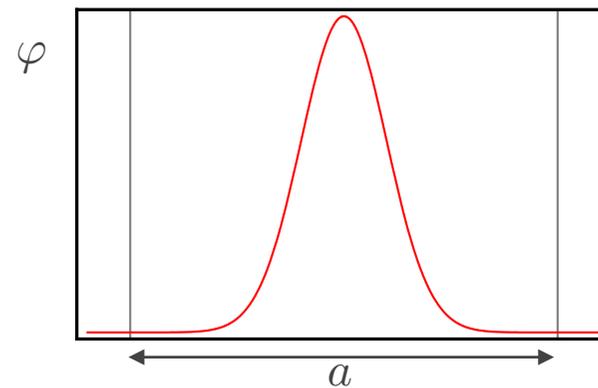


$$\Delta q < \frac{2\pi}{a}$$



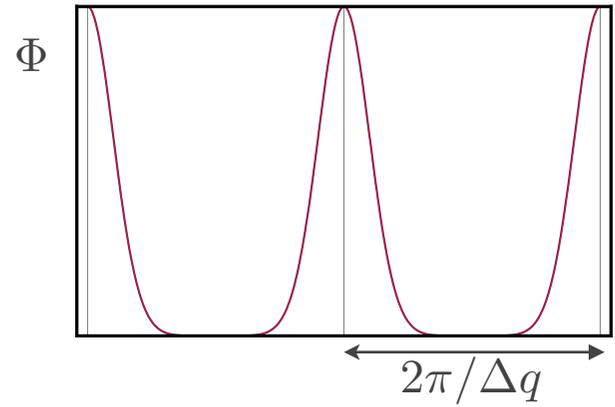
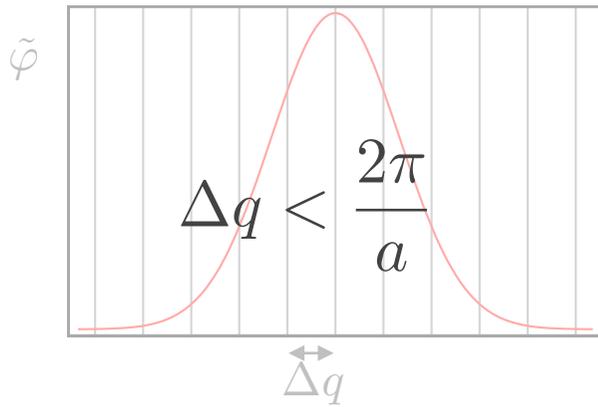
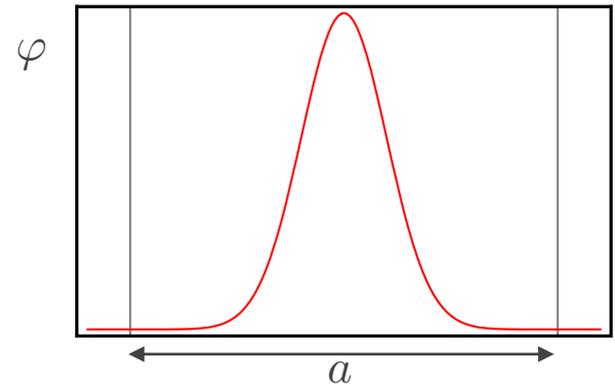
sampling theorem

$$\varphi(x) = 0 \quad \text{for} \quad |x| > \frac{a}{2}$$

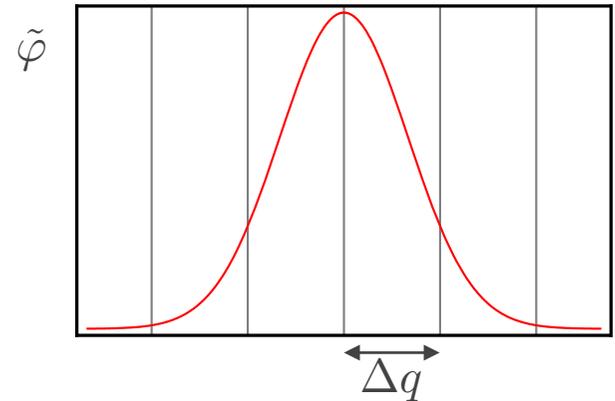


sampling theorem

$$\varphi(x) = 0 \quad \text{for} \quad |x| > \frac{a}{2}$$

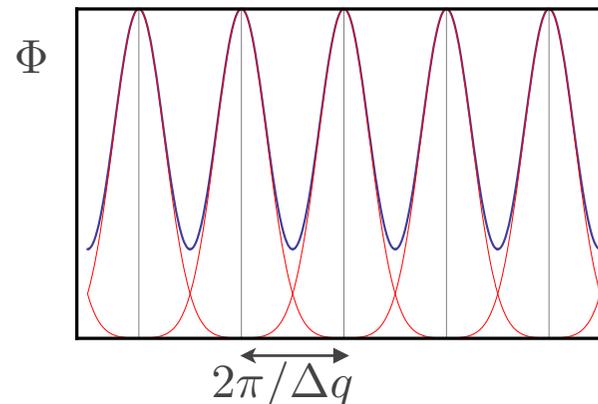
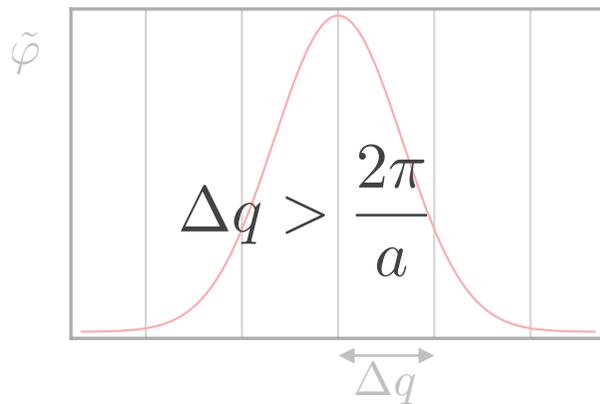
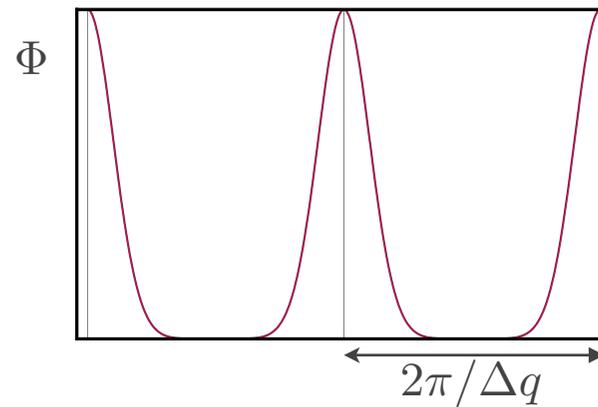
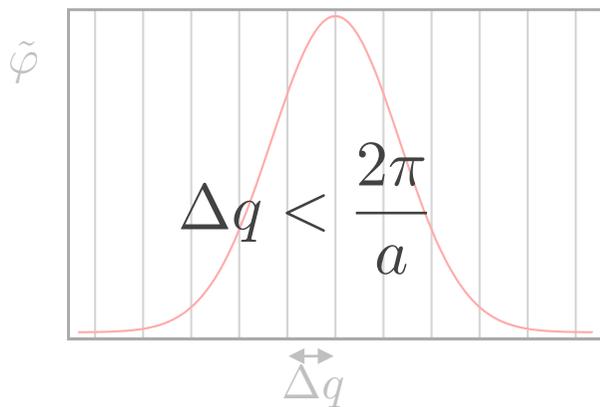
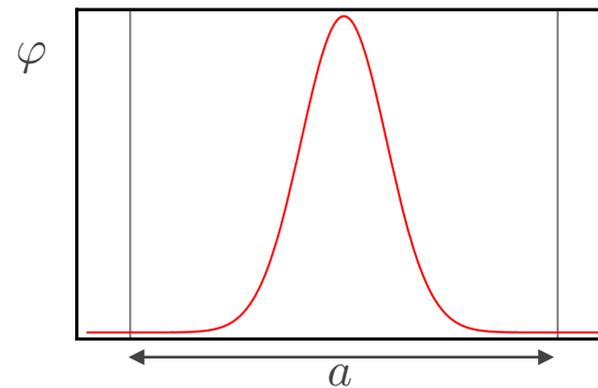


$$\Delta q > \frac{2\pi}{a}$$



sampling theorem

$$\varphi(x) = 0 \quad \text{for} \quad |x| > \frac{a}{2}$$



discrete Fourier transforms

$$f(t) = 0 \quad \text{for } t \notin [0, T] \quad \rightarrow \quad \Delta\omega = \frac{2\pi}{T}$$

discrete Fourier transforms

$$f(t) = 0 \quad \text{for } t \notin [0, T] \quad \rightarrow \quad \Delta\omega = \frac{2\pi}{T} \quad f(t) = \sum_k \tilde{f}\left(k\frac{2\pi}{T}\right) e^{-ik\frac{2\pi}{T}t} \quad K \geq \frac{T\Omega}{\pi}$$

discrete Fourier transforms

$$f(t) = 0 \quad \text{for } t \notin [0, T] \quad \rightarrow \quad \Delta\omega = \frac{2\pi}{T} \quad f(t) = \sum_k \tilde{f}\left(k\frac{2\pi}{T}\right) e^{-ik\frac{2\pi}{T}t} \quad K \geq \frac{T\Omega}{\pi}$$

$$\tilde{f}(\omega) = 0 \quad \text{for } \omega \notin [-\Omega, \Omega] \quad \rightarrow \quad \Delta t = \frac{2\pi}{2\Omega} \quad \tilde{f}(\omega) = \sum_n f\left(n\frac{2\pi}{2\Omega}\right) e^{in\frac{2\pi}{2\Omega}\omega} \quad N \geq \frac{T\Omega}{\pi}$$

discrete Fourier transforms

$$f(t) = 0 \quad \text{for } t \notin [0, T] \quad \rightarrow \quad \Delta\omega = \frac{2\pi}{T} \quad f(t) = \sum_k \tilde{f}\left(k\frac{2\pi}{T}\right) e^{-ik\frac{2\pi}{T}t} \quad K \geq \frac{T\Omega}{\pi}$$

$$\tilde{f}(\omega) = 0 \quad \text{for } \omega \notin [-\Omega, \Omega] \quad \rightarrow \quad \Delta t = \frac{2\pi}{2\Omega} \quad \tilde{f}(\omega) = \sum_n f\left(n\frac{2\pi}{2\Omega}\right) e^{in\frac{2\pi}{2\Omega}\omega} \quad N \geq \frac{T\Omega}{\pi}$$

$$t \rightarrow \left\{ t_l = l\frac{T}{N} \right\}_{l=0, \dots, N-1} \quad f(t) \rightarrow \{f_l = f(t_l)\}$$

$$\omega \rightarrow \left\{ \omega_k = k\frac{2\Omega}{N} \right\}_{k=-\frac{N}{2}, \dots, \frac{N}{2}-1} \quad \tilde{f}(\omega) \rightarrow \{\tilde{f}_k = \tilde{f}(\omega_k)\}$$

$$N = \frac{\Omega T}{\pi}$$

discrete Fourier transforms

$$f(t) = 0 \quad \text{for } t \notin [0, T] \quad \rightarrow \quad \Delta\omega = \frac{2\pi}{T} \quad f(t) = \sum_k \tilde{f}\left(k\frac{2\pi}{T}\right) e^{-ik\frac{2\pi}{T}t} \quad K \geq \frac{T\Omega}{\pi}$$

$$\tilde{f}(\omega) = 0 \quad \text{for } \omega \notin [-\Omega, \Omega] \quad \rightarrow \quad \Delta t = \frac{2\pi}{2\Omega} \quad \tilde{f}(\omega) = \sum_n f\left(n\frac{2\pi}{2\Omega}\right) e^{in\frac{2\pi}{2\Omega}\omega} \quad N \geq \frac{T\Omega}{\pi}$$

$$t \rightarrow \left\{ t_l = l\frac{T}{N} \right\}_{l=0, \dots, N-1} \quad f(t) \rightarrow \{f_l = f(t_l)\}$$

$$\omega \rightarrow \left\{ \omega_k = k\frac{2\Omega}{N} \right\}_{k=-\frac{N}{2}, \dots, \frac{N}{2}-1} \quad \tilde{f}(\omega) \rightarrow \{\tilde{f}_k = \tilde{f}(\omega_k)\}$$

$$N = \frac{\Omega T}{\pi}$$

$$\tilde{f}_k = \frac{1}{N} \sum_{l=0}^{N-1} f_l e^{-i2\pi \frac{kl}{N}}$$

$$f_l = \sum_{k=0}^{N-1} \tilde{f}_k e^{i2\pi \frac{kl}{N}}$$

dFt

properties of the dFt

$$\begin{aligned} f_{i+N} &= f_i \\ \tilde{f}_{k+N} &= \tilde{f}_k \end{aligned}$$

properties of the dFt

$$\begin{aligned} f_{i+N} &= f_i \\ \tilde{f}_{k+N} &= \tilde{f}_k \end{aligned}$$

discreteness in dual space



periodicity in the primary space

properties of the dFt

$$\begin{aligned} f_{i+N} &= f_i \\ \tilde{f}_{k+N} &= \tilde{f}_k \end{aligned}$$

discreteness in dual space



periodicity in the primary space

$$f_i \in \mathbb{R} \rightarrow \begin{aligned} \tilde{f}_k &= \tilde{f}_{-k}^* \\ &= \tilde{f}_{N-k}^* \end{aligned}$$

the fast Fourier transform

$$\tilde{f}_k = \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} \quad \mathcal{O}(N^2) \text{ ops}$$

the fast Fourier transform

$$\begin{aligned}\tilde{f}_k &= \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} && \mathcal{O}(N^2) \text{ ops} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{(2l+1)k}{N}}\end{aligned}$$

the fast Fourier transform

$$\begin{aligned}\tilde{f}_k &= \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} && \mathcal{O}(N^2) \text{ ops} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{(2l+1)k}{N}} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{lk}{N/2}} + e^{-2\pi i \frac{k}{N}} \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{lk}{N/2}}\end{aligned}$$

the fast Fourier transform

$$\begin{aligned}\tilde{f}_k &= \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} && \mathcal{O}(N^2) \text{ ops} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{(2l+1)k}{N}} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{lk}{N/2}} + e^{-2\pi i \frac{k}{N}} \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{lk}{N/2}}\end{aligned}$$

for $k \leq N/2-1$, this is the linear combination of two FFTs of order $N/2$

the fast Fourier transform

$$\begin{aligned}\tilde{f}_k &= \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} && \mathcal{O}(N^2) \text{ ops} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{(2l+1)k}{N}} \\ &= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{lk}{N/2}} + e^{-2\pi i \frac{k}{N}} \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{lk}{N/2}}\end{aligned}$$

for $k \leq N/2-1$, this is the linear combination of two FFTs of order $N/2$

for $k \geq N/2$, use:

$$\begin{aligned}\frac{N}{2} \tilde{f}_{k+\frac{N}{2}} &= \frac{N}{2} \tilde{f}_k \\ e^{-2\pi i \frac{k+N/2}{N}} &= -e^{-2\pi i \frac{k}{N}}\end{aligned}$$

the fast Fourier transform

$$\tilde{f}_k = \sum_{l=0}^{N-1} f_l e^{-2\pi i \frac{lk}{N}} \quad \mathcal{O}(N^2) \text{ ops}$$

$$= \sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{(2l+1)k}{N}}$$

$$\mathcal{O}\left(\sum_{l=0}^{N/2-1} f_{2l} e^{-2\pi i \frac{lk}{N/2}} + e^{-2\pi i \frac{k}{N}} \sum_{l=0}^{N/2-1} f_{2l+1} e^{-2\pi i \frac{lk}{N/2}}\right)$$

for $k \leq N/2-1$, this is the linear combination of two FFTs of order $N/2$

for $k \geq N/2$, use:

$$\begin{aligned} \frac{N}{2} \tilde{f}_{k+\frac{N}{2}} &= \frac{N}{2} \tilde{f}_k \\ e^{-2\pi i \frac{k+N/2}{N}} &= -e^{-2\pi i \frac{k}{N}} \end{aligned}$$

multivariate FFTs

$$F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}) \rightarrow \begin{cases} F(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{G}) \\ \tilde{F}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{r}) d\mathbf{r} \end{cases} \quad \mathbf{G} \cdot \mathbf{R} = 0 \pmod{2\pi}$$

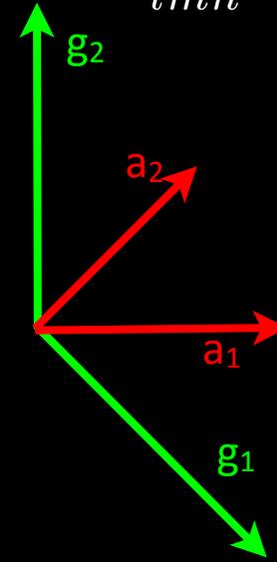
multivariate FFTs

$$F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}) \rightarrow \begin{cases} F(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{G}) \\ \tilde{F}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{r}) d\mathbf{r} \approx \frac{1}{N^3} \sum_{lmn} e^{-i\mathbf{G}_{pqS} \cdot \mathbf{r}_{lmn}} F_{lmn} \end{cases}$$

$$\mathbf{G}_{pqS} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

$$\mathbf{r}_{lmn} = \frac{l}{N}\mathbf{a}_1 + \frac{m}{N}\mathbf{a}_2 + \frac{n}{N}\mathbf{a}_3$$

$$\mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$



multivariate FFTs

$$F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}) \rightarrow \begin{cases} F(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{G}) \\ \tilde{F}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{r}) d\mathbf{r} \approx \frac{1}{N^3} \sum_{lmn} e^{-i\mathbf{G}_{pqS} \cdot \mathbf{r}_{lmn}} F_{lmn} \end{cases}$$

$$\mathbf{G}_{pqS} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

$$\mathbf{r}_{lmn} = \frac{l}{N}\mathbf{a}_1 + \frac{m}{N}\mathbf{a}_2 + \frac{n}{N}\mathbf{a}_3$$

$$\mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \rightarrow$$

$$\mathbf{G}_{pqS} \cdot \mathbf{r}_{lmn}$$

$$= \frac{2\pi}{N}(pl + qm + sn)$$

multivariate FFTs

$$F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}) \rightarrow \begin{cases} F(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{G}) \\ \tilde{F}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{G} \cdot \mathbf{r}} F(\mathbf{r}) d\mathbf{r} \approx \frac{1}{N^3} \sum_{lmn} e^{-i\mathbf{G}_{pq_s} \cdot \mathbf{r}_{lmn}} F_{lmn} \end{cases}$$

$$\mathbf{G}_{pq_s} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

$$\mathbf{r}_{lmn} = \frac{l}{N}\mathbf{a}_1 + \frac{m}{N}\mathbf{a}_2 + \frac{n}{N}\mathbf{a}_3$$

$$\mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \rightarrow$$

$$\mathbf{G}_{pq_s} \cdot \mathbf{r}_{lmn}$$

$$= \frac{2\pi}{N}(pl + qm + sn)$$

$$\begin{array}{c} \text{FFT} \\ \curvearrowleft \\ \tilde{F}(p\mathbf{g}_1, q\mathbf{g}_2, s\mathbf{g}_3) = \frac{1}{N^3} \sum_{klm} e^{-i2\pi \frac{pk+ql+sm}{N}} F\left(\frac{k}{N}\mathbf{a}_1, \frac{l}{N}\mathbf{a}_2, \frac{m}{N}\mathbf{a}_3\right) \\ F\left(\frac{k}{N}\mathbf{a}_1, \frac{l}{N}\mathbf{a}_2, \frac{m}{N}\mathbf{a}_3\right) = \sum_{pq_s} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p\mathbf{g}_1, q\mathbf{g}_2, s\mathbf{g}_3) \\ \curvearrowright \text{FFT}^{-1} \end{array}$$

multivariate FFTs (II)

$$F(k, l, m) = \sum_{pqs} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p, q, s)$$

multivariate FFTs (II)

$$\begin{aligned} F(k, l, m) &= \sum_{pqs} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p, q, s) \\ &= \sum_p e^{i2\pi \frac{pk}{N}} \sum_q e^{i2\pi \frac{ql}{N}} \sum_s e^{i2\pi \frac{sm}{N}} \tilde{F}(p, q, s) \end{aligned}$$

multivariate FFTs (II)

$$\begin{aligned}
 F(k, l, m) &= \sum_{pqs} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p, q, s) \\
 &= \sum_p e^{i2\pi \frac{pk}{N}} \underbrace{\sum_q e^{i2\pi \frac{ql}{N}} \underbrace{\sum_s e^{i2\pi \frac{sm}{N}} \tilde{F}(p, q, s)}_{N^2 \text{ FFT}(N)}}_{N^2 \text{ FFT}(N)} \\
 &\quad \underbrace{\hspace{15em}}_{N^2 \text{ FFT}(N)}
 \end{aligned}$$

multivariate FFTs (II)

$$\begin{aligned} F(k, l, m) &= \sum_{pqs} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p, q, s) \\ &= \sum_p e^{i2\pi \frac{pk}{N}} \underbrace{\sum_q e^{i2\pi \frac{ql}{N}} \underbrace{\sum_s e^{i2\pi \frac{sm}{N}} \tilde{F}(p, q, s)}_{N^2 \text{ FFT}(N)}}_{N^2 \text{ FFT}(N)} \end{aligned}$$

$N^2 \text{ FFT}(N)$

$$3N^2 \times N \log N = N^3 \log(N^3)$$

solving the Poisson equation

$$\Delta V(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

solving the Poisson equation

$$\Delta V(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

solving the Poisson equation

$$\Delta V(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$\tilde{V}(\mathbf{G}) = \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G})$$

$$\tilde{V}(\mathbf{G} = 0) = 0$$

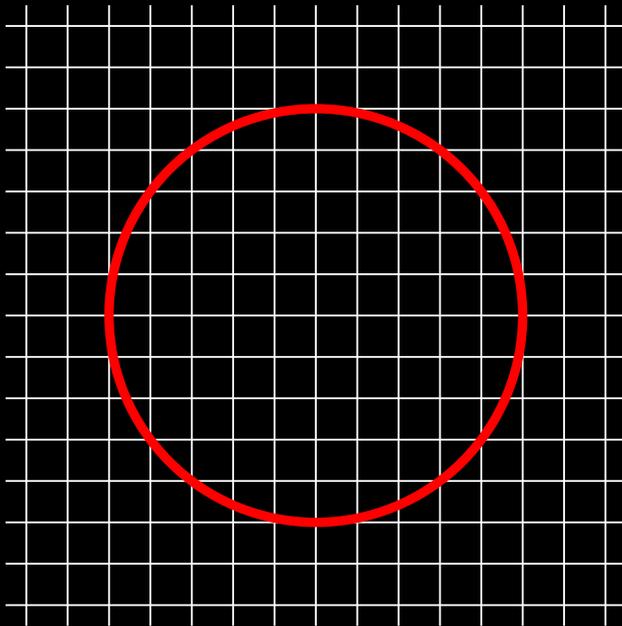
solving the Poisson equation

$$\Delta V(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$\tilde{V}(\mathbf{G}) = \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G})$$

$$\tilde{V}(\mathbf{G} = 0) = 0$$



$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

$$\mathbf{G}_{max} \sim \frac{2\pi}{h}$$
$$h \lesssim \frac{2\pi}{G_{max}}$$

PWs: pros & cons

PWs: pros & cons

- 😊 approach to completeness easily and systematically checked
($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked
($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and $H\psi$ products easily calculated

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and $H\psi$ products easily calculated
- ☺ density, Hartree, and XC potentials easily calculated

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and $H\psi$ products easily calculated
- ☺ density, Hartree, and XC potentials easily calculated
- ☺ orthonormality

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and $H\psi$ products easily calculated
- ☺ density, Hartree, and XC potentials easily calculated
- ☺ orthonormality
- ☹ basis set depends on volume shape/size (Pulay stresses)

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and $H\psi$ products easily calculated
- ☺ density, Hartree, and XC potentials easily calculated
- ☺ orthonormality
- ☹ basis set depends on volume shape/size (Pulay stresses)
- ☹ uniform spatial resolution (no core states!)

treating core states

1																	2
1																	2
Group 1																	Group 18
3																	10
11																	18
19																	36
37																	54
55																	86
87																	
88																	
89																	
104																	
105																	
106																	
107																	
108																	
109																	
110																	
111																	
112																	
113																	
114																	
115																	
58	59	60	61	62	63	64	65	66	67	68	69	70	71				
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
140.116	140.907 65	144.24	(145)	150.36	151.964	157.25	158.925 34	162.500	164.930 32	167.259	168.934 21	173.04	174.967				
90	91	92	93	94	95	96	97	98	99	100	101	102	103				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				
232.0381	231.036 88	238.028 91	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)				

* The systematic names and symbols for elements greater than 110 will be used until the approval of final names by IUPAC.

A team at Lawrence Berkeley National Laboratories reported the discovery of elements 116 and 118 in June 1999. The same team retracted the discovery in July 2001. The discovery of elements 113, 114, and 115 has been reported but not confirmed.

$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

treating core states

1																	2
1																	2
Group 1																	Group 18
3																	10
11																	18
19																	36
37																	54
55																	86
87																	
88																	
89																	
104																	
105																	
106																	
107																	
108																	
109																	
110																	
111																	
112																	
113																	
114																	
115																	
58	59	60	61	62	63	64	65	66	67	68	69	70	71				
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
140.116	140.907 65	144.24	(145)	150.36	151.964	157.25	158.925 34	162.500	164.930 32	167.259	168.934 21	173.04	174.967				
90	91	92	93	94	95	96	97	98	99	100	101	102	103				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				
232.0381	231.036 88	238.028 91	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)				

$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

$$E_{cut} \sim Z^2$$

* The systematic names and symbols for elements greater than 110 will be used until the approval of final names by IUPAC.
 A team at Lawrence Berkeley National Laboratories reported the discovery of elements 116 and 118 in June 1999. The same team retracted the discovery in July 2001. The discovery of elements 113, 114, and 115 has been reported but not confirmed.

treating core states

1																	2																			
1	H Hydrogen 1.007 94																2																			
2	Group 1																Group 18																			
2	3 Li Lithium 6.941																10 Ne Neon 20.1797																			
3	4 Be Beryllium 9.012 182																9 F Fluorine 18.998 4032																			
3	11 Na Sodium 22.989 770		12 Mg Magnesium 24.3050												17 Cl Chlorine 35.453		18 Ar Argon 39.948																			
4	19 K Potassium 39.0983		20 Ca Calcium 40.078		21 Sc Scandium 44.955 910		22 Ti Titanium 47.867		23 V Vanadium 50.9415		24 Cr Chromium 51.9961		25 Mn Manganese 54.938 049		26 Fe Iron 55.845		27 Co Cobalt 58.933 200		28 Ni Nickel 58.6934		29 Cu Copper 63.546		30 Zn Zinc 65.409		31 Ga Gallium 69.723		32 Ge Germanium 72.64		33 As Arsenic 74.921 60		34 Se Selenium 78.96		35 Br Bromine 79.904		36 Kr Krypton 83.798	
5	37 Rb Rubidium 85.4678		38 Sr Strontium 87.62		39 Y Yttrium 88.905 85		40 Zr Zirconium 91.224		41 Nb Niobium 92.906 38		42 Mo Molybdenum 95.94		43 Tc Technetium (98)		44 Ru Ruthenium 101.07		45 Rh Rhodium 102.905 50		46 Pd Palladium 106.42		47 Ag Silver 107.8682		48 Cd Cadmium 112.411		49 In Indium 114.818		50 Sn Tin 118.710		51 Sb Antimony 121.760		52 Te Tellurium 127.60		53 I Iodine 126.904 47		54 Xe Xenon 131.295	
6	55 Cs Cesium 132.905 43		56 Ba Barium 137.327		57 La Lanthanum 138.9055		72 Hf Hafnium 178.49		73 Ta Tantalum 180.9479		74 W Tungsten 183.84		75 Re Rhenium 186.207		76 Os Osmium 190.23		77 Ir Iridium 192.227		78 Pt Platinum 195.078		79 Au Gold 196.966 55		80 Hg Mercury 200.59		81 Tl Thallium 204.3833		82 Pb Lead 207.2		83 Bi Bismuth 208.980 38		84 Po Polonium (209)		85 At Astatine (210)		86 Rn Radon (222)	
7	87 Fr Francium (223)		88 Ra Radium (226)		89 Ac Actinium (227)		104 Rf Rutherfordium (261)		105 Db Dubnium (262)		106 Sg Seaborgium (266)		107 Bh Bohrium (264)		108 Hs Hassium (277)		109 Mt Meitnerium (268)		110 Ds Darmstadtium (281)		111 Uuu* Ununium (272)		112 Uub* Unubium (285)		113 Uut* Ununium (284)		114 Uuq* Unquadium (289)		115 Uup* Unpentium (288)							
	58 Ce Cerium 140.116		59 Pr Praseodymium 140.907 65		60 Nd Neodymium 144.24		61 Pm Promethium (145)		62 Sm Samarium 150.36		63 Eu Europium 151.964		64 Gd Gadolinium 157.25		65 Tb Terbium 158.925 34		66 Dy Dysprosium 162.500		67 Ho Holmium 164.930 32		68 Er Erbium 167.259		69 Tm Thulium 168.934 21		70 Yb Ytterbium 173.04		71 Lu Lutetium 174.967									
	90 Th Thorium 232.0381		91 Pa Protactinium 231.036 88		92 U Uranium 238.028 91		93 Np Neptunium (237)		94 Pu Plutonium (244)		95 Am Americium (243)		96 Cm Curium (247)		97 Bk Berkelium (247)		98 Cf Californium (251)		99 Es Einsteinium (252)		100 Fm Fermium (257)		101 Md Mendelevium (258)		102 No Nobelium (259)		103 Lr Lawrencium (262)									

* The systematic names and symbols for elements greater than 110 will be used until the approval of final names by IUPAC.

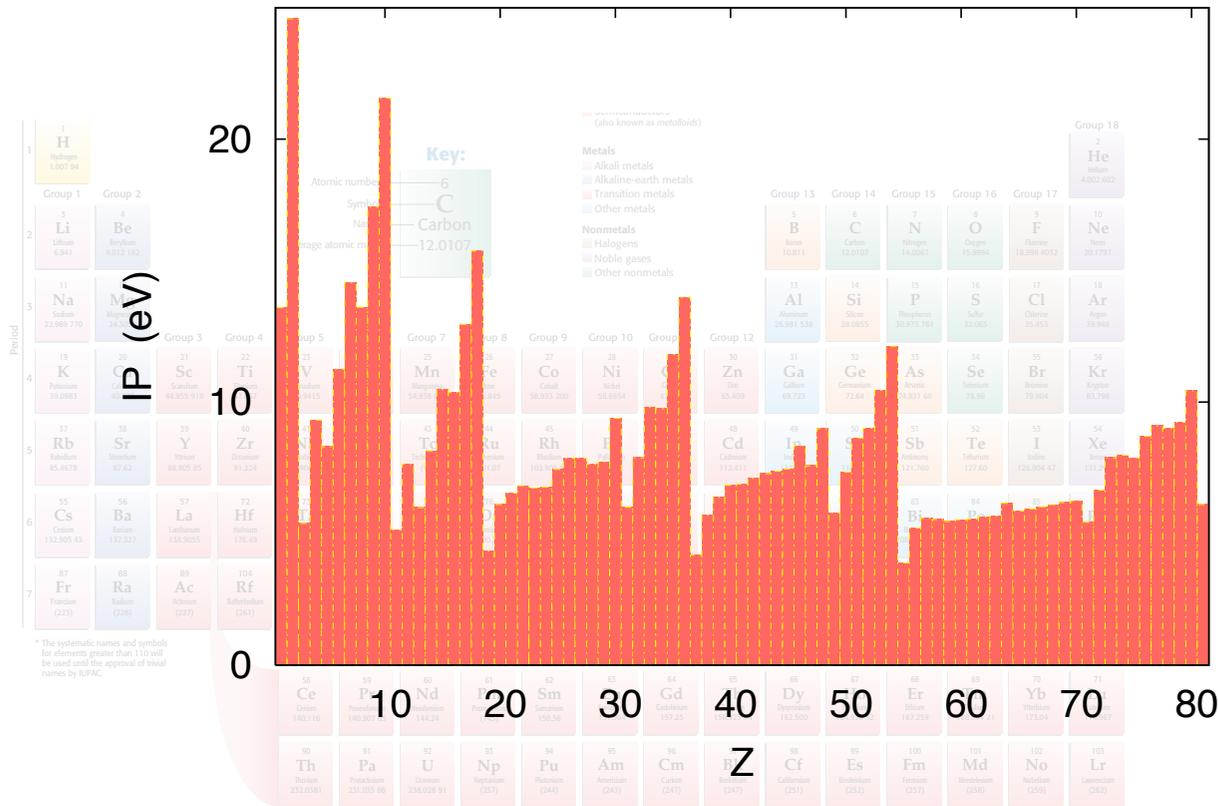
A team at Lawrence Berkeley National Laboratories reported the discovery of elements 116 and 118 in June 1999. The same team retracted the discovery in July 2001. The discovery of elements 113, 114, and 115 has been reported but not confirmed.

$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

$$E_{cut} \sim Z^2$$

$$N_{PW} = \frac{4\pi}{3} k_{cut}^3 \frac{\Omega}{(2\pi)^3} \sim Z^3$$

treating core states



$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

$$E_{cut} \sim Z^2$$

$$N_{PW} = \frac{I_{p\pi} \sim 1}{3} k_{cut}^3 \frac{a \sim 1}{(2\pi)^3}$$

$$\sim Z^3$$

trashing core states: pseudopotentials

trashing core states: pseudopotentials

pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

ϕ_{val}^{ps} is nodeless and smooth

trashing core states: pseudopotentials

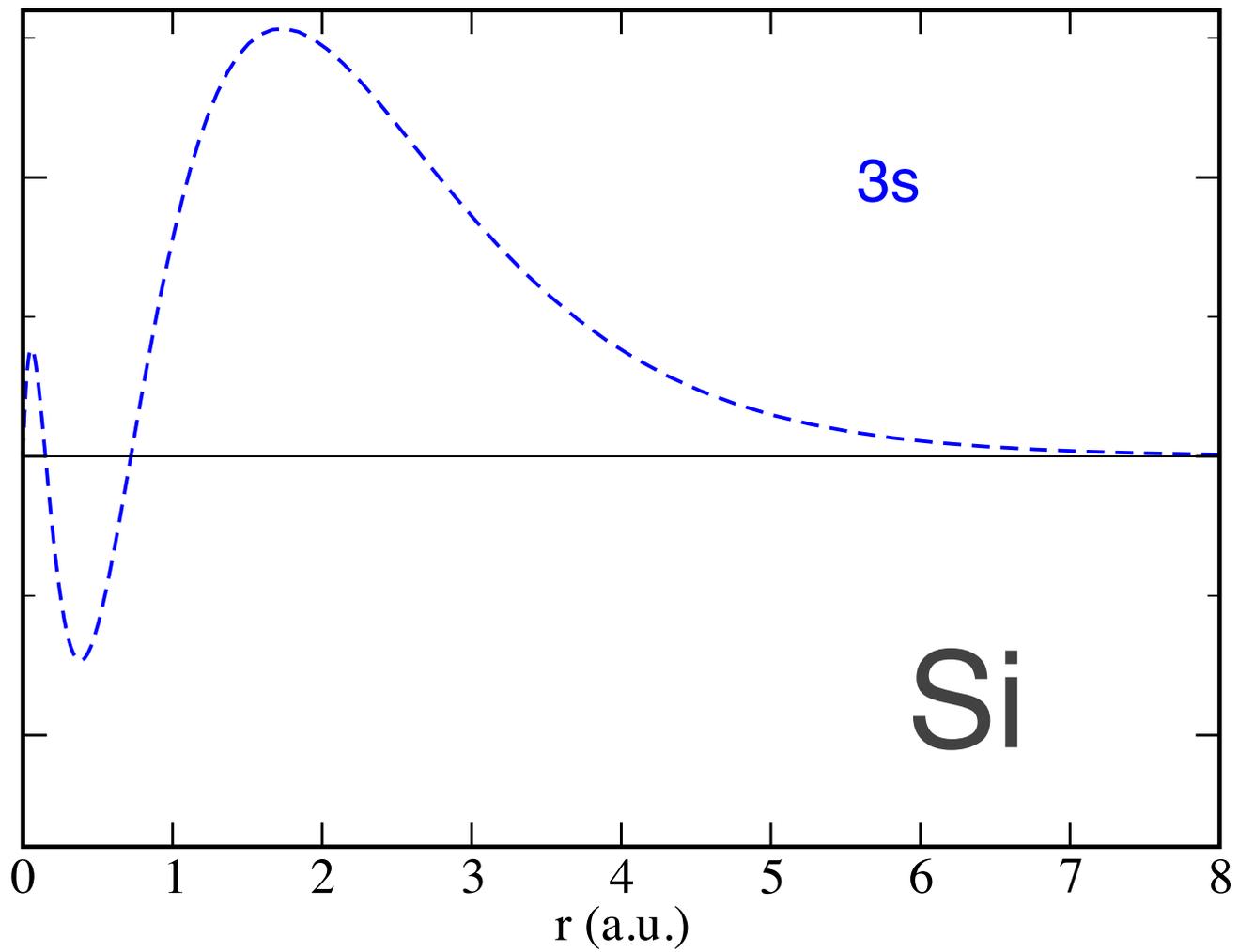
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

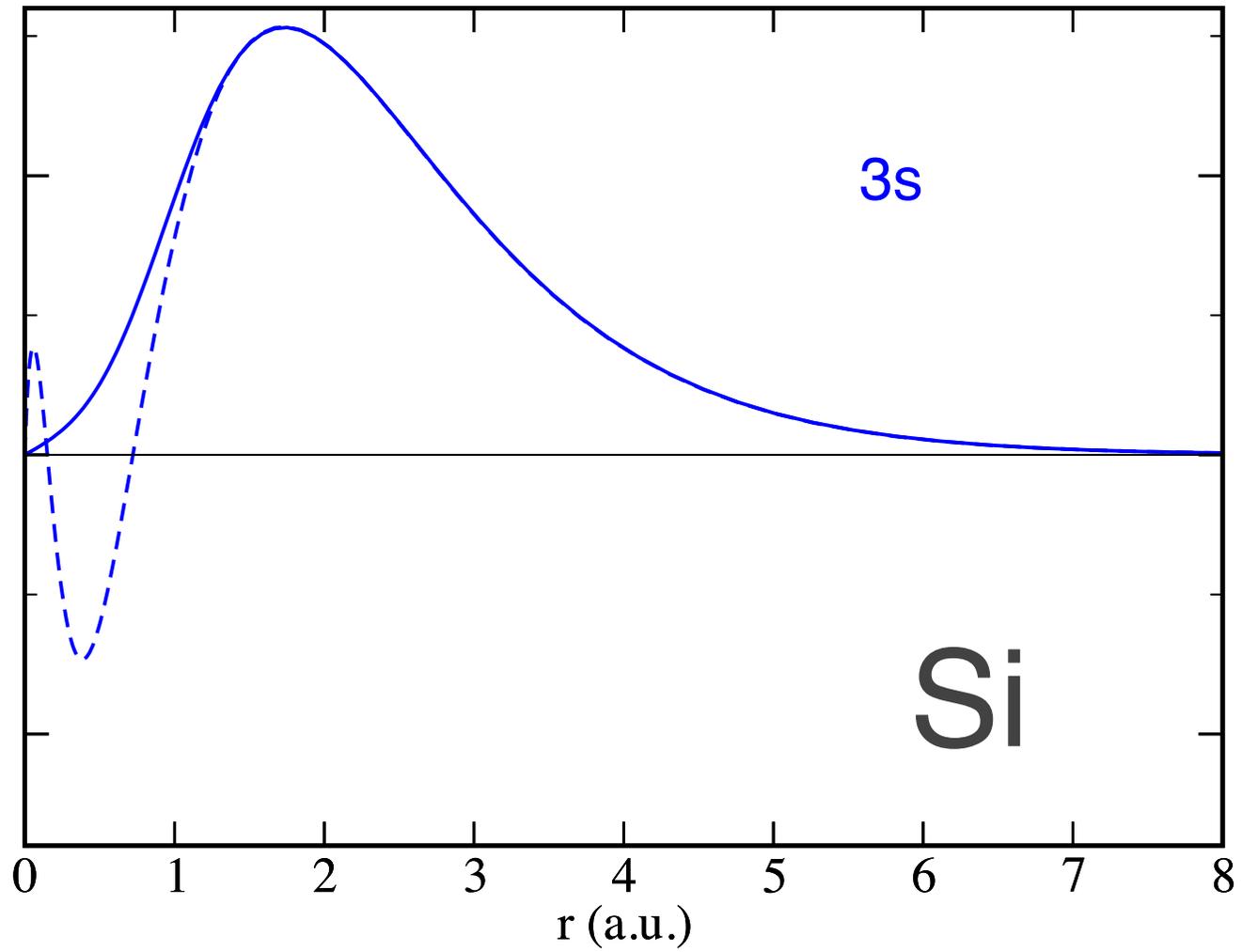
ϕ_{val}^{ps} is nodeless and smooth

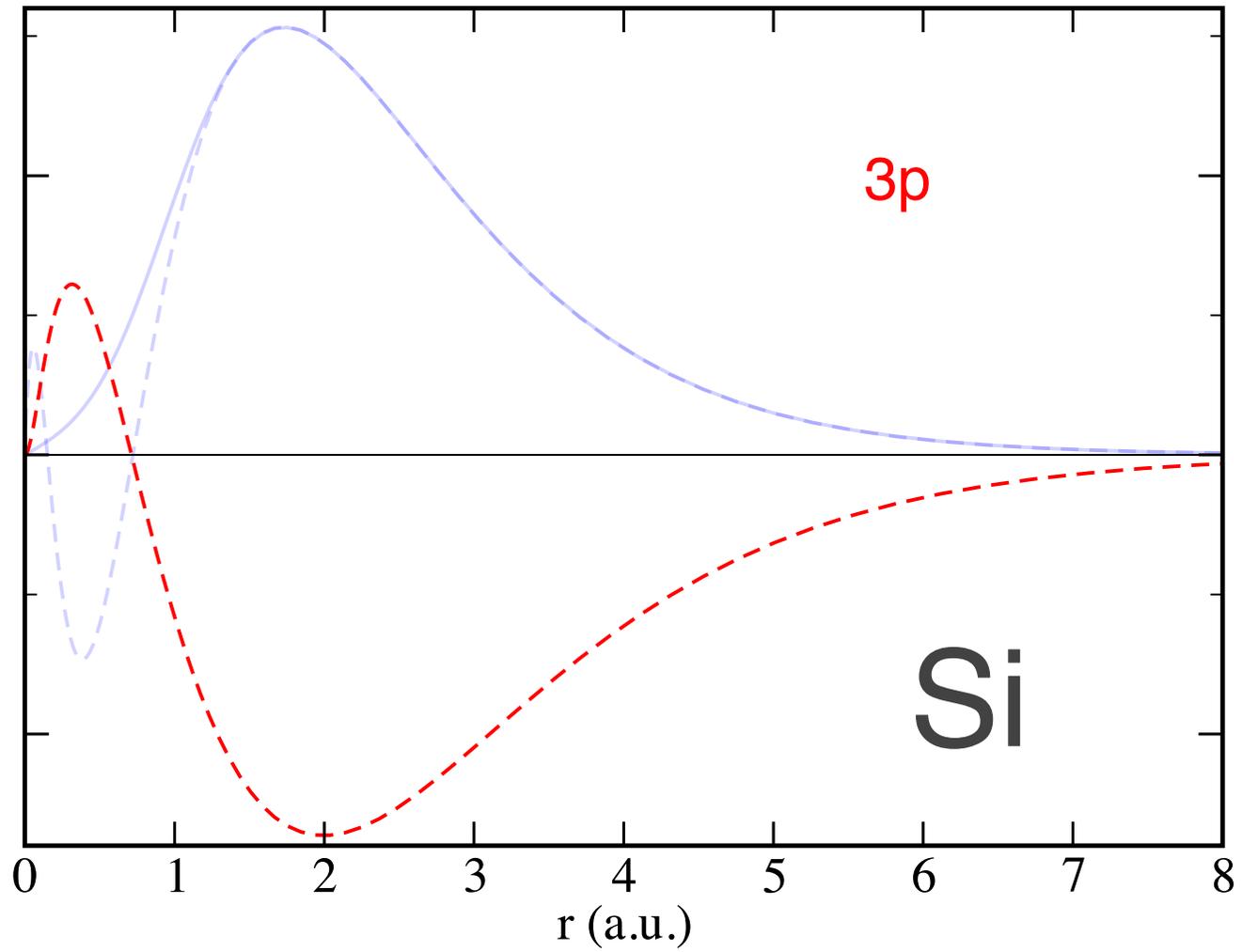
the chemical properties of the pseudo-atom are the same as those of the true atom:

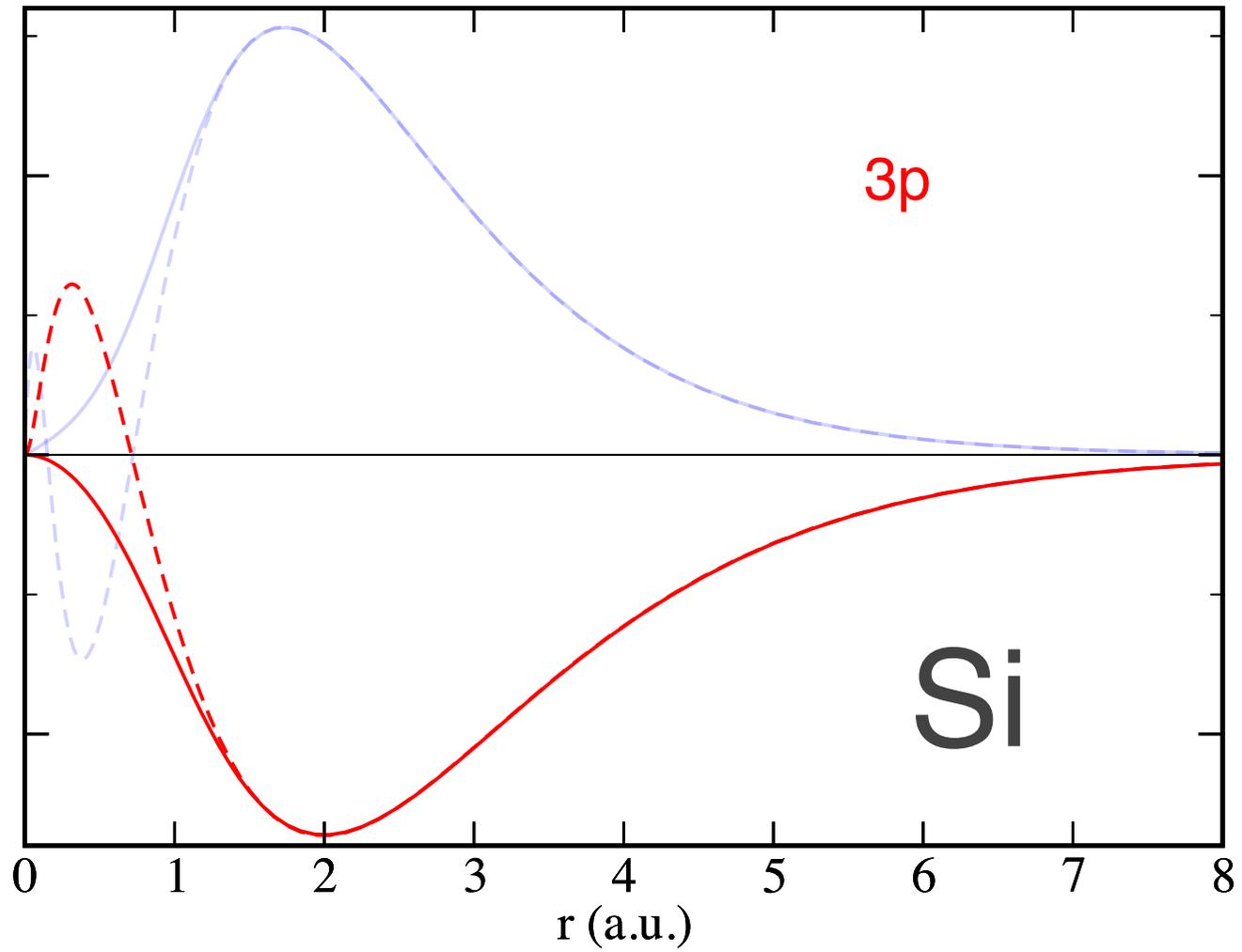
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

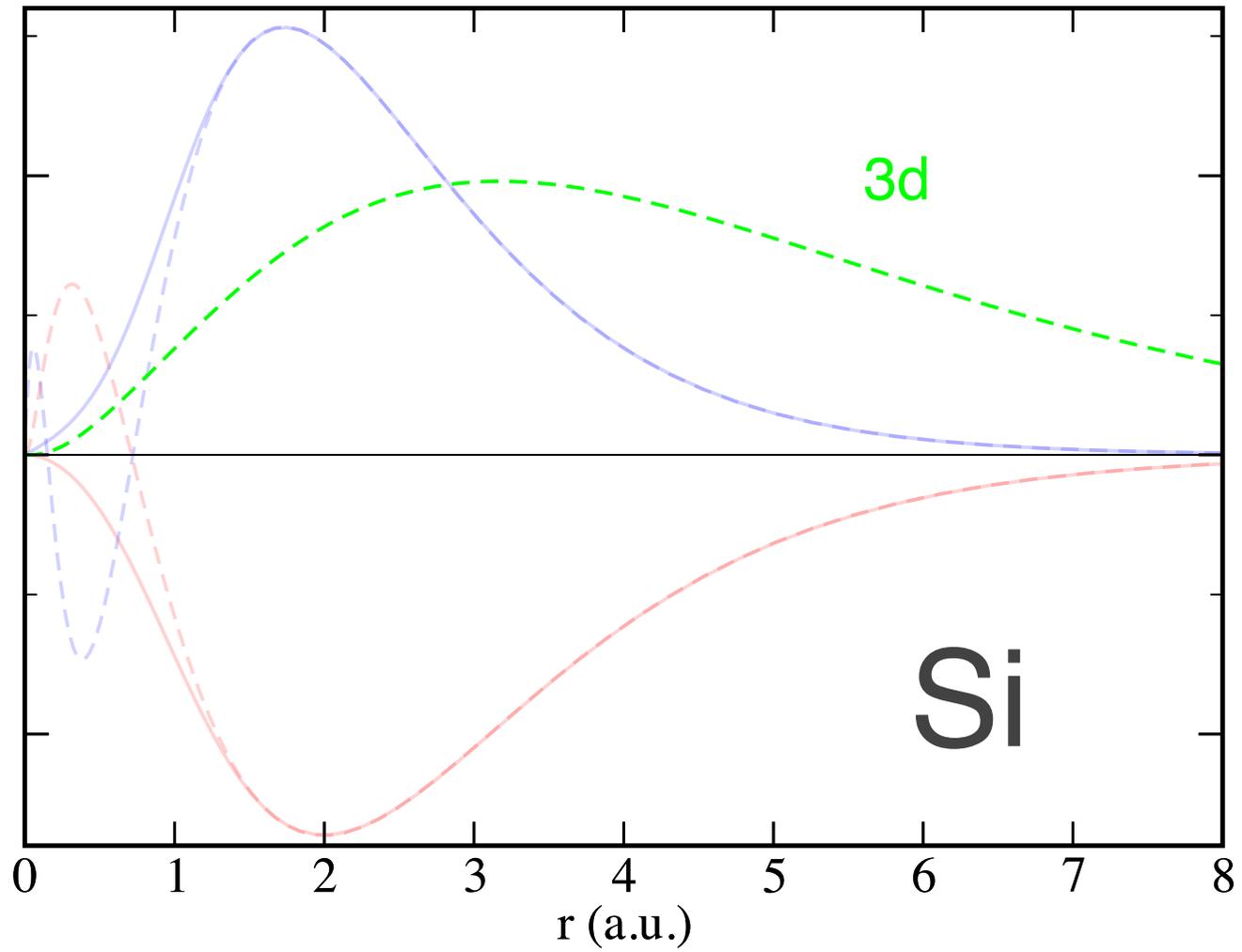
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for } r > r_c$$

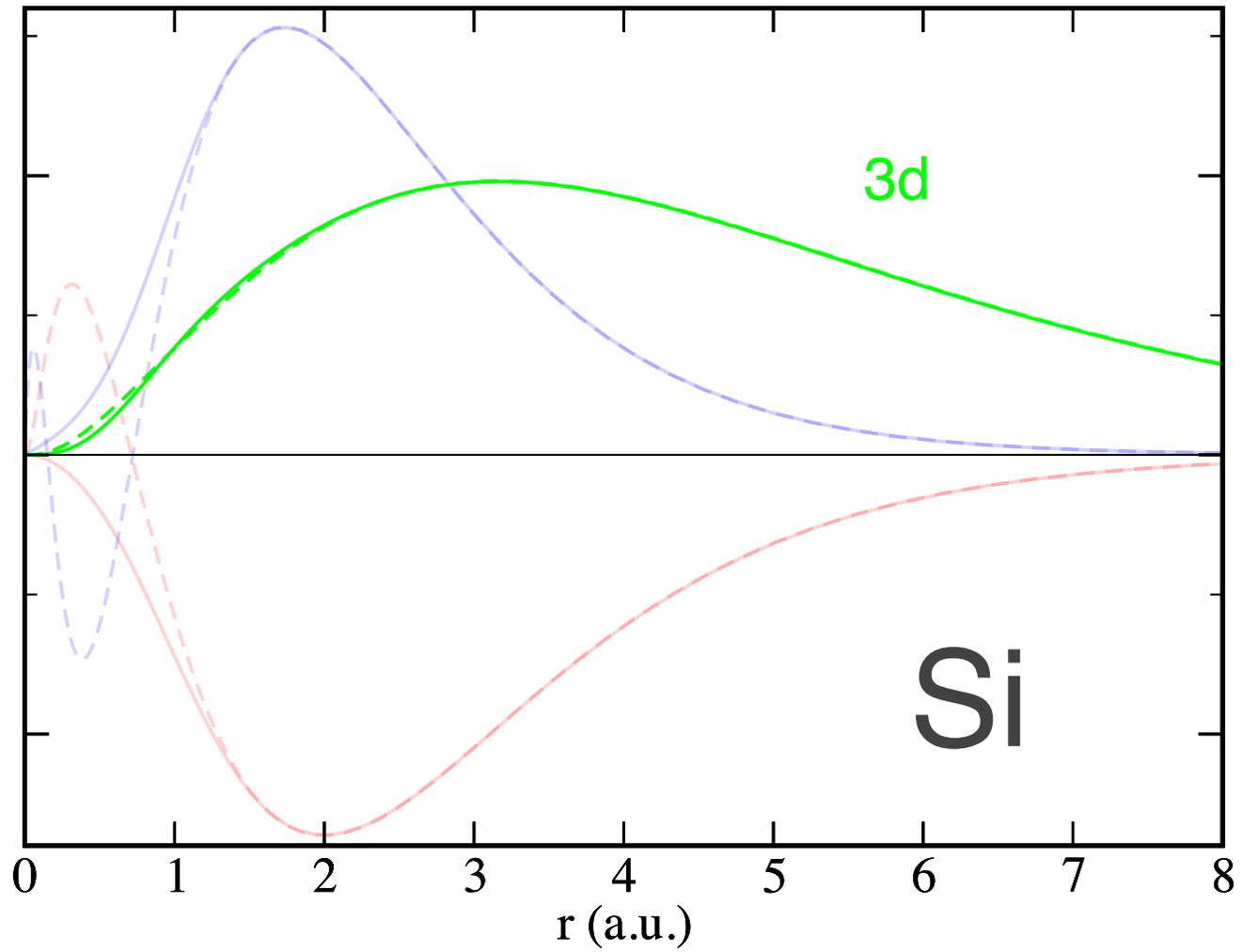




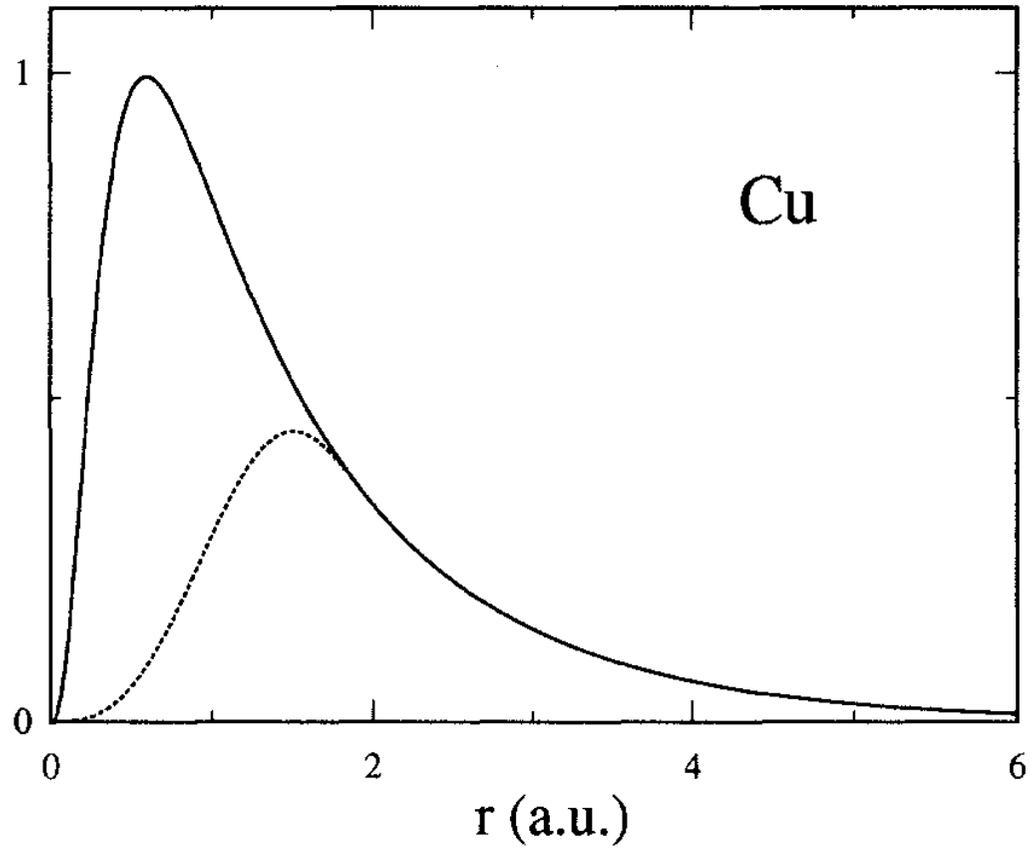




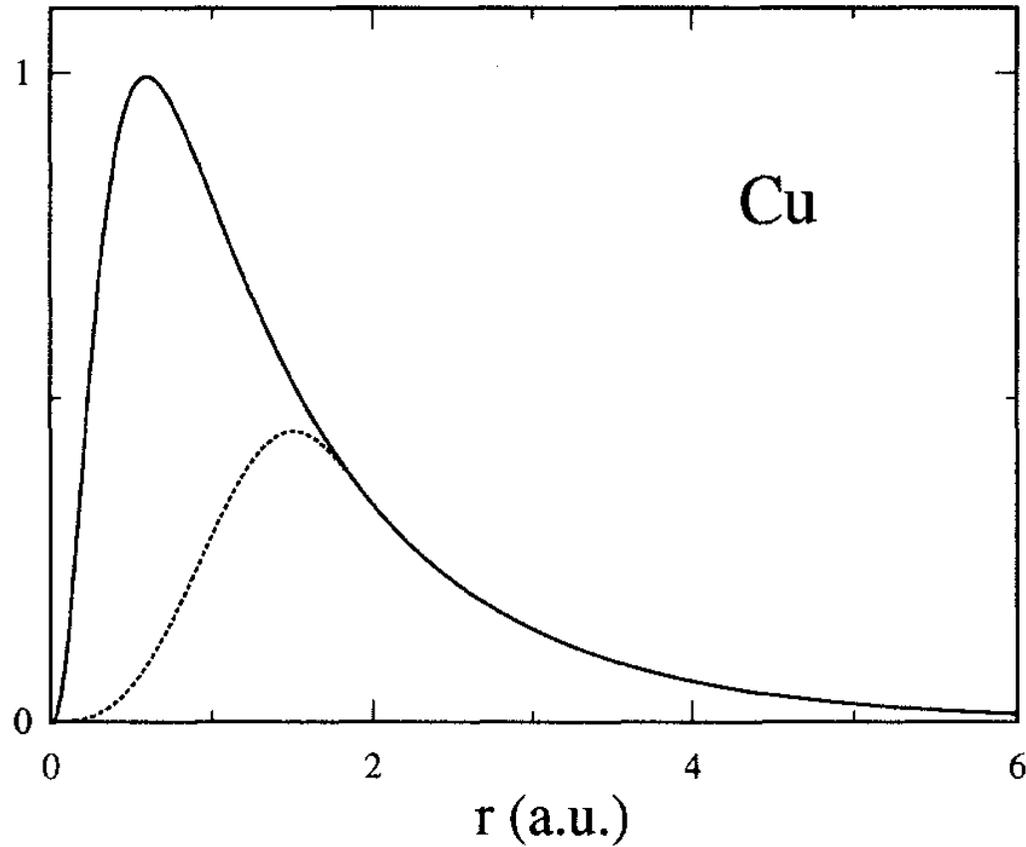




US pseudopotentials



US pseudopotentials



$$H_{US}\phi_n = \epsilon_n S\phi_n \quad \langle \phi_n | S | \phi_m \rangle = \delta_{nm}$$



That's all Folks!

these slides at
<http://talks.baroni.me>
baroni@sissa.it