

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

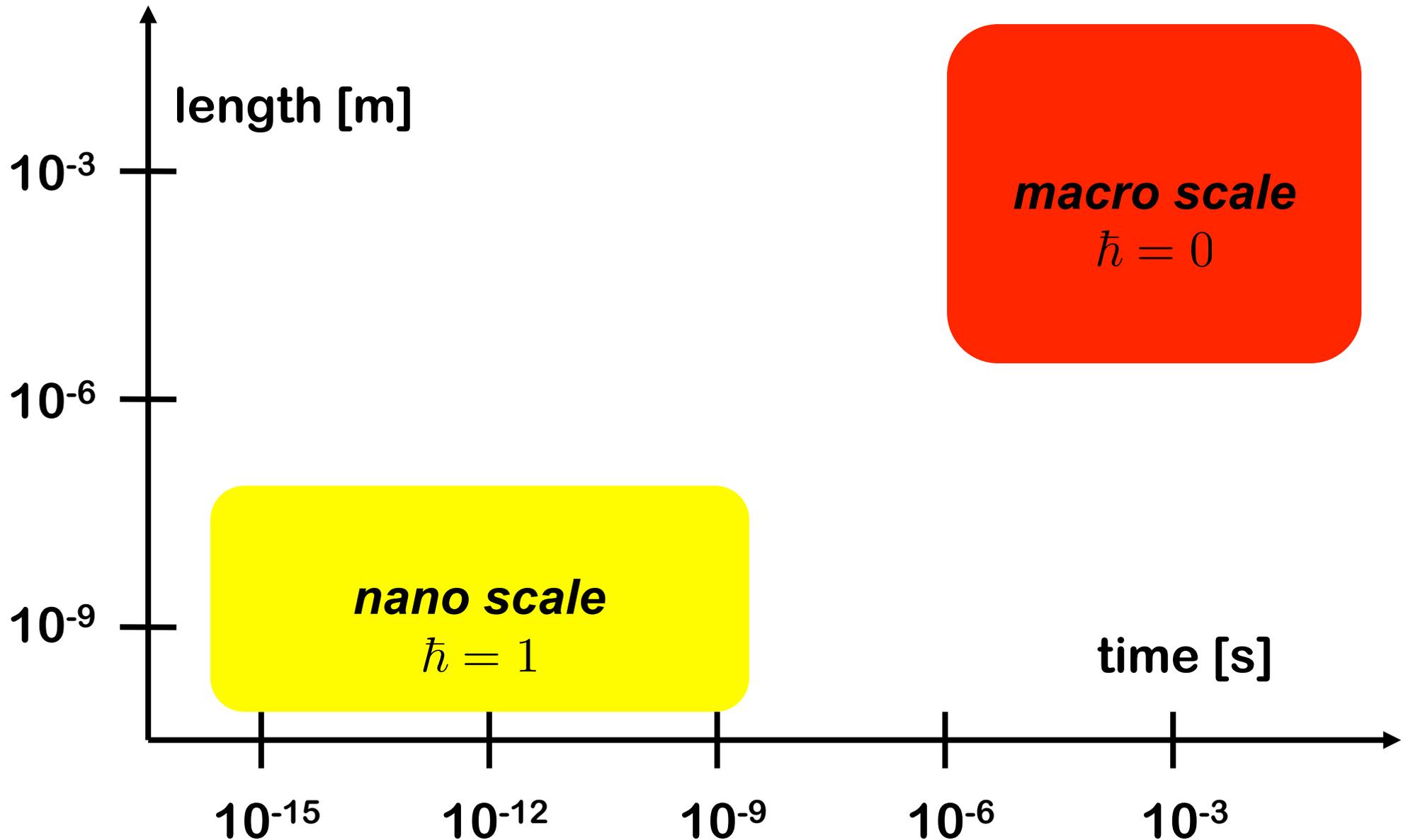
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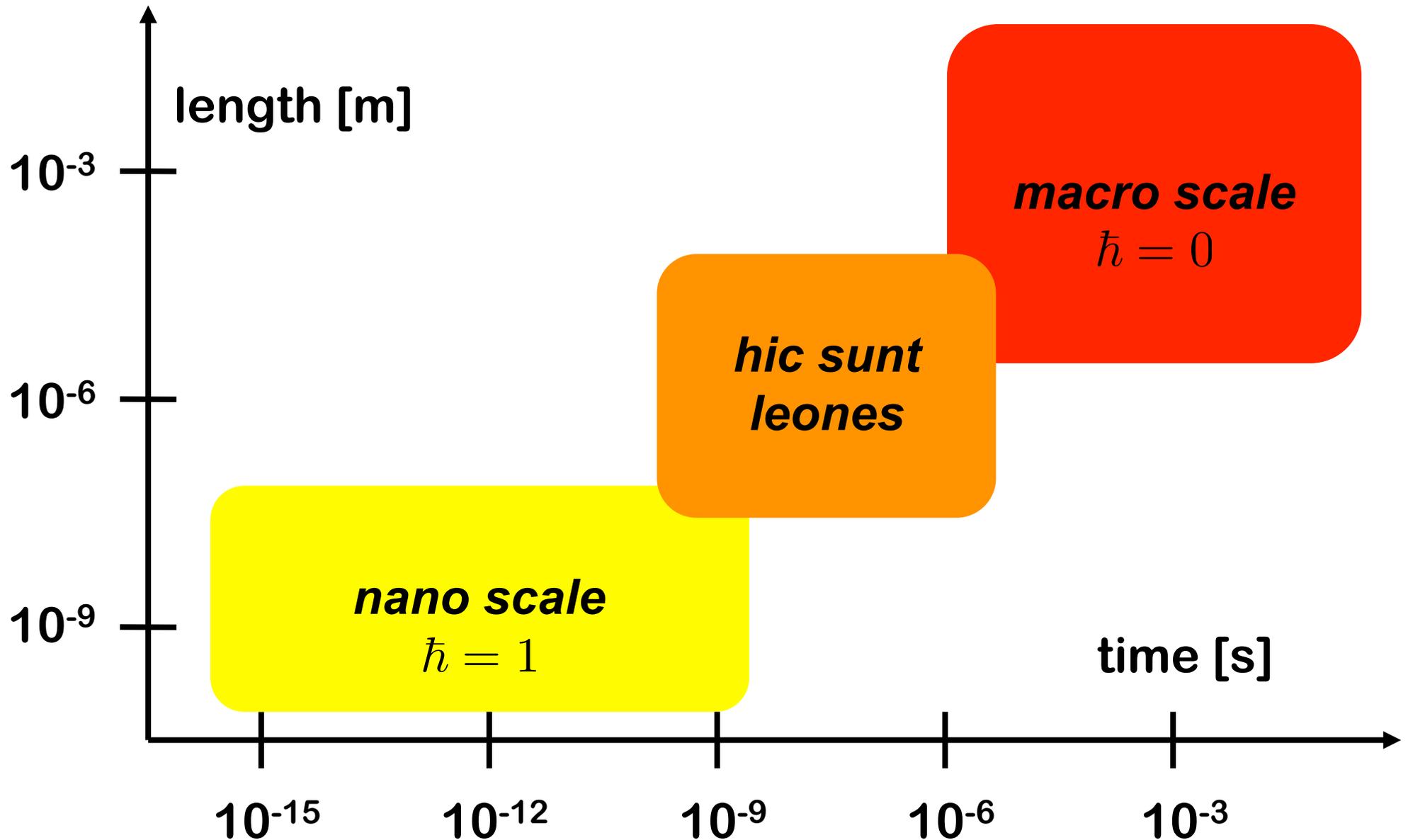
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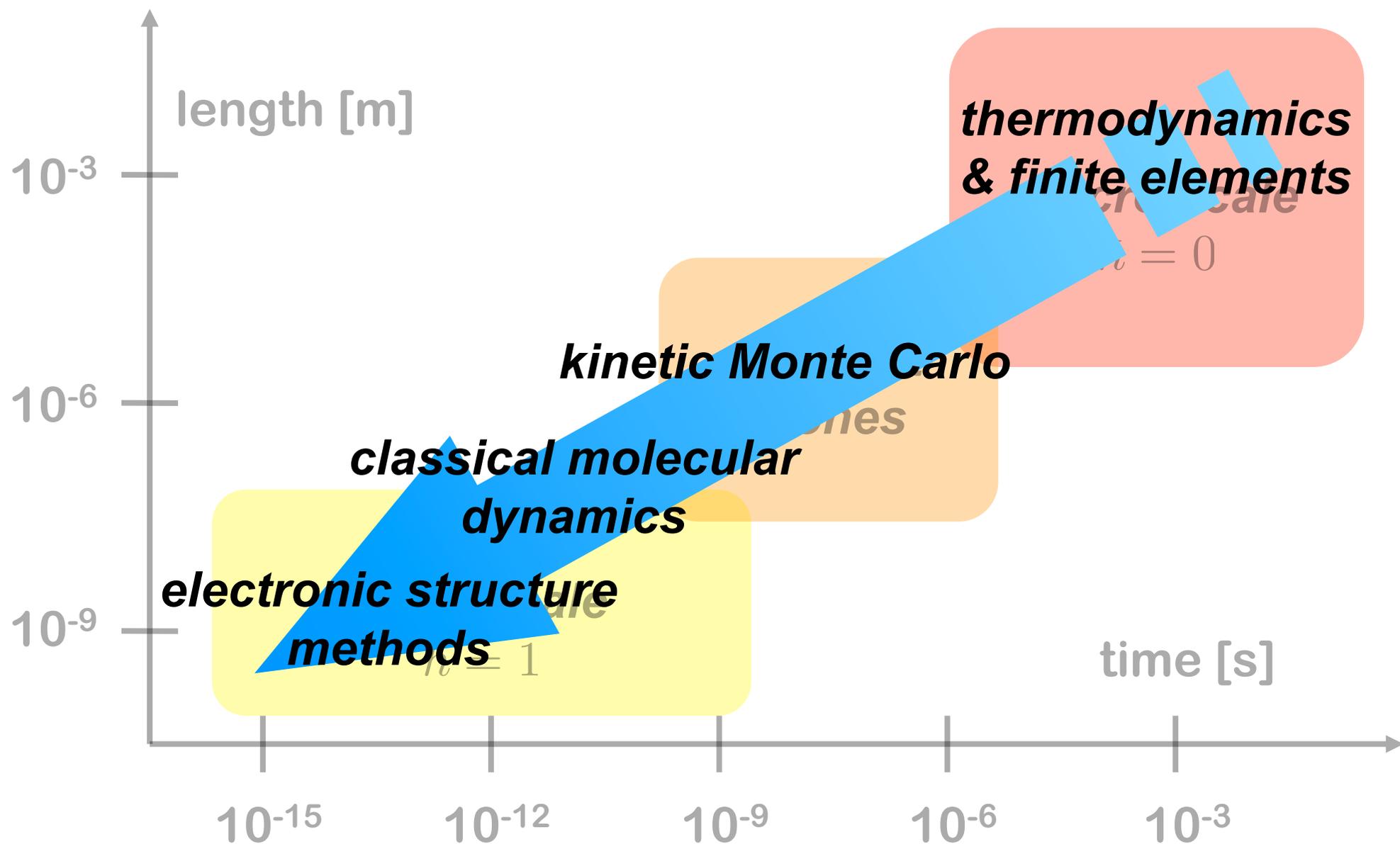
# the saga of time and length scales



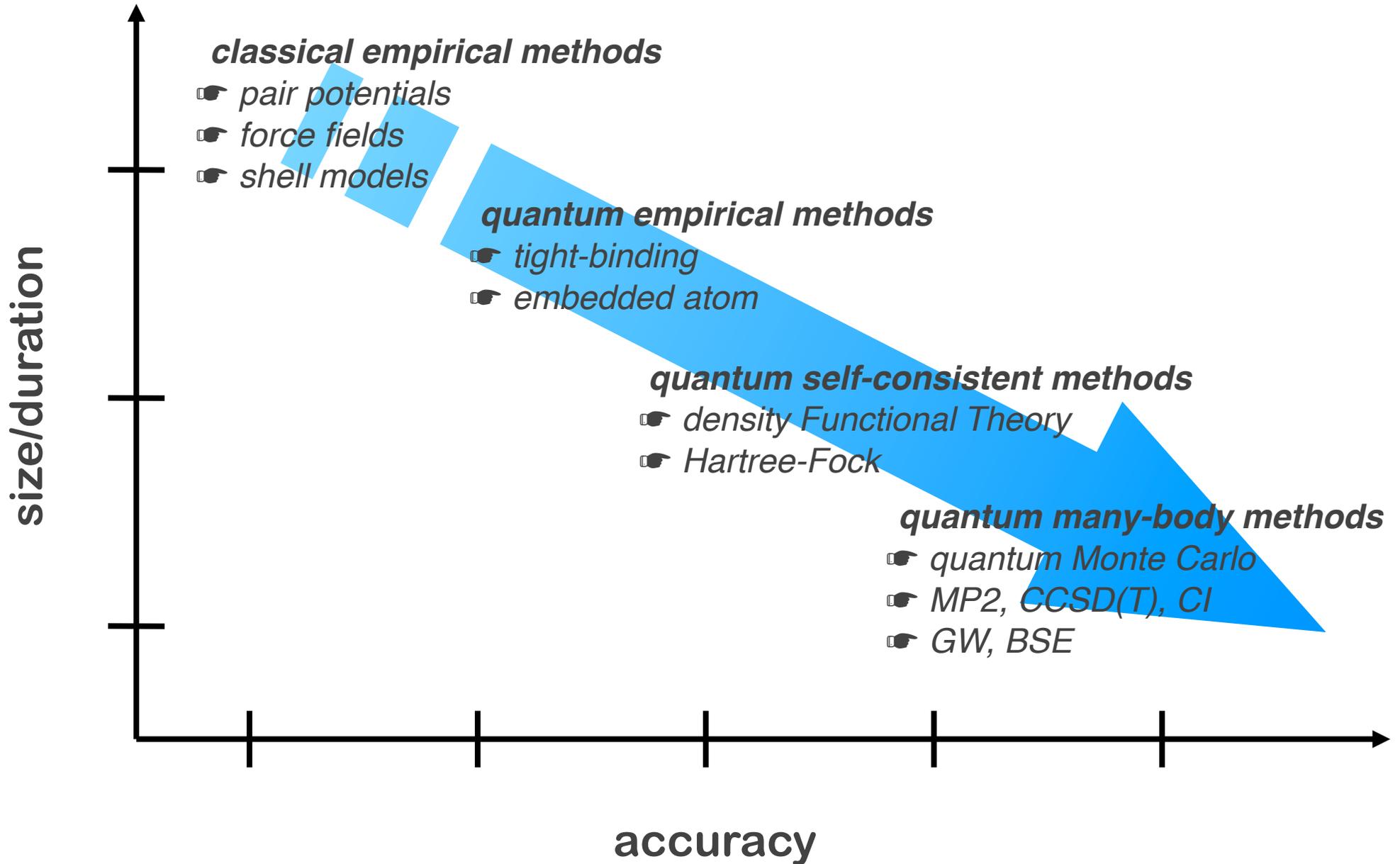
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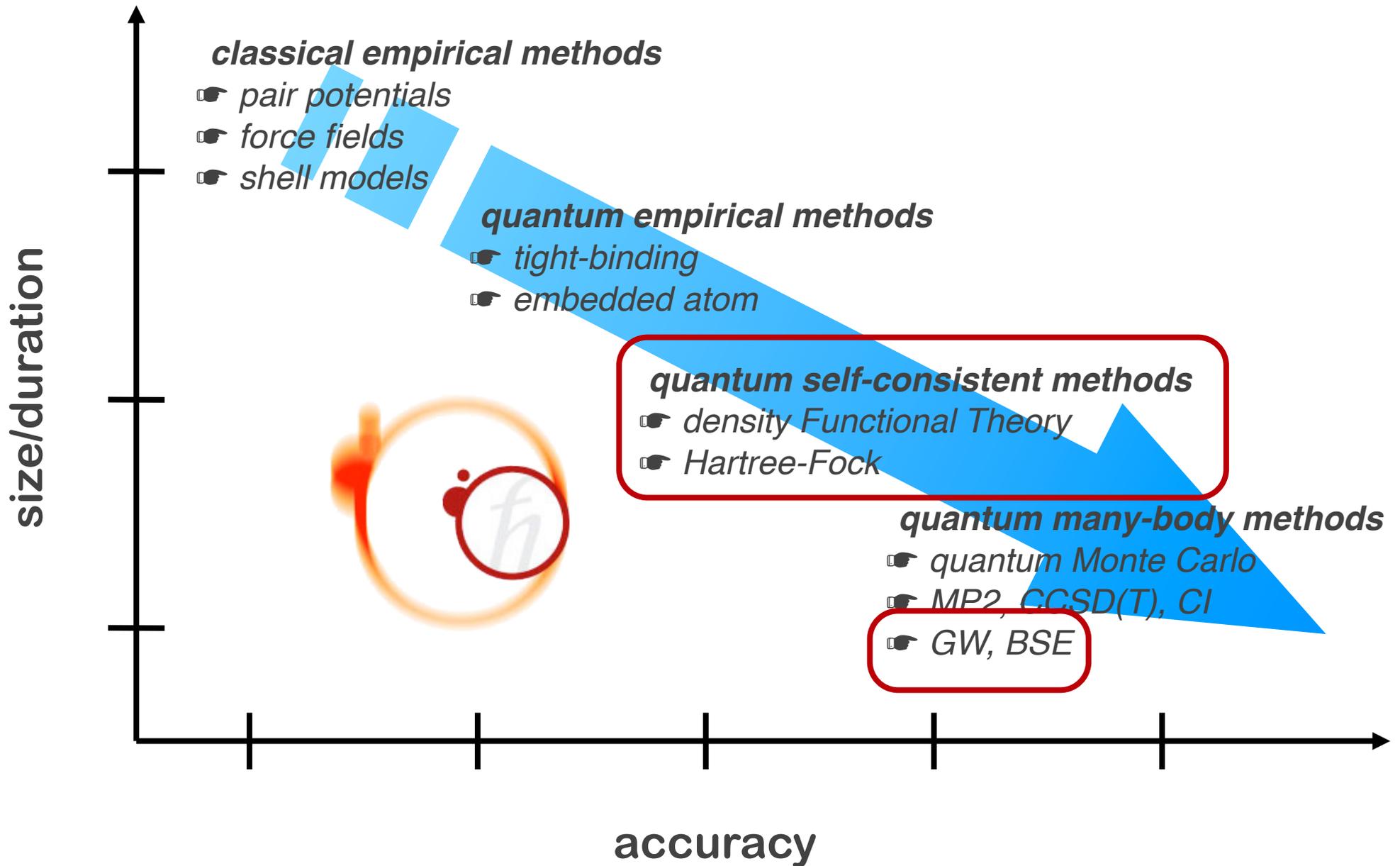
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# size vs. accuracy



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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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$M \gg m$ : 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

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

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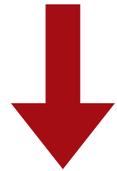
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$$V(\mathbf{r}, \mathbf{R}) \rightarrow \frac{e^2}{2} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + v_{[\rho]}(\mathbf{r})$$

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**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

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

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examples:

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

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

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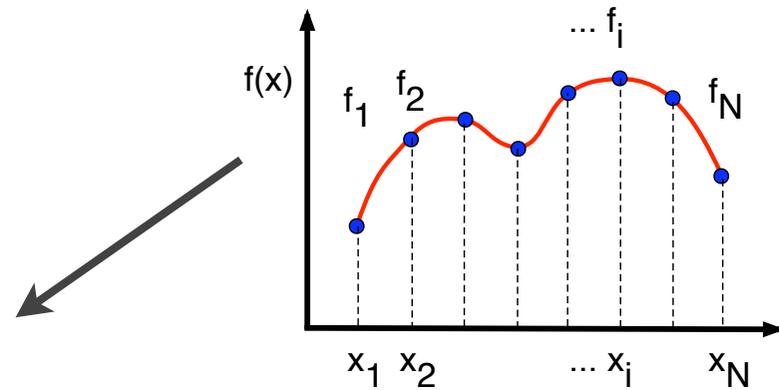
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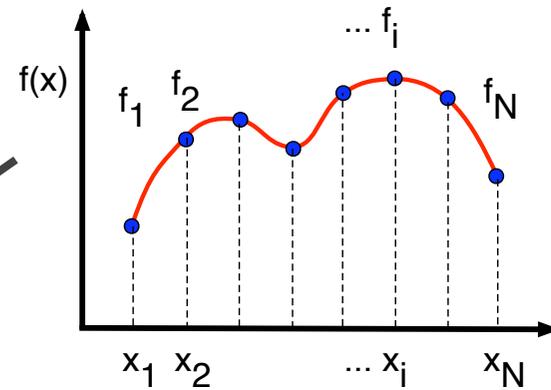
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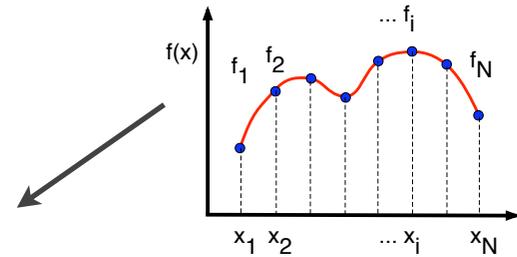


$$f(x) \approx \sum_n c_n \phi_n(x)$$

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

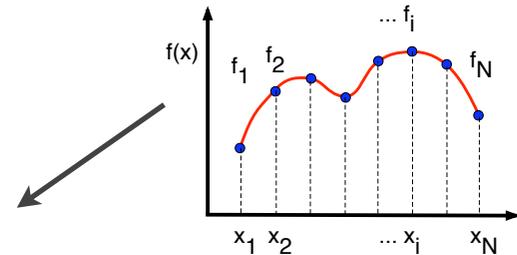
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$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \text{ “ = ” } \lim_{\epsilon \rightarrow 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

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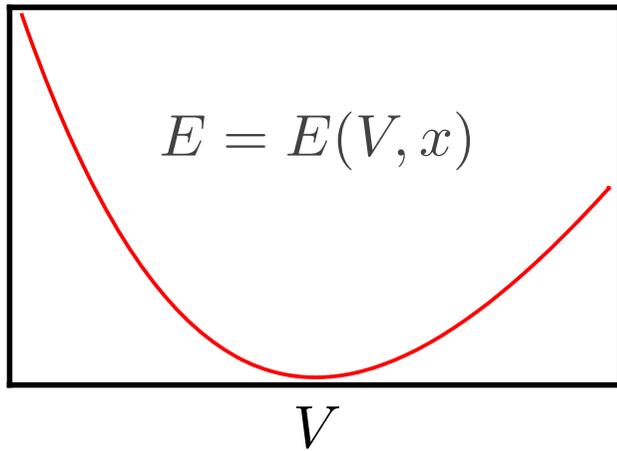


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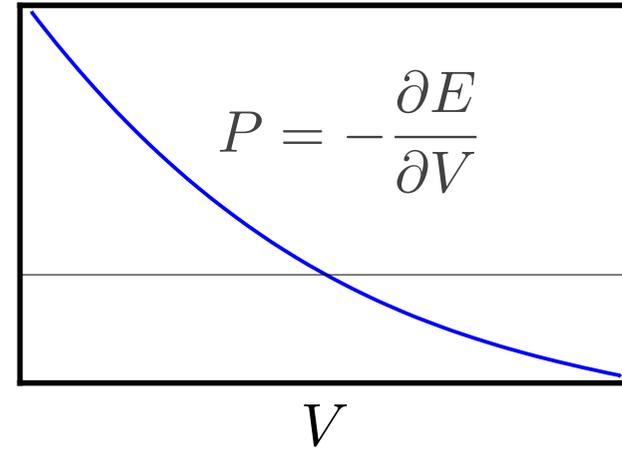
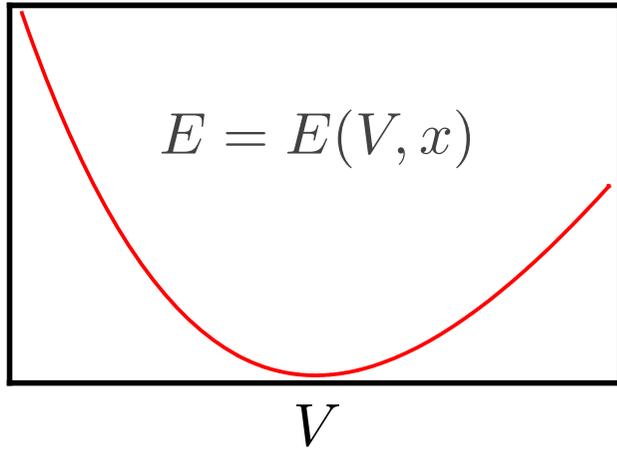


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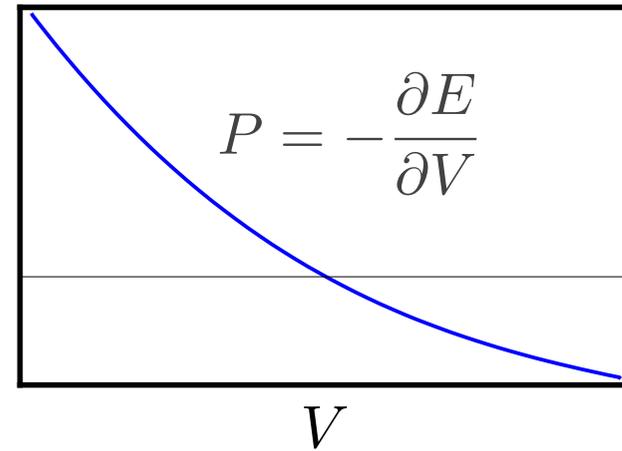
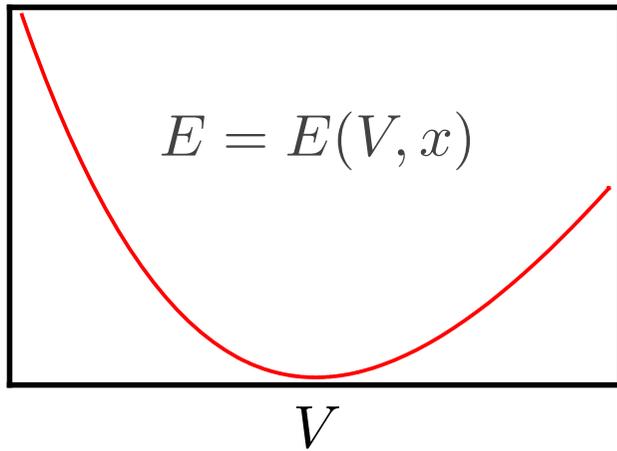
# conjugate variables & Legendre transforms



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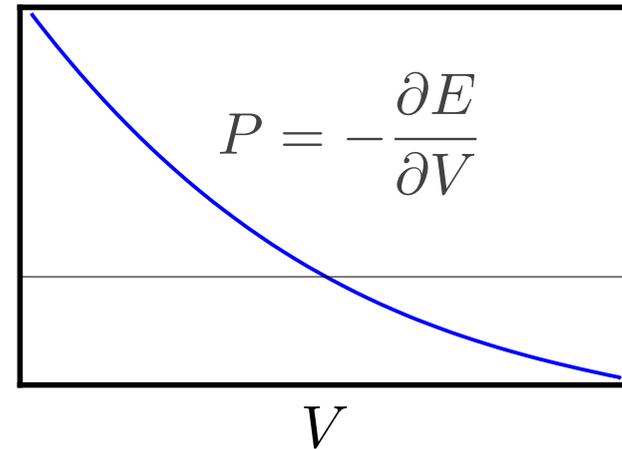
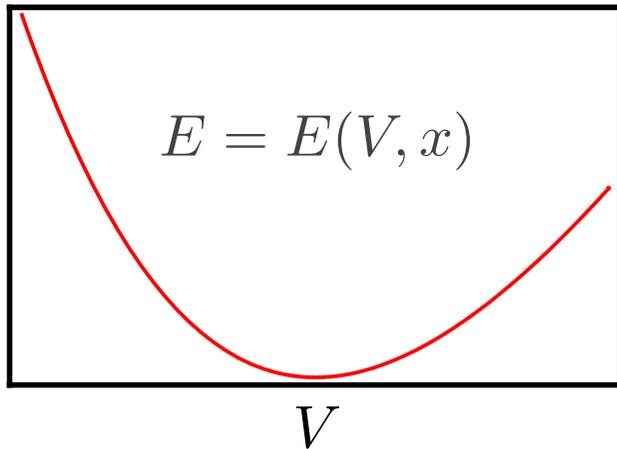


# conjugate variables & Legendre transforms



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

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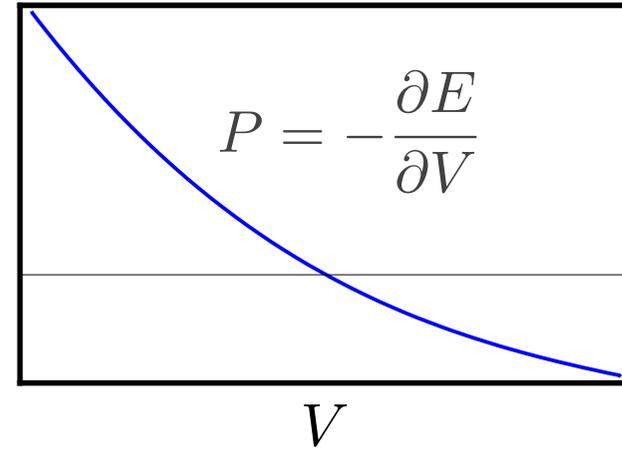
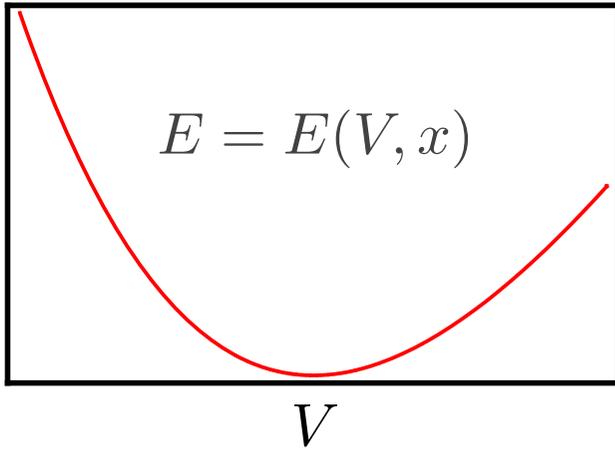


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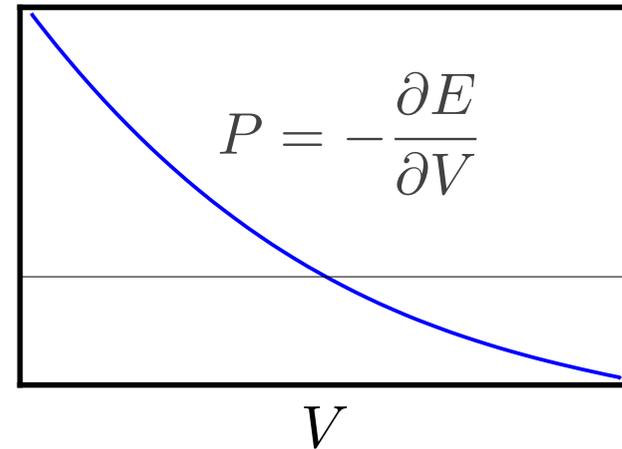
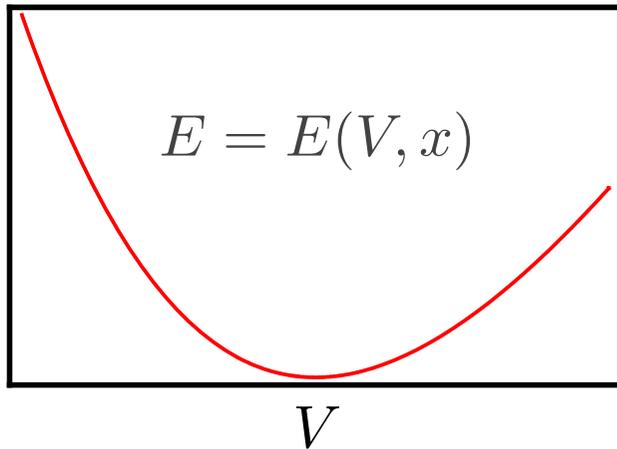


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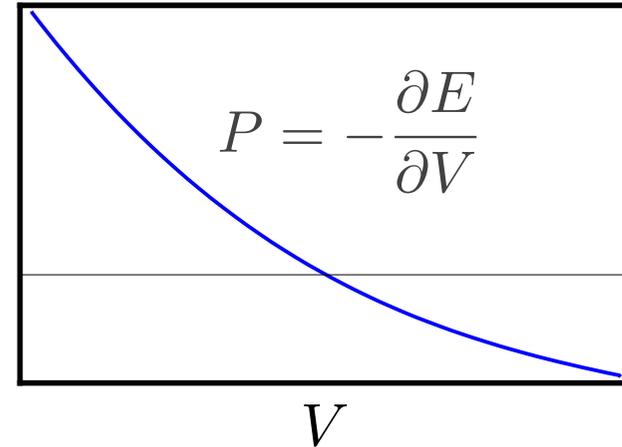
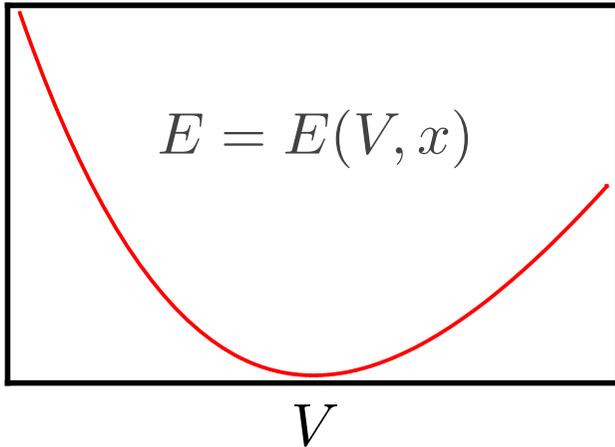


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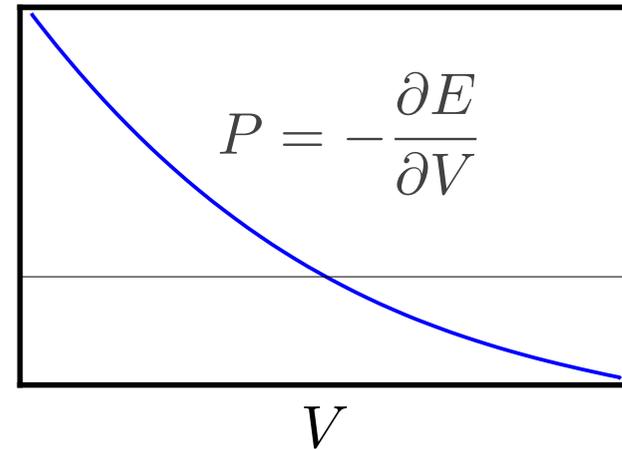
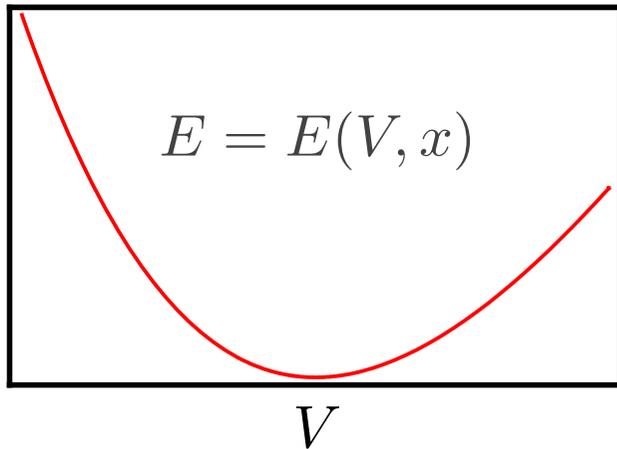


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# Hohenberg-Kohn DFT

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

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## 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*)

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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

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

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$\rho(\mathbf{r})$

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# 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

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

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# plane-wave basis sets

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

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

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

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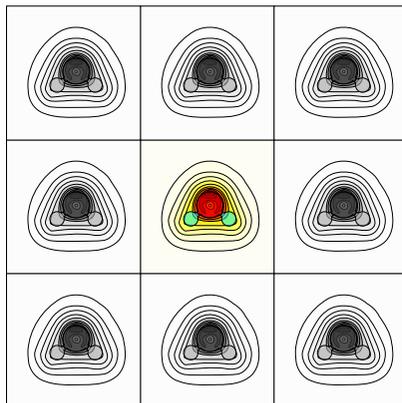
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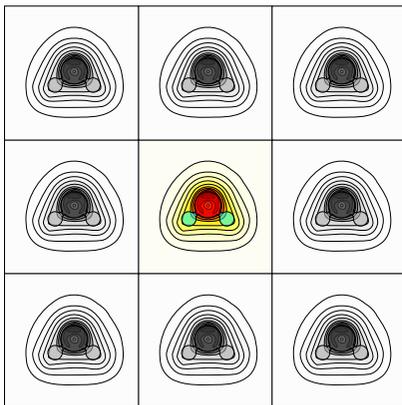
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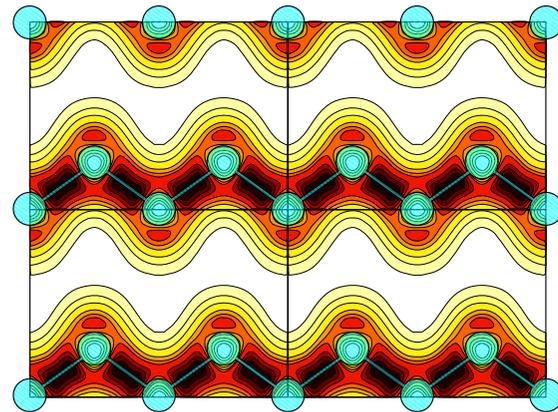
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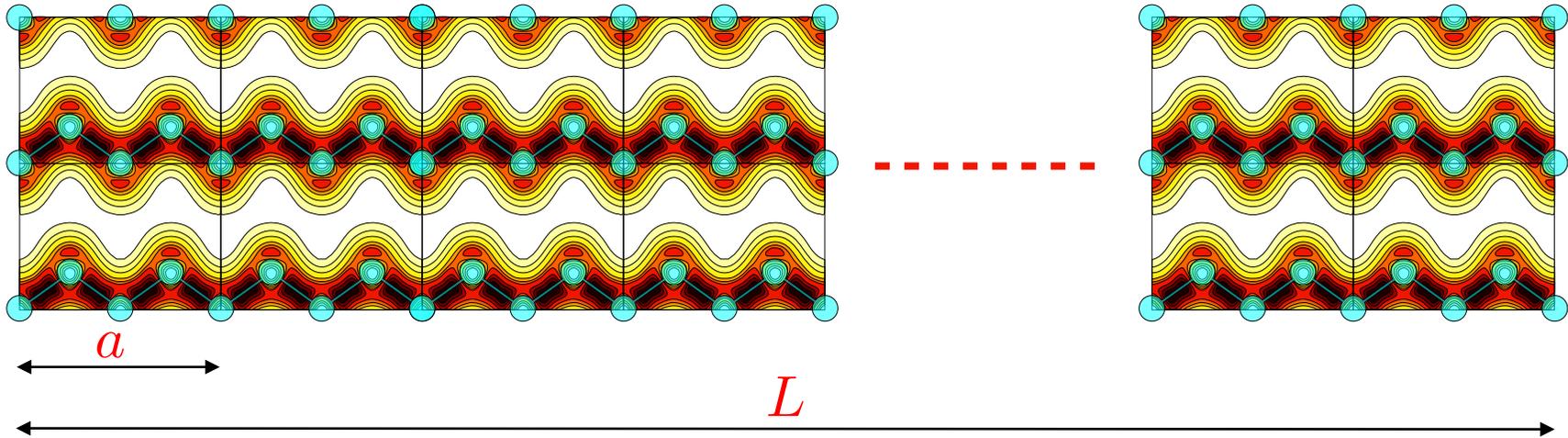
infinite crystals ( $\ell = L$ )



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

# 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

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

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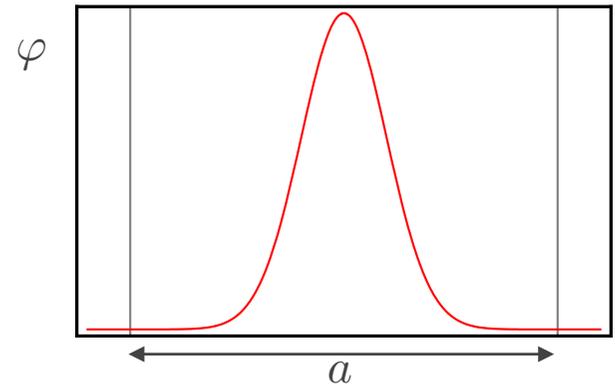
$$\rho(\mathbf{r}) = \sum_{v\mathbf{k}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

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

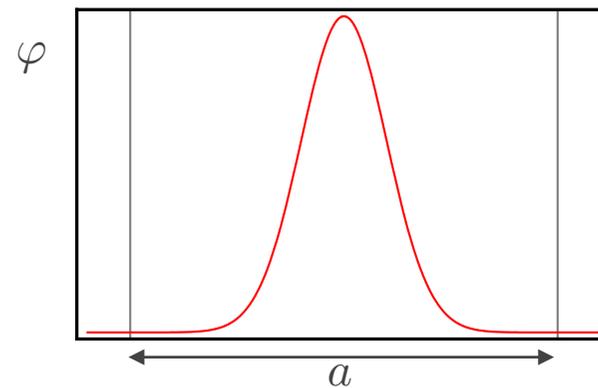
# sampling theorem

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

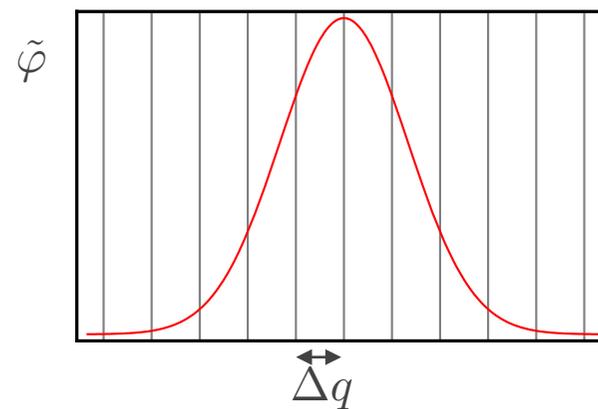


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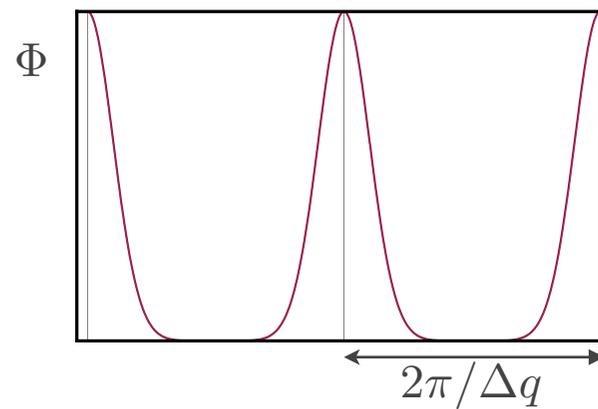
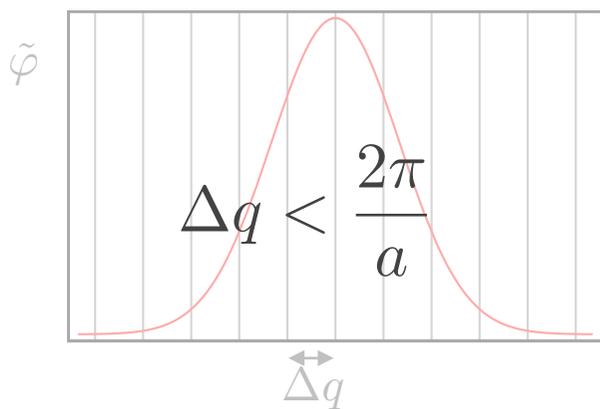
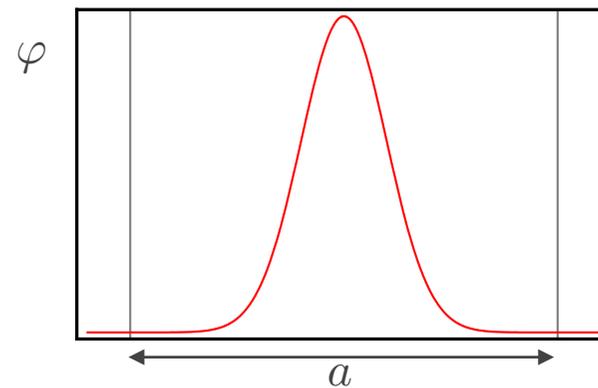


$$\Delta q < \frac{2\pi}{a}$$



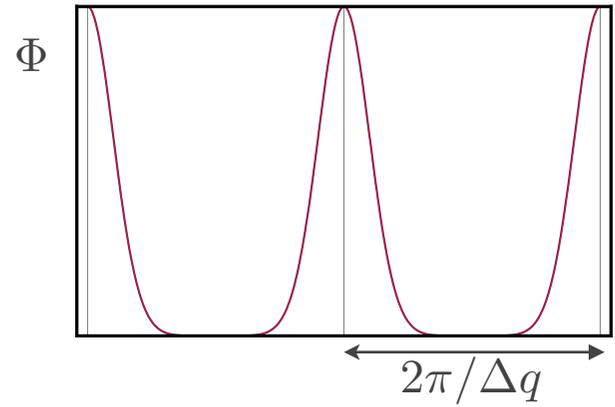
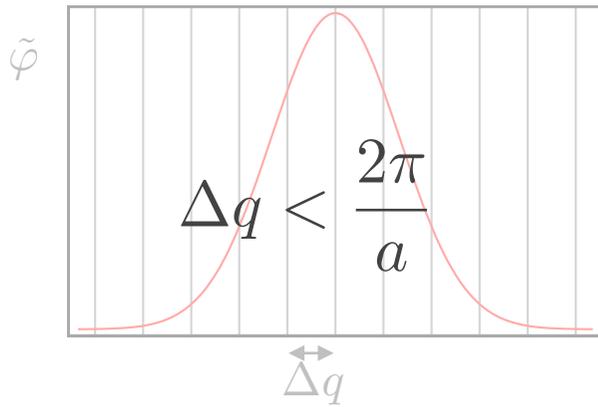
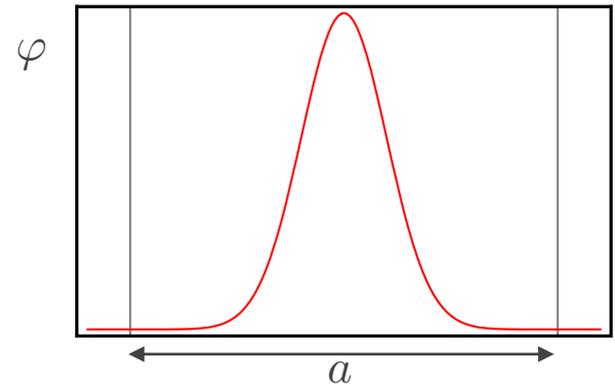
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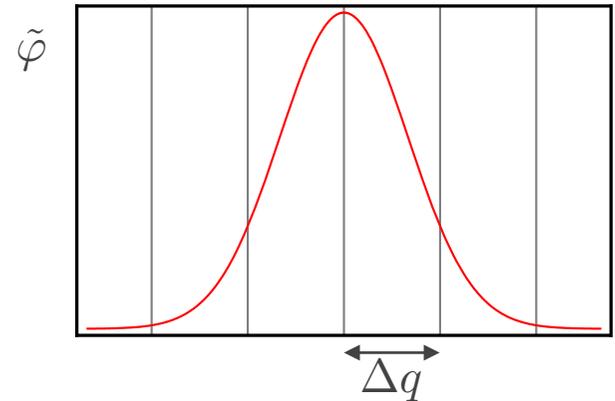


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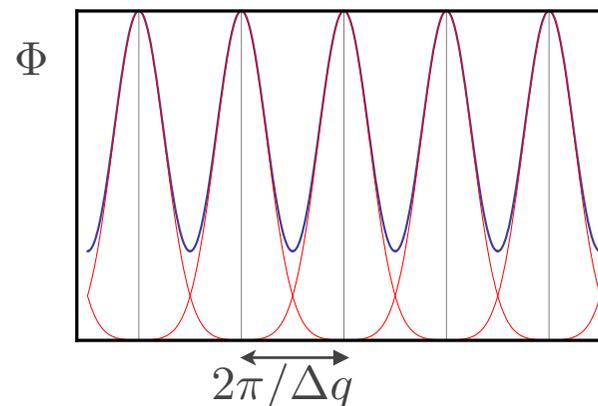
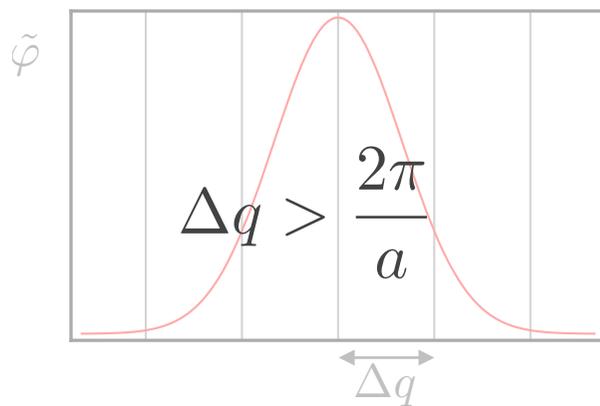
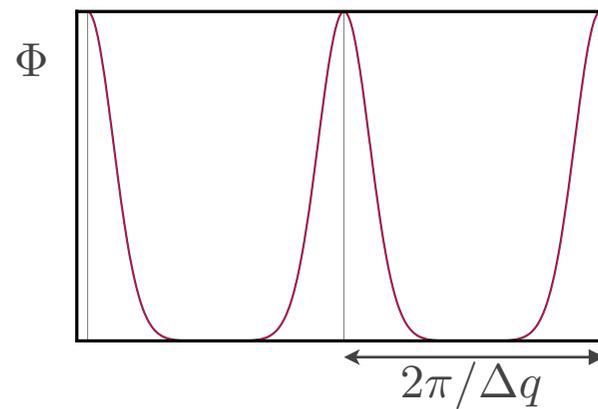
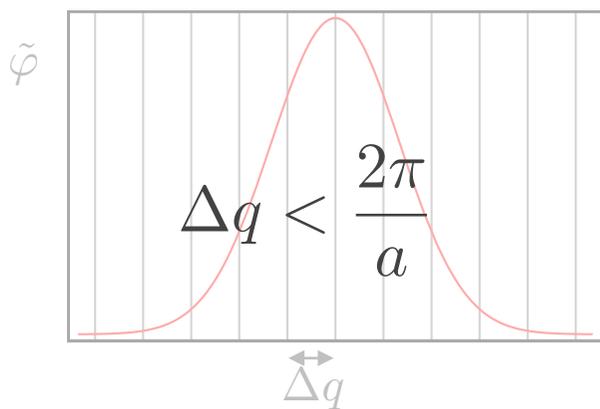
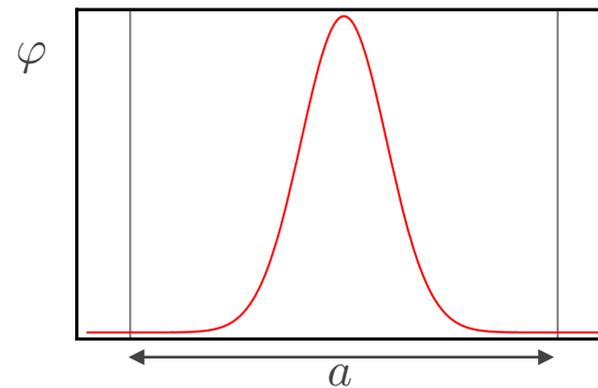


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# discrete Fourier transforms

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

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

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

# discrete Fourier transforms

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

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

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dFt

# properties of the dFt

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

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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

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# multivariate FFTs

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

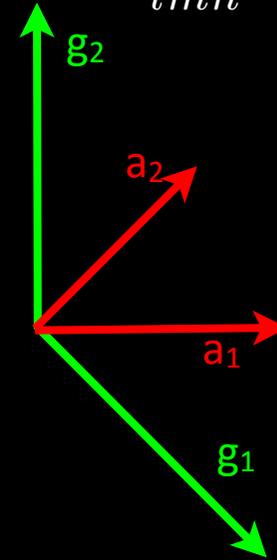
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$$\mathbf{G}_{pq s} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

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

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



## multivariate FFTs (II)

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

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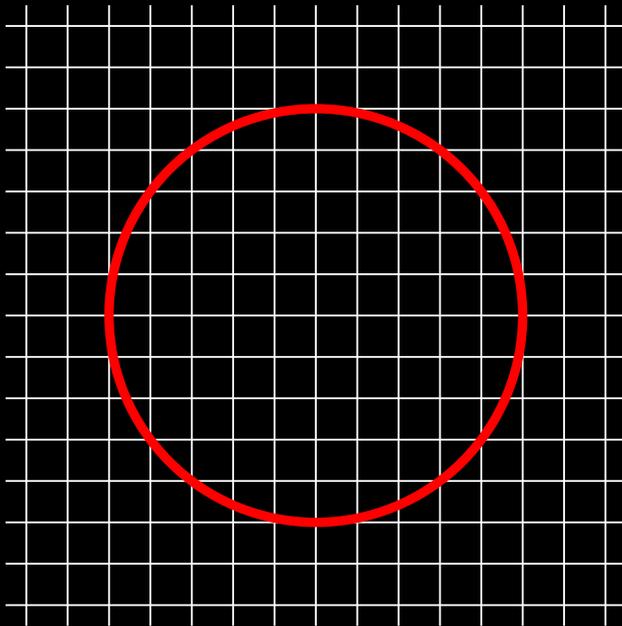
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$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

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

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- ☹ 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
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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)				

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

\* The systematic names and symbols for elements greater than 110 will be used until the approval of trivial 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

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5	Group 6																19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
6	Group 7																37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
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$$E_{cut} \sim Z^2$$

\* 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		4 Be Beryllium 9.012 182														10 Ne Neon 20.1797																			
3	11 Na Sodium 22.989 770		12 Mg Magnesium 24.3050														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)							
	98 Ce Cerium 140.116		99 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)									

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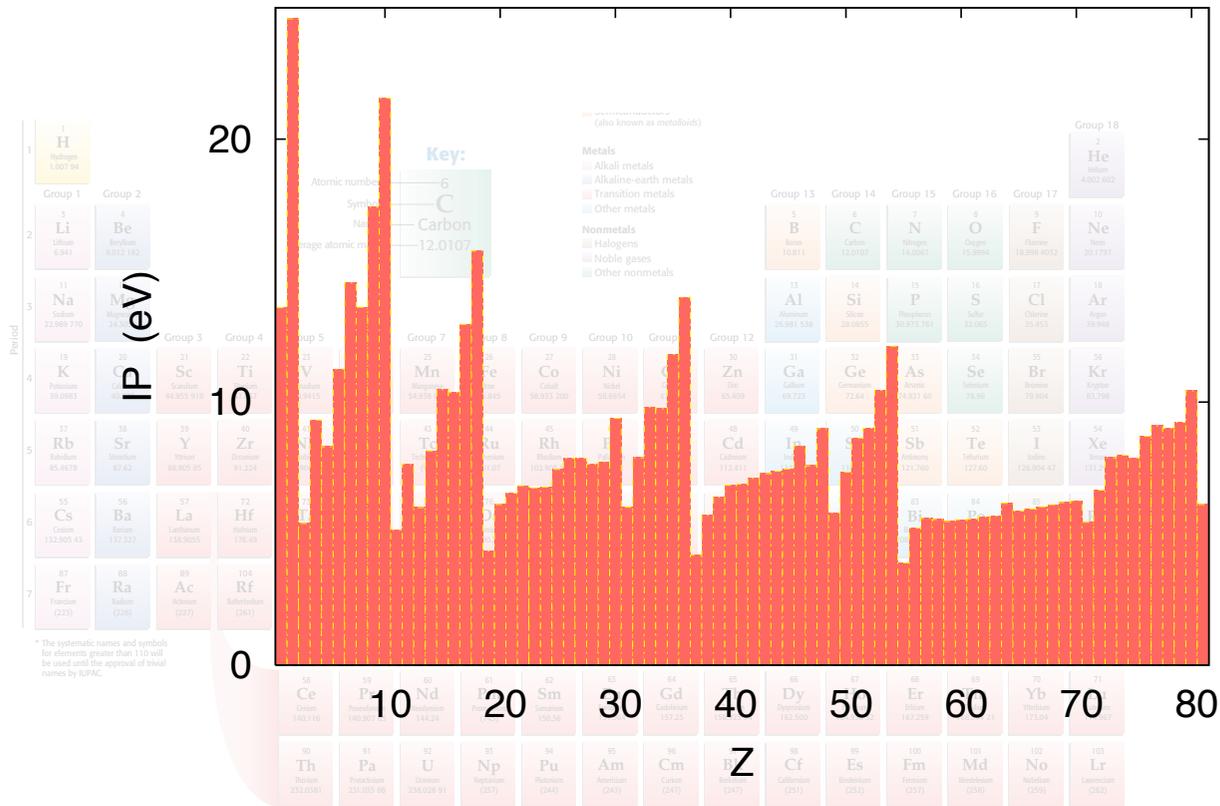
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$$E_{cut} \sim Z^2$$

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

# 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:

$\phi_{val}^{ps}$  is nodeless and smooth

# trashing core states: pseudopotentials

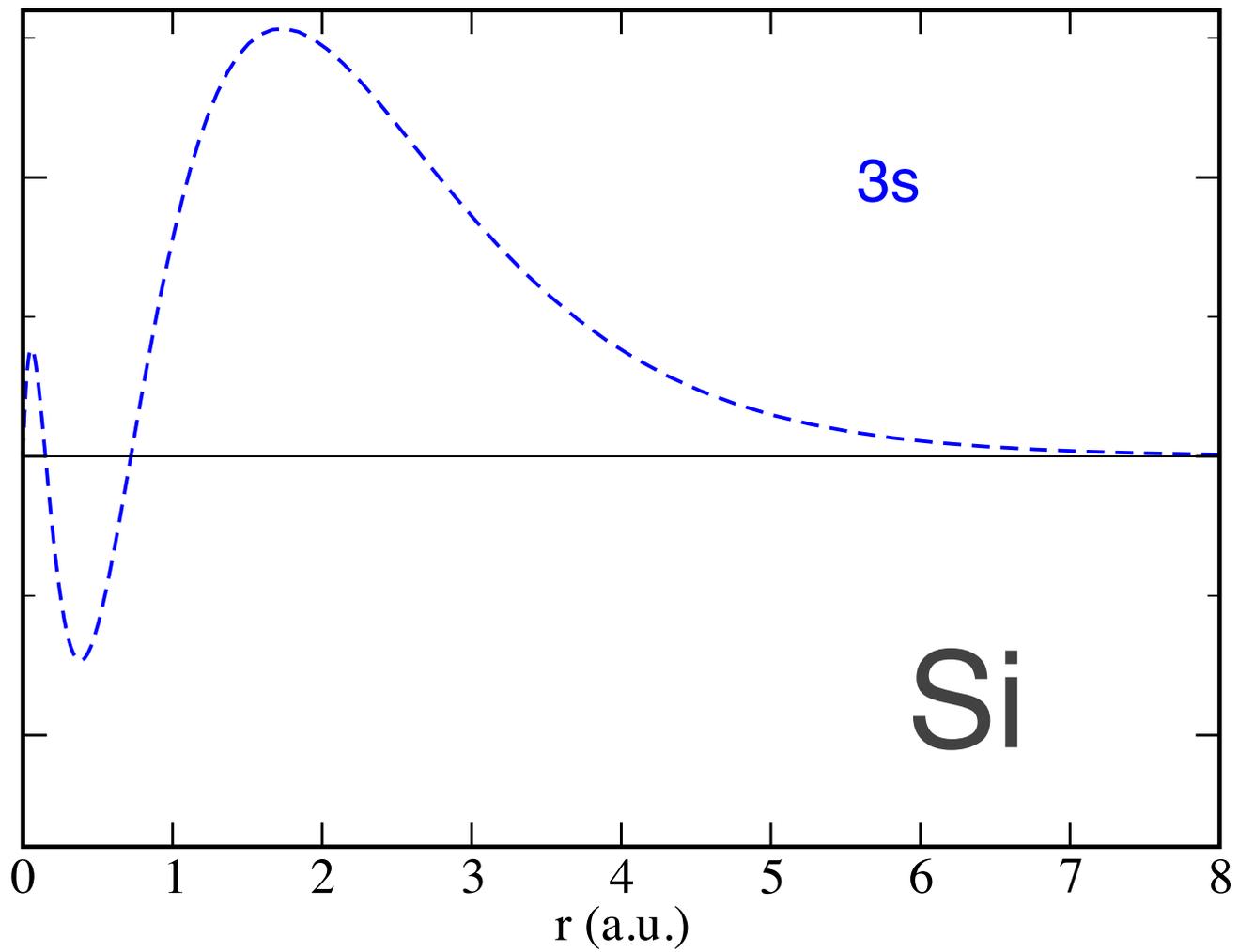
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

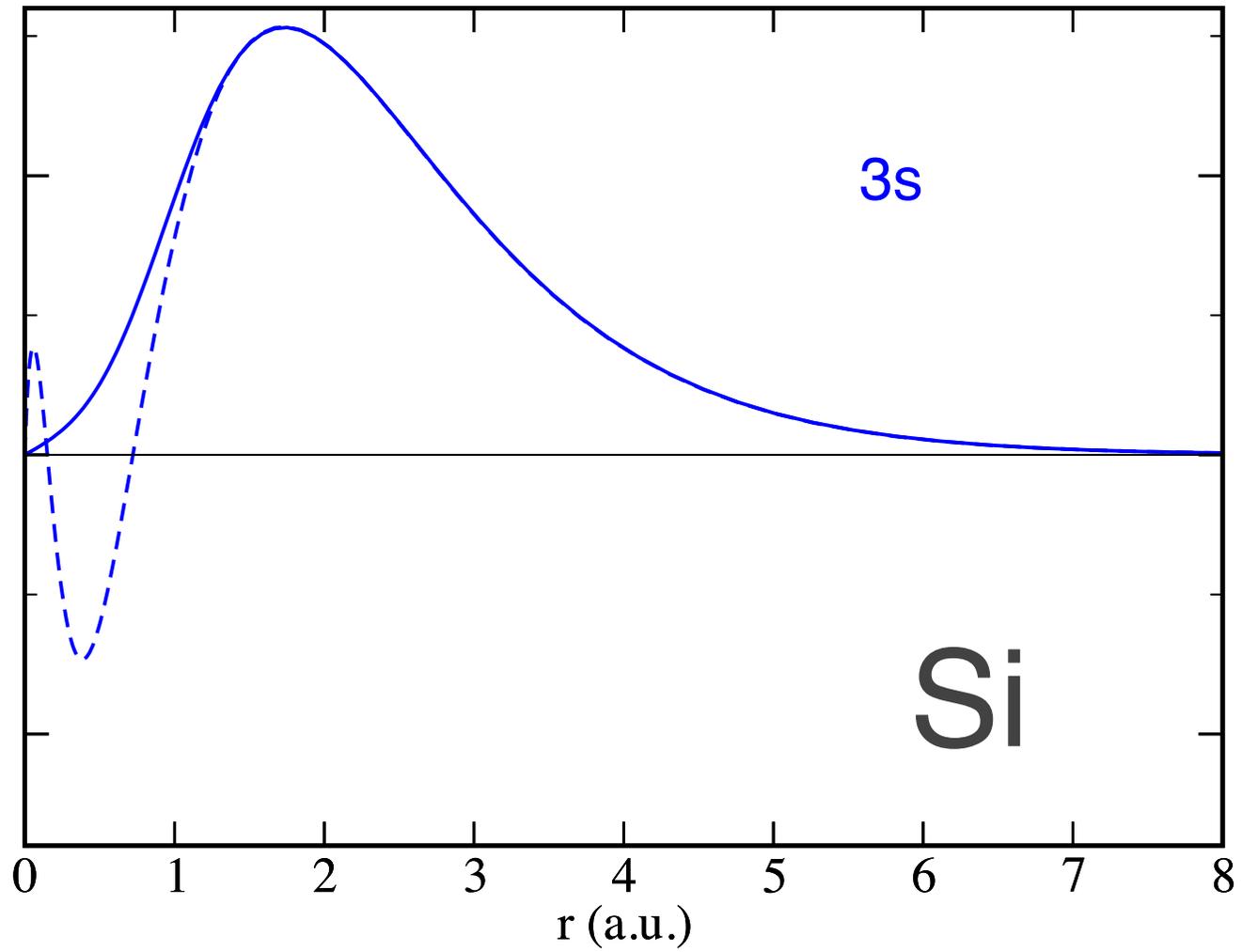
$\phi_{val}^{ps}$  is nodeless and smooth

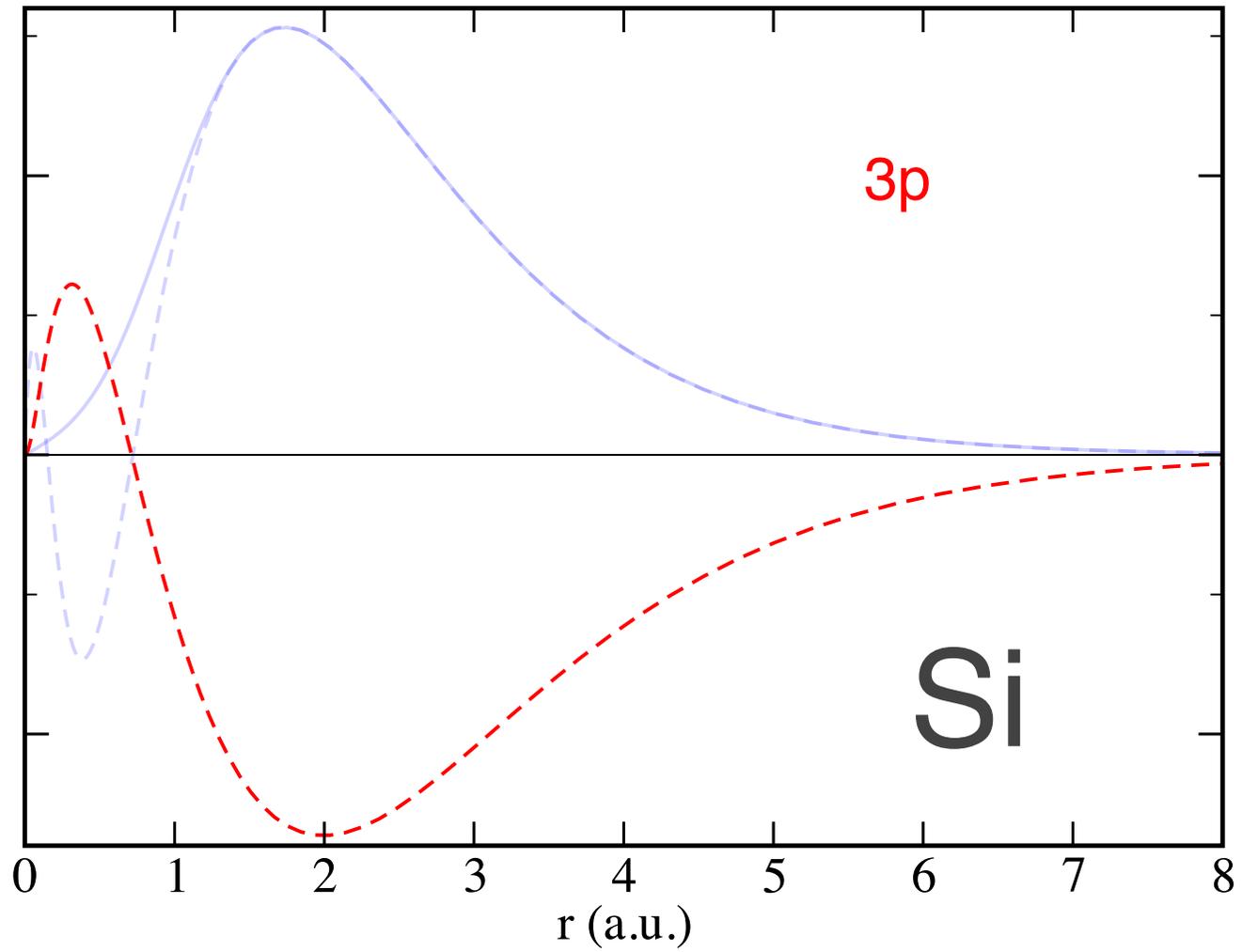
the chemical properties of the pseudo-atom are the same as those of the true atom:

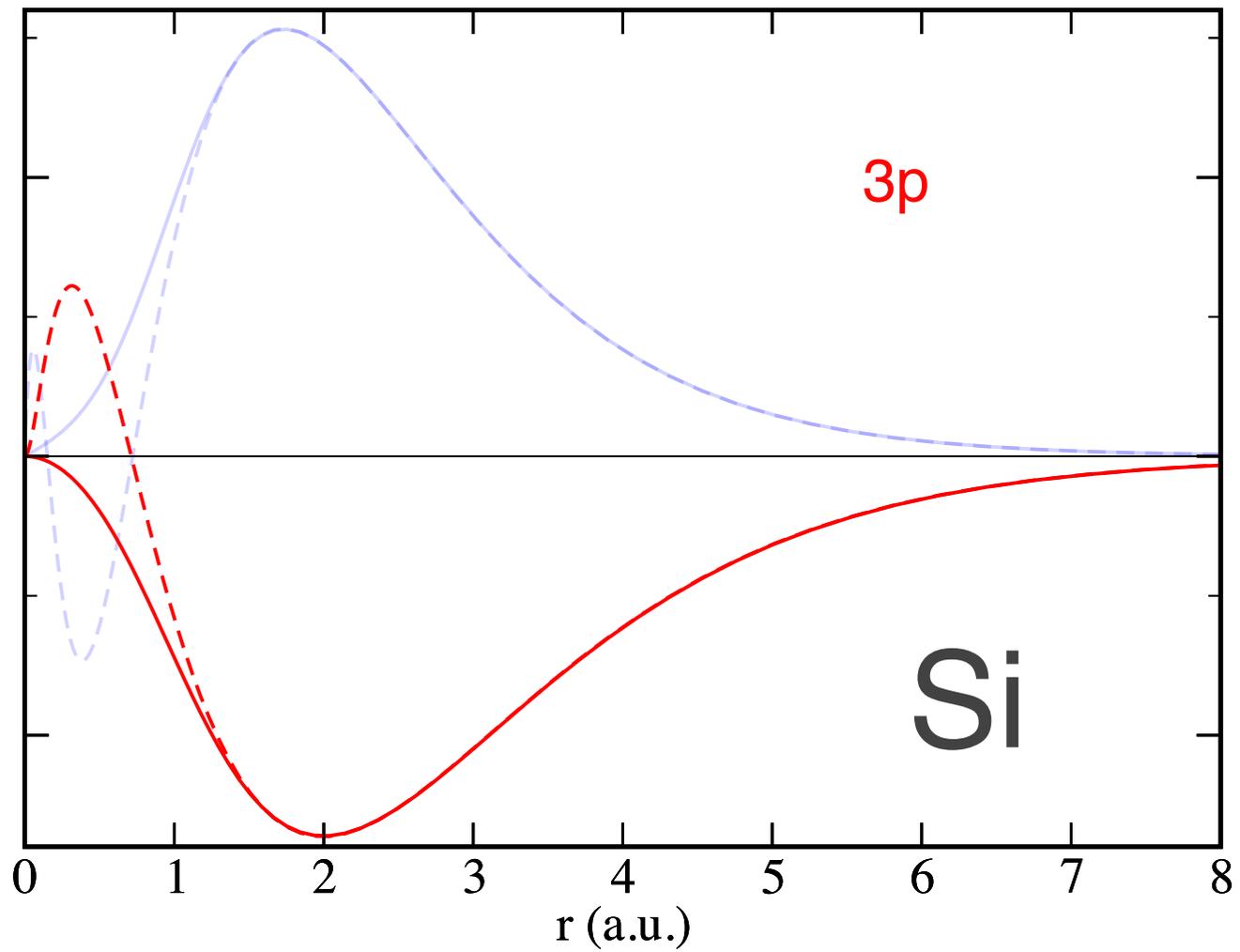
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

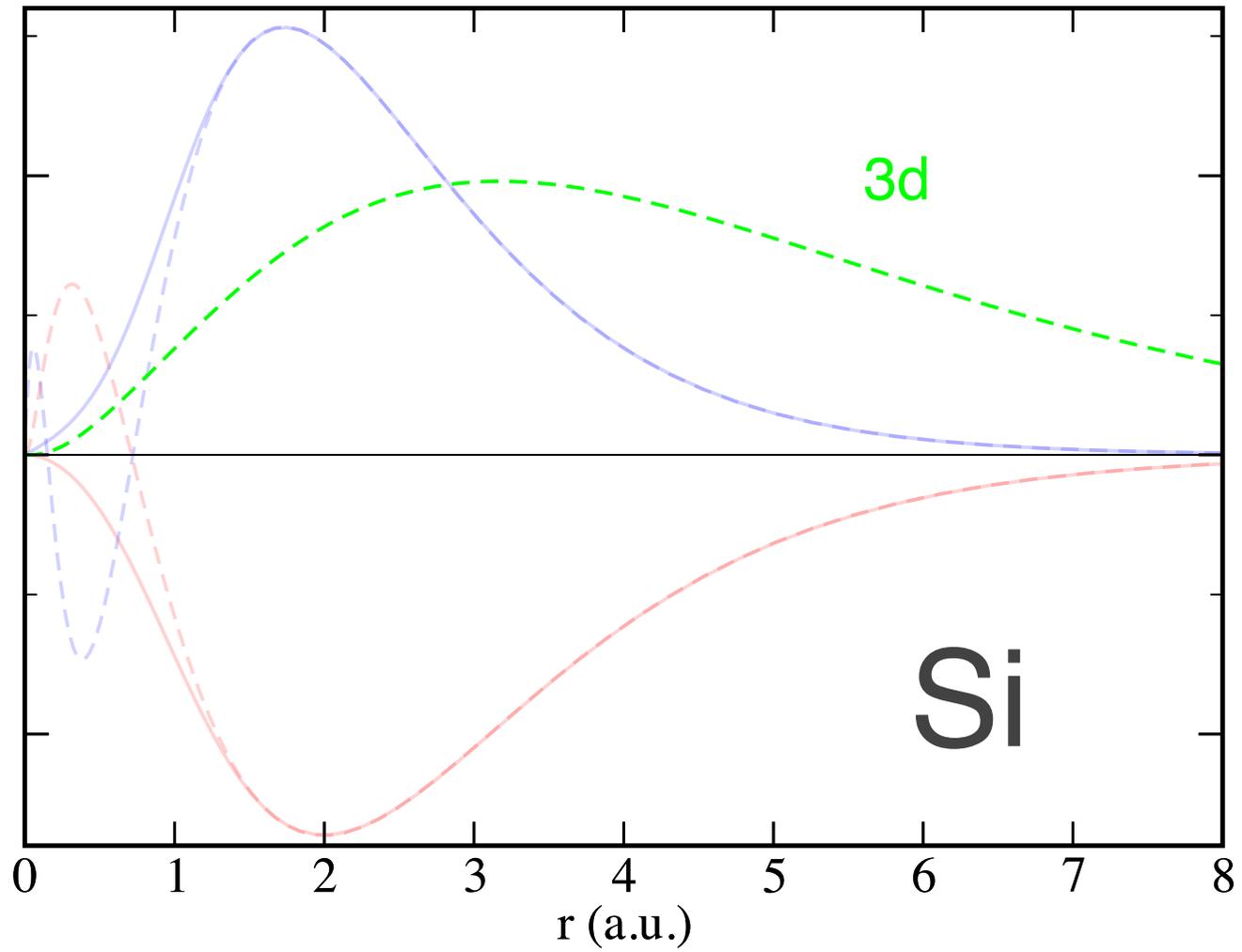
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for } r > r_c$$

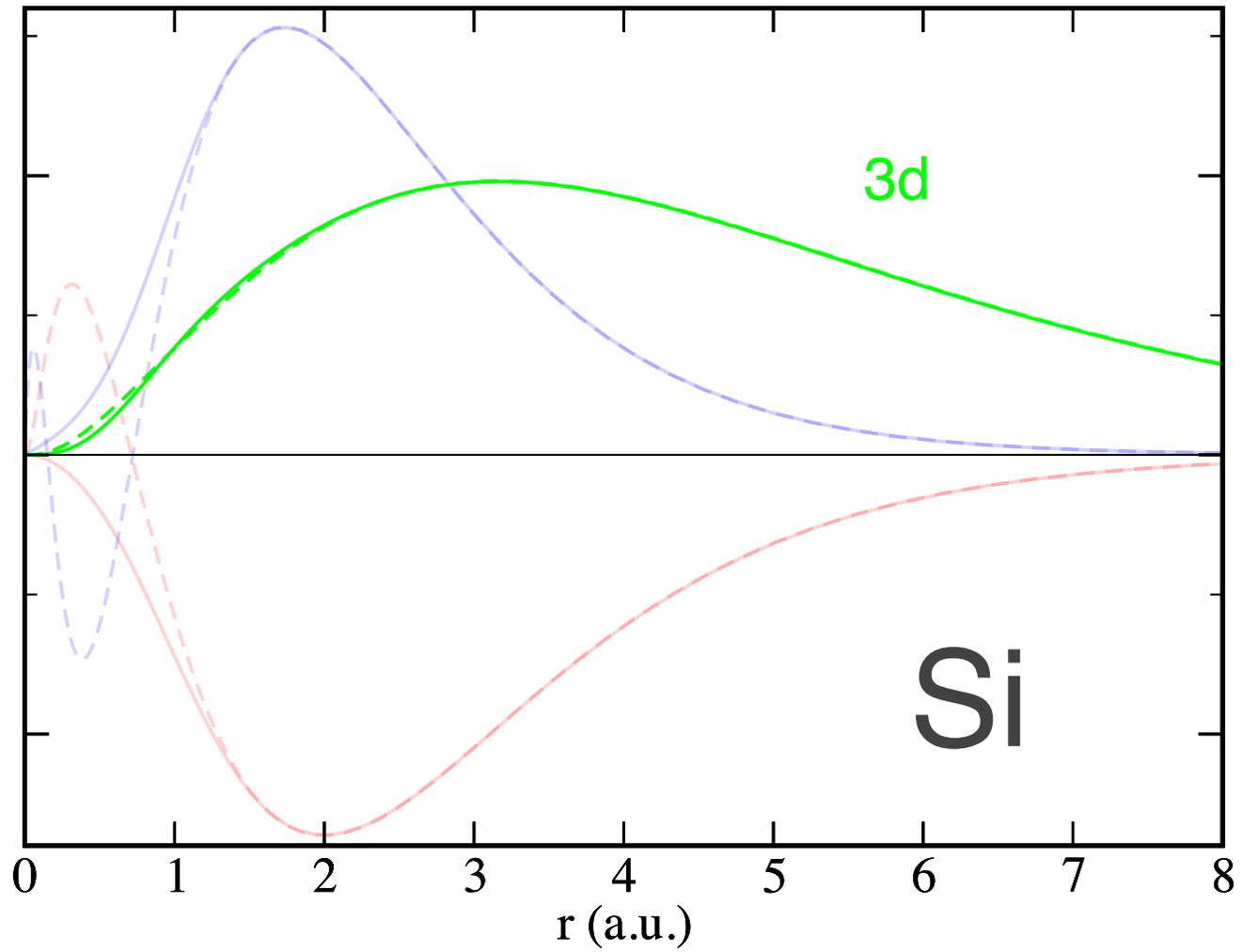




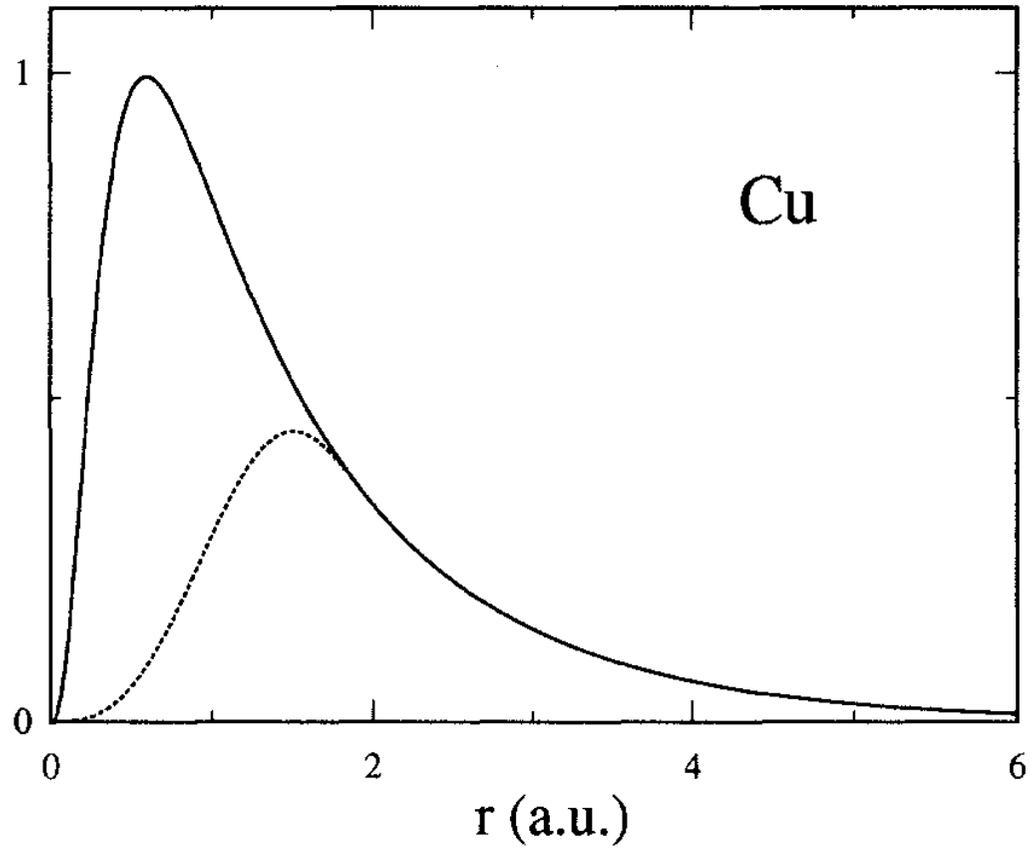




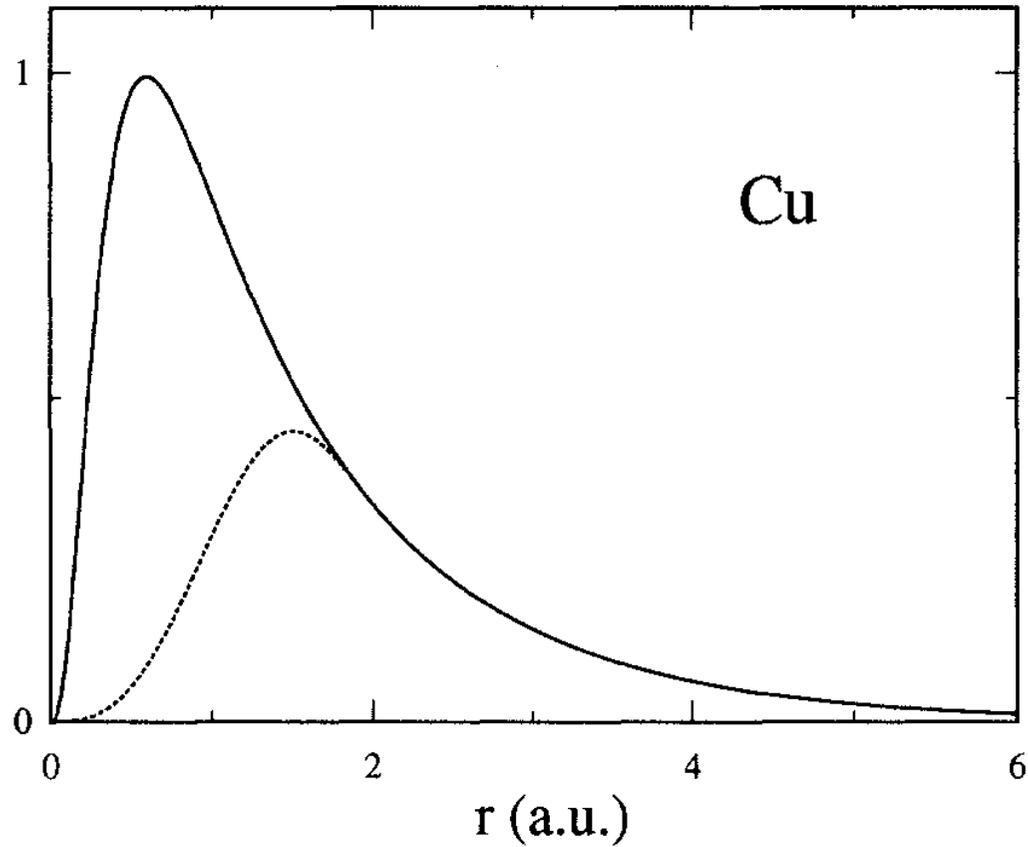




# US pseudopotentials



# 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