

modeling materials using quantum mechanics and digital computers

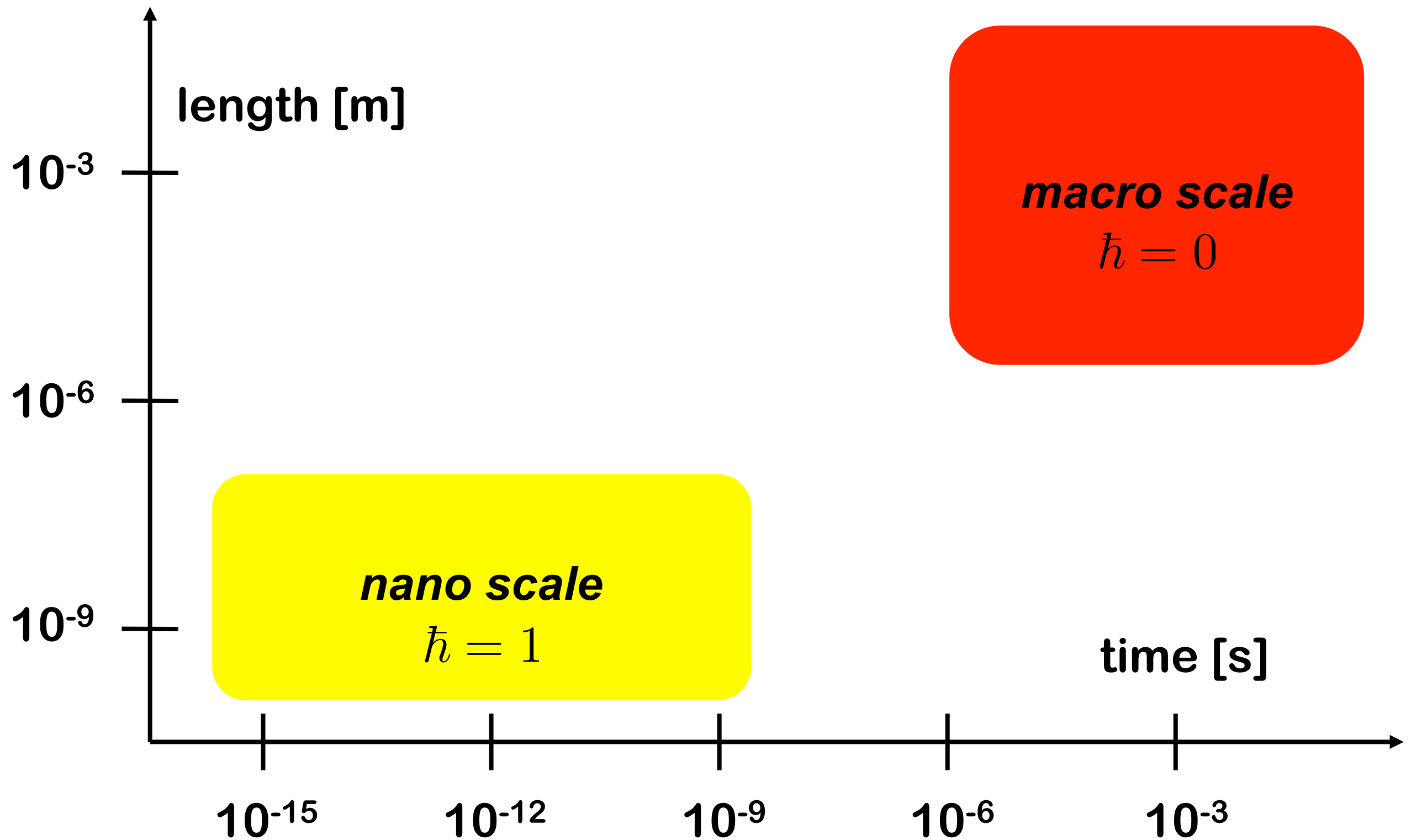
the plane-wave pseudo potential way

Stefano Baroni

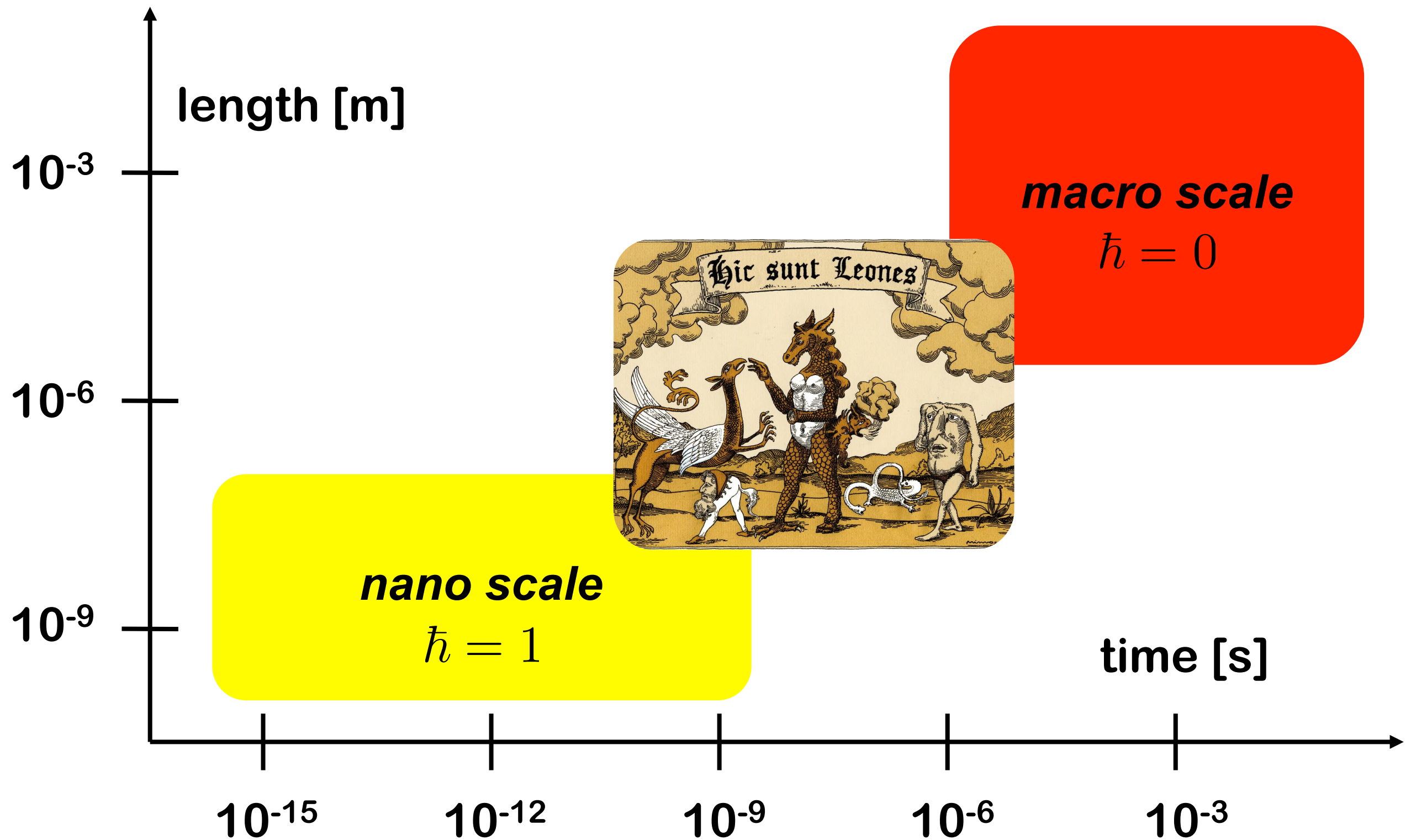
Scuola Internazionale Superiore di Studi Avanzati
Trieste - Italy

Lecture given at the *Advanced Workshop on High-Performance & High-Throughput Materials Simulations using QUANTUM ESPRESSO*,
the Abdus Salam International Centre for Theoretical Physics, Trieste, January 16- 27, 2017

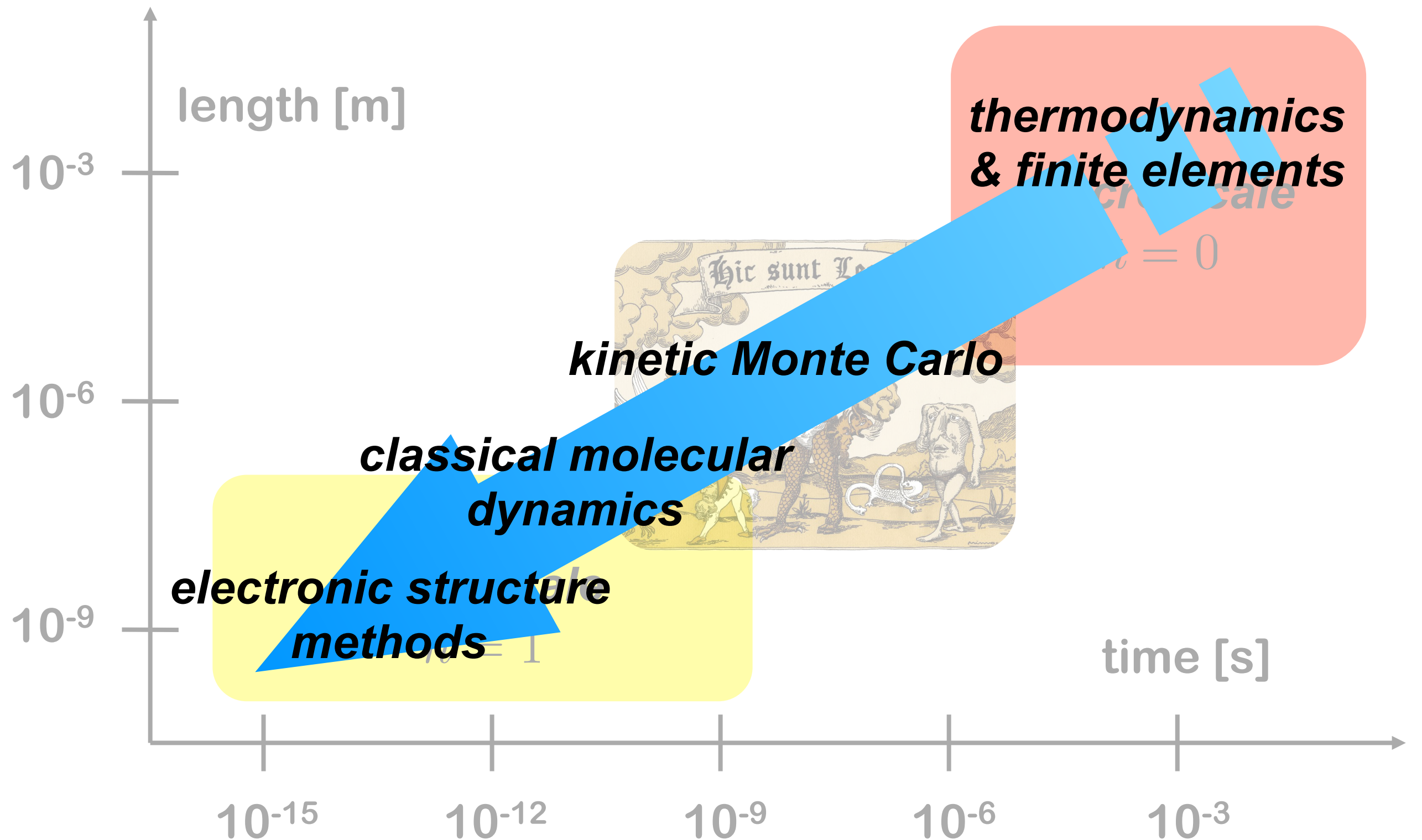
the saga of time and length scales



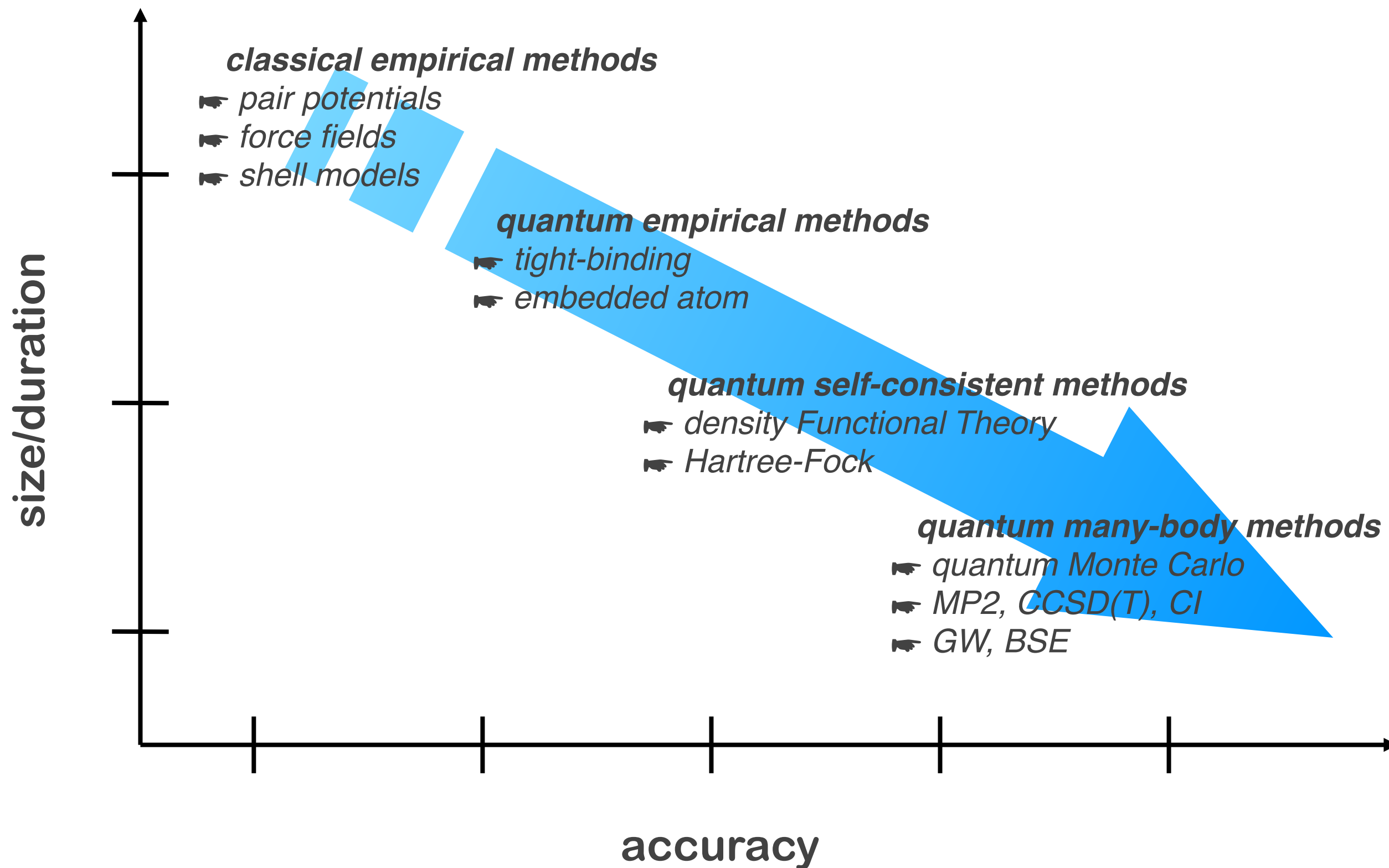
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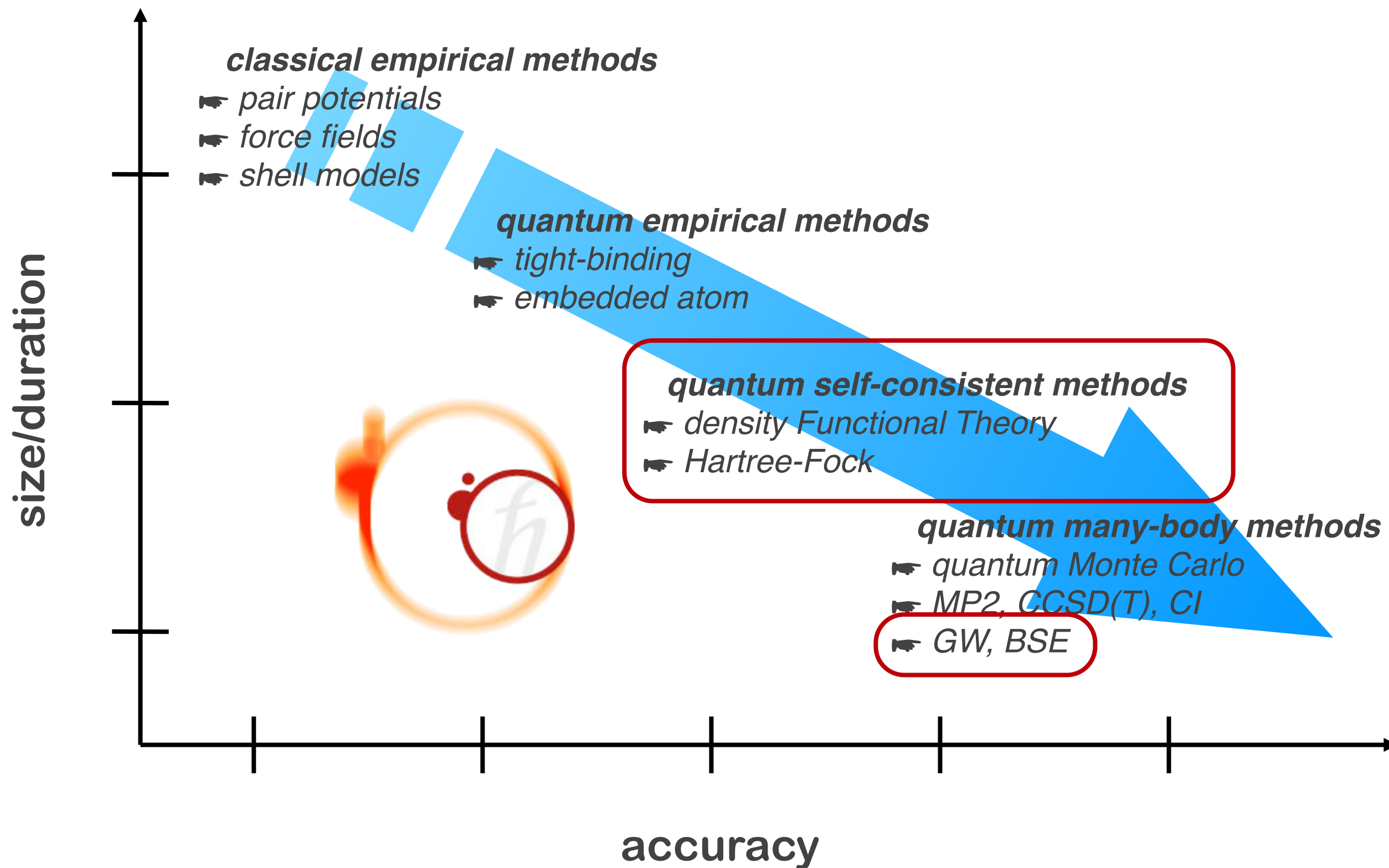
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size vs. accuracy



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ab initio calculations: what, why, when, how

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- what:** simulate the properties of materials using Schrödinger and Maxwell equations and chemical composition as the *sole* input ingredients
- why:** they are accurate and *unbiasedly 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 *unbiasedly 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

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

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

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

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density-functional theory

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 **DFT**

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

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**Kohn-Sham
equations**

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

functionals

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

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examples:

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

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

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

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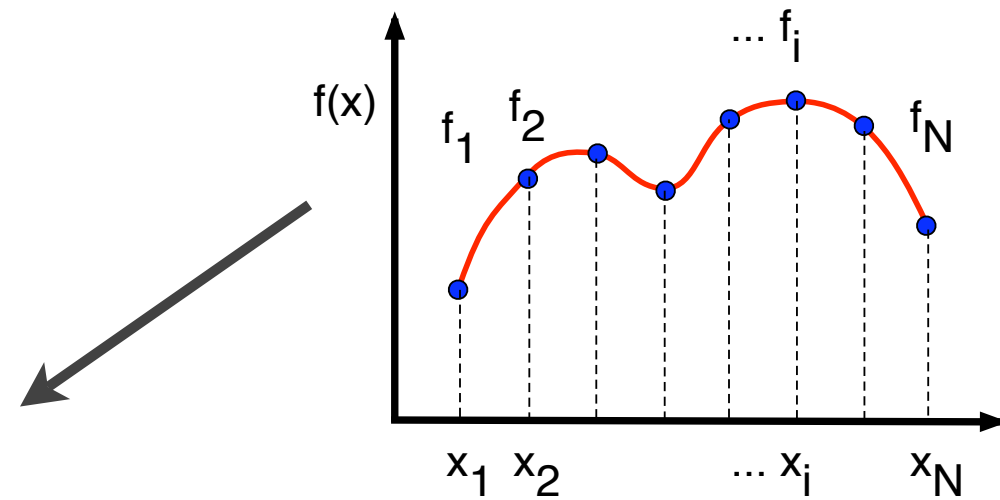
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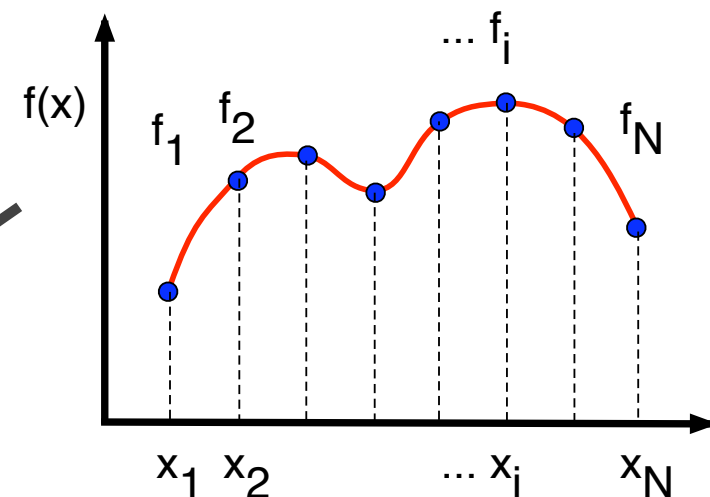
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$$G[f] \approx g(c_1, c_2, \dots, c_N)$$



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

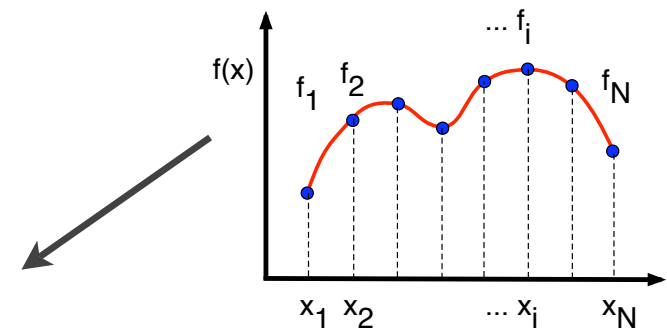
functional derivatives

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

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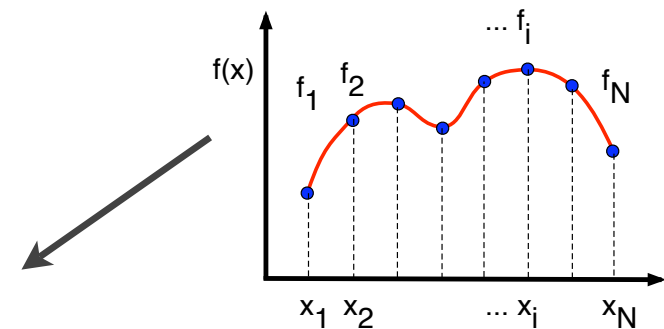
$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \approx \frac{1}{h} \frac{\partial g}{\partial f_i}$$



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

the Hellmann-Feynman theorem

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

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

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

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

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

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properties:

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

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

consequences:

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

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

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

exchange-correlation energy functionals

- ▶ **LDA** (Kohn & Sham, 60's)

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

- ▶ **GGA** (Becke, Perdew, *et al.*, 80's)

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

- ▶ **DFT+U** (Anisimov *et al.*, 90's)

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

- ▶ **hybrids** (Becke *et al.*, 90's)

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

- ▶ **meta-GGA** (Perdew, early 2K's)

$$E_{mGGA} = \int \rho(\mathbf{r}) \times \\ \epsilon_{mGGA}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \tau_s(\mathbf{r})) d\mathbf{r} \\ \tau_s(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla^2 \psi_i(\mathbf{r})|^2$$

- ▶ **VdW** (Langreth & Lundqvist, 2K's)

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

▶ ...

KS equations from functional minimization

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

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

solving the Kohn-Sham equations

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

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

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

basis set requirements

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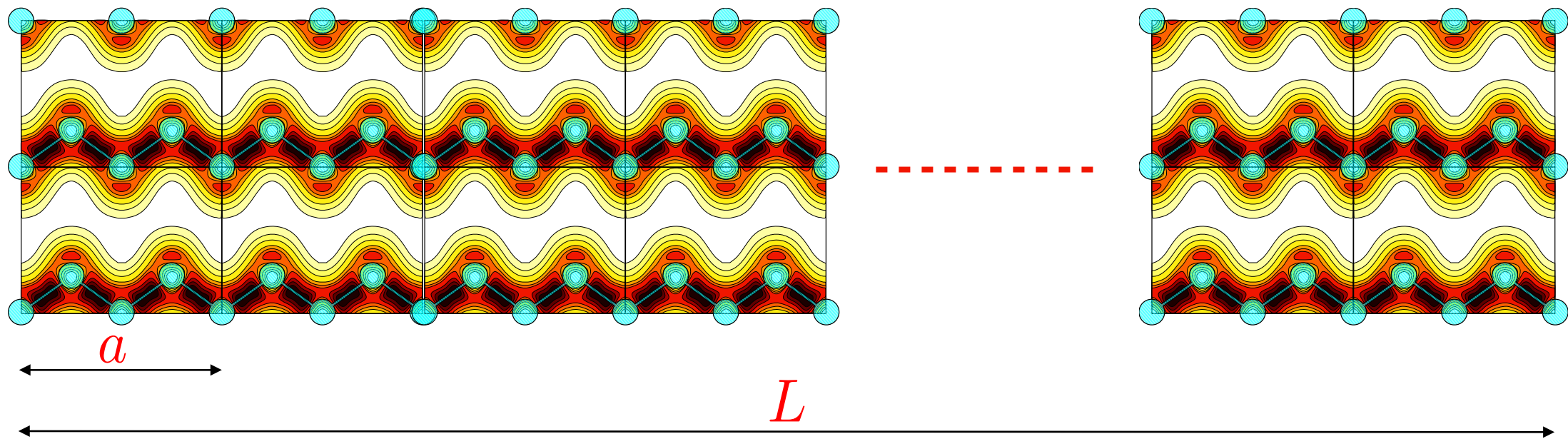
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- ▶ orthogonality is a plus

the Bloch theorem & plane waves

infinite crystals



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

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

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

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

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

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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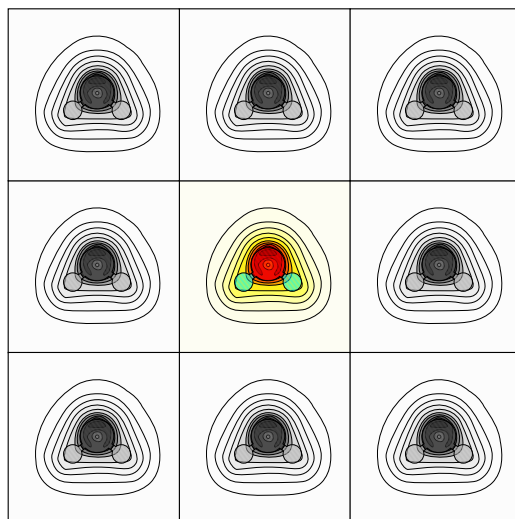
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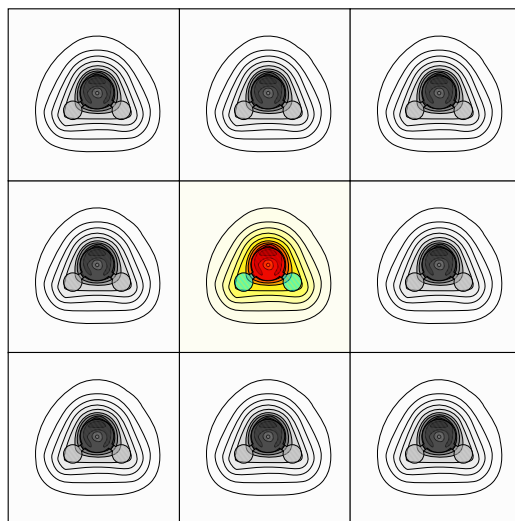
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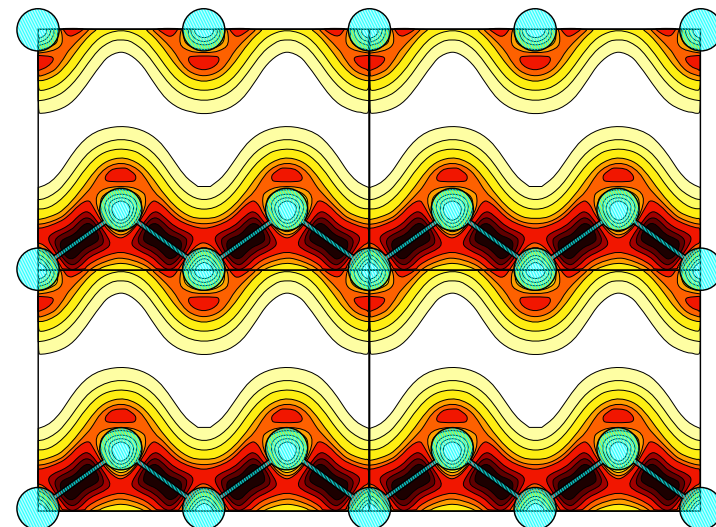
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finite systems ($\ell = a$)



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infinite crystals ($\ell = L$)



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

PWs: pros & cons

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- 😞 uniform spatial resolution (no core states!)

treating core states

Period	1	Group 1		Group 2								Group 13										Group 14		Group 15		Group 16		Group 17		Group 18								
	2	3		4												5		6		7		8		9		10												
	3	11		12												13		14		15		16		17		18												
	4	19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36		
	5	37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54		
	6	55		56		57		72		73		74		75		76		77		78		79		80		81		82		83		84		85		86		
	7	87		88		89		104		105		106		107		108		109		110		111		112		113		114		115								
	H		Li		Be												B		C		N		O		F		Ne											
	Hydrogen		Lithium		Beryllium												Boron		Carbon		Nitrogen		Oxygen		Fluorine		Neon											
	1.007 94		6.941		9.012 182												10.811		12.0107		14.0067		15.9994		18.998 4032		20.1797											
			Na		Mg												Al		Si		P		S		Cl		Ar											
	Sodium		Magnesium												Aluminum		Silicon		Phosphorus		Sulfur		Chlorine		Argon													
	22.989 770		24.3050												26.981 538		28.0855		30.973 761		32.065		35.453		39.948													
			K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
	Potassium		Calcium		Scandium		Titanium		Vanadium		Chromium		Manganese		Iron		Cobalt		Nickel		Copper		Zinc		Gallium		Germanium		Arsenic		Selenium		Bromine		Krypton			
	39.0983		40.078		44.955 910		47.867		50.9415		51.9961		54.938 049		55.845		58.933 200		58.6934		63.546		65.409		69.723		72.64		74.921 60		78.96		79.904		83.798			
			Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe	
	Rubidium		Strontium		Yttrium		Zirconium		Niobium		Molybdenum		Technetium		Ruthenium		Rhodium		Palladium		Silver		Cadmium		Indium		Tin		Antimony		Tellurium		Iodine		Xenon			
	85.4678		87.62		88.905 85		91.224		92.906 38		95.94		(98)		101.07		102.905 50		106.42		107.8682		112.411		114.818		118.710		121.760		127.60		126.904 47		131.293			
			Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn	
	Cesium		Barium		Lanthanum		Hafnium		Tantalum		Tungsten		Rhenium		Osmium		Iridium		Platinum		Gold		Mercury		Thallium		Lead		Bismuth		Polonium		Astatine		Radon			
	132.905 43		137.327		138.9055		178.49		180.9479		183.84		186.207		190.23		192.217		195.078		196.966 55		200.59		204.3833		207.2		208.980 38		(209)		(210)		(222)			
			Fr		Ra		Ac		Rf		Db		Sg		Bh		Hs		Mt		Ds		Uuu*		Uub*		Uut*		Uuq*		Uup*							
	Francium		Radium		Actinium		Rutherfordium		Dubnium		Seaborgium		Bohrium		Hassium		Meitnerium		Darmstadtium		Ununium		Ununbium		Ununtrium		Ununquadium		Ununpentium									
	(223)		(226)		(227)		(261)		(262)		(266)		(264)		(277)		(268)		(281)		(272)		(285)		(284)		(289)		(288)									
			Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu									
			Cerium		Praseodymium		Neodymium		Promethium		Samarium		Europium		Gadolinium		Terbium		Dysprosium		Holmium		Erbium		Thulium		Ytterbium		Lutetium									
			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									
			Thorium		Protactinium		Uranium		Neptunium		Plutonium		Americium		Curium		Berkelium		Californium		Einsteinium		Fermium		Mendelevium		Nobelium		Lawrencium									
			232.0381		231.035 88		238.028 91		(237)		(244)		(243)		(247)		(247)		(251)		(252)		(257)		(258)		(259)		(262)									

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treating core states

Period	1	1 H Hydrogen 1.007 94																2 He Helium 4.002 602																			
	2	Group 1 3 Li Lithium 6.941		Group 2 4 Be Beryllium 9.012 182																		Group 13 5 B Boron 10.811		Group 14 6 C Carbon 12.0107		Group 15 7 N Nitrogen 14.0067		Group 16 8 O Oxygen 15.9994		Group 17 9 F Fluorine 18.998 4032		Group 18 10 Ne Neon 20.1797					
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	4	19 K Potassium 39.0983		20 Ca Calcium 40.078		Group 3 21 Sc Scandium 44.955 910		Group 4 22 Ti Titanium 47.867		Group 5 23 V Vanadium 50.9415		Group 6 24 Cr Chromium 51.9961		Group 7 25 Mn Manganese 54.938 049		Group 8 26 Fe Iron 55.845		Group 9 27 Co Cobalt 58.933 200		Group 10 28 Ni Nickel 58.6934		Group 11 29 Cu Copper 63.546		Group 12 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 131.293	
	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 192.217		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* Unbium (285)		113 Uut* Ununtrium (284)		114 Uuq* Ununquadium (289)		115 Uup* Ununpentium (288)							
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					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						
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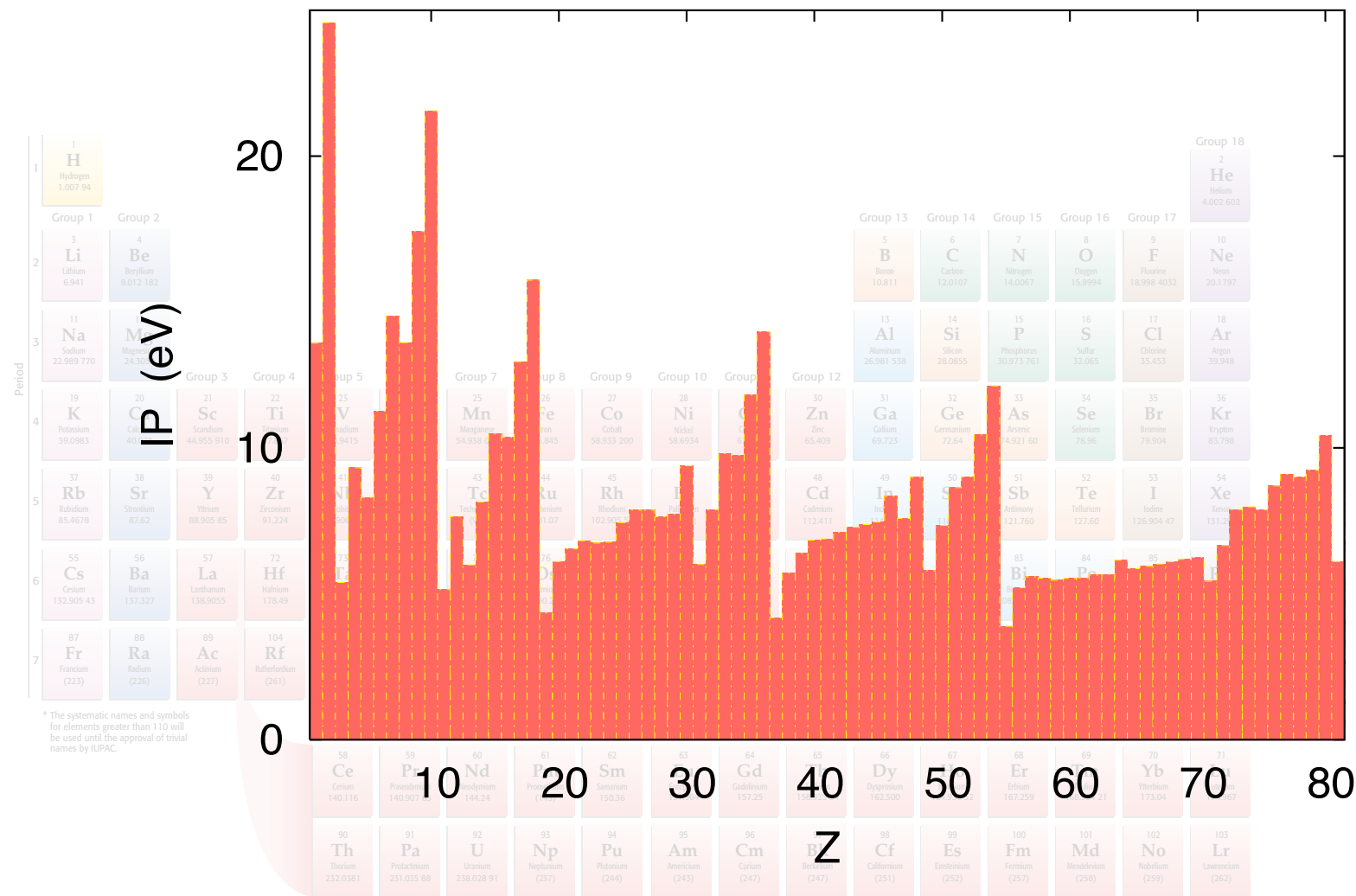
Period	1																	Group 18	
																		Group 18	
	2																	Group 18	
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$$\phi_{val}^{ps}$$

is nodeless and smooth

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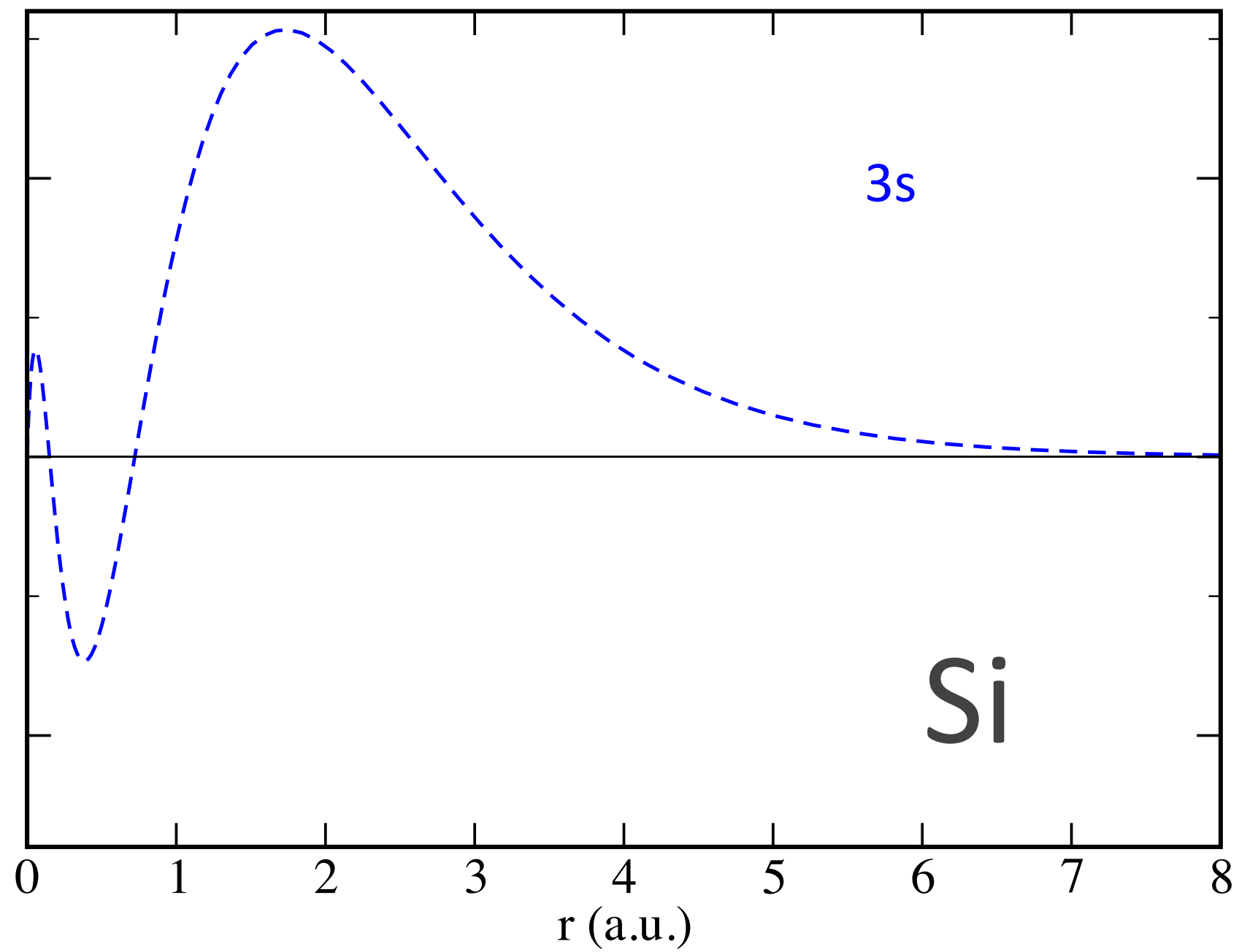
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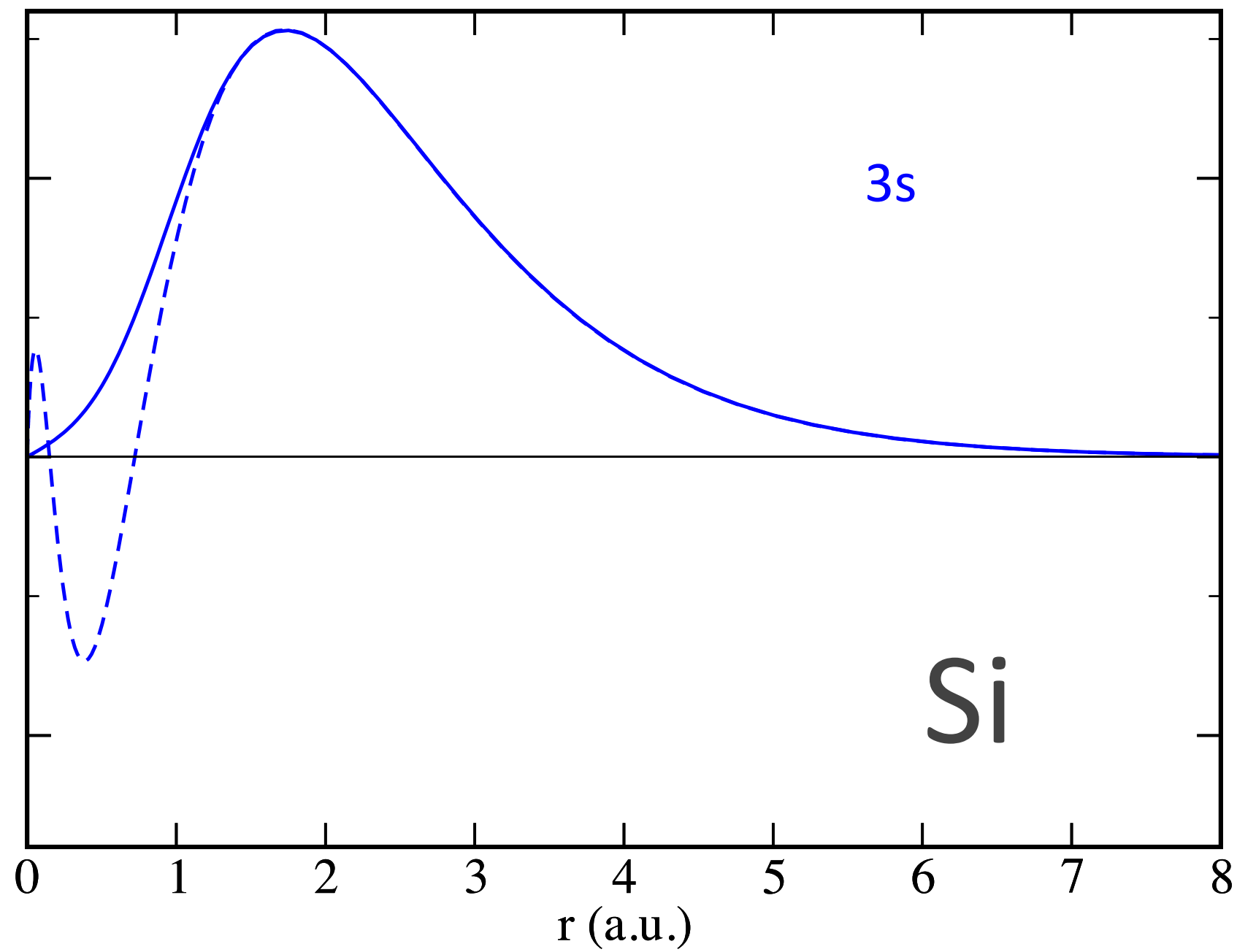
ϕ_{val}^{ps} is nodeless and smooth

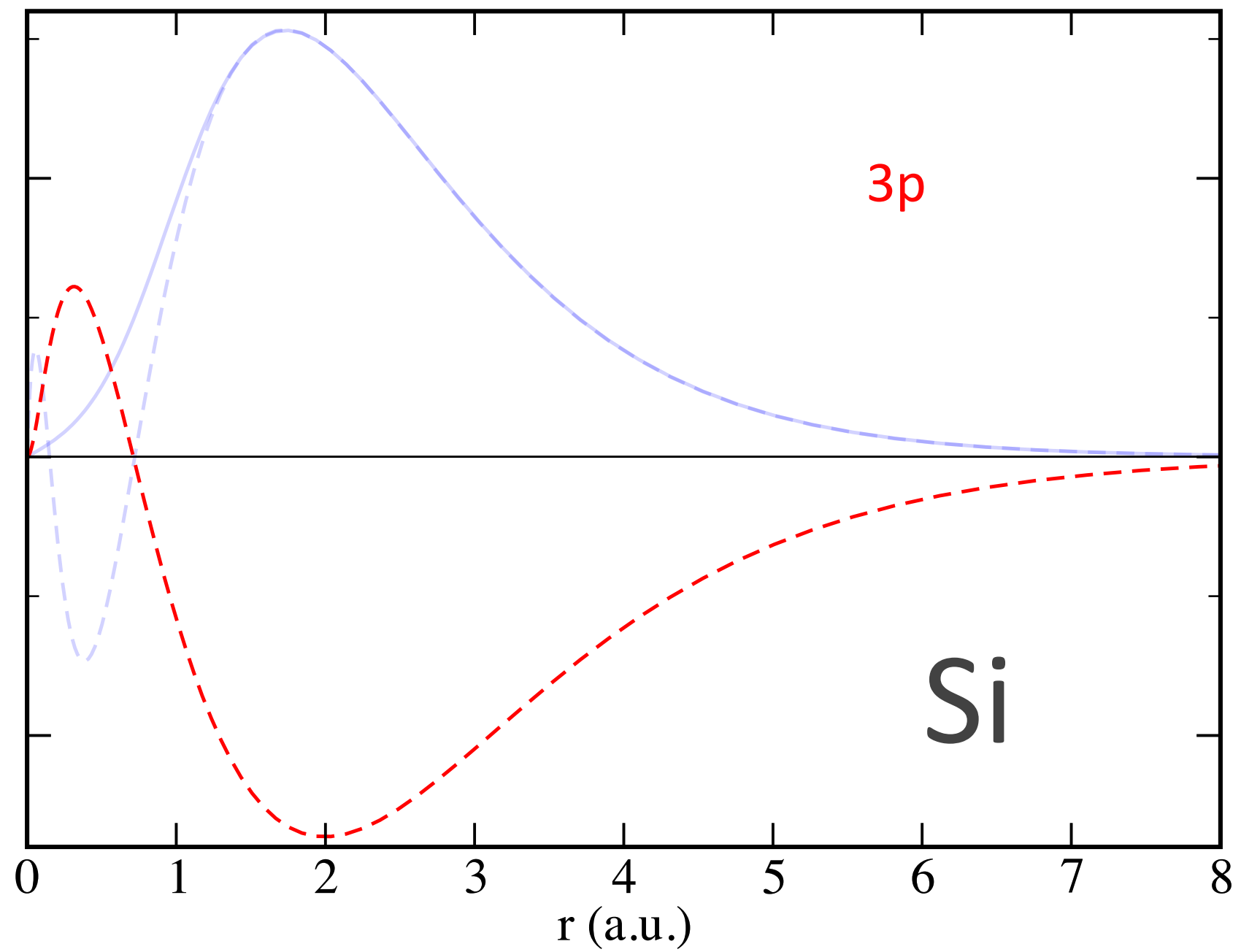
the chemical properties of the pseudo-atom are the same as those of the true atom:

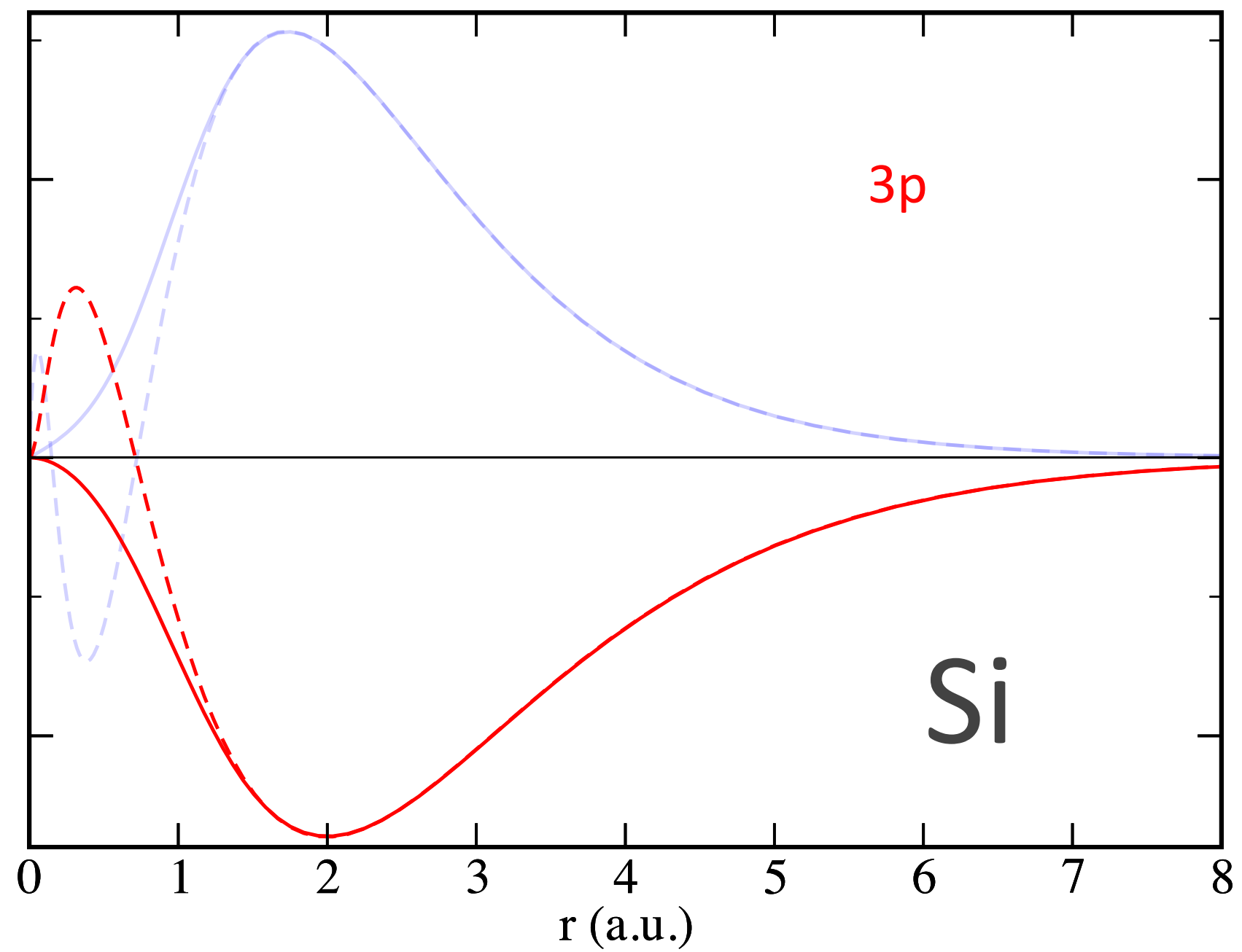
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

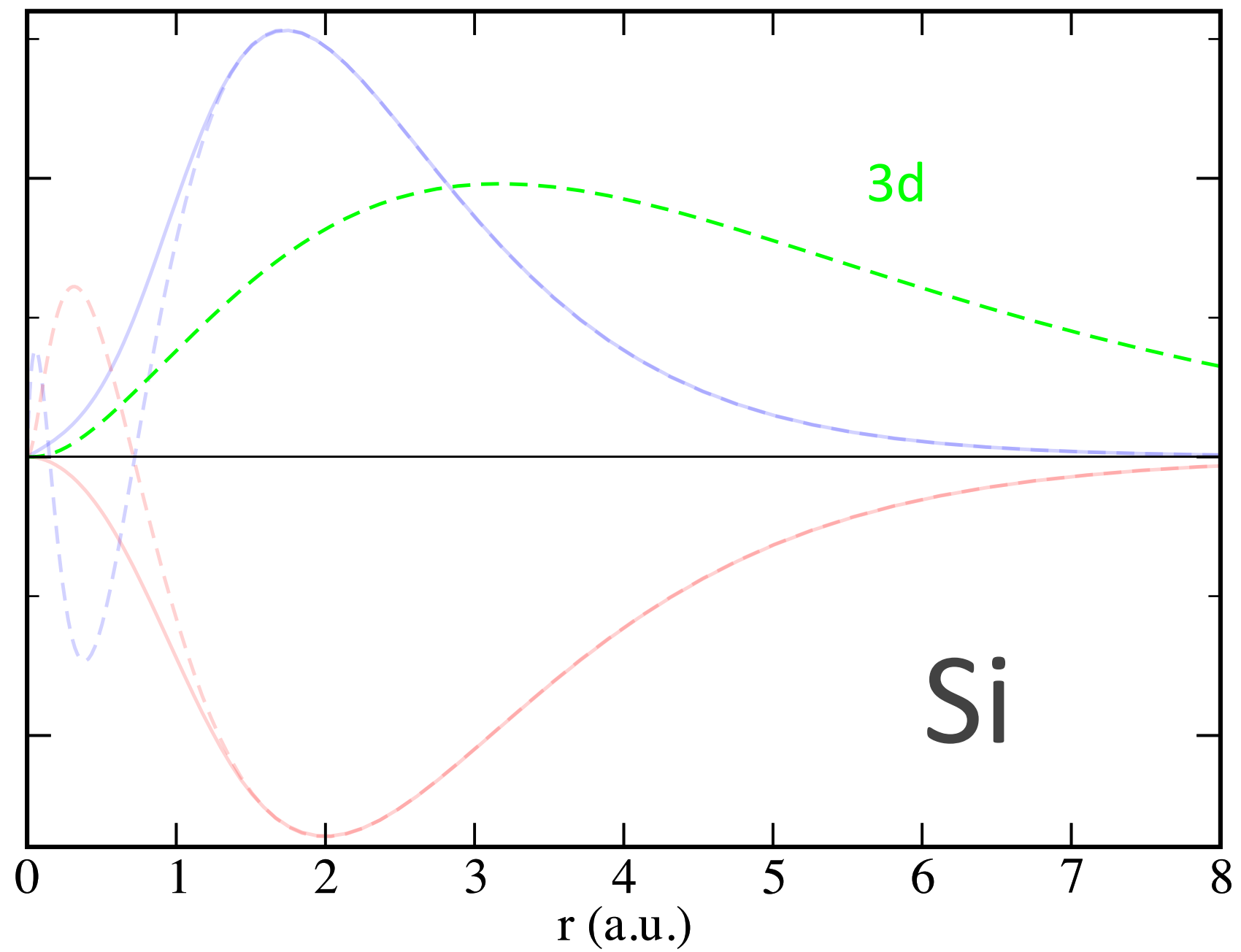
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for} \quad r > r_c$$

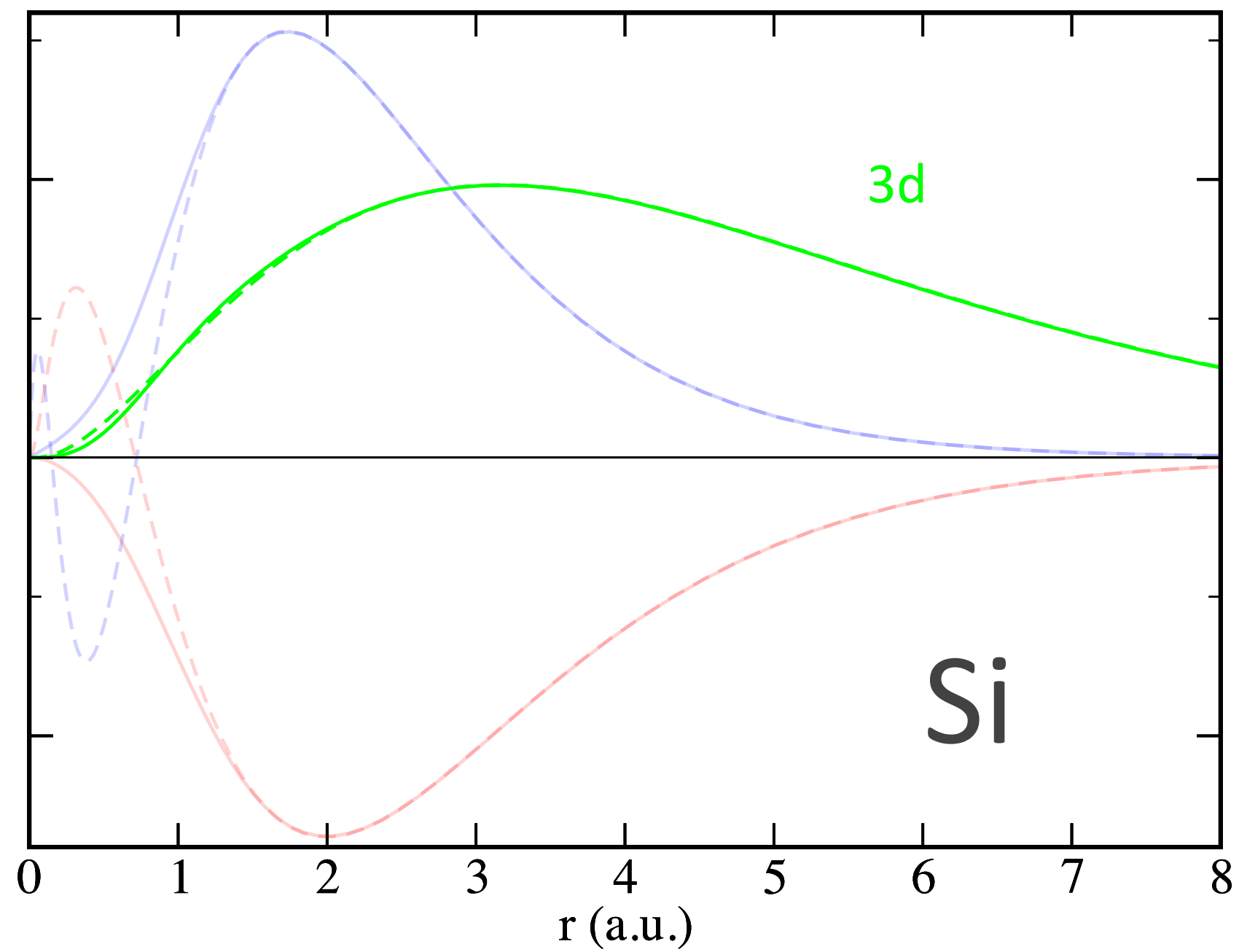




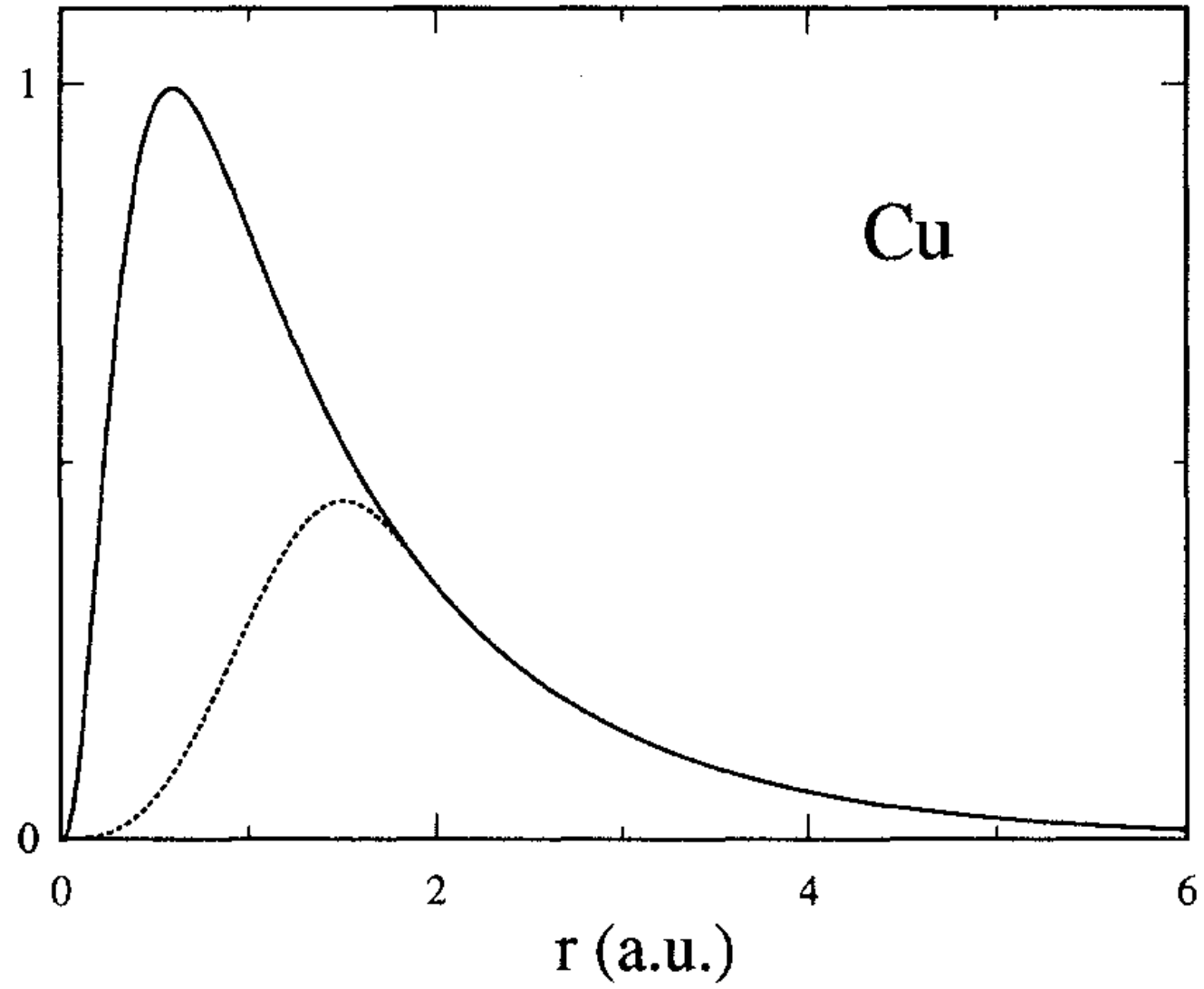




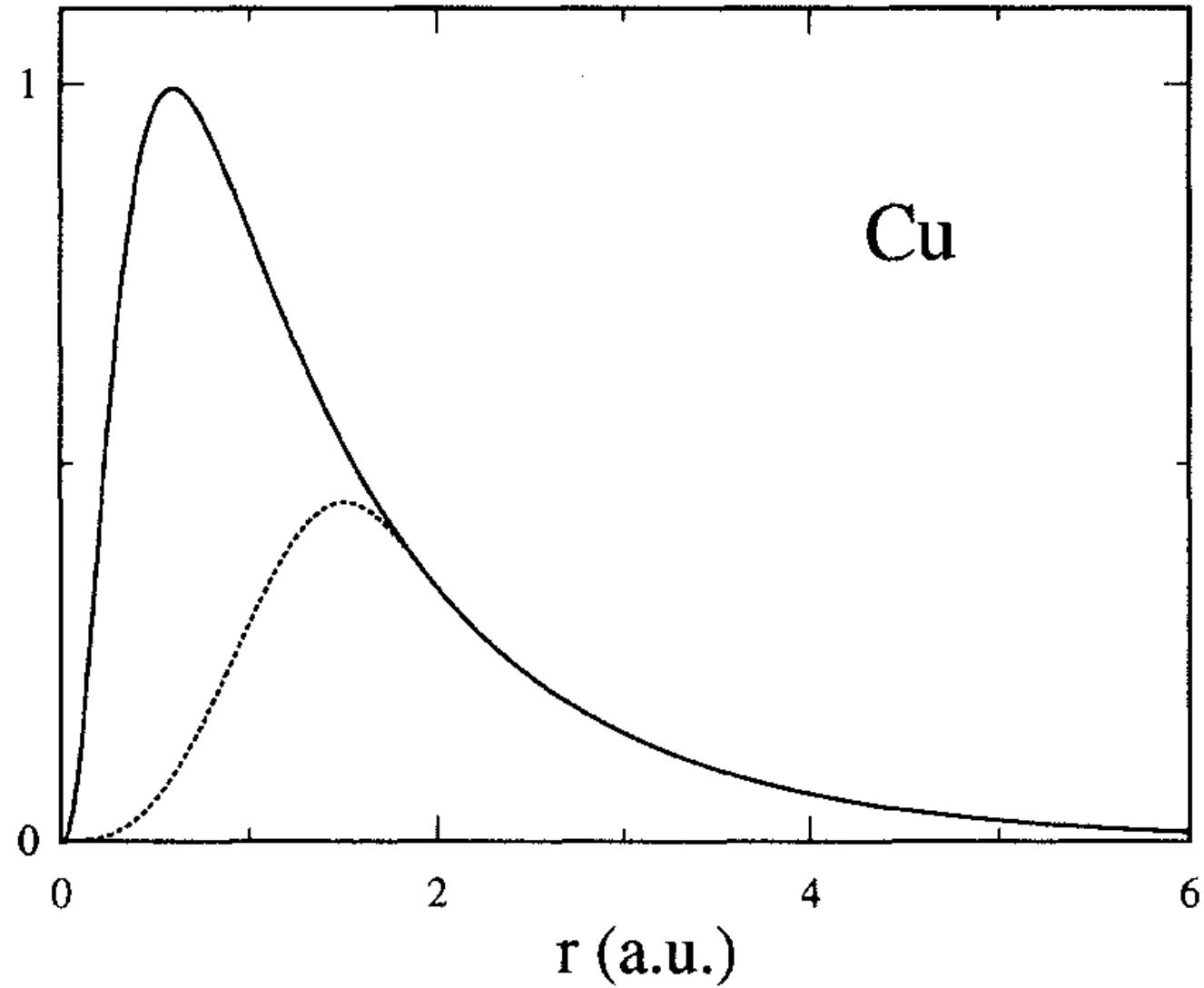




US pseudopotentials



US pseudopotentials



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



That's all Folks!

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