modeling materials using quantum mechanics and digital computers

the plane-wave pseudo potential way

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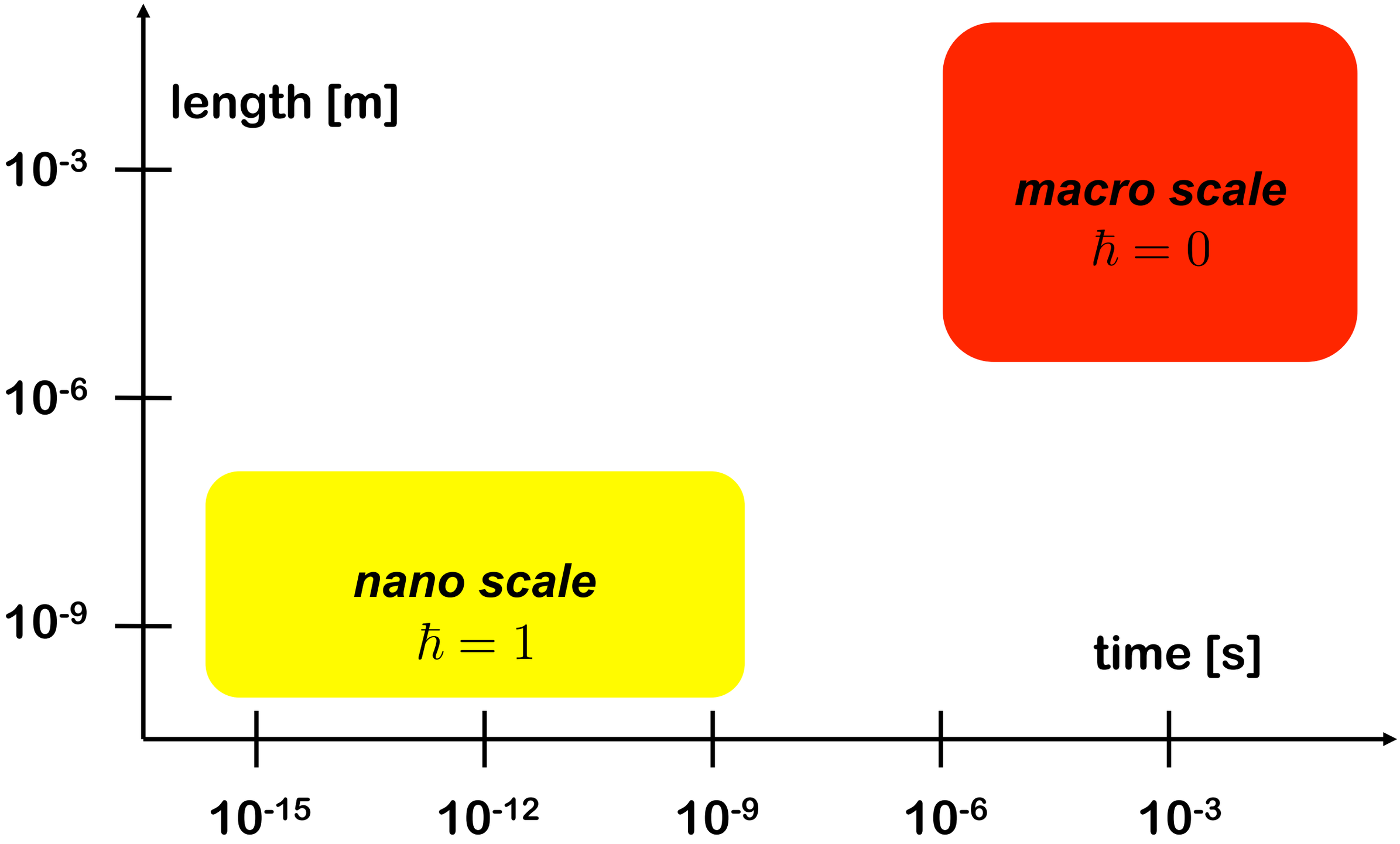
the saga of time and length scales



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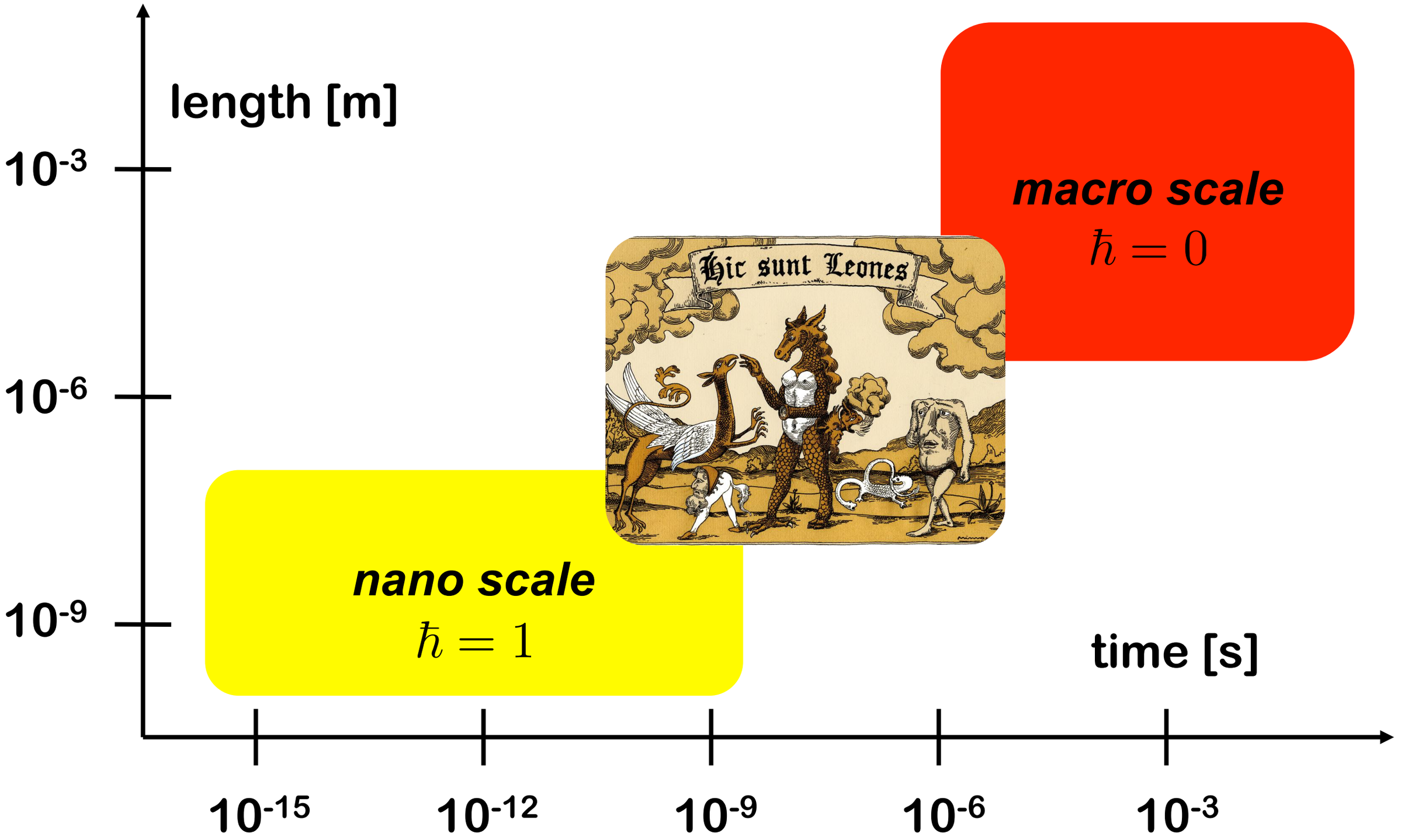

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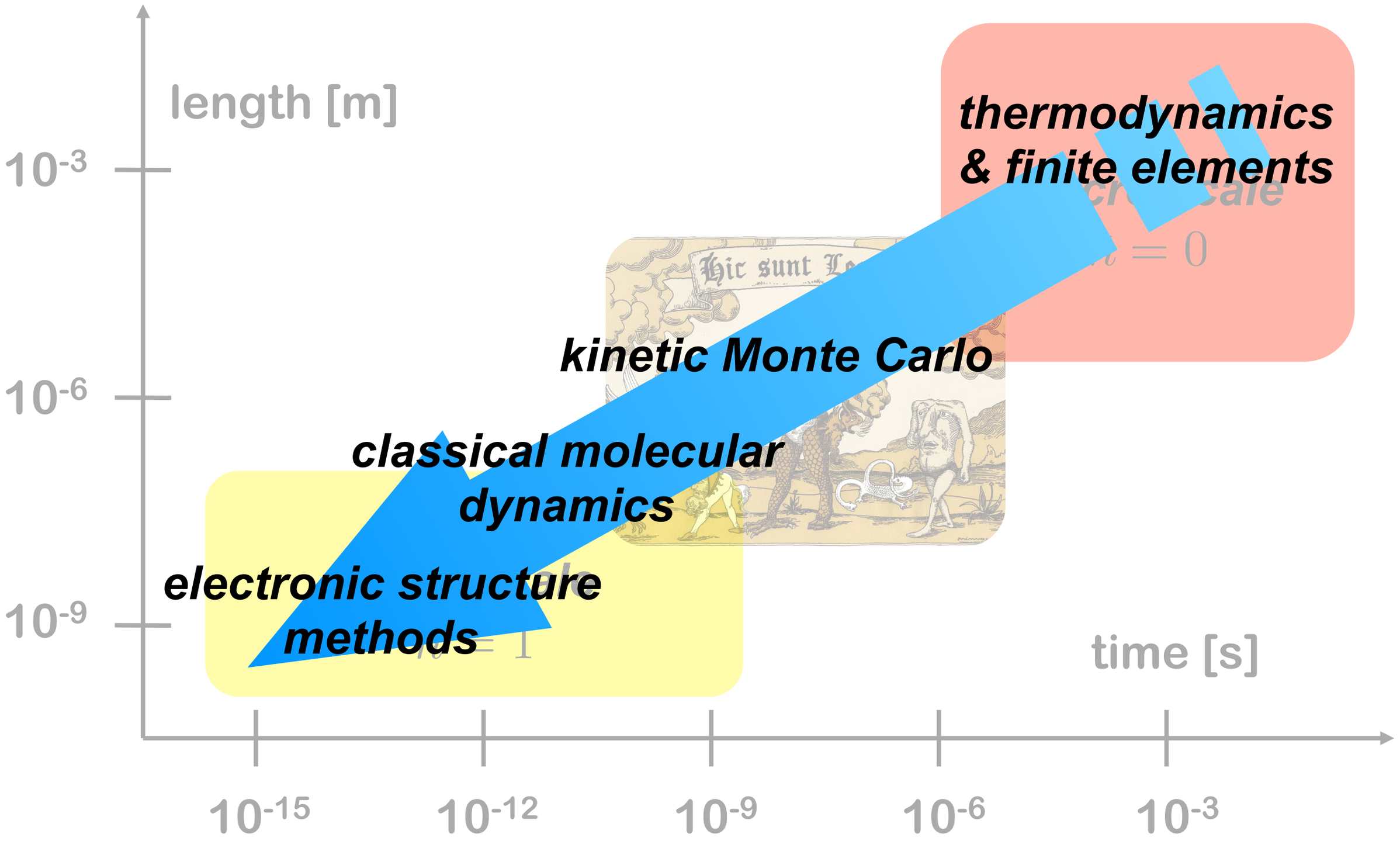
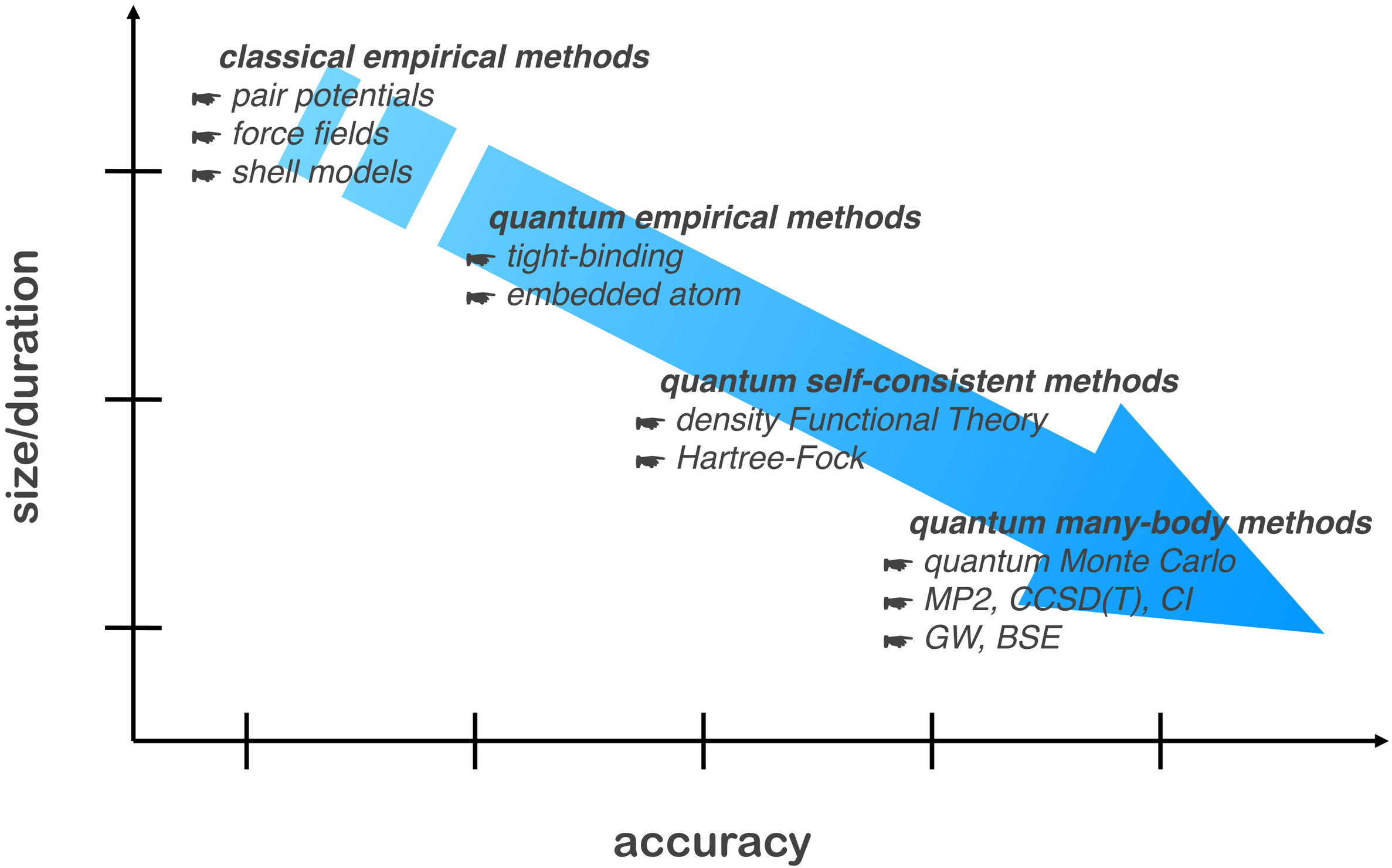


size vs. accuracy



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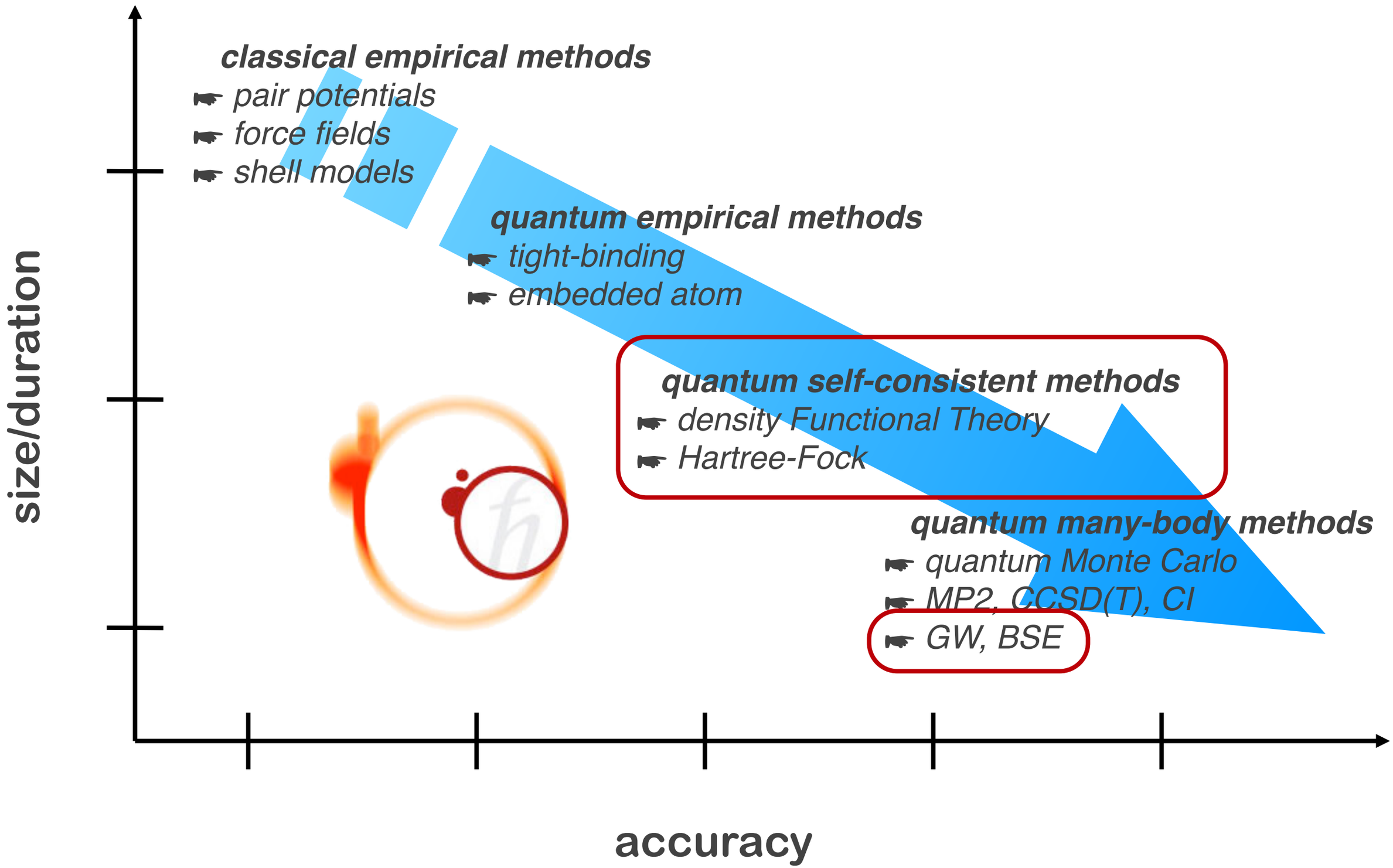

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how: using digital computers, clever algorithms, common sense, and *scientific rigor*

ab initio simulations

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

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M ≫ m: the Born-Oppenheimer approximation

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

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density-functional theory

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Kohn-Sham equations

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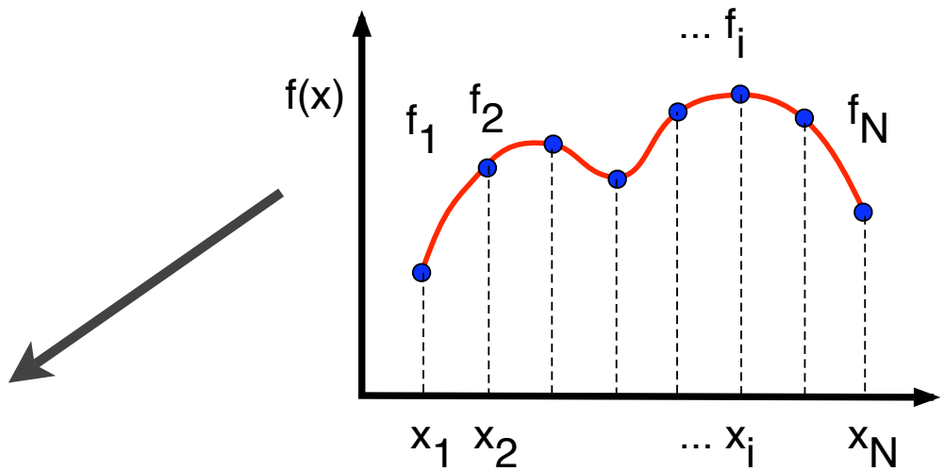
approximations:

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



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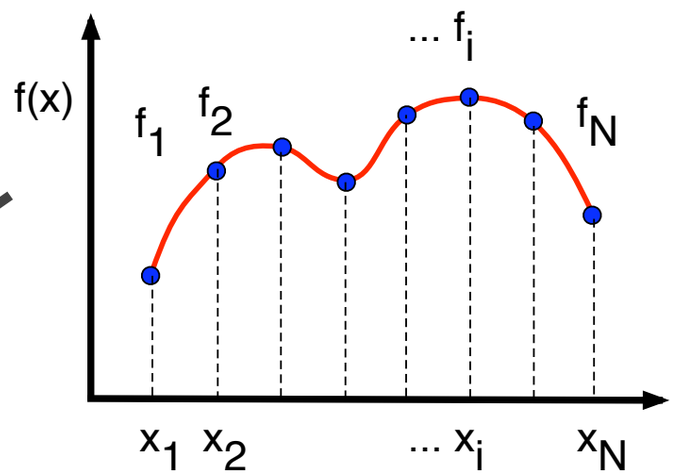

$$f(x) \approx \sum_n c_n \phi_n(x)$$

functional derivatives

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

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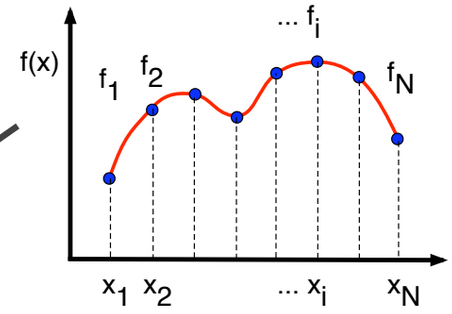
$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \approx \frac{1}{h} \frac{\partial g}{\partial f_i}$$



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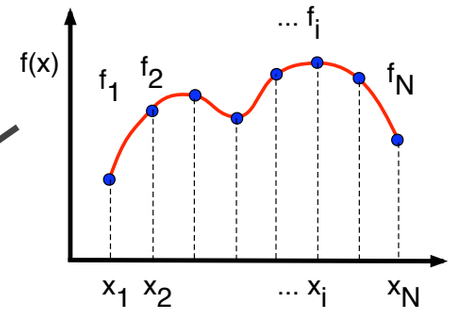

$$\frac{\delta G}{\delta f(x)} \text{“} = \text{”} \lim_{\epsilon \to 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

the Hellmann-Feynman theorem

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

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properties:

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

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consequences:

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

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Kohn-Sham DFT

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

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

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

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

exchange-correlation energy functionals

- LDA (Kohn & Sham, 60's)

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

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

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

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

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

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

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

- meta-GGA (Perdew, early 2K's)

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

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

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

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

- ...

KS equations from functional minimization

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

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basis set requirements

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- (effective) completeness easily checked and systematically improved

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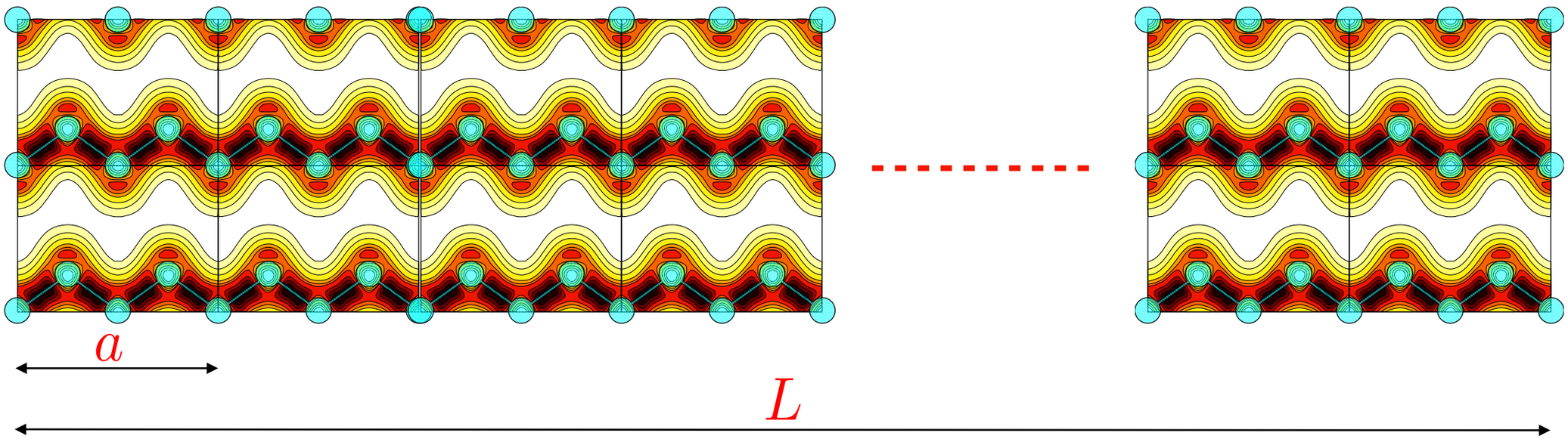
- orthogonality is a plus

the Bloch theorem & plane waves

infinite crystals



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

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

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

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

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

plane-wave basis sets

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

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

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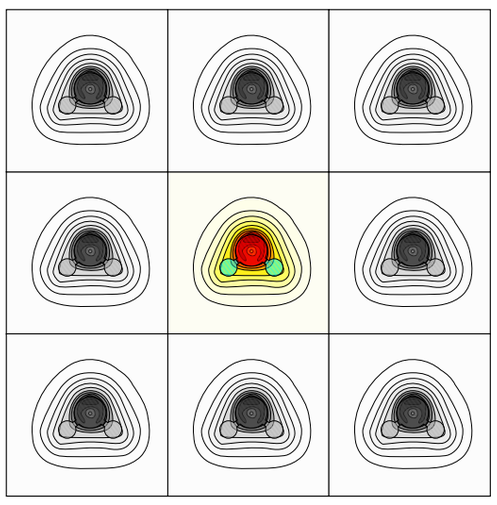
finite systems $(\ell = a)$



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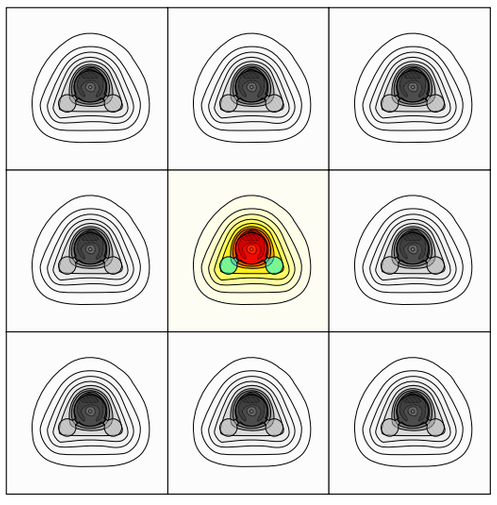
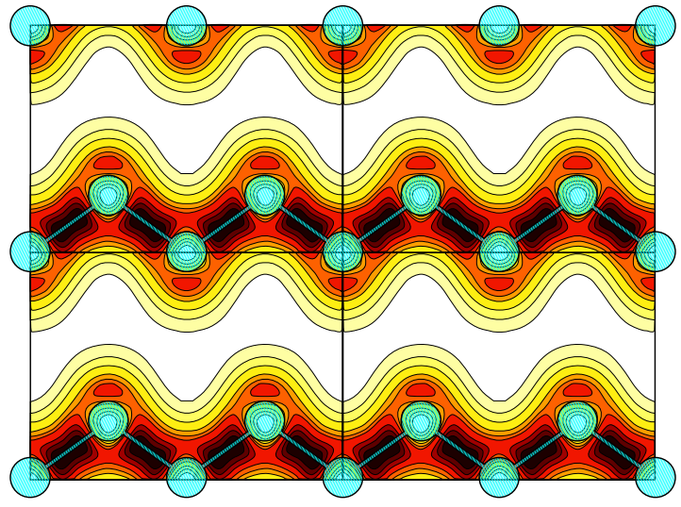


$\mathbf{q} = \mathbf{G}$

infinite crystals $(\ell = L)$



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

PWs: pros & cons

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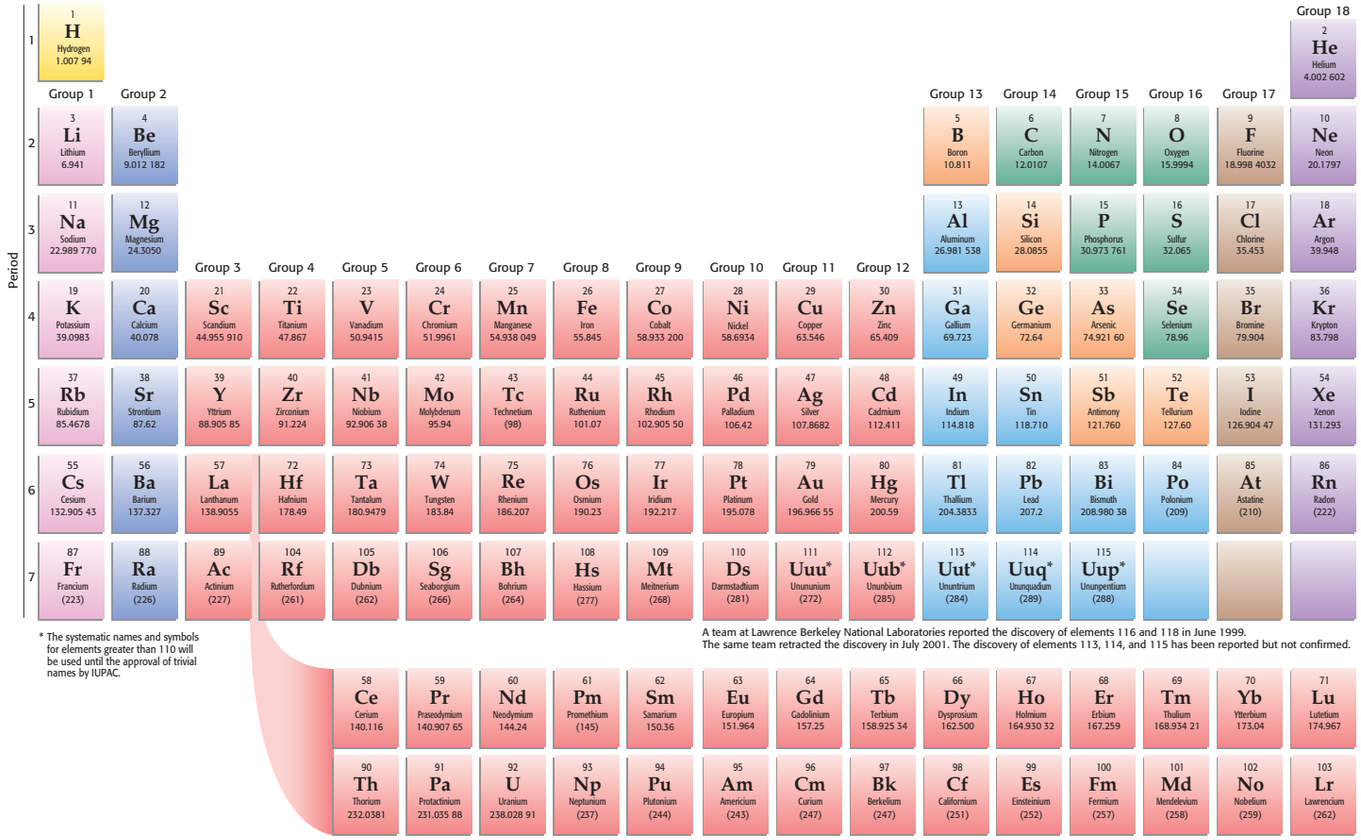
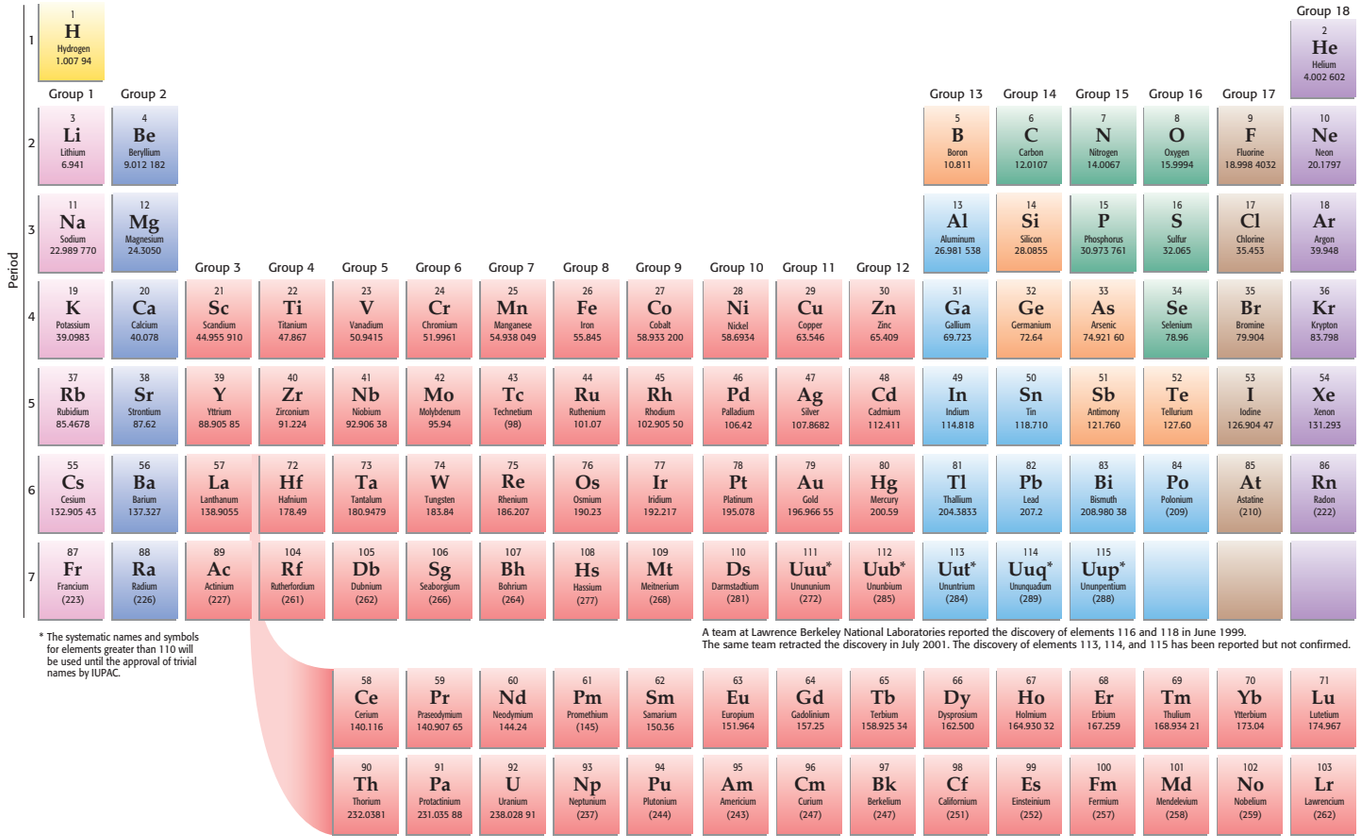
- ☹ uniform spatial resolution (no core states!)

treating core states



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

treating core states



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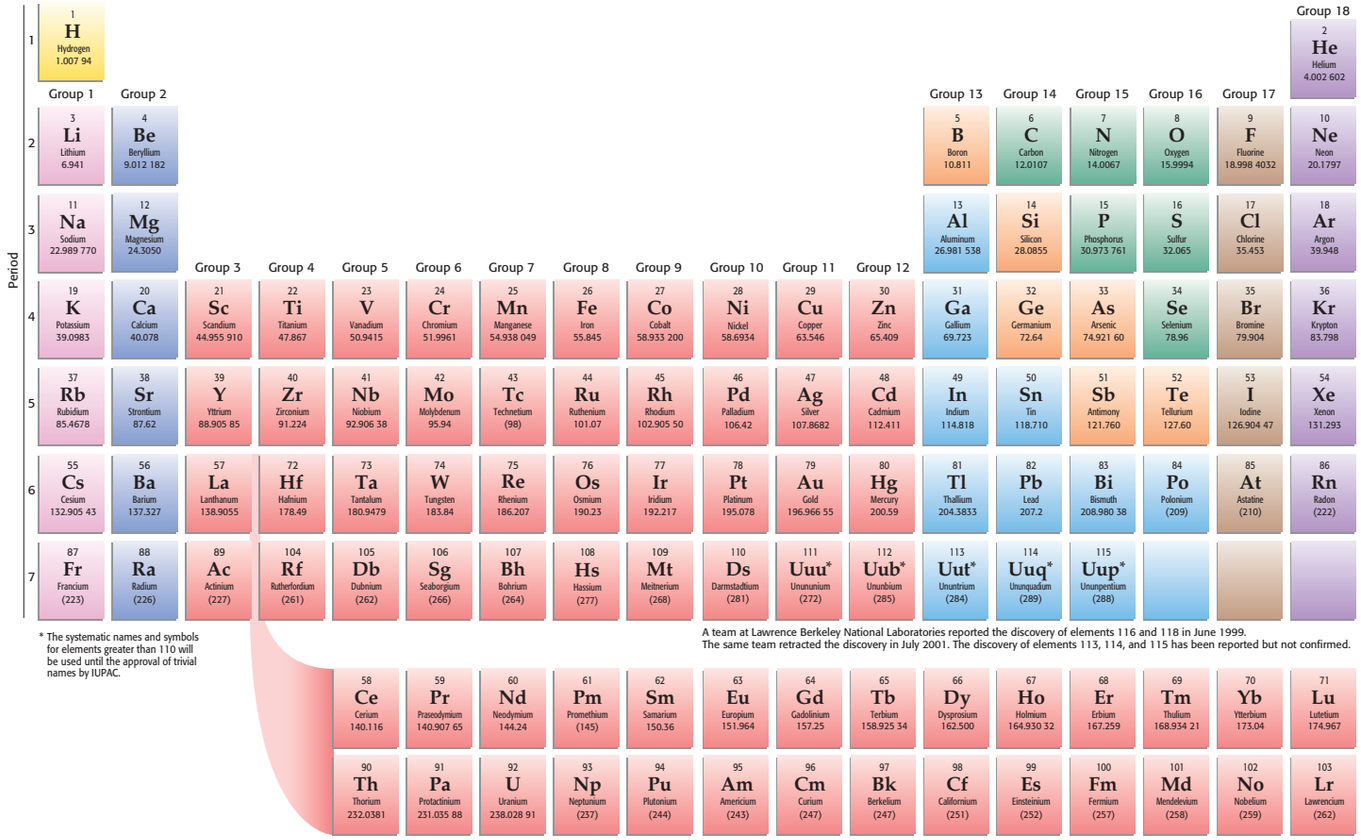


Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	1 H Hydrogen 1.007 94																	2 He Helium 4.002 602
2	3 Li Lithium 6.941	4 Be Beryllium 9.012 182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.998 4032	10 Ne Neon 20.1797
3	11 Na Sodium 22.989 770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981 538	14 Si Silicon 28.0855	15 P Phosphorus 30.973 761	16 S Sulfur 32.065	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 131.293
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* Unununium (272)	112 Uub* Ununbium (285)	113 Uut* Ununtrium (284)	114 Uuq* Ununquadium (289)	115 Uup* Ununpentium (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 231.035 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 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.

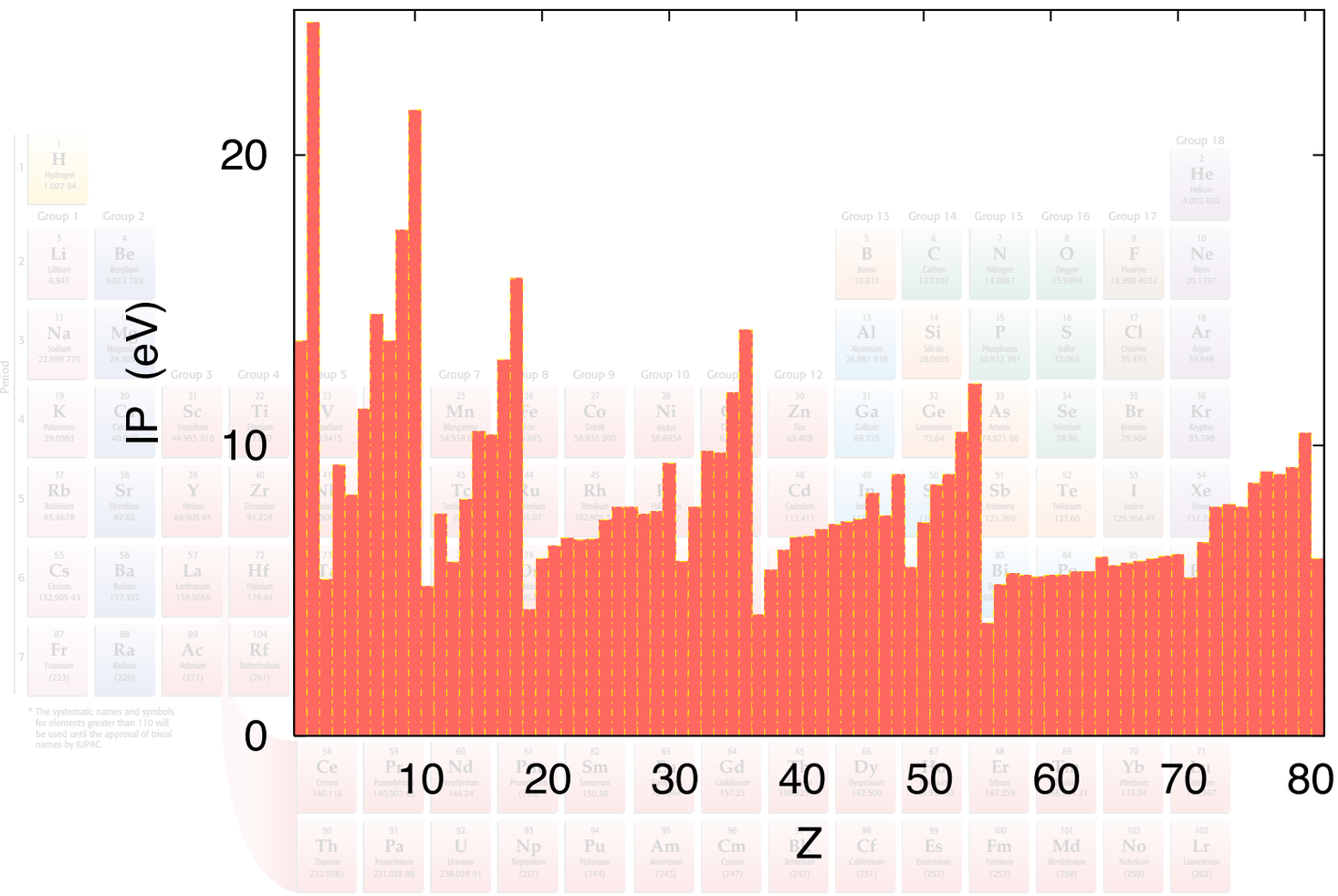
$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

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

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

$$\sim Z^3$$

treating core states



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trashing core states: pseudopotentials

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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

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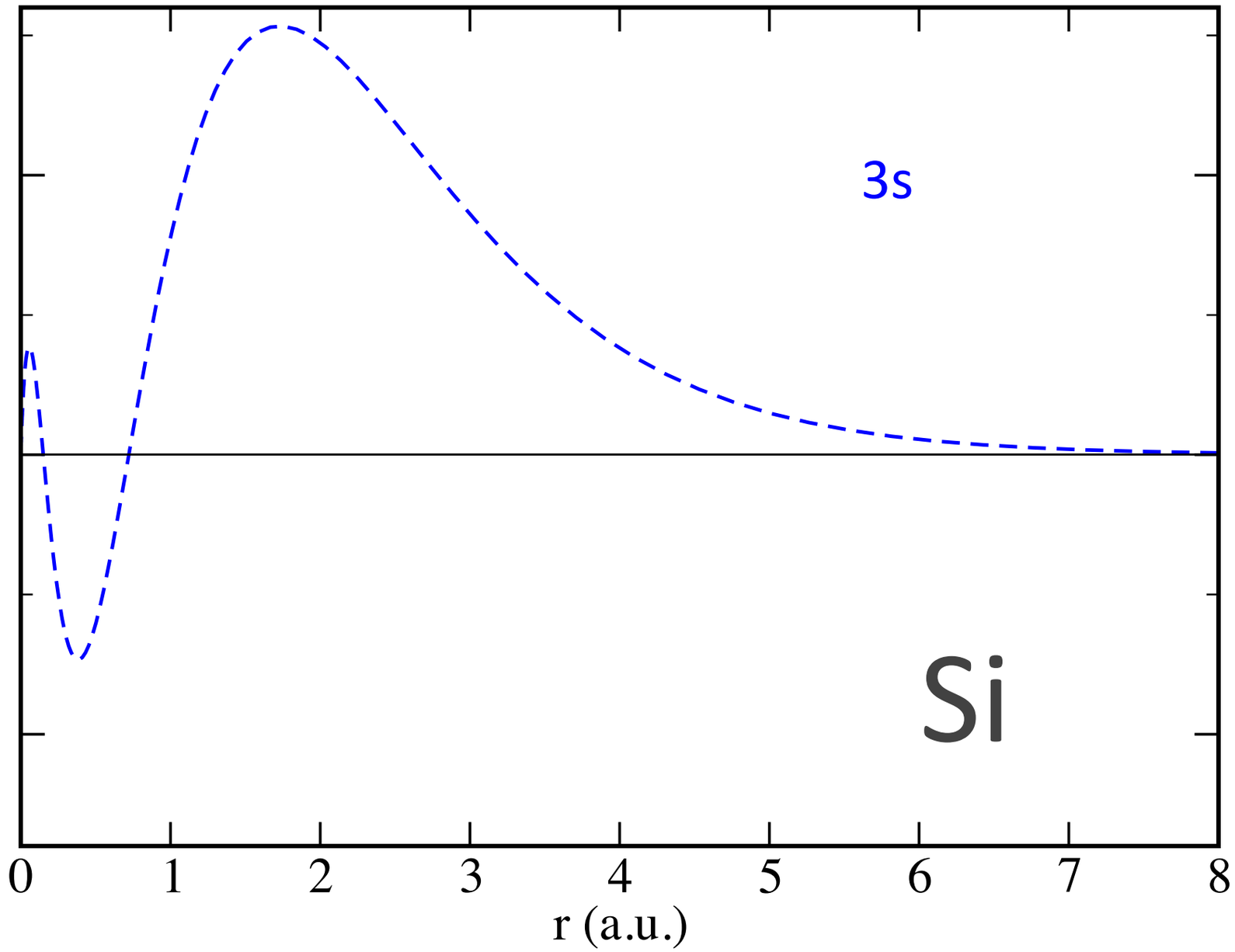
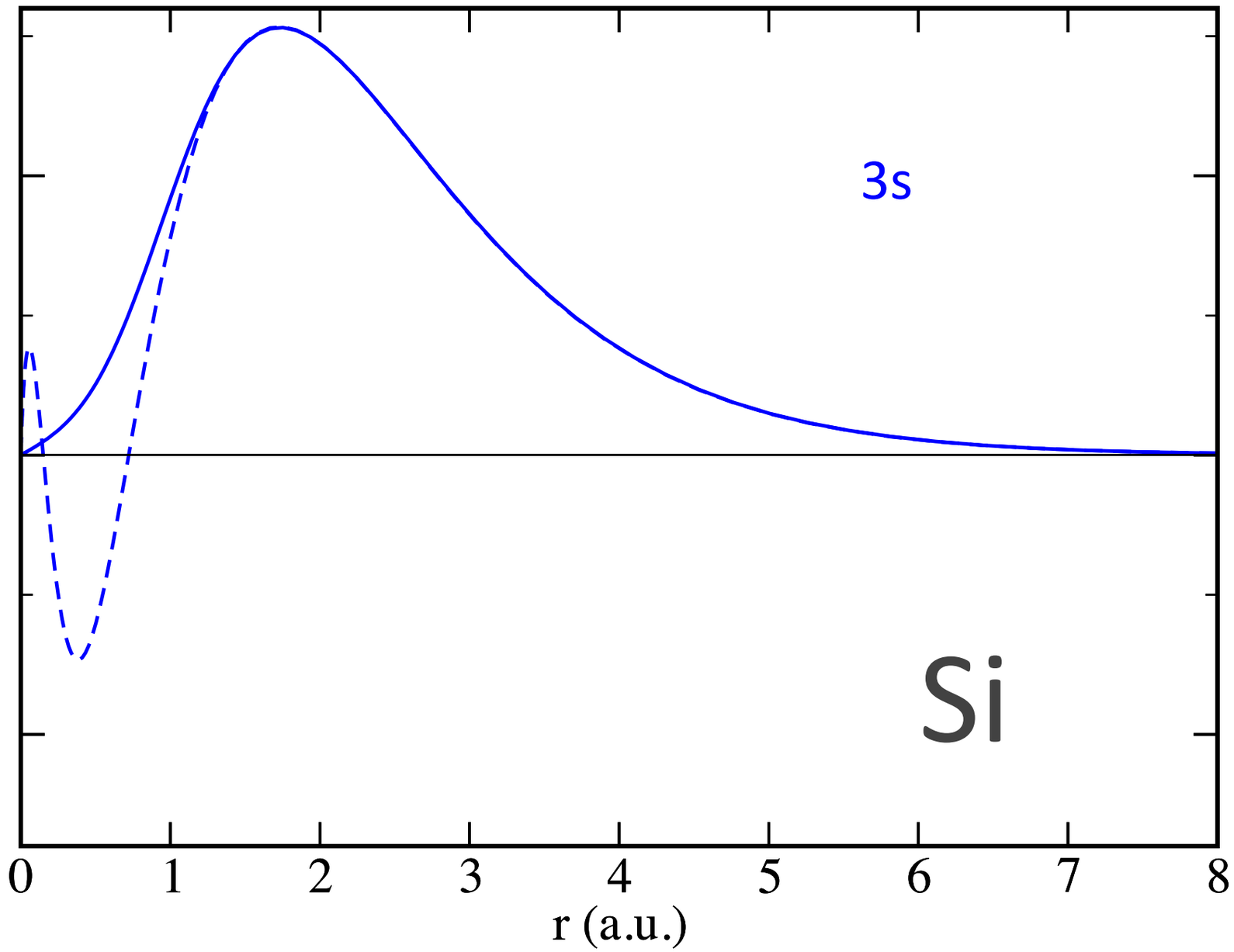
the chemical properties of the pseudo-atom are the same as those of the true atom:

$$\epsilon^{ps}_{val} = \epsilon^{ae}_{val}$$

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


3s
Si
0
1
2
3
4
5
6
7
8
r (a.u.)


3s
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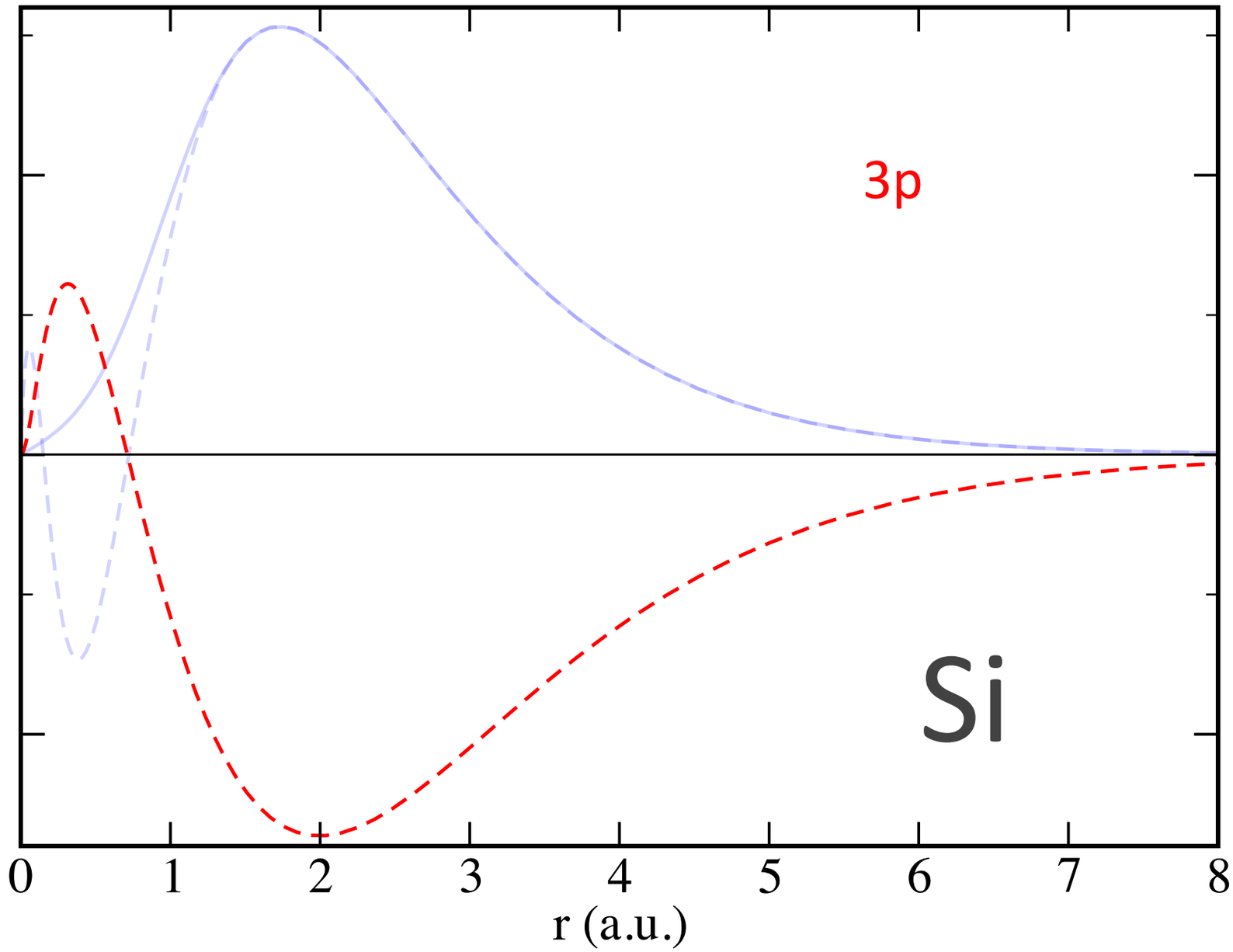
3p
Si
0
1
2
3
4
5
6
7
8
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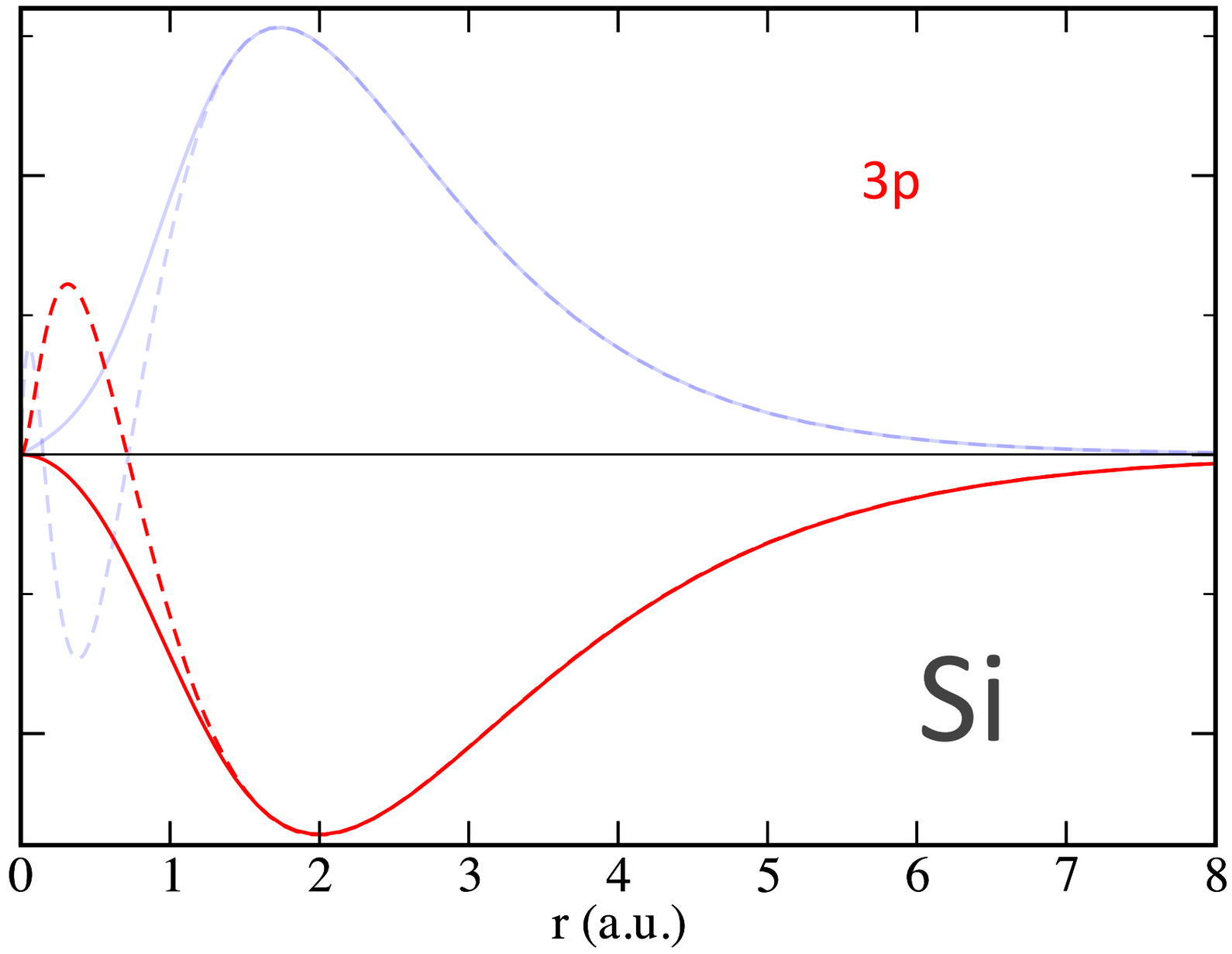
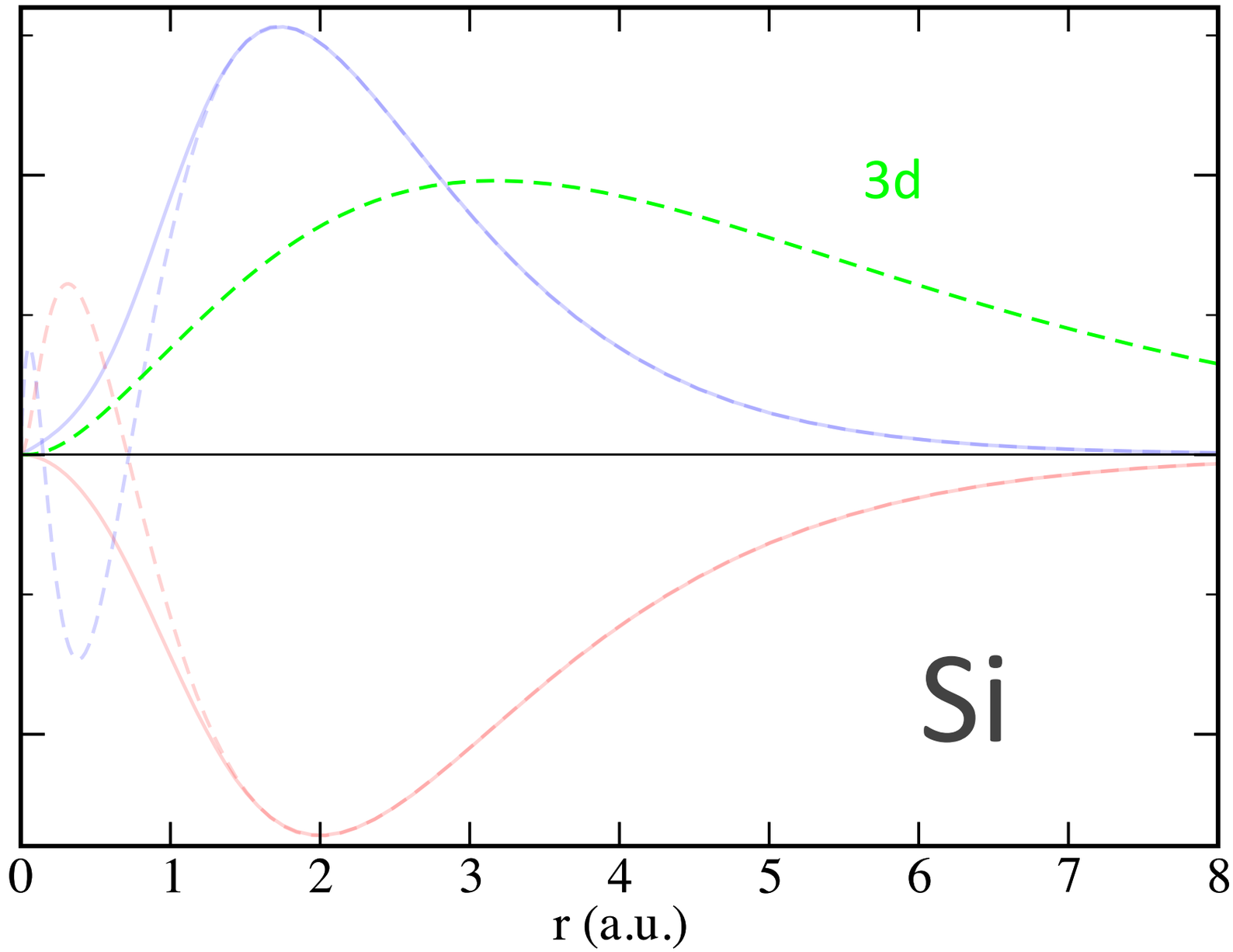

3p
Si
0
1
2
3
4
5
6
7
8
r (a.u.)


3d
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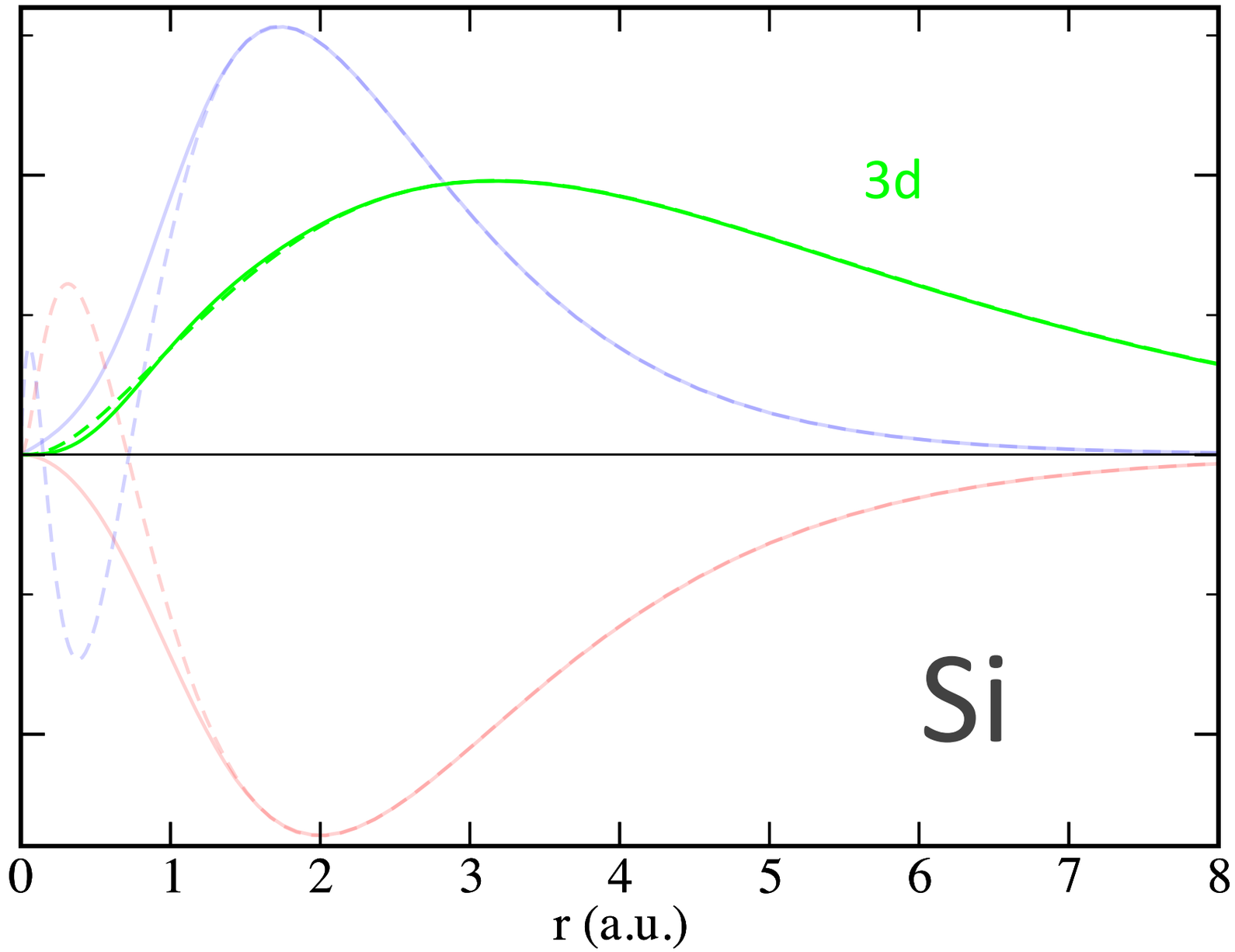
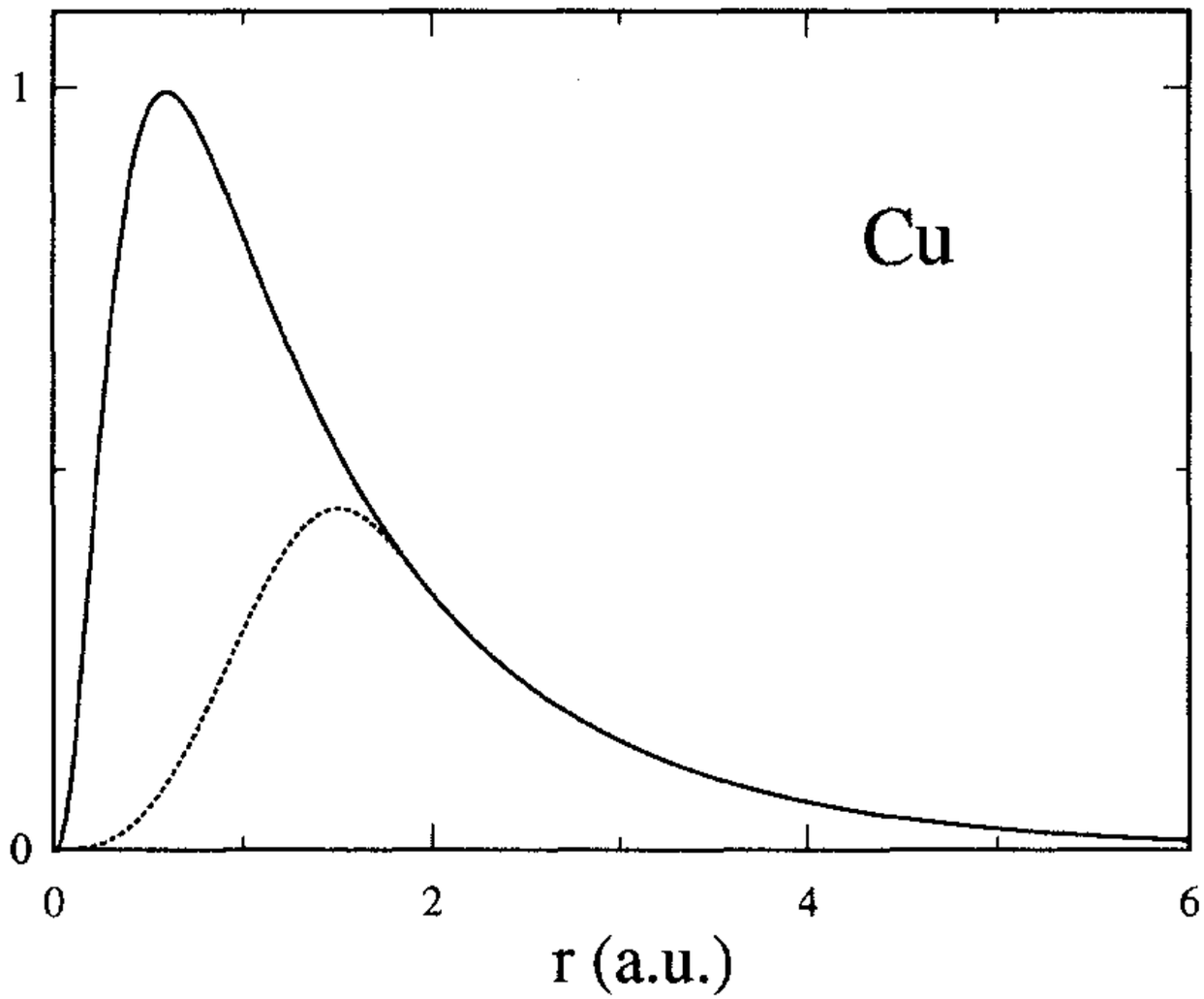

3d
Si
0
1
2
3
4
5
6
7
8
r (a.u.)

US pseudopotentials



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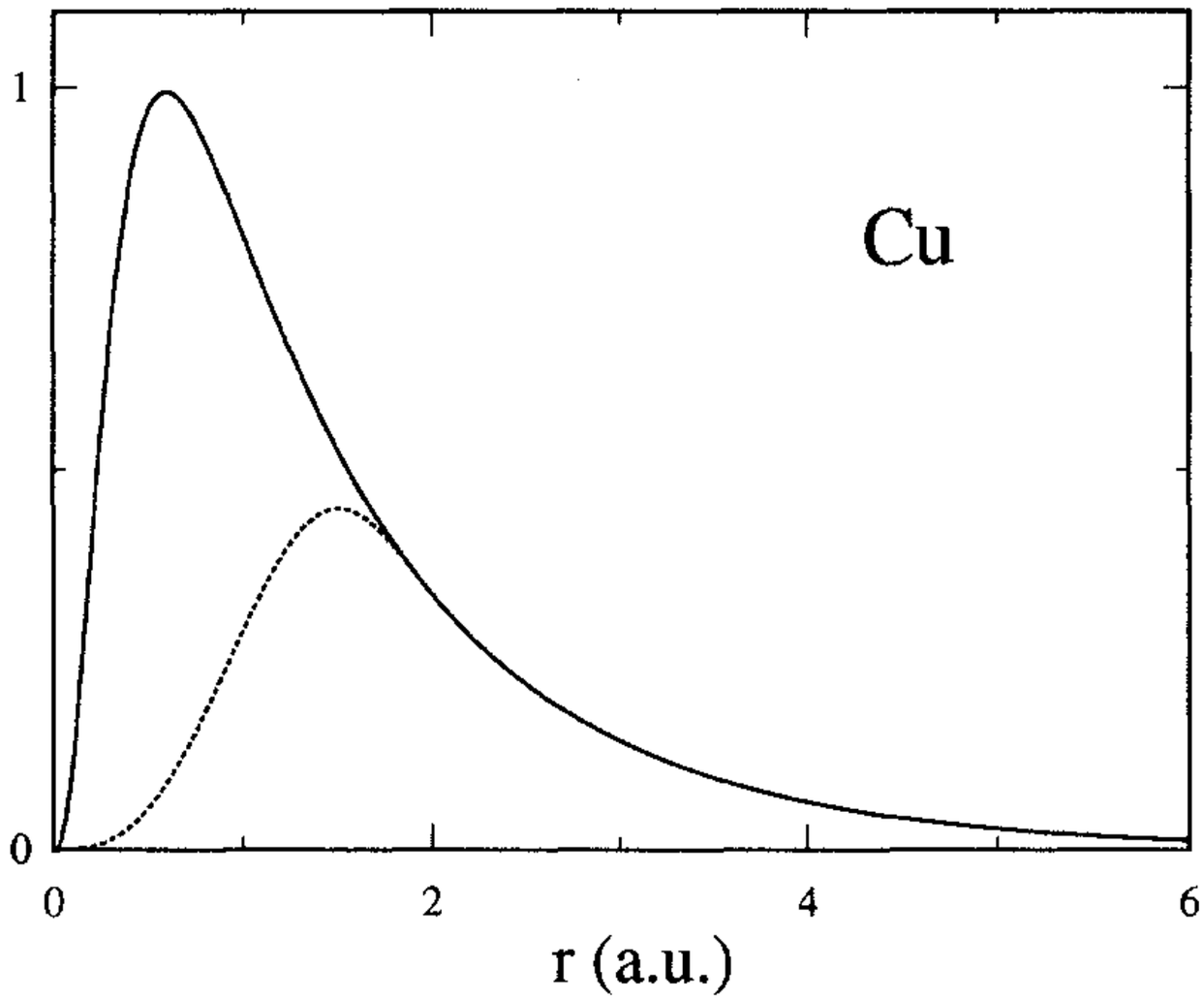

$$H_{US}\phi_n = \epsilon_n S\phi_n \qquad \langle\phi_n|S|\phi_m\rangle = \delta_{nm}$$

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