

# 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

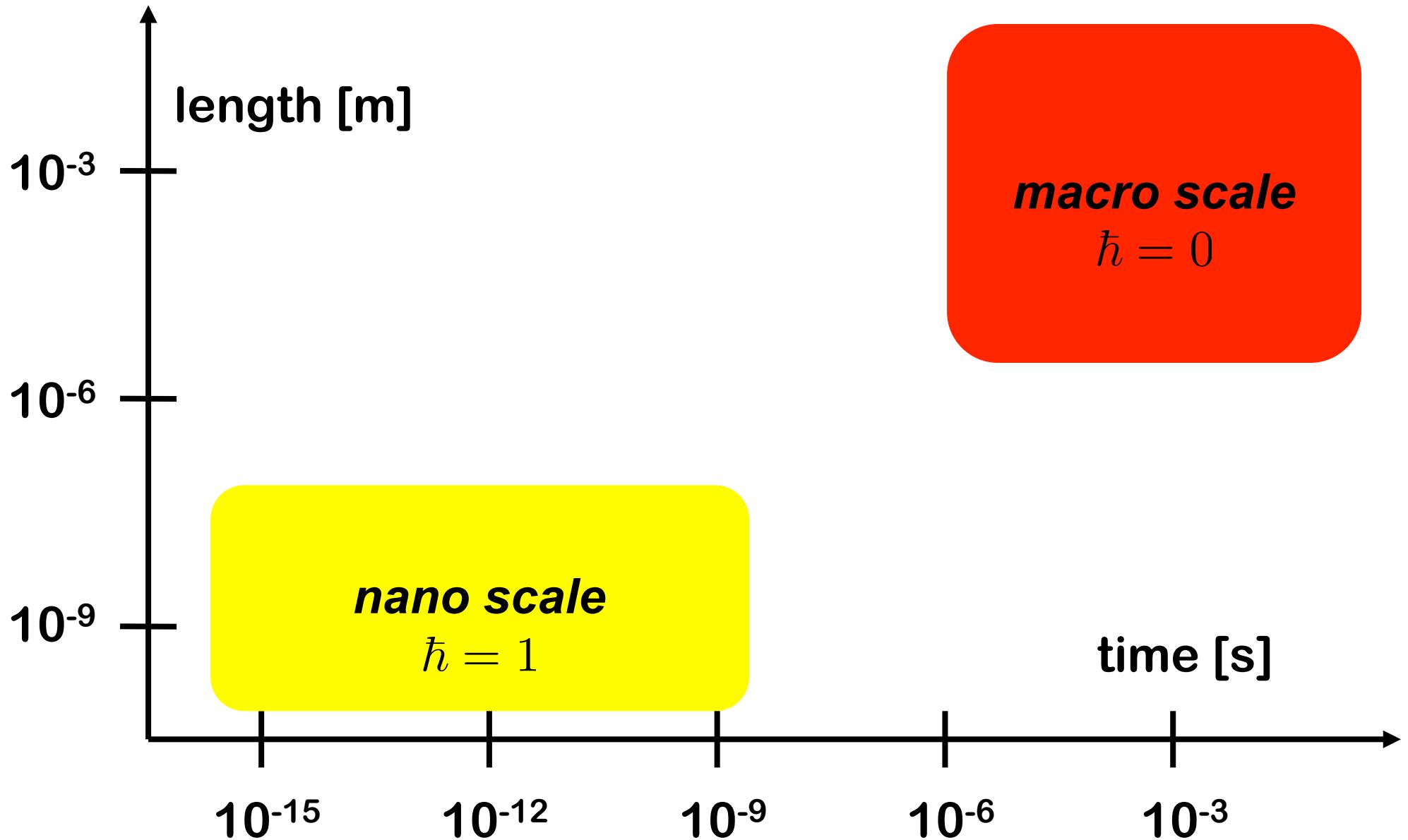
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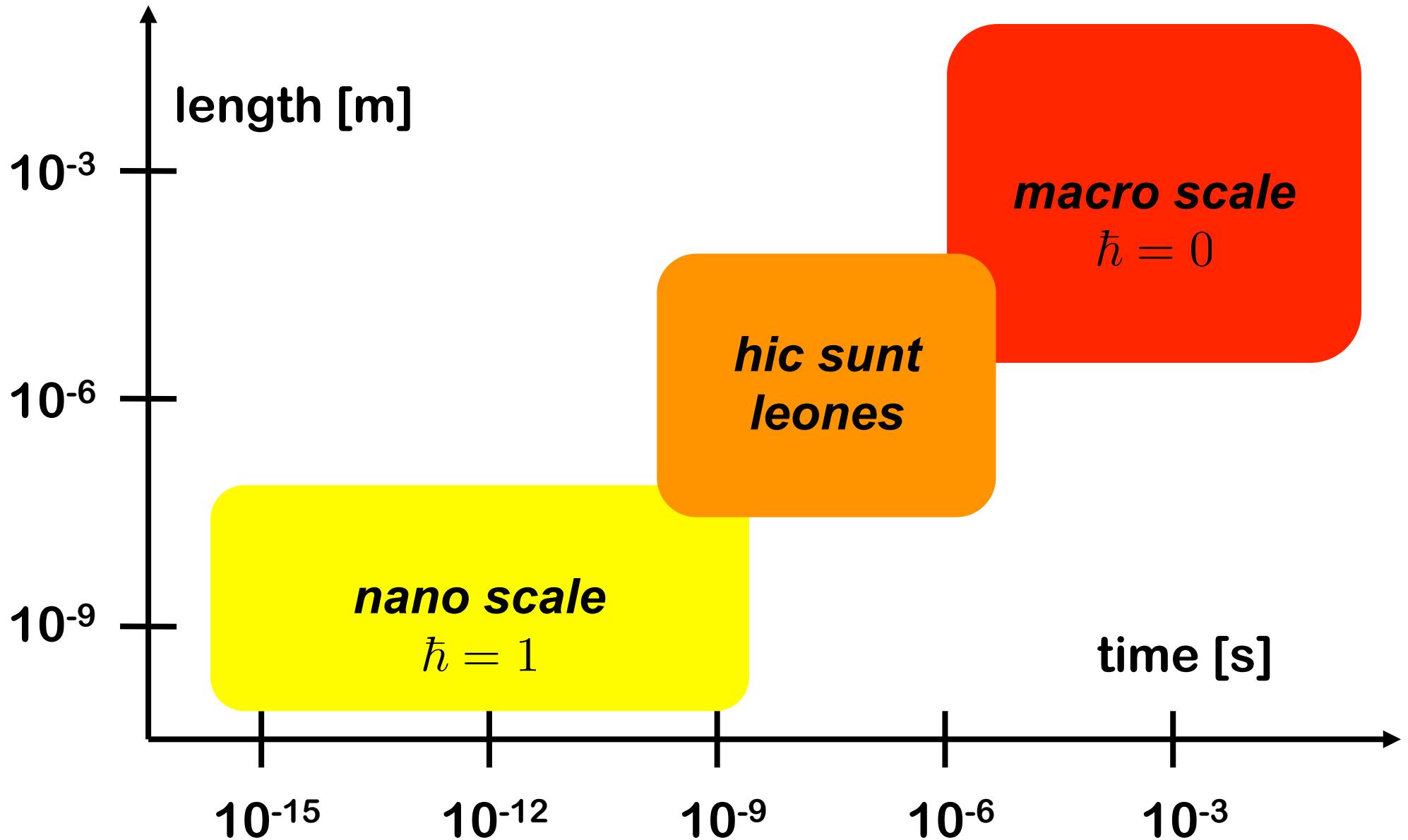
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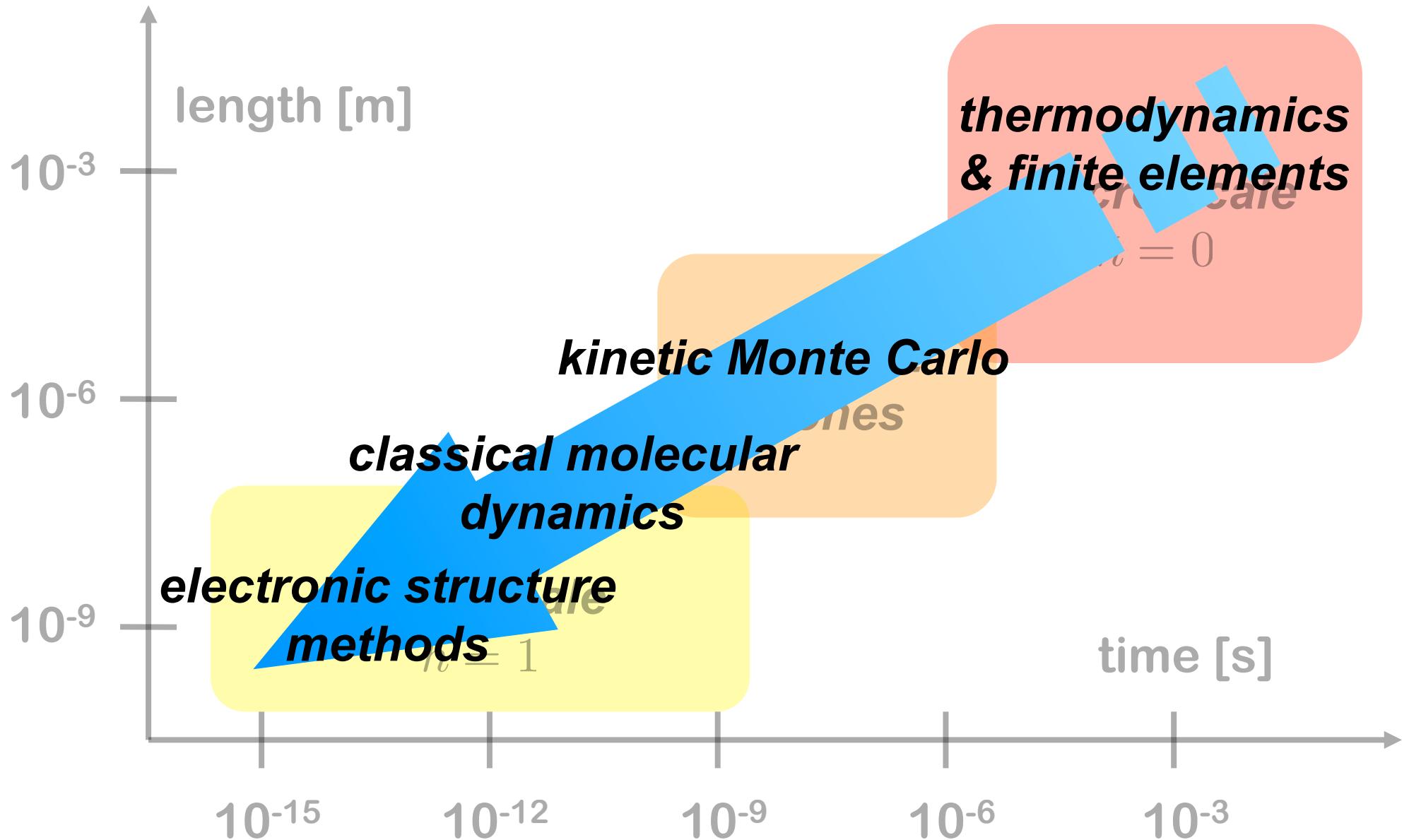
# the saga of time and length scales



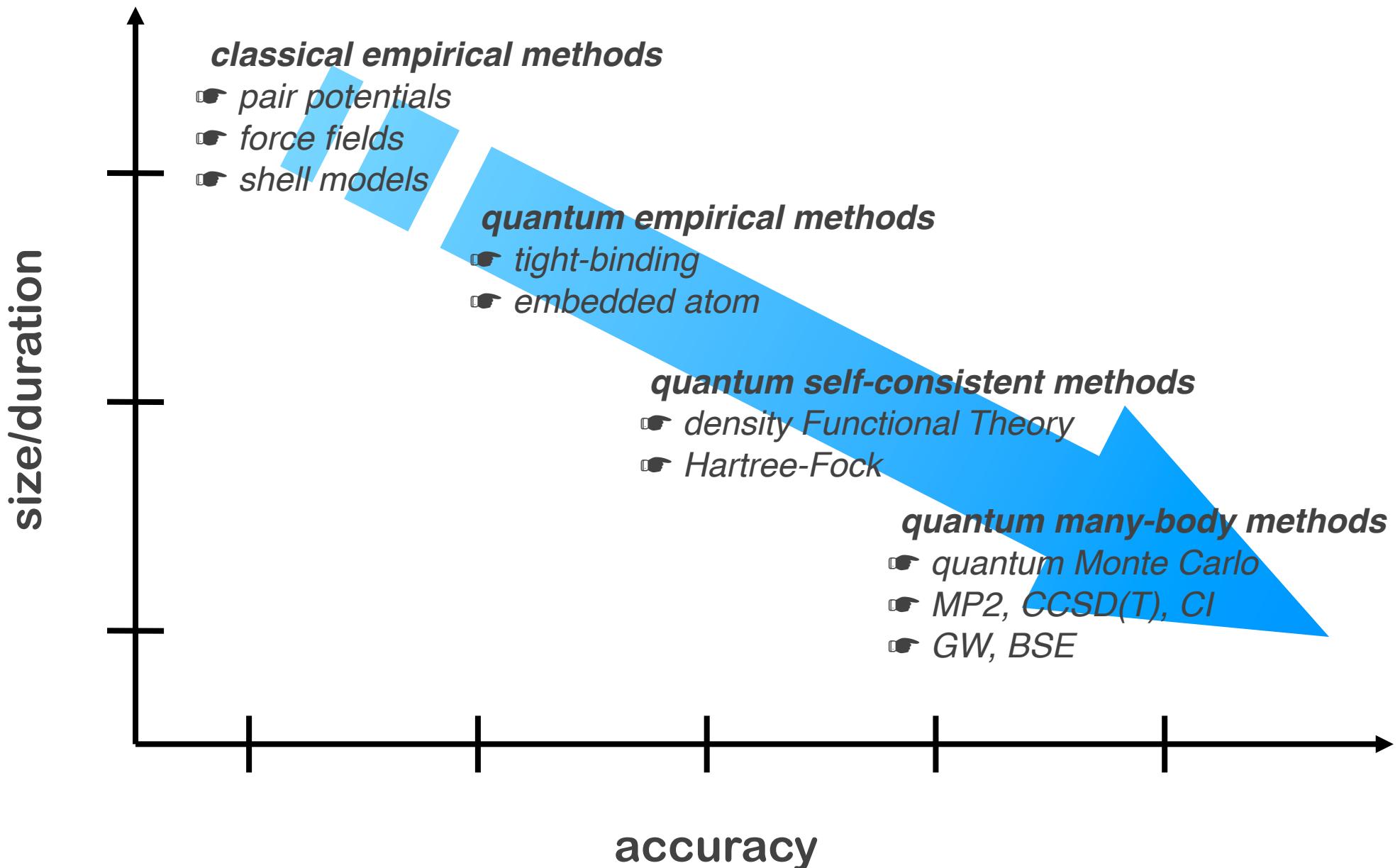
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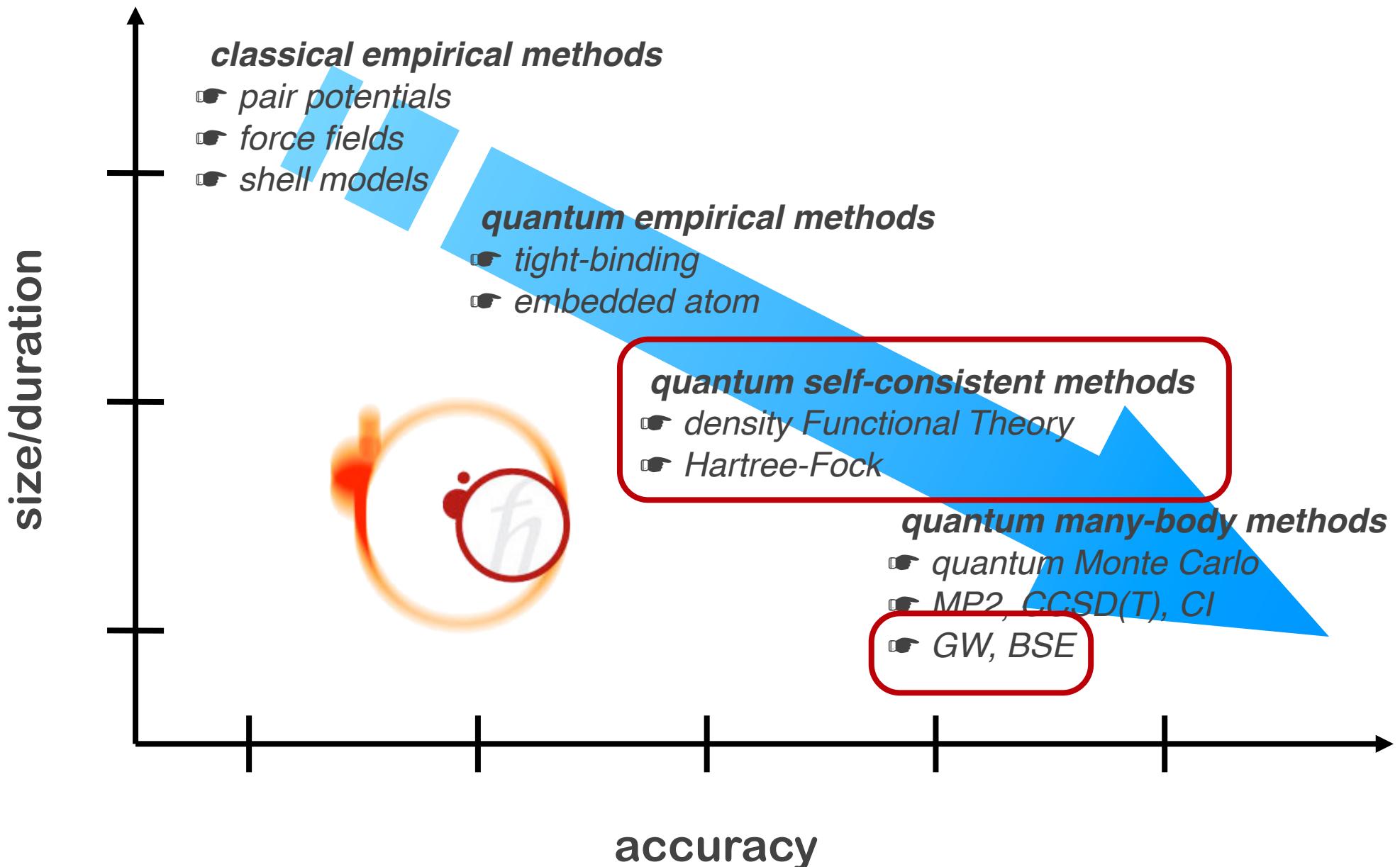
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# size vs. accuracy



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# *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
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# *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

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

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M»m: the Born-Oppenheimer approximation

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

# 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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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

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examples:

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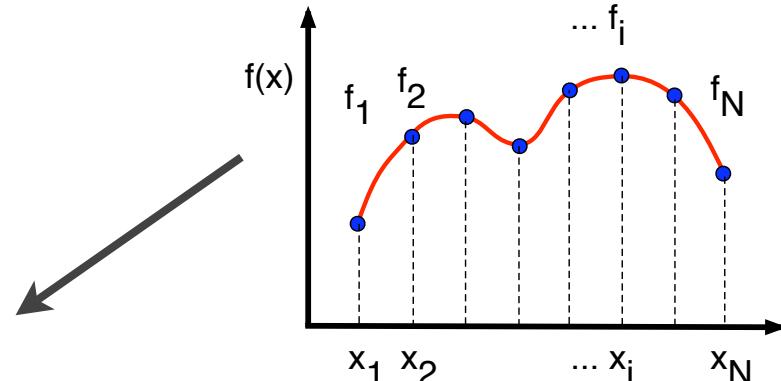
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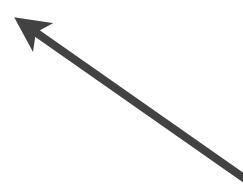
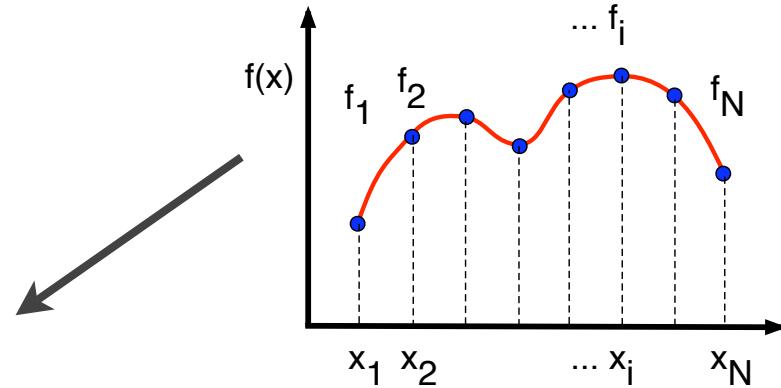
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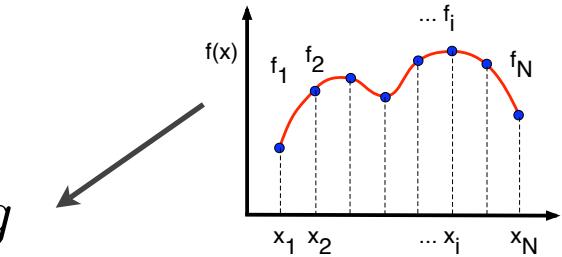


$$f(x) \approx \sum_n c_n \phi_n(x)$$

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

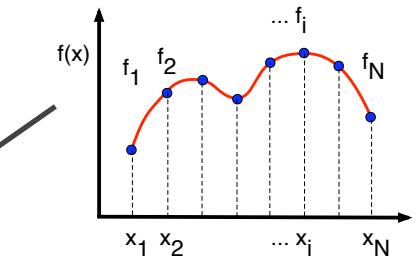
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$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \text{ ``=} \lim_{\epsilon \rightarrow 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

# the Hellmann-Feynman theorem

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

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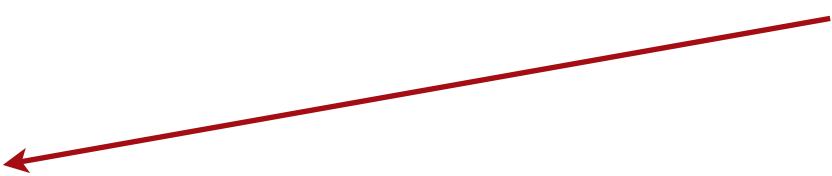
$$g(\lambda) = \min_x G[x, \lambda] \quad \longrightarrow \quad \left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)} = 0$$

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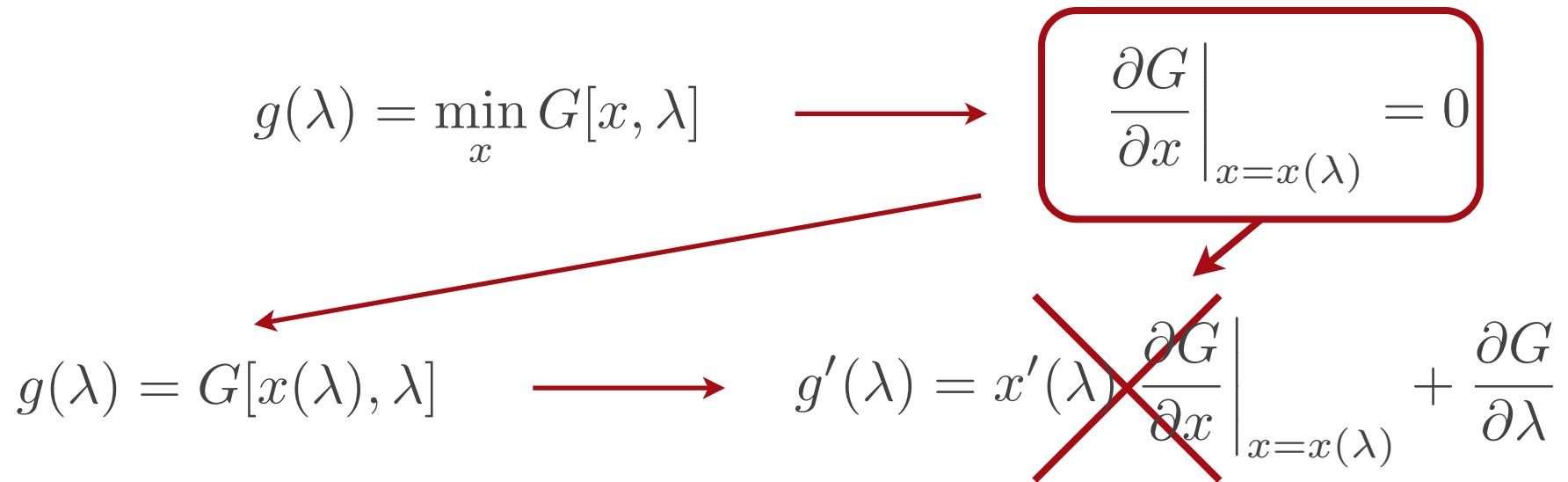
$$\begin{array}{ccc} g(\lambda) = \min_x G[x, \lambda] & \xrightarrow{\hspace{2cm}} & \left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)} = 0 \\ \downarrow & & \uparrow \\ g(\lambda) = G[x(\lambda), \lambda] & \xrightarrow{\hspace{2cm}} & g'(\lambda) = x'(\lambda) \left. \frac{\partial G}{\partial x} \right|_{x=x(\lambda)} + \frac{\partial G}{\partial \lambda} \end{array}$$

# the Hellmann-Feynman theorem

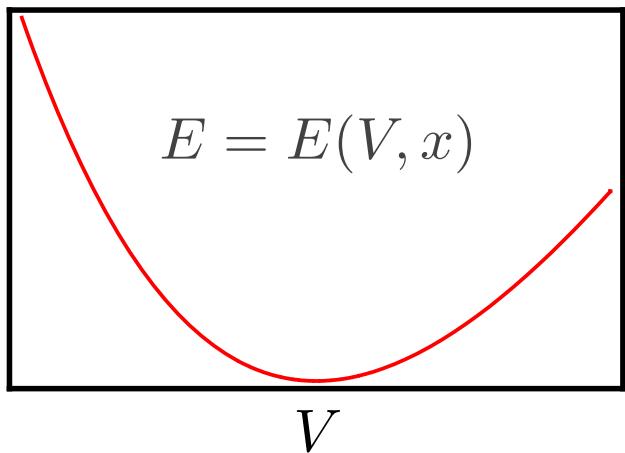
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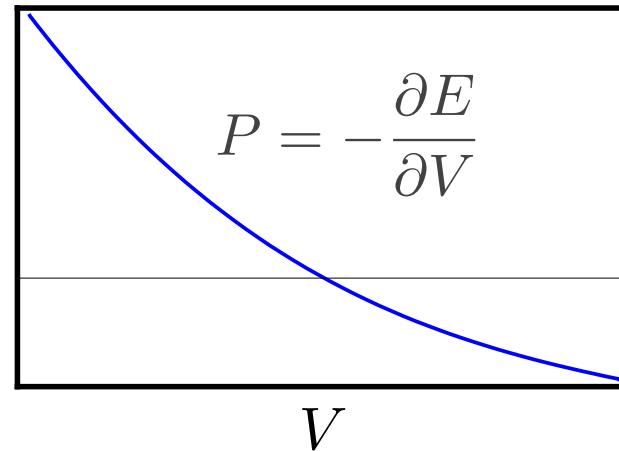
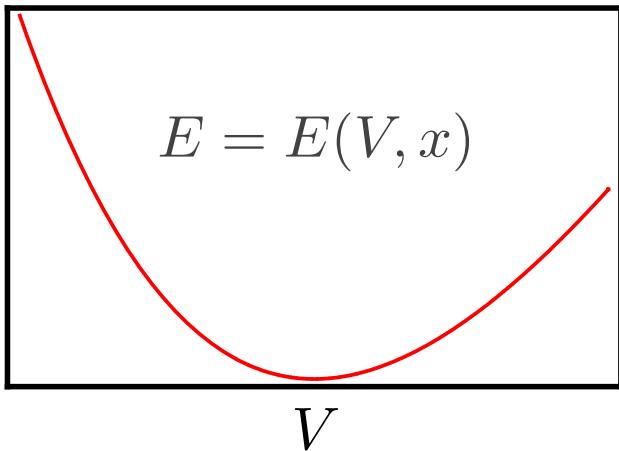
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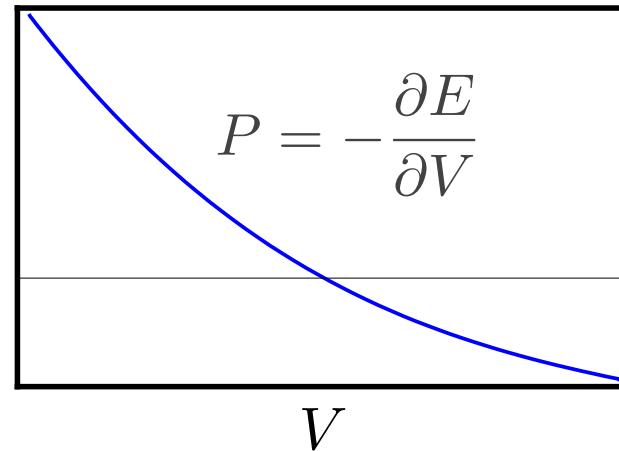
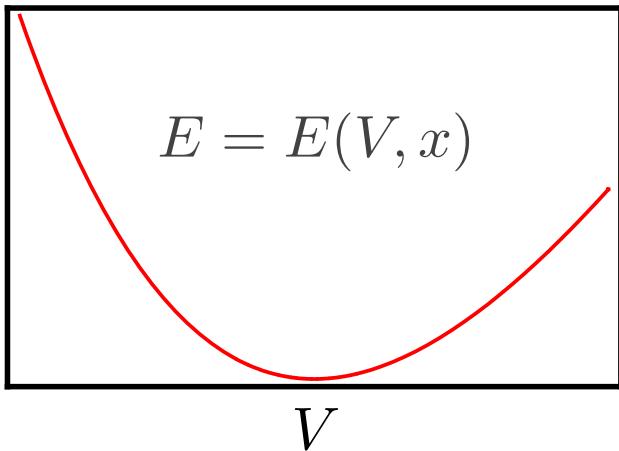
# conjugate variables & Legendre transforms



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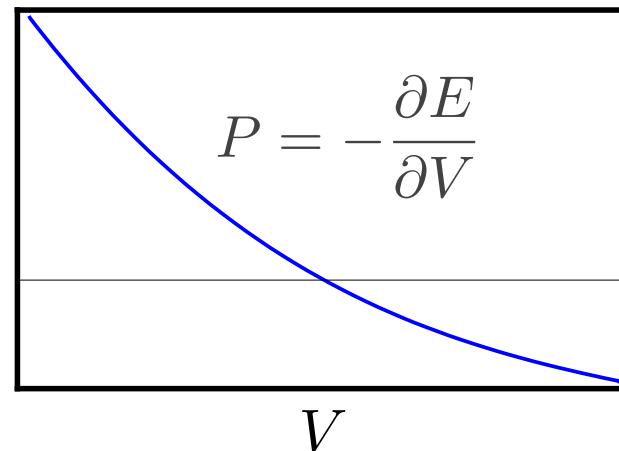
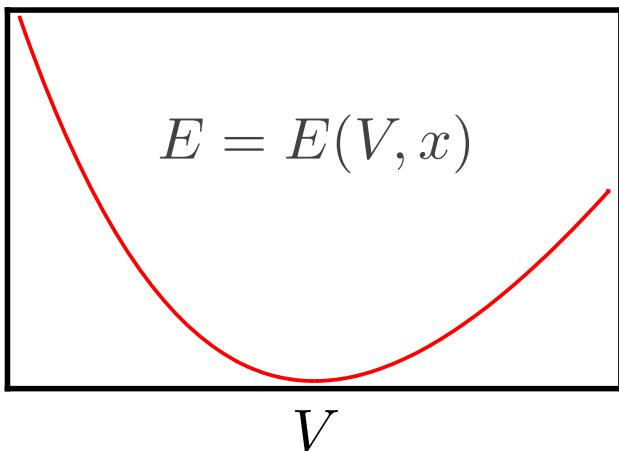


# conjugate variables & Legendre transforms



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

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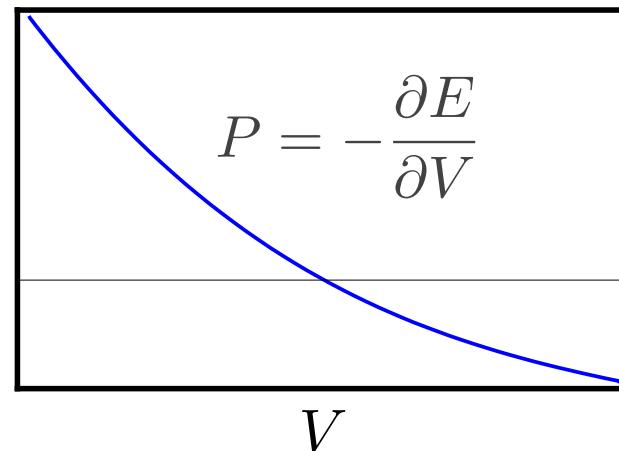
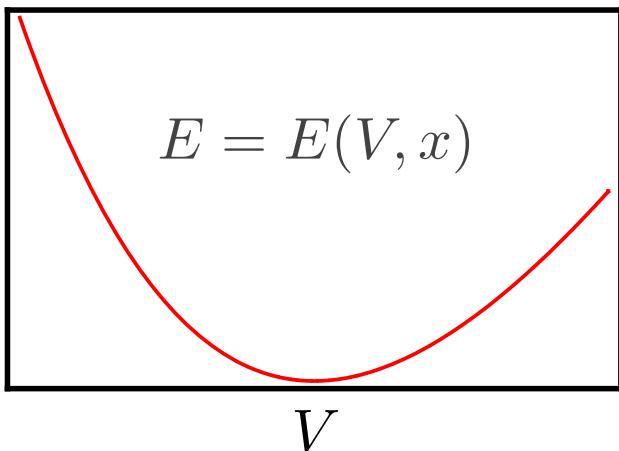


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properties:

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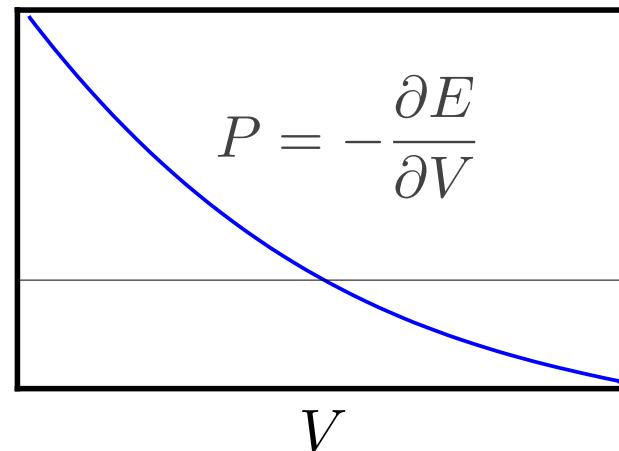
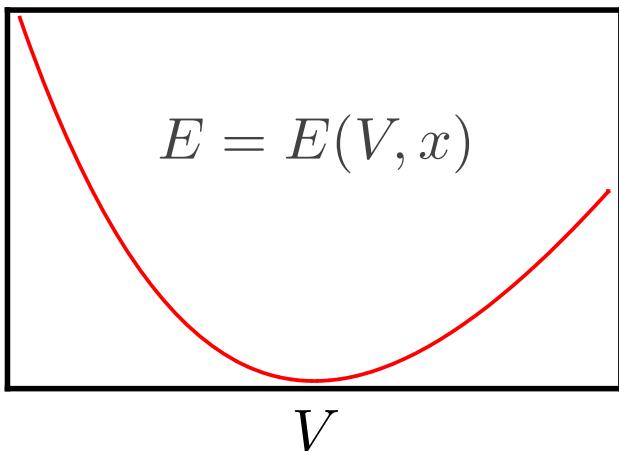


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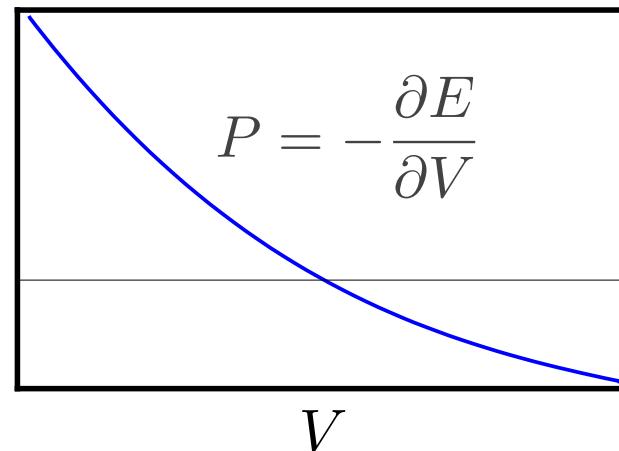
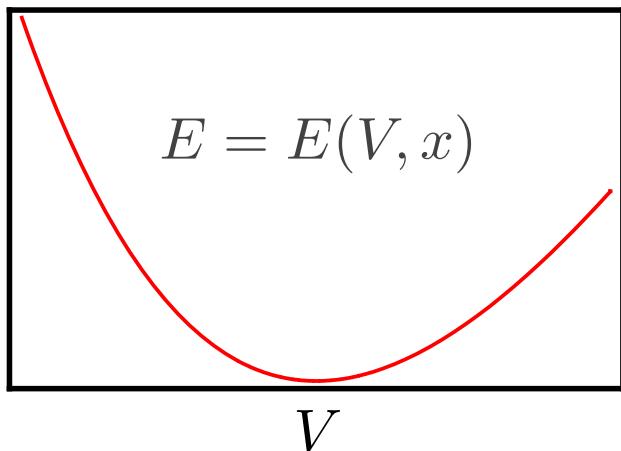


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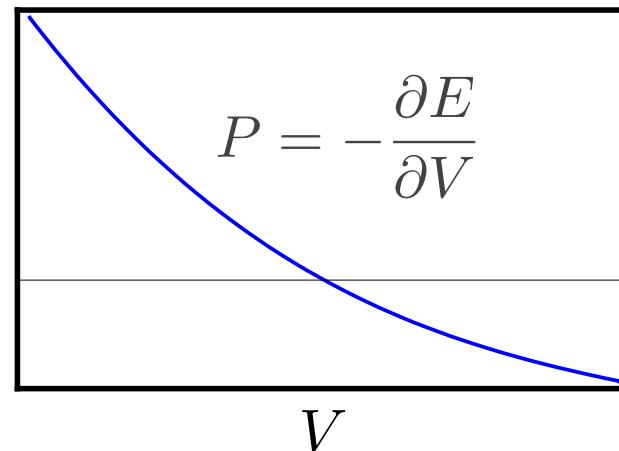
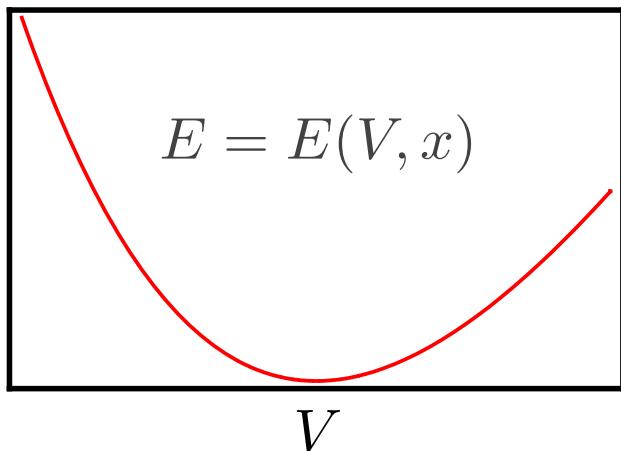


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# Hohenberg-Kohn DFT

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

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- $E[V]$  is convex (requires some work to demonstrate)
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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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*properties:*

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

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

- ▶ VdW (Langreth & Lundqvist, 2K's)

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

- ▶ ...

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

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

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- ▶ orthogonality is a plus

# plane-wave basis sets

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

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

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periodic boundary conditions

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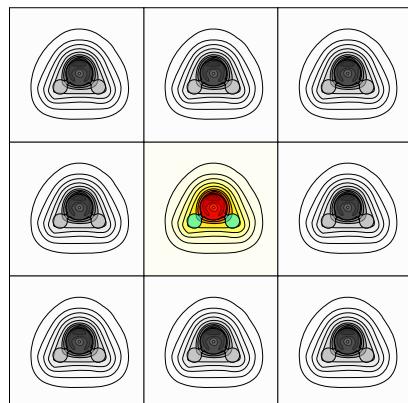
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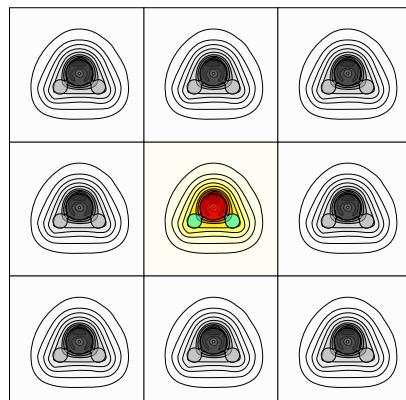
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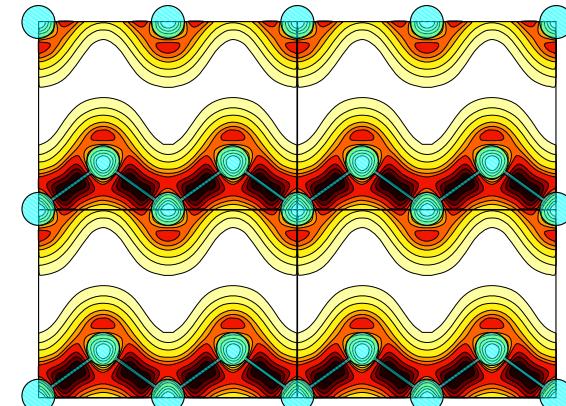
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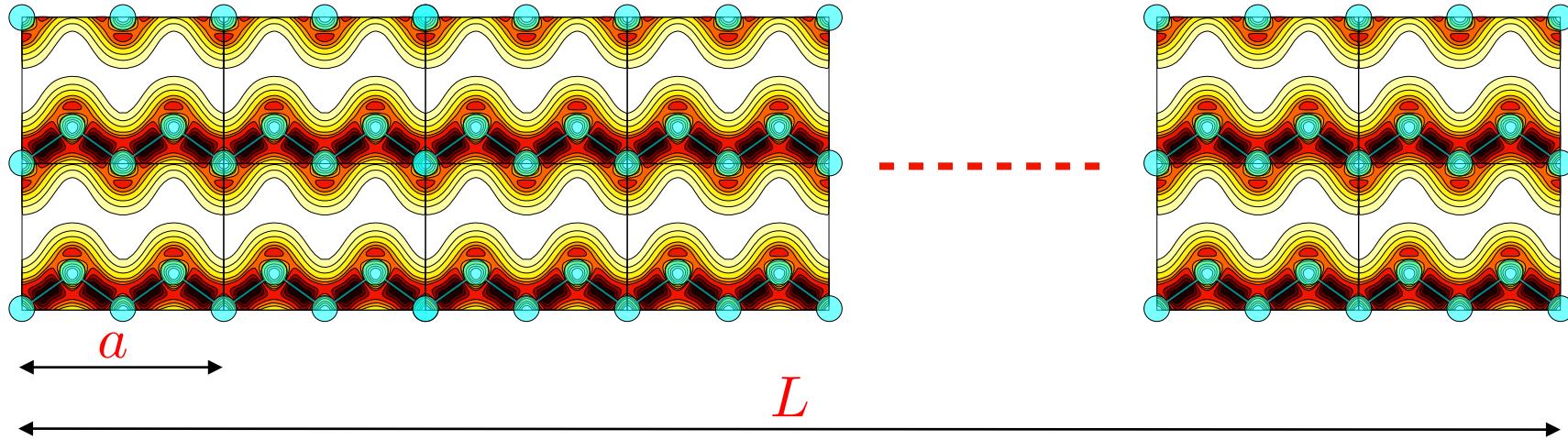
infinite crystals ( $\ell = L$ )



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

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

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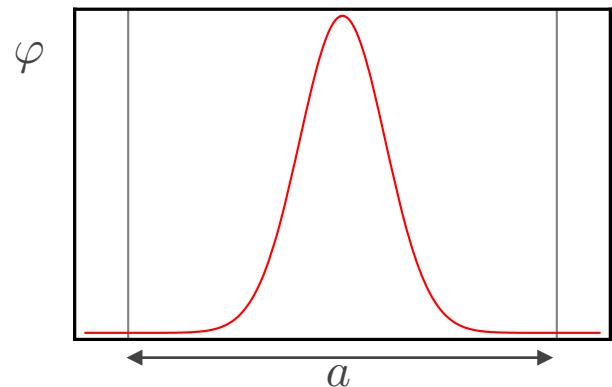
$$V_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r}))$$

$$V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$= e^2 \sum_{\mathbf{G} \neq 0} e^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G})$$

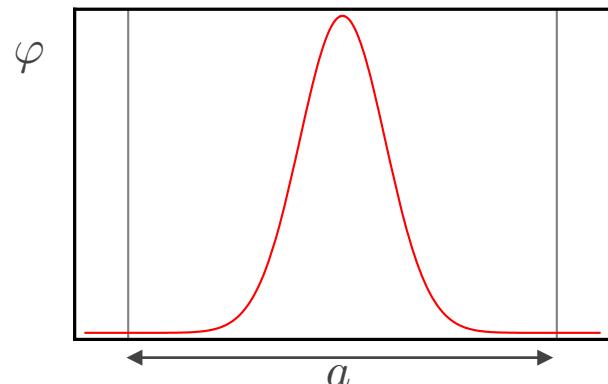
# sampling theorem

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

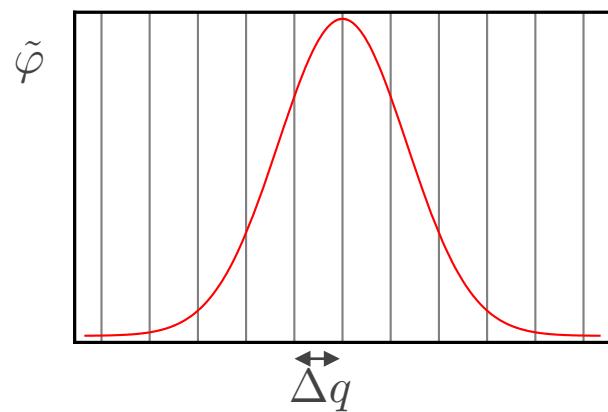


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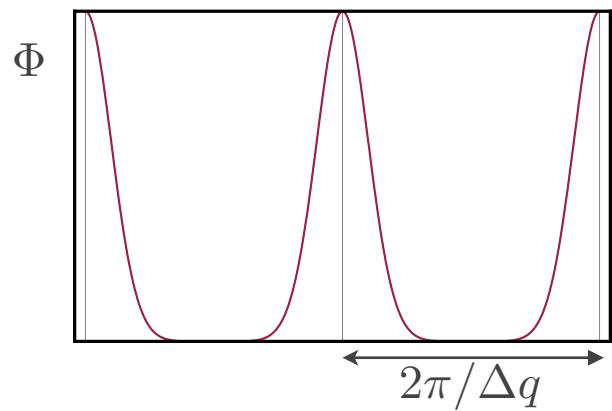
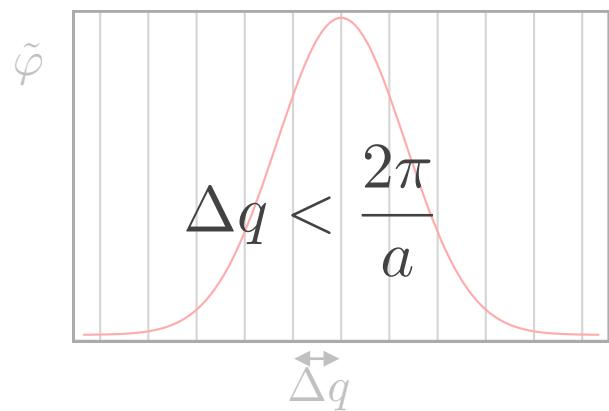
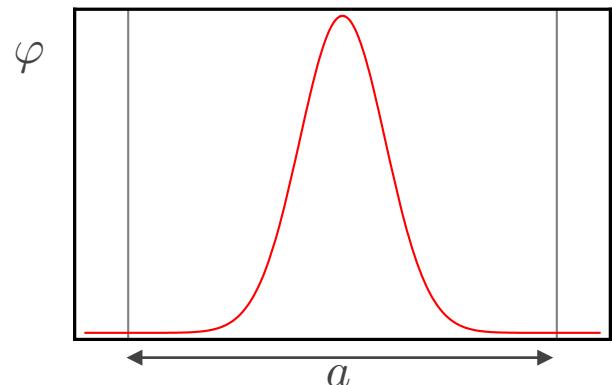


$$\Delta q < \frac{2\pi}{a}$$



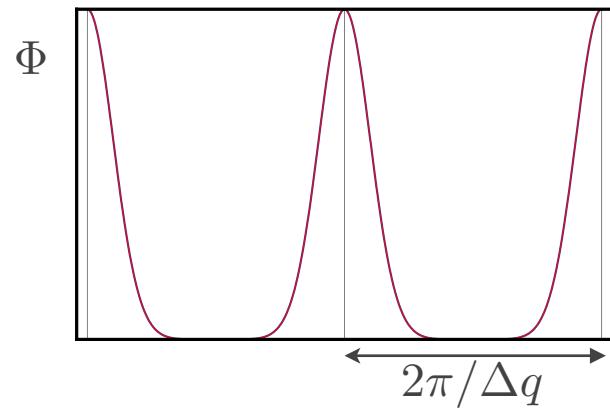
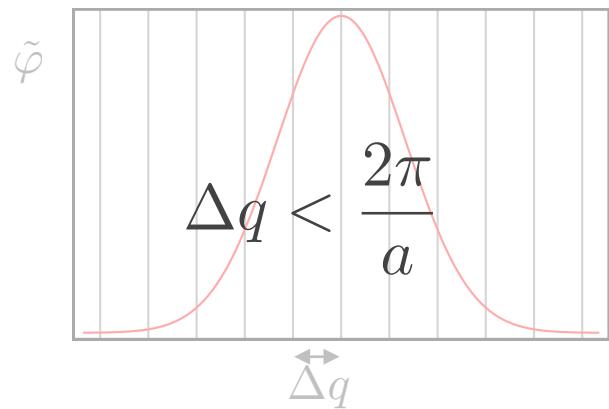
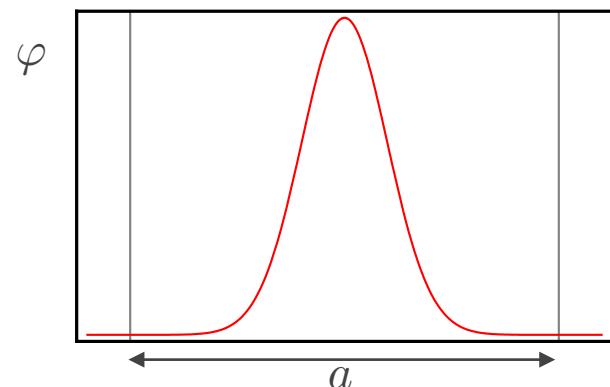
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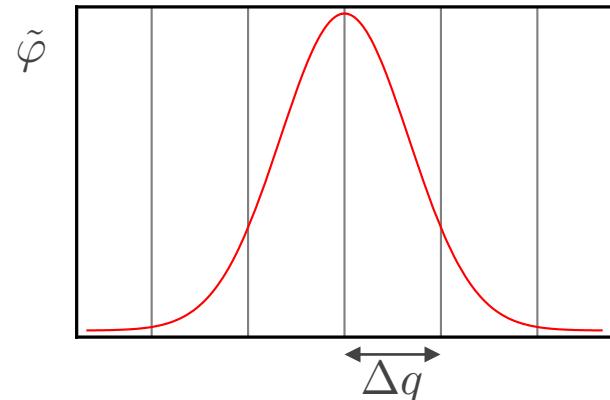


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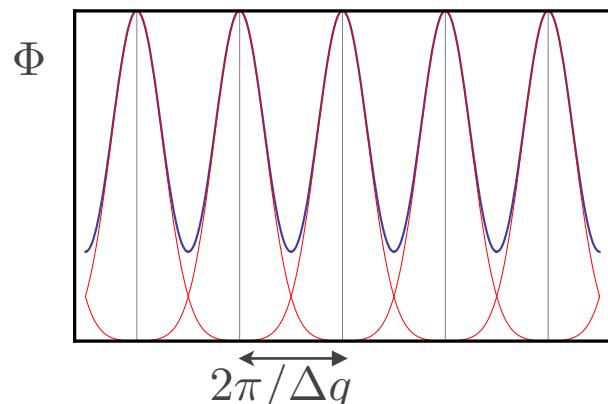
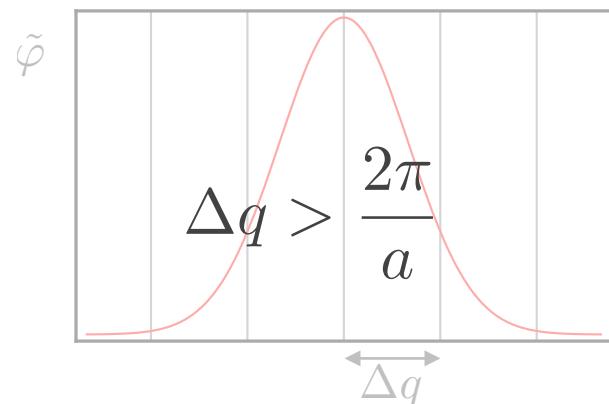
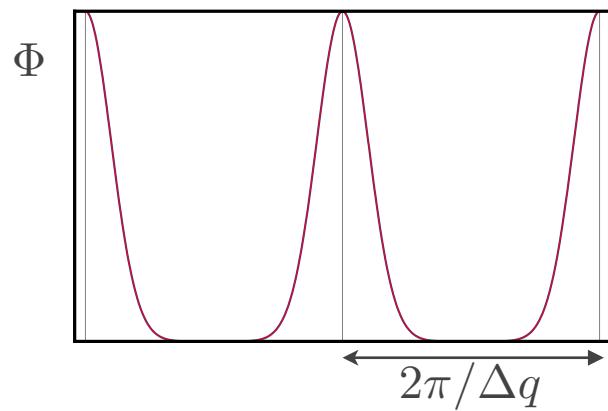
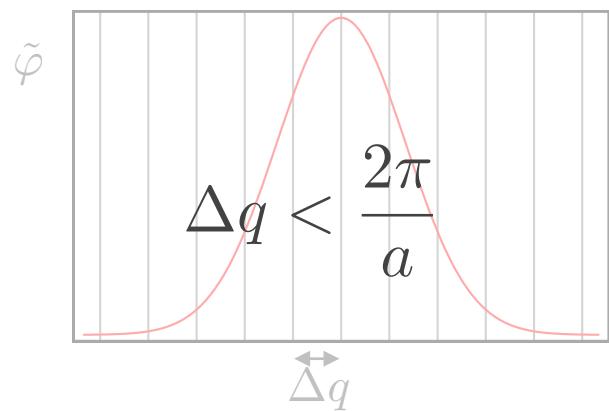
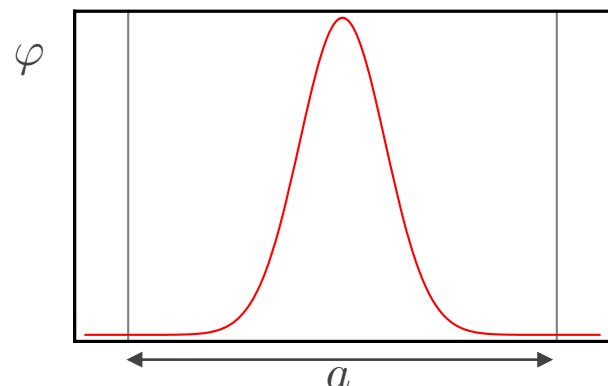


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# discrete Fourier transforms

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

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

$$\omega \rightarrow \left\{ \omega_k = k \frac{2\Omega}{N} \right\}_{k=-\frac{N}{2}, \dots, \frac{N}{2}-1}$$

$$f(t) \rightarrow \{f_l = f(t_l)\}$$

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

$$\tilde{f}(\omega) \rightarrow \{\tilde{f}_k = \tilde{f}(\omega_k)\}$$

# discrete Fourier transforms

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

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

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

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

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

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

dFt

# properties of the dFt

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

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periodicity in the primary space

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

# the fast Fourier transform

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

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

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

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

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

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# multivariate FFTs

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

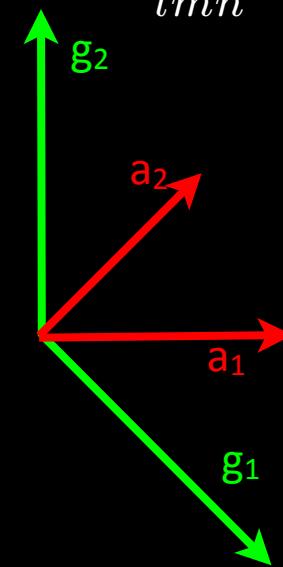
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$$\mathbf{G}_{pqrs} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

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

FFT   
 FFT<sup>-1</sup>

# multivariate FFTs (II)

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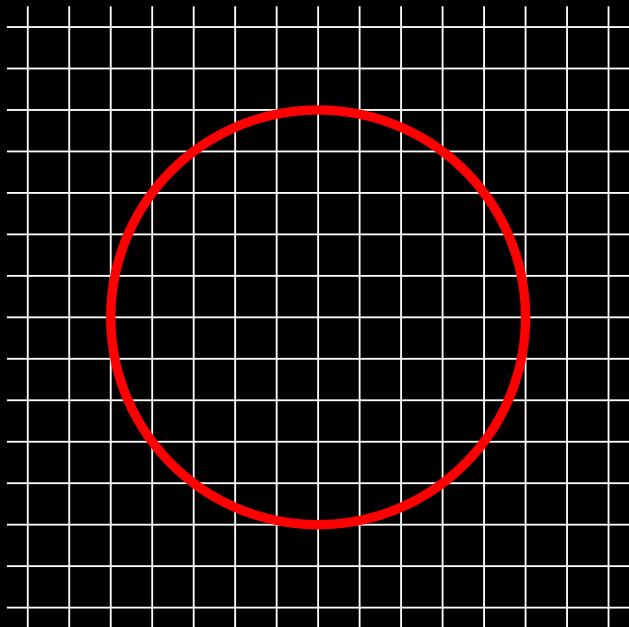
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$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

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

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- 😢 basis set depends on volume shape/size (Pulay stresses)
- 😢 uniform spatial resolution (no core states!)

# treating core states

1	H Hydrogen 1.007 94																	
2	Li Lithium 6.941	Group 2	Be Beryllium 9.012 182															
3	Na Sodium 22.989 770	Mg Magnesium 24.3050																
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955 910	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938 049	Fe Iron 55.845	Co Cobalt 58.933 200	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.409	Al Aluminum 26.981 536	Si Silicon 28.0855	P Phosphorus 30.973 761	S Sulfur 32.065	Cl Chlorine 35.453	Ar Argon 39.948
5	Rb Radium 85.4678	Sr Strontium 87.62	Y Yttrium 88.905 85	Zr Zirconium 91.224	Nb Niobium 92.906 38	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.905 50	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.904 47	Xe Xenon 131.293
6	Cs Cesium 132.905 43	Ba Barium 137.527	La Lanthanum 138.9055	Hf Hafnium 178.49	Ta Tantalum 180.9479	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.217	Pt Platinum 195.078	Au Gold 196.966 55	Hg Mercury 200.59	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.980 38	Po Polonium (209)	At Astatine (210)	Rn Radon (222)
7	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (268)	Ds Darmstadtium (281)	Uuo* Ununoctium (272)	Uub* Ununbium (285)	Uut* Ununtrium (284)	Uuu* Ununquadium (289)	Uup* Ununpentium (288)			
	* The systematic names and symbols for elements greater than 110 will be used until the approval of trivial names by IUPAC.																	
	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 173.64	71 Lu Lutetium 174.967				
	90 Th Thorium 232.0381	91 Pa Protactinium 231.035 68	92 U Uranium 238.028 91	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (245)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (252)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)				

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

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<b>4</b>	<b>19</b> <b>K</b> Potassium 39.0983	<b>20</b> <b>Ca</b> Calcium 40.078	<b>21</b> <b>Sc</b> Scandium 44.955 910	<b>22</b> <b>Ti</b> Titanium 47.867	<b>23</b> <b>V</b> Vanadium 50.9415	<b>24</b> <b>Cr</b> Chromium 51.9861	<b>25</b> <b>Mn</b> Manganese 54.938 049	<b>26</b> <b>Fe</b> Iron 55.845	<b>27</b> <b>Co</b> Cobalt 58.933 200	<b>28</b> <b>Ni</b> Nickel 58.6934	<b>29</b> <b>Cu</b> Copper 63.546	<b>30</b> <b>Zn</b> Zinc 65.409	<b>31</b> <b>Ga</b> Gallium 69.723	<b>32</b> <b>Ge</b> Germanium 72.64	<b>33</b> <b>As</b> Arsenic 74.931 60	<b>34</b> <b>Se</b> Selenium 78.96	<b>35</b> <b>Br</b> Bromine 79.904	<b>36</b> <b>Kr</b> Krypton 83.798	<b>Group 18</b>	
<b>5</b>	<b>37</b> <b>Rb</b> Rubidium 85.4678	<b>38</b> <b>Sr</b> Strontium 87.62	<b>39</b> <b>Y</b> Yttrium 88.905 85	<b>40</b> <b>Zr</b> Zirconium 91.224	<b>41</b> <b>Nb</b> Niobium 92.906 38	<b>42</b> <b>Tc</b> Technetium (98)	<b>43</b> <b>Ru</b> Ruthenium 101.07	<b>44</b> <b>Rh</b> Rhodium 102.955 50	<b>45</b> <b>Pd</b> Palladium 106.42	<b>46</b> <b>Ag</b> Silver 107.8862	<b>47</b> <b>Cd</b> Cadmium 112.411	<b>48</b> <b>In</b> Indium 114.818	<b>49</b> <b>Sn</b> Tin 118.710	<b>50</b> <b>Sb</b> Antimony 121.760	<b>51</b> <b>Te</b> Tellurium 127.60	<b>52</b> <b>I</b> Iodine 126.904 47	<b>53</b> <b>Xe</b> Xenon 131.293			
<b>6</b>	<b>55</b> <b>Cs</b> Cesium 132.905 43	<b>56</b> <b>Ba</b> Barium 137.327	<b>57</b> <b>La</b> Lanthanum 138.9055	<b>72</b> <b>Hf</b> Hafnium 176.49	<b>73</b> <b>Ta</b> Tantalum 180.9479	<b>74</b> <b>W</b> Tungsten 183.84	<b>75</b> <b>Re</b> Rhenium 186.207	<b>76</b> <b>Os</b> Osmium 190.23	<b>77</b> <b>Ir</b> Iridium 192.217	<b>78</b> <b>Pt</b> Platinum 195.078	<b>79</b> <b>Au</b> Gold 196.966 55	<b>80</b> <b>Hg</b> Mercury 200.59	<b>81</b> <b>Tl</b> Thallium 204.3833	<b>82</b> <b>Pb</b> Lead 207.2	<b>83</b> <b>Bi</b> Bismuth 208.980 38	<b>84</b> <b>Po</b> Polonium (209)	<b>85</b> <b>At</b> Astatine (210)	<b>86</b> <b>Rn</b> Radon (222)		
<b>7</b>	<b>87</b> <b>Fr</b> Francium (223)	<b>88</b> <b>Ra</b> Radium (226)	<b>89</b> <b>Ac</b> Actinium (227)	<b>104</b> <b>Rf</b> Rutherfordium (261)	<b>105</b> <b>Db</b> Dubnium (262)	<b>106</b> <b>Sg</b> Seaborgium (266)	<b>107</b> <b>Bh</b> Bohrium (264)	<b>108</b> <b>Hs</b> Hassium (277)	<b>109</b> <b>Mt</b> Meitnerium (268)	<b>110</b> <b>Ds</b> Darmstadtium (281)	<b>111</b> <b>Uuu*</b> Ununtrium (272)	<b>112</b> <b>Uub*</b> Ununbium (285)	<b>113</b> <b>Uut*</b> Ununtrium (284)	<b>114</b> <b>Uuq*</b> Ununquadium (289)	<b>115</b> <b>Uup*</b> Ununpentium (288)					
	<b>58</b> <b>Ce</b> Cerium 140.116	<b>59</b> <b>Pr</b> Praseodymium 141.907 65	<b>60</b> <b>Nd</b> Neodymium 144.24	<b>61</b> <b>Pm</b> Promethium (145)	<b>62</b> <b>Sm</b> Samarium 150.36	<b>63</b> <b>Eu</b> Europium 151.964	<b>64</b> <b>Gd</b> Gadolinium 157.25	<b>65</b> <b>Tb</b> Terbium 158.925 34	<b>66</b> <b>Dy</b> Dysprosium 162.500	<b>67</b> <b>Ho</b> Holmium 164.930 32	<b>68</b> <b>Er</b> Erbium 167.259	<b>69</b> <b>Tm</b> Thulium 168.934 21	<b>70</b> <b>Yb</b> Ytterbium 173.04	<b>71</b> <b>Lu</b> Lutetium 174.967						
	<b>90</b> <b>Th</b> Thorium 232.0381	<b>91</b> <b>Pa</b> Protactinium 231.015 88	<b>92</b> <b>U</b> Uranium 238.028 91	<b>93</b> <b>Np</b> Neptunium (237)	<b>94</b> <b>Pu</b> Plutonium (244)	<b>95</b> <b>Am</b> Americium (243)	<b>96</b> <b>Cm</b> Curium (247)	<b>97</b> <b>Bk</b> Berkelium (247)	<b>98</b> <b>Cf</b> Californium (251)	<b>99</b> <b>Es</b> Einsteinium (252)	<b>100</b> <b>Fm</b> Fermium (257)	<b>101</b> <b>Md</b> Mendelevium (258)	<b>102</b> <b>No</b> Nobelium (259)	<b>103</b> <b>Lr</b> Lawrencium (262)						

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.

\* The systematic names and symbols for elements greater than 100 will be used until the approval of trivial names by IUPAC.

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

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

# treating core states

	1 H Hydrogen 1.007 94																							
1	3 Li Lithium 6.941	4 Be Beryllium 9.012 182																						
2	11 Na Sodium 22.989 770	12 Mg Magnesium 24.3050																						
3	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 51.9861	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 74.931 60	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798						
4	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 102.955 50	46 Pd Palladium 106.42	47 Ag Silver 107.8862	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						
5	55 Cs Cesium 132.905 43	56 Ba Barium 137.327	57 La Lanthanum 138.9055	58 Hf Hafnium 176.49	59 Ta Tantalum 180.9479	60 W Tungsten 183.84	61 Re Rhenium 186.207	62 Os Osmium 190.23	63 Ir Iridium 192.217	64 Pt Platinum 195.078	65 Au Gold 196.966 55	66 Hg Mercury 200.59	67 Tl Thallium 204.3833	68 Pb Lead 207.2	69 Bi Bismuth 208.980 38	70 Po Polonium (209)	71 At Astatine (210)	72 Rn Radon (222)						
6	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* Ununtrium (272)	112 Uub* Ununbium (285)	113 Uut* Ununtrium (284)	114 Uuo* Ununoctium (289)	115 Uup* Ununpentium (288)									
7	58 Ce Cerium 140.116	59 Pr Praseodymium 141.907 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)										

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 114, 116, and 118 has been reported but not confirmed.

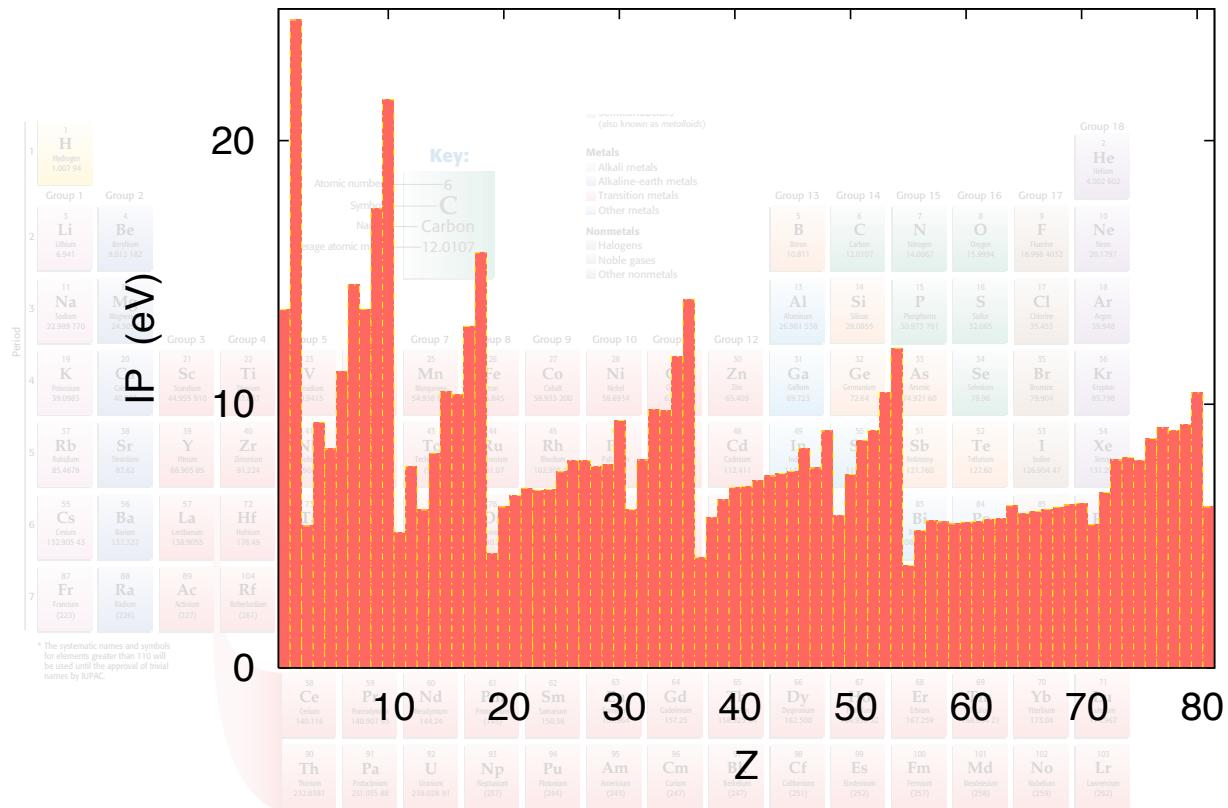
\* The systematic names and symbols for elements greater than 110 will be used until the approval of trivial names by IUPAC.

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

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

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

# treating core states



$$\begin{aligned}
 \epsilon_{1s} &\sim Z^2 & a_{1s} &\sim \frac{1}{Z} \\
 E_{cut} &\sim Z^2 & \\
 N_{PW} &= \frac{4\pi}{3} k_{cut}^3 \frac{1}{(2\pi)^3} & a &\sim 1 \\
 &\sim Z^3
 \end{aligned}$$

# 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

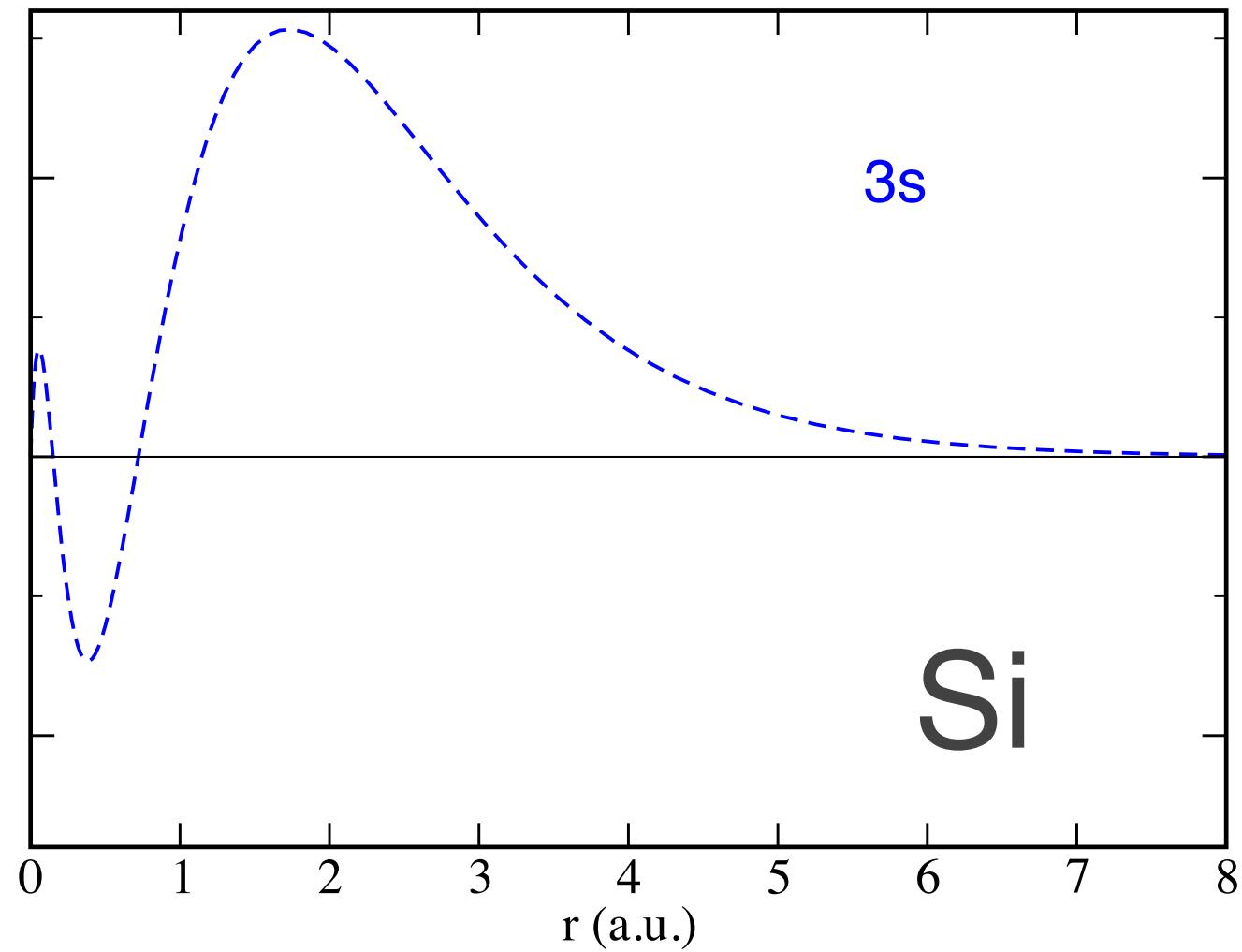
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

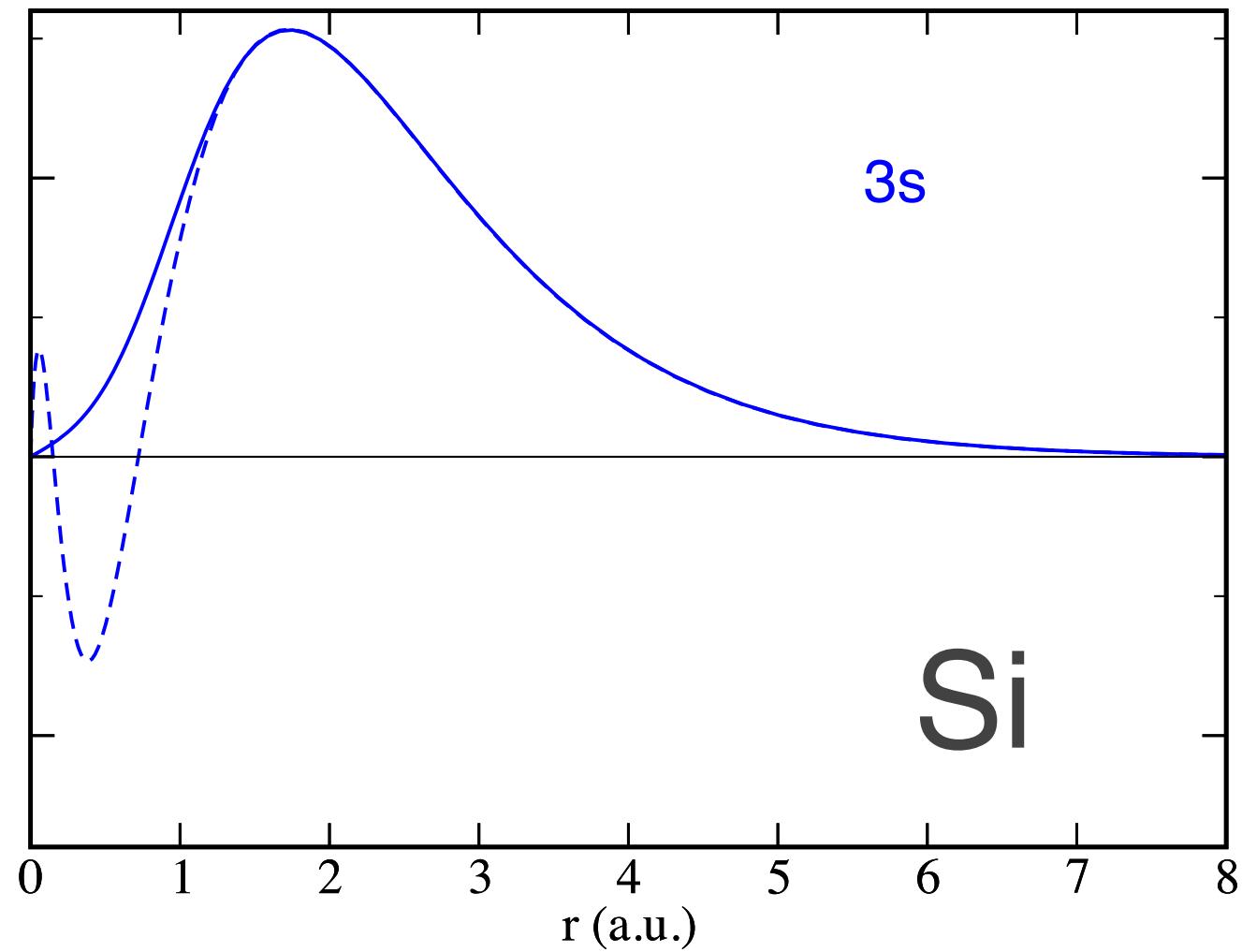
$$\phi_{val}^{ps} \quad \text{is nodeless and smooth}$$

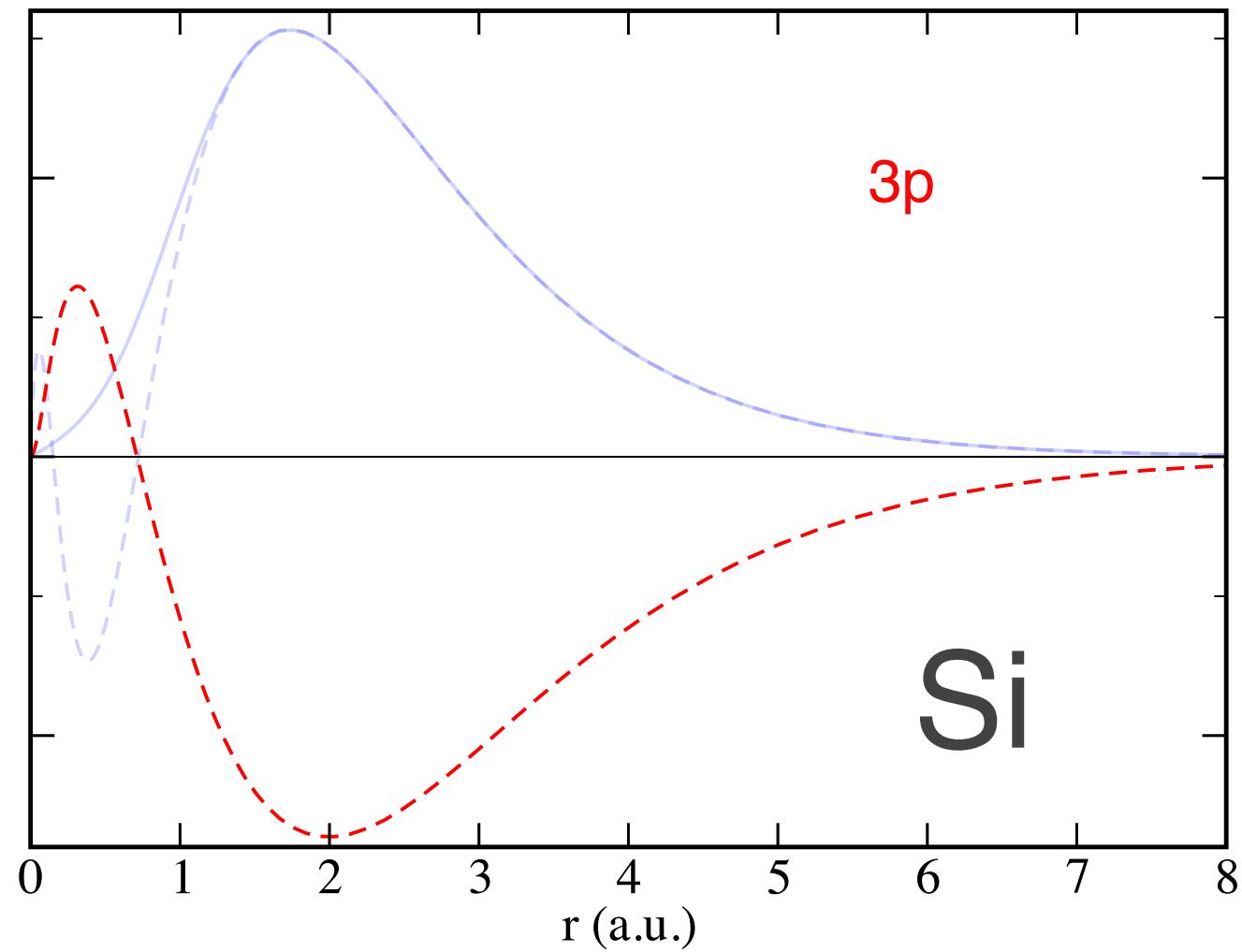
the chemical properties of the pseudo-atom are the same as those of the true atom:

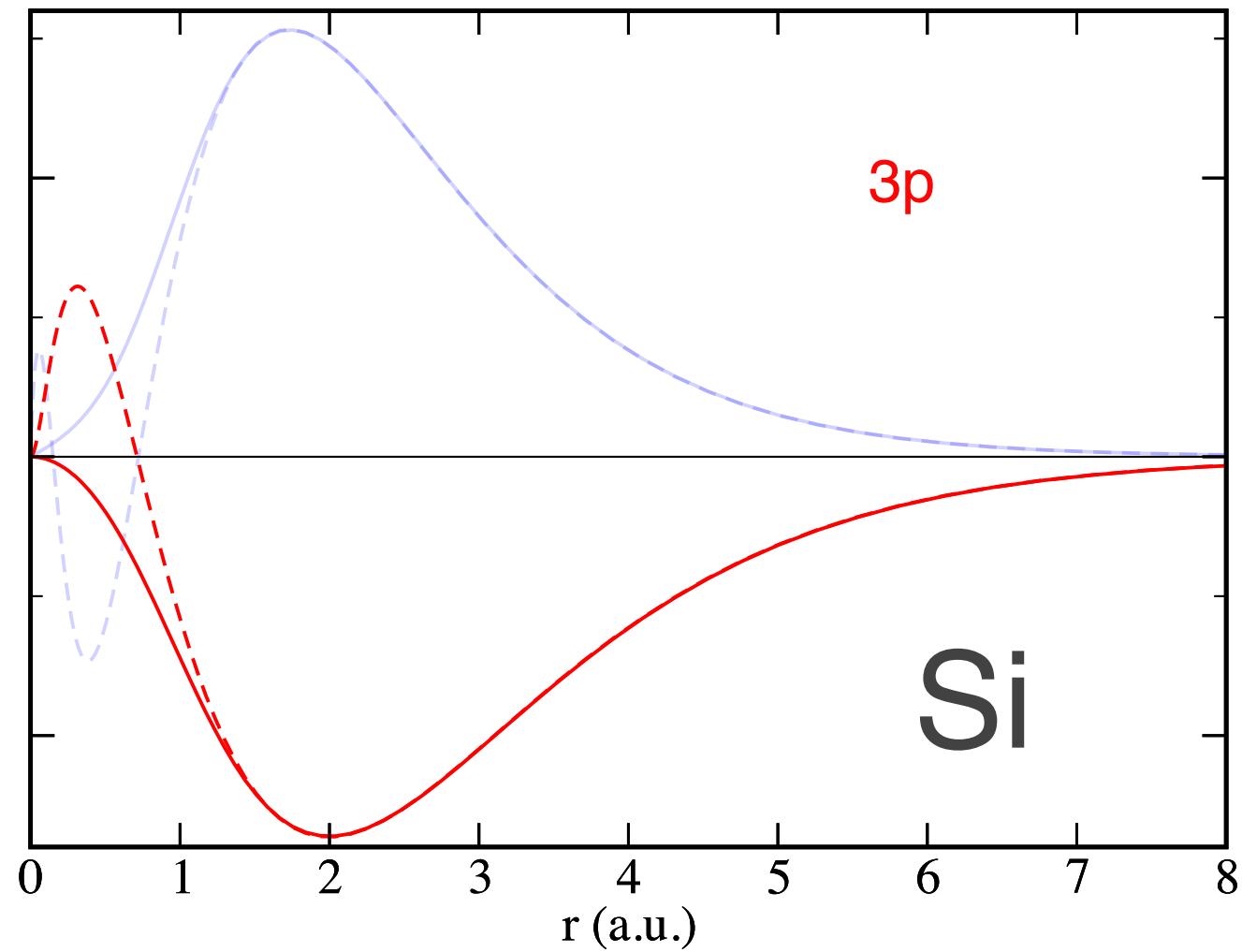
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

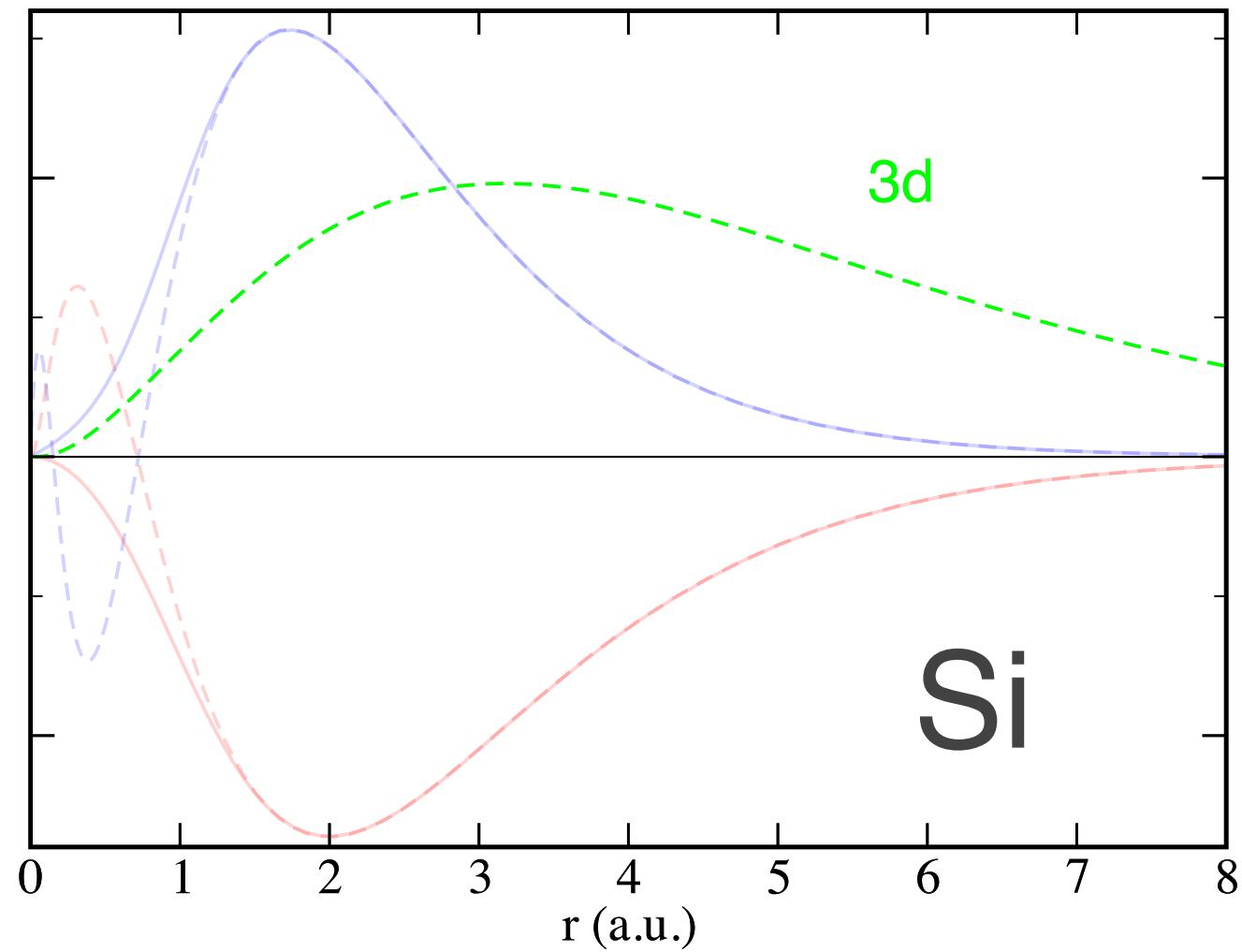
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for} \quad r > r_c$$

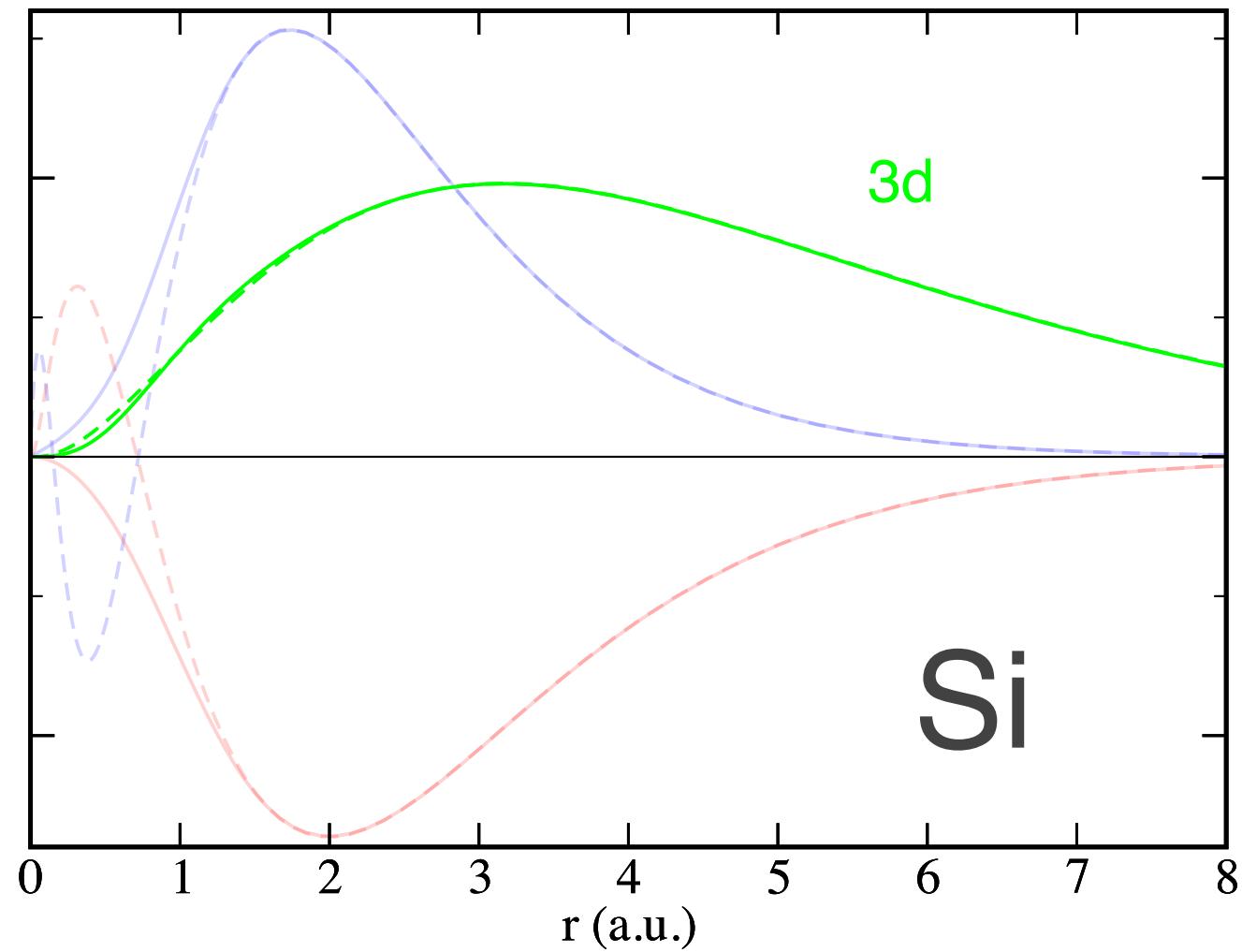




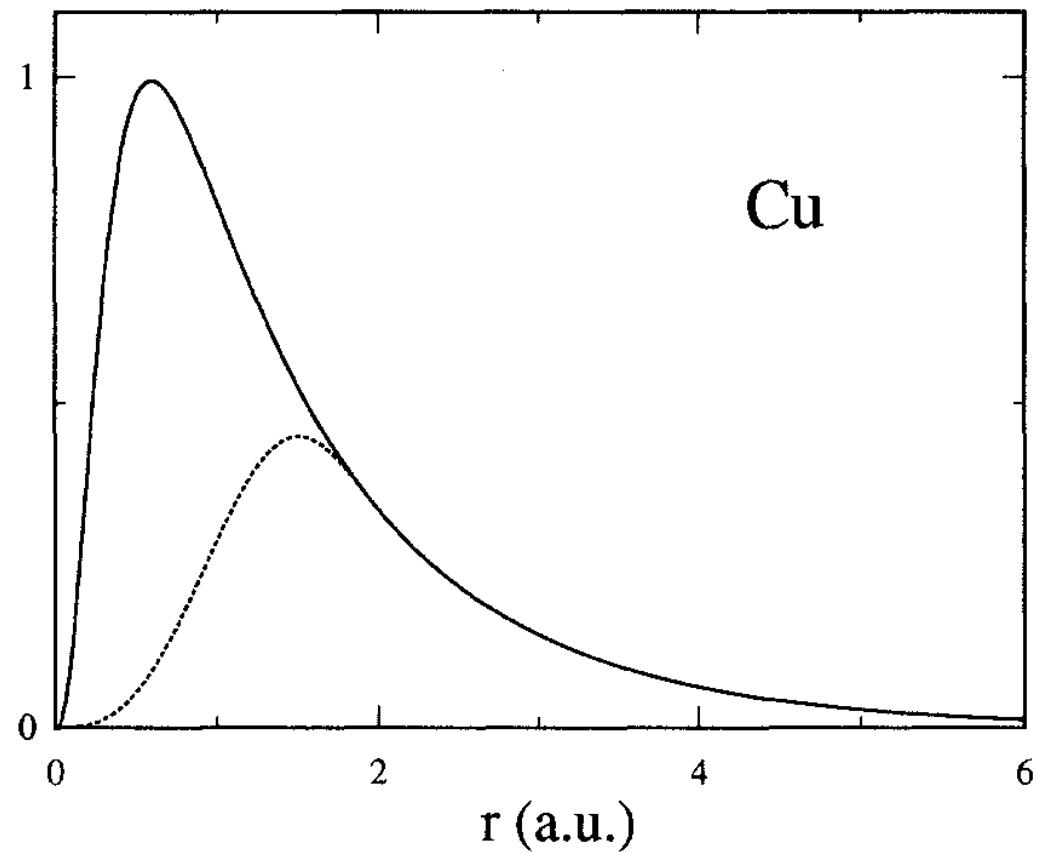




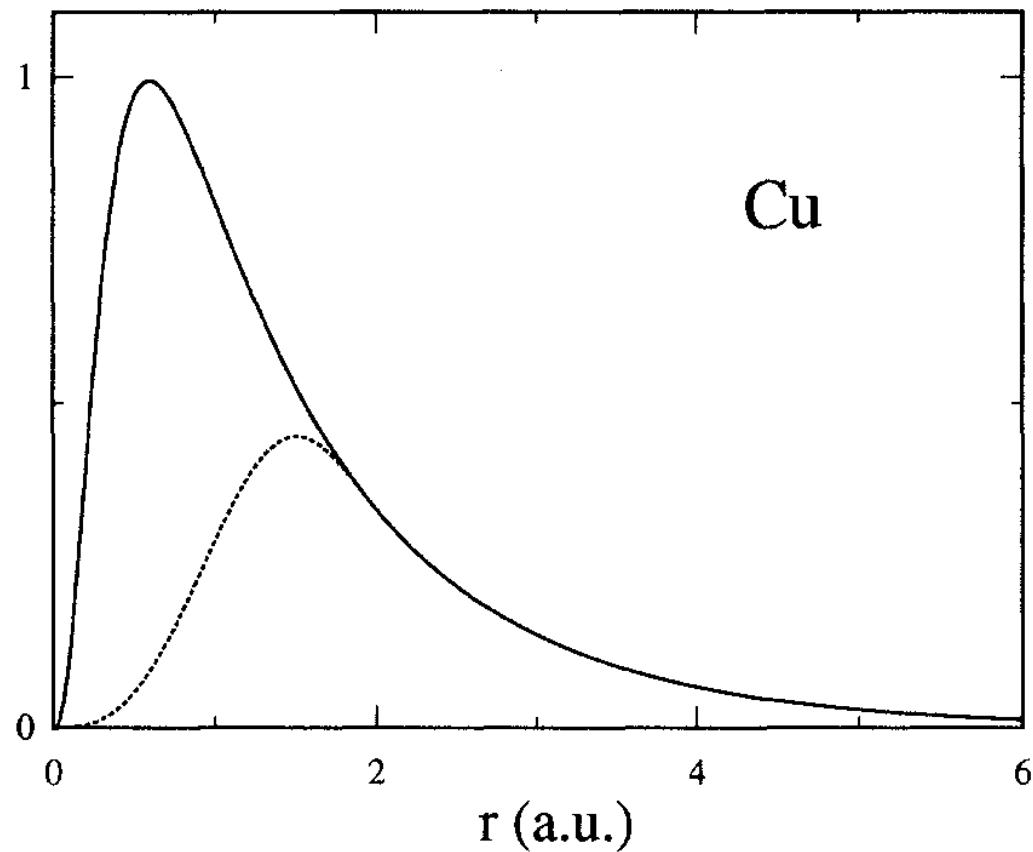




# US pseudopotentials



# US pseudopotentials



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

*That's all Folks!*

these slides at

<http://talks.baroni.me>

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