



modelling materials using quantum mechanics and digital computers

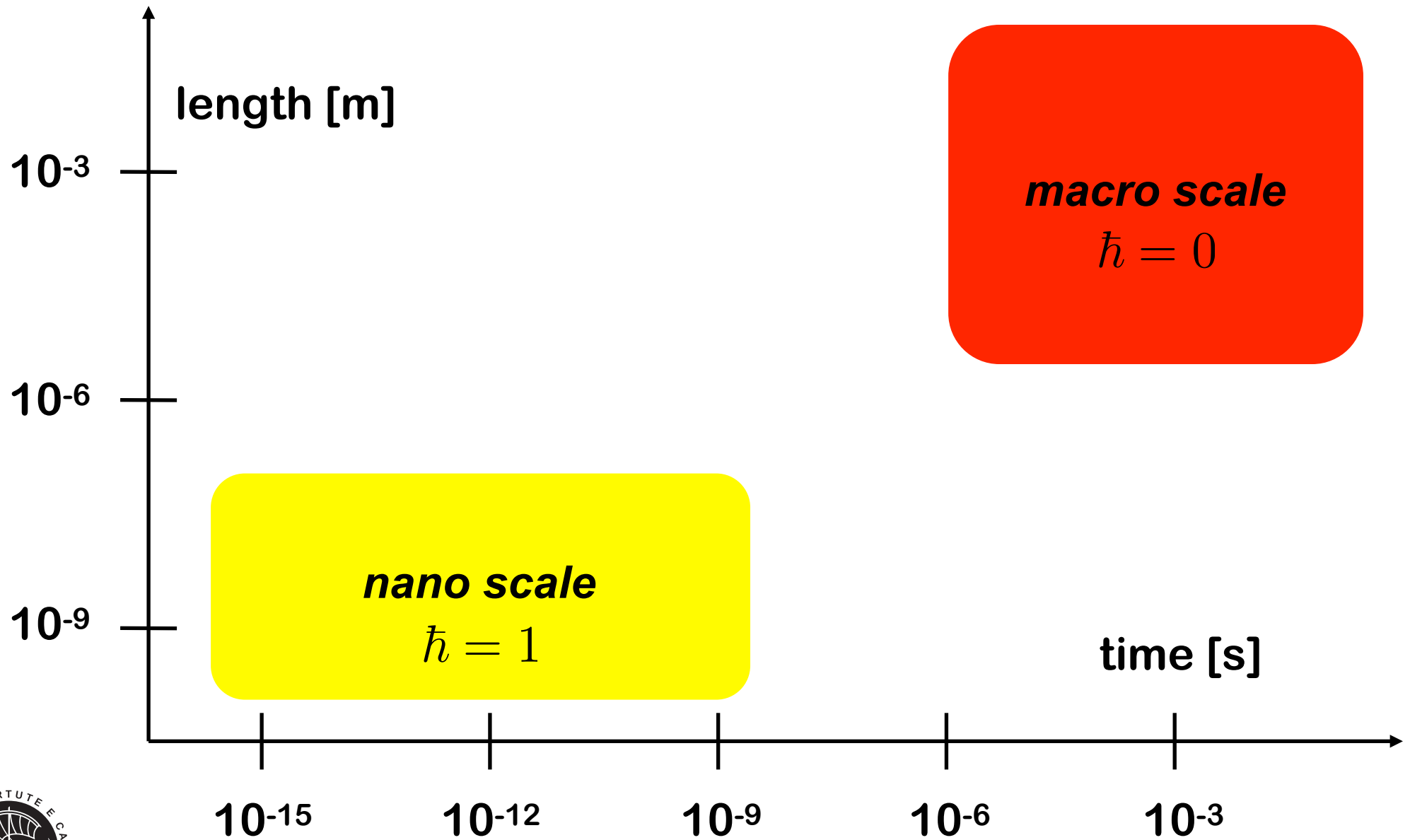
the plane-wave pseudo potential way

Stefano Baroni

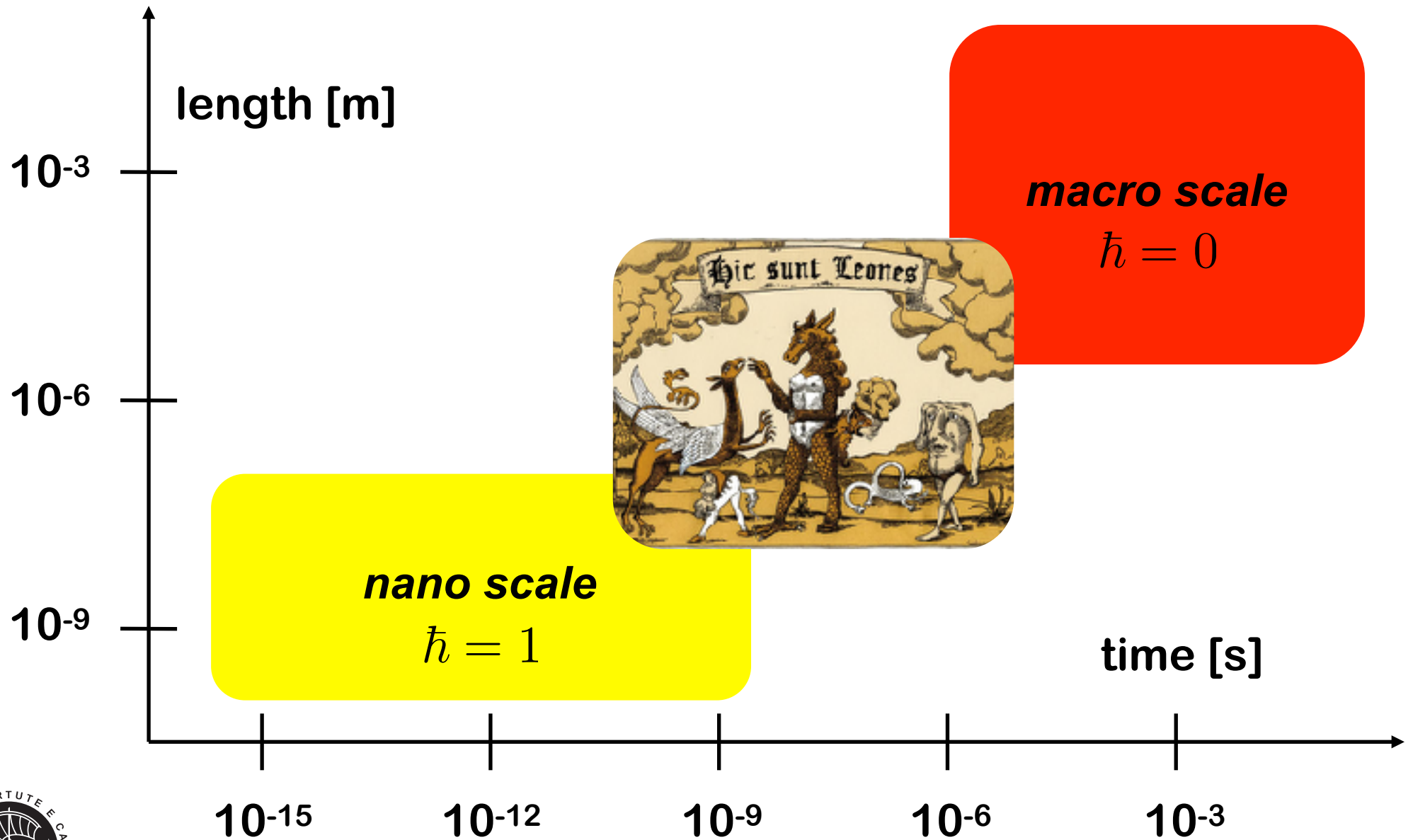
Scuola Internazionale Superiore di Studi Avanzati
Trieste - Italy

warm-up lecture given at the Summer School on Advanced and Materials and Molecular Modelling,
Jožef Stefan Institute, Ljubljana, September 16-20, 2019

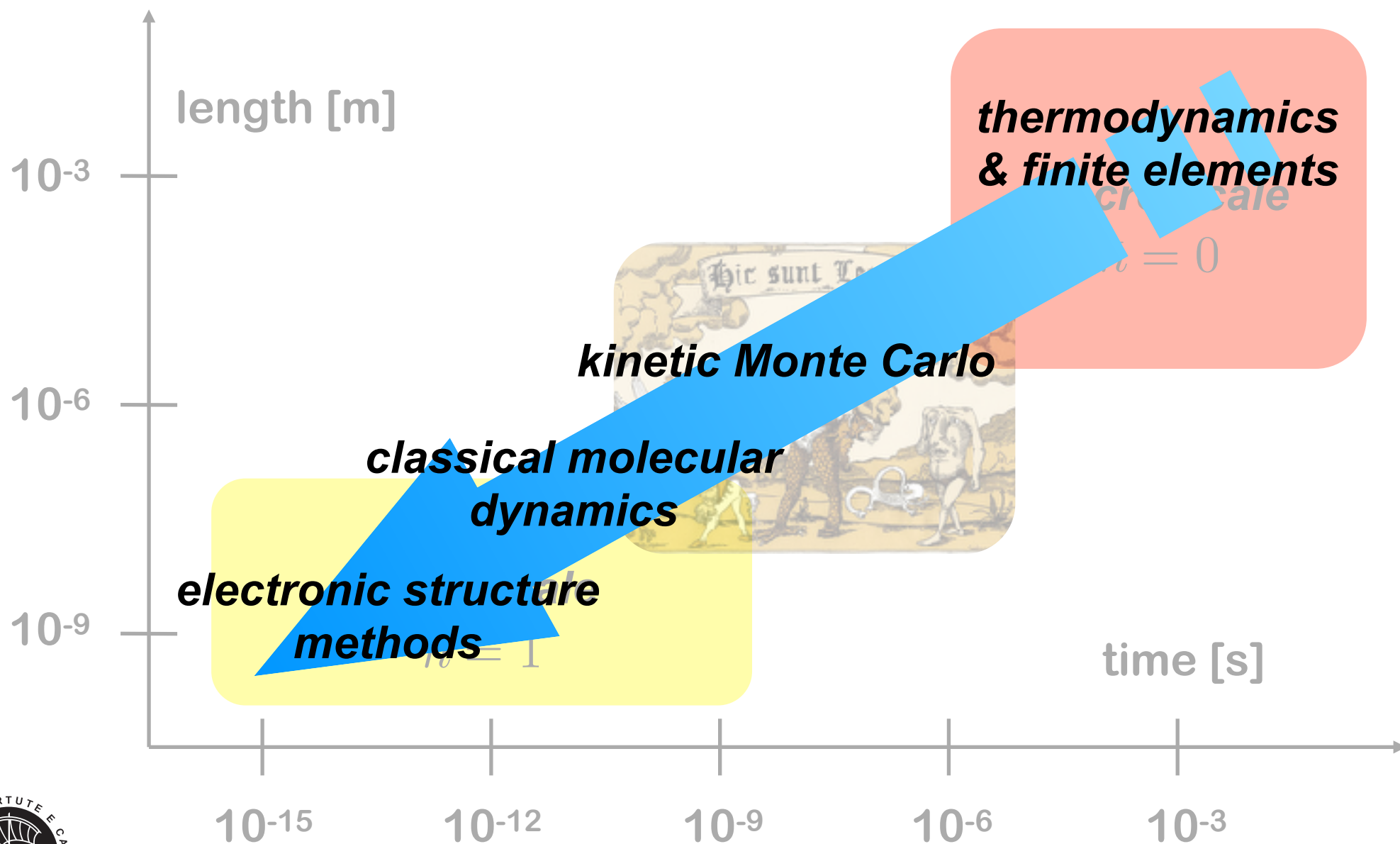
the saga of time and length scales



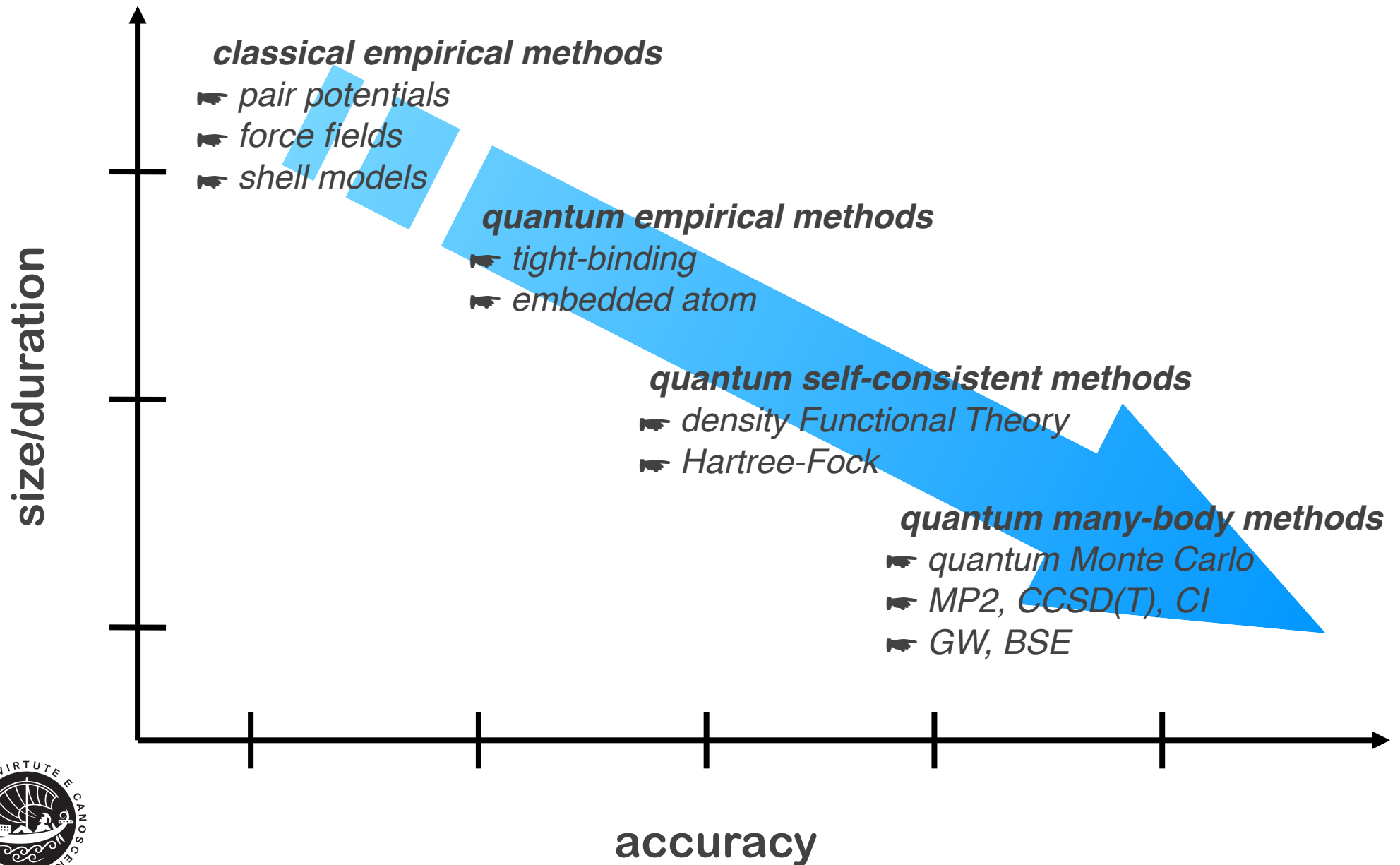
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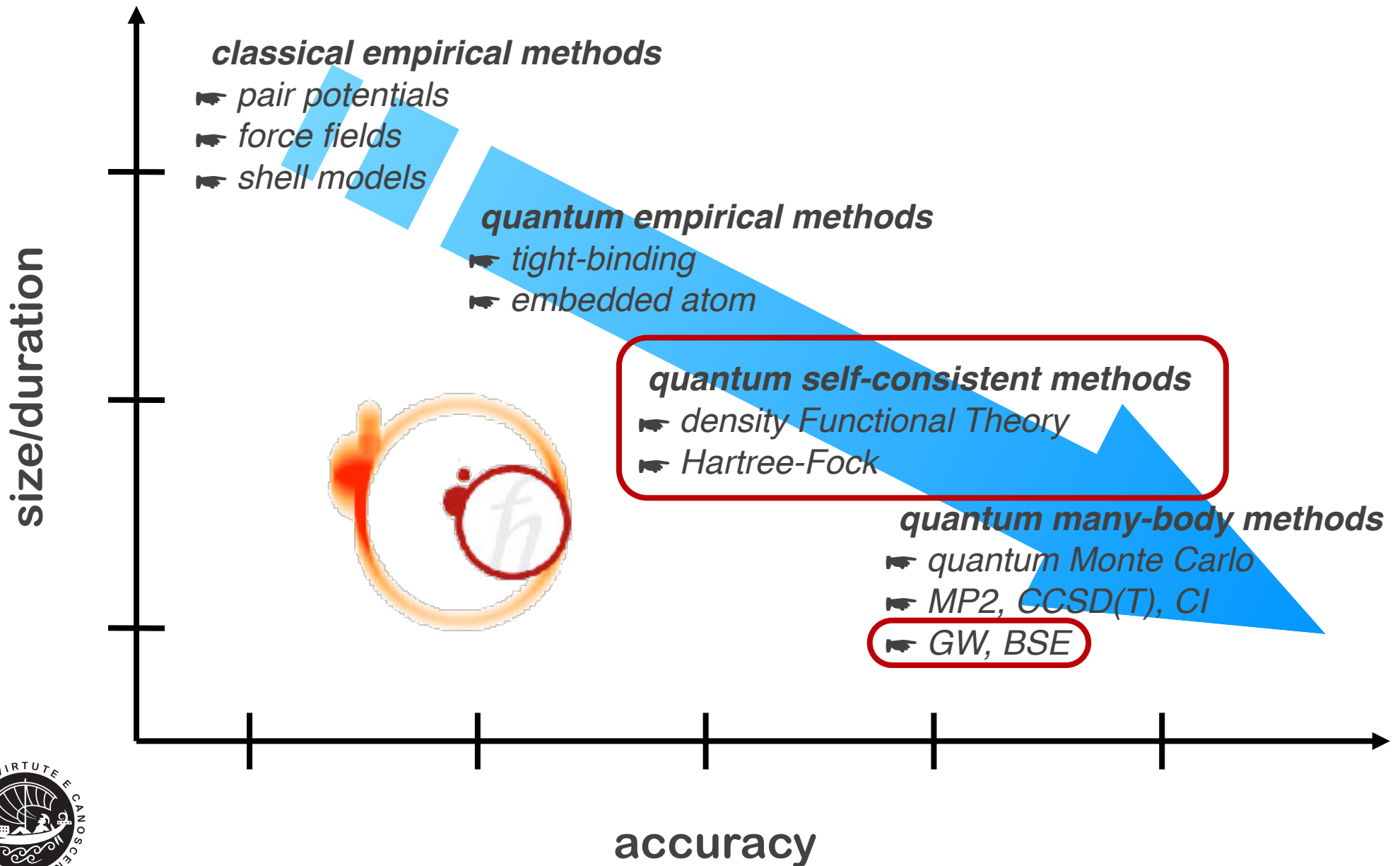
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size vs. accuracy



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

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Kohn-Sham
Hamiltonian

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functionals

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



functionals

examples:

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

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

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

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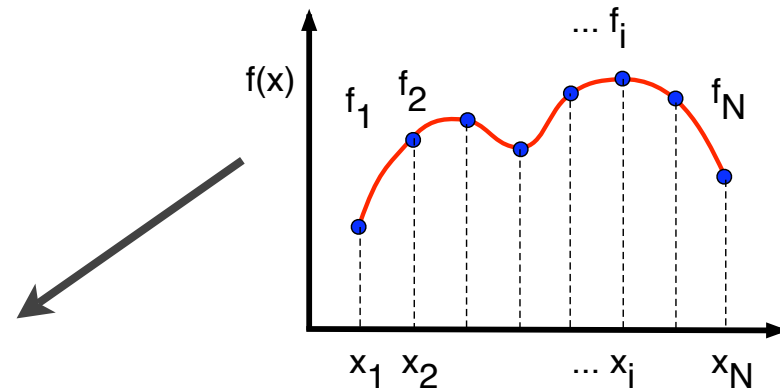
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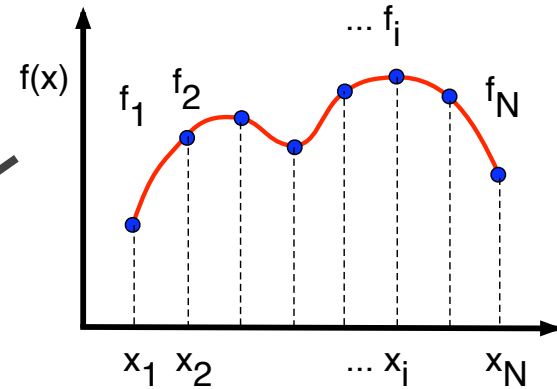
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$$f(x) \approx \sum_n c_n \phi_n(x)$$



functional derivatives

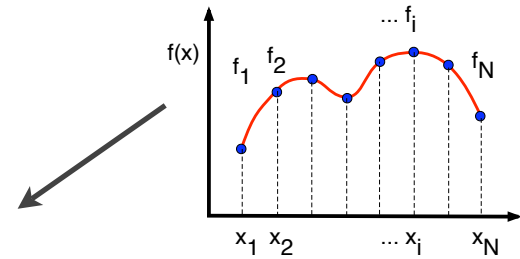
$$G[f_0 + \epsilon f_1] = G[f_0] + \epsilon \int f_1(x) \left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} dx + \mathcal{O}(\epsilon^2)$$



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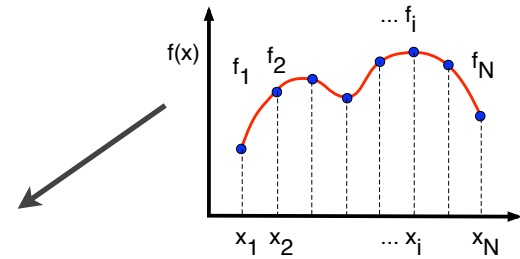
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$$\left. \frac{\delta G}{\delta f(x)} \right|_{f=f_0} \text{ “ = ” } \lim_{\epsilon \rightarrow 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

the Hellmann-Feynman theorem

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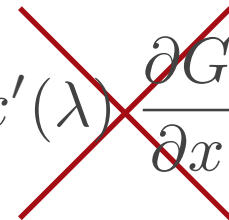
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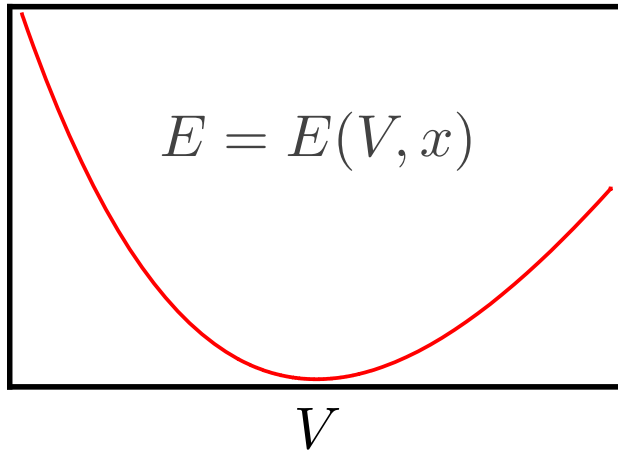
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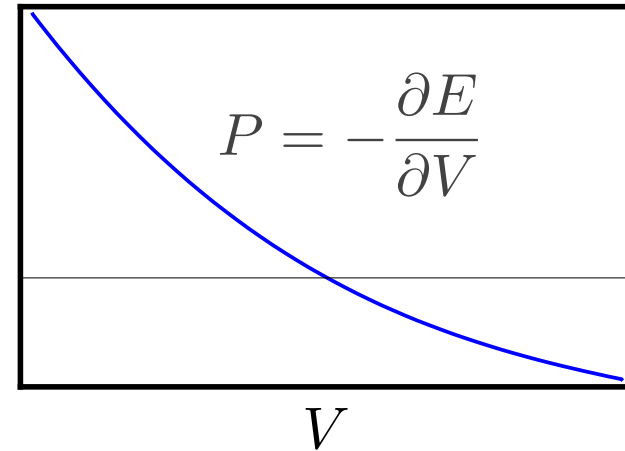
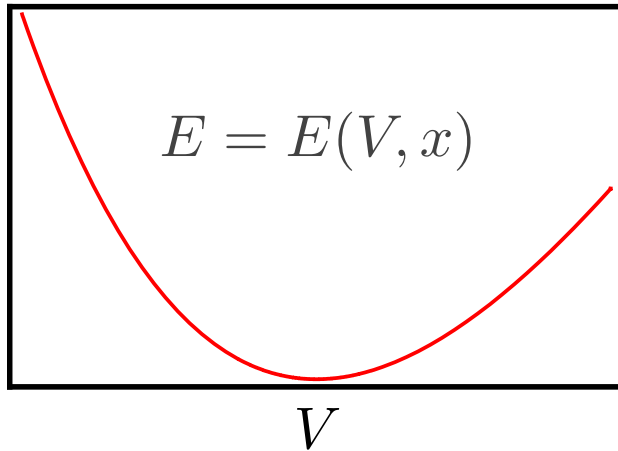
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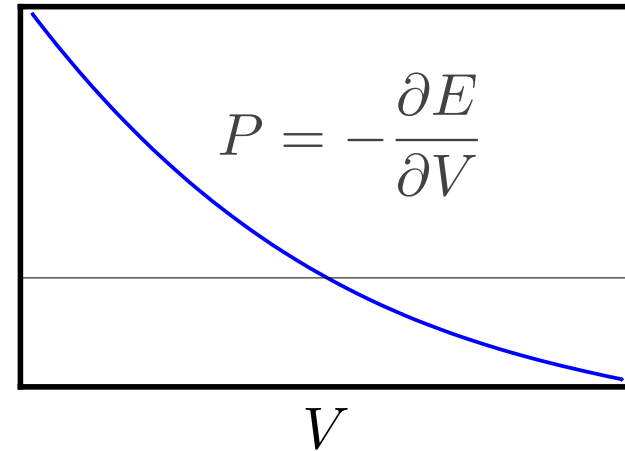
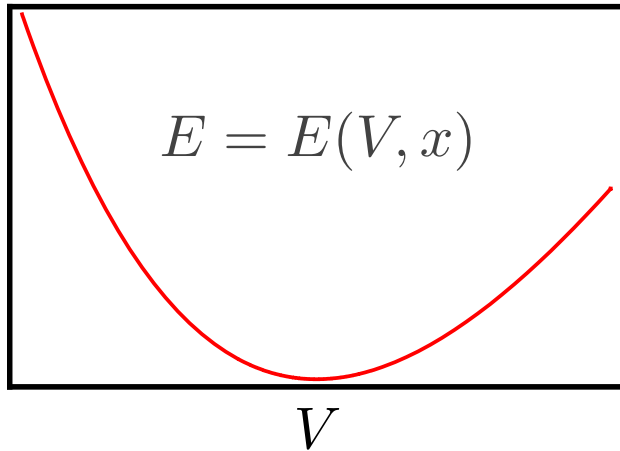
conjugate variables & Legendre



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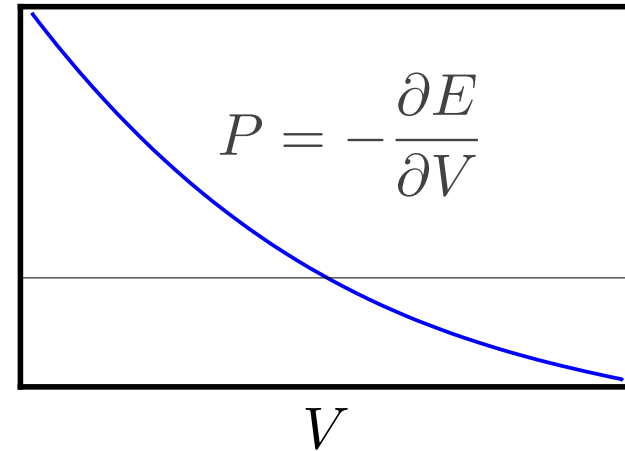
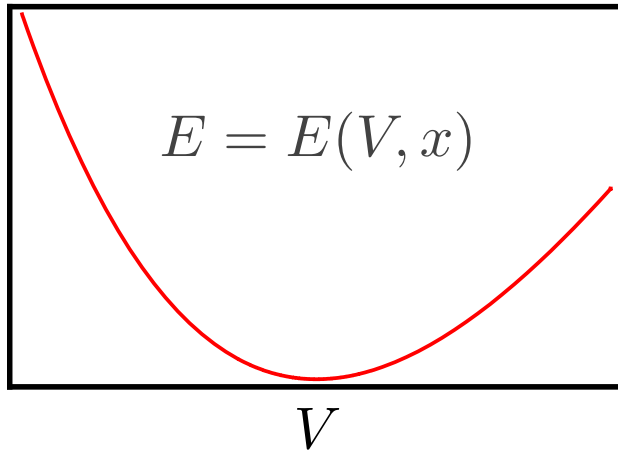


conjugate variables & Legendre



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

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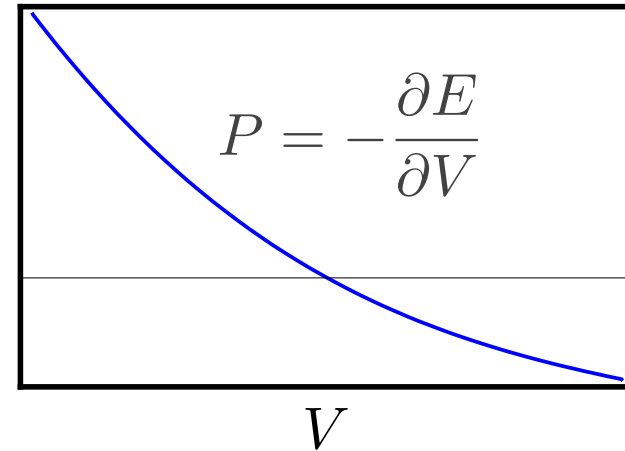
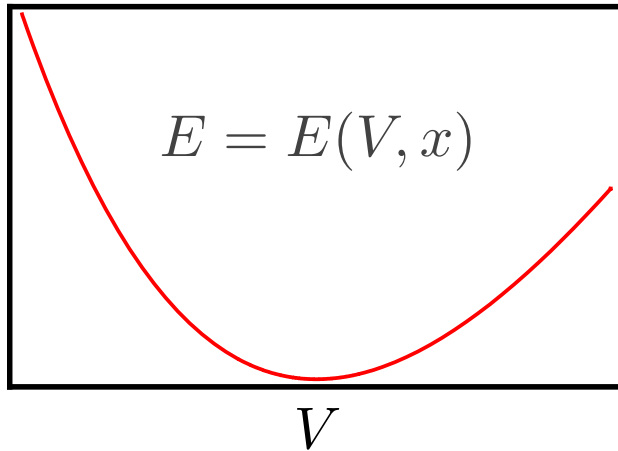


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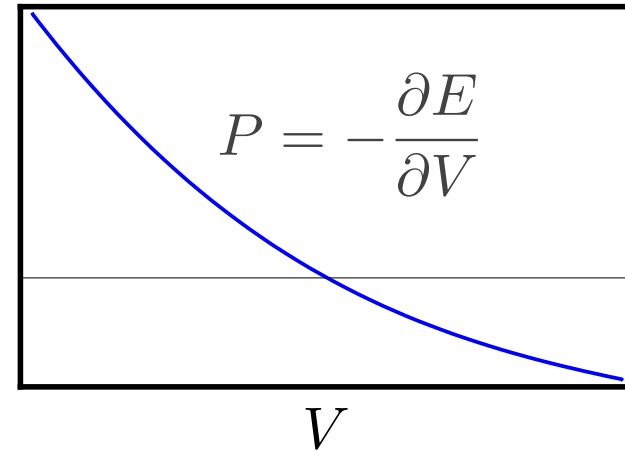
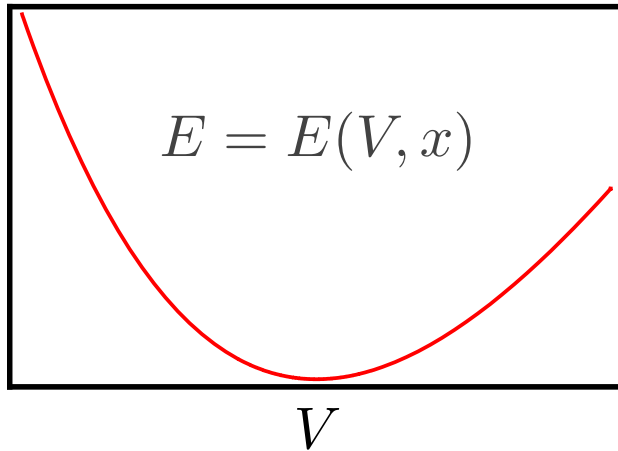


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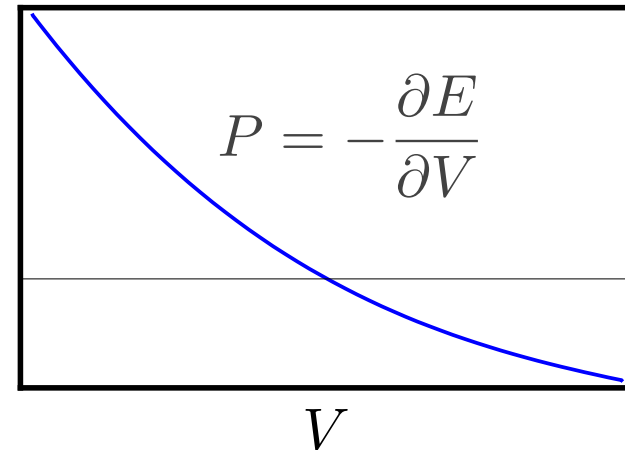
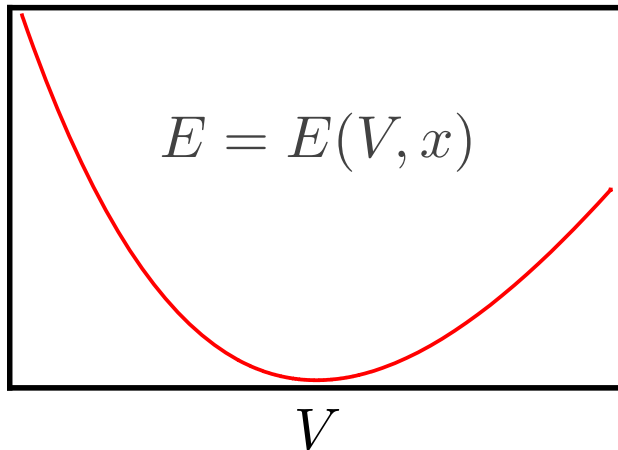


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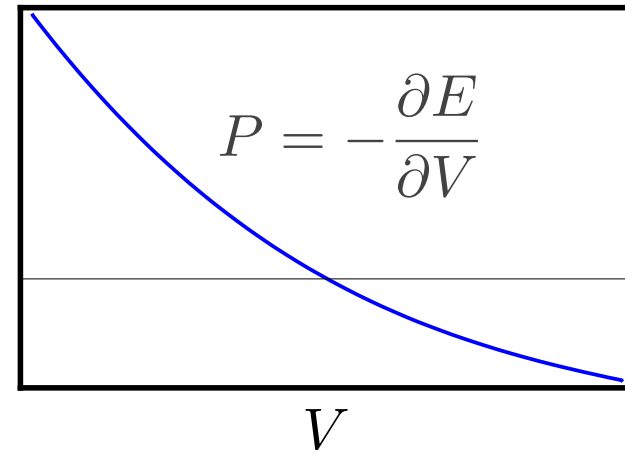
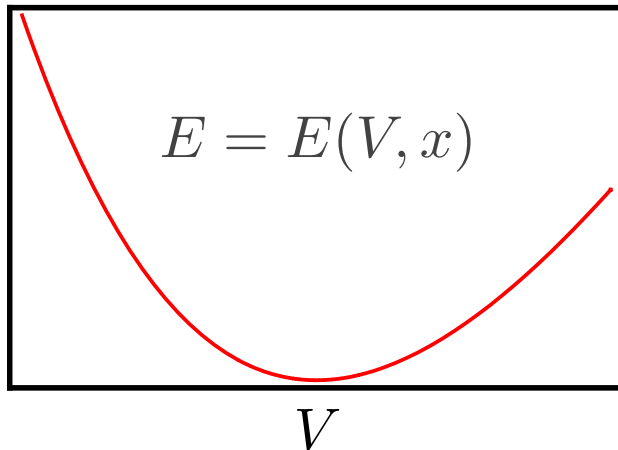


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Hohenberg-Kohn DFT

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



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



Kohn-Sham DFT

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

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

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



XC 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)

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

▶ ...



the Local-Density Approximation

on the blackboard



KS equations from functional

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



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

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



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solving the Kohn-Sham equations

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

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



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solving the Kohn-Sham equations

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requirements

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- ▶ (effective) completeness of the basis set easily checked and systematically improved

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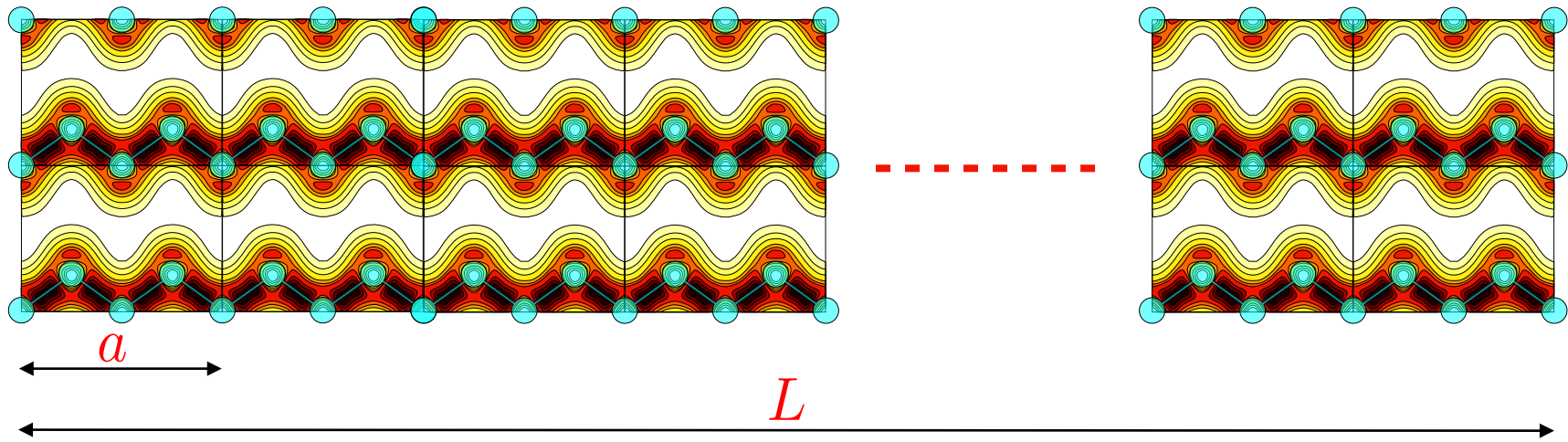
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- ▶ Hartree and XC potentials easy to represent and calculate
- ▶ orthogonality is a plus

the Bloch theorem & plane waves

infinite crystals

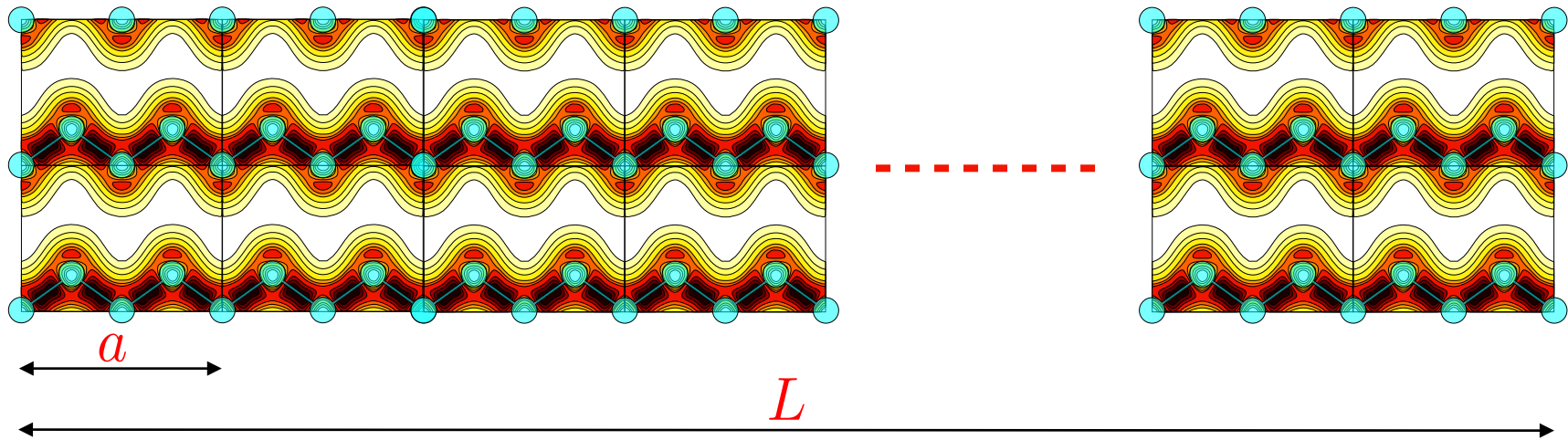


$$\psi(x + L) = \psi(x)$$

Born — von Kármán PBC

the Bloch theorem & plane waves

infinite crystals



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

Born — von Kármán PBC

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

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

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

} Bloch theorem

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

plane-wave basis sets

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

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

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



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periodic boundary conditions

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



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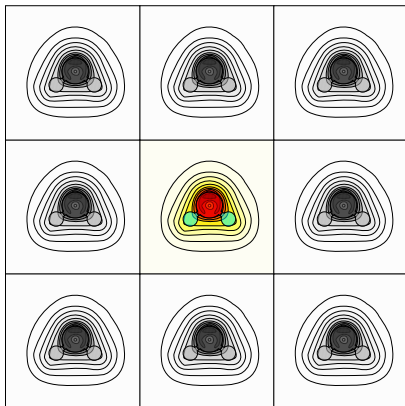
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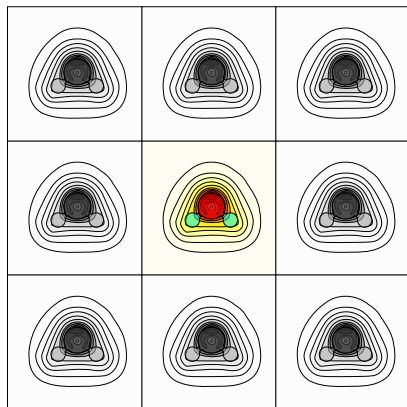
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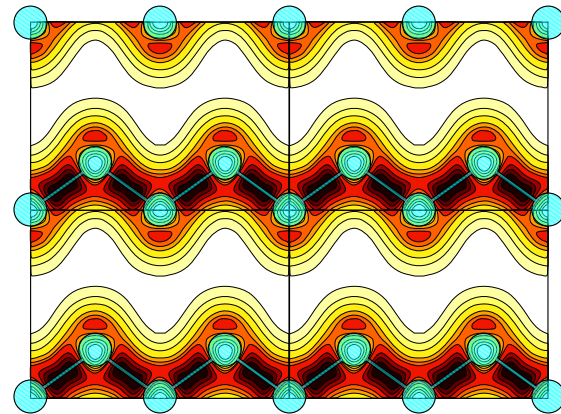
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finite systems ($\ell = a$)



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

infinite crystals ($\ell = L$)



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

plane-wave expansion of LCAO orbitals

on the blackboard



using plane waves

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



using plane waves

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

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

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



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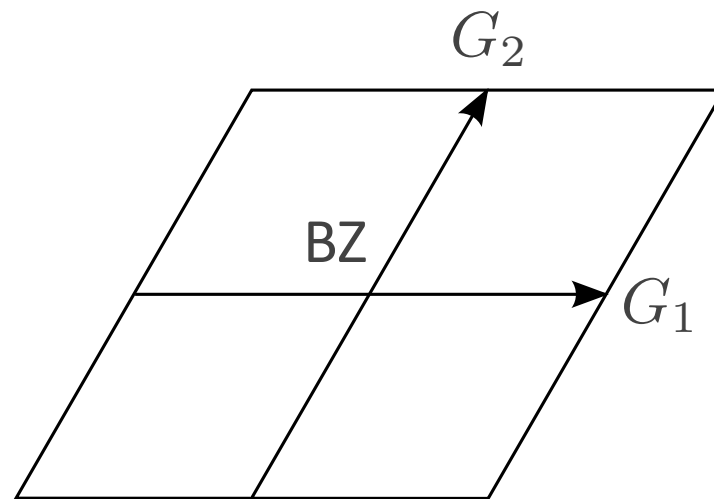
$$V_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r}))$$

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



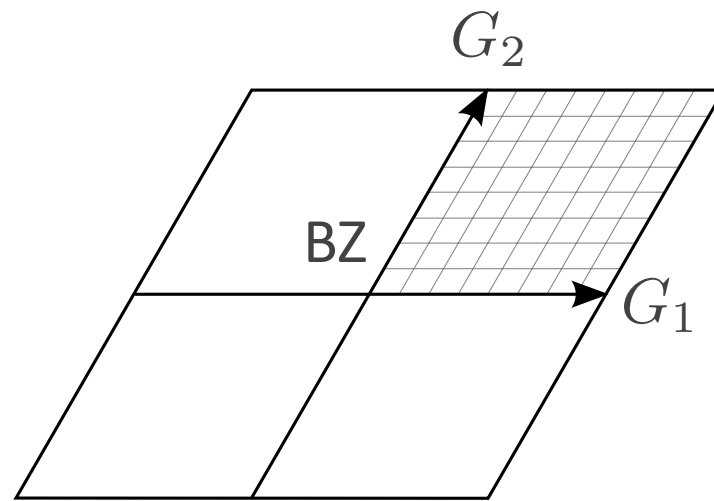
sampling the Brillouin zone: special points

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



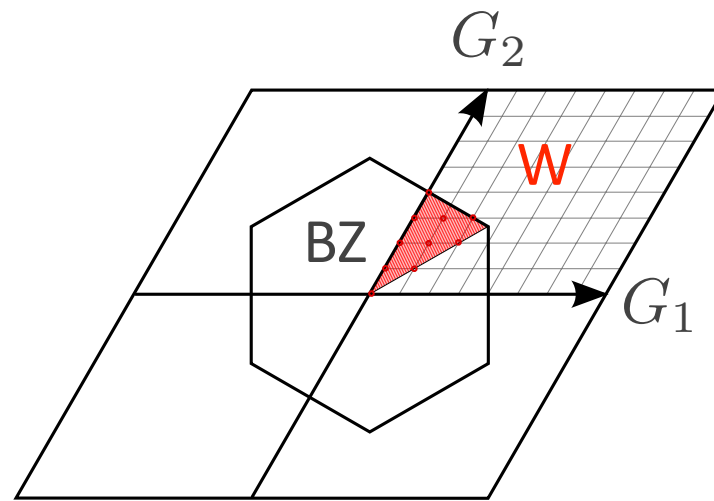
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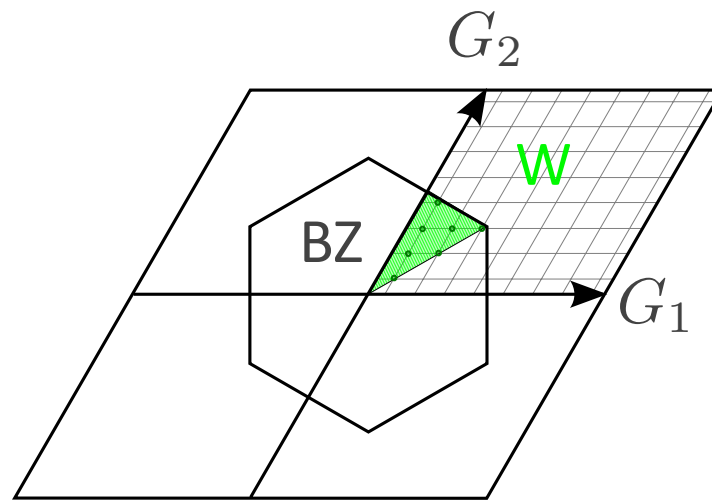
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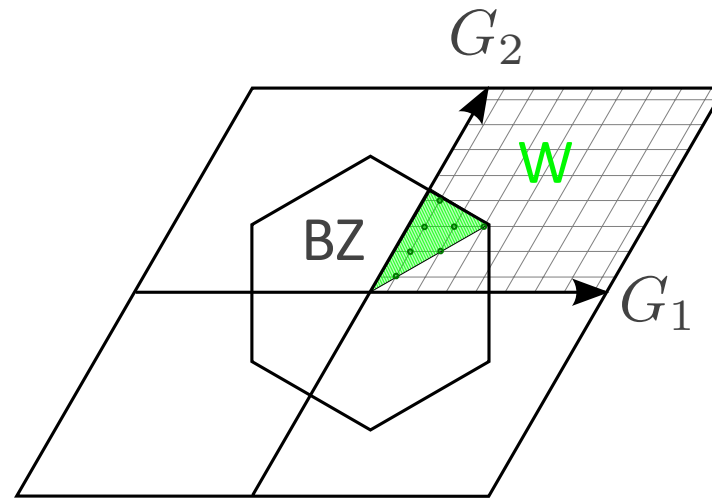


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sampling the Brillouin zone: special points



$$\begin{aligned}\rho(\mathbf{r}) &= \sum_v \sum_{\mathbf{k} \in \text{BZ}} |u_{v\mathbf{k}}(\mathbf{r})|^2 \\ &= \sum_v \sum_{S \in \mathcal{G}} \sum_{\mathbf{k} \in W} |u_{vS \cdot \mathbf{k}}(\mathbf{r})|^2 \\ &= \sum_v \sum_{S \in \mathcal{G}} \sum_{\mathbf{k} \in W} |u_{vS\mathbf{k}}(S^{-1} \cdot \mathbf{r})|^2 \\ &= \sum_{S \in \mathcal{G}} \rho_W(S^{-1} \cdot \mathbf{r})\end{aligned}$$

PWs: pros & cons



treating core states

1																	2	
1																	2	
Group 1	Group 2												Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
3	4											5	6	7	8	9	10	
Li	Be											B	C	N	O	F	Ne	
6.941	9.012 182											10.811	12.0107	14.0067	15.9994	18.998 4032	20.1797	
11	12											13	14	15	16	17	18	
Na	Mg											Al	Si	P	S	Cl	Ar	
22.989 770	24.3050											26.981 538	28.0855	30.973 761	32.065	35.453	39.948	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
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	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
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	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
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)	
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu*	Uub*	Uut*	Uuq*	Uup*				
(223)	(226)	(227)	(261)	(262)	(266)	(264)	(277)	(288)	(281)	(272)	(285)	(284)	(289)	(288)				
<p>* The systematic names and symbols for elements greater than 110 will be used until the approval of trivial names by IUPAC.</p>																		
<p>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.</p>																		
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)					

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



treating core states

1																	2																																																									
1	H Hydrogen 1.007 94																2																																																									
2	Group 1																Group 18																																																									
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4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																																								
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	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.921 60	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798																																																								
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																								
5	Rb Rubidium 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	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																																																								
6	Cs Cesium 132.905 43	Ba Barium 137.327	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	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115																																																											
7	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (288)	Ds Darmstadtium (281)	Uuu* Ununium (272)	Uub* Unubium (285)	Uut* Ununtrium (284)	Uuq* Ununquadium (289)	Uup* Ununpentium (288)																																																											
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$$E_{cut} \sim Z^2$$



treating core states

1																	2																																																								
1	H Hydrogen 1.007 94																2																																																								
2	Group 1																Group 18																																																								
2	3	4															9	10																																																							
2	Li Lithium 6.941	Be Beryllium 9.012 182															F Fluorine 18.998 4032	Ne Neon 20.1797																																																							
3	Group 2																Group 17																																																								
3	11	12															17	18																																																							
3	Na Sodium 22.989 770	Mg Magnesium 24.3050															Cl Chlorine 35.453	Ar Argon 39.948																																																							
4	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																																												
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																					
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	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.921 60	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798																																																							
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																							
5	Rb Rubidium 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	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																																																							
6	Cs Cesium 132.905 43	Ba Barium 137.327	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	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115																																																										
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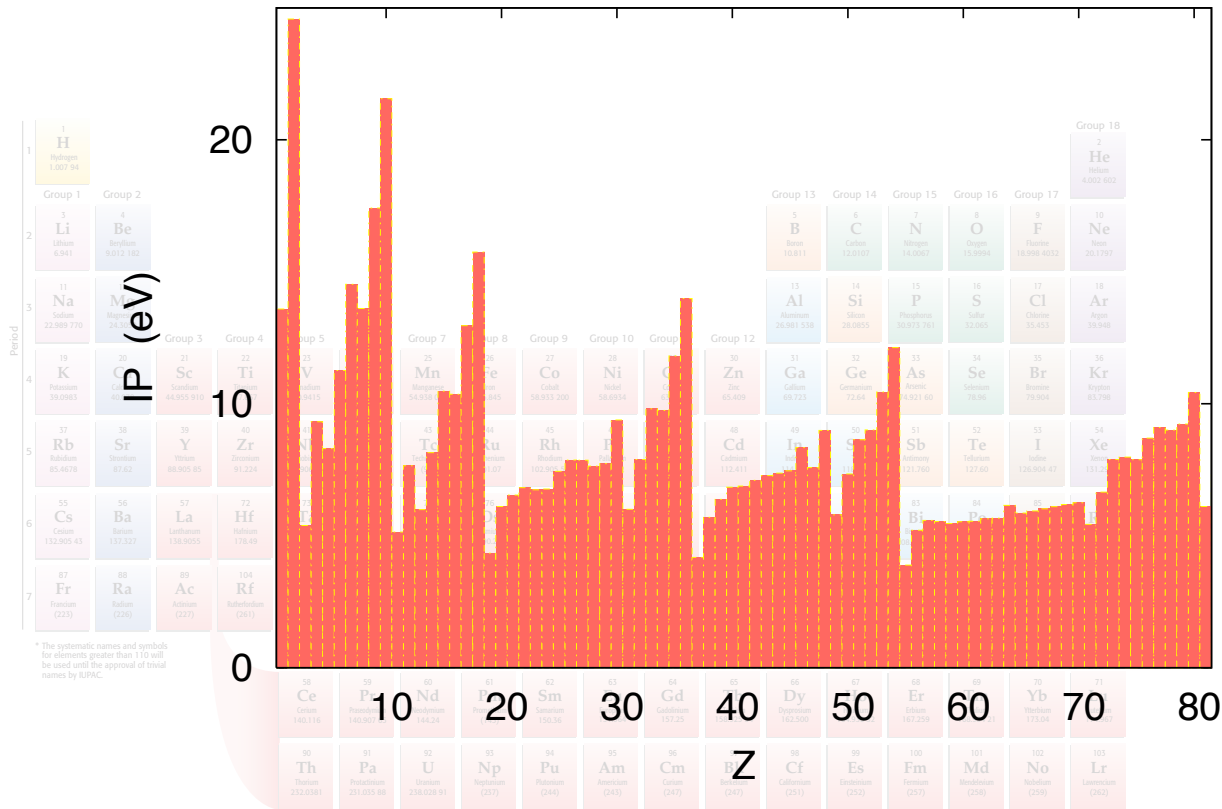
$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

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

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



treating core states



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

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

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



trashing core states: pseudopotentials



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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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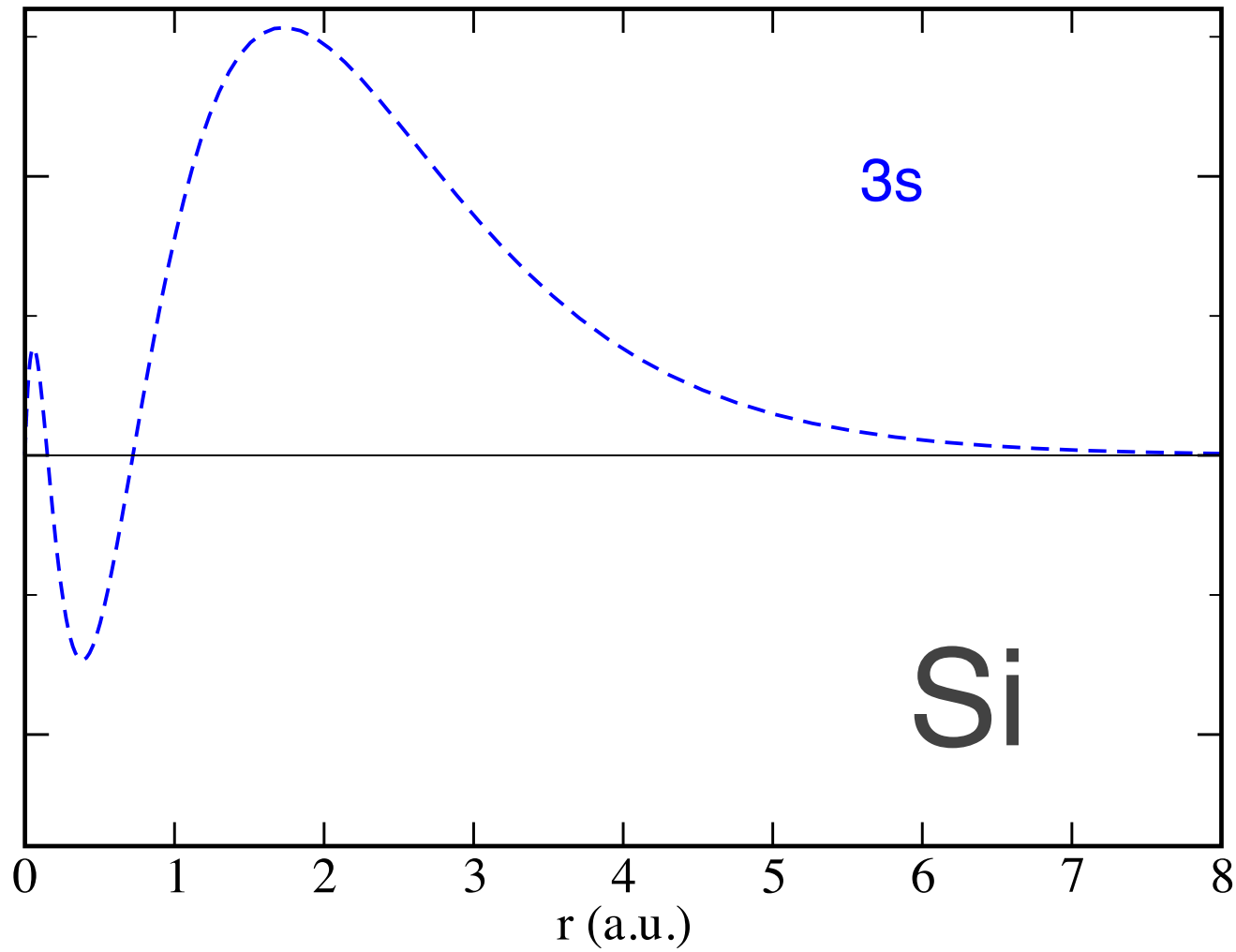
ϕ_{val}^{ps} is nodeless and smooth

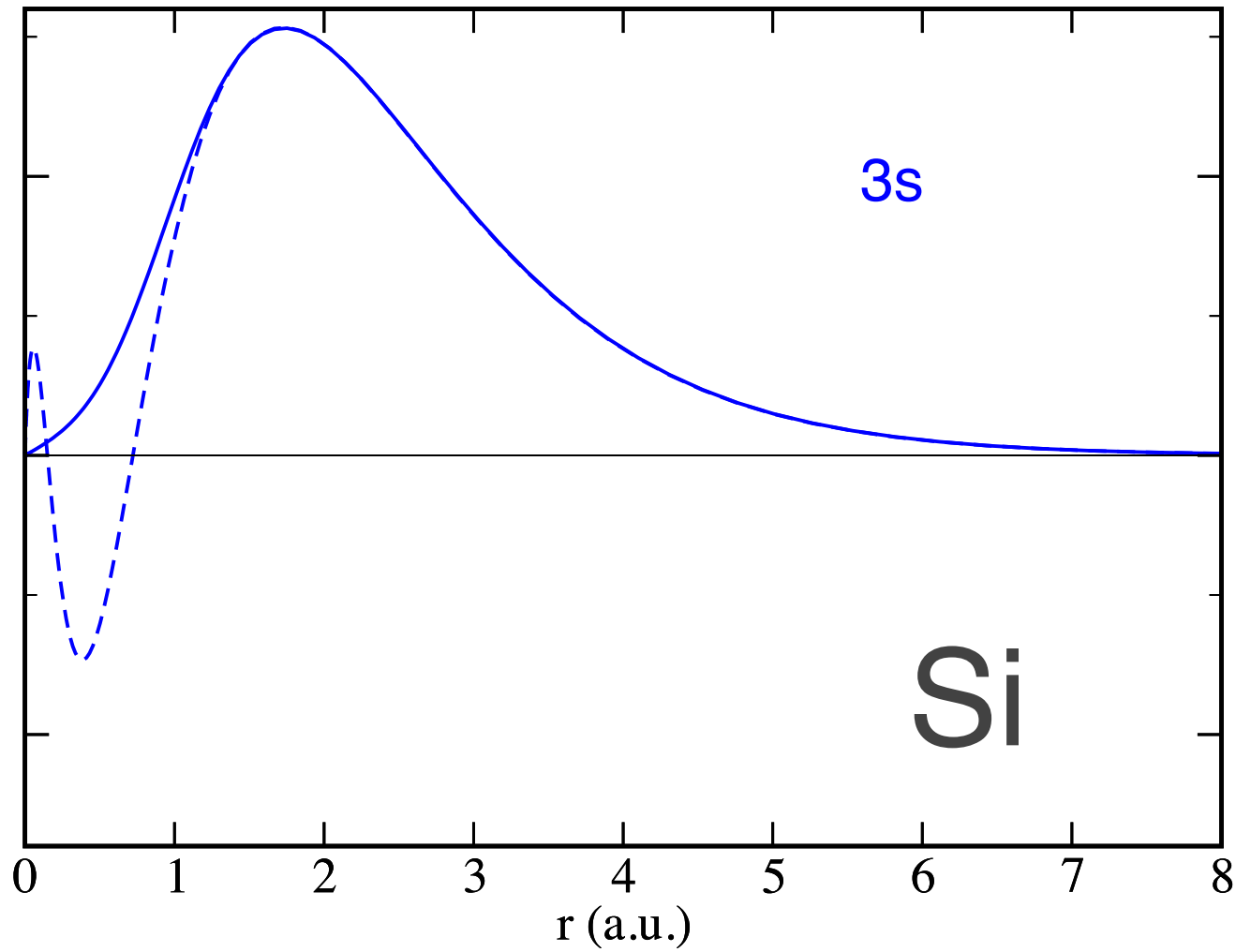
the chemical properties of the pseudo-atom are the same as those of the true atom:

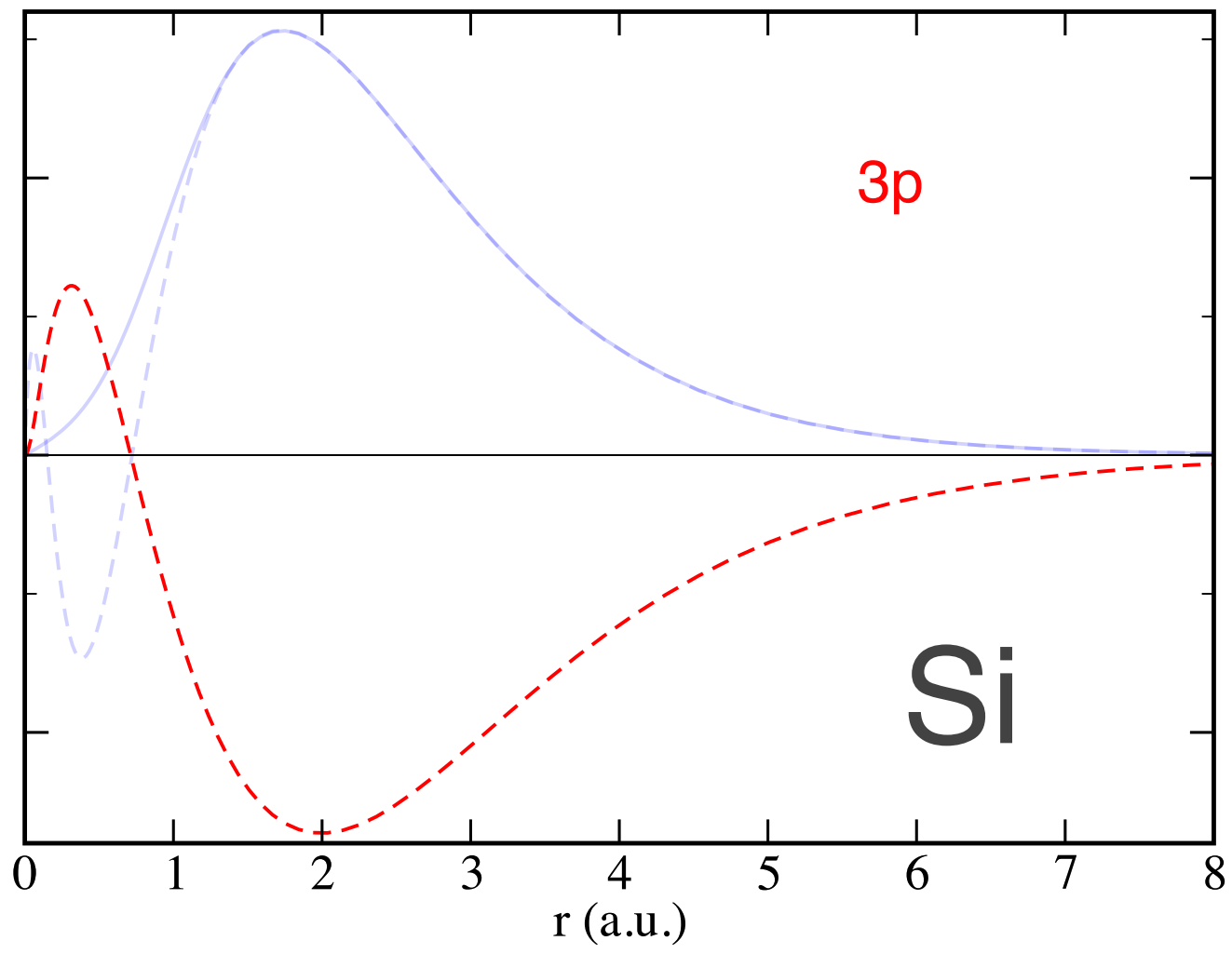
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

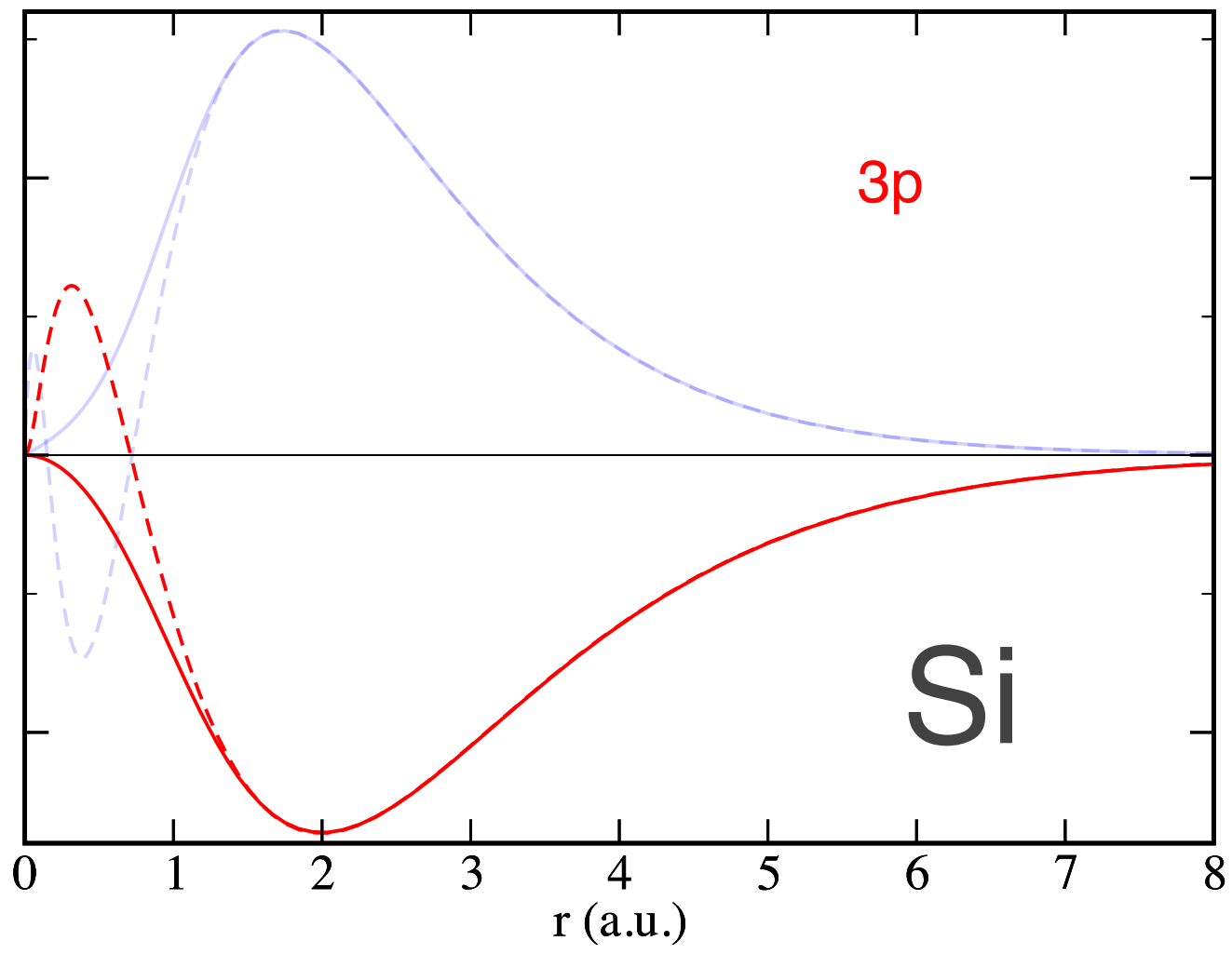
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for } r > r_c$$

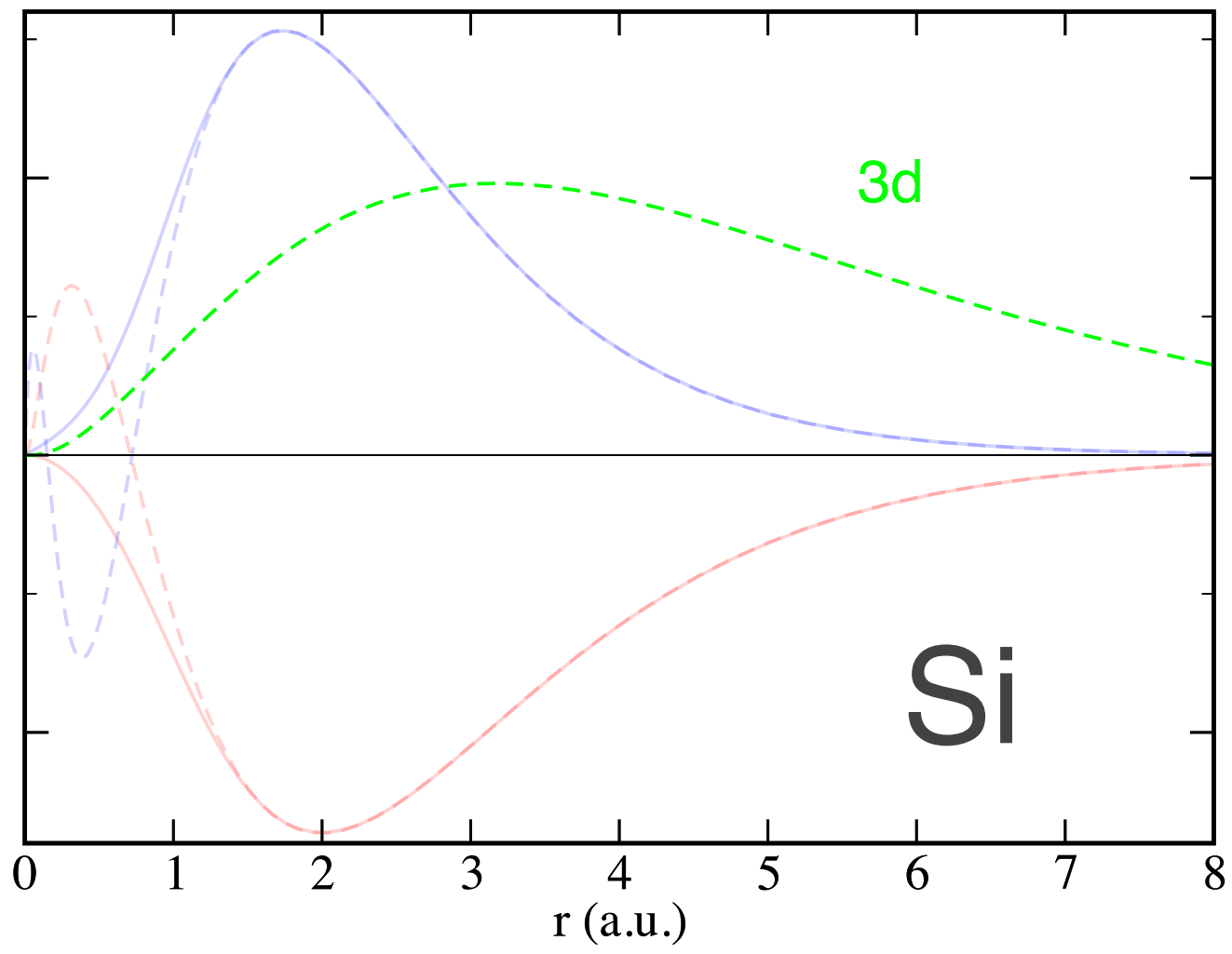


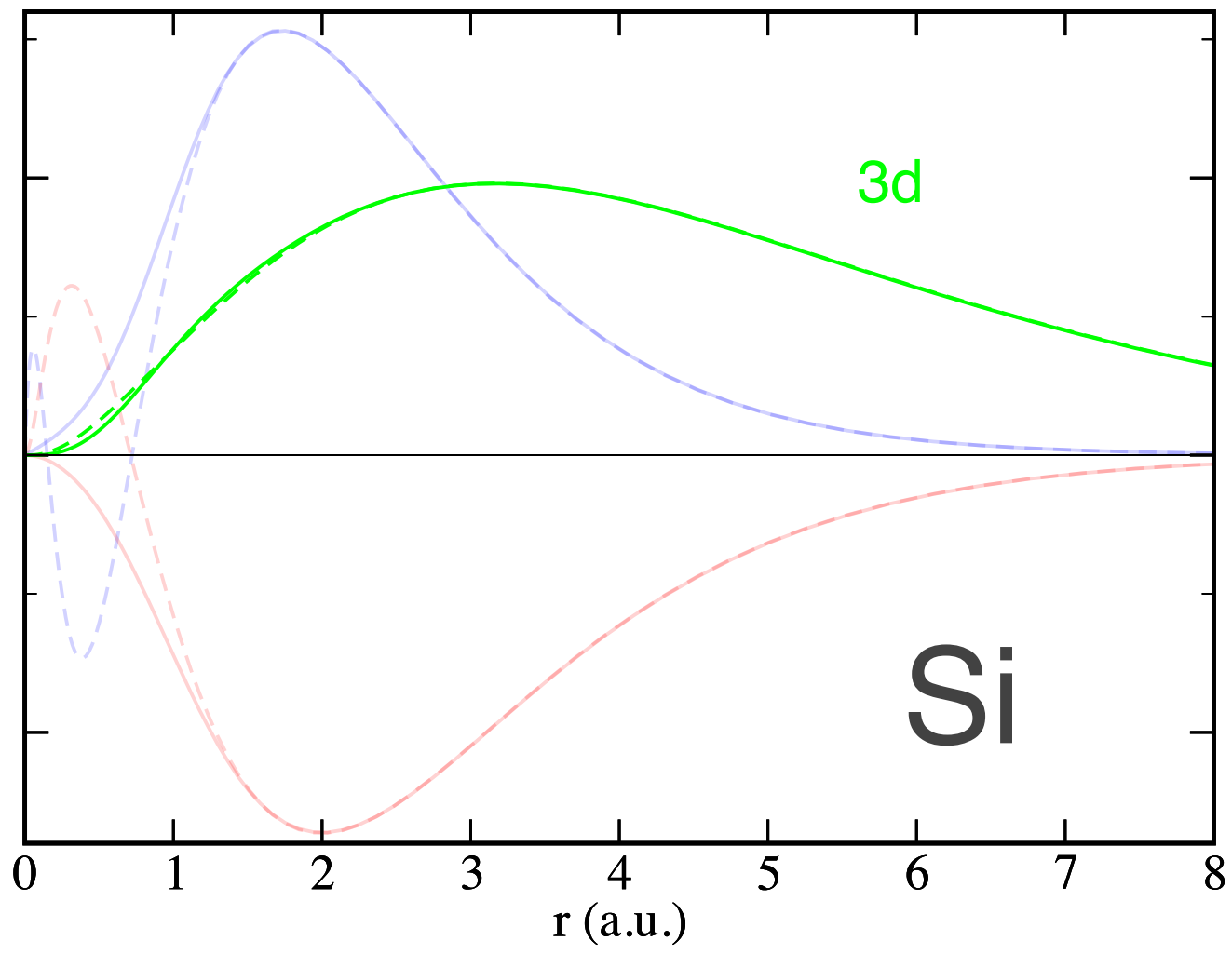




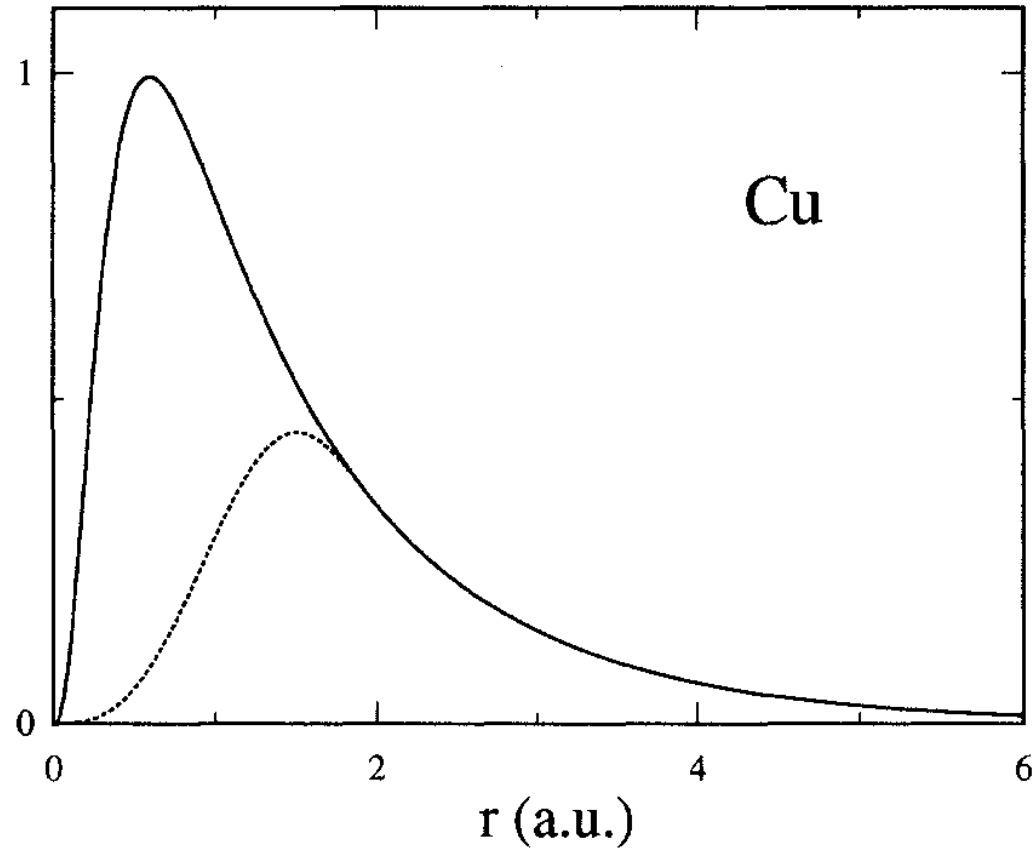




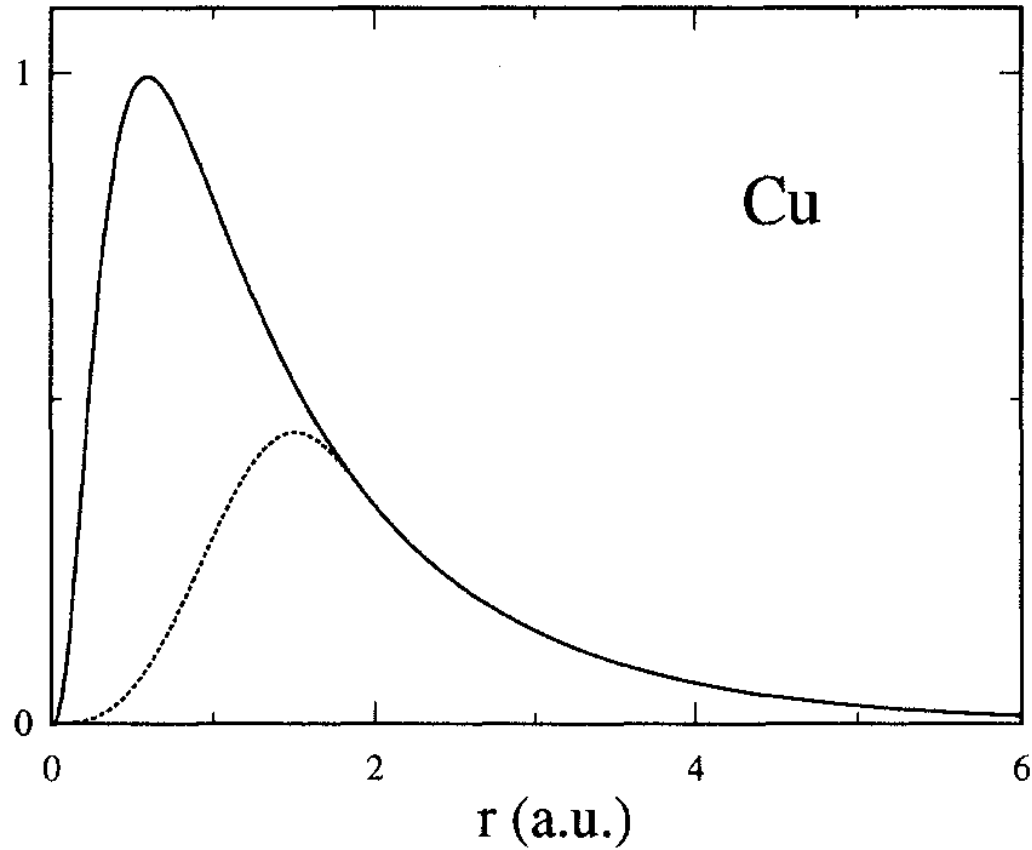




US pseudopotentials



US pseudopotentials



$$H_{US}\phi_n = \epsilon_n S\phi_n$$

$$\langle \phi_n | S | \phi_m \rangle = \delta_{nm}$$



watching the sound of waves

a short digression on signal analysis & Fourier transforms



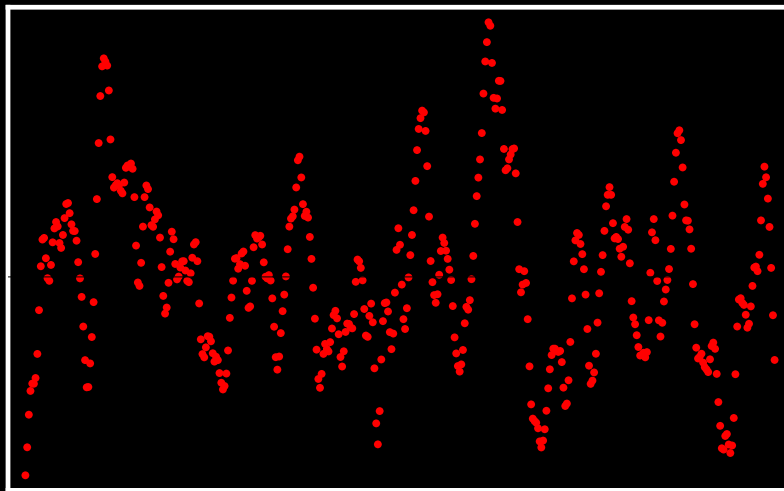
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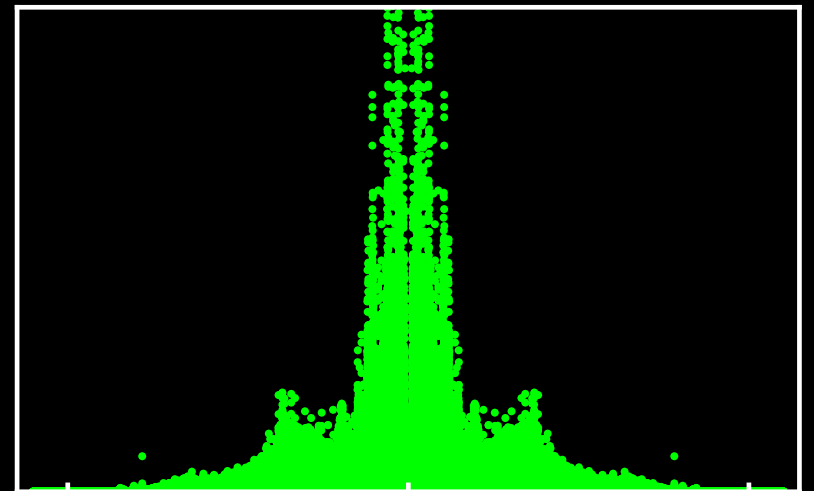


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10 msecs

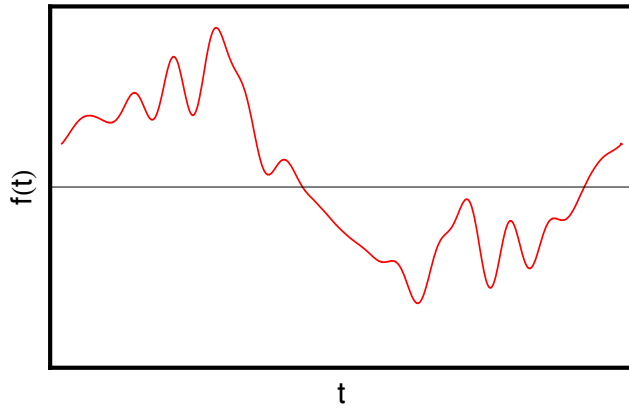


-20 000

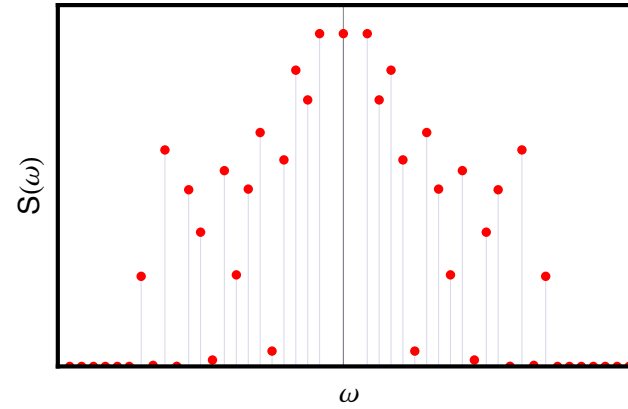
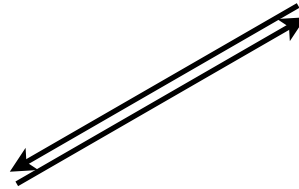
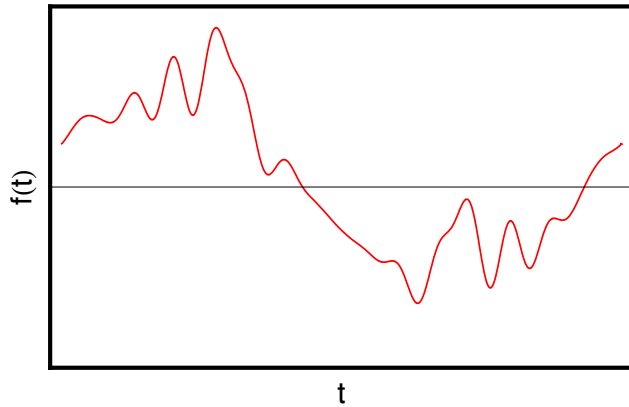
ν [Hz]

20 000

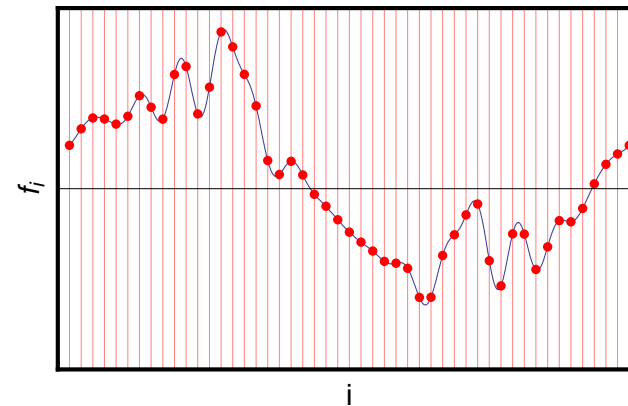
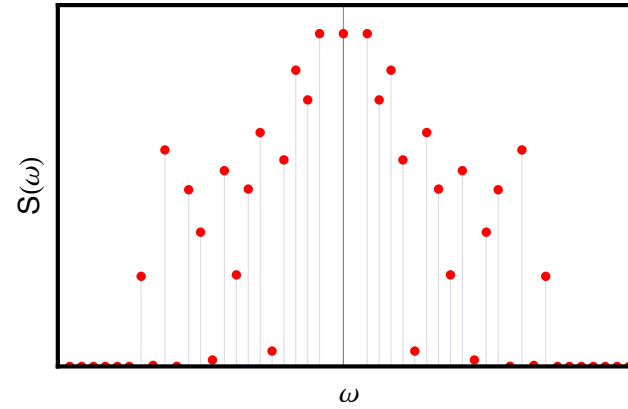
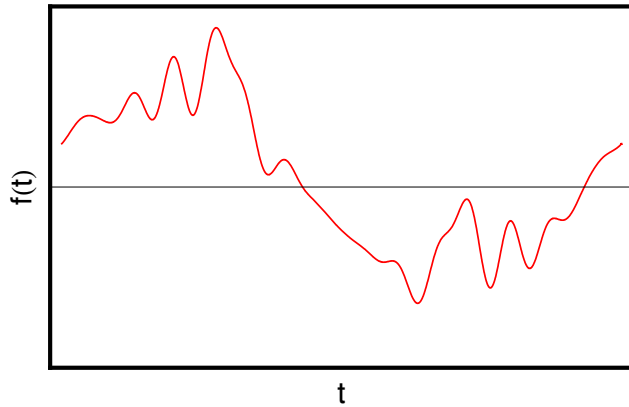
sampling signals



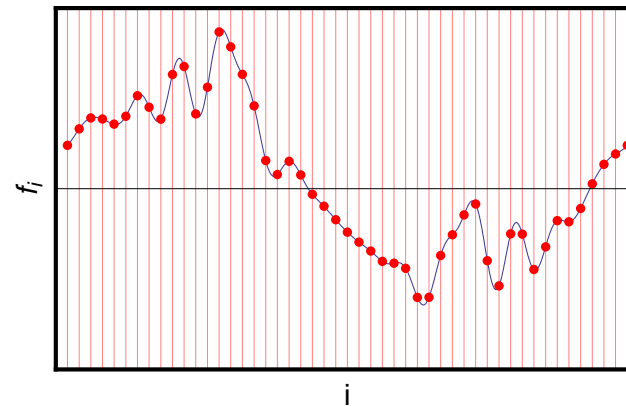
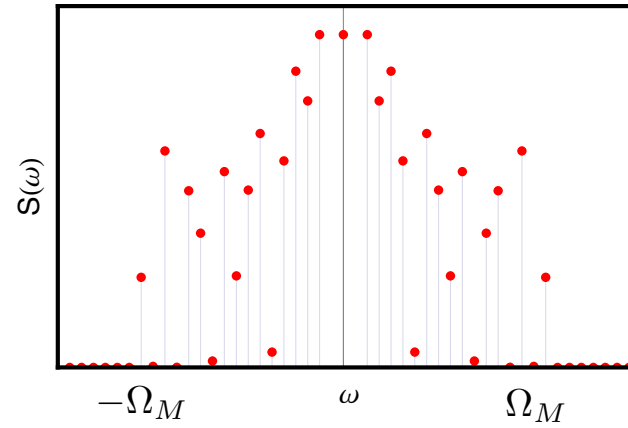
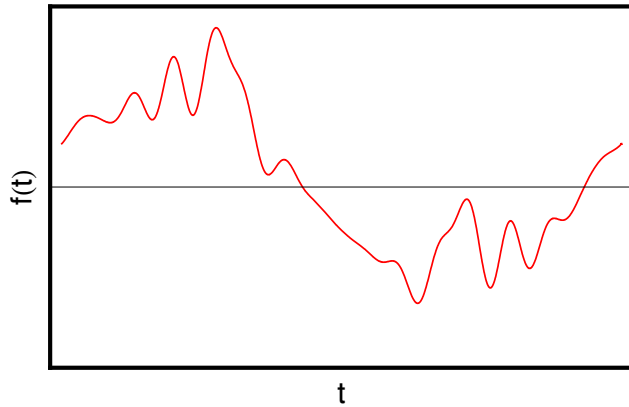
sampling signals



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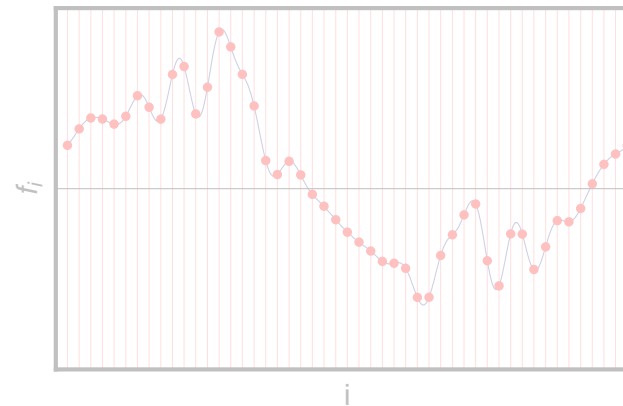
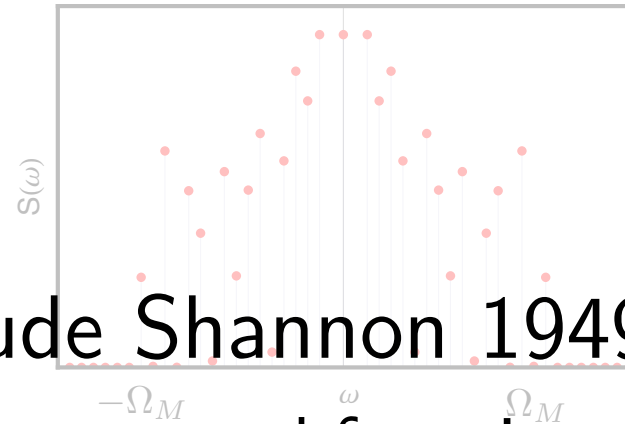
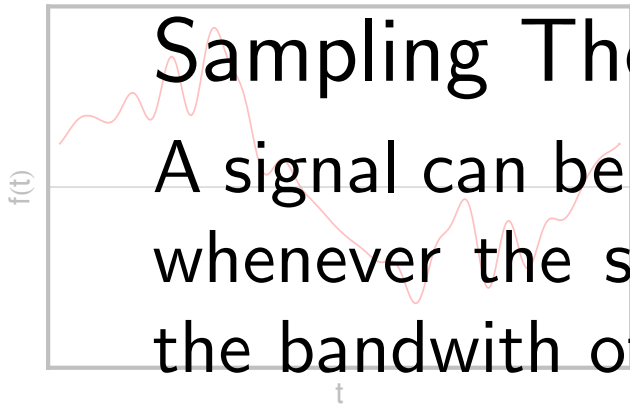
sampling signals



sampling signals

Sampling Theorem (Claude Shannon 1949)

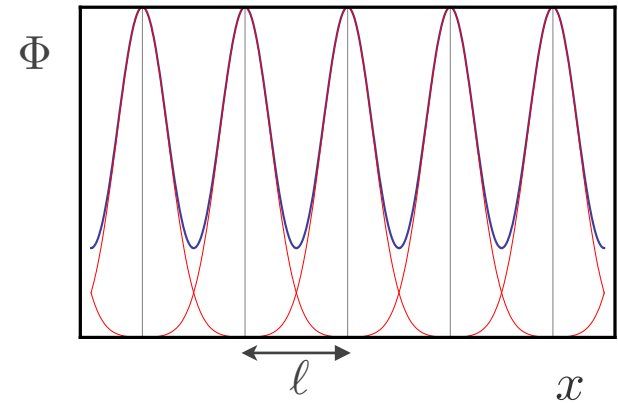
A signal can be faithfully reconstructed from its sample whenever the sampling frequency is larger than twice the bandwidth of the spectrum: $\nu_S > \frac{2\Omega_M}{2\pi}$



Fourier analysis

$$\Phi(x) = \sum_n \varphi(x - n\ell)$$

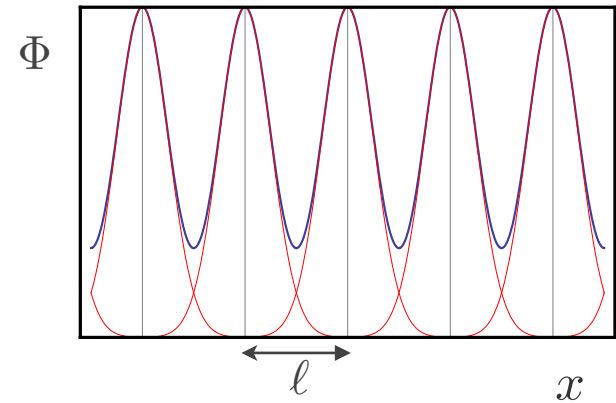
$$\Phi(x + \ell) = \Phi(x)$$



Fourier analysis

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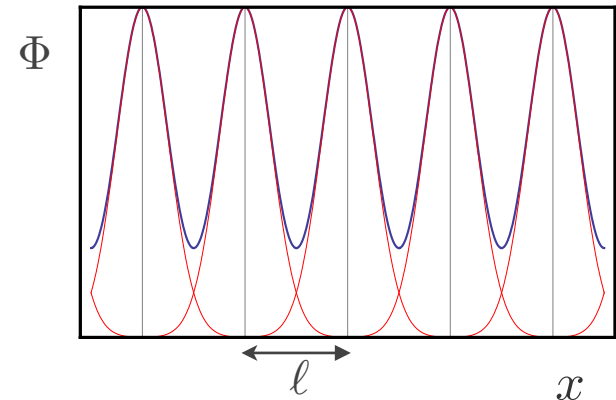


$$\Phi(x) = \sum_q \tilde{\Phi}(q) e^{iqx} \quad q_k = k \frac{2\pi}{\ell}$$

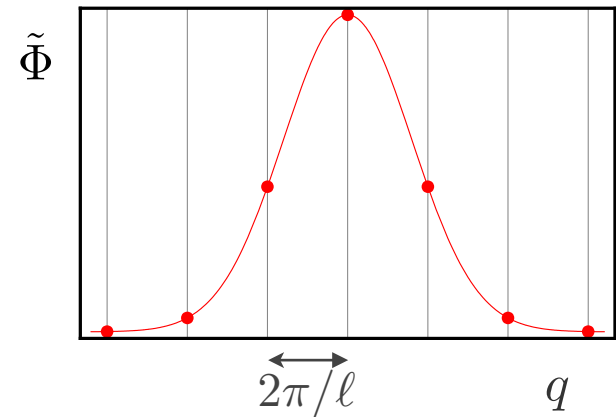
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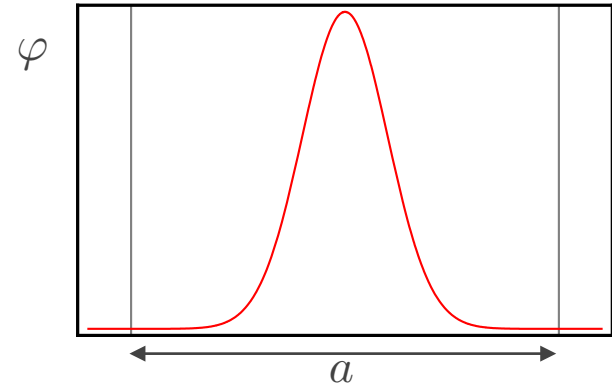
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$$\begin{aligned} \tilde{\Phi}(q) &= \frac{1}{\ell} \int_0^\ell \Phi(x) e^{-iqx} dx \\ &= \frac{1}{\ell} \int_{-\infty}^{\infty} \varphi(x) e^{-iqx} dx \\ &= \frac{1}{\ell} \tilde{\varphi}(q) \end{aligned}$$

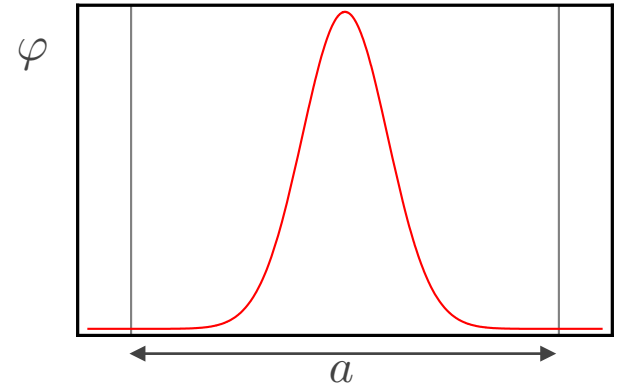
sampling theorem

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

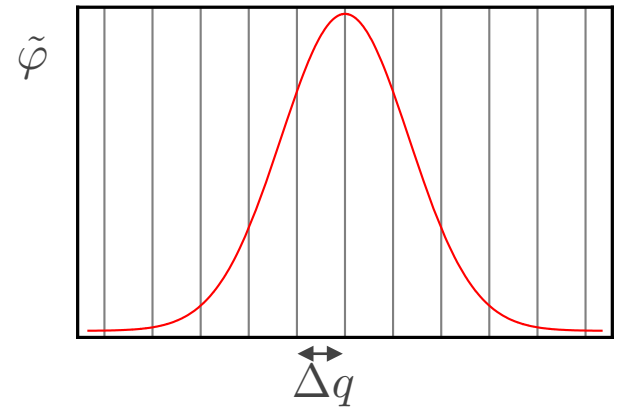


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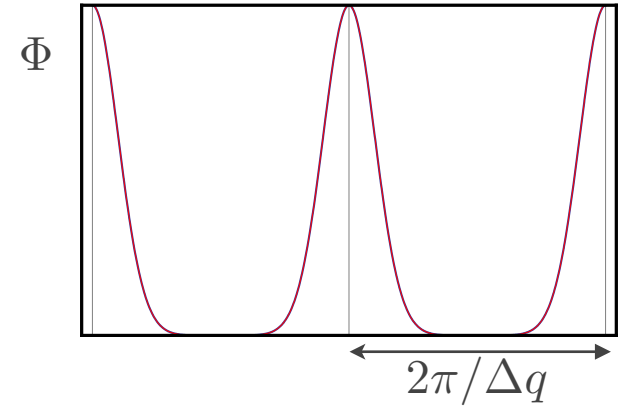
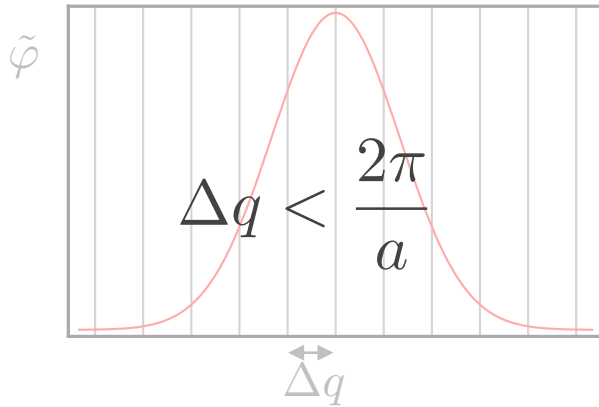
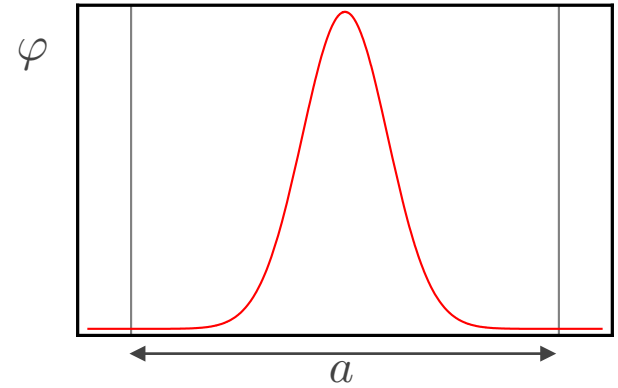


$$\Delta q < \frac{2\pi}{a}$$



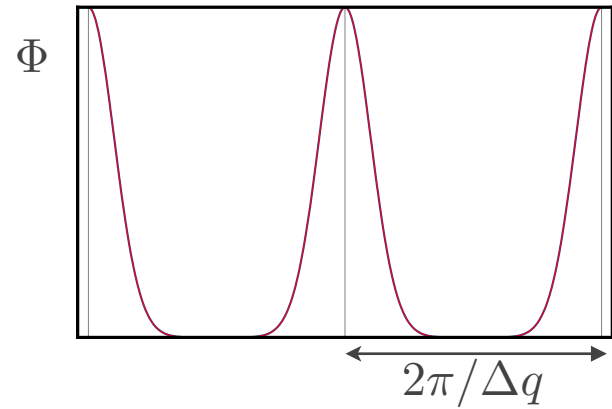
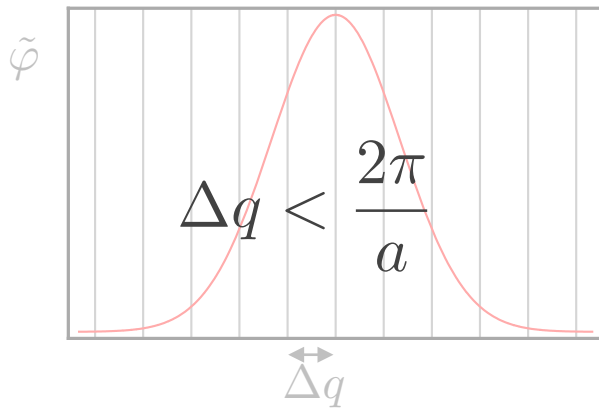
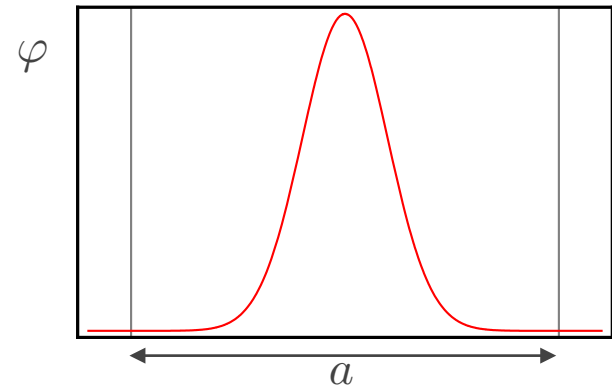
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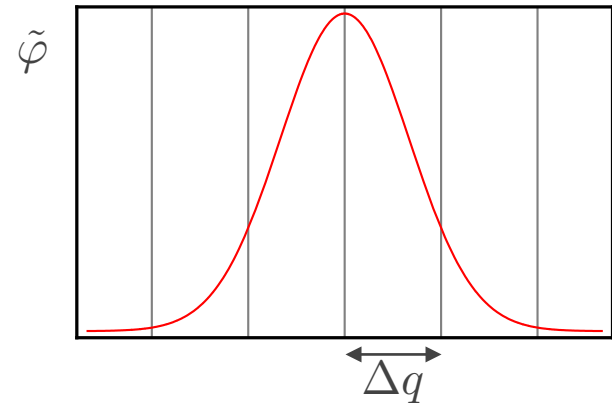


sampling theorem

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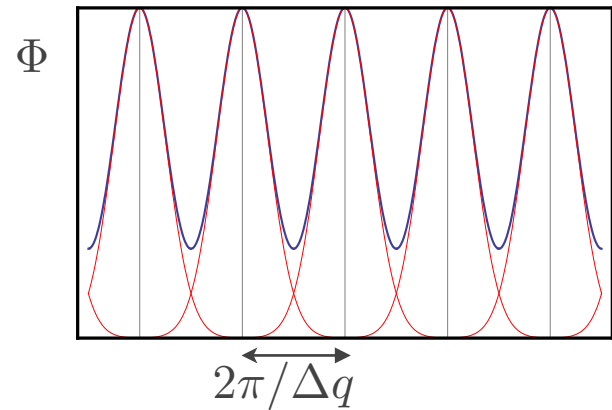
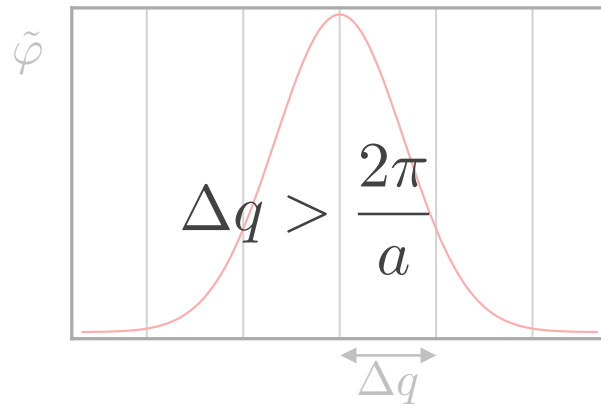
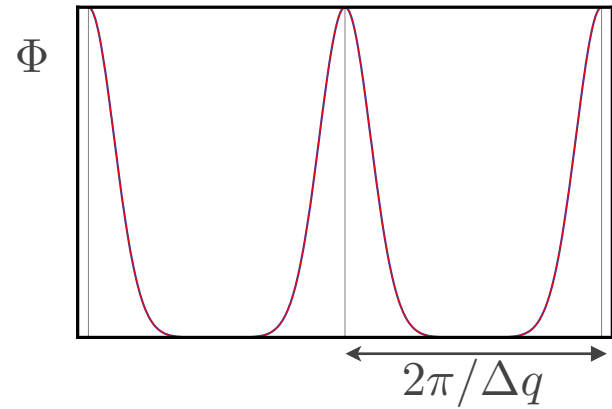
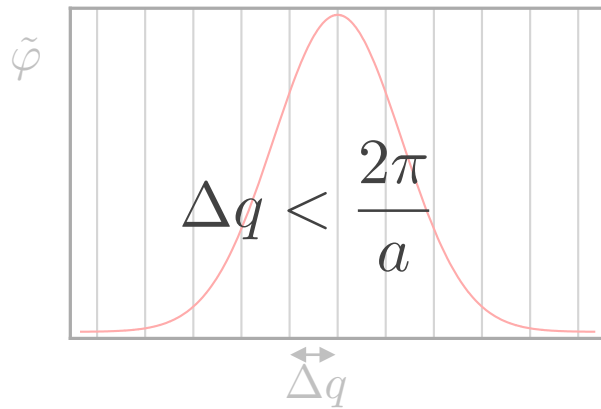
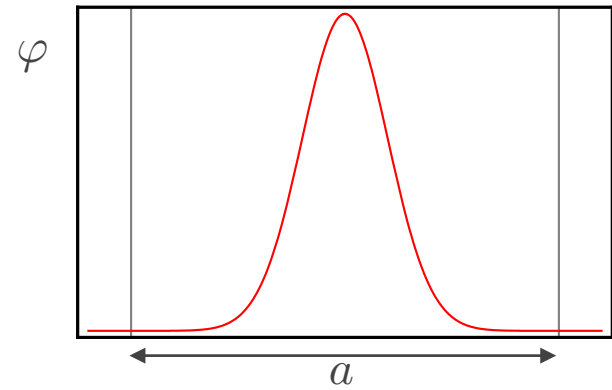


$$\Delta q > \frac{2\pi}{a}$$



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

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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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discreteness in dual space



periodicity in the primary space

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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

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

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

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

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FFT of real data sets

$$f_l \in \mathbb{R} \quad \rightarrow \quad \tilde{f}_{N-k} = \tilde{f}_k^*$$

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$$\tilde{g}_k = \frac{1}{2i} (\tilde{F}_k - \tilde{F}_{N-k}^*)$$

get two, pay one!

FFT of real data sets (II)

$$f_l \in \mathbb{R} \quad \rightarrow \quad \tilde{f}_{N-k} = \tilde{f}_k^*$$

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get one, pay half!

multivariate FFTs

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

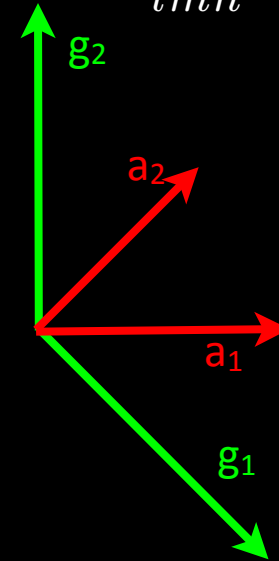
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$$\mathbf{G}_{pqS} = p\mathbf{g}_1 + q\mathbf{g}_2 + s\mathbf{g}_3$$

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

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

multivariate FFTs (II)

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

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 &\quad \underbrace{\hspace{10em}}_{N^2 \text{ FFT}(N)}
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$N^2 \text{ FFT}(N)$

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

correlation functions, convolutions, power spectra

$$C_A(t) = \langle A(t + t')A(t') \rangle$$

correlation functions, convolutions, power spectra

$$\begin{aligned} C_A(t) &= \langle A(t+t')A(t') \rangle \\ &= \frac{1}{T-t} \int_0^{T-t} A(t+t')A(t')dt' \end{aligned}$$

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$$A \otimes A(l) = \frac{1}{N} \sum_k A(k+l)A(k)$$

$\mathcal{O}(N^2)$ ops

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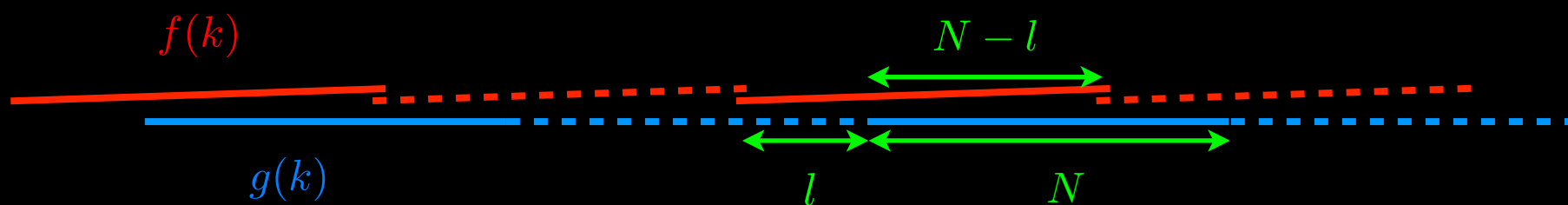
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convolutions (II)

$$h(l) = \frac{1}{N} \sum_k f(k+l)g(k)$$

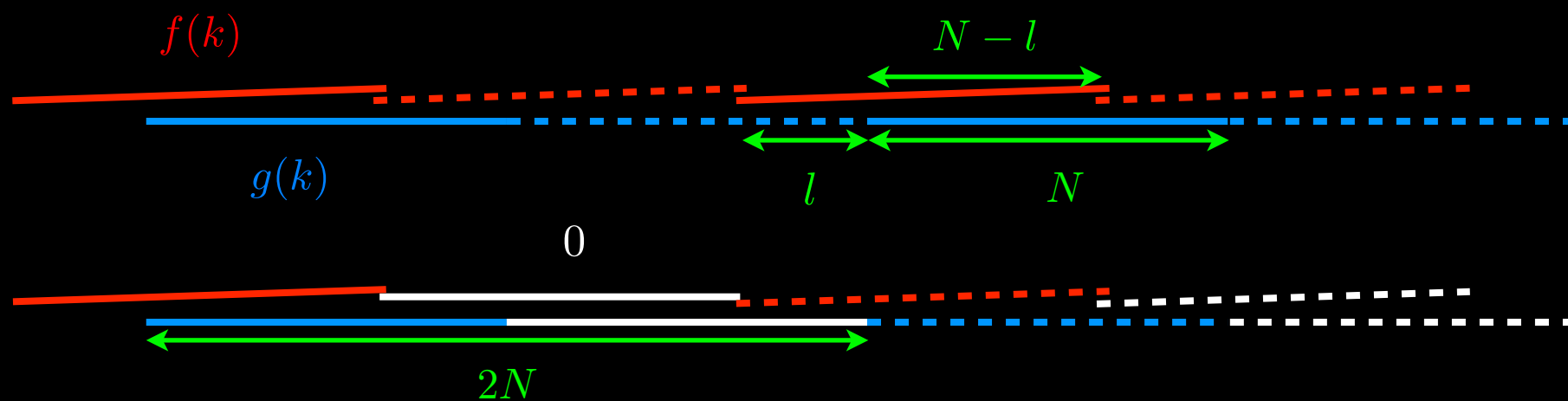
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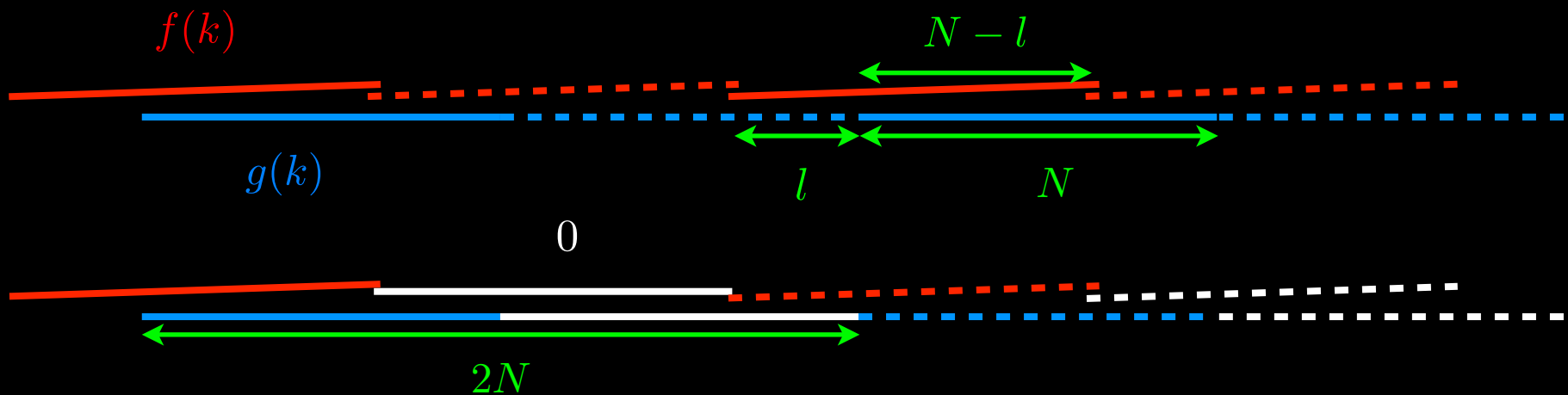
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$$h(l) = \frac{1}{2N} \sum_{k=0}^{2N-1} f(k+l)g(k)$$

solving the Poisson equation

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

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

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

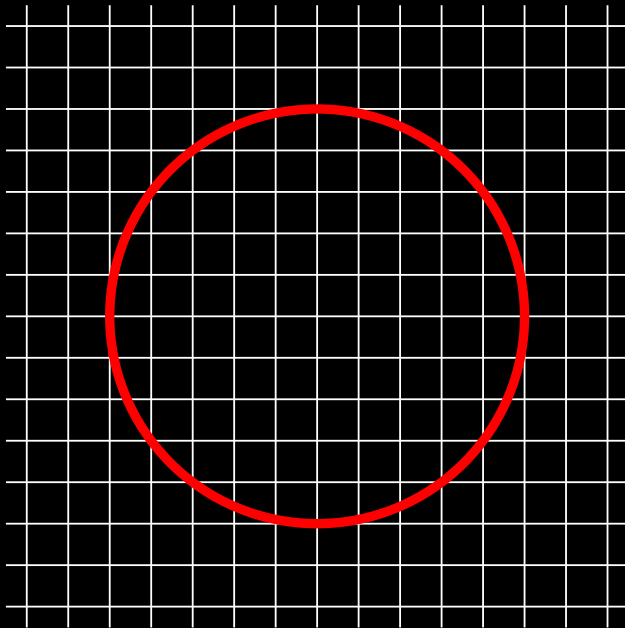
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$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

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

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



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

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



MAX





That's all Folks!

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