# 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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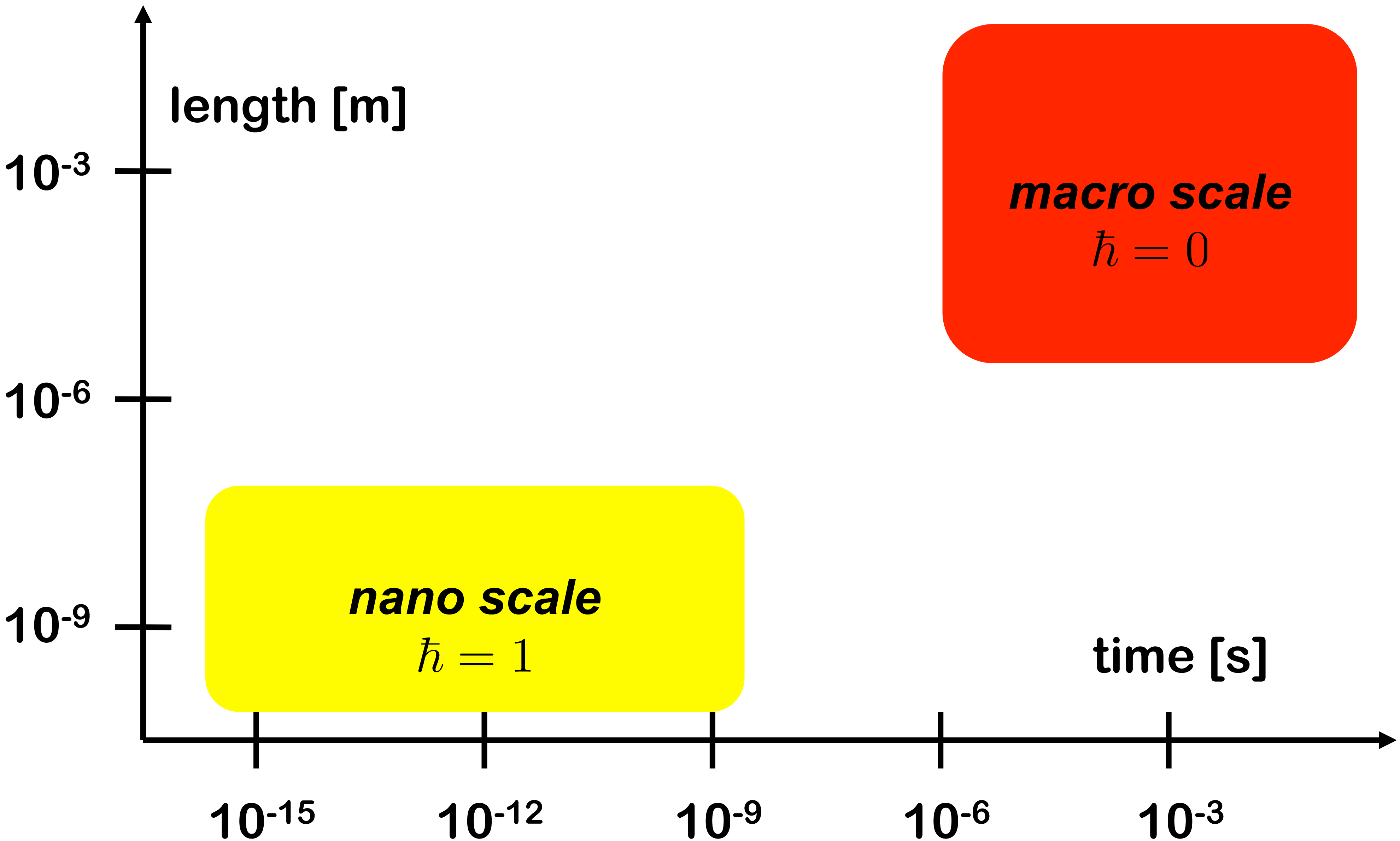
# the saga of time and length scales



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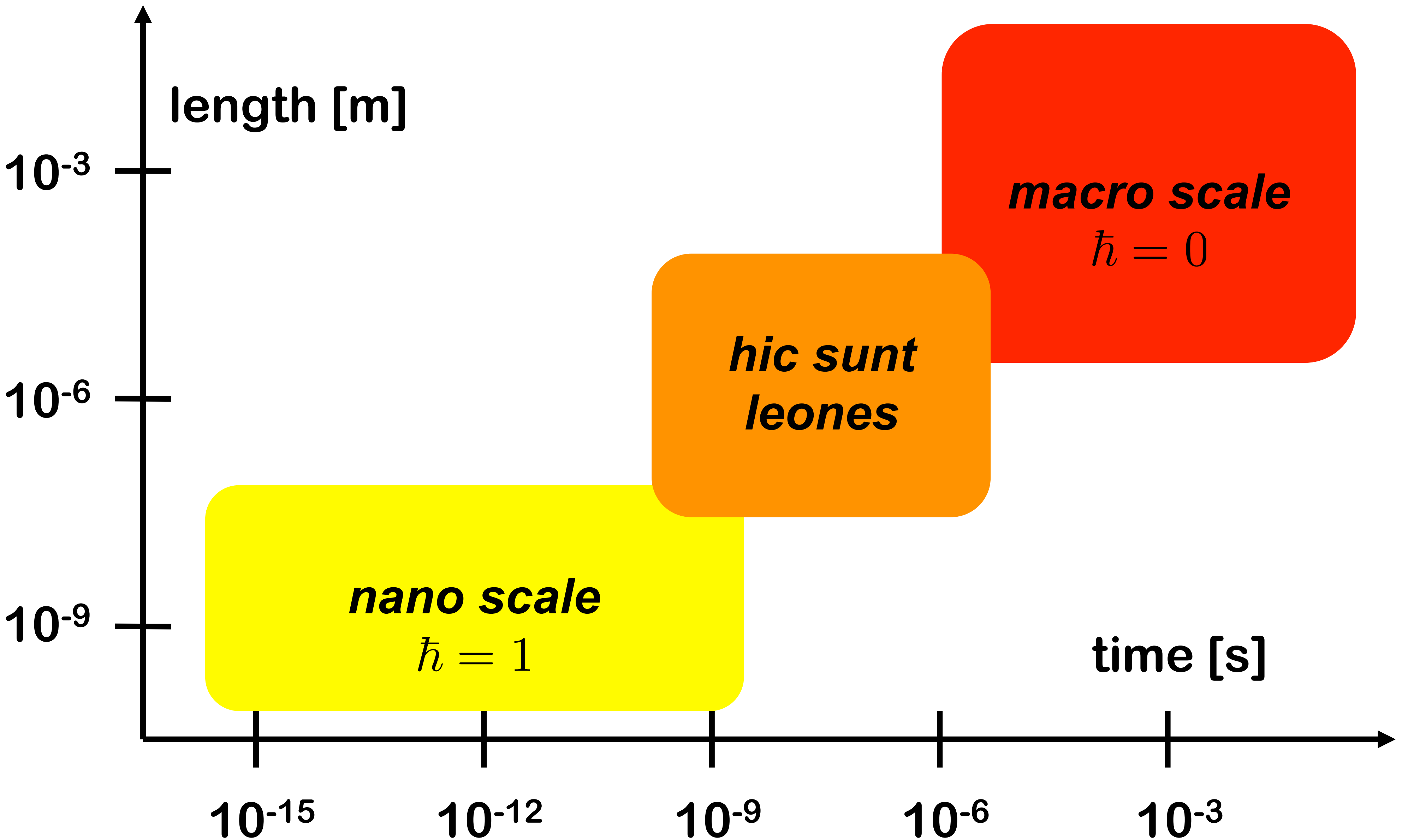

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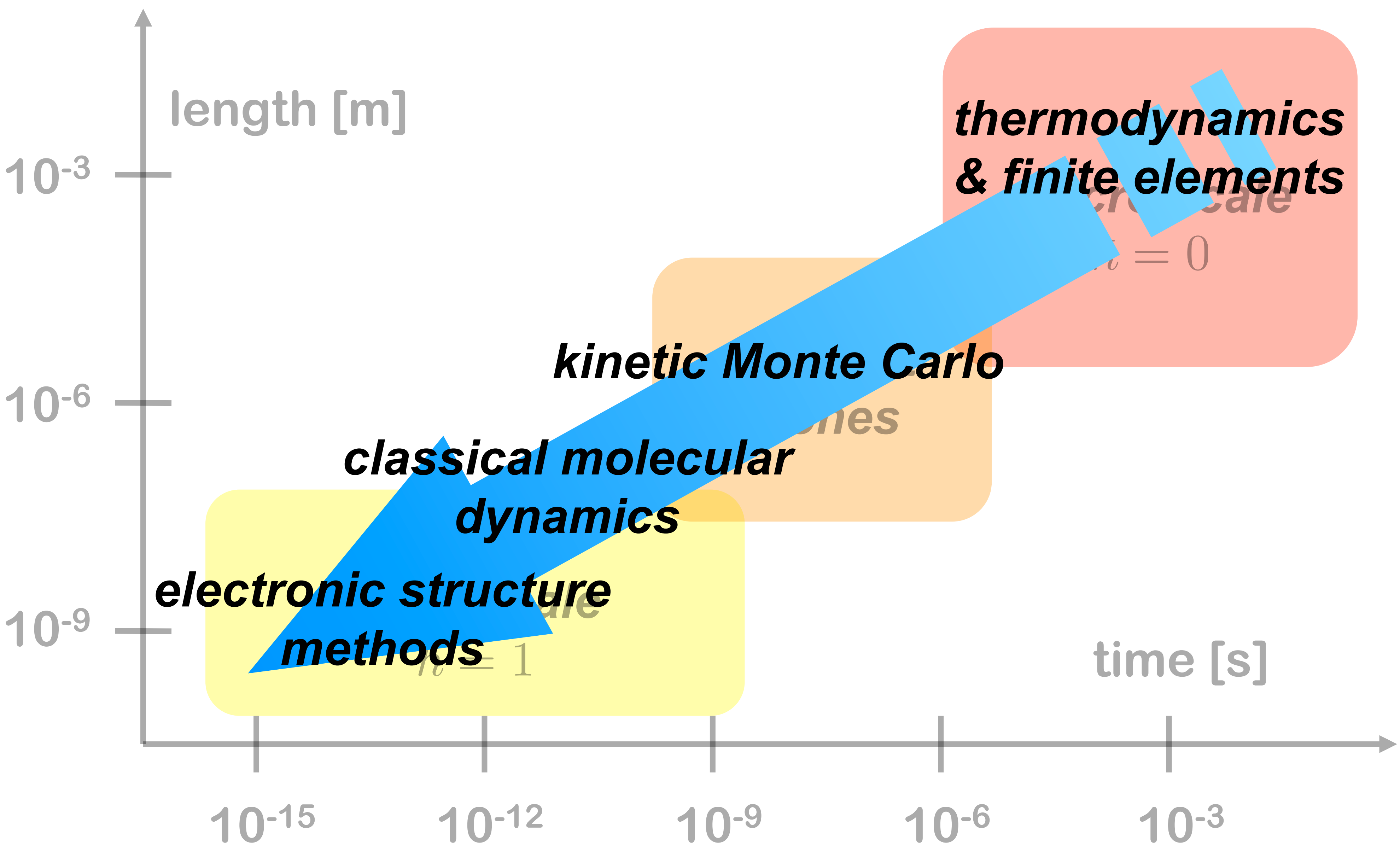
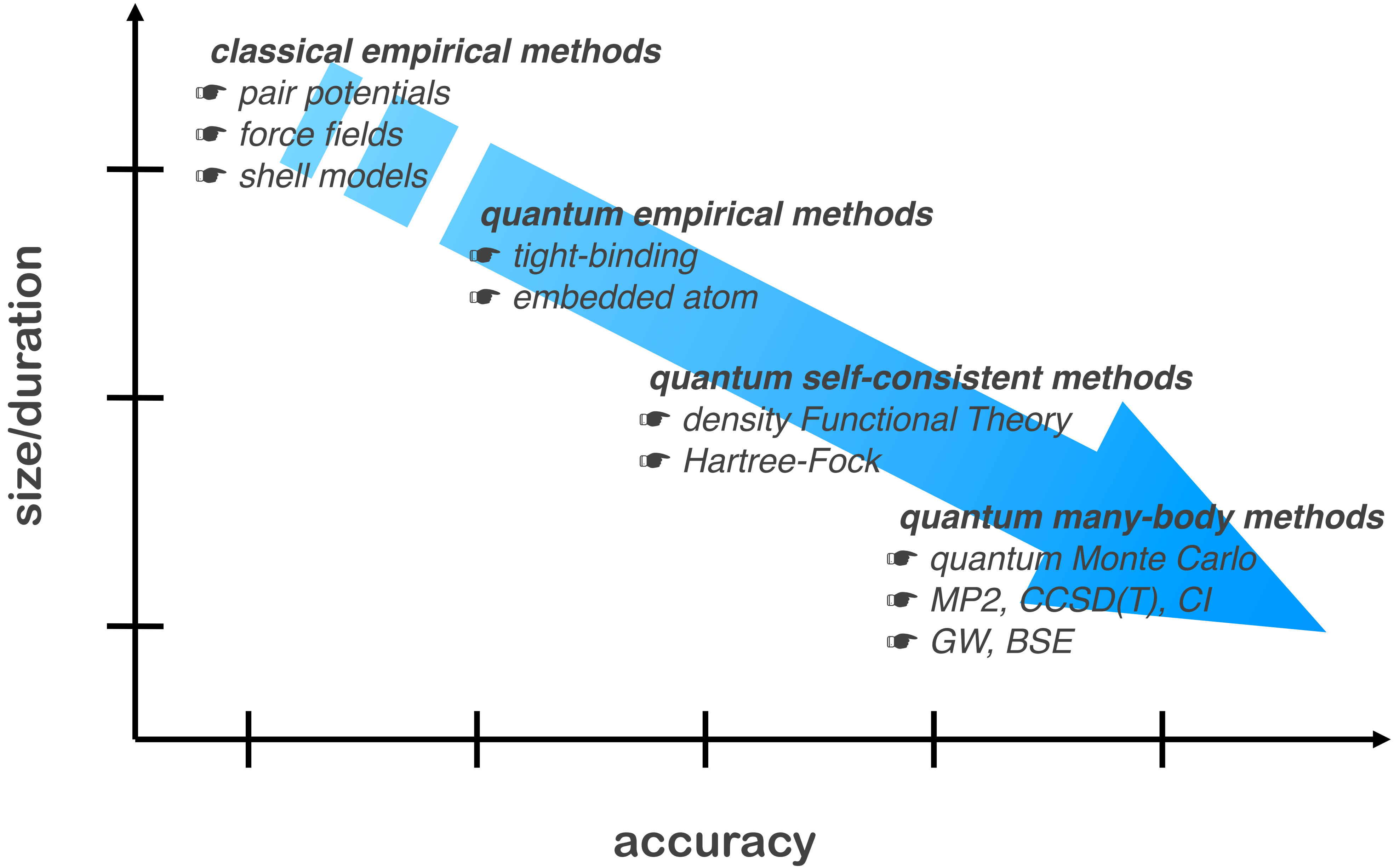


# size vs. accuracy



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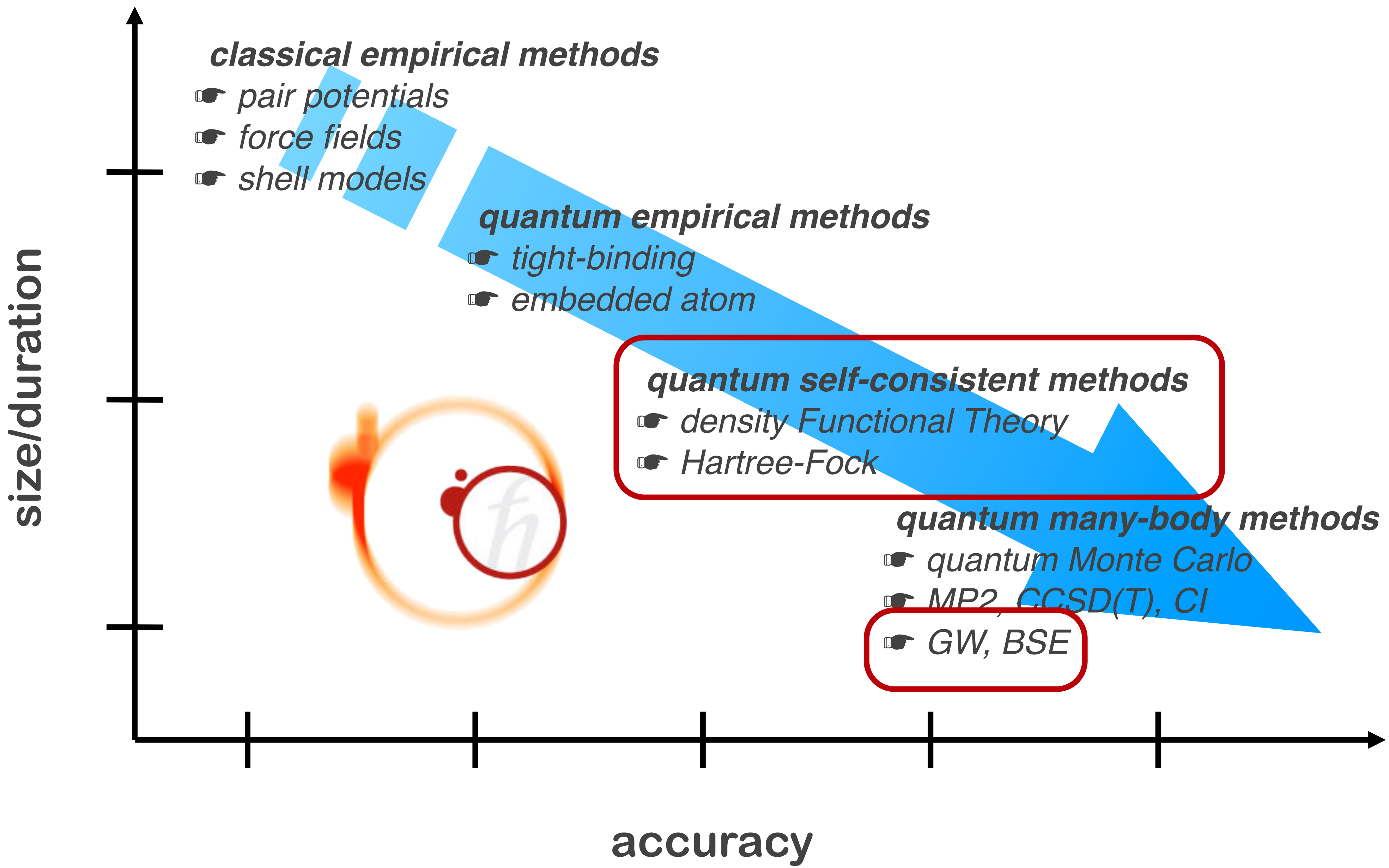

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how: using digital computers, clever algorithms, common sense, and *scientific rigor*

# 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

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

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

# 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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Kohn-Sham Hamiltonian

$$\rho(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2$$

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

# functionals

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

# functions

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examples:

$$
\begin{aligned}
G[f] &= f(x_0) \\
G[f] &= \int_a^b f^2(x)dx \\
G[f] &= \int_a^b |f'(x)|^2 dx \\
&\cdots
\end{aligned}
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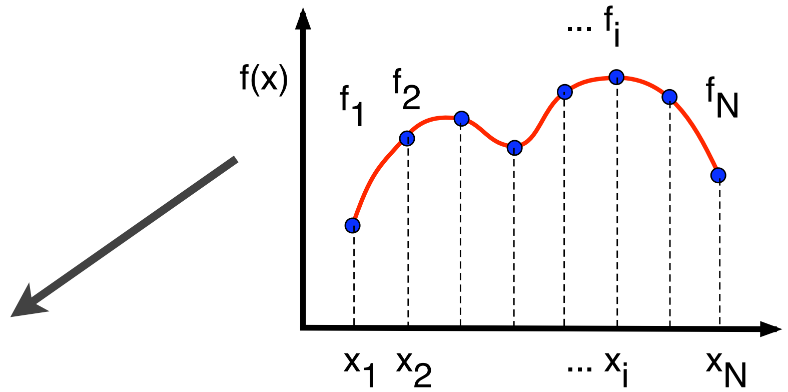


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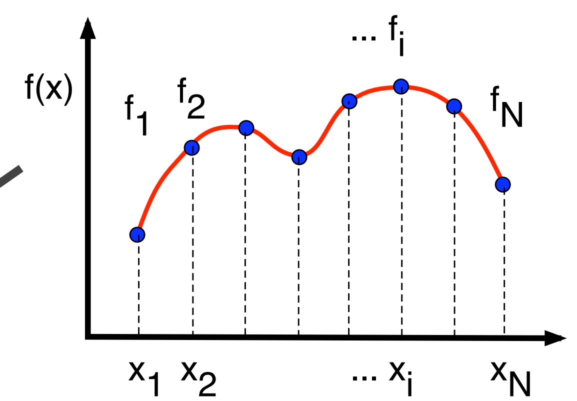


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$$G[f] \approx g(c_1, c_2, \cdots, c_N)$$

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

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

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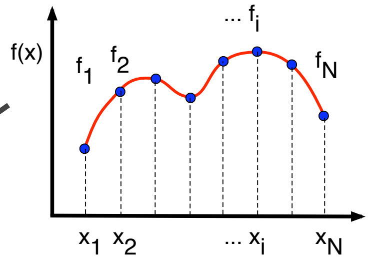


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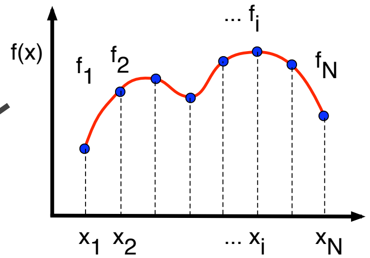


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$$\frac{\delta G}{\delta f(x)} \text{ “}=\text{” } \lim_{\epsilon \to 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

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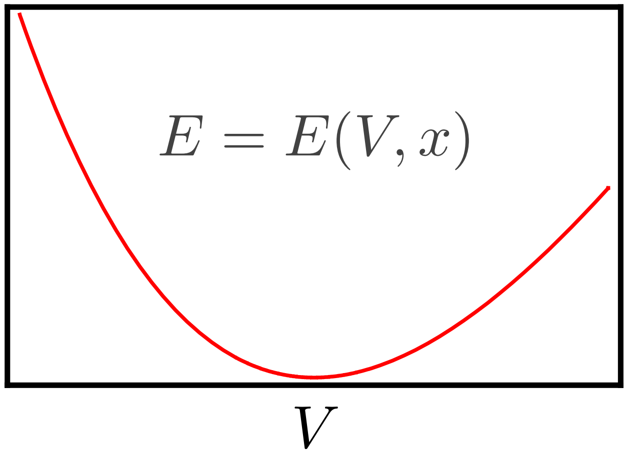
# conjugate variables & Legendre transforms



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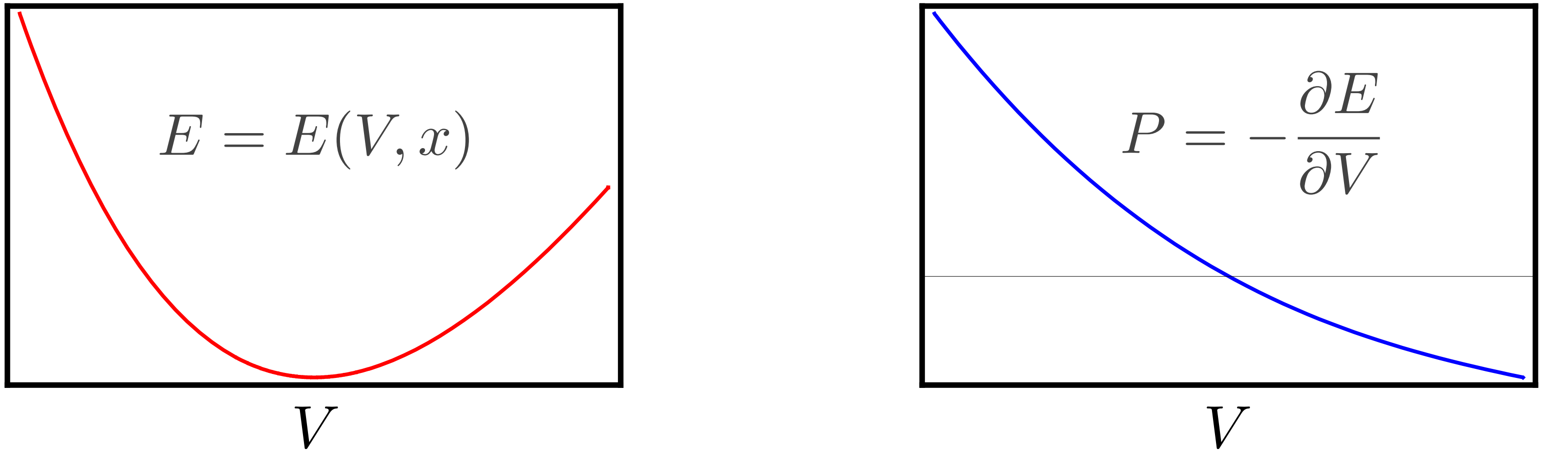

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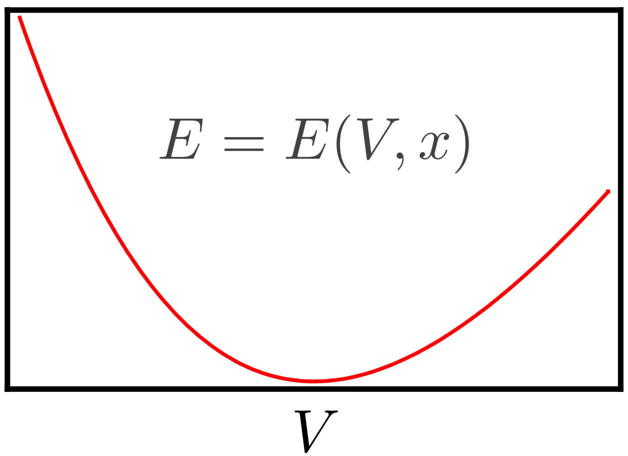


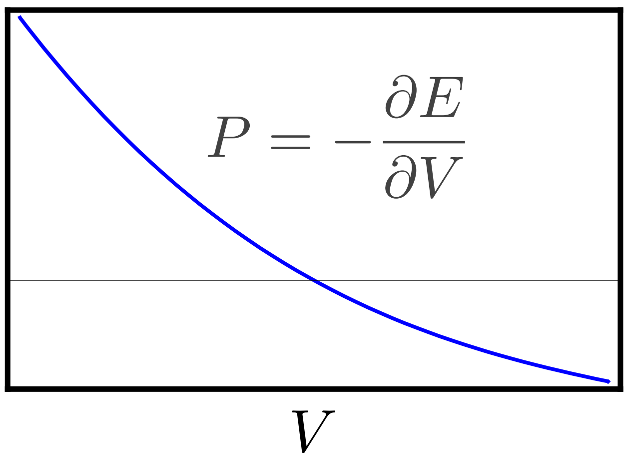


Legendre transform: $H(P, x) = E + PV$

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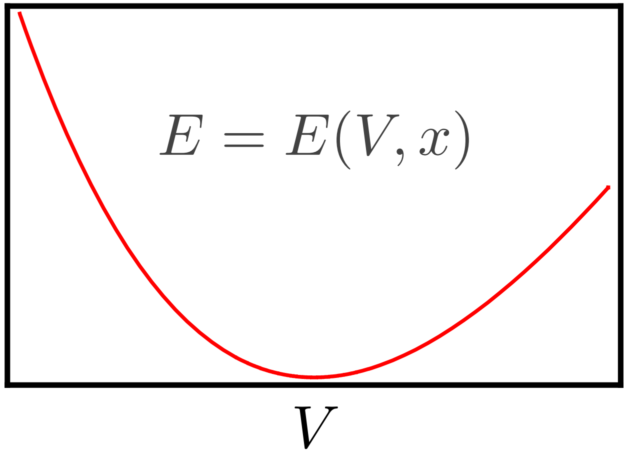


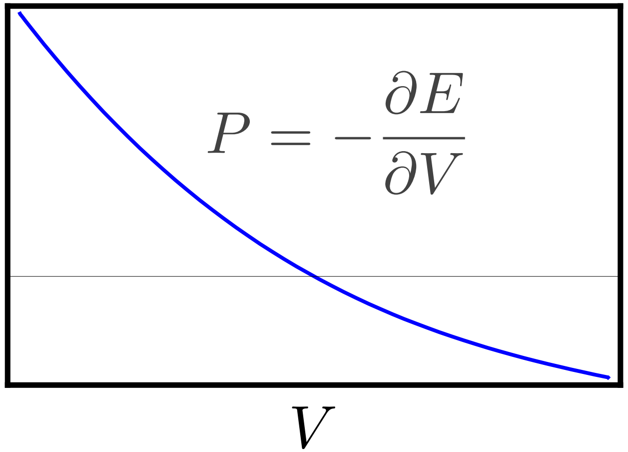


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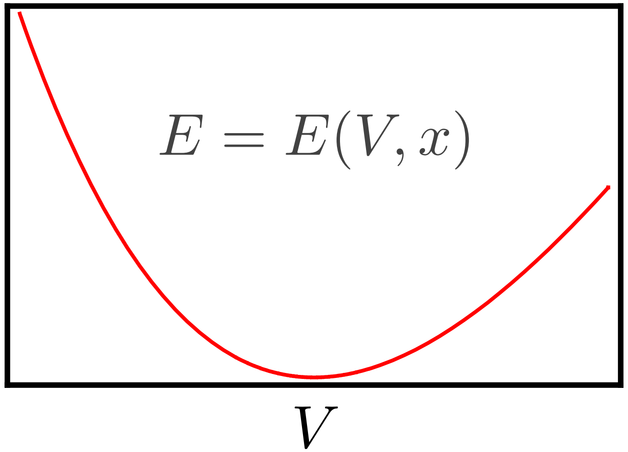


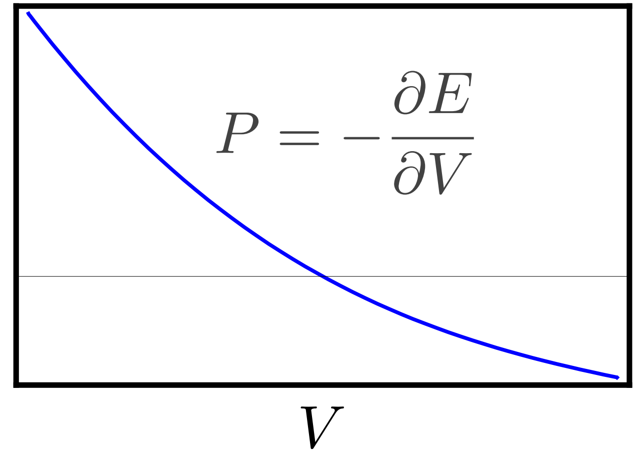


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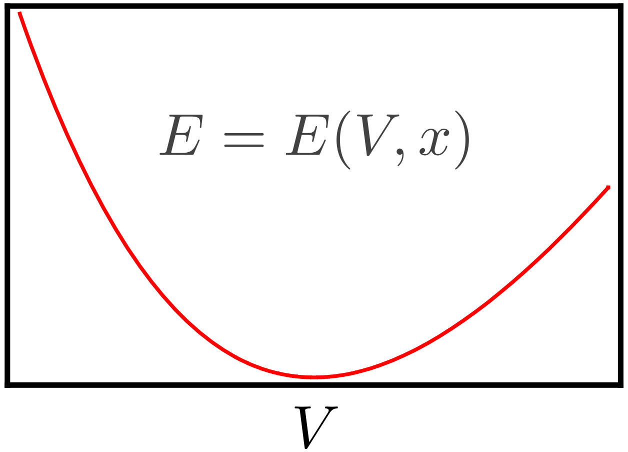


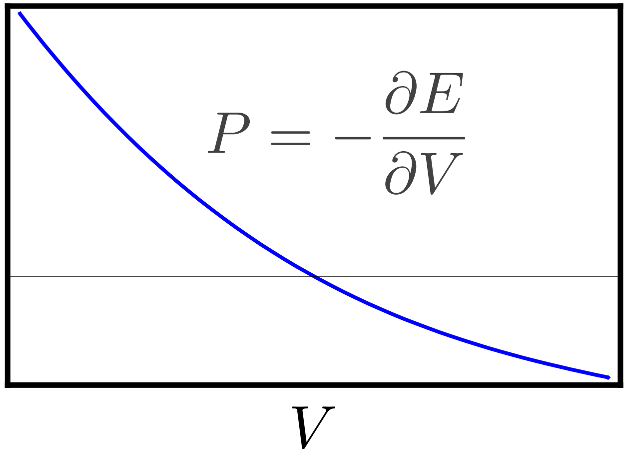


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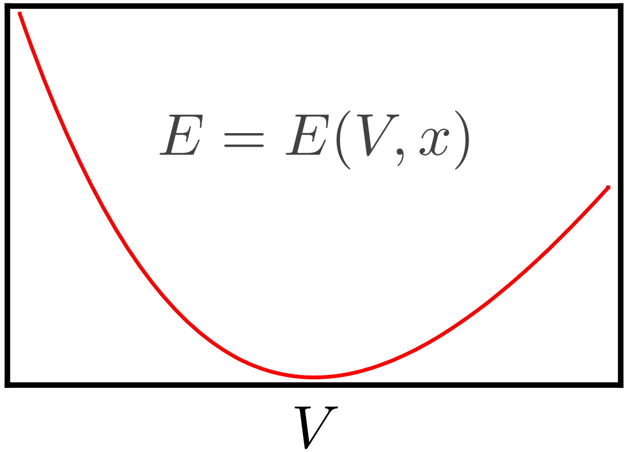


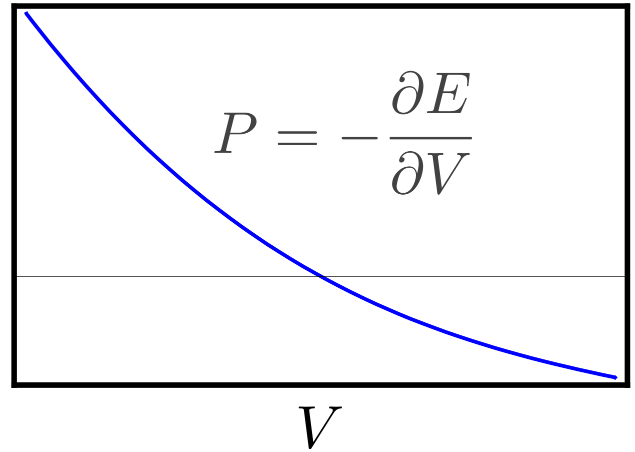


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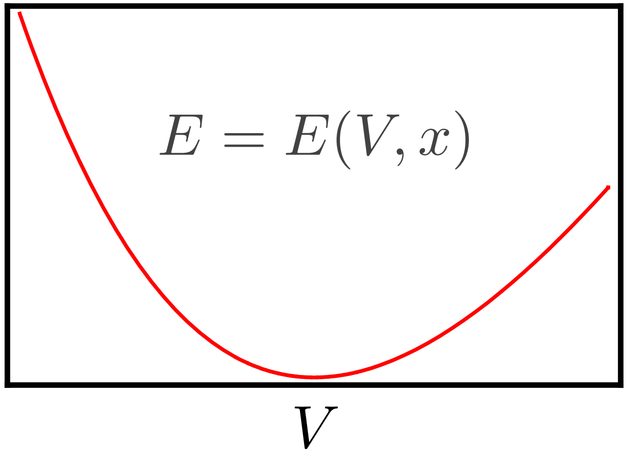


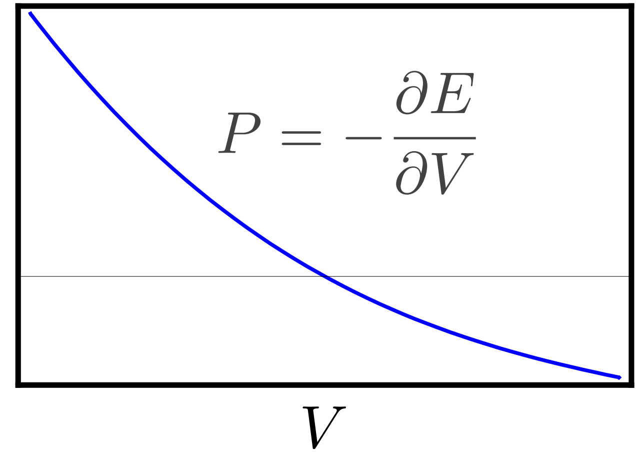


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# Hohenberg-Kohn DFT

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

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consequences:

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

# Kohn-Sham DFT

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

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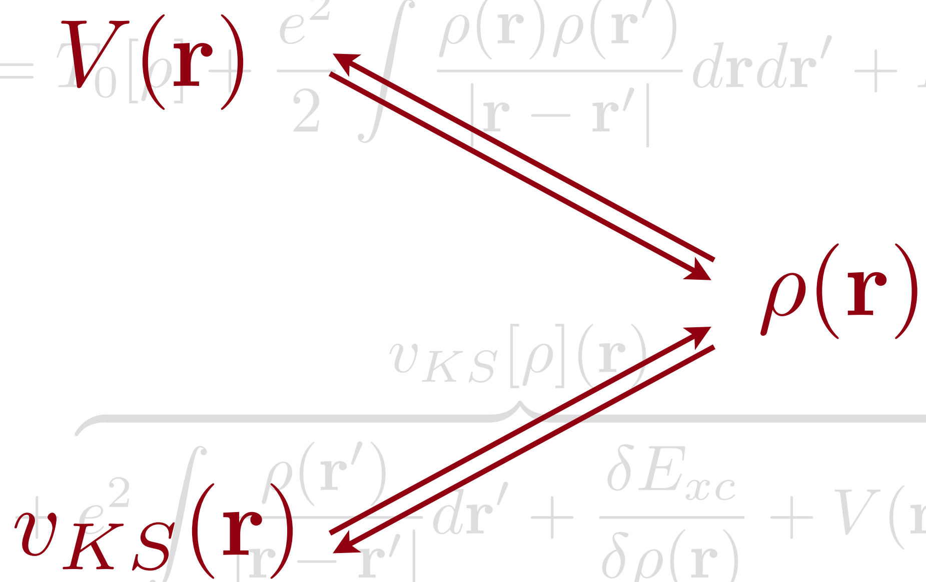


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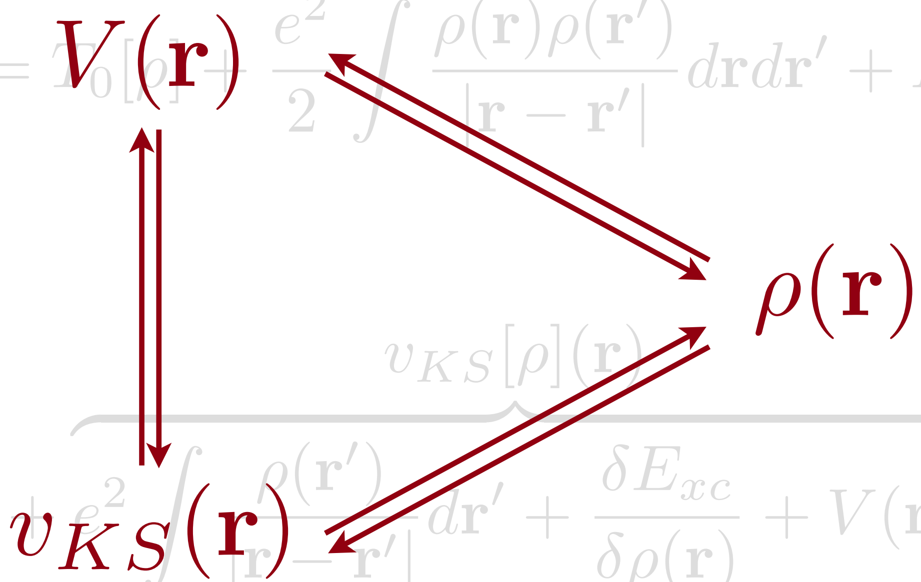


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# exchange-correlation energy functionals

- 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)

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

- 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)

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

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

- 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

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

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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

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

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

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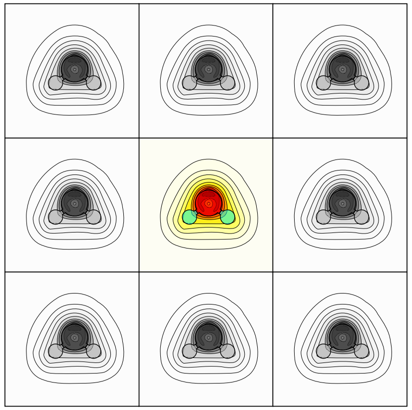
finite systems $(\ell = a)$



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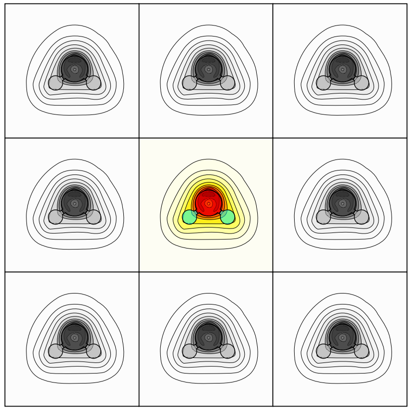

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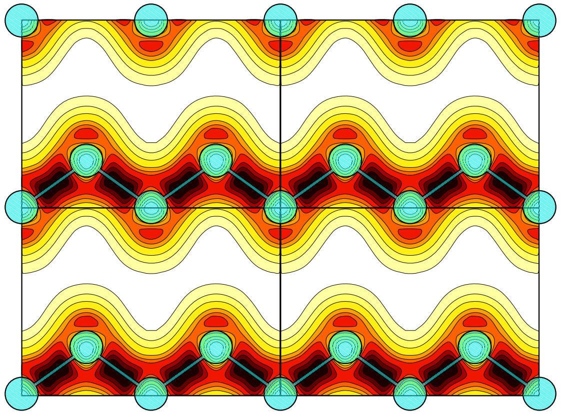
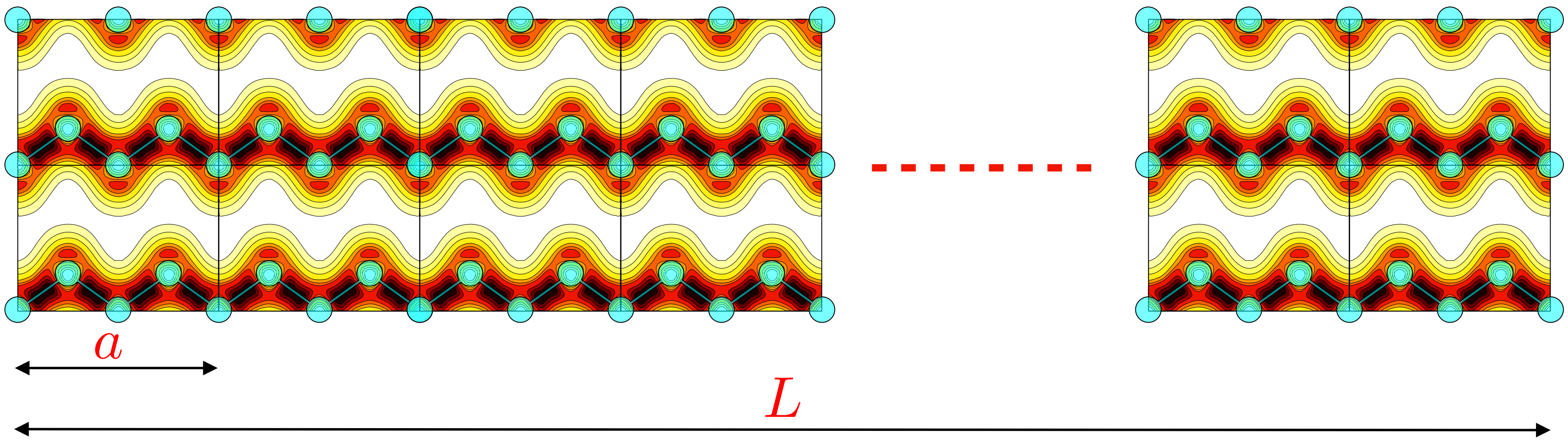
infinite crystals $(\ell = L)$



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

# the Bloch theorem & plane waves

infinite crystals




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

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

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

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

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

# using plane waves

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

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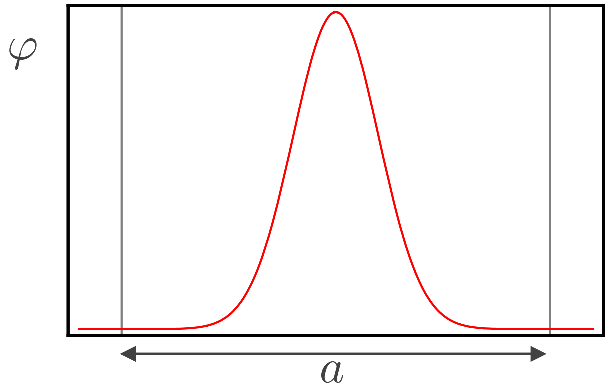
$$\begin{aligned} V_{xc}(\mathbf{r}) &= \mu_{xc}\big(\rho(\mathbf{r})\big) \\ V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ &= e^2 \sum_{\mathbf{G}\neq 0} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G}) \end{aligned}$$

# sampling theorem

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



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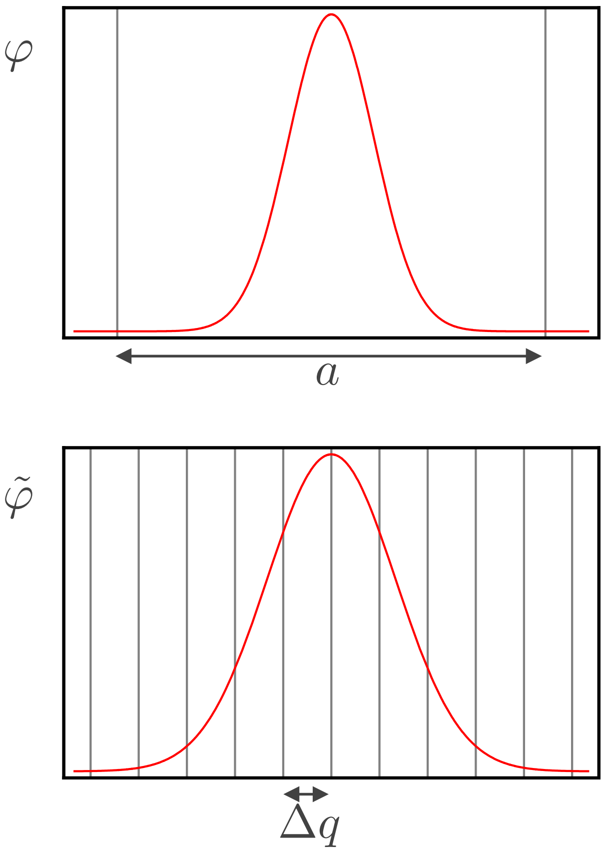

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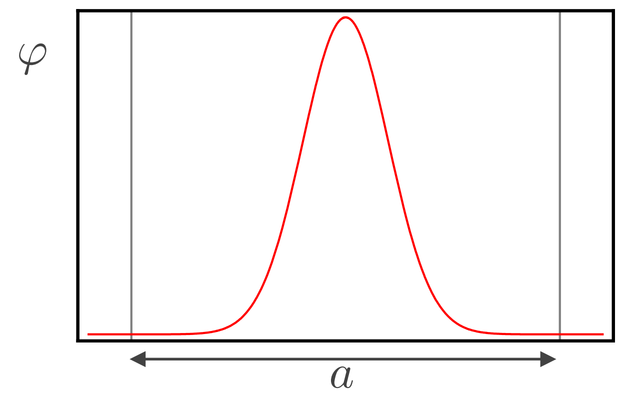


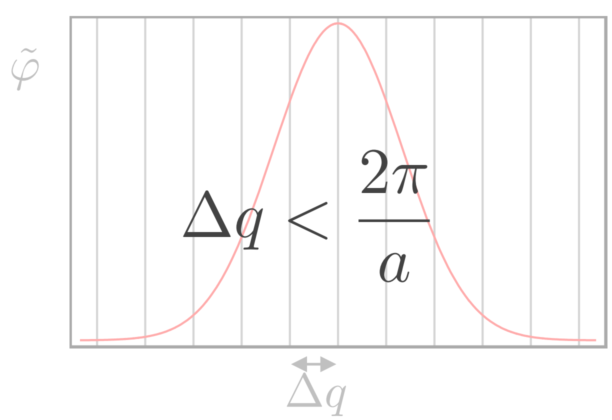


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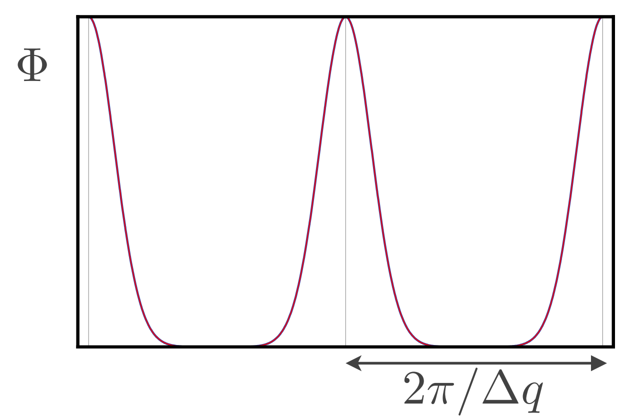

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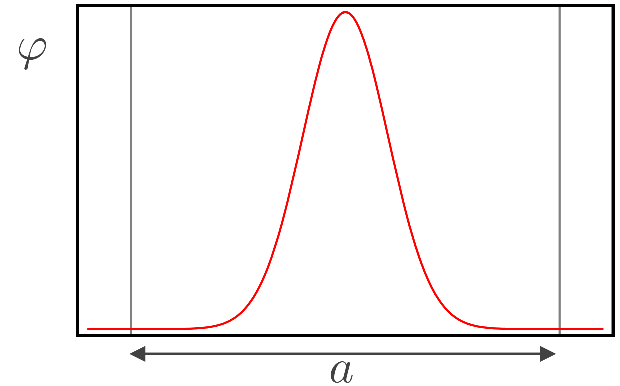


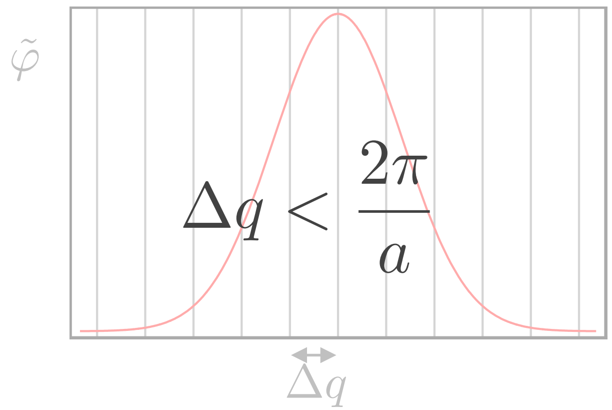


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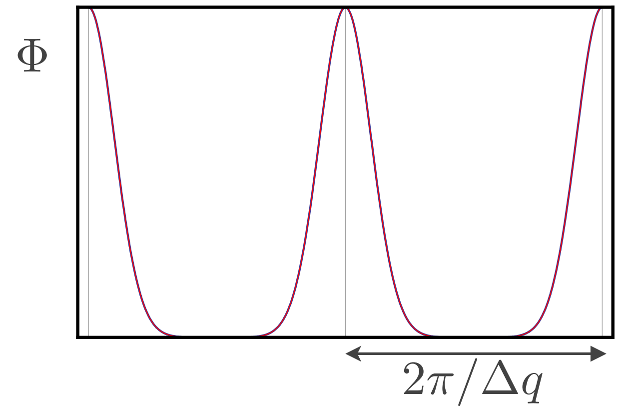


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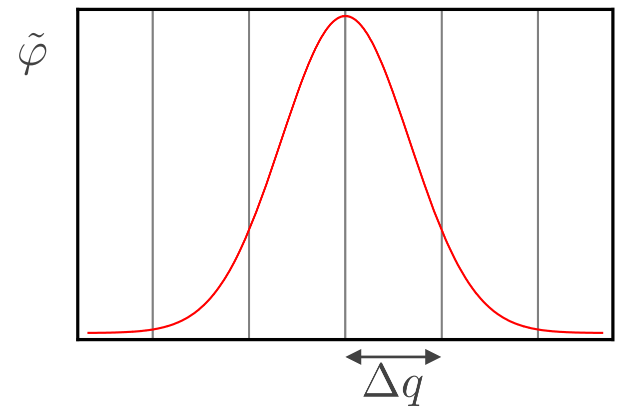

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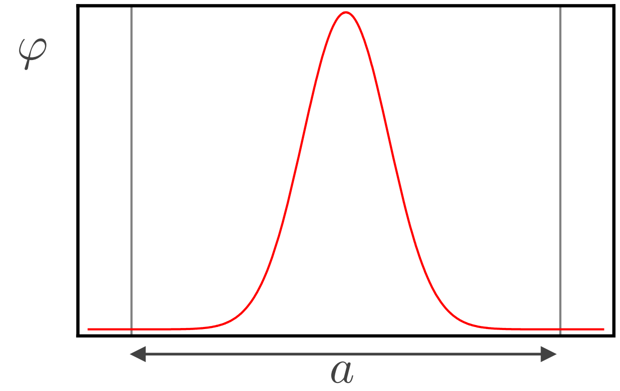


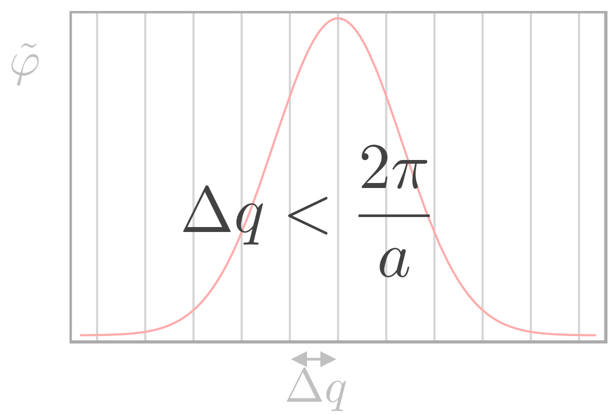


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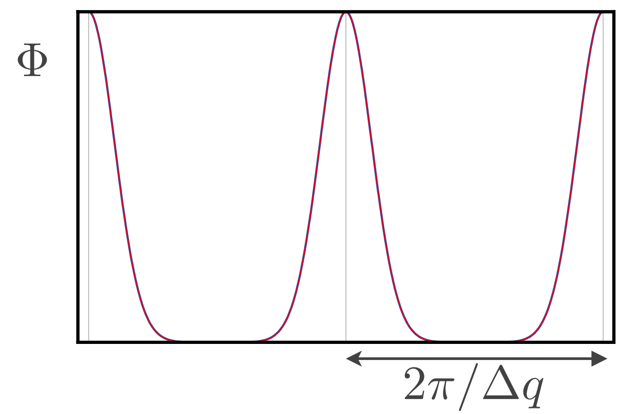


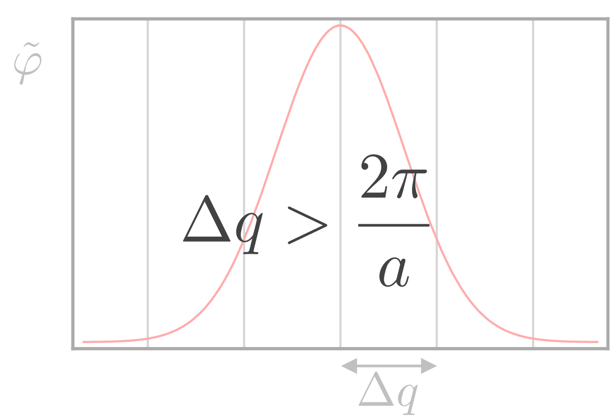


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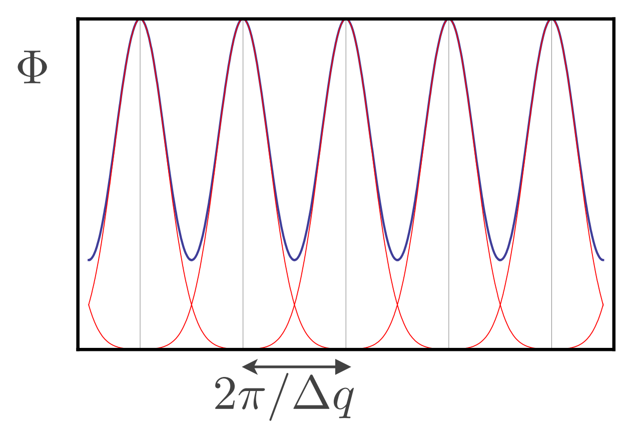

# discrete Fourier transforms

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

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dFt

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

# the fast Fourier transform

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# multivariate FFTs

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

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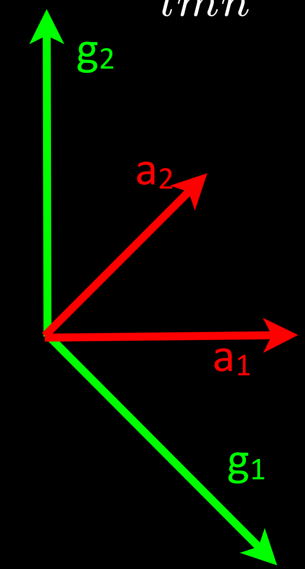

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FFT

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

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$\mathrm{FFT}^{-1}$

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

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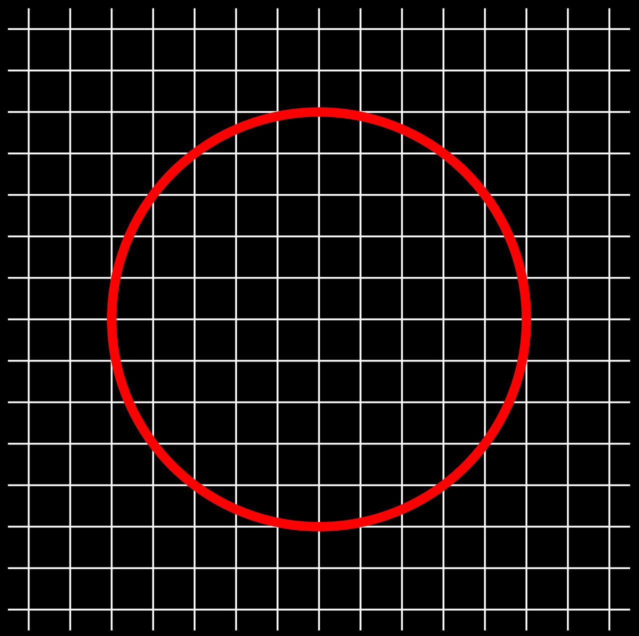

$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

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

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

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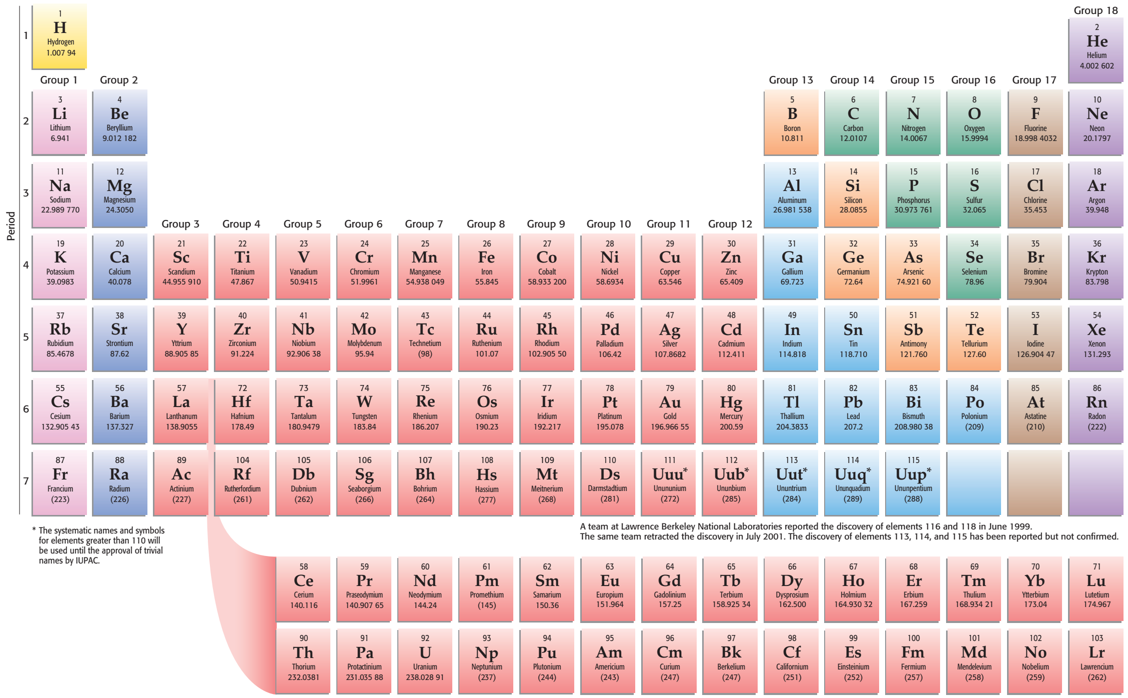
- ☹ uniform spatial resolution (no core states!)

# treating core states




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

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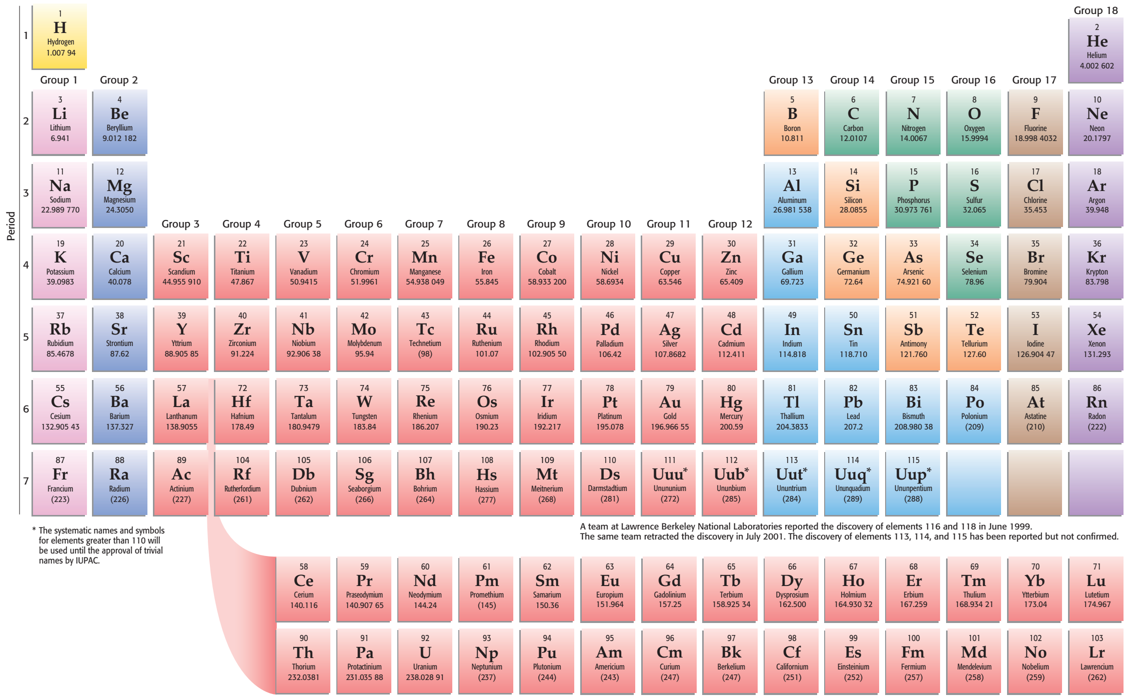


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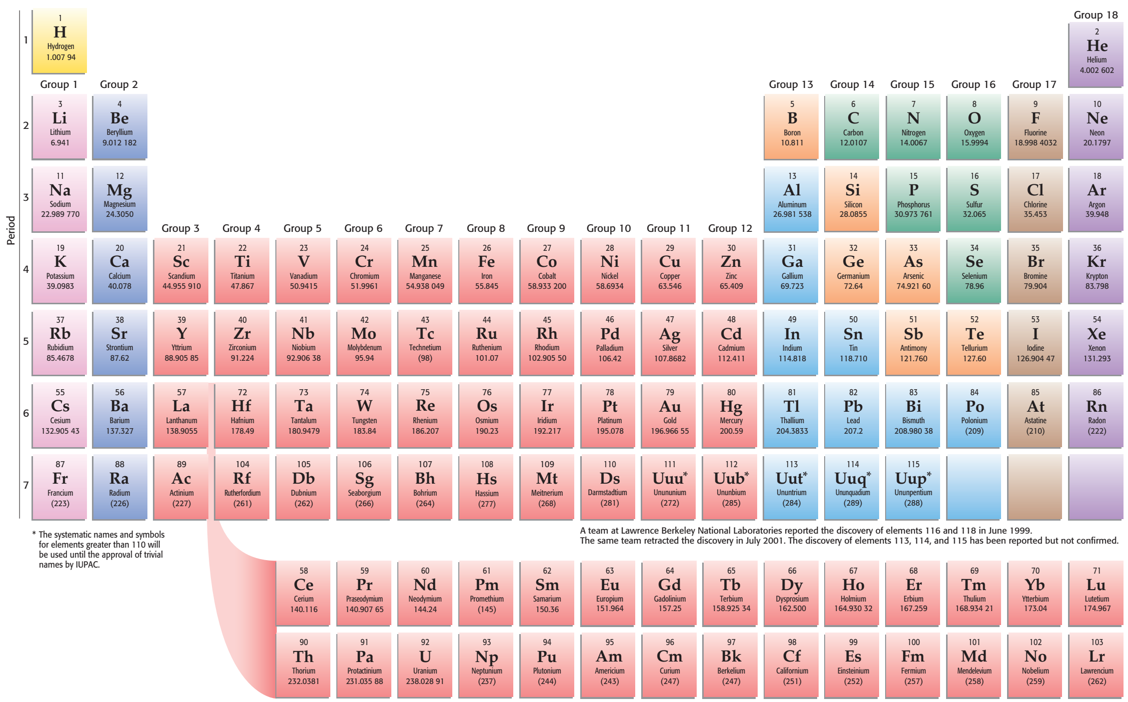


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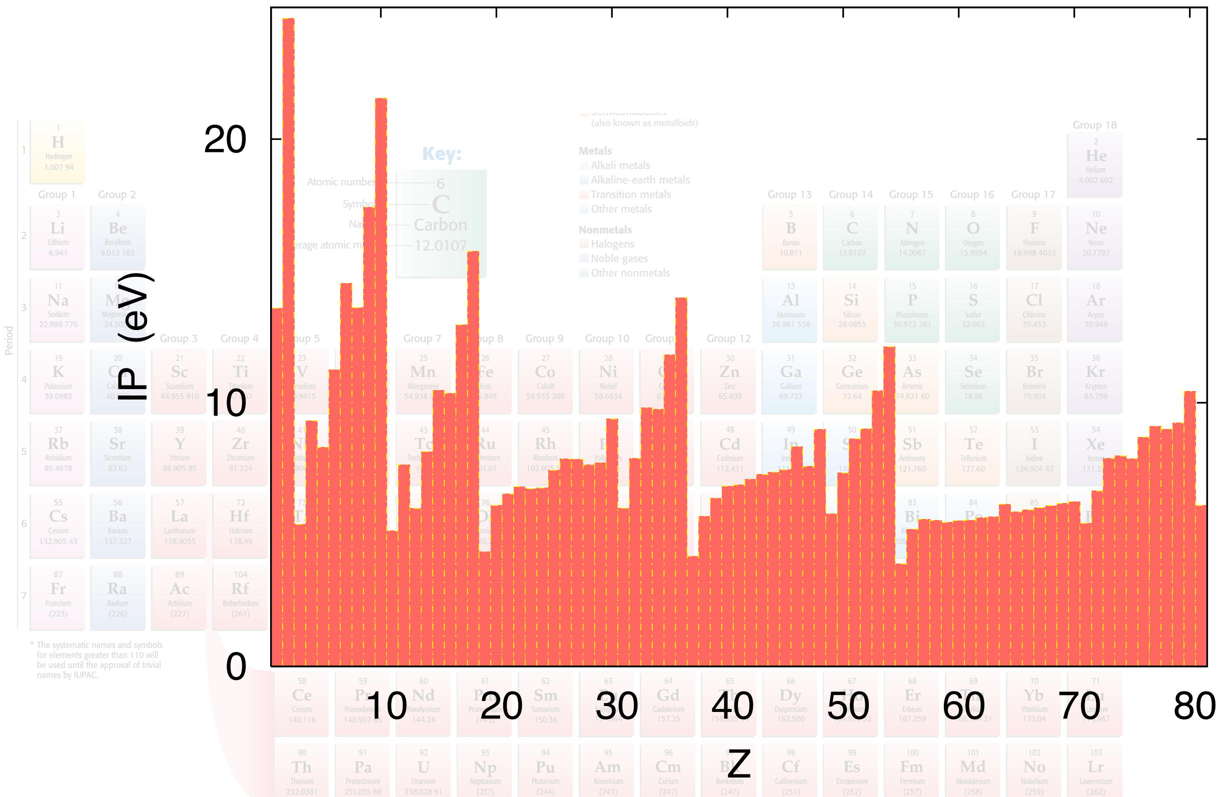


$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

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$$I_P \sim 1 \quad a \sim 1$$

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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:

$\phi^{ps}_{val}$ is nodeless and smooth

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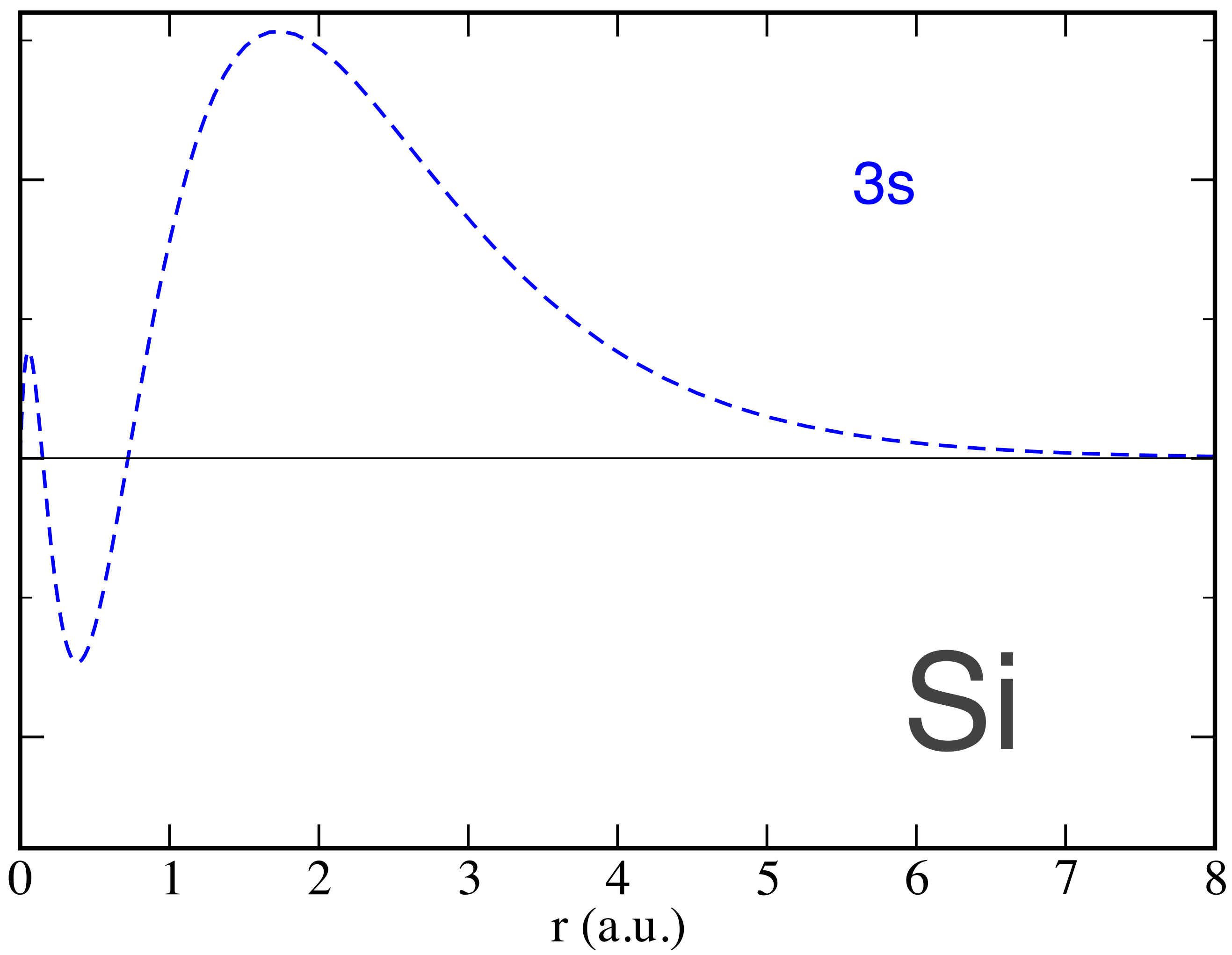
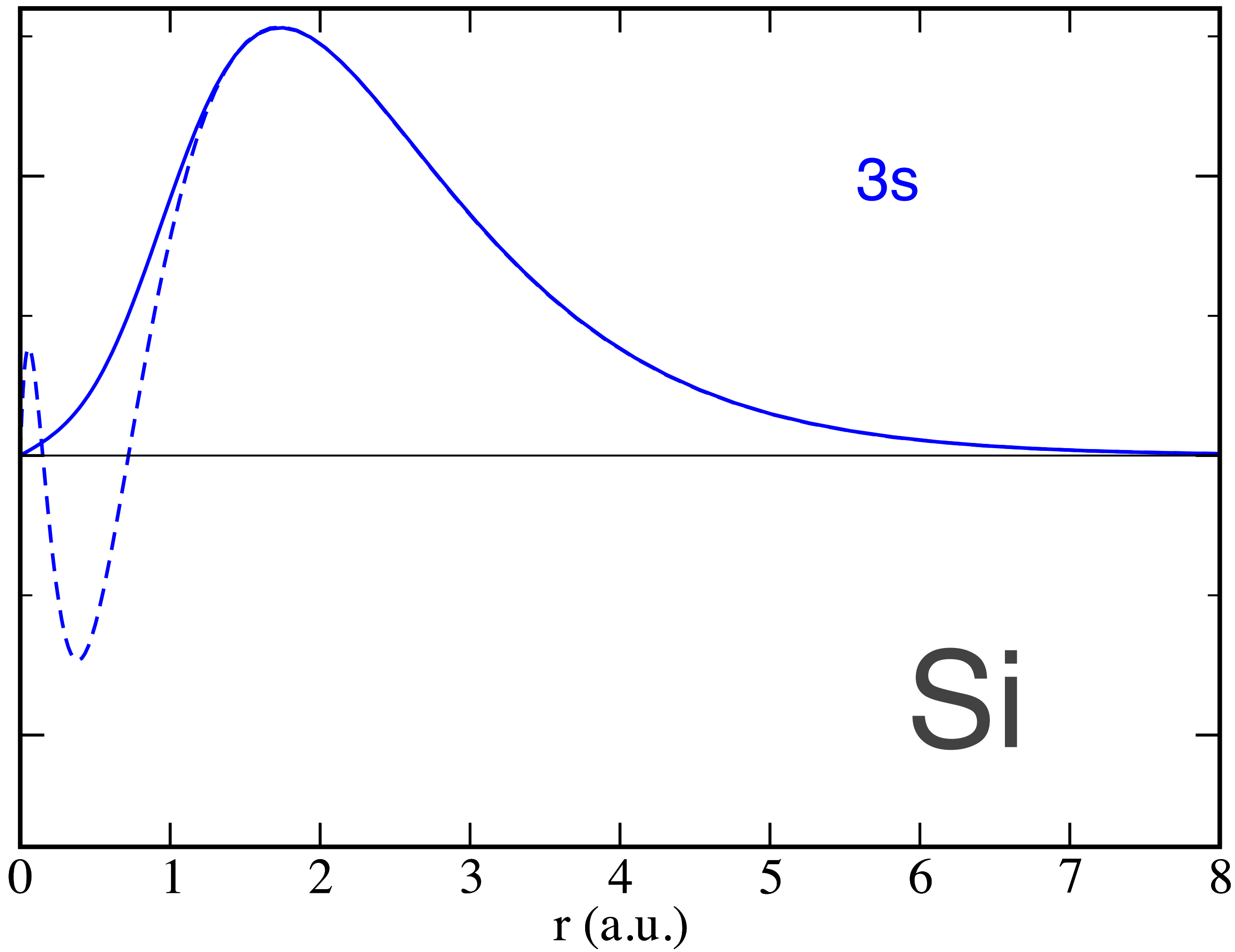
the chemical properties of the pseudo-atom are the same as those of the true atom:

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

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


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


3s
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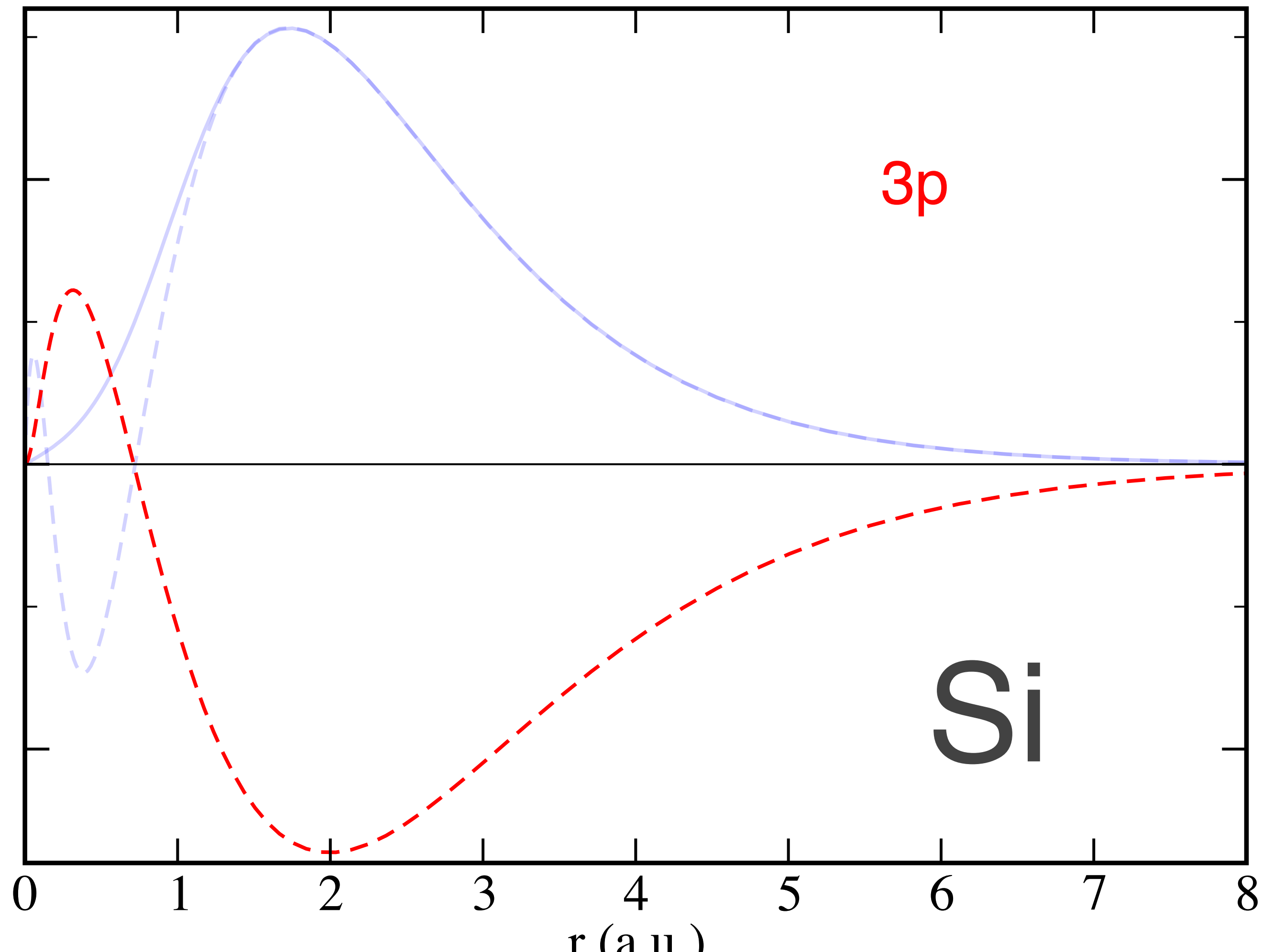
3p
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0
1
2
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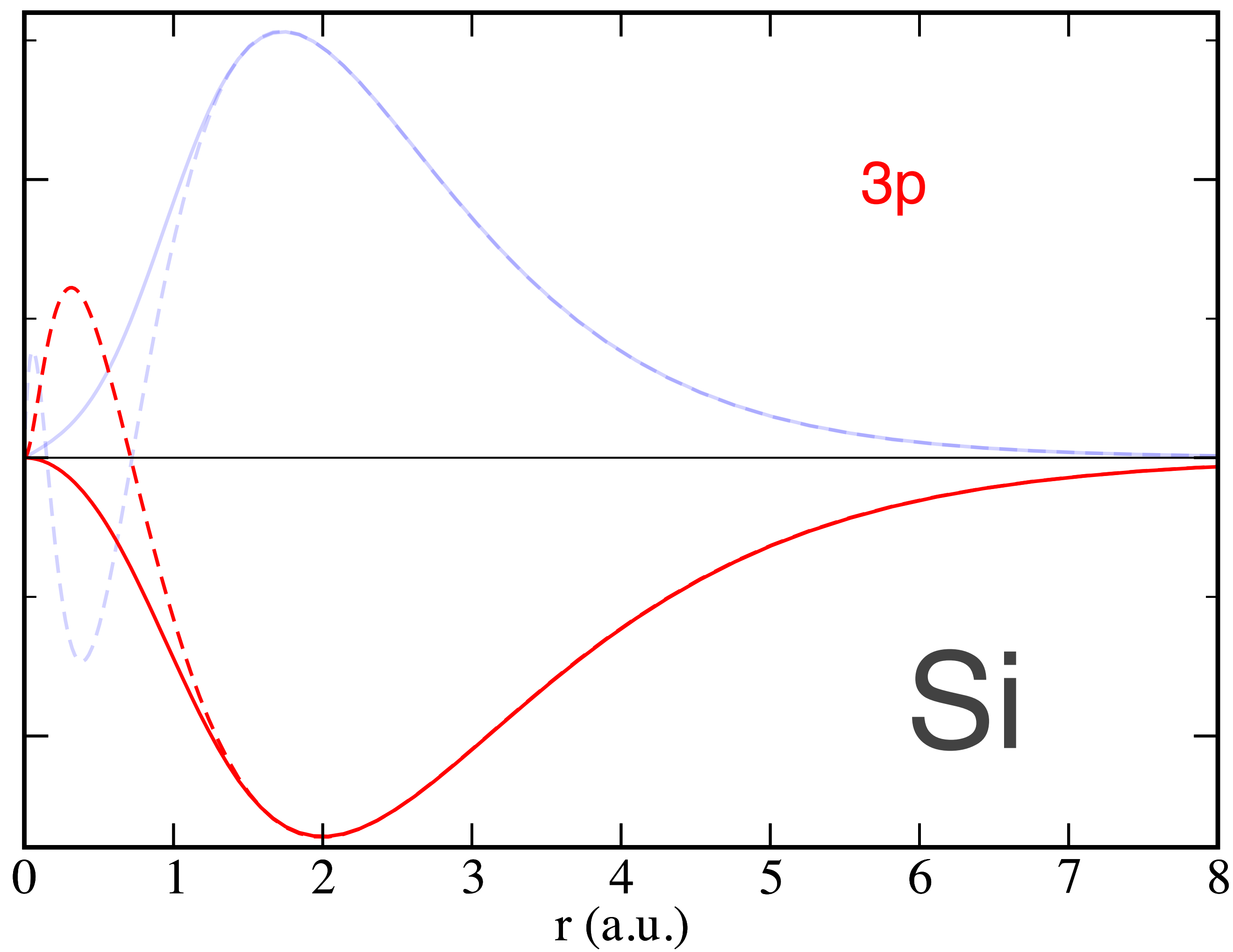
6
7
8
r (a.u.)


3p
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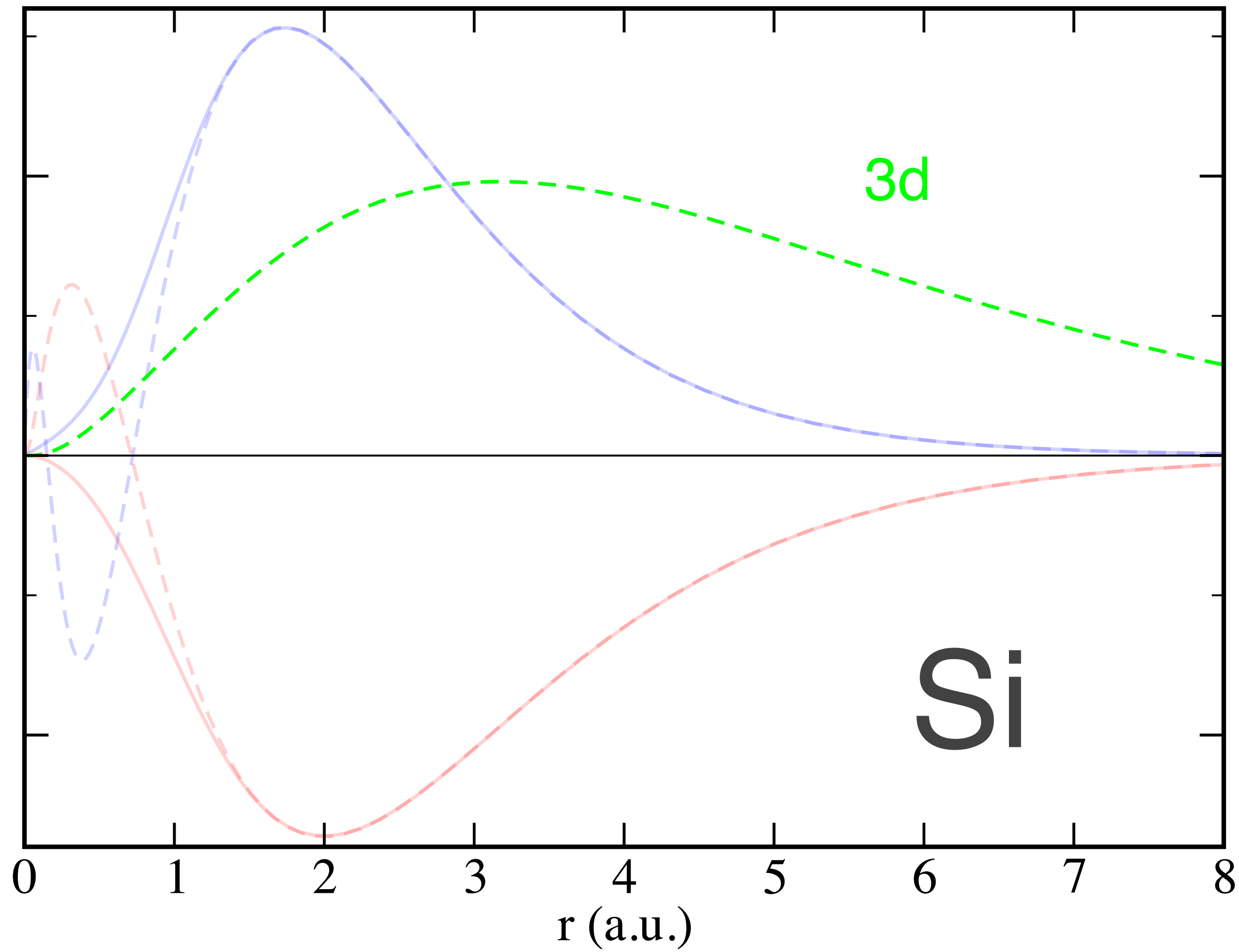
3d
Si
0
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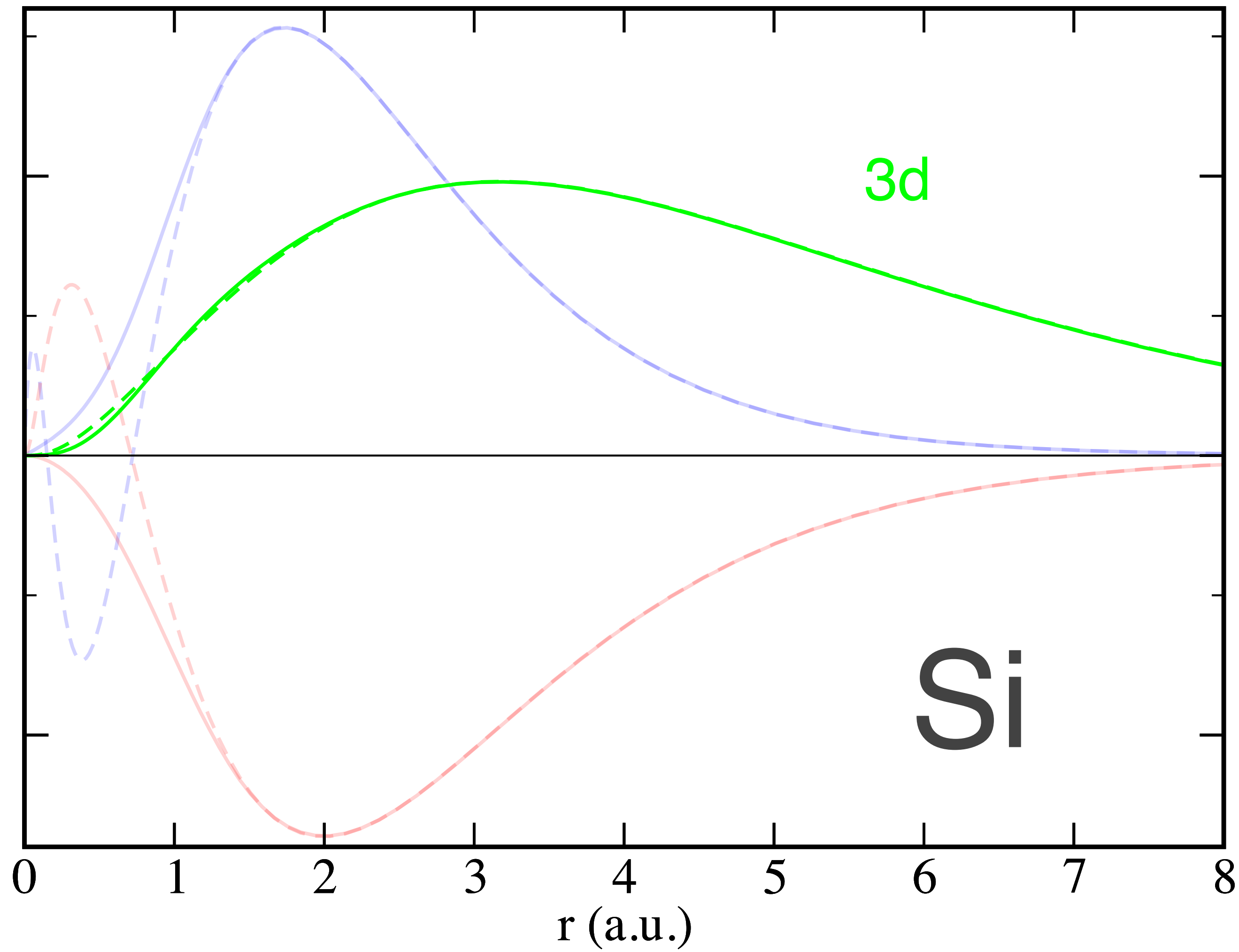
8
r (a.u.)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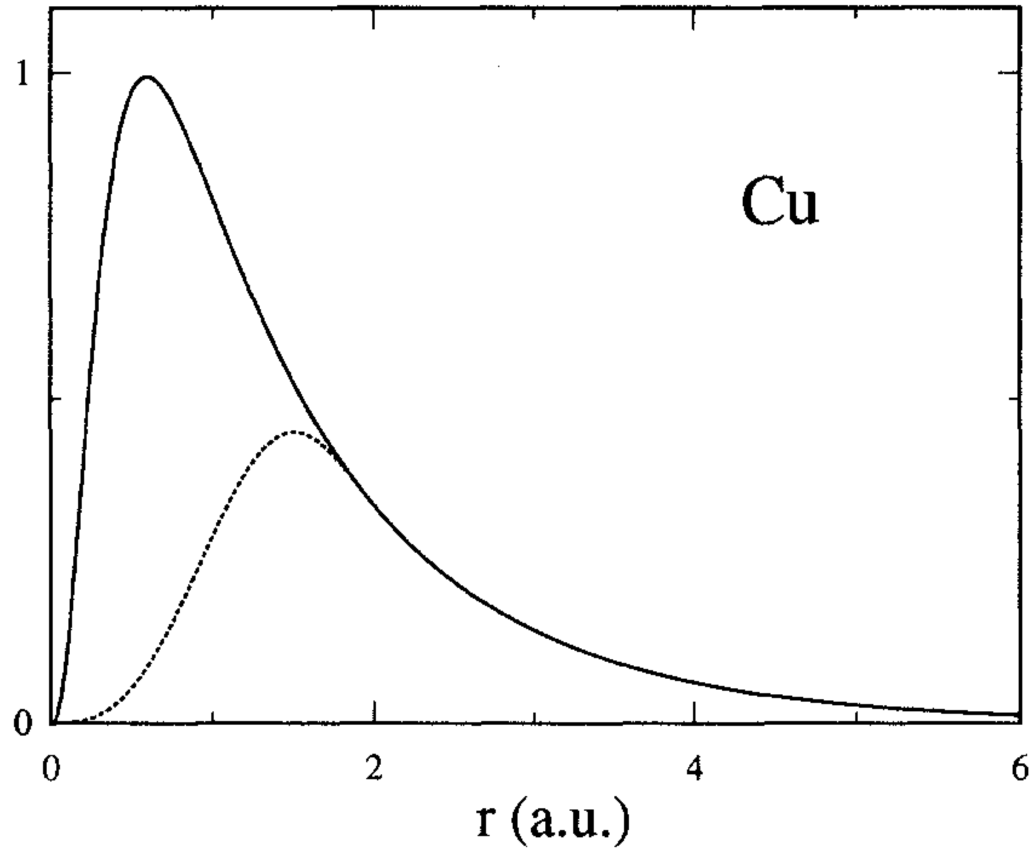
# US pseudopotentials



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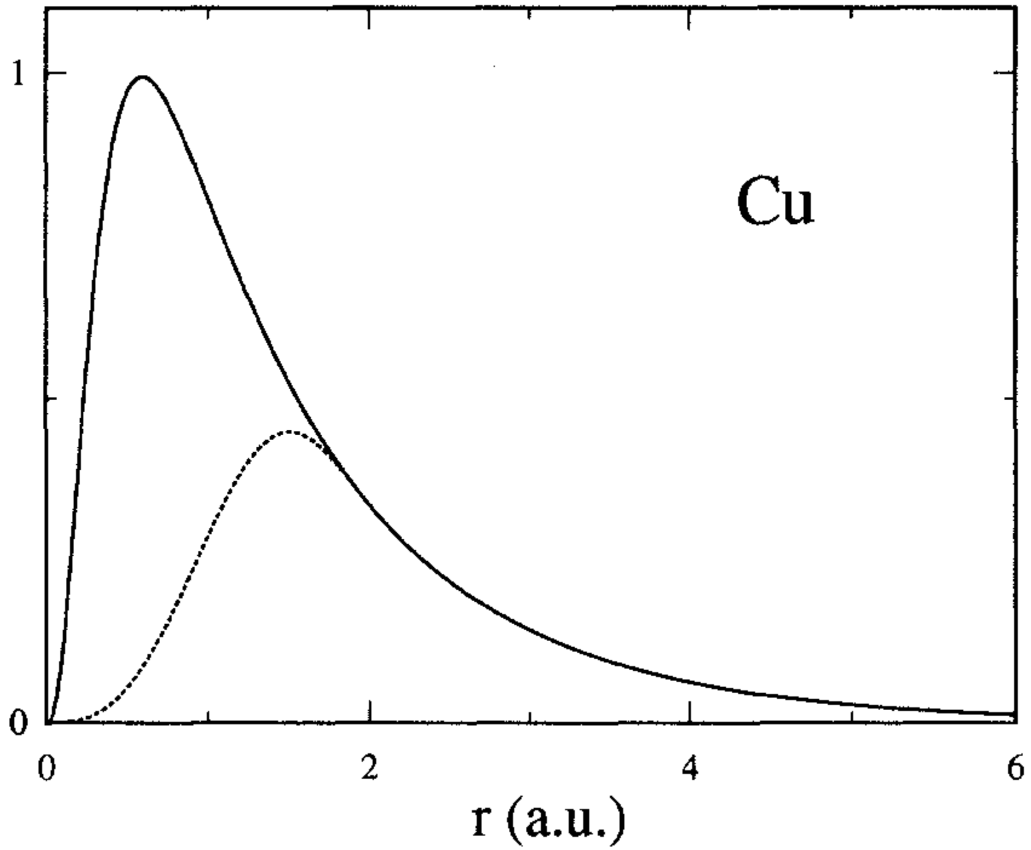


$$H_{US}\phi_n = \epsilon_n S\phi_n \qquad \langle\phi_n|S|\phi_m\rangle = \delta_{nm}$$


these slides at
http://talks.baroni.me
baroni@sissa.it