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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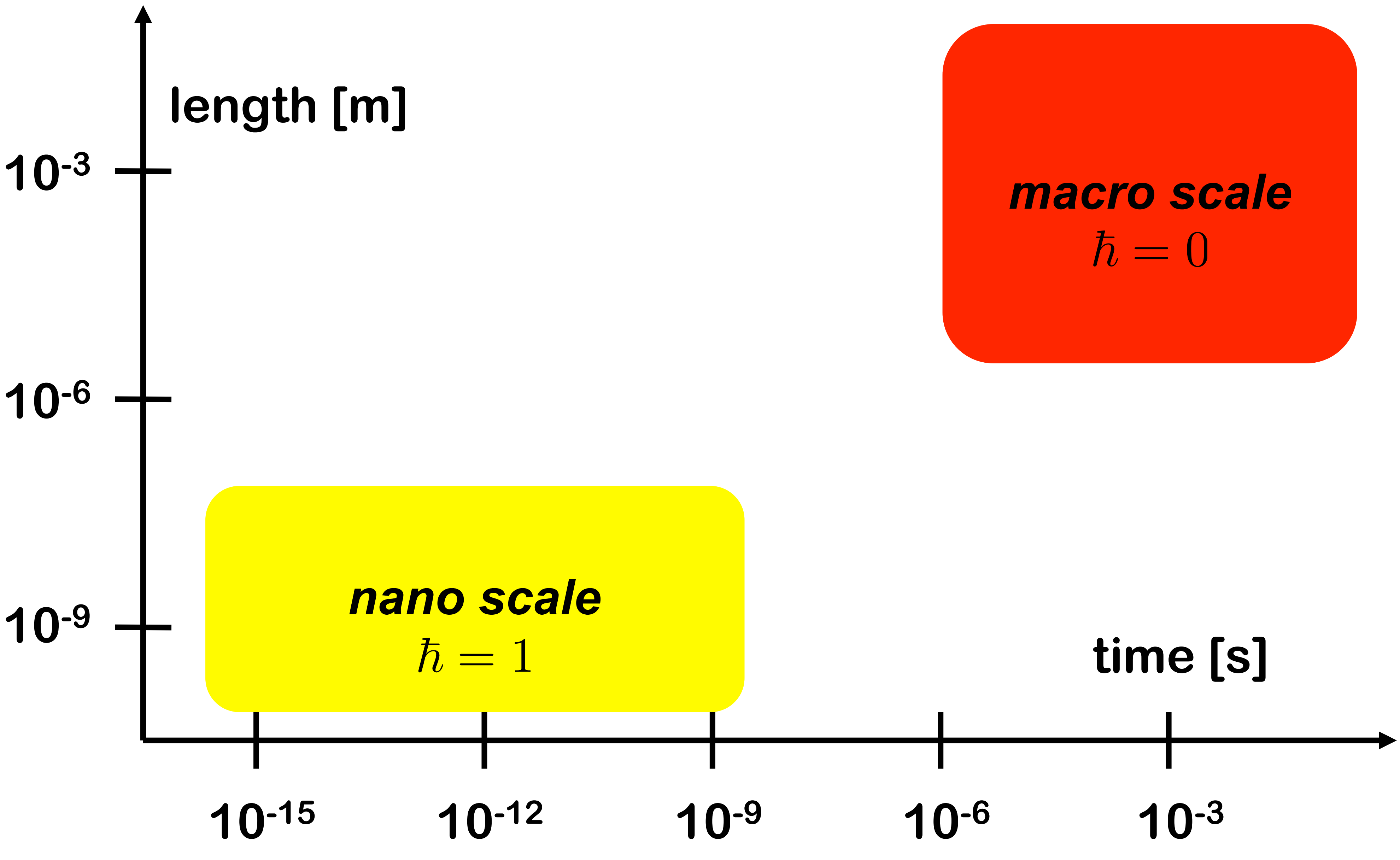
the saga of time and length scales



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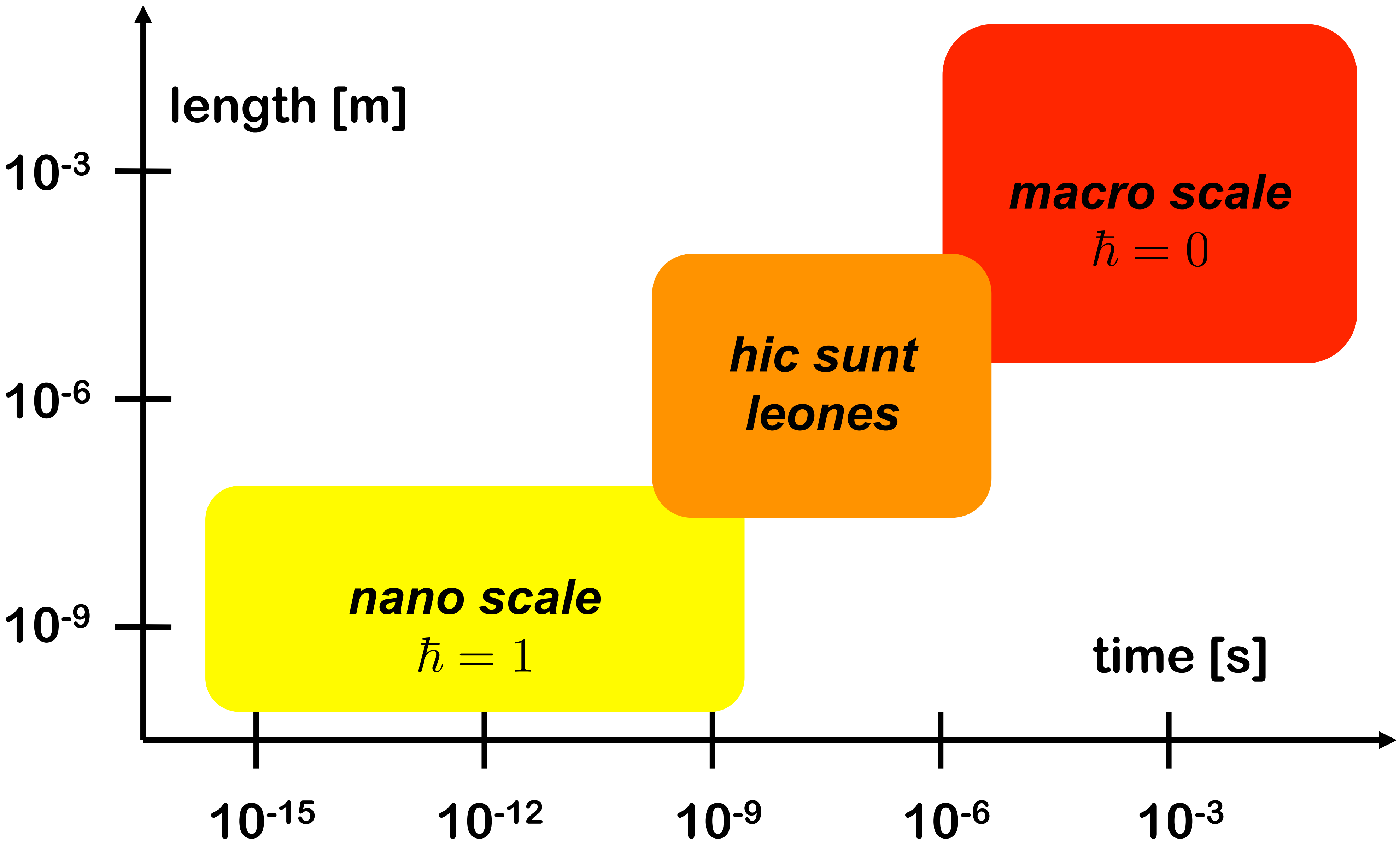

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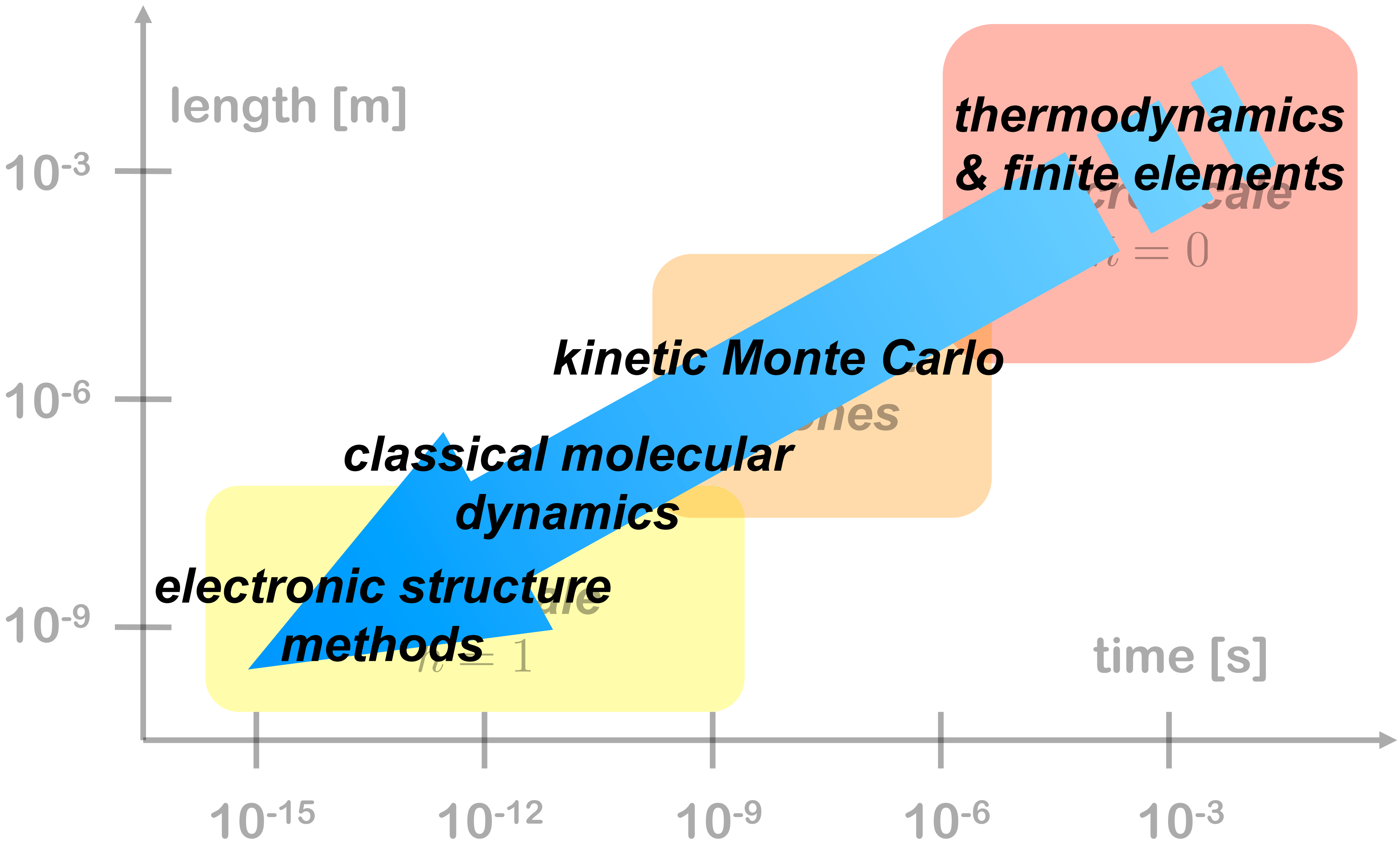
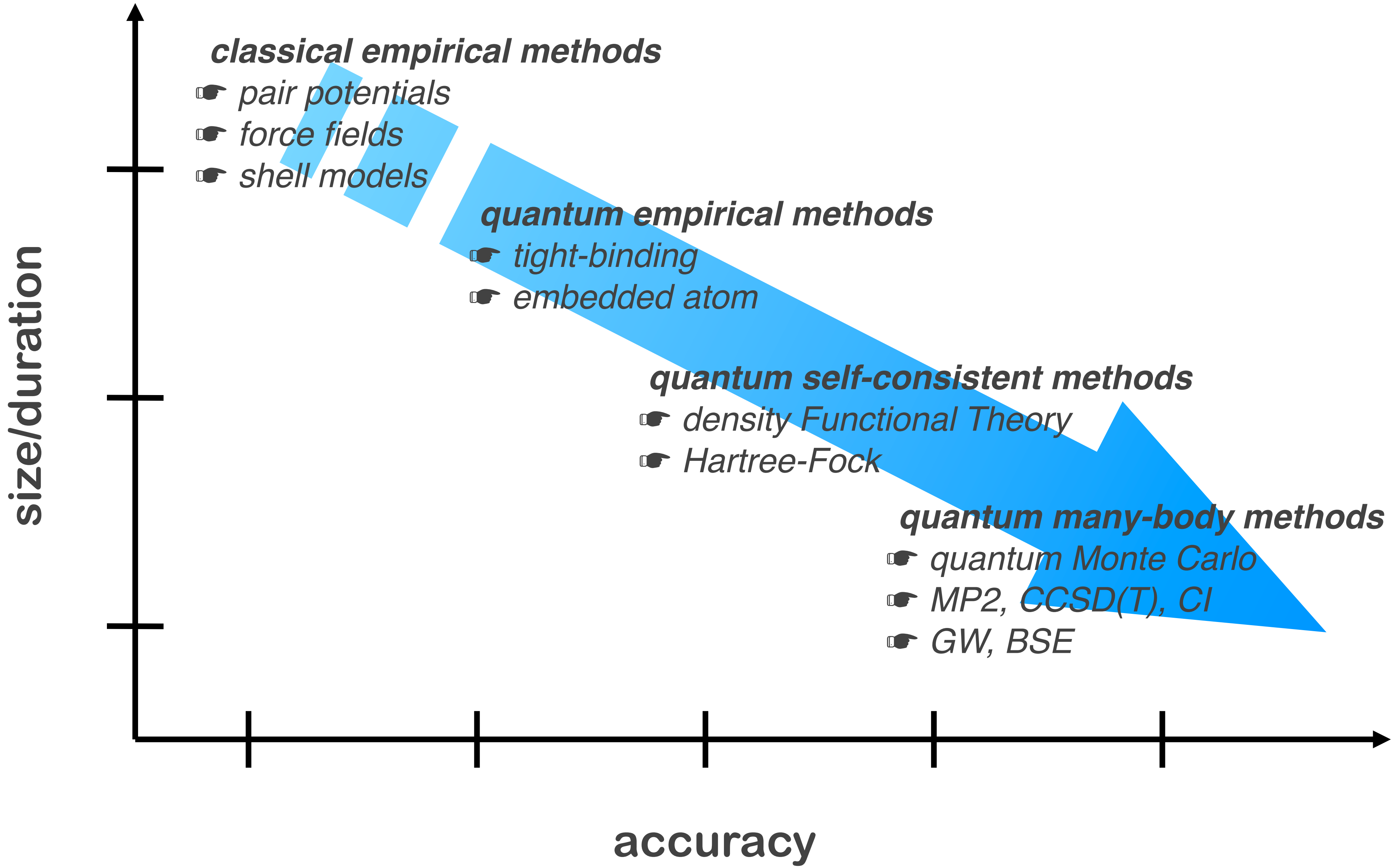


size vs. accuracy



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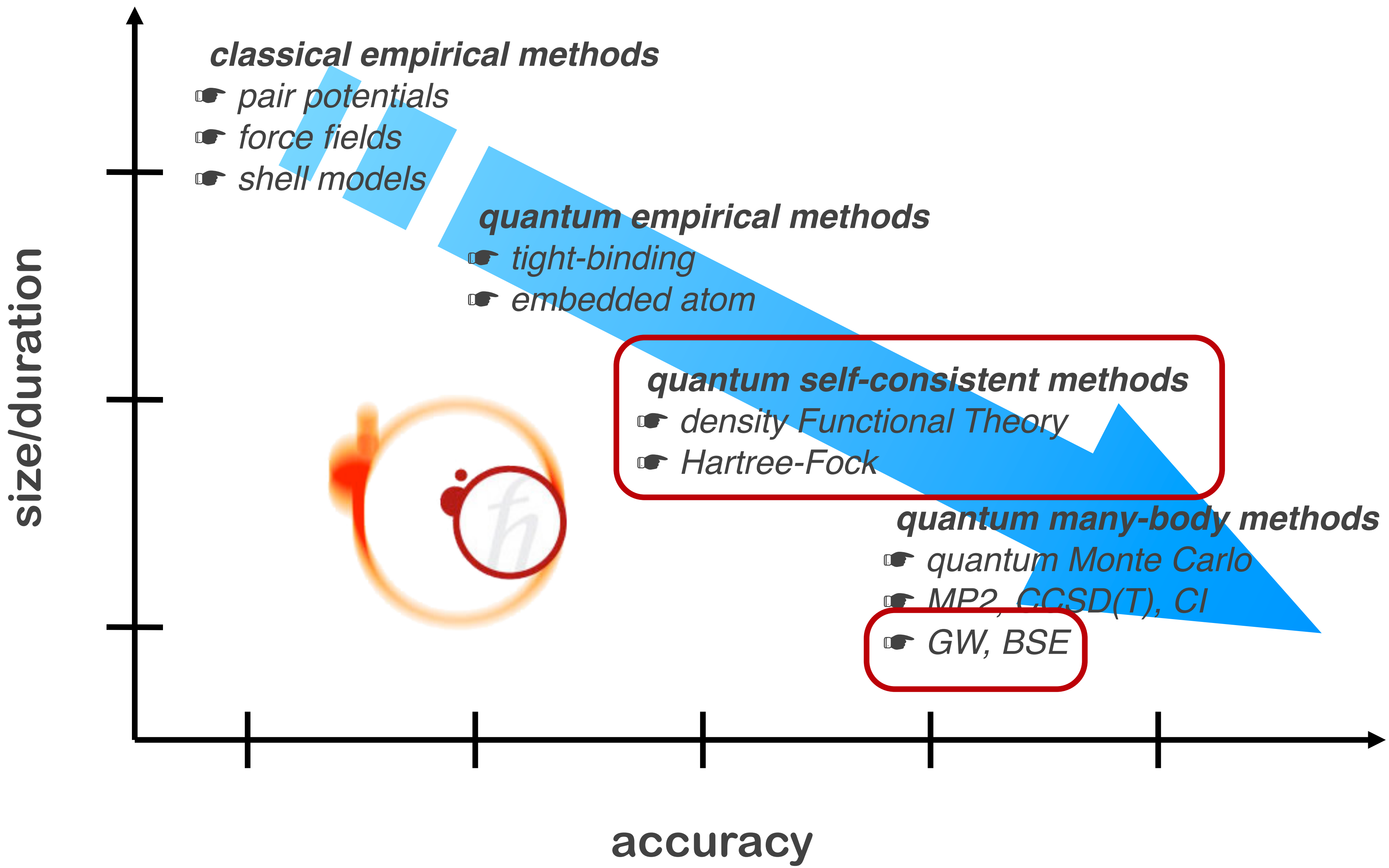

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when: if currently available approximations make the calculations feasible and the results meaningful (and no meaningful results can be obtained with cheaper methods)

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what: simulate the properties of materials using Schrödinger and Maxwell equations and chemical composition as the *sole* input ingredients

why: they are accurate and *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

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

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

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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DFT

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

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Kohn-Sham
Hamiltonian

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

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

functionals

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

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examples:

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

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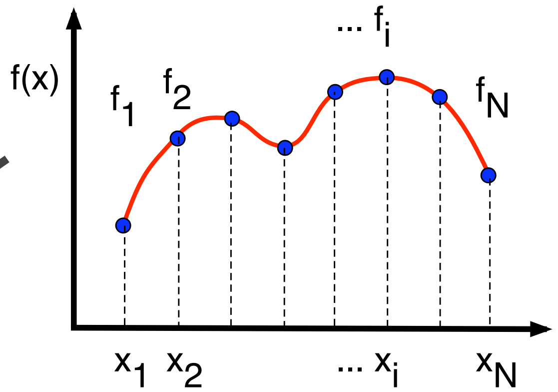

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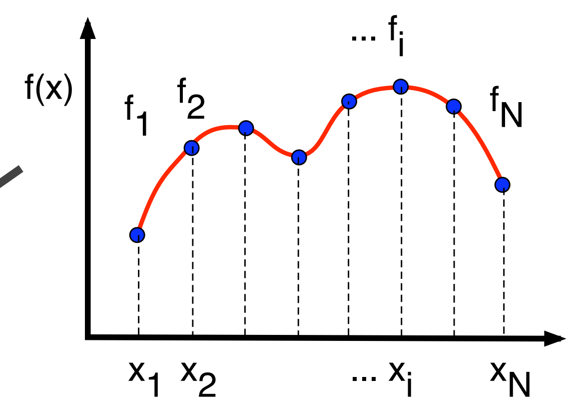

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$$

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

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

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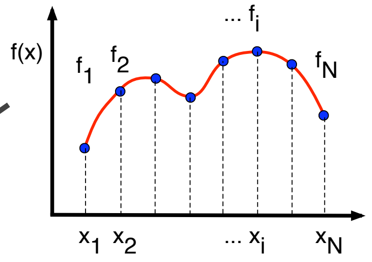

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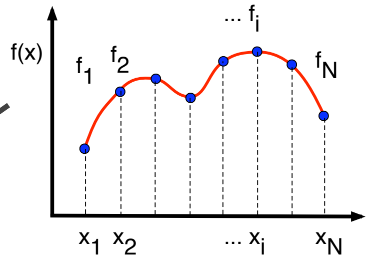

$$\frac{\delta G}{\delta f(x)} \text{``} = \text{''} \lim_{\epsilon \to 0} \frac{G[f(\bullet) + \epsilon \delta(\bullet - x)] - G[f(\bullet)]}{\epsilon}$$

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

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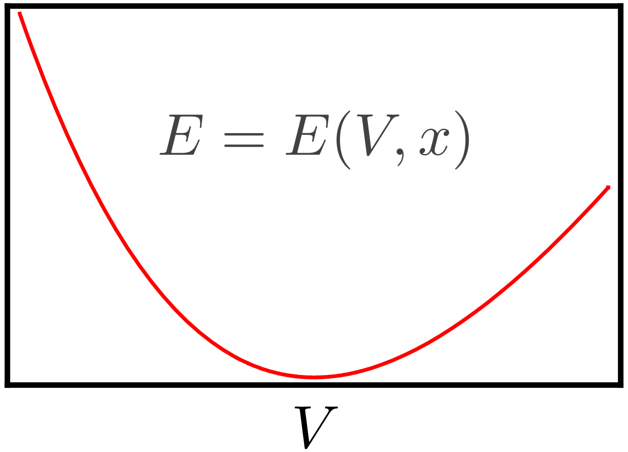
conjugate variables & Legendre transforms



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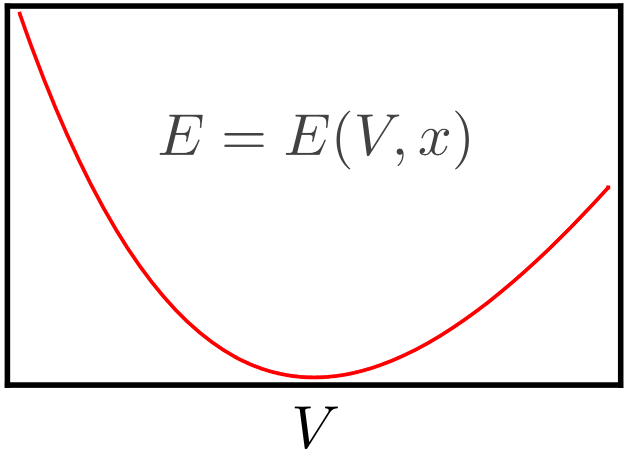

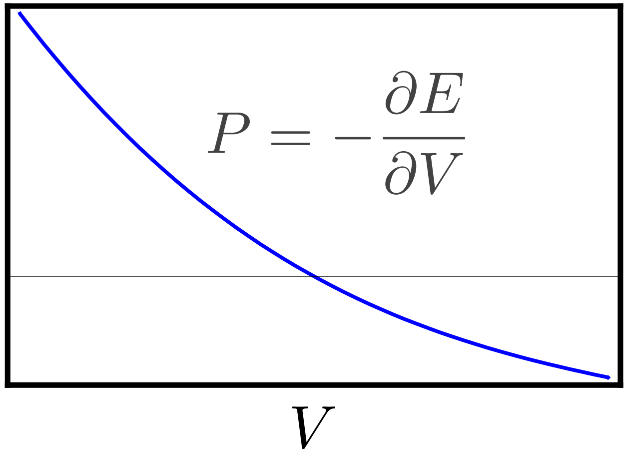

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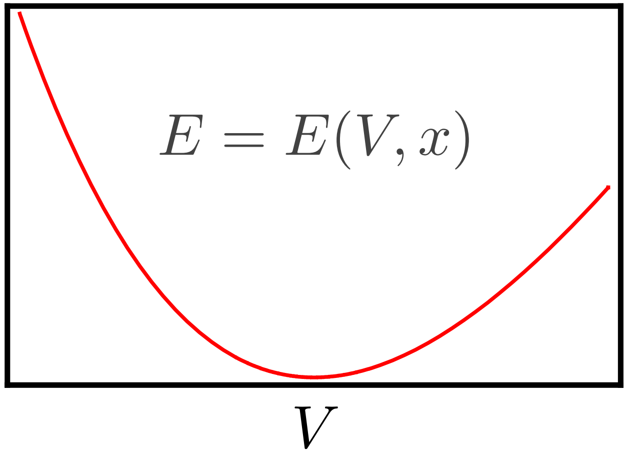
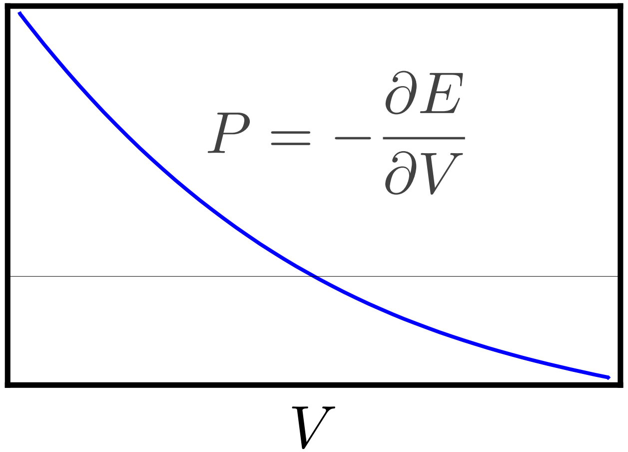
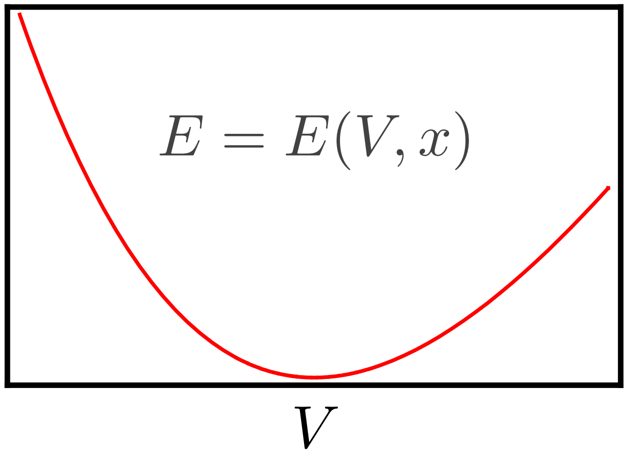
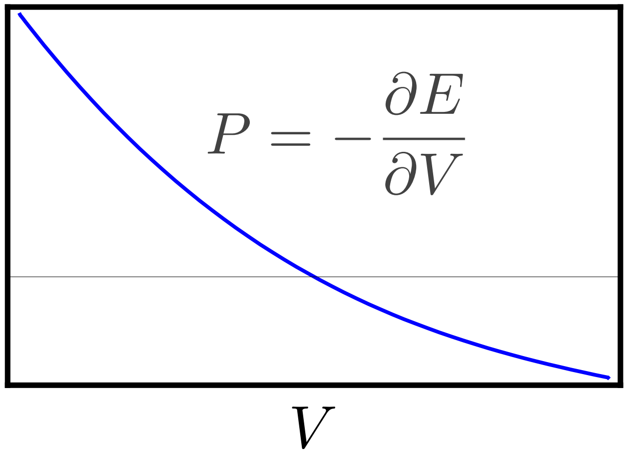




Legendre transform: $H(P, x) = E + PV$

conjugate variables & Legendre transforms





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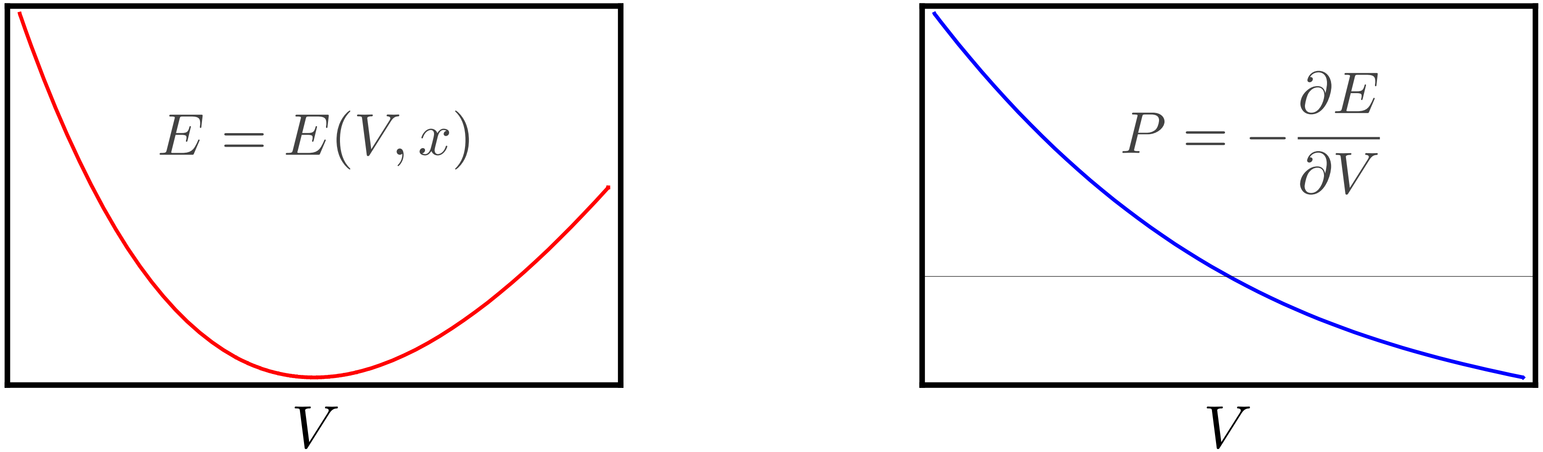

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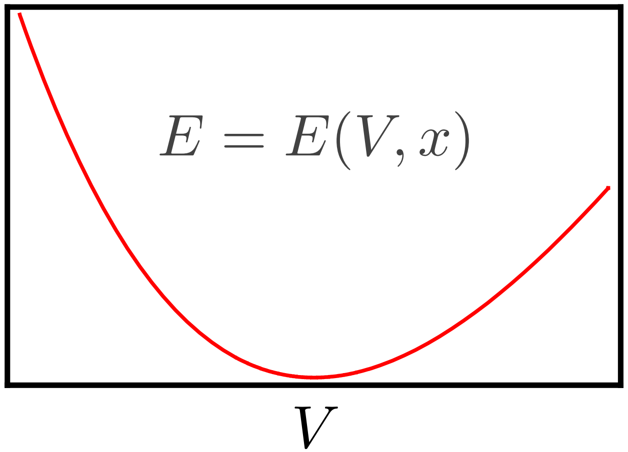

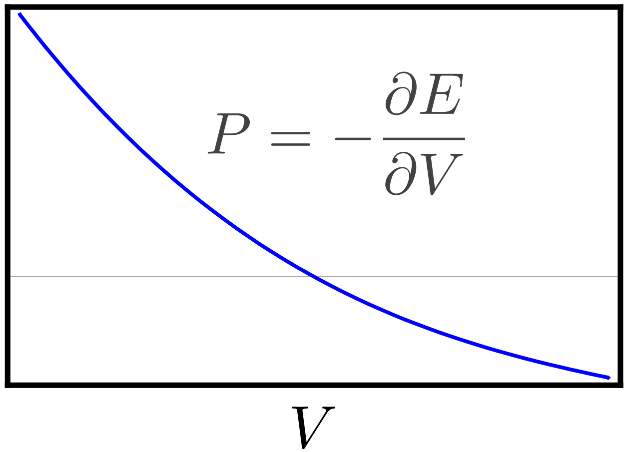

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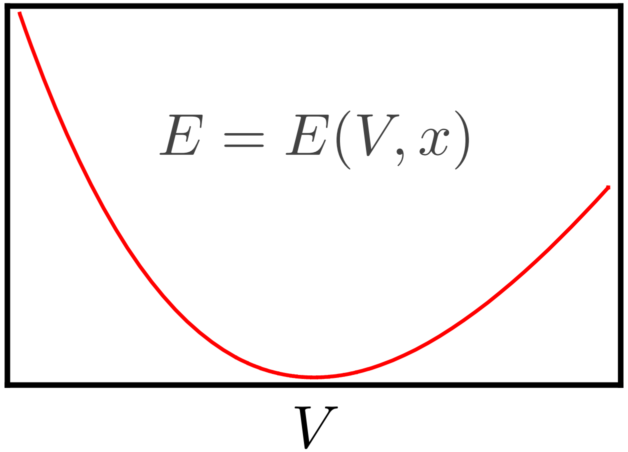

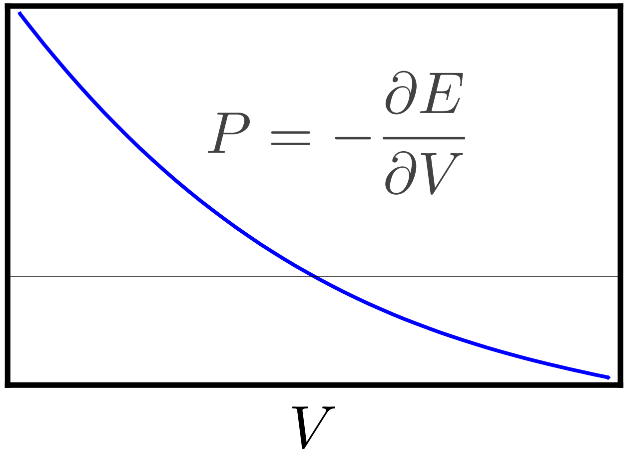

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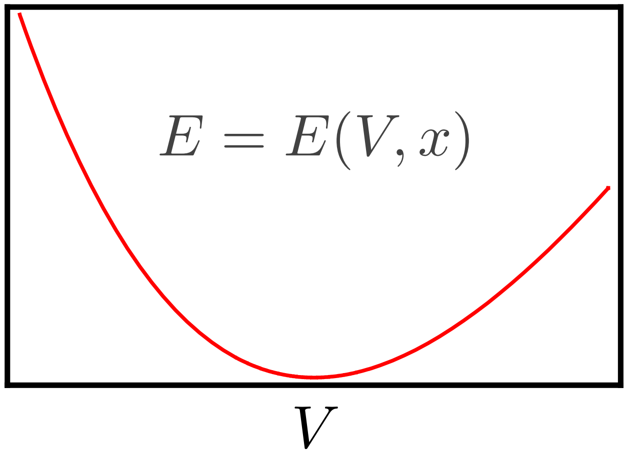

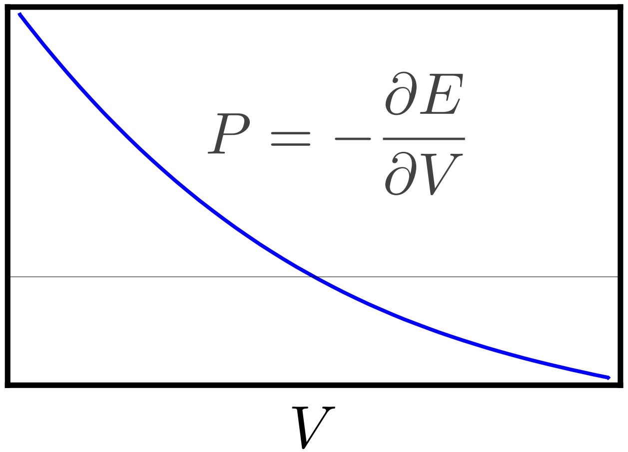

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Hohenberg-Kohn DFT

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

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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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- $E[V] = \min_{\rho}\left[F[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\right]$ (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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$$\frac{\delta T_0}{\delta \rho(\mathbf{r})} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + V(\mathbf{r}) = \mu$$

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

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

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$$\begin{tikzcd}
V(\mathbf{r}) \arrow[rd, shift left] \arrow[d, shift left] & \\
v_{KS}(\mathbf{r}) \arrow[u, shift left] \arrow[r, shift left] & \rho(\mathbf{r}) \arrow[lu, shift left] \arrow[l, shift left]
\end{tikzcd}$$

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exchange-correlation energy functionals

- LDA (Kohn & Sham, 60's)

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

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

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

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

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

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

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

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

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

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

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

- ...

KS equations from functional minimization

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

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

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

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solving the Kohn-Sham equations

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

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

requirements

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- (effective) completeness easily checked and systematically improved

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- orthogonality is a plus

plane-wave basis sets

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

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

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

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periodic boundary conditions

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

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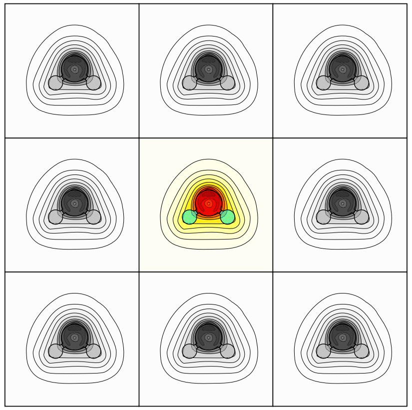
finite systems $(\ell = a)$



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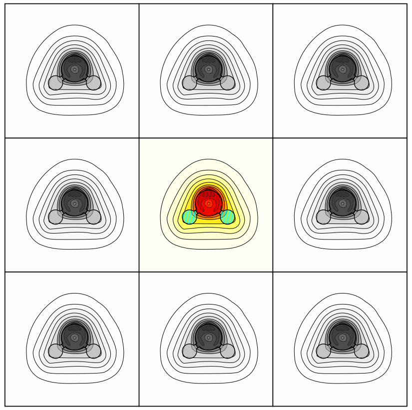
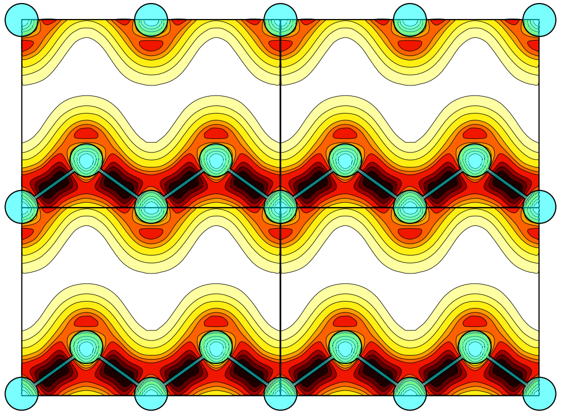


$$\mathbf{q} = \mathbf{G}$$

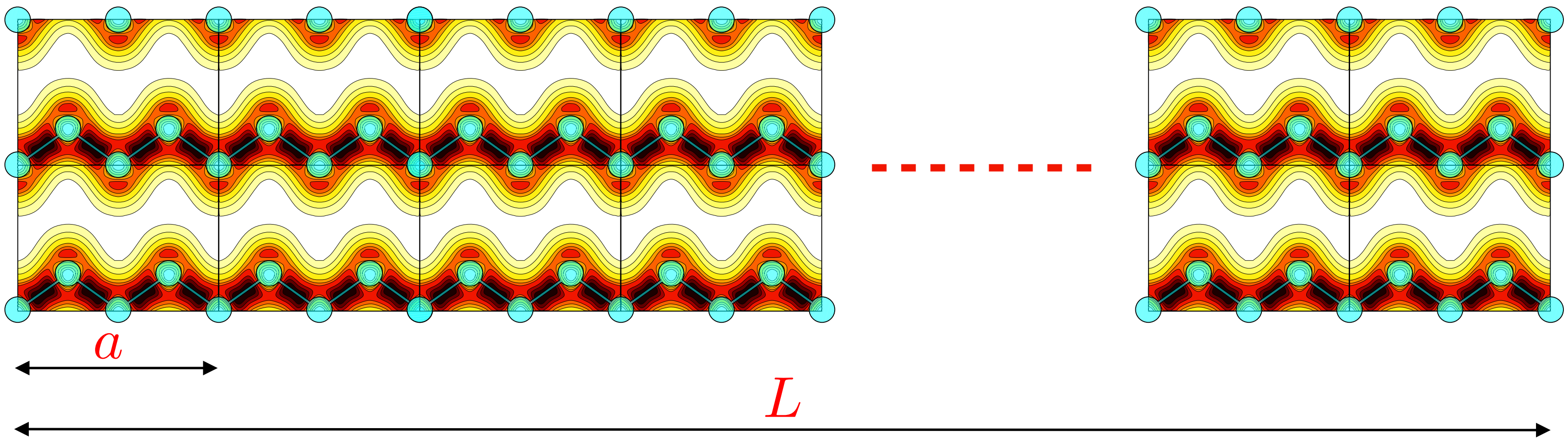
infinite crystals $(\ell = L)$



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

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

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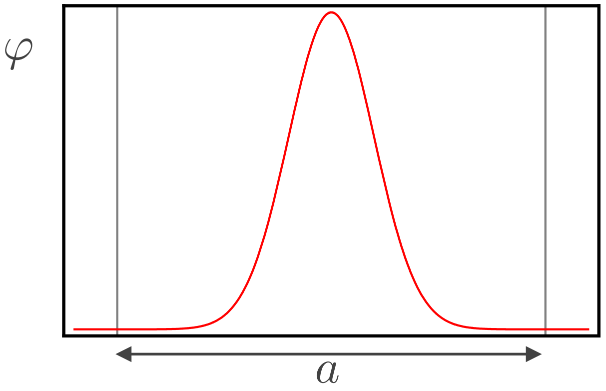
$$\begin{aligned}
V_{xc}(\mathbf{r}) &= \mu_{xc}\big(\rho(\mathbf{r})\big) \\
V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
&= e^2 \sum_{\mathbf{G}\neq 0} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G})
\end{aligned}$$

sampling theorem

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



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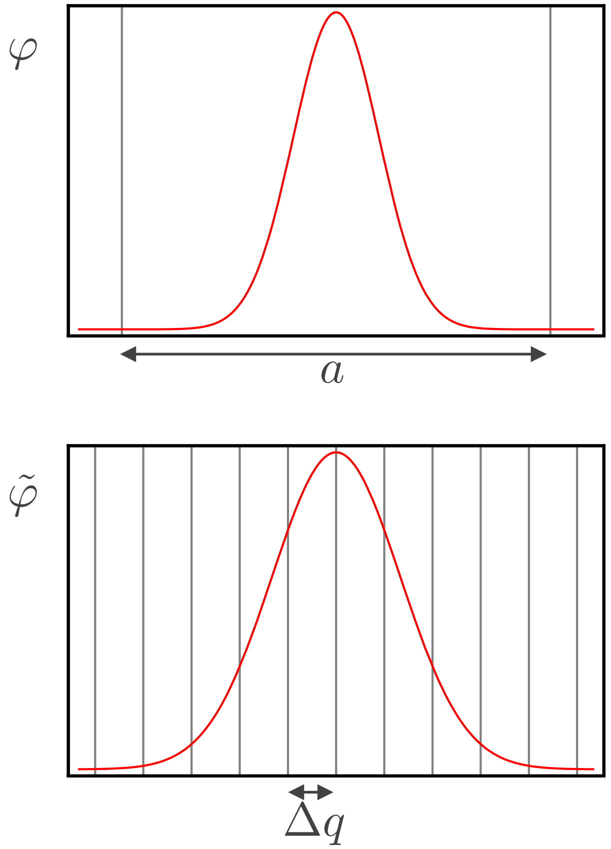

$$\Delta q < \frac{2\pi}{a}$$

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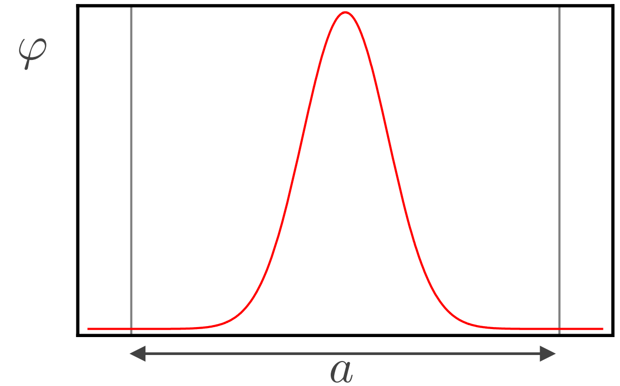

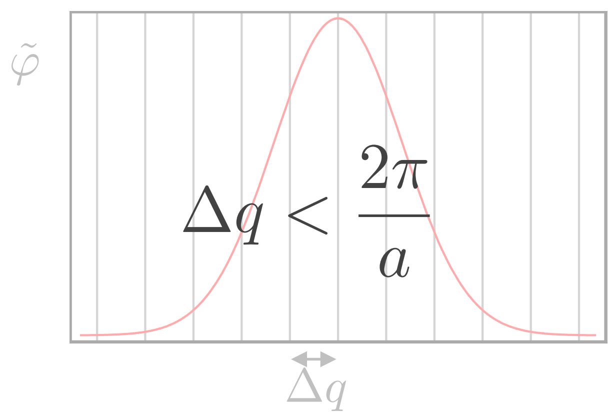

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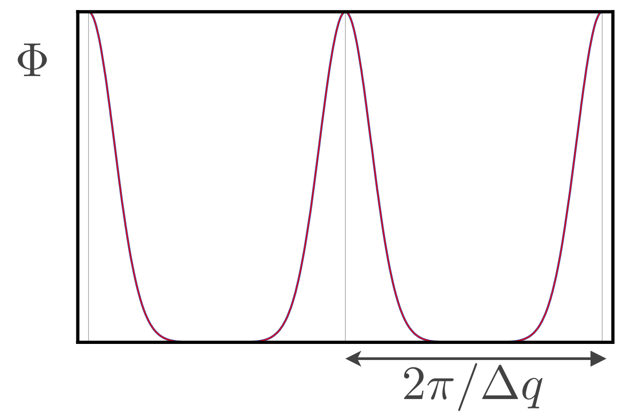

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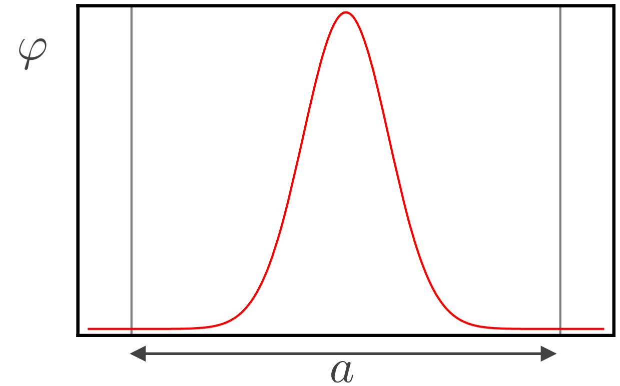

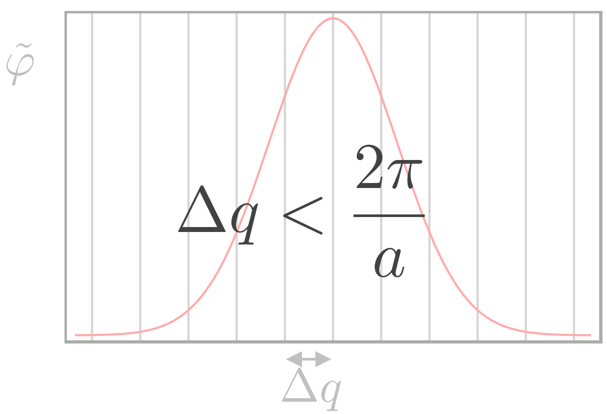

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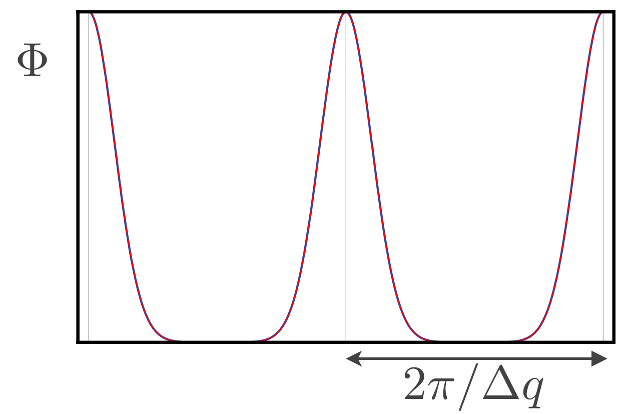

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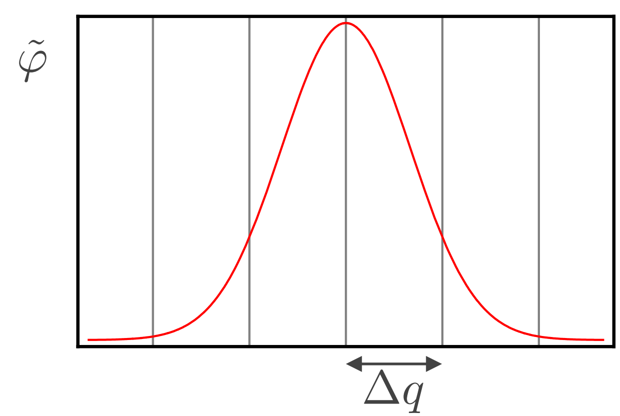

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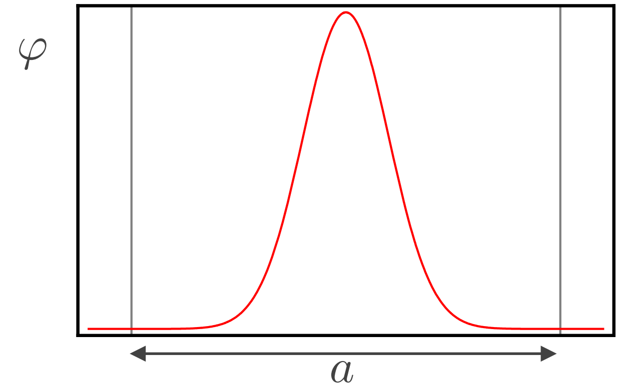

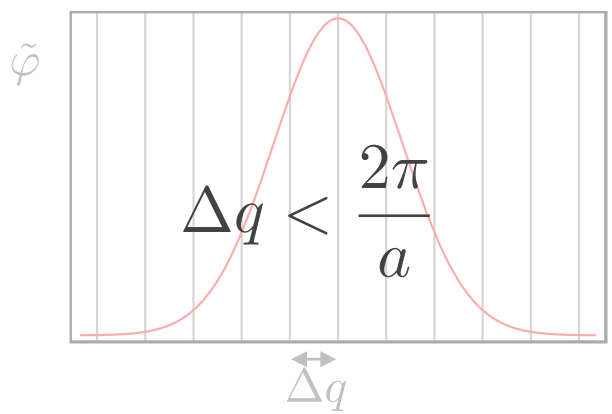

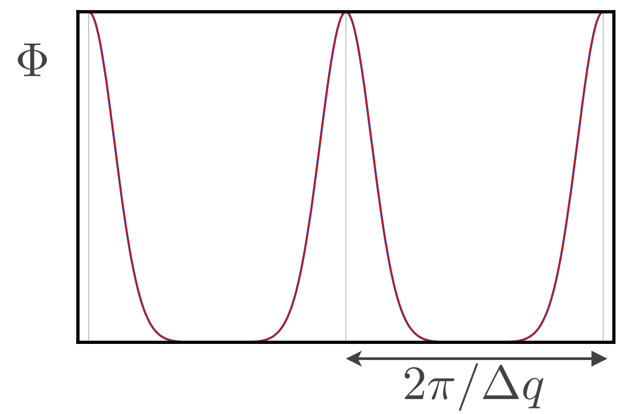

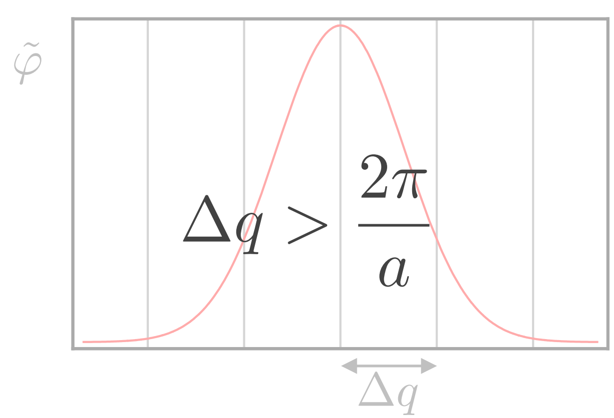

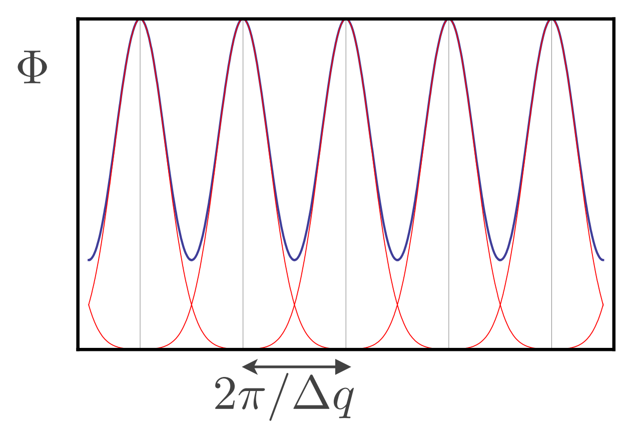

discrete Fourier transforms

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

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

discrete Fourier transforms

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

$$t \rightarrow \left\{t_l = l\frac{T}{N}\right\}_{l=0,\cdots N-1} \qquad f(t) \rightarrow \{f_l = f(t_l)\}$$

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dFt

properties of the dFt

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$\Downarrow$

periodicity in the primary space

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discreteness in dual space

$\Downarrow$

periodicity in the primary space

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

the fast Fourier transform

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

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

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$$\mathcal{O}\left(N^2\right) \longrightarrow \mathcal{O}\left(N \log(N)\right)$$

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

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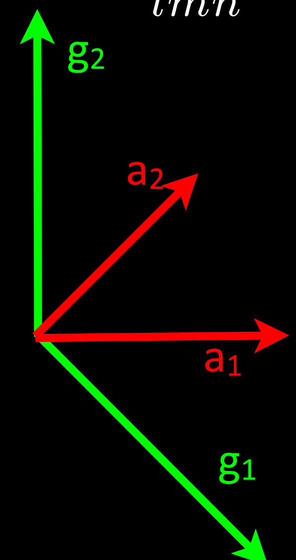
$$\mathbf{g}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$



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FFT

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FFT^{-1}

multivariate FFTs (II)

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

multivariate FFTs (II)

$$
\begin{aligned}
F(k,l,m) &= \sum_{pqs} \mathrm{e}^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p,q,s) \\
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$$3N^2 \times N \log N = N^3 \log\left(N^3\right)$$

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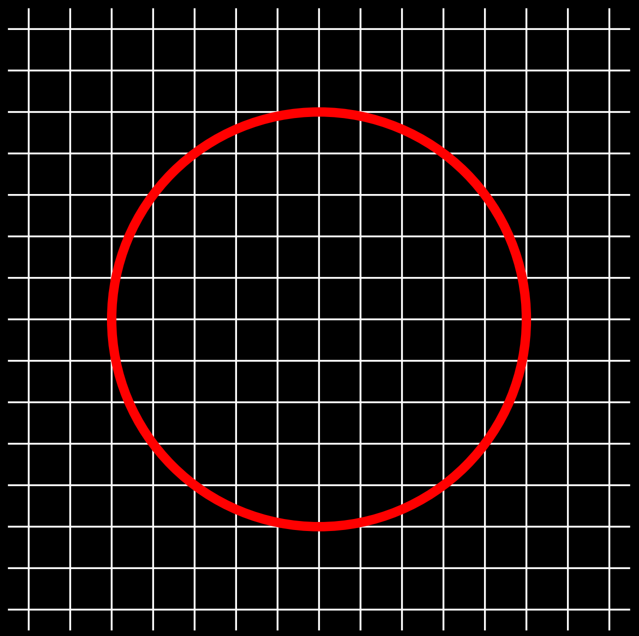

$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

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

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

PWs: pros & cons

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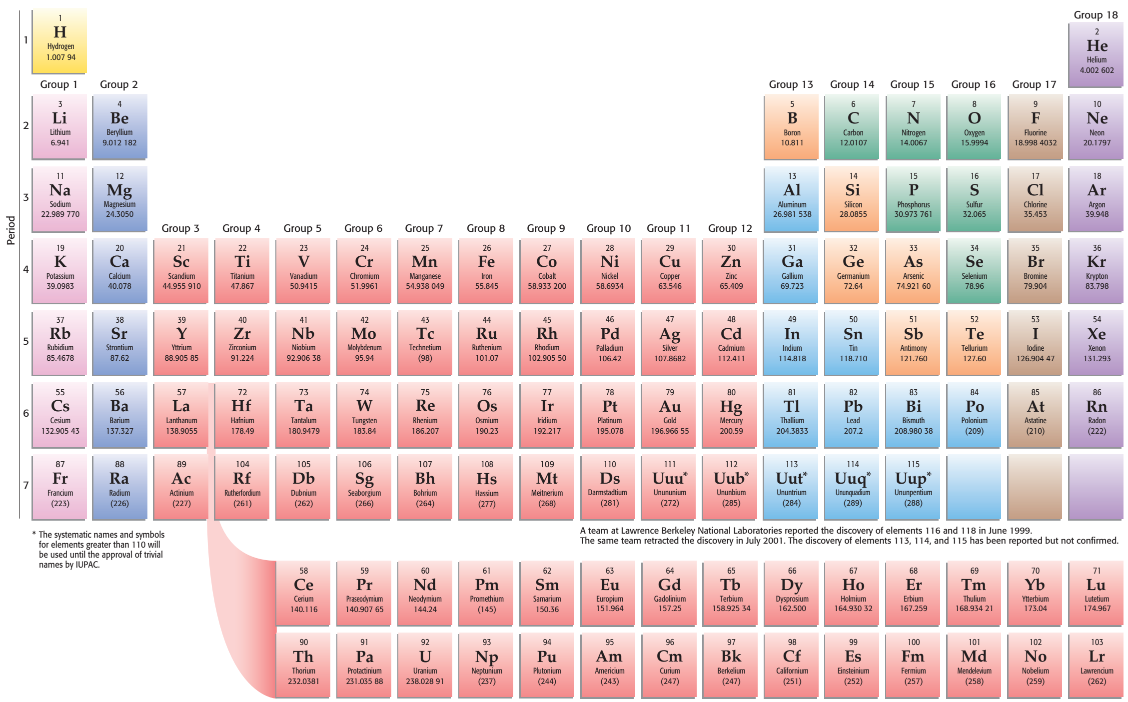
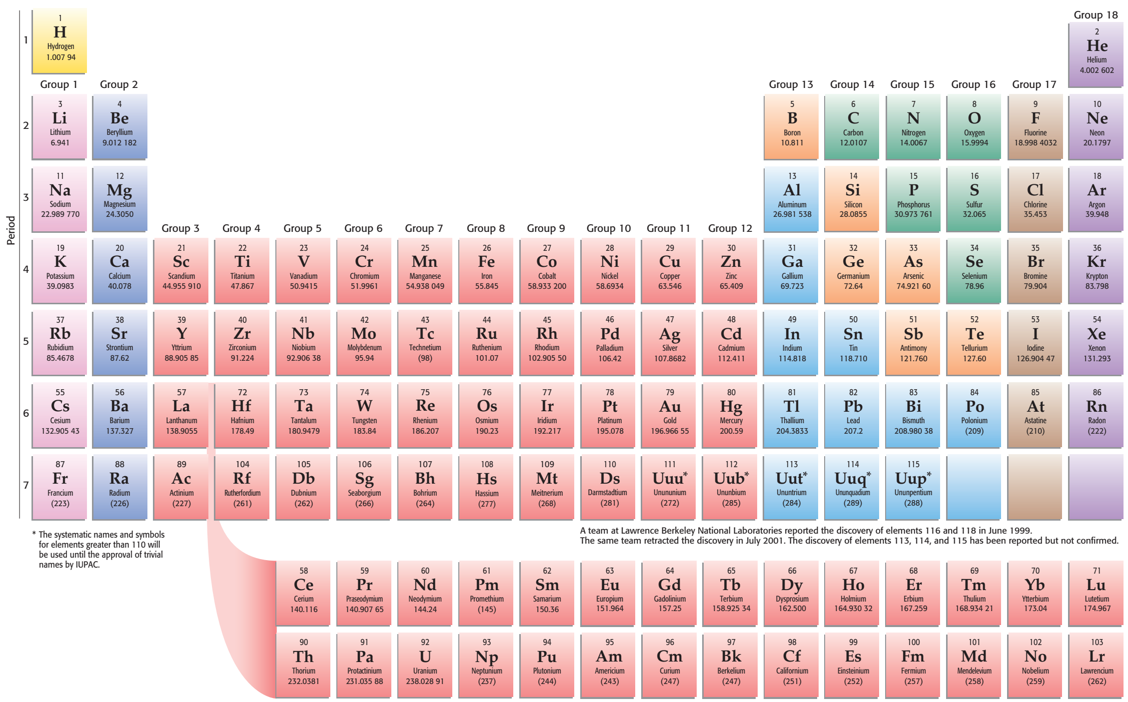
- ☹ basis set depends on volume shape/size (Pulay stresses)
- ☹ uniform spatial resolution (no core states!)

treating core states



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

treating core states



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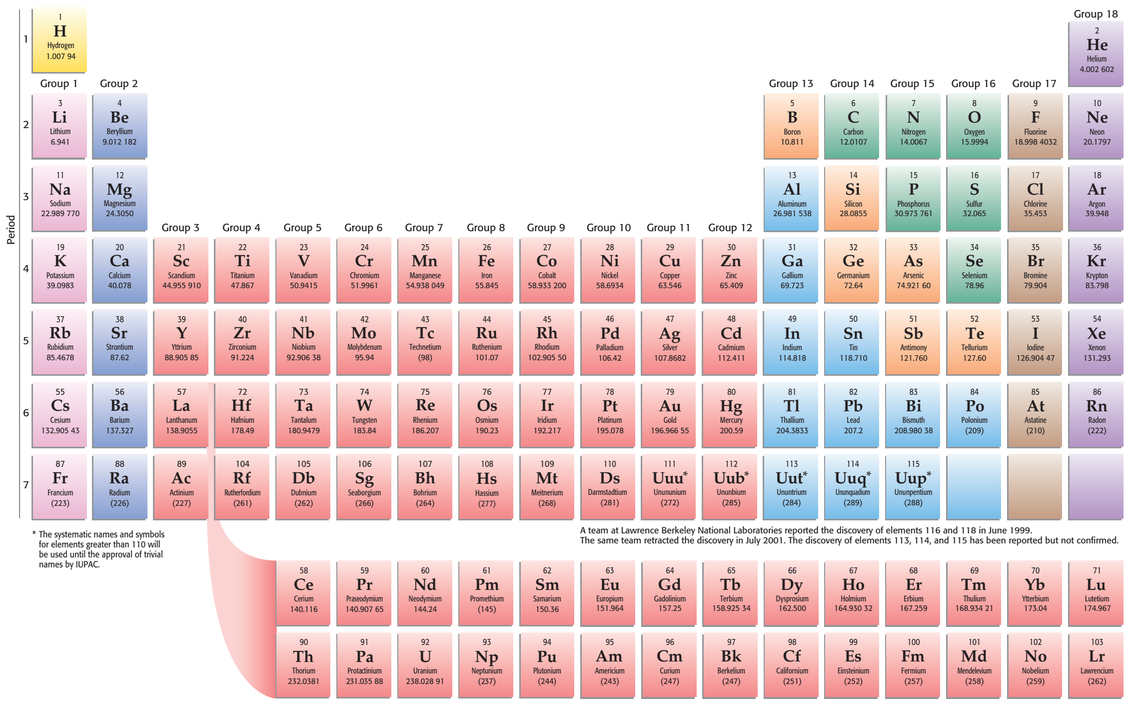


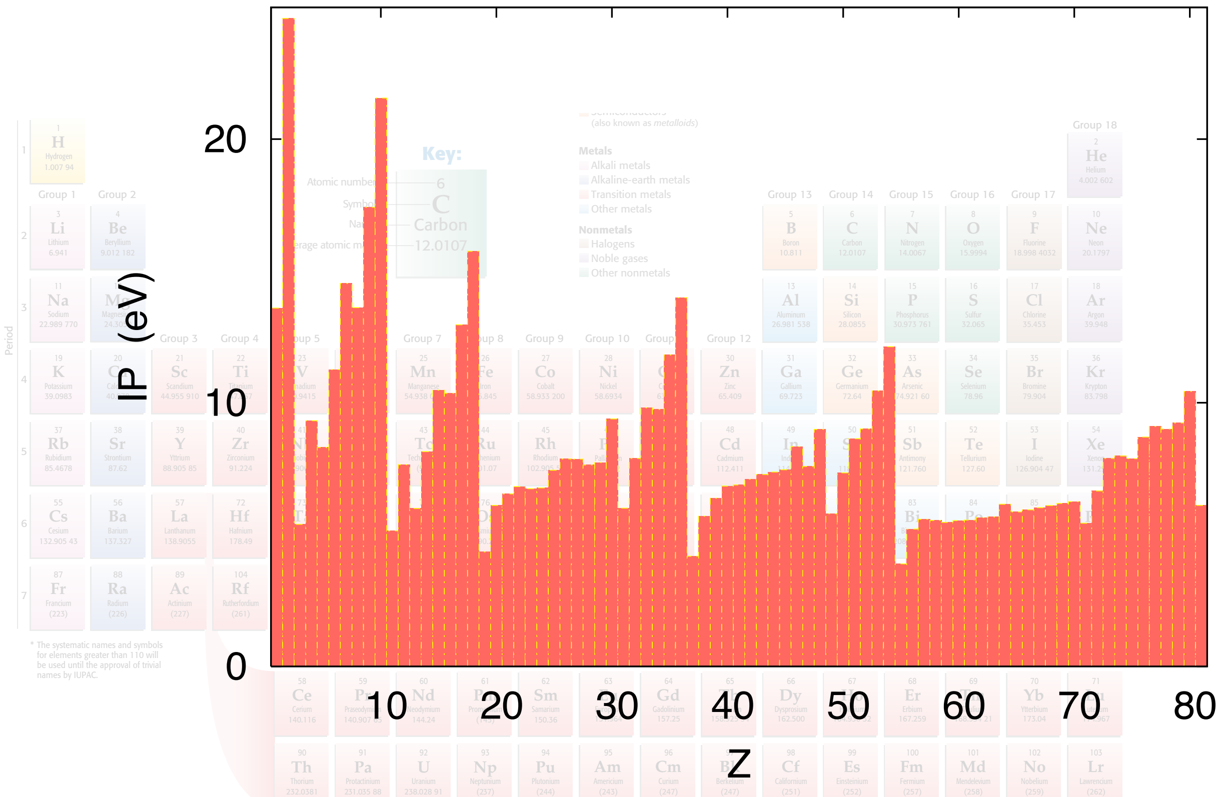
$$\epsilon_{1s} \sim Z^2 \qquad a_{1s} \sim \frac{1}{Z}$$

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

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

$$\sim Z^3$$

treating core states



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

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

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

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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:

ϕ_{val}^{ps} is nodeless and smooth

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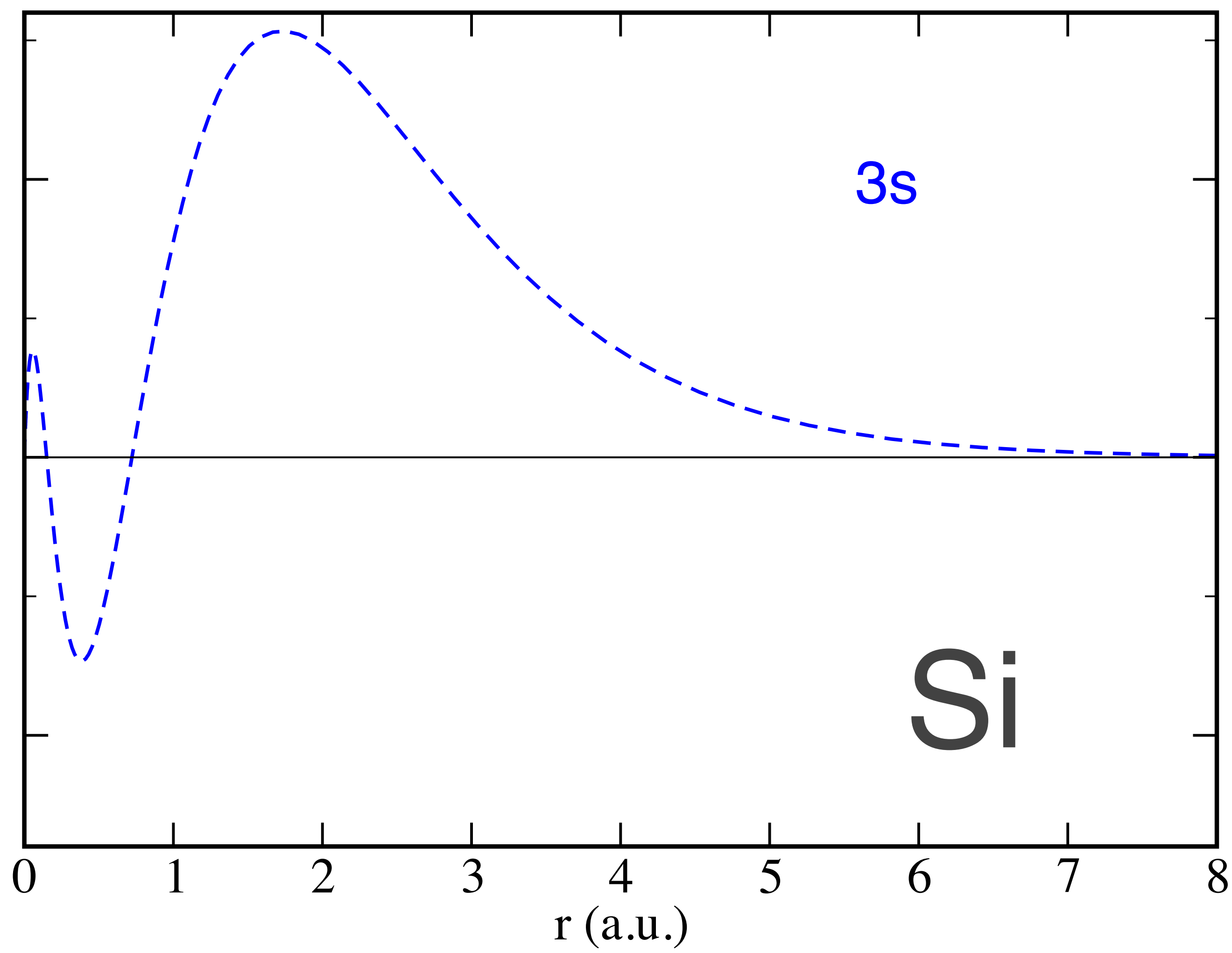
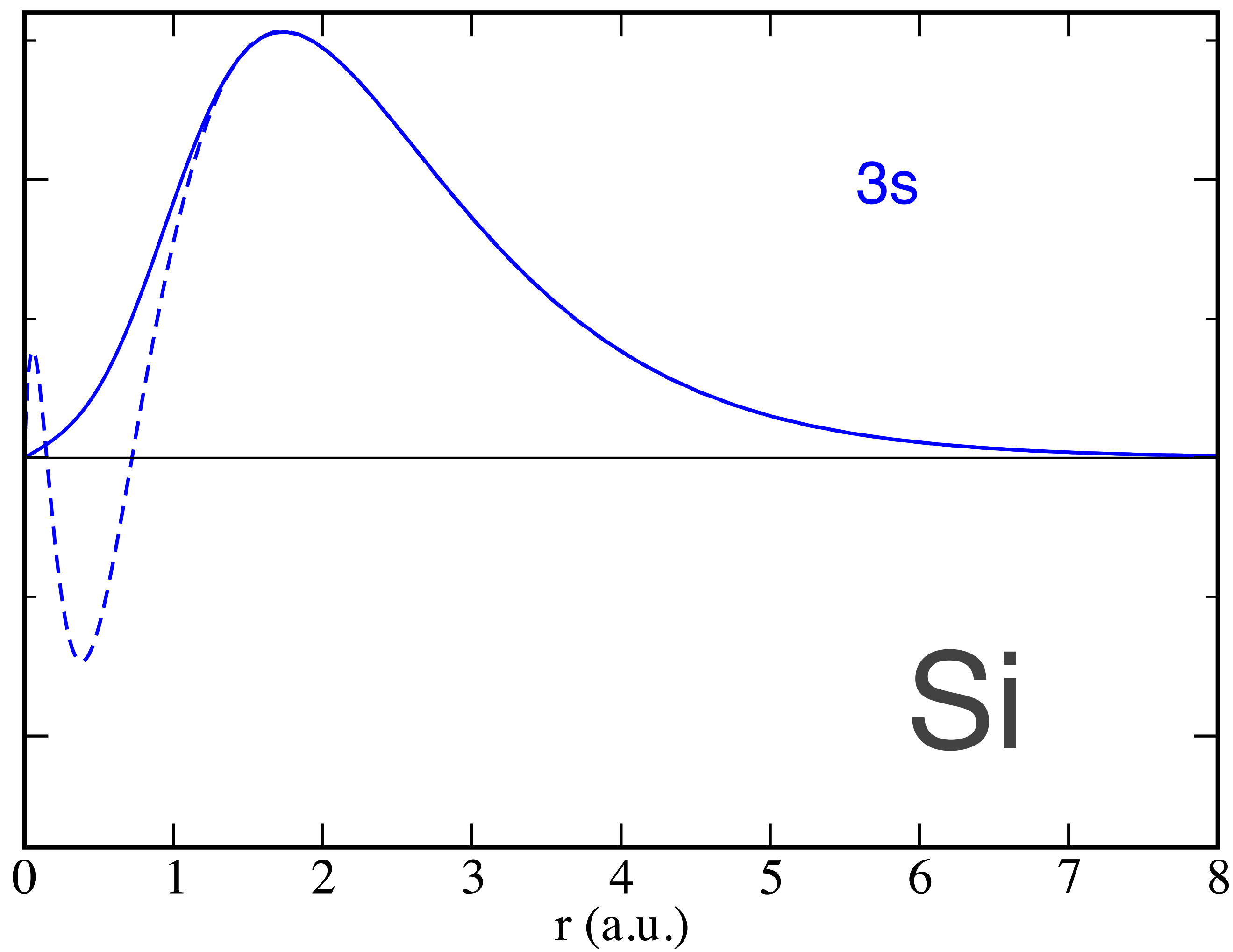
ϕ_{val}^{ps} is nodeless and smooth

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

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

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


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



3s
Si
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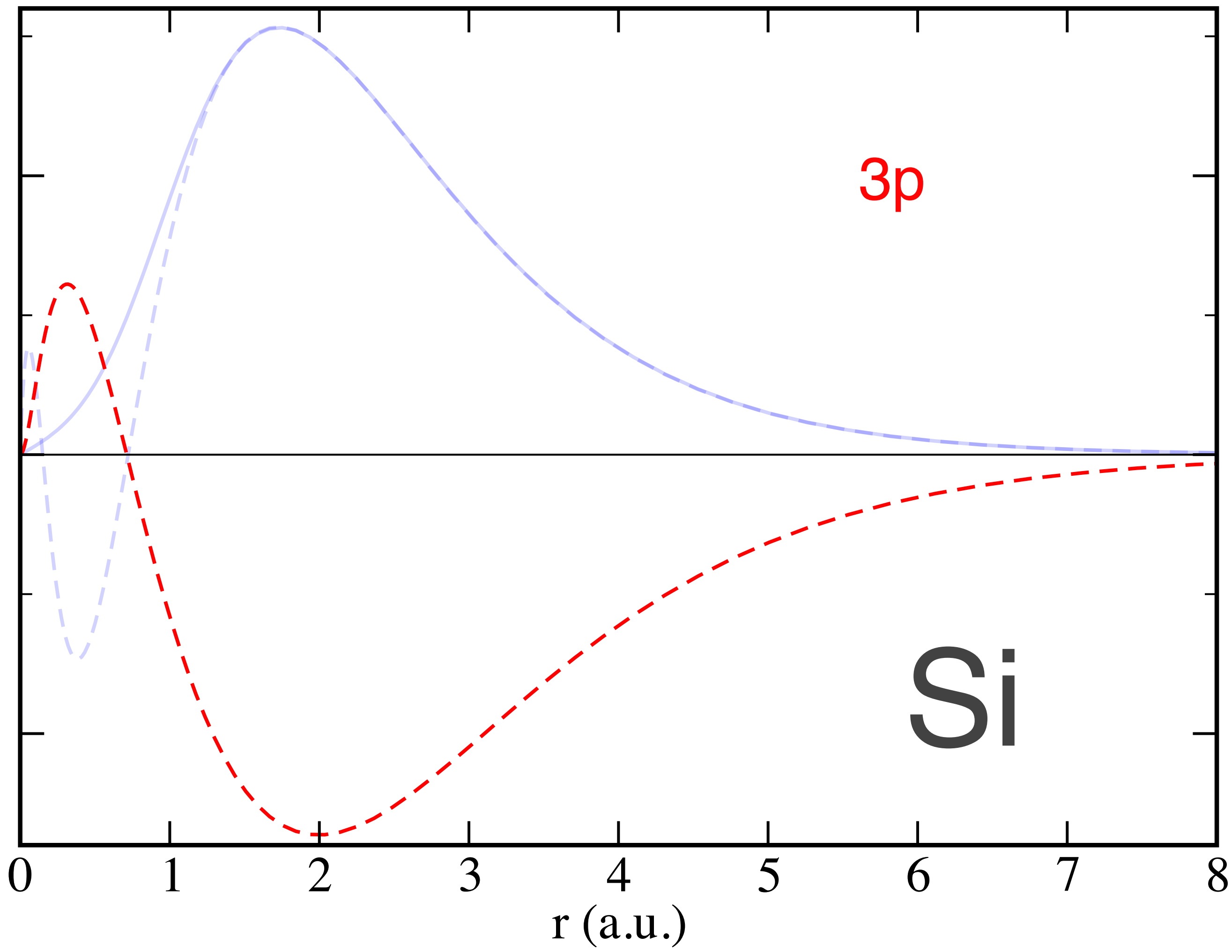
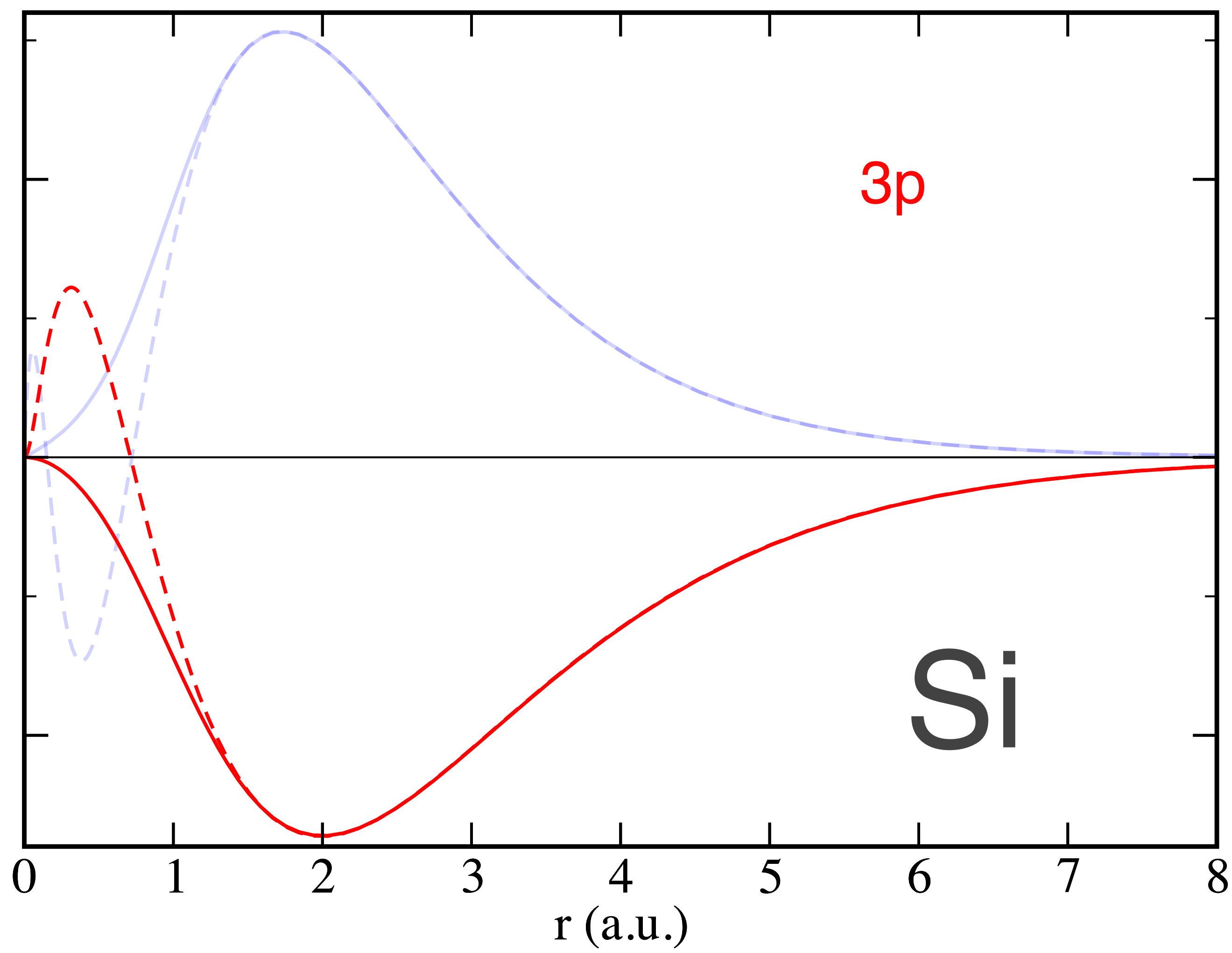
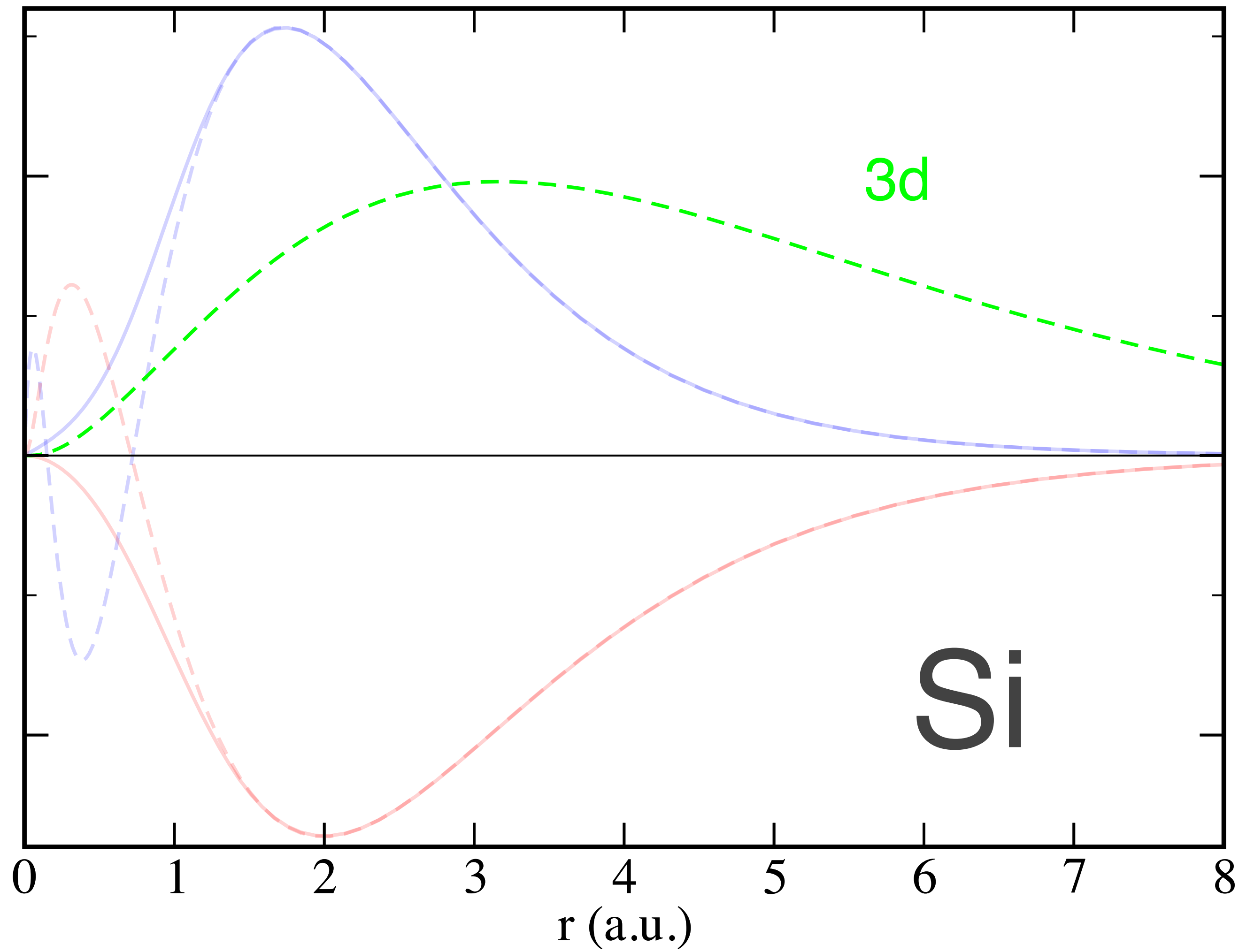
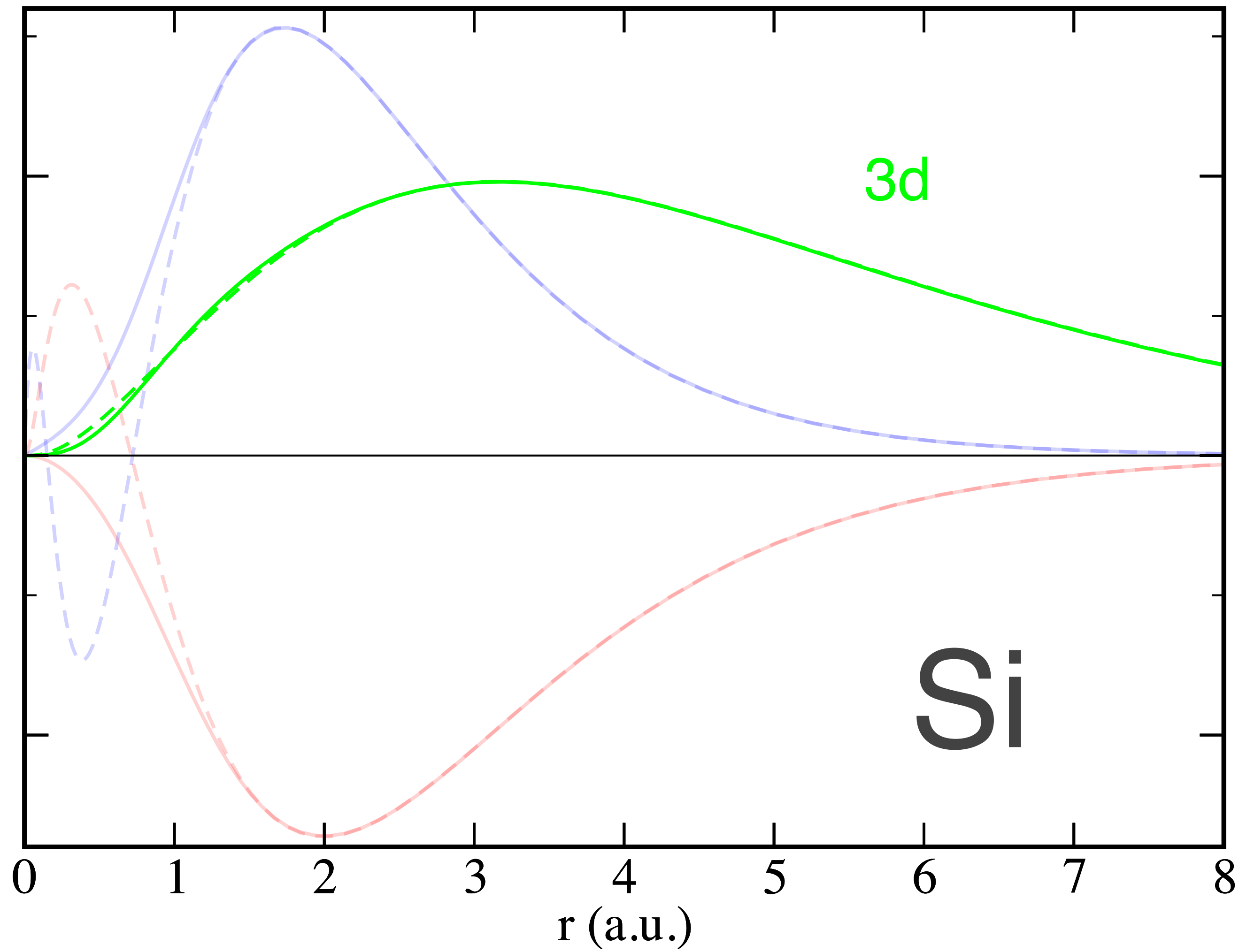

3p
Si
0
1
2
3
4
5
6
7
8
r (a.u.)



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



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


3d
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0
1
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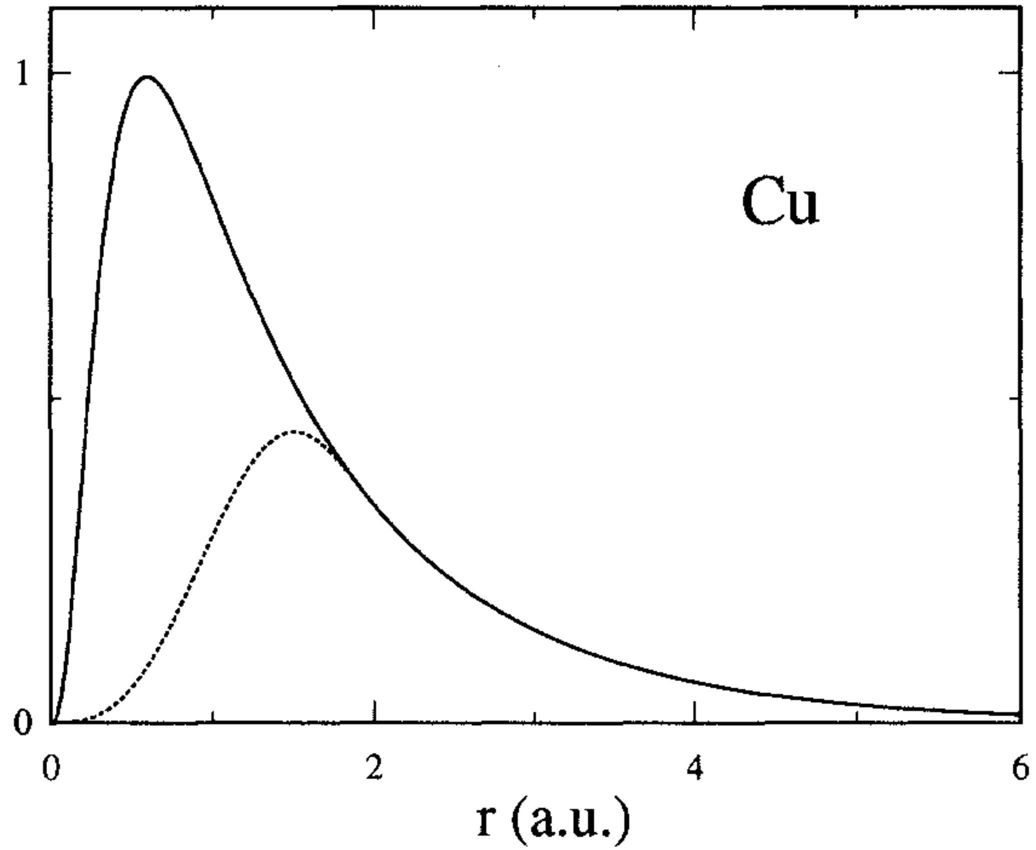
US pseudopotentials



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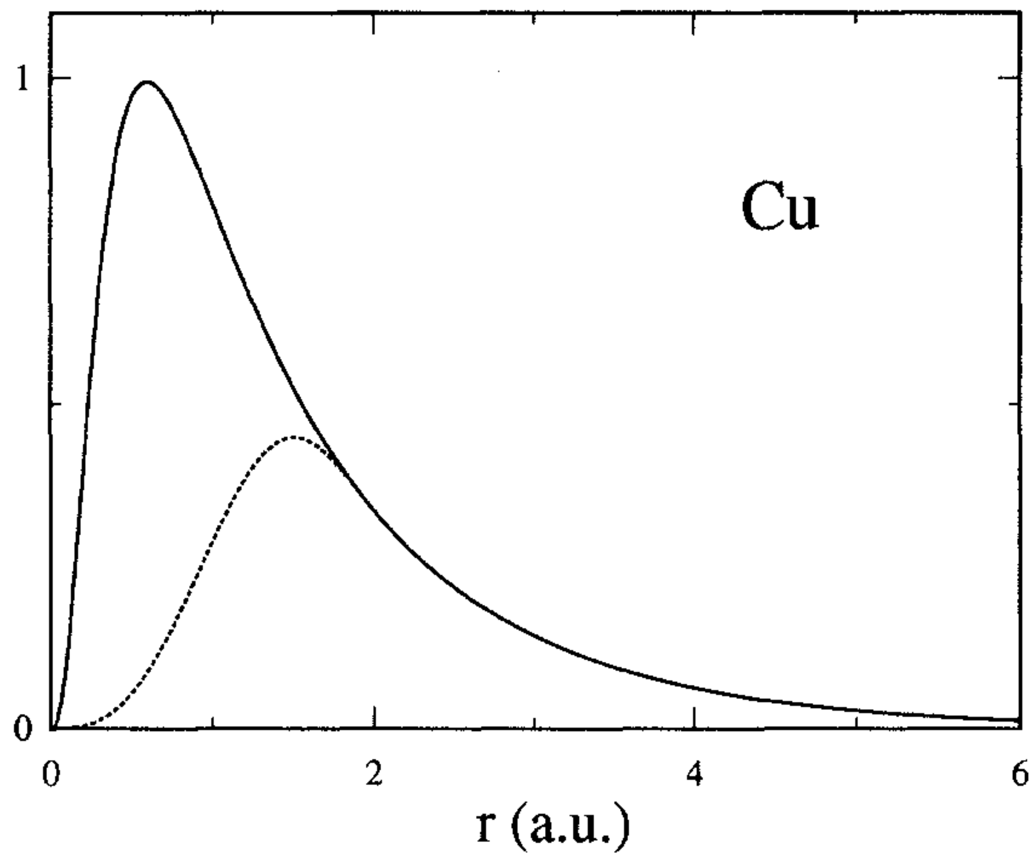

$$H_{US}\phi_n = \epsilon_n S \phi_n \qquad \langle \phi_n | S | \phi_m \rangle = \delta_{nm}$$

these slides at

http://talks.baroni.me

baroni@sissa.it