modelling materials using quantum mechanics and digital computers

the plane-wave pseudo potential way

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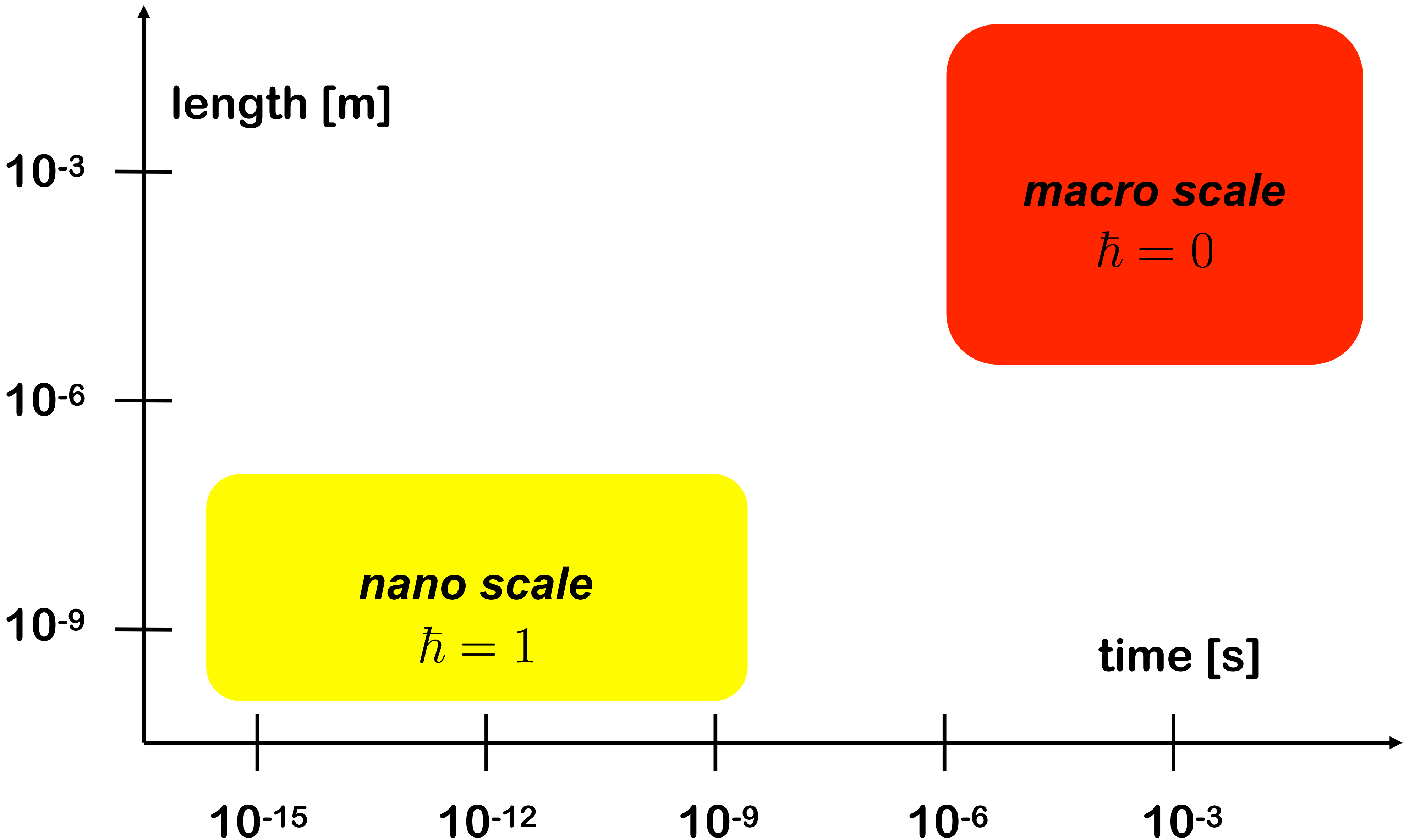
lecture given at the *Quantum ESPRESSO Workshop*, Penn State University, May 21-25, 2018

the saga of time and length scales



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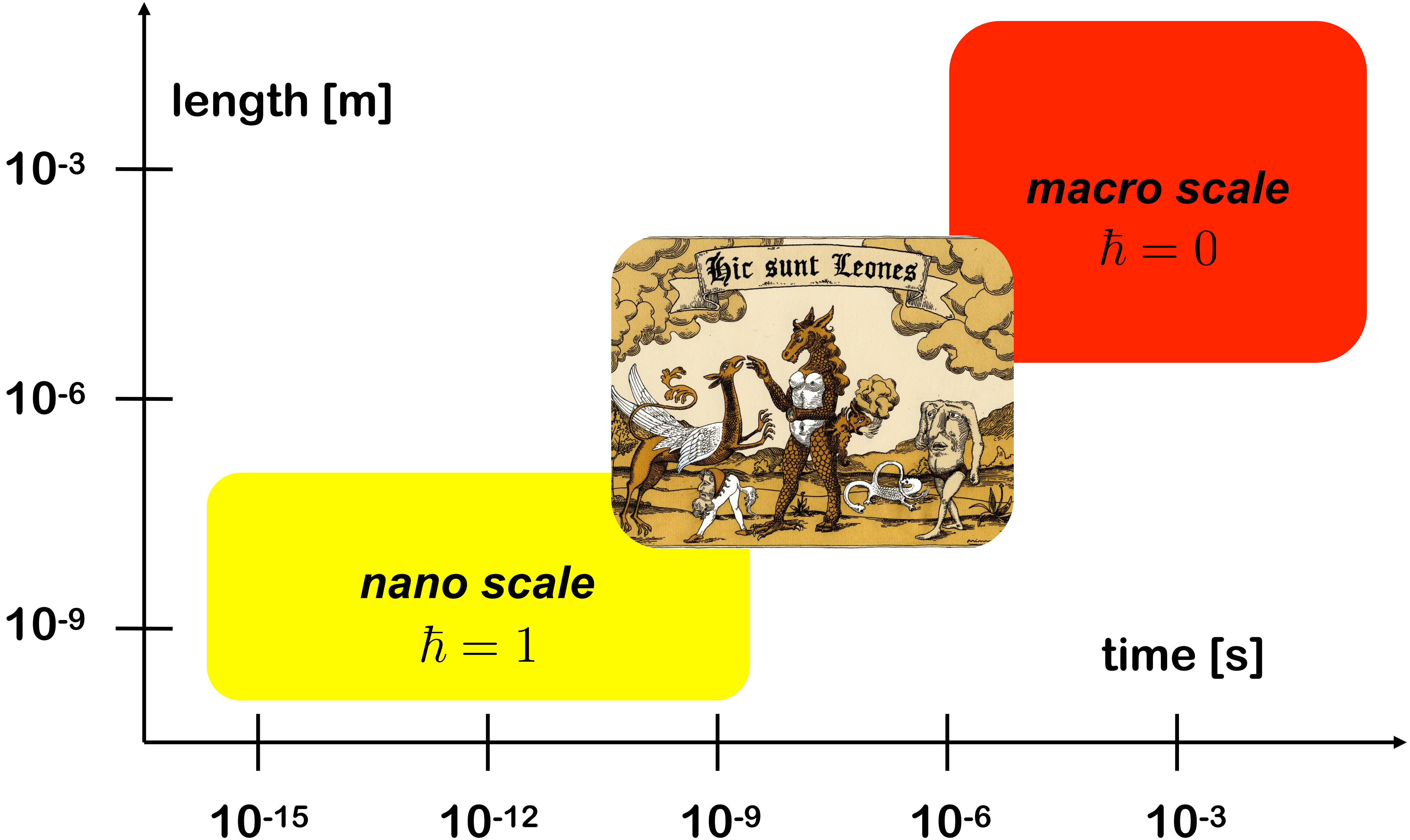

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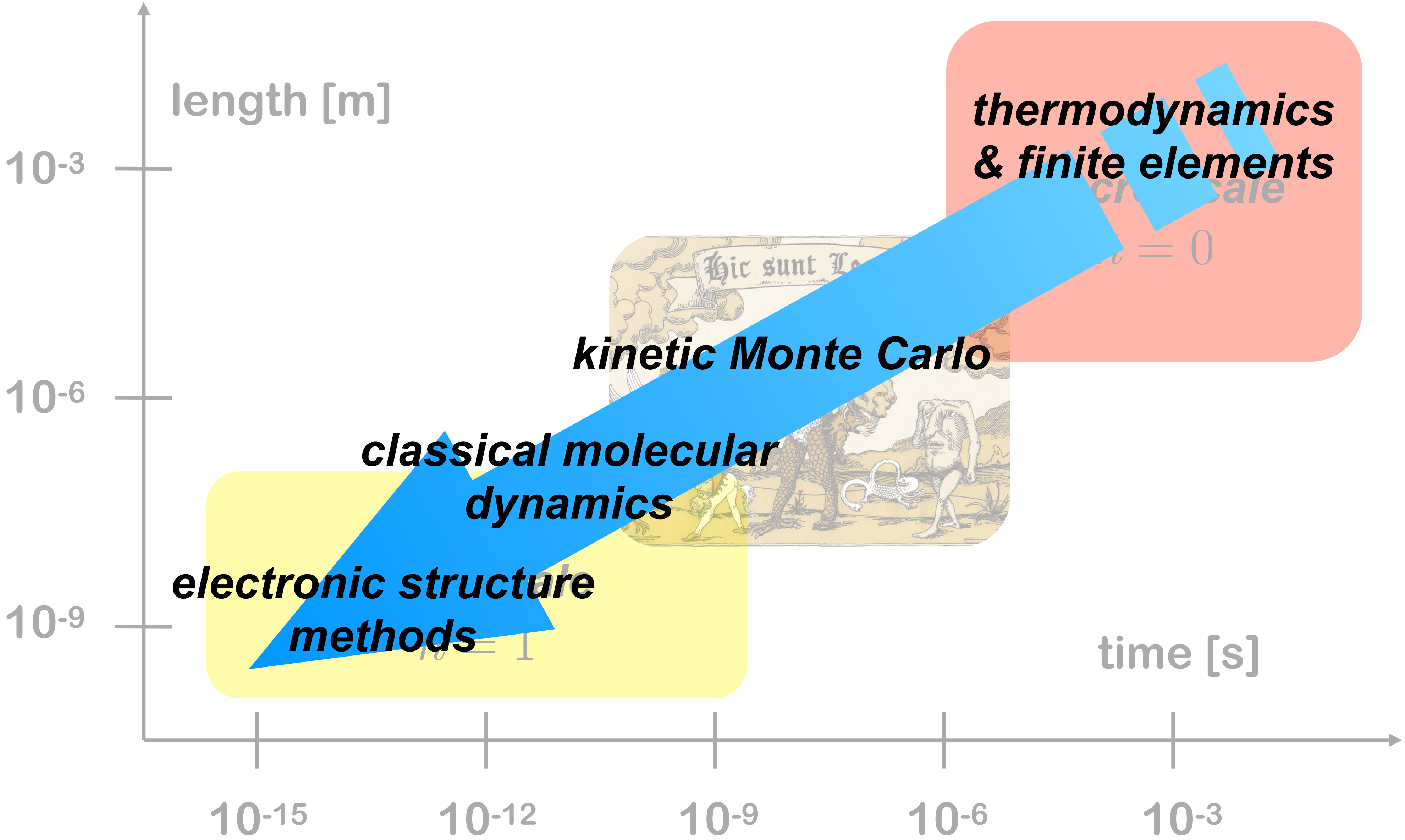
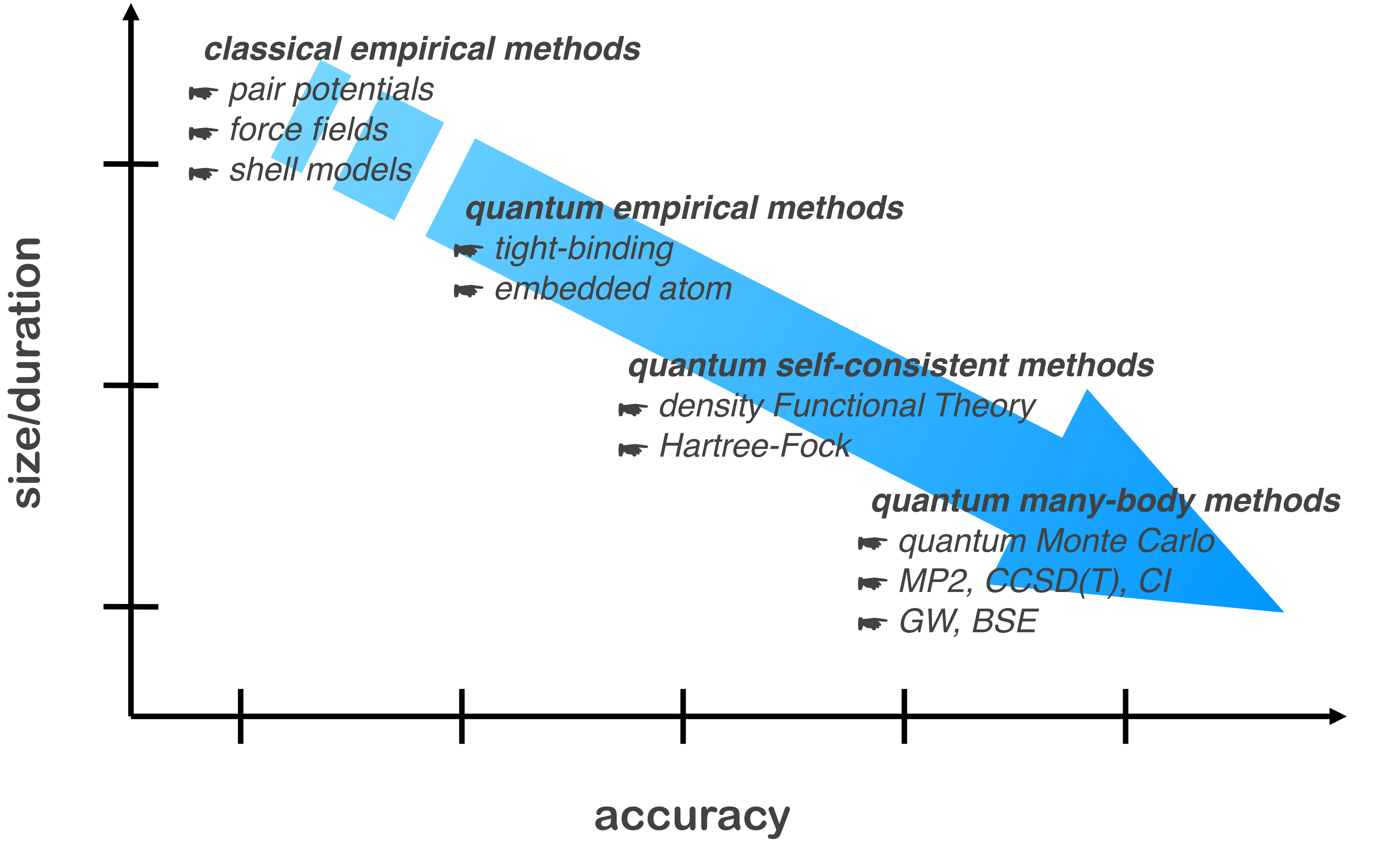


size vs. accuracy



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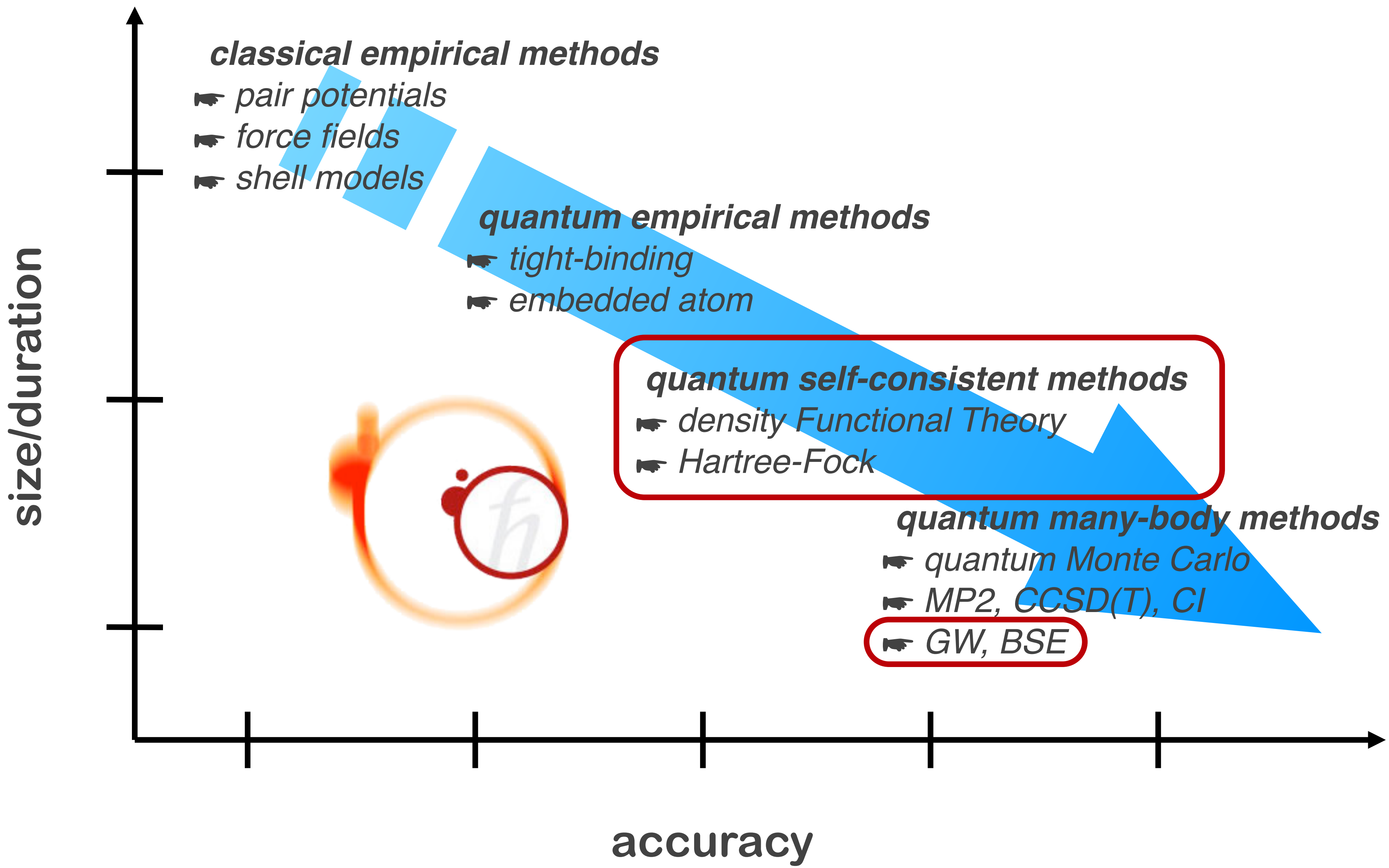

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why: they are accurate and *predictive*

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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$M \gg m$

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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

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

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examples:

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

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

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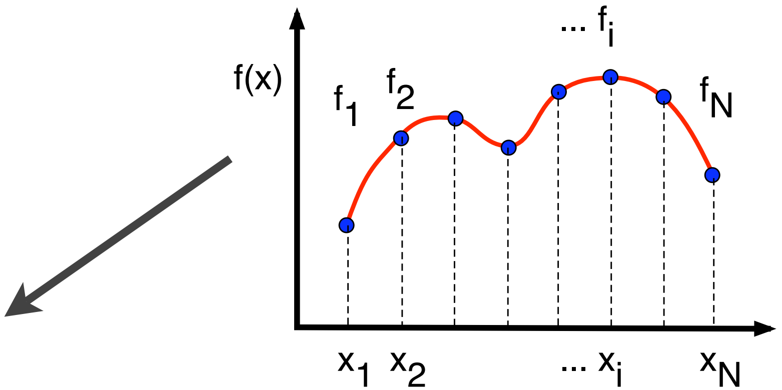

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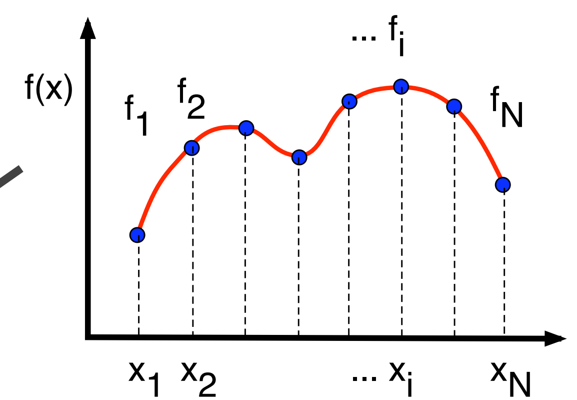

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$$G[f] \approx g(c_1, c_2, \cdots, c_N)$$

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

functional derivatives

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

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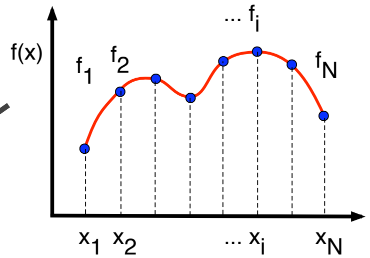

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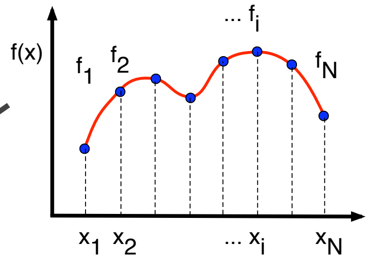

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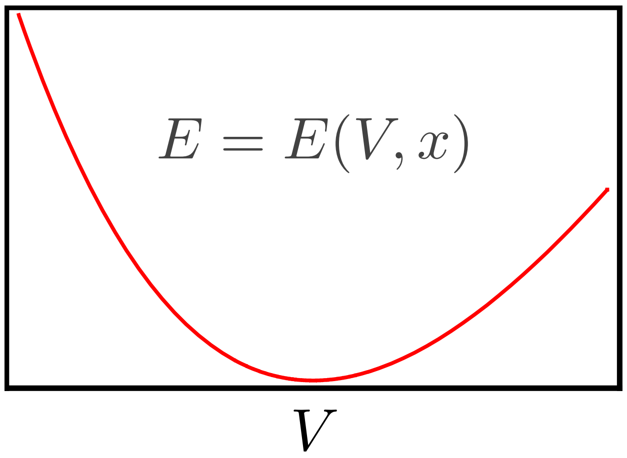
conjugate variables & Legendre transforms



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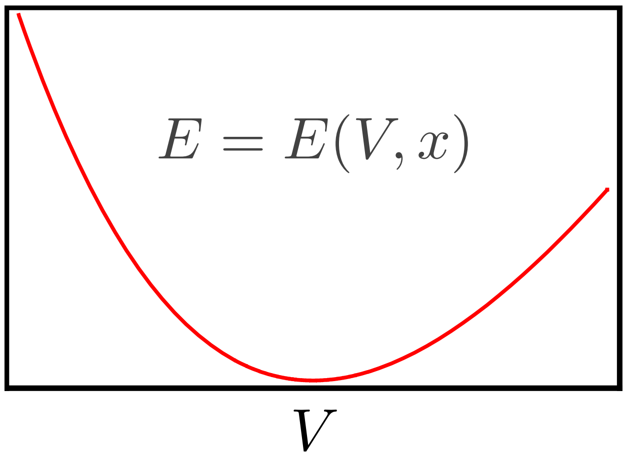

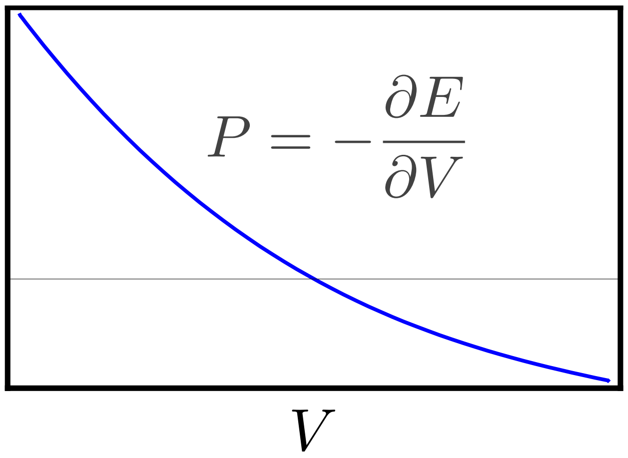

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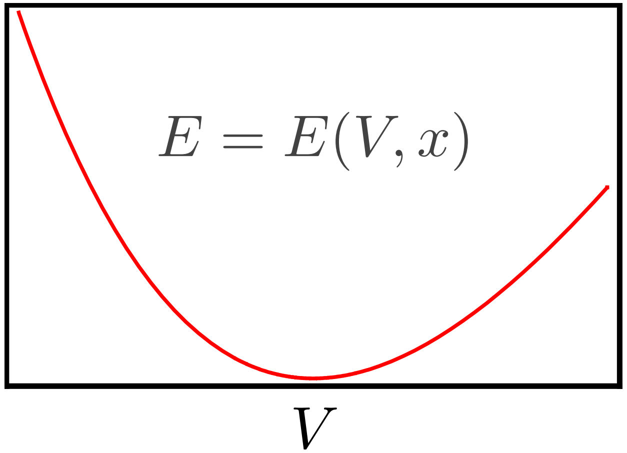
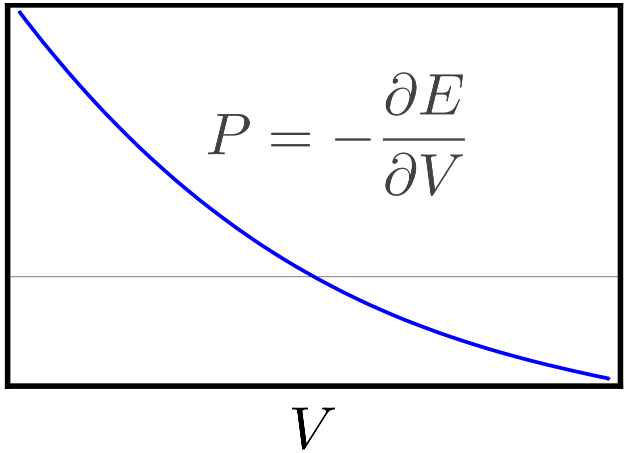
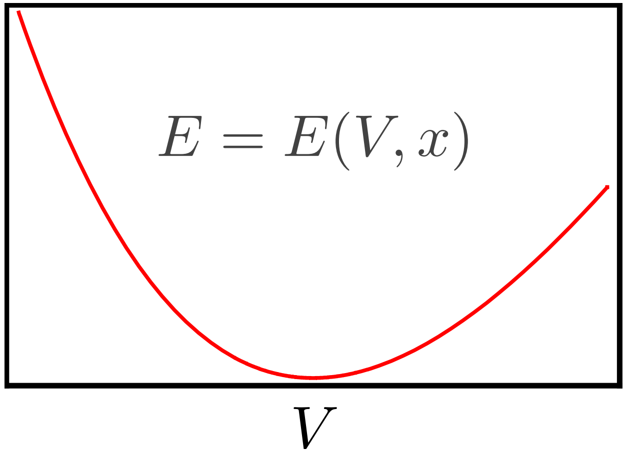
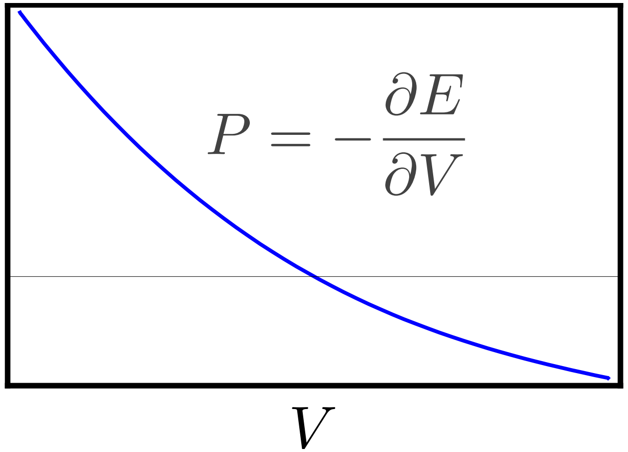




Legendre transform: $H(P, x) = E + PV$

conjugate variables & Legendre transforms





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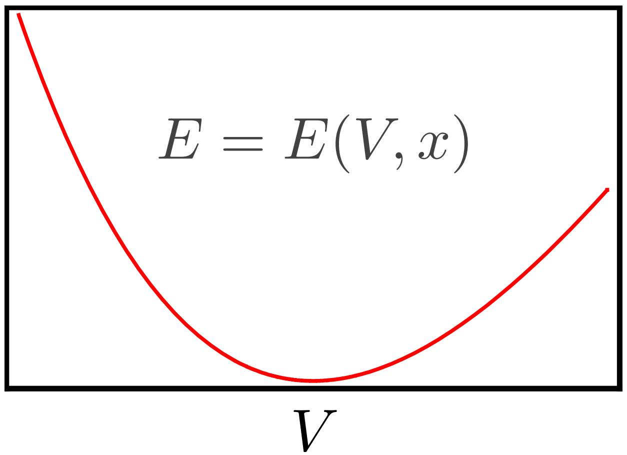

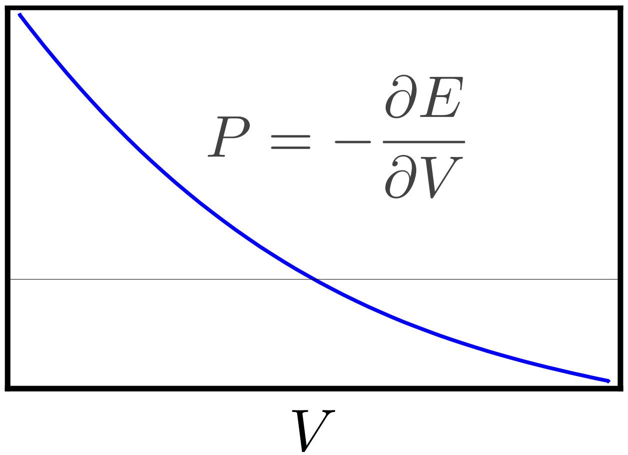

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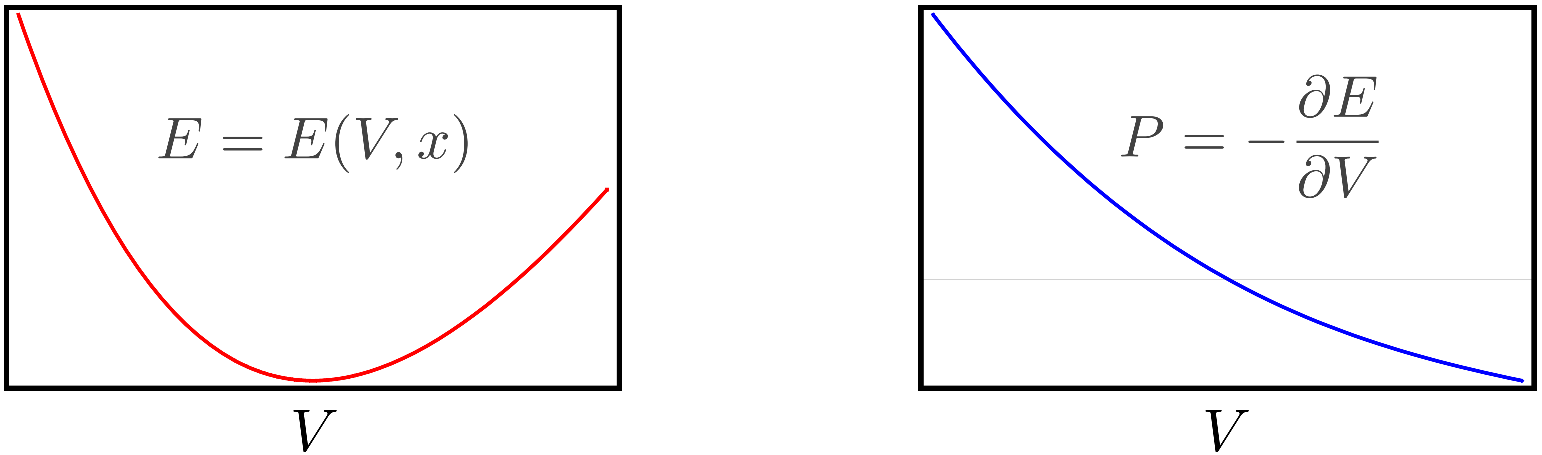

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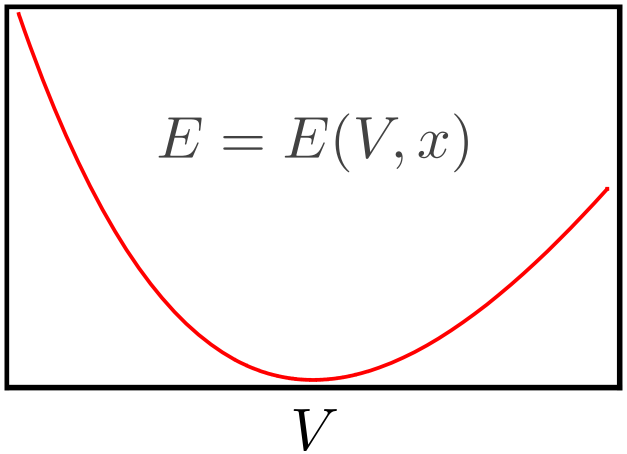

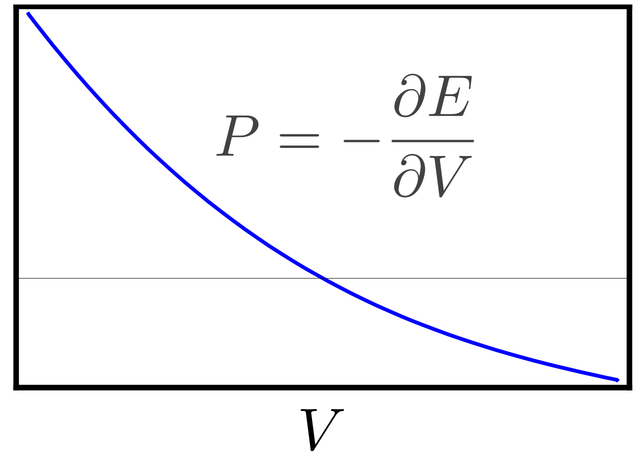

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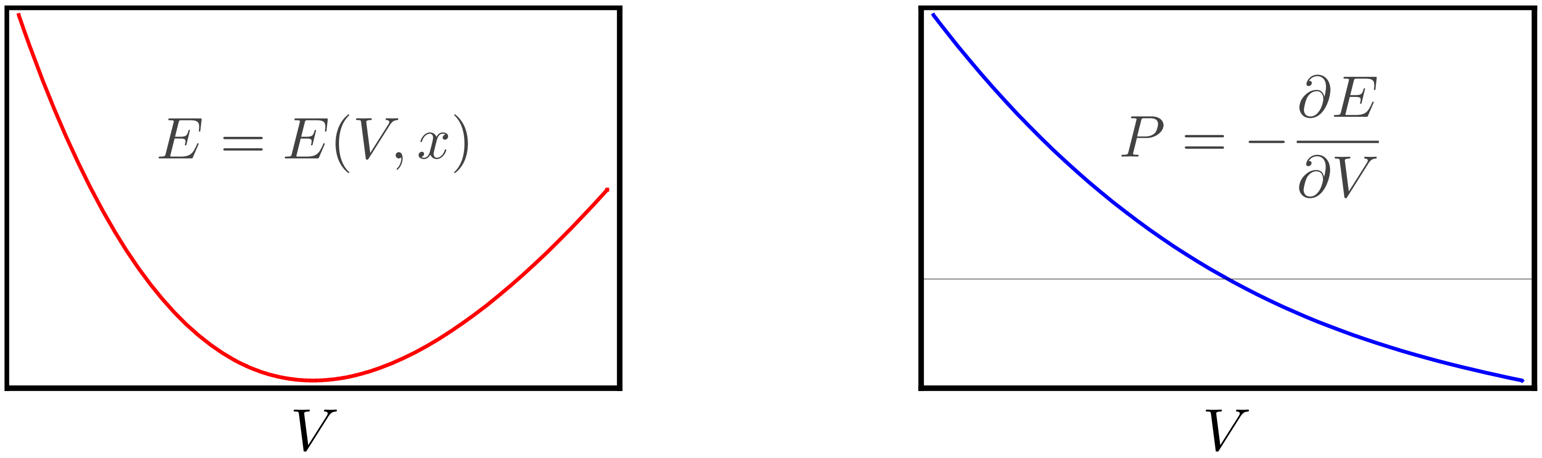

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Hohenberg-Kohn DFT

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

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- $V(\mathbf{r}) \rightleftarrows \rho(\mathbf{r})$ (1st *HK theorem*)
- $F[\rho] = E - \int V(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}$ is the Legendre transform of E
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Kohn-Sham DFT

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

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

exchange-correlation energy functionals

- LDA (Kohn & Sham, 60's)

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

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

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

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

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

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

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

- 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)

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

- ...

KS equations from functional minimization

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

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$\longrightarrow$

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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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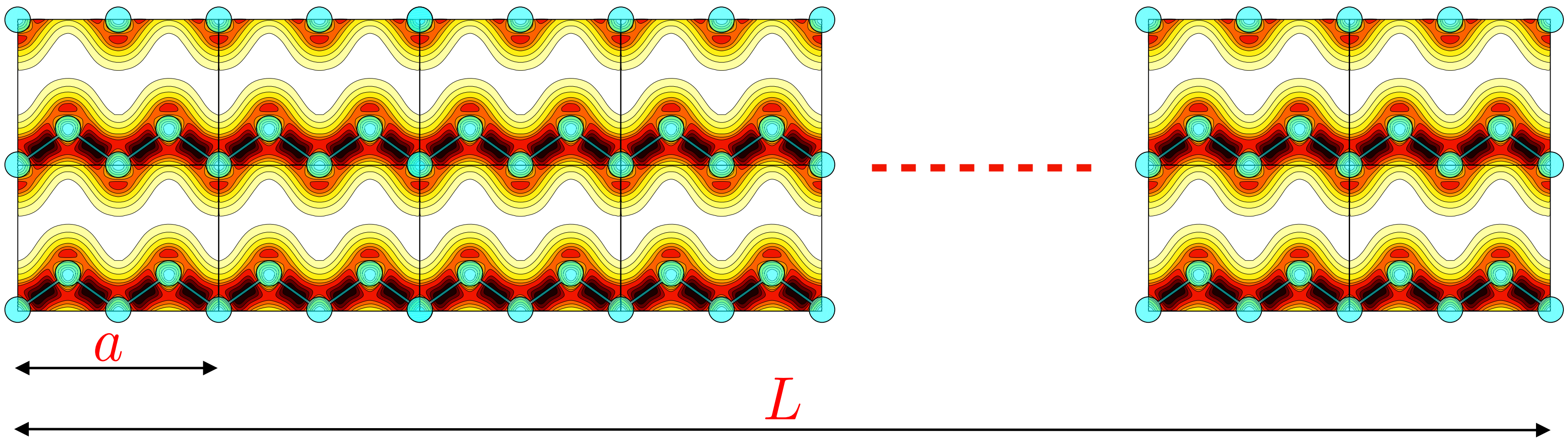
- matrix elements easy to calculate and/or Hψ products easily calculated on the fly
- Hartree and XC potentials easy to represent and calculate
- orthogonality is a plus

the Bloch theorem & plane waves

infinite crystals



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

Born — von Kármán PBC

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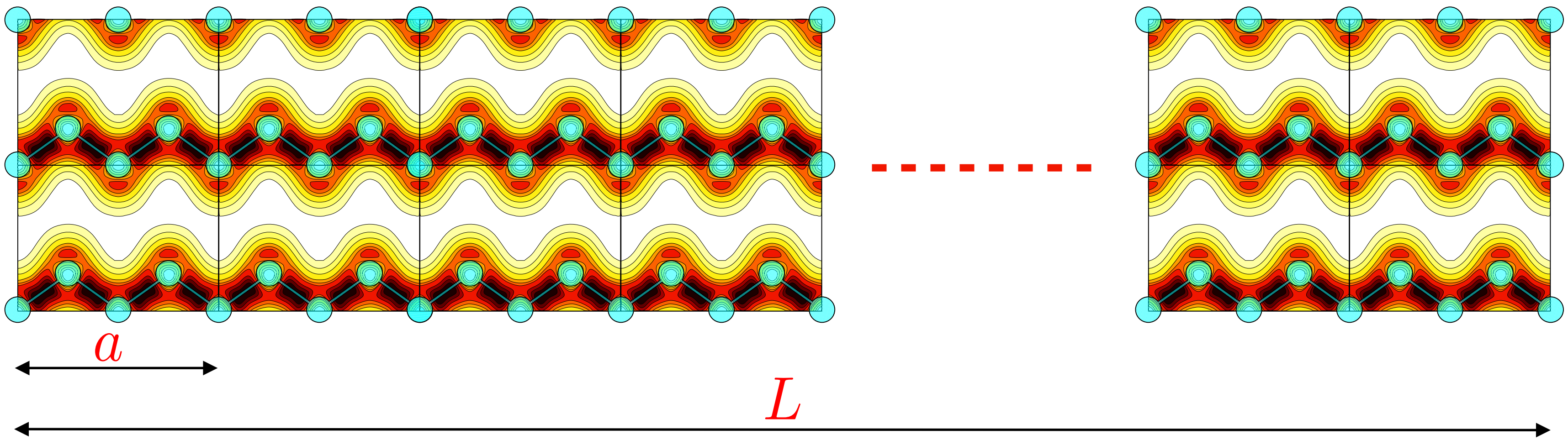

$$\psi(x + L) = \psi(x)$$ Born — von Kármán PBC

$$\left.\begin{aligned} \psi_k(x + a) &= e^{ika}\psi_k(x) \\ \psi_k(x) &= e^{ikx}u_k(x) \\ u_k(x + a) &= u_k(x) \end{aligned}\right\}$$ Bloch theorem

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

plane-wave basis sets

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

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

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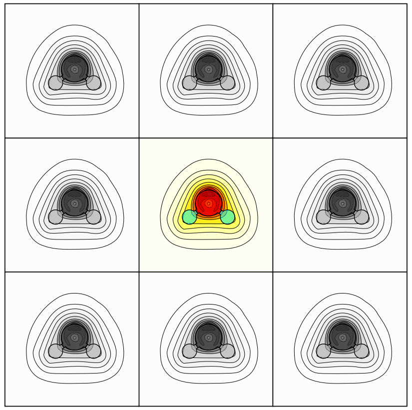
finite systems $(\ell = a)$



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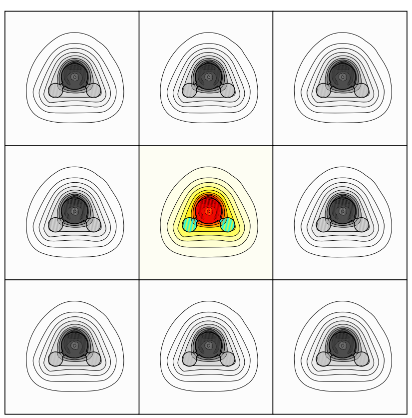

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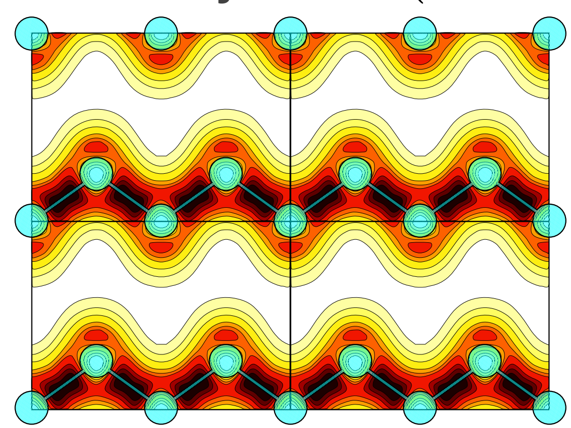

$$\mathbf{q} = \mathbf{k} + \mathbf{G}; \quad \mathbf{k} \in BZ$$

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

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

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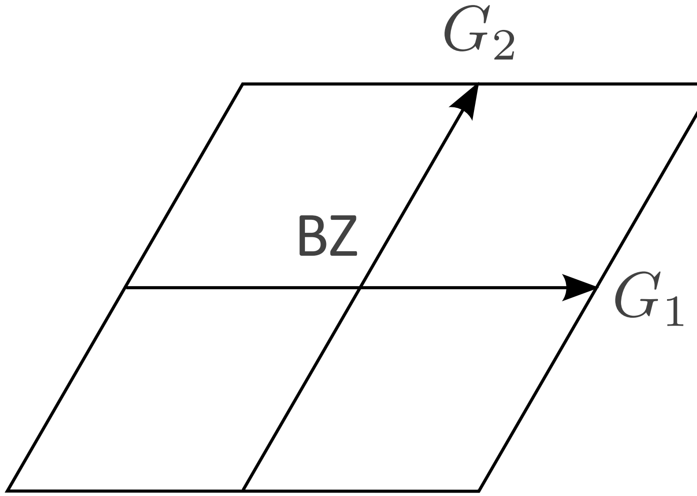
$$\begin{aligned} V_{xc}(\mathbf{r}) &= \mu_{xc}\big(\rho(\mathbf{r})\big) \\ V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ &= e^2 \sum_{\mathbf{G}\neq 0} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G}) \end{aligned}$$

sampling the Brillouin zone: special points

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



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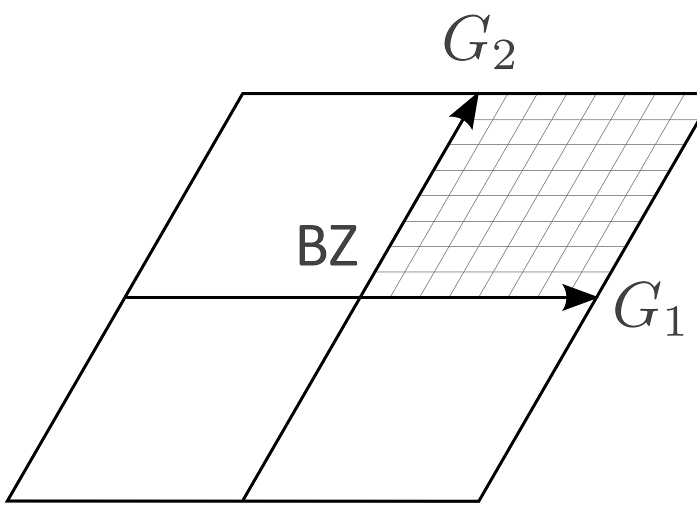

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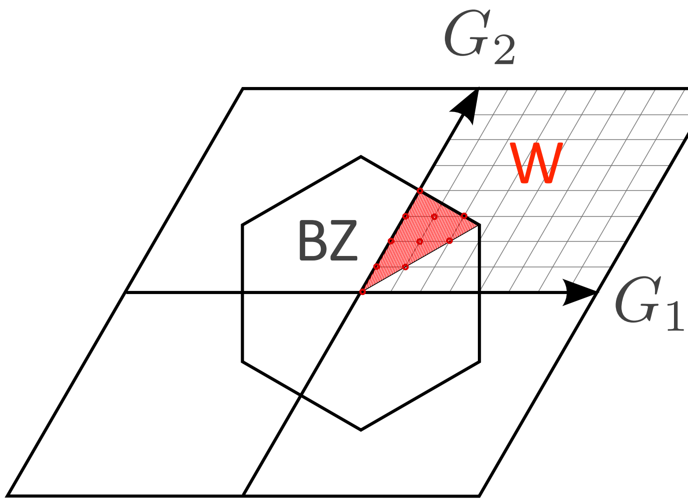

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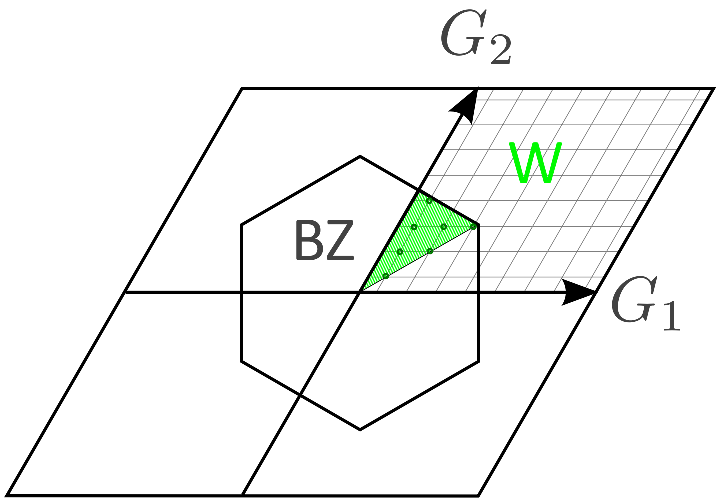

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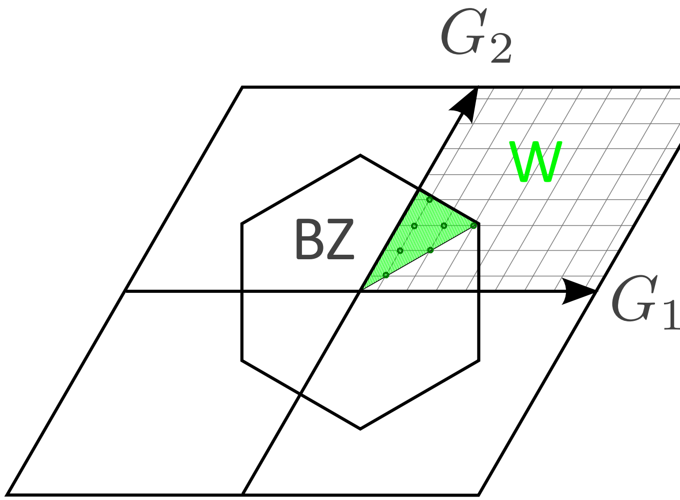

$$\rho(\mathbf{r}) = \sum_v \sum_{\mathbf{k}\in \mathrm{BZ}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

$$= \sum_v \sum_{S\in\mathcal{G}} \sum_{\mathbf{k}\in \mathrm{W}} |u_{vS\cdot\mathbf{k}}(\mathbf{r})|^2$$

$$= \sum_v \sum_{S\in\mathcal{G}} \sum_{\mathbf{k}\in \mathrm{W}} |u_{vS\mathbf{k}}(S^{-1}\cdot\mathbf{r})|^2$$

$$= \sum_{S\in\mathcal{G}} \rho_{\mathrm{W}}(S^{-1}\cdot\mathbf{r})$$

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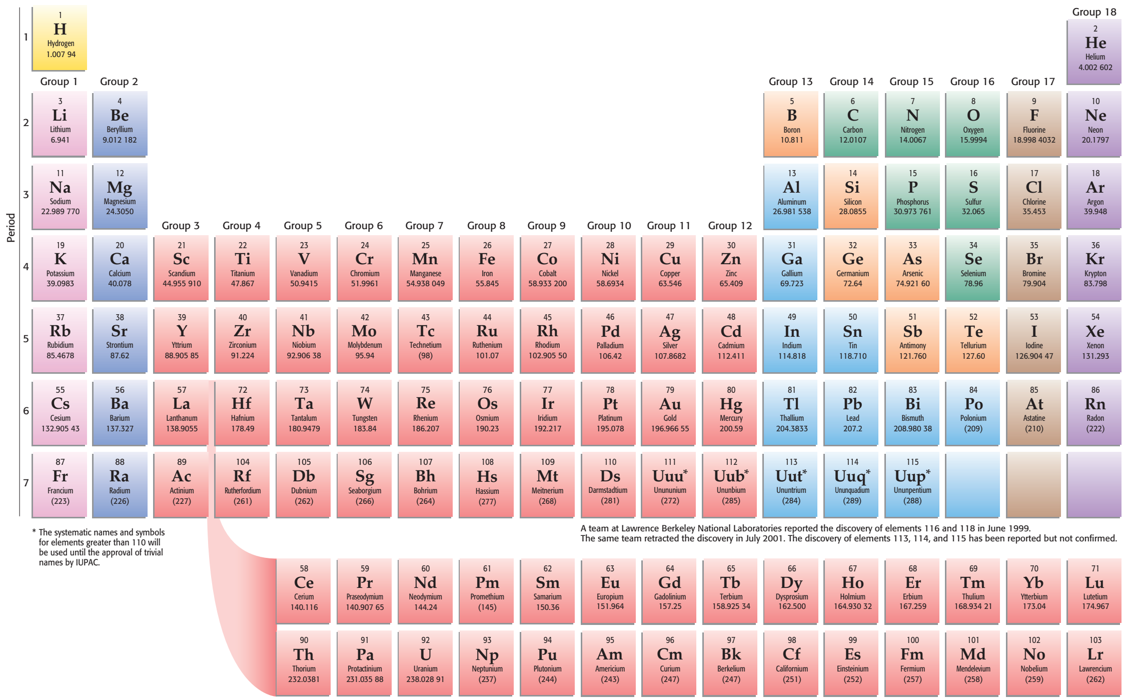
- ☹ uniform spatial resolution (no core states!)

treating core states



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

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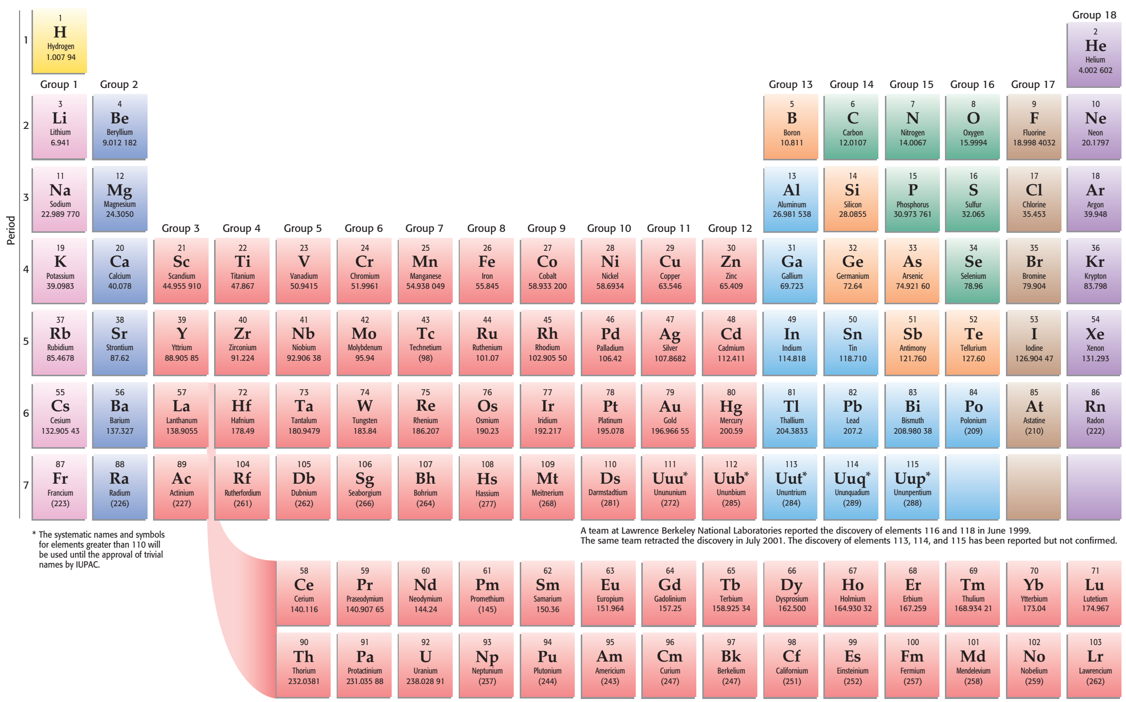

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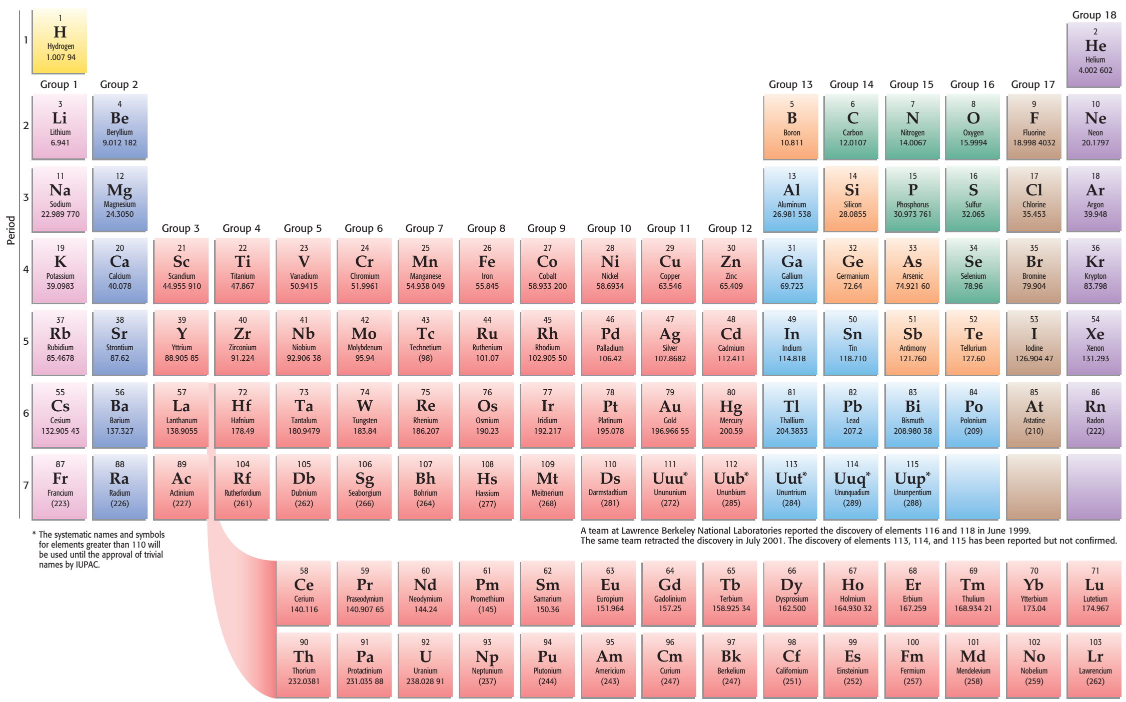

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$$\sim Z^3$$

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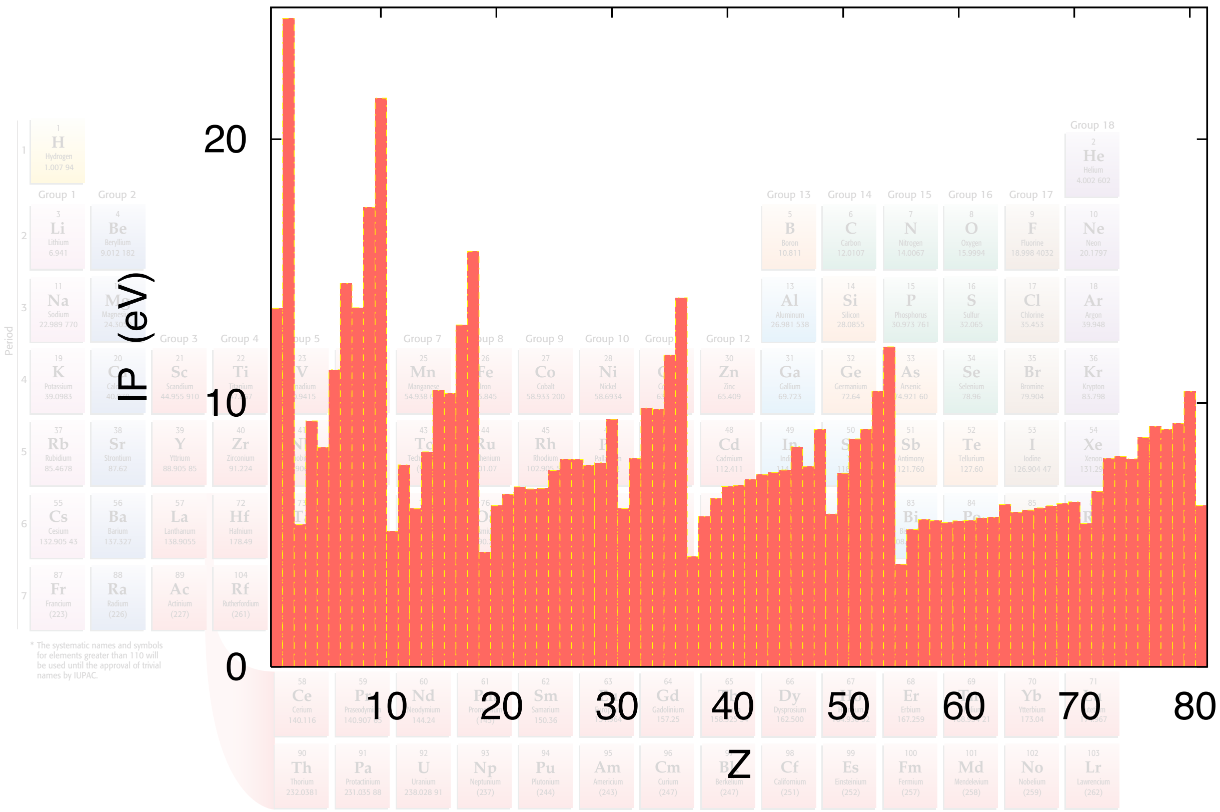

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$$I_P \sim 1 \quad a \sim 1$$

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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:

ϕ^{ps}_{val} is nodeless and smooth

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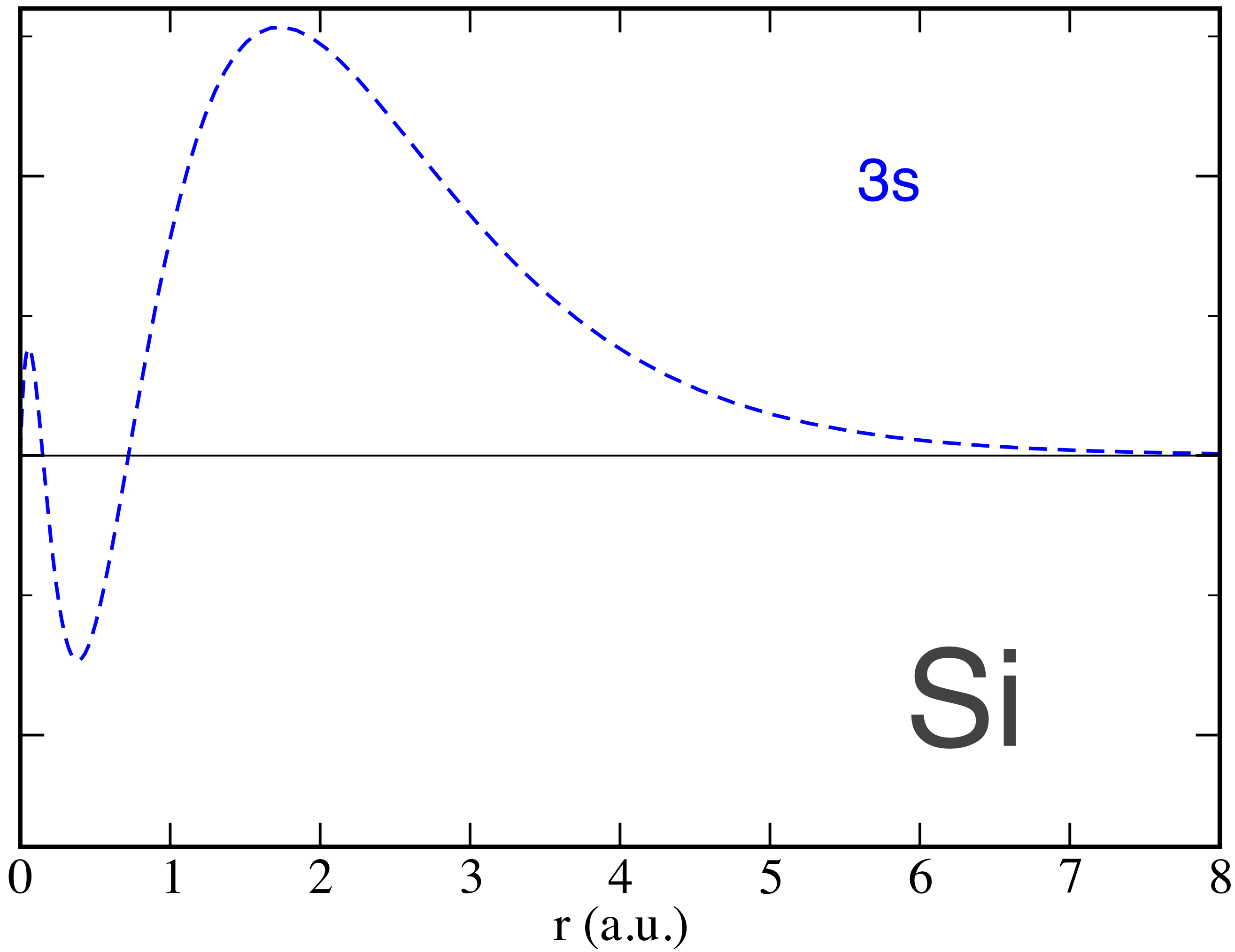
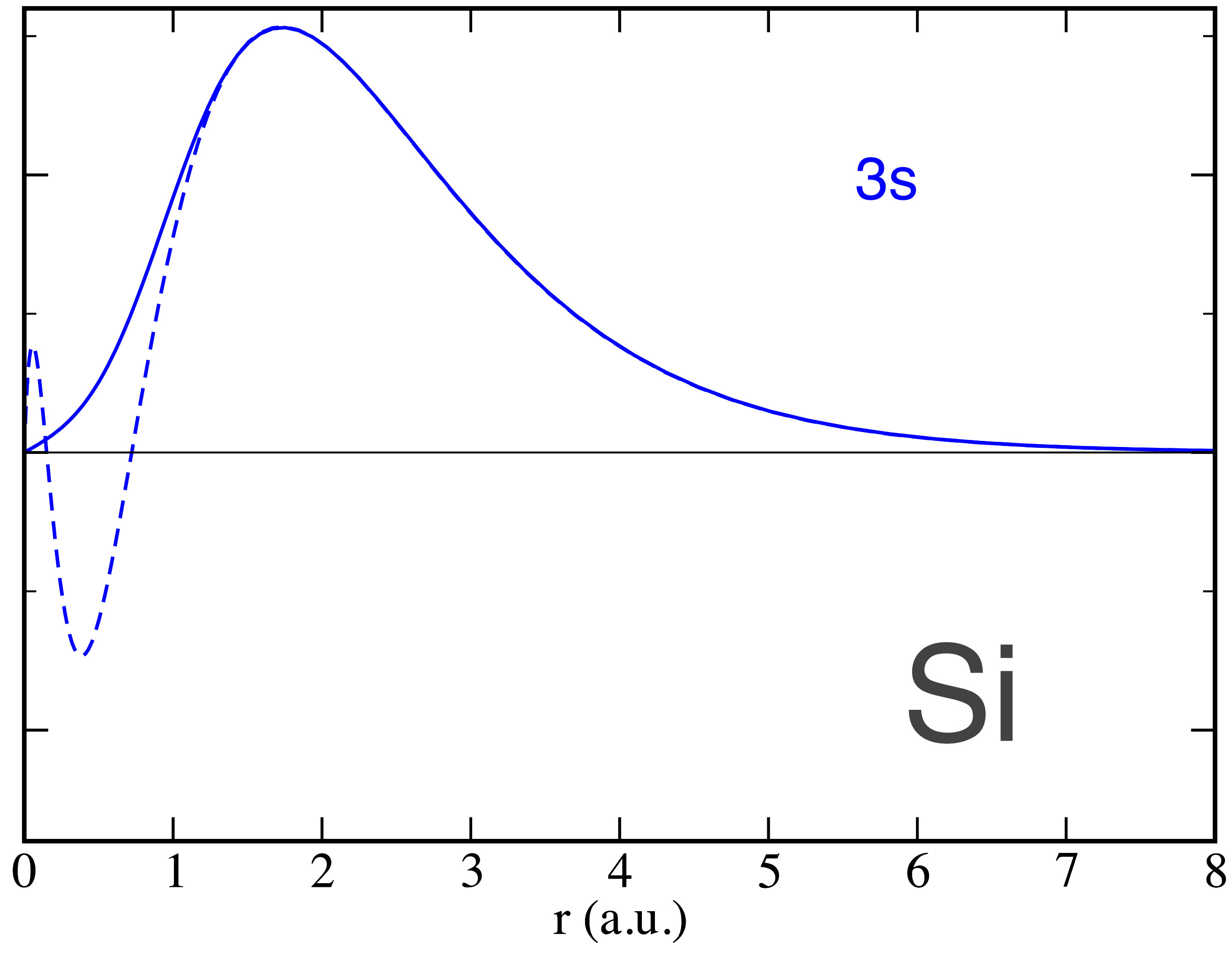
ϕ_{val}^{ps} is nodeless and smooth

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
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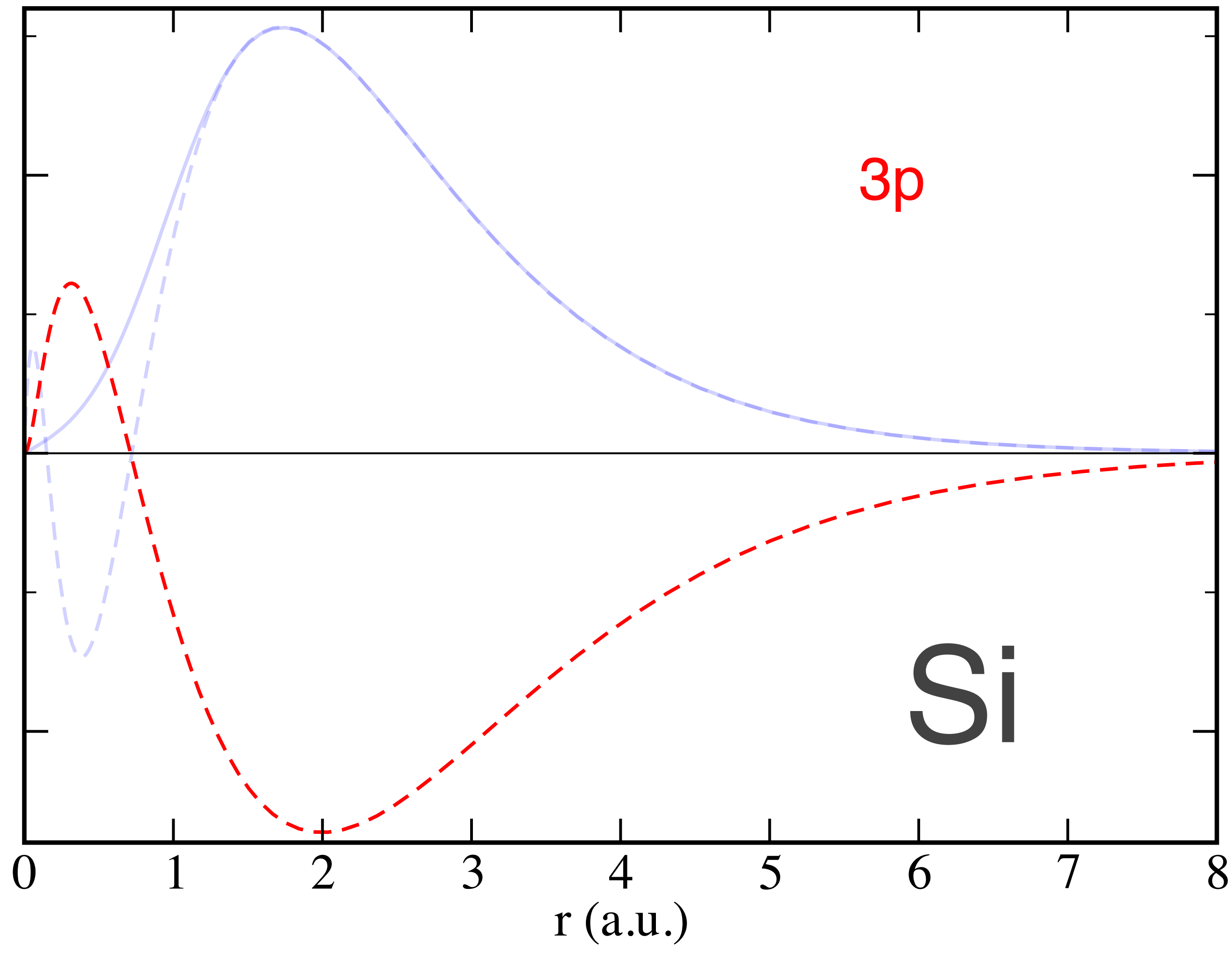
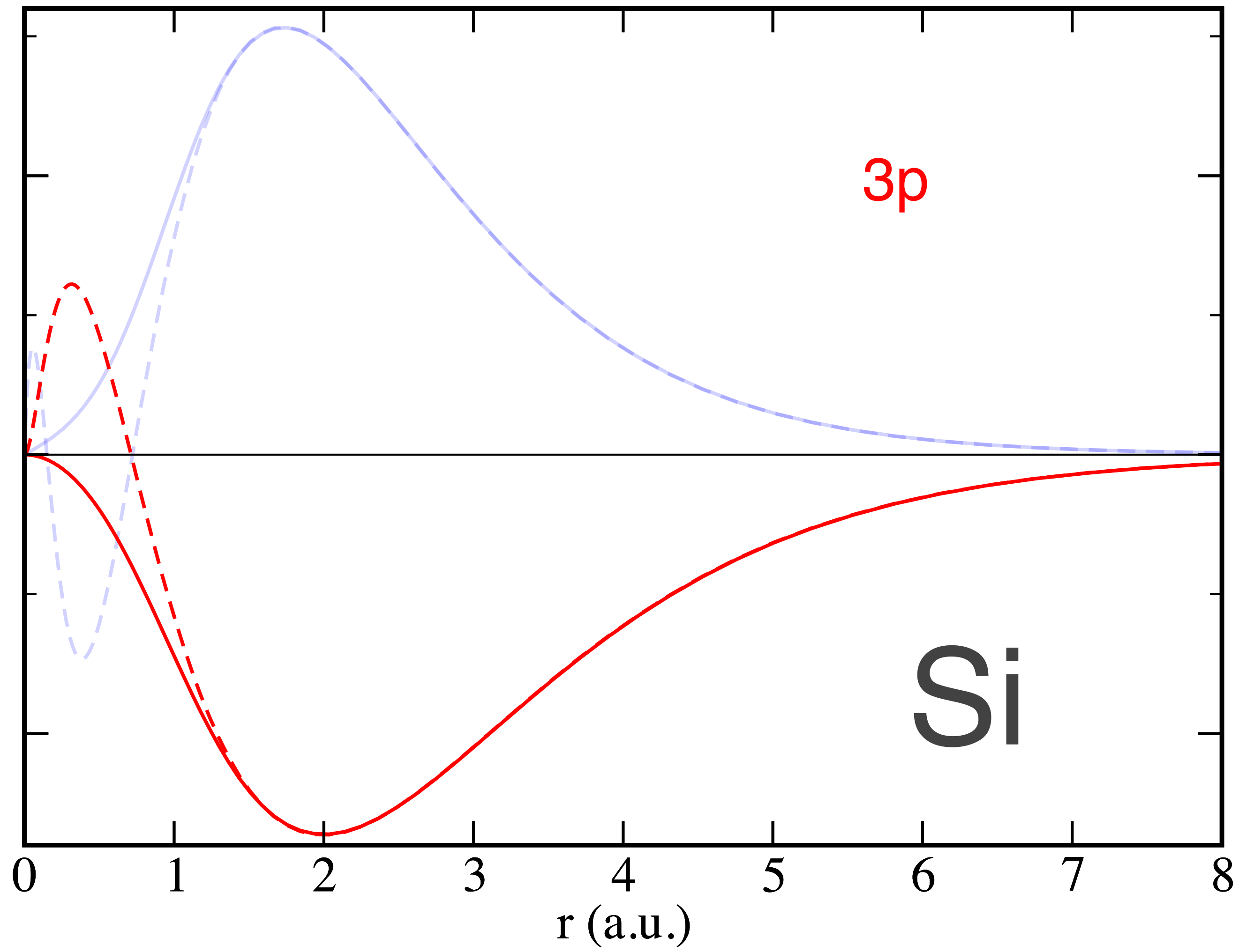

3p
Si
0
1
2
3
4
5
6
7
8
r (a.u.)


3p
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0
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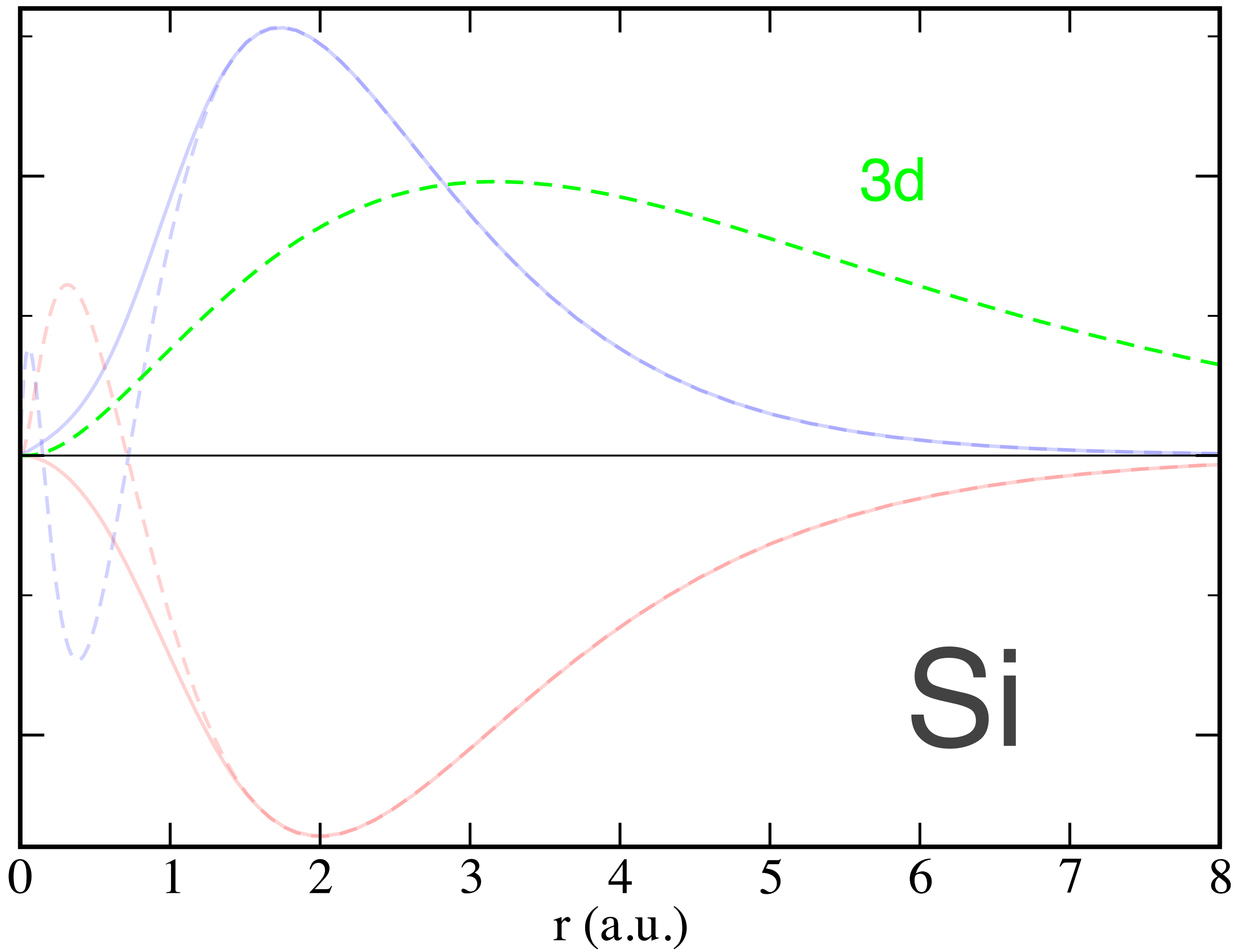
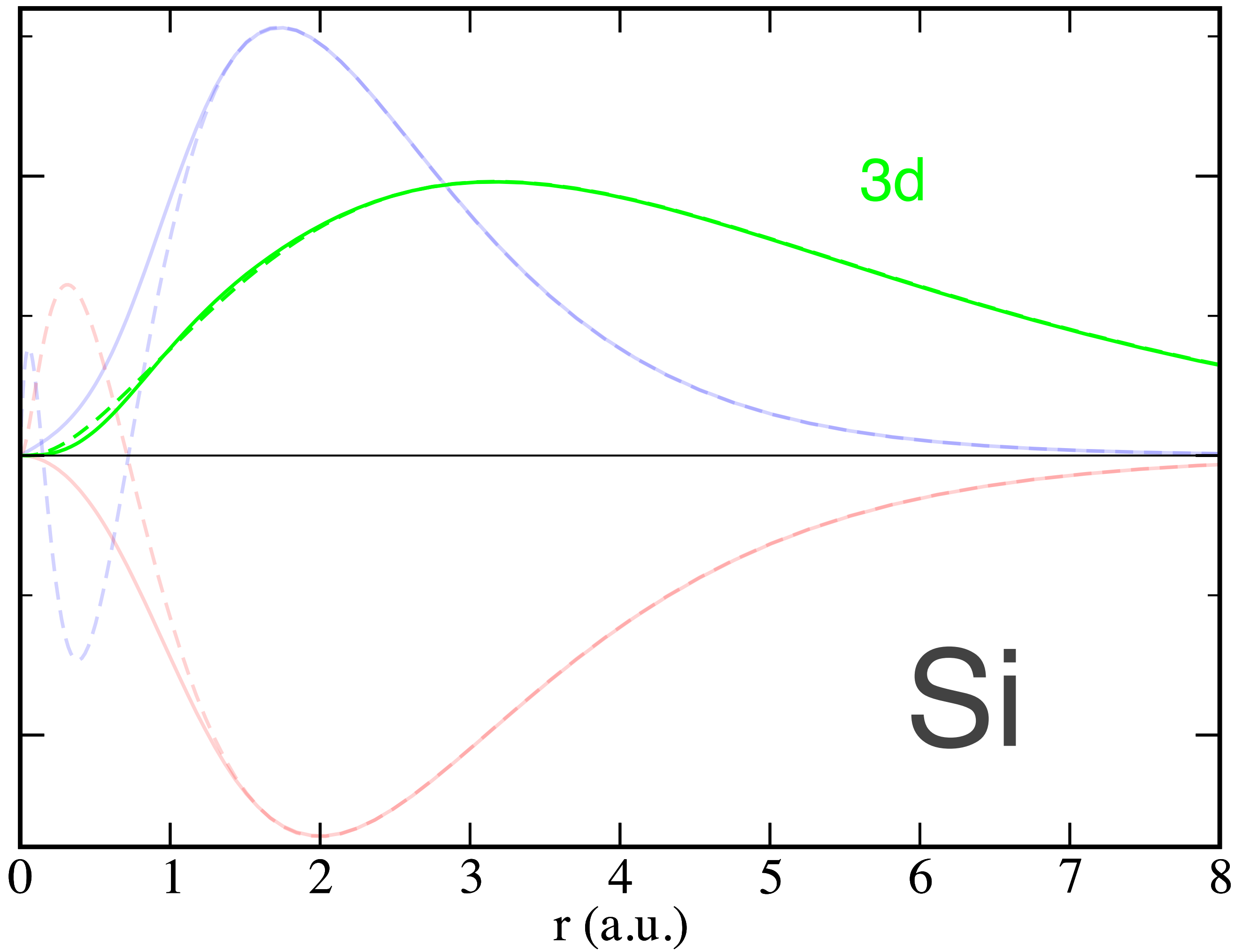
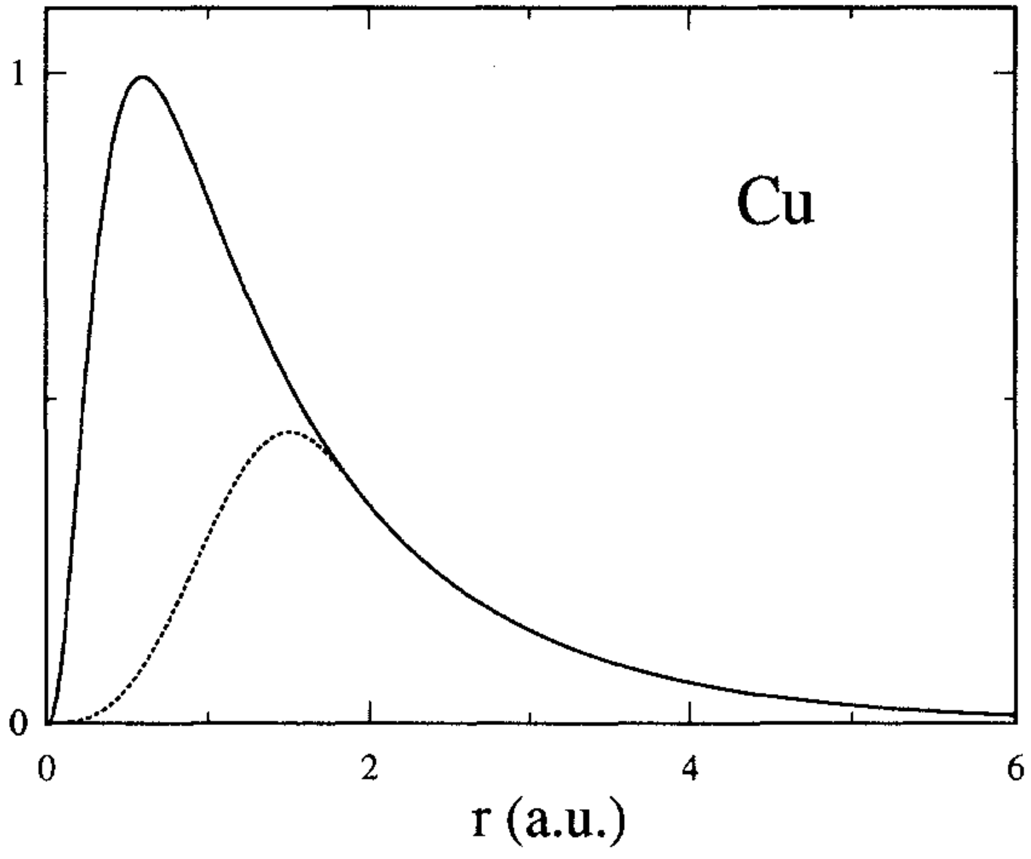

3d
Si
0
1
2
3
4
5
6
7
8
r (a.u.)

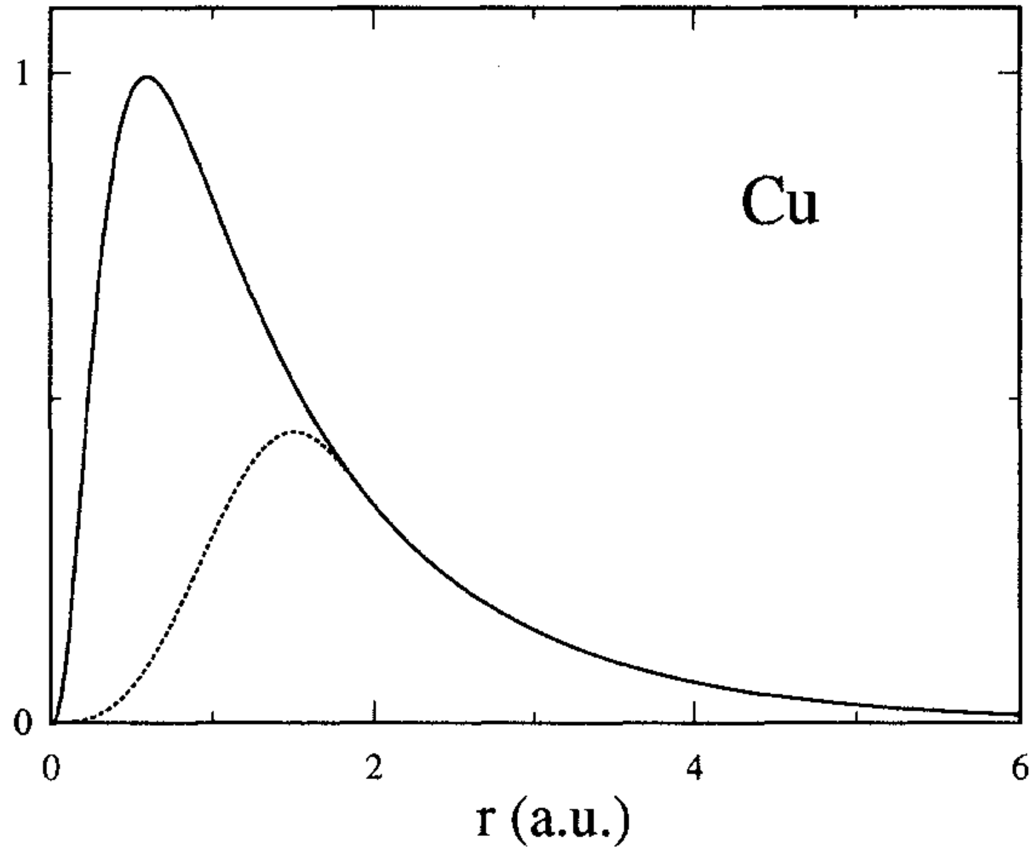


3d
Si
0
1
2
3
4
5
6
7
8
r (a.u.)

US pseudopotentials

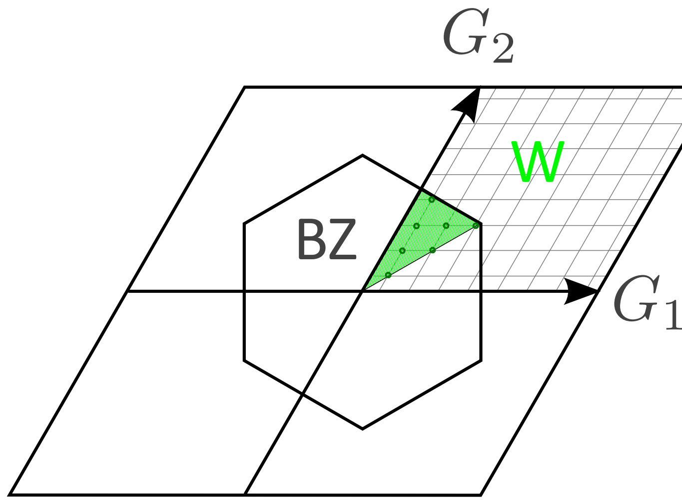


US pseudopotentials



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

sampling the Brillouin zone: special points



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

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