modelling materials using quantum mechanics and digital computers

the plane-wave pseudo potential way

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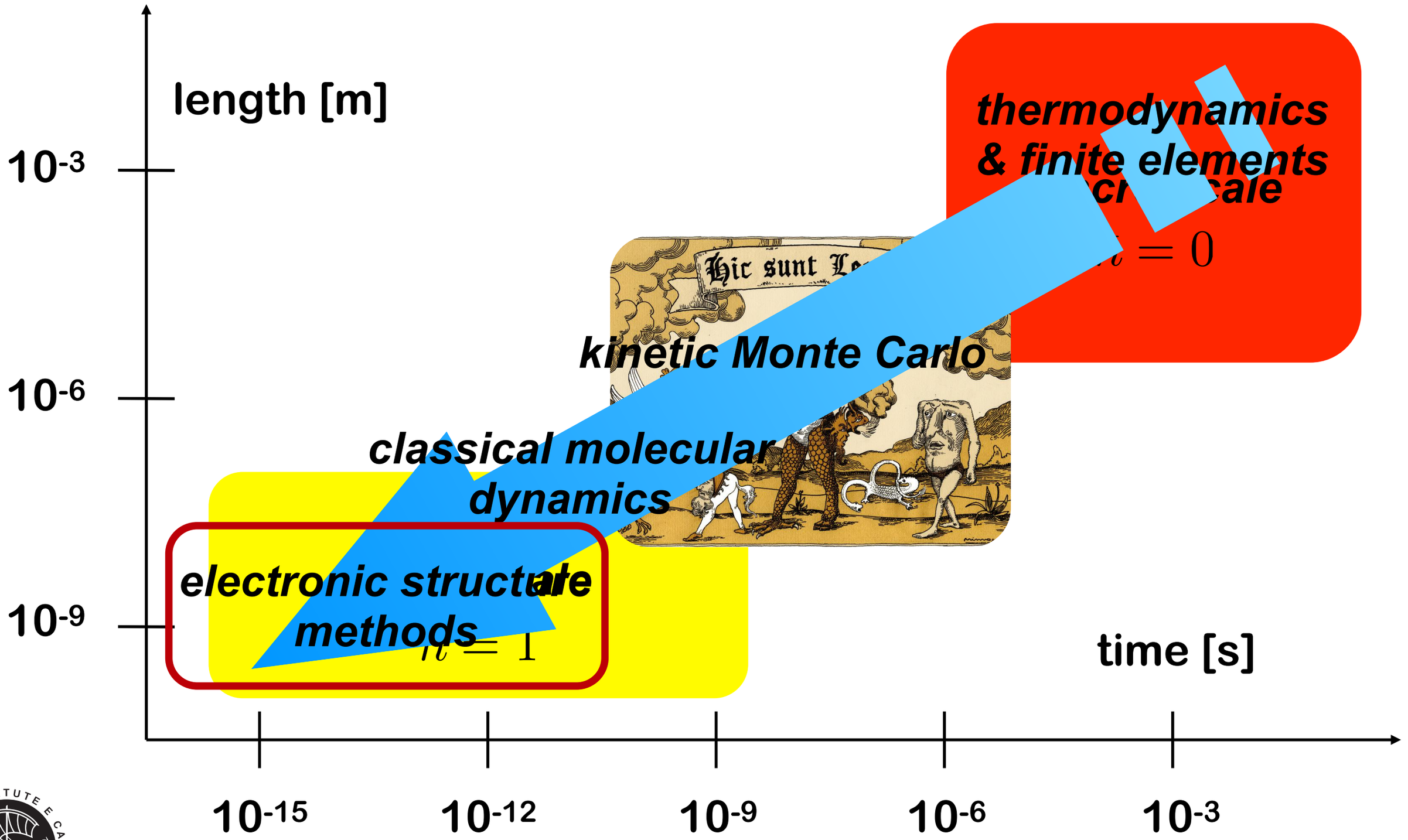
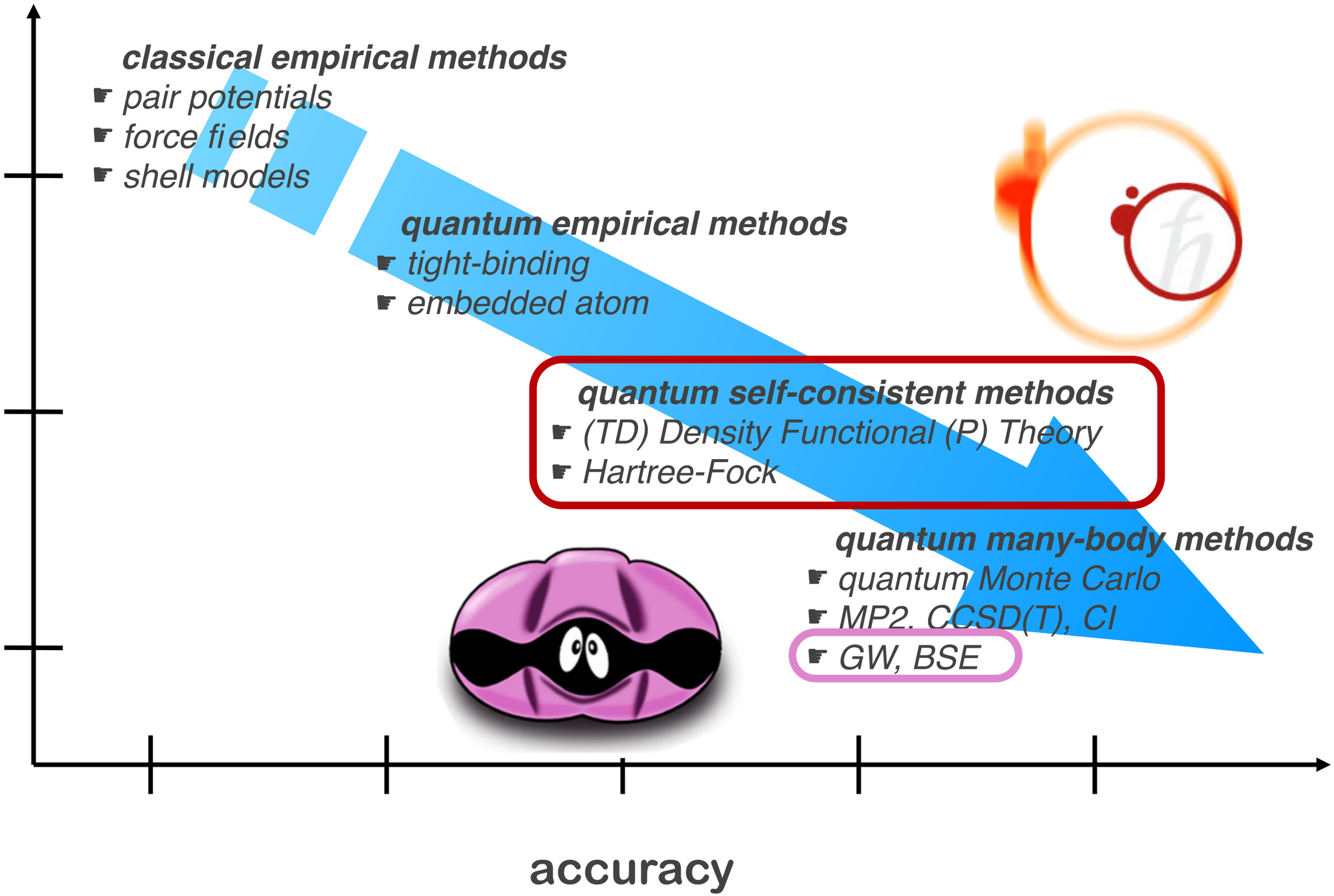
the saga of time and length scales



size *vs.* accuracy



ab initio calculations: what, why, when, how

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

why: they are accurate and *predictive*

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

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

ab initio simulations

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

M ≫ m: the Born-Oppenheimer approximation

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

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

density-functional theory

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

$$V(\mathbf{r},\mathbf{R})=\frac{e^2}{2}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}-\frac{Z_I e^2}{|\mathbf{r}_i-\mathbf{R}_I|}+\cancel{\frac{e^2}{2}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}$$

DFT

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

Kohn-Sham equations

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

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

Hohenberg-Kohn DFT

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

$$\begin{aligned} E[V] &= \min_\Psi \langle\Psi|\hat{K} + \hat{W} + \hat{V}|\Psi\rangle \\ &= \min_\Psi \left[\langle\Psi|\hat{K} + \hat{W}|\Psi\rangle + \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}\right] \end{aligned}$$

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

$$\rho(\mathbf{r}) = N\int |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

properties:

- $E[V]$ is convex (requires some work to demonstrate)
- $\rho(\mathbf{r}) = \dfrac{\delta E}{\delta V(\mathbf{r})}$ (from Hellmann-Feynman)

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*)

Kohn-Sham DFT

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

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

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

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

exchange-correlation energy functionals

- LDA (Kohn & Sham, 60's)

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

- 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)

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

- ...

solving the Kohn-Sham equations

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

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

$$\frac{\delta E_{KS}}{\delta \psi_v^*(\mathbf{r})} = \sum_{uv} \Lambda_{vu}\psi_u(\mathbf{r})$$

$$\sum_j h_{KS}[c](i,j)c(j,v) = \epsilon_v c(i,v)$$

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

requirements

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

plane-wave basis sets

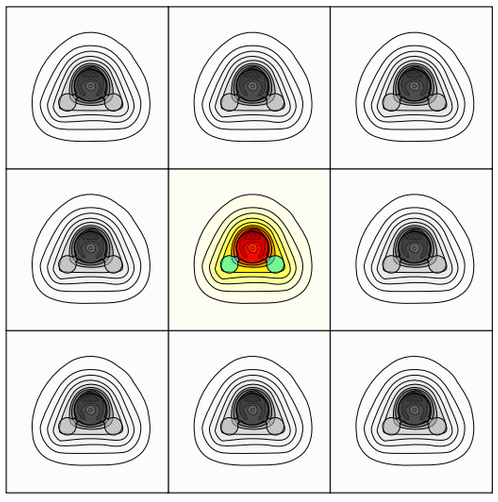
$$\psi(\mathbf{r}) = \sum_j c(j)\varphi_j(\mathbf{r})$$

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

periodic boundary conditions

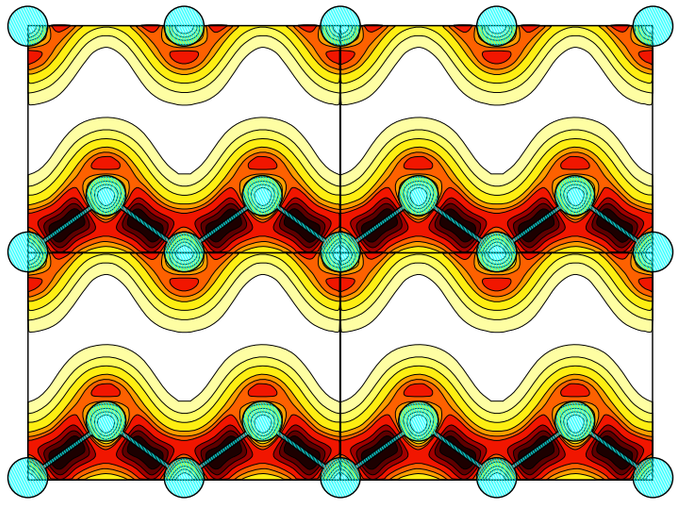
$$\varphi(x+\ell) = \varphi(x) \rightarrow q_j = \frac{2\pi}{\ell} j$$

finite systems $(\ell = a)$



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

infinite crystals $(\ell = L)$

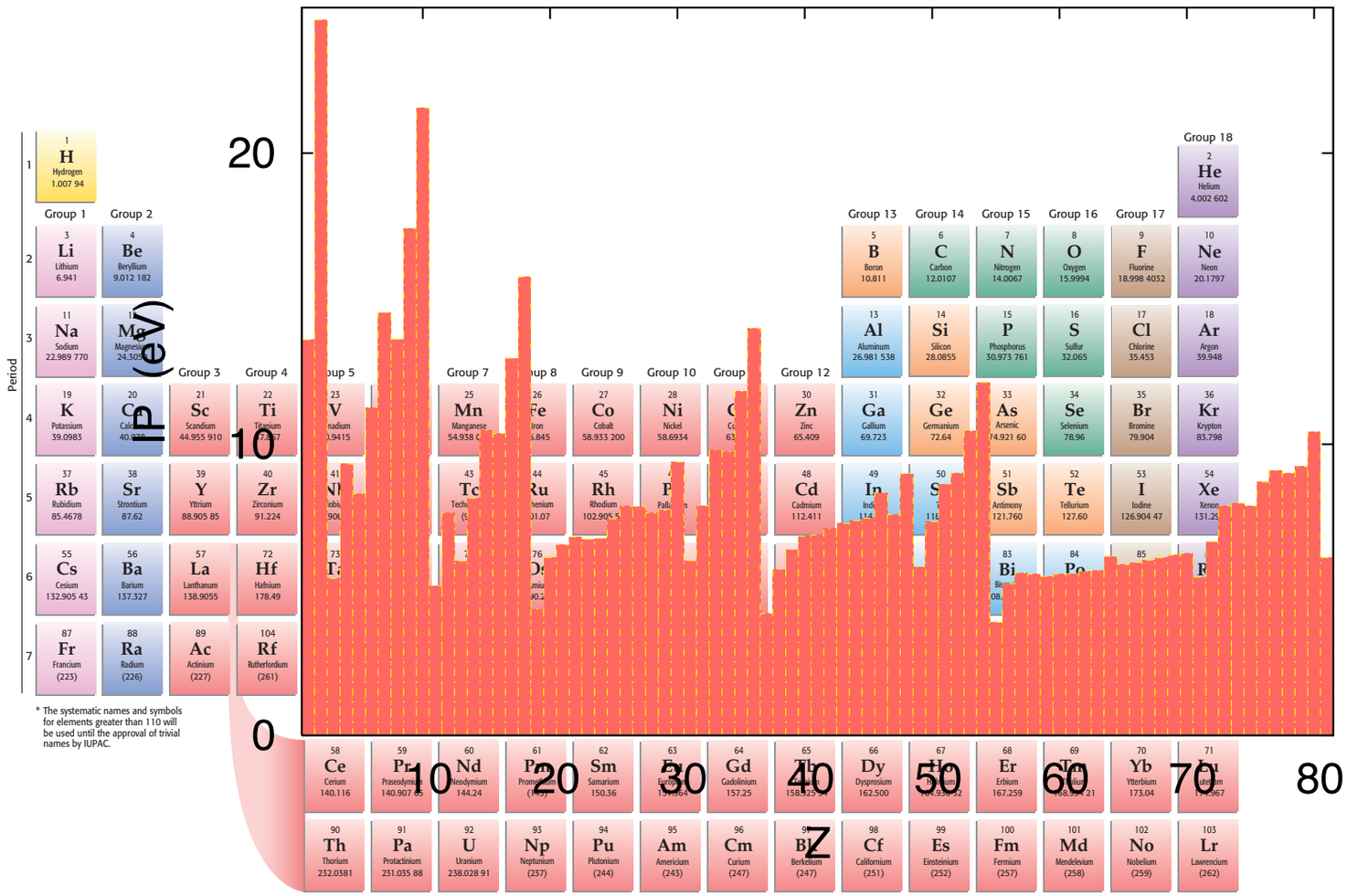


$$\mathbf{q} = \mathbf{k} + \mathbf{G}; \quad \mathbf{k} \in BZ$$

PWs: pros & cons

- ☺ approach to completeness easily and systematically checked ($|\mathbf{k}+\mathbf{G}|^2 < E_{cut}$)
- ☺ basis set independent of nuclear positions (no Pulay forces)
- ☺ matrix elements and Hψ products easily calculated
- ☺ density, Hartree, and XC potentials easily calculated
- ☺ orthonormality
- ☹ basis set depends on volume shape/size (Pulay stresses)
- ☹ uniform spatial resolution (no core states!)

treating core states



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

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

$$\frac{4\pi}{3} \sim 1 \qquad \Omega \sim 1$$

trashing core states: pseudopotentials

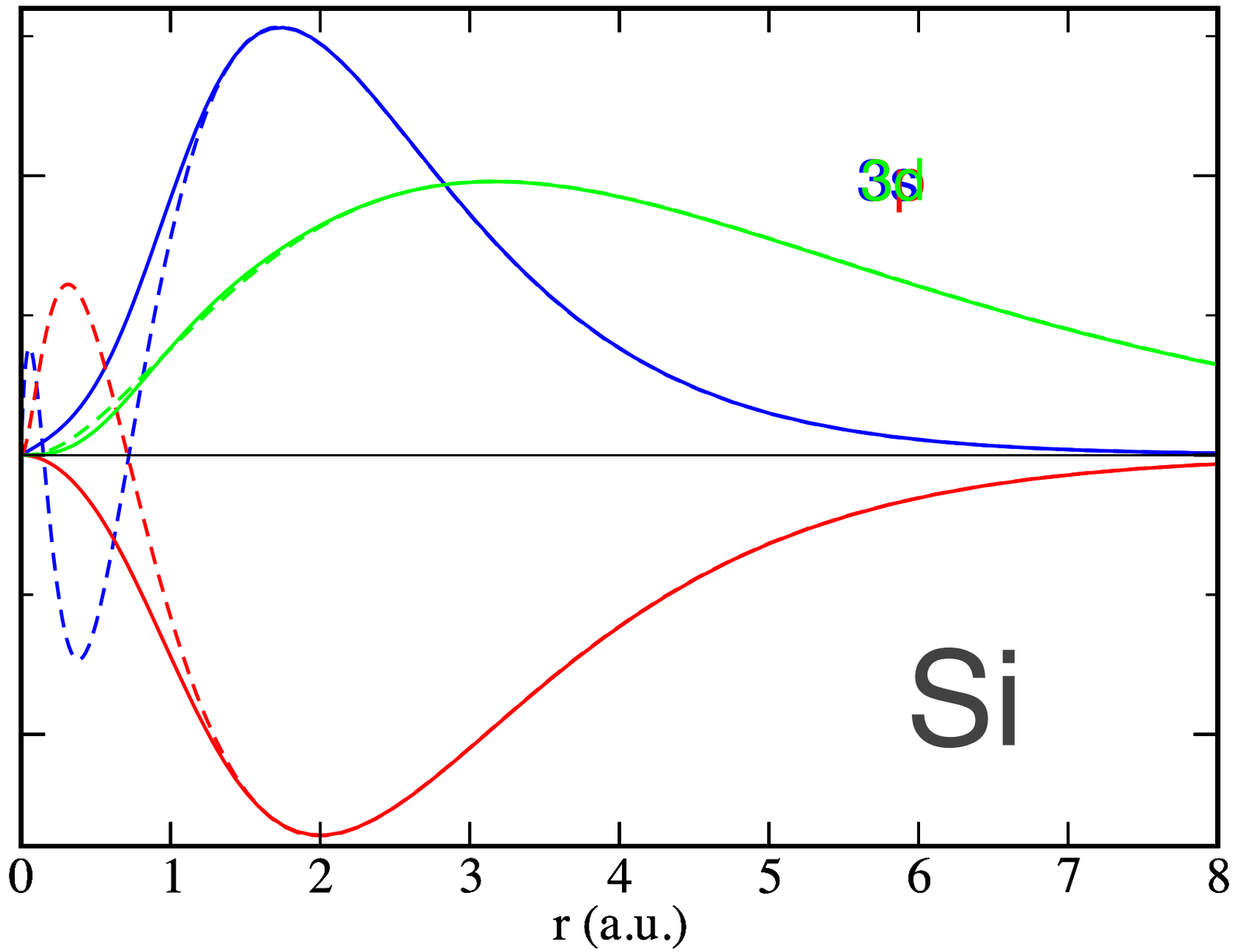
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

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

response functions

$$\text{property} = \frac{\partial(\text{variable})}{\partial(\text{strength})}$$

- polarizability, dielectric constant $\frac{\partial \mathrm{P}_i}{\partial \mathrm{E}_j}$
- elastic constants $\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$
- piezoelectric constants $\frac{\partial \mathrm{P}_i}{\partial \epsilon_{kl}}$
- interatomic force constants $\frac{\partial f_i^s}{\partial u_j^t}$
- Born effective charges $\frac{\partial d_i^s}{\partial u_j^s}$
- … …

susceptibilities as energy derivatives

$$\hat{H}_\alpha = \hat{H}^\circ + \alpha\hat{A}$$

$$\chi_{BA} = \frac{\partial\langle\hat{B}\rangle_\alpha}{\partial\alpha}$$

$$\langle\hat{B}\rangle = \frac{\partial E_\beta}{\partial\beta}$$

(Hellmann & Feynman)

$$\hat{H}_\beta = \hat{H}^\circ + \beta\hat{B}$$

$$\chi_{BA} = \frac{\partial^2 E_{\alpha\beta}}{\partial\alpha\partial\beta}$$

$$\hat{H}_{\alpha\beta} = \hat{H}^\circ + \alpha\hat{A} + \beta\hat{B}$$

energy derivatives

$$H = H_0 + \sum_i \lambda_i v_i$$

$$E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \cdots$$

- ☛ structural optimization & molecular dynamics

- ☛ (static) response functions
  - elastic constants
  - dielectric tensor
  - piezoelectric tensor
  - ...
- ☛ vibrational modes in the adiabatic approximation
  - interatomic force constants
  - Born effective charges
  - ...

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

$$E(\lambda) = \min_n \left(F[n] + \int V_\lambda(\mathbf{r}) n(\mathbf{r}) \right) \quad \int n(\mathbf{r}) d\mathbf{r} = N \quad \text{DFT}$$

$$\frac{\partial E(\lambda)}{\partial \lambda_i} = \int n_\lambda(\mathbf{r}) v_i(\mathbf{r}) d\mathbf{r} \quad \text{HF}$$

$$\frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r} \quad \text{DFPT}$$

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi'_v(\mathbf{r})$$

$$= 2\mathrm{Re}\sum_{cv} \rho'_{vc}\phi_v^{\circ *}(\mathbf{r})\phi_c^{\circ}(\mathbf{r})$$

$$\phi'_v = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

$$(H^{\circ} - \epsilon_v^{\circ})\phi'_v = -P_c V' \phi_v^{\circ}$$

calculating the response

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi'_v(\mathbf{r})$$

$$(H^\circ - \epsilon_v^\circ)\phi'_v = -P_c V' \phi_v^\circ$$

DFPT: the equations

DFT

DFPT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r}) \longrightarrow V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

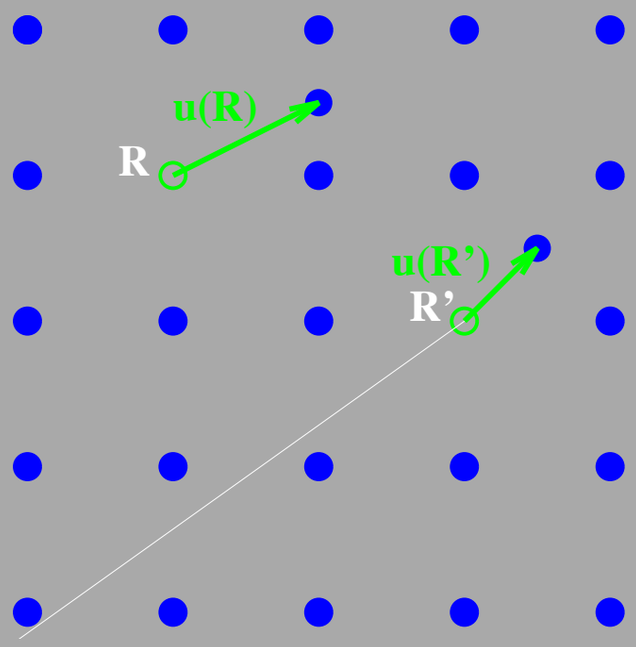
$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2 \longrightarrow n'(\mathbf{r}) = 2\ \mathrm{Re} \sum_{\epsilon_v < E_F} \phi^*_v(\mathbf{r}) \phi'_v(\mathbf{r})$$

$$\big(-\Delta + V_{SCF}(\mathbf{r})\big)\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r}) \longrightarrow \big(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v\big)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r}) \phi_v(\mathbf{r})$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

simulating atomic vibrations ...

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

DFT

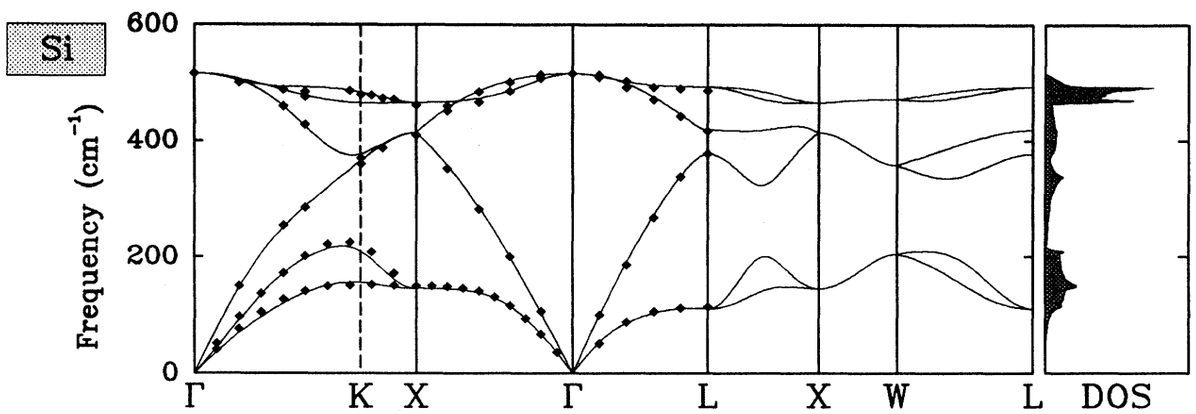
DPFT

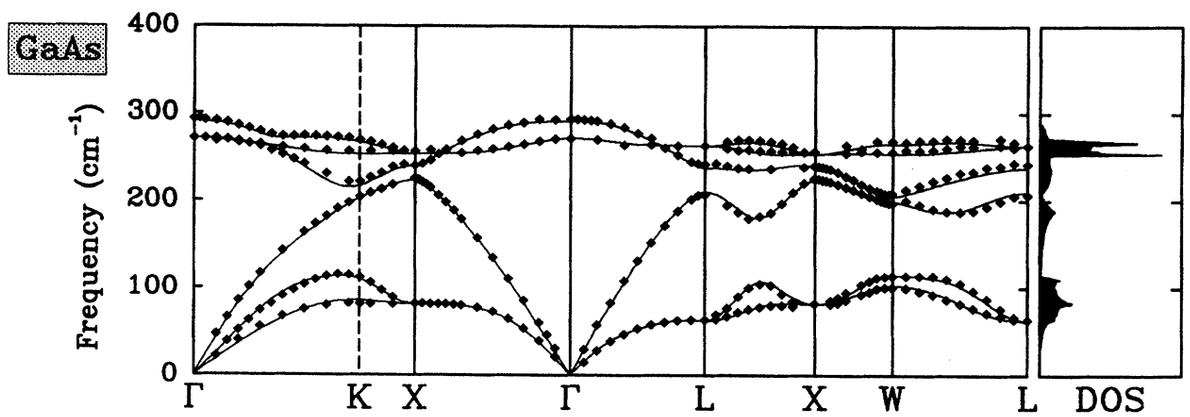
$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

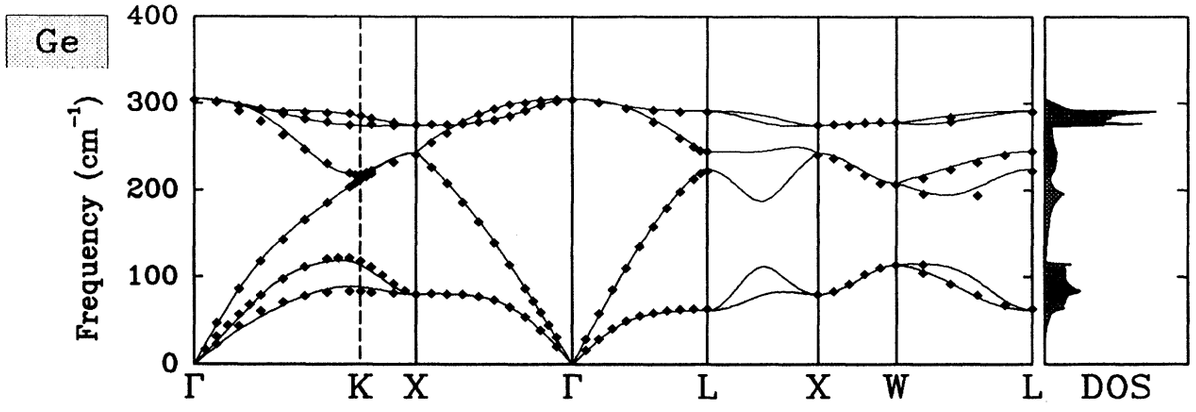
$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}') + \cdots$$

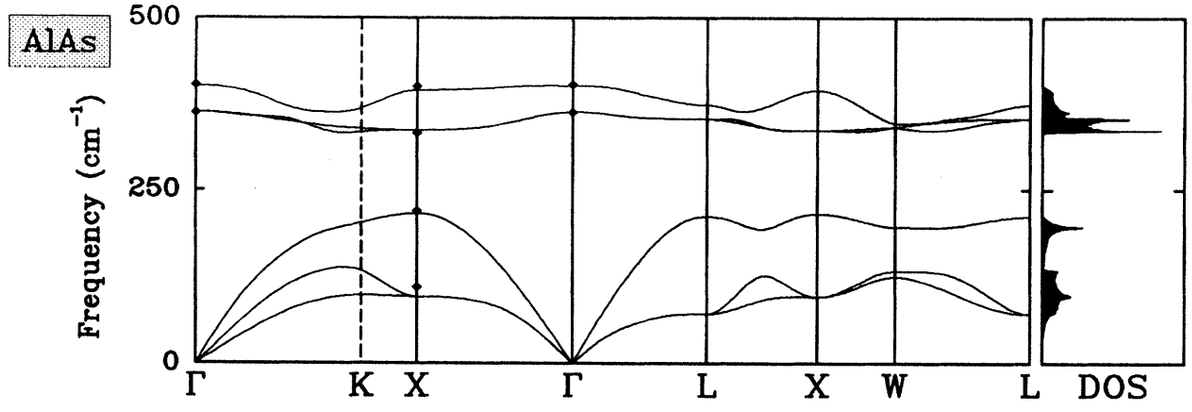
$$\det \left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R}) \delta_{\mathbf{R},\mathbf{R}'} \right] = 0$$

phonons from DFPT









P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)

you have (kind of) learnt how to simulate lattice fluctuations

this week you'll learn now how to simulate electronic charge fluctuations: *ENJOY!*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