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

- length [m]
  - $10^{-9}$
  - $10^{-6}$
  - $10^{-3}$

- time [s]
  - $10^{-15}$
  - $10^{-12}$
  - $10^{-9}$
  - $10^{-6}$
  - $10^{-3}$

- thermodynamics & finite elements
- classic molecular dynamics
- kinetic Monte Carlo
- electronic structure methods
size vs. accuracy

- **classical empirical methods**
  - pair potentials
  - force fields
  - shell models

- **quantum empirical methods**
  - tight-binding
  - embedded atom

- **quantum self-consistent methods**
  - (TD) Density Functional (P) Theory
  - Hartree-Fock

- **quantum many-body methods**
  - quantum Monte Carlo
  - MP2, CCSD(T), CI
  - GW, BSE
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

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

M \gg m: the Born-Oppenheimer approximation

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V(r, R) \right) \Psi(r|R) = E(R) \Psi(r|R) \]
\[ M\ddot{R} = -\frac{\partial E(R)}{\partial R} \]
density-functional theory

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

\[
V(r, R) = \frac{e^2}{2} \frac{Z_I Z_J}{|R_I - R_J|} - \frac{Z_I e^2}{|r_i - R_I|} + \frac{e^2}{2} \frac{1}{|r_i - r_j|}
\]

Kohn-Sham equations

\[
\rho(r) = \sum_v |\psi_v(r)|^2
\]

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

DFT

\[
V(r, R) \rightarrow \frac{e^2}{2} \frac{Z_I Z_J}{|R_I - R_J|} + v[\rho](r)
\]
Hohenberg-Kohn DFT

\[ H = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial r_i^2} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_i V(r_i) \]

\[ E[V] = \min_{\psi} \langle \psi | \hat{K} + \hat{W} + \hat{V} | \psi \rangle \]

\[ = \min_{\psi} \left[ \langle \psi | \hat{K} + \hat{W} | \psi \rangle + \int \rho(r)V(r)dr \right] \]

\[ E[V] = \min \left[ F[\rho] + \int V(r)\rho(r)dr \right] \]

properties:

- \( E[V] \) is convex \hspace{1em} (requires some work to demonstrate)
- \( \rho(r) = \frac{\delta E}{\delta V(r)} \) \hspace{1em} (from Hellmann-Feynman)

consequences:

- \( V(r) \Leftrightarrow \rho(r) \) \hspace{1em} (1st HK theorem)
- \( F[\rho] = E - \int V(r)\rho(r)dr \) \hspace{1em} is the Legendre transform of \( E \)
- \( E[V] = \min_{\rho} \left[ F[\rho] + \int V(r)\rho(r)dr \right] \) \hspace{1em} (2nd HK theorem)
Kohn-Sham DFT

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

\[ \frac{\delta T_0}{\delta \rho(r)} + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{xc}}{\delta \rho(r)} + V(r) = \mu \]

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

\[ \rho(r) = \sum_v |\psi_v(r)|^2 \theta(\epsilon_v - \mu) \]
exchange-correlation energy functionals

- **LDA** (Kohn & Sham, 60’s)
  \[ E_{xc}[\rho] = \int \epsilon_{xc}(\rho(r)) \rho(r) \, dr \]

- **GGA** (Becke, Perdew, et al., 80’s)
  \[ E_{xc} = \int \rho(r) \epsilon_{GGA}(\rho(r), |\nabla\rho(r)|) \, dr \]

- **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)
  \[ E_{mGGA} = \int \rho(r) \times \epsilon_{mGGA}(\rho(r), |\nabla\rho(r)|, \tau_s(r)) \, dr \]
  \[ \tau_s(r) = \frac{1}{2} \sum_i |\nabla^2 \psi_i(r)|^2 \]

- **VdW** (Langreth & Lundqvist, 2K’s)
  \[ E_{VdW} = \int \rho(r)\rho(r') \times \Phi_{VdW}[\rho](r, r') \, dr \, dr' \]

- **...**
solving the Kohn-Sham equations

\[ \psi_v(r) = \sum_j c(j, v) \varphi_j(r) \]
\[ \psi_v(r) \Leftrightarrow c(j, v) \]

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

- (effective) completeness of the basis set easily checked and systematically improved
- matrix elements easy to calculate and/or $H\psi$ products easily calculated on the fly
- Hartree and XC potentials easy to represent and calculate
- orthogonality is a plus
plane-wave basis sets

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

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

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

periodic boundary conditions

\[ \varphi(\mathbf{x} + \ell) = \varphi(\mathbf{x}) \rightarrow \mathbf{q}_j = \frac{2\pi}{\ell} j \]

finite systems \((\ell = a)\)

infinite crystals \((\ell = L)\)

q = G

q = k + G; k \in BZ
PWs: pros & cons

😊 approach to completeness easily and systematically checked \( |\mathbf{k} + \mathbf{G}|^2 < E_{\text{cut}} \)

😊 basis set independent of nuclear positions (no Pulay forces)

😊 matrix elements and \( \mathbf{H}\psi \) 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

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

\[ N_{PW} = \frac{4\pi}{3} k_{cut}^3 \frac{1}{(2\pi)^3} \Omega \sim 1 \]

\[ \sim Z^3 \]
trash 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:

\[ \phi_{val}^{ps} \text{ is nodeless and smooth} \]

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

\[ \epsilon_{val}^{ps} = \epsilon_{val}^{ae} \]

\[ \phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for} \quad r > r_c \]
response functions

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

- polarizability, dielectric constant
- elastic constants
- piezoelectric constants
- interatomic force constants
- Born effective charges

\begin{align*}
\frac{\partial P_i}{\partial E_j} & \quad \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \\
\frac{\partial \epsilon_{kl}}{\partial P_i} & \quad \frac{\partial f_i^s}{\partial u_j^t} \\
\frac{\partial d_i^s}{\partial u_j^s} & \quad \ldots
\end{align*}
susceptibilities as energy derivatives

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

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

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

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

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

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

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

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

\[ \frac{\partial E(\lambda)}{\partial \lambda_i} = \int n_\lambda(\mathbf{r}) v_i(\mathbf{r}) d\mathbf{r} \]

\[ \frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r} \]
calculating the response

\[ n(r) = \sum_v |\phi_v(r)|^2 \]

\[ n'(r) = 2\text{Re} \sum_v \phi_v^*(r)\phi_v'(r) \]

\[ = 2\text{Re} \sum_{cv} \rho'_{vc} \phi_v^*(r)\phi_c(r) \]

\[ \phi'_v = \sum_c \phi_c^o \frac{\langle \phi_c^o | V' | \phi_v^o \rangle}{\epsilon_v^o - \epsilon_c^o} \]

\[ (H^o - \epsilon_v^o)\phi'_v = -P_c V' \phi_v^o \]
calculating the response

\[ n'(r) = 2\text{Re} \sum_v \phi_v^*(r) \phi'_v(r) \]

\[ (H^\circ - \epsilon_v^\circ) \phi'_v = -P_c V' \phi_v^\circ \]
DFPT: the equations

**DFT**

\[ V_0(r) \leftrightarrow n(r) \]

\[ V_{SCF}(r) = V_0(r) + \int \frac{n(r')}{|r - r'|} dr' + \mu_{xc}(r) \]

\[ n(r) = \sum_{\epsilon_v < E_F} |\phi_v(r)|^2 \]

\[ (-\Delta + V_{SCF}(r)) \phi_v(r) = \epsilon_v \phi_v(r) \]

**DFPT**

\[ V'(r) \leftrightarrow n'(r) \]

\[ V'_{SCF}(r) = V'(r) + \int \frac{n'(r')}{|r - r'|} dr' + \mu'_{xc}(r) \]

\[ n'(r) = 2 \text{Re} \sum_{\epsilon_v < E_F} \phi_v^*(r) \phi_v(r) \]

\[ (-\Delta + V'_{SCF}(r) - \epsilon_v) \phi_v'(r) = P \epsilon_v V'_{SCF}(r) \phi_v(r) \]

simulating atomic vibrations ...
lattice dynamics

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

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

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

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

this week you’ll learn now how to simulate electronic charge fluctuations: *ENJOY!*
Designing the logo
download me at
http://talks.baroni.me