Computational Materials Science

$$\hat{H}\,\Psi_n(\{\underline{R}_I\},\{\underline{r}_k\}) = \mathcal{E}_n\,\Psi(\{\underline{R}_I\},\{\underline{r}_k\})$$

→ full description of electrons, nuclei

↘ plenty of interesting physics "beyond" Born-Oppenheimer
- friction in transport
- superconductivity
- ...

↙ Born-Oppenheimer

$$\hat{H}^e\,\Phi_\nu(\{\underline{R}_I\},\{\underline{r}_k\}) = E_\nu\,\Phi_\nu(\{\underline{R}_I\},\{\underline{r}_k\})$$

$$\left(\hat{H}^{nuc} + E_\nu(\{\underline{R}_I\})\right)\Lambda_n(\{\underline{R}_I\}) \approx \mathcal{E}_n\,\Lambda_n(\{\underline{R}_I\})$$

↘ "wave-function based"
- Hartree-Fock
- Perturbative (MP2, RPA, ...)
- "Exact" (CI, CCSDT...)
- "strong correlation" (Hubbard)
- Quantum Monte Carlo

↓ Density functional theory

$$E_{g.s.} = E[n_0(\underline{r})]$$

(Hohenberg-Kohn)

$$\left[-\frac{\nabla^2}{2} + V^{nuc}(\underline{r}) + V^e_{es}(\underline{r}) + V_{xc}(\underline{r})\right]\varphi_{ok}(\underline{r}) = \epsilon_{ok}\,\varphi_{ok}(\underline{r})$$

(Kohn-Sham)

↓ DFT

$E_{xc}[n]$?

⟹ remarkably accurate workhorses for many materials properties:
- geometry
- chemical bonding / trends
- structure, dynamics of molecules, materials from "first principles"

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7. Using "total energies and forces"

$E_0(\{\underline{R}_i\})$ of the electronic system

1) Nuclear wave function Λ_n properties i.e. $E_0(\{\underline{R}_I\})$ "effective potential"

2) "Classical" nuclei:

Qualitative estimate

de Broglie $\lambda = \frac{h}{p}$ but RT $E = \frac{p^2}{2M} \sim k_B T$

$$\lambda \overset{\text{at. units}}{=} \frac{1}{p} \overset{\leftarrow \hbar = 1}{=} \frac{1}{\sqrt{2 M k_B T}} \approx \frac{1}{\sqrt{2 \cdot 1836 \cdot 0.001}} \text{ a.u.} \approx \frac{1}{3.6} \text{ a.u} \approx 0.25 \text{ Å}$$

$M \sim M_{proton} = 1836 \; [m_e]$

$k_B T \underset{(RT)}{\sim} 0.025 \frac{1}{27.21} \text{ Ha} \sim 0.001 \text{ Ha}$

$\lambda \ll$ typ bond distances ($\sim$ 1-2 Å)

At RT, nuclei essentially "decoupled" wave packets

→ use classical approximation

$$H = \sum_I \frac{P_I^2}{2M_I} + \frac{1}{2} \sum_{\substack{J,I \\ I \neq J}} \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|^2} + \underbrace{E_0(\{\underline{R}_I\})}_{\text{electronic part, used as classical potential.}}$$

→ Equation of Motion, statistical mechanics etc. on "Born-Oppenheimer surface" $E_0(\{\underline{R}_I\})$

→ Obviously, not so for $T \to 0$ (phonons, heat capacity) but can still use gm. wave function Λ_n!

7.1 Total energy derivatives ("forces" on the nuclei)

$$E_{BO} := E_0(\{\underline{R}_I\}) + \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}} \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|}$$

- Minima of E_{BO} : $\frac{\partial E_{BO}}{\partial \underline{R}_I} = 0 \qquad I = 1, \dots, M$

(meta-) → "stable structures"

- "Forces" : $M_I \ddot{\underline{R}}_I = : \underline{F}_I = - \frac{\partial E_{BO}}{\partial \underline{R}_I}$ (classical !)

can use for • finite T dynamics (classical)

• even for "quantum dynamics" on BO surface

• simply to find minima $\frac{\partial E_{BO}}{\partial \underline{R}_I} = 0$

How to get $\underline{F}_I$?

• Nuclear part : $\underline{F}_I^{nuc-nuc} = - \frac{\partial}{\partial \underline{R}_I} \left[\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|} \right] = \sum_{J \neq I} \frac{Z_I Z_J}{|\underline{R}_I - \underline{R}_J|^3} (\underline{R}_I - \underline{R}_J)$

• Electronic part: Formally

$$\frac{\partial}{\partial \underline{R}_I} \langle \Phi_0 | \hat{H}^e | \Phi_0 \rangle = \langle \frac{\partial \Phi_0}{\partial \underline{R}_I} | \hat{H}^e | \Phi_0 \rangle + \langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial \underline{R}_I} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H}^e | \frac{\partial \Phi_0}{\partial \underline{R}_I} \rangle = (*)$$

Assume the exact $|\Phi_0\rangle$ (complete basis limit)

$$\hat{H}^e | \Phi_0 \rangle = E_0 | \Phi_0 \rangle \qquad \langle \Phi_0 | \hat{H}^e = \langle \Phi_0 | E_0$$

$$(*) = \langle \frac{\partial \Phi_0}{\partial \underline{R}_I} | \Phi_0 \rangle E_0 + \langle \Phi_0 | \frac{\partial \Phi_0}{\partial \underline{R}_I} \rangle E_0 + \langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial \underline{R}_I} | \Phi_0 \rangle$$

$$= \underbrace{\frac{\partial}{\partial \underline{R}_I} \underbrace{\langle \Phi_0 | \Phi_0 \rangle}_{\stackrel{!}{=} 1} E_0}_{0} + \underline{\underline{\langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial \underline{R}_I} | \Phi_0 \rangle}}$$

$$\langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial \underline{R}_I} | \Phi_0 \rangle = \frac{\partial}{\partial \underline{R}_I} \left(\int d^3 r \, n_0(\underline{r}) \sum_I \frac{Z_I}{|\underline{R}_I - \underline{r}|} \right)$$

$$= \int d^3r\, n_0(\underline{r}) \sum_I \frac{Z_I}{|\underline{r}-\underline{R}_I|^3} (\underline{r}-\underline{R}_I)$$

Hellmann-Feynman-theorem

$\Rightarrow$ in practice: Rigorously valid only for
(i) complete basis set
(ii) basis sets whose functions are not centered at atoms

Else: Extra terms from overlap matrix after all ("Pulay forces")

7.2. Applications: I Small vibrations
→ heat capacities, harmonic free energies etc.
→ "fingerprint" for structure in spectroscopy

Simple recipe: - Find metastable structure, $\frac{\partial E_{BO}}{\partial \underline{R}_I} = 0$ at $\{\underline{R}_I^0\}$

- Find Hessian $\left.\frac{\partial^2 E_{BO}}{\partial x_{I,i}\partial x_{J,j}}\right|_{\{\underline{R}_I^0\}} =: \underline{\underline{H}}_{IJ}$ $i,j = 1,\dots,3$

Taylor: $E_{BO}(\{\underline{R}_I^0 + \underline{u}_I\}) \approx E_{BO}(\{\underline{R}_I^0\}) + \sum_{I,J} \underline{u}_I \underline{\underline{H}}_{IJ} \underline{u}_J$

Classical mechanics $M_I \ddot{\underline{R}}_I = -\sum_J \underline{\underline{H}}_{IJ} \underline{u}_J$

$= M_I \ddot{\underline{u}}_I$

transform: $q_I = \sqrt{M_I}\, \underline{u}_I$

$\Rightarrow$ $\ddot{q}_I = -\sum_J \underbrace{\frac{\underline{\underline{H}}_{IJ}}{\sqrt{M_I M_J}}}_{\text{diagonalize}} q_J$

mass-weighted Hessian:

Eigenmodes ω_k, $\underline{\xi}_k$

c_{ik}: both classical, qm!

7.3 Application: II Classical Molecular Dynamics

$$M \ddot{\underline{R}}_I = -\frac{\partial E_{BO}}{\partial \underline{R}_I} \qquad \text{Newtonian Dynamics}$$

Could write: (1) $\underline{R}_I(t+\Delta t) = \underline{R}_I(t) + v(t)\cdot\Delta t + \frac{F_I(t)}{2M_I}\Delta t^2 + O(\Delta t^3)$ ++

(2) $\underline{R}_I(t-\Delta t) = \underline{R}_I(t) - v(t)\Delta t + \frac{F_I(t)}{2M_I}\Delta t^2 - O(\Delta t^3)$ +−+

$\Rightarrow$ (1) + (2):

$$\underline{R}_I(t+\Delta t) = 2\underline{R}_I(t) - \underline{R}_I(t-\Delta t) + \frac{F_I(t)}{M_I}\Delta t^2 + O(\Delta t^4)$$

essentially, free! no further $\frac{\partial E_{BO}}{\partial \underline{R}_I}$!

(with slight modifications: "Verlet algorithm"

Additional advantages:
- time-reversible! (no odd orders)
- "symplectic"
  (can show that there exists a discrete-time analogue to E that is conserved exactly! errors are bounded)

However: E conserved! Rarely the case in physics ...
(we always measure ensemble, system in a bath, etc.)
thermal equilibrium? finite T

→ "Thermostats": Add term to classical Hamiltonian that adds or subtracts ΔE like a bath

Simplest, canonical: Andersen:

Replace velocities of indv. nuclei stochastically with Maxwell-Boltzmann distributed random velocity!

Unphysical trajectory - but time average over ∞ trajectory = ensemble average over canonical ensemble of many identical systems.

7.4 Application (III) Multiscale Modelling

Multiphysics ??

Multiscience

First-principles accuracy is great.

but
- $O(1000)$ atoms [not 10^{23}]
- $O(10^{-9}s)$ timescale [not milliseconds, years]
  - milliseconds ↑ chemical reactions
  - years ↑ time it takes for (1) Your CPU to burn out (2) Your bridge to collapse
- $O(10^6)$ single calculations (not enough for statistical mechanics!)

Solution: for larger length, time, ensemble sizes, use often have well-understood models.

- choose a suitable empirical (?) Hamiltonian form
  - balls and springs for atoms
  - Ising model
  - continuum elasticity
  - many more ...

- compute key parameters from first principles
- use parameterized Hamiltonian for larger-scale predictions
- Verify key predictions by first principles! Accurate?

Note: "empirical" Hamiltonian can be rigorous: e.g. part of an exact expansion

Example: "Cluster expansion"