

Computational Materials Science

$$\hat{H} \Psi_n(\{\mathbf{R}_i\}, \{\mathbf{r}_k\}) = E_n \Psi(\{\mathbf{R}_i\}, \{\mathbf{r}_k\})$$

→ full description of electrons, nuclei

↙
Born-Oppenheimer

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

$$(\hat{H}^{nuc} + E_\nu(\{\mathbf{R}_i\})) \Lambda_n(\{\mathbf{R}_i\}) \approx E_n \Lambda_n(\{\mathbf{R}_i\})$$

↘
plenty of interesting physics
"beyond" Born-Oppenheimer

- friction in transport
- superconductivity
- ...

↓
Density functional theory

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

(Hohenberg-Kohn)

$$\left[-\frac{\nabla^2}{2} + V^{nuc}(\mathbf{r}) + V_{ext}^e(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_{\alpha}(\mathbf{r}) = \epsilon_{\alpha} \phi_{\alpha}(\mathbf{r})$$

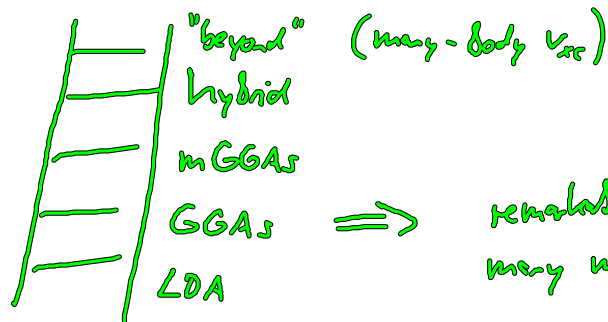
(Kohn-Sham)

↘ "Wave-function based"

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

↓ DFT

$$E_{xc}[n]?$$



⇒

reliably accurate workhorses for many material properties:

- geometry
- chemical bonding / trends
- structure, dynamics of molecules, materials from "first principles"

7. Using "total energies and forces"

$E_0(\{R_i\})$ of the electronic system

1) Nuclear wave function Δ_n properties in $E_0(\{R_i\})$ "effective potential"

2) "Classical" nuclei

Qualitative estimate

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

$\lambda \stackrel{\text{a.u. with } h=1}{=} \frac{1}{p} = \frac{1}{\sqrt{2M k_B T}} \approx \frac{1}{\sqrt{2 \cdot 1836 \cdot 0.001}} \text{ a.u.} \approx \frac{1}{3.6} \text{ a.u.} \approx 0.25 \text{ \AA}$

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

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

$\lambda \ll$ typ bond distances ($\sim 1-2 \text{ \AA}$)

At RT, nuclei essentially "decoupled" wave packets

→ use classical approximation

$$H = \sum_I \frac{p_I^2}{2M_I} + \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}} \frac{z_I z_J}{|R_I - R_J|^2} + \underbrace{E_0(\{R_I\})}_{\text{electronic part, used as classical potential.}}$$

→ Equation of Motion, statistical mechanics etc.

on "Born-Oppenheimer surface" $E_0(\{R_I\})$

→ Obvious, not so far $T \rightarrow 0$ (phonons, heat capacity) but can still use gen. wave function Δ_n !

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

$$E_{Bo} : = E_0(\{R_I\}) + \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}} \frac{z_I z_J}{|R_I - R_J|}$$

- Minima of E_{B0} : $\frac{\partial E_{B0}}{\partial R_I} = 0$ $I=1, \dots, M$
 (nuclei)
 \rightarrow stable structures

- "Forces": $M_I \ddot{R}_I = : F_I = - \frac{\partial E_{B0}}{\partial R_I}$ (classical!)

can use for finite T dynamics (classical)

• even for "quantum dynamics" on B_0 surface

• simply to find minima $\frac{\partial E_{B0}}{\partial R_I} = 0$

How to get F_I ?

• Nuclear part: $F_I^{\text{nuc-nuc}} = - \frac{\partial}{\partial R_I} \left[\frac{1}{2} \sum_{I \neq J} \frac{z_I z_J}{|R_I - R_J|} \right] = \sum_{J \neq I} \frac{z_I z_J}{|R_I - R_J|^3} (R_I - R_J)$

• Electronic part: Formally

$$\frac{\partial}{\partial R_I} \langle \Phi_0 | \hat{H}^e | \Phi_0 \rangle = \left\langle \frac{\partial \Phi_0}{\partial R_I} | \hat{H}^e | \Phi_0 \right\rangle + \langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial R_I} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H}^e | \frac{\partial \Phi_0}{\partial R_I} \rangle = (*)$$

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

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

$$(*) = \left\langle \frac{\partial \Phi_0}{\partial R_I} | \Phi_0 \right\rangle E_0 + \langle \Phi_0 | \frac{\partial \Phi_0}{\partial R_I} \rangle E_0 + \langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial R_I} | \Phi_0 \rangle$$

$$= \underbrace{\frac{\partial}{\partial R_I} \langle \Phi_0 | \Phi_0 \rangle}_{=1} E_0 + \underbrace{\langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial R_I} | \Phi_0 \rangle}$$

0

$$\langle \Phi_0 | \frac{\partial \hat{H}^e}{\partial R_I} | \Phi_0 \rangle = \frac{\partial}{\partial R_I} \left(\int d^3r u_0(r) \sum_I \frac{z_I}{|R_I - r|} \right)$$

$$= \int d^3r \psi_0(\underline{r}) \sum_I \frac{z_I}{I} \frac{z_I}{|\underline{r} - \underline{R}_I|^3} (\underline{r} - \underline{R}_I)$$

Hellmann-Feynman-theorem

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

Else: E 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 hope: - Find metastable structure, $\frac{\partial E_{B0}}{\partial \underline{R}_I} = 0$ at $\{\underline{R}_I^0\}$

- Find Hessian $\left. \frac{\partial^2 E_{B0}}{\partial x_{I,i} \partial x_{J,j}} \right|_{\{\underline{R}_I^0\}} =: \underline{H}_{IJ}$
 $i, j = 1, \dots, 3$

Taylor: $E_{B0}(\{\underline{R}_I^0 + \underline{u}_I\}) \approx E_{B0}(\{\underline{R}_I^0\}) + \sum_{I,J} \underline{u}_I \underline{H}_{IJ} \underline{u}_J$

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

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

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

mass-weighted Hessian:
 mass-weighted Hessian:

Eigenmodes $\omega_k, \underline{f}_k$

c_{ij} : both classical, qm!

7.3 Application: II Classical Molecular Dynamics

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

Could write:

$$(1) \underline{R}_I(t+\Delta t) = \underline{R}_I(t) + v(t) \Delta t + \frac{F_I(t)}{2M_I} \Delta t^2 + O(\Delta t^3) \dots$$
$$(2) \underline{R}_I(t-\Delta t) = \underline{R}_I(t) - v(t) \Delta t + \frac{F_I(t)}{2M_I} \Delta t^2 - O(\Delta t^3) \dots$$

\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 $\frac{\partial E_{\text{Bo}}}{\partial \underline{R}_I}$!

(with slight modifications: "Verlet algorithm")

Additional advantages: - time-reversible! (no odd order)

- "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 ensembles, system in a bath, etc.)

thermal equilibrium?, finite T

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

Simplest, canonical; Andersen:
Replace velocities of indiv. 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 (II) Multiscale Modelling

Multiphysics ??

Multiscience

First-principles accuracy is great.

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

Solution: for larger length, time, ensemble sizes, we 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 parametrized Hamiltonian for large-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"