LANL Summer School: Total Energy and Forces

Richard C. Remsing[1]
Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854

I. INTRODUCTION

Why think about total energy and forces? Many materials properties depend on energy and forces (derivatives of the total energy) tell us how atoms move. See the accompanying slides for more discussion and examples, including equations of state and dynamics.

Before talking about how to compute total energies and forces, let's quickly review density function theory (DFT).

II. DFT REVIEW

The total energy of our system is

$$E_{tot} = \min_{\{\psi_i\}} \left\{ \langle \Psi | \hat{H}_{ele} | \Psi \rangle \right\} \tag{1}$$

$$= \min_{\{\phi_i\}} E^{KS}[\{\phi_i\}] \tag{2}$$

$$E^{KS}[\{\phi_i\}] = T_s[\{\phi_i\}] + \int d\mathbf{r}\, V_{ext}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}\, V_H(\mathbf{r}) n(\mathbf{r}) + E_{xc}[n] \tag{3}$$

We have replaced a minimization with respect to all possible many-body wave functions, $\{\Psi\}$, by a minimization with respect to a set of orthonormal one-particle functions, Kohn-Sham orbitals $\{\phi_i\}$.

In the expression for E^{KS},

$$n(\mathbf{r}) = \sum_i^{occ} f_i |\phi_i(\mathbf{r})|^2, \tag{4}$$

$$T_s[\{\phi_i\}] = \sum_i^{occ} f_i \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle, \tag{5}$$

$$V_{ext}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}, \tag{6}$$

and

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{7}$$

such that $\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r})$

Within Kohn-Sham DFT, can write total energy as:

$$E^{KS} = \sum_i f_i \epsilon_i - \frac{1}{2} \int d\mathbf{r}\, V_H(\mathbf{r}) n(\mathbf{r}) + E_{xc}[n] - \int d\mathbf{r}\, \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) \tag{8}$$

Band structure energy comes from:

$$\hat{h}_e^{KS} \phi_i = \epsilon_i \phi_i \tag{9}$$

where $\hat{h}_e^{KS}$ is the effective one-body Hamiltonian.

The local exchange-correlation (XC) potential is

$$\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = V_{xc}(\mathbf{r}). \tag{10}$$

Functional derivative gives KS force on orbitals:

$$\frac{\delta E^{KS}}{\delta \phi_i^*} = f_i \hat{h}^{KS} \phi_i \tag{11}$$

Need approx for $E_{\mathrm{xc}}[n]$. E.g., GGA is

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \epsilon_{\mathrm{xc}}^{\mathrm{GGA}}\left(n(\mathbf{r}), \nabla n(\mathbf{r})\right) \tag{12}$$

In practice, to evaluate total energy or force, we need to represent orbitals and interactions in a numerically practical way. Need to discuss basis sets, pseudopotentials, etc. because our energy and force calculations will involve them.

III. BASIS SETS

We use basis sets to represent ϕ in terms of simple functions f_ν with well-known properties

$$\phi_i = \sum_\nu C_{i\nu} f_\nu(\mathbf{r}_i; \{\mathbf{R}^3\}) \tag{13}$$

Most widely used are Gaussian-type (GTOs)

$$f_m^G(\mathbf{r}) = N_m^G\, r_x^{m_x}\, r_y^{m_y}\, r_z^{m_z}\, e^{-\alpha_m r^2} \tag{14}$$

N_m, α_m usually held fixed so that only $C_{i\nu}$ are optimized.

GTOs or STOs are centered at nuclei. We will discuss "Pulay forces" that necessarily result for basis functions that are fixed at atoms and those atoms are allowed to move.

Could use "freely floating Gaussians" distributed in space, localized but not atom-fixed.

IV. PLANE WAVES

Periodic potential of lattice imposes periodicity on density

$\Rightarrow$ suggests using plane waves as basis set to expand periodic part of orbitals

$$f_G^{\mathrm{PW}}(\mathbf{r}) = N e^{i\mathbf{G}\cdot\mathbf{r}} \tag{15}$$

$$N = \frac{1}{\sqrt{\Omega}}, \quad \Omega = \text{Volume of periodic (super-) cell}$$

$\mathbf{G}$ is Fourier/reciprocal space vector

PWs form complete orthonormal set. Label $\mathbf{k}$ is replaced by $\mathbf{G}$.

PWs are originless $\Rightarrow$ Pulay forces vanish exactly even in finite basis.

Very unbiased basis set $\Rightarrow$ ultimately "balanced basis set". Can efficiently connect real and $\mathbf{G}$-space via FFTs. Can improve quality by increasing E_{cut} to increase largest $\mathbf{G}$-vector included in finite expansion.

$\Rightarrow$ Not all advantages: For structures on small length scales, need large Fourier components to resolve.

Often use PPs to replace core e^- and their rapid spatial variation. No way to include more basis functions in a particular region of space.

CP2K uses a dual Gaussian Plane Wave representation. This can be advantageous in many computational ways. One interesting approach is Gaussian-augmented PW (GAPW).

Replace $n(\mathbf{r})$ by

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_I n_I(\mathbf{r}) - \sum_I \tilde{n}_I(\mathbf{r}) \tag{16}$$

$\tilde{n}(\mathbf{r})$ is expanded in PWs and is the smooth part of density, i.e., in interatomic regions:

$$\tilde{n}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{17}$$

$n_I(\mathbf{r})$ and $\tilde{n}_I(\mathbf{r})$ expanded in products of atom-centered Gaussians:

$$n_I(\mathbf{r}) = \sum_{\mu\nu} P^I_{\mu\nu} \phi_\mu(\mathbf{r}) \phi^*_\nu(\mathbf{r}) \tag{18}$$

$$\tilde{n}_I(\mathbf{r}) = \sum_{\mu\nu} \tilde{P}^I_{\mu\nu} \tilde{\phi}_\mu(\mathbf{r}) \tilde{\phi}^*_\nu(\mathbf{r}) \tag{19}$$

P are functions of the density matrix.

$n(\mathbf{r})$ is correct if:

- Close to atom I: $n(\mathbf{r}) = n_I(\mathbf{r}), \quad \tilde{n}(\mathbf{r}) = \tilde{n}_I(\mathbf{r})$
- Far from atom I: $n(\mathbf{r}) = \tilde{n}(\mathbf{r}), \quad n_I(\mathbf{r}) = \tilde{n}_I(\mathbf{r})$
- Fulfilled exactly in complete basis set limit.

V. IMPLEMENTATION IN PERIODIC SYSTEMS

We will focus on the plane wave expansion.

KS potential,

$$V^{\mathrm{KS}}(\mathbf{r}) = V^{\mathrm{KS}}(\mathbf{r} + \mathbf{L}), \tag{20}$$

has periodicity of direct lattice.

KS orbitals can be written in Bloch form:

$$\phi_j(\mathbf{r}, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_j(\mathbf{r}, \mathbf{k}) \tag{21}$$

$\mathbf{k}$ = quantum number associated with crystal momentum, and is a vector in the first Brillouin zone.

$$u_j(\mathbf{r}, \mathbf{k}) = u_j(\mathbf{r} + \mathbf{L}, \mathbf{k}) \quad \text{have periodicity of lattice} \tag{22}$$

If we expand in PWs:

$$u_j(\mathbf{r}, \mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_j(\mathbf{G}, \mathbf{k}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{23}$$

$$\phi_j(\mathbf{r}, \mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_j(\mathbf{G}, \mathbf{k}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \tag{24}$$

$$\begin{aligned} n(\mathbf{r}) &= \frac{1}{\Omega} \sum_j \int d\mathbf{k}\, f_j(\mathbf{k}) \sum_{\mathbf{G},\mathbf{G}'} C^*_j(\mathbf{G}', \mathbf{k}) C_j(\mathbf{G}, \mathbf{k}) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \\ &= \frac{1}{\Omega} \sum_{\mathbf{G}} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \end{aligned} \tag{25}$$

In real calculations, need to truncate infinite sum over $\mathbf{G}$ and need to approximate integration over 1st Brillouin zone by discrete sum over a set of $\mathbf{k}$-points:

$$\int d\mathbf{k} \to \sum_{\mathbf{k}} w_{\mathbf{k}} \quad \text{(weights of integration points)} \tag{26}$$

$$V^{\mathrm{KS}}(\mathbf{G}) \quad \text{converges rapidly with increasing } |\mathbf{G}|$$

At each k-point, only $\mathbf{G}$-vectors with KE lower than max cutoff are included in basis

$$\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 \leq E_{\mathrm{cut}} \tag{27}$$

Precision of calc is controlled by E_{cut}
Number of PWs, N_{pw}, depends on unit cell & k-points. For a given E_{cut}:

$$N_{\mathrm{pw}} = \frac{\Omega}{2\pi^2} E_{\mathrm{cut}}^{3/2} \tag{28}$$

Number PWs at given density cutoff is 8 times number PWs needed for orbitals

VI. PSEUDOPOTENTIALS (PP)

Represent long range interactions of core e^- & produce pseudo WF that approach full WF outside core radius r_c. Inside r_c, PP & WF are as smooth as possible to allow small PW basis.

Smooth, nodeless WF close to nucleus.

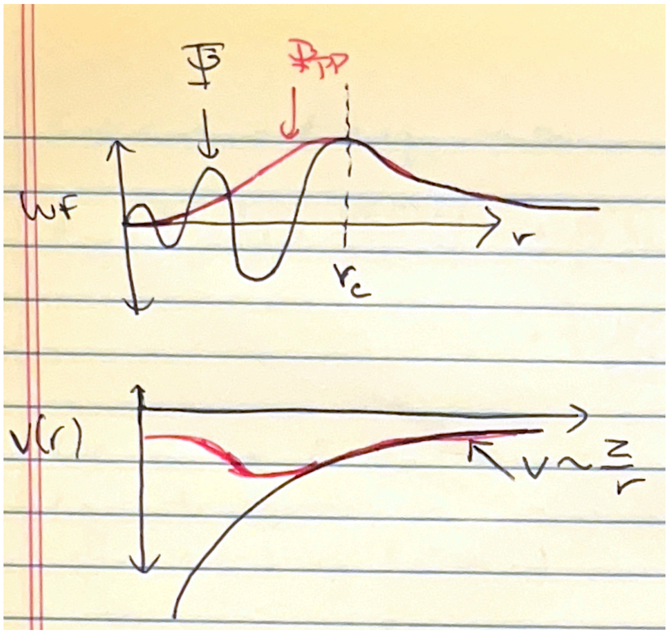


FIG. 1. Sketch of WF, PP WF, and resulting potentials.

Norm-conserving PPs are angular momentum-dependent and involve spherical harmonics.

Can use PPs with a separable form that contains a local part and a nonlocal part which give rise to local and non-local potentials.

Now we have set up the representation of our system: DFT, basis sets, PPs, PBCs.
Now we can compute the contributions to the energy, finally!

VII. ELECTROSTATIC ENERGY

First component of energy to think about is electrostatic

$$E_{\text{es}} = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \sum_I \int d\mathbf{r}\, V_I^{\text{core}}(\mathbf{r})\, n(\mathbf{r}) + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{29}$$

We can use Ewald method, but we want to use a single charge density for everything (e.g. nuclei). To do so, we associate a Gaussian core charge distribution with each nucleus

$$n_I^c(\mathbf{r}) = -\frac{Z_I}{(R_I^c)^3\pi^{3/2}}\exp\left[-\frac{|\mathbf{r}-\mathbf{R}_I|^2}{(R_I^c)^2}\right] \tag{30}$$

Then we make the core potential that of a Gaussian charge

$$V_I^{\text{core}}(\mathbf{r}) = \int d\mathbf{r}'\,\frac{n_I^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\,\text{erf}\left[\frac{|\mathbf{r}-\mathbf{R}_I|}{R_I^c}\right] \tag{31}$$

Then add and subtract energy of Gaussians to E_{es}

$$\begin{aligned} E_{\text{es}} = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\Big(n(\mathbf{r})n(\mathbf{r}') + n^c(\mathbf{r})n^c(\mathbf{r}') + 2n^c(\mathbf{r})n(\mathbf{r}')\Big) \\ + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{n^c(\mathbf{r})n^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{aligned} \tag{32}$$

$$n^c(\mathbf{r}) = \sum_I n_I^c(\mathbf{r}) \tag{33}$$

$$n^{\text{tot}}(\mathbf{r}) = n(\mathbf{r}) + n^C(\mathbf{r}) \tag{34}$$

Last two terms involve nuclei, including self-energy terms, which can be rewritten as

$$E_{\text{ES}} = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}'\,\frac{n^{\text{tot}}(\mathbf{r})\, n^{\text{tot}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\,\text{erfc}\left[\frac{|\mathbf{R}_I-\mathbf{R}_J|}{\sqrt{{R_I^c}^2 + {R_J^c}^2}}\right] - \sum_I \frac{1}{\sqrt{\pi}}\frac{Z_I^2}{R_I^c} \tag{35}$$

Total E per unit cell derived for periodic system by using sol'n to Poisson's Eq in Fourier space:

$$E_{\text{ES}} = 2\pi\Omega\sum_{\mathbf{G}\neq 0}\frac{|n^{\text{tot}}(\mathbf{G})|^2}{G^2} + E_{\text{overlap}} - E_{\text{self}} \tag{36}$$

$$E_{\text{overlap}} = \sum_{I\neq J}{}^{'}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J-\mathbf{L}|}\,\text{erfc}\left[\frac{|\mathbf{R}_I-\mathbf{R}_J-\mathbf{L}|}{\sqrt{{R_I^c}^2 + {R_J^c}^2}}\right] \tag{37}$$

Prime means $I \leq J$ for $\mathbf{L} = 0$ term.

$$E_{\text{self}} = \sum_I \frac{1}{\sqrt{\pi}}\frac{Z_I^2}{R_I^c} \tag{38}$$

In the end, our total energy is

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{loc}}^{\text{PP}} + E_{\text{nloc}}^{\text{PP}} + E_{\text{xc}} + E_{\text{ES}} \tag{39}$$

Now that we have the total energy, we can take derivatives to get forces!

VIII. HELLMAN-FEYNMAN FORCES

Force on atom I is

$$\mathbf{F}_I = -\nabla_I \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle \tag{40}$$

Direct evaluation with finite differences is too costly and too inaccurate.
Can we make progress analytically?

Hellman-Feynman Theorem (HFT)

$$\begin{aligned}
\nabla_I \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle &= \langle \nabla_I \Psi_0 | \hat{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{H}_e | \nabla_I \Psi_0 \rangle \\
&= E_0 \langle \nabla_I \Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle + E_0 \langle \Psi_0 | \nabla_I \Psi_0 \rangle \\
&= E_0 \nabla_I \langle \Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle \\
&= \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle
\end{aligned} \tag{41}$$

If wavefunction is exact eigenvalue of $\hat{H}_e$:

$$\mathbf{F}_I = -\langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle \tag{42}$$

If wavefunction is not exact eigenvalue of $\hat{H}_e$, which is always true in practice, we have additional terms in force.
Due to incomplete basis sets (IBS / Pulay Force) and non-self-consistency (NSC Force).
Can write down what these are (but we won't here).
Total force is:

$$\mathbf{F}_I = \mathbf{F}_I^{\mathrm{HFT}} + \mathbf{F}_I^{\mathrm{IBS}} + \mathbf{F}_I^{\mathrm{NSC}} \tag{43}$$

Self-consistency is never satisfied in numerical calc.

- If SC is exactly satisfied, $\mathbf{F}_I^{\mathrm{NSC}} = 0$, $\mathbf{F}_I^{\mathrm{IBS}}$ is not.
- IBS/Pulay force vanishes in limit of complete basis set (not possible in actual calc).
- If WF is expanded in originless basis like plane waves, Pulay force vanishes!
- If # PWs not constant (e.g., cell size changes w/ fixed energy cutoff), Pulay stress contributions appear.

To actually take these gradients to get $\mathbf{F}_I^{\mathrm{HFT}}$, need gradient for WF and nuclear positions:

$$\frac{\partial E_{\mathrm{tot}}}{\partial c^*(\mathbf{G})} \quad \text{and} \quad \frac{\partial E_{\mathrm{tot}}}{\partial \mathbf{R}_I}$$

Stress tensor:

$$\Pi_{u\nu} = -\frac{1}{\Omega} \sum_s \frac{\partial E_{\mathrm{tot}}}{\partial h_{us}} h_{s\nu}^T \qquad \frac{\partial \Omega}{\partial h_{u\nu}} = \Omega (h^{-1})_{u\nu} \tag{44}$$

WHAT CAN WE DO WITH FORCES?

Molecular dynamics simulations

- Want to do stat mech
- Want to compute ensemble average of an observable $O(\mathbf{R}, \mathbf{P})$

In canonical ensemble:

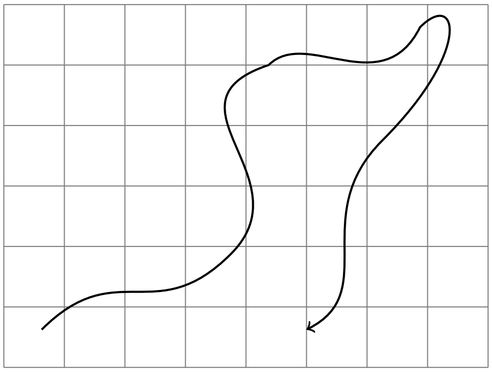
$$\langle O(\mathbf{R},\mathbf{P})\rangle = \frac{\int d\mathbf{R} \int d\mathbf{P}\, O(\mathbf{R},\mathbf{P}) e^{-\beta H(\mathbf{R},\mathbf{P})}}{\int d\mathbf{R} \int d\mathbf{P}\, e^{-\beta H(\mathbf{R},\mathbf{P})}} \tag{45}$$

Instead, we compute dynamics and observables along a trajectory.

Can replace ensemble average by time average under assumption of ergodicity:

$$\langle O(\mathbf{R},\mathbf{P})\rangle = \frac{\int d\mathbf{R} \int d\mathbf{P}\, O(\mathbf{R},\mathbf{P}) e^{-\beta H(\mathbf{R},\mathbf{P})}}{\int d\mathbf{R} \int d\mathbf{P}\, e^{-\beta H(\mathbf{R},\mathbf{P})}} \approx \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, O(\mathbf{R}(t),\mathbf{P}(t)) = \bar{O} \tag{46}$$

Ergodic hypothesis:



Can derive MD equations of motion for different “flavors” by starting w/ TDSE and making systematic approximations.

We only have time to discuss main features.

Let’s focus on 3 flavors of MD

IX. EHRENFEST MD

- Treat nuclei classically but electrons & their dynamics w/ Q.M.

Ehrenfest MD makes a “one-determinant” or “single configuration” ansatz for the total WF

$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \approx \Psi(\{\mathbf{r}_i\};t)\,\chi(\{\mathbf{R}_I\};t) \tag{47}$$

Must lead to mean field approx for coupled dynamics. Resulting coupled equations (TDSCF, Dirac 1930) are

$$i\hbar\frac{\partial}{\partial t}\Psi(\{\mathbf{r}_i\};t) = -\sum \frac{\hbar^2}{2m_e}\nabla^2\Psi + \chi\langle \hat{V}_{ne}\rangle\chi\,\Psi \tag{48}$$

$$i\hbar\frac{\partial}{\partial t}\chi(\{\mathbf{R}_I\};t) = -\sum \frac{\hbar^2}{2M_I}\nabla^2_{\mathbf{R}_I}\chi + \Psi\langle \hat{V}_{eI}\rangle\Psi\,\chi \tag{49}$$

e^- and nuclei move in presence of time-dependent effective fields (averages) and this is mean field description of quantum dynamics.

Take classical limit for nuclei:

$$M_\alpha \ddot{\mathbf{R}}_\alpha(t) = -\nabla_\alpha V_E^e\left(\{\mathbf{R}_\alpha(t)\}\right) \tag{50}$$

⇒ Newton’s Eq. for nuclei.

Nuclei move according to classical mechanics in effective potential V_E^e called *Ehrenfest potential*, given by quantum dynamics of e^- by solving electronic TDSE:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\Psi + V_{n-e}\left(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha(t)\}\right)\Psi \tag{51}$$

$$= \hat{H}_e\left(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha(t)\}\right)\Psi \tag{52}$$

$\hat{H}_e$ depends parametrically on classical nuclear positions $\{\mathbf{R}_\alpha(t)\}$ through V_{n-e}.
Feedback between classical and quantum DOFs incorporated in both directions at MF level.
Newton's Eq. for nuclei + TDSE for e^- = Ehrenfest MD
→ Paul Ehrenfest 1927
Ehrenfest MD allows transitions between electronic states:
⇒ Can expand WF in basis of electronic states

$$\Psi = \sum_{k=0}^{g} C_k(t)\varphi_k \tag{53}$$

X. BORN-OPPENHEIMER MD

Ehrenfest MD reduces to BOMD by restricting Ψ to G.S. adiabatic WF Φ_0 of $\hat{H}_e$ at each instant in time.
Good approx if $E_1 - E_0 \gg k_B T$ everywhere.
In this limit,

$$V^E = \int d\mathbf{r}\,\Phi_0^*\hat{H}_e\Phi_0 \equiv E_0(\{\mathbf{R}_I\}) \tag{54}$$

The ground state BO potential energy surface by solving the electronic TISE at each nuclear config $\{\mathbf{R}_I\}$ generated during MD:

$$V^E = E_0 \equiv V^{BO} \tag{55}$$

Can decouple generating classical nuc dynamics from computing quantum PES.
Do classical dynamics on nuclei and then solve electronic problem "on the fly" at each instant in time.
→ Ab initio MD
In BOMD, given set of nuclear positions $\{\mathbf{R}_i\}$ at an instant in time, solve static electronic structure problem.
Time-dependence of ES is imposed/dictated by parametric dependence on classical dynamics of nuclei:

$$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0}\left\{\langle\Psi_0|\hat{H}_e|\Psi_0\rangle\right\} \tag{56}$$

$$\hat{H}_e\Psi_0 = \mathcal{E}\Psi_0 \tag{57}$$

BOMD neglects both non-diagonal and diagonal corrections ⇒ it is **not** adiabatic MD because it does not include diagonal corrections.
Assume we represent Ψ_0 with some set of orbitals $\{\phi_i\}$, e.g., Kohn-Sham orbitals.
Constrained energy minimization becomes:

$$\min_{\{\phi_i\}}\left\{\langle\Psi_0|\hat{H}_e|\Psi_0\rangle\right\} \quad \text{s.t.} \quad \langle\phi_i|\phi_j\rangle = \delta_{ij} \tag{58}$$

Constraints become Lagrange multipliers in dynamics:

$$\mathcal{L} = \langle\Psi_0|\hat{H}_e|\Psi_0\rangle + \sum_{i,j}\Lambda_{ij}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right) \tag{59}$$

Minimization leads to EOM:

$$0 = -\hat{H}_e \phi_i + \sum_j \Lambda_{ij} \phi_j \tag{60}$$

BOMD EOM are

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \left\langle \Psi \middle| \hat{H}_e \middle| \Psi \right\rangle \tag{61}$$

$$\hat{H}_e \phi_i + \sum_j \Lambda_{ij} \phi_j \tag{62}$$

XI. CAR-PARRINELLO MD

BOMD allows for large time steps when integrating EOM but needs to solve ES problem at each time step.

Ehrenfest MD doesn't need to solve ES problem but needs to propagate electronic dynamics which requires small timestep.

Car and Parrinello tried to bridge these two methods with CPMD.

CPMD evolves electron dynamics efficiently and tries to get to large timestep for nuclear dynamics, but it's a compromise.

CPMD maps two-component quantum/classical problem onto two-component purely classical problem with two separate energy scales → loses physical time info of quantum subsystem dynamics.

Orbitals → classical field

CPMD EoMs:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle \Psi | \hat{H}_e^{KS} | \Psi \rangle \tag{63}$$

$$\mu \ddot{\phi}_i(t) = -\hat{H}_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j \tag{64}$$

μ is the effective mass / fictitious mass / adiabaticity parameter

For CPMD to work, vibrational DOS of nuc + e^- subsystems need to be sufficiently decoupled so that the two subsystems stay decoupled → essentially maintaining a metastable system.

Lowest possible e^- frequency:

$$\omega_e^{\min} \propto \left(\frac{E_{\text{gap}}}{\mu} \right)^{1/2} \tag{65}$$

$$\Delta t^{\max} \propto \left(\frac{\mu}{E_{\text{cut}}} \right)^{1/2} \tag{66}$$

CPMD needs fine tuning to maximize $\Delta t^{\max}$, $\omega_{\min}$, and $\omega_{\max} \propto \left(\frac{E_{\text{cut}}}{\mu} \right)^{1/2}$.

If $E_{\text{gap}} \to 0$, μ needs to go to zero $\Rightarrow \Delta t^{\max} \to 0$.

Use BOMD for metals!

XII. SUMMARY OF EOMS

BOMD:

$$\text{Nuclei}: \quad M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I E_{\text{tot}}\{\mathbf{R}_I(t)\} \tag{67}$$

$$\text{Electrons}: \quad 0 = \hat{H}\phi_i + \sum_j \lambda_{ij}\phi_j \tag{68}$$

CPMD:

$$\text{Nuclei}: \quad M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I E_{\text{tot}}[\rho] \tag{69}$$

$$\text{Electrons}: \quad \mu\ddot{\phi}_i(t) = -\hat{H}\phi_i + \sum_j \lambda_{ij}\phi_j \tag{70}$$

EMD:

$$\text{Nuclei}: \quad M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I E_{\text{tot}}[\rho] \tag{71}$$

$$\text{Electrons}: \quad i\hbar\dot{\psi}_n(t) = \hat{H}\psi_n \tag{72}$$

Alternatively we could treat everything classically by developing an approx of the total ground state PES:

$$V_e \simeq V_e^{FF}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} V_1(\mathbf{R}_I) + \sum_{I<J}^{N} V_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K}^{N} V_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \dots \tag{73}$$

This is a "forcefield" that reduces problem entirely to classical mechanics by replacing e$^-$ DOFs by effective interaction potentials.

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{FF}(\{\mathbf{R}_I(t)\}) \tag{74}$$

Latest revolution in materials is using ML to model the PES, e.g., with neural network (NN) potentials:

$$V_e \simeq V_e^{NN}(\{\mathbf{R}_I\}) \tag{75}$$

By "training" NN on *ab initio* energies and forces, NN can learn the PES with high accuracy and predict V_e much more efficiently than *ab initio* methods.