Mathematics

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Some math (or physics?)

- Schrodinger equation: minimize $E^{\mathrm{S}}\big(\varphi(R_1, \dots, R_N; r_1, \dots, r_n)\big)$
- Born-Oppenheimer: minimize $E^{\mathrm{BO}}\big(R_1, \dots, R_N;\ \varphi(r_1, \dots, r_n)\big)$
- Exact DFT functional: minimize $E^{\mathrm{dft}}\big(R_1, \dots, R_N; \rho(\xi)\big)$, where

$$E^{\mathrm{dft}}\big(R_1, \dots, R_N; \rho(\xi)\big) = \min_{\varphi} E^{\mathrm{BO}}\big(R_1, \dots, R_N;\ \varphi(r_1, \dots, r_n)\big)$$

$$\text{subject to } \rho(r_1) = n \int \varphi\bar{\varphi}\, \mathrm{d}r_2 \dots \mathrm{d}r_{\mathrm{n}}$$

- Interatomic potentials: minimize $E^{\mathrm{ip}}(R_1, \dots, R_N)$, where

$$E^{\mathrm{ip}}(R_1, \dots, R_N) = \min_{\rho} E^{\mathrm{dft}}\big(R_1, \dots, R_N; \rho(r)\big)$$

Hohenberg Kohn Sham

- Interested in ground state (potential energy surface)

$$\mathrm{PES}(R_1, \ldots, R_N) = \min_{\varphi} E^{\mathrm{BO}}\big(R_1, \ldots, R_N;\ \varphi(r_1, \ldots, r_n)\big)$$

- Let’s do the minimization in two steps:

$$\min_{\rho} \min_{\varphi:\,\varphi\sim\rho} E^{\mathrm{BO}}\big(R_1, \ldots, R_N;\ \varphi(r_1, \ldots, r_n)\big)$$

$$\min_{\rho} \underbrace{\min_{\varphi:\,\varphi\sim\rho} E^{\mathrm{BO}}\big(R_1, \ldots, R_N;\ \varphi(r_1, \ldots, r_n)\big)}_{=:E^{\mathrm{exact-dft}}\left(R_1,\ldots,R_N,\rho(r)\right)}$$

- Ground state problem now:

$$\min_{\rho} E^{\mathrm{exact-dft}}\big(R_1, \ldots, R_N, \rho(r)\big)$$

Some math (or physics?)

- Interatomic potentials: minimize $E^{\mathrm{ip}}(R_1, \ldots, R_n)$, where

$$E^{\mathrm{ip}}(R_1, \ldots, R_n) = \min_{\rho} E^{\mathrm{dft}}\big(R_1, \ldots, R_n; \rho(\xi)\big)$$

- Magnetic disorder: many local minima of $E^{\mathrm{dft}}\big(R_1, \ldots, R_n; \rho(\xi)\big)$. Then

$$E^{\mathrm{ip}}(R_1, \ldots, R_n; s_1, \ldots, s_n) = \min_{\rho} E^{\mathrm{dft}}\big(R_1, \ldots, R_n; \rho(\xi)\big)$$

$$\text{subject to } s_i = \int_{\text{around } x_i} (\rho^+(x) - \rho^-(x))\,\mathrm{d}x$$

On-lattice (cluster expansion) type potentials

- Start with $E^{\mathrm{ip}}(x_1, \dots, x_n; z_1, \dots, z_n)$, here by x_i I mean displacements from ideal lattice
- Define:

$$E^{\mathrm{lat}}(z_1, \dots, z_n) = \min_{x_1, \dots, x_n} E^{\mathrm{ip}}(x_1, \dots, x_n; z_1, \dots, z_n)$$

- Works if $z_1, \dots, z_n$ define well the corresponding minimum of energy

Provocative question: all we are doing is a botany of near-ground state – is it true?

On-lattice (cluster expansion) type potentials

- Finite temperature? No problem*:

$$E^{\mathrm{lat}}(z_1, \dots, z_n)$$
$$= -k_{\mathrm{B}}T \ \log \int \ \exp\left(-E^{\mathrm{ip}}(x_1, \dots, x_n; z_1, \dots, z_n)/(k_{\mathrm{B}}T)\right) \ \mathrm{d}\boldsymbol{x}$$

- Works if $z_1, \dots, z_n$ define well the corresponding minimum of free energy

* Conceptually

Hellmann Feynman aka 2n+1 theorem

- Ground state wrt electronic degrees of freedom (DoF):
$$E(\boldsymbol{x}) = \min_{\rho} \hat{E}(\boldsymbol{x}, \rho)$$
- Let’s denote by $\rho^*(\boldsymbol{x})$ the minimizer of $\hat{E}(\boldsymbol{x}, \rho)$ for a given $\boldsymbol{x}$.

  (Mathematicians say $E(\boldsymbol{x}) = \hat{E}\left(\boldsymbol{x}, \rho^*(\boldsymbol{x})\right)$,
  where $\rho^*(\boldsymbol{x}) = \mathrm{argmin}_{\rho}\, \hat{E}(\boldsymbol{x}, \rho)$)
- Minimum = derivatives are zero:
$$\nabla_{\rho} \hat{E}\left(\boldsymbol{x}, \rho^*(\boldsymbol{x})\right) = 0$$
- Hence forces:
$$\nabla_x E(\boldsymbol{x}) = \nabla_x \hat{E}\left(\boldsymbol{x}, \rho^*(\boldsymbol{x})\right) + \left\langle \underbrace{\nabla_{\rho} \hat{E}\left(\boldsymbol{x}, \rho^*(\boldsymbol{x})\right)}_{=0}, \nabla_x \rho^*(\boldsymbol{x}) \right\rangle$$

Equilibrium Thermodynamics

- Having energy $E(\boldsymbol{x})$ and inverse temperature $\beta = (k_\mathrm{B}T)^{-1}$, the probability (density) of seeing state $\boldsymbol{x}$ is proportional to $\exp\big(-\beta E(\boldsymbol{x})\big)$
- Hence probability density $= Z^{-1}\exp\big(-\beta E(\boldsymbol{x})\big)$, where the normalizing factor

$$Z = Z(\beta) = \int \exp\big(-\beta E(\boldsymbol{x})\big)\,\mathrm{d}\boldsymbol{x}$$

is called the partition function

Equilibrium Thermodynamics

- Imagine phase A given by a set of states A and phase B given by the set B
- Then probability of A is

$$p(A) = Z^{-1} \int_A \exp\big(-\beta E(\boldsymbol{x})\big)\, \mathrm{d}\boldsymbol{x}, \qquad \text{and}$$

$$p(B) = Z^{-1} \int_B \exp\big(-\beta E(\boldsymbol{x})\big)\, \mathrm{d}\boldsymbol{x}$$

- Free energy of *A* is $F(A) = -\beta^{-1} \log\left(\int_A \exp\big(-\beta E(\boldsymbol{x})\big)\, \mathrm{d}\boldsymbol{x}\right)$
- $p(A) \sim -\exp\big(F(A)\big)$. In fact, as number of DoF $\to \infty$, $p(A) \to 0$ or 1 (depending whether *A* is a ground state).

Thermodynamic integration

- Free energy $F(A) = -\beta^{-1} \log\left(\int \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}\right)$ is hard to compute directly (it is a multidimensional integral)
- But its derivative with respect to any variable *v* is easy:

$$\frac{\mathrm{d}F}{\mathrm{d}v} = \frac{\int \frac{\mathrm{d}E}{\mathrm{d}v} \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}}{\int \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}} = \mathbb{E}\left[\frac{\mathrm{d}E}{\mathrm{d}v}\right]$$

(Boltzmann average that is usually computed in MD)

Ergodicity

Theorem: integral over a long trajectory $=$ integral wrt Boltzmann distribution:

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T f\big(\boldsymbol{x}(t)\big)\mathrm{d}t = \mathbb{E}[f(x)]$$

- (You prove it for a realistic system -> Fields medal)

Example (sloppily done)

- Pressure as derivative of free energy wrt volume:

$$\frac{\mathrm{d}F}{\mathrm{d}V} = \frac{\int \frac{\mathrm{d}E}{\mathrm{d}V} \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}}{\int \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}} = \mathbb{E}[p(x)]$$

- can be done by averaging pressure over the course of MD

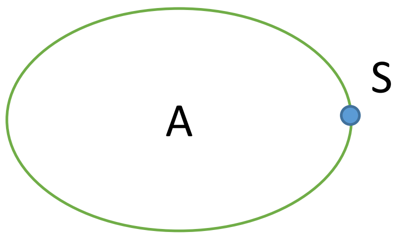
more carefully:

$$\frac{\mathrm{d}F}{\mathrm{d}V} = \frac{\int_{\boldsymbol{V}} \frac{\mathrm{d}E}{\mathrm{d}V} \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}}{\int_{\boldsymbol{V}} \exp\left(-\beta E(\boldsymbol{x})\right) \mathrm{d}\boldsymbol{x}} + \beta^{-1} \log(\beta^{-1} V)$$

$$= \mathbb{E}\left[p_{\text{virial}}(x) + \frac{\beta^{-1}}{V}\right] = \mathbb{E}[p_{\text{full}}(x)]$$

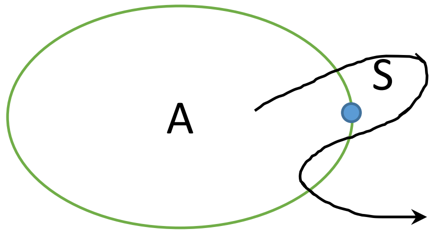
Transition state theory

- Count the number of times an infinite trajectory crosses surface S from state A:



$$\nu = \frac{\int_S \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}{\int_A \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}$$

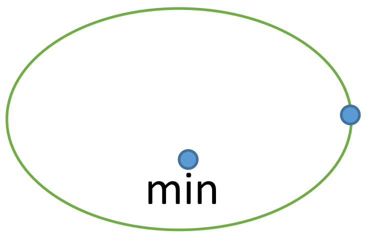
- Not entirely what we want: recrossings (counts as two)



Transition state theory

- TST:

$$\nu = \frac{\int_S \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}{\int_A \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}$$



- Harmonic TST: Taylor expansion in β^{-1}:

$$-\beta^{-1}\log(\nu) = E_{\mathrm{TS}}(\boldsymbol{x}) - E_{\min}(\boldsymbol{x}) - \beta^{-1}\log(\mathrm{pF}),$$

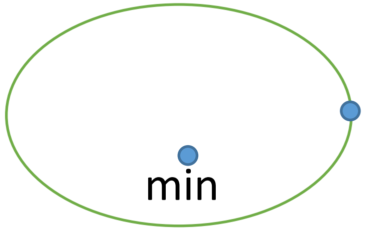
where pF is called the prefactor that depends on oscillation frequencies at min and TS. From here

$$\nu = \mathrm{pF}\exp\left(-\beta\left(E_{\mathrm{TS}}(\boldsymbol{x}) - E_{\min}(\boldsymbol{x})\right)\right) + O(\beta^{-1})$$

Idea:

- TST:

$$\nu = \frac{\int_S \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}{\int_A \exp(-\beta E(\boldsymbol{x}))\,\mathrm{d}\boldsymbol{x}}$$



$$\exp \int \left(-\beta E(x_{\min}) - \frac{\beta E''(x_{\min})(x - x_{\min})^2}{2}\right) \mathrm{d}x$$

$$= \exp(-\beta E(x_{\min})) \quad \sqrt{\frac{2\,\pi}{\beta\; E''(x_{\min})}}$$

Exponential factor

prefactor