Locality

self-consistent Coulomb interactions for MLIPs
w/ W. Baldwin
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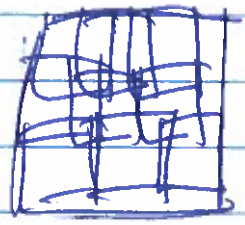
2025

~~2025~~
↗ e.g. Chen, Fang, Ortner arXiv 2025

Locality of Wannier functions ⟹ Density matrix "nearsightedness" $\rho(x,y) \to 0$ as $|x-y| \to \infty$ ⇝ $O(N)$ method "divide-and-conquer" etc...

e.g. insulators
$|\rho(x,y)| \lesssim e^{-\gamma|x-y|}$
$\gamma \leftrightarrow$ spectral gap



$O(n^3) \times N$ vs $O(N^3)$

Not sufficient to justify QM/MM methods or (ML) IPs

$$E^{QM} \approx \mathbb{E} = \sum_i \mathbb{E}_i$$ ← "local + simple"

Need locality of forces:

$$F_i := \frac{\partial E}{\partial r_i}$$

$$\left|\frac{\partial F_i}{\partial r_k}\right| \to 0 \text{ "sufficiently rapidly"}$$

e.g. Decay of IFC in rH
w/ Cances, Levitt
arXiv 2025

Stronger: Energy locality

$$E = \sum_l E_l, \quad \left|\frac{\partial E_l}{\partial r_m}\right| \lesssim e^{-\gamma r_{lm}} + \text{higher derivatives}$$

Tight binding models:

- Chen, Ortner 2016 ← QM/MM I
- Chen, Lu, Ortner 2018 ← Thermodynamic limits w/ defects
- Ortner, JT, Chen 2020 ← improved results for point defects in insulators

SCREENED COULOMB

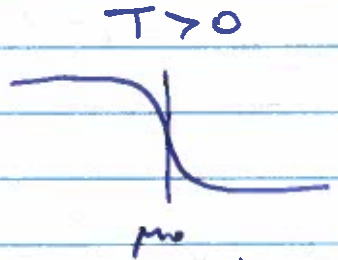
$|[H_0]_{lm}| \lesssim e^{-\gamma r_{lm}}$ ← improved results for point defects in insulators

- JT 2020 ← self-consistent model

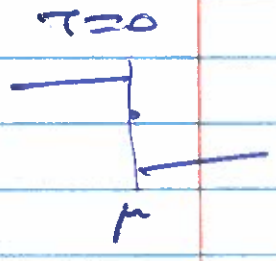
+ derivatives

e.g. band energy $E = \sum_n \varepsilon_n f(\varepsilon_n)$ ← Fermi-Dirac

where $H\psi_n = \varepsilon_n \psi_n$ ← Tight binding Hamiltonian

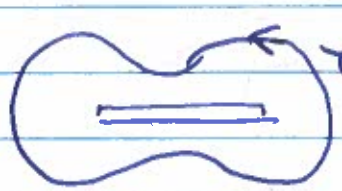


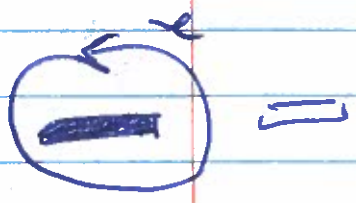
$$f(x) = \frac{1}{1+e^{(x-\mu)/T}}$$



$$\mathbb{1}_{(-\infty,\mu)}(x)$$

$$E = \sum_n e(\varepsilon_n) = \mathrm{Tr}\, e(H) = \sum_l e(H)_{ll}$$





$$E_l = \oint_e e(z)\,(z-H)^{-1}_{ll}\,\frac{dz}{2\pi i}$$

$$\frac{\partial E_l}{\partial r_m} = \oint_e e(z)\,\boxed{(z-H)^{-1}_{lm}}\,\frac{\partial H_{mn}}{\partial r_m}\,\boxed{(z-H)^{-1}_{nl}}\,\frac{dz}{2\pi i}$$

DECAY

Lemma [$|(z-H)^{-1}_{lm}| \lesssim e^{-\gamma r_{lm}}$

~~$\gamma \gtrsim \text{dist}(z, \sigma(H))$ as~~

$\gamma = c \min(1, \text{dist}(z, \sigma(H)))$]

Fun "proof" If $[H]_{lm} = 0 \quad \forall r_{lm} \geq n$ (simplify)

Then $(H^n)_{lm} = \sum_{l_1, \dots, l_{n-1}} H_{ll_1} H_{l_1 l_2} \cdots H_{l_{n-1} m} = 0$

$\forall r_{lm} \geq mn$

So $|(z-H)^{-1}_{lm}| = \min_{P_n \in \mathcal{P}_n} |(z-H)^{-1}_{lm} - P_n(H)_{lm}|$

(for $n \leq \frac{r_{lm}}{m}$)

polynomials of degree $\leq n$

$\leq \min_{P_n \in \mathcal{P}_n} \| (z-\cdot)^{-1} - P_n \|_{L^\infty(\sigma(H))}$

$\lesssim e^{-\gamma n} \approx e^{-\frac{\gamma}{m} r_{lm}}$. □

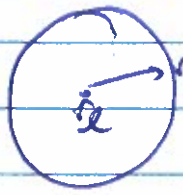
Approx. Theory

~~**Question** what is missing?~~

$E^{QM} \approx E = \sum_l E_l$

$E_l \approx E_l(\{r_{lm}\}_{r_{lm} \leq r_{cut}})$

Tight Binding — local — "simple"



[Body-ordered approx. atomic properties w/ Chen, Ortner, 2022]

ASSUMPTION

Coulomb interaction screened

$$E_i \approx V_0 + \sum_{u \neq i} V_1(\xi, r_{iu}) + \sum_{u_1, u_2 \neq i} V_2(r_{iu_1}, r_{iu_2}) + \cdots + \sum_{u_1, \ldots, u_N \neq i} V_N(r_{iu_1}, \ldots, r_{iu_N})$$

"body-ordered approximation"

Missing? Coulomb ⟶ (i) charge equilibriation
(ii) locally learnable

Example 1 (classical Electronegativity Equalization Method)

Add partial charges $q_i := Z_i - P_i$

(Z_i: atomic species, P_i: electron population)

Consider an extended PES $E(\underline{r}, q)$

$$= \sum_i \left[\varepsilon_i + \chi_i q_i + U_i q_i^2 \right] + \sum_{i<k} J_{ik} q_i q_k$$

$\varepsilon_i + \chi_i q_i + U_i q_i^2$: Taylor series expansion of individual atomic energies

J_{ik}: Coulomb

min to q "self-consistency" (linear-N-q + constraint)

χ_i electronegativity, U_i atomic hardnesses

- want a systematically improvable version of this.

Example 2 (CCENT Charge equilibriation via NN technique)

$\chi_i = \chi_i(\underline{r})$ – learn from NN

$$\{r_{ch}\}_{ch\neq e} \mapsto_{\text{local, NL}} \chi_e(\underline{r})$$

$$\chi \mapsto_{\text{linear}} q \mapsto_{\text{exact}} E, \nabla E$$

- can only describe systems where the ground state electron density is a smooth function of the geometry
- also not systematically improvable.

Example 3 (BpopNN)

↑ Behler population Neural Network

$$E(\underline{r}, q) = \sum_e \left[E_e(r, q) + \xi_e + \chi_e q_e + U_e q_e^2 \right] + \sum_{e<ch} J_{eh}\, q_e q_h$$

$$q_e = z_e - \int \rho_{n_I}(x)\, w(x - r_e)\, dx$$

Train: $E(\underline{r}, q) \approx \min_{\Psi \to q} \langle \Psi | \mathcal{H} | \Psi \rangle$

$\min_q$ → resembles the charge-equilibration in DFT models

→ self-consistently adapt part of electronic degrees of freedom

Aim: rigorously justify this approach

Idea: (Add atom-centred features) + minimise to SC. which provide a low-dimensional

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In our case, we write

$$E(\underline{r},\hat{v}) = \sum_\ell \left[E_\ell(\underline{r},\hat{v}) + E_{el}[\rho(r,\hat{v})] \right]$$

$$= \sum_\ell \left[\rho_\ell(r,\hat{v}) \right]$$

- E_ℓ: LOCAL AS A FUNCTION OF $\{\underline{r}_{\ell\alpha}, \hat{v}_\ell\}_\ell$
- E_{el}: explicit long-range functional

MR

Approximate:

$E_\ell \approx E_\ell^N$

$\rho_\ell \approx \rho_\ell^N$

Show: || minimizers $\hat{v}^*$ of $E(\underline{r},\hat{v})$ can be approached by minimizers $\hat{v}_N^*$ of $E^N(\underline{r},\hat{v})$

* systematically improvable
  ↳ convergence as we choose larger N

$$\mathcal{E}^{qm}(\gamma) = \mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] + \int \rho_\gamma V^{nuc} + \tfrac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} - \mu S[\rho_\gamma]$$

(← Grand canonical)

→ minimize over density matrices $\mathcal{P}$

$$\gamma^0 = f\left(-\tfrac{1}{2}\Delta + V_{eff}[\rho^0]\right)$$

$$V_{eff}[\rho] = V^{nuc} + V_c\rho = V_c(\rho - z)$$

Self-consistent!

* Tight binding
* + expand effective potential

⇒ local features

Tight binding $\gamma = \sum_i f_i |i\rangle\langle i|$
$(0 \le f_i \le 1, \ \sum_i f_i = N_el)$

Expand $|i\rangle = \sum_{la} c^i_{la} \phi_{la}$ ← atom centered fast decay.

$\Rightarrow \gamma = \sum_{lalbsb} \phi_{la}(x) [\gamma_{TB}]_{la,sb} \phi_{sb}(y)$

$\sum_i f_i c^i_{la} c^i_{sb}$

$\mathcal{E}^{QM}(\gamma)$ minimised over $P^{TB} \subseteq P$.

$= \mathrm{Tr}\, H_0 \gamma_{TB} + E_{el}[\rho_\gamma]$

$-\mu \int \mathrm{Tr}\, \gamma_{TB}$ ← Grand canonical ensemble

$\int \rho V^{nuc} + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|}$ ← explicit long range Hartree

$\rightsquigarrow \gamma^0_{TB} = f(H^{TB}[\rho^0_{TB}])$

$H^{TB}[\rho]_{lasb} = \int \phi_{la}(x) \left[-\frac{1}{2}\Delta + V_{eff}[\rho]\right] \phi_{sb}(x)$

$= (H_0 + V[\rho])_{lasb}$

Expand effective potential — atom-centred "features" — atom-centered

$V_{eff}[\rho] = \sum_{nc} \hat{V}_{nc} \equiv_{nc}(x)$

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$$\gamma^{\circ}_{\text{TB}} = f(H^{\text{TB}}[\rho^{\circ}])$$

$$H^{\text{TB}}[\rho]_{\text{thds}} = \int \phi_{\text{la}}(x)\left[-\tfrac{1}{2}\Delta + V_{\text{eff}}[\rho]\right]\phi_{\text{ls}}(x)$$

$$= (H_0 + V)_{\text{thds}} \qquad \textstyle\sum_{nc} \hat{V}_{nc} \equiv \Xi_{ss}$$

$\{\hat{V}_{nc}\}$ — atom-centred features $\longleftrightarrow$ $V \in (\mathbb{R}^{M\times M})^{N_b \times N_b}$ — effective potential

$$\mathcal{E} = \text{Tr}\, H_0 f(H_0+V) + E_{el}[\rho] - \mu \text{Tr}\, f(H_0+V)$$

$$\left(\rho(x) = \sum_{\text{thds}} \phi_{\text{la}}(x)\, f(H_0+V)_{\text{thds}}\, \phi_{\text{ls}}(x)\, ds\right)$$

$$E_l := \Sigma_l \left[(H_0-\mu) f(H_0+V)\right]_{ll}$$

LEARN!

$$\rho_l = \sum_l \int_{\text{ds}} \phi_{\text{la}}(x)\, f(H_0+V)_{\text{ds}}\, \phi_{\text{ls}}(x)$$

Claim

$$\left|\frac{\partial E_l}{\partial r_{lh}}\right| \lesssim e^{-\eta r_{lh}}, \quad \left|\frac{\partial E_l}{\partial \hat{V}_{lh}}\right| \lesssim e^{-\eta r_{lh}}$$

$$\left|\frac{\partial \rho_l}{\partial r_{lh}}\right| \lesssim e^{-\eta r_{lh}}, \quad \left|\frac{\partial \rho_l}{\partial \hat{V}_{lh}}\right| \lesssim e^{-\eta r_{lh}}$$