QM/MM Coupling for Crystalline Defects

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QM/MM coupling

Low speed fracture in a brittle crystal [Kermode, Albaret, Sherman, Bernstein, Gumbsch, Payne, Csányi, De Vita, Nature, 2008]

- **QM** (quantum mechanic): DFT, Hartree-Fock, QMC, Tight-binding ...
- **MM** (molecular mechanic): Lennard-Jones, EAM, Gupta ...
Quantum mechanical models

Tight-binding (TB): the minimal electronic structure model
Outline

- Strong Locality of Tight-Binding
- An Energy-Based QM/MM Scheme
Consider a system with $N$ atoms $y = (y_1, \cdots, y_N) \in (\mathbb{R}^d)^N$.

$$E(y) = ?$$
Tight-Binding total energy

Consider a system with $N$ atoms $y = (y_1, \cdots, y_N) \in (\mathbb{R}^d)^N$.

$E(y) = ?$

1. Construct a Hamiltonian matrix $H(y) \in \mathbb{R}^{N \times N}$

$$H_{\ell k}(y) = h(y_\ell - y_k)$$

with some empirical potential $h$.

2. Solve the matrix eigenvalue problem

$$H(y)\psi_s = \varepsilon_s \psi_s \quad s = 1, 2, \cdots$$

3. Calculate the Tight-binding (QM) energy

$$E(y) = \sum_s \varepsilon_s \cdot f(\varepsilon_s)$$

with $f(\varepsilon_s) = \left(1 + \exp[\beta(\varepsilon_s - \mu)]\right)^{-1}$ (smeared step function)
Tight-Binding site energy

\[ E(y) = \sum_{s=1}^{N} \epsilon_s f(\epsilon_s) \]
Tight-Binding site energy

\[ E(y) = \sum_{s=1}^{N} \varepsilon_s f(\varepsilon_s) \left\| \psi_s \right\|_2^2 \]

\[ \psi_s = \left( [\psi_s]_1, \cdots, [\psi_s]_\ell, \cdots, [\psi_s]_N \right) \text{ where } [\psi_s]_\ell \text{ relates to the } \ell \text{th atom} \]

\[ = \sum_{s=1}^{N} \varepsilon_s f(\varepsilon_s) \sum_{\ell=1}^{N} [\psi_s]_\ell^2 \]

\[ = \sum_{\ell=1}^{N} \sum_{s=1}^{N} \varepsilon_s f(\varepsilon_s) [\psi_s]_\ell^2 \quad =: \sum_{\ell=1}^{N} E_\ell(y) \]

where \( E_\ell(y) = \sum_{s=1}^{N} \varepsilon_s f(\varepsilon_s) [\psi_s]_\ell^2 \)
A tight-binding toy model: Hamiltonian

\[ H_{ij} = h(|y_i - y_j|) \quad \text{with} \quad h(r) = e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}. \]

\[ H = \begin{bmatrix}
0 & -1 & -0.225 \\
-1 & 0 & -0.225 \\
-0.225 & -0.225 & 0
\end{bmatrix} \]
A tight-binding toy model: Site energy

Solve the matrix eigenvalue problem

\[ H \psi_s = \varepsilon_s \psi_s \quad s = 1, 2, 3 \]

We have

\[ \varepsilon_1 = -1.1 \quad \psi_1 = [0.68, 0.68, 0.28] \]

\[ \varepsilon_2 = 0.1 \quad \psi_2 = [-0.19, -0.19, 0.96] \]

\[ \varepsilon_3 = 0.0 \quad \psi_3 = [0.71, -0.71, 0.0] \]

Then \[ E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \]
A tight-binding toy model: Site energy

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Then \[ E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = E_1 + E_2 + E_3 \]

with

\[ E_1 = -0.50 \quad E_2 = -0.50 \quad E_3 = 0.01 \]
QM Vs. MM

- MM potential is local: Range of potential $\leq R_{\text{cut}}$

$$E_{\ell}^{\text{MM}}(y) = E_{\ell}^{\text{MM}}(\{y_k, |y_k - y_\ell| \leq R_{\text{cut}}\})$$

- QM does not calculate energy per atom

Does $E_{\ell}^{\text{QM}}(y)$ have similar locality?
Theorem (Strong locality) [HC & Ortner 2015]

Assume that $H(y)$ is local:

$$|H_{\ell k}(y)| \lesssim e^{-cr_{\ell k}}, \quad \left| \frac{\partial H_{\ell k}(y)}{\partial y_m} \right| \lesssim e^{-c(r_{\ell m} + r_{km})}, \quad \partial^k H$$

then

$$\left| \frac{\partial E_\ell(y)}{\partial y_m} \right| \lesssim e^{-\gamma_1 r_{\ell m}}, \quad \left| \frac{\partial^2 E_\ell(y)}{\partial y_m \partial y_n} \right| \lesssim e^{-\gamma_2 (r_{\ell m} + r_{\ell n})}, \quad \partial^k E_\ell$$

- establish a bridge between QM and MM models
- required by QM/MM coupling [Csányi et al 2005]
Other QM models

- orbital-free DFT with Coulomb [Nazar & Ortner 2015]

- reduced Hartree-Fock with Yukawa [HC & Nazar & Ortner 2016]

- with long-range Coulomb potential, \( |\partial_{ym} H_{\ell k}| \lesssim (r_{\ell m}^{-2} + r_{km}^{-2}) e^{-\gamma r_{\ell k}} \),

we can only get \( |\partial_{ym} E_{\ell}(y)| \lesssim r_{\ell m}^{-2} \)
Numerical tests of a toy model

- 2D triangle lattice
- Left: perturb each position
- Right: remove some random lattice sites and perturb the remaining positions
Numerical tests of a toy model

- 2D triangle lattice
- \( H_{\ell k}(y) = h(|y_\ell - y_k|) \)
  with
  \[
  h(r) = \left( e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right) f_{\text{cut}}(r)
  \]
- \( \cdot \) : perturb each position
- \( \times \) : remove some random lattice sites and perturb the remaining positions
Outline

- Strong Locality of Tight-Binding
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An energy-based QM/MM coupling

Energy functional:

\[ E^H(y) = E_{QM} + E_{MM} = \sum_{\ell \in QM} E_{QM}^\ell(y) + \sum_{\ell \in MM} E_{MM}^\ell(y) \]

Equilibrium state:

\[ \bar{y} = \arg \min_y \{ E^H(y) \} \]

- MM potentials are taken off-the shelf, not matched to QM model
- Accuracy of the QM/MM method and its convergence with respect to possible parameters?
Test of principle: a vacancy in 2D triangular lattice

- Reference configuration:
  \[ \Lambda = s \begin{pmatrix} 1 & 1/2 \\ 0 & \sqrt{3}/2 \end{pmatrix} \mathbb{Z}^d \setminus \{0\} \]

- Displacement \( u : \Lambda \to \mathbb{R}^d \)

- \( y = y_0 + u \)
  with \( y_0(\ell) = \ell \ \forall \ \ell \in \Lambda \)
Energy difference functional and decay estimates

Only the energy-difference is meaningful

\[ E(u) = \sum_{\ell \in \Lambda} \left( E_\ell(y_0 + u) - E_\ell(y_0) \right) := \sum_{\ell \in \Lambda} E_\ell(u) \]

\[ E(u) \] is well defined on some energy space \( U^{1,2} \) and

\[ E \in C^k(U^{1,2}) \]

far-field structure of the minimizer

\[ \bar{u} \in \text{arg min}\{ E(u) \mid u \in U^{1,2} \} \]

\[ |\nabla \bar{u}(x)| \lesssim |x|^{-d} \]

[Ehrlacher & Ortner & Shapeev 2013] and [HC & Nazar & Ortner 2016]
Decomposition of reference configuration

Decomposition $\Lambda = \Lambda^{QM} \cup \Lambda^{MM} \cup \Lambda^{FF}$ with parameters $R^{QM}$, $R^{BUF}$, $R^{MM}$
Construction of MM potential

**MM site potential**
(Taylor’s expansion of TB site energy on reference configuration)

\[
\mathcal{E}_\ell^{MM}(u) = \mathcal{E}_\ell^{buf}(0) + u^T \nabla \mathcal{E}_\ell^{buf}(0) + \frac{1}{2} u^T \nabla^2 \mathcal{E}_\ell^{buf}(0) u + \cdots
\]

- \(\mathcal{E}_\ell^{buf}\) = Tight-Binding site energy difference in \(B_{R_{buf}}(\ell)\)

- Error can be controlled since \(|\nabla \bar{u}(x)| \lesssim |x|^{-d}||

- 2nd expansion for point defects (minimal requirement)
Convergence of energy-mixing

\[
\mathcal{E}^H(u) = \sum_{\ell \in \Lambda^{QM}} \mathcal{E}^\text{buf}_\ell (u) + \sum_{\ell \in \Lambda^{MM}} \mathcal{E}^\text{MM}_\ell (u) := \mathcal{E}^{QM} + \mathcal{E}^{MM}
\]

\[
\bar{u}^H \in \arg\min \left\{ \mathcal{E}^H(v) \mid v = 0 \text{ in } \Lambda^{FF} \right\}
\]

Theorem (Convergence rates) [HC & Ortner 2015]

Let \( \bar{u} \) be a strongly stable minimiser of \( \mathcal{E} \). Then for \( R^{QM} \) sufficiently large, there exists a strongly stable minimiser \( \bar{u}^H \) of \( \mathcal{E}^H \) such that

\[
\|\nabla \bar{u} - \nabla \bar{u}^H\|_{L^2} \leq C \left( (R^{QM})^{-3d/2} + (R^{MM})^{-d/2} + e^{-\gamma R^{\text{buf}}} \right),
\]

\[
|\mathcal{E}(\bar{u}) - \mathcal{E}^H(\bar{u}^H)| \leq C \left( (R^{QM})^{-2d} + (R^{MM})^{-d} + e^{-\gamma R^{\text{buf}}} \right).
\]

Balance the errors: \( R^{\text{buf}} \approx c \log R^{QM} \), \( R^{MM} \approx (R^{QM})^3 \) or \( R^{MM} \approx (R^{QM})^2 \)
Numerical tests

Vacancy in 2D triangular lattice, using a toy TB model.
Concluding remarks

- Decomposition of TB total energy into contributions from individual sites. Proof of locality of these contributions.

- New approaches to QM/MM coupling. **Key point:** do not use black-box potentials, but construct a potential specifically for good coupling with the QM model!

- Analogous constructions and error estimates for force-based QM/MM coupling.

- For dislocations, one has to use higher order expansion for the MM site energy construction.
References


Thank you for your attention!