Local Energies and Electrostatics from DFT

Albert Bartók-Pártay

TCM Group

Outline

- aim of research: classical potential with quantum mechanical accuracy

- local and non-local terms in the energy expression

- existing schemes: Electronegativity Equalization Method and Charge Equilibration

- atomic properties: charges, energies, multipoles

- how local are they?

QM-accurate classical potential?

Total energy expression:

$$E = \sum_{i}^{\text{atoms}} \epsilon_i \left(\mathbf{r}_{in_1}, \mathbf{r}_{in_2}, \ldots, \mathbf{r}_{in_i} \right) +$$

$$+ \frac{1}{2} \sum_{i,j}^{\text{atoms}} \hat{L}_i \hat{L}_j \frac{1}{r_{ij}}$$

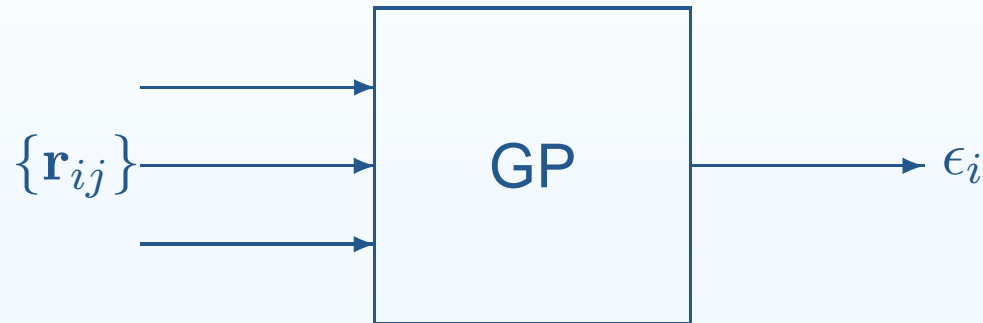where $\hat{L}_i = q_i + \mathbf{p}_i \cdot \nabla_i + \cdots$

first term: *local* term, function of positions of neigbouring atoms j

second term: classical Coulomb term in multipole expansion

Machine learning

$f : \mathbb{R}^N \mapsto \mathbb{R}$ may be learnt

- learning: high-dimensional interpolation by a Gaussian Process
- $N \approx 10 - 15$
- local energies
- local charges, polarizabilities etc.

Electronegativity Equalization Method[a]

total energy as atomic contributions: $E = \sum_A E_A$

'self' term and electrostatic term:

$$E_A = E_A^0 + \chi_A \Delta N_A + \eta_A (\Delta N_A)^2 - N_A \sum_B \frac{Z_B}{R_{AB}} + N_A \frac{1}{2} \sum_B \frac{N_B}{R_{AB}} + Z_A \frac{1}{2} \sum_B \frac{Z_B}{R_{AB}}$$

in equilibrium:

$$\mu = \frac{\partial E}{\partial N_A} = \frac{\partial E}{\partial N_B} = \cdots$$

$$\mu = \chi_A + \eta_A \Delta N_A + \sum_B \frac{N_B - Z_B}{R_{AB}} = \cdots$$

Nth equation from electroneutrality: $\sum_A \Delta N_A = 0$

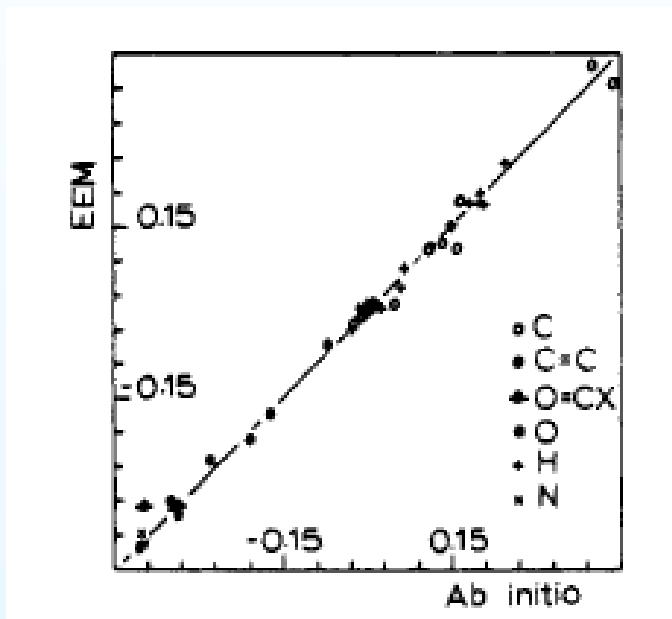local properties: E_A^0, χ (electronegativity) and η (atomic hardness)

EEM requires the fitting of parameters χ and η, then solving N linear equations

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[a]W. J. Mortier, S. K. Ghosh and S. Shankar J. Am. Chem. Soc. 1986, 108, 4315–4320
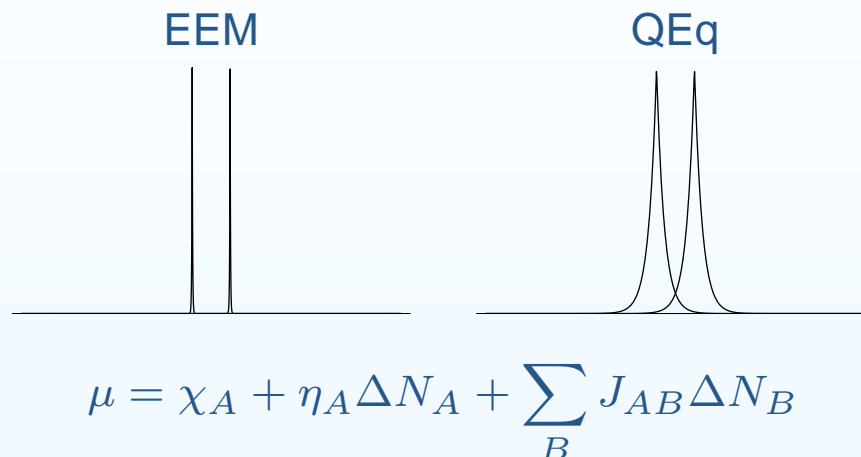
Electronegativity Equalization Method

- used for determining partial charges of atoms in molecules

- reasonable result for molecules

- parameters are not transferable

Charge Equilibration[b]

EEM   QEq

$$\mu = \chi_A + \eta_A \Delta N_A + \sum_B J_{AB} \Delta N_B$$

where J_{AB} is the 'shielded' Coulomb potential:

$$J_{AB} = \int\int d\mathbf{r}\, d\mathbf{r}' \frac{\phi_A(\mathbf{r})\phi_B(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Slater functions are used: $\phi_n = N_n r^n \exp(-\zeta r)$
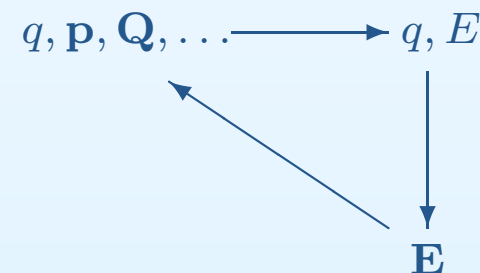all parameters are derived from experiments: ionization potentials, electron affinities

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[b]A. K. Rappé and W. A. Goddard III J. Phys. Chem. 1991, 95, 3358–3363

Electronegativities and atomic hardnesses to be learnt

$$E = \sum_{i}^{\text{atoms}} \epsilon_i^{(0)}(\mathbf{r}_{in_1}, \ldots) + \epsilon_i^{(1)}(\mathbf{r}_{in_1}, \ldots)q_i + \epsilon_i^{(2)}(\mathbf{r}_{in_1}, \ldots)q_i^2 +$$

$$+ \frac{1}{2} \sum_{i,j}^{\text{atoms}} \hat{L}_i \hat{L}_j \frac{1}{\mathbf{r}_{ij}}$$

$$\frac{\partial E}{\partial q_i} = \frac{\partial E}{\partial q_j} = \cdots$$

- electronegativities and atomic hardnesses depend on environment
- $\epsilon^{(n)}$ to be learnt
- equations similar to EEM
- elctrostatics: multipole moments from polarisabilities
- polarisabilities to be learnt
- self-consistent solution

$$q, \mathbf{p}, \mathbf{Q}, \ldots \longrightarrow q, E$$

$$\mathbf{E}$$

Atomic properties from ONETEP[c]

ONETEP:

- linear scaling DFT

- uses plane waves

- uses atomic basis set

properties calculated so far:

- atomic energies

- atomic charges, dipoles, quadrupoles, octupoles

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[c]C. K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne J. of Chem. Phys. 2005, 122, 084118

Atomic properties

Let $\hat{O}$ be an arbitrary operator:

$$\left\langle \hat{O} \right\rangle = \sum_i f_i \left\langle \psi_i \left| \hat{O} \right| \psi_i \right\rangle = \sum_{\alpha,\beta} K^{\alpha\beta} O_{\beta\alpha} = Tr\,(\mathrm{KO})$$

$$O_{\beta\alpha} = \left\langle \phi_\beta \left| \hat{O} \right| \phi_\alpha \right\rangle$$

$$\left\langle \hat{O} \right\rangle_A = \sum_{\alpha \in A} (\mathrm{KO})_{\alpha\alpha}$$

$\hat{O}$ can be:

- Hamiltonian

- position operator

- …

e.g.: $\hat{O} = \hat{1}$

$q_A = \sum_{\alpha \in A} (\mathrm{KS})_{\alpha\alpha}$

Long-range interactions in ONETEP

$$\rho_A(\mathbf{r}) = \sum_{\alpha \in A} \sum_{\beta} K^{\alpha\beta} \phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_A \rho_A(\mathbf{r})$$

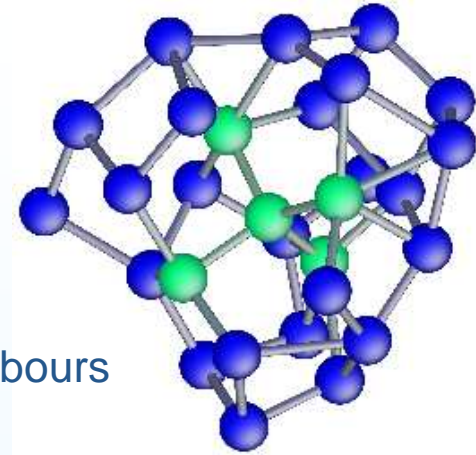$$E_{\rho_A \rho_B} = \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' \frac{\rho_A(\mathbf{r})\, \rho_B(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{\rho_A Z_B} = \int d\mathbf{r}\, \frac{\rho_A(\mathbf{r}) Z_B}{|\mathbf{r} - \mathbf{R}_B|}$$
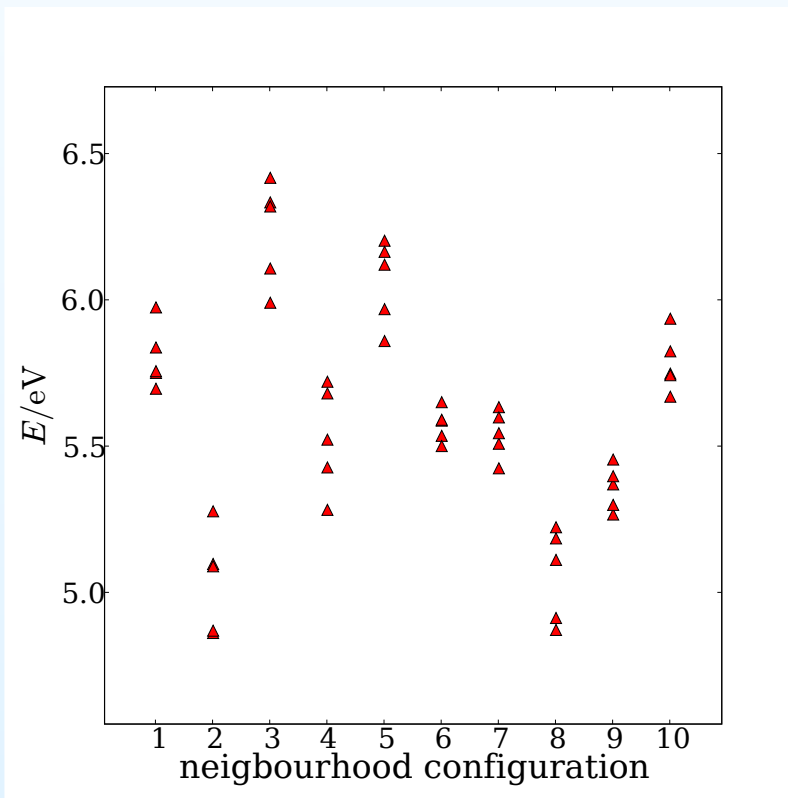
electrostatic interactions between atoms farther than 2 Wannier radii can be treated exactly by multipole expansion
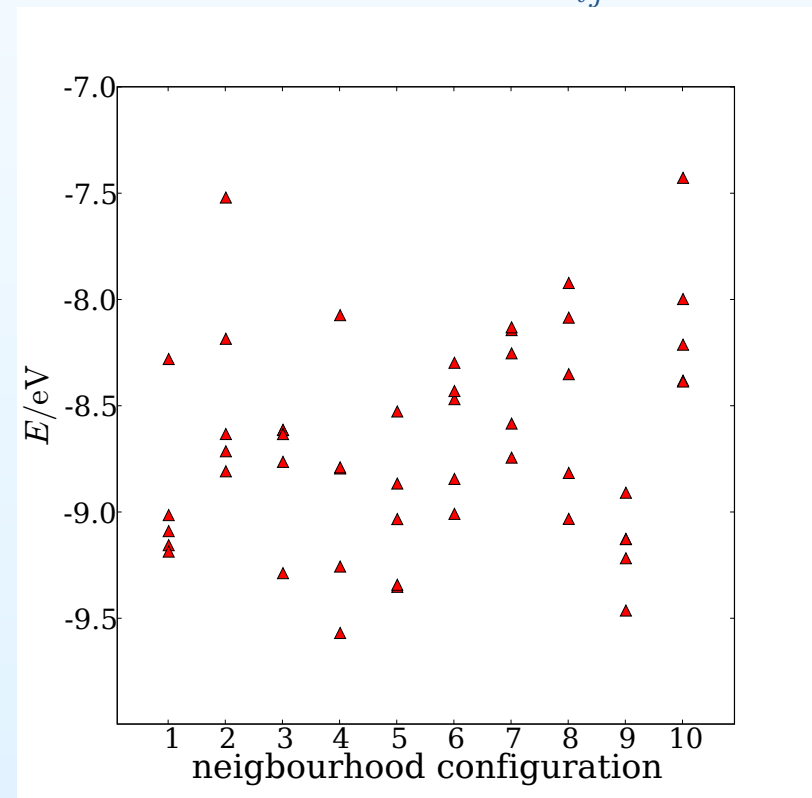
Locality of properties

- model system: small Si clusters

- evaluation of atomic energies with fixed nearest neighbours

$$E_{\text{kinetic}} + E_{\text{xc}}$$

$$E_i - \tfrac{1}{2} \sum_j \hat{L}_i \hat{L}_j \frac{1}{r_{ij}}$$

Conclusions

- derivation of useful formulas for local and long-range terms
- connection between EEM and our method
- atomic properties programmed into ONETEP
- investigation of locality in small systems
- local energies are influenced by second neighbours
- further work: examination of other systems, implementation of Gaussian Processes