#### From Electrons to Interatomic Potentials for Materials Simulation

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INTERDISCIPLINARY CENTRE FOR ADVANCED MATERIALS SIMULATION

#### Plan

- **1. Interatomic potentials for materials simulation**
- 2. Coarse graining the electronic structure for interatomic potentials
- 3. The moments theorem and local expansions
- 4. Many atom expansion
- **5. Summary and conclusions**

Lecture notes including references: https://www.cond-mat.de/events/correl20/manuscripts/drautz.pdf



#### 1. Interatomic Potentials



# 1.1 Motivation: numerical efficiency

**Example**: computation of phase diagram for an element

- Thermodynamic sampling requires about:
  - ~10<sup>3</sup> atoms
  - ~10<sup>9</sup> force evaluations at different pressures/temperatures
  - → ~10<sup>12</sup> atomic force calls
- Do do this within one year: ~30  $\mu$ s/atomic force call
- → Not possible with Density Functional Theory

**Example:** mechanical properties

- Dislocation interactions require large cells and long simulation times
  - ~10<sup>6</sup> atoms
  - ~10<sup>6</sup> molecular dynamics steps
  - → ~10<sup>12</sup> atomic force calls
- Do do this within one year: ~30  $\mu$ s/atomic force call
- → Not possible with Density Functional Theory

#### Need fast models of interatomic interaction. Fast models need to be accurate.



## 1.2 Motivation: insight and interpretation

Example: multi-component alloy phase stability

- Modern alloys contain many elements (>10)
- Impossible to sample combinatorial phase space
- $\rightarrow$  Need effective descriptors for guidance
  - Reproduce basic chemical trends
  - Key descriptors such as bandfilling, atomic size, electronegativity, etc. should emerge naturally

#### Need simplified models of bonding. Simplified models need to be accurate.



# 1.3 Development of potentials

- Electrons regarded as glue that mediates the interaction between atomic cores
- Until about the 1980s:
  - Development empirical, based on experience and intuition
  - Force fields for bio-systems different from potentials for materials
- Potentials based on or inspired by DFT and TB:
  - Second Moment Potentials, Effective Medium Theory, Embedded Atom Method, Finnis Sinclair Potential, Tersoff Potential, ...
- Increased complexity/formal derivation:
  - Modified Embedded Atom Method, and others
  - Reactive force fields
  - Bond-Order Potentials
- Machine learning potentials:
  - Learn DFT reference data
  - Neural network potentials, Gaussian approximation potentials, ...

# This lecture: 1. Derive potentials from DFT 2. Many atom expansion



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# 2. Coarse graining the electronic structure for interatomic potentials



# 2.1 Second-order expansion of the density functional

- Tight-binding (TB) approximation obtained from DFT
- Many developments about 20-40 years ago
- Names that you may come across: Pettifor, Ducastelle, Elstner, Finnis, Foulkes, Frauenheim, Harris, Haydock, Horsfield, Heine, Paxton, Sutton, ... and many others
- Several related but different representations and approaches
- Aim here: simple approach from DFT to TB

#### 2.2 Basis

- Represent DFT functional in basis
- Overlap

$$S_{ij} = \langle \varphi_i | \varphi_j \rangle$$

• One-electron eigenfunctions in basis

$$|\psi_n\rangle = \sum_i c^{i(n)} |\varphi_i\rangle$$

• For simplified notation introduce

$$|\varphi^i\rangle = \sum_j S_{ij}^{-1} |\varphi_j\rangle$$

• Therefore

$$\delta_{ij} = \langle \varphi^i | \varphi_j \rangle$$



#### 2.3 Example: density matrix

Density matrix element

$$\rho^{ij} = \langle \varphi^i | \hat{\rho} | \varphi^j \rangle = \sum_n f_n \langle \varphi^i | \psi_n \rangle \langle \psi_n | \varphi^j \rangle = \sum_n f_n c^{i(n)} (c^{j(n)})^*$$

Charge density

$$\rho(\boldsymbol{r}) = \sum_{ij} \rho^{ij} \varphi_i(\boldsymbol{r}) \varphi_j^*(\boldsymbol{r})$$



#### 2.4 Contributions to DFT functional

• Contributions to energy

$$E = T_S + E_H + E_{XC} + E_{ext}$$

Kinetic energy of non-interacting electrons

$$T_S = \sum_n f_n \langle \psi_n | \hat{T} | \psi_n \rangle = \boldsymbol{T} \boldsymbol{\rho}$$

$$\boldsymbol{T}\boldsymbol{\rho} = \sum_{ij} T_{ij} \rho^{ji} \qquad \qquad T_{ij} = \langle \varphi_i | \hat{T} | \varphi_j \rangle$$



#### 2.5 Contributions to DFT functional II

• External potential

$$E_{ext} = \int V^{ext}(\boldsymbol{r})\rho(\boldsymbol{r}) \, d\boldsymbol{r} = \boldsymbol{V}^{ext}\boldsymbol{\rho}$$

• Hartree energy

$$E_H = \frac{1}{2} \int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' = \sum_{ijkl} \frac{1}{2} J_{ijkl}^H \rho^{ij} \rho^{kl} = \frac{1}{2} \boldsymbol{J}^H \boldsymbol{\rho} \boldsymbol{\rho}$$

Series expansion of exchange correlation energy

$$E_{XC} = \boldsymbol{V}^{XC}\boldsymbol{\rho} + \frac{1}{2}\boldsymbol{J}^{XC}\boldsymbol{\rho}\boldsymbol{\rho} + \frac{1}{6}\boldsymbol{K}^{XC}\boldsymbol{\rho}\boldsymbol{\rho}\boldsymbol{\rho} + \cdots$$



#### 2.6 DFT functional expansion

- Group contributions according to their order
- First order

$$V = T + V^{ext} + V^{XC}$$

Second order

$$\boldsymbol{J} = \boldsymbol{J}^H + \boldsymbol{J}^{XC}$$

• Third order

$$K = K^{XC}$$

• Expansion of the energy

$$E = V\rho + \frac{1}{2}J\rho\rho + \frac{1}{6}K\rho\rho\rho + \cdots$$



#### 2.7 Band energy

Hamiltonian matrix

$$\boldsymbol{H} = \frac{\partial E}{\partial \boldsymbol{\rho}} = \boldsymbol{V} + \boldsymbol{J}\boldsymbol{\rho} + \frac{1}{2}\boldsymbol{K}\boldsymbol{\rho}\boldsymbol{\rho} + \cdots$$

• Energy represented as band energy and double counting correction

$$E = H\rho - \frac{1}{2}J\rho\rho - \frac{1}{3}K\rho\rho\rho - \cdots$$

• Band energy

$$E_{band} = H\rho$$



#### 2.8 Band energy and density of states

• Partition band energy for local expansion

$$E_{band} = \sum_{i} E_{band,i}$$

• Intersite representation

$$E_{band,i} = \sum_{j} H_{ij} \rho^{ij}$$

Onsite representation

$$E_{band,i} = \int^{E_F} E \, n_i(E) \, dE$$

Local density of states

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$$n_i(E) = \sum_n c_i^{(n)} (c^{i(n)})^* \delta(E_n - E)$$



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#### 2.9 Perturbation expansion

• Expand around reference density

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(0)} + \delta \boldsymbol{\rho}$$

• Energy

$$E = E^{(0)} + \boldsymbol{H}^{(0)}\delta\boldsymbol{\rho} + \frac{1}{2}\boldsymbol{J}'\delta\boldsymbol{\rho}\,\delta\boldsymbol{\rho} + \frac{1}{6}\boldsymbol{K}'\delta\boldsymbol{\rho}\,\delta\boldsymbol{\rho}\,\delta\boldsymbol{\rho} + \cdots$$

Hamiltonian

$$H = H^{(0)} + J'\delta\rho + \frac{1}{2}K'\delta\rho\delta\rho + \cdots$$

#### For TB: terminate expansion, typically after 2<sup>nd</sup> order



## 2.10 Tight-binding approximation

• Linear combination of atomic orbitals minimal basis

$$\varphi_{i\alpha}(\boldsymbol{r}) = R_{nl}(|\boldsymbol{r} - \boldsymbol{r}_i|)Y_l^m(\theta, \phi)$$

Optimal radial functions for minimal basis are determined from DFT



## 2.11 Tight-binding approximation

• Parameterize matrix elements

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• Example: Hamiltonian matrix elements for Fe in minimal basis



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## 2.12 Bond formation in TB

- Expansion needs reference: start from spherical, charge neutral atoms
- Shrink atoms, contract radial functions

$$E_{prep} = \sum_{i\alpha} (E_{i\alpha}^{(0)} - E_{i\alpha}^{(at)}) N_{i\alpha}^{(0)}$$



Overlap atomic charge densities



#### 2.13 Bond formation in TB

• Charge transfer, often simplified

$$E_{es} = \frac{1}{2} \sum_{ij}^{i \neq j} J_{ij} q_i q_j$$

$$E_{ion} = \bar{E}_i q_i + \frac{1}{2} \sum_i J_{ii} q_i^2$$

• Promotion energy

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$$E_{prom} = \sum_{i\alpha} E_{i\alpha}^{(0)} (N_{i\alpha} - N_{i\alpha}^{(0)})$$

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#### 2.14 Bond formation in TB

• Bond energy

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$$E_{bond} = \sum_{i\alpha j\beta} (H_{i\alpha j\beta} - E_{i\alpha} S_{i\alpha j\beta}) \rho_{j\beta i\alpha}$$
  
onsite  $E_{bond} = \sum_{i\alpha} \int_{-\infty}^{E_F} (E - E_{i\alpha}) n_{i\alpha}(E) dE$ 

• Binding energy in TB approximation (rewrite of 2<sup>nd</sup> order DFT expansion)

$$E_B = \underline{E_{bond}} + \underline{E_{prom}} + \underline{E_{ion}} + \underline{E_{es}} + \underline{E_{rep}}$$



#### 3. Moments theorem and local expansions



#### 3.1 Moments of the density of states

• Moments of the local density of states

$$\mu_{i\alpha}^{(N)} = \int E^N n_{i\alpha}(E) \, dE$$

Idea: reconstruct density of states from its moments

$$n_{i\alpha}(E) = n_{i\alpha}(E, \mu_{i\alpha}^{(0)}, \mu_{i\alpha}^{(1)}, \mu_{i\alpha}^{(2)}, \dots)$$

• Moments theorem (for orthonormal basis)

$$\mu_{i\alpha}^{(N)} = \langle i\alpha | \hat{H}^N | i\alpha \rangle = \sum_{j\beta k\gamma \dots} \langle i\alpha | \hat{H} | j\beta \rangle \langle j\beta | \hat{H} | k\gamma \rangle \langle k\gamma | \hat{H} \dots \hat{H} | i\alpha \rangle$$



#### 3.2 Moments theorem II

• Spectrally resolved density matrix

$$\rho_{i\alpha j\beta} = \int^{E_F} n_{i\alpha j\beta}(E) \, dE$$

• Interference paths

$$\xi_{i\alpha j\beta}^{(N)} = \int E^N n_{i\alpha j\beta}(E) \, dE = \langle i\alpha | \hat{H}^N | j\beta \rangle$$



#### 3.3 Local expansions

- Different methods make use of the relations provided by the moments theorem, explicitly or implicitly
- Next we will briefly look at:
  - 1. Recursion
  - 2. Numerical bond-order potentials
  - 3. Kernel polynomial method
  - 4. Fermi operator expansion
  - 5. Analytic bond-order potentials

#### 3.4 Recursion

• Recursively generate new states

$$b_{n+1}|u_{n+1}\rangle = (\hat{H} - a_n)|u_n\rangle - b_n|u_{n-1}\rangle$$

• Tridiagonal Hamiltonian matrix

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$$\langle u_n | \hat{H} | u_m \rangle = \begin{pmatrix} a_0 & b_1 & 0 & 0 & 0 & 0 & \cdots \\ b_1 & a_1 & b_2 & 0 & 0 & 0 & \cdots \\ 0 & b_2 & a_2 & b_3 & 0 & 0 & \cdots \\ 0 & 0 & b_3 & a_3 & b_4 & 0 & \cdots \\ 0 & 0 & 0 & b_4 & a_4 & b_5 & \cdots \\ 0 & 0 & 0 & 0 & b_5 & a_6 & \ddots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}$$

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Relation to moments

$$\begin{split} \mu_{i\alpha}^{(0)} &= 1 \,, \\ \mu_{i\alpha}^{(1)} &= a_0 \,, \\ \mu_{i\alpha}^{(2)} &= a_0^2 + b_1^2 \,, \\ \mu_{i\alpha}^{(3)} &= a_0^3 + (a_0 + a_1)b_1^2 \,, \\ \mu_{i\alpha}^{(4)} &= a_0^4 + b_1^4 + (a_0^2 + a_1^2 + a_0a_1 + b_2^2)b_1^2 \,, \end{split}$$

#### 3.6 Recursion

Green's function

$$\hat{G} = (E\hat{1} - \hat{H})^{-1}$$

Continued fraction expansion



Relation to density of states

$$n_{i\alpha}(E) = -\frac{1}{\pi} \mathrm{Im} G_{i\alpha i\alpha}(E) \qquad n_{i\alpha j\beta}(E) = -\frac{1}{\pi} \mathrm{Im} G_{i\alpha j\beta}(E)$$

#### 3.7 Numerical bond-order potentials

Terminate expansion

$$a_m = a_\infty, \quad b_m = b_\infty \quad \text{for } m > n$$

• Terminator

$$T(E) = \frac{1}{2} \left( E - a_{\infty} - \sqrt{E - a_{\infty} - 2b_{\infty}} \sqrt{E - a_{\infty} + 2b_{\infty}} \right)$$

• Bond energy

$$E_{bond,i\alpha} = -\frac{1}{\pi} \text{Im} \int^{E_F} \frac{E - E_{i\alpha}}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{\cdots - \frac{b_2^2}{E - a_{n-1} - T(E)}}}$$

# Plus a few tricks for convergence → Efficient local expansion of the TB energy

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polynomials of the first kind for n<sub>max</sub> = 50 (black squares), and the corresponding kernels, Eqs. (36) (red circles) and (40) (blue triangles), for Chebyshev polynomials of the second kind.
 Emansions), for Chebyshev polynomials of the second kind.

$$n_{i\alpha}(\epsilon) = \frac{1}{\pi} \frac{1}{\sqrt{1 - \epsilon^2}} \left( g_T^{(0)} + 2 \sum_{n=1}^{n_{max}} g_T^{(n)} T_n(\epsilon) \mu_n^T \right)$$

Chebyshev moments of the density of states

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$$\mu_n^T = \int_{-1}^1 T_n(\epsilon) n_{i\alpha}(\epsilon) \, d\epsilon$$

Chebyshev expansion may be integrated analytically for bond energy



#### 3.10 Fermi operator expansion

• Introduce temperature into band energy

$$E_{band} = \int \epsilon f(\epsilon, \mu) n(\epsilon) \, d\epsilon$$

Fermi-Dirac distribution function

$$f(\epsilon, \mu) = \frac{1}{1 + \exp(\frac{\epsilon - \mu}{k_B T})}$$

• Density matrix elements

$$\rho_{i\alpha j\beta} = \int f(\epsilon,\mu) n_{i\alpha j\beta}(\epsilon) d\epsilon$$



### 3.11 Fermi operator expansion

• Polynomial expansion of Fermi-Dirac distribution function

$$f(\epsilon,\mu) = \sum_{k} c_k \epsilon^k$$

• Use moments theorem

$$\rho_{i\alpha j\beta} = \sum_{k} c_k \xi_{i\alpha j\beta}^{(k)}$$

• Expansion for band energy

$$E_{band} = \sum_{i\alpha j\beta} \sum_{k} c_k \xi_{i\alpha j\beta}^{(k)} H_{j\beta i\alpha} = \sum_{i\alpha} \sum_{k} c_k \mu_{i\alpha}^{(k+1)}$$

• In practise the Fermi-Dirac function is expanded in Chebyshev polynomials

#### 3.12 Analytic bond-order potentials

- Make use of elements of Numerical Bond-Order Potentials and Kernel Polynomial Method
- Moments of the Chebyshev polynomials of the second kind

$$\sigma_{i\alpha}^{(n)} = \int_{-1}^{+1} U_n(\epsilon) n_{i\alpha}(\epsilon) \, d\epsilon$$

• Expansion of the density of states

$$n_{i\alpha}(\epsilon) = \sum_{n=0}^{n_{max}} \sqrt{1 - \epsilon^2} \sigma_{i\alpha}^{(n)} U_n(\epsilon) = \sum_{n=0}^{n_{max}} \sigma_{i\alpha}^{(n)} \sin(n+1)\phi$$
$$\epsilon = -\cos\phi$$

Close-packed structures recovered at low order



#### 3.13 Analytic bond-order potentials

Damp and terminate expansion

$$n_{i\alpha}(\epsilon) = \sum_{n=0}^{n_{max}} g_n \sigma_{i\alpha}^{(n)} \sin(n+1)\phi + \sum_{n=n_{max}+1}^{n_{exp}} g_n \sigma_{i\alpha}^{(n)} \sin(n+1)\phi$$

• Can be integrated analytically

$$E_{bond,i\alpha} = 2b_{\infty} \sum_{n=0}^{n_{exp}} g_n \sigma_{i\alpha}^{(n)} \left[ \hat{\chi}_{n+2}(\phi_F) - \gamma_0 \hat{\chi}_{n+1}(\phi_F) + \hat{\chi}_n(\phi_F) \right]$$

• With response functions

$$\hat{\chi}_n(\phi_F) = \frac{1}{\pi} \left[ \frac{\sin(n+1)\phi_F}{n+1} - \frac{\sin(n-1)\phi_F}{n-1} \right]$$

→ Efficient local expansion of the TB energy



#### 3.14 Examples: Analytic bond-order potentials

- Some properties of the density matrix/bond order ٠
- Introduce bonding and anti-bonding state •

$$|+\rangle = \frac{1}{\sqrt{2}}(|i\alpha\rangle + |j\beta\rangle)$$
$$|-\rangle = \frac{1}{\sqrt{2}}(|i\alpha\rangle - |j\beta\rangle)$$

Representation of density matrix element •

$$\rho_{i\alpha j\beta} = \langle i\alpha | \hat{\rho} | j\beta \rangle = \frac{1}{2} (N_{+} - N_{-})$$

$$N_{+} = \langle +|\hat{\rho}|+\rangle \qquad \qquad N_{-} = \langle -|\hat{\rho}|-\rangle$$

Envelope follows •

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$$|\rho_{i\alpha j\beta}| \le N_{i\alpha j\beta}$$
  $|\rho_{i\alpha j\beta}| \le 2 - N_{i\alpha j\beta}$ 



#### 3.15 Examples: Analytic bond-order potentials

 Density matrix elements across *sp* band for model Hamiltonian

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#### 3.16 Examples: Analytic bond-order potentials

 Structural energy differences for close packed structures across the *d* band

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#### 3.17 Examples: Analytic bond-order potentials







#### 4. Many atom expansion



# 4.1 Many atom expansion

#### **Until here:**

- Derived interatomic potentials from DFT
- Several approximations along the way
- → Cannot expect to reproduce DFT with meV accuracy

#### Next:

- Introduce formally complete representation of interatomic interactions
- Parameterized from large numbers of DFT reference data
- Reproduce DFT energy accurately, but no insight into bond formation

#### 4.2 Local atomic environment

- Descriptors key to machine learning
- Many different descriptors for atomic environment



#### → Formally complete descriptor desirable



## 4.3 Atomic energy

- Aim: represent atomic energy
- Energy is fully characterized by vectors to all other atoms

$$oldsymbol{\sigma} = \{oldsymbol{r}_{1i}, oldsymbol{r}_{2i}, \dots, oldsymbol{r}_{Ni}\}$$

→ Energy

$$E_i(\boldsymbol{\sigma}) = E_i(\boldsymbol{r}_{1i}, \boldsymbol{r}_{2i}, \dots, \boldsymbol{r}_{Ni})$$

with  $\boldsymbol{r}_{ji} = \boldsymbol{r}_j - \boldsymbol{r}_i$ 





#### 4.4 Basis

Inner product •

$$\langle f|g\rangle = \int f^*(\boldsymbol{\sigma})g(\boldsymbol{\sigma})\,d\boldsymbol{\sigma}$$

Complete single-bond basis •

$$\int \phi_v^*(\boldsymbol{r}) \phi_u(\boldsymbol{r}) \, d\boldsymbol{r} = \delta_{vu} \, ,$$
  
 $\sum_v \phi_v^*(\boldsymbol{r}) \phi_v(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$ 

Each basis function depends only ٠ on single bond vector





#### 4.5 Cluster expansion

• Cluster basis function

$$\Phi_{\alpha\nu} = \phi_{v_1}(\boldsymbol{r}_{j_1i})\phi_{v_2}(\boldsymbol{r}_{j_2i})\dots\phi_{v_K}(\boldsymbol{r}_{j_Ki})$$

• Orthogonality and completeness follow immediately

$$\langle \Phi_{\alpha\nu} | \Phi_{\beta\mu} \rangle = \delta_{\alpha\beta} \delta_{\nu\mu} ,$$
  
 $1 + \sum_{\gamma \subseteq \alpha} \sum_{\nu} \Phi^*_{\gamma\nu}(\boldsymbol{\sigma}) \Phi_{\gamma\nu}(\boldsymbol{\sigma}') = \delta(\boldsymbol{\sigma} - \boldsymbol{\sigma}')$ 

Cluster expansion

$$G(\boldsymbol{\sigma}) = J_0 + \sum_{\alpha\nu} J^{\alpha\nu} \Phi_{\alpha\nu}(\boldsymbol{\sigma})$$

• Expansion coefficients by projection

 $J^{\alpha\nu} = \langle \Phi^{\alpha\nu} | G(\boldsymbol{\sigma}) \rangle$ 





#### 4.6 Cluster expansion

• Cluster basis function

$$\Phi_{\alpha\nu} = \phi_{v_1}(\boldsymbol{r}_{j_1i})\phi_{v_2}(\boldsymbol{r}_{j_2i})\dots\phi_{v_K}(\boldsymbol{r}_{j_Ki})$$

• Cluster expansion

$$G(\boldsymbol{\sigma}) = J_0 + \sum_{\alpha\nu} J^{\alpha\nu} \Phi_{\alpha\nu}(\boldsymbol{\sigma})$$



• Inefficient for high body-order

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#### 4.7 Atomic cluster expansion

• Atomic density

$$\varrho_i = \sum_j \delta(\boldsymbol{r} - \boldsymbol{r}_{ji})$$

• Atomic base

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$$A_v = \langle \rho_i | \phi_v \rangle = \sum_j \phi_v(\mathbf{r}_{ji})$$

• Cluster expansion becomes polynomial in atomic base

$$G(\sigma) = \sum_{\nu}' c_{\nu} A_{\nu} \quad \text{with} \quad A_{\nu} = A_{v_1} \dots A_{v_N}$$
$$E = \underbrace{}_{\nu} + \underbrace{}_{\nu} \underbrace{}_{\nu} \underbrace{}_{\nu} \underbrace{}_{\nu} + \underbrace{}_{\nu} \underbrace{}$$

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#### 4.8 Rotational invariance

• Employ LCAO basis as irreducible basis of rotation group

 $\phi_v(\boldsymbol{r}) = R_{nl}(r) Y_l^m(\hat{\boldsymbol{r}})$ 

• Atomic base as before

$$A_v = \langle \rho_i | \phi_v \rangle = \sum_j \phi_v(\boldsymbol{r}_{ji})$$

Rotationally covariant basis functions

$$\boldsymbol{B}_{\nu} = \sum_{\boldsymbol{m}} \left( \begin{array}{c} \boldsymbol{l} \\ \boldsymbol{L} \end{array} \right)_{N} \prod_{k=1}^{N} A_{v_{k}}$$

Atomic cluster expansion

Generalized Glebsch-Gordan coefficients

$$oldsymbol{G}_i = \sum_
u' c_
u oldsymbol{B}_
u$$



#### 4.9 Example: Aluminium

- ~100000 DFT reference calculations
- up to 7-body interactions
- 514 parameters
- 525 radial function
   parameters
- RMSE ~ 4.3 meV
- MAE ~ 2.5 meV





#### 4.10 Application to small clusters

- Small Cu clusters with LDA and PBE, FHI-aims with 'tight' basis settings
- Complete sampling of phase space of clusters
- 575 two-atom clusters

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#### 4.11 Small clusters: trimers

• 3809 three-atom clusters (symmetric 3d space) + 575 dimers

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#### 4.12 Small clusters: four atoms

- 18864 four-atom clusters (symmetric 6d space) + 3809 trimers + 575 dimers
- LDA and PBE on top of each other

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#### 4.13 From free atoms to bulk

- Cu clusters and bulk
- More than 50000 structures in total
- Finnis-Sinclair-type potential



→ Errors of about 1-3 meV including up to four-body interactions

Difference in cohesive energy between LDA and PBE: 1eV (25%)

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#### 4.14 Reference vs. fit

Comparison of reference and fitted data



#### Transferable over three orders of magnitude in energy



## 5. Summary and conclusions

- Second moment expansion of DFT functional
  - Derivation of TB approximation
  - Parameterization of matrix elements
  - Bond formation in the TB approximation
- The moments theorem and local expansions
  - Moments theorem
  - Recursion
  - Numerical bond-order potentials
  - Kernel polynomial method
  - Fermi operator expansion
  - Analytic bond-order potentials
  - Applications: bond-orders, structural stability, phase diagrams, ...
- Many atom expansion
  - Formally complete atomic cluster expansion
  - Accurate representation of DFT reference energy

