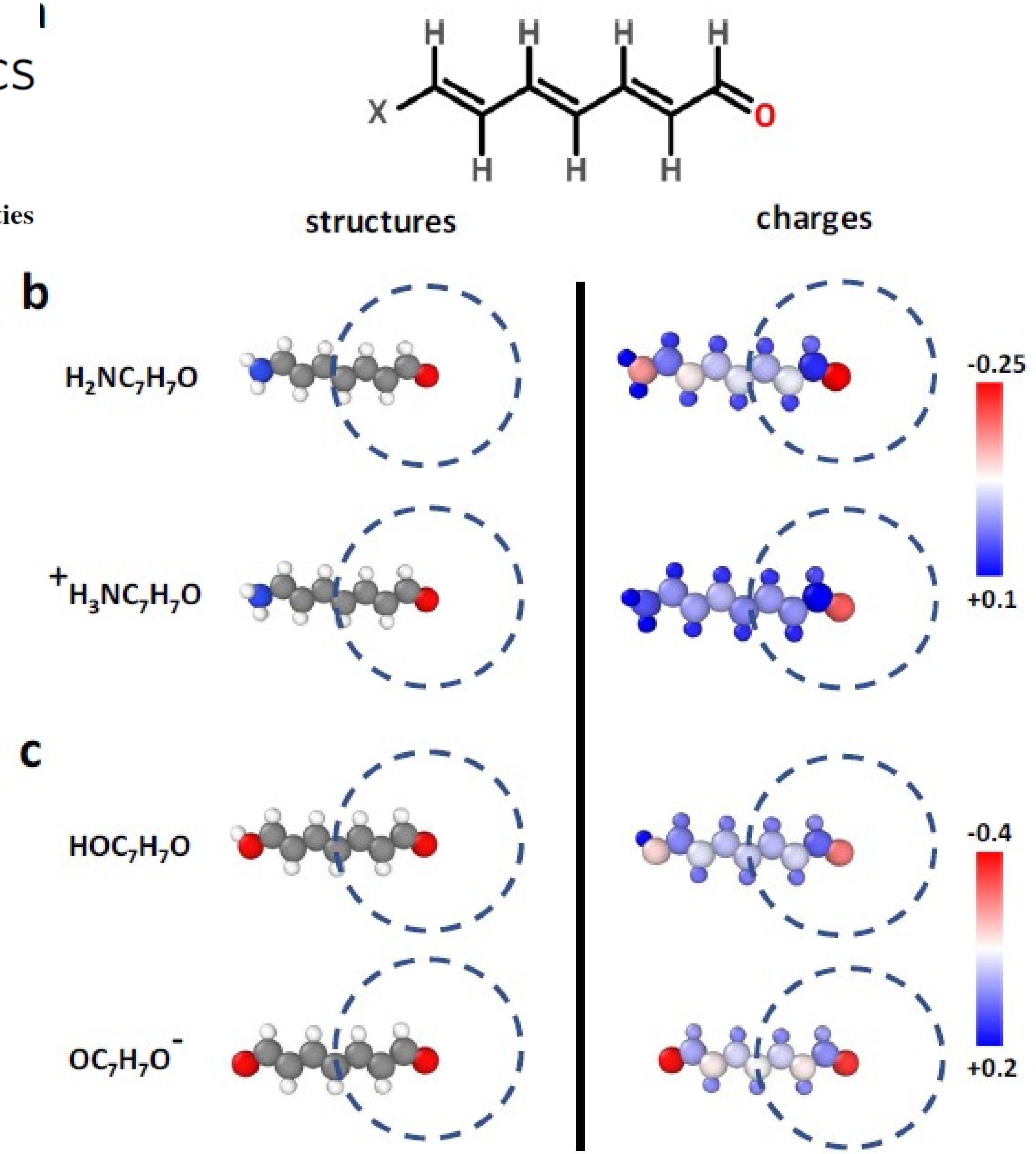
A fourth-generation high-dimensional neural network potential with accurate electrostatics including non-local charge transfer

Interatomic potentials for ionic systems with density functional accuracy based on charge densities obtained by a neural network

„In spirit of CENT“



Include description of global change in electronic structure from
Long-range charge transfer or different charge states

$$E_{\text{total}}(\mathbf{R},\mathbf{Q}) = E_{\text{elec}}(\mathbf{R},\mathbf{Q}) + E_{\text{short}}(\mathbf{R},\mathbf{Q}).$$

electronegativities $\{\chi_i\}$ that are adjusted to yield charges in agreement with the DFT reference charges, which here we choose to be Hirshfeld charges

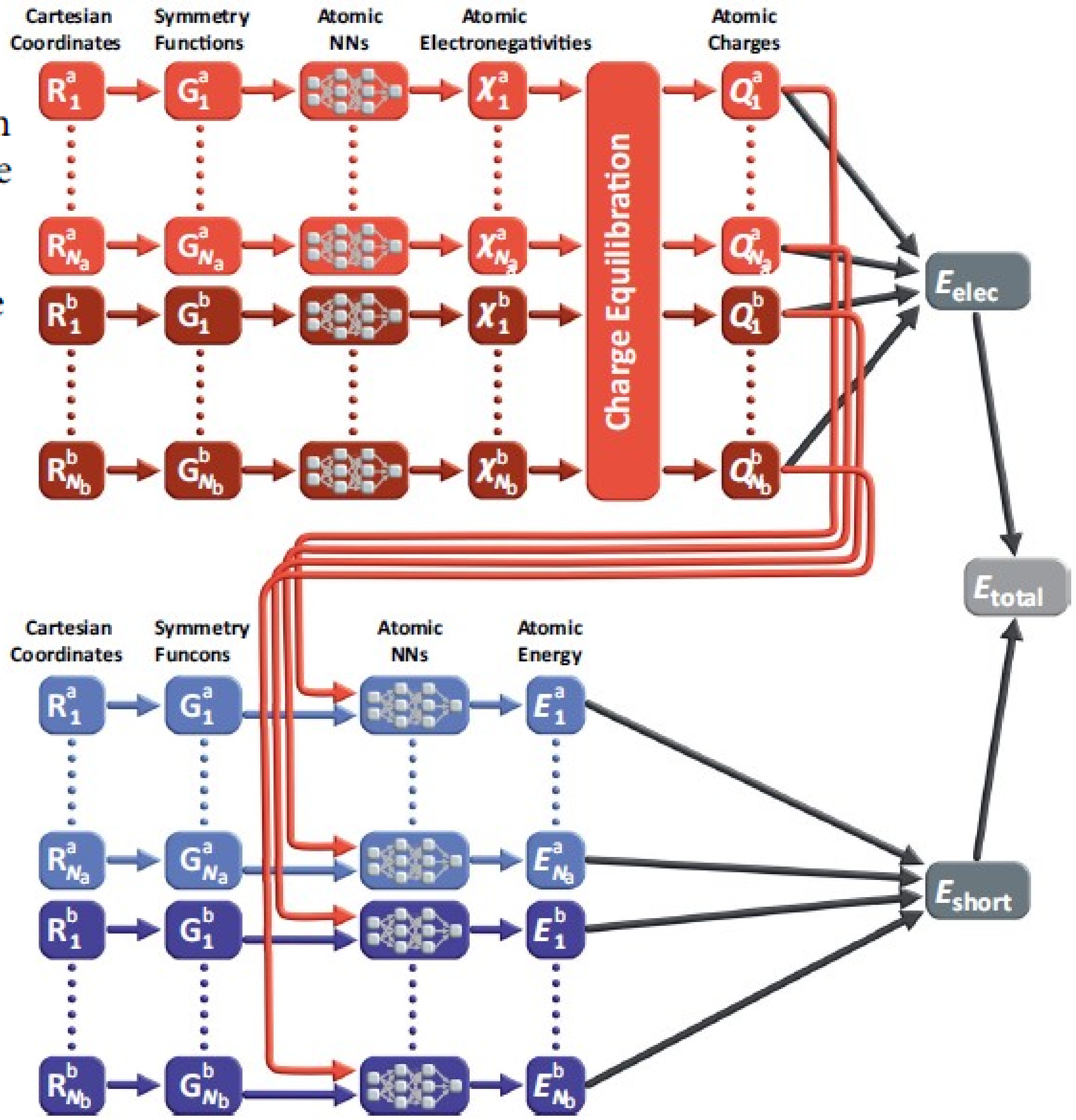
translational, rotational and permutational invariance of the electronegativities.

$$E_{\text{Qeq}} = E_{\text{elec}} + \sum_{i=1}^{N_{\text{at}}} \left(\chi_i Q_i + \frac{1}{2} J_i Q_i^2\right)$$

$$E_{\text{elec}} = \sum_{i=1}^{N_{\text{at}}} \sum_{j}^{N_{\text{at}}} \frac{\operatorname{erf}\left(\frac{r_{ij}}{\sqrt{2}\gamma_{ij}}\right)}{r_{ij}} Q_i Q_j + \sum_{i=1}^{N_{\text{at}}} \frac{Q_i^2}{2\sigma_i\sqrt{\pi}}$$

J is the hardness (here optimized during training)

$$\frac{\partial E_{\text{Qeq}}}{\partial Q_i} = 0, \forall i = 1, .., N_{\text{at}} \;\Rightarrow\; \sum_{j=1}^{N_{\text{at}}} A_{ij} Q_j + \chi_i = 0$$

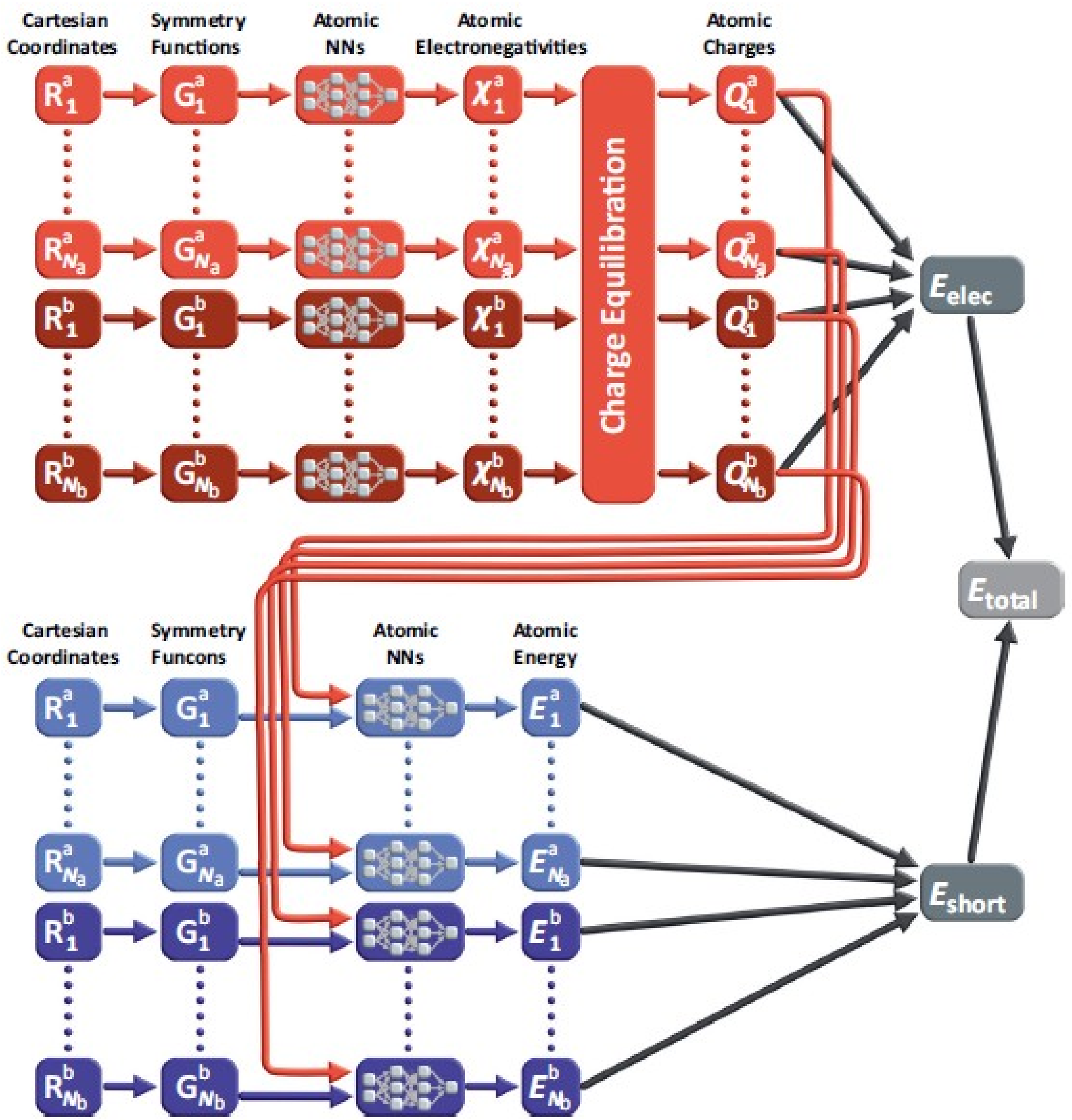


$$[\mathbf{A}]_{ij} = \begin{cases} J_i + \frac{1}{\sigma_i\sqrt{\pi}}, & \text{if i = j} \\ \frac{\operatorname{erf}\left(\frac{r_{ij}}{\sqrt{2}\gamma_{ij}}\right)}{r_{ij}}, & \text{otherwise} \end{cases}$$

$$\left(\begin{array}{c|c} \mathbf{A} & \begin{matrix} 1 \\ \vdots \\ 1 \end{matrix} \\ \hline 1 \;\ldots\; 1 & 0 \end{array}\right) \left(\begin{array}{c} Q_1 \\ \vdots \\ Q_{N_{\mathrm{at}}} \\ \hline \lambda \end{array}\right) = \left(\begin{array}{c} -\chi_1 \\ \vdots \\ -\chi_{N_{\mathrm{at}}} \\ \hline Q_{\mathrm{tot}} \end{array}\right)$$

Charges are trained vs DFT references

$$E_{\mathrm{elec}} = \sum_{i=1}^{N_{\mathrm{at}}} \sum_{j}^{N_{\mathrm{at}}} \frac{\operatorname{erf}\left(\frac{r_{ij}}{\sqrt{2}\gamma_{ij}}\right)}{r_{ij}} Q_i Q_j + \sum_{i=1}^{N_{\mathrm{at}}} \frac{Q_i^2}{2\sigma_i\sqrt{\pi}}$$



$$E_{\text{short}} = \sum_{i=1}^{N_{\text{at}}} E_i$$

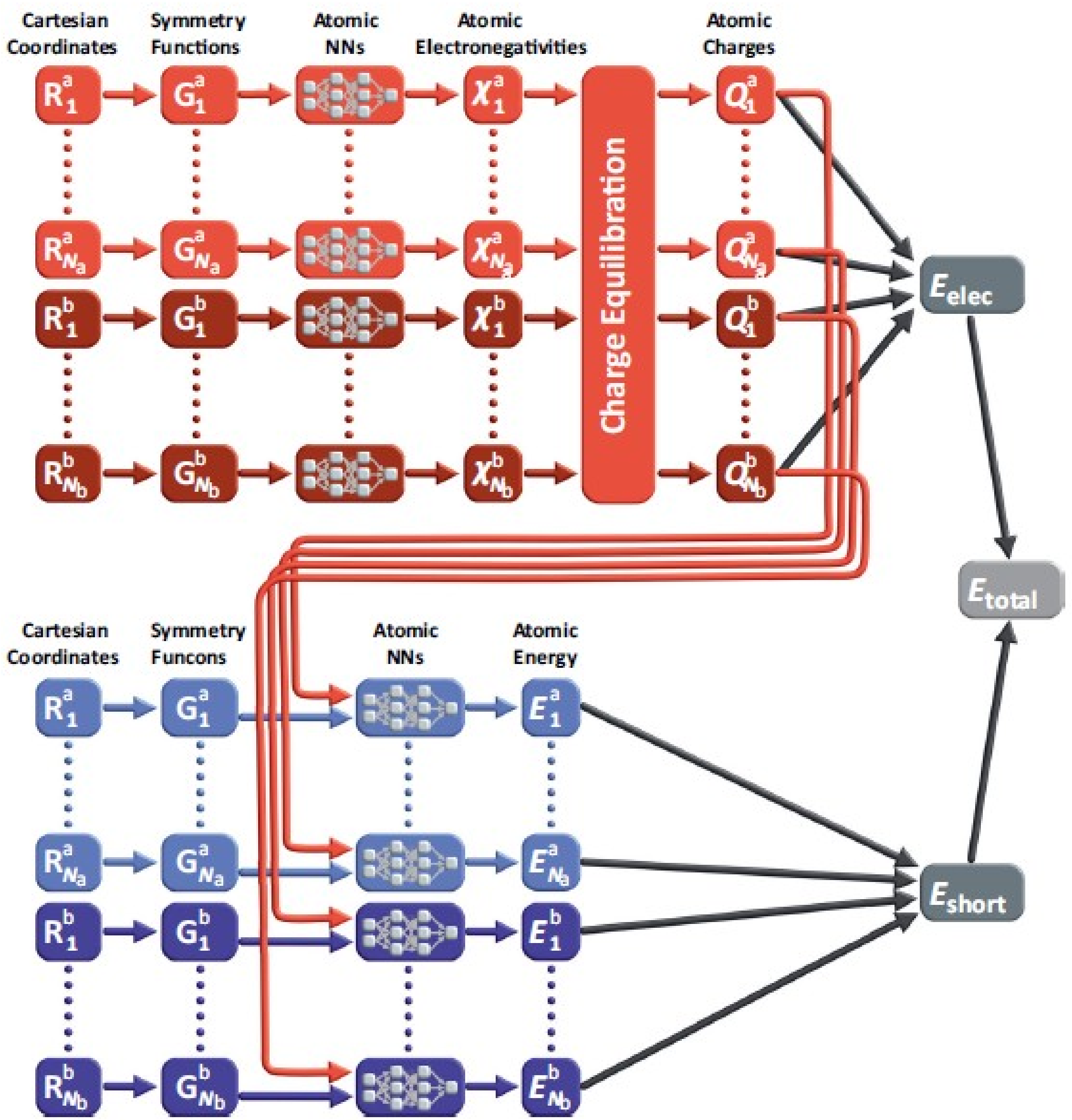
$$E_{\text{short}} = E_{\text{ref}} - E_{\text{elec}} = \sum_{i=1}^{N_{\text{at}}} E_i(\{\mathbf{G}_i\}, Q_i)$$

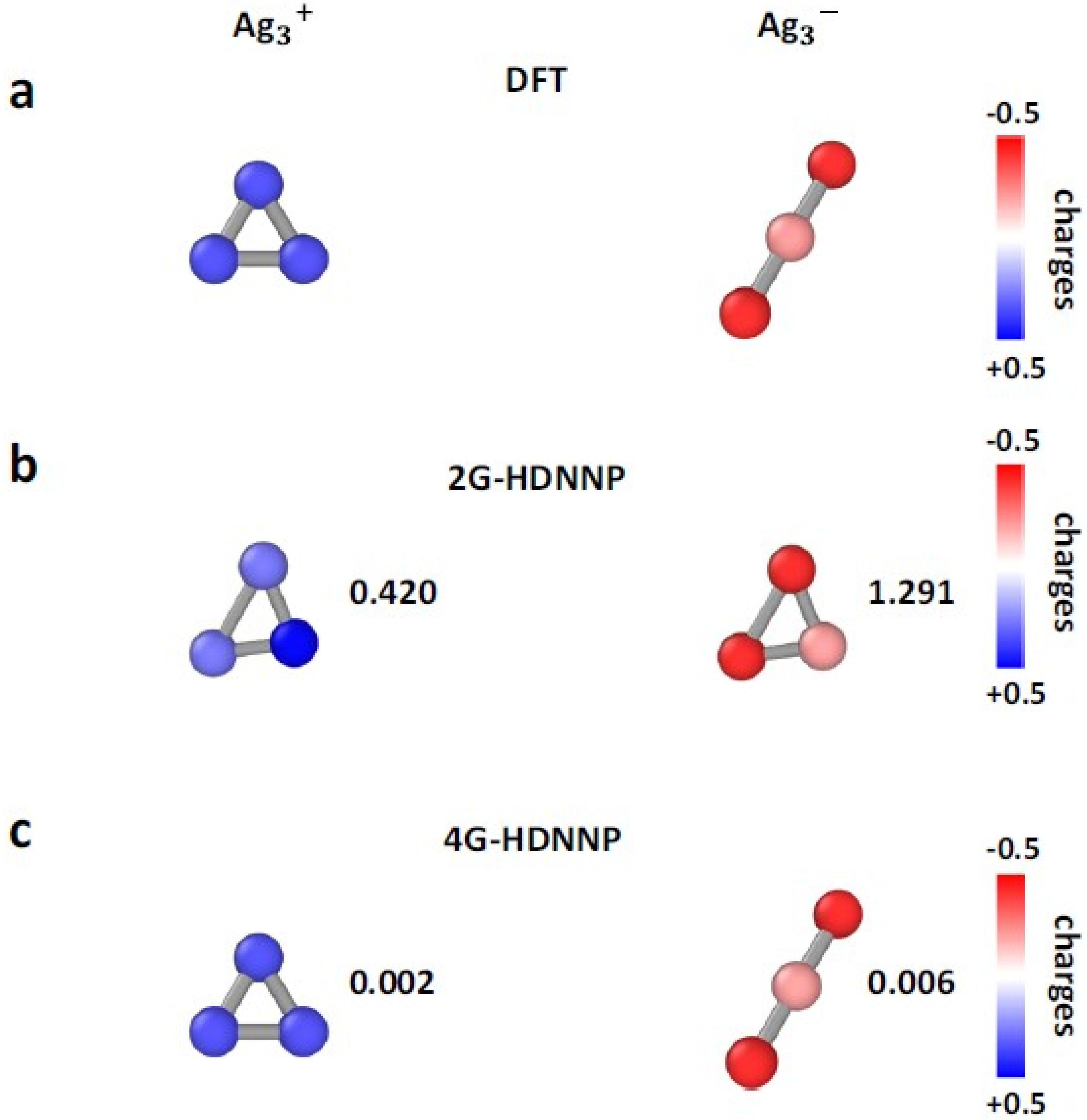
In Conclusion

Hardness included as parameter

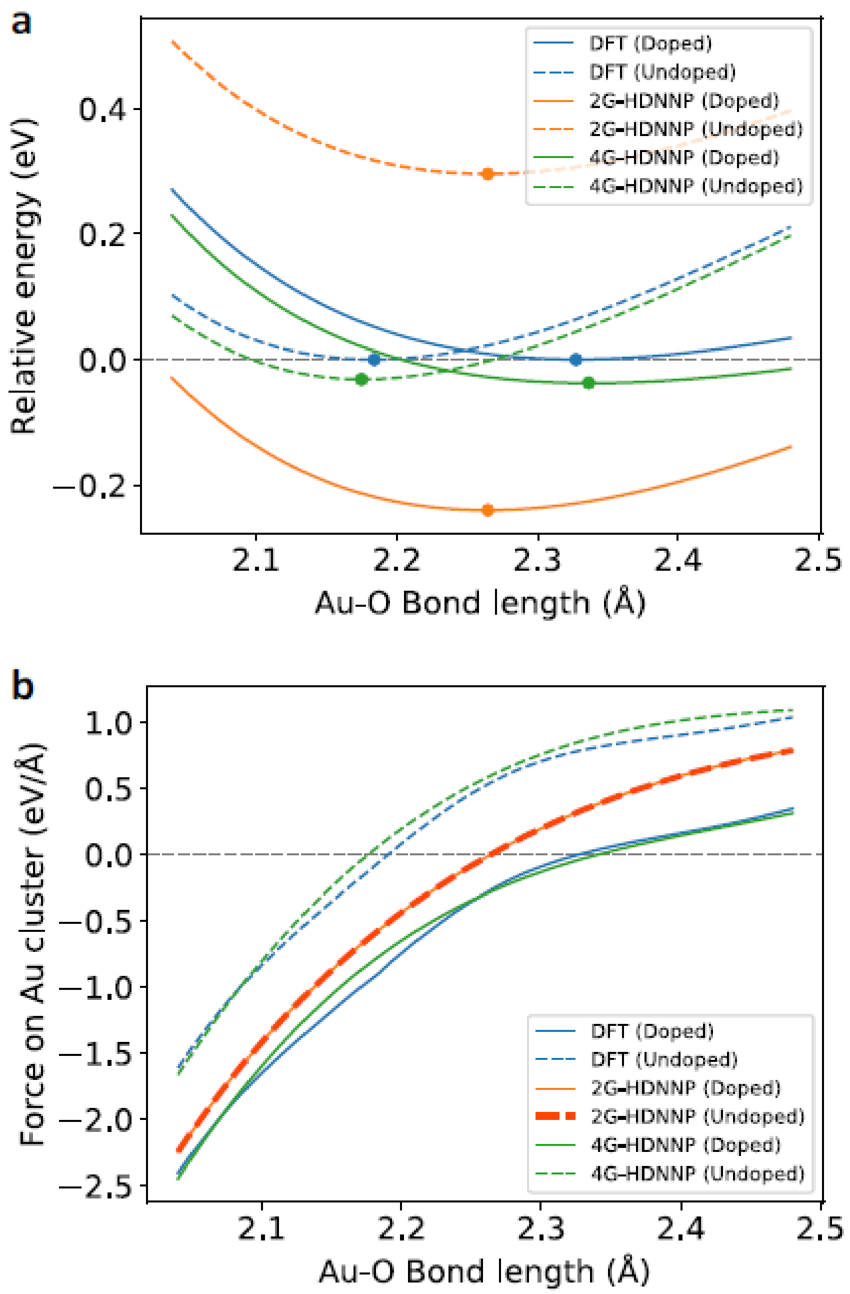
Charges trained with DFT charges

E short not described through charges but own neural network





Ag3+
Ag3−
a
DFT
-0.5
charges
+0.5
b
2G-HDNNP
0.420
1.291
-0.5
charges
+0.5
c
4G-HDNNP
0.002
0.006
-0.5
charges
+0.5



a
DFT (Doped)
DFT (Undoped)
2G-HDNNP (Doped)
2G-HDNNP (Undoped)
4G-HDNNP (Doped)
4G-HDNNP (Undoped)
Relative energy (eV)
0.4
0.2
0.0
−0.2
2.1
2.2
2.3
2.4
2.5
Au-O Bond length (Å)
b
Force on Au cluster (eV/Å)
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
DFT (Doped)
DFT (Undoped)
2G-HDNNP (Doped)
2G-HDNNP (Undoped)
4G-HDNNP (Doped)
4G-HDNNP (Undoped)
2.1
2.2
2.3
2.4
2.5
Au-O Bond length (Å)