Correct Vibrational Properties of Polar Materials from Neural Network Interatomic Potentials

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Abstract

The LO-TO splitting in the vibrational properties of polar materials results from the long-range nature of Coulomb interaction. The state-of-the-art neural network interatomic potentials (NNIP) are usually constructed based on the local chemical environment descriptors that are truncated at a finite spherical cutoff. This approach, by construction, neglects the electrostatic interactions whose long-wavelength limit contains the ingredients to account for the so-called non-analytic correction in the interatomic force constants. Here, we apply our recently developed incorporation of long-range electrostatics in NNIP to describe the LO-TO splitting in polar materials and, as a first example, compute the full phonon dispersion of NaCl.

Theory

This work focuses on phonon dispersion with long range correction. In order to implement the long range correction in NN potentials, an anology between DFT and NN energies can be considered[1]:

$$\mathrm{E^{DFT}}(\{\mathbf{R}\}) = \min_{\rho}[\mathrm{T_s}[\rho] + \int \mathrm{V_{ext}}(\mathbf{r}|\{\mathbf{R}\})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + \frac{e^2}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3\mathrm{r}\mathrm{d}^3\mathrm{r}' + \mathrm{E_{xc}}[\rho] + \mathrm{E_{ion}}(\{\mathbf{R}\})]$$

$$\mathrm{E^{VNN}}(\{\mathbf{R}\}) = \min_{\{q\}}[\sum_{\mathrm{I}} \mathrm{E_I^0}(\{\mathbf{R}\}) + \sum_{\mathrm{I}} \mathrm{E_I^1}(\{\mathbf{R}\})\ \mathrm{q_I} + \frac{1}{2}\sum_{\mathrm{IJ}} \mathrm{q_I}\ (\ \mathrm{E_I^2}(\{\mathbf{R}\})\ \delta_{\mathrm{IJ}} + \mathrm{V_{IJ}}(|\mathbf{R_I}-\mathbf{R_J}|)\ )\ \mathrm{q_J}],$$

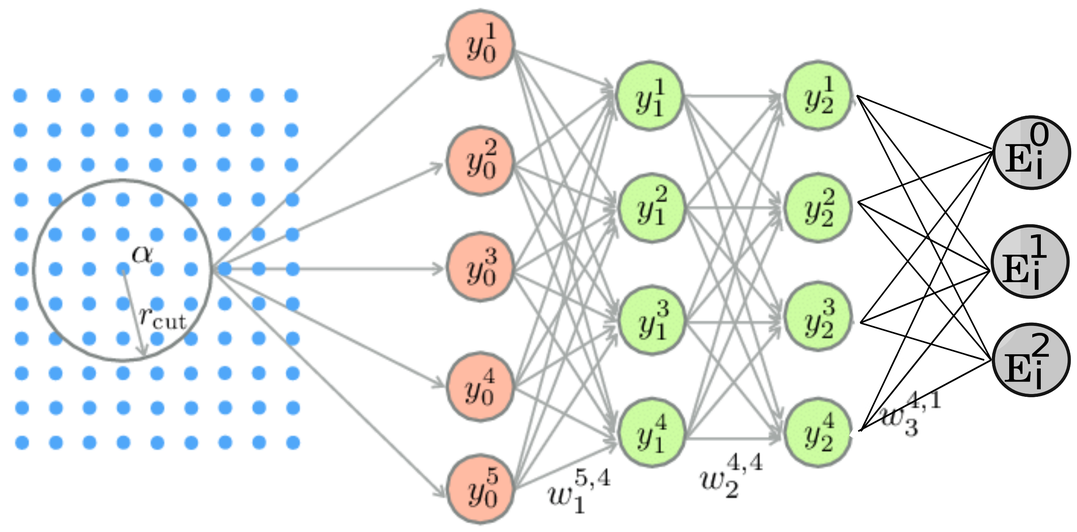

Figure 1. Schimatic neural network configuration to implement long range correction in NN potentials. Output has divided to 3 facors.

To distingush the long-range and short-range parts of the NN total energy, it can be written as follows:

$$\mathrm{E_{tot}} = \eta_{\mathrm{SR}}\ \mathrm{E_{SR}} + \eta_{\mathrm{LR}}\ \mathrm{E_{LR}}$$

$$\mathrm{E_{SR}} = \sum_{\mathrm{I}}^{\mathrm{N_{at}}} \mathrm{e_i}(\mathrm{G_i}(\{\mathbf{R}\})) \qquad \longrightarrow \mathrm{e_i} = \mathrm{E_i^0} + \mathrm{E_i^1} + \mathrm{E_i^2}$$

$$\mathrm{E_{LR}}[\rho] = \sum_{\mathrm{i}}[\chi_{\mathrm{i}}\mathrm{q_i} + \frac{1}{2}\mathrm{J_i}\mathrm{q_i^2}] + \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3\mathrm{r}\mathrm{d}^3\mathrm{r}'$$

One notice to calculate correct phonon dispersion for a polar semiconductor, which is determined by NN potential from this model, the LO - TO splitting at wavevector q =0 is required (Γ), since LO - TO splitting is a consequence of long-range effects of electric field in polar materials. There is an approach to tackle this problem, which is introduced in DFPT method[2] by considering non-analyticity at q = 0. This means we can write the mantrix of force constant as seen below:

$$\tilde{\mathrm{C}}_{\alpha\mathrm{i},\beta\mathrm{j}} = \tilde{\mathrm{C}}^{\mathrm{an}}_{\alpha\mathrm{i},\beta\mathrm{j}} + \tilde{\mathrm{C}}^{\mathrm{na}}_{\alpha\mathrm{i},\beta\mathrm{j}}$$

This separation let us to implement desired correction to phonon dispersion. Then dynamical matrix is defined as usual.

$$\tilde{\mathrm{D}}_{\alpha\mathrm{i},\beta\mathrm{j}}(\mathbf{q}) = \frac{\tilde{\mathrm{C}}_{\alpha\mathrm{i},\beta\mathrm{j}}(\mathbf{q})}{\mathrm{M_i}\mathrm{M_j^{\frac{1}{2}}}}$$

Results

We investigate the phonon dispersion of molten NaCl as an example of polar material. The structure has been relaxed with NN potential trained by PANNA code[3], which is implemented in LAMMAPS code[4]. After relaxation process and reach the ground state, phonon calculation is performed with phonpy and phonolammps libraries[5] of python. These libraries are used to implement Small displacement method to calculate phonon dispersion. One can add non-analytical correction (calculated with DFPT) as a flag to phonopy. Then it is possible to reach LO- TO splitting at Gamma Point (q=0), As shown in graph as follows (Fig 2):

PANNA training parameters: Size of discriptors per atom: 80 cutoff=5.3 Angstrom

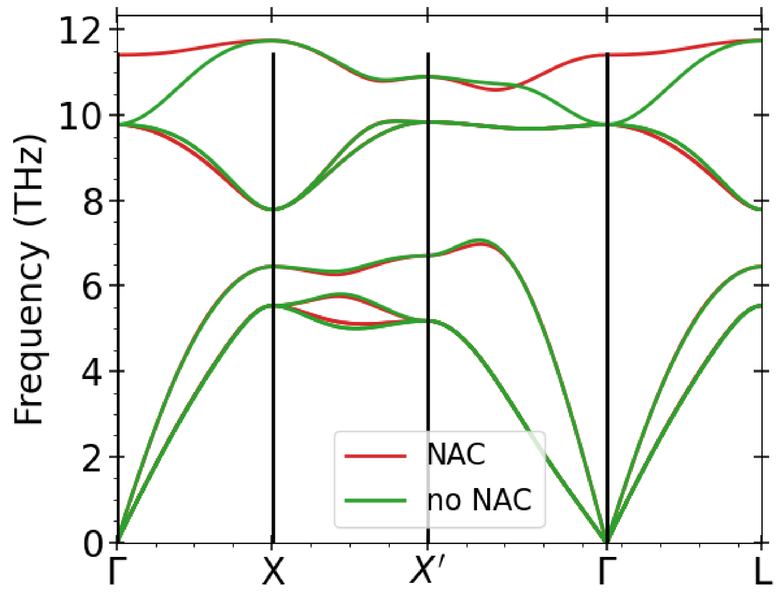

Figure 2. phonon dispersion of NaCl in molten phase , which is relaxed with NN potential trained with PANNA code. The LO-TO splitting in Gamma point is recognizable.

Conclusion

In summery we succeed to calculate the correct phonon dispersion for polar semiconductors, such as NaCl. The interatomic potential is neural network potential, trained by PANNA. The charge minimization was implemented in PANNA routine, introduced to LAMMPS, which is required for long-range effects simulation.
Although, this is an indirect way to reach the LO-TO splitting in Gamma point. Which means we still need an ab-initio code to calculate the Born Effective charge and dielectric constant. Finally, to generalize the results, our next step will be implementation of perturbation, and use response theory to find effective charge ($\mathbf{Z}^*$) and high-frequency static dielectric constant (ϵ_∞) directly.

$$\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$$

$$\mathrm{Z^*_{i,\alpha\beta}} = \frac{\Omega}{\mathrm{e}}\frac{\partial \mathrm{P^{tot}_\alpha}}{\partial \mathrm{u}_{\beta \mathrm{iq}=0}} \quad \longrightarrow \quad \tilde{\mathrm{C}}^{\mathrm{na}}_{\alpha\mathrm{i},\beta\mathrm{j}} = \frac{4\pi\mathrm{e}^2}{\Omega}\frac{(\mathrm{qZ^*_i})_\alpha(\mathrm{qZ^*_j})_\beta}{\mathrm{q}\epsilon^\infty_{\alpha\beta}\mathrm{q}}$$

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