

# Non-variational induced Multipoles for Polarizable Force Fields: Theory and Implementation for Molecular Dynamics Simulations

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Describing electrostatic polarization effects in Classical Molecular Dynamics simulations is an ongoing field of research aiming to make molecular simulations more accurate and realistic. Polarization effects are modelled by introducing induced charges, dipoles or in general multipoles, according to the specific model adopted, arising from intra- and inter-molecular electrostatic interactions. All existing polarization models can be considered variational since the induced multipoles are obtained by minimizing a polarization energy functional: this feature allows an easy evaluation of energy gradients required to perform Molecular Dynamics simulations, as the classical Hellman-Feynman theorem can be invoked. In the case of non-variational models, where the induced multipoles are not obtained by minimizing the polarization energy, energy gradients are formally cumbersome to compute as the multipolar response term needs to be evaluated. We here present a Lagrange formalism allowing the evaluation of energy gradients for non-variational polarization models at a computational cost comparable to that for variational ones. The theory is implemented and tested for the recently proposed Bond Capacity model which introduces polarization at the charge-level [1]. The model is implemented in the Tinker-HP package and long-range electrostatic interactions are treated with the Smooth Particle Mesh Ewald Method [2].

## References

1. P. P. Poier and F. Jensen, *Journal of Chemical Theory and Computation* **15** (2019), 3093.
2. L. Lagardere *et al.*, *Chemical Science* **9** (2018), 956.