

Efficient force field optimization methodology for high temperature metal alloys: application to W-Re systems

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ABSTRACT

While quantum chemical simulations have been increasingly used as an invaluable source of information for atomistic model development, the high computational expenses typically associated with these techniques often limit thorough sampling of the systems of interest. It is therefore of great practical importance to use all available information as efficiently as possible, and in a way that allows for consistent addition of constraints that may be provided by macroscopic experiments. Here we propose a simple approach that combines information from configurational energies and forces generated in a molecular dynamics (MD) simulation to increase the effective number of samples. Subsequently, this information is used to optimize a molecular force field by minimizing the statistical distance similarity metric. We illustrate the methodology on an example of a trajectory of configurations generated in equilibrium molecular dynamics simulations of argon and water, and compare the results with those based on the force matching method.

1. **Introduction**

Steady advances in both quantum chemical methods and molecular simulation techniques have made the development of sophisticated quantum chemistry-based force fields a common task. Over the past three decades a number of approaches have been proposed for translating the target *ab initio* data into effective potentials for classical simulations. These could be roughly divided into the efforts to match (i) the potential energy surface (PES) of small systems, such as dimers, single molecule adsorption, or sections of bulk solid,[1-4](#_ENREF_1) (ii) reproduce the energetics of select configurations, typically representing local energy minima, defects, or transition states,[5-7](#_ENREF_5) and (iii) matching the trajectories of quantum chemical MD simulations,[7-9](#_ENREF_7) usually generated under the Born-Oppenheimer approximation.[10](#_ENREF_10)

In this report, we will focus on molecular force fields developed on the basis of finite temperature MD simulations of the target system. These often employ the density functional theory (DFT) approach to the electronic structure calculation,[11](#_ENREF_11) and produce a trajectory of nuclear positions, configurational energies, and forces acting on the nuclei. Such data can be used for force field development in different approaches, including energy and force matching,[8](#_ENREF_8),[9](#_ENREF_9),[12-15](#_ENREF_12) or the Boltzmann inversion of pair distribution functions based on averaged structural data.[16](#_ENREF_16),[17](#_ENREF_17) Arguably, the most common way to use data from DFT-MD simulations for force field optimization is to apply the force matching method (FMM),[8](#_ENREF_8) whose main advantages are simplicity and the use of large amounts of information consisting of three force components per every atom in each generated configuration.

In our previous study we touched upon the limitation of the standard FMM,[18](#_ENREF_18) which tends to overweight otherwise statistically unimportant configurations if the model and target system forces differ significantly, such as for rare configurations with large atomic core overlaps. To remedy some of these deficiencies various weighting schemes are typically employed.[15](#_ENREF_15) Also, the asymmetry of the FMM loss function with respect to averaging over the target and model system trajectories is inconsistent with the symmetric auxiliary loss functions often used to incorporate macroscopic constraints.[18](#_ENREF_18) Instead, we proposed to base the optimization loss function on a similarity metric known in physics as statistical distance.[19](#_ENREF_19),[20](#_ENREF_20) We have recently shown that this metric could be used as a loss function consistently integrating quantum chemical and experimental data into effective models.[21](#_ENREF_21) Despite these advantages, we have only demonstrated how to utilize configurational energies, while we left the information contained in forces untapped.

Here we present a simple extension of the statistical distance minimization approach that can consistently incorporate information about forces (and higher derivatives of potential energy) generated in an MD simulation. Such a capability will not only increase the overall amount of information available for optimization, but will also allow for the optimization of interactions restricted to selected subsets of a given atomic system.

In the following section we review the basic ideas of statistical distance minimization and describe how forces can be incorporated into the framework. Then, in Section 3, we present the technical details of the optimization procedure as well as of classical and DFT MD simulations details. In Section 4, we demonstrate the principles on the examples of MD simulation of supercritical argon and liquid water, and conclude in Section 5 with the discussion of current limitations and possible extensions of the proposed approach.

1. **Theoretical background**
   1. *Defining model optimality criteria*

Throughout this report we will consider target systems whose atomic interactions may follow the laws of quantum mechanics, but whose nuclear motions can be tracked on a classical continuous phase space. The effective interaction potentials of the corresponding models are then designed so that the equilibrium probabilities of different nuclear configurations generated in simulations closely follow those of the target systems. For simplicity, we will restrict the discussion to systems with constant number of particles *N*, absolute temperature *T*, and volume *V*. The properties depending on the nuclear positions of one such system *P* are completely determined by the canonical partition function[22](#_ENREF_22)

 (1)

where  and  are the coordinates and momenta of *N* particles, respectively, *h* is the Planck constant,  is de Broglie wavelength, *HP* is the Hamiltonian of system *P*, *uP* is its configurational energy, and , with *kB* being the Boltzmann constant. While it is usually computationally prohibitive to evaluate the absolute value of the partition function, it is often possible to determine the ratio of partition functions of systems with a sufficient overlap of their probability distributions using the importance sampling or some more sophisticated method.[23](#_ENREF_23) The ratio of two partition functions corresponding to systems *P* and *Q*,

 (2)

where  denotes the ensemble average over all configurations of system *P*, , and  is the Helmholtz free energy difference between systems *Q* and *P.* In the case of importance sampling, the estimator of the ratio can be written as,

 . (3)

Here the summation runs over *MP* configurations generated in an equilibrium simulation of *P*.

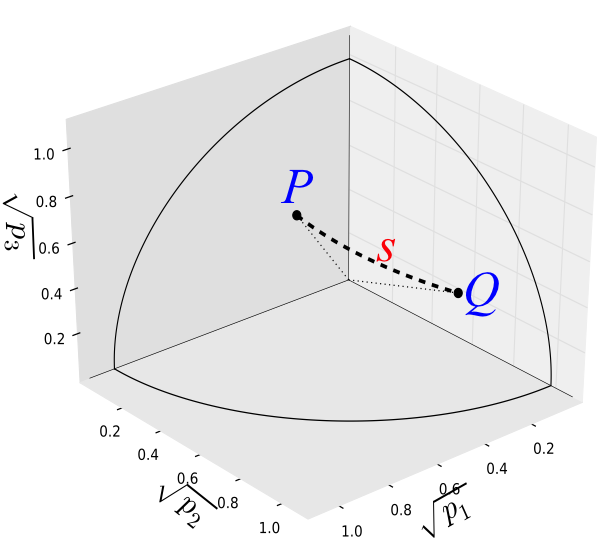
Since all measurable properties of systems considered in this study are determined by their partition functions given by Eq. (1), it is natural to require that the model’s partition function, or rather its microstate probability distribution, differs minimally from that of the target system. We have previously shown the advantages of using a model optimization loss function based on a similarity metric introduced to statistics by Rao,[24](#_ENREF_24),[25](#_ENREF_25) and known in physics as statistical distance,[19](#_ENREF_19) which quantifies distinguishability between two physical systems based on the results (sets of samples) of arbitrary measurements performed on those systems. The metric is closely related to relative entropy, which has been previously used in the design of atomistic and coarse-grained models,[22](#_ENREF_22),[26](#_ENREF_26) but does not suffer from divergence for hard body potentials and is more robust overall.[18](#_ENREF_18) Statistical distance between systems *P* and *Q* is defined as,[19](#_ENREF_19)

 (4)

where *CB* is the Bhattacharyya coefficient,

 (5)

with  and  being the probability densities of configurations  in systems *P* and *Q*, respectively. The form and meaning of Eq. (4) can be easily understood from its geometric interpretation as the geodesic distance between probability distributions on the shared probability space (Figure 1).



**Figure 1.** Statistical distance *s* between probability distributions *P* and *Q* on the probability space of three-state systems. The coordinates of points *P* and *Q* determine the square roots of microstate probabilities.

For equilibrium systems, which we are concerned with here, the probability density

 , (6)

leads to

 . (7)

The estimator of *CB* can be calculated from a finite number *MP* of samples from system *P* (or *Q*) as

 (8)

The corresponding force field optimization loss function based on statistical distance and using configurational energies as input (SDU), can be defined as the square of Eq. (4), *i.e.*, .

Given the limited amount of information that can be obtained from a finite set of samples of the target system, the judiciously chosen functional form of the model’s interaction potential is essential to provide the necessary regularization. However, as the complexity and number of adjustable parameters of the model increases, the risk of overfitting increases as well. It is therefore highly desirable to maximize information extracted from the available target data.

* + 1. *Relation to energy and force matching approaches*

Statistical distance minimization can be related to popular energy and force matching methods.

As discussed in our previous study, if forces are included in the target properties, optimization based on a single configuration, the SD loss function reduces to force matching. SD loss function can also be shown to reduce to energy matching.

As can be seen, energy matching can be seen as the first order approximation of SD, assuming equality of free energies.

While energy matching can suffer from and completely fail in general settings, it can provide a good starting point for further optimization for sufficiently flexible potentials with localized basis functions, as discussed here.

We must note that energy matching will produce reasonable results only in cases where the basis functions are sufficiently flexible across the full range of atomic configurations. Application of energy matching to more general force field forms, such as simple Lennard-Jones functions, will lead to large biases, and probability matching should always be preferred. The described methodology is equally applicable to all potentials from complex force fields to hard sphere models.

* 1. *General embedded atom models*

Basis functions

Underfitting and overfitting.

Ising model

* 1. *Optimization algorithm*

To find a set of parameters minimizing the loss function

Newton-Raphson iterations: Weighted least squares

Energy matching

Step 1: Energy matching: Linear regression, direct and step-wise

Step 2: N-R algorithm

1. **Simulation details**
   1. *Perturbation technique for parameter optimization*

The search for the optimal set of model parameters can be efficiently accomplished using the perturbation technique applied in our earlier studies.[27-30](#_ENREF_27) The approach uses the thermodynamic perturbation relations of statistical mechanics to predict changes of arbitrary properties *A* of system *P* as a function of interaction parameters. Here we want to predict the changes in the statistical distance of a model from its target system, so that we can find its minimum. This can be achieved by using Eq. (8), (12), or (13) after sampling system *P.*  In the present application, the samples come from the target system trajectory.

The accuracy of *CB* predictions based on Eq. (8) or (12) depends both on the overlap of the two systems’ probability distributions and on sufficient sampling of the configurational space. Since the best models are those with the largest overlaps with the target microstate distribution, the perturbation relations using the target system trajectories as a reference can be expected to produce accurate predictions for such models.

The key to avoiding the need for repeated reference system simulations for each new parameter combination is to express the energy and force differences,  and , in a form that separates the model parameters from quantities defined solely by configurations collected from the reference simulation. The concrete expressions will depend on the functional form of the model interaction potential. For instance, in a system of particles with Lennard-Jones (LJ) and point charge interactions,

 (14)

where is distance between particles *k* and *l*, *qk* is charge on particle *k* while  and  are size and energy parameters, respectively. The energy of configuration *i* can be then written as,

 (15)

Here numbers ,  and  are collected for each configuration *i* generated in the reference simulation. Subsequently, these quantities are multiplied by different combinations of model parameters *A*, *C* and *E*, and added together to obtain a series of configurational energies for the corresponding models at the comparably negligible cost of a few array operations rather than that of a full new simulation. The configurational energy difference between target *P* and model *Q* characterized by parameters *A* and *C* can be determined as

, (16)

and Eq. (8) can be then used to estimate statistical distance between the two systems.

To use forces in Eq. (11) - (13), we can follow the same ideas. For the above potential

 (17)

Here is the atom index,  is the one of the three spatial directions (*x* = 1, *y* = 2, *z* = 3), and  is the  component of a vector from atom *k* to atom *l*. The mapping between the indexes is given by prescription  and , where ‘\’ denotes integer division.

Similar expressions for configurational energies and forces can be obtained for other interaction potentials. For instance, in the following section we will deal with harmonic bonds, whose potential is defined as

 (18)

where *Kf* is the force constant and *R0* is the minimum energy bond distance.

The contribution of these harmonic interactions to the total configurational energy can be expressed as,

, (19)

where the summations run between bonded atoms. Forces can expressed as,

 (20)

The harmonic angle potential is defined as,

 (21)

where  is the bond angle between atoms *k*, *l*, and *m*,  is the minimum energy angle, and  is the force constant. The corresponding relations for the configurational energies and forces follow Eq. (17) and (20) with appropriate substitutions of  for  and  for .

The optimization procedure can be summarized as follows: (i) Collect atomic coordinates, configurational energy, and forces from a DFT-MD trajectory. (ii) Use atomic coordinates to calculate quantities  and  for each configuration *i* according to Eqs. (15)-(20). (iii) Multiply these quantities by trial force field parameters to determine energies and forces of the model for each configuration *i* according to Eqs. (15)-(20). (iv) Use these energies and forces along with the known configurational energies and forces of the target system to determine the SDF or FMM loss functions according to Eq. (12) or (13). (v) If convergence criteria are not reached, modify the force field parameters using a search algorithm, such as the conjugate gradient method.[31](#_ENREF_31) (vi) Return to (iii).

* 1. *DFT-MD simulations*

The *ab initio* molecular dynamics (AIMD) simulations at 300K were performed using the canonical ensemble with the Nosé thermostat[32](#_ENREF_32),[33](#_ENREF_33) implemented in Vienna *ab initio* simulation package (VASP)[34](#_ENREF_34) within the generalized gradient approximation, parameterized in the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.[35](#_ENREF_35) Interactions between electrons and nuclei were described by the projector-augmented wave (PAW) method.[36](#_ENREF_36) The criterion of the total energy convergence was 1E−5 eV. A plane-wave kinetic energy cutoff of 350 eV was employed. The Brillouin zone (BZ) was sampled using only the gamma point. A supercell containing 125 water molecules was used for the AIMD simulations, with the initial configurations generated from well-equilibrated classical molecular dynamics runs.  An additional 3ps of equilibration in AIMD was performed with the time step of 1 fs. Three independent simulations were performed for this set up and their trajectories were combined to obtain equilibrium samples.

* 1. *Classical simulations*

The classical molecular dynamics (CMD) simulations were performed using LAMMPS package.[37](#_ENREF_37) The canonical ensemble was used for all simulations with temperature maintained by the Nosé thermostat[32](#_ENREF_32),[33](#_ENREF_33) The equations of motion were integrated using the velocity Verlet algorithm with 1 fs time step. The particles were placed in a cubic simulation box with Coulombic interactions treated by the Ewald summation method, and non-Coulombic interactions cut off at the distance of the half of the simulation box.

For simulations of argon (Section 4.1), the system consisted of *N* = 123 particles, held at *T* = 160 K in a simulation box with side 24 Å. The target system atom-atom interactions were represented by the Buckingham potential,[38](#_ENREF_38) while the model system interactions were represented by the LJ potential, whose two parameters were optimized.

For simulations of water (Section 4.2), the system consisted of *N* = 125 molecules, held at *T* = 300 K in a simulation box with side 15.74298 Å. The functional form of the model water molecules consisted of the LJ interactions between O atoms, point charges located at O and H atoms, Eq. (14), harmonic O-H bonds, Eq. (18), and harmonic H-O-H angles, Eq. (21). All 7 force field parameters were simultaneously optimized.

1. **Results and discussion**

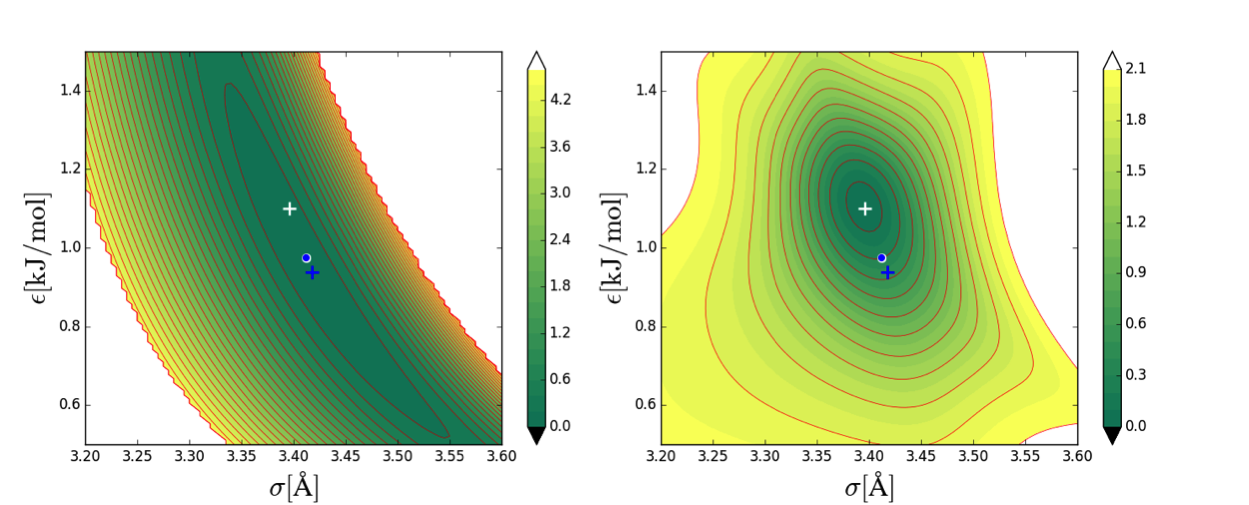
We demonstrate the application of the theoretical relations introduced in the preceding sections to the optimization of effective force fields for equilibrium fluids. To assess the basic behavior and features of the proposed approach, we first study a simple system of supercritical argon represented by a classical interaction potential, and to demonstrate its accuracy, efficiency, and flexibility we follow with a more complex problem of the DFT-MD trajectory of liquid water. In the last part of this section we try to draw more general (and somewhat speculative) observations about the proposed approach, its current limits, possible extensions, and its comparison with the FMM.

* 1. **Argon**

In this example we develop a simple model of supercritical argon, with the target system represented by the classical Buckingham potential.[31](#_ENREF_31) We have previously performed optimization of the identical system based on information from configurational energies,[30](#_ENREF_30) and the values of density and compressibility at different chemical potentials.[21](#_ENREF_21) In those studies we have established that a model based on SDU reproduces the structure, entropy, and the equation of state in better agreement with the target system than a model based on simple FMM. Here we want to investigate if the convergence to the SDU optimum can be achieved faster with the use of forces information.

The simulations of the target system spanned 2 ns and provided the total of 1000 independent samples, which were used for the optimization of the LJ model. To evaluate how information about atomic forces impacts the resulting models, we optimized the argon LJ force field based on different numbers of samples and compared different loss functions, which included (i) statistical distance based on configurational energies, SDU, Eq. (8), (ii) statistical distance based on energies and forces, SDF, Eq. (12), and (iii) simple force matching loss function without adjustable weights, FMM, Eq. (13).

First, to establish the optimal parameters in the limit of thorough sampling, we used all collected samples, *i.e.,* *MP* = 1000. In Figure 2 we plot the landscapes of SDU/SDF and FMM loss functions as a function of the LJ parameters, with the optimized parameter sets shown as white and blue crosses. At this level of sampling and for  Å, the SDF and SDU loss functions produce practically indistinguishable results because the substantial number of configurational energy samples renders the force information nearly redundant. Qualitative assessment of the shape and extent of the valley surrounding the minimum can also indicate how well the different loss functions constrain the interaction parameters. While the FMM landscape, Figure 2a, exhibits a long bent valley, which includes the SDU/SDF optimum near its bottom, *i.e.*, the parameters are reasonable even based on the FMM criteria, the near-spherical valley of the SDU/SDF landscape, Figure 2b, is more constraining, *i.e.*, the FMM-optimal parameters would not be acceptable according to the statistical distance criteria. We may speculate that the larger set of near-optimal models according to FMM is the consequence of the fact that many different systems will be similar in the linear approximation, which ignores their differences contained in the higher derivatives. (Note that the wavy shape of the landscape farther away from the minimum is most likely the result of statistical uncertainty and will be smoothed out with larger number of samples. However, this is immaterial for our purposes because we are interested in finding the minimum and the loss function in its close neighborhood.)



**Figure 2:** The landscapes of the FMM (left) and SDU/SDF (right) loss functions in the space of argon LJ parameters. The symbols indicate optimal parameters based on SDU/SDF for *MP* = 1000 samples (white cross), SDF for *MP* = 1 (white circle), FMM for *MP* = 1000 samples (blue cross), and FMM for *MP* = 1 (blue circle).

Next, we reduced the number of independent samples to *MP* =10, and averaging over 100 optimizations we calculated the mean values and standard deviations of the optimal parameters, which are given in Table I. It turns out that for this very simple system, such limited sampling is still sufficient to constrain well the two adjustable parameters in close agreement with the limiting case of *MP* =1000. The predictions of the SDF differ significantly from the limiting values only for larger  > 0.05 Å, for which the linear approximation is not accurate and leads to bias.

Table I: Optimal values of the argon LJ potential based on different loss functions and sample numbers. The values of  are given in Å, and  in kJ/mol. The numbers indicate mean values, with the standard deviations given in parentheses.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Samples | *MP = 1000* | | *MP = 10* | | *MP = 2* | | *MP = 1* | |
| Parameters |  |  |  |  |  |  |  |  |
| SDU | 3.396 | 1.088 | 3.397(3) | 1.10(2) | 3.46(9) | 1.15(26) | - | - |
| SDF() | 3.396 | 1.088 | 3.396(4) | 1.11(1) | 3.40(3) | 1.11(15) | 3.412(5) | 0.98(4) |
| SDF() | 3.395 | 1.088 | 3.396(4) | 1.11(1) | 3.39(3) | 1.10(15) | 3.412(5) | 0.97(4) |
| SDF() | 3.395 | 1.088 | 3.396(3) | 1.10(2) | 3.39(3) | 1.10(15) | 3.412(5) | 0.97(4) |
| SDF() | 3.408 | 0.979 | 3.388(1) | 1.08(4) | 3.39(4) | 1.05(15) | 3.409(11) | 0.93(3) |
| FMM | 3.418 | 0.937 | 3.417(3) | 0.94(2) | 3.415(5) | 0.96(4) | 3.412(5) | 0.98(4) |

Tests performed with optimizations based on 1 and 2 samples lead to noticeable differences from the limiting parameter values. In the case of a single sample, *MP* =1, the energy-based SDU loss function does not constrain the parameters at all since a perfect match of the energies of the target and model configurations can be always achieved by adjusting the reference zero of the potential energy. Thus only the forces provide information useful for optimization. The resulting sets of optimal parameters based on SDF and FMM for this single-sample case are indicated in Figure 2 as white and blue circles, respectively. The mean values and standard deviations based on 1000 1-sample optimizations for different  are given in Table I. It can be clearly seen that for *MP* = 1 as , the optimal parameters based on the SDF converge to those of the FMM. In Appendix B we show that indeed for this case, statistical distance minimization leads to the exact same optimum as the FMM.

For *MP* ≥ 2 the configurational energies provide increasingly more important constraints and the relative importance of forces decreases. The mean values and standard deviations of optimal parameters calculated from 500 *MP* = 2 measurements are listed in Table I. Unlike for *MP* = 1, the mean of the optimal values quickly converges to the large sample limit. The comparisons of the SDU and SDF outcomes for different  also show that inclusion of forces significantly reduces the statistical error of the estimates and speeds up the convergence to the correct limit. It can be expected that the extra information in the form of forces will have even larger impact on the speed of optimization convergence for more complex systems and interaction potentials.

* 1. **General discussion and comparison with the force matching method**

It is notable that while the FMM loss function tends to be less restrictive with respect to the choice of parameters compared to the proposed SDU/SDF loss functions (see Figure 2), it is at the same time more sensitive and restrictive with respect to the choice of the force field functional form. For instance, it cannot be applied to discrete or discontinuous potentials, and even better behaving potentials may produce suboptimal models by overemphasizing model inaccuracies in force description for configurations with low probabilities.[18](#_ENREF_18),[21](#_ENREF_21) Even though these limitations do not apply to the SDU loss function, the use of forces in the SDF may raise the question about its generality and possible limitations similar to the FMM.

The key to preserving the general applicability of the SDF lies in proper adjustment of the  parameter controlling the contribution of the force information. For this proof-of-principle study we have estimated suitable  by following the convergence of optimal parameters as a function of its magnitude, and set it to the largest value that still provided the same (within the statistical error) estimate for *MP* = 1 as . However, a more sophisticated (and more computationally expensive) approach should evaluate the expected error of the truncated Taylor expansion by explicitly comparing the exact configurational energies and its Taylor approximations as a function of  and then assign appropriate weights  to the extra 6*N* configurations. For instance the denominator of Eq. (12) could read as . With this adjustment, the average error in the predicted energy for hard body potentials would go to infinity for any , and therefore the statistical weights of configurations other than  would go to zero. Consequently, such weighting within the SDF loss function would automatically eliminate problems encountered by the FMM.

It is also straightforward to incorporate seamlessly information from higher order energy derivatives, such as the Hessian matrix, into the Taylor expansion, making the extrapolated energies of neighboring configurations more accurate, and thus allowing setting larger . Adding the second order derivative information would be especially useful for improving the description of the PES around local energy minima and saddle points in the vicinity of transition states. While energies, forces, and the Hessian have been combined in a single loss function in past studies,[2](#_ENREF_2) the relative weights of these contributions were left as adjustable parameters. In the present approach the relative weights are determined by the Taylor expansion coefficients, with the only adjustable parameter being the range parameter , whose value can be, in principle, rigorously estimated from the Taylor series error.

Another significant advantage of the statistical distance-based loss function is the well-defined way for integrating different sources of information, offering thus the possibility of complementing DFT-MD data by experimental constraints using the very same theoretical principles.[21](#_ENREF_21) However, to fully and correctly implement this scheme, it will be necessary to include the effects of uncertainty resulting from the systematic errors of quantum chemical methods and various sources of noise in the experimental measurement.

1. **Summary**

We have proposed and tested principles for the incorporation of configurational energies and forces into a force field optimization loss function based on the statistical distance metric. This allows us to exploit the generality and robustness of the statistical distance minimization approach along with the large amounts of target information contained in the forces (and possibly higher energy derivatives) generated in molecular dynamics simulations. Importantly, this atomically resolved information from quantum chemical calculations can be consistently combined with macroscopic constraints, which may come from experimentally determined structural or thermodynamic properties.[21](#_ENREF_21) The resulting efficiency and wide applicability of the proposed force field optimization methodology will especially facilitate developing interaction potentials of complex systems for which only a limited amount of high-level quantum calculations can be performed. Other applications may involve on-the-fly model optimization in which every new configuration provides meaningful refinement of interaction parameters, or design of hybrid classical-quantum simulations techniques in which the continuously updated model predicts the next equilibrium configuration. By extending the approach to use higher order energy derivatives, e.g., the Hessian matrix, it should be possible to develop efficiently models accurately describing transition states and the related kinetic properties. Further refinement of the proposed principles will focus on the quantification of the Taylor approximation error and the corresponding assignment of weights to the extrapolated configurations.

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