

**NEW FUNCTIONAL FORMS AND PARAMETERIZATION METHODS FOR AB  
INITIO, INTERMOLECULAR FORCE FIELD DEVELOPMENT**

by

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*Soli Deo gloria.*

## ACKNOWLEDGMENTS

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*It is customary for authors of academic books to include in their prefaces statements such as this: "I am indebted to ... for their invaluable help; however, any errors which remain are my sole responsibility." Occasionally an author will go further. Rather than say that if there are any mistakes then he is responsible for them, he will say that there will inevitably be some mistakes and he is responsible for them....*

*Although the shouldering of all responsibility is usually a social ritual, the admission that errors exist is not — it is often a sincere avowal of belief. But this appears to present a living and everyday example of a situation which philosophers have commonly dismissed as absurd; that it is sometimes rational to hold logically incompatible beliefs.*

— DAVID C. MAKINSON (1965)

Above is the famous “preface paradox,” which illustrates how to use the `wbepi` environment for epigraphs at the beginning of chapters. You probably also want to thank the Academy.

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# NEW FUNCTIONAL FORMS AND PARAMETERIZATION METHODS FOR AB INITIO, INTERMOLECULAR FORCE FIELD DEVELOPMENT

Mary J. Van Vleet

Under the supervision of Professor J.R. Schmidt

At the University of Wisconsin-Madison

**FIXME: basically a placeholder; do not believe**

I did some research, read a bunch of papers, published a couple myself, (pick one):

1. ran some experiments and made some graphs,
2. proved some theorems

and now I have a job. I've assembled this document in the last couple of months so you will let me leave. Thanks!

J.R. Schmidt

## ABSTRACT

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and now I have a job. I've assembled this document in the last couple of months so you will let me leave. Thanks!

PUBLISHED WORK AND WORK IN PREPARATION

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- [1] Van Vleet, M. J.; Misquitta, A. J.; Stone, A. J.; Schmidt, J. R. *J. Chem. Theory Comput.* **2016**, *12*, 3851–3870.

# **Part I**

## **Introduction**

## 1 INTRODUCTION

---

### 1.1 The Importance of Molecular Simulation

This ref<sup>2</sup> is super cool!

What is molecular simulation? What types of problems can it solve? How does molecular simulation work? (Be sure to include solving Newton's EQs of motion and relevant details on the partition function and interaction energies!)

## 2 BACKGROUND

---

### 2.1 Molecular Mechanics and the Theory of Intermolecular Forces

What is a force field? What are the important components of a force field, and how do we model them?

#### 2.1.1 The Many-Body Expansion

How do we break apart a force field into manageable pieces? Why does it make sense to break a force field into 2- and many-body components?

#### 2.1.2 Energy Decomposition Schemes

##### Intramolecular Interactions

Brief commentary on the non-intermolecular portions of a force field

##### Electrostatics

Conceptual description of electrostatics: long-range multipoles and charge penetration

##### Exchange

Quantum-mechanically-based Pauli Exclusion. Theoretical grounds for exponential behavior

##### Induction

Charge transfer. Polarization. Polarization Damping.

## **Dispersion**

Theoretical Formulation. Damping.

## **2.2 Ab-Initio Force Field Development**

### **2.2.1 Electronic Structure Benchmarks**

#### **SAPT**

General SAPT methodology. DFT-SAPT.

#### **Coupled-Cluster Methods**

CCSD(T). CCSD(T)-f12.

## **2.3 ISA-based methods for force field development**

What is ISA? How can ISA be used to generate parameters for intermolecular force field development? What progress has been made from this approach?



# **Part II**

## **Published Work**

### 3 ISOTROPIC AB INITIO FORCE FIELDS

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## 4 ANISOTROPIC AB INITIO FORCE FIELDS

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# **Part III**

## **Unpublished Work**

## 5 AB INITIO FORCE FIELDS USING LMO-EDA

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### 5.1 Preface

The preceding sections have been devoted to a development of various methodologies for ab initio intermolecular force field development, all generally assuming that Symmetry-Adapted Perturbation Theory (SAPT) can be used as a benchmark electronic structure theory. Critically, and especially given the developments discussed in Chapter 4, we can now usually expect our model force field energies to be within  $\sim 1$  kJ/mol of the SAPT reference values! In spite of this success, this high precision between the model and SAPT energies can only lead to experimentally-accurate molecular simulation provided that the SAPT energies themselves are accurate, either with respect to the exact underlying potential energy surface (PES) or (in practice) with respect to gold-standard CCSD(T) calculations. Indeed, for systems where SAPT and CCSD(T) disagree by several kJ/mol, there is little point in developing SAPT-based force fields with sub- kJ/mol accuracy! This limitation raises to two fundamentally important questions. First, for what types of systems might we expect SAPT to be inaccurate? Second, for the systems where SAPT and the exact PES are in disagreement, how must we modify our typical methodology for ab-initio force field development?

The purpose of this chapter is to partially address these questions, all within the specific context of force field development for Metal-Organic Frameworks (MOFs). Note that the results presented here were gathered from 2012–2014, so some important advances (namely those presented in Chapters 3 and 4) haven't been incorporated into the force fields presented here. This is probably to the detriment of the accuracy and transferability that might be possible with the LMO-EDA-based methodology, and (should this project be picked up in the future) it may be necessary to refit these force fields to the functional forms and monomer-based parameters discussed in Chapter 4.

## 5.2 Introduction

Metal-Organic Frameworks (MOFs) are an increasingly important class of compounds that are defined as porous materials which contain inorganic nodes connected by organic linkers. Within this general motif, more than 20,000 compounds have been reported and studied,<sup>3</sup> and this vast diversity of MOF materials shows great promise for chemical customization and optimization. Within the past two decades, a huge body of research has been devoted to the design and study of MOFs, and current applications range from gas separation and storage to catalysis and biomedical imaging.<sup>3</sup>

Somewhat recently, it has been discovered that so-called Coordinatively-Unsaturated (CUS) MOFs can be created by activation of solvent-coordinated inorganic nodes to yield exposed (or 'open') metal sites.<sup>4-6</sup> These CUS-MOFs have been shown to exhibit excellent uptakes and selectivities in a number of gas separation and storage problems,<sup>4,5,7</sup> making this family of compounds an excellent target for future investigation and materials design. Owing to the vast scope of hypothetical CUS-MOF materials, however, and the number of chemically-distinct targets for gas separation/storage, it is unlikely that experiment alone can be used to screen for new and promising CUS-MOF materials.<sup>8</sup> Rather, a combination of experiment and computational modeling will be required to find (or possibly even rationally design) optimal CUS-MOFs.<sup>7-9</sup>

Despite the utility of computational studies, it remains challenging to develop molecular models for CUS-MOFs.<sup>6</sup> Because the strong binding between metal and adsorbate leads to chemical environments substantially different from typical coordinatively-saturated MOFs, many standard force fields (such as UFF and DREIDING) which yield good predictions for these MOFs frequently (and substantially!) underpredict adsorption in CUS-MOFs, especially at low pressures.<sup>8-10</sup> While CUS-MOFs can sometimes be studied using quantum mechanical means,<sup>9,11</sup> clearly new and improved force fields will be required to perform in-depth simulations and large-scale screenings of these materials.

The goal of the present chapter is to present a general methodology for devel-

oping accurate and transferable force fields for CUS-MOFs. The current study is limited to a discussion of the MOF-74 series (a prototypical and well-studied CUS-MOF), however it is expected that the methods presented herein might also be applicable to other systems. After outlining this methodology (Sections 5.3 and 5.4), we next show how our force fields can be applied to accurately predict CO<sub>2</sub> adsorption isotherms in Mg-MOF-74. At the present time, we do not have results for other compounds in the M-MOF-74 series (M = Co, Cr, Cu, Fe, Mn, Ni, Ti, V, and Zn), largely as a result of technical challenges in the force field parameterization itself. We discuss these technical challenges in some detail, and conclude with our perspective on the challenges and opportunities associated with developing transferable force fields for these and other CUS-MOF systems.

### 5.3 Background and Motivation

Prior work in our group has shown how, at least for coordinatively-saturated MOFs, accurate and transferable force fields can be generated for a wide variety of systems by fitting force field parameters on a component-by-component basis to reproduce an ab initio SAPT energy decomposition.<sup>12,13</sup> While full details for this force field development methodology can be found in refs. 13, 14, a short workflow is as follows:

1. Generate a representative cluster model from which interaction parameters can be determined for each pairwise interaction. An example cluster, used to parameterize Mg-CO<sub>2</sub> interactions in Mg-MOF-74, is shown in Fig. 5.1.
2. Using DFT-SAPT (a variant of SAPT with monomer densities given by Density Functional Theory (DFT)), compute a series of representative dimer interaction energies for the model cluster. For the cluster model in Fig. 5.1, representative dimers were generated by varying the position of CO<sub>2</sub> with respect to the MOF cluster, and the corresponding DFT-SAPT total interaction energies are shown for a subset of representative points.

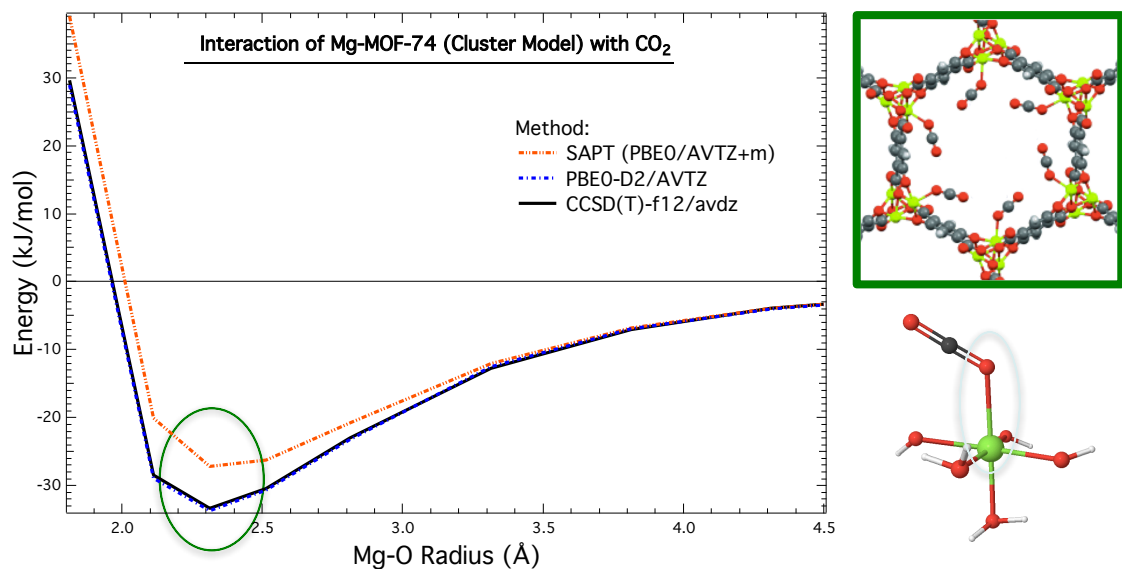


Figure 5.1: Model PES for interactions between  $\text{CO}_2$  and Mg-MOF-74. (Left) Interaction energies between  $\text{CO}_2$  and a cluster model of Mg-MOF-74 (shown bottom right), computed at a CCSD(T)-f12 (black), SAPT (orange), and/or PBE0-D2 (blue) level of theory. Discrepancies between SAPT and CCSD(T)-f12 in the minimum-energy region of the potential have been highlighted. (Top right) The structure of  $\text{CO}_2$ -bound Mg-MOF-74. (Bottom right) The structure of the cluster model used for Mg-MOF-74, where the circled atom pair indicates the relevant Mg-O radius from the x-axis in the leftmost figure.

3. To determine partial charges for the system, generate representative clusters (as described in Section 5.5) for each the organic ligand and the inorganic node, and perform a Distributed Multipole Analysis (DMA) analysis on each cluster to determine partial charges for the overall system.
4. For each component of the DFT-SAPT interaction energy, parameterize the relevant functional forms (as detailed in ref. 13 and Section 5.4) to reproduce the DFT-SAPT component energy.

Once parameterized, these SAPT-based MOF force fields can be used for calculating individual adsorption isotherms or even for high-throughput screening.<sup>14</sup>



In the generation of force fields for CUS-MOFs, we expect that many of the advantages of the above workflow for coordinatively-saturated MOFs (such as the component-by-component based parameterization and method for partial charge determination) will also translate well to CUS-MOF materials. Nevertheless, there are two reasons why a SAPT-based methodology cannot be used to generate such force fields. First, and as shown in Fig. 5.1 for a representative Mg-MOF-74 cluster model, we have empirically found SAPT to be in error for CUS-MOF-like systems compared to benchmark CCSD(T)-f12 calculations. DFT-SAPT has been known to struggle with highly ionic systems (relative to CCSD(T) or DFT methods),<sup>15,16</sup> and so this error is perhaps not surprising. (Possible sources of the discrepancy between SAPT and CCSD(T)-f12 will be discussed in Section 5.8.) Nevertheless, and in the absence of fortuitous error cancellation, predictions from an *ab initio* force field can only be as good as the level of theory that they are parameterized against. Consequently, because SAPT underbinds CO<sub>2</sub> by a full 6 kJ/mol compared to CCSD(T)-f12, we would not expect to see good predictions for the CO<sub>2</sub> adsorption isotherm with a SAPT-based methodology, and a new strategy will be required.

As a second barrier to using a SAPT-based methodology, many of the compounds in the M-MOF-74 series are open-shell. Though this poses no fundamental issue, in practice most implementations of SAPT (aside from the seldom-used SAPT 2012 package developed in Krzysztof Szalewicz’s group at Delaware) do not allow for computations of open-shell systems, and indeed SAPT-based studies of open-shell compounds are very rare.<sup>17</sup> For these reasons, a new, open-shell-compatible electronic structure benchmark is highly preferable.

## 5.4 New Methods for CUS-MOF force fields

Based on the results for Mg-MOF-74, it is clear that, at least for CUS-MOFs, a new methodology is required which simultaneously keeps the important advantages of the old workflow (especially the component-by-component based parameterization, which is essential for generating transferable force fields) while overcoming the limitations of SAPT itself. Put differently, for CUS-MOFs we should seek a

new electronic structure theory benchmark and associated Energy Decomposition Analysis (EDA) with the following qualities:

1. High accuracy with respect to CCSD(T)-f12 benchmark energies
2. Physically-meaningful energy decomposition into (at least) electrostatics, exchange, induction, and dispersion
3. For systems where SAPT and CCSD(T)-f12 agree, a quantitative correspondence between the energy decompositions of SAPT and the new method

Assuming these three qualities are met, we expect to be able to generate force fields for CUS-MOFs that are both highly accurate and maximally-compatible with previous force fields developed for coordinatively-saturated MOF systems.

A substantial number of EDAs exist in the literature, and the interested reader is referred to ref. 16 for a review and comparison of various popular methods. Aside from SAPT, which is a perturbative method, most EDAs are ‘variational’, meaning that the various energy components are calculated in stages from a series of constrained relaxations of the monomer wavefunctions into the optimized dimer wavefunction. For this reason, all variational EDAs are guaranteed to have total energies that match the result from a supermolecular interaction energy calculation. Furthermore, these EDAs are often implemented for wavefunction and DFT methods, thus allowing for significant flexibility (compared to the SAPT EDA) in terms of finding an EDA whose total energy closely matches CCSD(T)-f12. Indeed, and as shown in Fig. 5.1, PBE0-D2 shows excellent agreement with CCSD(T)-f12 for a Mg-MOF-74 cluster model, and so any DFT-compatible EDA should meet our first criteria from above.

Although all variational EDAs yield the same total interaction energy for a given level of theory, many EDAs can differ substantially in terms of how this total energy is decomposed into chemically-meaningful components. At the time this research was completed, only a handful of variational EDAs distinguished each electrostatics, exchange, induction, and dispersion. (Notably, the recent second-generation ALMO-EDA<sup>18</sup> now separates their ‘frozen’ energy term into electrostatic, exchange, and

dispersion components, and might thus be worth re-investigation.) Of the popular EDA methods available as of 2014, we found that LMO-EDA,<sup>19,20</sup> GKS-EDA,<sup>21</sup> and PIEDA<sup>22</sup> decompose the total interaction in a manner philosophically similar to SAPT, and include each electrostatic, exchange, induction, and dispersion terms. These three methods thus meet our second criteria for an optimal energy decomposition scheme for CUS-MOFs, and complete formalisms and details for the methods can be found in refs. 19–22.

As for the last criterion, that of maximum correspondence between SAPT and a variational EDA, we have performed component-by-component analyses to compare SAPT to both LMO-EDA and GKS-EDA. PIEDA is known to overestimate the relative magnitude of the polarization energy, compared to SAPT, and thus was not considered in detail.<sup>16</sup> As for LMO-EDA and GKS-EDA (both of which are based on very similar theories, and tend to yield similar energy decompositions), we have in general found semi-quantitative to quantitative agreement with the SAPT energy decomposition, particularly for the electrostatic and exchange energies. Comparisons between LMO-EDA and SAPT are shown for the CO<sub>2</sub> dimer (Fig. 5.2) and for CO<sub>2</sub> interacting with a model Mg-MOF-74 compound (Fig. 5.3). GKS-EDA results are not shown, as the LMO-EDA and GKS-EDA results tend to be very similar, with the GKS-EDA results in slightly worse agreement with SAPT. For this reason, and because LMO-EDA does the best job of meeting our three criteria above, we choose in this work to use LMO-EDA as our new benchmark EDA for fitting CUS-MOF force fields.

In addition to describing the advantages of the LMO-EDA method, it is worthwhile to overview some of its relevant shortcomings, and limitations. As with most variational EDA methods,<sup>16</sup> and especially for DFT-based methods, it becomes difficult to precisely assign and separate out the true ‘dispersion’ energy for a system. This limitation is also true of LMO-EDA, where the dispersion energy is defined as the difference in correlation energy between the monomer and dimer wavefunctions. For density functionals employing Grimme’s –D dispersion correction, this correction is also added to the LMO-EDA dispersion energy. For functionals that have a well-defined and theoretically-grounded distinction between the

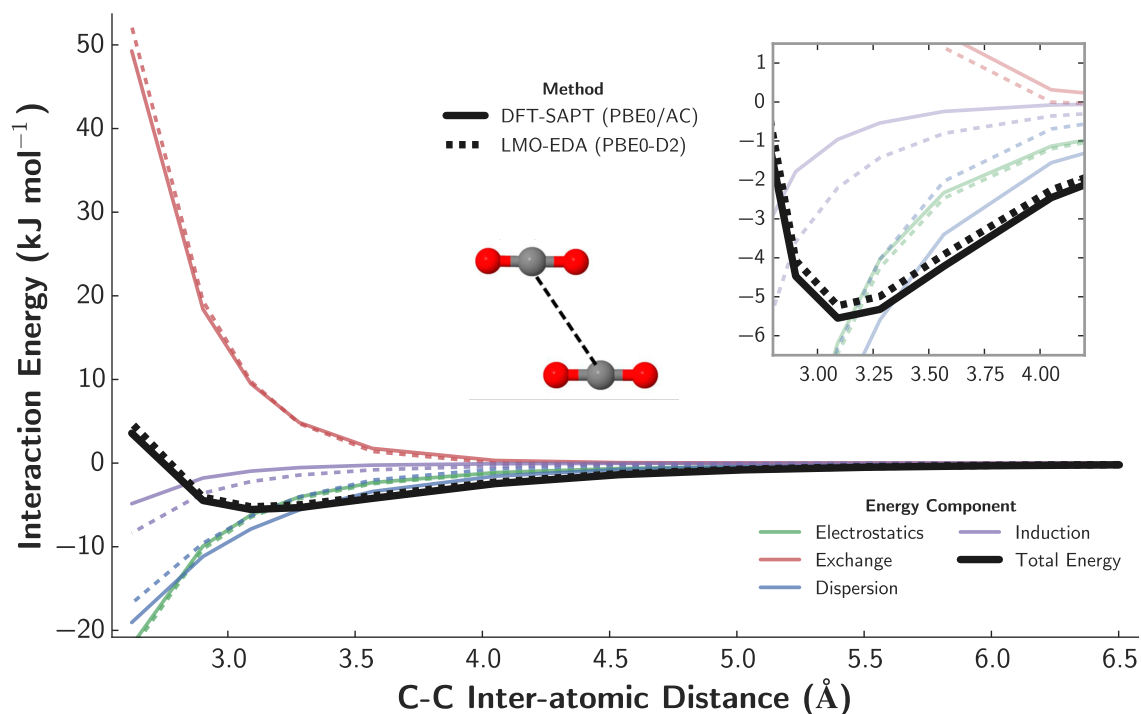


Figure 5.2: PES and associated energy decomposition for the slipped parallel geometry of the CO<sub>2</sub> dimer as a function of the C-C interatomic distance. The PES has been computed by both DFT-SAPT (PBE0) (solid lines) and LMO-EDA-PBE0-D2 (dashed lines), and each electrostatics (green), exchange (red), dispersion (blue), induction (purple), and total energy (black) components are displayed. Note that, for the DFT-SAPT energies, the  $\delta$ HF contribution has been incorporated into the induction energy.

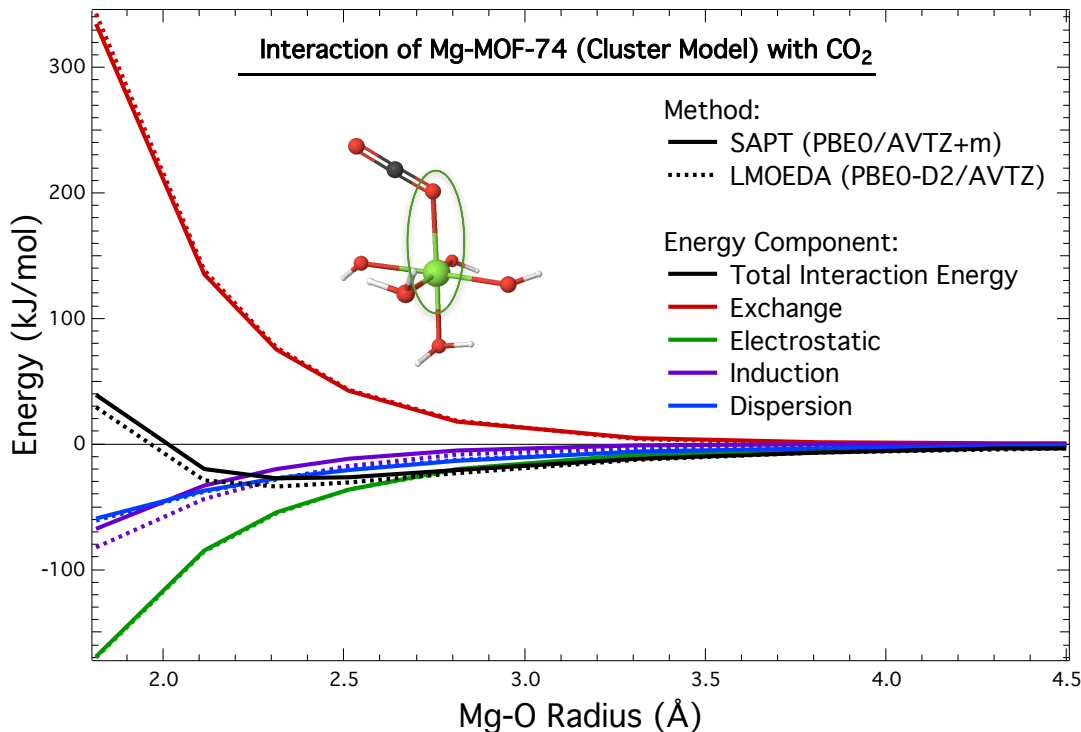


Figure 5.3: PES and associated energy decomposition for a  $\text{CO}_2 + \text{MgO}_5$  cluster, as a function of the highlighted Mg-O interatomic distance. The PES has been computed by both DFT-SAPT (PBE0) (solid lines) and LMO-EDA-PBE0-D2 (dashed lines), and colors and labels for the energy decomposition are as in Fig. 5.2.

exchange and correlation functionals, the LMO-EDA energies tend to agree well with SAPT, and we have found good agreement (for instance) between SAPT and LMO-EDA-PBE0-D2. With other functionals, such as with our tests using the M06 functional, there is no separation between the exchange and correlation functionals, and LMO-EDA gives unphysical values for both the exchange and dispersion energies in this case. (GKS-EDA attempts to rectify this issue by changing the LMO-EDA formalism for dispersion. While this leads to qualitative agreement between SAPT and GKS-EDA for a wider variety of functionals, the quantitative agreement for the PBE0-D2 functional is somewhat worsened for the systems studied herein, and we instead use LMO-EDA-PBE0-D2 for all results in this work.)

A second, and purely practical, limitation of LMO-EDA is its memory-intensive implementation in GAMESS. As will be discussed in detail later, calculations on a large (43 heavy atom) cluster model of Mg-MOF-74 were infeasible for us (using the Phoenix cluster in 2014) in all but the smallest VDZ basis set, and calculations on an identical cluster model of Co-MOF-74 could not be completed at all. For this reason, the LMO-EDA method is practically restricted to studies of smaller systems and/or basis sets.

## 5.5 Computational Methods

### 5.5.1 Partial Charge Determination

Partial charges for Mg-MOF-74 were determined in a manner analogous to ref. 14 using the  $Q_{\text{SBU}}$  method. Two cluster models, one a hydrogen-capped DOBDC ligand environment, and one a capped  $\text{MgO}_5$  inorganic chain, were constructed and analysed using a Distributed Multipole Analysis (DMA). The resulting DMA charges were then used to obtain charge parameters for the ligand and inorganic SBU, respectively. See Section 5.A for final charge parameters.

### 5.5.2 Force Field Fitting

Two types of force field functional forms were considered in this work. The first, a ‘single-exponential’ functional form, exactly matches that used in ref. 23, with the exception that  $\delta\text{HF}$  parameters were not fit to the Mg atomtype. This fitting choice was due to the fact that LMO-EDA only provides a total induction term (rather than splitting into 2<sup>nd</sup>- and higher-order induction energies, as with SAPT).

For the ‘double-exponential’ functional form used to fit the Mg-MOF-74-Yu cluster model, the same functional form was used as in the single-exponential case, with the exception that two sets of short-range interaction parameters (labeled Mg and Du in Section 5.A) were assigned to the Mg atomic center. This effectively

meant that Mg was described by two separate exponential decays, which enabled the much more accurate force field fits discussed in Section 5.6.

In all cases, force fields were fit using the Fortran code described in the Appendix of ref. 24.

## 5.6 Results

### 5.6.1 Initial Force Field and Cluster Model Analysis

Originally, we attempted to fit Mg parameters on the basis of a small, 6 heavy atom cluster ('Mg-MOF-74-small', see Fig. 5.4 for chemical structure), which we felt would be representative of the Mg environment in Mg-MOF-74. Using the functional forms discussed in Section 5.5, force field parameters were fit to reproduce LMO-EDA-PBE0-D2 energies for a variety of CO<sub>2</sub>/Mg-MOF-74-small interactions, with results shown in Fig. 5.4. Though some interaction energies disagree by several kJ/mol between LMO-EDA-PBE0-D2 and the force field energies, overall the agreement is reasonable, and the force field correctly reproduces trends in the interaction energies without significant systematic error.

Based on the agreement between PBE0-D2 and the force field, as well as between PBE0-D2 and CCSD(T)-f12, we expected to obtain good CO<sub>2</sub> adsorption isotherm predictions for the Mg-MOF-74 system itself. By contrast, our computed isotherm substantially underpredicts the experimental adsorption at low pressures, where Mg-CO<sub>2</sub> interactions are known to dominate. This underprediction strongly suggests that we had originally underestimated the magnitude of the Mg-CO<sub>2</sub> binding, a result which we were then able to attribute to our choice of cluster model (*vide infra*).

Cluster models for the M-MOF-74 series have been investigated by several groups, and it has been found in general that computed binding energies are sensitive both to the size of the cluster model as well as the treatment of geometry relaxation effects.<sup>26,27</sup> Consequently, we calculated the CO<sub>2</sub> binding energies and geometries of both our original Mg-MOF-74-small cluster as well as for two larger

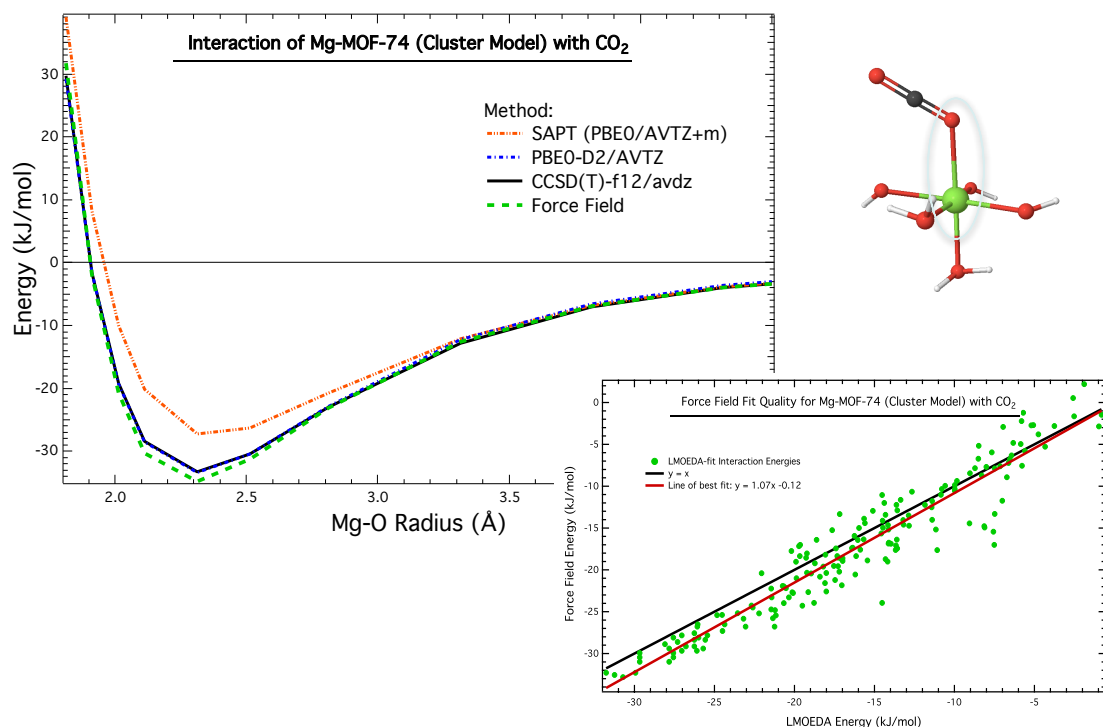
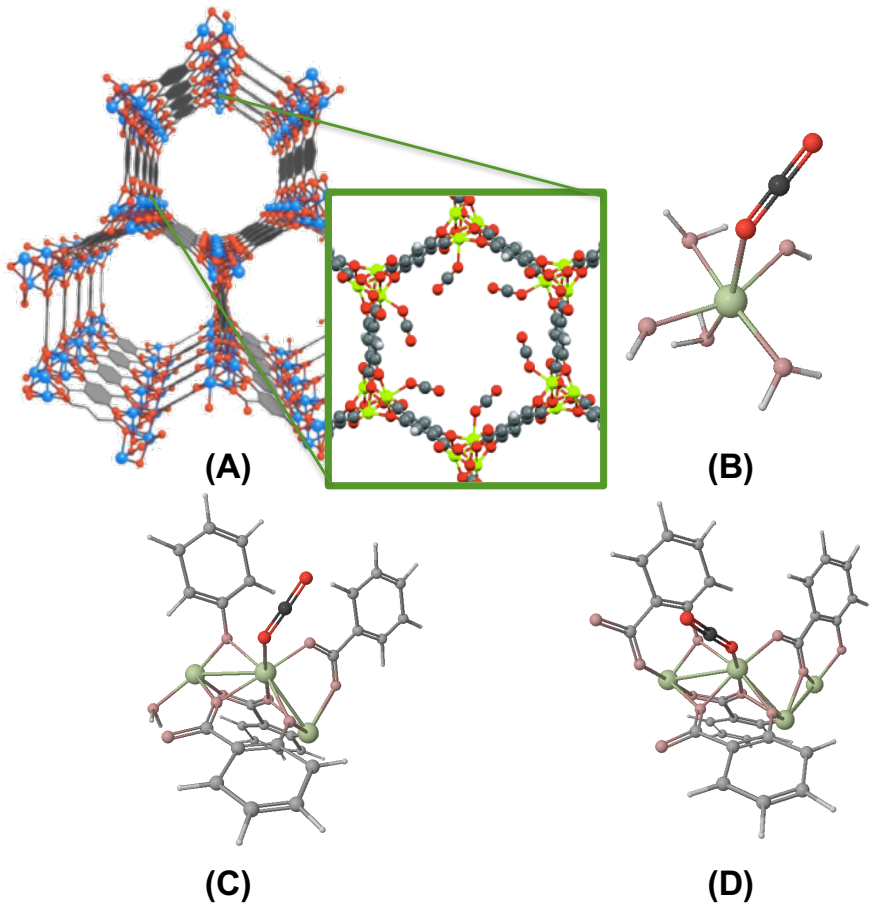


Figure 5.4: Force field fitting quality for the Mg-MOF-74-small cluster. (Top left) Various electronic structure benchmarks for Mg-MOF-74-small along with the classical potential. Each DFT-SAPT (orange dot-dashed), PBE0-D2 (blue dot-dashed), CCSD(T)-f12 (black solid), and the LMO-EDA-based force field (green dashed) are shown as a function of the Mg-O interatomic distance (non-bonding pair highlighted at top right). (Bottom right) Force field fit quality, as benchmarked against LMO-EDA-PBE0-D2, for a semi-random set of dimer configurations of the Mg-MOF-74-small cluster model interacting with CO<sub>2</sub>. The black line establishes the  $y = x$  benchmark, and the red line represents the line of best fit.





Model	CO <sub>2</sub> Binding Energy (kJ/mol)	Mg–O Interatomic Distance (Å)	Mg–O–C Tilt Angle (°)
<b>A</b> <sup>11</sup>	<b>-41.5</b>	<b>2.31</b>	<b>129</b>
B	-23.3	2.31	122
C	-31.4	2.28	123
D	-41.7	2.20	149

Figure 5.5: Various structures and cluster models for Mg-MOF-74 interacting with CO<sub>2</sub>. (A) Full periodic Mg-MOF-74 structure with inset showing adsorbed CO<sub>2</sub> positions. (B) Mg-MOF-74-small cluster, containing 6 heavy atoms (not including CO<sub>2</sub>). (C) Yu et al. cluster model for Mg-MOF-74, denoted in text as Mg-MOF-74-Yu. (D) Dzubak et al. cluster model for Mg-MOF-74, denoted in text as Mg-MOF-74-Dzubak. All cluster models as shown with optimized CO<sub>2</sub> positions, and bond lengths and angles for adsorbed CO<sub>2</sub> are given in the bottom table. Data for (A) was taken from Valenzano et al. using a B3LYP-D level of theory,<sup>11</sup> whereas data for (B-D) was computed in this work using PBE0-D2. Finally, note that the binding energy for (A) includes framework geometry relaxation effects, whereas (B-D) were computed using semi-rigid cluster geometries and only optimizing the CO<sub>2</sub> position and exposed MgO<sub>5</sub> pocket.

clusters developed in refs. 6, 25. These latter two clusters, respectively denoted Mg-MOF-74-Yu and Mg-MOF-74-Dzubak, are the same size (each with 60 atoms), but have made different choices as to the number of included magnesium atoms (three vs. four) and number/location of capping atoms. To test the influence of model cluster on the CO<sub>2</sub> binding energy/geometry, we performed two sets of optimizations of the Mg-MOF-74-Yu and Mg-MOF-74-Dzubak clusters: one in which only the CO<sub>2</sub> position was optimized, and one in which the exposed MgO<sub>5</sub> pocket was additionally relaxed. Binding geometries were relatively insensitive to the geometry relaxation, though binding energies varied by 2-5 kJ/mol, in agreement with other studies that have tested geometry relaxation effects.<sup>26</sup> Results for the CO<sub>2</sub> + MgO<sub>5</sub> relaxation are shown in Fig. 5.5.

Of the three studied cluster models, both Mg-MOF-74-small and Mg-MOF-74-Yu correctly reproduce the Mg-O interatomic distance and Mg-O-C tilt angle. These geometrical parameters arise primarily from electrostatic interactions between CO<sub>2</sub> and the MgO<sub>5</sub> pocket,<sup>11</sup> suggesting that both of these models capture such important interaction features. By contrast, the Mg-MOF-74-Dzubak model predicts a substantially shorter binding distance and increased tilt angle, both in contrast to results from the periodic system. In part, these deficiencies can be attributed to spurious CO<sub>2</sub> interactions with the exposed carbonyl capping groups in the Mg-MOF-74-Dzubak model which are not present in the periodic system or the other two cluster models. Additionally, a Mulliken charge analysis of the Mg-MOF-74-Dzubak cluster yields larger partial charges for the surrounding Mg atoms as compared to the Mg-MOF-74-Yu model, which may help explain the increased binding and shortened Mg-O contact in the Mg-MOF-74-Dzubak model. As for binding energies, there are substantial differences in binding energies between the various cluster models, with Mg-MOF-74-small severely underbinding. These results for the Mg-MOF-74-small cluster indicate the inadequacy of such a small model, and likely explain the underprediction of the CO<sub>2</sub> adsorption isotherm from above. The Mg-MOF-74-Dzubak model shows best energetic agreement with the periodic system. Nevertheless, some of the Mg-MOF-74-Dzubak binding energy arises from truncation effects (as described above), and the energetic agreement

is thus due (at least in part) to error cancellation. Indeed, some of the binding energy in the periodic system arises from (attractive) long-range interactions, and thus we should expect to see a cluster model somewhat underpredict the binding energy. Primarily for its good agreement in binding geometries, and reasonable agreement in binding energy, we opt to use the Mg-MOF-74-Yu cluster model for the remainder of this work.

### 5.6.2 Final Mg-MOF-74 CO<sub>2</sub> Adsorption Isotherm

Using our new Mg-MOF-74-Yu cluster model, we next attempted to fit new force field parameters for Mg. As discussed earlier, and because of the size of this new cluster (60 atoms), LMO-EDA-PBE0-D2 calculations became cost prohibitive in all but the smallest VDZ basis set and for a limited set of points. Starting from the minimum energy configuration shown in Fig. 5.5, we fit Mg parameters to a 12-point scan along the Mg-O bond vector, with fit results shown in Fig. 5.6. Interestingly, though the functional form used in this fit was sufficient to accurately parameterize the interaction energies in the Mg-MOF-74-small cluster, the same force field methodology proved unsuccessful in parameterizing Mg-MOF-74-Yu interactions. We knew at the time that this inaccuracy was probably a consequence of uncertainties in correctly parameterizing the Mg short-range exponent. (See Chapter 3 for a full discussion of new methods for parameterizing the short-range potential.) Nevertheless, because the Slater-ISA methodology for short-range interactions had not yet been developed, we opted instead to fit the Mg interactions to a double exponential functional form, with each exponent corresponding to the ionization potential for either Mg<sup>+</sup> or Mg<sup>2+</sup>, the two chemical environments that we thought might correctly represent the Mg cation. As shown in Fig. 5.6, this form could excellently reproduce the Mg-MOF-74-Yu model PES.

Using the double exponential functional form from above, we recomputed the Mg-MOF-74 CO<sub>2</sub> adsorption isotherm. Before comparing to experiment, and as recommended by others,<sup>28</sup> we scaled the experimental isotherm in order to account for the pore blocking effects that are common in the M-MOF-74 series. Using this

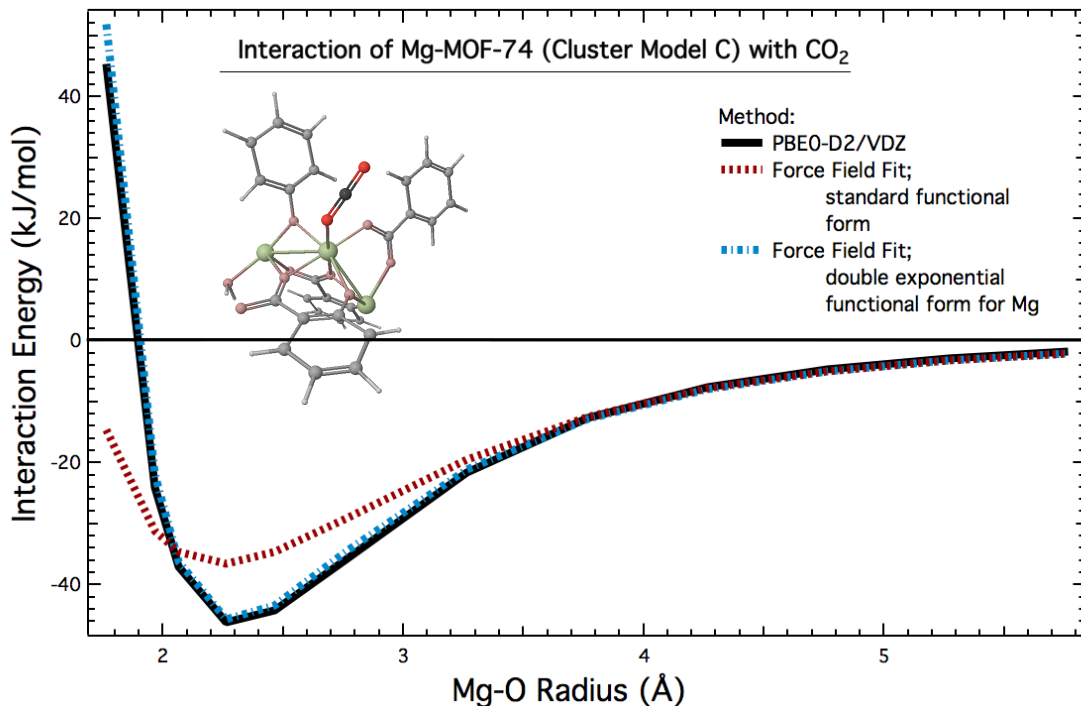


Figure 5.6: Force field fitting quality for the Mg-MOF-74-Yu cluster. A PBE0-D2 benchmark (black solid) is displayed along with two force field fits: single-exponential (red dashed) and double-exponential for Mg (blue dash-dotted). In either case, a cut of the PES is shown along the interatomic distance between the central Mg atom and the closest-contact oxygen atom in CO<sub>2</sub>.

scaled isotherm, we then obtain excellent agreement between our model potential and experiment (Fig. 5.7). Crucially, this accuracy is seen both at low- and high-pressure ranges, indicating the accuracy of the force field in modeling both the strong Mg-CO<sub>2</sub> binding as well as the weaker physisorption regime.

### 5.6.3 Transferability to Other Adsorption Isotherms

In addition to using our Mg parameters to compute the CO<sub>2</sub> adsorption isotherm, we also used our Mg force field in conjunction with the N<sub>2</sub> parameters developed by Yu et al.<sup>29</sup> to predict the N<sub>2</sub> adsorption isotherm. These predictions were generally

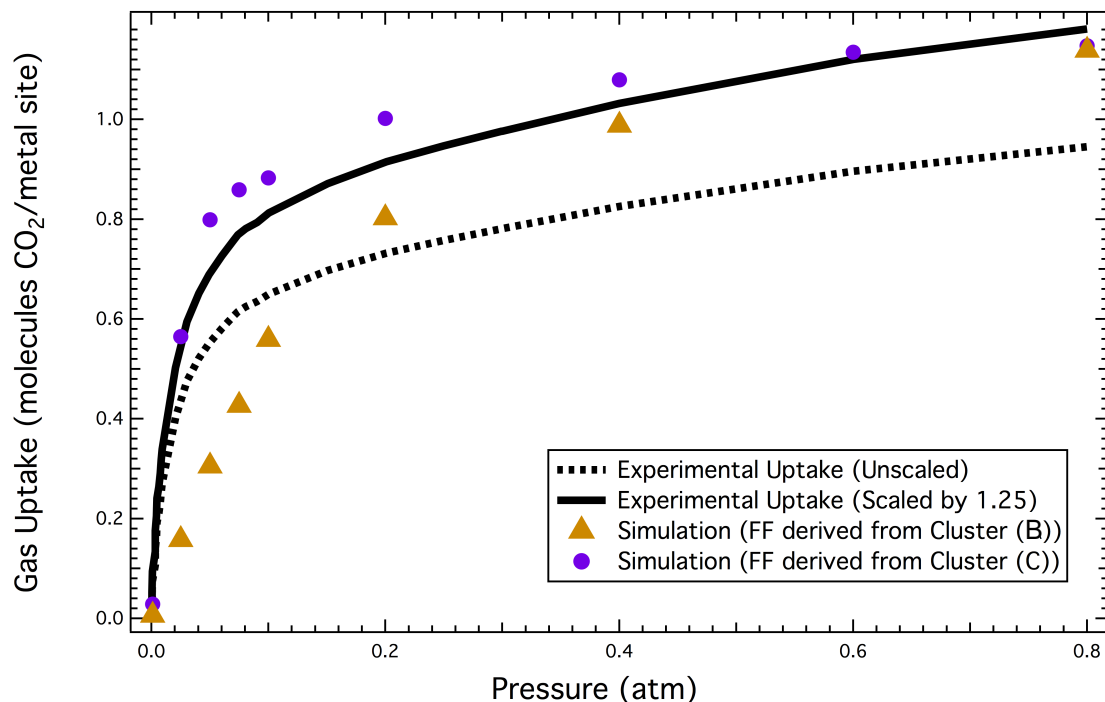


Figure 5.7: Predicted  $\text{CO}_2$  adsorption isotherm for Mg-MOF-74. Two experimental isotherms are shown, one as directly measured by experiment (dashed line) and one scaled to account for pore block effects (solid line). Predictions from two force fields are also shown, where Mg parameters for each force field were fit either to the Mg-MOF-74-small cluster (gold triangles) or to the Mg-MOF-74-Yu cluster (purple circles). Cluster geometries are given in ??.

poor, and results are not shown. Nevertheless, the poor  $\text{N}_2$  results suggest a lack of transferability of our Mg parameters, possibly (and as discussed in the section on Future Work) due to unphysical double-exponential functional form used to parameterize Mg.

#### 5.6.4 Transferability to Other M-MOF-74 systems

As a second test of transferability, we also attempted to develop force fields for other compounds in the M-MOF-74 series, starting with Co-MOF-74. Unfortunately, the

open-shell nature and increased electron count of Co-MOF-74 made LMO-EDA calculations computationally prohibitive for any reasonable basis set, and these systems were not investigated further.

## 5.7 Conclusions

In this unpublished work, we have determined a new methodology for fitting force fields to CUS-MOFs. While largely following our previous methodology for MOF force field development, we have shown how an LMO-EDA Energy Decomposition Analysis can be used in lieu of SAPT to generate accurate ab initio benchmark energies in cases where SAPT itself is inaccurate. Using this new methodology, we have successfully modeled CO<sub>2</sub> interactions in Mg-MOF-74, and have simulated the adsorption isotherm for CO<sub>2</sub> in Mg-MOF-74 with good accuracy compared to experiment.

Ultimately, the methods presented herein suffered from a number of practical and fundamental issues (see Section 5.8). Unless these limitations can be fully addressed, we do not anticipate that the LMO-EDA method can be broadly used to develop force fields for CUS-MOFs or other large systems where SAPT is in error.

## 5.8 Future Work

Throughout this manuscript, we have attempted to highlight some of the key limitations of our force field development methodology for CUS-MOFs. In summary, the following issues would need to be resolved in order to expand the scope of the present research:

1. **Memory Limitations in GAMESS:** As evidenced in this work, relatively large (60+ atom) cluster models are required to correctly parameterize force fields for the M-MOF-74 system. While these cluster sizes do not present difficulties for standard DFT calculations with reasonable basis sets, the corresponding LMO-EDA calculations were, as implemented in the GAMESS software pack-

age, infeasible due to memory requirements. Some time was spent attempting to address these memory issues, particularly for the memory-intensive Edmiston-Ruedenberg localization subroutine that is the source of the problem. However, due to our lack of familiarity with the GAMESS software and the LMO-EDA source code, this pursuit was eventually dropped.

2. **Fundamental Issues with LMO-EDA:** As discussed in Section 5.4, the LMO-EDA method has several theoretical limitations. In particular, and especially for functionals with no defined separation between exchange and correlation functionals, LMO-EDA does not offer a clean separation between the exchange and dispersion energies. Furthermore, and unlike some recent EDA methods, LMO-EDA cannot separate induction into charge transfer and polarization components.
3. **Transferability of the Force Field Functional Form:** While our final force field for studying CO<sub>2</sub> interactions in Mg-MOF-74 was highly accurate (both with respect to *ab initio* theory and with respect to experiment), it does not appear that this accuracy extends to models for the adsorption of other small molecules, such as N<sub>2</sub>. This transferability limitation is almost certainly due to the chosen double-exponential functional form and/or the parameterization process used to obtain Mg parameters, and improvements to this methodology will be essential to make our work on the CO<sub>2</sub>-Mg-MOF-74 system applicable to general force field development for CUS-MOFs. In particular, we will require a better force field for describing short-range interactions, as the functional forms and parameters used in this work struggled to model the Mg-MOF-74 exchange energies.

While several of these issues (particularly practical limitations with the LMO-EDA implementation) have yet to be addressed in a meaningful fashion, several recent theoretical advances may pave the way for continued work on this project. Thus for CUS-MOFs and other systems where DFT-SAPT might be in error, we offer the following recommendations:

1. **Improved SAPT energies:** Recently, it has been proposed that the commonly used single-exchange (“ $S^2$ ”) approximation can lead to errors in the description of the induction energy,<sup>30</sup> particularly for ionic systems.<sup>15</sup> While it is difficult to attribute errors in SAPT to a particular energy component, it may well be that SAPT poorly describes Mg-MOF-74 due to the  $S^2$  treatment of the induction energy. In this case, eliminating the  $S^2$  approximation might improve the DFT-SAPT total interaction energies, thus enabling SAPT to be used for (at least) closed-shell CUS-MOFs.
2. **New SAPT Correction Schemes:** As discussed in Chapter 4, deviations between SAPT and CCSD(T) can be rectified by adding a  $\delta\text{CCSD(T)}$  correction to the total SAPT energy. Thus far, we have had good success modeling this  $\delta\text{CCSD(T)}$  correction as part of the dispersion energy, though this is an empirically-justified choice, and may need modification for treating Mg-MOF-74. Regardless, the results in Chapter 4 indicate that correcting (rather than entirely ignoring) the DFT-SAPT energies is a promising strategy for transferable force field development.
3. **New EDA schemes:** Since this work was completed, a second-generation ALMO-EDA scheme has been implemented in the Q-Chem software package.<sup>18</sup> Crucially, and unlike its predecessor, this ALMO-EDA scheme now breaks up the interaction energy into electrostatic, exchange, polarization, charge-transfer, and dispersion components. While there is no guarantee that such an EDA could serve as the basis for CUS-MOF force field development (see Section 5.4), these and other recently developed EDAs may be worth investigation, and could eventually replace the (practically problematic) LMO-EDA method.
4. **Improved Force Field Functional Forms:** Since 2014, we have made significant progress in developing more accurate and transferable intermolecular force fields (see Chapters 3 and 4), and many of these advances particularly improve the description of the short-range potential itself. There is a good



chance that either the Slater-ISA FF or MASTIFF methodologies would yield high-quality force fields for Mg-MOF-74 and other systems. In this case, continued work on this project might be an exciting avenue for showcasing the MASTIFF methodology in the context of accurate inorganic/organometallic force field development.

## 5.A Force Field Parameters for CO<sub>2</sub> and Mg-MOF-74

Final force field parameters, fit using the double-exponential functional form above and the Mg-MOF-74-Yu cluster model, for CO<sub>2</sub> and Mg-MOF-74. These parameters should be read in as input into our group's lattice simulation code, see <http://schmidt.chem.wisc.edu/montecarlosimulationcodes> for details.

```
lennard_jones_type 1 "1 for buckingham, 2 for lennard jones"

" parameters are listed as charge, A,B,C, polarizability
" units are A:kJ/mol, B:A^-1, C: KJ/mol*A^6  epsilon:KJ/mol,  sigma:A,  polarizability: A^3 "
" polarizability is defined as q^2/k, spring constant is set to .1*1.8897^3 e^2/A^3"

solute_species
atom_type_parameters  ( q, Aexch, Aelec, Aind, Adhf, Adisp, C6, C8, C10, alpha )
2
CO      0.6573800      95510.43      -27846.98      -13425.1  2065.044
        0.0      6.891E02 0.0 0.0 1.1926153
O0      -0.328690      521902.066      -163908.84      -4475.8095      -26042.04
        0.0      1.8341E03 0.0 0.0 0.9009290

solute parameters for framework cross terms  ( Aexch, Aelec, Aind, Adhf, Adisp, B, C6, C8, C10, C12 )
CO 74376.65 24130.18      12513.37      795.36
        0.0 3.4384      1147.41867      6329.41038      29659.50100      183546.714
O0 354373.13 108208.5      2544.89      -18178.7
        0.0 3.7795      867.27598      4266.54582      28761.10636      132581.301

solute dhf cross terms (check code for input format if more than one cross term)
-6124.0

solute-solute exponents ( Bii, Bij, Bjj)
3.5105206 3.6993494 3.9288490
```

framework\_species

atom\_type\_parameters ( q, Aexch, Aelec, Aind, Adhf, Adisp, B, C6, C8, C10, C12, alpha )

9

C1	-0.1639350	612892.611	229850.679	-6511.529	-60036.930			
	0.000	3.438	1628.820002	6821.530007	44464.989999	193602.980000	0.0	
H1	0.2637500	8538.651	1678.771	-612.739	-502.639			
	0.000	3.778	129.439978	679.640001	4995.299998	0.000000	0.0	
C2	-0.3191850	612892.611	229850.679	-6511.529	-60036.930			
	0.000	3.438	1628.820002	6821.530007	44464.989999	193602.980000	0.0	
C3	0.4964850	612892.611	229850.679	-6511.529	-60036.930			
	0.000	3.438	1628.820002	6821.530007	44464.989999	193602.980000	0.0	
O3	-1.0339500	3398.424	1965.168	-182.412	-178.025			
	0.000	2.457	2237.635879	29956.090890	561056.184030	7451461.601923	0.0	
C4	0.9468300	263600.161	112896.479	-11.681	-2837.170			
	0.000	3.438	772.870024	2349.180008	27539.189998	102366.260000	0.0	
O4	-0.8903225	656757.170	174054.351	-45410.640	-33954.271			
	0.000	3.779	1799.560008	11576.089993	50164.639999	0.000000	0.0	
Mg	1.5906500	917.037	2417.463	-12542.799	0.000			
	0.000	2.834	630.723467	0.000000	0.000000	0.000000	0.0	
Du	0.0000000	29176.333	0.000	142260.481	0.000			
	0.000	3.973	0.000000	0.000000	0.000000	0.000000	0.0	

## 5.B Simulation Parameters CO<sub>2</sub> Adsorption in Mg-MOF-74

Lattice simulation parameters for CO<sub>2</sub> adsorption in Mg-MOF-74. Of particular importance is the 'orientation\_try' keyword, which is necessary to sample the specific binding geometries CO<sub>2</sub> adopts when binding to the open-metal site. These simulation parameters should be read in as input into our group's lattice simulation code, see <http://schmidt.chem.wisc.edu/montecarlosimulationcodes> for details.

### Simulation Methodology

```
energy_decomposition yes      ! yes for our force fields, no for UFF LJ, etc.
solute_cross_parameter_set yes ! this should be set to yes if using different solute parameters
                             ! for solute-solute and solute-framework interactions as in our force fields, no otherwise
C8_10_dispersion_terms yes   ! set to yes if using C8, C10 dispersion terms as in our force fields
C12_dispersion yes
electrostatic_type pme       ! either "pme" for particle-mesh ewald, "cutoff", or "none"
lj_comb_rule ZIFFF          ! "opls" or "standard" for lj, "standard" or "ZIFFF" for bkgbm
```

### Simulation Parameters

```
temperature 296.0 ! temperature in Kelvin
too_close 1.8 ! reject move if molecules are within this separation in Angstroms.
               ! helpful to avoid unnecessary energy calculations and to prevent drude oscillator catastrophes
lj_bkgbm 1 ! 1 for bkgbm force field, 2 for lj
screen_type 1 ! screening for coulomb potential: 0 = no screening, 1 = Tang-Toennies type screening for our force fields
springconstant 0.1 ! spring constant for drude oscillators (au). set to 0.1 for our CO2/N2 force fields
thole 2.0 ! thole parameter for intra-molecular drude oscillator screening. Set to 2.0 for our CO2/N2 force fields.
drude_simulation 1 ! set to 1 if drude-oscillators are being used, 0 otherwise

pme_grid 100 ! size of the pme grid
alpha_sqrt 0.6 ! alpha sqrt for the electrostatic interactions
lj_asqrt 0.6 ! alpha sqrt for the pme dispersion
lj_cutoff 7.5 ! cutoff for long range LJ or C6,C8,C10 dispersion interactions
ewald_cutoff 5.0 ! cutoff for real space pme
cav_grid_a 30
cav_grid_b 30
cav_grid_c 30
na_nslist 30 ! neighbour list searching grid
nb_nslist 30 ! neighbour list searching grid
nc_nslist 30 ! neighbour list searching grid
orientation_try 2000 ! max number of orientation samplings
REL_THRSH 0.05 ! sampling threshold
ABS_THRSH 3.0
BZ_CUTOFF 100.0
```

## 6 BENCHMARK DATABASE FOR AB INITIO FORCE FIELD DEVELOPMENT

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# **Part IV**

## **Practical Matters**

## 7 WORKFLOW FOR INTERMOLECULAR FORCE FIELD DEVELOPMENT

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## **7.1 Overview**

## **7.2 Codes**

### **7.2.1 Molpro**

### **7.2.2 CamCASP**

### **7.2.3 Scripts**

## **7.3 Geometry Generation**

## **7.4 SAPT Calculations**

## **7.5 Monomer-Based Parameterization**

### **7.5.1 Multipoles**

### **7.5.2 ISA Exponents**

### **7.5.3 Polarization Charges**

### **7.5.4 Dispersion Coefficients**

Jesse's Method

Alston's Method

## **7.6 Dimer-Based Parameterization**

Refer to POInter Code section

## 8 POINTER: A PROGRAM FOR INTERMOLECULAR FORCE FIELD OPTIMIZATION

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### 8.1 Overview

### 8.2 Documentation

### 8.3 Examples



## **Part V**

# **Conclusions and Future Work**

## 9 FUTURE WORK

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## 10 CONCLUSIONS

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## ACRONYMS

---

### Symbols | C | D | E | M | P | S

#### Symbols

**δHF** Delta-Hartree Fock. 16, 18

#### C

**CUS** Coordinatively-Unsaturated. iv, 10, 11, 13–15, 26–28

#### D

**DFT** Density Functional Theory. 11, 13–15, 26

**DFT-SAPT** Density Functional Theory Symmetry-Adapted Perturbation Theory.  
11–13, 16, 17, 20, 27, 28

**DMA** Distributed Multipole Analysis. 12, 18

#### E

**EDA** Energy Decomposition Analysis. 14, 15, 26–28

#### M

**MOF** Metal-Organic Framework. iv, 9–15, 26–28

#### P

**PES** potential energy surface. vii, 9, 12, 16, 17, 23, 24, 43

#### S

**SAPT** Symmetry-Adapted Perturbation Theory. vii, 9, 11–15, 17, 18, 26, 28, *Glossary:*  
SAPT

## GLOSSARY

---

### C | I | L | S

#### C

**CCSD(T)** Coupled Cluster methods including singles, doubles, and perturbative triples excitations. CCSD(T). Given a sufficiently large (aVQZ or better) basis set, can be used as a ‘gold-standard’ estimate of the exact potential energy surface. 9, 13, 28

**CCSD(T)-f12** Explicitly-correlated CCSD(T). Given a sufficiently large (aVDZ or aVTZ) basis set, used throughout this work as a ‘gold-standard’ estimate of the exact potential energy surface. 12–14, 19, 20

#### I

**induction** FILL . 16, 18

#### L

**LMO-EDA** FILL . iv, vii, 9, 15–20, 23, 26–28

#### S

**SAPT** Symmetry-Adapted Perturbation Theory, a perturbative treatment of inter-molecular interactions which is pretty cool. vii, 9