

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

by

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Soli Deo gloria.

ACKNOWLEDGMENTS

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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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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PUBLISHED WORK AND WORK IN PREPARATION

- [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 ref² 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.

Part II

Published Work

3 ISOTROPIC AB INITIO FORCE FIELDS

4 ANISOTROPIC AB INITIO FORCE FIELDS

Part III

Unpublished Work

5 AB INITIO FORCE FIELDS USING LMOEDA

5.1 Preface and Motivation

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 ~ 1 kJ/mol of the SAPT reference values! In spite of this success, it is important to realize that such high precision between the model and SAPT can only lead to improved molecular simulation provided that the SAPT energies *themselves* are accurate, either with respect to the exact underlying Potential Energy Surface (PES) or (for practical purposes) with respect to gold-standard CCSD(T) calculations. This raises to two fundamentally important questions regarding our methodology for force field development. First, where might we expect SAPT to be inaccurate? Secondly, for systems where SAPT does not achieve a desired level of accuracy, how should our general methodology for ab-initio force field development be modified?

The purpose of this chapter is to answer, in part, these above questions.

Nevertheless (and as discussed in Chapter 4 and below), significant SAPT

5.2 Introduction

What, however, should be done for systems where SAPT itself is in significant error??

Back in 2013, at the start of this project, we encountered a series of systems for which SAPT did indeed seem to be breaking down.

Introduction

=====

Symmetry-Adapted Perturbation Theory (SAPT) SAPT ab-initio force field

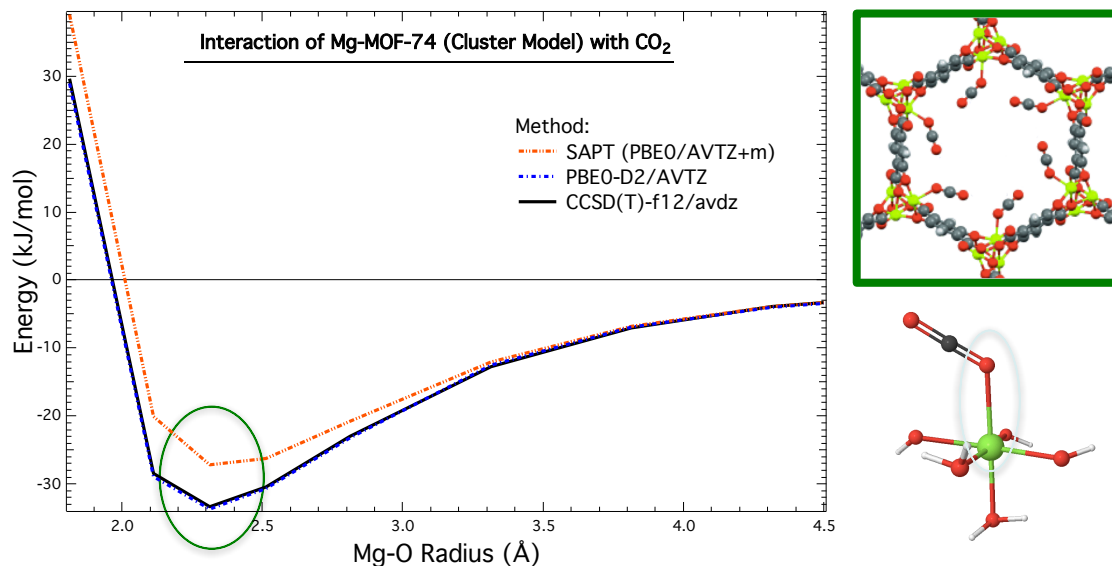


Figure 5.1: Model PES for interactions between CO₂ and Mg-MOF-74. (Left) Interaction energies between CO₂ and a cluster model of Mg-MOF-74 (shown bottom right), computed at a CCSD(T)-f12 (black), SAPT (orange), and/or PBE0-D2 (blue) level of theory. Discrepancies between SAPT and CCSD(T)-f12 in the minimum-energy region of the potential have been highlighted. (Top right) The structure of CO₂-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.

6 BENCHMARK DATABASE FOR AB INITIO FORCE FIELD DEVELOPMENT

Part IV

Practical Matters

7 WORKFLOW FOR INTERMOLECULAR FORCE FIELD DEVELOPMENT

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

8.1 Overview

8.2 Documentation

8.3 Examples

Part V

Conclusions and Future Work

9 FUTURE WORK

10 CONCLUSIONS

BIBLIOGRAPHY

- [2] Stone, A. J. *The Theory of Intermolecular Forces*, 2nd ed.; OUP Oxford, 2013.

ACRONYMS

P | S

P

PES Potential Energy Surface. vii, 9, 10, 21

S

SAPT Symmetry-Adapted Perturbation Theory. vii, 9, 10, *Glossary*: SAPT

GLOSSARY

A | C | S

A

ab-initio force field force field developed from first-principles by fitting parameters to electronic structure calculations. 9

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

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.. vii, 10

S

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