

Ammonium Fluoride Nanoparticle Modelling: Independent Study Report and Documentation

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Table of Contents

[Table of Contents](#)

[Abstract](#)

[Introduction](#)

[Phase 1: Background Research and Survey of Literature](#)

[Overview](#)

[Description of Relevant Literature](#)

[Phase 2: Quantum Mechanics Calculations](#)

[Overview](#)

[Description of Calculations](#)

[Results and Discussion](#)

[Phase 3: U-r Grapher](#)

[Overview](#)

[Results, Discussion and Conclusions](#)

[Phase 4: Partial Charge Optimization](#)

[Overview](#)

[Results, Discussion and Conclusions](#)

[Phase 5: CHF-DHF Parameter Optimization](#)

[Overview](#)

[Results, Discussion and Conclusion](#)

[Alternatives Considered](#)

[Improvements and Directions for Further Research](#)

[Acknowledgements](#)

[Annotated Bibliography](#)

[Appendices](#)

[Appendix 1: Initial Estimates for Topper-Freeman Interaction Potential Parameters for NH₄F](#)

[Appendix 2: Partial Charges on Lone Ammonium Ion from Hartree-Fock / 6-31G** Calculation](#)

[Appendix 3: Graphs of optimum distance, well depth and Euclidean distance as functions of CHF and DHF](#)

Abstract

The present work can be considered in five “phases”, each of which is presented in a separate section. In the first phase, background research was conducted to understand the interaction model that would be used to model it, and obtain initial estimates for parameters of the interaction model. In the second phase, quantum mechanics calculations were performed on an ammonium fluoride nanoparticle on Spartan to determine the optimum distance (at which the total interaction potential was minimized) and the depth of the potential well. In the third phase, a MATLAB program was written to plot the $U - r$ graph of any pair of atoms in an NH_4F nanoparticle. It was found that the initial estimates gave an interaction that was globally repulsive, instead of having a finite range of distances over which the interaction was attractive. However, this error was overlooked, and the project continued as if the interaction model had the same qualitative behavior as the quantum results. In the fourth phase, the partial charges within the ammonium were optimized using another MATLAB program. It was found that varying the partial charges on the ammonium was not enough to make the interaction attractive at some interval of distances. Finally, in the fifth phase, the values the C_{HF} and D_{HF} parameters were optimized. Again, it was found that varying the values of C_{HF} and D_{HF} were not enough to make the interaction attractive at some interval of distances.

Introduction

Caustic nanoparticles of ammonium chloride are formed in polluted marine atmospheres in coastal environments off the Pacific, North Atlantic and Indian Oceans. In order to model their formation and growth, accurate models of their intermolecular forces must be developed and tested (Topper 2016).

Beyond its application to caustic nanoparticles, the behavior of hydrogen bonds in ammonium halide nanoclusters is of fundamental chemical interest. It is known that different kinds of hydrogen bonding (e.g. classical and bridging) manifest themselves within such ammonium halide nanoclusters, and exhibit fascinating properties¹. A force field of ammonium halide nanoclusters would therefore provide insight into the nature of the intermolecular forces.

In the present phase of this research project, the framework for modelling and analyzing $(\text{NH}_4\text{Cl})_n$ clusters will be modified to also handle $(\text{NH}_4\text{F})_n$ clusters, which thus far have proved to be more complex and difficult to characterize than the chloride and bromide clusters, due to the extreme electronegativity of the fluoride ion. This will involve the development and implementation of an intermolecular force model which can describe mixed clusters of NH_4^+ , F^- , NH_3 and HF .

¹ For example, it is known that for the ammonium bromide and chloride nanoparticles, all hydrogen bonds are “classical”: i.e. all hydrogens are closer to the nitrogen than they are to the halide. However, adding anything else to the system - be it another hydrogen, another ammonium halide, even another electron - will cause the hydrogen bond to “bridge”. The hydrogen will move closer to the halide so that it is roughly equidistant from the nitrogen and the halide. This is known to be true for the bromide and chloride clusters, but it remains to be seen what, if anything, will cause the hydrogen bonds in the fluoride cluster to “bridge”.

Phase 1: Background Research and Survey of Literature

Overview

In the first phase of the research project, background research was done of existing scientific literature on ammonium halide nanoclusters. Please refer to the Annotated Bibliography and Works Cited. Below is a brief description of the critical pieces of literature.

Description of Relevant Literature

(Topper and Freeman, 1994) outlines the equation for the interaction model for NH_4Cl , and provides the parameters for the interaction model². This interaction model consists of an exponential repulsive term, the Lennard-Jones (6-12) potential, and the Coulombic interaction term. The force field is thus

$$U(r_{ij}) = A_{ij}e^{-\alpha_{ij}r_{ij}} + \frac{C_{ij}}{r_{ij}^{12}} - \frac{D_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}^2}$$

where r_{ij} is the distance between atoms i and j , $U(r_{ij})$ is the pairwise potential of the atom pair, given that they are a distance r_{ij} apart, q_i and q_j are the partial charges of atoms i and j , respectively, and A_{ij} , α_{ij} , C_{ij} and D_{ij} are all parameters. This exact same interaction model was used, except the parameters for chlorine had to be replaced by the corresponding parameters for fluorine.

The erratum notes (Topper 2014) revised the values of the interaction model parameters (especially the values of the D parameters).

² The terms “interaction potential” and “force field” will be used interchangeably to refer to a function together with the set of parameters that can calculate the potential energy of a system of atoms.

In order to estimate (i.e. get initial guesses for) the parameters for the interactions between the fluoride ions, several papers were referred to:

1. The values of C_{FF} and D_{FF} were found from (Mao and Pappu, 2012)
2. The value of q_F was found from (Chandrasekhar, Spellmeyer and Jorgensen, 1983)
3. Finally, the values of C_{HH} and D_{HH} for the hydrogen-hydrogen interactions were found from (Oobatake and Ooi, 1972).

From the above papers, estimates for all necessary parameters had either been obtained or could be calculated using the Lorentz-Berthelot combination rules³ for the Lennard-Jones parameters. The initial estimates for the parameters are included in Appendix 1.

Furthermore, crystallographic data on ammonium fluoride was obtained from (Adrian and Feil, 1969). Of particular interest were the interatomic distances within an ammonium fluoride crystal: these figures could later be used to comparison and reference.

All papers and literature cited here and in the bibliography may be found in the folder entitled "Papers and Literature".

³ a.k.a. "the standard combination rules", although this name is misleading, as there are several alternative sets of combination rules.

Phase 2: Quantum Mechanics Calculations

Overview

Having found initial estimates for all necessary parameters, the next step was to find a method of testing the interaction model. It was decided to simulate a NH_4F nanoparticle using quantum mechanics with the Spartan software package, and compare the predictions of the interaction model with those given by quantum mechanics: in particular, the optimum N-F distance and the potential well depth^{4,5} predicted by the force field would be compared with those calculated using Spartan.

Description of Calculations

On Spartan, two builds of ammonium fluoride were created. For the first, molecular mechanics (specifically, MMFF, the Merck Molecular Force Field) was used to create a build of an ammonium fluoride nanoparticle. For the second, a “rigid” ammonium ion was built from scratch, with all N-H distances equal to 1.012 angstroms, and a fluoride ion was added to the build⁶. The difference between the two builds is solely in the geometry of the ammonium ion⁷.

The H-F bond distances for both builds was then constrained, and driven to range from 0.5 to 3.5 angstroms, resulting in energy profiles. Both energy profiles were then subjected to all

⁴ Which is defined as the difference between the minimum energy achieved by the cluster and the asymptotic potential achieved when the separation between the two ions approaches infinity. This definition allows for the computation of the well depth for the density functional theory and Møller-Plesset calculations, whose asymptotic potentials are not zero.

⁵ The N-F distance that gives the minimum interaction potential and the depth of the potential well will herein be referred to as “the optimum distance” and the “well depth”, respectively.

⁶ The two different builds will herein be referred to as the “MM build” and the “rigid-ammonium build”.

⁷ Note that, since nitrogen is an extremely electronegative atom, it is not likely that the hydrogens will stray very far from it. Thus, it is very likely that the rigid-ammonium build models the nanoparticle more accurately. However, since the fluoride ion is even more electronegative, this may not be the case: thus, for safety, both the MM build and the rigid-ammonium build were subjected to quantum mechanics calculations.

of the following quantum calculations, in order to determine the potential of the nanoparticle as a function of the H-F distance.

Quantum Mechanics Calculations:

1. Semi-Empirical Methods
 - a. AM1
 - b. PM3
2. Density Functional Theory
 - a. M06 6-31G*
 - b. M06-2X/6-31G**
3. Møller-Plesset Perturbation Theory⁸
 - a. MP2 6-31G*
 - b. MP2 6-311+G(2df, 2f)
 - c. MP2 aug-cc-pVTZ

Furthermore, the density functional theory M06-2X/6-31G** calculation was reproduced for the NH₄Cl cluster, for which there was an interaction model (from previous work on the project) with which to compare results.

Finally, MMFF and SYBYL (two different families of force fields used for molecular modelling) were used to model an ammonium fluoride nanoparticle. This was done purely to see what the resulting optimum distance and well depth would be.

The MM build and rigid-ammonium build, the outputs of the various quantum calculations and a spreadsheet collating all the quantum calculations can be found in the folder entitled “Spartan Calculations”. The MM build and rigid-ammonium build for the NH₄Cl cluster can be found under the same folder, as well as the M06-2X/6-31G** calculation for the aforementioned

⁸ A few technical errors were experienced when running the 6-311+G(2df, 2f) and the aug-cc-pVTZ calculations: Spartan threw an SCF convergence error. This was resolved by invoking the GUESS=CORE keyword. Even so, there was one anomalous point that was given by the aug-cc-pVTZ calculation: the eighth data point for the rigid-ammonium build is anomalously large. This was simply disregarded: the computer used may not have been reliable enough for such high-caliber calculations.

two builds. Finally, the MMFF and SYBYL builds of an ammonium fluoride nanoparticle can also be found in the same folder.

Results and Discussion

It was found that all the quantum calculations roughly agreed with one another, placing the H-F distance at around 1.167 angstroms. This agreement corroborates the reliability of the results from the quantum mechanics calculations. The well depth for the M06-2X/6-31G** calculation was computed to be around -623 kJ/mol; while the well depths for all other calculations were not computed, they can be generally expected to agree closely with this value.

Interestingly, the quantum results also agreed very well with the results from the MMFF model of ammonium fluoride, but not the SYBYL model. This was believed to be due to the fact that the MMFF parameters had been optimized to agree with quantum results, whereas the SYBYL parameters had not. It was thus concluded that the parameters of the interaction model had to be similarly optimized to agree with the quantum results from Spartan.

Phase 3: $U - r$ Grapher

Overview

Having found the “true” values of the optimum distance and the well depth, it now remained to be determined whether the H-F distance given by the interaction model, with the initial estimates for the parameters, agreed with the H-F distance given by quantum mechanics.

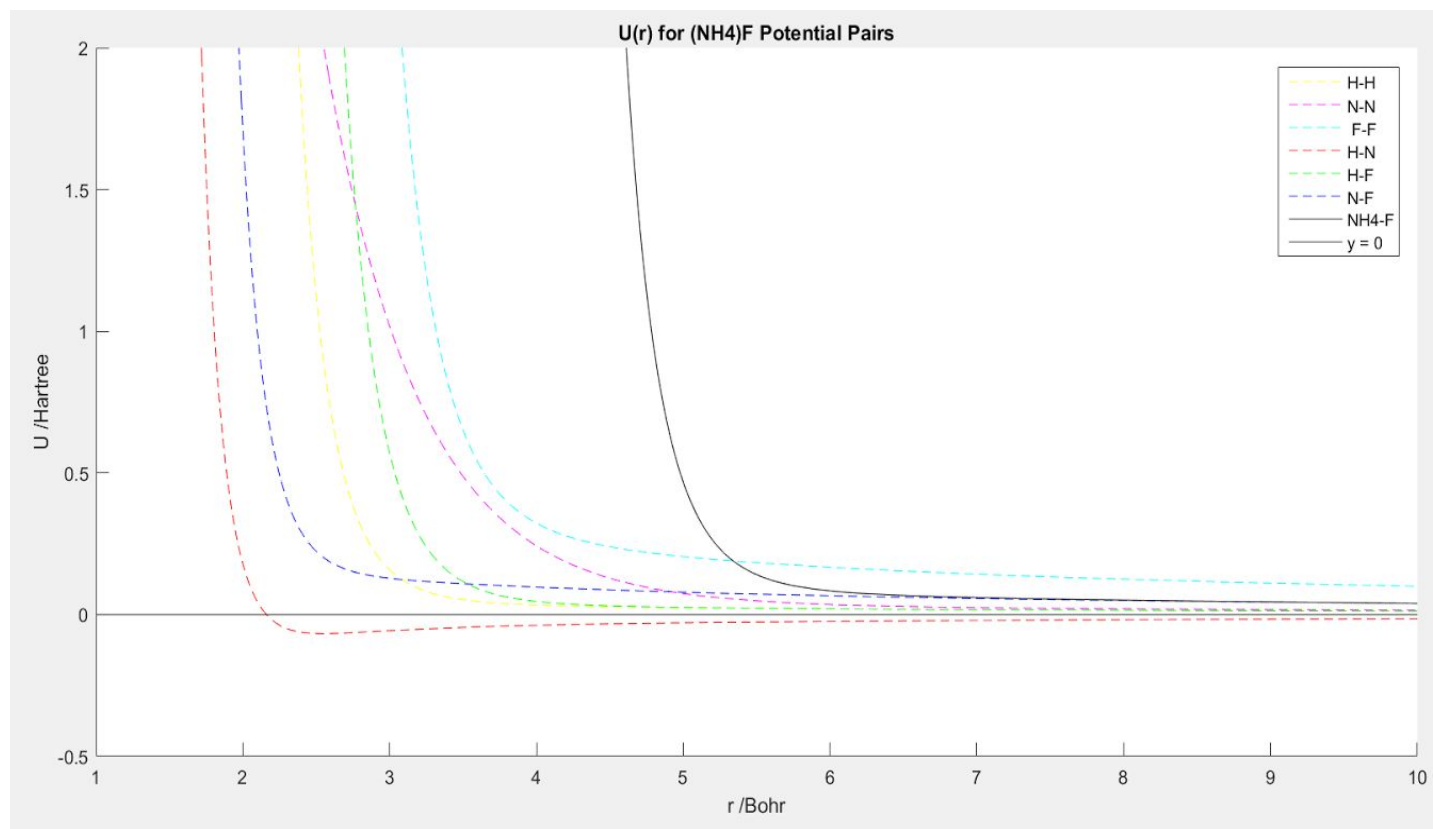
To this end, a MATLAB program was written that graphs the pairwise potential for of atoms as a function of their separation: i.e. graph the potential of any two pairs of atoms in the ammonium fluoride cluster (U) as a function of the distance between them (r)⁹. This is done by storing all parameters in a matrix, and defining all pairwise interaction potential functions at once, accessing the matrix whenever necessary. The total interaction between the ammonium ion and the fluoride ion was calculated by assuming that the ammonium oriented one of its hydrogens to point directly at the fluorine ion (Pauling, 1960). Then, by calling the N-F distance r , and through elementary trigonometry, the distances from F to all atoms in the ammonium ion - and thus, the corresponding pairwise potential - can be found in terms of r . These pairwise potentials are summed to find the total interaction between the ammonium ion and fluoride ion. This total interaction is also graphed.

This MATLAB program, named “Ur_Grapher” may be found in the folder entitled “MATLAB programs”.

⁹ Note that all MATLAB code handles distances and energies in atomic units (i.e. bohr and hartree). This is simply for convenience's sake: the numbers are on the first order of magnitude and are therefore easily comparable by human eyes. Furthermore, the Coulomb constant in the Coulombic interaction term becomes unity, which is computationally more efficient.

Results, Discussion and Conclusions

With the initial estimates, the Topper-Freeman interaction model produced the following graph:



As can be seen, the interaction is globally repulsive: the graph never dips below zero.

This is clearly incorrect, as disagrees with all of the previously performed quantum calculations, and it is known that NH_4F exists as a stable compound (Pauling, 1960). Thus, one or more of the parameters must be adjusted so as to get a finite range of distances over which the potential is actually negative¹⁰. It was decided to first try and modify the partial charges of the nitrogen

¹⁰ A short Monte Carlo calculation was performed on the $n=4$ cluster using these initial parameter estimates and, sure enough, gave terrible results in which ions were attracted to each other but without N-H bonds pointing towards the fluorides and adopting ring structures in some cases. Remarkably, when the same test was applied to OPLS parameters, a cubic structure in decent agreement with MP2 calculations was obtained. So the next step is to use the code to test the OPLS parameters: either the OPLS will show up as

and hydrogens on the ammonium ion, as it was hitherto the only set of parameters that did not have a reference in the literature. Therefore, it is the one that falls under suspicion first and will therefore be optimized first.

Phase 4: Partial Charge Optimization

Overview

In order to optimize the partial charges on the atoms within the ammonium ion, another MATLAB program was written to handle such an optimization. This program worked in very much the same way as the previous program: that is, there was a matrix of parameters which was accessed when defining the necessary pairwise potential functions. However, since the total potential only requires the pairwise potential between fluorine and hydrogen, and between fluorine and nitrogen all other potential functions were simply left out of the code. Similarly, since the values of A and α were both zero for the two aforementioned pairwise potential function, those two parameters were also left out of the code.

Since the partial charges on the ammonium ion must sum to +1, the partial charges on the hydrogens and nitrogen may be expressed as

$$q_H = 1 - d \qquad q_N = -3 + 4d$$

where d is a number between 0 and 1. Thus, the code is structured around a for loop: for every value of d between 0 and 1 that is a multiple of 0.05, redefine the partial charges and pairwise potential functions, find the optimum distance, and store the values of d , q_H , q_N , and the optimum distance in separate arrays, and reiterate. When done, output a table of the arrays of said variables.

attractive, or there is a bug in the code. In the end, OPLS, or something very close to it, should be able to model the mixed cluster systems of present interest.

It was decided that the ultimately goal would be to get the interaction model to approximate the optimum length and well depth to within 0.01 angstroms and 0.1 kJ/mol, respectively. Approximations to these tolerances would be sufficient to allow the subsequent quantum calculations on Annie and Spartan to accurately and correctly model an ammonium fluoride nanocluster (Topper, 2016).

This MATLAB program, named “dCharge_Opt” may be found in the folder entitled “MATLAB programs”.

Results, Discussion and Conclusions

The table produced by MATLAB (described in the previous section) is overleaf.

At first glance, the results are good: reasonable distances are generated for all d . It also appears that the optimum distance is a continuous function of d , which agrees with intuition.

However, unfortunately, the values of 5.8 - 6.1 bohr that the MATLAB program produces by varying the values of the partial charges is nowhere near the “target value” of 1 - 1.5 angstrom (2 - 2.5 bohr) that Spartan produced. Thus, the conclusion is more or less the same as in Phase 3: more (or other) parameters must be modified and optimized so as to achieve better agreement with the quantum calculations. The values of C_{ij} and D_{ij} for the H-F interaction were chosen to be optimized next. The choice (both of which parameters to optimize next, and which pairwise interaction to focus on) was completely arbitrary (Topper, 2016).

Note that varying the partial charges also does not solve the problem presented in Phase 3. That is, changing the partial charges within the ammonium ion does not make the interaction attractive at any range of distances: the interaction is still globally repulsive. However, this was overlooked by the author: the research project thus continues as if the interaction had the qualitative behavior of diverging towards infinity as the distance approaches

zero, intersecting the x-axis at some finite distance, attaining a global (negative) minimum, before asymptotically approaching zero as the distance approaches infinity. For a detailed account of this mistake, please consult the author's research log.

d	q_H	q_N	Optimum distance /bohr
0	1	-3	5.806
0.05	0.95	-2.8	5.8163
0.1	0.9	-2.6	5.8268
0.15	0.85	-2.4	5.8377
0.2	0.8	-2.2	5.849
0.25	0.75	-2	5.8606
0.3	0.7	-1.8	5.8726
0.35	0.65	-1.6	5.8851
0.4	0.6	-1.4	5.898
0.45	0.55	-1.2	5.9114
0.5	0.5	-1	5.9254
0.55	0.45	-0.8	5.9399
0.6	0.4	-0.6	5.9551
0.65	0.35	-0.4	5.9709
0.7	0.3	-0.2	5.9874
0.75	0.25	0	6.0047
0.8	0.2	0.2	6.0229
0.85	0.15	0.4	6.0421
0.9	0.1	0.6	6.0622
0.95	0.05	0.8	6.0836
1	0	1	6.1061

Phase 5: $C_{HF} - D_{HF}$ Parameter Optimization

Overview

Attention was now turned to the values of C_{HF} , D_{HF} . As explained above, both the choice of C_{ij} , D_{ij} and the choice of the H-F interaction was completely arbitrary. For this phase of the project, the values of q_H and q_N were held constant at 0.5 and -1, respectively. A Hartree-Fock / 6-31G** calculation was performed on an isolated ammonium ion using Spartan: the conventional wisdom is that such a calculation is a good level of theory for determining the partial charges within a molecule. A table of the results can be found Appendix 2. Of the results, the “Natural” charges are generally held in the greatest confidence, with the “Electrostatic” charges a close second. Thus, setting q_H and q_N to be 0.5 and -1, respectively, seems eminently reasonable.

Again, to optimize the values of C_{HF} and D_{HF} , a MATLAB program was written. This program was, once again, very much like the previous program. There is still a parameter matrix which is accessed when defining the pairwise potential parameters; there is also a for loop, in which the values of C_{HF} , D_{HF} , the optimum distance, the well depth and the Euclidean distance for every (C_{HF} , D_{HF}) pair are stored in separate arrays, and at the end of which a table and three graphs are outputted. The table includes the values of C_{HF} , D_{HF} , the optimum distance, the well depth and the Euclidean distance for every (C_{HF} , D_{HF}) pair, and the graphs plot the latter three variables as a function of C_{HF} and D_{HF} . The only aspect of the code that is not self-explanatory is the computation of the “target” values for the optimum distance and the well depth. Their method of computation is outlined below.

The Møller-Plesset MP2 6-311+G(2df, 2f) calculation was chosen to be the quantum calculation to which the results of the interaction model would be compared. The results of the MP2 6-311+G(2df, 2f) calculation are tabulated and graphed in Appendix 3. However, the main problem is that the Møller-Plesset Theory compares energies to a different basis, and therefore does not have an asymptotic potential of zero: the asymptotic potential is on the order of -4×10^5 kJ/mol. Therefore, the main obstacle is to “normalize” the Møller-Plesset data so that it is as the same qualitative behavior as the interaction model (Topper, 2016).

First, Spartan was used to calculate the asymptotic potential of a NH_4F nanoparticle, using the MP2 6-311+G(2df, 2f) calculation. This was done by separately calculating the energy of an isolated ammonium ion and an isolated fluoride ion, and summing them. The data points from the quantum mechanics calculations could then be shifted upwards by the absolute energy of the minimum data point, so that the minimum data point will have a potential of zero. The same data points could then be shifted down by the difference between the asymptotic potential and the absolute energy of the minimum data point. This will ensure that the quantum calculation data points will have an asymptotic potential equal to zero, and therefore have the same qualitative behavior as the interaction model. The quantitative behavior of the two models can now be compared.

Below are the results for the calculation described above:

- Isolated NH_4^+ potential = -149087.84 kJ/mol (from Spartan)
- Isolated F^- potential = -261827.69 kJ/mol (from Spartan)
- Asymptotic potential = sum of isolated NH_4^+ and F^- potentials = -410915.53 kJ/mol
- Minimum potential¹¹ = -411538.56 kJ/mol

¹¹ Note that this potential may not actually be the minimum. Since only 10 data points were taken, it is possible that the true minimum lies between the 2nd and 3rd, or 3rd and 4th, data points... In other words, since only a finite number of distances were sampled, it is entirely possible that the optimum distance was

- Well depth = asymptotic potential - |minimum potential| = -623.03 kJ/mol
= -0.2372 hartree

This MATLAB program, named “CD_Opt” may be found in the folder entitled “MATLAB programs”.

A spreadsheet named “Normalized MP2 6-311+G” details this normalization of the MP2 6-311+G data can be found in the folder entitled “Spartan Calculations”.

Results, Discussion and Conclusion

The MM build and rigid-ammonium build, the outputs of the various quantum calculations and a spreadsheet collating all the quantum calculations can be found in the folder entitled “Spartan Calculations”. The builds and quantum mechanics calculations are in Spartan files, under various subfolders; the spreadsheet collating all results is simply named “Spartan Data”.

The graphs for the optimum distance, the well depth and the Euclidean distance as a function of C_{HF} and D_{HF} may be found in Appendix 3. Note, however, that these graphs were made under the mistaken assumption that the total interaction potential function had the same qualitative behavior as the desired interaction model: that is, it starts off diverging to infinity as the distance approaches zero, intersects the x axis and attains a negative global minimum, before asymptotically approaching zero as the distance approaches infinity. However, as explained in Phase 4, this is not the case: the interaction potential is globally repulsive. While this does not completely invalidate the results found in this phase of the project, it does mean that they will only become a relevant concern once this problem of global repulsiveness has been solved. In other words, the results are not wrong, they simply miss the point.

“missed”. A small (but perhaps appreciable) improvement would therefore be to sample more distances using Spartan to find a value closer to the true minimum potential.

However, that notwithstanding, the program does execute the desired task: it iterates over a large number of (C_{HF}, D_{HF}) pairs, and calculates the optimum length, well depth, and Euclidean distance, and can therefore theoretically find the (C_{HF}, D_{HF}) pair that gives the best agreement with the quantum calculations.

Note that care must be taken when comparing the optimum N-F distance, as given by the MATLAB interaction model calculations, to the optimum H-F distance, as given by the Spartan quantum mechanics calculations. In all cases, the former distance will be greater than the latter distance by 1.012 angstroms: this is the common value of all N-H distances in a rigid-ammonium build (refer to the Description of Calculations in Phase 2). This computation assumes that the ammonium is, indeed, rigid. However, as outlined in Phase 2, it is not certain that this is still the case with ammonium fluorides. Thus, this assumption may or may not need to be revisited.

Alternatives Considered

An alternative to optimizing the values C_{HF} and D_{HF} was considered: modifying the attractive term of the Lennard-Jones. Instead of the term involving a r^6 denominator, it would be changed to be an r^{10} denominator. Furthermore, the attractive term would be multiplied by a $\cos^2\theta_{AHD}$, where θ_{AHD} is the angle between the proton acceptor, hydrogen ion, and proton donor. However, this idea was nixed, as the computation of the $\cos^2\theta_{AHD}$ would slow the execution of Annie down to an unacceptable extent (González, 2011).

Two alternative methods of optimizing the values of C_{HF} and D_{HF} were considered. The first method was that, for every (C_{HF}, D_{HF}) pair, the total potential curve (between the ammonium ion and the fluoride ion) would be graphed, and compared to the total potential curve produced by the quantum mechanics calculations. A least squares regression could then

be performed to find the (C_{HF}, D_{HF}) pair that gives the curve that fits closest to the curve given by quantum mechanics. The second method was that, for every (C_{HF}, D_{HF}) pair, the optimum distance and well depth would be calculated, and compared to the optimum distance and well depth found from the quantum mechanics calculations. The Euclidean distance between the interaction model values and the quantum mechanics values could then be used as a measure of how well the (C_{HF}, D_{HF}) pair produces results that resemble the quantum mechanics results.

Although the former method is much more conventional and widely accepted, it was rejected due to the sheer computational load it would involve: a least squares regression for every single (C_{HF}, D_{HF}) pair would slow down computations immensely. However, it may be a fruitful line of inquiry to try adopting the former method of optimizing the values of C_{HF} and D_{HF} .

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Improvements and Directions for Further Research

There are several improvements that can be made to the current work, and several lines along which future work may be directed. They are detailed below.

The first priority should be to get the interaction potential to have the correct qualitative behavior. It is currently globally repulsive, when there should be a finite range of distances over which is attractive. This problem was presented in Phase 3 of the project but was overlooked by the author throughout Phases 4 and 5. This does not necessarily mean that the work done in Phases 4 and 5 are now useless: rather, it simply means that once the problem of Phase 3 has been resolved, Phases 4 and 5 will be very short work, since all the necessary software has been made, and the relevant behavior has been studied.

Secondly, even after performing Phase 5, it may be found that while the optimum distance and the well depth do move in the right direction (i.e. move closer to the “target values”), they still do not approximate the “target values” to a satisfactory degree of accuracy. Furthermore, it was decided that it was more important that the interaction model produce an accurate optimum distance than it was to produce an accurate well depth. This is because the subsequent calculations done by Annie and Spartan can cope with an incorrect well depth much better than an incorrect optimum distance. Therefore, one line of attack to make the model fit the data would be to multiply the entire total interaction potential function by a switch function¹². In particular, a switch function of the form

$$S(r) = \frac{1}{1+e^{-b(r-m)}}$$

¹² A switch function is a term that can “turn on” or “turn off” a term or terms in a force field. It is best illustrated by example. Consider $S(x) = \cos^2(x/c)$. Then, if an arbitrary $f(x)$ is multiplied by $S(x)$, the switch function will have the effect of leaving the output untouched at $x = 0$, and gradually diminishing the output to 0 as x approaches c .

where b is a parameter to be optimized, and m is the point at which the switch function will turn the interaction potential function completely off. It will then be possible to completely determine where the optimum distance occurs. Unfortunately, this means that we must accept whatever well depth accompanies that potential function; however, as mentioned before, it is more important to achieve an accurate optimum length than it is to achieve an accurate well depth.

An alternative to this would be to optimize the exponents on the Lennard-Jones terms. Instead of 6-12, perhaps it would be advantageous to try a 6-14 potential. Changing the exponents would change the placement of the optimum length, which may be an alternative to using a switch function, as described above.

Finally, it may be fruitful to revisit the assumptions or alternative methods outlined in the project: in particular, the method of graphing a separate potential curve for every (C_{HF}, D_{HF}) pair, and using a least squares regression to determine the optimal value of (C_{HF}, D_{HF}) (refer to Alternatives Considered, Phase 5). Also, the assumption that the ammonium ion is perfectly rigid and has four identical N-H distances may need to be revisited, as that assumption underlies the comparison between the H-F distances produced by the Spartan quantum calculations and the N-F distances produced by the MATLAB interaction potential calculations.

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Mao, Albert H., and Rohit V. Pappu. "Crystal Lattice Properties Fully Determine Short-Range Interaction Parameters for Alkali and Halide Ions." *Journal of Chemical Physics* 137 (2012): n. pag. Print. This paper was referenced for initial estimates of C and D (the Lennard-Jones coefficient parameters) for the fluoride ion. These values were propagated on using the Lorentz-Berthelot combination rules to find the C and D values for all interactions involving fluoride ions.

Oobatake, Motohisa, and Tatsuo Ooi. "Determination of Energy Parameters in Lennard-Jones Potentials from Second Virial Coefficients." *Progress of Theoretical Physics* 48.6B (1972): n. pag. Print. This paper was used to calculate the values of C and D (Lennard-Jones coefficient parameters) for the hydrogen-hydrogen interaction. Note that the force field used by the authors do not include an exponential repulsive term, which may introduce error.

Pauling, Linus. *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell UP, 1960. Print. This book provided a diagram illustrating the crystal structure of NH_4F . This was helpful when computing the interaction potential between an ammonium and a fluoride ion, as the geometry of the cluster affects its energy.

Topper, Robert Q. *Ammonium Halide Nanoparticle Modelling*. N.p.: n.p., 2016. Print. This was a summary of the research project, submitted by Prof. Topper to the Registrar of The Cooper Union in fulfillment of the requirement of the CH-391 class.

Topper, Robert Q. "Independent Study Meetings." Personal interview. Spring 2016. Weekly meetings for research progress updates. These meetings were invaluable in providing new directions and ideas for research.

Topper, Robert Q., and John Biswakarma. *Erratum Notes for 2011 J. Phys. Chem. A Article*. N.p.: n.p., 2014. Print. These erratum notes revised the values of D (Lennard-Jones coefficient parameter) for the Topper-Freeman 2014 article.

Topper, Robert Q., and David L. Freeman. "Monte Carlo Studies of the Orientational Order-Disorder Phase Transition in Solid Ammonium Chloride." *Journal of Chemical Physics* (1994): n. pag. Print. This paper provided the interaction model that was used throughout the entire project, and the values of the A, α , C and D parameters for the ammonium chloride

interaction model. It also outlines the Lorentz-Berthelot combination rules, which was used to calculate the parameters for any interaction involving the fluoride ion.

Appendices

Appendix 1: Initial Estimates for Topper-Freeman Interaction Potential Parameters for NH_4F

The following table presents the initial estimates of the parameters used in the Topper-Freeman interaction model.

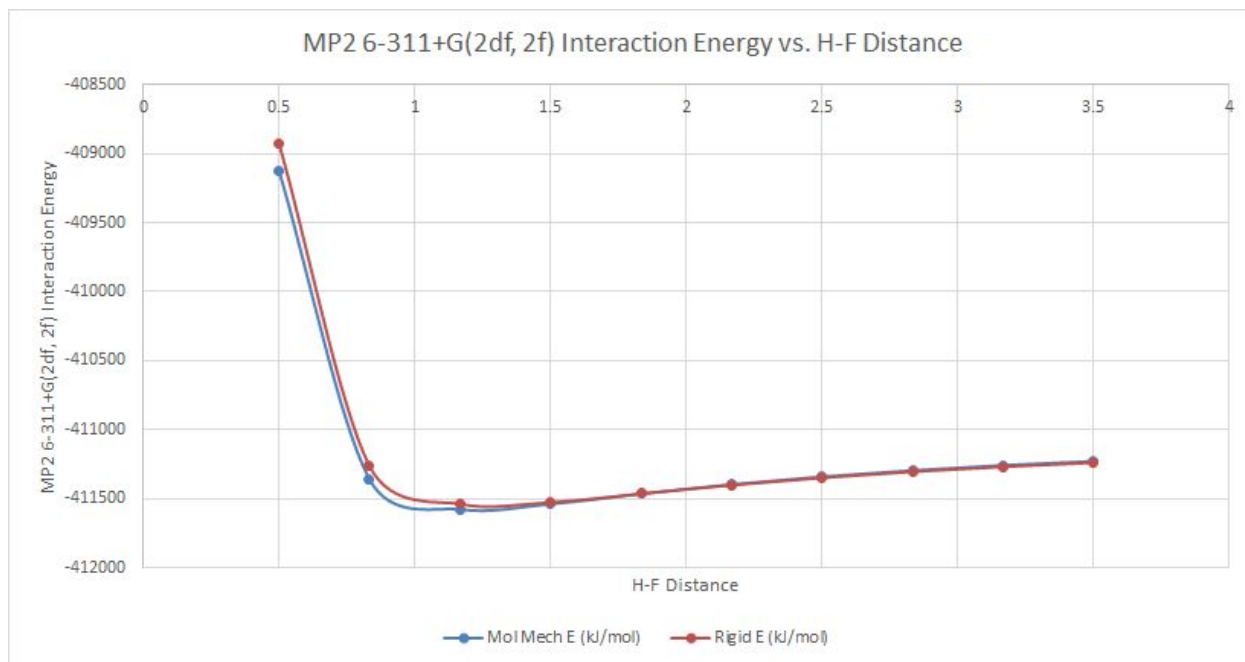
	A_{ij}	α_{ij}	C_{ij}	D_{ij}	q_i	q_j
H-H	0	0	3.3384	6.4895e+04	0.35	0.35
N-N	104.74	1.5611	25.393	40.0	-0.4	-0.4
F-F	0	0	7.1717	1.2481e+06	-1.0	-1.0
H-N	0	0	9.2072	1.6111e+03	0.35	-0.4
H-F	0	0	4.8931	2.8460e+05	0.35	-1.0
N-F	0	0	13.4948	7.0656e+03	-0.4	-1.0

Appendix 2: Partial Charges on Lone Ammonium Ion from Hartree-Fock / 6-31G** Calculation

The following table presents the partial charges on an ammonium ion, as calculated from a Hartree-Fock 6-31G** calculation on Spartan.

	Natural	Electrostatic	Mulliken
N1	-0.983	-0.822	-0.655
H1	+0.496	+0.456	+0.414
H2	+0.496	+0.456	+0.414
H3	+0.496	+0.456	+0.414
H4	+0.496	+0.456	+0.414

Appendix 3: Results of MP2 6-311+G(2df, 2f) Calculation



H-F Distance (Å)	Mol Mech Energy (kJ/mol)	Rigid Energy (kJ/mol)
0.500	-409121.82	-408923.35
0.833	-411358.63	-411262.17
1.167	-411577.19	-411538.56
1.500	-411537.99	-411525.28
1.833	-411464.34	-411463.34
2.167	-411395.93	-411400.7
2.500	-411339.71	-411347.52
2.833	-411294.56	-411303.97
3.167	-411257.95	-411268.22
3.500	-411227.88	-411238.57

Appendix 4: Graphs of optimum distance, well depth and Euclidean distance as functions of C_{HF} and D_{HF}

The following graphs plot the dependences of the optimum distance, the well depth and the Euclidean distance on the values of C_{HF} and D_{HF} , in that order.

The following graphs are named “optLength”, “wellDepth” and “euclidean”, respectively, and may be found in the folder entitled “MATLAB Calculations”.

