Ab initio investigations of the dynamic and thermodynamic properties of atmospherically relevant strong acids

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Helsinki 2017
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Acknowledgements

While a casual observer might find this page to be one of the least significant of this thesis, from my own subjective perspective it is without a doubt the most important one. Perhaps in accordance with our nature, in our scientific ventures we tend to emphasize the role of the individual, while leaving out the multiverse of interactions and discussions that facilitated the conception of the ideas now buttressing our scientific world view. In my experience, however, it is largely through interactions with those around us that we slowly, and sometimes painstakingly, come to know and understand ourselves and the universe around us.

I owe a huge debt of gratitude to the people who worked with me on the publications: The supervisors of my thesis, Lauri Halonen and Vesa Hänninen, with whom I have had several vigorous and productive discussions and who were always able to find time for me and my work; Garold Murdachaew who provided me with an endless supply of helpful tips and a seemingly limitless patience for my questions; Janne Pesonen who introduced me to the strange world of geometric algebra (I shall never forget that falling cat); Hanna Vehkamäki and all the others. Furthermore, I am thankful for all the people at the Laboratory of Physical Chemistry and the Laboratory for Instruction in Swedish for creating a stimulating and relaxed work environment. It has been a pleasure to do research alongside you.

Several teachers have also had a profound influence on me along the way. I am grateful to Sari Kolo-Vartiainen and Petra Luukko, who encouraged me on my path to study science in the secondary primary school, and to my English teacher Minna Oittinen, who went far beyond the call of duty reading my texts and helping me to develop as a writer. Of my teachers at the university, I am indebted to Aino-Maija Lahtinen and Juha Taina who opened to me a new window into science by helping me develop my pedagogical thinking.

A heartfelt thanks also goes to my closest friends. Make and Emmi, you have provided me with much needed perspectives and distractions whenever the day-to-day chores of pursuing a PhD seemed bleak; Mika, your positive and carefree attitude towards life seems to have rubbed on me over the years and made my life a lot more enjoyable. Taneli, I think that
since those first few weeks in the organic chemistry laboratory we have influenced each other’s thinking and lives in countless ways and I know that had I not met you I would not be the person I am today.

Last but not least, this thesis would not have been completed without the enduring support of my parents and my sister. The bonds that we share have given me so much strength and perseverance, I cannot imagine my life without them. Finally, I am indebted to Pau Rodriguez-Ruiz - you were there for the most difficult stretch of this journey holding me up with your love and understanding. Thank you.

Helsinki, December 17, 2016
Abstract

Sulfuric and hydrochloric acids participate in several important chemical processes occurring in the atmosphere. Due to its tendency to react with water molecules, sulfuric acid is an important factor in cloud formation and related phenomena. Hydrochloric acid is heavily implicated in stratospheric ozone depletion because of its role as a temporary reservoir for chlorine radicals.

In this thesis, the thermodynamics and dynamics of these two acids are investigated. The dynamic part focuses on the chemical processes following collision of HCl on water and amorphous ice surfaces at different temperatures. By utilizing ab initio molecular dynamics, it is observed that the surface temperature and the initial kinetic energy of the HCl molecule have important and not wholly overlapping effects on its ionization behaviour. The results add to the understanding of hydrochloric acid dissociation on water surfaces in various parts of the atmosphere, potentially illuminating new pathways for related chemical reactions, such as the formation of ClNO on amorphous ice surfaces.

The thermodynamic studies revolve around the impact of multiple low-lying stable conformers, or global anharmonicity, on the thermodynamic properties. The studies for this part focus on complexes of sulfuric acid, especially sulfuric acid monohydrate. Due to the relatively small size of the monohydrate, high-level ab initio methods can be employed to obtain accurate values for its thermodynamic properties, thus providing a reliable basis for comparison with less accurate approaches. New ways of accounting for global anharmonicity are developed both for small- and medium-sized clusters. For small clusters, an approximation is presented where the large amplitude motions connecting different conformers are treated separately from the rest of the vibrations, resulting in direct quantum mechanical accounting of the different conformers. In the case of medium-sized clusters, an equation based on statistical mechanics is derived to replace the erroneous Boltzmann averaging formula that has seen wide use in the literature.
List of publications

This thesis consists of five original publications in scientific journals:


In Article I, the three-dimensional water potential energy surface and energy level calculations as well as all geometry optimizations and harmonic frequency calculations were performed by the candidate. In the second article, all calculations and derivations were performed by the candidate based on the general results derived by Pesonen.\(^1\) In the third article, almost all of the molecular dynamics simulations and analysis of the results were done by the candidate, utilizing pre-existing programs written by Dr. G. Murdachaew. In Article IV, the candidate derived the main theoretical formula and did most of the analysis of the computational results. The candidate wrote all computer programs dealing with nuclear motion in Article V. He also derived the necessary equations, performed most of
the electronic structure calculations, and analyzed all results. He wrote the manuscripts for Articles I, II, III, and V and the majority of Article IV. The original research ideas for Articles IV and V were conceived chiefly by the candidate.
Errata

Article III

1. Equation (1) on page 13434 should read

\[ \rho(z) = \frac{\rho_l + \rho_v}{2} - \frac{\rho_l - \rho_v}{2} \tanh \left( \frac{z - z_{GDS}}{\delta} \right) \]

Article V

1. Equation (23) on page 5516 should read

\[ E_k^0 = U_k^0 + \epsilon_k - \epsilon_0, \]

and the instances of \( E_{k,0} \) and \( E_{0,0} \) immediately following that sentence should be changed to \( \epsilon_k \) and \( \epsilon_0 \), respectively.

2. On page 5516, the symbols \( E_{k,0}, E_{1,0}, \) and \( E_{0,0} \) in Figure 2 and its caption should be changed to \( \epsilon_k, \epsilon_1, \) and \( \epsilon_0 \), respectively.
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<tr>
<td>AIMD</td>
<td><em>Ab initio</em> molecular dynamics</td>
</tr>
<tr>
<td>AMBER</td>
<td>Assisted model building with energy refinement, a family of empirical force fields for molecular dynamics</td>
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<tr>
<td>AO</td>
<td>Atomic orbital</td>
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<tr>
<td>aug</td>
<td>Augmented basis set</td>
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<tr>
<td>aug-cc-pVmZ</td>
<td>Augmented correlation consistent polarized valence double ((m=D)), triple ((m=T)), quadruple ((m=Q)) or pentuple ((m=5)) zeta basis set with diffuse functions</td>
</tr>
<tr>
<td>aug-cc-pV(m+d)Z</td>
<td>Augmented correlation consistent polarized valence double ((m=D)), triple ((m=T)), quadruple ((m=Q)) or pentuple ((m=5)) zeta basis set with diffuse functions and an extra tight (d) function for the third row atoms</td>
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<td>See aug-cc-pVmZ and aug-cc-pV(m+d)Z</td>
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<td>BLYP</td>
<td>A Density functional combining the Becke exchange functional with the correlation functional by Lee, Yang, and Parr</td>
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<td>BLYP-D2</td>
<td>The BLYP functional with Grimme-type dispersion corrections</td>
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<tr>
<td>BO</td>
<td>Born–Oppenheimer</td>
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<tr>
<td>BSSE</td>
<td>Basis set superposition error</td>
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<tr>
<td>B3LYP</td>
<td>Becke, 3-parameter, Lee–Yang–Parr hybrid density functional</td>
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<tr>
<td>cc-pV(T+d)Z</td>
<td>Correlation consistent polarized valence triple zeta basis set with an extra tight (d) function for the third row atoms</td>
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<tr>
<td>CC</td>
<td>Coupled cluster</td>
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<tr>
<td>CCSD</td>
<td>Coupled cluster singles and doubles</td>
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<tr>
<td>CCSD-F12a or b</td>
<td>Explicitly correlated coupled cluster singles and doubles with some of the contributions from the explicitly correlated configurations to the doubles residual neglected.</td>
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<td>CCSD(T)</td>
<td>Coupled cluster singles and doubles with perturbative triples</td>
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<tr>
<td>CCSD(T)-F12</td>
<td>Explicitly correlated coupled cluster singles and doubles with perturbative triples</td>
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<tr>
<td>CCSD(T)-F12a or b</td>
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<td>CC-VSCF</td>
<td>Correlation corrected vibrational self-consistent field</td>
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<td>Contracted gaussian type orbitals</td>
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<td>CFC</td>
<td>Chlorofluorocarbon</td>
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<td>CHARMM</td>
<td>Chemistry at Harvard Macromolecular Mechanics, an empirical set of force fields for molecular dynamics</td>
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<td>CIP</td>
<td>Contact ion pair</td>
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<td>CP</td>
<td>Counterpoise</td>
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<td>Density fitting</td>
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<td>Density functional theory</td>
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<td>DZVP</td>
<td>Double zeta valence polarized basis set</td>
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<td>GGA</td>
<td>Generalized gradient approach</td>
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<td>GVPT2</td>
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<td>GTH</td>
<td>Goedecker–Teter–Hutter</td>
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<td>GTO</td>
<td>Gaussian type orbitals</td>
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<td>G3(MP2)</td>
<td>Gaussian-3 composite quantum chemistry method</td>
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<td>HBB</td>
<td>Huang–Braams–Bowman water dimer potential</td>
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<td>HDCPT2</td>
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<td>HF</td>
<td>Hartree–Fock</td>
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<td>LMP2</td>
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<td>MP</td>
<td>Møller–Plesset perturbation theory</td>
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<td>MP(m)</td>
<td>Møller–Plesset perturbation theory of (m)th order</td>
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<td>PBC</td>
<td>Periodic boundary conditions</td>
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<td>PES</td>
<td>Potential energy surface</td>
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<td>P(_{VMWC12})</td>
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<td>PW91</td>
<td>Perdew–Wang exchange and correlation functional</td>
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<td>QZ</td>
<td>Quintuple zeta basis set</td>
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<td>RMS</td>
<td>Root mean square</td>
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<td>Spin component scaling</td>
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<td>Simple perturbation theory</td>
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<td>SSIP</td>
<td>Solvent separated ion pair</td>
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<td>STO</td>
<td>Slater type orbital</td>
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<td>TIP&lt;sub&gt;mP&lt;/sub&gt;</td>
<td>A force field for H&lt;sub&gt;2&lt;/sub&gt;O where the molecules are modelled by &lt;i&gt;m&lt;/i&gt; interaction sites</td>
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<td>TZ</td>
<td>Triple zeta basis set</td>
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<tr>
<td>T1</td>
<td>A composite quantum chemistry method developed for calculating accurate heats of formation</td>
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<td>VDZ</td>
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<td>Vibrational configuration interaction</td>
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<td>Vibrational self-consistent field theory</td>
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<tr>
<td>ZPE</td>
<td>Zero point energy</td>
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<td>Valence triple zeta basis set with diffuse functions on all atoms and two additional d polarization functions on second row atoms, one d function on first row atoms and a p function on hydrogen atoms</td>
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1 Introduction

Sulfuric acid has a crucial role in environmental chemistry as a central component in both acid rain and cloud formation.\textsuperscript{2,3} In the atmosphere, H$_2$SO$_4$ is typically formed by the oxidation and possible hydration of gaseous sulfur containing compounds such as sulfur dioxide and dimethyl sulfide. These compounds, in their turn, can have either anthropogenic or natural origins. For example, while substantial amounts of SO$_2$ are released to the atmosphere from volcanoes, the predominant contribution comes from the combustion of sulfur containing fuels.\textsuperscript{4}

In cloud formation, atmospheric aerosols can originate either from primary sources, like sea spray, or form directly in the atmosphere via nucleation in the gas phase. This new particle formation occurs in two distinct stages:\textsuperscript{5} First, a critical cluster is formed mainly by the complexation of sulfuric acid and water with trace gases such as ammonia,\textsuperscript{6–11} amines,\textsuperscript{12–17} ions,\textsuperscript{18–27} and volatile organic compounds.\textsuperscript{5,28–37} This is followed by subsequent spontaneous growth of the critical cluster to sizes larger than a few nanometers, accompanied by, for example, coagulation with pre-existing aerosols. Due to its low vapour pressure and large mixing enthalpy with water,\textsuperscript{38–40} a significant portion of the sulfuric acid molecules in the atmosphere is found in hydrates\textsuperscript{41} with the exact amount changing with the altitude.\textsuperscript{42,43} Consequently, sulfuric acid is one of the most important nucleating species in the atmosphere.\textsuperscript{5} This fact is of great significance to models seeking to predict the nucleation rates because reliable estimation of the hydrate effects requires accurate values for the thermodynamic properties for the hydration reactions.\textsuperscript{44,45} As the new particles potentially impact rain fall, ozone depletion in polar stratospheric clouds, and the net radiative forcing due to increased albedo,\textsuperscript{46,47} understanding the nucleation process is of paramount importance.

Experimentally, the equilibrium constants for the individual hydrate reactions are challenging to measure partly due to the difficulties associated with estimating the amounts of different hydrates formed upon reaction of water with sulfuric acid. In terms of the temperature dependence of the equilibrium constant and thus the reaction enthalpy $\Delta H$, several purely ex-
perimental techniques ranging from nuclear magnetic resonance spectroscopy, \(^{48,49}\) microwave spectroscopy, \(^{50}\) pressure measurements, \(^{51–54}\) and IR-spectroscopy \(^{53,55–61}\) have been employed to obtain \(\Delta H\) values. However, the variation between the results of different methods can be large. \(^{48,53,54,59}\) In light of this host of issues, it is appealing to use quantum chemical calculations to obtain the equilibrium constants.

In addition to \(\text{H}_2\text{SO}_4\), various other strong acids such as \(\text{HNO}_3\) participate in important atmospheric processes like acid rain. \(^2\) Furthermore, surface reactions of compounds like \(\text{HCl}\) on aqueous or wetted mineral and organic surfaces enable a host of chemical processes that are slow to occur in the gas phase. For example, one of the most studied mechanisms of ozone hole formation starts with the adsorption of \(\text{HCl}\) and \(\text{ClONO}_2\) on ice, followed by their bimolecular reaction to form \(\text{Cl}_2\) \(^{62–64}\) which during the polar spring photolyses to form chlorine atoms, setting the stage for ozone destruction. \(^{65}\)

With the advent of supercomputers and linear-scaling quantum mechanical methods like density functional theory (DFT), the exact mechanisms of surface processes can now be studied by \textit{ab initio} molecular dynamics (AIMD) simulations. For example, in the case of \(\text{HCl}\), it is known that collisions with a water surface can be succeeded by direct inelastic scattering, trapping succeeded by prompt desorption, or, in the majority of cases, \(\text{HCl}\) dissociation followed by long-term trapping. \(^{66,67}\) As shown in panels (a)–(c) of Figure 1 adapted from Article III, the dissociation process typically starts with the approaching hydrogen in \(\text{HCl}\) donating a hydrogen bond to a surface molecule, followed by the Cl anion accepting two hydrogen bonds, leading to \(\text{HCl}\) ionic dissociation in the picosecond timescale. The resulting contact ion pair (CIP) often rapidly transforms into a solvent-separated ion pair (SSIP) depicted in panel (d) in which the ions are separated by at least one solvent molecule. \(^{68–72}\) This process occurs via the Grotthuss mechanism in which the serendipitous oscillations of the hydrogen-bonded water network enable the relaying of the proton from the acid to a suitably bonded neighbouring water molecule. \(^{73,74}\) The SSIP formation can be followed by solvation of the Cl anion deeper into the bulk or by a process of fast proton exchange and
recombination with another hydrogen. In rare cases, the Cl anion can also resurface from the bulk, reform HCl, and escape into the gas phase in a process of slow evaporation.\textsuperscript{75}

Whereas HCl and HNO\textsubscript{3} are small enough molecules that their potential energy surfaces only contain a single energetically low-lying conformer, already in the case of H\textsubscript{2}SO\textsubscript{4} two such conformers exist as described in Article II. Because the different volatile organic compounds and prenucleation clusters may contain several tens of atoms, there are often multiple low-lying minimum energy configurations in these systems and their number tends to increase with the size of the system.\textsuperscript{76,77} Thus, a major challenge in the theoretical treatment of critical cluster formation is the location and incorporation of the relevant cluster configurations in the calculation. The location of the conformers is typically done in successive stages starting with less accurate approaches based on classical properties. This is followed by more accurate determination of vibrational frequencies, energies, and other properties necessary for the calculation of the conformers’ partition functions using \emph{ab initio} methods.\textsuperscript{26,78,79}

After the different conformations have been located, an increasingly common approach in the calculation of thermodynamic properties has been to employ a process called Boltzmann averaging to obtain a thermal average over the energetically relevant conformers.\textsuperscript{18,26,76,77,79–93} However, as demonstrated in Article IV, this approach yields erroneous results even at the qualitative level, as the incorporation of additional conformers increases the Gibbs free energy of the species, corresponding to an effective decrease in the number of available microstates. In reality, the existence of several conformers increases the number of energy levels and available microstates, which corresponds to an increase in the molecular partition function and a consequent decrease in the value of the Gibbs free energy.

Generally speaking, the accuracy to which the partition function of a molecule can be determined depends inversely on its size. For very small systems, such as a water or an ammonia molecule, it is possible to reliably calculate all relevant energy levels using sophisticated electronic structure methods\textsuperscript{94,95} and thus obtain the partition function accurately as a simple sum over these levels. Upon increasing the size of the system, already for small
Figure 1: A series of snapshots from an AIMD simulation of a thermal collision of HCl with a slab consisting of 72 water molecules at 390 K. Chlorine atoms are marked in green, hydrogens in white, and oxygens in red. The hydronium defects are marked by red circles. Panel (a) shows the system before collision, in panel (b) HCl has a D bonding pattern, in panel (c) a CIP is formed and the Cl anion is solvated by two H-bonds, in panel (d) an SSIP is formed, in panel (e) the hydrogen defect moves further away, and finally ends up at the bottom of the surface in panel (f). This figure is reprinted here with the permission of Physical Chemistry Chemical Physics.
complexes such as the water dimer, water–ammonia cluster, and water–sulfuric acid cluster the complete variational treatment becomes very challenging. In these cases the presence of other conformers can be accounted for by reserving high-accuracy variational calculations only for the large amplitude vibrational motions that connect the separate local minima. This approach was followed in Articles I, II, and V. By treating the high-frequency vibrations separately from the low-frequency ones, it is possible to reduce the dimensionality of the large amplitude motion potential energy surface to a manageable size. This enables a direct quantum mechanical accounting of the different conformers. For larger clusters, more rudimentary approaches based on statistical mechanics become necessary such as the quasi-harmonic approximation where the large amplitude motions connecting the different conformers are treated approximately as rotations.

This thesis focuses on the dynamics and thermodynamics of two strong acids, HCl and H$_2$SO$_4$. The dynamical calculations were performed for HCl, where AIMD was used to study the effects of impact energy and surface temperature on collision outcomes in the case of HCl scattering from a water or an amorphous ice surface. The simulations were performed at three different temperatures: 390, 300, and 212 K. Due to the high vapor pressure of water, experimental studies of molecular scattering from the water surface have been limited to low temperatures, even though some progress has been made in studying processes on high vapor pressure surfaces by employing micron-thin water jets. Thus, the first goal for this line of research was to investigate how the dissociation and the subsequent picosecond timescale chemical processes of HCl are affected by the temperature of the slab, i.e., how the reactivity changes in different parts of the atmosphere. The second goal was to find out how changes in the impact kinetic energy affect the process because the kinetic energy is typically varied in the gas–liquid scattering experiments such as the ones conducted by the Nathanson group.

The thermodynamic calculations were mainly focused on complexes of H$_2$SO$_4$, especially H$_2$SO$_4$-H$_2$O. The fundamental research question was the impact of global anharmonicity,
i.e., the presence of multiple low-lying conformers, \(^\text{108}\) on the thermodynamic properties. A secondary question was the impact of local anharmonicity, i.e., the anharmonicity of the vibrational modes within a given conformer on the thermodynamic properties. Of the different complexes of sulfuric acid, the small size of the sulfuric acid monohydrate makes it possible to accurately account for both local and global anharmonicities resulting in highly accurate values for the thermodynamic properties. These properties can then be compared with more approximate methods of treating global anharmonicity, such as Boltzmann averaging, and the correct statistical mechanical formula described in Article IV.
2 Hydrochloric and sulfuric acids in the atmosphere

2.1 Sources of sulfuric acid

The origins of atmospheric $\text{H}_2\text{SO}_4$ are manifold: Several compounds containing sulfur in the lowest oxidation state such as $\text{H}_2\text{S}$, SCO, CS$_2$, CH$_3$SH, S(CH$_3$)$_2$, and S$_2$(CH$_3$)$_2$ can function as precursors for sulfuric acid. These molecules get released to the air, for example, from the oceans and the soil as byproducts of reactions occurring within microbiological organisms.$^3$

In many cases, the first step in the atmospheric transformation of the $\text{H}_2\text{SO}_4$ precursors is the oxidation of sulfur and the formation of $\text{SO}_2$. While the reaction pathways are often complex, the hydroxyl radical is typically an important contributor to the oxidation process.$^{2,109-111}$ Most of the sulfuric acid in the atmosphere is formed from $\text{SO}_2$. In addition to $\text{SO}_2$ obtained from oxidation of sulfur-containing compounds, around 90% of the sulfur in fossil fuels is released to the atmosphere directly as $\text{SO}_2$. As industrial activities and fuel combustion constitute around 76% of the global emissions of sulfur compounds,$^4$ these direct emissions are in actuality the predominant source for $\text{SO}_2$. Additionally, significant amounts of $\text{SO}_2$ also originate from volcanoes and underwater fissures.$^{112}$

The oxidation of $\text{SO}_2$ to sulfuric acid can in principle occur homogenously within the gas phase, or heterogenously within liquid droplets and on the surfaces of aerosols. The reaction rate and mechanism depend, for example, on the nature and presence of an aqueous phase, or the concentration of oxidizing species like $\text{H}_2\text{O}_2$ and $\text{O}_3$. In the gas phase, the only relevant oxidation pathway occurs via a reaction with hydroxyl radical, for example, through$^2$

$$\text{SO}_2(g) + \text{OH}(g) \xrightarrow{M} \text{HOSO}_2(g)$$  \hspace{1cm} (1a)

$$\text{HOSO}_2(g) + \text{O}_2 \xrightarrow{M} \text{HOO}(g) + \text{SO}_3(g).$$  \hspace{1cm} (1b)

Sulfuric acid is then produced by the dissolution of $\text{SO}_3$ into water via the formation of an intermediate $\text{SO}_3 \cdot \text{H}_2\text{O}$ complex and its reaction with an additional water molecule.$^{113,114}$
The heterogenous pathway in water droplets begins by the solvation of sulfur dioxide and its reactions in water

\[
\begin{align*}
\text{SO}_2(g) & \rightleftharpoons \text{SO}_2(aq) \\
\text{SO}_2(aq) + 2 \text{H}_2\text{O} & \rightleftharpoons \text{HSO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \\
\text{HSO}_3^-(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq).
\end{align*}
\]

As the equilibria in reactions (2a)–(2c) is rapidly established,\textsuperscript{115} \(\text{SO}_2\) is involved in three different chemical forms, all with distinct reactions with different oxidizing agents. The three predominant oxidizing agents in the liquid phase are \(\text{O}_2\), \(\text{O}_3\) and \(\text{H}_2\text{O}_2\).\textsuperscript{115,116} The key difference between the oxidation processes of \(\text{H}_2\text{O}_2\) compared to \(\text{O}_2\) and \(\text{O}_3\) is that the rate coefficient of \(\text{H}_2\text{O}_2\) is inversely dependent on pH.\textsuperscript{2} Concurrently, while increasing the available sulfur species in the usual manner, a decrease in proton concentration results in a decrease in this rate coefficient. As the two effects cancel each other out, the rate of the peroxide oxidation stays relatively constant for pH 1–5, whereas the oxidation rates of both \(\text{O}_2\) and \(\text{O}_3\) show a sharp decrease with decreasing pH.\textsuperscript{117–119} The end result is that due to the high Henry’s law constant of \(\text{H}_2\text{O}_2\)\textsuperscript{i} and thus its relative abundance in water droplets, the peroxide oxidation pathway dominates in the pH region 1-5. At higher pH values the oxidation is dominated by \(\text{O}_3\) and the various catalysed \(\text{O}_2\) pathways.\textsuperscript{115,116}

Compared to the gas phase and droplet oxidation pathways, the current understanding of the surface oxidation of \(\text{SO}_2\) is limited. Part of the reason for this is the plethora of factors influencing surface reactivity. The relative rates depend, among other things, on the physicochemical nature of the surfaces including surface defects, surface areas, and the presence of other adsorbed species.\textsuperscript{2} So far, studies have been able to show that oxidation on surfaces does take place\textsuperscript{120–122} and may have a significant impact on the total oxidation of the various sulfur dioxide species.\textsuperscript{122,123}

2.2 Sulfuric acid and cloud formation

Once formed, H$_2$SO$_4$ can photodissociate or react with a number of airborne species giving rise to a wealth of different environmental effects. In a gas containing water vapor, sulfuric acid reacts with water via

$$\text{H}_2\text{SO}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}(g).$$  \hspace{1cm} (3)

Equation (3) is an example of binary homogenous nucleation reaction, in which two compounds merge in the gas phase. Usually this reaction is followed by the addition of water to form sulfuric acid embedded in water clusters

$$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_{n-1}(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_n(g).$$  \hspace{1cm} (4)

Moreover, additional sulfuric acid molecules, ammonia, amines, or different organic compounds can accumulate to the clusters as well.$^5$–$^{37}$ Once a critical size is reached through this nucleation process, the cluster starts to rapidly and spontaneously grow due to enhanced vapour uptake of, for example, organic vapours and coagulation with other pre-existing clusters.$^5$,$^{124}$

Due to its large mixing enthalpy with water and low vapour pressure,$^{38}$–$^{40}$ extremely small amounts of H$_2$SO$_4$ are capable of inducing nucleation, even in relative humidities of less than 100%.$^{125}$,$^{126}$ As a result, the reaction system of (3) and (4) has turned out to be the most important binary nucleation process in the atmosphere.$^{44}$

An enduring challenge in atmospheric research is the accurate determination of the rates at which the condensation nuclei are formed. In terms of classical nucleation theories,$^{127}$ the sulfuric–acid water system is problematic as the existence of the already hydrated H$_2$SO$_4$ species has to be taken into account. As the formation free energy of the hydrates is negative, it is much more difficult to form clusters out of them than from pure monomers$^{128}$ making it
important to know the relative amount of free H$_2$SO$_4$ compared to the total amount present. This can be obtained from equation
\[ \frac{\rho_{a}^{\text{total}}}{\rho_{a}^{\text{free}}} = 1 + \sum_{i=1}^{N} \left( \frac{\rho_{\text{free}}^{w}}{\rho_{0}} \right)^{i} \prod_{j=1}^{i} K_{j}, \] (5)

where $\rho_{a}^{\text{total}}$ is the total concentration of sulfuric acid in the gas phase, $\rho_{a}^{\text{free}}$ is the concentration of free sulfuric acid molecules, $\rho_{\text{free}}^{w}$ is the concentration of free water molecules, and $N$ is the number of water molecules for the largest hydrate considered. The equilibrium constants $K_{j}$ correspond to the reactions (3) and (4). The $\rho_{0}$ term in the denominator is the reference vapor concentration $\rho_{0} = p_{0}/kT$, where $p_{0}$ is usually chosen as $p_{0} = 1$ atm = 101325 Pa.

Because most sulfuric acid molecules in the atmosphere are hydrated, inclusion of hydrate formation into the nucleation rate models can reduce the rates by a factor of $10^{5} - 10^{6}$. In most nucleation models for the sulfuric acid systems, the addition of hydrates requires the knowledge of the $K_{j}$ equilibrium constants as shown in equation (5), making it imperative that these are known with high accuracy.

### 2.3 Hydrochloric acid in the atmosphere and the formation of the ozone hole

In the atmosphere, hydrochloric acid is an important reservoir species for the chlorine radical chemistry. The formation of HCl can include a reaction between the halogen radical and a hydrocarbon, or it can occur through the displacement of HCl by stronger acids from chlorine containing aerosol particles such as airborne sea salt particles. The chlorine radical can then be released, for example by a reaction with OH:

\[ \text{OH}(g) + \text{HCl}(g) \rightarrow \text{H}_{2}\text{O}(g) + \text{Cl}(g). \] (6)
After their formation, the Cl atoms can react further, for example, with tropospheric ozone or hydrocarbons. These reactions lead to secondary HO\(_x\) radical production and provide a mechanism in which halogen radicals can be converted into HO\(_x\) radicals within the troposphere.\(^{132}\)

Due to the short lifetimes of most of the chlorine compounds formed in the troposphere, few of these compounds get transported into the stratosphere. In fact, the most important source of chlorine in the stratosphere are chlorofluorocarbon (CFC) compounds which are made out of carbon, chlorine, and fluorine. Due to their exceptional inertness and non-toxicity, CFCs have been used extensively as primary propellants in aerosol cans, refrigerants, and blowing agents.\(^{ii}\) These compounds in general do not absorb low energy light of wavelengths above 290 nm and do not react with the three principal oxidizing agents in the troposphere: NO\(_3\), O\(_3\) and OH. Consequently, the tropospheric lifetimes of CFCs are of the order of tens or hundreds of years\(^{133}\) implying that significant amounts of these compounds can escape into the stratosphere.

After their transport into the stratosphere, the increased solar radiation can break the strong C-Cl bonds in the CFC compounds such as CF\(_2\)Cl\(_2\), releasing chlorine

\[
\text{CF}_2\text{Cl}_2(g) + h\nu \rightarrow \text{Cl}(g) + \text{CF}_2\text{Cl}(g).
\]  

The Cl atom can then react with ozone in the lower stratosphere through the following mechanism

\[
\begin{align*}
\text{Cl}(g) + \text{O}_3(g) & \rightarrow \text{ClO}(g) + \text{O}_2(g) \quad (8a) \\
\text{ClO}(g) + \text{HO}_2(g) & \rightarrow \text{HOCl}(g) + \text{O}_2(g) \quad (8b) \\
\text{HOCl}(g) + h\nu & \rightarrow \text{Cl}(g) + \text{OH}(g) \quad (8c) \\
\text{OH}(g) + \text{O}_3(g) & \rightarrow \text{HO}_2(g) + \text{O}_2(g). \quad (8d)
\end{align*}
\]

The net result of this chain reaction is the loss of two ozone molecules and the formation of three oxygen molecules. This cycle is responsible for about 30% of the ozone loss due to halogens in the lower stratosphere with a similar contribution from the analogous cycle for bromine.\textsuperscript{134}

Several pathways compete with ozone destroying chain reactions in the stratosphere by tying up Cl or ClO in temporary reservoirs such as HCl and ClONO\textsubscript{2}. For example, the reaction

\[
\text{Cl}(g) + \text{CH}_4(g) \rightarrow \text{HCl}(g) + \text{CH}_3(g)
\]  

leads to the formation of HCl. The analogous reaction does not occur for bromine which is one of the reasons why it is particularly efficient in destroying ozone.\textsuperscript{2}

The reason why ozone destruction takes place mostly on the poles is the result of their unique meteorology: During the antarctic winter, a polar vortex develops where the air remains relatively isolated from the rest of the stratosphere, enabling the build-up of photochemically active compounds.\textsuperscript{135,136} This build-up then sets the stage for the rapid destruction of ozone when the sun appears and the polar vortex dissipates. In addition to the concentrations of the ozone depleting compounds, several other factors influence the severity of the ozone destruction including temperature and aerosol particle concentrations.\textsuperscript{137–140}

As mentioned, HCl inhibits ozone destruction by tying up chlorine atoms from the stratosphere. The key point is that the recombination of HCl and ClONO\textsubscript{2} via

\[
\text{HCl}(g/\text{ads}) + \text{ClONO}_2(g/\text{ads}) \rightarrow \text{Cl}_2(g) + \text{HNO}_3(g/\text{ads})
\]  

is slow in the gas phase\textsuperscript{141} but occurs rapidly on ice surfaces such as on polar stratospheric clouds where it may proceed through several different steps.\textsuperscript{62–64} These clouds are readily formed in the low winter temperatures of the antarctic and consist mostly of water, HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{46}
Because HNO$_3$ sticks to the surface, reaction (10) also effectively removes oxides of nitrogen from the gas phase, which are able to remove ClO by forming ClONO$_2$. Thus, during the polar winter, reaction (10) together with the similar reaction

$$\text{HCl}(\text{g}/\text{ads}) + \text{N}_2\text{O}_5(\text{g}/\text{ads}) \rightarrow \text{ClNO}_2(\text{g}) + \text{HNO}_3(\text{g}/\text{ads}),$$

which also occurs much faster on aerosol surfaces than in the gas phase, result in the conversion of chlorine from photochemically inert reservoir species HCl and ClONO$_2$ into photochemically active Cl$_2$ and ClNO$_2$ species. When the sun comes up in the polar spring the large amounts of Cl$_2$ and ClNO$_2$ compounds generated by (10) and (11) are rapidly photolysed, resulting in the massive loss of ozone displayed in Figure 2.

Figure 2: Illustration of the ozone hole formation based on aircraft measurements of ClO and O$_3$ in August 23 and September 16 in 1987 over Antarctica. This Figure has been reproduced with the permission of Science.
3 Principles of computational quantum chemistry

In quantum mechanics, the state of a system is completely described by its wavefunction \( \Psi \) in the sense that from the wavefunction the expectation values of the energy, particle locations, and all other physical properties can be deduced. Quantum chemical calculations thus revolve around finding the wavefunction by solving its Schrödinger equation

\[
\hat{H} \Psi = i\hbar \frac{\partial \Psi}{\partial t},
\]

(12)

where \( \hat{H} \) is the system’s Hamiltonian operator, \( \hbar \) is Planck’s constant \( h \) divided by \( 2\pi \), and \( i \) is the imaginary unit. The wave function depends on the locations of all \( N \) particles \( \{r_i\} \) in the system and time: \( \Psi = \Psi (r_1, r_2, \ldots, r_N, t) \).

Often we are interested in systems where the probabilistic aspects of the wavefunction do not vary with time. In these stationary states, the separability of equation (12) makes it possible to write the wavefunction as a product of its time and space components: \( \Psi = \psi(r_1, r_2, \ldots, r_N) \tau(t) \). The resulting time dependence has the form \( \tau(t) = \exp(-iEt/\hbar) \) where \( E \) is the system’s energy.\(^{143}\) With this notation, the time-independent Schrödinger equation becomes

\[
\hat{H} \psi = E \psi.
\]

(13)

Ignoring relativistic effects,\(^{144}\) the Hamiltonian operator in equation (13) consists of the operators for kinetic and potential energy, and in Cartesian coordinates for a system of \( N \) charged particles it can be written as

\[
\hat{H} = \hat{K} + \hat{V} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{4\pi \epsilon_0} \sum_{i=1}^{N} \sum_{i<j}^{N} \frac{q_i q_j}{r_{ij}},
\]

(14)

where \( q_i \) is the charge of the particle \( i \), \( r_{ij} \) is the interparticle distance between \( i \) and \( j \), \( m_i \) is the mass of particle \( i \), \( \epsilon_0 \) is the vacuum permittivity constant and \( \nabla_i \) the the gradient with respect to particle \( i \). For systems larger than two particles, the second order differential
equation (13) cannot be solved analytically. In fact, just to obtain numerical solutions one has to resort to a number of approximations, the first of which are the Born–Oppenheimer (BO) and adiabatic approximations.

3.1 Separating the nuclear and electronic motions with the Born–Oppenheimer and adiabatic approximations

Because the nuclei in the system are three orders of magnitude more massive than the electrons, the electrons are likely to respond instantaneously to any change in the nuclear configuration. It is therefore of great practical use to separate these two motions. This separation can be introduced by noting that for a system of $N_e$ electrons and $N_n$ nuclei, the Hamiltonian of equation (14) can, in a center of mass coordinate system, be represented in the form $\hat{H} = \hat{K}_n + \hat{H}_e + \hat{H}_{mp}$. It consists of the nuclear kinetic energy operator $\hat{K}_n$ and the electronic Hamiltonian operator $\hat{H}_e$ which contains all the electron coordinate dependent terms of $\hat{H}$ and the nuclear repulsion term.\textsuperscript{144–146} The mass-polarization operator $\hat{H}_{mp}$ arises because it is impossible to rigorously separate the center of mass motion from the internal motion in a system containing more than two particles.

Because $\hat{H}_e$ is Hermitian, the electronic wave functions $\psi_{e,i}(x; y)$ that are solutions to the Schrödinger equation

$$\hat{H}_e \psi_{e,i}(x; y) = E_i(y) \psi_{e,i}(x; y)$$  \hspace{1cm} (15)

form a complete orthogonal set of functions. In equation (15), the symbol $x$ represents the electron coordinates and $y$ represents the nuclear coordinates. Due to the completeness of the $\psi_{e,i}$ function set, the wave functions of the Hamiltonian $\hat{H}$ can be expressed as a linear combination:

$$\psi(x; y) = \sum_{i=1}^{\infty} \psi_{n,i}(y) \psi_{e,i}(x; y).$$  \hspace{1cm} (16)

The expansion coefficients $\psi_{n,i}(y)$ are found by operating on $\psi$ with the Hamiltonian of equation (13), multiplying from the left by a specific $\psi_{e,k}^*$ and integrating over all electronic
coordinates. In the Dirac bracket notation, the resulting expression is

\[ E_{\text{tot}} \psi_{n,k} = \hat{K}_n \psi_{n,k} + E_k \psi_{n,k} \]

\[ + \sum_{i=1}^{\infty} \left( \langle \psi_{e,k} | \hat{K}_n | \psi_{e,i} \rangle + \langle \psi_{e,k} | \hat{H}_{\text{mp}} | \psi_{e,i} \rangle - \sum_{j=1}^{N_n} \frac{1}{m_j} \langle \psi_{e,k} | \nabla_j | \psi_{e,i} \rangle \nabla_j \right) \psi_{n,i}, \tag{17} \]

where the energy \( E_i \) is obtained from equation (15), and the operator \( \hat{K}_n \) is defined by equation

\[ \hat{K}_n = - \sum_{j=1}^{N_n} \frac{1}{2m_{a,j}} \nabla_j^2, \tag{18} \]

where \( m_j \) is the atomic mass associated with the nuclei \( j \). It should be noted that to simplify notation, all the equations are given in atomic units in Sections 3.1-3.7.3.

In equation (17), the terms under summation represent the coupling between different electronic states. In the adiabatic and Born–Oppenheimer approximations, the first two terms in the sum are set equal to zero. The last term disappears because the mass-polarization operator depends inversely on the total mass of the molecule so its effect is negligible in most cases. With these approximations the Schrödinger equation becomes

\[ \hat{K}_n \psi_{n,k}(y) + E_k(y) \psi_{n,k}(y) = E_{\text{tot}} \psi_{n,k}(y). \tag{19} \]

The motion of the nuclei, as described by the nuclear wave functions \( \psi_{n,k} \), is seen to occur on a potential energy surface \( E_k(y) \) that can be obtained by solving the electronic Schrödinger equation for each nuclear geometry \( y \).

The BO and adiabatic approximations work well for most systems, but fail, for example, when two states of the system become energetically close or when the reaction contains spin-forbidden transitions, as in many photochemical reactions.\(^{144,147}\) The errors resulting from the use of the BO approximation are largest in systems containing hydrogen nuclei\(^{148}\) but even there they are often small. For example, in the H\(_2\) molecule, the BO approximation
causes a 3 cm$^{-1}$ shift in the harmonic wavenumbers.$^{149}$

Because the coming sections will concentrate mainly on the methods devised for solving equation (15), the electronic Hamiltonian and wavefunction will simply be written as $\hat{H}$ and $\psi$, respectively. Thus, for a system consisting of $N_e$ electrons and $N_n$ nuclei we may write

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{k=1}^{N_n} \frac{q_k}{r_{ik}} + \sum_{i=1}^{N_e} \sum_{j<i}^{N_e} \frac{1}{r_{ij}} + \sum_{k=1}^{N_n} \sum_{l>k}^{N_n} \frac{q_k q_l}{r_{kl}},$$

(20)

where the first potential energy term describes the nuclear–electron attractions, the second the electron–electron repulsions, and the third for the nuclear–nuclear repulsions. Because for any given nuclear configuration the third term is a constant, it can be added to the energy at the end of the calculation.

3.2 The Hartree–Fock approach – laying the groundwork for computational chemistry

After the BO and adiabatic approximations, the next host of complications in the solution of equation (15) arise from the electron–electron interaction term in equation (20). In the Hartree–Fock (HF) approach, this interaction is modelled so that each electron moves in the mean electric field generated by all other electrons and nuclei. The Hartree–Fock method is rooted in the variational theorem, which states that for any trial wave function $\psi_t$ the following holds$^{144}$

$$\frac{\langle \psi_t | \hat{H} | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle} \geq E_0,$$

(21)

i.e., the expectation value of the Hamiltonian operator is always greater than or equal to the lowest energy $E_0$ of the system.

Given that the electronic wave function has to fulfill the Pauli principle, a natural choice for the HF trial wave function is a Slater determinant:

$$\Phi_0 = \frac{1}{\sqrt{N_e!}} \det |\varphi_a(1)\varphi_b(2)\varphi_c(3)\ldots\varphi_z(N_e)|,$$

(22)
where \( \phi_a, \phi_b, \ldots, \phi_z \) are the occupied molecular orbitals. These one-electron wave functions are also known as spinorbitals as they are generally obtained by multiplying the spatial orbital with a spin function.\(^{150}\) Customarily, each spinorbital is expanded as a linear combination of a set of \( n \) basis functions \( \xi_p \):

\[
|\phi_u\rangle = \sum_{p=1}^{n} c_{pu} |\xi_p\rangle ,
\]

(23)

where \( c_{pu} \) are coefficients that need to be determined. The different forms of these basis functions will be discussed in detail in Section 3.4.

The solution to the electronic Schrödinger equation in the HF approach is obtained by minimizing the energy functional \( \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \) under the constraint that the spinorbitals remain orthonormal. This results in a series of Hartree–Fock equations of the type\(^{145}\)

\[
\hat{f}_i |\phi_u(i)\rangle = \epsilon_u |\phi_u(i)\rangle ,
\]

(24)

where the Fock operator \( \hat{f}_i \) is defined as

\[
\hat{f}_i = \hat{h}_i + \sum_{u=a}^{z} \left[ \hat{J}_u(i) - \hat{K}_u(i) \right].
\]

(25)

In equation (25), \( \hat{h}_i \) is a one-electron core Hamiltonian which consists of the kinetic energy of the electron and its interactions with the nuclei. Strictly speaking, the spinorbitals appearing in equations (24) and (25) are not the same as those appearing in (22), but rather linear combinations called canonical spinorbitals. The Coulomb operator \( \hat{J}_u(i) \) accounts for the electrostatic repulsions between electrons whereas the exchange operator \( \hat{K}_u(i) \) takes into account the spin correlation effect between electrons. The exact definitions for the different terms in equation (25) can be found elsewhere.\(^{144}\)

Insertion of equation (23) and operation from the left by \( \langle \xi_q | \) allows one to write the Fock equations concisely as

\[
\mathbf{FC} = \mathbf{SCE},
\]

(26)
where $C$ is an $n \times n$ matrix of the coefficients, $E$ is an $n \times n$ diagonal matrix of the orbital energies, and the elements in the Fock and overlap matrices, $F$ and $S$, have the following forms

$$F_{qp} = \langle \xi_q (i) | \hat{f}_i | \xi_p (i) \rangle, \quad S_{qp} = \langle \xi_q (i) | \xi_p (i) \rangle. \quad (27)$$

This transforms the problem of determining the best possible single-determinantal wave function into one of finding $C$. In practice, the generation of an initial set of coefficients is followed by the calculation of the Fock and the overlap matrices from equation (27). From these a new set of orbital energies and coefficients are obtained, which can then be used to recalculate the Fock and overlap matrices forming an iterative cycle. Usually the cycle is repeated until the difference between subsequent sets of coefficients is negligible and the system has achieved self-consistency.

### 3.3 Taking the next step with electron correlation

It has been approximated that with a large set of basis functions, the HF method accounts for about 99% of the total energy. The remaining percent comes from the instantaneous Coulombic and other correlation effects, which cause the electrons to avoid each other more than what the mean-field treatment predicts. The difference between the HF energy and the lowest possible energy for a given basis function set is called the electron correlation energy and is essential for the accurate treatment of molecular properties and chemical reactions.

As the HF solution yields the best non-relativistic one-determinantal wave function $\Phi_0$ within the BO approximation for the ground state, additional determinants have to be added to account for electron correlation. These determinants can be constructed from the leftover $n - N_e$ virtual orbitals that result from filling the lowest of our $n$ spinorbitals with $N_e$ electrons. The different types of excited determinants are formed by promoting electrons to the virtual spinorbitals $\varphi_\alpha$, indicated by greek subscripts. For example, in the case of two-electron promotion from spinorbitals $b$ and $c$ in equation (22) to the virtual orbitals $\varphi_\alpha$
and \( \varphi_{\beta} \), we would have one of the doubly excited determinants:

\[
|\Phi_{bc}^{\alpha\beta}\rangle = \frac{1}{\sqrt{N_e!}} \det |\varphi_a \varphi_a \varphi_\beta \ldots \varphi_z|.
\]  

(28)

These determinants are eigenfunctions of all operators that commute with \( \hat{H} \).

The three most common ways to deal with electron correlation are configuration interaction, Møller-Plesset many-body perturbation (MP), and coupled cluster (CC) methods. Here, only MP and CC methods will be explored, due to their relevance for this thesis.

### 3.3.1 Adding electron correlation with MP2

The Møller–Plesset approach \(^{151}\) (MP) applies many-body perturbation theory to the electron correlation problem. It makes use of the property that for small perturbations, the Hamiltonian together with the ground state wave function and energy can be expanded as

\[
\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)} + \ldots, 
\]

(29a)

\[
E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots, 
\]

(29b)

\[
\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots, 
\]

(29c)

where the \( \hat{H}^{(0)} \) Hamiltonian represents a good guess of the ground state of the system. In the MP method, it is chosen as the sum of the Fock operators of equation (25). To correct for the double counting of the electron–electron repulsion arising from this choice, the first order correction \( \hat{H}^{(1)} \) has the form

\[
\hat{H}^{(1)} = \hat{H} - \sum_{i=1}^{N_e} \hat{f}_i, 
\]

(30)

where \( \hat{f}_i \) is the Fock operator defined by equation (25). All higher order perturbations are set to zero, i.e., \( \hat{H}^{(2)} = \hat{H}^{(3)} = \ldots = 0 \).
The perturbation wave functions of equation (29) are expanded as a linear combination of the excited Slater determinants \( \Phi_J \). Because first order perturbation is required to reach just the HF energy, the first improvement is obtained from second order perturbation. By the application of Brillouin’s theorem and Slater–Condon rules, the energy correction can be expressed as a sum over two-electron integrals:

\[
E^{(2)} = \sum_{\text{occ}} \sum_{u<v} \sum_{\alpha<\beta} \frac{\left( \phi_\alpha \phi_u | \phi_\beta \phi_v \right)}{(\epsilon_u + \epsilon_v)} - \frac{\left( \phi_\beta \phi_u | \phi_\alpha \phi_v \right)}{(\epsilon_\alpha + \epsilon_\beta)} \left( \epsilon_u + \epsilon_v \right),
\]

(31)

where the spinorbital energies are symbolized by \( \epsilon \), and the sums go over all occupied and virtual orbitals. The Mulliken integral notation for some arbitrary electrons \( i \) and \( j \) is defined by

\[
\left( \phi_\alpha \phi_u | \phi_\beta \phi_v \right) = \left\langle \phi_u(i) \left| \phi_v(j) \right\rangle \frac{1}{r_{ij}} \left| \phi_\alpha(i) \right\rangle \left| \phi_\beta(j) \right\rangle.
\]

(32)

The determination of second order perturbation energy requires no knowledge of the second order wave function, and in general the knowledge of the \( m \)th order wave function allows one to calculate the perturbed energy up to the order \( 2m + 1 \). The most popular method employs only the second order correction to the energy and is called MP2. Physically, the second order perturbation accounts for interactions between the two electrons, which corresponds to \( 80 - 90 \% \) of the electron correlation energy. The calculation consists of three parts: An initial HF calculation is used to obtain the reference Slater determinant. The computational effort here scales as \( n^4 \) where \( n \) is the size of the basis set. The bottleneck of the calculation is the \( n^5 \) scaling in the second part where the transformation of integrals from the atomic orbitals (AOs) or basis functions of equation (23) into the molecular orbital basis occurs. Lastly, the calculation of the energy scales as \( n^4 \).

The convergence behaviour of different MP methods depends on whether the electron pairs of the system are well separated or cluster together in some regions. In systems with separated electron pairs, pair correlation effects dominate the correlation energy and the convergence is usually monotonous. In clustered systems, correlation arises mainly from
three electron interactions and pair correlation effects in the areas of high electron density resulting in oscillating convergence behavior. \textsuperscript{153} Because the convergence properties of the MP series vary greatly with the number of diffuse functions within the basis set used and generally diverges for a diffuse enough basis, the use of higher order MP-calculations is questionable in systems where a diffuse basis is necessary for chemical reasons.\textsuperscript{154,155}

The MP methods are both size extensive and size consistent. In size extensive methods, the energy of the system scales properly with the number of particles in the system, so that all particles in the system can be allowed to interact. In size consistent methods, the energy of the system scales properly with the number of electrons, i.e., a simultaneous calculation of two non-interacting systems yields the sum of the individual energies of the systems. Because the perturbational corrections to the ground state energy can be either positive or negative, MP-methods are not variational. Due to the lack of iterative procedures, the MP methods are computationally in general about an order of magnitude more efficient than the corresponding CI or CC methods.\textsuperscript{156}

### 3.3.2 Adding electron correlation with coupled cluster methods

Whereas in the MP-methods all types of electron excitations in equation (28) are included to a certain order, the CC-methods incorporate all orders of electron excitations up to a given type. This is done with the help of the cluster operator $\hat{T}$:\textsuperscript{143}

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N,
\]

where $\hat{T}_n$ are excitation operators. When operating on the HF wave function, the $\hat{T}_n$ generate a set of excited determinants of a given order $n$. For example, $\hat{T}_2$ operating on the HF reference wave function results in an series of determinants of the form

\[
\hat{T}_2 \Phi_0 = \sum_{\text{occ}} \sum_{\alpha<\beta} \rho_{\alpha\beta}^{uv} \Phi_0^{\alpha\beta} |\Phi^{\alpha\beta}_{uv}\rangle,
\]

where $\Phi_0$ is the HF wave function.
where the expansion coefficients $t_{uv}^{\alpha\beta}$ are called amplitudes. The CC wave function is defined as

$$|\psi_{CC}\rangle = e^{T} |\Phi_{0}\rangle = \left[ 1 + \hat{T}_{1} + \left( \hat{T}_{2} + \frac{1}{2!} \hat{T}_{1}^{2} \right) + \left( \hat{T}_{3} + \hat{T}_{2}\hat{T}_{1} + \frac{1}{3!} \hat{T}_{1}^{3} \right) + \ldots \right] |\Phi_{0}\rangle. \quad (35)$$

Each term in the parenthesis is responsible for incorporating all orders of a given type of excitation (single, double, etc.). The different terms of a given order account for different physical phenomena, for example in $\hat{T}_{3}$, the excitations are connected, meaning that they interact with each other, while the disconnected term $\hat{T}_{2}\hat{T}_{1}$ describes interaction between a single electron and a pair. Because it becomes increasingly unlikely to have a large number of electrons interacting at the same time, the importance of the $\hat{T}_{k}$ terms decreases as $k$ increases. In line with the successes of MP2, with a canonical set of molecular orbitals, the most important interaction arises from the $\hat{T}_{2}$ term. Due to Brillouin’s theorem, the sole inclusion of the $\hat{T}_{1}$ term yields the HF energy, so the typical approach is to cut equation (33) after the double excitations, leading to the CCSD method.

Because the full variational solution of the Schrödinger equation within the coupled cluster scheme is unfeasible except for the smallest systems,\(^{157}\) a typical method is to project it to the reference wave function by $\langle \Phi_{0} |$:

$$E_{CC} = E_{0} + \sum_{u<v}^{\text{occ}} \sum_{\alpha<\beta}^{\text{vir}} \left( t_{uv}^{\alpha\beta} + t_{u}^{\alpha} t_{v}^{\beta} - t_{v}^{\beta} t_{u}^{\alpha} \right) \left[ (\varphi_{\alpha} \varphi_{u} | \varphi_{\beta} \varphi_{v}) - (\varphi_{\beta} \varphi_{u} | \varphi_{\alpha} \varphi_{v}) \right]. \quad (36)$$

The unknown amplitudes $t_{uv}^{\alpha\beta}$, $t_{u}^{\alpha}$, and $t_{v}^{\beta}$ are found by projecting the Schrödinger equation onto the space spanned by the excited determinants after a similarity transform of the Hamiltonian.

Due to the iterative processes involved in the calculation of the amplitudes, already the CCSD method scales as $n^{6}$ and the addition of higher excitations causes an increase in computational effort that is two orders of magnitude per level. However, because the effects of the $\hat{T}_{1}$ terms are small, most of the effect from the triple excitations arise from
the $\hat{T}_3$-term in (35). This most important triples contribution can be implemented into standard CCSD by using perturbation theory. In the most effective formulation of the different perturbational approaches, denoted CCSD(T) and introduced by Raghavachari et al.,\textsuperscript{158} the $\hat{T}_3$-term is evaluated from an MP4 formula with the original CCSD amplitudes and then added to the final energy.\textsuperscript{159} This process increases the computational scaling to $n^7$, but also markedly increases the amount of correlation energy obtained. Compared with the MP2 methods, CCSD and CCSD(T) give substantially more accurate results, but at a higher cost.

3.3.3 Further modifications on MP2 and CCSD(T)

3.3.3.1 Local approaches

The canonical orbitals obtained from an HF calculation are generally delocalized over the molecule or system. This delocalization is partly to blame for the rapid, non-physical scaling of the standard electron correlation methods.\textsuperscript{156} From a physical point of view, electron correlation effects arise primarily from electrons that are near one another\textsuperscript{160} meaning that the scaling issues can be mitigated by performing calculations in a localized set of orbitals.

Local correlation methods simplify calculations by omitting those two electron integrals where the differential overlaps $\langle \varphi_u | \varphi_\alpha \rangle$ and $\langle \varphi_v | \varphi_\beta \rangle$ are small. This is done by restricting the virtual space to the atomic orbital subspace in the neighbourhood of the orbitals to be correlated separately for each electron. For example, in the local formulation by Pulay and Saebø,\textsuperscript{156,161–163} a domain $D(u)$ which is independent of molecular size is assigned for each of the correlated occupied orbitals $| \varphi_u \rangle$. For a lone electron pair, the domain consists of the valence AOs of the atom associated with the pair, whereas, for a bond localized to $n$ atom centers, $D(u)$ consists of valence atomic orbitals of the $n$ atoms. In both cases, the AOs are projected onto the virtual orbital basis to ensure orthogonality between the virtual and the occupied subspaces. The local basis for a pair of occupied orbitals $| \varphi_u \rangle$ and $| \varphi_v \rangle$ is defined as $D(u) \cup D(v)$. The aim is to choose the virtual basis so that it includes all pair correlations
and leads to smooth potential energy surfaces while resulting in computational savings.

Because the correlation energies of orbitals separated by one bond are approximately an order of magnitude smaller than of those located on the same atom, further savings are achieved by imposing a hierarchy upon the electron pairs of the molecule. In the localized MP2 treatment employed in Article I, the electron pairs are divided into four groups according to the minimum distance \( R \) between the two correlated localized occupied molecular orbitals of the electrons:\textsuperscript{164–166} Strong pairs have \( R \leq 1 \) bohr (where 1 bohr = 52.92 pm), and the pairs are treated at the CCSD level. Weak pairs with \( 1 < R \leq 8 \) bohr are treated by local MP2. For distant pairs with \( 8 < R \leq 15 \) bohr, long range ionic excitations are neglected and a multipole expansion is used.\textsuperscript{165,167} Finally, very distant pairs for which \( R > 15 \) bohr are completely neglected.

In addition to the radical reduction in computational cost from an \( n^5 \) dependence for MP2 to a linear one with the size of the system,\textsuperscript{165} the truncation of the virtual space greatly reduces both the intermolecular and intramolecular basis set superposition errors (BSSEs),\textsuperscript{168} making the counterpoise (CP) correction\textsuperscript{169} unnecessary. For a fraction of the computational cost, the local correlation methods produce geometries of comparable accuracy and vibrational frequencies that are slightly closer to the experimental values than their non-local counterparts.\textsuperscript{170,171}

\subsection*{3.3.3.2 Density fitting}

Even though the local approximations can be used to achieve linear scaling with molecular size,\textsuperscript{171} they do nothing to the steep fourth-order scaling of the computational cost with the basis set size per atom.\textsuperscript{172} To tackle with this issue, density fitting (DF) approaches facilitate the calculation of the problematic four electron integrals by transforming these into a sum over three electron integrals via the resolution of the identity:\textsuperscript{173,174}

\[
(f_{\alpha\beta}|v_{\alpha\beta}) = \sum_x (f_{\alpha}|x_x) (x_x|v_{\beta}),
\] (37)
where the $\xi_x$ functions in principle form a complete orthonormal set. The first integral on the right is a three-index one-electron overlap integral and the second integral is defined analogously to equation (32) with the product of the $r_i$ dependent functions $\varphi_u \varphi_\alpha$ replaced by the sum over $\xi_x(r_i)$. Because three-index integrals are easier to compute and store than the original ones, savings in computation time are achieved.\(^\text{174}\)

The obvious practical issue with equation (37) is the impossibility of utilizing a complete basis set for $\xi_x$. As the products of the two molecular orbitals $\varphi_\alpha \varphi_u = \rho_{\alpha u}$ can be interpreted as electron densities for the single electron, one can use the auxiliary basis set $\{\xi_x\}$ to approximate $\rho_{\alpha u}$ by the formula\(^\text{172,175}\)

$$\tilde{\rho}_{\alpha u} = \sum_x \rho_{\alpha u}^{\xi_x} \xi_x. \quad (38)$$

Usually, the functions $\xi_U$ are chosen to be the atom-centered Gaussian type orbitals described in Section 3.4. The coefficients $d_{\alpha u}^{\xi_x}$ are calculated by minimizing the Coulomb energy fitting residual:\(^\text{176,177}\)

$$\epsilon_{ab} = \int \int \frac{[\rho_{ab}(r_i) - \tilde{\rho}_{ab}(r_i)] [\rho_{ab}(r_j) - \tilde{\rho}_{ab}(r_j)]}{r_{ij}} dr_i dr_j, \quad (39)$$

which also minimizes the least squares error of the electric field.\(^\text{177}\)

With a proper choice of the auxiliary basis set, the error from the DF approximation becomes negligible\(^\text{178}\) and, therefore, third order scaling with the basis set size per atom is achieved.\(^\text{172}\) In the literature, local DF approximations have, for example, enabled the HF energy calculation of large systems with about 4000 basis functions.\(^\text{179}\)

### 3.3.3.3 Spin component scaling

A known problem with the canonical MP series is that it contains a biased description of the electron pairs with different and same electron spins. This arises because at the HF level the Fermi correlation between spin-parallel pairs is taken into account, whereas the Coulomb
correlation of spin-anti-parallel pairs is not. The bias continues at the MP2-level resulting in a systematic overestimation of the static electron correlation energy and a corresponding underestimation of the dynamic electron correlation.

Since the Hamiltonian in (20) is independent of spin, it is possible to separate the MP2 correlation energy into a sum of parallel and anti-parallel spin pair terms. In the spin component scaling approximation (SCS), the two energies are calculated separately and the total correlation energy is then obtained by individually scaling the two contributions:

$$E^{(2)} = p_T E_T^{(2)} + p_S E_S^{(2)},$$

where $E_T^{(2)}$ and $E_S^{(2)}$ are the MP2 correlation energies for electrons with parallel and antiparallel spin pairs, respectively, and $p_T$ and $p_S$ are the corresponding scaling coefficients.

The SCS method improves the accuracy of the original MP2 method practically without any increase in computational cost. It creates a more uniform distribution of results than MP2 for both bond lengths and vibrational frequencies, and also recovers somewhat more correlation energy on average. The optimal values for the scaling coefficients depend on the set of basis functions employed, the chemical nature of the problem, and the properties of interest. Suggested values have been obtained, for example, by minimizing the error between the intermolecular binding energies predicted by the SCS methods and by a higher level computational method such as CCSD(T) using multivariate linear least squares analysis.

### The explicitly correlated F12 methods

The problematic electron–electron interaction terms in equation (20) cause singularities in the potential energy, which introduce cusps to the wave function at points where two of the electrons coincide. Because the kinetic energy has to cancel the infinity of the potential energy this results in the wave function behaving linearly around the points $r_{ij}$. Most of the convergence problems in the standard methods arise because the slowly varying orbital
product, \( \varphi_u(r_i) \varphi_v(r_j) \), is ill-suited for describing the cusp when the electrons \( i \) and \( j \) are near each other.

To implement the correct cusp behaviour, the F12 methods in both MP2 and CCSD(T) incorporate configurations that improve the performance near the correlation hole. In the MP2 case, making use of the Einstein summation rule where summation over indexes not present on both sides of the equation is implied, the first order wave function has the form

\[
|\psi^{(1)}\rangle = \frac{1}{2} \left( T_{uv}^{\alpha \beta} \hat{C}_{\alpha \beta}^{uv} + T_{uv}^{xy} F_{xy}^{RS} \hat{C}_{RS}^{uv} \right) |\Phi_0\rangle,
\]

where \( T_{uv}^{ij} = T_{vi}^{ji} \) for any molecular orbitals \( i, j \), and \( T_{av}^{\alpha x} = T_{av}^{\alpha x} = 0 \). It is composed of the conventional \( \hat{C}_{\alpha \beta}^{uv} |\Phi_0\rangle \) configurations and the explicitly correlated configurations \( \hat{C}_{RS}^{uv} |\Phi_0\rangle \), where \( \hat{C}_{\alpha \beta}^{uv} = \hat{C}_u^{\alpha} \hat{C}_v^{\beta} \) is the two-electron excitation operator and \( \hat{C}_u^{\alpha} \) is the one-electron excitation operator from the orbital \( u \) to the orbital \( \alpha \). The capital letters in equation (41) designate a formally complete virtual space \( \{R, S, ...\} \), which is employed for the explicitly correlated expansion coefficients \( F_{xy}^{RS} \).

In the CCSD case, the wavefunction is defined by

\[
|\psi_{\text{CCSD-F12}}\rangle = \exp \left( \hat{T}_1 + \hat{T}_2 \right) |\Phi_0\rangle,
\]

where the cluster operators \( \hat{T}_1 \) and \( \hat{T}_2 \) are defined by equations

\[
\hat{T}_1 = t_u^{\alpha} \hat{C}_u^{\alpha}
\]

\[
\hat{T}_2 = \frac{1}{2} T_{uv}^{\alpha \beta} \hat{C}_{\alpha \beta}^{uv} + \frac{1}{2} T_{uv}^{xy} F_{xy}^{RS} \hat{C}_{RS}^{uv}
\]

The right hand side in equation (43) and the first term on the right in equation (44) present the standard first and second order excitations to virtual orbitals encountered in equation (35). Both equations (41) and (42) contain the expansion coefficients \( F_{xy}^{RS} \) which are defined.
\[
\mathcal{F}_{xy}^{RS} = \langle \varphi_x \varphi_y | \hat{F}_{12} \hat{Q}_{12} | \varphi_R \varphi_S \rangle ,
\]

where \( \hat{F}_{12} \) is a short-range correlation factor. It has been found that the most intuitive choice of setting \( F_{12} = r_{12} \), as done originally by Kutzelnigg et al.,\(^{187,189,190}\) is not the optimal one when using relatively small basis sets of around triple zeta quality.\(^{191}\) According to Tew and Klopper,\(^{192}\) the best correlation factor comes in the form of a Slater function, which can be further fitted to a set of Gaussian geminals\(^{193}\) to make the computations easier:

\[
F_{12} = -\frac{1}{\gamma} e^{-\gamma r_{12}} \approx \sum_k c_k e^{-a_k r_{12}^2} ,
\]

where the coefficients \( c_k \) and \( a_k \) are determined by a least squares fitting\(^{188}\) and \( \gamma \) is a parameter. The form of the projector operator \( \hat{Q}_{12} \) in equation (45) can be found elsewhere.\(^{194}\)

It ensures that the different \( F_{12} \) configurations

\[
| \Phi_{uv}^{xy} \rangle = \mathcal{F}_{xy}^{RS} \hat{\mathcal{C}}_{uv}^{RS} | \Phi_0 \rangle
\]

are orthogonal with the configurations in the standard molecular orbital space.

In summary, the effect of the additional amplitudes is to introduce new functions into the conventional CC expansion where the products \( | \varphi_u(1) \varphi_v(2) \rangle \) have been replaced with a negative short-range correlation function

\[
| \chi_{uv}(1, 2) \rangle = T_{uv}^{xy} \hat{Q}_{12} \hat{F}_{12} | \varphi_x(1) \varphi_y(2) \rangle .
\]

This both decreases the chance of finding two electrons in the same place and improves the behaviour of the wave function in the vicinity of the cusp. The most important terms in (48) are those for which \( xy = uv \) or \( xy = vu \). It is possible to simplify calculations by ignoring less important terms in the configurations \( T_{uv}^{xy} \hat{\varphi}_{xy}^{uv} \) while treating the rest constant.\(^{194}\) In this fixed amplitude scheme, the amplitudes \( T_{xy}^{uv} \) in the wave function are set to zero for
all terms except $T_{uu}$, $T_{uv}$, and $T_{vu}$, which are given fixed values so that the wave function fulfills the cusp conditions. The advantages of this kind of fixed amplitude ansatz is that it is unitary invariant, free of the geminal basis set superposition error, and size consistent.\textsuperscript{195}

Resulting from all of the rather technical approximations involved in the MP2-F12 and CCSD(T)-F12 methods, the nominal scaling with the molecular size of the corresponding MP2 and CCSD(T) approaches is retained, but marked improvements are observed in the accuracy of results, for example, in terms of reaction energies.\textsuperscript{188,194} With minimal additional computational cost, calculations performed using the CCSD(T)-F12a method at the aug-cc-pVDZ level are often comparable to calculations performed at the CCSD(T)/aug-cc-pVQZ level, while an aug-cc-pVTZ basis set gives results similar to CCSD(T)/aug-cc-pV5Z calculations,\textsuperscript{194,196,197} implying a much faster convergence towards accurate results. Moreover, the method reduces basis set errors of atomization energies, reaction energies, electron affinities, ionization potentials, equilibrium structures, and vibrational frequencies all by an order of magnitude.\textsuperscript{194} It has been demonstrated that similar advantages are also found in equilibrium geometries and anharmonic vibrational frequencies for large molecules.\textsuperscript{198} For these small basis sets, the good performance is probably the result of a cancellation of errors regarding overshooting the F12 correlation energies and undershooting the noncorrected triples contribution.\textsuperscript{194} However, as this cancellation is systematic, the results are reliable to a high accuracy.

### 3.4 Decreasing the computational effort with a smart choice of basis functions

As described in Section 3.2, the spinorbitals of equation (23) are almost always expanded in terms of a set of predetermined basis functions $\xi_i$. This choice of basis is as integral a part of the computational procedure as is the choice of the method. Three types of basis functions are commonly used in quantum chemical calculations: Slater orbitals\textsuperscript{199,200} (STOs), plane waves, and Gaussian type orbitals. Of these three, STOs are used, for example, in the
commercial Amsterdam density functional DFT code,\(^{iii}\) whereas plane waves are employed in DFT calculations of systems with periodic boundary conditions (PBCs). The QUICKSTEP program,\(^{201}\) applied to study HCl dissociation on a water surface in Article III, exploits a dual representation of the electron density both in terms of Gaussian functions and plane waves, for example.

Most of the quantum chemical calculations of molecules in this thesis make use of GTOs which, in Cartesian coordinates, have the general form\(^ {143}\)

\[
\zeta_{ijk}(x, y, z) = (x - x_c)^i (y - y_c)^j (z - z_c)^k e^{-\zeta|\vec{r} - \vec{r}_c|^2},
\]

where the point \(\vec{r}_c = (x_c, y_c, z_c)\) defines the center of the Gaussian function, \(\zeta\) determines how quickly the GTO decays to zero, and \(i, j, k \in \mathbb{N}\) determine the nodes of the GTO. Typically, the centers of the GTOs coincide with the locations of the nuclei, although GTOs centered at the bonds can also be used. This type of basis is well-suited for calculation of multicenter integrals, as the product of two GTOs with different centers yields another one-center Gaussian function.\(^ {202}\) A minor downside of GTOs is that owing to the \(r^2\) dependence in the exponential term, they tend to decay too fast compared with the actual wave functions, and have a zero slope at \(\vec{r}_c\). Thus, utilization of these functions necessitates the use of relatively large basis sets. In practice, the computational basis typically consists of a group of linear combinations of GTOs known as Gaussian contractions (CGTOs). This is because in the standard variational calculations used to obtain the \(\zeta\) coefficients, the GTOs become mainly optimized around the chemically uninteresting core electrons of the system due to the large contribution these have on the system energy.\(^ {144}\)

Minimally, each atomic orbital is represented by one function but especially when correlation effects are concerned it is necessary to use several times larger basis sets for valence orbitals to achieve reliable results. Depending on the multiplicative factor, this leads to the double, triple, quadruple etc zeta-sized basis sets (DZ), (TZ), (QZ). As the computational


31
effort typically grows rapidly with the size of the basis, it is common to use split valence basis sets where only the number of basis functions for the valence electrons is increased.

There are several reasons why adding more functions of the same type to increase the basis set size is not optimal for improving the accuracy of the results. First, because these functions are unable to account for the deformation of the atomic orbitals caused by adjacent atoms, they should be complemented by polarization functions which have higher values of angular momentum. Second, especially for extrapolation purposes, it is useful if the shift from any basis to a larger one leads to a systematic increase in the percentage of the total correlation energy obtained. This is achieved, for example, in the correlation consistent (cc) basis sets of Dunning, where those angular momentum functions that have similar contributions to the energy are added simultaneously as the size of the basis increases. Third, if the system contains hydrogen bonding or other significant long distance interactions it is necessary to further refine the basis set by adding diffuse functions which have small values for the ζ parameter in equation (49). Implementations include the augmented correlation consistent (aug-cc) variant of the Dunning cc-basis set.

3.5 Cheaper alternatives to the Hartree–Fock based methods: density functional theory

The foundation of density functional theory (DFT) rests on two theorems by Hohenberg and Kohn. The first of these theorems states that the electron density ρ uniquely defines both the ground state energy and the wavefunction ψ of the system, even though ρ depends only on 3 coordinates and ψ on 3Ne. In other words, the ground state energy of the system is a bijective functional of the electron density, which for an Ne electron system is defined by

\[ \rho(r_1) = \int \psi^*(r_1, r_2, \ldots, r_{Ne}) \psi(r_1, r_2, \ldots, r_{Ne}) \, dr_2 \ldots dr_{Ne}. \]  (50)
While the exact form of the energy functional is unknown it can be divided into different parts

\[
E_{\text{DFT}}[\rho] = K_S[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho], \tag{51}
\]

where \(E_{\text{ne}}[\rho]\) corresponds to the attraction between the nuclei and the electrons and \(J[\rho]\) is the Coulomb part of the electron-electron repulsion. The first functional, \(K_S[\rho]\), is the kinetic energy calculated by expanding \(\rho\) in terms of one-electron orbitals \(\phi_i\) corresponding to a system where the electrons do not interact:

\[
\rho = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2. \tag{52}
\]

The actual functional is then calculated in atomic units as

\[
K_S[\rho] = \sum_{i=1}^{N_e} \left\langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \right\rangle \tag{53}
\]

as suggested by Kohn and Sham.\textsuperscript{208} The reason for this expansion is that while according to the first Hohenberg–Kohn theorem the kinetic energy is directly related to \(\rho\), the kinetic energy is typically poorly represented in orbital free models. On the other hand, even for non-interacting orbitals, equation (53) recovers most of the kinetic energy, which results in the exchange-correlation functional

\[
E_{\text{xc}}[\rho] = (K[\rho] - K_S[\rho]) + (E_{\text{ee}}[\rho] - J[\rho]) \tag{54}
\]

having an absolute value of approximately 10 times smaller than the kinetic energy. In equation (54), \(K[\rho]\) and \(E_{\text{ee}}[\rho]\) represent the correct kinetic and electron correlation energies, respectively. It should be noted that by definition \(E_{\text{ee}}[\rho]\) contains the Coulomb correlation between electrons. As the expressions for the other terms in equation (51) are known, the problem of finding the energy functional has been reduced into deriving approximations for the exchange-correlation part. According to the second Hohenberg–Kohn theorem, the total
energy obtains its minimum value for the correct \( \rho \), so the variational principle can be used to solve the problem iteratively. Analogously to the HF method, minimization of energy under the orbital orthonormality condition leads to a series of Kohn–Sham equations:

\[
\mathbf{h}_{\text{KS}} \phi_i = \epsilon_i \phi_i, \tag{55}
\]

where

\[
\mathbf{h}_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}, \rho(\mathbf{r})). \tag{56}
\]

The effective potential \( V_{\text{eff}}(\mathbf{r}, \rho(\mathbf{r})) \) contains the nuclear contribution, the electronic Coulomb repulsion, and the exchange–correlation potential. It is defined by

\[
V_{\text{eff}}(\mathbf{r}, \rho(\mathbf{r})) = V_{\text{ne}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}. \tag{57}
\]

Because the effective potential depends on \( \rho \) and thus on the orbitals obtained from (55) the Kohn–Sham orbitals are solved numerically by an iterative process analogously to the HF orbitals.

Several different forms of the exchange–correlation potential functional have been developed. In the simplest of these, the local density approximation, it is assumed that the density can be locally treated as a uniform electron gas. In this case, \( E_{\text{xc}} \) is obtained by integrating the corresponding local exchange–correlation energy per atom, multiplied by the electron density. For molecular systems, the local density approximation leads to an underestimation of the exchange energy by about 10 %, resulting in errors that are larger than the whole correlation energy.\textsuperscript{144}

Significant improvement over the local density approach can be obtained by allowing the exchange correlation energy to depend on the gradient of the electron density as well as \( \rho \) itself. This is the starting point of the generalized gradient approximation (GGA) methods. Many different forms have been separately developed for the exchange and corre-
lation energy parts of the exchange correlation functional. One of the earliest of these is the Becke exchange functional,\(^{209}\) which is often coupled with the correlation functional by Lee, Yang, and Parr\(^{210}\) to form the widely used BLYP-functional. Further improvements can be achieved by incorporating a fraction of the exact HF exchange energy in the total exchange–correlation energy calculation as done, for example, in the popular B3LYP method.\(^{211}\) While the inclusion of exact exchange is now a standard feature, giving rise to the hybrid family of methods, the optimum fraction depends on the specific properties of interest.

### 3.6 How the different electronic structure methods and basis sets were employed in this thesis

Several different combinations of basis set and electronic structure methods were employed in this thesis. The most accurate calculations were done using the CCSD(T)-F12a and CCSD(T)-F12b methods\(^{194}\) described in Section 3.3.3, which were combined with the VDZ-F12 to VQZ-F12 basis sets of Peterson et al.\(^{212}\) These basis sets are similar in size to the corresponding AV\(n\)Z and AV\((n+d)\)Z correlation consistent polarized valence triple zeta basis sets of Dunning\(^{203,204,206}\) but have been particularly optimized for explicitly correlated calculations. These types of calculations were employed for the electronic energy calculations and the crucial segments of the PESs corresponding to the large amplitude motions in Articles I, II, and V. A sample PES is displayed in Figure 3 for the two motions connecting different conformers of the sulfuric acid monohydrate.

Lower level methods were employed for the geometry optimizations, harmonic frequency calculations, and the PES calculations of the vibrational second order perturbational theory (VPT2) and self-consistent-field (VSCF) anharmonic frequencies in Articles I, II, IV, and V. This is justified because these properties are generally less sensitive to the level of computation as demonstrated by the success of the various composite quantum chemistry procedures,\(^{144}\) such as T1\(^{213}\) and G3(MP2).\(^{214}\) With T1, for example, high-quality heats of formation can be obtained as a result of consecutive quantum chemical calculations where
methods of different accuracies are used to obtain the optimized geometries, vibrational frequencies, and energies of molecules. According to the test calculations during the course of these studies, the mean difference was less than 1 cm$^{-1}$ between the two-dimensional H$_2$SO$_4$ PES, where the geometry optimization was done at the DF-MP2-F12/VDZ-F12 level followed by a single point calculation at CCSD(T)-F12a/VDZ-F12, and a PES where the geometry optimizations were also performed at the CCSD(T)-F12a/VDZ-F12-level. The first of these PESs is displayed in Figure 4. In addition to DF-MP2-F12/VDZ-F12 calculations, DF-SCS-LMP2/AV(T+d)Z$^{215}$ calculations were also employed for the geometry optimizations and harmonic frequency calculations in Article I, while regular MP2 calcula-
lations described in Section 3.3.1 with the partially augmented jun-cc-pV(T+d)Z basis of Papajak and Truhlar\textsuperscript{216} or the AV(T+d)Z basis were used for the anharmonic frequency calculations with VPT2 in Article V.

Figure 4: The two dimensional PES connecting the different conformers of H$_2$SO$_4$ obtained in Article II. The angles are given in radians.

In the larger sulfuric acid complexes of Article IV containing several tens of atoms, calculation of anharmonic frequencies quickly becomes impossible and DFT methods have to be used for the calculation of geometries and harmonic frequencies. In the case of the pinic acid –H$_2$SO$_4$ cluster, the M06-2X\textsuperscript{217} functional was utilized based on its performance in calculating the Gibbs free energies and binding energies of sulfuric acid containing clusters\textsuperscript{218–220} together with the DZ 6-31+G(d) basis set.\textsuperscript{221} For the (H$_2$SO$_4$)$_3$(NH$_3$)$_3$(H$_2$O)$_4$ cluster the
calculations were performed using the hybrid B3LYP functional mentioned in Section 3.5 with the CBSB7 (6-311G(2d,d,p)) basis set as this level of theory has shown to yield reliable quantitative trends for atmospheric molecular cluster formation.

The largest system under investigation, the HCl molecule reacting with a water slab, consisted of 216 atoms within a simulation cell employing PBCs. While non-hybrid DFT functionals such as the BLYP functional introduced in Section 3.5 with Grimme type dispersion corrections (BLYP-D2) are still applicable for systems of this size, the use of pseudopotentials for the core electrons is necessary to make the calculations feasible. For example, in Article III, the Kohn-Sham orbitals were expanded in a double-valence polarized basis set (DZVP) with core electrons represented by the Goedecker–Teter–Hutter pseudopotentials (GTH) while the BLYP-D2 functional was used as it has been shown to reliably reproduce water properties.

3.7 How to solve the nuclear Schrödinger equation?

After the potential energy surface $E_i(y)$ has been obtained with the electronic structure calculation methods described in the previous sections, it can be used to find the solution of the nuclear Hamiltonian of equation (19). For the methods employed in this thesis, the calculation of thermodynamical properties mandates the calculation of equilibrium geometries for the rotational constants and vibrational frequencies for the vibrational partition function. Most of the geometry optimization algorithms employ a Taylor series expansion of the PES which can be written in terms of the nuclear positions $y - y_e$ as

$$E(y) = E(y_e) + \left(\frac{\partial E}{\partial y}\right)^T(y - y_e) + \frac{1}{2}(y - y_e)^T\frac{\partial^2 E}{\partial y^2}(y - y_e) + \ldots$$

The convergence behaviour of the energy minimization procedure in terms of (58) improves when higher order derivatives are included in the calculation at the expense of the time taken for the single point calculations.
3.7.1 Harmonic approximation and the calculation of vibrational energy levels

One of the most problematic open questions for the calculation of thermodynamic properties is how to accurately model the oscillatory motion of the nuclei around the equilibrium structure. As a starting point, observe that for a deviation from the equilibrium nuclear locations $y_e$, the first derivative of equation (58) disappears. Setting the zero of potential energy to $E(y_e)$ and ignoring all terms of third and higher order, substitution into the nuclear Schrödinger equation (19) yields in atomic units

$$\left[ -\sum_{j=1}^{3N_n} \left( \frac{1}{2m_j} \frac{\partial^2}{\partial y_j^2} \right) + \frac{1}{2} (y - y_e)^T \frac{\partial^2 E}{\partial y^2} (y - y_e) \right] \psi_n = E_n \psi_n. \quad (59)$$

When this equation is recast in terms of mass-dependent coordinates $z_j = \sqrt{m_j}(y_j - y_{e,j})$ one obtains

$$\left[ -\sum_{j=1}^{3N_n} \left( \frac{1}{2} \frac{\partial^2}{\partial z_j^2} \right) + \frac{1}{2} z^T (F \cdot G) z \right] \psi_n = E_n \psi_n, \quad (60)$$

where $F$ is the matrix of force constants ($\partial^2 E/\partial z^2$) and $G$ is defined by $G_{jk} = 1/\sqrt{m_j m_k}$. This Schrödinger equation can be transformed into a set of $3N_n$ one-dimensional harmonic oscillator equations by defining $q = Uz$ where $U$ is the unitary matrix that diagonalizes $F \cdot G$:

$$\left[ -\sum_{j=1}^{3N_n} \left( \frac{1}{2} \frac{\partial^2}{\partial q_j^2} + \frac{1}{2} \varepsilon_j q_j^2 \right) \right] \psi_n = E_n \psi_n. \quad (61)$$

From the eigenvalues of the unitary transformation $U$, the harmonic frequencies are obtained by $\nu_j = \sqrt{\varepsilon_j}/2\pi$ and $q$’s are the mass-weighted normal coordinates. Physically, these normal modes correspond to independent motions of groups of atoms in the sense that each normal mode can be excited without exciting any of the other modes. The general process of calculating vibrational energy-levels is summarized in Figure 5.
Figure 5: A flowchart of a typical vibrational energy level calculation.
3.7.2 Beyond the harmonic approximation: standard methods for anharmonicity calculations

Based on equation (59) and the discussion in the previous section, the harmonic approximation works well when the true potential curve is reasonably approximated by a second order polynomial. As illustrated in Figure 6 where the ratio of VPT2 anharmonic and harmonic frequencies of the different species of reaction (3) is displayed as a function the harmonic frequency, the harmonic frequencies typically overestimate the anharmonic and experimental ones. This is due the lack of higher-order terms in equation (59). While for high frequencies the agreement is fairly good, there are evidently many cases where the harmonic approximation is not applicable. For example, it is incapable of describing the process of bond breaking both due to the form of the harmonic PES and because this process cannot be described in terms of a single normal mode. Additionally, in systems with multiple low-lying potential energy minima, the splitting of states caused by tunneling effects means that the harmonic approximation can fail badly even for the lowest vibrational states. This is a frequently encountered issue when dealing with the large amplitude intermolecular motions of weakly bound complexes with multiple PES minima such as the sulfuric acid hydrates formed through reactions (3) and (4). In these cases, the higher order derivatives of equation (58) cannot be ignored, and a more complete representation of the PES becomes necessary. Fortunately, two families of standard methods can nowadays be used to account for anharmonicity: The vibrational self-consistent-field (VSCF) based approaches and the methods based on second order vibrational perturbation theory (VPT2).

3.7.2.1 VSCF and its derivatives

In VSCF, the vibrational problem is treated analogously to the HF approach and, at least in principle, the full form of the potential is retained. This means that, in any given vibrational state of the molecule, each vibrational mode is described by the averaged potential due to all of the other modes. Like its Hartree-Fock analogue, VSCF possesses multiple
Figure 6: Ratio of the harmonic and anharmonic fundamental wavenumbers as a function of the harmonic wavenumber. The anharmonicity corrections were performed using HDCPT2 at the MP2/AVTZ-level. The different conformers are represented by the symbols $g_i$.

advantages: it is easily interpreted in terms of single-mode potentials, energies, and eigenstates, it can be combined with essentially any form of the molecular Hamiltonian, it can be employed either in time dependent form to examine dynamics or static form to study eigenstates, and it is applicable for the study of quite large systems.\(^{230}\)

In this approach as well as in the VPT2 based approaches, the nuclear wave function is represented in terms of the mass-weighted normal mode coordinates $\psi_n = \psi_n(q_1, \ldots, q_{N_n})$. In this case, the Schrödinger equation has the form

$$\left[ -\frac{1}{2} \sum_{j=1}^{N_n} \frac{\partial^2}{\partial q_j^2} + V(q_1, \ldots, q_{N_n}) \right] \psi_n = E \psi_n. \quad (62)$$
where \( V(q_1, \ldots, q_{N_n}) \) is the PES in normal coordinates. Upon minimization of the energy functional \( \langle \psi_n | \hat{H}_n | \psi_n \rangle \), expansion of the nuclear wavefunction as \( \psi_n = \Pi_{j=1}^{N_n} \psi_j^{(n)}(q_j) \) together with the constraint that each \( \psi_j^{(n)}(q_j) \) remains normalized leads to the single-mode VSCF equations

\[
\left[ -\frac{1}{2} \frac{\partial^2}{\partial q_j^2} + V_j^{(n)}(q_j) \right] \psi_j^{(n)}(q_j) = \epsilon_j^{(n)} \psi_j^{(n)}(q_j),
\]

(63)

where

\[
V_j^{(n)}(q_j) = \left\langle \Pi_{l \neq j}^{N_n} \psi_l^{(n)}(q_l) \right| V(q_1, \ldots, q_{N_n}) \left| \Pi_{l \neq j}^{N_n} \psi_l^{(n)}(q_l) \right\rangle.
\]

(64)

In practice, the wave functions \( \psi_l^{(n)}(q_j) \) are generated numerically on a grid and the potential energy is typically cut after the second order interaction term, i.e.,

\[
V(q_1, \ldots, q_{N_n}) = \sum_{j=1}^{N_n} V_j^{\text{diag}}(q_j) + \sum_{i=1}^{N_n-1} \sum_{i<j}^{N_n} V_{ij}^{\text{coup}}(q_i, q_j).
\]

(65)

This avoids the prohibitively costly multidimensional integrals. After an initial VSCF calculation, several methods can be used to add correlation between the different modes including vibrational second order Møller-Plesset perturbation theory (VMP2), and configuration interaction (VCI). Compared to the VSCF results, these different approaches generally offer corrections that can significantly improve the accuracy of the calculations with varying increases in computational effort.

### 3.7.2.2 VPT2 and its derivatives

While the VSCF methods yield good zero point energies (ZPEs) and anharmonic frequencies for the majority of fundamental modes, their nonlinear scaling with the number of normal modes and the number of modes being correlated can make them expensive to utilize. In VPT2 calculations, the vibrational Hamiltonian is represented in reduced normal coordinates
\[ Q_i = (2\pi \omega_i)\frac{1}{2} q_i \] as\textsuperscript{240}

\[
\hat{H}_{\text{vib}} = \frac{1}{2} \sum_r \omega_r (P_r^2 + Q_r^2) + \frac{1}{6} \sum_{rst} \phi_{rst} Q_r Q_s Q_t \\
+ \frac{1}{24} \sum_{rstu} \phi_{rstu} Q_r Q_s Q_t Q_u + \sum_{\alpha} B_{\alpha}^e j_{\alpha}^2, \tag{66}
\]

where

\[
j_{\alpha} = \sum_{i<j} \zeta_{ij}^\alpha (Q_i P_j - Q_j P_i), \tag{67}\]

\[ P_r = -i \frac{\partial}{\partial Q_r}, \] and \( \alpha \) identifies a rotational axis. The symbol \( B_{\alpha}^e \) marks the corresponding equilibrium rotational constant, and \( \zeta_{ij}^\alpha \) is a Coriolis coupling constant between the vibrational modes \( i \) and \( j \). The coefficients \( \phi_{rst} \) are defined by the derivatives of the force constant matrix over normal coordinates \( \Phi = U^T F \cdot GU \) as \( \phi_{rst} = (\omega_r \omega_s \omega_t)^{-1/2} \Phi_{rst} \) and analogously for \( \phi_{rstu} \). In VPT2, these third order energy derivatives and the semidiagonal fourth order derivatives are calculated by finite differentiation which scales linearly with the number of normal modes. Typically this results in at least an order of magnitude savings in computational time compared to the VSCF calculations.\textsuperscript{239} If desired, ro-vibrational couplings can be obtained by adding the rotational energy terms to \( \hat{H}_{\text{vib}} \).\textsuperscript{240}

There have been numerous refinements to the original VPT2 outlined above. For example, the generalized VPT2 (GVPT2), is able to account for resonance effects arising from the singularities caused when one vibrational frequency is either close the sum of two others or twice another.\textsuperscript{241-244} A more recent development was the extension of the GVPT2 into a hybrid degeneracy-corrected VPT2 (HDCPT2) by Bloino,\textsuperscript{245} which unlike its predecessors performs well even when the couplings between the high- and low-frequency modes are large.

### 3.7.3 Alternative approaches to anharmonicity

Aside from the VSCF and VPT2-based methods, several alternatives have been used to account for anharmonicities: One typical approach is simply to scale the harmonic frequencies
by suitable factors to more closely agree with experimental or computationally obtained frequencies or thermodynamic data.\textsuperscript{81,239,246,247} A more recent alternative is the quasi-harmonic approximation where the large amplitude low-frequency motions are treated approximately as rotations.\textsuperscript{96,248} Specifically in hydrogen bonded systems, approaches such as the harmonically coupled anharmonic oscillator,\textsuperscript{249} \textit{ab initio} molecular dynamics\textsuperscript{250} (see section 4.1), the parallel variational multiple window configuration interaction wave functions method (P\textsubscript{VMWCI}\textsubscript{2}),\textsuperscript{251} and the Huang–Braams–Bowman water dimer potential (HBB)\textsuperscript{252} have seen use. Recent attempts have also combined experimental measurements of the integrated absorbance with theoretically calculated oscillator strengths to obtain accurate values for the free energies of complexation.\textsuperscript{61,253–255}

Generally speaking, a fundamental issue with several of the mentioned approaches is the inaccurate treatment of the large amplitude motions partly due to the problems in the representation of the PES in cases where more than one low lying potential energy minima are present. In the case of VPT2, the problematic behaviour at low wavenumbers is illustrated, for example, in Figure 6 where the relative differences between harmonic and anharmonic frequencies are large for the lowest vibrational states. This is a common occurrence in large amplitude intermolecular modes of atmospheric complexes and is exacerbated because, due to the high density of states for these motions, a large number of vibrational overtones are needed for the accurate calculation of the vibrational partition function and thus the thermodynamic properties. For this reason, the focus of this section is on variational approaches to the nuclear Schrödinger equation that enable the calculation of an arbitrary number of excited states within the boundaries of the basis set size and accuracy of the PES.

In practice, the dimensionality of the vibrational PES increases by three with each added atom. The complete anharmonic treatment requires calculations of vast areas of this PES making it difficult if not impossible already to treat systems the size of sulfuric acid and sulfuric acid monohydrate complex fully variationally. On the other hand, for small systems such as a single water molecule, the complete anharmonic treatment of the potential
energy surface has been doable for a long time and the results are in good agreement with experiment.\textsuperscript{256}

For larger molecules than water, it is possible to circumvent the difficulties in the anharmonic treatment, for example, by dividing the systems into smaller uncoupled sub-systems (domains) where variational calculations are feasible. In Articles I, II, and V, this approach is referred to as the anharmonic domain (AD) approximation. For example in Article I, it was used to investigate the motions connecting the different conformers and the bending and stretching motions of the water molecule of \( \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \). The vibrational frequencies obtained from these calculations are reproduced in Table 1 together with comparable results from both VSCF and HDCPT2 calculations and show that the AD values are closest to the experimental ones. In Article II, the AD approximation was employed to look at the conformational change in \( \text{H}_2\text{SO}_4 \) and in Article V, all of the large amplitude motions in \( \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \) were treated with ADs to obtain as accurate thermodynamical properties as possible. In addition to these publications, for example Fábri et al.\textsuperscript{94} and Mátyus et al.\textsuperscript{95} have looked at reduced dimensional models and concluded that with a reasonable choice of the coordinates included in the treatment, energy levels with good accuracy can be obtained.

As opposed to the normal coordinates utilized in Sections 3.7.1 and 3.7.2 in the variational calculations of Articles I, II, and V the nuclear Hamiltonian was expressed in terms of curvilinear internal coordinates. The two major advantages associated with the use of curvilinear coordinates are that they facilitate a more accurate representation of the potential energy surface and make the potential energy surface parameters independent of the isotopes within the Born–Oppenheimer approximation.\textsuperscript{257} The foremost drawback is that the kinetic energy operator becomes more complicated both as a result of using curvilinear internal coordinates and of imposing rigid constraints on the system in the form of the ADs.
Table 1: The fundamental wavenumbers for free water and water bound in the g1 conformer of the sulfuric acid monohydrate complex compared with experimental values. All values are in cm$^{-1}$. The anharmonic domain calculations are abbreviated by AD. The shifts in wavenumber for the anharmonic $\Delta\tilde{\nu}_a$ and experimental $\Delta\tilde{\nu}_e$ values are defined as the free water fundamental wavenumber minus the fundamental wavenumber in the hydrate. The HDCPT calculations were performed at the MP2/AVTZ level.

<table>
<thead>
<tr>
<th></th>
<th>isolated H$_2$O</th>
<th>bounds H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDCPT2</td>
<td>AD</td>
</tr>
<tr>
<td>HOH bend</td>
<td>1578.2</td>
<td>1594.5</td>
</tr>
<tr>
<td>sym. stretch (bonded)</td>
<td>3655.1</td>
<td>3652.4</td>
</tr>
<tr>
<td>asym. stretch (free)</td>
<td>3770.6</td>
<td>3761.5</td>
</tr>
</tbody>
</table>

$^a$ Engdahl and Nelander$^{258}$ in Ar matrix

$^b$ Tennyson et al.$^{259}$ in the gas phase

$^c$ Tennyson et al.$^{260}$ in the gas phase

$^d$ CCSD(T)/AVQZ calculation by Salmi et al.$^{261,262}$

$^e$ Givan et al.$^{263}$ in Ar matrix

$^f$ Rozenberg and Loewenschuss$^{264}$ in Ar matrix.
3.7.3.1 Kinetic energy operator

In the AD approximation, the \(3N_n\)-dimensional coordinate space is effectively partitioned into a set of active coordinates \(A = \{q_1, q_2, \ldots, q_A\}\) that constitute the AD and a set of \(P = 3N_n - A\) passive coordinates \(P = \{q_{A+1}, q_{A+2}, \ldots, q_{A+P}\}\). The presence of rigid constraints alters the kinetic energy operator within the anharmonic domain. Specifically, the presence of rigid constraints changes the contravariant metric tensors \(g^{(i,j)}\) where

\[
g^{(i,j)} = \sum_{\alpha=1}^{N_n} g^{(i)}_{\alpha} \cdot g^{(j)}_{\alpha}.
\] (68)

The sum over the inner products of the measuring vectors \(g^{(i)}_{\alpha}\) goes over all nuclei \(N_n\) in the molecule and \(i, j \in A\). In the unconstrained case, the measuring vectors for the vibrational coordinates, \(h^{(i)}_{\alpha}\), are obtained by taking the mass-weighted gradient of the vibrational coordinate

\[
h^{(i)}_{\alpha} = \frac{1}{\sqrt{m_\alpha}} \nabla q_i.
\]

As shown in Ref. 1, in the rigidly constrained case \(g^{(i)}_{\alpha}\) are obtained by adding the frozen-mode correction term to \(h^{(i)}_{\alpha}\):

\[
g^{(i)}_{\alpha} = h^{(i)}_{\alpha} - \sum_{I=1}^{P} \lambda^{(i[I])} \frac{k^{(I)}_{\alpha}}{k^{(I)[I]}},
\] (69)

where

\[
k^{(ij)} = \sum_{\beta=1}^{N_n} k^{(i)}_{\beta} \cdot k^{(j)}_{\beta},
\] (70)

\[
\lambda^{(ij)} = \sum_{\beta=1}^{N_n} h^{(i)}_{\beta} \cdot k^{(j)}_{\beta}.
\] (71)

The bracketed index counter is defined by the equation \([I] = A + P + 1 - I\), and the vectors \(k^{(1)}_{\alpha}, k^{(2)}_{\alpha}, \ldots, k^{(P)}_{\alpha}\) are related to the unconstrained measuring vectors of the passive coordinates \(h^{(1)}_{\alpha}, h^{(2)}_{\alpha}, \ldots, h^{(P)}_{\alpha}\) through the recursive formula

\[
k^{(I+1)}_{\alpha} = h^{(I+1)}_{\alpha} - \sum_{J=1}^{I} \lambda^{(I+1)[J]} \frac{k^{(J)}_{\alpha}}{k^{(J)[J]}},
\] (72)
with $k^{(1)}_\alpha = h^{(1)}_\alpha$ for all nuclei $\alpha$.

The translational motion is completely separated from the vibrational and rotational degrees of freedom. Consequently, the total kinetic energy operator can be written as a sum of two parts, one associated with the internal motion of the molecules and the other with the translational motion of the molecule as a whole. Once the measuring vectors have been calculated from equation (69), the kinetic energy operator for the internal motions can be written for the zero angular momentum states as

$$\hat{K}_n = \frac{1}{2} \sum_{ij} A^{-3} p_i^\dagger \alpha^{(ij)} p_j = -\frac{1}{2} \sum_{ij} A^{-3} \left( \frac{\partial}{\partial q_i} + \frac{1}{g^{-1/2}} \frac{\partial g^{-1/2}}{\partial q_i} \right) \alpha^{(ij)} \frac{\partial}{\partial q_j},$$  \hspace{1cm} (73)

where $g = \det g^{(ij)}$, and $p_j = -i \frac{\partial}{\partial q_j}$. Because the total angular momentum quantum number is zero, the rotational coordinates included in the active coordinate space make no contributions and the sum is only over the active vibrational degrees of freedom. The contravariant metric tensor is connected to the Jacobian of the coordinate transformation via $J = g^{-1/2}$.

For equation (73), the volume element of integration is $d\tau = J dq_1 dq_2 \ldots dq_A$. If one prefers to use a weight function of unity, i.e., $d\tau = dq_1 dq_2 \ldots dq_A$, the kinetic energy becomes

$$\hat{K}_{n,1} = g^{-1/4} \hat{K}_n g^{1/4}. \hspace{1cm} (74)$$

Following simplification, this transforms into

$$\hat{K}_{n,1} = \frac{1}{2} \sum_{ij} A^{-3} p_i \alpha^{(ij)}(q) p_j. \hspace{1cm} (75)$$

It should be noted that the pseudopotential term $\hat{V}'(q)$ has been neglected in equation (75). It arises solely from setting the weight function equal to one, and its effect on the energies is usually small. By comparing the relative magnitudes of the effects of the $g$-matrix-elements, this kinetic energy operator can be further simplified by neglecting those elements $\alpha^{(ij)}$ which do not significantly affect the energy levels. In Article II, it was found
that for the vibrational energy levels of the H$_2$SO$_4$ large amplitude motions it was sufficient to include only the frozen mode corrected diagonal g-matrix elements as the values of the off-diagonal terms were substantially smaller in this case, as shown in Figure 7. Furthermore, sufficient accuracy for the calculation of thermodynamic properties is maintained even when the diagonal elements are treated as constants by taking the average over the $g^{(ij)}$ obtained with different values for the active coordinates. In this case, the kinetic energy operator becomes

$$\hat{K}_{n,1} = \frac{1}{2} \sum_{i}^{4-3} g_{e}^{(ii)} p_i^2,$$

where the subindex $e$ indicates that the g-matrix element is a constant, and not a function of the active coordinates $A$.

![Figure 7](image)

Figure 7: The frozen mode corrected diagonal and off-diagonal matrix elements of H$_2$SO$_4$ in u$^{-1}$ Å$^{-2}$ obtained in Article II when the geometry was fixed to that of the lowest energy conformer at each point except for $\phi_1$ and $\phi_2$. The angles are given in radians. This Figure has been reproduced with the permission from Journal of Chemical Physics.

### 3.7.3.2 Potential energy operator

Three different types of functions were used to represent the PESs within the ADs in Articles I, II, and V. After the functional representation of PES was decided, the basis set was usually chosen in a way to make the evaluation of integrals as easy as possible.
For torsional angles where the potential energy surface was broad and the full rotation from 0 to $2\pi$ was possible, the potential energy was usually represented in terms of sine and cosine terms and the basis set employed was a product of one-dimensional free rotor eigenfunctions. For example, in the case of sulfuric acid in Article II, the PES of the two-dimensional AD connecting the different rotomers had the form

$$
\hat{V}(\phi_1, \phi_2) = \sum_{n=0}^{3} A_n^{(1)} \cos(n\phi_1) \cos(n\phi_2) + \sum_{n=1}^{5} A_n^{(2)} [\cos(n\phi_1) + \cos(n\phi_2)]
$$

$$
+ \sum_{n=1}^{3} A_n^{(3)} \sin(n\phi_1) \sin(n\phi_2) + \sum_{n=2}^{4} A_n^{(4)} [\cos(n\phi_1) \cos(\phi_2) + \cos(\phi_1) \cos(n\phi_2)]
$$

$$
+ \sum_{n=3}^{4} A_n^{(5)} [\cos(n\phi_1) \cos(2\phi_2) + \cos(2\phi_1) \cos(n\phi_2)] + \sum_{n=2}^{4} A_n^{(6)} [\sin(n\phi_1) \sin(\phi_2) + \sin(\phi_1) \sin(n\phi_2)]
$$

$$
+ \sum_{n=3}^{4} A_n^{(7)} [\sin(n\phi_1) \sin(2\phi_2) + \sin(2\phi_1) \sin(n\phi_2)],
$$

(77)

where $\phi_1$ and $\phi_2$ were the two torsional angles within $\text{H}_2\text{SO}_4$ defined by the chain $\text{H-O-S-O}$ of singly bonded atoms. For the more rigid bending and torsional motions, where the periodicity of the potential is not relevant, the PES can be represented in terms of a simple polynomial as was done for both of the three-dimensional ADs in Article V covering most of the intermolecular modes. In this case, the PES had the form

$$
\hat{V}(q_1, q_2, q_3) = \hat{V}_1(q_1) + \hat{V}_2(q_2) + \hat{V}_3(q_3) + \hat{V}_{12}(q_1, q_2) + \hat{V}_{23}(q_2, q_3) + \hat{V}_{13}(q_1, q_3),
$$

(78)

where $q_i = Q_i - Q_{i,e}$ is the bond angle displacement coordinate, $Q_i$ is an instantaneous bond angle, and $Q_{i,e}$ is its equilibrium value. The terms on the right of equation (78) were defined by

$$
\hat{V}_i(q_i) = \sum_{k=2}^{12} D_k^{(i)} q_i^k
$$

(79)
\[
\hat{V}_{ij}(q_i, q_j) = \sum_{k=1}^{11} \sum_{l=1}^{11} D_{k,l}^{(q_i q_j)} k_i^l j_i^l.
\]

This type of potential was used in conjunction with a basis set of harmonic oscillator wave functions \(\xi^h(\theta)\) of the type

\[
\xi^h(\theta) = \left(\frac{\alpha}{2v!\pi^{1/2}}\right)^{1/2} H_v(\alpha \theta) e^{-\alpha^2 \theta^2/2},
\]

where \(\alpha\) is a parameter that depends on the form of the Hamiltonian and \(H_v(\alpha \theta)\) is a Hermite polynomial. This choice makes the analytic evaluation of the matrix elements possible.

For stretching motions, the variation in the coordinate generally ranges from 0 to \(\infty\). In this case, a widely employed method is to expand the PES in terms of the Morse variable

\[
z_i = 1 - e^{-a_i R_i},
\]

where \(R_i = r_i - r_{i,e}\) is the difference in the bond length and \(a_i\) is the Morse parameter. For example, in the case where the water molecule in the H\(_2\)SO\(_4\)-H\(_2\)O complex was treated by the AD approximation in Article I, both of the stretching motions were described in terms of these variables, and they were coupled to the HOH bending motion and each other via the PES:

\[
V(z_b, z_f, \theta) = \sum_{k=2}^8 T_k^{(b)} z_b^k + \sum_{k=2}^8 T_k^{(f)} z_f^k + \frac{f_{r_b r_f}}{a_b a_f} z_b z_f
\]

\[
+ \frac{1}{2} \left( \frac{f_{r_b r_f}}{a_b^2 a_f} + \frac{f_{r_b r_f}}{a_b a_f^2} \right) z_b^2 z_f^2 + \frac{1}{2} \left( \frac{f_{r_b r_f}}{a_b^2 a_f} + \frac{f_{r_b r_f}}{a_b a_f^2} \right) z_b^2 z_f^2
\]

\[
+ \sum_{k=2}^4 \frac{f_{\theta^k}}{k!} z_b^k + \frac{f_{r_b \theta}}{a_b} z_b \theta + \frac{f_{r_f \theta}}{a_f} z_f \theta + \frac{f_{r_b \theta}}{2a_b} z_b \theta^2 + \frac{f_{r_f \theta}}{2a_f} z_f \theta^2
\]

\[
+ \frac{1}{2a_b^2} (f_{r_b r_b \theta} + a_b f_{r_b \theta}) z_b^2 \theta + \frac{1}{2a_f^2} (f_{r_f r_f \theta} + a_f f_{r_f \theta}) z_f^2 \theta
\]

\[
+ \frac{1}{4a_b^2} (f_{r_b r_f \theta} + a_b f_{r_f \theta}) z_b^2 \theta^2 + \frac{1}{4a_f^2} (f_{r_f r_f \theta} + a_f f_{r_f \theta}) z_f^2 \theta^2,
\]

where \(z_b\) refers to the hydrogen bonded OH-stretch, \(z_f\) refers to the free OH-stretch, and
\(\theta\) is the bond displacement coordinate for the HOH-bend. In this case, Morse oscillator eigenfunctions of the form

\[
\xi_n^m(x) = n! \left[ \frac{a(2\lambda - 2n - 1)}{\Gamma(n + 1)\Gamma(2\lambda - n)} \right]^{\frac{1}{2}} x^{\lambda - n - \frac{1}{2}} e^{-\frac{1}{2}x^2} L_{2n-2\lambda}^2(x)
\]  

(83)

were used for the stretches. In equation (83), \(L\) is the Laguerre polynomial, \(\Gamma\) is the gamma function, and \(x = 2\lambda e^{-a(R-R_e)}\), where \(a\) is the Morse parameter. The parameter \(\lambda\) is related to the depth of the potential well \(D_e\) via \(\lambda = \sqrt{2mD/e}\). In all the AD calculations, the total wave function was expressed as a linear combination of the products of individual basis functions, for example in the case of equation (82) it had the form

\[
|\psi\rangle = \sum_{n_b} \sum_{n_f} \sum_v c_{n_b n_f v} \left( |\xi_n^m(x_b)\rangle |\xi_n^m(x_f)\rangle |\xi_v^h(\theta)\rangle \right),
\]

(84)

where the coefficients \(c_{n_b n_f v} \in \mathbb{R}\). In the variational calculations, insertion of the wave function of type (84) into the Schrödinger equation followed by multiplication from the left with \(\langle \xi_n^m(x_b) | \langle \xi_n^m(x_f) | \langle \xi_v^h(\theta) | \hat{H} | \xi_n^m(x_b) \rangle | \xi_n^m(x_f) \rangle | \xi_v^h(\theta) \rangle = c_{n_b n_f v} E\),

(85)

from which the energies are obtained by diagonalizing the corresponding matrix.
4 Statistical thermodynamics – the link between quantum chemistry and thermodynamics

Statistical thermodynamics provides the link between the microscopic quantities quantum mechanics is concerned with, and the macroscopic quantities that are the topic of thermodynamics. This section deals with the basics of statistical thermodynamics, introducing the formulae used in the calculation of thermodynamic properties from microscopic data.

4.1 The building blocks of statistical mechanics: ensembles and partition functions

The macroscopic state of a system where the number of particles is of the order of one mole (or $6 \cdot 10^{23}$), can be defined by specifying a small number of the system’s physical quantities such as $n$, $T$, and $p$. These quantities are then connected to other macroscopic properties by the equation of state. In contrast, the identification of the microscopic state of a system requires specification of all of its quantum numbers, and is utterly unfeasible for systems of macroscopic size. Thus, the first fundamental challenge in statistical thermodynamics is that in order to ascend from the microscopic to the macroscopic, ostensibly the microscopic state of the system has to be to specified.

A second challenge arises because the measuring process of thermodynamic quantities takes a finite amount of time implying that the measured properties are essentially time averages. For relatively small systems of few hundreds or thousands of atoms, direct simulation of the system’s time evolution is possible using molecular dynamics (MD) where the system evolves in discretized time according to Newton’s equations of motion. For all nuclei, the force on nucleus $j$, $F_j = -\nabla_j V$, is re-evaluated from the potential $V$ at new atomic positions at every interval $\Delta t$ as illustrated in the flowchart of Figure 8, depicting a typical MD simulation. The form of the potential and the magnitude of the time-step $\Delta t$ depend on the size of the system and the phenomena under investigation. In large chemical systems, where
the focus is on structural properties like in protein folding, time steps of 2-5 fs are regularly utilized. These steps can be further extended with the help of time-split algorithms. The potential $V$ is usually represented by a parametrized function tailored for the needs of the simulation. In empirical force fields such as AMBER and CHARMM, the force is directly calculated instead of the potential and the aqueous solvent around the protein is treated either explicitly with potentials such as the different TIPnP water potentials or implicitly by, for example, making use of the generalized Born surface area approach. In small systems and when chemical reactions are under investigation, a common approach is to obtain the potential by solving the electronic Schrödinger equation under the BO-approximation for each new nuclear configuration with an affordable quantum mechanical method such as DFT. Especially when the system includes explicitly treated water molecules, following chemical reactions on the atomic level, the computational procedure requires the use of small time-steps of around 1 fs as the size of the step needs to be about an order of magnitude smaller than the smallest nuclear vibrational period in the system.

To deal with the second challenge more generally, statistical mechanics introduces the concept of an ensemble, which is an arbitrarily large collection of systems that cover all of the possible microstates for a given macrostate. The first postulate of statistical thermodynamics is that the average of a property calculated over such an ensemble corresponds to the time average obtained as a result from a thermodynamical measurement. This ergodic postulate is, for example, put to use in Monte Carlo simulations where the ensemble averages are computed instead of the time averages obtained in MD simulations.

The problem in the specification of the system state is harder to resolve. The solution starts with the postulate of equal a priori probabilities according to which the system is equally likely to be found in any of its possible quantum states. For now, the ensemble is thought to have a constant number of particles $N$, volume $V$, and energy $E$. The value of a
Input all initial coordinates and velocities $q(t_0), v(t_0)$

Obtain new forces $F_i(q)$ from DFT, force-fields, etc.

Solve the equations of motions numerically for the time-step $\Delta t$
$q(t_n), v(t_n) \rightarrow q(t_{n+1}), v(t_{n+1})$

Take the time-step $t \rightarrow t + \Delta t$

Calculate relevant physical properties at $t_{n+1}$

Calculate averages and other results from frames and finish

Figure 8: A flowchart depiction of a typical molecular dynamics simulation.
macroscopic thermodynamic variable $X$ for any ensemble is simply

$$\bar{X} = \sum_j X_j P_j,$$

(86)

where $P_j$ is the average probability of finding a system in a certain energy state where the value of $X$ is $X_j$. Looking at a canonical ensemble where $T$, $V$, and $N$ in each system are kept constant, the largest contribution to the average comes from the term that has the largest $P_j$, i.e., the term that can be achieved in the greatest number of ways. In fact, as the size of the ensemble increases, this term so overwhelms the others that the average probability can be replaced by the one corresponding only to the most likely state of the entire ensemble.\(^{278}\)

In addition to the canonical ensemble, both microcanonical and grand canonical ensembles are commonly employed. In the microcanonical ensemble, the constants of the systems are $E$, $V$, and $N$ and in the grand canonical ensemble they are $T$, $V$, and the chemical potential $\mu$. Regardless of the ensemble used, the computation of $P_j$ leads to the introduction of the partition function. For example, in the case of the canonical ensemble, the partition function has the form

$$Q(N, V, T) = \sum_j e^{-\frac{E_j(N, V)}{k_B T}},$$

(87)

where the sum is over the different energy levels.

Because all of the fundamental thermodynamic properties can be relatively easily represented in terms of the partition function, it is of central importance to statistical mechanics. For example, in terms of the canonical partition function, the Helmholtz free energy is

$$A - A(0) = -k_B T \ln Q(N, V, T),$$

(88)

where $A(0)$ is the Helmholtz free energy at zero Kelvin.

The direct evaluation of the partition functions in equation (87) still requires a complete knowledge of the system’s energy levels. To make use of these equations in practice, a number
of simplifying assumption have to be made. In low enough densities and high temperatures, the intermolecular interactions between the gas molecules can be neglected and, therefore, the gas can be treated as ideal. This makes it possible to separate the Hamiltonian for the system into a sum of single molecule Hamiltonians and the energy of the state \( E_j \) can be represented as a sum of the molecular energy levels \( \epsilon_i \). Thus, the partition function can be written as

\[
Q(N, V, T) = \sum_{a, b, c, d, \ldots} e^{-\frac{\epsilon_a + \epsilon_b + \epsilon_c + \cdots}{k_B T}}. \tag{89}
\]

If the particles are distinguishable the summing can be done separately for each \( i = a, b, \ldots \). With indistinguishable particles, problems arise because two or more particles can occupy the same molecular state. Fortunately, for gas systems at approximately room temperature, the number of permissible translational states is usually so large that it vastly outnumbers the molecules in the system, making it extremely improbable to find a multiply occupied state. In this case, the canonical partition function becomes

\[
Q(N, V, T) = \frac{q^N}{N!}, \tag{90}
\]

where \( q \) is the molecular partition function

\[
q = \sum_i e^{-\frac{\epsilon_i}{k_B T}}, \tag{91}
\]

and the summation index \( i \) goes over all molecular states. Thus, the problem of calculating the energy states for the whole system has been transformed into a calculation of the energy states of a single molecule. This much simpler problem can be solved accurately in the case of small molecules and atoms. It should be noted that equation (91) ignores all the additional requirements the wavefunction may have, such as the antisymmetry requirements for fermions. Accounting for these effects leads to a different form of the canonical partition function, but it can be shown that in the Boltzmann limit of high temperature and low
density, all these partition functions reduce to equation (91).  

4.2 Evaluation of partition functions

In order to evaluate the molecular partition function \( q \) for even medium-sized molecules, some additional approximations need to be employed. As a starting point, it is common to assume that the molecular Hamiltonian can be separated into the five parts corresponding to the different types of molecular motion and the electronic and nuclear contributions:

\[
\hat{H} = \hat{H}_t + \hat{H}_r + \hat{H}_v + \hat{H}_e + \hat{H}_n. 
\]  

(92)

In equation (92), the subindex \( t \) refers to translational motion, \( r \) refers to rotational motion, \( v \) refers to vibrational motions, \( e \) refers to the electronic contribution, and \( n \) to the nuclear contribution. As the separations between the nuclear energy levels are typically millions of electron volts\(^{iv} \) (where 1 eV = 96.5 kJ mol\(^{-1} \)) and because the nuclear energy states seldom change in chemical reactions, the nuclear partition function can often be ignored altogether. In this case, the molecular energy can be represented as a sum of the different terms \( \epsilon_t \) through \( \epsilon_e \) and the molecular partition function becomes a product of the different terms

\[
q = q_t q_r q_v q_e. 
\]  

(93)

Because the overall motion of the molecule can be separated into the movement of the center of mass of the molecule through space and the relative displacement of the nuclei with respect to the center of mass, it is clear that the translational motion can be treated separately from all the other contributions to the energy as described in Section 3.7.3. The form of \( q_t \) can then be obtained by applying the energies from the particle in a box model

\(^{iv}\text{Energy levels of Light Nuclei, } A = 3 – 20, \ http://www.tunl.duke.edu/nuclidata/, \ accessed 23.11.2016\)
to the definition of the molecular partition function (91), and is simply

\[ q_t = \left( \frac{2\pi mk_B T}{\hbar^2} \right)^\frac{3}{2} V, \]  

(94)

where the zero point of the translational energy has been chosen to be that of the lowest translational level and \( m \) is the total mass of the molecule.

The electronic effects of the total Hamiltonian of the molecule can be separated away from the rest of the degrees of freedom as well and the partition functions can be treated simply according to definition (91). For the electronic partition function, we choose the zero of energy as the ground state electronic energy of the molecule. With this choice the electronic partition function has the form

\[ q_e = \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}}, \]  

(95)

where \( \epsilon_j \)'s are measured from the ground state of the molecule, the sum is over the electronic levels, and \( g_j \) is the degeneracy of the level \( j \).

The temperatures required for the lowest electronically excited states to be significantly populated are much lower than those for the nuclear states, but are still often high enough so that \( q_e \) can be well approximated simply by the first term in equation (95). For example in the case of diatomic molecules, the introduction of these terms to equation (95) typically becomes important only for temperatures over 5000 K.\(^{279}\)

The separation of the rotational and vibrational parts in the Hamiltonian is more problematic than the separation of the translational motion because of the well-known interconnectedness of the two motions. Equation (92) is therefore only the starting point of accurate calculations, but it turns out that for most problems the corrections can be made by adding some terms with small effects to the equation that account for centrifugal distortion effects, anharmonic effects, and others.\(^{278}\)

A simple form of the rotational partition function can be derived by first making the
rigid rotor assumption, in which the movement of the molecule around principal axes of inertia has no effect on its shape, and by assuming that the density of the rotational states is so large that the sum in equation (91) can be approximated by an integral. This can be done when the ratio $\frac{\epsilon_i}{kB}$ is small, which is satisfied when $T$ is large enough. With these approximations, the rotational partition function becomes

$$q_r = \frac{1}{\sigma} \left( \frac{k_B T}{\hbar c} \right)^{\frac{3}{2}} \left( \frac{\pi}{ABC} \right)^{\frac{1}{2}},$$

(96)

where $\sigma$ is the symmetry number, which is simply the sum of the pure rotational symmetry elements of the molecule. The quantities $A$, $B$, and $C$ are called rotational constants and they are defined by the formula

$$A = \frac{\hbar}{8\pi c I_A},$$

(97)

where $I_A$ is the moment of inertia around one of the three principal axes, such that $I_A \leq I_B \leq I_C$. In Article V, the moments of inertia and rotational constants were obtained as a part of the VPT2 anharmonic calculations described in Section 3.7.2. For rotational degrees of freedom, the energies are generally small and the temperatures required for the approximation to be valid are only some tens of Kelvins. Thus, equation (96) produces accurate values of the partition function for ordinary temperatures.

The separation between the energy levels is so large for vibrational degrees of freedom that in most cases the integral approximation is invalid even at room temperature. As demonstrated before, by applying the harmonic oscillator model and treating the system in normal coordinates, it becomes possible to separate the $3N_n - 6$ vibrational degrees of freedom for a non-linear molecule, or $3N_n - 5$ vibrational degrees of freedom for a linear one. For non-linear molecules, the vibrational partition function becomes a product of $3N_n - 6$ independent harmonic oscillators:

$$q_{\text{vib}} = \prod_{i=1}^{3N_n-6} q_{\text{vib},i} = \prod_{i=1}^{3N_n-6} \frac{1}{1 - e^{-\frac{\hbar \nu_i}{k_B T}}},$$

(98)
where \( \nu_i \) is the frequency of the \( i \)th vibrational degree of freedom and the zero of energy corresponds to the vibrational ZPE of the molecule.

For systems where the harmonic approximation is inapplicable, numerous other approaches have been developed for the vibrational partition function. In simple perturbation theory (SPT),\(^{280–282}\) the equal spacing of the energy levels that is present in the harmonic approximation is retained, but the spacing corresponds to the anharmonic fundamental frequency instead. In other words, the \( \nu_i \) in equation (98) is replaced with the fundamental anharmonic frequency which is obtained, for example, from a VSCF or a VPT2 calculation as shown in Section 3.7.2. Another alternative is to start from the general anharmonic expression for energy when no degeneracies are present:

\[
E(\{n_i\}) = \sum_{i=1}^{3N_n-6} h\nu_i n_i + \sum_{i=1, \ j<i}^{3N_n-6} X_{ij}(n_in_j + \frac{1}{2}(n_i + n_j)), \tag{99}
\]

where \( n_i \) is the quantum number of the mode \( i \), \( \nu_i \) is the harmonic frequency of mode \( i \), and \( X_{ij} \) is the anharmonic coefficient between modes \( i \) and \( j \). This equation can be inserted into the definition of the partition function. By the use of a Taylor expansion to the final term in equation (99) after plugging it into the definition of the partition function, this results in a vibrational partition function of the form:\(^{18}\)

\[
q_{\text{vib}} = q_{\text{vib},0} \left( 1 - \sum_{i=1}^{3N_n-6} \chi_{ii} e^{-\xi_i} \frac{(1 + e^{-\xi_i})}{(1 - e^{-\xi_i})^2} - \sum_{i=1}^{3N_n-6} \chi_{ii} \frac{e^{-\xi_i}}{1 - e^{-\xi_i}} \right) - q_{\text{vib},0} \left( \sum_{i=1, \ j<i}^{3N_n-6} \chi_{ij} \frac{e^{-\xi_i}}{1 - e^{-\xi_i}} \left( \frac{e^{-\xi_j}}{1 - e^{-\xi_j}} \right) - \sum_{i=1, \ j<i}^{3N_n-6} \chi_{ij} \frac{e^{-\xi_i} + e^{-\xi_j}}{1 - e^{-\xi_i} + 1 - e^{-\xi_j}} \right), \tag{100}
\]

where \( \chi_{ij} = X_{ij}/k_B T \), \( \xi_i = h\nu_i/k_B T \), and \( q_{\text{vib},0} \) is the harmonic partition function.

If the presence of multiple conformers in the molecule is accounted for by the use of anharmonic domains as described in Section 3.7.3, then the vibrational partition function for these domains has to be evaluated directly from equation (91), which is easy enough
provided that the sum is convergent and the vibrational states are readily available. In this case, the vibrational partition function corresponding to the passive degrees of freedom can be calculated with either the SPT approximation or equation (100) with the sum running only over the passive vibrational states as was done in Article V.

4.3 Statistical mechanics of equilibrium systems: free energies, entropies, and enthalpies

After the molecular partition function is known, its relation to the Gibbs free energy and the equilibrium constant can be established through the connection between the Helmholtz free energy and the canonical partition function:

\[ A - A(0) = -k_B T \ln Q = -Nk_B T \ln \frac{q}{N} - Nk_B T, \]  

(101)

where the second equality follows from the insertion of \( Q = \frac{q^N}{N!} \) and the use of Stirling’s approximation. For an ideal gas, \( G = A + pV = A + Nk_B T \) resulting in the expression

\[ G - G(0) = -Nk_B T \ln \frac{q}{N}, \]  

(102)

where \( G(0) \) is the Gibbs free energy at absolute zero.

In the case where the molecule possesses multiple stable conformers which cannot be feasibly accounted for by quantum mechanical methods such as the anharmonic domain approximation, a statistical mechanical method can be used. The molecular partition function is then written in terms of the different conformers as:

\[ q = \sum_k q_k e^{-\frac{E_k^0}{k_B T}}, \]  

(103)

where the index \( k \) runs over all different conformers, with \( k = 0 \) corresponding to the global minimum. The term \( E_k^0 \) is the zero point of energy of the conformer relative to the absolute
ground state (i.e., the ground state of the lowest energy conformer). It is defined as

$$E_k^0 = U_k^0 + \varepsilon_k - \varepsilon_0,$$

where $U_k^0$ is the separation between the global minimum of the potential energy surface $U_0$ and the local minima $k$. Finally, $\varepsilon_k$ is the zero point vibrational energy of the minima $k$ as illustrated in Figure 9.

Figure 9: Generic energy level diagram of a molecule with multiple isomers along the general reaction coordinate $d$. The quantity $U_0^k$ is the value of the global minimum of the potential energy surface, $\varepsilon_k$ is the zero point energy of the conformer $k$, $E_{k,j}$ is the energy of the $j$th energy level measured from the quantum mechanical ground state of the system, $U_k^0$ is the energy difference between the electronic energy of the $k$th conformer and the global minimum energy, and $E_k^0$ is the energy difference between the zero point energies of the $k$th conformer and the global minimum energy. The figure has been reproduced from Article IV with the permission of the Journal of Physical Chemistry A.

Starting with equation (103), one obtains an equation for the Gibbs free energy in terms
of the Gibbs free energies of the conformers

\[ G_m = -RT \ln \sum_{k=0} e^{-\frac{G_{m,k}}{RT}}. \]  

(105)

Once the molar free energies of both products and reactants \( G_{m,k} \) have been calculated with equations (102) or (105), the equilibrium constant \( K \) can be directly evaluated from

\[ -RT \ln K = \Delta_r G_m^\circ = \sum_i v_i G_{m,i}^\circ, \]  

(106)

where the sum goes over the reactants and products, and \( v_i \) is the stoichiometric coefficient of species \( i \).

A popular alternative to equation (105) is to calculate so called Boltzmann averaged free energies via

\[ \langle G_m \rangle = \frac{\sum_k G_{m,k} e^{-\frac{G_{m,k}}{RT}}}{\sum_k e^{-\frac{G_{m,k}}{RT}}}, \]  

(107)

where \( G_{m,k} \) is the Gibbs free energy of the conformer \( k \). Figure 10 depicts the application of both equations (105) and (107) for the calculation of the reaction Gibbs free energy of the pinic acid–sulfuric acid complex from its constituent molecules as a function of the product conformers included in the calculation. The data are based on the results obtained in Article IV. For concreteness, four of the product conformers are displayed in Figure 11. The dashed lines depicting the free energy when all higher energy conformers are neglected for the reactants, show that the Boltzmann averaging scheme yields free energies larger than when no extra conformers are included. As mentioned in the Introduction, this behaviour is unphysical, since the presence of multiple minima on the PES introduces new vibrational states to the system, which should result in a more negative Gibbs free energy for the products and thus for the reaction overall. When the conformers of the reactants are also incorporated in the calculation, it becomes more difficult to predict what will happen to the free energies.
Figure 10: The formation free energies of the pinic acid - sulfuric acid complex when only product conformers (P) or both product and reactant conformers are taken into account (P+R) as a function of the number of product conformers incorporated.

Similarly to the free energies, the enthalpy, and entropy are also connected to the canonical partition function and thus to the molecular partition function. In the case of the enthalpy, this connection is

$$H = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B T V \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}.$$  

Using the SPT approximation for the passive degrees of freedom and the anharmonic domain approximation to account for the presence of higher order conformers, one obtains, for
example, the following expression for the enthalpy

\[
H - H(0) = 4Nk_B T + Nh \sum_{i=1}^{P} \frac{\nu_i e^{-\frac{h\nu_i}{k_B T}}}{1 - e^{-\frac{h\nu_i}{k_B T}}} + Nh \sum_{j=1}^{A} \sum_{k=1}^{N_j} \frac{\nu_{jk} e^{-\frac{h\nu_{jk}}{k_B T}}}{\sum_{k=1}^{N_j} e^{-\frac{h\nu_{jk}}{k_B T}}},
\]

(109)

where the index \(i\) goes over the passive coordinates \(P\) with the fundamental frequencies symbolized by \(\nu_i\), \(j\) goes over all the active coordinates \(A\), and \(k\) goes over the \(N_j\) energy levels \(\nu_{jk}\) of the anharmonic domain \(j\).

Figure 11: The molecular structure of four different conformers (#1, #5, #12, and #38) of the pinic acid - sulfuric acid complex. The relative stability is given in the brackets in kJ/mol. This figure has been reproduced with the permission from Journal of Physical Chemistry A.
The effects of different approaches to both local and global anharmonicities on the thermodynamic properties are summarized for H$_2$SO$_4$·H$_2$O in Figure 12 which shows the free energies, enthalpies, and entropies as a function of temperature. The final panel depicts how the temperature changes in the atmosphere with increasing altitude. Interestingly, the entropies and enthalpies are worst predicted by the teal line representing pure harmonic calculations, but at 298 K these effects cancel, leading to a good agreement with the most accurate AD calculations of the Gibbs free energy. The SPT calculation represented by the black line gives worse predictions for free energy, due to its abysmal prediction for the enthalpy. For the harmonic calculation coupled with equation (105) and represented by the red lines, the results are fairly good as the errors in the reaction entropy and enthalpy approximate cancel at all temperatures. Again, introduction of local anharmonicity to this treatment with SPT is seen to improve the entropy but not enthalpy, leading to a poorer agreement in terms of free energies. In all cases, the entropies and enthalpies are almost independent of temperature within the studied range, resulting in a linear temperature dependence of the free energy.
Figure 12: The free energies, enthalpies, and entropies compiled from Article V as a function for temperature for the formation of the sulfuric acid monohydrate complex from its constituent molecules together with the atmospheric temperature profile measured from the sea level.\(^2\) In the Harm calculations, the harmonic approximation was used to obtain the vibrational partition function via equation (98) whereas in the SPT calculations anharmonic vibrational frequencies were combined with the SPT approximation. The anharmonic frequency calculations all made use of VPT2. Calculations where the presence of higher energy conformers was accounted for with equation (105) are indicated by SG. Finally, C+AD indicates that the anharmonic domain approximation was employed together with couplings from the anharmonic domain to the passive degrees of freedom for the ZPE.
5 Summary and conclusions of the individual research articles

5.1 Article I: Structure and vibrational motions of H$_2$SO$_4$·H$_2$O

In this study, the CCSD(T)-F12a method was employed to obtain optimized geometries of H$_2$SO$_4$·H$_2$O and its individual monomer components as well as the equilibrium energies and PESs. The geometry optimizations confirmed the previously found ground state structures, but it was discovered that the second stable conformer of H$_2$SO$_4$·H$_2$O was only 0.41 kJ mol$^{-1}$ above the global minimum energy structure. While this geometry had been reported in earlier studies its presence was yet to be accounted for in the calculation of the thermodynamic properties. The DF-SCS-LMP2/AV(T+d)Z and CCSD-F12a/VDZ-F12 methods were used for the calculation of harmonic frequencies. The results overestimated the experimental ones for the high-frequency OH-stretches due to the neglect of anharmonicity, but the DF-SCS-LMP2/AV(T+d)Z method gave good agreement in the middle range of frequencies. For the large-amplitude motions, significant differences between the methods used and anharmonic calculations were observed.

The work employed the AD approximation to investigate some of the most important anharmonicities in H$_2$SO$_4$·H$_2$O. The first of the domains consisted of the three-dimensional space spanned by the internal coordinates of the bound water molecule. The second domain covered the two-dimensional space spanned by the wagging angle of the free hydrogen in the hydrogen-bound water molecule and the HOSO torsional angle of the free OH group in the sulfuric acid molecule. These two motions connect the two low-energy conformers of H$_2$SO$_4$·H$_2$O. Results for the second domain showed radical deviation from the harmonic case as the zero-point energy almost doubled and the density of low-lying energy levels decreased, indicating large changes in the vibrational partition function. This discredits the commonly held belief that adding anharmonic corrections leads to a lowering of the wavenumbers. According to the results, for a system with many energetically close minima, it is essential
to employ an anharmonic treatment that takes all of these minima into account.

The vibrational wavenumbers from the three-dimensional AD calculation on complexed and free water molecules agreed well with previous experiments, though the lack of couplings to the other vibrational degrees of freedom was evident in the OH stretch of the bonded hydrogen and the HOH bend in H$_2$SO$_4$:H$_2$O. Based on the two ADs, it was concluded that approaches of this type make it possible to obtain large numbers of fundamental and overtone anharmonic states, with enough accuracy for thermodynamic property calculations. However, in order to obtain sufficiently many vibrational states accurately, the domains must include all strongly coupled vibrational modes. Finally, the vibrational approach used in this study together with the electronic energy calculations provide a systematic way through which more accurate thermodynamic properties can be obtained for small atmospheric clusters.

5.2 Article II: Frozen-mode correction and the rotamer energy levels of H$_2$SO$_4$

In this study, the frozen mode correction derived by Pesonen$^1$ was employed to calculate rotamer energy levels and the vibrational partition function of sulfuric acid. An AD was defined encompassing the two OH-torsional angles which connect the different conformers. Several different approximations to the kinetic energy operator were tested to see which ones would yield energy levels accurate enough for the calculation of thermodynamic properties. For the AD employed, omitting the passive degrees of freedom introduces an increase of around 8.7 cm$^{-1}$ for the ZPE and an additional increase of 9.6 cm$^{-1}$ on the average for the 17 lowest excited states, with increases larger than 18 cm$^{-1}$ for several states. This is unacceptable for accurate calculations. On the other hand, with the frozen mode correction, one can obtain quantitative estimates of the significance of the different terms within the kinetic energy operator, incorporating them in calculations as necessary. The anharmonic vibrational frequencies for the passive degrees of freedom were computed with VSCF, where
the potential energy surface was calculated at the DF-MP2-F12/VTZ-F12-level. Within the AD, the density of states with respect to the harmonic case was significantly increased, which resulted in more than a doubling of the vibrational partition function when moving from the harmonic picture to the anharmonic one. This effect was even more pronounced when the VSCF anharmonic values were compared with the AD ones. Thus, proper accounting for the second H$_2$SO$_4$ conformer should have a marked effect on the thermodynamical properties for all reactions where it is involved.

5.3 Article III: Effects of temperature and collision energy on HCl dissociation on water surfaces

Article III focused on the chemical processes subsequent to the collision of HCl with a water slab as a function of incident kinetic energy and the slab temperature using AIMD and dispersion-corrected DFT. Several different reaction pathways were observed with the relative importance of specific pathways varying with the slab temperature and impact energy. The simulation temperatures studied were 212, 300, and 390 K. As summarized in Figure 13 when the temperature and/or impact energy increased, dissociation time decreased. At the same time, the donated hydrogen atom and the proton defect showed more mobility, mostly due to the increased thermal motion in the surface. In contrast to the other trajectories where dissociation was the predominant reaction pathway, for thermal collisions at the simulation temperature of 212 K approximately corresponding to an experimental temperature of 122 K, nondissociative surface trapping dominated, and there was only a single dissociation event in the five scattering trajectories calculated. This finding corroborates the experimental work of Devlin et al. and Kang et al. according to which almost no ionization occurs at 50 K, as the decrease in temperature and surface porosity from the 212 K calculations should decrease the reactivity of the surface leading to less ionization.

With increased impact energy, all trajectories ended in dissociation even at 212 K, though dissociation at this simulation temperature is slower than at higher temperatures. As colli-
sions are typically thermal in the atmosphere, on surfaces resembling the coldest low density amorphous ice slab of this study HCl could remain undissociated at least on the picosecond timescale, whereas at the higher temperatures encountered, for example, in the troposphere and upon high energy impacts with the surfaces, it should, in most cases, dissociate quickly and dissolve into the droplet.

Direct scattering occurred only in a single trajectory at 390 K, with $10kT$ kinetic energy added to the center of mass of HCl. This indicates that the scattering pathway becomes relevant only at higher temperatures and kinetic energies when HCl has enough energy to escape from the HCl–water potential energy well. By far the most commonly observed reaction path was dissociation on the surface, followed by Grotthuss migration and the formation of solvent-separated ion pair. Due to the existence of a minimum in the free energy profile at the surface for both $\text{H}_3\text{O}^+$ and $\text{Cl}^-$, the majority of the $\text{Cl}^-$ ions stayed at the interface region. In contrast, the hydronium defect showed a tendency to stay on the surface or move to the opposite face of the slab in the 390 K cases. With increased kinetic energy, the Cl anion penetrated into the slab, in some trajectories ending up in the bulk where it was solvated by approximately six hydrogen bonds as opposed to three or four on the surface. The picosecond-scale dissociation together with the tendency of $\text{Cl}^-$ to stay in the surface region sheds some light on the mechanism of the fast proton exchange channel. In this pathway, the HCl molecule is reformed in a sub-microsecond timescale, probably from one of these surface sticking Cl anions.

5.4 Article IV: Effects of conformers on the free energies of atmospheric complexes

This article described how to correctly incorporate the presence of multiple conformers into reaction free energy calculations using statistical mechanics. It gave a thorough accounting of why the thermal or Boltzmann averaging-type approaches that are gaining popularity in the field of atmospheric cluster calculations are incorrect. Furthermore, it provided numerical
Figure 13: The dissociation times at different slab temperatures and different impact energies presented in Article III. This figure is reproduced with the permission of Physical Chemistry Chemical Physics.

evidence that the use of these erroneous formulae can result in errors larger than 4 kJ/mol, especially if coupled with the widespread approach of only taking product conformers into account. When both reactants and products have multiple conformers, the differences between the thermal averaging approaches and the correct method are difficult to predict beforehand. In general, if the free energies of all the energetically low lying conformers of both reactants and products are unavailable, one should neglect the presence of higher energy conformers. If free energies can be calculated for all the conformers then the accurate equation should be employed.

Due to the logarithmic dependence on free energies in the correct formulae, the number of conformers making significant contributions to the free energy of the molecule or cluster was smaller than predicted by the incorrect equations. Even though this implies that only a handful of conformers are important in terms of the free energy values, one will still need to perform a large conformational search to ensure that the true global minimum
structure is discovered. Based on the calculations, a Gibbs free energy threshold criterion of approximately 12.6 kJ/mol relative to the free energy of the global minimum energy structure should be adopted. At this point the addition of one extra conformer will change the Gibbs free energy by less than 0.017 kJ/mol at 298.15 K when using the accurate equation. In terms of electronic energies, this corresponds to performing free energy calculations on all conformers roughly within 16 kJ/mol of the global minimum.

5.5 Article V: Calculation of accurate thermodynamic properties of H$_2$SO$_4$·H$_2$O

In Article V, the effects that the presence of multiple conformers has on the thermodynamic properties of H$_2$SO$_4$·H$_2$O at different temperatures were studied. The higher energy conformers were incorporated in the calculations either quantum mechanically by using the AD approximation or by statistical mechanics. The impact of different local anharmonicity approaches on the thermodynamic properties was also investigated, with the ultimate goal of obtaining thermodynamic properties that are accurate within 1 kJ/mol. While the reaction free energies were well reproduced just at the harmonic level, both the reaction entropy and enthalpy were significantly off compared to the most accurate results. This discrepancy was mitigated by the inclusion of global anharmonicity. For the electronic basis sets studied, further inclusion of local anharmonic effects by HDCPT2 corrected the entropy but not the enthalpy, resulting in a worse agreement in terms of the Gibbs free energies. Even in a small system like the sulfuric acid monohydrate, global and local anharmonicities had similar impacts on the thermodynamic properties. For example, in the case of the reaction enthalpy, these effects were around 3-4 kJ/mol.

Generally speaking, after the relevant low-lying conformers have been identified, global anharmonicity is easy to account for by using statistical mechanical methods. In contrast, despite the development of approaches like HDCPT2, the accurate treatment of local anharmonicity remains a challenge. As observed in Article V, this is due to the large differences
in the fundamental wavenumbers of anharmonic large amplitude motions between different basis sets, which result in large differences in the thermodynamic properties. Furthermore, comparing the regularly employed SPT approximation with the Taylor series approach, it was observed that in some cases the thermodynamic properties are dependent on the method of calculation of the partition function. On the other hand with the AD calculations, the Gibbs free energies and enthalpies obtained with different methods and basis sets all agree within 1 kJ/mol.

6 Overarching conclusions and implications for further research

With respect to molecular processes occurring on water surfaces in the atmosphere, the results of this thesis show that at least in the case of HCl, the collision energy and temperature of the slab play important and not fully overlapping roles in the ionization behaviour. It would be an interesting venue for future research to look at the effects of kinetic energy and temperature for other systems, such as some of the organic acids prevalent in the atmosphere, to see whether the results obtained in this work are generalizable. In the broader context, hydrochloric acid ionization on amorphous ice surfaces may have consequences for several atmospherically relevant reactions. For example, Cl\(^-\) is known to react with NO and NO\(_2\) species adsorbed on liquid water surfaces. This reaction is thought to produce ClNO and ClNO\(_2\) which are precursors of atomic chlorine in the atmosphere. According to the results in Article III, this mechanism should also be operative on amorphous ice surfaces, contributing to the total amount of the pollutant Cl.

In contrast to the computational results of Article III and the experimental ones by Devlin et al.\(^{286}\) and Kang et al.,\(^{287}\) the AIMD simulations by Riikonen et al. on HNO\(_3\) and HI on a quasi-liquid layer of ice\(^{291}\) and HNO\(_3\) on a defect containing ice surface\(^{292}\) at low and cryogenic temperatures, together with the experimental work by Ayotte\(^{293}\) indicate that HCl
dissociation occurs rapidly in accordance. In general, these various and often contradicting experimental and theoretical works support the conclusion that the method of preparation in both experimental and theoretical work determines the nature of the ice surface which subsequently specifies its reactivity.

In recent studies, there has been some indications that the free energy barrier heights of acid deprotonation on the surface differ from those within the bulk.\textsuperscript{294–296} This is an interesting phenomenon and it would be well suited for study with the slab model employed in Article III, perhaps in conjunction with a temperature effect study on the surface $\text{pK}_a$ values. For weak acids like formic acid, these kinds of free energy calculations with MD require enhanced sampling as provided by, for example, the well-tempered metadynamics method.\textsuperscript{297–299}

In terms of calculation of thermodynamic properties of atmospheric clusters, the four such studies within this thesis raise serious doubts about the predominant ways we treat anharmonicity in atmospheric cluster modeling. First, regardless of whether it is possible to obtain free energies for higher energy conformers, a thorough conformational search for both reactants and products should be used to ensure that the correct global minimum is identified. Secondly, if higher energy conformers can be incorporated, free energy calculations should be performed for all the reactant and product conformers approximately within 16 kJ/mol of the global minima. Finally, all the calculated conformers should be included in the free energy calculations using the correct statistical mechanical formula as presented in Article IV. It should be noted that while the results of this thesis place the impact of global anharmonicity at around 4 kJ/mol for the free energies, it might be substantially larger than this for systems with several low free energy minima.

Pertaining to local anharmonicity, due to the difficulties in its treatment and the unfeasibility of doing a full AD calculation on the intermolecular vibrational modes of large systems, future studies should prioritize including global anharmonicity and only afterwards consider a local anharmonicity treatment with, for example, HDCPT2. The tentative hypothesis
presented in Article V, i.e., that harmonic calculations coupled with a global anharmonicity treatment might give superior results to calculations where standard local anharmonicity methods are coupled with global ones, deserves further study. This line of research could be pursued by looking at the differences of these two approaches in small complexes such as NO·H₂O, (H₂O)₂, H₂O·NH₃, and H₂SO₄·NH₃ where more accurate energy level calculations are already available²⁶¹,3⁰⁰,3⁰¹ or can be performed with relative ease.

This thesis calls for a re-evaluation of the thermodynamic properties published in several recent papers due to their use of the incorrect Boltzmann averaging formula and neglect of the reactant conformations. In this light, a review summarizing the current trends in atmospheric cluster calculations as well as presenting the corrected thermodynamic properties for the wide range of clusters treated in these studies seems warranted.

Regarding the broader atmospheric implications of this work, as mentioned in the Introduction, accurate calculation thermodynamic properties is necessary for the reliable modeling of new particle formation within the atmosphere. As the sulfuric acid containing aerosols potentially impact rain fall, ozone depletion in polar statospheric clouds, and the net radiative forcing due to increased albedo,⁴⁶,⁴⁷ the tools developed in this thesis for the calculations of accurate thermodynamic properties take us a firm step forward in our understanding of the atmosphere. In addition to helping us predict the behaviour of our atmosphere, a thorough knowledge of atmospheric processes also opens up the possibility geoengineering, for example to mitigate the effects of climate change³⁰²
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Appendix