Dynamics of van der Waals Clusters: Theoretical and Computational Studies

Jordan Aleksander Ramilowski
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DYNAMICS OF VAN DER WAALS CLUSTERS:
THEORETICAL AND COMPUTATIONAL STUDIES

by

Jordan Aleksander Ramilowski

A dissertation submitted in partial fulfillment
of the requirements for the degree
of
DOCTOR OF PHILOSOPHY
in
Chemistry

Approved:

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UTAH STATE UNIVERSITY
Logan, Utah

2010
ABSTRACT

Dynamics of van der Waals Clusters:
Theoretical and Computational Studies

by

Jordan Aleksander Ramilowski, Doctor of Philosophy
Utah State University, 2010

Major Professor: Dr. David Farrelly
Department: Chemistry and Biochemistry

The marriage of two very powerful techniques – cryogenic matrix isolation spectroscopy and seeded supersonic molecular beams – has led to the development of a novel type of cryogenic matrix isolation spectroscopy in ultracold, near 0 K, He droplets. The technique known as helium nanodroplet isolation (HENDI) has seen tremendous experimental interest over the past 20 years; this in turn has resulted in the availability of spectroscopic data for many molecules and clusters embedded in He clusters. The experimental findings have motivated a large number of theoretical calculations.

This dissertation focuses on theoretical and computational studies of the rotational dynamics of weakly bound van der Waals clusters with its main theme being the dynamics of molecules and small molecular dimers embedded in superfluid $^4$He nanodroplets.

The single molecular dopant systems studied were clusters of HCN-(He)$_N$, HX-(He)$_N$, where X = F, Cl, Br as well as NH$_3$-(He)$_N$, with $N = 1 \approx 20$. Ground and excited state calculations were performed using the rigid body diffusion Monte Carlo (RBDMC) algorithm. For the excited state calculations a new approach was developed: adiabatic-node DMC (ANDMC).

The ANDMC method was used to study the renormalization of molecular rotational constants in He droplets. It revealed that the dynamics depend on a delicate interplay
between the gas phase rotational constant value and the anisotropies in the potential energy interaction between the He atom and the dopant.

Also presented are the results of the first DMC simulations of the ammonia dimer doped into a small droplet of $^4\text{He}$. Further, a new approach to finding nodal surfaces for DMC simulations was developed that involved using a genetic algorithm (GA). This method was implemented to systematically and automatically compute nodal surfaces of excited states of the HCN-$^4\text{He}$ complex and of the interchange tunneling splitting in the hydrogen-bonded HCl-HCl complex. The classical rotational dynamics of HX-$^4\text{He}$ complexes with X = F, Cl, Br, CN were studied to gain insight into quantum simulations and revealed highly chaotic dynamics for states with $J > 0$. Fractal Weyl law behavior in an open, chaotic Hamiltonian system is the subject of the final chapter.

(205 pages)
ACKNOWLEDGMENTS

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Jordan Ramilowski
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CHAPTER 1

INTRODUCTION

The study of the quantum and classical dynamics of very floppy van der Waals complexes is an area of active research [1–8]. Of particular current interest is the behavior of the weakest possible van der Waals molecules, especially those involving He atoms. Nowadays much of this research is performed inside nanodroplets of liquid $^4\text{He}$ [9].

The experimental study of helium droplets has a long history, possibly extending back to 1908 [10,11]; however, two developments have triggered the recent explosion in the number of experimental and theoretical studies of molecules – or small molecular clusters – seeded into $^4\text{He}$ droplets. The first, in 1992, was the creation of the technology that allowed helium nanodroplets to be used to do cluster isolation spectroscopy [12]. The second was the so-called microscopic Andronikashvili experiment [13,14] in which the effect of the helium environment on the rotational motion of a molecular probe seeded into a $^4\text{He}$ droplet was studied. Surprisingly, in the early Andronikashvili-type experiments using SF$_6$ and OCS probe molecules [14,15], sharp rotational features, characteristic of free (gas-phase) molecular rotation, were observed but with renormalized (reduced) rotational constants. For example, in the case of SF$_6$ the renormalized rotational constant is approximately one-third of its gas phase value. Since these early experiments, many dopant molecules have been studied both experimentally and theoretically [16–20]. One persistent objective of these studies has been to try to relate the extent by which the rotational constants are renormalized to general properties such as (i) the anistropy of the molecule-helium interaction potential, (ii) the local superfluidity of the helium around the molecule, and (iii) whether the rotational constants are large (as in the case of “light rotors,” e.g., HF, H$_2$O, NH$_3$) or small (as in the case of “heavy rotors,” e.g., SF$_6$, OCS). Nevertheless, a clear connection has still not been found between any one of these three factors and the degree of renormalization.

The first calculations of the rotational structure of a molecule in a $^4\text{He}$ cluster were
diffusion Monte Carlo (DMC) simulations for SF$_6$($^4$He)$_N$ clusters [21]. The DMC method is an accurate and straightforward way of finding ground state energies of quantum systems [22]. Although the method is numerically exact for the ground state, this is not the case for excited states [23,24]. Prominent among the various approaches for adapting DMC to the calculation of excited states is the fixed-node method [22,23]. In this algorithm, any DMC walkers that cross a predetermined nodal plane are eliminated. If the exact nodal surface is known in advance, the DMC algorithm can be used to compute excited state energies with good accuracy. Unlike for the ground state, however, fixed node calculations are no longer numerically exact. In general, the fixed-node method is somewhat paradoxical: to compute an excited state its nodal surface must already be known. At times, symmetry or approximations can be used to estimate the topology of the node but no general procedure exists.

Small molecular homo- and heterodimers have also been an active area of study in superfluid helium droplets [25], in particular to study hydrogen bonding [26]. For example, as noted by Lin et al. [27], the ammonia dimer is one of the three textbook examples of hydrogen bonding, the other two being (HF)$_2$ and (H$_2$O)$_2$. Of these three, (NH$_3$)$_2$ has been the most problematic and is, therefore, the most interesting example. Early molecular beam experiments by Odutola et al. [28] discovered the polar nature of the ammonia dimer, which was believed to have a classical hydrogen-bonded structure; i.e., one of the monomers acts as a proton donor with an NH bond pointed towards the lone pair of the other monomer. Subsequent experiments by Nelson et al. [29] contradicted this expectation and suggested a more cyclic structure as opposed to a linear hydrogen-bonded structure. The current consensus seems to be that ammonia dimer is a hydrogen-bonded structure but with the twist that the structure is nonlinear as reflected by the ease with which the the donor/acceptor behavior of the molecules can be interchanged [30]. The uncertainties associated with the structure of the ammonia dimer were part of the motivation for Behrens et al. [26] to study this system in ultra-cold nanodroplets of $^4$He. The main conclusion drawn from their study is that the interchange tunneling splitting (ITS) is quenched considerably, by a factor of
2-5, as compared to the gas phase. This was interpreted as the two ammonia monomers being more equivalent than in the gas-phase which, in turn, suggests a more cyclic structure in a $^4$He droplet.

This dissertation addresses a number of these issues and is organized as follows.

In Chapter 2 the microscopic mechanism of the rapid quantum solvation of HCN is traced directly to angular momentum coupling – and decoupling – between identical bosons and the molecular rotor. This is accomplished using a fixed-node DMC procedure in which a Born-Oppenheimer-like separation of radial and angular motions is used to compute estimates of many-body wavefunction nodal surfaces at each cluster size. Excited rotational states are calculated for HCN($^4$He)$_N$, $N = 1 - 20$, and good agreement is obtained with other calculations. Similar to the situation observed in experiments on CO, HCN-seeded droplets display two series of transitions that correlate with the $a$-type ($\Delta K = 0$) and $b$-type ($\Delta K = \pm 1$), lines of the binary complex HCN-He; here $K$ is the projection of the total angular momentum $J$ on to the molecular symmetry axis. Using an adiabatic nodal approach, physical mechanisms are proposed for the predicted disappearance of the $b$-type series and the rapid convergence of the $a$-type series to the nanodroplet limit as a function of cluster size.

In Chapter 3 DMC calculations are performed for ground and excited rotational states of HX($^4$He)$_N$, complexes with $N \leq 20$ and $X = F, Cl, Br$. The calculations are done using $ab$ initio He-HX intermolecular potentials whose computation is described. Intermolecular energies and He radial and angular probability density distributions are computed as a function of the number of solvent atoms. Excited states are calculated using fixed-node DMC methods, and molecule-solvent angular momentum coupling is studied as a function of cluster size and potential anisotropy. Nodal surfaces of the many-body wave function are computed approximately by making an adiabatic Born-Oppenheimer-like separation of radial and angular degrees of freedom of the cluster. The procedure is then extended to include radial dependencies in the adiabatic nodal function. This study predicts that the observed decrease in the gas-phase rotational constants for HCl and HBr in a $^4$He nan-
odroplet will be smaller than that observed for HF, despite HF having the largest (by far) gas-phase rotational constant of the three molecules. This suggests that the specifics of the solvation dynamics of a molecule in a $^4$He cluster are the result of a delicate interplay between the magnitude of the gas-phase rotational constant of the molecule and the anisotropic contributions to the atom-molecule potential energy.

In Chapter 4 the solvation dynamics of an ammonia molecule doped into a droplet of $^4$He containing $N = 1 - 25$ $^4$He atoms are studied using the DMC method. Excited states are computed using the adiabatic fixed-node procedure. The computed renormalization (a reduction of $\approx 5\%$) of the rotational constants of the ammonia molecule is in quantitative agreement with the recent experiments of Slipchenko and Vilesov [31] and disagrees with the much larger renormalization (a reduction of $\approx 25\%$) originally reported by Behrens et al. [32]. For the symmetric top ammonia molecule it was predicted that the asymptotic limit is not reached until $N > 25$; this is similar to the case for the linear molecules HF, HCl and HBr, which also have relatively large rotational constants. These results were interpreted as providing support for the prediction that rotors with large rotational constants should (i) exhibit a smaller renormalization of their moments of inertia and (ii) exhibit a slower rate of renormalization as a function of $N$ as compared to heavy rotors.

In Chapter 5 the DMC method is used to study the interchange tunneling of $(\text{NH}_3)_2$ embedded in $^4$He clusters. The interchange tunneling splittings are reported as a function of the number of $^4$He atoms in the droplet. The results are in agreement with previous experimental findings by Behrens et al. [26], which indicate that the presence of helium impedes the large amplitude interchange tunneling motion. This suggests a structure in which the two ammonia monomers are more equivalent in the droplet than in the free gas phase dimer.

In Chapter 6 the utility of a genetic algorithm is investigated to systematically and automatically compute nodal surfaces for use in fixed-node DMC calculations. Application is made to the computation of excited states of the HCN-$^4$He complex and to the computation of tunneling splittings in the hydrogen-bonded HCl-HCl complex.
In Chapter 7 the classical rotational dynamics of a series of van der Waals complexes $\text{HX}^-\text{He}$ with $X = \text{F}, \text{Cl}, \text{Br}, \text{CN}$ are studied. In all cases, the ground state dynamics are found to be almost entirely chaotic, in sharp contrast to other floppy complexes, such as $\text{HCl-Ar}$, for which chaos sets in only at relatively high energies. The consequences of this result for quantum solvation in liquid helium are discussed. Also investigated are rotationally excited states with $J = 1$ which, except for $\text{HCN}^-\text{He}$, are actually resonances that decay by rotational pre-dissociation.

Chapter 8 presents a theoretical study of the semiclassical dynamics of a model of rotational dynamics in an open Hamiltonian system, one that contains no bound states. This was motivated by the recognition that, as noted, $J > 0$ states of many helium-containing complexes are resonances. Additionally, fractal Weyl law behavior is shown in this system, which is described by a smooth potential and supports numerous above-barrier resonances. This behavior holds even relatively far away from the classical limit. The complex resonance wave functions are found to be localized on the fractal classical repeller.
CHAPTER 2
QUANTUM SOLVATION DYNAMICS OF HCN IN A $^4\text{He}$ DROPLET

Abstract

Ultracold nanodroplets of $^4\text{He}$, containing several thousands of He atoms, offer considerable promise as microscopic cryogenic chambers. Potential applications include the creation of tailor-made chemical or biomolecular complexes and studies of superfluidity in nanoscale systems. Recent experiments have succeeded in interrogating droplets of quantum solvent that consist of as few as 1 − 20 $^4\text{He}$ atoms and contain a single solute molecule. This allows the transition from a floppy, but essentially molecular, complex to a dissolved molecule to be followed and, surprisingly, the transition is found to occur quite rapidly, in some cases for as few as $N = 7 − 20$ solvent atoms. For example, in experiments on $^4\text{He}$ droplets seeded with CO molecules [Tang and McKellar, J. Chem. Phys. 119, 754 (2003)], two series of transitions are observed that correlate with the $a$-type ($\Delta K = 0$) and $b$-type ($\Delta K = \pm 1$) lines of the binary complex CO-He ($K$ is the quantum number associated with the projection of the total angular momentum onto the vector connecting the atom and the molecular center of mass). The $a$-type series, which evolves from the end-over-end rotational motion of the CO-He binary complex, saturates to the nanodroplet limit for as few as 10 − 15 $^4\text{He}$ atom; the effective moment of inertia of the molecule converges to its asymptotic (solvated) value quite rapidly. In contrast, the $b$-type series, which evolves from the free-molecule rotational mode, disappears altogether for $N \approx 7$ atoms. Similar behavior is observed in recent computational studies of HCN($^4\text{He}$)$_N$ droplets [Paolini et al., J. Chem. Phys. 123, 114306 (2005)]. In this article the quantum solvation of HCN in small $^4\text{He}$ droplets is studied using a new fixed-node diffusion Monte Carlo (DMC) procedure. In this approach, a Born-Oppenheimer-type separation of radial and angular motions is introduced as a means of computing nodal surfaces of the many-body wavefunctions that are required in the fixed-

node DMC method. Excited rotational energies are calculated for HCN(\(^{4}\)He)\(_N\), \(N = 1 - 20\); the adiabatic node approach also allows concrete physical mechanisms to be proposed for the predicted disappearance of the \(b\)-type series as well as the rapid convergence of the \(a\)-type series to the nanodroplet limit with increasing \(N\). The behavior of the \(a\)-type series is traced directly to the mechanics of angular momentum coupling and decoupling between identical bosons and the molecular rotor. For very small values of \(N\) there exists significant angular momentum coupling between the molecule and the He atoms; at \(N \approx 10\) solvation appears to be complete as evidenced by significant decoupling of the molecule and solvent angular momenta. The vanishing of the \(b\)-type series is predicted to be a result of increasing He-He repulsion as the number of solvent atoms increases.

2.1 Introduction

A molecule dissolved in a liquid is not normally expected to rotate freely as it might in the gas phase. However, in an ultra-cold (\(T \approx 0.37\) K) droplet of \(^{4}\)He atoms, coherent molecular rotation over many periods is not only possible, it appears to be the norm [11, 14, 18, 19, 33–39]. The gentleness of this unique quantum solvent opens up the possibility of employing superfluid \(^{4}\)He-droplets as ultra-clean nano-laboratories for making and characterizing novel species [35], (e.g., nanoscale oligomers [38] or complexes of bio-molecules [19]). Because solvated molecules can serve as antennae with which to relay information to and from the droplet; (e.g., structural information about species being formed in the droplet [35] or information about the onset of superfluidity as a function of droplet size [14, 40]), it is critical to understand how molecules become solvated in a quantum solvent. However, a major shortcoming of the helium-droplet matrix method remains the generally large, and as yet little understood, apparent increase in the moments of inertia of solvated molecules as compared to their gas-phase values [11, 18, 19].

A good working definition of quantum solvation is that dissolved molecules are coated by a solvation shell with which they exchange little or no angular momentum. This circumstance allows for effectively free rotational motion, albeit with altered spectroscopic constants [11, 21, 41, 42]. Recent experiments advances have allowed the solvent to be built
up atom by atom [34,36,37] and have shown that the transition from a “molecular complex” to a “dissolved molecule” can occur rapidly as a function of cluster size; (e.g., for $N \approx 7-12$ in $N_2O( ^4 \text{He})_N$ clusters [37]).

The first calculations of the rotational structure of a molecule seeded in a $^4\text{He}$ cluster were DMC simulations for $\text{SF}_6( ^4\text{He})_N$ clusters [21]. These calculations reproduced the decrease in the rotational constant and led to a physical explanation for the origin of this effect: Essentially, a fraction of the He density in the droplet follows the relatively slow rotation of the $\text{SF}_6$ molecule adiabatically [18,21,39,41,43]. In “adiabatic following,” the observed decrease in the rotational constant is expected to correlate roughly inversely with $B_0$. However, an explicit caveat was added [21]; the extent of adiabatic following will be significantly modulated by the anisotropy of the molecule-He interaction potential.

The expectation has, nevertheless, developed that the observed reduction in rotational constant can be related to crude parameters such as rotational constant, molecular weight or the size of the potential anisotropy. For example, Paolini et al. [42] compare the solvation dynamics of light versus heavy molecular rotors to understand how molecular weight and potential anisotropy affect the extent of adiabatic following. Despite these (and earlier) simulations [21,36,42–45], the underlying physics remains poorly understood. For example, the putative view that, in general, light rotors (e.g., HCN) solvate slowly ($N \gtrapprox 20$) whereas heavy rotors (e.g., OCS) solvate quickly ($N \approx 10-20$) [19,41] has been challenged [42] as being precisely the opposite of the actual situation. Reptation Monte Carlo (RMC) calculations for HCN($^4\text{He})_N$ clusters suggest solvation as early as $N \approx 10$ [42] in contrast to earlier predictions that the nanodroplet limit would not yet be achieved at $N = 25$ [46].

The success of experimental studies [34,36,37] that start from a molecular point of view suggests that analogous theoretical approaches might be fruitful. Here such a view is adopted and used to investigate the solvation of an HCN molecule in a $^4\text{He}_N$ droplet with $N = 1-20$. Our particular focus is the extent and nature of angular momentum coupling between bosonic $^4\text{He}$ atoms and HCN as a function of cluster size. For HCN-seeded droplets two series of transitions have been predicted [42] that correlate with the
a-type ($\Delta K = 0$) and $b$-type ($\Delta K = \pm 1$) lines of the binary complex, HCN-He [42, 47]; here $K$ is the projection of the total angular momentum $J$ on to the molecular symmetry axis. This is rather similar to the situation observed experimentally for CO, where two series of lines are also observed; in the CO-He binary complex the $b$-type series disappears abruptly [45, 48] while the $a$-type series rapidly settles down to the nanodroplet limit. This behavior is addressed using fixed-node DMC methods, [21] which have the important advantage of providing direct knowledge of the many-body wavefunction. Nodal topologies are estimated using an adiabatic (Born-Oppenheimer-like [49]) separation of radial and angular motions at each cluster size.

The paper is organized as follows: Sec. 2.2 introduces the Hamiltonian and potential energy surface for the HCN-He binary complex. Because the potential is anisotropic, the molecular rotational and He orbital angular momentum are not separately conserved. Thus a state labeling scheme is introduced that correlates with a hypothetical (but useful) situation: the HCN-He binary with an isotropic interaction potential for which the rotor and atomic angular momenta are separately conserved. In Sec. 2.2 coupled-channel and matrix diagonalization methods are employed to compute ground and excited state energy levels and wavefunctions. These results serve as benchmarks with which to compare DMC computations and also provide important information about the nodal topologies of the wavefunctions. In Sec. 2.3 the DMC approach is described. To compute excited states using DMC methods, knowledge of the nodal topology of the wavefunction is needed. This is a difficult problem, in general, although it can sometimes be solved using known symmetries of the system. For many-body molecule-$^4$He$_N$ clusters, however, it is necessary to resort to approximations. A new approach to computing nodes is described in which estimates of nodal surfaces are obtained using a Born-Oppenheimer-like separation of radial and angular motions [49]. For the binary HCN-He complex, a direct comparison is made between adiabatic and accurate nodal topologies. The results of using this procedure – adiabatic node diffusion Monte Carlo (ANDMC) – are presented in Sec. 2.4 and are shown to provide a physical explanation for (i) the convergence of the $a$-type series to the asymptotic limit
and (ii) the disappearance of the \( b \)-type series as previously reported in RMC simulations. Conclusions are in Sec. 2.5.

2.2 Hamiltonian

In the space-fixed frame, the Hamiltonian for \( N \) He atoms interacting with an HCN molecule (treated as a linear rigid rotor) is:

\[
H = -\frac{\hbar^2}{2M} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + B_0 j^2 + \sum_{i<j}^{N} V_{He}(r_{ij}) + \sum_{i=1}^{N} V(R_{iI}, \Theta_{iI}) \quad (2.1)
\]

where \( r_{ij} \) and \( R_{iI} \) denote He-He and He-molecule separations respectively; \( \Theta_{iI} \) is the angle between the molecular axis and the \( i \)’th He atom (for \( N = 1; R_{iI} \rightarrow R; \Theta_{iI} \rightarrow \Theta \)); \( M = 27.011 \) amu and \( m = 4.00260 \) amu are the masses of HCN and He, respectively. \( V_{He}(r_{ij}) \) and \( V(R_{iI}, \Theta_{iI}) \) are the He-He [50] and the HCN-He [51] potential energy surfaces (PESs), respectively. The molecular rotational angular momentum operator is \( j \) and, for HCN, \( B_0 = 1.478 \ 221 \ 834 \ \text{cm}^{-1} \). All DMC calculations were done in the rigid-body approximation [21, 52].

2.2.1 Potential energy surfaces

All the calculations were done using pairwise molecule-He and He-He interaction potentials. The He-He PES of Aziz \et al. was used [50]. This potential is simply a function of the distance between any two He atoms. Several HCN-He potentials exist in the literature, each of which leads to slightly different spectra [47, 51, 53, 54]. The only completely \textit{ab initio} PES is that of Toczyłowski \et al. [51]. The PES in Refs. [53] and [54] use observed microwave and millimeter-wave transitions of the HCN-He complex to refine their surfaces. The 1E8 and 2E8 potential energy surfaces of Atkins and Hutson [53] have significantly deeper wells than the \textit{ab initio} surface of Drucker \et al. but both forms reproduce the spectroscopic data with similar accuracy. The potential of Harada \et al. [54] starts from the PES of Toczyłowski \et al. [51] and scales the well depth and radial separation to improve agreement with spectroscopic data. Recent molecular scattering calculations [55] for the
He-HCN system suggest that the Harada potential *et al.* [54] provides the best agreement with the observed spectrum of the bound complex, whereas the 1E8 potential (which has been used in previous Monte Carlo studies [42, 46]) provides the poorest agreement. The Harada *et al.* [54] and Toczylowski *et al.* [51] PESs provide similar predictions for pressure broadening and frequency shifts. Generally, the 2E8, Harada and Toczylowski provide comparable agreement with each other in reproducing spectroscopic data. In the current study the potential of Toczyowski *et al.* [51] is used.

### 2.2.2 Isotropic binary complex

If the molecule-^4^He interaction potential is isotropic, the molecular rotational angular momentum and the atomic orbital angular momentum quantum numbers, \( j \) and \( \ell \), respectively, are separately conserved; for the isotropic binary complex (IBC) the labeling scheme \([j\ell J]\) is exact. For the IBC, the molecular part of the wavefunction is the Wigner rotation matrix \( D_{m_{j_{k}}}(\alpha, \beta, \gamma) \) where \( \alpha, \beta, \gamma \) are Euler angles and the atomic part is a spherical harmonic \( Y_{m_{\ell}}^{m_{j}}(\theta, \phi) \) where \( \theta \) and \( \phi \) are the usual spherical polar angles in the space-fixed frame and \( m_{j} \) and \( m_{\ell} \) label the magnetic numbers corresponding to \( j_{z} \) and \( \ell_{z} \). This labeling scheme is introduced because, in later discussion of nodal surfaces, it will be necessary to refer to nodal surfaces of the IBC. For example, the nodal functions for the isotropic states are \( \Psi_{iso}^{(a)} = \cos \theta \) and \( \Psi_{iso}^{(b)} = \cos \beta \). While it is legitimate to refer to the nodal function \( \Psi_{iso}^{(b)} \) as the “free-rotor” node because this node is identical to that of the free molecule, analogous terminology for \( \Psi_{iso}^{(a)} \) is inappropriate because the orbital angular momentum of the atom has to be referred to some center – in this case the center-of-mass (c.o.m) of the molecule. Thus this node is neither a “free-atom” nor a “free-rotor” node. The IBC limit thus provides a precise labeling scheme with which to correlate the levels of the anisotropic binary complex.

In this notation, the \( a \)- and \( b \)-type series correspond to the transitions \((0,1,1) \leftarrow (0,0,0)\) and \((1,0,1) \leftarrow (0,0,0)\) respectively [47, 53]. For simplicity, the anisotropic states that correlate with the IBC states \(|011\rangle\) and \(|101\rangle\) will be referred to as \(|a\rangle\) and \(|b\rangle\), respectively (see Table 2.1).
2.2.3 Energy levels and wavefunctions

To test our DMC procedure, it is useful to have accurate eigenvalues and eigenstates of the binary complex, HCN-He, to hand. In particular, knowing the topology of the binary eigenfunctions is invaluable for generating estimates of the nodal surfaces needed for excited-state DMC calculations. Accurate eigenvalues were computed in two ways: (i) coupled-channel (CC) calculations using the BOUND computer program and (ii) matrix diagonalization using a product basis as will be described.

Coupled-channel calculations

To implement the BOUND procedure, the potential is expanded in Legendre polynomials

\[ V(R, \Theta) = \sum_{\lambda} v_\lambda(R) P_\lambda(\cos \Theta). \]  (2.2)

The expansion was truncated at \( \lambda = 12 \) and the quality of the expansion was checked by comparing contour plots of the accurate potential with those obtained from the expansion. The radial expansion functions were generated using Gauss-Legendre quadrature. CC results for several eigenvalues with \( J = 0 \) and \( J = 1 \) are shown in Table 2.1.

Matrix diagonalization

Previous DMC calculations have indicated that the nodal functions of the IBC do not provide good eigenvalues for the \( |b\rangle \) states, which implies that the actual node of the \( |b\rangle \) state is significantly different from that of the free-rotor. To gain insight into the distortion of the IBC nodal topologies due to the potential anisotropy, accurate eigenfunctions for the binary complex were computed using a basis set that is a product of \( |\text{radial}\rangle \times |\text{angular}\rangle \) functions. The total wavefunction is expanded

\[ \Psi = R^{-1} \sum_{a} c_{J,\ell,M}^{a} \Phi_{J,\ell,M}^{a}(\Omega, \theta, \phi) \chi^{(n)}(R) \]  (2.3)

where \( R \) is the intermolecular distance; \( \Omega \) are the angular coordinates of the molecule (i.e., the set of Euler angles), \((\theta, \phi)\) are the spherical polar angular coordinates of the atom and
\{c_{j,\ell}^{JM}\} are expansion coefficients. The radial basis functions, \(\chi^{(n)}(R)\), where \(n\) is the radial quantum number, were chosen to be Morse eigenfunctions. The Morse parameters were obtained by fitting a Morse potential

\[
V_M(R) = D_0 \{1 - \exp[-a(R - R_0)]\}^2 - D_0
\]

(2.4)
to the radial expansion function \(v_0(R)\) in Eq. (2.2). The parameters so obtained are \(a = 0.95\) bohr\(^{-1}\), \(R_0 = 7.29\) bohr and \(D_0 = 20.35\) cm\(^{-1}\). The angular basis functions \(\Phi_{j,\ell}^{JM}(\Omega, \theta, \phi)\) are defined as follows

\[
\Phi_{j,\ell}^{JM}(\Omega, \theta, \phi) = \sum_{m_j, m_\ell} (-1)^{j-\ell+M} \sqrt{2J+1} \begin{pmatrix} j & \ell & J \\ m_j & m_\ell & -M \end{pmatrix} Y_j^{m_j}(\Omega) Y_\ell^{m_\ell}(\theta, \phi)
\]

(2.5)

where \(
\begin{pmatrix} \ldots \\ \ldots \end{pmatrix}
\) is a Wigner 3-\(j\) symbol and \(Y_j^{m_j}(\Omega)\) and \(Y_\ell^{m_\ell}(\theta, \phi)\) are Spherical Harmonics. Using the expansion in Eq. (2.2), the matrix elements of the potential can be expressed in closed form in terms of Percival-Seaton coefficients. The size of the basis is determined by the maximum size of \(j = j_{max}\) for a given \(J\). Convergence was achieved using \(n = j_{max} = 16\). The matrix diagonalization results in Table 2.1 compare favorably with CC and literature values for states with \(J = 0, 1\) [51,56].

2.3 Diffusion Monte Carlo

DMC calculations were done using the rigid-body diffusion Monte Carlo (RBDMC) method originally developed by Buch [52] and later extended [21,57]. This procedure reduces the number of degrees-of-freedom and allows larger diffusive time steps to be used. The RBDMC approximation is possible for weakly bound complexes (e.g., van der Waals complexes) because of the large disparity in the strengths of the intramolecular and inter-
molecular forces. That is, the HCN molecule can be treated as a rigid rotor. The RBDMC method has been described in detail elsewhere [52, 57, 58]. The basic idea is to recognize that for “small” rotations the rotational energy propagator is analogous to the translational kinetic energy propagator with a diffusion constant $D_R = 1/2I$ where $I$ is the moment of inertia of the molecule. This procedure takes advantage of the fact that components of angular momentum commute for sufficiently small rotations. In the current application, all translations and rotations are made in the space-fixed Cartesian frame, (i.e., rotational moves are done around a set of axes originating in the molecular c.o.m. and aligned with the space-fixed axes). However, this is only possible for spherical top and linear molecules; in the case of symmetric and asymmetric tops, the rotational moves must be made around the principal axes of the molecule.

In RBDMC excited rotational states can be computed using the fixed-node method [23, 59]; in its simplest form this involves “killing” walkers that cross nodal surfaces. In practice, importance sampling is used in which the nodal structure is built into the trial wavefunction. The most immediate problem is how to obtain estimates of the nodal surfaces of the (a priori unknown) excited state wavefunctions.

2.3.1 Adiabatic nodal surfaces

In the original calculations for SF$_6$ it was assumed that the nodal surface were well approximated by the nodal functions of the free rotor. In practice, this produced excellent agreement with experimental results and, for the binary complex, with accurate CC computations [21]. However, subsequent DMC calculations using free-rotor nodal surfaces, (e.g., for HCN-He), have failed to provide accurate results, even for the binary complex [46]. This failure was attributed to poor estimates of the actual nodal topologies. This is confirmed in Table 2.1 which shows the results of DMC calculations using the “isotropic” nodal functions, $\Psi_{\text{iso}}^{(a,b)}$. Nodes of the IBC lead to good results for the $|a\rangle$ state but fail for the $|b\rangle$ state. To understand the actual nodal topology, accurate wavefunctions for the binary complex were calculated using the MD procedure already described.

Various sections through the probability densities corresponding to the $|a\rangle$ and $|b\rangle$
states are shown in Fig. 2.1. The plots do not vary greatly with the relative azimuthal angle. Note that, even though the potential does not depend on the azimuthal angle, because the molecule is free to rotate the wavefunctions will, in general, depend explicitly on angles $\alpha$ and $\phi$. Whereas in the ground $|a\rangle$ and excited $|b\rangle$ states (Fig. 2.1) the He density is localized at the H end of the molecule, with $R \approx 8$ bohr, in the $|b\rangle$ state the complex has a more T-shaped geometry and the atom lies somewhat closer to the molecular c.o.m. Furthermore, the nodal topology is quite noticeably distorted from that of the isotropic complex (i.e., $\beta = \pi/2$).

The topologies of the wavefunctions can best be understood by considering the expansion of the PES in Legendre polynomials in Eq. (2.2). Plots of the three dominant $v_\lambda(R)$-functions are shown in Fig. 2.2. Note that the anisotropic terms arising from $P_1$ and $P_2$ cross at a value of $R$ very close to the maximum of the $b$-type density – (see the inset). The $P_1$ term mixes zero-order basis states with $\Delta j, \Delta \ell = \pm 1$ and to lowest order, the $a$- and $b$-type states have the form $|a\rangle = c_1 |011\rangle + c_2 |101\rangle$, $|b\rangle = -c_2 |011\rangle + c_1 |101\rangle$ with $c_1^2 + c_2^2 = 1$ and $c_1 >> c_2$. The $P_2$ anisotropy leads to admixtures containing $|211\rangle$ and $|121\rangle$, etc. and this is responsible for the approximately T-shaped geometry in Fig. 2.1 (b). Hutson [2] provides a thorough discussion of the effect of the sign and magnitude of the various anisotropies on the geometry of the complex.

Unlike for SF$_6$-He [21], the wavefunction is not approximately separable into $|\text{molecule}\rangle \times |\text{atom}\rangle$ ruling out the use of isotropic nodes. However, good estimates for nodal surfaces can be obtained from an adiabatic separation of radial and angular motions. This approximation was first developed by Holmgren et al. [49], who used a Born-Oppenheimer angular-radial separation (BOARS) in the molecule fixed frame. In BOARS, the radial degree of freedom of frozen ar $R = R_0$ and the angular part of the resulting Schrödinger equation is then solved; this is repeated for different values of $R_0$, which generates families of adiabatic radial potentials. As in the conventional Born-Oppenheimer approximation, the adiabatic potentials are then used to solve for the radial wavefunctions. Various modifications to this method have been developed, such as the inclusion of non-adiabatic corrections [60].
The BOARS approach is rarely used in contemporary work because it is straightforward to solve the Schrödinger equation for binary complexes using coupled-channel approaches. However, as will be demonstrated, it provides a useful way of generating good estimates of nodal surfaces for small molecule-He clusters. The method is computationally quite efficient for small clusters because the angular matrix elements can be computed analytically or semi-analytically [2,61].

Here the BOARS method is extended by (i) applying it in the space-fixed frame and (ii) applying it to clusters containing more than a single atom. In this approach, the following approximations are made: (i) ignore He-He interactions (for the ground state with \( N = 10 \), these contribute < 4% to the energy), (ii) fix \( R = R_0 \), (iii) pin the molecular c.o.m. in place.

To illustrate the procedure, consider the binary complex for which the wavefunction is approximated

\[
\psi_{\text{bend}} = \lambda(\Omega, \theta, \phi; R)\rho^{(n_j \ell J)}(R)
\]  

(2.6)

where the angular functions \( \lambda(\Omega, \theta, \phi; R) \) depend parametrically on \( R \) in analogy with the Born-Oppenheimer approximation and \( \rho^{(n_j \ell J)}(R) \) is a radial function. The angular functions are eigenfunctions of the Hamiltonian

\[
H_{\text{rot}} = B_0 J^2 + \frac{l^2}{2mR_0^2} + V(R_0, \Theta).
\]  

(2.7)

This approach differs from the usual BOARS procedure in that the molecular c.o.m. has been clamped and so the \(^4\text{He} \) mass, \( m \), appears rather than the reduced mass, \( \mu \). This is done to the method so that it can be extended to treat more than a single \(^4\text{He} \) atom. In practice, the nodal topology is relatively insensitive to using \( m \) or \( \mu \). Solving Eq. (2.7) at a series of \( R_0 \) values yields a set of effective potentials, \( U^{j,\ell,J} \) for the radial motion. These potentials, two of which are illustrated in Fig. 2.3, are then used solve for the radial functions \( \rho^{(n_j \ell J)}(R) \) and eigenstates. The lowest such radial eigenfunction in the \( J = 1 \) manifold is also illustrated in Fig. 2.3. This procedure leads to eigenvalues for the \(|a\rangle \) and \(|b\rangle \) states.
of -7.84 cm\(^{-1}\) and -5.35 cm\(^{-1}\), which are in moderately good agreement with the accurate results in Table 2.1. However, the point of this approach is to generate good estimates of nodal topologies rather than to estimate eigenvalues. Fig. 2.4 compares the adiabatic and accurate nodal topologies directly and good agreement is observed.

The generalization of Eq. (2.7) to more than a single He atom, neglecting He-He interactions, is the following

\[ H_{rot} = B_0 j^2 + \sum_{i=1}^{N} \kappa l_i^2 + \sum_{i=1}^{N} V(R_0, \Theta_{iI}) \]  

(2.8)

where \( \kappa = 1/2mR_0^2 \). Diagonalizing \( H_{rot} \) at fixed \( J \) and \( N \) thus produces estimates for the nodes. The value of \( R_0 \) was chosen to be the minimum of the appropriate adiabatic radial potential. For the binary, as noted, adiabatic separation in the body-fixed frame is also possible [49] and yields similar results. However, for more than a single He atom it is necessary to perform the adiabatic separation in the space-fixed frame.

2.3.2 Diagonalization of \( H_{rot} \) for \( N \) He atoms

To diagonalize \( H_{rot} \), it is first necessary to develop an appropriate set of basis functions. Because the total angular momentum quantum number \( J \) and its projection on the space-fixed axes are conserved, a reduced basis is employed that has fixed values of \( J \) and \( M \), in analogy with Eq. (2.5). Essentially the problem reduces to the coupling of an arbitrary number of angular momenta. Assume, for illustration, that four (rotor + three He atoms) angular momenta are involved: \( j, l_1, l_2, l_3 \) where the quantum numbers \( j, m_j \) refer to the rotor and \( \ell_i, m_i, i = 2, 3, 4 \) to the three He atoms. First it is necessary to form intermediate angular momenta. Because the He atoms are equivalent, the angular momentum coupling scheme is as follows: Form the intermediate angular momenta \( l_{12} = l_1 + l_2, l_{123} = l_{12} + l_3 \) and then form the total angular momentum \( J = j + l_{123} \). The basis functions can then be expressed in terms of generalized Clebsch-Gordan coefficients. For example, for \( N = 3 \) the
basis functions can be written [62–65]

\[
\psi_{j_1\ell_1\ell_2\ell_3\ell_12}^{JM} = \sum_{m_j,m_1,m_2,m_3} C(\ell_1m_1...\ell_123m_123jm_jJM) \\
\times Y_j^{m_j}(\Omega_j) Y_{\ell_1}^{m_1}(\Omega_1) Y_{\ell_2}^{m_2}(\Omega_2) Y_{\ell_3}^{m_3}(\Omega_3)
\]  

(2.9)

where \(C(\ell_1m_1...\ell_123m_123jm_jJM)\) is a generalized Clebsch-Gordan coefficient [62] and \(\Omega_{j,i}\) refer to the space-fixed coordinates of the several rotors. Explicitly–

\[
C(jm_j\ell_1m_1\ell_2m_2\ell_3m_3\ell_12m_123m_123JM) = \sum_{m_{12},m_{123}} (-1)^{\ell_12-m_{12}+\ell_123-m_{123}} \\
\times \begin{pmatrix}
\ell_1 & \ell_2 & \ell_12 \\
m_1 & m_2 & -m_{12}
\end{pmatrix} \\
\times \begin{pmatrix}
\ell_3 & \ell_12 & \ell_123 \\
m_3 & m_{12} & -m_{123}
\end{pmatrix} \\
\times \begin{pmatrix}
j & \ell_123 & J \\
m_j & m_{123} & -M
\end{pmatrix}
\]  

(2.10)

Employing Eq. (2.2), the matrix elements of \(H_{\text{rot}}\) are computed using the Wigner-Eckhardt theorem [2,62,65].

2.3.3 Importance sampling in the space-fixed frame

Importance sampling, in which a trial wavefunction, \(\Psi_T\), is introduced to guide the diffusion, improves the efficiency of the DMC method and, in general, reduces the size of the error bars on the computed energies [23]. Further, unless importance sampling is used,
He clusters might undergo unphysical dissociation for larger cluster sizes. In importance sampling the trial wavefunction leads to a diffusion-like equation for the mixed function \( f(R, r_i) = \Psi(R, r_i)\Psi_T(R, r_i) \) where \( R \) and \( r_i \) are the molecular and He atom coordinates, respectively. In particular, additional drift terms (quantum forces) are introduced into the diffusive process, which guide the walkers to regions of high probability density. The first application of importance sampling within the RBDMC context was made in Ref. [21] and a thorough review of this method is provided by Viel et al. [58].

In this work, trial wavefunctions were chosen to have the form

\[
\psi_T = \left\{ \prod_{i=1}^{N} f(R_i) \prod_{i \neq j}^{N} \Xi(r_{ij}) \right\} \Upsilon(\Omega, \theta_i, \phi_i) \tag{2.11}
\]

where \( R_i \) is the radial distance from the molecular c.o.m. to He-atom \( i \) and \( r_{ij} \) is the distance between He atoms \( i \) and \( j \). As in previous work [21,46] the radial functions were chosen to have the form

\[
f(R) = b \exp \left(-\frac{c}{R^5} - aR\right) \tag{2.12}
\]

where the parameters \( a, b, c \) were obtained by fitting the function \( f(R) \) to (i) accurate binary wavefunctions obtained from MD or (ii) adiabatic radial functions obtained as described previously. The two approaches provided essentially identical results. For ground state calculations, the angular function \( \Upsilon(\Omega, \theta_i, \phi_i) \) was set to unity whereas for excited states this function was obtained from diagonalizing Eq. (2.8), (i.e., it contained the nodal topology). The He-He part of the trial wavefunction, \( \Xi(r_{ij}) \), was the same as used in previous studies [21,46].

2.4 Results

A comparison between DMC results obtained using adiabatic and accurate nodal functions for the binary complex is made in Table 2.1. For \( N = 1 \), adiabatic nodes substantially improve DMC estimates for the \( b \)-type state as compared to the “free-rotor” (IBC) node [46].
Fig. 2.3 shows energies obtained using adiabatic nodes for \( N = 1 - 20 \). As additional \(^4\)He atoms are added, the Bose symmetry of the wavefunction must be taken into account (i.e., symmetric linear combinations of the functions in Eq. (2.9) need to be formed). Rotational energies for \( N \leq 4 \) (and for the \( a \)-type state, \( N = 7 \)) using adiabatic nodes obtained this way are shown in Fig. 2.3, and they agree quite well with previous results from RMC calculations [42] and, for \( N < 10 \) with the projection operator imaginary time Schrödinger equation (POITSE) method [46]. Beyond \( N = 4 \) it becomes increasingly difficult to compute adiabatic nodes because of the very rapid growth in basis size. Further, the \( b \)-type state becomes harder to identify because of extensive mixing with higher energy states. However, the form of the eigenvectors for \( N \leq 4 \) and the fact that the molecule couples identically to each atom suggests an additional approximation best suited for the \( a \)-type states.

2.4.1 Two-level approximation for the \( a \)-type series

With \( N = 1, J = 1 \) the dominant states are \( |011\rangle \) and \( |101\rangle \): For \( N \) He atoms \( |011\rangle \) is replaced by a symmetric linear combination of states having a single quantum of angular momentum permuted over the \( N \) He atoms, (e.g., \( |j\ell_1\ell_2\ell_3\ell_12\ell_123JM\rangle = |01001JM\rangle \)). Denoting these normalized states by \( |s\rangle /\sqrt{N} \) and those of the form \( |10\ldots00\ldots0JM\rangle \) by \( |j\rangle \) the eigenvector mixtures to lowest order are the same as for \( N = 1 \), for example,

\[
|a\rangle \approx \frac{c_1}{\sqrt{N}} |s\rangle + c_2 |j\rangle
\]  

(2.13)

and similarly for \( |b\rangle \). In this approximation, the nodal functions simplify to

\[
\psi_{node}^{(a)} \approx c_2 \cos \beta + \sum_{i=1}^{N} \sqrt{\frac{1-c_2^2}{N}} \cos \theta_i.
\]  

(2.14)

The factor of \( 1/\sqrt{N} \) diminishes the contribution of each individual He atom as \( N \) increases. Further, as \( N \) increases the sum of cosines will, on average, cancel out and the molecular
and solvent nodal function decouple. This “two-level” approximation agrees rather well with DMC calculations using adiabatic nodes (Fig. 2.3), and the $a$-type states converge rapidly to the asymptotic (nanodroplet) limit [39]. The initial decline observed for the $a$-states agrees qualitatively with projection operator results [46], although this trend is not captured in RMC studies [42]. While exchange symmetry has been implicated in the approach to solvation, [21, 66] these results identify the specific microscopic mechanism of wavefunction decoupling that leads to quantum solvation. For fermionic $^3$He atoms antisymmetric wavefunctions will have to be constructed (e.g., as Slater determinants). It is apparent that this will involve progressively higher He atom angular momentum states and a clean uncoupling of solvent, and solute will not occur [14].

### 2.4.2 $b$-type series

At this point something of a paradox arises; by the above arguments, the $|b\rangle$ states should also approach the free-rotor limit. In fact, this happens in the “two-level” nodal approximation. However, in RMC calculations the $b$-type series increases in energy and vanishes altogether at $N \approx 7$ [42]. This is similar to experimental observations of CO seeded clusters. Recall that the $b$-type state for $N = 1$ is approximately T-shaped and lies relatively close to the molecular c.o.m. Initially, as He atoms are added, the important He-He interactions are, primarily, attractive; For example, these forces cause clumping of the atoms which, given the T-shape of the $b$-type state – (see Fig. 2.1 b) – give rise to a “longitudinal asymmetry” as discovered in RMC calculations [42, 45]. As more atoms are added, the roughly torus-shaped region of He density becomes crowded – closest packing suggests $\approx 7–8$ atoms will fit into this ring. Consequently, the torus starts to expand and samples the region where $v_1$ and $v_2$ become most strongly negative – (see Fig. 2.2).

This effect cannot be captured directly in the adiabatic Hamiltonian of Eq. (2.3) because He-He interactions are there neglected (but not in the DMC simulations). However, it is possible to simulate this effect as follows: (i) For the binary complex, replace the repulsive branch only of $v_0$ with a Morse potential $V_M(R) = D_0\{1-\exp[-a(R-R_0)]\}^2-D_0$ with $a = a_0 = 0.95 \text{ bohr}^{-1}$, $R_0 = 7.29 \text{ bohr}$ and $D_0 = 20.35 \text{ cm}^{-1}$. These parameters
reproduce the levels in Table 2.1 to within 0.1 cm$^{-1}$ or better. (ii) Increase $a$ from $a_0$ to $a_1 = 1.15$ bohr$^{-1}$ and $a_2 = 1.5$ bohr$^{-1}$ to simulate the average isotropic repulsion produced by He-He repulsions. As Fig. 2.4 shows, the $a$-states are robust to this procedure while the $b$-type state topology is dramatically destabilized even for $a = a_1$. The $b$-type state now assumes a linear geometry – characteristic of $v_2 < 0$ – at $R \approx 8$ bohr, and is a stronger mixtures of $|011\rangle$ and $|121\rangle$. Overall, the $K = \pm 1$ character of the state is diminished as can be seen by re-expanding the states in body-fixed $|jJK\rangle$ basis vectors [2]. It seems reasonable to conclude that this mixing – induced by the physical expansion of the cluster – is the fundamental reason that the $b$-type series disappears suddenly, effectively eliminating symmetry-breaking longitudinal asymmetries arising from He-He attractive interactions at smaller cluster sizes [42,48].

2.5 Conclusions

In conclusion, these calculations have demonstrated explicitly that quantum solvation of HCN in $^4$He droplets proceeds through decoupling of the solvent and solute angular wavefunctions. This is a direct result of the bosonic nature of the $^4$He atoms. These results predict similar decoupling behavior for CO-seeded clusters, since the CO-He and HCN-He interaction potentials are similar, as are the molecular constants [48]. The calculations relied on the introduction of a new DMC approach in which nodal topologies are approximated using an adiabatic separation of angular and radial motions. This approach could probably be refined by including nonadiabatic corrections. However, it was also necessary to neglect He-He interactions, and it seems likely that this is a larger source of error. Neglecting these interactions in the first solvation shell appears to be a reasonable approximation, however, in that the adiabatic and two-level nodal functions provide good agreement with previous calculations. It will clearly be necessary to study other systems to determine how accurate this procedure is in general. In principle, He-He interactions could be introduced, possibly using mean field or other approximations, and work to this end is underway. The adiabatic node approach allowed physical mechanisms to be proposed for the previously predicted [42] disappearance of the $b$-type series, as well as the rapid convergence of the $a$-type series to
the nanodroplet limit as a function of cluster size. In particular, the behavior of the a-type series was traced directly to the mechanics of angular momentum coupling – and decoupling – between identical bosons and the molecular rotor. For very small values of N there exists significant angular momentum coupling between the molecule and the He atoms. This coupling diminishes quickly and for N \( \approx 10 \) solvation appears to be essentially complete as evidenced by significant decoupling of the molecule and the solvent angular momenta.

It was suggested that the vanishing of the b-type series is a consequence of He-He repulsion causing the states most strongly associated with the b-type transition to sample the negative P2 anisotropy of the potential more strongly. This leads to a change in their geometry that eliminates longitudinal bumps (i.e., the dynamical asymmetry required to observe two, rather than one, lines in the spectrum [42]). These results lead to the prediction that the equivalent states for DCN-He clusters will vanish slightly later than do those for the equivalent HCN complex. This is because of the greater reduced mass of the DCN complex, which results in a slightly more localized T-shaped geometry that, by these arguments, will be somewhat more resilient to size expansion of the cluster.

While all heliophilic molecules will eventually solvate, the speed at which this happens, as a function of cluster size, appears to depend delicately on the specifics of the molecule. Previous studies have attempted to understand the importance of the bare moment of inertia and the strength of the potential anisotropy on the extent of adiabatic following. For example, Paolini et al. [42] compared the solvation of OCS and HCN with so-called fudged versions, f-OCS and f-HCN, having artificially altered moments of inertia (or, equivalently, altered gas-phase rotational constants). They concluded that it is the strength and anisotropy of the He-molecule interaction, rather than the bare molecular inertia, that is mainly responsible for the renormalization of the rotational constant in the nanodroplet regime. While we do not disagree with this conclusion, and it is certainly not inconsistent with the original statements by Lee et al. [21], which emphasized the relative roles of the potential anisotropy and the gas-phase rotational constant, it appears that the dynamics are rather more intricate. For example, the vanishing of the b-type series seems to be re-
lated not only to the overall anisotropy of the potential but also to the precise point at which the P1 and P2 anisotropies cross each other. Similarly, the convergence of the a-type series to the nanodroplet limit is a result of how the P1 and P2 anisotropies (especially) mix the IBC basis vectors. In DMC, this is reflected in the resulting distortions in the nodal topologies. The existence of various exceptions to light–(versus heavy)–rotor rules of thumb [19, 41, 42] suggests that further studies of a wide variety of molecules in $^4\text{He}$ droplets are needed to understand the interplay between the nature and strength of the potential anisotropies and the size of the bare molecular moment of inertia in controlling the approach to solvation. As noted very recently by Toennies and Vilesov: [19] “One of the shortcomings of the helium-droplet matrix is the large and as yet little understood increase in the moments of inertia compared to the free molecules.” While this is a complication, the complexity of the dynamics also widens the scope for creating clusters that are tailor-made to have particular properties [19].
Table 2.1: Ground and excited state energies for HCN-He in cm$^{-1}$. CC: Coupled-channel; MD: Matrix diagonalization; DMC: Fixed-node DMC using $^1$isotropic, $^2$adiabatic and $^3$exact nodal functions. The $|j\ell J\rangle$ labeling scheme is exact only for the isotropic binary complex.

| $|j\ell J\rangle$ | CC    | MD    | DMC$^1$ | DMC$^2$ | DMC$^3$ |
|----------------|-------|-------|---------|---------|---------|
| $|000\rangle$  | -8.867| -8.844| -8.88±0.05|         |         |
| $|a\rangle = |011\rangle$ | -8.342| -8.316| -8.33±0.05| -8.30±0.06| -8.34±0.06 |
| $|b\rangle = |101\rangle$ | -5.554| -5.528| -6.46±0.08| -5.55±0.06| -5.55±0.06 |
| $|111\rangle$  | -5.019| -4.997| -       | -       | -       |
| $|121\rangle$  | -4.084| -4.044| -       | -       | -       |
Figure 2.1: Density maps of $|\Psi^{(a),(b)}(r)|^2$; (a)–(d): from matrix diagonalization; (e) and (f): adiabatic approximation. In (a) and (b) $\beta = 0$ and in all cases $\phi = 0$. The densities have all been scaled to have the same maximum value. In color: the color bar shows the range of density values. In black and white; white (black) regions indicate large (small) density amplitudes. The broad black bands in (a), (c)–(f) bound the nodal surfaces.
Figure 2.2: Radial expansion functions, $v_\lambda(R)$, for the HCN-He PES of Toczyński et al. J. Chem. Phys. 114, 851 (2001). The inset shows $|\Psi^{(0)}(r)|^2$ - arbitrarily scaled to a maximum of unity - in the roughly equatorial (solid line) $(\beta = 0, \theta = 114^\circ)$ and polar (dashed line) $(\beta = 0, \theta = 0)$ directions.

Figure 2.3: Adiabatic radial potentials $U^{(j\ell J)}(R)$ obtained from Eq. (2.7) with $(j\ell J) = (011)$ and $(j\ell J) = (101)$. Also shown is the adiabatic radial function $\rho^{(n\ell J)}(R)$ for $(n\ell J) = (001)$. 
Figure 2.4: Rotational energies, $\Delta E = 2B$, as a function of cluster size ($N$) from DMC using different fixed-nodes; $\diamondsuit - \psi_{iso}^{(b)}$, $\bigcirc$ – adiabatic; $\square$ – “two-level” nodes: $+$ – origins of the $a$- and $b$-type series at $N = 1$. The horizontal dot-dashed line at $\Delta E = 2.4 \text{ cm}^{-1}$ is the nanodroplet limit.
CHAPTER 3
ROTATIONAL STRUCTURE OF SMALL $^4\text{He}$ CLUSTERS SEEDED WITH HF, HCl AND HB$\text{r}$ MOLECULES

Abstract

Diffusion Monte Carlo (DMC) calculations are performed for ground and excited rotational states of HX($^4\text{He})_N$, complexes with $N \leq 20$ and $X = F, \text{Cl}, \text{Br}$. The calculations are done using \textit{ab initio} He-HX intermolecular potentials whose computation is described. Intermolecular energies and He radial and angular probability density distributions are computed as a function of the number of solvent atoms. Excited states are calculated using fixed-node DMC methods and molecule-solvent angular momentum coupling is studied as a function of cluster size and potential anisotropy. Nodal surfaces of the many-body wavefunction are computed approximately by making an adiabatic Born-Oppenheimer-like separation of radial and angular degrees of freedom of the cluster. This procedure is extended to include radial dependencies in the adiabatic nodal function. We predict that the observed decrease in the gas-phase rotational constants for HCl and HB$\text{r}$ in a $^4\text{He}$ nanodroplet will be smaller than that observed for HF, despite HF having the largest (by far) gas-phase rotational constant of the three molecules. This suggests that the specifics of the solvation dynamics of a molecule in a $^4\text{He}$ cluster are the result of a delicate interplay between the magnitude of the gas-phase rotational constant of the molecule and the anisotropic contributions to the atom-molecule potential energy.

3.1 Introduction

Helium is a singular substance for various reasons. It has no triple point and so is the only material known that can exist as a liquid at absolute zero [10,67–69]. Below 2.17 K $^4\text{He}$ behaves as a superfluid but is not a pure Bose-condensate [70]. Liquid $^4\text{He}$ has a thermal conductivity $\approx 30$ times greater than copper [19,67,68], and it apparently has a supersolid...
phase [71–74]. The $^4$He dimer is renowned for its small binding energy [75] ($\approx 1$ mK) and large bond length [75] ($\langle r \rangle \approx 100$ bohr). $^4$He$_3$ has been predicted to exhibit the long sought after Efimov state [76, 77]. In contrast, fermionic $^3$He does not achieve superfluidity until 0.0025 K, and bound states of the dimer and trimer do not exist at all because of the higher zero-point energy of $^3$He complexes [10, 11]. The threshold for the appearance of $^3$He$_N$ droplets appears to be in the range $20 < N < 40$ [11, 78].

The peculiarities of the properties of helium are only exaggerated by confining the geometry of the system as in a film or droplet [11, 18, 19, 79]. Due to the very weak He-He interaction, He droplets containing $\approx 10^3 − 10^8$ atoms cool down very efficiently by evaporation and achieve temperatures of 0.37 K ($^4$He) and 0.15 K ($^3$He) in a free jet expansion [18,19,38]. Consequently, droplets of $^4$He are superfluid, whereas those of $^3$He behave as conventional liquids [11,19]. Nanodroplets of $^4$He have been called the “ultimate spectroscopic matrix” [9] and also offer potential as ultra-cold [17], ultra-clean, nano-reactors [19] (e.g., for making and characterizing novel chemical species [38]; performing high-resolution spectroscopy of van der Waals complexes [80, 81]; studying, or creating, complexes of biomolecules [19,82]; monitoring chemical reactions between individual molecules [19]; isolating reaction intermediates or precursors [83]; and studying the onset and nature of superfluidity in finite-sized systems [14,84]).

The usefulness of $^4$He droplets can be traced in part to their superfluid nature and in part to the efficiency of evaporative cooling as the droplet expels atoms [11,19]. Consider, for example, the formation of molecular clusters. In a typical free jet expansion, cluster formation occurs early in the expansion and is followed by relatively slow cooling through two-body collisions. The opposite happens in a $^4$He droplet experiment. Here the droplet picks up molecules sequentially (according to Poisson statistics [18]) with the average time between capture events greatly exceeding the time needed for each molecule to cool through evaporation of He atoms from the droplet. Thus, in a droplet, molecular clusters are built from already cold molecules, and this can produce novel arrangements (e.g., linear chains of HCN molecules oriented by long range dipole-dipole interactions [38]). This procedure
rather neatly avoids the usual problem of rotational motion swamping dipole-dipole interactions. In other – actual or prospective – applications, molecules seeded into nanodroplets can serve as antennae with which to relay information to and from the droplet (e.g., structural information about species being formed in the droplet [35] or information about the onset of superfluidity as a function of droplet size [14,40,84]).

Indications of the utility of $^4$He droplets as ultra-gentle cryogenic matrices were apparent even in the earliest pioneering spectroscopic studies. In 1992 Goyal et al. [12] observed unusually narrow absorption line widths in SF$_6$-seeded nanodroplets. This work was followed by high-resolution infrared ($\text{ir}$) studies by Hartmann et al. [15] who observed rovibrational fine structure more typical of gas- than liquid-phase spectra. While it is exceptional for a molecule dissolved in a liquid to present rotationally resolved lines (HF being one exception [85]) in a $^4$He nanodroplet, coherent free rotation over many periods appears to be the norm [18]. Still, the liquid and gas-phase spectra are not identical. In most cases the spectroscopic constants of the solvated molecule are shifted from their gas-phase values. For example, SF$_6$ in a $^4$He nanodroplet exhibits a spherical top spectrum but with a rotational constant, $B$, approximately one-third of $B_0$ – its gas-phase value [15].

The first calculations of the rotational structure of a molecule in a $^4$He cluster were DMC simulations for SF$_6(^4\text{He})_N$ clusters [21]. From these calculations it emerged that a fraction of the helium density in the droplet follows the rotation of the SF$_6$ molecule adiabatically. In the “adiabatic following” model, the observed decrease in the rotational constant is due to the molecule dragging a fraction of the helium density along as it rotates, thereby increasing its moment of inertia.

A good definition of quantum solvation is that dissolved molecules are coated by a solvation shell and, at some point, as a function of number of solvent atoms, angular momentum coupling with the solvent atoms saturates. This situation then allows for apparent free rotational motion, albeit with altered spectroscopic constants [11,21,41,42]. Recently this has been studied in more detail in experiments that effectively build up the quantum solvent He–atom by He–atom - more precisely clusters containing specific numbers of He atoms (e.g.,
from 1 – 20) can be individually interrogated [34,37,42,86]. It turns out that the transition from a “molecular complex” to a “dissolved molecule” can occur for as few as $\approx 7 – 12 \ ^4\text{He}$ atoms. Various simulations of the onset of solvation have been made [6,21,36,42–44] and the underlying physical mechanism for this transition continues to be a subject of active research [6,19,41,42].

Because the experiments are conducted at ultra-low temperatures, only the lowest rotational excited states are typically accessed. However, while this simplifies simulations, the many-body nature of the system rules out most computational procedures. DMC methods are ideal for studying such clusters because they can be used to compute accurate ground state energies for very large systems. However, DMC suffers from the drawback that the calculation of excited states is not straightforward and approximations must usually be introduced. The situation is alleviated somewhat by the observation that experiments involve only the lowest-lying excited states. One approach for computing excited states is fixed-node DMC, in which knowledge of the nodal topology of the wavefunction is built into the simulations. The nodal topology of the excited state being sought after can sometimes be obtained using known symmetries of the system. For many-body molecule-$^4\text{He}_N$ clusters, however, it is necessary to resort to approximations. A new approach to computing nodes has recently been developed in which estimates of nodal surfaces are obtained using a Born-Oppenheimer-like separation of radial and angular motions [6,49]. This approach, called adiabatic-node-diffusion Monte Carlo (ANDMC), was applied to the quantum solvation of HCN in small $^4\text{He}$ droplet [6]. For the binary He-HX complexes considered in this article, we will utilize ANDMC, and a direct comparison will be made between adiabatic and accurate nodal topologies.

In ANDMC, radial and angular motions are separated, and the resulting angular Hamiltonian is diagonalized. Using this method, accurate excited state rotational energies were calculated for HCN($^4\text{He})_N$ droplets. The adiabatic node approach also has the advantage of allowing the mechanics of angular momentum coupling – and decoupling – between identical bosons and the molecular rotor to be mapped out explicitly. For HCN($^4\text{He})_N$ complexes, it
was found that, for small values of $N$, there exists significant angular momentum coupling between the molecule and the helium atoms. However, because of the bosonic symmetry requirement, as $N$ is increased and solvation becomes almost complete, the degree of atom-molecule angular-momentum coupling saturates. In particular, the details of angular momentum coupling and decoupling were related to (i) the angular symmetry of the potential energy surface (PES); for example, which Legendre polynomials contribute to the PES in an expansion of the angular coordinates and (ii) the size of the rotational constant of the gas-phase molecule.

The reasons why – and how – these factors are expected to affect the solvation dynamics can be understood by thinking of seeded $^4$He-clusters as bosonic “super-atoms.” Imagine that the molecular rotor has infinite mass and the atom-molecule potential is isotropic. In this limit, the Hamiltonian is essentially that of an atom except that the “electrons” (i.e., the $^4$He atoms), are bosons and the form of the “electron-electron” interaction is quite different from a real atom. Neglecting He-He interactions results in a rough analog of an atom in the central-field approximation but with bosonic “electrons.” This model has few computational merits – although it is a useful limit to use in tests of algorithms – but it does bring into focus the importance of understanding angular momentum coupling in a seeded $^4$He cluster. This is entirely analogous to how angular momentum coupling is central to understanding electronic structure [63].

In the actual physical situation, anisotropies of the interaction potential will couple rotational states of the molecule with the orbital angular momentum of the He atoms. However, this will be modulated by the size of the gas-phase rotational constant. As was shown in an earlier study of SF$_6$ [21], artificially increasing the gas-phase rotational constant tends to decouple the molecule adiabatically from the He atoms, and the system effectively becomes more isotropic. In general, the details of quantum solvation are expected to depend on the competition between large $B_0$ values – which tend to encourage decoupling of the molecule, and the solvent and large potential anisotropies – which tend to increase the coupling. The current study is directed to quantifying the importance of these factors.
by studying clusters seeded with HF, HCl and HBr molecules. Two important caveats apply: (i) It is not only the size of the anisotropy that matters but also its symmetry, (i.e., which Legendre polynomials contribute to the angular anisotropy) and (ii) the bosonic symmetry of the solvent requires that all of the He atoms couple identically to the molecule. Eventually, the coupling of the atom and molecular angular momentum saturates and the molecule solvates [6].

In recent work Paolini et al. [42] have investigated the convergence of the apparent rotational constant of a molecule seeded into a $^4$He cluster as a function of cluster size. They found that, for HCN seedants, the effective rotational constant did not change significantly upon further growth of the cluster beyond $N \sim 15$. This is similar to the case of CO [45] and also in agreement with high resolution $ir$ spectra recently obtained for He clusters seeded with CO [48,86]. However, these results differed from earlier expectations of relatively slow convergence to the nanodroplet limit for light rotors [46].

To understand further the relative roles of the size of the gas-phase rotational constant and the strength and anisotropy of the He-molecule interaction potential, Paolini et al. [42] performed computations of the solvation of two so-called “fudged” molecules $f$-OCS and $f$-HCN, (i.e., OCS and HCN) in which artificially small or large values of the gas-phase rotational constant were used. This approach is similar to that employed in the earlier study of SF$_6$ [21]. They concluded that it is the strength and anisotropy of the He-molecule interaction, rather than $B_0$, that is mainly responsible for the reduction of the rotational constant in the nanodroplet regime. Therefore, the classification into heavy and light rotors relies upon the coincidence that heavier molecules tend to have stronger and more anisotropic interactions with He.

To make the competing roles of $B_0$ and the potential anisotropy more explicit, ANDMC was used [6] to trace the saturation of the bosonic solvent and solute angular wavefunctions in HCN-seeded clusters. Convergence of the effective rotational constant to its asymptotic limit (as a function of cluster size) was explained in terms of the specific anisotropic contributions to the interaction potential that lead to specific couplings between angular momentum
basis vectors. It was also shown that adiabatic nodes substantially improve DMC estimates in this system. This allowed an explanation to be put forward to explain the observed convergence of the \(a\)-series of lines observed experimentally to the nano-droplet and free-rotor limits as well as the sudden disappearance of the \(b\)-series [6]. While the ultimate explanation for the vanishing of the \(b\)-series was similar to that proposed in other studies [45, 87], it was arrived at differently: the mechanism was couched explicitly in terms of angular momentum coupling arguments. Similar behavior is expected for CO-seeded clusters since the CO-He and HCN-He interaction potentials are similar, as are the molecular constants [48].

Rather than using fudged molecules, in the current study the solvation dynamics of the three molecules – HF, HCl and HBr – are studied. The molecules have rather different gas-phase rotational constants, and the interaction potentials differ in several subtle but significant ways. An aim of the study is to test how good variously proposed rules of thumb, (e.g., “light-rotor” versus “heavy-rotor,” [42]) are at predicting system properties. It might, for example, be expected that HF, having the largest \(B_0\) value, will, on solvation, exhibit the smallest reduction in rotational constant of the three molecules. Although several potential energy surfaces for He-HX, \(X = F, Cl, Br\) already exist in the literature [88–92], to make a more consistent and even-handed comparison, \textit{ab initio} PESs for all three complexes are computed and fitted them to the same functional form.

The paper is organized as follows: The Hamiltonian is introduced in Sec. 3.2. Details of the calculation of the intermolecular PESs are provided in Sec. 3.2 together with the parameters and functions used in an analytical fit to each surface. The energies of the binary He-HX complexes are computed in Sec. 3.3 using coupled-channel (CC) and diagonalization procedures. Comparison is also made with DMC results. Details of the DMC approach are contained in Sec. 3.4. In Sec. 3.6, He radial and angular density probability distributions are computed as a function of cluster size. Rotational excited state DMC calculations are presented in Sec. 3.7. Conclusions are in Sec. 3.8.
3.2 Hamiltonian and Intermolecular Potentials

In the space-fixed frame the Hamiltonian for $N$ helium atoms interacting with an HX molecule (treated as a linear rigid rotor) is

$$H = -\frac{\hbar^2}{2M} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + B_0 \mathbf{j}^2 + \sum_{i<j}^{N} V_{He}^{He}(r_{ij}) + \sum_{i=1}^{N} V(R_{iI}, \theta_{iI}) \quad (3.1)$$

where $r_{ij}$ and $R_{iI}$ denote He-He and He-HX separations, respectively; $\theta_{iI}$ is the angle between the molecular axis and the $i$'th He atom (in the case of the dimer complex $\theta_{1I} \to \theta$); $M$ and $m$ are the masses of the HX molecule and the He atom, respectively; $V_{He}^{He}(r_{ij})$ and $V(R_{iI}, \theta_{iI})$ are the He-He [50] and the HX-He PESs, respectively. The molecular rotational angular momentum operator is $\mathbf{j}$, and $B_0$ is the gas-phase rotational constant. The various physical constants are collected together in Table 3.1 [93, 94]. All calculations are done in the rigid-body approximation.

All the calculations to be described assume pairwise molecule-He and He-He interaction potentials. For the He-He interaction, the potential energy surface of Aziz et al. was used [50]. The potential is simply a function of the distance between any two He atoms. *Ab initio* PESs of the three He-HX van der Waals complexes are calculated directly. The He-HF PES has been reported elsewhere along, with details of the approach taken [92]. Essentially, the three PES, were obtained by fitting a considerable number of interaction energies obtained at the *Coupled Cluster Singles and Doubles* level, including connected triple corrections; this was done using the augmented correlation consistent polarized valence quintuple zeta (He-HF and He-HCl) and the SDB-aug-cc-pVQZ (He-HBr) basis sets extended with a set of 3s3p2d1f1g midbond functions. These basis sets were selected after systematic studies carried out at representative intermolecular geometries.

The potentials are each found to be characterized by two minima corresponding to linear configurations, (i.e., He-HX and He-XH). The *ab initio* single point interaction energies were then fitted to the analytical function $V(R, \theta)$ originally suggested by Bukowski et al. [95]. Here, $R = |\mathbf{R}|$ is the distance from the He atom to the molecular center-of-mass (c.o.m.)
and \( \theta \) is the angle between \( \mathbf{R} \) and the molecular axis; \( \theta = 0 \) corresponds to the linear He-HX configuration. The potential energy function is the sum of two terms, a short range term \( V_{sh} \) and an asymptotic term \( V_{as} \)

\[
V(R, \theta) = V_{sh}(R, \theta) + V_{as}(R, \theta)
\]  

where

\[
V_{sh}(R, \theta) = G(R, \theta)e^{B(\theta)+D(\theta)R}
\]  

and

\[
V_{as}(R, \theta) = \sum_{n=6}^{7} \sum_{l=0}^{n-4} f_n(D(\theta)R) \times \frac{C_{nl}^l}{R^n} P_l(\cos \theta).
\]

The functions \( D(\theta), B(\theta), \) and \( G(R, \theta) \) are represented as expansions in Legendre polynomials, \( P_l(\cos \theta) \)

\[
B(\theta) = \sum_{l=0}^{5} b_l P_l(\cos \theta)
\]

\[
D(\theta) = \sum_{l=0}^{5} d_l P_l(\cos \theta)
\]

\[
G(R, \theta) = \sum_{l=0}^{5} (g_{0l} + g_{1l} R + g_{2l} R^2 + g_{3l} R^3) P_l(\cos \theta)
\]

and

\[
f_n(x) = 1 - e^x \sum_{k=0}^{n} \frac{|x|^k}{k!}
\]

is a Tang-Toennies damping function \([96]\) with \( x = R \times D(\theta) \); \( b_l, d_l, g_{kl} \) and the \( C_{nl}^l \) parameters are adjustable. The fitted values of the corresponding PES parameters are presented in Tables 3.2–3.4.

The three resulting PESs are shown in Fig. 3.1. Table 3.5 shows the locations and well
depths of the two global minima for each complex. Several observations can be made. As the halogen atom increases in the size, the He-HX minimum becomes shallower and moves farther out. Essentially, the complex is becoming more spherically symmetric as the halogen atom increases in radius. This observation can be made more quantitative by expanding the PES in Legendre polynomials

$$V(R,\theta) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos \theta). \quad (3.9)$$

Several of the lowest-order radial strength functions, \( v_{\lambda}(R) \), are shown in Fig. 3.2 for each of the three binary complexes. It is readily apparent that the contributions of \( v_1, v_2 \) and \( v_3 \) decrease relative to \( v_0 \) as one goes from HF to HCl to HBr. This observation will prove useful for understanding the excited state dynamics of these molecules in small \(^4\)He clusters.

It is also notable that the deeper minimum corresponds to the He-HF geometry in the He-HF complex but to He-BrH in the He-HBr dimer. The He-HCl complex falls in between with both minima having rather similar binding energies.

3.3 Energy Levels of the HX-He Complexes

Before proceeding to study droplets containing many He atoms, it is essential to understand the level structure and the nodal topology of the wavefunction of the binary complex. This is achieved by using (a) CC calculations [56] and, so as to obtain accurate wavefunctions and nodal surfaces, (b) matrix diagonalization using a product basis of radial \( \times |j\ell JM \rangle \) basis vectors where \( j, \ell \) and \( J \) are the rotor, atom, and total angular momentum quantum numbers respectively and \( M \) is the projection of the total angular momentum on the space-fixed z-axis [2,3].

First, it is useful to consider a particular limit – the “isotropic binary complex” (IBC): If the molecule-\(^4\)He interaction potential is isotropic, the molecular rotational angular momentum and the atomic orbital angular momentum quantum numbers, \( j \) and \( \ell \), respectively, are separately conserved. For the IBC, the labeling scheme \(|j\ell J\rangle\) is exact and the wave-
function is separable; the molecular and atomic parts of the wavefunction are spherical harmonics involving the spherical polar angles in the space-fixed frame. The IBC is used to generate a set of basis vectors.

Of particular interest, both theoretically and experimentally, are the nodal functions for the lowest lying rotational states, (e.g., levels with $J = 1$, for which the nodal surfaces of IBC states of most interest, $|011\rangle$ and $|101\rangle$ are $\Psi^{(a)}_{iso} = \cos \theta_2$ and $\Psi^{(b)}_{iso} = \cos \theta_1$ where $\theta_1$ and $\theta_2$ are the space fixed polar angles of the molecule and atom, respectively). While it is legitimate to refer to the nodal function $\Psi^{(b)}_{iso}$ as the “free-rotor” node because this node is identical to that of the free molecule, analogous terminology for $\Psi^{(a)}_{iso}$ does not exist because the orbital angular momentum of the atom has to be referred to some center – in this case the c.o.m. of the molecule. Thus this node is neither a “free-atom” nor a “free-rotor” node. The IBC limit also provides a useful labeling scheme with which to correlate the levels of the anisotropic binary complex in the space-fixed frame.

Tables 3.6–3.8 show a selection of energy levels for the three dimers using CC, diagonalization and various DMC methods to be described.

### 3.3.1 Coupled-Channel calculations for the dimers

CC calculations were performed for the three dimers using the BOUND program [56]. In this procedure the potential must be expanded as in Eq. (3.9). The quality of the expansion was checked by (i) comparing contour plots of the accurate potential with those obtained from the expansion, and (ii) examining the convergence of the computed eigenvalues as a function of $\lambda$. The radial strength functions were generated using a Gauss-Legendre quadrature. CC results for several eigenvalues with $J = 0$ and $J = 1$ are shown in Tables 3.6–3.8 for the three molecules.

### 3.3.2 Matrix diagonalization for the dimers

In the fixed-node DMC calculations (to be described) for excited states, it is necessary to have good estimates of nodal surfaces. Previous work for the HCN-He complex has shown that the nodal functions of the IBC do not necessarily provide accurate estimates
of the actual nodal geometries \cite{6,46}. To gain insight into the distortion of the IBC nodal
topologies due to the potential anisotropy, accurate eigenfunctions for the binary complex
were computed using a basis set that is a product of $|\text{radial}\rangle \times |\text{angular}\rangle$ functions. The
total wavefunction is expanded

$$\Psi = R^{-1} \sum_a c_{J,M}^{J,M} \Phi_{j,\ell}^{J,M}(\Omega_1, \Omega_2) \chi_n^{(n)}(R) \quad (3.10)$$

where $R$ is the intermolecular distance; $\Omega_1 = (\theta_1, \phi_1)$ are the angular coordinates of the
molecule, and $\Omega_2 = (\theta_2, \phi_2)$ are the spherical polar angular coordinates of the atom and
$\{c_{J,M}^{J,M}\}$ are expansion coefficients. The radial basis functions, $\chi_n^{(n)}(R)$, where $n$ is the radial
quantum number, were chosen to be harmonic oscillator eigenfunctions. The angular basis
functions $\Phi_{j,\ell}^{J,M}(\Omega_1, \Omega_2)$ are defined as follows

$$\Phi_{j,\ell}^{J,M}(\Omega_1, \Omega_2) = \sum_{m_j,m_\ell} (-1)^{j-\ell+M} \sqrt{2J+1} \begin{pmatrix} j & \ell & \ell J \\ m_j & m_\ell & -M \end{pmatrix} Y_{j,m_j}^{m_j}(\Omega_1) Y_{\ell,m_\ell}^{m_\ell}(\Omega_2) \quad (3.11)$$

where $\begin{pmatrix} \ldots \end{pmatrix}$ is a Wigner $3-j$ symbol and $Y_{j,m_j}^{m_j}(\Omega_1)$ and $Y_{\ell,m_\ell}^{m_\ell}(\Omega_2)$ are spherical har-
monics. Using the expansion in Eq. (3.9), the matrix elements of the potential can be
expressed in closed form in terms of Percival-Seaton coefficients \cite{2}. The size of the basis
is determined by the maximum size of $j = j_{\text{max}}$ for a given $J$. The matrix diagonalization
results in Tables 3.6–3.8 compare favorably with CC and literature values for states with $J = 0, 1$.

### 3.4 Rigid-Body DMC Calculations

The DMC calculations were done using the rigid-body diffusion Monte Carlo (RBDMC)
method originally developed by Buch \cite{52} and later extended to compute excited states using
importance sampling [21,57]. This procedure reduces the number of degrees of freedom and allows larger diffusive time steps to be made. The RBDMC approximation is especially suitable for very weakly bound complexes because of the large difference in the strengths of the intramolecular and intermolecular forces – and, therefore, time scales of the various motions. The basic idea in RBDMC is to recognize, that for sufficiently small rotations, the rotational energy propagator is analogous to the translational kinetic energy propagator with a diffusion constant $D_R = 1/2I$ where $I$ is the moment of inertia of the molecule. This procedure takes advantage of the fact that components of angular momentum commute for sufficiently small rotations. In the current application, all translations and rotations are made in a rotor-fixed frame (i.e., rotational moves are done around the set of principal axes of the HX c.o.m. and rotate along with the rigid HX molecule).

In RBDMC, excited rotational states are computed using the fixed-node method [23,59]; this involves “killing” walkers that cross nodal surfaces. In the simulations, importance sampling was used as is now described.

3.5 Importance sampling

In importance sampling, a trial wavefunction, $\Psi_T$, is introduced to guide the diffusion. This improves the efficiency of the DMC method and increases the precision of the computed energies [23]. For larger He clusters, unphysical dissociation might occur unless importance sampling is used. Use of a guiding trial wavefunction leads to a diffusion-like equation for the mixed function $f(R_i, r_i) = \Psi(R_i, r_i)\Psi_T(R_i, r_i)$ where $R_i$ and $r_i$ are the molecular and He atom coordinates, respectively. Additional drift terms – quantum forces – are introduced into the diffusive process to guide the walkers to regions of high-probability density [58]. In this work trial wavefunctions were chosen to have the form

$$\psi_T = \prod_{i=1}^{N} f(R_i) \prod_{i \neq j}^{N} \Xi(r_{ij})$$  \hspace{1cm} (3.12)

where $R_i$ is the radial distance from the molecular c.o.m. to helium atom $i$ and $r_{ij}$ is the distance between helium atoms $i$ and $j$. As in previous work [6,21,46] the radial functions
were of the following form

\[ f(R) = b \exp\left(-\frac{c}{R^6} - aR\right). \]  

(3.13)

The parameters \( a, b, c \) were obtained by fitting the function \( f(R) \) to (i) accurate binary wavefunctions obtained from diagonalization or (ii) to adiabatic radial functions. The two approaches provided similar results. For excited state calculations the replicas where killed when they were crossing the nodal surface. The He-He part of the trial wavefunction, \( \Xi(r_{ij}) \), was the same as that used in previous studies [21,46].

3.6 Ground State Properties

We performed systematic studies of ground states properties (i.e. energy levels, radial and angular distributions) for all He-HX complexes with various number of helium atoms, by means of unbiased RBDMC. Parameters used in simulations such as rotational constants, molecular masses are summarized in Table 3.1. This section contains obtained results and relative conclusions. Specific interplays between some DMC results and independently calculated potentials energy surfaces are subject to the following.

3.6.1 Dimers configuration

The most obvious difference between the three dimers He-HF, He-HCl and He-HBr is in the ordering of the potential minima. Table 3.5 indicates that for He-HF the configuration He-HF has a deeper well than does He-FH; for He-HCl and He-HBr this ordering is inverted. Figs. 3.3–3.5 compare the He density, for the three complexes, computed for the rotational constant \( B_0 = 0 \) with the ones computed for its physical values. In the case of no rotation \( (B_0 = 0) \), the density for HF and HCl is primarily concentrated at the H atom end of the HX molecule while for HBr the opposite is the case. The finding that the HeHCl configuration is favored over the HeClH configuration agrees with the results of Murdachaew et al. [90] obtained using a different PES. They attributed it to the greater volume of the shallower well in the He-HCl configuration (i.e., despite the well being shallower, the volume of phase space is greater at the H-end of the molecule). It should also be noted that the ground
state actually lies above the saddle point of the PES.

3.6.2 Radial and angular distributions

Figs. 3.6–3.8 show the radial correlation functions as a function of number of He atoms. The corresponding angular correlation functions are shown in Figs. 3.9–3.11. These plots were obtained by projection the He density from converged unbiased RBDMC calculations into a frame in which the molecule is aligned along the space-fixed $z$–axis and were all normalized to 1.

For a given He-HX complex, all radial correlation functions peak out around the same R value and only a fraction of density is observed as R tends to larger values. This finding suggests that up to $N=15$, He atoms fill up only the first solvation shell around the molecule, and the second solvation shell has not yet begun. Additionally, no unphysical 'dissociation', which was elsewhere [46] observed for HCN-(He)$_N$ where $N \geq 10$, is noticed here.

It is apparent from Figs. 3.9–3.11 that for $N = 1$, though delocalized, the density switches primarily from the H-end of the molecule in HF and HCl to the halogen end in HBr. For larger number of He atoms, the majority of the density in all cases is concentrated not close to one end of the molecule but in a broad donut shape corresponding to $\theta \sim \pi/2$. This can be explained by taking into account growing repulsive interactions between He atoms as their number increases, which result in spatial arrangements that allow them to avoid each other.

The effect of the relatively large value of $B_0$ for all three molecules is clearly reflected in the significant delocalization of the He density as compared to the case that $B = 0$. Given the large $B_0$ values one would expect a rather modest decrease in the effective rotational constant in a $^4$He nanodroplet. For HF, in fact, $B_{\text{eff}} \sim 98\%$ of $B_0$ [18,97]. Based simply on the size of $B_0$, one would expect somewhat larger percentage reductions for HCl and HBr. This is the subject of the next section.
3.7  Excited States

Excited states were computed using fixed-node DMC and, in particular, the ANDMC method proposed by Mikosz et al. [6]. In this approach, improved as compared to the IBC, estimates of nodal surfaces are obtained by making an adiabatic separation of radial and angular motions.

3.7.1  Nodal surfaces of the dimers, He-HX

The topologies of the wavefunctions can best be understood by considering the expansion of the PES in Legendre polynomials in Eq. (3.9). Plots of the first four dominant \( v_\lambda(R) \)-functions are shown in Fig. 3.2. The \( P_1 \) term mixes zero-order basis states with \( \Delta j, \Delta \ell = \pm 1 \). For the three dimer complexes, the free-rotor state \(|101\rangle\) is coupled most strongly to \(|011\rangle\) by the \( P_1 \) anisotropy, whereas the \( P_2 \) anisotropy leads to admixtures containing primarily \(|121\rangle\) [2]. Unlike in the case of He-HCN [6], the dominant potential anisotropy for the three complexes arises from the \( P_2 \) term in Eq. (3.9). Furthermore, as one moves through the series HeHF - HeHCl - HeHBr, the minimum in the corresponding strength function, \( v_2(R) \) moves closer to the minimum in \( v_0(R) \) while its well-depth becomes shallower in comparison to \( v_0 \).

Fig. 3.12 is a representation of the probability density of the space-fixed wavefunction, \(|\langle x|101\rangle|^2\) for the HeHF. The nodal surface is clearly apparent. The plots are similar for the HeHCl and HeHBr dimers. In these three cases – and again, unlike for HCN, – the “free-rotor” nodal surface provides a reasonable approximation to the actual dimer node. Note that the “free-rotor” approximation improves as one goes from HF - HCl - HBr. This is apparent when comparing the rotational energies obtained using the free-rotor nodal function in DMC with accurate results in Tables 3.6–3.8. As the mass of the system increases, the wavefunction becomes somewhat more localized, which tends to “clean–up” the node. In addition, the system is becoming somewhat more isotropic (i.e., the non-spherical radial strength functions contribute less). For more than a single He atom, the nodal surfaces can be estimated using the adiabatic procedure now described.
3.7.2 Adiabatic nodal functions

Holmgren et al. [49] developed an adiabatic (i.e., Born-Oppenheimer-like) angular-radial separation (BOARS) in the molecule fixed frame for van der Waals atom-molecule dimer complexes. In BOARS, the radial degree of freedom is frozen at $R = R_0$, and the angular part of the resulting Schrödinger equation is then solved; this is repeated for different values of $R_0$, which generates families of adiabatic radial potentials. The adiabatic potentials are then used to solve for the radial wavefunctions. Although the BOARS approach has generally been superseded for atom-molecule (dimer) van der Waals complexes it, nevertheless, can be adapted to provide a convenient and accurate way of generating good estimates of nodal surfaces for small molecule-helium clusters [6]. The method is also computationally quite efficient because the angular matrix elements can be computed analytically or semi-analytically [2,61].

Adiabatic nodal functions are computed by making the following assumptions: (i) He-He interactions are ignored (for ground states with $N = 10$, e.g., these contribute $<5\%$ to the energy); (ii) fix $R = R_0$; (iii) pin the molecular c.o.m. in place; (iv) for more than a single He atom, the adiabatic separation is done in the space-fixed frame.

The resulting Hamiltonian is the following

$$H_{rot} = B_0 j^2 + \sum_{i=1}^{N} \kappa l_i^2 + \sum_{i=1}^{N} V(R_0, \theta_i)$$

where $\kappa = 1/2mR_0^2$. Diagonalizing $H_{rot}$ at fixed $J$ and $N$ thus produces estimates for the nodes. The value of $R_0$ is chosen to be the minimum of the appropriate adiabatic radial potential.

Diagonalization involves the coupling of an arbitrary number of angular momenta; for example, consider the case where four (rotor + three He atoms) angular momenta are involved (i.e., $j, l_1, l_2, l_3$ where the quantum numbers $j, m_j$ refer to the rotor and $\ell_i, m_i, i = 2, 3, 4$ to the He atoms). Because the He atoms are equivalent, the following angular momentum coupling scheme is used: Form the intermediate angular momenta $l_{12} = l_1 + l_2, l_{123} = l_{12} + l_3$
and then form the total angular momentum $J = j + l_{123}$. The basis functions can then be expressed in terms of generalized Clebsch-Gordan coefficients. For example, for $N = 3$ the basis functions can be written [62–65]

$$\psi^{JM}_{j_1 l_2 l_3 l_{123}} = \sum_{m_j, m_1, m_2, m_3} C(\ell_1 m_1 ... \ell_{123} m_{123} j m_J M)$$

$$\times Y_j^{m_j}(\Omega_j) Y_1^{m_1}(\Omega_1) Y_2^{m_2}(\Omega_2) Y_3^{m_3}(\Omega_3)$$

$$(3.15)$$

where $C(\ell_1 m_1 ... \ell_{123} m_{123} j m_J M)$ is a generalized Clebsch-Gordan coefficient [62] and $\Omega_{j,i}$ refer to the space-fixed coordinates of the several rotors. Explicitly,

$$C(j m_j \ell_1 m_1 \ell_2 m_2 \ell_3 m_3 \ell_{12} m_{12} \ell_{123} m_{123} j m_J M) = \sum_{m_{12}, m_{123}} (-1)^{\ell_{12}-m_{12}+\ell_{123}-m_{123}}$$

$$\times \begin{pmatrix} \ell_1 & \ell_2 & \ell_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix}$$

$$\times \begin{pmatrix} \ell_3 & \ell_12 & \ell_{123} \\ m_3 & m_{12} & -m_{123} \end{pmatrix}$$

$$\times \begin{pmatrix} j & \ell_{123} & J \\ m_j & m_{123} & -M \end{pmatrix}$$

$$(3.16)$$

The matrix elements of $H_{rot}$ are computed using the Wigner-Eckhardt theorem [2,62,65].

In previous work on HCN complexes, the value of $R$ used was chosen to correspond to the minimum of the adiabatic radial potential [6]. Inspection of the PESs in Fig. 3.1
indicates that as one moves from HF - HCl - HBr, the two potential minima move to different $R$ values relative to each other. This radial distortion suggests that use of a single $R$ value to define the node might be a less good approximation in HF than HBr. In fact, for the nominal $|101\rangle$ state, both the free-rotor $(\cos \theta_1)$ and “single-$R$” adiabatic nodes provide reasonable agreement with accurate results. However, some improvement can be achieved by using the following procedure to generate adiabatic nodal surfaces.

1. Generate adiabatic wavefunctions on a grid of $R$-values.

2. The adiabatic wavefunction is then expressed

$$\psi(\Omega_1, \Omega_2; R) = \sum c(R) \psi_{J^M}^{\ell_1 \ell_2 \ell_3 \ell_{12} \ell_{123}} (\Omega_1, \Omega_2; R).$$

(3.17)

3. The expansion coefficients, $c(R)$, are then fit to an analytical form. In practice, Morse potential forms provide an accurate numerical fit over the range of interest.

The function $\psi$ in Eq. (3.17) is then used to define the nodal function in the trial wavefunction.

The result of using adiabatic nodes is shown for the three dimer complexes in Tables 3.6–3.8. For more than a single He atom, adiabatic nodes provide very similar results as when the free-rotor node is employed. Fig. 3.13 shows values of the rotational energy of the states that evolve from $|101\rangle$ for the three HX molecules, as a function of the number of He atoms, $N$. Energies are expressed in terms of “$2B_{\text{eff}}$” where $B_{\text{eff}}$ is the effective rotational constant. The horizontal dashed lines show the value of $2B_0$ (i.e., the gas-phase values). Note that by $N = 20$ both HCl and HBr $B_{\text{eff}}$ has restored to its gas-phase value, whereas the reduction in $B_0$ for HF is similar to the experimental nanodroplet limit. The results shown in Fig. 3.13 were obtained using a free-rotor nodal function. In this case adiabatic nodal functions give the same results to within the error bars in the figure. This differs considerably from the situation with HCN, where the free-rotor node provides poor
agreement with accurate results for small number of He atoms [6]. This can be understood in terms of the contributions of the different anisotropic components of the PES; He-HCN and He-CO are “$P_1$” type dimers, whereas the He-HX complexes are dominantly $P_2$-type – see Fig. 3.2.

3.7.3 Nodal decoupling

The transition from the relatively strong coupling in the dimer to the solvated molecule can be understood in terms of angular momentum or nodal decoupling between the molecule and the He atoms. Consider first the dimer with $N = 1$. For $J = 1$ the dominant states are $|011\rangle$ and $|101\rangle$. The $P_1$ term mixes zero-order basis states with $\Delta_j, \Delta \ell = \pm 1$ and to lowest order, the resulting states have the form $|a\rangle = c_1 |011\rangle + c_2 |101\rangle, \ |b\rangle = -c_2 |011\rangle + c_1 |101\rangle$ with $c_1^2 + c_2^2 = 1$. By contrast, the $P_2$ anisotropy leads to admixtures of $|101\rangle$ with $|121\rangle$.

The corresponding wavefunctions can be written explicitly as follows:

$$
\psi_{101} = \frac{\sqrt{3} \cos \theta_1}{4\pi} \\
\psi_{121} = -\frac{1}{4\pi} \sqrt{\frac{3}{2}} \left(3 \cos^2 \theta_2 - 1\right) + 3 \cos \phi \cos \theta_2 \sin \theta_1 \sin \theta_2
$$

where $\phi = \phi_1 - \phi_2$ and the subscript “1” (2) refers to the angular coordinates of the molecule (atom). For $N$ He atoms, the $|121\rangle$ state is replaced by a symmetric linear combination of states having He orbital angular momentum permuted over the $N$ He atoms (e.g., $|j \ell_1 \ell_2 \ell_3 \ell_{123} JM\rangle = |120020JM\rangle$). Denoting these normalized “solvent” states by $|s\rangle / \sqrt{N}$ and “molecule” states of the form $|10...000JM\rangle$ by $|j\rangle$ the eigenvector mixtures to lowest order are the same as for $N = 1$

$$
|\alpha\rangle \approx \frac{c_1}{\sqrt{N}} |s\rangle + c_2 |j\rangle.
$$

The factor of $1/\sqrt{N}$ diminishes the contribution of each individual He atom as $N$ increases. Furthermore, as $N$ increases the trigonometric terms will approach their average values,
i.e., the free-rotor “$\cos \theta_1$” term will emerge. In fact, as Fig. 3.12 shows the free-rotor node is quite good even for $N = 1$.

### 3.8 Conclusions

Ground and excited state properties were computed for the $\text{H}X(\text{He})_N$, complexes with $N = 1 - 20$ and $X = \text{F, Cl, Br}$. The calculations used pairwise intermolecular potentials computed for the He-HX interactions and fitted to similar functional forms. Intermolecular energies and ground-state He radial and angular probability density distributions were computed. Excited states were calculated using fixed-node DMC procedure and molecule-solvent angular momentum coupling was studied as a function of cluster size and potential anisotropy. The calculations suggest that the observed decrease in the gas-phase rotational constants for HCl and HBr in a $^4\text{He}$ nanodroplet will be smaller than for HF, despite HF having a considerably larger rotational constant than the other two molecules.

Generally, these results can be explained in terms of the interplay between the various anisotropies of the potential energy surfaces shown in Fig. 3.2 for the HF-He, HCl-He and HBr-He potentials. In contrast to HCN \[6\] and CO, for which the $P_1$ and $P_2$ anisotropies compete, for quantum solvated hydrogen halides the $P_2$ anisotropy dominates. The solvation behavior of the three molecules can be traced to how the potential anisotropies couple angular momentum states between the molecule and the bosonic $^4\text{He}$ atoms. Although HF has a rotational constant that is almost double that of HCl, the somewhat larger anisotropy of the PES leads to a small asymptotic decrease in the effective rotational constant whereas, HCl and HBr approach their gas-phase values in the nanodroplet limit.
Table 3.1: Atomic and molecular masses and molecular rotational constants.

<table>
<thead>
<tr>
<th>Atom/Molecule</th>
<th>Mass (a.m.u.)</th>
<th>Rotational Constant (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^4)He</td>
<td>4.00260</td>
<td>——</td>
</tr>
<tr>
<td>HF</td>
<td>20.00634</td>
<td>20.560</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46094</td>
<td>10.403</td>
</tr>
<tr>
<td>HBr</td>
<td>80.91194</td>
<td>8.473</td>
</tr>
</tbody>
</table>

Table 3.2: Parameters of the analytical PES fitted to the \textit{ab initio} interaction energies of the He-HF complex. This set of parameters requires distances (R) to be in Å and will result in potential values in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_0^0)</td>
<td>-0.01401238000863</td>
<td>(g_{05})</td>
<td>-0.02516881784584</td>
</tr>
<tr>
<td>(C_2^2)</td>
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<td>(g_{10})</td>
<td>-3.73235058315367</td>
</tr>
<tr>
<td>(b_0)</td>
<td>13.351403479292370</td>
<td>(g_{11})</td>
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</tr>
<tr>
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<td>(g_{12})</td>
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</tr>
<tr>
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<td>(g_{13})</td>
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</tr>
<tr>
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<td>(g_{14})</td>
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</tr>
<tr>
<td>(b_4)</td>
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<td>(g_{15})</td>
<td>0.02744036687153</td>
</tr>
<tr>
<td>(b_5)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>(d_1)</td>
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<td>(g_{22})</td>
<td>0.20171778104730</td>
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<tr>
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<td>(g_{23})</td>
<td>0.16229578225988</td>
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<tr>
<td>(d_3)</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>(g_{00})</td>
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<td>(g_{31})</td>
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<tr>
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<td>(g_{32})</td>
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<tr>
<td>(g_{02})</td>
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<td>(g_{33})</td>
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</tr>
<tr>
<td>(g_{03})</td>
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<td>-0.00145052999200</td>
</tr>
<tr>
<td>(g_{04})</td>
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</tbody>
</table>
Table 3.3: Parameters of the analytical PES fitted to the *ab initio* interaction energies of the He-HCl complex. This set of parameters requires distances (R) to be in Å and will result in potential values in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0^6$</td>
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<td>$g_{05}$</td>
<td>0.17984821</td>
</tr>
<tr>
<td>$C_6^5$</td>
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<td>$g_{11}$</td>
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<td>$g_{12}$</td>
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<tr>
<td>$b_2$</td>
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<td>$g_{13}$</td>
<td>-1.1149131</td>
</tr>
<tr>
<td>$b_3$</td>
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<td>$g_{14}$</td>
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</tr>
<tr>
<td>$b_4$</td>
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<td>$g_{15}$</td>
<td>-0.0821105</td>
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<td>$g_{20}$</td>
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</tr>
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<td>$g_{21}$</td>
<td>-0.08245550</td>
</tr>
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<td>$g_{02}$</td>
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<td>$g_{03}$</td>
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</tr>
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Table 3.4: Parameters of the analytical PES fitted to the \textit{ab initio} interaction energies of the He-HBr complex. This set of parameters requires distances (R) to be in Å and will result in potential values in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>C_0^6</td>
<td>-320.525651759542</td>
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<td>-0.076662339377</td>
</tr>
<tr>
<td>C_1^7</td>
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<tr>
<td>C_2^3</td>
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<tr>
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<td>g_12</td>
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</tr>
<tr>
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<td>g_13</td>
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<td>b_2</td>
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<tr>
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<tr>
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<td>-0.14874579592</td>
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<tr>
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<td>g_23</td>
<td>0.103244893893</td>
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<tr>
<td>d_2</td>
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<td>g_24</td>
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<tr>
<td>d_3</td>
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<td>g_34</td>
<td>-0.006071430979</td>
</tr>
<tr>
<td>g_03</td>
<td>0.912749039267</td>
<td>g_35</td>
<td>0.003520180843</td>
</tr>
</tbody>
</table>

Table 3.5: Well depths and atom-molecule separations at the two minima in the three dimer PESs. (\textit{*}) signifies the global minimum.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>$\theta$ (deg)</th>
<th>$R$ (bohr)</th>
<th>$V$ (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>He-HF</td>
<td>0.0\textit{*}</td>
<td>5.983\textit{*}</td>
<td>-43.844\textit{*}</td>
</tr>
<tr>
<td></td>
<td>180.0</td>
<td>5.667</td>
<td>-26.169</td>
</tr>
<tr>
<td>He-HCl</td>
<td>180.0\textit{*}</td>
<td>6.340\textit{*}</td>
<td>-32.736\textit{*}</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>7.242</td>
<td>-31.160</td>
</tr>
<tr>
<td>He-HBr</td>
<td>180.0\textit{*}</td>
<td>6.446\textit{*}</td>
<td>-37.103\textit{*}</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>7.783</td>
<td>-27.666</td>
</tr>
</tbody>
</table>
Table 3.6: Ground and excited state energies for the He-HF dimer in cm$^{-1}$. CC: Coupled-channel; MD: Matrix diagonalization; DMC: Fixed-node DMC using 1 the appropriate IBC node, 2 adiabatic and 3 accurate nodal functions. The $|j\ell J\rangle$ labeling scheme is exact only for the isotropic binary complex.

| Dominant $|j\ell J\rangle$ | CC    | D     | DMC$^1$ | DMC$^2$ | DMC$^3$ |
|-------------------------|-------|-------|---------|---------|---------|
| 000                     | -6.718| -6.723| -6.720 ± 0.033 |
| 011                     | -5.967| -5.974| -5.987 ± 0.053  | 32.776 ± 0.107 | 33.569 ± 0.142 |
| 101                     | 33.951| 33.980| 32.392 ± 0.117 | 32.776 ± 0.107 | 33.569 ± 0.142 |
| 111                     | 36.758| 36.755| 32.392 ± 0.117 | 32.776 ± 0.107 | 33.569 ± 0.142 |
| 121                     | 37.148| 37.144| 32.392 ± 0.117 | 32.776 ± 0.107 | 33.569 ± 0.142 |

Table 3.7: Ground and excited state energies for the He-HCl dimer in cm$^{-1}$. CC: Coupled-channel; MD: Matrix diagonalization; DMC: Fixed-node DMC using 1 the appropriate IBC node, 2 adiabatic and 3 accurate nodal functions. The $|j\ell J\rangle$ labeling scheme is exact only for the isotropic binary complex.

| Dominant $|j\ell J\rangle$ | CC    | D     | DMC$^1$ | DMC$^2$ | DMC$^3$ |
|-------------------------|-------|-------|---------|---------|---------|
| 000                     | -7.753| -7.761| -7.648 ± 0.033 |
| 011                     | -7.214| -7.213| -7.206 ± 0.041  | 13.526 ± 0.057 | 12.505 ± 0.061 |
| 101                     | 12.765| 12.805| 12.328 ± 0.057 | 13.526 ± 0.057 | 13.526 ± 0.057 |
| 111                     | 14.964| 14.977| 12.328 ± 0.057 | 13.526 ± 0.057 | 12.505 ± 0.061 |
| 121                     | 15.220| 15.251| 12.328 ± 0.057 | 13.526 ± 0.057 | 12.505 ± 0.061 |

Table 3.8: Ground and excited state energies for the He-HBr dimer in cm$^{-1}$. CC: Coupled-channel; MD: Matrix diagonalization; DMC: Fixed-node DMC using 1 the appropriate IBC node, 2 adiabatic and 3 accurate nodal functions. The $|j\ell J\rangle$ labeling scheme is exact only for the isotropic binary complex.

| Dominant $|j\ell J\rangle$ | CC    | D     | DMC$^1$ | DMC$^2$ | DMC$^3$ |
|-------------------------|-------|-------|---------|---------|---------|
| 000                     | -7.873| -7.881| -7.861 ± 0.076 |
| 011                     | -7.406| -7.414| -7.412 ± 0.034 | 8.561 ± 0.057 | 7.781 ± 0.131 |
| 101                     | 8.078 | 8.091 | 8.322 ± 0.142 | 8.561 ± 0.057 | 7.781 ± 0.131 |
| 111                     | 10.463| 10.455| 8.322 ± 0.142 | 8.561 ± 0.057 | 7.781 ± 0.131 |
| 121                     | 10.569| 10.548| 8.322 ± 0.142 | 8.561 ± 0.057 | 7.781 ± 0.131 |
Figure 3.1: Contour plots of potential energy: (a) He-HF, (b) He-HCl, (c) He-HBr. $\theta$ is the angle between molecular axis and a vector connecting c.o.m. of a molecule and a helium atom. The H-atom lies along the positive $z$-axis, i.e. $\theta = 0^\circ$ for He-HF and $\theta = 180^\circ$ for He-FH.
Figure 3.2: Radial strength (expansion) functions for: (a) He-HF, (b) He-HCl, (c) He-HBr PES. As one moves from HF (a) to HBr (c), the importance of $v_2$ term decreases. $R$ is a distance of He atom to the c.o.m. of a molecule.
Figure 3.3: Plots showing density of DMC walkers superimposed on the PES of He-HF in cylindrical coordinates $\rho = \sqrt{x^2 + y^2}$ for the rotational constant (a) $B = 0$ and (b) $B = B_0$ where $B_0$ is the physical (gas-phase) value. The H-atom of the HF molecule lies along the positive $z$–axis. In panel (a) walkers gather around the potential minimum, whereas in panel (b) walkers spread out more as a result of rotation of the molecule, therefore larger decoupling between the molecule and helium. Darker color corresponds to a higher density of walkers.
Figure 3.4: Same as Fig. 3.3 but for He-HCl.
Figure 3.5: Same as Fig. 3.3 but for He-HBr.
Figure 3.6: Radial correlation functions for HF-He$_N$ clusters where $R$ is the distance between the c.o.m. of the molecule and the He atom and $N$ is the number of He atoms solvating the diatom. All areas under the curves are normalized to 1.
Figure 3.7: Same as Fig. 3.6 but for He-HCl.
Figure 3.8: Same as Fig. 3.6 but for He-HBr.
Figure 3.9: Angular correlation functions for HF-He$_N$ clusters where $\theta$ is the angle between the molecular axis and the vector $\mathbf{R}$ connecting the molecule c.o.m. and the He atom. $0^\circ$ corresponds to the H-end of the molecule. All areas under the curves are normalized to 1.
Figure 3.10: Same as Fig. 3.9 but for He-HCl.
Figure 3.11: Same as Fig. 3.9 but for He-HBr.
Figure 3.12: Three-dimensional scatterplot of the probability density of the $|101\rangle$ space-fixed state obtained from diagonalization for the He-HF dimer (i.e., $|\langle x|101\rangle|^2$). The angles $\theta_1$ and $\theta_2$ are the space fixed polar angles of the HF molecule and the He atom, respectively; $\phi = \phi_1 - \phi_2$ is the relative azimuthal angle; $R$ is the distance, in atomic units, between the He atom and the HF center of mass. To generate the plot 20,000 points were chosen randomly in $(\theta_1, \theta_2, \phi, R)$ with $4 < R < 10$. Points in $R,\theta_1,\theta_2$ space are represented by spheres whose size is proportional to $|\langle x|101\rangle|^2$. Each sphere is colored according to its value of $R$. The equilibrium value of $R$ is $\sim 6$ bohr. The plane $\theta_2 = \pi/2$ does not correspond to a nodal surface because the wave function does not change sign as one crosses this surface. The nodal surface is roughly the same as the “free-rotor” node (i.e., the plane $\theta_1 = \pi/2$).
Figure 3.13: Values of the rotational energy of the states which evolve from $|101\rangle$ for the three HX molecules, as function of number of He atoms, $N$. Energies are expressed in terms of “$2B_{\text{eff}}$” where $B_{\text{eff}}$ is the effective rotational constant. The horizontal dashed lines show the value of $2B_0$ (i.e., the gas-phase values).
CHAPTER 4

RENORMALIZATION OF THE ROTATIONAL CONSTANTS OF NH$_3$

IN A $^4$He DROPLET

Abstract

The solvation dynamics of an ammonia molecule doped into a droplet containing of $N = 1-25$ $^4$He atoms are studied using the diffusion Monte Carlo (DMC) method. Excited states are computed using the adiabatic fixed-node procedure. The computed renormalization – a reduction of $\approx 5\%$ – of the rotational constants of the ammonia molecule is in quantitative agreement with recent experiments of Slipchenko and Vilesov [Chem. Phys. Lett., 412, 176, (2005)] and disagrees with the much larger renormalization – a reduction of $\approx 25\%$ – originally reported by Behrens et al. [J. Chem. Phys., 109, 5914, (1998)]. For the symmetric top ammonia molecule, we predict that the asymptotic limit is not reached until $N > 25$, similar to the case for the linear molecules HF, HCl and HBr, which also have relatively large rotational constants. We interpret these results as providing support for the prediction that rotors with large rotational constants should (i) exhibit a smaller renormalization of their moments of inertia and (ii) exhibit a slower rate of renormalization as a function of $N$ as compared to heavy rotors.

4.1 Introduction

The experimental study of He droplets has a long history, possibly extending back to 1908 [10, 11]. However, two developments in the 1990s have triggered a large number of experimental and theoretical studies of molecules – or small molecular clusters – seeded into $^4$He droplets: The first, in 1992, was the creation of the technology that allowed He nanodroplets to be used to do cluster isolation spectroscopy [12]. The second was the so-called microscopic Andronikashvili experiment [13, 14] in which the effect of the He environment on the rotational motion of a molecular probe seeded into a $^4$He droplet was studied. Surprisingly, in the early Andronikashvili-type experiments using SF$_6$ and OCS probe molecules [14, 15], sharp rotational features, characteristic of free (gas-phase)
molecular rotation, were observed but with renormalized (reduced) rotational constants. For example, in the case of SF$_6$, the renormalized rotational constant is approximately one-third of its gas phase value.

Since these early experiments, many dopant molecules have been studied both experimentally and theoretically [16–20]. One persistent objective of these studies has been to try to relate the extent by which the rotational constants are renormalized to general properties such as (i) the anisotropy of the molecule-He interaction potential; (ii) the local superfluidity of the He around the molecule; and (iii) whether the rotational constants are large (as in the case of “light rotors” such as HF, H$_2$O, NH$_3$) or small (as in the case of “heavy rotors” such as SF$_6$, OCS). Nevertheless, a clear connection has still not been found between any one of these three factors and the degree of renormalization.

Probably the most generally applicable rule of thumb, suggested by Lee et al. [21], is that light rotors tend to experience a smaller (and slower [41]) renormalization of their rotational constants as compared to heavier rotors. The explanation is that light rotors, because of their large rotational constants, in effect average the interaction potential so that the rotor appears to the $^4$He atoms as if the potential were almost spatially isotropic. Therefore, angular momentum transfer between the He atoms and the rotor is relatively inefficient. This is in contrast to the situation for heavy rotors, for which a fraction of the He density is able to follow the rotor adiabatically. It is this dragging of the He density that leads to the relatively large renormalization observed for heavy rotors.

However, exceptions exist; in a study using “fudged” molecules (i.e., molecules with non-physical values for their rotational constants) Paolini et al. [42] came to the conclusion that the molecular anisotropy is more important than the size of the rotational constants. In particular, Paolini et al. [42] compared the solvation dynamics of OCS and HCN with their fudged counterparts, f-OSC and f-HCN, for which the intermolecular potentials were kept the same but the rotational constants were interchanged. Their study compared the degree of renormalization experienced by the two molecules with their fudged versions; this was measured by $\Delta = B/B_0$ where $B$ is the apparent (renormalized) rotational constant.
observed in the droplet. For OCS, $\Delta = 0.36$ and for f-OSC, $\Delta = 0.33$. Similarly, for HCN, $\Delta = 0.90$ and for f-OCS, $\Delta = 0.81$. Thus, even though the rotational constant of OCS is about 7 times smaller than that of HCN, interchanging these constants in the fudged molecules produces relatively little change in $\Delta$. This suggests that the molecular anisotropy is more important than the size of the gas-phase rotational constant.

It is worth pointing out that HCN and OCS are similar to each other – but dissimilar to many other molecules that have so far been studied – in exhibiting both $a$-type and $b$-type states. For HCN, in an earlier study, the behavior of the solvation dynamics was traced to significant state mixing caused by anisotropies in the potential energy function [6]. In fixed-node DMC calculations, this manifests itself as a noticeable distortion of the nodal topologies. Though usually considered a light rotor, the rotational constant of HCN, $B_0 = 1.48$ cm$^{-1}$, is not exceptionally large when compared to molecules such as such as HF, HCl, HBr, H$_2$O, NH$_3$ and CH$_4$. It is therefore possible that the conclusions of Paolini et al. [42] apply to an intermediate regime for which the molecular anisotropy competes with the effect of the size of the bare, gas-phase rotational constant.

Some weight is given to this argument by recent path integral Monte Carlo computations of the rotational dynamics of CH$_4$ ($B_0 = 5.1$ cm$^{-1}$) and f-CH$_4$ ($B_f = 0.105$ cm$^{-1}$, where $B_f$ is the gas-phase rotational constant of the fudged molecule) in $^4$He nanodroplets [98]. These calculations observed a “rotational smearing” effect for large values of the rotational constant similar to that first pointed out for SF$_6$ ($B_0 = 0.091$ cm$^{-1}$) and f-SF$_6$ ($B_f = 10 \times B_0$) [21]. For larger rotational constants, the molecule becomes almost completely decoupled from the He shell because the interaction potential appears essentially isotropic due to orientational averaging. That is to say, for light rotors the renormalization is not directly the result of adiabatic following – a conclusion that echoes that of the earlier SF$_6$ study where adiabatic following was posited specifically for heavy rotors [21].

Similar conclusions can also be drawn from a study [7] of the solvation dynamics of HF, HCl and HBr in $^4$He nanodroplets in which (i) the transition to the nanodroplet limit [i.e., the saturated value of the observed value(s) of the rotational constant(s)] was observed
to be much slower than for heavier rotors, and (ii) the renormalization experienced was also quite small as compared to heavier rotors. Curiously, the renormalization observed for HF was larger than those seen for HCl and HBr, despite the fact that HF has the largest gas-phase rotational constant of the three molecules. This was attributed to the slightly stronger anisotropy of the HF-He intermolecular potential. Nevertheless, comparing the actual extent of renormalization for the three molecules – HF ($\Delta = 0.98$), HCl ($\Delta \approx 1$) and HBr ($\Delta \approx 1$) – shows that this effect is relatively weak in comparison to that induced by the size of the rotational constants.

Taken together, this suggests that one can identify three regimes: In Regime I – the adiabatic following regime (very small rotational constants) – the He atoms experience a slowly rotating anisotropic potential (i.e., significant density is dragged along as the molecule rotates). Regime I is characterized by strong renormalization and a relatively fast approach to the nanodroplet limit. In Regime II – intermediately sized rotational constants – there exists a complex interplay between the effect of the size of the gas-phase rotational constant of the molecule and the anisotropic contributions to the atom-molecule potential energy. In this regime, very little can be predicted based solely on the size of the gas-phase rotational constants and the degree of anisotropy of the potential. Finally, in Regime III – in the limit of very large rotational constants – there is no significant adiabatic following, and a relatively small renormalization is observed together with a comparatively slow approach to the nanodroplet limit.

According to this view, the ammonia molecule should fall into Regime III, the light rotor limit, because its gas-phase rotational constants are $B_0 = 9.945\text{cm}^{-1}$ and $C_0 = 6.229\text{cm}^{-1}$. The case of NH$_3$ is, however, somewhat peculiar in that an early experiment by Behrens et al. [32] measured a renormalized rotational constant $B = 7.5\text{cm}^{-1}$ that represents a 25% reduction in $B_0$. In contrast, a much more recent experiment [31] found only a 5% reduction in $B_0$; this is much more in line with expectations. Even though it is likely that the more recent experiment is correct, it is, nevertheless, of interest to study the quantum solvation dynamics of NH$_3$ in a $^4$He droplet for at least two reasons: (i) To definitively decide
between the two experiments, and (ii) to test further the validity of the “three-regimes” picture proposed above.

To that end, in this paper we perform fixed-node DMC simulations for NH$_3$-He$_N$ clusters with $N = 1 - 25$. Because there are two sets of conflicting experimental results in regard to the extent of renormalization, it is important to carefully study the nodal structure of the excited rotational states. In particular, given the relatively large gas-phase rotational constants of ammonia, it would seem reasonable that it would be sufficient to a so-called “isotropic node” (a nodal function appropriate to a hypothetical complex in which the NH$_3$-He potential is assumed to not depend on the angles). This is because, as noted, a large amount of orientational averaging of the already weakly anisotropic potential is expected because of the large rotational constants of the NH$_3$ monomer. This should tend to make the effective potential more isotropic [21]. However, the experimental results of Behrens et al. [32] imply significant state mixing and, therefore, possible distortion of the nodal topologies in the excited states. This would be similar to the case of HCN-He, despite HCN often being thought of as a “light” rotor [6].

For these reasons, we have computed the nodal functions for the $J = 1$ excited states using the recently developed adiabatic node DMC (ANDMC) technique, in which an adiabatic separation of radial and angular motions is made to estimate the nodal geometry of the states in question [6, 7]. As it turns out, we find that the adiabatic node is essentially indistinguishable from the nodal functions of the hypothetical isotropic complex. Using these nodes we obtain quantitative agreement with the $\approx 5\%$ renormalization observed in the experiments of Slipchenko and Vilesov [31] together with relatively slow convergence to the nanodroplet limit as a function of $N$. We also perform calculations for f-NH$_3$ for which the rotational constants are chosen to be 100 times smaller than the physical values – these are comparable in size to the physical value of the rotational constant for SF$_6$.

The paper is organized as follows: Sec. 4.2 introduces the Hamiltonian and describes the potential energy functions used. A brief overview of the RBDMC method is given in Sec. 4.3 together with a description of how importance sampling [23] was implemented.
We also describe the ANDMC method in this section. Sec. 4.4 contains our results and conclusions.

4.2 Hamiltonian

Working in the space-fixed frame and neglecting three-body effects, three Euler angles, \((\alpha, \beta, \gamma)\), define the orientation of the \(\text{NH}_3\) molecule (mass \(M\)), and two more, \((\theta_i, \phi_i)\), specify the angular location of the \(i^{th}\) He atom (mass \(m_i\)). The distance of the \(i^{th}\) He atom from the center-of-mass (c.o.m.) of \(\text{NH}_3\) is \(R_i\). Assuming a rigid \(\text{NH}_3\) molecule, the PES is \(V(R_i, \Theta_{iI}, \Phi_{iI})\) where \(\Theta_{iI}\) and \(\Phi_{iI}\) relate the \(\mathbf{R}\)-vector of the \(i^{th}\) He atom to an axis system that coincides with the principal axes of the \(\text{NH}_3\) molecule, here denoted as “\(I\)”. The \(\text{NH}_3\) potential is due to Hodges and Wheatley [99], and the interaction potential between two He atoms \(i\) and \(j\), \(V_{HeHe}^{He}(r_{ij})\) is that of Aziz and Slaman [100] (see also Ref. [50]). In the potential of Hodges and Wheatley, the N atom of the \(\text{NH}_3\) molecule is used as the origin rather than the center-of-mass of the \(\text{NH}_3\) molecule, and so this has to be accounted for in the calculations.

In the space-fixed frame the Hamiltonian can be written:

\[
H = -\frac{\hbar^2}{2M} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + H_I + \sum_{i<j}^{N} V_{HeHe}^{He}(r_{ij}) + \sum_{i=1}^{N} V(R_i, \Theta_{iI}, \Phi_{iI}) \tag{4.1}
\]

where

\[
H_I = B_0 \mathbf{j}^2 + (C_0 - B_0) j_z^2 \tag{4.2}
\]

and \(\mathbf{j}\) is the angular momentum vector of the molecule.

4.3 Rigid-Body DMC Calculations

The DMC calculations were done using the rigid-body diffusion Monte Carlo (RBDMC) method originally developed by Buch [52] (i.e., the ammonia monomer is treated as a rigid
body fixed at its equilibrium geometry). This procedure, though approximate, eliminates the vibrational degrees of freedom and thus allows larger diffusive time steps to be made. The RBDMC approximation is especially suitable for very weakly bound complexes because of the large difference in the strengths of the intramolecular and intermolecular forces—and, therefore, time scales of the various motions. The RBDMC method exploits the fact that, for sufficiently small rotations, the rotational energy propagator is analogous to the translational kinetic energy propagator with a diffusion constant \( D_{\omega} = 1/2I_{\omega} \) where \( I_{\omega} \) is the moment of inertia of the molecule around the principal axis corresponding to \( L_{\omega} \). This procedure takes advantage of the fact that components of angular momentum commute for sufficiently small rotations.

Excited rotational states can be computed in the RBDMC method by use of the fixed-node method [23, 59], which involves “killing” walkers that cross nodal surfaces. However, this procedure requires that accurate estimates of the nodal surfaces be available. In general, it is difficult to compute accurate nodal surfaces because, obviously, the wave function itself is unknown. Sometimes symmetries can be used to estimate nodal surfaces or, more usually, one must resort to approximations. Here nodal surfaces are calculated using the ANDMC procedure, as will be described. In the simulations, importance sampling was used to guide the walkers.

4.3.1 Importance sampling

In importance sampling, a trial wave function, \( \Psi_T \), is introduced to guide the DMC walkers. This improves the efficiency of the DMC method as well as increases the precision of the computed energies [23]. In addition, for clusters containing larger numbers of He atoms unphysical dissociation may occur unless importance sampling is used. Use of a guiding trial wave function leads to a diffusion-like equation for the mixed function \( f(R, r_i) = \Psi(R, r_i)\Psi_T(R, r_i) \) where \( R \) and \( r_i \) are the molecular and He atom coordinates, respectively. Additional drift terms – quantum forces – are introduced into the diffusive process to guide the walkers to regions of high probability density [58]. In this work trial wave functions were chosen to have the form
\[
    \psi_T = \left\{ \prod_{i=1}^{N} f(R_i) \prod_{i \neq j}^{N} \Xi(r_{ij}) \right\} \Upsilon(\Omega, \theta_i, \phi_i) \tag{4.3}
\]

where \( \Omega \) denotes the Euler angles. As in previous studies [6,21,46,101], the radial functions were chosen to have the form

\[
    f(R) = b \exp\left(-\frac{c}{R^5} - aR\right) \tag{4.4}
\]

where the parameters \( a, b, c \) were obtained by fitting the function \( f(R) \) to adiabatic radial functions, as will be described. For ground state calculations, the angular function \( \Upsilon(\Omega_1, \Omega_2) \) was set to unity, whereas for excited states this function contains the nodal topology. The He-He part of the trial wave function, \( \Xi(r_{ij}) \), was the same as that used in previous studies [7].

4.3.2 Nodal functions

The ANDMC procedure is based on the original idea of Holmgren et al. [49] in which an adiabatic (i.e., Born-Oppenheimer-like, angular-radial separation (BOARS) is made in the molecule fixed frame). That is, the radial degree of freedom is frozen at some value \( R = R_0 \) and the angular part of the resulting Schrödinger equation is then solved; this is then repeated for different values of \( R_0 \), which generates families of adiabatic radial potentials. The adiabatic potentials are then used to solve for the radial wave functions. Although the BOARS approach is no longer routinely used for van der Waals complexes, it nevertheless turns out to provide a useful way of generating good estimates of nodal surfaces for small molecule-He clusters. The method is also computationally quite efficient because the angular matrix elements can be computed analytically or semi-analytically [2,61].

Adiabatic nodal functions are computed by making the following assumptions: (i) He-He interactions are ignored; (ii) the He-molecule distance \( R \) is fixed at \( R = R_0 \); (iii) the molecular c.o.m. is fixed in place; and (iv) for more than a single He atom, the adiabatic separation is done in the space-fixed frame.
The resulting adiabatic Hamiltonian is the following

$$H_{\text{adiab}} = H_I + \sum_{i=1}^{N} \kappa l_i^2 + \sum_{i=1}^{N} V(R_0, \Theta_{iI}, \Phi_{iI}) \quad (4.5)$$

where $\kappa = 1/2mR_0^2$. Diagonalizing $H_{\text{adiab}}$ at fixed $J$ and $N$ thus produces estimates for the nodes.

For more than a single He atom, this approach differs from the usual BOARS method in that the molecular c.o.m. has been clamped, so the $^4He$ mass, $m$, appears rather than the reduced mass, $\mu$. In practice the nodal topology is relatively insensitive to using $m$ or $\mu$. Solving Eq. (4.5) at a series of $R_0$ values yields a set of effective potentials that are then used to solve for the radial functions $\rho(R)$ and eigenvalues. For a single He atom, the value of $R_0$ used to compute the nodal surface of the angular wave function was calculated in two different ways: (i) For $N = 1$, the expectation value of $R$ for the appropriate radial eigenfunction in the BOARS procedure was computed; and (ii) for $N > 1$, we set $R_0$ to be the expectation of value of $R$ in the ground state (i.e., $\langle R \rangle_{gs}$, which is computed using descendant weighting in the DMC computations). This procedure is somewhat inconsistent in that, strictly, the value of $\langle R \rangle$ for the excited state should be used: however, in DMC, this is unavailable without first knowing the nodal function. To check that this procedure does not introduce large errors, we varied $R_0$ over a range of values and found that (i) for $N = 1$, $\langle R \rangle$ is similar for ground and $J = 1$ excited states, and (ii) the results did not depend strongly on the exact value of $R_0$ used unless $R_0$ was chosen to be significantly smaller than the minimum in the adiabatic potential. Fig. 4.2 shows the distribution of $R$ values obtained from DMC computations for three different values of $B$. As expected, the distributions peak at smaller values of $R$ as the rotational constant is reduced.

For the NH$_3$-He dimer, the angular basis functions used are the following [2]

$$\Phi_{jkl}^{JM}(\alpha, \beta, \gamma, \theta, \phi) = \sum m_j, m_L \langle jLm_jm_L|JM \rangle Y_{Lm_L}(\theta, \phi) \phi_{m_j,k}(\alpha, \beta, \gamma) \quad (4.6)$$
where \( \phi_{m_j,k}^j(\alpha, \beta, \gamma) = [(2j + 1)/8\pi^2]^{1/2} \times D_{Kk}^j(\alpha, \beta, \gamma) \) and \( D_{KK}^j \) is a rotation matrix.

Diagonalization involves the coupling of an arbitrary number of angular momenta. For example consider the case where four (rotor + three He atoms) angular momenta are involved (i.e., \( J, I_1, I_2, I_3 \) where the quantum numbers \( j, m_j \) refer to the rotor and \( \ell_i, m_i, i = 2, 3, 4 \) to the He atoms). This procedure has been described for the case of linear rotors in Ref. [7].

4.4 Results and Conclusions

For calibration, we computed the ground and excited \((J = 1)\) states for the NH\(_3\)-He dimer using nodal functions for the hypothetical isotropic complex, adiabatic nodal functions and coupled channel calculations obtained using the program BOUND [56]. The results in Table 4.1 show excellent agreement for the ground and excited states of the NH\(_3\)-He dimer. Fig. 4.3 shows the percentage reduction in the \( B_0 \) and \( C_0 \) rotational constants for NH\(_3\) and f-NH\(_3\) as a function of the number of \(^4\)He atoms using the “isotropic” node. For both cases, there was little or no difference observed between results obtained using the “isotropic” and adiabatic nodal functions. This is interesting, as for the value of \( R_0 \) used to obtain the adiabatic-node, there is a substantial state mixing in the \( J = 1 \) excited states for f-NH\(_3\). It can be seen from Fig. 4.2 that the radial probability distribution for the f-NH\(_3\) peaks out at smaller distances as compared to that of NH\(_3\) with gas-phase rotational constants values. This, in turn, leads to a larger mixing of the rotationaly excited states. Also, it is apparent from Fig. 4.3 that the asymptotic, \( \approx 5\% \) reduction in \( B_0 \) and \( C_0 \) is not achieved until \( N \approx 25 \) and is reached for \( N \approx 8 \) for f-NH\(_3\). The latter case may require additonal work to decrease statistical uncertainties.

Fig. 4.1 shows a projection of the He density at fixed \( R_0 \) obtained from the DMC calculations. Two cases are presented: In Fig. 4.1 (top) the rotational constants of the ammonia molecule are set to those of f-NH\(_3\)-He whereas in Fig. 4.1 (bottom) the physical (gas-phase) values are used. In both cases the density is computed in the principal axis frame of the ammonia monomer. The anisotropy of the potential, clearly apparent in Fig. 4.1 (top), has been almost completely averaged in Fig. 4.1 (bottom). This is in contrast to the
situation for the SF$_6$ molecule, which has considerably smaller rotational constants [21].
Table 4.1: Ground and excited state energies for the He-NH$_3$ dimer considered in this work (in cm$^{-1}$) and as obtained from coupled-channel calculations and DMC. The $|jk\ell J\rangle$ labeling scheme is exact only in the isotropic limit (i.e., when the PES is assumed not to depend on the angles).

| $|jk\ell J\rangle$ | coupled-channel | cDMC        |
|-----------------|----------------|-------------|
| |0000$|$        | - 5.244       | - 5.298±0.077 |
| |1101$|$        | 10.600         | 10.786±0.097  |
| |1001$|$        | 14.224         | 14.148±0.103  |
Figure 4.1: Projection into the $\theta - \phi$ plane of $\rho = \sqrt{\left|\Psi(R_0, \theta, \phi)\right|^2}$ as obtained from the DMC calculations. In the top panel the rotational constants are 1/20th of the physical (gas-phase) values: the physical values are used in constructing the lower panel. Notice the different scales of the $\rho$ axis between the two panels.
Figure 4.2: Normalized radial probability density for NH$_3$-He for two values of the rotational constants: Gas-phase values (black) $B_0$ and $C_0$; fudged (red) $B_0/20$ and $C_0/20$. 
Figure 4.3: Effective rotational constants (RC), $B_0$ (black circles) and $C_0$ (red diamonds), for NH$_3$ (top) and f-NH$_3$ (bottom) as a function of the number, N, of $^4$He atoms. The error bars represent standard deviations of the computed values.
CHAPTER 5
INTERCHANGE TUNNELING SPLITTING IN THE NH₃ DIMER IN A
⁴He DROPLET

Abstract

The diffusion Monte Carlo (DMC) method is used to study the interchange tunneling of \((\text{NH₃})_2\) embedded in \(^4\text{He}\) clusters. The interchange tunneling splittings are reported as a function of the number of \(^4\text{He}\) atoms in the droplet. Our results are in agreement with previous experimental findings by Behrens et al. \([J. \text{Chem. Phys.}, \textbf{107}, 7179 (1997)]\) which indicate that the presence of He impedes the large amplitude interchange tunneling motion. This suggests a structure in which the two ammonia monomers are more equivalent in the droplet than in the free gas-phase dimer.

5.1 Introduction

The experimental and theoretical study of atoms, molecules and small molecular clusters doped into nano- (or smaller) sized droplets of \(^4\text{He}\) can be traced to two important advances: The first, in 1992, was the creation of the technology that allowed He nanodroplets to be used to do cluster isolation spectroscopy \([12]\). The second was the so-called microscopic Andronikashvili experiment \([13,14]\) in which the effect of the He environment on the rotational motion of a molecular probe seeded into a \(^4\text{He}\) droplet was studied. In the early Andronikashvili-type experiments using SF₆ and OCS probe molecules \([14,15]\), sharp rotational features, characteristic of free (gas-phase) molecular rotation, were observed but with renormalized (reduced) rotational constants. For example, in the case of SF₆, the renormalized rotational constant is approximately one-third of its gas phase value. Since these early experiments, a large number of dopant molecules have been investigated both experimentally and theoretically \([16–20]\).

Despite the large number of studies of these systems, the effect of the quantum solvent on the dopant species, though gentle, is, nevertheless complicated and only partially understood. For this reason, recent experiments have begun to look at large amplitude motions
of van der Waals clusters immersed in such droplets. The first such study by Behrens et al. [26], in 1997, examined the ammonia dimer spectrum in cold He clusters. In particular, this experiment probed the interchange tunneling splitting (ITS) and found that this splitting was quenched by the He environment. This study was soon followed by a study of the HF dimer in $^4$He droplets by Nauta and Miller [102] and, again, a substantial quenching of the ITS, by approximately 40%, in both the ground and vibrationally excited states of the $\text{(HF)}_2$ was observed. The reduction of the ITS in the HF dimer was confirmed in calculations by Jiang et al. [91]. However, using the same computational procedure as for HF dimer (i.e., fixed-node DMC) Jiang et al. found no reduction in the ITS for the HCl dimer. This result is curious because of the similarities between the HF and HCl dimers and the fact that the computations between the two systems were essentially identical. A recent experiment on HCl dimer solvated in $^4$He only complicates the picture [103]: This experiment finds a significant reduction in the ITS, albeit for the $\nu_1$ and $\nu_2$ vibrationally excited states rather than that in the ground vibrational state. Although a direct comparison with the ITS in the ground vibrational state cannot be made, based on several reasonable assumptions, Skvortsov et al. predicted a 40 - 50% reduction of the ITS in the ground vibrational state. These results are puzzling and suggest that it is worthwhile to pursue experimental and theoretical studies of large amplitude tunneling motions in hydrogen-bonded complexes.

As noted by Lin et al. [27], the ammonia dimer is one of the three textbook examples of hydrogen bonding, the other two being $\text{(HF)}_2$ and $\text{(H}_2\text{O)}_2$. Of these three, $\text{(NH}_3\text{)}_2$ has been the most difficult to understand and, is therefore, the most interesting example. Early molecular beam experiments by Odutola et al. [28] discovered the polar nature of the ammonia dimer, which was believed to have a classical hydrogen-bonded structure (i.e., one of the monomers acts as a proton donor with an NH bond pointed towards the lone pair of the other monomer); see Fig. 5.1 (top). Subsequent experiments by Nelson et al. [29] contradicted this expectation and suggested a more cyclic structure as opposed to a linear hydrogen-bonded structure. The current consensus seems to be that ammonia dimer is a hydrogen-bonded structure but with the twist that the structure is nonlinear as reflected by
the ease by which the donor/acceptor behavior of the molecules can be interchanged [30].

The uncertainties associated with the structure of the ammonia dimer were one of the motivations for Behrens et al. [26] to study this system in ultra-cold nanodroplets of $^4$He. The main conclusion drawn from their study was that the ITS is quenched considerably, by a factor of 2-5, as compared to the gas phase. In particular, the difference between the $\nu_1$ and $\nu_2$ bands is much smaller for NH$_3$ in He (14 cm$^{-1}$) than in the free dimer (25 cm$^{-1}$). This was interpreted as the two ammonia monomers being more equivalent than in the gas phase which, in turn, suggests a more cyclic structure in a $^4$He droplet. The linear and cyclic structures are shown in Fig. 5.1. The potential energy curves for the ground and excited states of the free ammonia dimer are shown in Fig. 5.3 and in Ref. [26]. The excited state consists of two double-well potentials that would be asymmetric due to the non equivalence of the two monomers except that they are coupled by an interaction term proportional to $\nu_{01}/R^3$ where $\nu_{01}$ is the transition dipole moment and $R$ is the distance between the two dimers. This coupling has the effect of producing two symmetric double well potentials in the excited state with different barrier heights. The $\nu_1$ and $\nu_2$ ir bands correspond to transitions from the ground state to these two excited states. The smaller the difference between these bands, the smaller the difference between the two excited states and the more equivalent the monomers [26]. This analysis is based mainly on the discussion of Linnartz et al. [104].

In this article, we perform the first simulations of the ammonia dimer doped into a small droplet of $^4$He. Our goal is to compute the ITS for the ammonia dimer so as to make comparison with the experimental results.

The paper is organized as follows: Sec. 5.2 describes the Hamiltonian and potential energy surface. The details of the fixed-node DMC approach are outlined in Sec. 5.3. Results and conclusions are in Sec. 5.4.

5.2 Hamiltonian

Working in the space-fixed frame and neglecting three-body effects, six Euler angles, $(\alpha_k, \beta_k, \gamma_k)$, $k = 1, 2$, define the orientation of the two NH$_3$ molecules (mass $M$), and two
more, \((\theta_i, \phi_i)\), specify the angular location of the \(i^{th}\) He atom (mass \(m\)). The distance of the \(i^{th}\) He atom from the center-of-mass (c.o.m.) of each NH\(_3\) monomer is \(R_{ik}\). Assuming a rigid NH\(_3\) molecule, the atom-monomer potential energy surface (PES) is \(V(R_{ik}, \Theta_{ik}, \Phi_{ik})\) where \(\Theta_{ik}\) and \(\Phi_{ik}\) relate the \(R_i\)-vector of the \(i^{th}\) He atom to an axis system that coincides with the principal axes of each NH\(_3\) molecule. The NH\(_3\) potential is due to Hodges and Wheatley [99], and the interaction potential between two He atoms \(i\) and \(j\), \(V_{He}^{He}(r_{ij})\) is that of Aziz and Slaman [100] (see also Ref. [50]). The ammonia-ammonia potential is due to Olthof et al. [105]. In the potential of Hodges and Wheatley [99] the N atom of the NH\(_3\) molecule is used as the origin, rather than the center-of-mass of the NH\(_3\) molecule, so this has to be accounted for in the calculations. The coordinate system used is shown in Fig. 5.2.

In the space-fixed frame the Hamiltonian can be written:

\[
\hat{H} = \frac{-\hbar^2}{2M} \sum_{k=A<B} \nabla_k^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{k=A,B} H_k + \sum_{i<j} V_{He}^{He}(r_{ij}) \\
+ \sum_{i=1}^{N} V(R_{ik}, \Theta_{ik}, \Phi_{ik}) + V(R, \alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2) \tag{5.1}
\]

where \(R\) is the ammonia-ammonia distance and

\[
\hat{H}_k = B_0 j_z^2 + (C_0 - B_0) j_z^2 \tag{5.2}
\]

and \(j\) is the angular momentum vector of the molecule.

The largest source of uncertainty in the computations is the accuracy of the PES for the ammonia-ammonia interaction. The PES computed by Olthof et al. [105] contains the permanent dipole, quadrupole and octupole moments. The exchange and dispersion contributions were modeled by a site-site exp-6 interaction. However, the PES is a relatively crude model that was designed to understand then-available dimer spectroscopic data. Later
applications showed that it does not work so well when one considers geometries that were not probed in the original experimental data. However, it remains the best potential available, and we find that it is sufficient to model the main features of the experiment by Behrens et al. [26].

5.3 Diffusion Monte Carlo Calculations

All of the computations were done using the rigid-body diffusion Monte Carlo (RBDMC) method [52] (i.e., the ammonia monomers are each treated as a rigid body fixed at its equilibrium geometry). This procedure, though approximate, eliminates the vibrational degrees of freedom and thus allows larger diffusive time steps to be made. The RBDMC approximation is especially suitable for very weakly bound complexes because of the large difference in the strengths of the intramolecular and intermolecular forces – and, therefore, time scales of the various motions.

Excited rotational states are computed in the RBDMC method by use of the fixed-node method [23, 59] that involves “killing” walkers that cross nodal surfaces. This procedure requires that accurate estimates of the nodal surfaces are available. In the case of ammonia dimer, the nodal surface appropriate to the tunneling state in question can be obtained by symmetry. We have also computed the nodal surface of this state in an adiabatic approximation in which the ammonia-ammonia intermolecular distance is frozen at its equilibrium value. For convenience of computation, only the dipole, quadrupole and octupole moments were retained in the PES. This is a fairly dramatic approximation but it provides a relatively good trial wavefunction for the excited state of interest. The reason for retaining only the electrostatic contributions to the potential is that the matrix elements of the Hamiltonian of the free dimer can be computed analytically.

The electrostatic potential energy, at fixed $R$, can be expanded in terms of the complete orthogonal set of angular functions:
\[ A_{\{\Lambda\}}(\alpha_A, \beta_A, \gamma_A, \alpha_B, \beta_B, \gamma_B) = \sum_M \begin{pmatrix} L_A & L_B & L \\ M & -M & 0 \end{pmatrix} D^{L_A}_{MK_A}(\alpha_A, \beta_A, \gamma_A)D^{L_B}_{MK_B}(\alpha_B, \beta_B, \gamma_B) \]

where \( \{\Lambda\} \) is \( \{L_a, K_A, L_B, L\} \); the \( D \) functions are Wigner rotation matrix elements and

\[
\begin{pmatrix} \cdot & \cdot & \cdot \end{pmatrix}
\]

is a Wigner 3-j symbol. The potential is expanded as

\[ V(R, \Omega_A, \Omega_B) = \sum_{\{\Lambda\}} v_{\{\Lambda\}}(R) A_{\{\Lambda\}}(\Omega_A, \Omega_B) \]

where \( \Omega_A, \Omega_B \) represent the Euler angles of the two ammonia monomers. The matrix elements of the electrostatic potential can then be written analytically as follows.

\[ v_{\{\Lambda\}}(R) = \delta_{L_A+L_B,L}(-1)^{L_A}(2L+1)^{1/2} \times \left( \begin{array}{c} 2L \\ 2L_A \end{array} \right)^{1/2} x Q^{L_A}_{K_A} Q^{L_B}_{K_B}/R^{L_A+L_B+1} \]

where \( \begin{pmatrix} 2L \\ 2L_A \end{pmatrix} \) is a binomial symbol.

Fig. 5.3 shows a slice through the electrostatic potential and the ground and excited state wavefunctions, \( A_1 \) and \( A_4 \), associated with the ITS motion. This wavefunction was used to guide the walkers in the fixed-node DMC procedure.

5.4 Importance sampling

In importance sampling, a trial wavefunction, \( \Psi_T \), is introduced to guide the DMC walkers. This both improves the efficiency of the DMC method and increases the precision
of the computed energies [23]. In addition, for clusters containing larger numbers of He atoms, unphysical dissociation can occur unless importance sampling is used. Use of a guiding trial wavefunction leads to a diffusion-like equation for the mixed function $f(R, r_i) = \Psi(R, r_i)\Psi_T(R, r_i)$ where $R$ and $r_i$ are the molecular and He atom coordinates, respectively. Additional drift terms – quantum forces – are introduced into the diffusive process which guide the walkers to regions of high-probability density [58]. In this work the He-ammonia trial wavefunctions were chosen to have the form for each ammonia monomer

$$\psi_T = \left( \prod_{i=1}^{N} f(R_i) \prod_{i \neq j}^{N} \Xi(r_{ij}) \right) \Upsilon(\Omega, \theta_i, \phi_i)$$

(5.6)

where $\Omega$ are the Euler angles $R_A (R_B)$ is the radial distance from the molecular c.o.m. to He atom $i$ and $r_{ij}$ is the distance between He atoms $i$ and $j$. As in previous studies [6, 21, 46, 101], the radial functions were chosen to have the form

$$f(R) = b \exp\left(-\frac{c}{R^5} - aR\right),$$

(5.7)

where the parameters $a, b, c$ were obtained by fitting the function $f(R)$ to adiabatic radial functions, as described elsewhere. For ground state calculations, the angular function $\Upsilon(\Omega_1, \Omega_2)$ was set to unity, whereas for excited states this function contains the nodal topology. The He-He part of the trial wavefunction, $\Xi(r_{ij})$, was the same as that used in previous studies [7].

5.5 Results and Conclusions

For the bare NH$_3$ dimer, our DMC calculations agree favorably with the basis set results reported by Olthof et al. [105] – (see Table 5.1). Fig. 5.5 shows the reduction in the interchange tunneling splitting as a function of the number of He atoms. While the reduction is smaller than that observed experimentally, the basic trend is as observed in the experiment. We note that recent experiments [31] on the NH$_3$-He dimer have shown that previous experiments on that system [32] by the same authors as Ref. [26] overestimated
the renormalization of the rotation constant in that system. Therefore, it is possible that the reduction in the tunneling splitting observed experimentally in Ref. [26] might also overestimate the reduction, most likely due to using the CO$_2$ laser in both experiments (private communication).

Nevertheless, our results indicate that the scheme proposed in [26] captures the basic mechanism responsible for the reduction in the tunneling splitting, which, in turn, suggests a more cyclic structure in the $^4$He solvent. Future work will explore the use of a genetic algorithms to investigate whether the He environment distorts the nodal surface of the dimer. The procedure developed in this paper also opens up the way to explore other complexes that have very recently been studied in a He droplet (e.g., (H$_2$O)$_2$HCl. Vilesov et al. [25] have shown that He droplets provide a unique host that can be used for the isolation and study of single chemical acts). For example, they recently studied the formation of hydrogen bonds in water and ammonia clusters. This work has been extended to study the mechanism of ionization of acids such as HCl upon solvation. Here the idea is to attach water molecules one by one to an HCl molecule trapped in a He droplet so as to study the structure and the ionic state of the obtained clusters. We propose to combine the methods developed in this paper with the genetic-algorithm-DMC method developed earlier to study this system.
Table 5.1: Energies of the ground ($A_1$) and excited ($A_4$) states associated with the ITS. Basis set results are those reported by Olthof et al., J. Chem. Phys. 101, 8430 (1994).

<table>
<thead>
<tr>
<th>State</th>
<th>Basis Set</th>
<th>DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>-638.51</td>
<td>-639.35 ± 0.34</td>
</tr>
<tr>
<td>$A_4$</td>
<td>-622.66</td>
<td>-623.16 ± 0.38</td>
</tr>
</tbody>
</table>
Figure 5.1: Schematics showing the linear (top) and the cyclic (bottom) structures proposed for the free ammonia dimer.

Figure 5.2: Coordinate system used for the ammonia dimer. The dimer axis is denoted as z. The Euler angles are described in the text.
Figure 5.3: Projections of the ammonia-ammonia PES (top) and the $A_4$ wave function on to the $(\pi - \beta_2) - \beta_1$ plane (bottom). The nodal surface is apparent in (bottom).
Figure 5.4: Interchange tunneling splitting of $(\text{NH}_3)_2$ as a function of the number of $^4\text{He}$ atoms.
CHAPTER 6

COMPUTATION OF NODAL SURFACES IN FIXED-NODE DIFFUSION MONTE CARLO CALCULATIONS USING A GENETIC ALGORITHM

Abstract

The fixed-node diffusion Monte Carlo (DMC) algorithm is a powerful way of computing excited state energies in a remarkably diverse number of problems in quantum chemistry and physics. The main difficulty in implementing the procedure lies in obtaining an estimate of the nodal surface of the excited state in question. Sometimes the nodal surface can be obtained from symmetry or by making approximations. In any event, nodal surfaces are usually obtained in an ad hoc way. In fact, the search for nodal surfaces can be formulated as an optimization problem within the DMC procedure itself. Here we investigate the use of a genetic algorithm to systematically and automatically compute nodal surfaces. Application is made to the computation of excited states of the HCN-\(^4\)He complex and to the computation of tunneling splittings in the hydrogen bonded HCl-HCl complex.

6.1 Introduction

The DMC method is an accurate and straightforward way of finding ground state energies of quantum systems [22]. The main practical advantage of the method is that it can be applied to systems containing a large number of particles. For example, recent applications have included studies of the solvation of molecules and molecular clusters in droplets of \(^4\)He where the droplets might contain 20 or more helium atoms [6, 7, 21, 46, 57, 101, 106, 107]. Excellent reviews of the DMC algorithm and its implementation are available [23, 24].

Although the DMC method is numerically exact for the ground state, this is not the case for excited states [23, 24]. Prominent among the various approaches for adapting DMC to the calculation of excited states is the fixed-node method [22, 23]. In this algorithm, any DMC walkers that cross a predetermined nodal surface are eliminated. If the exact node
is known in advance, the DMC algorithm can be used to compute excited state energies with good accuracy. Unlike for the ground state, however, fixed-node calculations are no longer numerically exact. In general, the fixed-node method is somewhat paradoxical: To compute an excited state, the nodal surface of that excited state must already be known. At times, symmetry or approximations can be used to estimate the topology of the node but no general procedure exists. For example, recent computations of the interchange tunneling splitting in the HF and HCl dimers solvated into He droplets took advantage of symmetry to construct the nodal surface even though the full excited state wavefunction was itself unknown [91,108]. However, calculations of the equivalent tunneling splitting (e.g., for the mixed dimer HCl-HBr) cannot use symmetry to construct the nodal surface.

A number of approximations have also been developed to construct nodal surfaces, although these can be computationally intensive and difficult to implement [23,109]. Again, take as an example the HCl-HBr dimer doped into a He droplet. One could, for example, compute the nodal surface for the gas-phase HCl-HBr complex using basis set methods and then assume that the same node can be used for the solvated dimer. However, this is clearly an uncontrolled procedure.

All of this raises the question of whether it is possible to compute nodal surfaces on-the-fly during the DMC calculation. An elegant way of doing this has already been proposed by Sandler et al. [110], who recognized that certain conditions hold at the node in a DMC calculation. Because DMC walkers that cross a node are eliminated, one is, in effect, performing two DMC computations, one on each side of the node. Therefore, the energies obtained from these two computations, here denoted $E_+$ and $E_-$, should be equal if the nodal surface used is correct. Further, because the derivative of the wavefunction must be continuous across the node, the local density of DMC walkers crossing the node in each direction should be equal. Finally, the excited state must be orthogonal to the ground state. To impose these conditions, Sandler et al. [110] computed so-called flux histograms from DMC computations performed on each side of the node. By adjusting parameters in the nodal surface until (i) $E_+ = E_-$ and (ii) the flux histograms were identical, they were able
to obtain accurate estimates for the nodes of various excited states of the CO-H$_2$O complex. A later study by Severson and Buch used the same approach to compute intermolecular excited vibrational states in the cage water hexamer [111].

Although the histogram comparison method is, in principle, an excellent approach, it suffers from a number of practical drawbacks, the main one being that it is very difficult to compare multidimensional histograms. Even for 1D histograms, if the histograms have to be compared by eye, as was done in the papers by Buch and co-workers [110,111], the method is extremely tedious to implement and, in reality, is essentially impossible to do unless one has made a very good initial guess at the topology of the nodal surface.

In this article, we propose using a genetic algorithm (GA) [112] to compute nodal surfaces automatically based on the criteria outlined above. The key ingredient in a GA is to develop a fitness function that guides the evolution of an initially random population of “individuals” – in this case, each individual represents a guess at the correct nodal surface. The criteria developed by Buch and co-workers [110,111] are used to construct the fitness function: Because the fitness function involves comparing histograms of fluxes across the node then a way has to be developed to do this automatically. This is an important problem in the field of pattern recognition and a variety of approaches have been developed (e.g., the earth mover algorithm [113]).

Using this method, we are able to find automatically good estimates for nodal surfaces in several test problems including (i) the HCN-$^4$He dimer, (ii) the HCl-dimer and (iii) a “fudged” version of the HCl-dimer, f-(HCl)$_2$, for which the two monomers are artificially assigned different rotational constants so as to break the symmetry and distort the nodal topology of the symmetric dimer. For simplicity, in the case of the HCl dimers we make an adiabatic approximation in which the radial distances are frozen and concentrate solely on the angular part of the wavefunction. Doing this allows the exact node for each system to be calculated accurately using basis set methods, so as to make a comparison with the GA-DMC approach.

The method works best if an initial estimate of the node can be made (e.g., as is often
the case in van der Waals systems due to the weak interactions present). For example, the
nodes of certain rotationally excited states of the HCN-$^4$He dimer are quite close to the
corresponding nodes of the free HCN molecule treated as a rigid rotor [6,7,21,46,101,106].
In principle, the dimensionality of the problem is not a restriction in that multidimensional
histogram comparison is possible; however, the computational expense grows with the di-
mensionality of the problem. While the GA-DMC method is not a universal solution to
the problem of estimating nodal surfaces, there are many problems of current interest for
which it might be worth considering. In particular, a large number of recent experimental
studies have investigated the rotational dynamics of molecules or small molecular clusters
doped into $^4$He droplets [16–20]. A striking feature of these experiments is that the dopant
appears to undergo free rotation but with renormalized rotational constants. Therefore, one
objective of these studies has been to try to relate the extent by which the rotational con-
stants are re-normalized to general properties such as (i) the anisotropy of the molecule-$^4$He
interaction potential, (ii) the local superfluidity of the helium around the molecule and, (iii)
whether the rotational constants are large (as in the case of “light rotors” such as HF, H$_2$O,
NH$_3$) or small (for heavy rotors such as SF$_6$, OCS). Because of the very low temperatures
in $^4$He droplets, only very low lying rotational states are probed. These systems are, there-
fore, ideal candidates for the GA-DMC method for three reasons: (i) The DMC method
can handle the relatively large number of particles involved, (ii) The nodal surfaces of the
low lying rotational states (typically $J = 1$) are topologically simple as compared to highly
excited states, and (iii) the greatest distortion of the free rotor node often occurs upon the
addition of the first He atom with little further distortion upon the addition of subsequent
He atoms. For these reasons, we concentrate on these types of problems although, in future
work, we intend to investigate applications of the GA-DMC algorithm to higher excited
states of more complicated systems.

The paper is organized as follows: Sec. 6.2 describes the test problems to be considered
and, for calibration, presents accurate computations of various low lying excited states.
The details of the GA-DMC approach are outlined in Sec. 6.3, as well as our approach for
comparing flux histograms. Results and conclusions are in Sec. 6.4.

6.2 Model Problems

This section describes the model systems to be studied. In each case, accurate nodal surfaces and excited states can be computed. These are then used to test the efficacy of the GA-DMC approach.

6.2.1 HCN-\(^4\)He dimer

The HCN-\(^4\)He system was chosen because there is an appreciable distortion of the nodal surface of the excited state as compared to the nodes of the gas-phase HCN molecule treated as a rigid rotor [38,39].

In the space-fixed frame, the Hamiltonian for a He atom interacting with an HCN molecule (treated as a linear rigid rotor) is

\[
\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(R, \Theta) + B_0 \hat{j}^2
\]  

(6.1)

where \(R\) is the \(^4\)He-molecule separation; \(\Theta\) is the angle between the molecular axis and the He atom, \(\mu = 3.486\) amu) is the reduced mass and \(V(R, \Theta)\) is the HCN-\(^4\)He potential energy surface (PES) [51]. The molecular rotational angular momentum operator is \(\hat{j}\) and, for HCN, the gas-phase rotational constant, \(B_0 = 1.478\) cm\(^{-1}\). All DMC calculations were done in the rigid-body approximation in which the vibrations are frozen [21,52].

It is useful first to consider a hypothetical complex for which the intermolecular potential is assumed to be isotropic; we call this the isotropic binary complex (IBC). If the molecule-\(^4\)He interaction potential were actually isotropic, the molecular rotational angular momentum quantum number, \(j\), and the helium orbital angular momentum quantum numbers, \(\ell\), would be separately conserved, i.e., the labeling scheme \(|j\ell J\rangle\) would be exact where \(J\) is the total angular momentum quantum number. For the IBC, the molecular part of the wavefunction is \(Y^m_j(\alpha, \beta)\) where \(\alpha\) and \(\beta\) are the Euler angles (with the Euler angle \(\gamma = 0\) for diatomics) of the rotor [2,64]; the atomic part is also a spherical harmonic \(Y^{m\ell}_\ell(\theta, \phi)\).
with \( \theta \) and \( \phi \) being the spherical polar angles of the atom in the space-fixed frame. This labeling scheme can be used to label states of the full complex approximately. For example, the nodal functions for the two IBC states of interest with \( J = 1 \) (i.e., \(|011\rangle \) and \(|101\rangle \)) are \( \Psi_{iso}^{(a)} = \cos \theta \) and \( \Psi_{iso}^{(b)} = \cos \beta \), respectively. We shall refer to these nodal functions as IBC nodes.

Previous DMC calculations have indicated that the nodal functions of the IBC do not provide good eigenvalues for the \(|b\rangle = |101\rangle\) state, which implies that the actual node of the \(|b\rangle\) state is significantly different from that of the free-rotor [6, 46]. To gain insight into the distortion of the IBC nodal topologies due to the potential anisotropy, accurate eigenfunctions for the binary complex were computed using a basis set that is a product of \(|\text{radial}\rangle \times |\text{angular}\rangle\) functions. The total wavefunction is expanded [2]

\[
\Psi = R^{-1} \sum_{\alpha} c_{j,\ell}^{J,M} \Phi_{j,\ell}^{J,M}(\alpha, \beta, \theta, \phi) \chi^{(n)}(R)
\]

where \( R \) is the intermolecular distance and \( \{c_{j,\ell}^{J,M}\} \) are expansion coefficients [2, 114]. The radial basis functions, \( \chi^{(n)}(R) \), where \( n \) is the radial quantum number, were chosen to be Morse eigenfunctions as described elsewhere [6]. The angular basis functions \( \Phi_{j,\ell}^{J,M}(\alpha, \beta, \theta, \phi) \) are defined as follows:

\[
\Phi_{j,\ell}^{J,M}(\alpha, \beta, \theta, \phi) = \sum_{m_j, m_\ell} (-1)^{j-\ell+M} \sqrt{2J+1} \times \begin{pmatrix}
  j & \ell & J \\
  m_j & m_\ell & -M
\end{pmatrix} Y_j^{m_j}(\alpha, \beta) Y_\ell^{m_\ell}(\theta, \phi)
\]

where \( \begin{pmatrix}
  \ldots & \ldots & \ldots
\end{pmatrix} \) is a Wigner 3-\( j \) symbol. By expanding the potential in Legendre poly-
nominals as follows
\[ V(R, \Theta) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos \Theta). \] (6.4)

the matrix elements of the potential can be expressed in closed form in terms of Percival-Seaton coefficients [6]. The size of the basis is determined by the maximum size of \( j = j_{\text{max}} \) for a given \( J \). Convergence was achieved using \( n = j_{\text{max}} = 16 \). The basis set results in Table 6.1 compare favorably with coupled channel (CC) and literature values for states with \( J = 1 \) [6,46,51,56]. By contrast, DMC computations for the \( |101\rangle \) state using the IBC the nodal function \( \Psi_{\text{iso}}^{(b)} = \cos \beta \) provide relatively poor agreement with accurate computations, suggesting that there is appreciable nodal distortion of this state as compared to the equivalent IBC node.

Fig. 6.1 shows the nodal surfaces of the two \( J = 1 \) states as obtained by diagonalization in the radial-angular basis set just described. Also shown are the nodal functions obtained by diagonalization after making an adiabatic separation of radial and angular motions. This type of approximation was first developed by Holmgren et al. [49], who used a Born-Oppenheimer angular-radial separation (BOARS) in the molecule-fixed frame. In BOARS, the radial degree of freedom of frozen is frozen at some \( R = R_0 \) and the angular part of the resulting Schrödinger equation is then solved; this is repeated for different values of \( R_0 \), which generates families of adiabatic radial potentials. This approach is the basis of the recently developed adiabatic node DMC procedure in which the same angular node, obtained using the BOARS approximation, is used for all \( R \) values [6,7].

It turns out that the nodal surfaces are quite insensitive to the value of \( R_0 \) used. For example, over the range of \( R \) values sampled in a DMC calculation, the adiabatic nodal surfaces, also shown in Fig. 6.1, provide good agreement with accurate results [6]. For that reason, in the GA-DMC computations, we will assume that the same angular nodal surface applies for all values of \( R \). This approximation is not needed but it simplifies the computations and discussion considerably.
6.2.2 Interchange tunneling in (HCl)$_2$ dimer

The study of hydrogen-bonded hydrogen halide dimers has been an area of active experimental and theoretical interest for a number of years [103, 115–120]. More recently, interchange tunneling in these complexes has been studied in $^4$He nanodroplets. For example, theoretical and experimental studies of the HF dimer in He droplets suggest that the interchange tunneling splitting (ITS) is reduced by approximately 40% in both the ground and vibrationally excited states. Using the same computational procedure as for HF dimer – (i.e., fixed-node DMC) – Jiang et al. [91] predict no reduction in the ITS for the HCl dimer. This result is curious because of the similarities between the HF and HCl dimers and the fact that the computations between the two systems were essentially identical. Two recent experiments on HCl dimer solvated in $^4$He only add to the puzzle [103,120]; they have found a significant reduction in the ITS albeit for the $\nu_1$ and $\nu_2$ vibrationally excited states rather than that in the ground vibrational state. Although a direct comparison with the ITS in the ground vibrational state cannot be made, based on several reasonable assumptions, Skvortsov et al. predict a 40 - 50% reduction of the ITS in the ground vibrational state [103]. One explanation of the apparent discrepancy between theory and experiment is that the DMC calculations only examined clusters with up to 14 He atoms while the experiments studied clusters containing ca. 4000 atoms. However, essentially all previous studies suggest that the nanodroplet limit is achieved relatively quickly (i.e., for $N \leq 30$ He atoms). The calculated zero reduction in the ITS for $N = 14$ He atoms therefore seems extraordinary and worthy of further study. While this question will not be considered here, we will study the use of the GA-DMC procedure to locate the nodal surfaces of the free complexes, and, in particular, for mixed dimers for which the nodal surface cannot be obtained using symmetry. Our hope is that a future systematic study of HX-HY dimers (X, Y = F, Cl, Br) using the GA-DMC method might provide insights into the ITS puzzle posed by the HCl-dimer.

With the HCl bond lengths held fixed, the molecule frame Hamiltonian for the HCl
dimer is, in Jacobi coordinates

\[
\hat{H} = B_1 \hat{j}_1^2 + B_2 \hat{j}_2^2 - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R - \frac{\hat{j}_1^2 + \hat{j}_2^2 - 2\hat{j}_{12} \cdot \hat{J}}{2\mu R^2} + V(R, \theta_1, \phi_1, \theta_2, \phi_2)
\]  

(6.5)

where \(\mu\) is the reduced mass, \(R\) is the intermolecular vector, \((\theta_1, \phi_1)\) and \((\theta_2, \phi_2)\) are the spherical polar angles of the two monomers, \(\hat{j}_{1,2}\) are the individual rotor angular momenta vectors, and \(\hat{j}_{12} = \hat{j}_1 + \hat{j}_2\). For \((\text{HCl})_2\) obviously \(B_1 = B_2\), but this is not the case in \(f-(\text{HCl})_2\).

We also employ an adiabatic approximation in which \(R\) is fixed at some value \(R_0\) [116]. The eigenvalues and eigenfunctions are computed using the following basis functions

\[
\Psi_{K_a}^{j_{11},j_{12},j_{21},j_{22}}(\theta_1, \phi_1, \theta_2, \phi_2) = \sum_{k_1,k_2} \langle j_{11} k_1 j_{21} k_2 | j_{12} k_{12} \rangle \times Y_{j_{11},k_1}(\theta_1, \phi_1) Y_{j_{21},k_2}(\theta_2, \phi_2)
\]

(6.6)

where, for simplicity, purely electrostatic potential energy surfaces were used. The parameters are the same as those used in a previous study by Althorpe et al. [116]. Doing this allows the potential to be expanded analytically as

\[
V = \sum_{\ell_1,m_1,\ell_2,m_2} A_{\ell_1,m_1,\ell_2,m_2} Y_{\ell_1,m_1}(\theta_1, \phi_1) Y_{\ell_2,m_2}(\theta_2, \phi_2)
\]

(6.7)

which, in turn, means that the matrix elements of the adiabatic Hamiltonian can be computed analytically. We used the helicity decoupling approximation because we are interested in relatively low lying excited states; the Coriolis terms that have been neglected couple different \(K_a\) states and are unimportant for the states of interest.

With the HCl bond lengths frozen, the states might be labeled by the vibrational quantum numbers \(|\nu_3 \nu_4 \nu_5 \nu_6\rangle\) and the rotational quantum numbers \(J, K_a\). The excited state of interest here is that corresponding to the interchange tunneling mode and corresponds to
\[ \nu_3 \nu_4 \nu_5 \nu_6 \rangle = |0010\rangle \] [118]. Our objective is to compute the nodal surface of this state for a model of a mixed dimer for which the node cannot be obtained by symmetry.

Fig. 6.2 shows a projection of the density corresponding to the \(|0010\rangle\) state of \((\text{HCl})_2\) on the \(\theta_1 - \theta_2\) plane with the angle \(\phi = \phi_1 - \phi_2 = \pi\). The node is apparent as the straight line \(\theta_1 = \pi - \theta_2\); this straight-line node might be obtained by symmetry arguments [91, 108, 121]. In the case of f-(HCl)\(_2\), the rotational constant of one of the dimers was artificially doubled, which leads to pronounced nodal distortion of the \(|0010\rangle\) state as is apparent in the equivalent projection shown in Fig. 6.3.

This problem and the HCN-\(^4\)He dimer discussed earlier will now be used as test cases for the GA-DMC procedure.

6.3 Finding Nodal Surfaces with a GA

Genetic algorithms are simulations in which a population of “individuals” is allowed to interbreed in the hope that they will evolve to an optimal solution as governed by a fitness function which is constructed according to the problem at hand. Each individual is a representation (or chromosome) of a possible solution to the optimization problem. The individual is encoded as a string of binary bits (i.e., 0s and 1s). Initially, a population of randomly chosen individuals is created, and the fitness of each individual is then evaluated. This constitutes the first generation. The next generation is formed by selecting individuals from the previous generation, based on their fitness, and randomly forming new individuals by recombination and mutation. The new population is then used in the next iteration of the algorithm and so on. The algorithm terminates after a certain predetermined number of generations. If a satisfactory solution has not been found, the last generation might be used as the starting point for the evolution of further generations. In practice, the two most important steps are (i) encoding a representation of a potential solution and (ii) defining a fitness function against which to evaluate the individuals. The GA then proceeds to initialize a population of solutions randomly and then improves it through repetitive applications of mutation, crossover, inversion and selection operators. Several excellent discussions of the details of the procedure are available (e.g., the recent book by Goldberg [112]).
6.3.1 Encoding of the representation

Here the problem is to map the topology of a nodal surface onto a bit string of 0s and 1s. Because algorithms exist to convert numbers into bit strings, the problem reduces to encoding an arbitrary nodal surface by a set of parameters. Our approach is best explained by a concrete example that can be generalized to more or fewer dimensions.

Imagine that, as is the case with the HCl dimers in the adiabatic approximation, the wavefunction is a function of three angles: \( \Psi = \Psi(\theta_1, \theta_2, \phi) \); here \( \phi = \phi_1 - \phi_2 \). The nodal surface is the surface for which \( \Psi(\theta_1, \theta_2, \phi) = 0 \). We can re-write this condition, as, for example, \( \theta_2(\theta_1, \phi, c) = 0 \) where \( c \) is a constant. The encoding is done as follows:

1. Decide how many parameters will be used to represent the surface. Too few parameters might fail to capture the details of the surface while too many will increase the computational effort involved. If a rough approximation to the nodal surface is already known, this information can be used to choose a reasonable number of parameters. Alternatively, trial and error can be used or, in principle, the GA itself can be allowed to choose the number of parameters to use, although doing so can increase the computational expense of the procedure.

2. In the exemplary problem, we chose a \( 4 \times 4 \) grid of index points in the \( \theta_1 \) and \( \phi \); the ranges of the angles \( \theta_1 \) and \( \phi \) are divided into the following intervals: \( \theta_1 = (0, \theta_1^{(a)}, \theta_1^{(b)}, \pi) \) and \( \phi = (0, \phi^{(a)}, \phi^{(b)}, 2\pi) \). The intersections of these points are referred to as the knots. At each knot, a random value of \( \theta_2 \) in the range \( (0, \pi) \) is then chosen. The GA was allowed to choose the knot locations in-between the boundaries—(i.e., \( \theta_1^{(a)}, \theta_1^{(b)} \) and \( \phi^{(a)}, \phi^{(b)} \)). Altogether, this means that the GA has 20 free parameters—(i.e., the locations of 2 of the 4 grid points per angle together with the 16 values assigned to \( \theta_2 \) at the knots).

3. A bicubic spline was then fitted through the knot points; this defines the nodal surface for that particular individual. Occasionally, the spline fit for \( \theta_2 \) can produce values that lie outside the allowed range of, in this application, \( (0, \pi) \); even though the knot
points themselves do not lie outside this range. These individuals were immediately rejected.

6.3.2 Evaluation of the fitness function

Each individual corresponds to a particular estimate of the nodal surface. The fitness function for that individual is evaluated as follows:

1. Two different DMC runs are made for each individual (i.e., for each nodal surface). In the first one, the initial population of walkers is distributed on one side of the node while in the second the walkers are started on the opposite side of the node. This produces two energies, $E_+$ and $E_-$, which, if the node were exact, would be equal. However, as noted by Buch and co-workers [110,111], equality of energies is a necessary but not a sufficient condition to pin down the node.

2. During the two DMC runs, the number of walkers crossing the node in the “+” and “−” directions are kept track of and binned. This allows for the construction of two flux histograms, which for the exact node would be identical.

3. The flux histograms are normalized and then a histogram comparison measure is generated (i.e., we ask how similar are the histograms are). Various ways of comparing histograms are available including, for example, the $L_1$ measure and the earth mover algorithm [113]. In the examples described here, the histograms were normalized and divided up into $n$ boxes. The so-called $L_1$ measure was used to compare the histograms. This is defined as follows

$$L_1 = \sum_{j=1}^{n} |h^+_j - h^-_j|$$  \hspace{1cm} (6.8)

where $h^+_j$ and $h^-_j$ represent the number of walkers passing in the “+” and “−” directions through box $j$. $L_1$ was normalized to lie in the range (0,1). For 2- or higher dimensional histograms the same measure can be used.
4. The fitness of the individual is then generated using an appropriately defined fitness function. This was chosen to depend on (i) $E_+$ and $E_-$ and (ii) $L_1$. The following simple functional form was used

$$f = \frac{2}{L_1 + \epsilon} - 1$$  \hspace{1cm} (6.9)

where \(\epsilon = 1 - \min(E_+, E_-)/\max(E_+, E_-)\) and for the examples presented here we also require that \((E_+, E_-) < 0\). The best nodal function maximizes $f$.

In practice, the more information built into the fitness function, the faster the GA convergence. For example, if one is searching for the $|j\ell J\rangle = |101\rangle$ state of the HCN-\(^4\)He dimer, it is likely that the energy is relatively close to $E = E_{gs} + 2B_0$ where $E_{gs}$ is the ground-state energy. Thus the fitness function might include a cost function (e.g., \(\exp(-\delta|\epsilon_a - E_{gs} - 2B|)\)), where $\epsilon_a = (E_+ + E_-)/2$ with $\delta$ chosen empirically). This is done to discriminate against higher excited states and also to prevent the GA from converging to the ground state; the latter could happen by the GA converging to a node for which, for example $\theta_2 = 0$ or $\theta_2 = \pi$ for all values of the other angles in the problem. An alternative approach to avoid convergence to the ground state is to allow the GA to search for a node only in a predefined region (e.g., centered on an approximation to the node in question.) Of course, these details will depend on the problem under consideration and require some preliminary experimentation.

In general, the GA need not converge to a single excited state, so the procedure is implemented in practice in an epochal fashion.

6.3.3 Epochal GA

The epochal procedure is as follows:

1. In the first “epoch,” a given number of generations are evolved. The DMC calculations in the initial epoch use a relatively small number of walkers and a relatively large time step. The precise values used are determined by the problem and initial
experimentation. No attempt is made to compute standard deviations.

2. At the end of the first epoch, the individuals with the highest fitness are examined. Typically, these can cluster around several different excited states. The average value of the energy inside the cluster of interest, $E_{\text{ave}}$, is then computed and a new fitness function is created that includes a cost function $\exp(-\delta|E - E_{\text{ave}}|)$.

3. A new GA run is then performed in a second epoch. Generally, in the second epoch, more walkers are used together with a smaller time step.

4. The process is repeated for a number of epochs until satisfactory convergence and standard deviations are achieved.

In principle, the epochal procedure could be automated, but in the simulations reported here each epoch was initiated manually.

6.4 Results and Conclusions

The first application made was to the HCN-$^4$He dimer. Nodes corresponding to the $J = 1$ states $|a\rangle$ and $|b\rangle$ were computed. Because the procedure is similar for the two cases, a detailed analysis is presented only for the $|b\rangle$ state. In these calculations, only the angles $\beta$ and $\theta$ were considered in the construction of the nodes. The details of the DMC calculations in the different epochs are given in the caption to Fig. 6.3. In these calculations, the IBC node was used as an initial guess and the GA allowed to search in a band centered on the node. The band was defined to be, in this case, $\beta = \pi/2 \pm \pi/4$ and equivalently for the node lying close to $\theta = \pi/2$.

Fig. 6.3 shows scatter plots of the energies $E_+$ and $E_-$ over the three epochs used. It is apparent, that after only two epochs, excellent convergence has been achieved. Also shown are typical flux histograms from each of the three epochs. In practice, there is some fluctuation in the precise topology of the nodal surface between individuals as shown in Fig. 6.5. It turns out that it is not necessary to pin the nodal surface down accurately at all points in space. Because the parts of the nodal surface through which most of the flux
passes carry the most weight, with other regions being less important. Note also that in the DMC computations $R$ was allowed to vary, although $R$ was frozen in the actual computation of the node by the GA algorithm.

A similar procedure was used in the simulations for the HCl dimer except that no initial constraints were imposed. In these computations, our target was to locate the nodal surface $\text{(HCl)}_2$ and $f$-$(\text{HCl})_2$, which is significantly distorted in comparison to that of $(\text{HCl})_2$ (compare Figs. 6.2 and 6.3). Our objective here is to simulate finding the nodes of mixed dimers (e.g., HF-HBr). We chose to use a fudged version of $(\text{HCl})_2$ because this allows us to artificially distort the topology of the nodal surface quite strongly. Although the nodal plane can be located exactly by symmetry for $(\text{HCl})_2$, we performed an unconstrained search using the GA for both versions of the dimer. The results are shown in Table 6.2, and good agreement is achieved with basis set computations. In principle, the accuracy could be improved by (a) first finding a population of good nodal surfaces in the adiabatic approximation and (b) using this population to initiate a search using the full potential in which $R$ is allowed to vary.

Future work will investigate the use of more sophisticated histogram comparison methods (e.g., combining the earth mover algorithm with other measures, as well as extending the method to higher dimensional problems and higher excited states). However, the results presented here already seem to suggest that finding nodes in DMC calculations using a genetic algorithm holds promise when symmetry arguments fail, (e.g., for isotope-substituted water trimers [122]).
Table 6.1: Ground and excited state energies for the HCN-\textsuperscript{4}He dimer in cm\textsuperscript{−1}. CC: Coupled channel; RABS: Radial-angular basis set; DMC: Fixed-node DMC using IBC nodal functions; GA-DMC: The genetic algorithm DMC method described in the text. For the ground state, the DMC and GA-DMC results are identical since no nodal surfaces are involved, so these results are not shown. The $|j\ell J\rangle$ labeling scheme is exact only for the isotropic binary complex.

$$
|j\ell J\rangle \\
|a\rangle = |011\rangle \\
\begin{array}{c|c|c|c|c}
|CC| & |RABS| & |DMC| & |GA-DMC| \\
\hline
-8.342 & -8.316 & -8.33 \pm 0.05 & -8.43 \pm 0.08 \\
\hline
-5.554 & -5.528 & -6.46 \pm 0.08 & -5.63 \pm 0.06 \\
\end{array}
$$

Table 6.2: Energies of the $|0010\rangle$ state of the (HCl)\textsubscript{2} and f-(HCl)\textsubscript{2} dimers in cm\textsuperscript{−1}. ABS: Angular basis set; GA-DMC: The genetic algorithm DMC method described in the text.

$$
|\text{Dimer}| & |\text{ABS}| & |\text{GA-DMC}| \\
\hline
\text{(HCl)}\textsubscript{2} & -255.67 & -255.45 \pm 0.60 \\
\text{f-(HCl)}\textsubscript{2} & -213.80 & -214.20 \pm 0.32 \\
\hline
$$
Figure 6.1: Probability density maps corresponding to the $|a\rangle$ and $|b\rangle$ states of the HCN-$^4$He dimer. The top rows show states obtained using a radial-angular basis set. The bottom rows show the same states but obtained in an adiabatic approximation in which $R$ is frozen as described by Mikosz et al., J. Chem. Phys. 125, 014312 (2006). The densities have all been scaled to have the same maximum value. The color bar shows the range of density values. The broad black bands bound the nodal surfaces. The IBC nodes are straight lines corresponding to $\theta = \pi/2$ and $\beta = \pi/2$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.1.png}
\caption{Probability density maps corresponding to the $|a\rangle$ and $|b\rangle$ states of the HCN-$^4$He dimer. The top rows show states obtained using a radial-angular basis set. The bottom rows show the same states but obtained in an adiabatic approximation in which $R$ is frozen as described by Mikosz et al., J. Chem. Phys. 125, 014312 (2006). The densities have all been scaled to have the same maximum value. The color bar shows the range of density values. The broad black bands bound the nodal surfaces. The IBC nodes are straight lines corresponding to $\theta = \pi/2$ and $\beta = \pi/2$.}
\end{figure}
Figure 6.2: Projection of the $|0010\rangle$ state of $(\text{HCl})_2$ onto the $\theta_1 - \theta_2$ plane with $\phi = \phi_1 - \phi_2 = \pi$. The intermolecular distance was frozen at $R = 7.33$ au. In this case the node corresponds to the line $\theta_2 = \pi - \theta_1$. The wavefunction has been scaled to lie in the interval (-1,1) as shown in the color bar.

Figure 6.3: As for Fig. 6.2 except for $f-(\text{HCl})_2$. Note the distortion of the nodal plane as compared to $(\text{HCl})_2$. 
Figure 6.4: Frames (a) and (c) and (e) are scatterplots of the energies $E_+$ and $E_-$ for the first, second and third epochs respectively for the $^4$He-HCN calculation. Frames (b), (d) and (f) show typical histograms from each epoch. The black and white bars correspond to DMC walkers crossing the nodal plane in opposite directions. The grey shading corresponds to regions where the histograms overlap. The number of walkers, $N_w$, the time step, $\tau$ and the total number of time steps, $N_{\tau}$ for each epoch were as follows. Epoch 1: $N_w = 500$, $\tau = 15$, $N_{\tau} = 30,000$; Epoch 2: $N_w = 2000$, $\tau = 10$, $N_{\tau} = 40,000$; Epoch 3: $N_w = 5000$, $\tau = 5$, $N_{\tau} = 60,000$. The first epoch consisted of 30 generations, the second consisted of 20 generations and the third consisted of 10 generations. For each epoch, each generation contained 60 individuals.
Figure 6.5: Density plot showing the superposition of the 60 nodal surfaces corresponding to the final generation of the third epoch for the $^4$He-HCN calculation. This figure should be compared to the node of the $|b\rangle$ state in Fig. 6.1.
Abstract

The quantum and classical dynamics of floppy van der Waals complexes have been, in general, extensively studied in the past except for the weakest of all (i.e., those involving He atoms). These complexes are of considerable current interest in light of recent experimental work focused on the study of molecules trapped in small droplets of the quantum solvent $^4$He. Despite a number of quantum investigations, details on the dynamics of how quantum solvation occurs remains unclear. In this paper, the classical rotational dynamics of a series of van der Waals complexes HX-$^4$He with X = F, Cl, Br, CN are studied. In all cases, the ground state dynamics are found to be almost entirely chaotic, in sharp contrast to other floppy complexes, such as HCl-Ar, for which chaos sets in only at relatively high energies. The consequences of this result for quantum solvation are discussed. We also investigate rotationally excited states with $J = 1$ which, except for HCN-$^4$He, are actually resonances that decay by rotational pre-dissociation.

7.1 Introduction

The study of the quantum and classical dynamics of very floppy van der Waals complexes such as HCl-Ar continue to be, despite its long history, an area of active research [1–8]. In particular, these systems can be thought of as laboratories for the study of quantum chaos [123]. However, the classical and semiclassical behavior of the weakest possible van der Waals molecules, (those involving He atoms, for example HF-$^4$He), has been much less studied. In part, this might be due to the fact that these systems are considered to be so far from the classical limit that classical studies cannot provide any insight into their dynamical behavior. Indeed, much of the interest in these systems stems from the utility

of $^4$He as a quantum solvent, as shown in recent experiments. For example, ultra-cold nanodroplets of $^4$He offer considerable promise as microscopic cryogenic chambers, with possible applications including the formation of tailor-made chemical or bio-molecular complexes as well as studies of superfluidity in nanoscale systems [9, 35] (e.g., nanoscale oligomers [38] or complexes of bio-molecules [19]). However, despite the essential quantal nature of these systems, classical mechanical studies have the potential to provide insight into some relevant aspects of their dynamics. One such aspect is the angular momentum coupling between the molecule and the $^4$He atom, which is important as a way to understand quantum solvation.

A reasonable working definition of quantum solvation is the following: As molecules dissolved in $^4$He droplets become surrounded by an increasing number of solvent atoms, angular momentum coupling with the solvent atoms eventually saturates [6, 7]. Normally, a molecule dissolved in a liquid is not expected to rotate freely as it might in the gas-phase. However, in an ultra-cold ($T \approx 0.37$ K) droplet of $^4$He atoms the molecule appears to rotate freely but with a different spectroscopic constant – typically the gas-phase rotational constant, $B_0$, seems to decrease [11, 21, 41, 42].

Diffusion Monte Carlo (DMC) simulations for SF$_6$-($^4$He)$_N$ clusters [21] suggested a physical explanation for this effect: Essentially, a fraction of the helium density in the droplet follows the relatively slow rotation of the SF$_6$ molecule adiabatically. In this “adiabatic following,” the observed decrease in the rotational constant is caused by the molecule dragging a fraction of the helium density along with it as it rotates, thereby increasing its moment of inertia. This model suggests that the magnitude of $B_0$ is an important factor in determining how fast quantum solvation will occur and how big the change in the rotational constant will be. Moreover, while this model captures some of the essential physics, other factors are also important; for example, Paolini et al. [42] investigated the solvation of OCS and HCN as well as the so-called “fudged” molecules f-OCS and f-HCN (i.e., OCS and HCN with artificially small or large values of the gas-phase rotational constant). They concluded that it is the strength and anisotropy of the He-molecule interaction, rather than the gas-phase rotational constant itself, that is mainly responsible for the reduction of the rotational con-
stant in the nanodroplet regime. A more recent study [7] of HX-He complexes with X = F, Cl, and Br obtained results in agreement with the conclusions of Ref. [42]. This study predicted that the observed decrease in the gas-phase rotational constants for HCl and HBr in a \(^{4}\)He nanodroplet will be smaller than for HF, despite HF having the largest (by far) gas-phase rotational constant of the three molecules. The solvation behavior of these molecules was traced to how the potential anisotropies couple angular momentum states between the molecule and the bosonic helium-4 atoms. Although HF has a rotational constant that is almost double that of HCl, the somewhat larger anisotropy of the potential energy surface (PES) leads to a small asymptotic decrease in the effective rotational constant, whereas HCl and HBr approach their gas-phase values in the nanodroplet limit.

The twofold objective of the present study is (i) to try to understand if any insight into the quantum solvation behavior of molecules in helium-4 can be gleaned from a purely classical study of the dimer HX-\(^{4}\)He complexes with X = F, Cl, Br, CN, and (ii) to study the classical mechanics of very weakly bound clusters for which the ground state lies above all saddle points in the PES and whose lowest lying rotationally excited states are found about the dissociation threshold. This is in contrast, with the more well-studied case of the HCl-Ar dimer, for which chaos does not develop until energies relatively high above the minimum in the PES are reached [1].

We also investigate rotationally excited states with \(J = 1\) which, except for HCN-\(^{4}\)He and due to its relatively small rotational constant, are actually resonances that decay by rotational pre-dissociation. The existence of these resonances is a classical effect, due to the presence of a set of long-living orbits immersed in a chaotic sea that exist high above the dissociation limit of the dimer. In some cases large, permanently bound Kolmogorov-Arnold-Moser (KAM) islands are discovered in this chaotic sea. These islands are similar in nature to those found in the circular restricted three-body (CRTBP) problem of celestial mechanics [124] and are central to the chaos-assisted capture mechanism developed in planetary physics to explain the formation of binary objects in the Kuiper-belt [125] and the capture of irregular moons at the giant planets [126]. These events have been proposed
to take place through the formation of transitory objects whose long – but finite – life-
times are controlled by the existence of so-called sticky KAM islands [127] in phase space;
their stickiness is the result of thin chaotic layers that can trap particles long enough for
permanent capture to take place through other processes. In quantum physics these states
correspond to resonances. Because the resonances lie higher in energy than the classical
saddle point they are similar to above-barrier orbiting or shape resonances which, in quan-
tum mechanics, can exist even in 1-dimension (1D) [128]. However, resonances associated
with above-barrier KAM islands depend on essentially non-linear structures in the classi-
cal phase space and, therefore, cannot exist in 1D. These islands are rotational analogs
of above-dissociation limit KAM structures in vibrational problems [129, 130] and may be
important in the creation of rotational Feshbach molecules and complexes [131].

The paper is organized as follows: In Sec. 7.2 the Hamiltonian is introduced and a set of
canonical transformations is developed to facilitate examination of the classical mechanics
for arbitrary values of the total angular momentum. Sec. 7.3 compares the classical behav-
ior of the four complexes in their ground and rotationally excited states. The specific four
molecules considered in this work were chosen to span a wide range of gas-phase rotational
constants and also because they have already been the subject of previous quantum
studies. Conclusions are summarized in Sec. 7.4.

7.2 Hamiltonian

Working in the laboratory frame in three dimensions (3D) and neglecting three-body
effects, there are two angles that define the orientation of the linear HX molecule – ($\theta_1, \phi_1$)
and two more that specify the location of the He atom – ($\theta_2, \phi_2$). The distance of the He-
atom from the center-of-mass of HX is $R$, and the angle between He and HX is $\gamma = \theta_R - \theta_r$.
The PES is $V(r, R, \theta_R, \theta_r)$ but the H-X coordinate, $r$, is frozen at its equilibrium distance:
$r = r_e$, and so $V = V(R, \theta_R, \theta_r)$ (in the case of HCN the CN moiety is also frozen at its
equilibrium distance).

After separation of the motion of the center-of-mass, the Hamiltonian for our system
is given by

$$H = -\frac{\hbar^2}{2\mu_1} \nabla^2 + \frac{j_z^2}{2\mu_2 r_e^2} + V(R, \theta_R, \theta_r)$$  \hspace{1cm} (7.1)$$

where \(j\) is the HX rotational angular momentum operator, \(\gamma = \theta_R - \theta_r\) is the Jacobi angle, \(\mu_1\) is the reduced mass of the complex, and \(\mu_2\) is the reduced mass of the HX molecule. The values of the physical parameters defining these magnitudes are given in Table 7.1.

Alternatively, Hamiltonian (7.1) can be expressed in polar coordinates as

$$H = -\frac{\hbar^2}{2\mu_1} R^{-1} \left( \frac{\partial^2}{\partial R^2} \right) R + \frac{l_z^2}{2\mu_1 R^2} + \frac{j_z^2}{2\mu_2 r_e^2} + V(R, \theta_R, \theta_r)$$  \hspace{1cm} (7.2)$$

where \(J = j + l\). For the case that \(J = 0\), the dynamics are rigorously constrained to the plane containing the molecule and the atom. Although this is not necessarily the case when \(J \neq 0\), in this study we will consider only the planar limit even when \(J\) is different from zero.

### 7.2.1 Planar configuration

Now we specialize to a planar configuration such that \(l \to \ell_z\) and \(j \to j_z\). In this case, the Hamiltonian can be written in Cartesian coordinates and is given by the following expression

$$H = \frac{(p_x^2 + p_y^2)}{2\mu_1} + \frac{j_z^2}{2\mu_2 r_e^2} + V(R, \theta_R, \theta_r).$$  \hspace{1cm} (7.3)$$

Changing to polar coordinates

$$x = R \cos \theta_R$$ \hspace{1cm} (7.4)$$

$$y = R \sin \theta_R,$$ \hspace{1cm} (7.5)$$

we obtain

$$H = \frac{P_R^2}{2\mu_1} + \frac{\ell_z^2}{2\mu_1 R^2} + \frac{j_z^2}{2\mu_2 r_e^2} + V(R, \theta_R, \theta_r).$$  \hspace{1cm} (7.6)$$
The corresponding quantum Hamiltonian operator is given by

\[ H = -\frac{\hbar^2}{2\mu_1} R^{-1} \left( \frac{\partial^2}{\partial R^2} \right) R + \frac{\ell_z^2}{2\mu_1 R^2} + \frac{j_z^2}{2\mu_2 r_e^2} + V(R,\theta_R,\theta_r). \]  

(7.7)

For \( J = 0 \) and since \( J = j + 1 \), we have \( j_z = -\ell_z \), and then expressions (7.6) and (7.7) change to

\[ H = \frac{P_R^2}{2\mu_1} + \left( \frac{1}{2\mu_1 R^2} + \frac{1}{2\mu_2 r_e^2} \right) \ell_z^2 + V(R,\gamma) \]  

(7.8)

and

\[ H = -\frac{\hbar^2}{2\mu_1} R^{-1} \left( \frac{\partial^2}{\partial R^2} \right) R + \left( \frac{1}{2\mu_1 R^2} + \frac{1}{2\mu_2 r_e^2} \right) \ell_z^2 + V(R,\gamma) \]  

(7.9)

respectively.

7.2.2 Action-angle variables

Next we make the following transformation to action-angle variables

\[ j_1 = (j_z + \ell_z), \quad \gamma_1 = (\theta_R + \theta_r)/2 \]  

(7.10)

\[ j_2 = (j_z - \ell_z), \quad \gamma_2 = (\theta_R - \theta_r)/2. \]  

(7.11)

In this way, the classical Hamiltonian (7.6) becomes

\[ H = \frac{P_R^2}{2\mu_1} + \frac{(j_1 - j_2)^2}{8\mu_1 R^2} + \frac{(j_1 + j_2)^2}{8\mu_2 r_e^2} + V(R,\gamma_2). \]  

(7.12)

As a check, one can set \( J = 0 \) so that \( j_1 = 0 \) and \( j_2 = 2\ell_z \); this gives

\[ H = \frac{P_R^2}{2\mu_1} + \left( \frac{1}{2\mu_1 R^2} + \frac{1}{2\mu_2 r_e^2} \right) \ell_z^2 + V(R,\gamma_2) \]  

(7.13)

in agreement with Eq. (7.8) for \( \gamma = 2\gamma_2 \).
7.2.3 Potential energy surfaces

All calculations described in this paper assume pairwise molecule-He interaction potentials. The PESs for the HF-He, HCl-He and HBr-He dimers have been described elsewhere \[7\] and consist of the following expansion in Legendre polynomials

\[
V(R,\gamma) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos\gamma).
\]  \hspace{1cm} (7.14)

For the HCN-He case, a different potential expression, taken from Ref. \[51\], is used. The four PESs are shown as contours plots in Fig. 7.1; in all cases, the minimum energy path (MEP) connecting the two linear configurations He-HX and HX-He, or alternatively $\gamma = 0$ and $\gamma = \pi$, has also been added to the figure. Along this line two minima exist. The corresponding well depths and atom-molecule separations are given in Table 7.2 for the four dimers. In the first three cases, namely for $X = HF$, HCl, and HBr, the two minima are located at the linear configurations, and they both correspond to stable isomer wells. Moreover, along the MEP at saddle point is found at some intermediate geometry. However, in the case of He-HCN, the second minimum is not located at the linear configuration, but at an angle slightly smaller: $\gamma = 108.5^\circ$. Consequently, two different saddle points exist along the MEP, one of them corresponding to the linear (unstable) configuration HCN-He.

To complete the basic spectroscopic information about the systems under study, we report in Table 7.3 the numerical values for the energies of the ground and first three excited rotational states with $J = 1$. These values have been computed using the coupled channel method described in Ref. \[56\]. It should be remarked that, in all cases, the quantum ground state energy lies above the saddle points in the PESs of Fig. 7.1.

7.3 Classical Dynamics

This section compares the classical dynamics of the four complexes over a range of different energies values considering the cases $J = 0$ and $J = 1$.

The primary method for understanding the classical motion of a dynamical system is through the use of a Poincaré surface of section (SOS). This method is specially powerful
for systems of two degrees of freedom. The SOS are computed as the intersection of actual trajectories with a suitable surface, thus reducing the dimensionality of the geometrical object under examination. Usually, the results corresponding to a swarm of trajectories all propagated at the same energy are plotted together in a single picture, thus obtaining the so-called composite SOS. Because of the very floppy nature of the angular motion of the complexes that are being considered here, it is not feasible in general to obtain a good global view of the dynamics by fixing one of the coordinates at a certain value, as it is usually done in similar studies. An alternative approach, which has been successfully used for LiCN and similar molecules, is to use the MEP, $R_e(\gamma)$, to define the SOS (see Fig. 7.1). In our case, this requires the use of a new set of coordinates [132]

$$\rho = R - R_e(\gamma), \quad \Psi = \gamma$$

(7.15)

$$P_\rho = P_R, \quad P_\Psi = P_\gamma + P_\rho \left( \frac{\partial R_e}{\partial \gamma} \right)$$

to make the SOS an area-preserving map [133]. In practice, the MEPs are found numerically and then fitted, using non-linear least squares, to a Fourier expansion in $\cos \gamma$.

Now we proceed to examine SOS plots for the different title dimers calculated by the procedure outlined above with the Hamiltonian of Eq. (7.12) [which reduces to Eq. (7.13) for $J = 0$].

7.3.1 Case $J = 0$

In this subsection, we concentrate on the results corresponding to $J = 0$, which are presented in the left tier of Figs. 7.2–7.5. The results for $J = 1$ are not very different, and most of the comments given here are also valid for this value of the total angular momentum. Some peculiarities, however, are worth discussing, and we defer this task to the next subsection.

Three different values of the energy will be considered (in the figures, going from top to bottom). The first corresponds to an energy slightly above the global minimum of the PES. As can be seen, at this energy value, classical motion in the least stable well is forbidden for
HF-He and HCN-He but allowed for the two other dimers (structures centered at $\gamma = \pi$). The middle panels in Figs. 7.2–7.5 are computed at an energy that is halfway between the global minimum in the PES and the saddle point. The third value chosen corresponds to the quantum ground state energy as computed using CC methods [56]. Examination of the results in these figures reveals that at the lowest energy, considered (bottom panels), the dynamics are essentially regular, with the vast majority of the available phase space foliated with invariant tori. As energy increases (middle panels), the motion becomes more irregular due to the perturbation (i.e., anharmonic regions of the PES are explored) and a substantial part of these tori are destroyed, producing bands of stochasticity. Now noticeable are chains of islands – (these are very conspicuous in the cases of HF-He and HCl-He) – the centers of which correspond to vibrational motion in which the $R$ and $\gamma$ modes are in exact resonance (periodic orbits). Finally, at the highest energy considered (bottom panels), the motion is almost entirely irregular, and chaos appears widespread. Nevertheless, some regular structures are apparent. Most of these are located in the periphery and correspond to trajectories in which the He atom mostly rotates around the HX molecule. Particularly interesting are those found for HCN-He at $\gamma = 0$; this is the only dimer considered that exhibits an island of regularity at the energy of the ground state. All characteristics of the behavior described above are in agreement with the predictions dictated by the KAM theorem [133] for the destruction of invariant tori in perturbed Hamiltonian systems.

The main result that can be extracted for our purposes from Figs. 7.2–7.5 is that chaos is widespread in the systems being considered in this paper, even at energies corresponding to the ground state. This behavior is unexpected and somewhat counterintuitive, especially when one takes into account that in the isotropic limit the dynamics are entirely regular (i.e. $j$ and $\ell$ are exact invariants). Therefore, one might also expect that in view of the very large rotational constant for HF, at least for the ground state, the system would approach the isotropic limit adiabatically. As can be seen, this is not the case since the most regular structured phase space is observed for the case of the molecule with the smallest rotational constant of the four cases considered here. This difference might be attributable to the
different relative contributions in the Legendre expansion of the potential see Eq. (7.14), as discussed in Ref. [2].

Another interesting observation is the following: Dynamically, the presence of widespread chaos implies relatively facile angular momentum transfer between the atom and the rotor. This is a potentially important fact for the issue of quantum solvation. In Refs. [6, 7] it was shown that convergence of the effective reduction in the gas-phase rotational constant as a function of number of \(^4\)He atoms quickly saturates to the asymptotic limit for a relatively small number of them. Due to the bosonic symmetry of the wavefunction of the system, the molecule must couple identically to each of the atoms. Furthermore, this is true even in the limit in which the \(^4\)He-\(^4\)He interaction is neglected. In the case of regular dynamics, the transfer of angular momentum between each atom and the rotor would be quasi-periodic and, therefore, there would be a strong correlation between the rotational angular momentum of the molecule and the atoms. Of course, the indirect coupling among atoms through the molecule could, in principle, induce chaos in the dynamics. However, because the motion is almost completely chaotic, even for the dimer, one can expect little correlation in the case of a complex with more He atoms, and then an effective decoupling of the molecule from the atoms.

To numerically check this idea, we developed a simplified classical model for quantum solvation in which all \(^4\)He-\(^4\)He interactions are neglected. Although this approximation might seem at first sight too crude, notice that this is not the case since actual DMC calculations show that the contribution of these interactions in the first solvation shell is relatively small [7]. For a system consisting of an HX molecule and \(N\) He atoms, the corresponding “toy” Hamiltonian can be written as

\[
H = \frac{J_z^2}{2 \mu_2 r_e^2} + \sum_i \left( \frac{P_z^{(i)} \gamma_i}{2 \mu_1} + \frac{\ell_z^{(i)} \gamma_i}{2 \mu_1 R_i^2} + V(R_i, \gamma_i) \right) + V_1(R) \quad (7.16)
\]

where \(\ell_z^{(i)}\) represents the orbital angular momentum of each He atom. An extra term,
\( V_1(R) = D \exp[-(R - R_a)^2] \), (with \( D = 50 \text{ cm}^{-1} \) and \( R_a = 20 \text{ a.u.} \) for HBr) has been included in the potential with the purpose of preventing non-physical dissociation of the He atoms from the complex structure. The situation is similar to the well-known problem that arises in classical dynamics simulations where, specially in the case of many degrees of freedom, there can be enough zero-point energy to cause the system to dissociate. It should also be noticed that model (7.16) also neglects the fact that the center-of-mass of the complex cannot be separated except for the \( N = 1 \) case. This approximation is again not very important since the purpose of our exercise is only to get a qualitative understanding of the differences in the angular momentum exchange among molecule and He atoms that exist when \( N > 1 \) between the dynamical regime is chaotic or regular. Finally, because He-He interactions are neglected, the He atoms can only exchange angular momentum in an indirect way, such as through interactions with the molecule HX.

Classical trajectories for Hamiltonian (7.16) have been propagated for the case of a HBr molecule surrounded by \( N = 20 \) atoms of \(^4\text{He} \). For this choice adequate values for the parameters defining the \( V_1(R) \) term in Eq. (7.16) are: \( D = 50 \text{ cm}^{-1} \) and \( R_a = 20 \text{ a.u.} \), respectively. Data of the angular momenta of the molecule and the atoms were collected as a function of time during the calculation for further analysis. Two values of the energy were chosen for the simulations. HBr trajectories were run at an energy of \( E = 535.3 \text{ cm}^{-1} \), corresponding to \( N \) times the energy of the energy shown in the upper left panel of Fig. 7.4 when the dynamics are regular. An analogous calculation was performed at \( E = -20 \times 7.783 = -155.7 \text{ cm}^{-1} \) corresponding to the actual ground state energy (shown in the lower left panel of Fig. 7.4) for which highly chaotic dynamics are found. The results are presented in Figs. 7.6, panel (a) and (b), respectively, where the time evolution of the HBr molecular angular momentum, \( j_z \), and the different \(^4\text{He} \) atom angular momenta, \( \ell_{z}^{(i)} \) are plotted. Direct inspection of these figures might not be very conclusive, although the results in panel (b), at least in the case of the \(^4\text{He} \) atoms, appear to be much more complicated than those in (a). To make the analysis quantitative, we have also computed the power spectra of the HX angular momentum, \( j_z(t) \); the results are shown in panels (c) and (d) of the same
figure for the two working energies, respectively. Here, we can definitively conclude that the dynamics for the lowest energy remains regular even when 20 atoms are included in the complex, so that this number is not an issue concerning dynamical complexity of the motion. As a comparison, we can state that the dynamics at the highest energy [panel (d)] are seen to be chaotic, a result that cannot be considered unexpected since that was so in the $N = 1$ case (i.e. for the dimer). Moreover, it is apparent that the angular momentum of the molecule is strongly correlated with that of the He atoms in the regular regime, while when the dynamics are chaotic there is little correlation between them, although some correlation between the atoms is observed. Obviously, a classical simulation cannot capture the true boson statistics, and despite the existence of ground state chaos, no explicit signature of irregularity can be found in the corresponding quantum wavefunctions [7]. Nevertheless, the present results seem to suggest that the experimentally observed decoupling of the molecule from the helium density can be partially explained as the result of the chaotic nature of the motion on the ground (and low-lying) rotational states.

7.3.2 Case $J = 1$

The SOS results for rotationally excited ($J = 1$) dynamics of the HX-$^4$He dimers are shown in the right-hand columns of Figs. 7.2–7.5. The results are qualitatively similar to $J = 0$. Nevertheless, it is observed that the dynamics for the higher value of the momentum are somewhat more stable, especially at intermediate energies (see the middle panels). This stabilizing effect is often seen in rovibrational systems, with the double pendulum being an extreme case of this phenomenon. However, what is more important for our purposes is that the classical dynamics at the quantum ground state energies (bottom panels) also show a widespread chaotic nature, so that the conclusions and discussions given in the previous subsection also hold here.

On the other hand, there is an added distinct fact in the present case. Since the magnitude of the gas-phase rotational constants of the dimers, except in the case of He-HCN, states $|j\ell J\rangle = |101\rangle$ lie above their dissociation thresholds, thus corresponding to rotational resonances [128]. Moreover, these states, in which the molecule is excited to
its nominally $j = 1$ level, are the ones most often accessed in experimental studies. It is, therefore, of interest to understand how the presence of quantum resonances is reflected in the classical dynamics. Again, it should be remarked that the origin of these resonances is the anisotropy of the PES. For example, when the potential $V$ in Eq. (7.1) depends only on $R$, no angular momentum can be transferred between the atom and the molecular rotor and then the quantum numbers $j$ and $\ell$ are separately conserved. The anisotropy allows angular momentum coupling to take place and, if the rotational energy is high enough – and for $j = 1$ this essentially depends only on the magnitude of $B_0$ in the rigid-rotor approximation – the complex will eventually dissociate [134–136].

However, for rotationally excited states, the SOS used so far is inadequate because large amplitude motions, far from the MEP, are possible. An alternative SOS is, therefore, constructed by plotting the $R - P_R$ intersections of the computed trajectories with the $\gamma_2 = 0$ plane, taking only the positive branch of the conjugate momentum $j_2$. As before, initial conditions are randomly selected in the surface of section, at each energy.

The corresponding SOS results for the four molecules at selected values of the energy are shown in Figs. 7.7–7.10. In the first three, corresponding to dimers with the hydrogen halides HF, HCl and HBr, three values of $E$ are considered, ranging from $E = 0$, which is slightly below the dissociation limit to the energy of the excited state $|101\rangle$. As stated before in the case of the dimer with HCN this state is bounded, and then in the corresponding figure only the SOS at this energy is presented. Several comments are in order.

First, it is observed that qualitatively the dynamics for the HX-He become more chaotic as one considers higher masses, that is, when going from HF to HBr (see Figs. 7.7–7.9). Of particular interest is the existence of KAM islands embedded in a sea of unbounded chaos for the HF-He complex. These structures are highly reminiscent of those found in the CRTBP [125, 126], which suggests that these structures, which have been observed in vibrational dynamics [129], might be generic. Similar comments apply to the HCN-$^4$He dimer, for which a typical SOS is shown in Fig. 7.10.

Second, the chaotic sea observed for energies $E > 0$ is unbounded, but trajectories
can live for very long times before the dissociation occurs. The empty regions inside the bounding curves correspond to direct scattering trajectories, which do not survive for long enough to intersect the SOS in the region of interest. The apparent structure in the chaotic sea, visible in Figs. 7.7–7.9, is the signature of the existence of a fractal classical repellor [137] that controls the dissociation dynamics. In studies of quantum maps, it has recently been shown numerically that the complex resonant eigenvalues obey a fractal Weyl law [138–141]. The conventional Weyl law [142] applies to closed systems and associates quantum states with phase space volumes $\hbar^D$, where $D$ is the actual dimensionality of phase space [142]. In open maps, the number of resonance states is found to obey a similar law except that $D$ is no longer an integer (i.e., it is an effective phase space dimension). In addition, quantum quasiprobability distributions in phase space [143], such as the Husimi function [144], are observed to cling into a classical phase space object, which is fractal and is known as the repellor. This repellor is observable as a set of points in phase space that remain trapped for infinite times in the future (or in the past) [140]. The quantum consequences of the existence of a repellor for van der Waals clusters, such as those studied here, are at present under investigation.

7.4 Conclusions

In this article, the classical rotational dynamics of a series of van der Waals complexes HX-4He with X = F, Cl, Br, CN were studied. In each case, the ground state dynamics were found to be almost entirely chaotic. The chaotic nature of the low-lying states, including the ground state, seems to be partially responsible for the observed decoupling of the molecule and the He atoms that is observed experimentally. We also investigated rotationally excited states with $J = 1$ which, except for HCN-4He, are actually resonances that decay by rotational pre-dissociation. The existence of resonances was reflected classically in the presence of a series of long-living orbits embedded in the chaotic sea, which exist even above the dissociation limit of the dimer. Certain features of the chaotic sea are characteristic of the existence of a fractal classical repellor. In some cases large, permanently bound, KAM islands were discovered in the chaotic sea. These islands are similar to those of the chaos-
assisted capture mechanism of irregular moons at the giant planets, and they are expected to have important consequences for the quantum scattering dynamics of these complexes.
Table 7.1: Atomic and molecular masses and molecular rotational constants used in this work.

<table>
<thead>
<tr>
<th>Atom/Molecule</th>
<th>Mass (a.m.u.)</th>
<th>Rotational Constant (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4$He</td>
<td>4.00260</td>
<td>—</td>
</tr>
<tr>
<td>HF</td>
<td>20.00634</td>
<td>20.560</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46094</td>
<td>10.403</td>
</tr>
<tr>
<td>HBr</td>
<td>80.91194</td>
<td>8.473</td>
</tr>
<tr>
<td>HCN</td>
<td>27.02568</td>
<td>1.478</td>
</tr>
</tbody>
</table>

Table 7.2: Well depths and atom-molecule separations at the two minima in the four dimer PESs. Global minima are denoted by (*).

<table>
<thead>
<tr>
<th>Dimer</th>
<th>$\theta$ (deg)</th>
<th>$R$ (bohr)</th>
<th>$V$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-HF</td>
<td>0.0*</td>
<td>5.983*</td>
<td>-43.844*</td>
</tr>
<tr>
<td></td>
<td>180.0*</td>
<td>5.667</td>
<td>-26.169</td>
</tr>
<tr>
<td>He-HCl</td>
<td>180.0*</td>
<td>6.340*</td>
<td>-32.736*</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>7.242</td>
<td>-31.160</td>
</tr>
<tr>
<td>He-HBr</td>
<td>180.0*</td>
<td>6.446*</td>
<td>-37.103*</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>7.783</td>
<td>-27.666</td>
</tr>
<tr>
<td>He-HCN</td>
<td>0.0*</td>
<td>7.974*</td>
<td>-29.901*</td>
</tr>
<tr>
<td></td>
<td>108.5</td>
<td>6.782</td>
<td>-22.067</td>
</tr>
</tbody>
</table>

Table 7.3: Ground and excited state energies for the He-HX dimers considered in this work (in cm$^{-1}$) and as obtained from coupled channel calculations. The $|j\ell J\rangle$ labeling scheme is exact only in the isotropic limit (i.e., when the PES is assumed not to depend on the angle $\gamma$).

| $|j\ell J\rangle$ | HF   | HCl  | HBr  | HCN  |
|------------------|------|------|------|------|
| $|000\rangle$    | -6.718| -7.763| -7.873| -8.867|
| $|011\rangle$    | -5.967| -7.214| -7.406| -8.342|
| $|101\rangle$    | -33.951| 12.765| 8.078 | -5.554|
| $|111\rangle$    | 36.758| 14.964| 10.455| -5.019|
Figure 7.1: Contour plots of the potential energy surfaces: (a) HF-He, (b) HCl-He, (c) HBr-He, (d) HCN-He. Contours are labeled in cm\(^{-1}\). The solid line (red in color) shows the minimum energy path which connects the two linear configurations of the dimer.
Figure 7.2: Composite Poincaré surfaces of section (SOS) for He-HF computed along the minimum energy path as described in the text. The left column shows a selection of energies corresponding to $J = 0$ 20 while the right column compares the corresponding SOS for $J = 1$. From top to bottom the energies correspond to being slightly above the minimum in the PES, half way between the minimum and the saddle point in the potential and, finally, the ground state energy. The bounding curve (red in color) is shown in each case.
Figure 7.3: Same as Fig. 7.2 but for He-HCl.
Figure 7.4: Same as Fig. 7.2 but for He-HBr.
Figure 7.5: Same as Fig. 7.2 but for He-HCN.
Figure 7.6: Traces of the angular momenta $j_z(t)$ (black) and $\ell_z^{(i)}(t), i = 1, 20$ (colored) from classical trajectory simulations. The data shown are for HBr-$^4$He$_N$, $N = 20$, at total energies (a) $-535.3$ cm$^{-1}$ and (b) $-155.67$ cm$^{-1}$. Times are scaled by $10^6$. Frames (c) and (d) show the corresponding power spectra of $j_z(t)$. 
Figure 7.7: Composite Poincaré SOS computed in the $R - P_R$ plane as described in the text. The data shown are for He-HF for $J = 1$. From top to bottom the energies increase from $E = 0$ up to the energy of the state $|j\ell J\rangle = |101\rangle$. The bounding curve (red in color) is shown in each case.
Figure 7.8: Same as Fig. 7.7 but for He-HCl.
Figure 7.9: Same as Fig. 7.7 but for He-HBr.
Figure 7.10: Same as Fig. 7.7 but for He-HCN and only for the energy corresponding to the state $|j\ell J\rangle = |101\rangle$. 

E = 5.554 cm$^{-1}$ $J = 1$
CHAPTER 8
FRACCTAL WEYL LAW BEHAVIOR IN AN OPEN, CHAOTIC
HAMILTONIAN SYSTEM

Abstract

We numerically show fractal Weyl law behavior in an open Hamiltonian system that is described by a smooth potential and which supports numerous above-barrier resonances. This behavior holds even relatively far away from the classical limit. The complex resonance wavefunctions are found to be localized on the fractal classical repeller.

8.1 Introduction

The classical and quantum dynamics of open Hamiltonian systems is relevant to a variety of topics of current interest in macroscopic and microscopic physics. For example, in planetary physics, the formation of binaries in the Kuiper-belt might have proceeded through the formation of transitory objects in chaotic layers of phase space trapped close to above-barrier Kolmogorov-Arnold-Moser (KAM) islands [125–127]. The analogs of these states in open quantum Hamiltonians are resonances (quasibound states) that, in general, are predicted to be localized on an object known as the classical repeller [137]. The repeller is the intersection of two fractal sets of classical trajectories, one of which remains trapped in the infinite past and the other in the infinite future, denoted as $K_-$ and $K_+$, respectively. The fractal nature of these sets has led to the prediction of a fractal Weyl law for flows in which the number of long-living quantum resonances scales as $h^{-(1+d_H)}$ where $d_H$ is the partial Hausdorff dimension of the repeller [138].

In open maps, the number of resonances has already been found to obey a similar fractal Weyl law, $h^{-d}$, except that $d$ is now the partial fractal dimension of the trapped set. This relates to the original Weyl law [142] conceived for closed systems, which states that the number of eigenstates up to energy $E$ that fits into the available phase-space volume
of the classical system scales as $h^{-d}$, with $d$ being the actual (integer) dimensionality of quantum space. In addition, in open maps the associated quantum Husimi distributions are observed to cling to the classical repeller [140,145]. Although the fractal Weyl law has been observed in particular maps like the baker map and the kicked rotor [138–141, 145–147], there have been few previous studies of this problem in open Hamiltonian systems [148] even though such systems are of direct physical interest (e.g., the chaotic ionization of hydrogen atom interacting with a circularly polarized microwave exhibits above-barrier chaotic trapping [149]).

Here we present an examination of above-barrier quantum resonance (Gamow) states in a model Hamiltonian whose classical dynamics is chaotic. The system is described by a smooth potential, and numerous above-barrier resonances are supported. The model we use is chosen to capture essential features of the chaotic ionization dynamics of atoms in rotating fields; further, we propose that this mechanism might also be important in complex formation in certain chemical reactions. We find that, not only does the fractal Weyl law hold for a typical (generic) open Hamiltonian system [150], but it also holds even in the vicinity of $\hbar = 1$, (i.e., far from the classical limit).

The investigation of a fractal law for open analytical Hamiltonian systems is problematic for a number of technical reasons, including the larger dimensionality of phase space $N$ needed to observe the chaotic repeller. Unlike in unidimensional maps, for which $N = 2$, in an autonomous Hamiltonian the repeller exists only if $N \geq 4$, which compounds the computational challenges involved. An additional computational difficulty is the calculation of resonance eigenfunctions in the limit $\hbar \to 0$ because of the attendant growth in the size of the basis needed to converge the calculations. Some of these obstacles have been overcome in a previous study that reported fractal Weyl law behavior in an open Hamiltonian whose potential energy surface (PES) consisted of three gaussian bumps [148]. However, for computational reasons, only a rather limited number of resonances were included in the analysis and the structure of the resonance eigenstates themselves was not examined.
8.2 System Under Investigation

The model chosen here provides a realistic model of the chaotic ionization of atoms and of resonances in chemical reactions in that the PES features a potential well together with saddle points and, depending on the energy, the classical dynamics can be mixed (i.e., regular and chaotic) even above the saddle points. Computation of quantum complex (resonance) eigenvalues and quantum surfaces of section (QSOS; see, for example, Ref. [147, 151]), based on Husimi distributions, reveals that the above-barrier resonance energies are localized on the classical repeller. For values of $\hbar$ away from the asymptotic limit, there is progressively more delocalization. The advantage of the model used is that the calculations are more tractable than for, say, the H atom interacting with rotating fields for which the Coulomb term complicates the computations.

The model is a modification of the Hénon-Heiles (HH) Hamiltonian [152]

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(x^2 + y^2) + \lambda(x^2y - \frac{1}{3}y^3) - \omega(xy - yp_x)$$  \hspace{1cm} (8.1)

where, throughout, $\lambda = 0.1$ and $\omega = 0.1$. The modification is the presence of a Coriolis term – the term in $\omega$, which is designed to simulate the addition of, for example, a CPM field or a magnetic field to a Rydberg atom [153]. Because the Hamiltonian does not have rotational symmetry, this angular-momentum-like term is not a conserved quantity. Furthermore, the presence of the Coriolis term means that it is no longer possible to define a potential energy surface; instead one can resort to using the device of a zero velocity surface (or ZVS, see, for example, Ref. [149]). Finally, time reversal symmetry of the system is broken.

Energies and widths are scaled by the energy of the three saddle points in the ZVS, i.e., $E_s = (1 - \omega^2)^3/6\lambda^2 = 16.17165$.

8.3 Structure of the Repeller

The structure of the repeller is shown in Fig. 8.1 for $\omega = 0.1$ and an energy rather high above the saddle point energy. The repeller was computed by integrating trajectories forward and backward in time. The initial conditions of trajectories that survived (i.e., did
not escape) for a time $\tau_0$ were saved. Survivors were then reintegrated for a time $20\tau_0$ and their intersections with an appropriate Poincaré surface of section (SOS) were recorded. In this case, the SOS chosen is defined by $x = 0, \dot{x} < 0$.

The effect of adding the Coriolis term is that, for nonzero $\omega$, relatively large KAM islands can co-exist with – but are not part of – the repeller for energies considerably above the energy of the saddle points. Here we do not consider resonances directly associated with these islands. However, the Coriolis terms has the effect of bringing out the structure of the repeller more clearly than for the pure HH system ($\omega = 0$ [152]). Thus, varying $\omega$ allows for the fine tuning of the dynamics in the energy regime of interest.

8.4 Computations of the Complex Resonances

The method of complex rotation was used to compute the complex resonance energies $E_n = E_r - i\Gamma_n/2$ where $\Gamma_n$ is the resonance width [154]. This was accomplished by rotating the coordinates into the complex plane by an angle $\theta$ ($q_i \rightarrow q_i e^{i\theta}$) and then diagonalizing the resulting Hamiltonian matrix in a two-dimensional isotropic oscillator basis $|n, m \rangle$ [152]. In principle, the procedure is straightforward although care must be exercised to ensure that resonances are distinguished from scattering states. This can be accomplished by examining so-called $\theta$-trajectories; as the angle $\theta$ is varied the resonances, as distinct from scattering states, converge. A large number of resonances lying above the saddle points are required to achieve the quality of statistics needed to determine how the number of resonances scales with $\hbar$.

The complex energy spectrum for the Hamiltonian of Eq. (8.1) contains resonances lying below as well as above the saddle points. Sub-saddle states decay by tunneling. However, the states of interest lie above the saddle points and, therefore, a large basis set must be used to converge these resonances. As $\hbar$ is decreased, the number of states below the saddles grows and, therefore, the size of the basis must be increased. For this reason, it is difficult to access the very small values of $\hbar$ – or equivalently, the very high-lying states – for which it is normally assumed that the fractal Weyl law will hold. Working on the observation that, in general, asymptotic expansions often provide good agreement
even outside their strict domains of validity, we examined resonance statistics for \( h \) in the vicinity of \( h = 1 \). Numerically, resonances were computed by direct diagonalization and also, as a check, by using the Arnoldi method which takes advantage of the sparsity of the Hamiltonian matrix \([148]\). The Arnoldi method has the twin merits that (i) a larger basis can be employed, and (ii) it allows access to selected portions of the spectrum. However, only a relatively small subset of resonances can be computed in this way \([155]\).

Distributions of resonances in the range \( 0.9 \leq h \leq 1 \) were then computed. Fig. 8.2 shows the complex resonance eigenvalues obtained for \( h = 1 \). By counting the number of states, \( N(h) \), in 8 different rectangular boxes of size \((1, 1.24h)\) located around \( E_r = 1.8E_s \) and averaging over these sets of data, we were able to establish that the number of states follow a Weyl law with \( d = 1.231 \pm 0.028 \) (see lower inset in Fig. 8.2). Similarly, and also as shown in the figure, the dimension of the classical repeller of Fig. 8.1 computed from the Poincaré map is fractal with correlation dimension \( d_2 = 1.442 \pm 0.008 \) where \([156]\)

\[
d_2 = \lim_{s \to 0} \frac{\ln C_2(s)}{\ln s}.
\]  

(8.2)

Here \( s \) is the edge length of an \( n \)-dimensional cube and \( C_2(s) \) is the correlation sum \([156]\)

\[
C_2(s) = -\lim_{M \to \infty} \frac{1}{M^2} \sum_{k,\ell=1}^{M} \Theta (s - ||q^n_k - q^n_\ell||)
\]

(8.3)

where \( M \) is the number of points in the repeller, \( \Theta \) is the Heaviside step function and \( q_k \) are the points of the repeller. The fractal dimension, \( m \), is related to the correlation dimension computed from a Poincaré map as \( m = 1 + d_2 \) \([156]\). Using the classical data we found that \( d_2 = 1.442 \pm 0.008 \), which leads to a fractal dimension for the repeller of \( m = 2.44 \).

According to Ref. \([138]\), the quantum resonances in an energy interval should scale as \( h^{-m/2} \) where \( m \) is the dimension of the trapped set for the energies in that interval. This is in excellent agreement with quantum box counting since \( m/2 = 1.22 \) while the quantum box counting gives \( d = 1.23 \). This prediction is borne out remarkably well by Fig. 8.2 and
8.5 Fractal Weyl Law

In addition to the conjecture that for generic open systems fractal Weyl law behavior will be observed, it is also expected that Husimi functions will coagulate onto fractal sets (i.e., onto the repeller) in the limit $\hbar \to 0$ [140]. For finite $\hbar$ Husimi functions will not truly be confined to fractal sets and will appear somewhat blurred due to quantum effects. However, as $\hbar$ is decreased, classical structures, on progressively finer scales, will become apparent in the Husimi functions. The $\hbar \to 0$ limit is itself of physical interest in that this limit corresponds, for example, to the ionization of ultrahigh Rydberg states.

Because the Hamiltonian is complex and non-Hermitian, the left, $\Psi_L^{(i)}$, and right, $\Psi_R^{(i)}$ eigenfunctions do not satisfy the usual (Hermitian) identity $\Psi_L^{(i)} = \Psi_R^{(i)*}$ and, consequently, $\rho_i = \Psi_L^{(i)} \Psi_R^{(i)*}$ is a complex quantity. In fact, observables are associated with neither $\Psi_L^{(i)}$ nor $\Psi_R^{(i)}$ but with $\sqrt{\Psi_L^{(i)} \Psi_R^{(i)}}$ [157]. This complicates the computation of Husimi distributions as has been discussed by Buchleitner et al. [158], who pointed out that Husimi distributions for individual complex eigenstates have the peculiar property that they can be negative and a sum needs to be made, in principle, over all complex energies [158]. For this reason, and, in analogy with previous computations in quantum maps, Husimi distributions are averaged over an energy range of finite width. We use the following definition of the averaged Husimi function, whose derivation includes both left and right eigenstates, and which is in the spirit of Bogomolny [140,158,159]

$$|\langle \Omega | \phi_E \rangle|^2 = \frac{1}{\pi} \Im \sum_i \frac{\langle \Psi_L^{(i)} | R(\theta) | \Omega \rangle \langle \Psi_L^{(i)} | R(\theta) | \bar{\Omega} \rangle}{E_{i\theta} - E}.$$  \hspace{1cm} (8.4)

Here $\phi_E$ represents the probability amplitude at real energy $E$ and $|\Omega\rangle$ is a coherent state; $\Psi_L$ is a complex rotated eigenstate expressible in terms of the isotropic oscillator basis vectors; $E_{i\theta}$ is the complex energy of the eigenstate and the overbar notation signifies (e.g., that $\langle \bar{\Psi} |$ is the complex conjugate of $\langle \Psi |$); and $R(\theta)$ is the complex rotation operator [158].
Very recently, Ermann et al. have proposed a different, although related, phase space representation for open quantum systems [147].

8.6 Husimi Distributions

For narrow resonances, simplifications of Eq. (8.4) are possible. By projecting the states onto a basis of isotropic oscillator functions, one avoids computing basis vectors in the complex coordinate plane, a procedure that is numerically unstable since basis vectors that are oscillatory along the real axis may diverge exponentially in the complex plane [158]. In this case, one then needs to compute matrix elements of $R(\theta)$ in the basis used, although these matrix elements themselves ultimately diverge – the resonance eigenfunctions are not $L^2$ functions.

We adopted the following procedure to project the 4-dimensional Husimi distribution onto a 2-dimensional hypersurface in phase space so as to generate a QSOS: A narrow interval of energy was selected around some energy of interest $E_0$. Eq. (8.4) was then used with the resonance eigenstates projected onto the isotropic oscillator basis. Only resonance states with widths smaller than some width, $\Gamma_0$, were included in the summation, and the matrix elements $\langle n | R(\theta) | m \rangle$ were approximated by their lowest order (i.e., diagonal) expansion in $\theta$. For states with narrow widths, as is the case here, this is an excellent approximation. The QSOS was then computed by fixing $x = 0$ and computing the conjugate momentum $p_x$ using the classical Hamiltonian at energy $E$. Because the boundary of the classically allowed region itself changes with energy, this procedure is not entirely satisfactory when computing an average Husimi QSOS. However, provided that the energy range is kept sufficiently small, the errors so introduced are expected to be minimal; this was verified by direct computation.

Fig. 8.3 shows a typical example of a QSOS computed in this way. The averaged Husimi distribution is clearly localized on the fractal repeller sets $K_+$ and $K_-$, which are also shown in the figure. However, this tendency for the Husimi to coagulate onto the repeller is mitigated by the relatively large value of $\hbar = 1$ used in constructing the figure. The Husimi distribution is somewhat delocalized over the repeller and does not precisely...
follow the contours of the fine-scale classical structures. It is also apparent in Fig. 8.3 that the quantum density builds up close to the saddle point. The reason for this is that the quantum particle senses the presence of classical turning points in the complex plane and, therefore, slows down, which leads to a buildup in probability density in the vicinity of the saddle point. This is consistent with the recent findings of Keating et al., who note that for longer living states, the long lifetime allows interference and diffraction effects to accumulate, thereby washing out the fractal structure to some extent [141].

8.7 Conclusions

In summary, the fractal Weyl law was found to hold in an open Hamiltonian system. Despite working far from the asymptotic limit $h \to 0$, the resonance energies manifested clear fractal behavior, and averaged Husimi distributions reflected rather faithfully the structure of the classical repeller.
Figure 8.1: Superposition of the two branches of the repeller computed as described in the text and projected onto the SOS defined by $x = 0, \dot{x} < 0$ and $E = 1.8E_s$. The bounding curve, solid line (red in color), of the SOS is also shown. Both axes have been scaled to the interval (0,1) to allow for comparison with the Husimi plot of Fig. 8.3.
Figure 8.2: Frame (a) shows resonance positions ($E_r$) and widths ($\Gamma$) (scaled by the saddle point energy $E_s$) for $\hbar = 1$. In (b) the classical quantity $\ln C_2(s)$ is shown vs. $\ln s$ together with a best fit to a line whose slope is the correlation dimension [see Eq. (8.2)] (i.e., $d_2 = 1.442 \pm 0.008$). Frame (c) shows a best fit to box counted quantum resonances with slope $d = 1.231 \pm 0.028$. The quantum resonances scale as $\hbar^{-m/2}$ or $\hbar^{-1.22}$ where $m = (1 + d_2)$ is the dimension of the trapped set; the quantum box counting dimension is 1.23. Despite considering a relatively narrow range of $\hbar$, lying far from the classical limit the classical and quantum fractal dimensions agree well.
Figure 8.3: Contours of the averaged Husimi function calculated as described in the text superimposed on a representation of the classical repeller. Twenty resonance states on each side of $E = 1.8E_s$ were included. The points which represent the classical repeller on the SOS have been kernel smoothed which, in essence, assigns a local density of points and then colors that section of the plot accordingly – compare to Fig. 8.1. The color scale runs from white through light grey (yellow and light blue in color) to dark grey (dark blue in color) and represents the density from low to high accordingly.
CHAPTER 9

SUMMARY

The study of the quantum and classical dynamics of very floppy van der Waals complexes is an area of active research [1–8]. Of particular current interest is the behavior of the weakest possible van der Waals molecules, especially those involving He atoms. Nowadays much of this research is performed inside nanodroplets of liquid $^4$He [9]. The nanodroplets offer considerable promise as microscopic cryogenic chambers, with potential applications including the creation of tailor-made chemical or bio-molecular complexes and studies of superfluidity in nanoscale systems.

While it is exceptional for a molecule dissolved in a liquid to present rotationally resolved lines (HF being one exception [85]) in a $^4$He nanodroplet, coherent free rotation over many periods appears to be the norm [18]. Still, the liquid and gas-phase spectra are not identical. In most cases the spectroscopic constants of the solvated molecule are shifted from their gas-phase values. One persistent objective of the studies of molecules doped in helium droplets has been to try to relate the extent by which the rotational constants of molecules are renormalized to general properties such as (i) the anisotropy of the molecule-helium interaction potential, (ii) the local superfluidity of the helium around the molecule, and (iii) whether the rotational constants are large (as in the case of “light rotors,” e.g., HF, H$_2$O, NH$_3$) or small (as in the case of “heavy rotors,” e.g., SF$_6$, OCS). Nevertheless, a clear connection has still not been found between any one of these three factors and the degree of renormalization and the existence of various exceptions to light–(versus heavy)–rotor rules of thumb [19, 41, 42] suggests that further studies of a wide variety of molecules in $^4$He droplets are needed to understand the interplay between the nature and strength of the potential anisotropies and the size of the bare molecular moment of inertia in controlling the approach to solvation.

Most of the research described in this dissertation focused on tracing the microscopic mechanism of the quantum solvation of various molecules in small $^4$He clusters and relating
it directly to angular momentum coupling - and decoupling - between identical Bosons and the molecular rotor. The calculations were performed using DMC methods – an accurate and straightforward way of finding ground state energies of quantum systems [22]. Due to the large differences in the strengths of the intramolecular and intermolecular forces of weakly bound complexes, the bond distances were frozen at the equilibrium distance. This procedure, the rigid-body DMC method (RBDMC), allows for larger diffusive time steps to be used [23]. To avoid unphysical dissociation of larger clusters, and to speed up the convergence, importance sampling technique [23] was implemented. For calibration, the ground and excited \((J = 1)\) states for each molecule-He dimer were computed, using nodal functions for the hypothetical isotropic complex, and coupled channel calculations using the program BOUND [56].

Although the DMC method is numerically exact for the ground state, this is not the case for excited states. In this work, excited states computations relied on the fixed-node approximation [22, 23]. In general, the fixed-node method is somewhat paradoxical: To compute an excited state its nodal surface must already be known. At times, symmetry or approximations can be used to estimate the topology of the node but no general procedure exists. To study excited states, a new approach was developed – adiabatic-node diffusion Monte Carlo method, which relies on Born-Oppenheimer-like angular-radial separation (BOARS) developed by Holmgren et al. [49]. To compute adiabatic nodal functions, in this work, the following assumptions were made: (i) He-He interactions were ignored (for ground states with \(N = 10\) these contribute \(< 5\%\) to the energy); (ii) \(R\) was fixed at \(R_0\); (iii) the molecular c.o.m. was pinned in place; (iv) for more than a single He atom, the adiabatic separation was done in the space-fixed frame.

The calculations of HCN in \(^4\)He droplets demonstrated explicitly that quantum solvation of HCN in \(^4\)He droplets proceeds through decoupling of the solvent and solute angular wavefunctions. The adiabatic node approach allowed physical mechanisms to be proposed for the previously predicted [42] disappearance of the \(b\)-type \((\Delta K = \pm 1)\) series, as well as the rapid convergence of the \(a\)-type \((\Delta K = 0)\) series to the nanodroplet limit as a function
of cluster size. In particular, the behavior of the a-type series was traced directly to the mechanics of angular momentum coupling – and decoupling – between identical bosons and the molecular rotor. For very small values of $N$ there exists significant angular momentum coupling between the molecule and the He atoms. This coupling diminishes quickly and for $N \approx 10$ solvation appears to be essentially complete as evidenced by significant decoupling of the molecule and the solvent angular momenta. It was suggested that the vanishing of the b-type series is a consequence of He-He repulsion causing the states most strongly associated with the b-type transition to sample the negative P2 anisotropy of the potential more strongly. This leads to a change in their geometry that eliminates longitudinal bumps (i.e., the dynamical asymmetry required to observe two, rather than one, lines in the spectrum [42]).

For HX-$^4$He complexes, where X=F, Cl, Br, the calculations observed that the decrease in the gas-phase rotational constants for HCl and HBr in a $^4$He nanodroplet was smaller than for HF, despite HF having a considerably larger rotational constant than the other two molecules. This traced the solvation behavior of the three molecules to how the potential anisotropies couple angular momentum states between the molecule and the bosonic $^4$He atoms. Although HF has a rotational constant that is almost double that of HCl, the somewhat larger anisotropy of the PES leads to a small asymptotic decrease in the effective rotational constant whereas, HCl and HBr approach their gas-phase values in the nanodroplet limit.

Also, the solvation dynamics of an ammonia molecule doped into a droplet containing of $N = 1 − 25$ $^4$He atoms was studied. The computed renormalization – a reduction of $\approx 5\%$ – of the rotational constants of the ammonia molecule is in quantitative agreement with recent experiments of Slipchenko and Vilesov [Chem. Phys. Lett., 412, 176, (2005)] and disagrees with the much larger renormalization – a reduction of $\approx 25\%$ – originally reported by Behrens et al. [J. Chem. Phys., 109, 5914, (1998)]. For the symmetric top ammonia molecule, it was predicted that the asymptotic limit is not reached until $N \approx 25$, similar to the case for the linear molecules HF, HCl and HBr, which also have relatively
large rotational constants. These results provide support for the prediction that rotors with large rotational constants should (i) exhibit a smaller renormalization of their moments of inertia and (ii) exhibit a slower rate of renormalization as a function of $N$ as compared to heavy rotors.

Small molecular homo- and heterodimers have also been an active area of study in superfluid helium droplets [25], in particular to study hydrogen bonding [26]. Early molecular beam experiments by Odutola et al. [28] discovered the polar nature of the ammonia dimer, which was believed to have a classical hydrogen-bonded structure; i.e., one of the monomers acts as a proton donor with an NH bond pointed towards the lone pair of the other monomer. Subsequent experiments by Nelson et al. [29] contradicted this expectation and suggested a more cyclic structure as opposed to a linear hydrogen-bonded structure. The current consensus seems to be that ammonia dimer is a hydrogen-bonded structure but with the twist that the structure is nonlinear as reflected by the ease with which the the donor/acceptor behavior of the molecules can be interchanged [30]. The uncertainties associated with the structure of the ammonia dimer were part of the motivation for Behrens et al. [26] to study this system in ultra-cold nanodroplets of $^4$He. The main conclusion drawn from their study is that the interchange tunneling splitting (ITS) is quenched considerably, by a factor of 2-5, as compared to the gas phase. This was interpreted as the two ammonia monomers being more equivalent than in the gas-phase which, in turn, suggests a more cyclic structure in a $^4$He droplet.

This work studied a phenomenon of the reduction in the interchange tunneling splitting of the ammonia dimer as a function of the number of He atoms. While the reduction was smaller than that observed experimentally, the basic trend is as observed in the experiment. It was noted by the recent experiments on the NH$_3$-He dimer by Slipchenko et al. [31] that previous experiments [32] by the same authors as Ref. [26], overestimated the renormalization of the rotational constants for that system. It is possible that the reduction in the tunneling splitting observed experimentally in Ref. [26] might have also been overestimated, most likely due to using the CO$_2$ laser in both experiments (private communication). Never-
theless, the results indicate that the scheme proposed in [26] captures the basic mechanism responsible for the reduction in the tunneling splitting, which, in turn, suggests a more cyclic structure in the $^4$He solvent. Future work will explore the use of a genetic algorithms to investigate whether the He environment distorts the nodal surface of the dimer. The procedure developed in this paper also opens up the way to explore other complexes that have very recently been studied in a He droplet (e.g., $(\text{H}_2\text{O})_2\text{HCl}$. Vilesov et al. [25] have shown that He droplets provide a unique host that can be used for the isolation and study of single chemical acts). To study this system, this work proposes to combine the methods developed here with the genetic-algorithm-DMC method developed earlier.

As apparent from the previous discussion, the biggest challenge all DMC methods face are the computations of the excited states. This raises the question of whether it is possible to compute nodal surfaces on-the-fly during the DMC calculation. An elegant way of doing this has already been proposed by Sandler et al. [110], who recognized that certain conditions hold at the node in a DMC calculation. Because DMC walkers that cross a node are eliminated, one is, in effect, performing two DMC computations, one on each side of the node. Therefore, the energies obtained from these two computations, should be equal if the nodal surface used is correct. Further, because the derivative of the wavefunction must be continuous across the node, the local density of DMC walkers crossing the node in each direction should be equal. Finally, the excited state must be orthogonal to the ground state. The key ingredient in a GA is to develop a fitness function that guides the evolution of an initially random population of “individuals” – in this case, each individual represents a guess at the correct nodal surface. The criteria developed by Buch and co-workers [110, 111] are used to construct the fitness function: Because the fitness function involves comparing histograms of fluxes across the node then a way has to be developed to do this automatically. This is an important problem in the field of pattern recognition and a variety of approaches have been developed (e.g., the earth mover algorithm [113]).

In this work, a genetic algorithm (GA) [112] was used to compute nodal surfaces automatically based on the criteria outlined above. Using this method, good estimates were
found for nodal surfaces in several test problems including (i) the HCN-4He dimer, (ii) the HCl-dimer and (iii) a “fudged” version of the HCl-dimer, f-(HCl)2, for which the two monomers are artificially assigned different rotational constants so as to break the symmetry and distort the nodal topology of the symmetric dimer. For simplicity, in the case of the HCl dimers an adiabatic approximation, in which the radial distances are frozen, were made and concentrated solely on the angular part of the wavefunction. Doing this allows the exact node for each system to be calculated accurately using basis set methods, so as to make a comparison with the GA-DMC approach. Future work will investigate the use of more sophisticated histogram comparison methods (e.g., combining the earth mover algorithm with other measures, as well as extending the method to higher dimensional problems and higher excited states). However, the results presented here already seem to suggest that finding nodes in DMC calculations using a genetic algorithm holds promise when symmetry arguments fail, (e.g., for isotope-substituted water trimers [122]).

Also, the classical rotational dynamics of a series of van der Waals complexes HX-4He with X = F, Cl, Br, CN were studied. In each case, the ground state dynamics were found to be almost entirely chaotic. The chaotic nature of the low-lying states, including the ground state, seems to be partially responsible for the observed decoupling of the molecule and the He atoms that is observed experimentally. Rotationally excited states with \( J = 1 \) which, except for HCN-4He, are actually resonances that decay by rotational pre-dissociation, were also investigated. The existence of resonances was reflected classically in the presence of a series of long-living orbits embedded in the chaotic sea, which exist even above the dissociation limit of the dimer. Certain features of the chaotic sea are characteristic of the existence of a fractal classical repeller. In some cases large, permanently bound, KAM islands were discovered in the chaotic sea. These islands are similar to those of the chaos-assisted capture mechanism of irregular moons at the giant planets, and they are expected to have important consequences for the quantum scattering dynamics of these complexes.

The final chapter presents a theoretical study of the semiclassical dynamics of a model of rotational dynamics in an open Hamiltonian system (i.e., one that contains no bound
states). The system is described by a smooth potential and supports numerous above-barrier resonances. The research was motivated by the recognition that, as noted, $J > 0$ states of many helium-containing complexes are resonances. It was shown for this system that fractal Weyl law behavior holds even relatively far away from the classical limit. Additionally, the complex resonance wave functions were found to be localized on the fractal classical repeller.
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Department of Chemistry and Biochemistry
Utah State University
6200 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramilowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. *Rotational Dynamics of Small $^4$He Clusters Seeded with HF, HCl, HBr Molecules:*
   Jordan A. Ramilowski, Aleksandra A. Mikoss, David Farrelly, José Luis Caguide
   Fajín and Berta Fernández

2. *Quantum solution dynamics of HCN in a helium-4 droplet:*
   Aleksandra A. Mikoss, Jordan A. Ramilowski, and David Farrelly

Sincerely,

[Signature]

Aleksandra A. Mikoss
Permission Letter

Berta Fernández

Facultad de Química, Avda. das Ciencias s/n
Universidade de Santiago de Compostela
E-15782 Santiago de Compostela, Spain

April 27, 2010

Jordan A. Ramíowski
Department of Chemistry and Biochemistry
Utah State University
0300 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramíowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. Rotational Dynamics of Small 4He Clusters Seeded with HE, HCl, HBr Molecules:
   Jordan A. Ramíowski, Aleksandra A. Mitrocz, David Farrelly, José Luis Cagide Fajín and Berta Fernández

Sincerely,

\[Signature\]

Berta Fernández
Permission Letter
José Luis Cagide Fajín

Facultad de Química, Avda. das Ciencias s/n
Universidad de Santiago de Compostela
E-15782 Santiago de Compostela, Spain

April 27, 2010

Jordan A. Ramíowski
Department of Chemistry and Biochemistry
Utah State University
0900 Old Main Hill
Logan, UT 84322

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1. Rotational Dynamics of Small 4He Clusters Seeded with HF, HCl, HBr Molecules: Jordan A. Ramíowski, Aleksandra A. Mikosz, David Farrelly, José Luis Cagide Fajín and Berta Fernández

Sincerely,

José Luis Cagide Fajín
Permission Letter
Antonio Gamboa

Departamento de Física y Mecánica, Escuela Técnica Superior de Ingenieros Agrónomos
Universidad Politécnica de Madrid
28040 Madrid, Spain

April 24, 2010

Jordan A. Ramilowski
Department of Chemistry and Biochemistry
Utah State University
0300 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramilowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. *Chaos in the classical mechanics of bound and quasi-bound HX – 4He complexes with X = F, Cl, Br, CN.*

Sincerely,

[Signature]

Antonio Gamboa
Permission Letter
R. M. Benito

Departamento de Física y Mecánica, Escuela Técnica Superior de Ingenieros Agrónomos
Universidad Politécnica de Madrid
28040 Madrid, Spain

April 24, 2016

Jordan A. Ramilowski
Department of Chemistry and Biochemistry
Utah State University
0000 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramilowski to use the following publications in part or in full for inclusion in his PhD dissertation:


Sincerely,

R. M. Benito
Permission Letter
Henar Hernández

Departamento de Física y Mecánica, Escuela Técnica Superior de Ingenieros Agrónomos
Universidad Politécnica de Madrid
28040 Madrid, Spain

April 24, 2010

Jordan A. Ramilowski
Department of Chemistry and Biochemistry
Utah State University
0360 QDM Main HRE
Logan, UT 84322

This letter grants my permission to Jordan A. Ramilowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. *Chaos in the classical mechanics of bound and quasi-bound $^4$He complexes with $X = F, Cl, Br, CN$*.

Sincerely,

Henar Hernández
Permission Letter
J. C. Losada

Departamento de Física y Mecánica, Escuela Técnica Superior de Ingenieros Agrónomos
Universidad Politécnica de Madrid
28040 Madrid, Spain

April 24, 2010

Jordan A. Ramikowski
Department of Chemistry and Biochemistry
Utah State University
0000 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramikowski to use the following publications in part or in full for inclusion in his Ph.D. dissertation:

1. *Chaos in the classical mechanics of bound and quasi-bound HX – ⁴He complexes with X = F, Cl, Br, CN:*

Sincerely,

[Signature]

J. C. Losada
Permission Letter
F. Borondo

Departamento de Química, Instituto Mixto de Ciencias Matemáticas CSIC-UAM-IJCM-UCM
Universidad Autónoma de Madrid
Cantoblanco 28049, Madrid, España.

April 24, 2010

Jordan A Ramíkowski
Department of Chemistry and Biochemistry
Utah State University
0300 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A Ramíkowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. Fractal Wegzell behavior in open Hamiltonian systems:
   Jordan A. Ramíkowski, S. D. Prado, F. Borondo, and David Farrelly,

2. Chaos in the classical mechanics of bound and quasi-bound HX – X = F, Cl, Br, CN,
   Antonio Gamboa, Benar Hernández, Jordan A. Ramíkowski, J. C. Loisada, R. M. Benito, F. Borondo and David Farrelly, 

Sincerely,

F. Borondo
Permission Letter
S. D. Prado

Instituto de Física
Universidade Federal do Rio Grande do Sul, PO Box 15051
91501-970 Porto Alegre, RS, Brasil

April 27, 2010

Jordan A. Ramlowski
Department of Chemistry and Biochemistry
Utah State University
6380 Old Main Hill
Logan, UT 84322

This letter grants my permission to Jordan A. Ramlowski to use the following publications in part or in full for inclusion in his PhD dissertation:

1. Fractal Weyl law behavior in open Hamiltonian systems;
   Jordan A. Ramlowski, S. D. Prado, Florentino Borondo, and David Farrelly,

Sincerely,

S. D. Prado
Instituto de Física - UFRGS
Av. Bento Gonçalves, 9500 - Campus do Vale
CP: 15051
91501-970 Porto Alegre - RS Brasil
Jordan Ramilowski

CURRICULUM VITAE

Dept. of Chemistry and Biochemistry
Utah State University
Logan, UT 84322

Phone (435) 764-2243
Email jordan.ramilowski@aggiemail.usu.edu

Degrees
2010 Ph.D. in Theoretical Chemistry, Utah State University (USU), Logan, UT
2002 M.Sc. (Eng.) in Technology of Organic Chemistry, Silesian Technical University (STU), Gliwice, Poland

Computational Skills
Programming Perl, R statistical package, FORTRAN, Python, \LaTeX, multi-language interfacing, bash scripting, basic parallelization
Other MySQL, CHEMCAD, Maple, Mathematica, Gaussian
Platforms Linux, Mac, UNIX, Windows, basic administrative skills for all platforms

Research Skills and Interests
- Diffusion Monte Carlo Methods
- Reaction Dynamics. Quantum and Classical Chaos
- Artificial Intelligence Methods: Decision Trees, Genetic Algorithms
- Parallel computing. Graphical User Interface Programming
- Bioinformatics

Research and Teaching Experience
2004-Present PhD Research Assistant, USU
Jan-Sept 2008 Visiting Researcher: The Department of Chemistry and the Institute of Mathematical Sciences, Universidad Autónoma de Madrid, Madrid, Spain
2001-2002 MSc Thesis in the Department of Technology of Chemistry at STU, Poland

Simulations of the technology of the oxidative coupling of methane by means of CHEMCAD 5.2
2004-2010 Teaching Assistant Principles of Chemistry I/II (Recitation and Laboratory), USU
Awards

2010  USU Graduate Student Senate Travel Award for the 239-th ACS meeting
2010  USU Graduate Student Senate Travel Award for the APS March Meeting
2009  Outstanding Graduate Student In Chemistry Award in the Department of Chemistry and Biochemistry at USU
2009  USU Graduate Student Senate Travel Award for the 237-th ACS meeting
2006-2007 The AAAS/Science Program Award for Excellence in Science: AAAS/Science one-year sponsored membership
2000-2002 Scholarship for Outstanding Chemistry Student in the Department of Technology of Chemistry at STU

Publications

in Peer-Reviewed Journals

1. Fractal Weyl law behavior in the decay dynamics of atoms and molecules  
   Jordan A. Ramilowski, Sandra D. Prado, Florentino Borondo, and David Farrelly  

2. Classical and quantum chaos of weakly bound van der Waals clusters of He-HCl, He-HCN:  
   Antonio Gamboa, Henar Hernandez, Jordan A. Ramilowski, Maria R. Benito, Florentino Borondo, and David Farrelly  
   PCCP, 11, 8203, (2009)

3. Rotational dynamics of small $^4$He clusters seeded with HF, HCl, HBr molecules  
   Jordan A. Ramilowski, Aleksandra A. Mikosz, David Farrelly, Jose Luis Cagide Fajin, and Berta Fernandez  
   (Invited article to a special issue dedicated to Professor Giacinto Scoles)

4. Quantum solvation dynamics of HCN in a helium-4 droplet  
   Aleksandra A. Mikosz, Jordan A. Ramilowski, and David Farrelly  

5. Automated computations of nodal surfaces in diffusion Monte Carlo using a genetic algorithm  
   Jordan A. Ramilowski and David Farrelly  
   (accepted for publication in PCCP)

6. Renormalization of the rotational constants of an ammonia molecule seeded into a $^4$He droplet  
   Antonio Gamboa, Jordan A. Ramilowski, Maria R. Benito, and David Farrelly  
   (submitted to Chem. Phys. Lett.)

7. Computations of interchange tunneling splittings of $(NH_3)_2$ in superfluid $^4$He droplets  
   Jordan A. Ramilowski and David Farrelly  
   (to be submitted to PCCP)
At Professional Meetings (lead author)
1. Rotational dynamics in small superfluid He-4 droplets: Monte Carlo simulations
   Jordan A. Ramilowski
   2010 Intermountain Graduate Research Symposium, Logan, UT
2. Structure of (NH₃)₂ in superfluid He droplets
   Jordan A. Ramilowski and David Farrelly
   239th, American Chemical Society Meeting (2010), San Francisco, CA
3. Fractal Weyl law in an open, chaotic hamiltonian system
   Jordan A. Ramilowski and David Farrelly
   American Physical Society March Meeting (2010), Portland, OR
4. Quantum solvation of molecules and small molecular dimers in superfluid He-4 droplets
   Jordan A. Ramilowski and David Farrelly
   237th, American Chemical Society Meeting (2009), Salt Lake City, UT

Languages
- Polish: native language
- English: fluent
- Spanish: proficient
- Russian: basic

Functions and Positions Held
- 2001-2002: Member of the Graduate Student Senate of STU
- 1999-2002: Member and the President (2001-2002) of the Student Board of the Department of Chemistry of STU