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Modelling Magnetic Bonds for Di- and Triatomic Hydrogen-Helium Molecules in the Atmospheres of White Dwarfs

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Magnetiske bindinger er en nylig foreslått type binding som dannes i ekstremt sterke magnetfelt, som de som finnes i atmosfærene til Magnetiske Hvite Dverger. I motsetning til tradisjonelle bindinger, som er basert på Coulomb-interaksjoner, oppstår magnetiske bindinger på grunn av orbital- og spinn-avhengige effekter, og de er sterkt påvirket av molekylets orientering i forhold til det ytre feltet. Tidligere studier har hovedsakelig forsket på homonukleære molekyler, men ingen har forsket på heteronukleære molekyler av hydrogen og helium. hensikten med denne studien er å modellere diatomisk og triatomisk hydrogen-helium-molekyler i sterke magnetfelt ved bruk av kvantemekanisk modellering. stabiliteten til disse molekylene ble analysert ved ulike bindingslengder, elektronspinnkonfigurasjoner og magnetfeltorienteringer. Resultatene viser at molekylstabiliteten øker når bindingen blir mer vinkelrett til magnetfeltet, og at spinntilstanden spiller en kritisk rolle i å senke energien. Disse funnene gir innsikt i mulige molekylære sammensetninger i MHD-atmosfærer og kan bidra til å forutsi deres spektroskopiske signaturer.

Introduction

For decades, the most well-known and prevalent intramolecular bonds were considered to be covalent, ionic, and metallic. The majority, if not all, of known molecules were composed of at least one of these bonds, and in environments too violent for one of these three to form, we thought no molecule would be created. However, in recent years, studies have shown that there is another type of bond: A magnetic bond. These bonds will likely never be observed on Earth, in large part due to their dependence on strong magnetic fields that are $>10^5$ T (Lange, Tellgren, Hoffman, & Helgaker, 2012). The strongest continuous magnetic field generated in a lab, achieved with the use of a Bitter electromagnet, only reached 45 T (Wikipedia, 2024a), which is considerably lower than what is required for magnetic bonds to form. As such, we cannot expect to find examples of magnetic bonds on earth, but we can nonetheless predict their existence in outer space. In the atmospheres of certain stellar objects, such as Magnetic White Dwarfs (MWDs), the conditions for a magnetic bond to form are met, allowing molecules to form in environments that may be too extreme for traditional bonds (Lange, Tellgren, Hoffman, & Helgaker, 2012).

At a field strength of 10^5 T, the strength of the magnetic field and the strength of the Coulomb forces are about equal in magnitude. This leads to a competition between the two, and previous studies have shown that atoms in strong magnetic fields can create stable bonds using the magnetic forces (Lange, Tellgren, Hoffman, & Helgaker, 2012). However, these studies have primarily been for homonuclear (single element) molecules. Additionally, the element in question tends to be either hydrogen or helium, largely due to the complexity of the calculations rising considerably with each new electron. Though less common, studies on larger molecules, such as ammonia, still exist (Tellgren, Reine, & Helgaker, 2012). Though H-H bonds

already exist on Earth, even if it is with traditional Coulomb interactions rather than magnetism, He-He bonds are largely unheard of as helium is a noble gas. However, several studies have already shown that such molecules are possible, and that they are relatively stable in strong magnetic fields (Lange, Tellgren, Hoffman, & Helgaker, 2012). Despite this, studies on hydrogen-helium molecules are rather limited, with the only known study being from 2006, which only looked at ions of H-He rather than neutral molecules (Turbiner & Vieyra, 2006). This allowed them to study molecules containing only a single electron, considerably reducing the complexity of the calculations as technological limitations likely made it difficult to simulate more complex systems.

Traditional bonds, which operate based on Coulomb interactions between the electrons and nuclei, are independent of their orientation relative to their environment. Magnetic bonds, on the other hand, can vary greatly in strength depending on their orientation against the magnetic field. Previous studies have shown that a perpendicular orientation of the magnetic field relative to the bond is preferred (Lange, Tellgren, Hoffman, & Helgaker, 2012). Another factor that is typically studied is the difference in the amount of spin up to spin down electrons in the molecule. Spin is a property of electrons that can be interpreted as the electrons spinning around their own axis, much like planets do. As this counts as an electric charge in motion, electron spin generates a magnetic field. Spin up refers to electrons whose magnetic field is oriented the same way as the external field, whilst spin down is the opposite. In the absence of a magnetic field, the ground state of atoms and molecules is made by filling up the atom's orbitals with spin up and spin down electrons. The ground state therefore has equal amounts of spin up and spin down electrons, or as close to it as possible, due to the electrons being filled in pairs of spin up and spin down electrons to neutralize each other's effects. However, this is not the case for atoms and molecules in strong magnetic fields. Instead, having as many spin down electrons as possible is ideal. This allows the magnetic field generated from spin to counteract the external one, lowering the overall energy of the system.

Studies on magnetic bonds have to be theoretical due to limitations in generating strong enough magnetic fields, but it nonetheless has a number of practical uses. The most relevant use is likely within the field of astronomy, as accurate data for what bonds can form in the atmospheres of MWDs allows researchers to predict their emission and absorption spectra. This would thus make it possible to confirm the existence of these bonds through observation, and as such, we would be able to learn considerably more about the environments near MWDs. This study therefore aims to model hydrogen and helium atoms in strong magnetic fields to find out if they can form bonds, and how strong – and therefore stable - those bonds would be.

Method

In order to model the magnetic bonds of hydrogen-helium molecules, the LONDON code was run through SAGA, a supercomputer, via the Linux terminal emulator PuTTY. The LONDON code, the main author of which is Erik I. Tellgren, uses the Hartree-Fock method to generate single-electron states for each of the electrons before combining them to calculate the energy of the many-electron state (Wikipedia, 2024b). The basis set used was aug-cc-pVTZ, which determines the precision of the single-electron states. Several variables can be altered in simulations using the LONDON code, with the variables used in this study being: The orientation of the magnetic field, bond length, the amount of spin up compared to spin down electrons, and the number of atoms.

The strength of the magnetic field was held constant at 1 atomic unit (au). This was based on previous studies, which also used 1 au, including the study that first proved the existence of magnetic bonds (Lange, Tellgren, Hoffman, & Helgaker, 2012). For the diatomic bond (H-He), the orientation of the field ranged between 0° and 90° with intervals of 22.5°. This interval proved to be a good middle ground between showing a smooth progression from a parallel to a perpendicular field and not adding too many data points. Additionally, the bond length was altered from 2 bohr to 10 bohr, which was largely based on the bond lengths for single-element magnetic bonds from previous studies. The magnetic field for the triatomic bond (H-H-He), however, was kept at the same orientation throughout, with only the location of the atoms being

altered. The bond lengths ranged from 2 to 5 bohr. These assumptions were based on the diatomic H-He molecules, such as the locations of the atoms relative to one another. The bond length used was based on the diatomic H-He molecules as well. The last variable was the spin of the electrons, and more accurately, the difference between the number of spin up and the number of spin down electrons, called spin projection. For the diatomic molecule, this corresponded to spin projections s = -1 and s = -3, whilst the triatomic molecule had s = -2 and s = -4. These correspond to the ground and excited states of these molecules under normal conditions, respectively. The only difference between a positive and negative spin projection is that a positive value contributes positively to the energy, increasing it, whilst a negative value decreases it (Wikipedia, 2024c). All calculations were therefore done with a negative spin projection, as the more stable state for electrons in a magnetic field is spin down.

The LONDON code would return the energy levels for each molecule, which was then imported into Python to graph the values. The energy minimum for the various states and the energy difference, which is the energy difference from the minimum to where the energy plateaus, would also be returned. However, to find the lowest energy state for the triatomic molecule, the bond length of the helium atom to either of the hydrogen atoms would be altered separately from the bond length between the two hydrogen atoms. First, the He-H bond length would remain constant with the energy values being modelled as a function of the H-H bond length increasing. A quadratic regression would then be used to find the bond length for the energy minimum, before repeating the process with the H-H bond length being the constant instead. This was done several times until the value from the quadratic regression did not significantly differ from the minima in the energy graphs. As nothing was experimentally measured, with all numbers being taken from mathematical models, the results can be repeated with no variation. Thus, the number of significant figures is only dependent on the variables used. The number of decimals was nonetheless limited to eight for clarity, which is still enough to compute the energy differences. Additionally, for data sets where the energy levels had a significant difference between the minimum and when the energy plateaus due to the atoms being too far away from each other, additional data points were modelled for a more precise minimum value.

Results

The diatomic s = -1 and s = -3 states had the lowest energy minima at a perpendicular orientation, as well as the largest energy difference between the minima and where the energy plateaus (Table 1 & 2, Figure 1). The highest energy minimum, as well as the smallest energy difference, is at a 22.5° orientation for both states (Table 1 & 2, Figure 1). The s = -3 state shows a sudden 'dip' for the parallel orientation (Table 2, Figure 1b). The s = -1 states have energy differences that are approx. in the -10^{-4} to -10^{-3} range (Table 1), whilst the s = -3 states have energy differences that are approx. $-2*10^{-2}$ (Table 2).

Table 1. Energy minima for the diatomic s = -1 states with their corresponding bond length. Ediff refers to the difference between the minimum and where the energies plateau.

	Magnetic Field Orientation				
	90°	67.5°	45°	22.5°	0°
Bond length (bohr)	2.80	3.00	3.50	5.00	5.50
Energy minimum (hartree)	3.51941162	3.51916206	3.51869766	3.51854674	3.51859535
Ediff (hartree)	0.00092864	0.00069777	0.00021404	0.00008277	0.00011100

Table 2. Energy minima for the diatomic s = -3 states with their corresponding bond length. Ediff refers to the difference between the minimum and when the energies plateau.

	Magnetic Field Orientation				
	90°	67.5°	45°	22.5°	0°
Bond length (bohr)	2.88	3.10	3.75	5.00	2.88
Energy minimum (hartree)	3.76758783	3.76344314	3.75269839	3.74464476	3.76087809
Ediff (hartree)	0.02486413	0.02056019	0.00998255	0.00175408	0.01814659

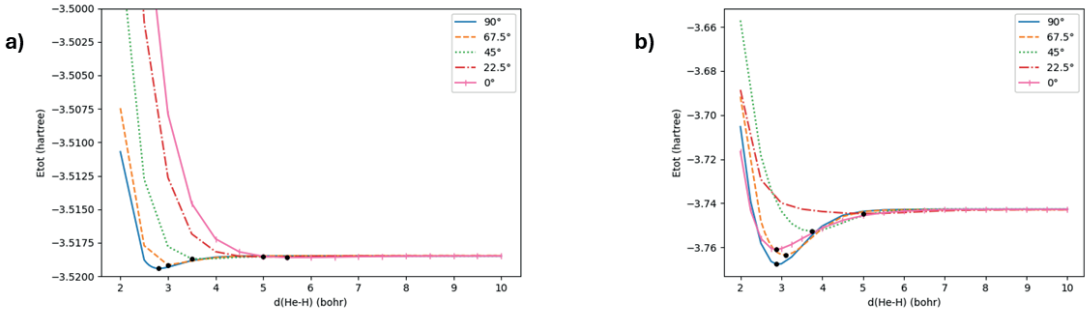

Figure 1. Energy values for the a) s = -1, and b) s = -3 states, alongside their corresponding bond lengths. Energy minima are marked with a dot.

The triatomic s = -2 and s = -4 states, with both showing an asymmetry in the bond lengths between the H-H and He-H bonds (Figure 2). The s = -2 state has a difference in bond length that is <0.5 bohr (Figure 2a & 2b), whilst the s = -4 state has a difference in bond length that is >0.5 bohr (Figure 2c & 2d)

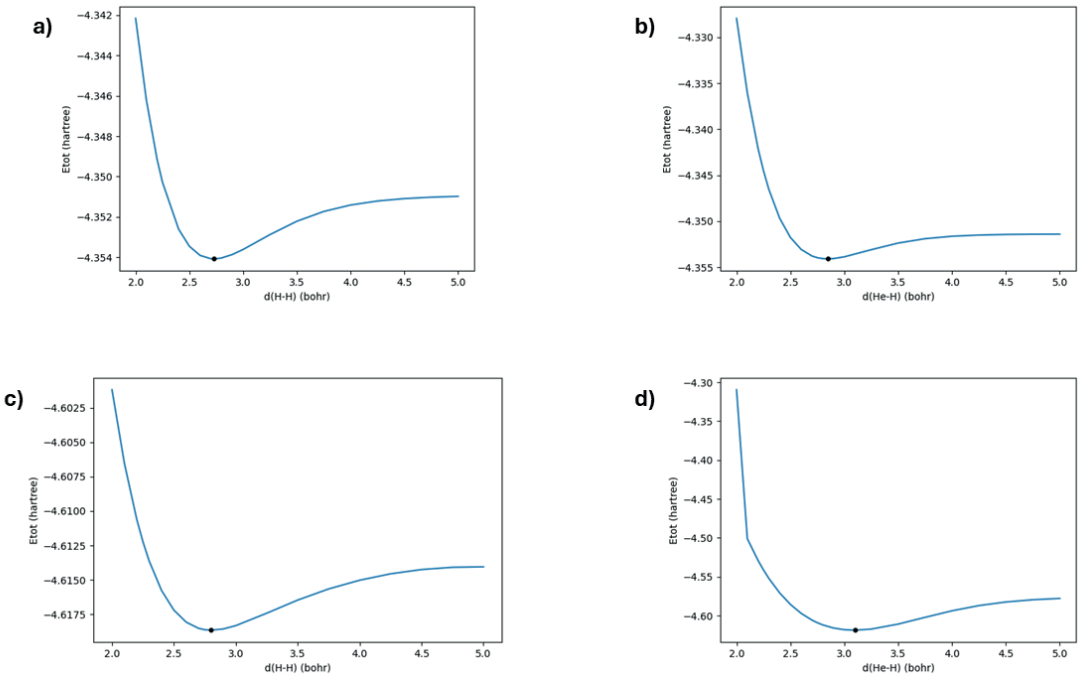

Figure 2. Energy values for the triatomic molecule and their corresponding bond lengths. a) & c) show the bond length between the helium and either hydrogen atom constant with the H-H bond length being varied, with a) being s = -2 and c) being s = -4. b) & d) show the bond H-H bond length as constant, with the bond length between the helium and either hydrogen atom being varied, with b) being s = -2 and d) being s = -4. Minima are marked with a dot.

Discussion

This study attempted to find out if bonds can form between hydrogen and helium atoms in magnetic fields, and how stable those bonds would be. The results largely coincided with previous studies despite this study being for a multi-element molecule, whilst previous ones were mostly for single-element molecules. As such, the bond is predicted to become increasingly more stable the closer the orientation of the magnetic field came to being perpendicular, much like H-H or He-He molecules (Lange, Tellgren, Hoffman, & Helgaker, 2012). For the molecule with s = -1, a parallel magnetic field resulted in an unstable bond, one that is either unlikely to form or, if it does form, would break quickly. This is due to the energy of the bond being negligibly lower than if the atoms were to exist on their own, and there is thus no incentive for a bond to form. The perpendicular orientation, however, had an energy difference that was ten times greater than the parallel orientation, allowing the bond to form and remain relatively stable.

Though the energy levels consistently decreased as the orientation went from being parallel to being perpendicular, this was not the case for s = -3. This was still within expectations, with some studies showing a similar 'dip' in the energy level for a parallel field (Tellgren, Reine, & Helgaker, 2012). This is due to the existence of some states the molecule can be in which prefer a parallel, or close to parallel, orientation. One can assume that the orientation with the lowest energy for this state would be somewhere between a parallel and a 22.5° orientation considering previous studies. Additionally, this energy minimum will likely still be higher than for the perpendicular orientation.

Though the results for the triatomic molecule did not coincide with previous studies due to the molecule not being an equilateral triangle (Tellgren, Reine, & Helgaker, 2012), this was not unexpected. An equilateral triangle for a molecule composed of only one element is expected, as each of the atoms would have an equal influence on the molecule's shape. The triatomic molecule in this study, however, contains a helium atom alongside two hydrogen atoms. As such, the helium's larger nucleus leads to a greater bond length between the helium and either of the hydrogen atoms than the bond length between the two hydrogen atoms. Otherwise, there was little deviation from previous findings, though there are a variety of uncertainties for the triatomic molecule that makes this difficult to conclude. Had it not been for time limitations, asymmetrical bond lengths between the He and the two H atoms would have also been modelled. Similarly, the orientation of the magnetic field was kept the same throughout due to time constraints. As a result, the findings of this study may not be the ideal structure nor the lowest energy state of the triatomic molecule. Thus, a definitive conclusion cannot be made, but from what was tested, the triatomic molecule behaved as expected.

These results indicate that complex molecules consisting of both hydrogen and helium can, in fact, form in the atmospheres of MWDs. A perpendicular orientation is preferred for diatomic molecules, with a non-equilateral form being preferred for the triatomic molecules. This initial study can be complemented by studies of excited states, allowing astronomers to predict the spectroscopic signatures of hydrogen-helium molecules based on the differences between the ground and excited states.

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