Density Functional Theory Study of Dilute Transition Metal Phthalocyanines

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DENSITY FUNCTIONAL THEORY STUDY OF DILUTE TRANSITION METAL PHTHALOCYANINES

A Thesis Presented
by
Daniel James Burrill
to
The Faculty of the Graduate College
of
The University of Vermont

In Partial Fulfillment of the Requirements
for the Degree of Master of Science
Specializing in Physics

May, 2015

Defense Date: March 26, 2015
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Organometallic (OM) crystals are studied in fields ranging from spintronics to photovoltaics. This thesis focuses on studying a particular class of OM crystals known as transition metal-phthalocyanines (TM-Pc) - a molecular crystal composed of chains of planar OM molecules with a transition metal center and four coordinated pyrrole-aromatic rings joined by nitrogen atoms, similar to porphyrin. The structure resembles a dish rack pattern where the planar TM-Pcs of adjacent chains are oriented nearly perpendicular to each other. While TM-Pcs have been studied for decades due to their interesting optical properties and applications as dyes, there has been recent interest in understanding the magnetic properties with various transition metals.

Due to crystal arrangement, inter-chain interactions among TM-Pcs are relatively weak when compared to intra-chain interactions. This property allows the chains of TM-Pcs to be isolated and approximated as a pseudo 1D system. The electronic structure and spin exchange are computationally examined along chains of CuPc when they have been diluted with the metal-free variant, H₂Pc. Density functional theory is employed with the Hubbard U correction to account for electron interactions on the copper d-orbitals. Since the diluted systems are effectively 1D with narrow bands along their stacking axis, a 1D Heisenberg model is applied where the exchange coefficient is determined through the Broken Symmetry method. Additionally, the effect of non-local corrections, used to determine structural features, on the Hubbard U and Heisenberg exchange coefficient, J, are discussed.
Acknowledgments

Over the course of three years I have accumulated a number of people I am indebted to for guiding me through this project. To give adequate acknowledgement to their assistance I think it is most appropriate to mention them in chronological order. Even before beginning this project I had help and advice from my previous advisor Dr. Ravindra Pandey. During my time searching for a meaningful career path in the world of computational physics he steered me towards density functional theory (DFT) and gave me great opportunities to pursue this path. Secondly, I would like to thank Dr. Ping Yang for her help and guidance towards understanding the theory side of DFT. With her oversight I was able to move from being a practitioner to a researcher able to make informed decisions about what data means. Lastly, I would like to thank my thesis advisor Dr. Adrian Del Maestro for the many insightful conversations and opportunities he has provided over the years.

*Science, great, mighty and in the end unerring [...] has fallen into many errors - errors which have been fortunate and useful rather than otherwise, for they have been the steppingstones to truth.*

Jules Verne, *A Journey to the Center of the Earth*
To my parents
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Chapter 1

Introduction

1.1 Introduction

Phthalocyanines (Pcs) have been applied in various applications such as industrial
dyes [1], molecular electronics [2–6], and photovoltaics [3,4] for many decades. These
organometallic molecules have been studied since the 1930’s for use as pigments when
British chemical corporations began characterization experiments to determine what
produced the vivid range of colors attributable to the crystalline form. Since phthalocy-
cyanines are large planar molecules with a coordination site located at the center, it
was found that the color depended largely on the transition metal placed in this cen-
tral site [1,7]. Recently, other areas such as spin and band gap engineering have been
useful in driving progress towards understanding the role played by the transition
metal [8–11].

Atoms located at the central site in phthalocyanine span the periodic table from
the metal-free variant H₂Pc to silicon Pc [1]. However, it is the transition metals
which give the phthalocyanines their vivid colors. The energy levels created by the
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d-orbitals and D$_{4h}$ symmetry give rise to energy transitions in the visible spectrum where the choice of transition metal governs the spacing of the energy levels. Some transition metal phthalocyanines (TMPcs, TM-C$_{32}$H$_{16}$N$_8$ [12]) such as MnPc, CoPc, and CuPc [12–16] have been well-studied in both their molecular as well as crystalline forms. This thesis focuses on the structural, electronic, and magnetic properties of CuPc and H$_2$Pc which are shown in Fig. 1.1.

![Figure 1.1: H$_2$Pc and CuPc molecules](image)

There are two major variants of the crystalline form of CuPc: the $\alpha$ and $\beta$ phases. These are characterized by the stacking and sliding angles as defined by Wu et al. [17] along the Pc chains which are shown in the Fig. 1.2 where $\phi$ represents the stacking angle and $\psi$ is the sliding angle. Note that the sliding angle, $\psi$, is within the plane of the molecule to the effect that the molecules can be rotated while the stacking angle, $\phi$, lies in the $xz$ plane and is used to define the overlap of the phthalocyanines. The $\beta$ phase is characterized by a stacking and sliding angle at about 45° and is stable at room temperature and pressure [12]. Additionally, CuPc is one of the most well-studied Pc variants due in part to its resilience and interesting magnetic properties.
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The crystals are formed by chains of stacked phthalocyanine molecules where electron interactions between the chains is negligible compared to intra-chain interactions [6].

While being well studied in the molecular, pure crystalline, as well as in various doped forms, dilute samples of CuPc have yet to be examined. This research explores the orbital and spin characteristics of CuPc diluted with H$_2$Pc in ratios of 75%, 50%, and 25%. When placed at the central site in a phthalocyanine, Cu loses two electrons to the ligand N states thus creating a d$^9$ open-shell. Due to ligand symmetry (D$_{4h}$) the occupied energy levels of interest are a singly occupied $b_{1g}$ state and a doubly occupied HOMO of $a_{1u}$ [16]. The ordering of the unoccupied states warrants more discussion but the two possibilities are an ordering of $e_g$ and $b_{1g}$ for semi-local exchange correlation functionals while the ordering flips for functionals which explicitly contain Hartree exchange. The order flipping is generally attributed to a self-interaction error in semi-local functionals [18].

Interactions between Pc molecules are mainly the result of $\pi$ orbital overlap, but the d-orbitals of the central transition metal can also contribute. The various dilute
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cases represent a change in the environment which effects the out-of-plane d-orbitals and can lead to a change the characteristics of the in-plane orbitals as well. By using the dilute cases as a means of understanding how the environment due to adjacent Pc molecules affects the d-orbitals, insight can be gained into how different types of dilution TMPcs can change the electronic properties.

Meanwhile, H$_2$Pc has reduced symmetry, D$_{2h}$, due to two H atoms located around the central site. An orbital with symmetry a$_u$ lies at the HOMO while the LUMO consists of a b$_{2g}$ state closely followed by b$_{1g}$. The HOMO-LUMO gap is reported to be about 2.1 eV [19]. These states provide a good benchmark for understanding how the states of the Cu d-orbitals change the orbital structure especially in the diluted cases.

Since the copper atoms in CuPc possess an unpaired electron the material exhibits weak magnetic ordering for the $\beta$-phase. Previous studies have shown that magnetic interaction is largely due to the overlap of the phthalocyanine molecules where the largest magnetic ordering is found for phthalocyanines which are directly stacked [17]. The exchange constant was found in the $\beta$-phase through SQUID measurements to be 0.15K while previous DFT studies have calculated a value of $-0.15$K [17]. The signs are different due to the fact that experimental uncertainty and the accuracy of DFT at these energy scales are similar. Therefore, pure $\beta$-CuPc is found to be paramagnetic.

Density functional theory is applied in this research to understand structural features, orbital energies, and spin interactions within dilute CuPc systems. Due to weak inter-chain interactions, the systems are approximated as pseudo 1D chains of phthalocyanines. Since van der Waals interactions play a large part in the in-
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Interactions of planar organic molecules, the Grimme dispersion correction is used to semi-empirically increase long-range interactions [20]. Orbital alignment is studied first in the molecular CuPc and then for the H$_2$Pc system. Upon understanding the orbital alignment the density of states (DOS) of the periodic 1D systems is examined. Spin interaction is studied here through the calculation of exchange constants through a polynuclear extension of the 'broken symmetry' method. Diluting CuPc with H$_2$Pc is proposed as a method of quenching the spin interaction between molecules.

This thesis is organized as follows: Chapter 2 is dedicated to describing the theory and implementation used to conduct calculations. Chapter 3 presents the results of the calculations first with the molecular systems followed by the 1D systems where spin exchange and DOS are shown. Chapter 4 concludes the thesis by discussing the implications of the results in terms of orbital and spin interaction engineering.
Chapter 2

Theory & Implementation

2.1 Density Functional Theory

In a system described by quantum mechanics, understanding both the wave function and its energy eigenvalues is comparable to the classical mechanics description of finding the equation of motion and determining its solution. The time-independent Schrödinger equation provides a method of determining the wave function analytically for a few choices of external potential, while most other solutions must be tackled numerically. Early numerical solutions focused on using the Hartree-Fock method which posed the solution in the form of a Slater determinant \[21\]. In the 1960’s Hohenberg, Kohn, and Sham formulated density functional theory (DFT) as a means to determine the properties of a system through the electron density rather than the wave function \[22,23\]. While it may seem trivial that the properties would depend on the electron density, it was not clear that a knowledge of electron density was enough information to determine any ground state property which could also be determined with knowing the external potential. Essentially, they showed that for any given
2.1. DENSITY FUNCTIONAL THEORY

external potential, there was a one-to-one mapping onto an electron density.

However, before a formulation of DFT is shown, first consider a system consisting of nuclear cores and electrons. The Hamiltonian for such a system is:

\[ H = \sum_{l} \left( -\frac{\hbar^2 \nabla_{l}^2}{2M} \right) + \frac{1}{2} \sum_{l,m: l \neq m} \frac{Z^2 e^2}{|\mathbf{R}_l - \mathbf{R}_m|} + \sum_{i} \left( -\frac{\hbar^2 \nabla_{i}^2}{2m} \right) + \frac{1}{2} \sum_{i,j: i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,l} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_l|} \tag{2.1} \]

where \( M, Z, \) and \( \mathbf{R} \) are the nuclear mass, charge, and positions. The symbols \( m, e, \) and \( \mathbf{r} \) refer to the electron equivalent. Here the electron charge, \( e, \) is defined to be a negative value. The first and third terms refer to the kinetic energies of the nuclear charge and electrons. The second and fourth terms give the Coulomb interactions between the nuclear charges and electrons, respectively. The last term gives the Coulomb interaction of the electrons with the nuclear charges.

A few approximations can be applied to simplify this Hamiltonian. First, the Born-Oppenheimer approximations states that in the time scale relevant to the properties due to electrons, the kinetic energy of the nuclear charges does not make a large contribution to the energy. Second, due to screening of the nuclear charges by the core electrons, the nuclear-nuclear interactions contribute relatively little. And, for the purposes of notational consistency with other authors, the electron-nuclear interaction can be approximated as the electrons interacting with an electric potential generated by all of the nuclear charges. Therefore, Eq. 2.1 reduces to:
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\[ \mathcal{H} = \sum_i \left( -\frac{\hbar^2 \nabla_i^2}{2m} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i eV_{\text{ext}}(\mathbf{r}_i) \]  

(2.2)

Despite the application of various approximations, this is still quite an intractable problem due to the book keeping of electron positions. If the number of degrees of freedom could be reduced, such as through a density function, the problem would be more approachable. Hohenberg and Kohn solved this problem through \textit{Reductio ad absurdum} and the Rayleigh-Ritz variational principle.

To prove that each external potential maps to a unique density we will consider two different potentials, \( V_1(\mathbf{r}) \) and \( V_2(\mathbf{r}) \) which are assumed to give rise to the same charge density, \( n(\mathbf{r}) \). If we can disprove this assumption then we know that two arbitrary \( V(\mathbf{r}) \) cannot lead to the same \( n(\mathbf{r}) \); therefore, each \( V(\mathbf{r}) \) has a unique density associated with it. From the solution of the Schrödinger equation we know that the corresponding wave functions, \( \psi_1(\mathbf{r}) \) and \( \psi_2(\mathbf{r}) \), are different due to the difference in \( V(\mathbf{r}) \).

Using the Rayleigh-Ritz variational principle, Hohenberg and Kohn proposed that the energies of the two states satisfy the relation:

\[ E_2 = \langle \psi_2 | \mathcal{H}_2 | \psi_2 \rangle < \langle \psi_1 | \mathcal{H}_2 | \psi_1 \rangle \]  

(2.3)

which can be reformulated in terms of \( \mathcal{H}_1 \) by considering the following change:

\[ \mathcal{H}_2 = \mathcal{H}_1 - V_1(\mathbf{r}) + V_2(\mathbf{r}) \]  

(2.4)

such that
2.1. DENSITY FUNCTIONAL THEORY

\[ E_2 < \langle \psi_1 | \mathcal{H}_1 - V_1(\mathbf{r}) + V_2(\mathbf{r}) | \psi_1 \rangle = E_1 + \langle \psi_1 | V_2(\mathbf{r}) - V_1(\mathbf{r}) | \psi_1 \rangle \]  

(2.5)

At this point it is useful to relate the charge density with the probability density \( \psi^* \psi \). We will posit the following relation:

\[ n(\mathbf{r}) = \sum_i n_i(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \]  

(2.6)

This relation allows us to rewrite Eq. 2.5 in terms of the density:

\[ E_2 < E_1 + \int (V_2(\mathbf{r}) - V_1(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \]  

(2.7)

If the converse situation is considered we find that:

\[ E_1 < E_2 - \int (V_2(\mathbf{r}) - V_1(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \]  

(2.8)

where the relation \( n_1(\mathbf{r}) = n_2(\mathbf{r}) = n(\mathbf{r}) \) was applied. Through the addition of Eqs. 2.7 and 2.8 a contradiction arises:

\[ E_1 + E_2 < E_2 + E_1 \]  

(2.9)

Therefore, the initial assumption is incorrect and it is true that each \( V(\mathbf{r}) \) has a uniquely defined \( n(\mathbf{r}) \). Now that we have shown that the potential due to the interactions with the ions in the system corresponds to a unique charge density we must formulate Eq. 2.2 in terms of this density.

Before this, however, it is useful to examine the Schrödinger equation resulting from Eq. 2.2 and digress into Hartree-Fock theory. Due to the interactions between
2.1. DENSITY FUNCTIONAL THEORY

each of the electrons in the Coulomb term the solution for the eigenstates is not straight forward and presents a considerable obstacle. Prior to the formulation of DFT the Hartree-Fock method was relied upon to generate solutions to a non-interacting version of the many-body Hamiltonian. The Hartree-Fock method used the Hartree approximation to define a self-consistent procedure where the ground state of a system was found iteratively.

The non-interacting wave function that the Hartree approximation leads to is a misnomer. In fact the electrons are interacting, it is only the dynamics of the system which is not captured in the calculation of the wave function for the single electron. The direct Coulomb interactions are replaced by a potential of the form shown in Eq. 2.10. This is equivalent to calculating the potential due to all of the other, \( j \), electrons in the system and calculating the wave function of the electron at \( i \). In reality the electrons of a system are all adjusting due to interactions with other electrons, but this method utilizes the non-interacting approach by fixing all electrons except for a single electron solution.

\[
V_i (r_i) = \sum_{j \neq i} \frac{e^2 |\psi_j (r_i)|^2}{r_i - r_j} \, dr_j \tag{2.10}
\]

Within the Hartree approximation the Schrödinger equation is resolved into a set of \( N \) single electron equations where \( N \) is the total number of electrons in the system. The total wave function is then found through the product state of all of the single electron wave functions. The self-consistent cycle to find the ground state solution is composed of the following steps:

1. Guess an initial wave function.
2.1. DENSITY FUNCTIONAL THEORY

2. Compute Hartree potential

3. Solve the set of single electron equations

4. Populate occupied orbitals according to Aufbau and Hund’s rules

5. Find the total wave function and calculate the energy.

6. Compare energies generated from initial guess and result. If energy difference is within tolerance then the ground state has been found. Otherwise, update the wave function and repeat the process.

In a sense, the requirement that the solution must be found self-consistently is a method of manually updating the non-interacting potential in place of the real, interacting picture.

An additional constraint is placed on the wave functions generated from this method by forcing all solutions to obey the Pauli exclusion principle. To reproduce the antisymmetric solutions Slater determinants are utilized where the elements are the single electron wave functions. As an example, a two electron system, such as H\textsubscript{2}, the well known solution is:

\[ \Psi (\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\psi_A (\mathbf{r}_1) \psi_B (\mathbf{r}_2) - \psi_B (\mathbf{r}_1) \psi_A (\mathbf{r}_2)) \quad (2.11) \]

which can be written as a Slater determinant:

\[ \Psi (\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_A (\mathbf{r}_1) & \psi_A (\mathbf{r}_2) \\ \psi_B (\mathbf{r}_1) & \psi_B (\mathbf{r}_2) \end{vmatrix} \quad (2.12) \]
2.1. **DENSITY FUNCTIONAL THEORY**

The Hartree-Fock method is still in use today by some chemists to understand the properties of molecules and smaller systems. Despite the power of such a method it still has severe draw backs when applied to metals and periodic systems. This failing is largely attributed to the absence of correlation effects in the Hartree Hamiltonian. DFT enters the picture again with its unique method of solving this shortcoming.

Following the groundbreaking work of Hohenberg and Kohn on the uniqueness of the charge density and form of the exchange-correlation functional, Kohn and Sham proposed the following equation (aptly named the Kohn-Sham equation) [23]:

\[
\begin{aligned}
\psi_i(r) & = E_i \psi_i(r) \\
\left[ -\frac{\hbar^2 \nabla^2}{2m} - eV_{\text{ext}}(r) + \int \frac{n_i(r')}{|r - r'|} dr' + V_{xc}[n_i](r) \right] \psi_i(r) & = E_i \psi_i(r)
\end{aligned}
\]

(2.13)

which is a single-particle equation similar to the Hartree equation with the added $V_{xc}[n](r)$ exchange-correlation potential term which is a functional of the electron density and encapsulates all effects which are not accounted for in the other terms. Note that in the Hartree-Fock formalism the exchange is treated explicitly while correlation effects are neglected. It should also be noted that the kinetic term is the non-interacting kinetic term where the unknown interacting term is moved to $V_{xc}$. In theory, this should produce an exact solution of the system given that the correct form of $V_{xc}$ is known. However, this is not the case in practice as the exchange-correlation is approximated.

As shown by Hohenberg and Kohn through a variational technique, the energy for a system represented by the Hamiltonian in Eq. 2.13 is given by the expression [22–24]:

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\[ E[n] = T[n] + \int V_{\text{ext}}(r) n(r) \, dr + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}') n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] \]  \tag{2.14}

where \([n]\) denotes a quantity which is a functional of the density function, \(V_{\text{ext}}\) is the system dependent potential due to the ionic positions, and \(E_{\text{xc}}\) is the exchange correlation energy functional which incorporates all of the information not contained in the non-interacting scheme. The \(E_{\text{xc}}\) is used to define \(V_{\text{xc}}\) from Eq. 2.13 as shown in Eq. 2.15

\[ V_{\text{xc}} = \frac{\delta E_{\text{xc}}[n](\mathbf{r})}{\delta n(\mathbf{r})} \]  \tag{2.15}

which states that \(V_{\text{xc}}\) can be determined if we know the form of the variation of \(E_{\text{xc}}\) with respect to the density. If \(E_{\text{xc}}\) were known, we could use Eqs. 2.14 and 2.13 to solve for the eigenstates and eigenvalues of any system exactly. However, as previously stated, this is not the case as models and approximations are used to define \(E_{\text{xc}}\).

Despite the limitation posed by a lack of knowledge of the form of \(E_{\text{xc}}\) Eqs. 2.14, 2.13, and 2.6 define a set of equations which can be solved self-consistently similarly to the Hartree-Fock method. The difference is that an extra step is added to calculate the density from eigenfunctions of the Kohn-Sham equations. By minimizing the energy of the system with respect to the density, a ground state density can be achieved within the limits of the chosen \(E_{\text{xc}}\) functional.
2.2 Spin Exchange

Spin exchange in a crystal is the virtual transfer of a spin unrestricted electron through a given mechanism between two sites. This exchange mechanism can take many forms ranging from the direct transfer of an electron to the propagation of spin through an intermediary. In 1D TMPcs, the exchange mechanism varies depending on the choice of TM. Since CuPc is examined in this work, the exchange mechanism and strength of the interaction can be calculated through examination of the electronic structure as well as comparisons to exchange models. The model used to understand the strength of the exchange interaction is the 1D nearest-neighbor Heisenberg model where interactions occur only between electrons on adjacent sites. This model is derived from the more general Hubbard model which describes the energy of an electron as being comprised of the kinetic energy and a repulsion term at each site. Finally, there will be a discussion of how to calculate the strength of interactions that will employ the Broken Symmetry method originally developed by Noodleman for use in transition metal dimers.

2.2.1 The Hubbard Model

Understanding the electronic and magnetic properties of crystals is a major goal of condensed matter physics. However, due to the complexity of most systems, approximations must be made in an effort to build a qualitative model which can be used to understand quantitative data. The band theory of solids was one of the most successful early models at understanding well known conductors and insulators based on the bond overlap between atoms. The bands used in this formalism represent the
available energies for a given momentum of the valence electrons. Metals were easily identified by the overlap of the bands formed between the valence and conduction bands while insulators possessed a large band gap representing a region of energy electrons could not occupy no matter their momentum.

For many materials band theory is sufficient, but it fails when describing more exotic effects such as Mott insulators. This class of insulator is typically comprised of a transition-metal oxide which band theory predicts incorrectly to be a metal. The effort to understand why band theory failed led to the Hubbard model which took into account the on-site coulomb repulsions felt by an electron [25–29]. By contrast, band theory only considers the kinetic energy of an electron. That is, band theory calculates the ability of an electron to hop between sites based only on its given energy at a certain momentum without consideration of the interaction with electrons on the site to which it is moving. The Hubbard model adds a cost of an electron to move to another site based on how many electrons are currently occupying the site. The Hamiltonian for the Hubbard model is shown in Eq. 2.17

\begin{equation}
H_{\text{Hub}} = -\sum_{\langle i,j \rangle,\sigma} t_{i,j} \left( c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma} \right) + U \sum_{i=1}^{N} n_{i,\uparrow} n_{i,\downarrow} \tag{2.16}
\end{equation}

For the purposes of this thesis, it is considered standard notation that \(\langle i, j \rangle\) represents the double sum over \(i\) and \(j\) where \(i \neq j\) and \(i\) and \(j\) are adjacent. In the left term \(i\) and \(j\) reference lattice site, \(\sigma\) is the spin operator, \(c_{i,\sigma}^\dagger\) and \(c_{j,\sigma}\) are the creation and annihilation operators at the given site with spin, and \(t_{i,j}\) gives the strength of interaction between the two sites. In the right term the sum is over all of the sites \(i\), \(n_{i,\uparrow}\) and \(n_{i,\downarrow}\) refer to the number operator at the site with given spin, and \(U\) is the strength of interaction on the site. The first term corresponds to the kinetic energy an
2.2. SPIN EXCHANGE

electron would have moving through a material whereas the second is the potential energy due to the electrons on a given site. The latter term is also known as the repulsive term due to it representing the energy cost of adding another electron to the orbital on the \( i^{th} \) site.

Without the repulsive term this model reduces to the Tight Binding model and represents the band theory of a solid. The kinetic part can be understood as the energy required to create a particle on site \( i \) and remove it from site \( j \) (plus the Hermitian conjugate). The repulsive term can be understood in terms of interacting d-orbitals between neighboring transition metals in a crystal. If the d-orbitals are completely occupied except for the highest associated energy state which is left with a single unpaired electron, any additional electrons added to the orbital would interact with the existing electrons through Coulomb repulsion. The more occupied the d-orbitals, the higher the energy cost of adding another electron. This effect leads to Mott insulators exhibiting a non-conducting behavior even though they have unfilled orbitals.

To illustrate the concept in light of the 1D TMPc case, consider the diagram shown in Fig. 2.1. This is a one dimensional crystal with lattice spacing \( a \) and site labels \( i \). Additionally, Fig. 2.2 shows how \( t \) and \( U \) are connected as explained above.

\[ \text{Figure 2.1: 1D Site Labels} \]
2.2. SPIN EXCHANGE

2.2.2 Heisenberg Model

In order to understand the spin exchange mechanism in 1D TMPcs the Hubbard model is applied within an approximation suitable to the band characteristics of these materials. Since the width of the valence bands is much smaller than the energy scale, taken as the band gap in this case, an approximation can be made such that \( t \ll U \). This stems from the width of the bands being tied to the kinetic interaction between overlapping orbitals. Therefore, we can apply second order perturbation theory to gain insight into this situation where the unperturbed Hamiltonian is the repulsive term subject to a kinetic perturbation.

Consider a situation similar to that shown in Fig. 2.1 except that each site is singly occupied. If the unperturbed, zero \( t \), case is considered the system can exist in a ferromagnetic (FM) state such as shown in Fig. 2.3. Here there are no allowed transitions from one site to the next due to the Pauli exclusion principle, and the electrons are stationary.

However, if we consider a state where the electrons are able to move, finite \( t \), we must set as the ground state a ferromagnetic system as shown in Fig. 2.4. This allows
2.2. SPIN EXCHANGE

electrons to move to nearest neighbor sites with a perturbation. These perturbed states leave some sites unoccupied and others doubly occupied as shown in Fig. 2.5.

![Figure 2.4: AFM State](image1)

So far, we have defined the Hamiltonian in perturbation theory as:

\[
H_{ub} = - \sum_{\langle i,j \rangle,\sigma} t_{i,j} (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma}) + U \sum_{i=1}^{N} n_{i,\uparrow} n_{i,\downarrow} = H_1 + H_0
\]  

(2.17)

where \( H_1 \) is the perturbation and \( H_0 \) is the unperturbed Hamiltonian. Considering only nearest neighbor interactions, the possible states are:

\[
|\uparrow, \uparrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\downarrow, \downarrow\rangle, |\uparrow, \downarrow, 0\rangle, |0, \uparrow, \downarrow\rangle
\]

where the top states exist in the unperturbed system and states listed on the bottom are due to perturbations. Since there are no interactions between states in the unperturbed system, each of these states are degenerate in energy. This implies that degenerate perturbation theory must be applied when determining the kinetic energy corrections. In the notation of Sakurai, the energy of a perturbed system is shown in Eq. 2.18 [30].
2.2. SPIN EXCHANGE

\[ E = E_D + \sum \left( E^{(0)} + \sum_{k \notin D} \frac{\left| \mathcal{H}_{1,kl}^{(0)} \right|^2}{E^{(0)}_D - E^{(0)}_k} \right) \]  \hfill (2.18)

where the subscript \( D \) denotes the unperturbed, degenerate subspace of systems, the superscript \( (0) \) labels the unperturbed quantities (from non-degenerate perturbations), and \( l \) & \( k \) are states. In this case, \( l \) refers to the degenerate ground states while \( k \) represents the perturbed states. The \( kl \) subscripts in the third term give the expectation value of the perturbed Hamiltonian with respect to \( k \) and \( l \), for example:

\[ \mathcal{H}_{1,kl}^{(0)} = \langle k | \mathcal{H}_1 | l^{(0)} \rangle \]

Also, note that the summation over \( l \) in the last term corresponds to:

\[ \sum_l \Rightarrow \sum_{i,j} \sum_{\sigma,\sigma'} \]

Considering Eq. 2.18, the \( E_D \) term can be set to zero because it is a constant which does not depend on the perturbation. The second term goes to zero because the \( \mathcal{H}_1 \) was constructed to only have off-diagonal terms, which leaves only the third term to represent the energy of the perturbed system. Through explicitly solving this term and using the definition of the spin operator in terms of creation and annihilation operators, the Heisenberg model is found where the interactions between nearest neighbors are only dependent on the relative spins. The Hamiltonian for this model is shown in Eq. 2.19.

\[ \mathcal{H}_{\text{Heisenberg}} = -\sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j \]  \hfill (2.19)
2.2. **SPIN EXCHANGE**

where $J_{ij}$ is the strength of interaction and the $\vec{S}$ operators refer to the spin at a specific site. With this sign convention, a positive value of $J$ would correspond to a FM ground state. Note that the interaction strength, $J$, is found to be:

$$J_{ij} = \frac{4t_{ij}^2}{U}$$

where the non-interacting model is recovered by applying the limit $U \rightarrow \infty$.

### 2.2.3 Broken Symmetry Method

**Dimer Model**

To determine the value of the exchange constant, $J$, a method developed by Noodleman and Ruiz will be followed where the difference in energies of two different spin states of the same system are used within the Broken Symmetry (BS) framework [31,32]. The BS method was developed for understanding the spin interaction between the transition metal centers of a molecular dimer system. For the purposes of deriving the expression proposed by Noodleman we will consider a generic dimer system with sites $A$ and $B$ as shown in Fig. 2.6. In this system the different spin states corresponding the the high symmetry wave functions and broken (lower) symmetry wave functions will be utilized to find the interactions between the two spin wave functions. Additionally, since the Heisenberg model concerns spin interactions, only the unpaired valence (HOMO) electrons are considered in the following equations where the interactions with core states are assumed to be negligible.

From quantum mechanics we know that the energies of a given system can be found through the expectation value of the Hamiltonian with respect to the system
2.2. SPIN EXCHANGE

![Figure 2.6: Symmetry States of Dimer](image)

wave function. Since we know the Hamiltonian from the Heisenberg model we must determine the wave functions which are eigenstates of the spin operators for the dimer model. For the symmetric case, Noodleman proposed that the wave function may be written as the Slater determinant of the spin wave functions associated with each site [31]:

\[ \Psi_S = \frac{|AB|}{\sqrt{2 - 2 \langle A | B \rangle^2}} \]  

(2.20)

where \(|AB|\) is short hand notation for the Slater determinant of the wave functions associated with \(A \& B\) and \(\langle A | B \rangle\) is the overlap between the two states. We can see that in the limit that the overlap goes to zero Eq. 2.20 reduces to the expected Slater wave function with normalization constant \(1/\sqrt{2}\). To describe the BS states there are two possible wave functions due to interchanging the spin:

\[ \psi_{BS}^1 = \frac{|\bar{A}B|}{\sqrt{2}} \quad \text{or} \quad \psi_{BS}^2 = \frac{|A\bar{B}|}{\sqrt{2}} \]  

(2.21)

However, these states alone are not eigenstates of the spin operators. To determine the eigenstates we use the superposition of the two components from Eq. 2.21 which yields the \(S = 0\) state, analogous to Eq. 2.20:
2.2. \textit{SPIN EXCHANGE}

\[
\Psi_{BS} = \frac{\psi_{1,BS} - \psi_{2,BS}}{\sqrt{2 - 2 \langle \psi_{1,BS} | \psi_{2,BS} \rangle}} \tag{2.22}
\]

By finding the expectation value with respect to each of these states and taking the difference, the exchange constant is found to be:

\[
J_{1,2} = \frac{2 (E_{BS} - E_{S})}{1 - \langle \psi_{1,BS} | \psi_{2,BS} \rangle} \tag{2.23}
\]

where \( E \) corresponds to the energy of each state. For a general expression of dimer systems with \( S \geq 1 \), \( J \) can be found in terms of the \( S \) of the HS state:

\[
J_{1,2} = \frac{2 (E_{BS} - E_{S})}{S^2} \tag{2.24}
\]

Before using Eq. 2.24 to start calculating the values of \( J \), consideration must be given to how the energies of these states are calculated. Due to the nature of how the orbitals were defined there should be an inclination towards using the Hartee-Fock method of calculating the energies which utilizes Slater determinants. However, since DFT is being employed in this research a relation between the Hartree-Fock and DFT calculated \( J \) must be found. The main concern is how the BS state is calculated within DFT. Rather than provide a superposition solution as in Eq. 2.22 only the single BS wave function from Eq. 2.21 is calculated. This problem was explored culminating in Eq. 2.25 for the \( H_2 \) system \((S = 1)\) calculated with DFT [33]. Ultimately, the results showed that despite being an approximation to \( \Psi_{BS} \) the individual state \( \psi_{BS} \) contained all of the electron correlation effects which need to be present given that the exchange-correlation functional adequately describes the system.
2.2. SPIN EXCHANGE

\[ J_{1,2} = E_{BS} - E_S \]  \hspace{1cm} (2.25)

Polynuclear Model

Applying Noodleman’s dimer model to the case of dilute CuPc requires the extension of the interactions to include effects for a polynuclear system. Ruiz et al. proposed a method of examining the exchange constant for multiple geometries with \( H \) at each site by approximating the polynuclear system as a series of dimers [32]. In essence, the interactions between each pair in the new model lead to different values of \( J \). However, an ambiguity arises when attempting to describe the BS system. Previously, the BS state corresponded to AFM state where the spins were anti-aligned, but a polynuclear system has numerous different combinations of possible spins. To resolve this issue each of the possible BS states are redefined as a low symmetry (LS) state with an index to count the number of non-symmetry related states are possible. Once all possible LS states are resolved, the \( J_{i,j} \) can be found by comparing the pairs of the HS state to each of the JS states.

For example, consider the case of 100% CuPc. There are four CuPc subunits in the supercell each with a single unpaired electron in the d-orbital of the Cu atoms. In the 1D approximation, this reduces to 4 singly occupied sites interacting along a chain. Figure 2.7 shows the four non-symmetry related states of the system. It is important to note that these calculated must be carried out in a finite system to adequately account for the finiteness of the original dimer system.

where HS denotes the high symmetry state and LS is used to label the different low symmetry states. For the purposes of understanding the exchange constants,
2.3. **HUBBARD CORRECTED DFT**

\[
\begin{array}{c|c|c|c|c|c}
|\uparrow\uparrow\uparrow\uparrow\rangle & |\uparrow\uparrow\uparrow\downarrow\rangle & |\uparrow\uparrow\downarrow\uparrow\rangle & |\uparrow\uparrow\downarrow\downarrow\rangle & |\uparrow\downarrow\uparrow\downarrow\rangle \\
HS & LS1 & LS2 & LS3 & LS4
\end{array}
\]

*Figure 2.7: Polynuclear CuPc Spin States*

the sites in each systems are labeled sequentially such that $J_{12}$ corresponds to the coupling between the first and second spin. By noting that interactions can only take place between sites with opposite spins, we find the following set of equations relating $J_{i,j}$ with the energies:

\[
\begin{align*}
E_{LS1} - E_{HS} &= J_{14} + J_{24} + J_{34} \\
E_{LS2} - E_{HS} &= J_{13} + J_{23} + J_{43} \\
E_{LS3} - E_{HS} &= J_{13} + J_{14} + J_{23} + J_{24} \\
E_{LS4} - E_{HS} &= J_{12} + J_{14} + J_{23} + J_{34}
\end{align*}
\]

(2.26)

This procedure was carried out on a number of the dilute systems being studied to examine the effects of long-range interaction as well as difference in the interaction due to the type of adjacent molecules. An extensive list of the exchange relations can be found in Appendix A.

### 2.3 Hubbard Corrected DFT

While DFT is, in theory, an exact method it relies on approximations which may emphasize one aspect of the energy calculation over another. In the case of strongly correlated systems we find that DFT regularly fails to reproduce some aspects of the electronic structure. As previously explained, DFT will typically miscalculate the band gap of Mott insulators to the extent that it predicts them to be metallic.
2.3. **HUBBARD CORRECTED DFT**

The Hubbard model, discussed in the previous section, gives insight into the failing of DFT. Even though the exchange-correlation energy functional should contain all effects not accounted for in the single particle terms, the results from Mott insulators hint to the fact that standard DFT functionals overemphasize the kinetic exchange term while suppressing on-site repulsion [34]. Therefore, the Hubbard U must be explicitly incorporated into the energy functional.

Before proceeding to understand the form of the functional it is useful to consider the meaning of the Hubbard U in the context of DFT. Strongly correlated systems typically involve the transition metal elements where the value of U corresponds to the Coulomb repulsion felt by an electron added to the partially occupied d-orbital due to the occupied states. While the interactions between core s- and p-states play a role in the value of U, we will consider these interactions as being implicitly included such that only Coulomb interactions within the d-orbitals are considered. This is known as screening the value of the Hubbard U.

Additionally, even though planewave solutions to the Kohn-Sham eigenfunctions were used in calculations, all conversation with respect to the U value is based on the atomic orbital eigenstates. Therefore, the calculated solutions are projected onto the atomic orbital basis which allows for a more fruitful discussion of orbital occupancy. In terms of the occupancy, the value of U can be understood as [34]:

\[
U = E\left(d^{n+1}\right) + E\left(d^{n-1}\right) - 2E\left(d^n\right)
\]  

(2.27)

where the last term corresponds to the energy of the initial state with \( n \) electrons on identical orbitals \( d \) and the first two terms are the energy due to adding and removing an electron from two different sites. This gives the cost of an electron moving to an
2.3. HUBBARD CORRECTED DFT

occupied site.

Considering the previous discussion of the ability of DFT to calculate on-site repulsion and the projection onto atomic orbitals, we can write a new model for the exchange-correlation energy functional [35],

\[
E_{DFT+U} \left[ n(\mathbf{r}) \right] = E_{DFT} \left[ n(\mathbf{r}) \right] + E_{Hub} \left[ n_{I\sigma}^{l} \right] - E_{dc} \left[ n_{I\sigma}^{l} \right] 
\]  \hspace{1cm} (2.28)

where the first term on the left is the standard DFT energy functional, \( n_{I\sigma}^{l} \) is the density matrix for orbital state \( \langle m \mid m \rangle \) at site \( I \) with spin \( \sigma \), and the function of the last term is given as,

\[
n_{I\sigma}^{l} = \sum_{m} n_{m}^{l\sigma}
\]  \hspace{1cm} (2.29)

Eq. 2.28 states that the standard energy functional is augmented by an explicit Hubbard term minus a double counting term necessary to remove the portion of \( E_{DFT} \) which already accounts for on-site repulsion. Since the density matrices represent the projected occupation onto the states \( m \) we see that the energy now depends on the cost of adding (or subtracting) an electron from an orbital state.

To determine the form of \( E_{Hub} \) and \( E_{dc} \) it is typically assumed that for the orbitals in question the contribution of the kinetic exchange term from the Hubbard model is negligible compared to the value of U. This represents the case for systems where the band width is much smaller than the on-site repulsion. Using the method of Cococcioni et al. we find that [35]:

2.3. HUBBARD CORRECTED DFT

\[ E_U \left[ n^{I\sigma}_{mm'} \right] = E_{Hub} \left[ \{ n^{I\sigma}_{mm'} \} \right] - E_{dc} \left[ \{ n^{I} \} \right] \]

\[ = \frac{U}{2} \sum_I \sum_{m,\sigma}^{n^{I\sigma}_{mm}} - \sum_{m,m',\sigma}^{n^{I\sigma}_{mm},n^{I\sigma}_{m'm}} \]

\[ = \frac{U}{2} \sum_{I,\sigma}^{n^{I\sigma}} \text{Tr} \left[ n^{I\sigma} \left( 1 - n^{I\sigma} \right) \right] \quad (2.30) \]

where \( n^{I\sigma} \) represents the tensor composed of the density matrices and Tr is the trace of the resulting expression. Therefore, the calculation of the Hubbard U and the sum are the necessary variables to capture the physics introduced by on-site repulsion.

Based on this model for the exchange-correlation energy there are two ways which we can calculate U. Since the density matrices can be calculated from projection into the appropriate basis, we can use experimental quantities such as the bandgap to fit the value. Or, it can be determined self-consistently by observing the response of the energy to artificially changing the occupations. The latter method is chosen in this thesis to preserve the self-consistent nature of the results.

Within the semi-local density approximations to DFT the energy of a system scales quadratically with the occupation of the orbital states \([35]\). Using this knowledge we can understand the Hubbard U in terms of how the energy changes with occupation, \( n_I \), as:

\[ U = \frac{\partial^2 E [n_I]}{\partial n_I^2} \quad (2.31) \]

that is, U can be determined from the concavity of the quadratic \( E \) vs \( n_I \) relation. However, this does not give the full picture as calculated by DFT.

During a DFT calculation a starting wavefunction is changed such that the energy
2.3. HUBBARD CORRECTED DFT

is minimized as discussed previously. Throughout this process the orbitals are allowed to interact and hybridize - this process is known as charge screening. The first cycle of the SCF loop is special in that it returns a wavefunction which has not gone through the screening process - returning the unscreened wave function. These two processes come into play when calculating U because the unscreened wave function adds an unphysical contribution to the energy which must be subtracted out. Therefore U may be found from the following expression:

\[
U = \frac{\partial^2 E[n_I]}{\partial n_I^2} - \frac{\partial^2 E^K_S[n^K_S]}{\partial n_I^2} - \frac{\partial^2 E^K_S[n_J^K_S]}{\partial n_J^2}
\]

(2.32)

where \( K_S \) refers to the screened (non-interacting) Kohn-Sham solution.

Through invoking the Janak theorem to recast these two terms as first derivatives of eigenvalues, \( \alpha \), Cococcioni proposes the following relation [35]:

\[
U = \frac{\partial \alpha^K_S}{\partial n^K_S} - \frac{\partial \alpha_I}{\partial n_I} = \chi^{-1} - \chi^{-1}
\]

(2.33)

where the subscripts \( I \) and \( J \) represent two atomic sites where the U value is being calculated. The \( \chi \) matrices are found by calculating the change in occupation of the orbital state on site \( I \) when an arbitrary potential has been applied to the site \( J \). Once both \( \chi \) have been calculated, the U values may be determined through the diagonal elements of the resulting matrix.

This method of calculation is used in this thesis for the variety of different systems necessary to calculate \( J \) values. Since the value of U is linked to the crystal environment in which the orbital resides it is appropriate to determine a value of U in each system differentiated both by dilution and spin. Therefore, the U for each
2.3. HUBBARD CORRECTED DFT

Cu atom must be calculated while taking into account symmetry considerations to reduce the amount of calculations.

As previously discussed, Hubbard U values are found through the calculation of the $\chi^{\prime}$ matrices. Each element is found through the linear proportionality factor relating $\alpha$ to $n$. Since most of the systems contain more than one site where we wish to calculate U, the interactions between the sites must be calculated through Eq. 2.33. The $KS$ term corresponds to finding the occupations after the first SCF cycle where the orbitals have not yet been allowed to hybridize. The off-site interactions are given by the terms where $I \neq J$. These relations are shown in Fig. 2.8 where the plot on the left corresponds to the case where $I = J$ while the plot on the right is $I \neq J$.

![Graph](image)

(a) On-Site Repulsion  
(b) Off-Site Repulsion

Figure 2.8: Repulsion due to $\alpha$

For the ferromagnetic CuPc system, the calculated U matrix is shown in Eq. 2.34 where the diagonal terms correspond to the U values on each site. Important to note is that the off-diagonal terms are much smaller than the diagonal values. For the case
2.3. *HUBBARD CORRECTED DFT*

of weakly interacting systems such as CuPc the magnitudes of the off-diagonal are a good indication of the uncertainty of the value. In this case symmetry causes all of the diagonal terms to be equal. The matrices were generated for each system used to calculate the Heisenberg $J$ values and can be found in Appendix B.

\[
\begin{bmatrix}
6.17 & 0.01 & 0.00 & 0.01 \\
0.01 & 6.17 & 0.01 & 0.00 \\
0.00 & 0.01 & 6.17 & 0.01 \\
0.01 & 0.00 & 0.01 & 6.17
\end{bmatrix}
\] (2.34)
Chapter 3

Results & Discussion

3.1 Structure

As mentioned previously, CuPc crystallizes into three major phases. The most stable of the three is $\beta$-CuPc which is characterized by a slipping and sliding angle of about $45^\circ$. Since the phthalocyanines studied here will be approximated as 1D chains the angles of the $\beta$-phase will be used for simulating only a single chain.

First, the structure of the the single molecules will be examined to ensure that the choice of functional and pseudopotentials yields accurate results for the molecular case. Once the molecules are optimized they will be placed into the 1D chains with fixed molecular structure. The atoms are fixed within a molecule because adjacent molecules are known to have little effect on the atomic spacing.

Several dilute systems will be studied where the ratio of CuPc to H$_2$Pc are 100%, 75%, 50%, 25%, and 0%. The structure of the pure cases have the same angles but slightly different values of the inter-planar spacing between molecules. Due to the organic, planar structure of the phthalocyanines the main mode of interaction
3.1. **STRUCTURE**

between molecules is van der Waals dispersion. Since this is a non-local interaction which DFT fails to accurately reproduce, Grimme’s dispersion correction is used to semi-empirically increase the attraction between molecules [20].

3.1.1 **MOLECULE**

To optimize the molecules atomic positions were first optimized by molecular dynamics where $D_{4h}$ symmetry was observed. These atomic positions were then used as the basis of a starting geometry for the DFT optimization procedure. Structural optimization was carried out using the BFGS optimization algorithm with convergence criteria on the force set to $10^{-3}$ a.u and energy at $10^{-4}$ Ry. Fig. 3.1 shows the results in units of Ångströms.

![Optimized Molecular CuPc Geometry](image)

*Figure 3.1: Optimized Molecular CuPc Geometry*

The numbers in parenthesis are experimental results according to Brown [12] while the top numbers represent the results of the optimization. Such good agreement between theoretical and experimental results suggests that, at least in terms of geometry, the GGA functional with PAW pseudopotentials represent a decent approximation to
3.1. STRUCTURE

the bonding characteristics within a molecule. It should be noted that D$_{4h}$ symmetry was lost in the optimization as there was a slight anisotropy of bond lengths along a direction passing through the center of the molecule. That is, the molecule was stretch along one direction and perpendicularly compressed.

Due to the similarity between H$_2$Pc and CuPc in terms of structure, the metal-free Pc was found by substituting the central Cu atom by two H atoms placed 1.02108 Å away from two opposite N atoms on the central ring.

3.1.2 CRYSTAL

Optimization of the planar distance between Pc molecules was carried out through Brent optimization where the planar distance was used as the minimization variable. This method was chosen over BFGS as the specialized nature to 1D cases reduced the number of optimization steps necessary to reach an energy minimum.

As stated, inter-molecular bonding in phthalocyanines is dominated by van der Waals forces which present an obstacle for DFT calculations. In order to produce a more accurate representation of the bonding characteristics the Grimme dispersion correction was applied to all calculations. The effect of such an addition greatly reduced the inter-planar distance to the point of overbinding.

Since several systems were necessary to understand exchange coupling constants, structure optimization was applied to several spin configurations at each dilution. Listed in Table 3.1 are the results from structure optimization with dispersion corrections applied. The structure on the right represent the periodic system being optimized where arrows denote spin on Cu atoms and 0 represent H$_2$Pc molecules.

Including the Hubbard U in structure optimizations did not affect the optimized
3.1. STRUCTURE

Table 3.1: Structure Optimization Results

<table>
<thead>
<tr>
<th>Structure</th>
<th>Planar Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑↑↑↑</td>
<td>3.24338</td>
</tr>
<tr>
<td>↑↑↑↑↓</td>
<td>3.24368</td>
</tr>
<tr>
<td>↑↑↑↑0</td>
<td>3.24762</td>
</tr>
<tr>
<td>↑↑↑↑↑0</td>
<td>3.24726</td>
</tr>
<tr>
<td>↑↑↓0</td>
<td>3.24726</td>
</tr>
<tr>
<td>↑↑00</td>
<td>3.25225</td>
</tr>
<tr>
<td>↑↓00</td>
<td>3.25325</td>
</tr>
<tr>
<td>↑0↑0</td>
<td>3.25134</td>
</tr>
<tr>
<td>↑0↓0</td>
<td>3.25325</td>
</tr>
<tr>
<td>↑000</td>
<td>3.26055</td>
</tr>
<tr>
<td>0000</td>
<td>3.26055</td>
</tr>
</tbody>
</table>

distance, but the energies were shifted as shown in Fig. 3.2. Since only the minimum of the energy is required, all structure calculations were performed without the Hubbard U to reduce the cost of calculation.

Optimization of the structure without dispersion corrections yields a far larger planar distance than is observed. Structure optimization was carried out on the FM CuPc system with and without the dispersion corrections to illustrate the difference. Fig. 3.3 shows the results of this trial where there is clearly a difference in the optimal planar distance.

Two features of the effect of the dispersion corrections on structural optimization are useful to understand. First, the energies at different planar distances with no dispersion corrections form a shallower curve than the dispersion corrected counterpart. This indicates that in order to adequately account for interactions between molecules dispersion corrections are necessary. Second, the optimal planar distance for the dispersion correction is considerably smaller, 3.2Å, compared to the non-corrected value, 4.1Å. Spin interaction and electronic structure are closely connected to the overlap...
of the $\pi$-orbitals of adjacent molecules. Closing the distance between them allows for more apparent electronic characteristics which might otherwise be negligible when the distance is too large.

3.2 SPIN EXCHANGE

Understanding the spin exchange within dilute CuPc presents difficulties both in technical aspects as well as in attributing a physical meaning to the calculated value. From a technical standpoint the values of $J$ are typically measured in Kelvin rather than eV which is the scale of DFT. This presents a problem due to the fact that slight changes in numerics or the description of the system have a large impact on $J$. As explained in Chapter 2, exchange coupling constants are determined through a series
3.2. SPIN EXCHANGE

![Graph showing the effect of dispersion corrections on structure](image)

*Figure 3.3: Effect of Dispersion Corrections on Structure*

of energy calculations on different spin configurations for a given dilution. However, the model presented is only constructed to deal with finite systems such as dimers or polynuclear molecules. Therefore, values derived for J are those within the finite case only. These may be used as a benchmark in the periodic system, but interpretation of the values should be carried out with care.

Since calculation of the exchange constants relies on an accurate representation of the energy of a system the Hubbard U was calculated for each system used determine J. Sensitivity of J to energy variations between systems presents a problem because different values of U can cause relatively large energy differences. This was accounted for by using the average value of U throughout a dilution rather than employing the self-contently calculated U values. The average value of U can be justified through the assumption that in the neighborhood of any given CuPc molecule the adjacent
molecules are randomly chosen.

### 3.2.1 Hubbard U

The calculated values of the Hubbard U are shown in Table 3.2. For the 50% dilution cases there were two systems studied where (1) corresponds to $|↑↑00\rangle$ and (2) denotes $|↑00↑\rangle$. While the value of U calculated for the dimer case has been previously reported to be about 5 eV [17], variations in the values are dependent on the choice of functional and basis. Therefore, values of about 6 eV are reasonable compared to previous results. For a full list of calculated U matrices see Appendix B.

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Average Hubbard U (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>6.16</td>
</tr>
<tr>
<td>3 CuPc, 1H$_2$Pc</td>
<td>6.13</td>
</tr>
<tr>
<td>(1) 2 CuPc, 2H$_2$Pc</td>
<td>6.11</td>
</tr>
<tr>
<td>(2) 2 CuPc, 2H$_2$Pc</td>
<td>6.13</td>
</tr>
<tr>
<td>1 CuPc, 3H$_2$Pc</td>
<td>6.13</td>
</tr>
</tbody>
</table>

### 3.2.2 Exchange Constants

Exchange constants calculated for finite systems within the polynuclear method are shown in Table 3.3 where the value in parenthesis correspond to the same systems used in Table 3.2. These values indicate two properties about the interactions between spin centers in β-CuPc. First, the magnitude of interactions is evident of a paramagnetic system. With such small coupling between spin centers, the temperature of a sample must be quite low to observe any magnetic ordering. Second, the signs of
3.2. SPIN EXCHANGE

The exchange constants lead to an anti-ferromagnetic ground state which agrees with previous calculations on CuPc [17].

<table>
<thead>
<tr>
<th>Table 3.3: Exchange Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>CuPc</td>
</tr>
<tr>
<td>3 CuPc, 1H$_2$Pc</td>
</tr>
<tr>
<td>2 CuPc, 2H$_2$Pc</td>
</tr>
<tr>
<td>1 CuPc, 3H$_2$Pc</td>
</tr>
</tbody>
</table>

The effect of diluting CuPc with H$_2$Pc has the effect of quenching the exchange interactions between CuPc molecules. The metal-free molecules placed between CuPc have the effect of increasing the range at which the spin centers interact which leads to lower interaction strengths. An interesting result of this is the preservation of the anti-ferromagnetic state which is seen in the $J_{14}$ interaction of the 50% dilute sample.

While these values were calculated for a finite system, this result corresponds to two CuPc molecules clustered together in a periodic system. That is, with periodicity taken into account, two adjacent CuPc molecules would remain anti-ferromagnetic.

A note on the error of the exchange constants is useful to understanding the accuracy of these results. The energy ranges of these values falls barely within the accuracy of DFT methods. Values such as $J_{15}$ reported for the 25% dilute case are at the limit of resolution and should be interpreted as indicating a paramagnetic state. Compared to experimental results, SQUID measurements have shown that the magnetic state of CuPc should be weakly ferromagnetic ($J \approx 0.15K$) [36,37], but experimental uncertainty means that the difference between a paramagnetic and ferromagnetic state at such a low energy scale is not discernible.
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3.3 Electronic Structure

Perhaps most important to understanding dilute systems is to investigate how the electronic structure changes based on dilution. Ultraviolet photoelectron spectroscopy (UPS) measurements are simulated for the CuPc and H$_2$Pc molecules to gain an understanding of the orbital alignment in each near the HOMO-LUMO gap. Then, the effect of the Hubbard U on the states is shown through the UPS of CuPc for a range U values. This is done to illustrate the importance of the parameter for open-shell phthalocyanine systems.

Following UPS measurements, the density of states (DOS) is calculated for a number of systems so that changes in the valence states and d-orbitals can be observed. First, benchmark DOS calculations are shown for the CuPc and H$_2$Pc 1D crystals followed by the DOS for dilute systems. Examining the DOS is important because it builds a connection between the interactions of the d-orbitals with the Pc ligand and the changes introduced through dilution.

Ultraviolet Photoelectron Spectroscopy Measurements

UPS is a technique which measures the energy of electrons excited from the valence bands of a material. Computationally, the spectra are determined through a Gaussian fit of the Kohn-Sham eigenvalues generated by a Gamma-point calculation. In the following figures, Gaussian broadening of 0.7 eV is used to build the spectra where the intensities are indicative of the number of states contributing to any one Gaussian feature.

Measurement of the highest occupied states is of interest because these states
3.3. **ELECTRONIC STRUCTURE**

provide the interesting optical and magnetic properties of phthalocyanines. If these states can be changed through dilution there exists the possibility to engineer the orbital alignment by choosing the dopant molecule and fixing the dilution. The orbital alignment of pure CuPc is best understood through the UPS shown in Fig. 3.4 where the Hubbard U of 6.17 eV is used from the self-consistent procedure.

![CuPc UPS; U=6.16eV](image)

*Figure 3.4: UPS of CuPc with self-consistent Hubbard U*

The highest two occupied states in CuPc are the half-filled $b_{1g}$ and $a_{1u}$ orbitals. These are represented as the two peaks left of the Fermi energy where the lower energy state clearly has a larger spin component that the HOMO state. The large difference in spin indicates that the lower state is only partially occupied which leads to its identification as the $b_{1g}$ state. The HOMO state has an equal portion of both spin such that it is identified as the fully occupied $a_{1u}$ state. The identification of these states through UPS calculations presents an improvement over previous PBE-GGA
3.3. ELECTRONIC STRUCTURE

calculations such that by simply resolving the difference comparisons can be made to more accurate functional methods [16].

Despite the ability to resolve the highest occupied states, GGA+U still fails to reproduce the correct ordering of the unoccupied states. In the molecular form of CuPc the lowest two unoccupied states should be a doublet $e_g$ followed by the the spin singlet $b_{1g}$. This indicates that upon the addition of an extra electron the $b_{1g}$ will remain singly occupied while the electron will move into a doubly degenerate state. From the two states to the right of the Fermi energy in Fig. 3.4 it is evident that the ordering is reversed. Rather than a doubly degenerate LUMO state, the $b_{1g}$ state takes the lowest energy indicating that with the addition of an extra electron the $b_{1g}$ state will be fully occupied. To better reproduce the ordering of LUMO states hybrid functionals must be used [16].

The splitting in the two HOMO states can be understood in terms of the Hubbard U. The Hubbard correction effectively adds an energy cost to occupying d-orbital states. Since the HOMO $a_{1g}$ state is composed of the nitrogen states interacting with the planar d-orbitals the interaction cost becomes higher for larger U. At zero U, there is no interaction cost and the $b_{1g}$ and $a_{1u}$ states become degenerate, but as U is increased they begin to separate. The splitting of these states is shown in Fig. 3.5 where the UPS of CuPc has been calculated for various values of the Hubbard U.

In Fig. 3.5 the energy level splitting develops as the value of U is increased from 0 to 7 eV. For lower values of U the shift in the peaks is hardly discernible, but around 3 or 4 eV the separation is clear. Despite increasing the Hubbard U correction, the orbital ordering of the LUMO states does not seem to be affected. This indicates that either a higher level of theory or different functional must be used to account for
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Figure 3.5: UPS of CuPc for Range of Hubbard U

other effects leading to a different ordering.

In both Figs. 3.4 and 3.5 there is considerable spin polarization shown for lower energy molecular orbitals. For the most part these are governed by the states of the constituent atoms of the phthalocyanine rings which indicates that the spin from
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the Cu d-orbital has a large effect on polarizing the molecular states. In terms of spin exchange, this shows that an indirect mechanism may be the dominant form of exchange in line with previous results [17].

The UPS of H$_2$Pc is shown in Fig. 3.6. The HOMO state is a fully-occupied $a_u$ orbital with two singlet $b_{1g}$ and $b_{2g}$ states at the LUMO. Here the LUMO states are close enough in energy to be indistinguishable. This UPS is presented as a benchmark where the majority of molecular orbitals are due to the phthalocyanine ligand. These can be compared to the CuPc states which is similar but distinguished by the effect of spin polarization among the core states.

![Figure 3.6: UPS of H$_2$Pc](image)

Lastly, the HOMO-LUMO gaps as calculated through PBE-GGA+U must be discussed. The gaps indicated in the previous figures are in the range of about 1 eV. This is slightly smaller than experimental results [38] and much smaller than
3.3. **ELECTRONIC STRUCTURE**

Theoretical results carried out with hybrid functionals [17]. GGA is known to produce smaller gaps, so the values were expected, but the Hubbard U typically increases that gap values as well. The effect of the Hubbard U on the gap is clearly not observed here which could indicate an inability to calculate the unoccupied states. This is further supported by the fact that orbital ordering for the LUMO states is not changed either. Efforts to understand the size of the gap would be best if carried out with hybrid functionals which explicitly incorporate Hartree-Fock exchange.

**Density of States**

Similar to UPS, the DOS can be used to gain an understanding of the orbital structure within a material. In this case the DOS of pure CuPc, H\(_2\)Pc, and various dilute samples will be shown. Partial density of states (PDOS) allows the DOS to be decomposed into the various composite orbitals. This will be utilized to show the contribution from d-orbitals to the overall DOS character.

The DOS for pure, ferromagnetic CuPc is shown in Fig. 3.7 on the left where negative values correspond to the spin down component on the states. As a comparison to the ligand states, the figure on the right shows the DOS of H\(_2\)Pc. The occupation of the states is determined by matching the number of spin up and down states at a given energy. Similar to UPS, the two highest occupied states of CuPc are characterized by a singly-occupied state followed by a doubly-occupied HOMO where the splitting between them is about 0.4 eV.

By projecting the total DOS onto only the d-orbital states contributed from the Cu atom, the local density of states (LDOS) can be attained which is shown for FM CuPc in Fig. 3.8. Due to the highly molecular nature of the states shown in the DOS,
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The peaks near the HOMO level can be compared directly with UPS data. In this case we see that the partially occupied \( b_{1g} \) state is composed of the single electron d-orbital while the HOMO peak must be entirely formed from ligand states. This agrees with previous calculations where the highest occupied d-state lies below the fully occupied ligand states.

The figure on the left of Fig. 3.9 shows the partial density of states (PDOS) of the in-plane \( d_{xy} \) orbital. The highest occupied peaks indicate that the \( b_{1g} \) orbital contributions come from the interaction of in-plane orbitals with the ligand. As a comparison, the out-of-plane \( d_{z^2} \) orbital is shown on the right which clearly only contributes to the core states in the DOS. Therefore, the HOMO-LUMO states are largely governed by the orbitals within the molecule rather than through interactions with adjacent molecules.

To understand how these states change based on dilution Fig. 3.10 shows the \( d_{xy} \) orbitals for the \( |\uparrow\uparrow\uparrow\uparrow\rangle \), \(|\uparrow\uparrow00\rangle\), and \(|\uparrow0\uparrow0\rangle\) systems, respectively. Since the out-of-plane interactions are important to understanding the interactions between
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Figure 3.8: CuPc d-Orbital LDOS

Figure 3.9: d-Orbital Contribution to Ferromagnetic CuPc

molecules, changes in the d_{xy} state indicate such interactions. Since the environment is changing in each of the cases, we see that the lack of a d-orbital to interact with from adjacent molecules does have an effect on the out-of-plane states available to
3.3. ELECTRONIC STRUCTURE

occupy. In particular, the available states are at the maximum when there is a single CuPc adjacent and a minimum when both of the adjacent molecules are CuPc.

![Figure 3.10: CuPc $d_{zy}$ Dilute Range PDOS](image)

The changes in the $d_{zy}$ orbital have a direct influence on the features present in the DOS. Presented in Figs. 3.11 and 3.12 are the DOS for the latter two systems shown in Fig. 3.10. It is obvious that the HOMO state undergoes a change as a function of the environment where there single HOMO state in pure CuPc has split into two states when there are H$_2$Pc molecules on both sides of a CuPc. Since interactions between molecules occur out-of-plane, the corresponding $d_{zy}$ orbitals seem fit to describe this change. While the d-orbitals of adjacent phthalocyanines may not directly overlap due to the geometry of the $\beta$-phase, there is still interaction observed between the phthalocyanine molecular orbitals. Similar results are found for the AFM systems which can be found in Appendix C.
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Figure 3.11: CuPc $|\uparrow\uparrow 00\rangle$ DOS

Figure 3.12: CuPc $|\uparrow 0 \uparrow 0\rangle$ DOS
Chapter 4

Conclusion

Understanding the physics of dilute samples of CuPc presents an opportunity to gain insight into such areas as organometallic interactions, orbital alignment engineering, and one dimensional long range order to name a few. With the application of the Hubbard model in one dimension, the structural, electronic, and magnetic properties were examined through density functional theory. Since both CuPc and H₂Pc are well studied in both the molecular and crystalline form, dilute samples of these two molecules represents a basis for understanding the interactions introduced by the transition metal centers and exchange interactions.

At the level of PBE-GGA+U it was found that the structural properties are heavily influenced by non-local dispersion forces as one would expect. From structure optimizations along the stacking axis it was found that the introduction of Grimme’s dispersion correction created a situation where over-binding was present in contrast to calculations performed in its absence which yielded under-binding. While experimental parameters are typically used to fix the planar distances between molecules the element of self-consistency is lost by doing so. Therefore, structural optimiza-
tion with the dispersion correction is necessary to adhere to self-consistent principles. Since the dispersion correction was designed for use in organic molecular crystals, it can be assumed that the introduction of a transition metal center leads to the over-binding. Further work may be done optimizing the correction for organometallic crystal not just in terms of the structure, but also in its ability to predict electronic structure as well.

Following the structural optimization the Hubbard U was calculated for a range of possible structure necessary to calculate the exchange constants from the Heisenberg model. Calculating the value of U can proceed in two directions: First, the U can be calculated by fitting to experimental results such as the magnitude of the band gap. Or, U can be calculated self consistently by observing the energy cost to occupation of the d-orbitals when an arbitrary potential cost is applied. The latter method was adopted to more accurately describe the U in terms of the chosen functional and pseudopotentials. While a value of U could be taken from literature, there is currently no direct method of using results calculated from a different set of functionals and basis. The Hubbard U was found to be about 6.1-6.17 eV over the range of systems which is not different from 4 eV which is reported in literature. Additionally, the influence of U corrections to the ligand states was neglected so that the calculated U could be understood from the value found rather than through an interaction between two competing values.

Calculation of the exchanges constants followed by implementing the polynuclear broken symmetry (BS) method. While the original BS method was developed only for dimer cases, the polynuclear method extends this by considering the energy differences between spin states to be a superposition of all dimer interactions. Spin configurations
were found for samples of various dilutions where only symmetry unrelated systems were used to calculate the set of equations necessary to finding the exchange constants. The values found indicated that CuPc systems of all dilutions were paramagnetic or weakly anti ferromagnetic. Nearest neighbor (nn) interactions were the largest in magnitude and next-nearest neighbor (nnn) interactions were quickly quenched. While the values are on the order of the error in energy as calculated by DFT, exchange structure was still preserved such that nn interactions had a negative sign indicating anti ferromagnetic behavior while nnn values were positive. The effect of diluting the samples served to increase the spacing between CuPc as more H$_2$Pc were placed between them. Through increased spacing, the J values decreased. Therefore, diluting the samples with the non-magnetic metal-free phthalocyanine can be used as a method of quenching spin interactions.

Within 1D chains of phthalocyanines the main mode of interaction is due to overlap of the $\pi$ orbitals perpendicular to the plane of the molecules. To understand the interplay between the single molecule orbitals and the change due to interactions with adjacent phthalocyanines the ultraviolet photoelectron spectra (UPS) for single molecules of CuPc and H$_2$Pc are calculated. The spectra showed the presence of the highest two occupied states which are the half-filled $b_{1g}$ and fully occupied $a_{1u}$ orbitals in CuPc whereas a single $a_u$ state for the HOMO is present in H$_2$Pc. The singly occupied state in CuPc is attributable to the half-filled d-orbital of the Cu center. Splitting between the $b_{1g}$ and $a_{1u}$ states was observed to be a result of the occupation cost introduced by the Hubbard U on the copper atom. While this interesting behavior aligns with other theoretical experiments well, the orbital alignment of the LUMO states is reverse of the reported values using hybrid functions. This
indicates that while the Hubbard U should heavily influence the unoccupied $b_{1g}$ state, the inclusion of exchange is necessary to fully describe the situation.

Upon understanding the single molecules, the density of states was calculated for several dilute samples in the 1D crystalline form to illustrate the effect of dilution. Similarly to the UPS, the higher occupied states were identified through the spin present at a given energy. Throughout diluting the samples an interesting feature emerged for the HOMO which resolved into two separate energy levels possibly due to the interaction with adjacent molecules. To fully understand this character, the projected d-orbitals in the molecular plane were shown first. The $d_{xy}$ orbital was attributed to the $b_{1g}$ state while $d_{x^2−y^2}$ interacted with core ligand states. However, throughout the dilution samples neither of these changed in a way that would suggest the splitting of energy levels at the HOMO. Instead, the out-of-plane $d_{zy}$ orbital showed characteristics of being affected by the presence of difference adjacent phthalocyanine molecules. By concluding that the nature of the non-planar orbitals is the main cause behind changing the states near the HOMO the effect of dilution has been observed.

Through inducing changes near the HOMO in crystalline phthalocyanine by dilution the possibilities to change fundamental behavior are great. Diluting CuPc with H$_2$Pc was presented as a benchmark system between two well-studied systems where magnetic interactions only occurred between Cu atoms. If, rather than the metal-free phthalocyanine, another magnetic molecule such as MnPc were used to dilute the system there could be fundamentally more interesting interactions as the exchange constants become more complex and the out-of-plane orbitals interact. Additionally, the orbital alignment at the HOMO and LUMO levels bears notice because the
alignment is systems such as CuPc and MnPc are reversed. This provides a possibility of engineering the orbital alignment through controlling the interactions between d-orbitals. While this may be an indirect method of affecting electronic structure, results from this research suggest that this method shows promise.
APPENDIX A

EXCHANGE CONSTANT RELATIONS

As illustrated in Chapter 2, the polynuclear model of spin exchange allows the exchange constants of systems beyond the dimer model to be calculated. The following is a comprehensive list of the relations found by applying this method to the dilute cases studied in this thesis.

100% CuPc

Spin States

\[
\begin{array}{c|c|c|c|c}
\uparrow\uparrow\uparrow\uparrow & \uparrow\uparrow\uparrow\downarrow & \uparrow\uparrow\downarrow\uparrow & \uparrow\uparrow\downarrow\downarrow & \uparrow\downarrow\uparrow\downarrow \\
HS & LS1 & LS2 & LS3 & LS4
\end{array}
\]
Exchange Constant Relations

\[
\begin{align*}
\alpha &= E_{LS1} - E_{HS} = J_{14} + J_{24} + J_{34} \\
\beta &= E_{LS2} - E_{HS} = J_{13} + J_{23} + J_{34} \\
\gamma &= E_{LS3} - E_{HS} = J_{13} + J_{14} + J_{23} + J_{24} \\
\delta &= E_{LS4} - E_{HS} = J_{12} + J_{14} + J_{32} + J_{34}
\end{align*}
\]

(A.1)

Symmetry Relations

\[
\begin{align*}
J_{12} &= J_{34} \quad \text{← Nearest Neighbors} \\
J_{13} &= J_{24} \quad \text{← Next Nearest Neighbors}
\end{align*}
\]

(A.2)

Exchange Constant Values

\[
\begin{align*}
J_{12} &= \frac{1}{2} (\beta - \gamma + \alpha) \\
J_{23} &= \frac{1}{2} (\gamma - 2\alpha + \delta) \\
J_{13} &= \frac{1}{2} (\alpha + \beta - \delta) \\
J_{14} &= \frac{1}{2} (\delta + \gamma - 2\beta)
\end{align*}
\]

(A.3)
75% CuPc Configuration 1

Spin States

Exchange Constant Relations

\[
\begin{align*}
\alpha &= E_{LS1} - E_{HS} = J_{13} + J_{23} \\
\beta &= E_{LS2} - E_{HS} = J_{12} + J_{23} \\
\gamma &= E_{LS3} - E_{HS} = J_{12} + J_{13}
\end{align*}
\]

(A.4)

Exchange Constant Values

\[
\begin{align*}
J_{12} &= \frac{1}{2} (\beta + \gamma - \alpha) \\
J_{13} &= \frac{1}{2} (\alpha - \beta + \gamma) \\
J_{23} &= \frac{1}{2} (\alpha + \beta - \gamma)
\end{align*}
\]

(A.5)
75\% CuPc Configuration 2

Spin States

Exchange Constant Relations

\[
\begin{align*}
\alpha &= E_{LS1} - E_{HS} = J_{14} + J_{24} \\
\beta &= E_{LS2} - E_{HS} = J_{12} + J_{24} \\
\gamma &= E_{LS3} - E_{HS} = J_{12} + J_{14}
\end{align*}
\] (A.6)

Exchange Constant Values

\[
\begin{align*}
J_{12} &= \frac{1}{2} (\beta + \gamma - \alpha) \\
J_{14} &= \frac{1}{2} (\alpha - \beta + \gamma) \\
J_{24} &= \frac{1}{2} (\alpha + \beta - \gamma)
\end{align*}
\] (A.7)
\[ |\uparrow\uparrow~00\rangle \quad |\uparrow\downarrow~00\rangle \]

**50% CuPc Configuration 1**

**Spin States**

**Exchange Constant Relations**

\[ \{ \alpha = E_{LS1} - E_{HS} = J_{12} \} \] (A.8)

**50% CuPc Configuration 2**

**Spin States**

\[ |\uparrow~00\uparrow\rangle \quad |\uparrow~00\downarrow\rangle \]

**Exchange Constant Relations**

\[ \{ \alpha = E_{LS1} - E_{HS} = J_{14} \} \] (A.9)
25% CuPc

Spin States

\[ |↑000⟩_\text{HS} \quad |↑000⟩_\text{LS1} \]

Exchange Constant Relations

\[
\begin{aligned}
\alpha &= E_{LS1} - E_{HS} = J_{15} \\
&= (A.10)
\end{aligned}
\]
APPENDIX B

DFT+U MATRICES

Listed are the calculated U matrices for each systems used to calculate the exchange constants. All values are in eV and the error is about ±0.02eV

|↑↑↑↑⟩

\[
\begin{bmatrix}
6.17 & 0.01 & 0.00 & 0.01 \\
0.01 & 6.17 & 0.01 & 0.00 \\
0.00 & 0.01 & 6.17 & 0.01 \\
0.01 & 0.00 & 0.01 & 6.17 \\
\end{bmatrix}
\]

|↑0 ↑↑⟩

\[
\begin{bmatrix}
6.12 & 0.01 & 0.01 \\
0.01 & 6.12 & 0.01 \\
0.00 & 0.00 & 6.11 \\
\end{bmatrix}
\]

|↑0 ↓↑⟩

\[
\begin{bmatrix}
6.12 & 0.00 & 0.00 \\
0.00 & 6.12 & 0.00 \\
0.01 & 0.00 & 6.14 \\
\end{bmatrix}
\]
\begin{align*}
|\uparrow \downarrow \downarrow\rangle &= \begin{pmatrix} 6.14 & 0.00 & 0.00 \\ 0.00 & 6.14 & 0.00 \\ 0.00 & 0.01 & 6.13 \end{pmatrix} \\
|\uparrow \uparrow 00\rangle &= \begin{pmatrix} 6.10 & 0.01 \\ 0.01 & 6.10 \end{pmatrix} \\
|\uparrow \downarrow 00\rangle &= \begin{pmatrix} 6.11 & 0.01 \\ 0.01 & 6.11 \end{pmatrix} \\
|\uparrow 0 \uparrow 0\rangle &= \begin{pmatrix} 6.15 & 0.01 \\ 0.01 & 6.15 \end{pmatrix} \\
|\uparrow 0 \downarrow 0\rangle &= \begin{pmatrix} 6.11 & 0.02 \\ 0.02 & 6.11 \end{pmatrix} \\
|\uparrow \uparrow \uparrow \downarrow \rangle &= \begin{pmatrix} 6.16 & -0.01 & 0.01 & -0.01 \\ -0.01 & 6.16 & -0.01 & 0.01 \\ 0.01 & -0.01 & 6.16 & -0.01 \\ -0.01 & 0.01 & -0.01 & 6.16 \end{pmatrix}
\end{align*}
$|\uparrow\uparrow\uparrow\downarrow\rangle$

\[
\begin{pmatrix}
6.15 & -0.01 & 0.02 & 0.00 \\
0.00 & 6.14 & 0.00 & 0.00 \\
0.02 & -0.01 & 6.15 & 0.00 \\
0.00 & -0.00 & 0.00 & 6.14 \\
\end{pmatrix}
\]
Appendix C

AFM Density of States

The density of states for the AFM dilute systems show the same effects as the FM system with the difference that the change in out-of-plane $d_{z^y}$ shows a different trend. This trend, however, illustrates the same effect that $d_{z^y}$ orbitals change due to the environment in which they are located. Figures C.1-C.3 show the AFM total DOS for similar systems as shown in the FM case. Each of these represents a different environment for the CuPc which should change the out-of-plane interactions.

The d-orbital LDOS is shown in Fig. C.4 where the similar feature of the highest singly-occupied state corresponding to a d-orbital while the bulk of the contribution is found in core states. Both the in-plane and out-of-plane d-orbitals are shown in Fig. C.5 where we see that the in-plane orbitals interacting with the ligand are responsible for the singly-occupied state.

Finally, the out-of-plane $d_{z^y}$ orbital changes based on the environment as shown in Fig. C.6 where the systems are $|\uparrow\downarrow\downarrow\rangle$, $|\uparrow\uparrow\downarrow\rangle$, and $|\uparrow\downarrow\downarrow\rangle$, respectively. A more obvious trend arises where the out-of-plane DOS grows in magnitude as the environment changes from completely CuPc to adjacent H$_2$Pc molecules. The same
A conclusion can be drawn where the interaction of the out-of-plane states creates a change within the in-plane states.

*Figure C.1: Pure AFM CuPc TDOS*
Figure C.2: AFM $|\uparrow 0 \uparrow\downarrow\rangle$ CuPc TDOS

Figure C.3: AFM $|\uparrow 0 \downarrow\rangle$ CuPc TDOS
Figure C.4: AFM CuPc d-Orbital LDOS

Figure C.5: d-Orbital Contribution to Anti-Ferromagnetic CuPc

(a) $d_{xy}$ Orbital

(b) $d_{zy}$ Orbital
Figure C.6: AFM CuPc $d_{zy}$ Dilute Range PDOS


BIBLIOGRAPHY


