Valence bond theory and organic molecules

Bachelor Project in Physics

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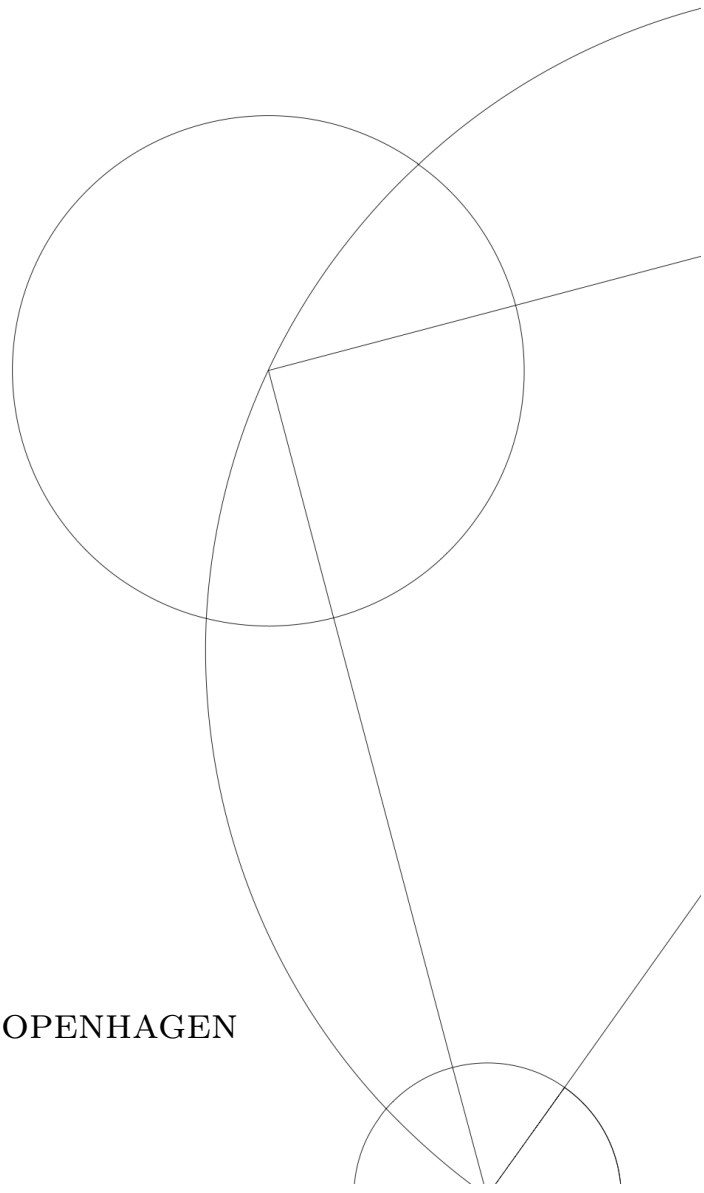

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Abstract

In this thesis a model for analyzing organic molecules is developed using valence bond theory. This was done by first considering a simple interaction between two overlapping electrons and afterwards introducing the Hubbard model. This model reflects the ability of interacting valence electrons on a lattice to move from site to site as well as taking into account their on-site repulsion. From this an effective Hamiltonian acting on a certain subspace of the Hilbert space is derived. A picture formalism for analyzing the bonds between lattice sites is developed that greatly simplifies the work of finding specific molecule's ground state energies. Lastly, the spin density of free radicals is analyzed.

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1 Introduction

The nature of the chemical bond has been widely studied for a long time and since the beginning of the last century with the formulation of Quantum Mechanics, the study of matter on the smallest of scales, along with Quantum Chemistry a more qualitative description of this bond has been given. The introduction of atomic orbitals helped describe the bonds that atoms form across molecules and the concept of orbital hybridization – a mixing of different orbitals, such as (mainly) s and p orbitals – made it possible to describe many types of valence bonds.

When an atom bonds with several other atoms in a molecule, such as methane CH_4, the valence electrons of the carbon atom can create hybridized orbitals equal in energy in order to bond to the four hydrogen atoms in so called bonding orbitals. This demands a small excitation of one s orbital but the energy to be gained by going into a bonding orbital strongly outweighs this excitation.

Valence bond theory is one of two theories developed using Quantum Mechanics to describe chemical bonds. This theory allows us to look at how organic molecules act and what the representation of a chemical bond is through a Quantum Mechanical perspective. Chemists have been drawing these molecules and their bonds for years but their fundamental property is as much of interests to physicists as well as chemists.
In organic molecules the valence electrons of each atom interact and their wave functions overlap. This overlap is crucial to valence bond theory as it allows electrons to move across atoms in the molecule instead of remaining fixed at their constituent atom. This hopping motivates the Hubbard model, reminiscent of the tight binding model, but one that also takes into account the electron-electron repulsion of doubly occupied atoms. In this model each atom is considered as a single orbital which only two electrons can occupy, as electrons are fermions and therefore obey the Pauli exclusion principle.

Organic molecules can be modelled as simple lattices with sites arranging themselves in different configurations, so this is very much an issue of relevance in the field of solid-state physics.

2 Chemical bonds in Quantum Mechanics

The chemical bond that exists between two atoms can be described using the Quantum Mechanical wave function of the valence electrons of the constituent atoms. The electrons are characterised by their quantum numbers: the principal quantum number n, the azimuthal quantum number l, the magnetic quantum number m and the spin quantum number s. n describes the orbital in which the electrons are found, s their spin, l their rotational angular momentum and m the projection of angular momentum along the $\hat{z}$-axis. In organic molecules the relevant orbitals are s ($l = 0$) and p ($l = 1$) orbitals as well as hybridized versions of the two. The electronic quantum state belonging to $l = 1$ (i.e. ψ_{21-1}, ψ_{210} and ψ_{211}) allow for a p_z orbital and linear combinations allow for p_x and p_y orbitals. Carbon, the most important element in organic molecules, will be bound to different amount of atoms in different molecules – the hybridizations (if there are any) will vary dependent on the amount of bonds. The electron configuration of Carbon is

$1s^2 2s^2 2p^2$ with four valence electrons (the 2s and 2p electrons), so the orbitals will be sp, sp^2 and sp^3 hybridized, taking the form of asymmetrical dumbbells (the p orbitals alone are symmetrical dumbbells). For example in methane, where carbon bonds with four Hydrogen atoms, one of the 2s electrons is excited and the four unpaired valence electrons go together to form four sp^3 hybridized orbitals equal in energy.

2.1 Bonding and anti-bonding orbitals

The electrons in hybridized orbitals of different atoms can overlap and their single particle quantum states are the eigenstates the Hamiltonian represented by a 2x2 matrix

$$h = \begin{bmatrix} \varepsilon_1 & -t \\ -t & \varepsilon_2 \end{bmatrix} \tag{1}$$

where t is the overlap of the wavefunctions defined as such

$$t = -\langle 1| \mathcal{H} |2\rangle = -\langle 2| \mathcal{H} |1\rangle \tag{2}$$

and ε_1 and ε_2 the orbital energies of the two atoms.

The eigenvalues are

$$\varepsilon_\pm = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \sqrt{\left(\frac{\varepsilon_1 - \varepsilon_2}{2}\right)^2 + t^2}$$

giving rise to so called bonding and antibonding states. The energy decreases and increases as $\sqrt{\Delta^2 + t^2}$ (Δ is the half the difference between ε_1 and ε_2) as a function of t of the bonding and antibonding states respectively, such that the bonding state is the natural ground state of the system, as it allows the electrons to move across the molecule (effectively creating a larger potential well to move across and thus lowering the kinetic energy).

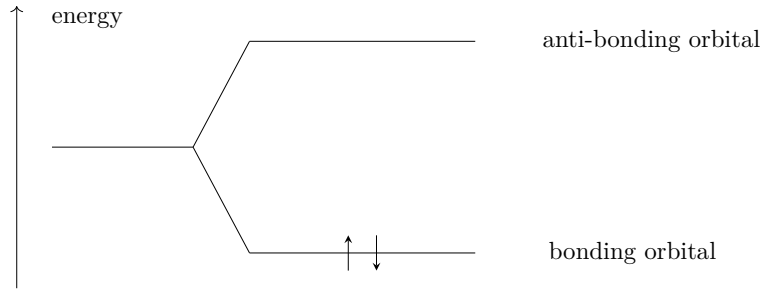


Figure 1: When an overlap of the wavefunctions of two electrons is present they have the ability to go into one common orbital – one that lowers both of their energies and one that raises them.

From the Slater determinant we find the total wavefunction of two electrons in the bonding orbital

$$\Psi = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)(u^2 |11\rangle + v^2 |22\rangle + uv\{|12\rangle + |21\rangle\}) \tag{3}$$

where $|21\rangle$ refers to the second electron occupying the first atom and the first electron occupying the second atom. The consequence of this is that both electrons can be found on the same atom. In this there is a Coulomb interaction that must be accounted for, which motivates the introduction of a two electron Hamiltonian that takes this into account:

$$h_2 = \begin{array}{c} \\ \langle 11| \\ \frac{1}{\sqrt{2}}(\langle 12|-\langle 21|) \\ \langle 22| \end{array} \begin{array}{c} \begin{array}{ccc} |11\rangle & \frac{1}{\sqrt{2}}(|12\rangle-|21\rangle) & |22\rangle \end{array} \\ \begin{bmatrix} 2\varepsilon_1+U & -\sqrt{2}t & 0 \\ -\sqrt{2}t & \varepsilon_1+\varepsilon_2 & -\sqrt{2}t \\ 0 & -\sqrt{2}t & 2\varepsilon_2+U \end{bmatrix} \end{array} \tag{4}$$

ε_i is the energy of an electron on the i^{th} atom and U is the Coulomb interaction. To solve this analytically we must set $\varepsilon_1 = \varepsilon_2 = \varepsilon$, giving the eigenstates of the total system as well as the total ground state energy

$$E_{\text{gs}} = 2\varepsilon + \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2} \tag{5}$$

$$|gs\rangle = \frac{1}{2}\sqrt{1-\frac{U}{2\epsilon}}(|11\rangle + |22\rangle) + \frac{1}{2}\sqrt{1+\frac{U}{2\epsilon}}(|12\rangle - |21\rangle) \tag{6}$$

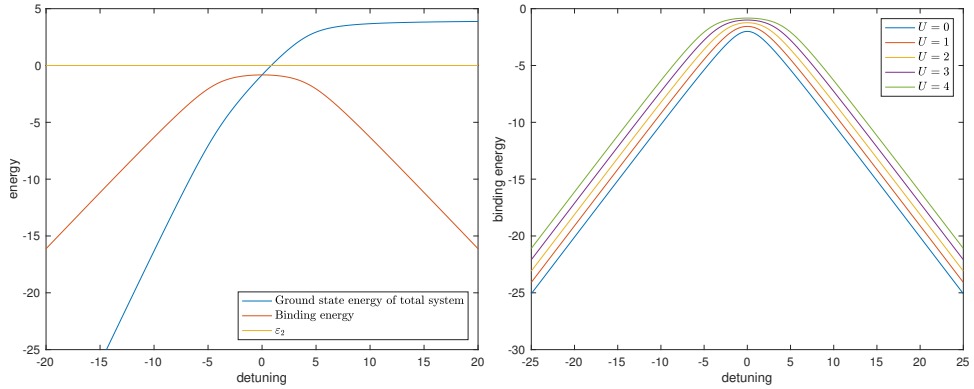
where $\epsilon = \sqrt{(U/2)^2 + 4t^2}$. From the ground state we find that for $U \to \infty$ the probability of the electrons being on the same atom goes to zero, and for $U \to 0$ it goes to $\frac{1}{2}$; for large electron-electron repulsion we do not expect to find them on the same atom. When there is no interaction there should be no preference. We note that the eigenstate is a superposition of two singlet states ($|11\rangle+|22\rangle$ is also a singlet state, i.e. $S^+[|11\rangle+|22\rangle] = 0$, since the electrons must have opposite spins to occupy the same atom).

The Hamiltonian in Eq. 4 is not simple to solve analytically but its eigenvalues and eigenstates can be found using numerical analysis.

3 Numerical analysis of 3x3 Hamiltonian

While we had to set $\varepsilon_1 = \varepsilon_2 = \varepsilon$ to solve the 3×3 Hamiltonian of Eq. 4 analytically we can still analyze it numerically without this restriction. Doing this it is natural to set the zero point of the energy scale at one of the orbital energies and the coupling constant $t = 1$. We can thus analyse the ground state energy and bonding energy of the system where $E_{\text{bonding}} = E_{\text{gs}} - \varepsilon_1$, if we set $\varepsilon_2 = 0$. Then ε_1 measures the detuning of the two orbitals, allowing us to vary this as well as the interaction U for fixed (normalized) t.

Figure 2 indicates that the binding energy of the two atoms is largest around $\varepsilon_1 - \varepsilon_2 = 0$, and that the peak around this maximum increases for increasing U – thus for larger Coulomb repulsion the binding energy increases and the energy to be gained by forming a bond decreases. The binding energy decreasing for increased detuning seems to indicate very frequent ionization between atoms and molecules. However, when the detuning becomes larger the physical picture of one orbital pr. atom becomes unrealistic as other energy levels on each atom will come into play and thus we cannot expect this kind of random ionization to occur.



(a) (b)

Figure 2: The binding and ground state energy measured as a function of detuning, for $U = 4t$ and for $U = 0$, $U = 1t$, $U = 2t$, $U = 3t$ and $U = 4t$. All energies measured in t.

4 Second quantization and the Hubbard Model

4.1 Creation and annihilation operators

We found that the total state of a two electron system required a 3x3 Hamiltonian (or in the full basis a 4x4 Hamiltonian). Most interesting molecules contain more than two atoms, so using the same procedure for larger systems would be rather tedious. It is therefore useful to introduce the formalism of second quantization. In this formalism we introduce the annihilation and creation operators $c_{i\sigma}$ and $c^\dagger_{i\sigma}$, that annihilate and create electrons respectively in the i^{th} orbital (referring to the i^{th} atom) with spin σ. Accounting for the antisymmetric nature of electrons the operators obey the following anticommutation relations

$$\{c_{i\sigma}, c^\dagger_{j\sigma'}\} = \delta_{ij}\delta_{\sigma\sigma'} \tag{7a}$$

$$\{c_{i\sigma}, c_{j\sigma'}\} = \{c^\dagger_{i\sigma}, c^\dagger_{j\sigma'}\} = 0 \tag{7b}$$

where the anticommutator is defined $\{A, B\} \equiv AB + BA$. One important consequence of the anticommutator relations (or rather an important fact reflected by these relations) is that applying the same creation (or annihilation) operator twice to any state annihilates it:

$$(c_{i\sigma})^2 |\psi\rangle = (c^\dagger_{i\sigma})^2 |\psi\rangle = 0$$

This is a reflection of the Pauli exclusion principle stating that no two fermions can occupy the same quantum state, i.e. that their set of quantum numbers cannot be identical. Thus we cannot create a state with two electrons in the same orbital with the same spin and neither can one exist for us to annihilate in the first place.

These operators can be used to formulate spin states by acting on an empty vacuum state, such that e.g. $|\uparrow\downarrow\rangle = c^\dagger_{1\uparrow}c^\dagger_{2\downarrow}|0\rangle$ corresponds to a state with spin up and down electrons on the first and second atom respectively and $|\uparrow\downarrow\ 0\rangle = c^\dagger_{1\uparrow}c^\dagger_{1\downarrow}|0\rangle$ contains both

electrons on the first atom. The order in which the operators act in defining the state is arbitrary but must be consistent.
This formalism motivates the introduction of the Hubbard model, the (reduced, $\varepsilon_1 = \varepsilon_2 = 0$) Hamiltonian expressed in matrix form in Eq. 4. The model can be expressed as

$$\mathcal{H} = -t \sum_{<ij>,\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{8}$$

The first term is the hopping term representing the energy of electrons moving between neighboring sites equivalent to the tight binding Hamiltonian which does not take electron-electron interaction into account. $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$ counts the number of electrons of spin σ on the i^{th} atom, such that the second term annihilates the state unless site i is doubly occupied, in which case it has eigenvalue U - thus the two terms can be (as in most Hamiltonians) thought of as a kinetic (hopping) term and a potential (Coulomb) term. It is clear that using the Hubbard model on the basis in which the Hamiltonians in Eqs. 1 and 4 was written (e.g. if $|12\rangle \to |\uparrow\downarrow\rangle$, $|21\rangle \to |\downarrow\uparrow\rangle$, etc.) indeed yields the matrix elements given (or rather the tight binding model for the one-particle Hamiltonian in Eq. 1).

Note that the Hubbard model could easily incorporate different on-site orbital energies by including the term $\sum_i (n_{i\uparrow} + n_{i\downarrow})\varepsilon_i$.

4.2 The effective Hamiltonian

The Hubbard model in Eq. 8 is very useful for many organic molecules where the bond being analyzed is between different Carbon atoms. Before moving on to specific examples of this we introduce the projection operators $\mathcal{P}$ and $\mathcal{Q}$, that are idempotent, mutually orthogonal, and their sum identity

$$\mathcal{Q} = \mathcal{Q}^2 \qquad \mathcal{P} = \mathcal{P}^2 \tag{9a}$$

$$\mathcal{Q}\mathcal{P} = 0 \qquad \mathcal{P} + \mathcal{Q} = \mathcal{I} \tag{9b}$$

$$\mathcal{Q} = n_\uparrow n_\downarrow \qquad \mathcal{P} = 1 - n_\uparrow n_\downarrow \tag{9c}$$

The function of these operators is to project states in a $N \times N$ Hilbert space into $n \times n$ and $m \times m$ subspaces, in which sites are either singly occupied (P) or doubly occupied (Q), i.e. states where there is no Coulomb interaction and states where there is Coulomb interaction. Using the relations in Eq. 9 we obtain an effective Hamiltonian $\mathcal{H}_{\text{eff}}$ working on differently projected states $|\psi_P\rangle = \mathcal{P}|\psi\rangle$ and $|\psi_Q\rangle = \mathcal{Q}|\psi\rangle$ with its own eigenvalues, $\mathcal{H}_{\text{eff}}|\psi_P\rangle = E|\psi_P\rangle$ (in this case acting on the P subspace). The effective Hamiltonian comes directly from the Schrödinger equation $\mathcal{H}|\psi\rangle = E|\psi\rangle$

$$\mathcal{P}\mathcal{H}|\psi\rangle = \mathcal{P}\mathcal{H}(\mathcal{P}+\mathcal{Q})|\psi\rangle = \mathcal{P}\mathcal{H}\mathcal{P}|\psi_P\rangle + \mathcal{P}\mathcal{H}\mathcal{Q}|\psi_Q\rangle = E|\psi_P\rangle \tag{10a}$$

$$\begin{aligned}\mathcal{Q}\mathcal{H}|\psi\rangle = \mathcal{Q}\mathcal{H}(\mathcal{Q}+\mathcal{P})|\psi\rangle = \mathcal{Q}\mathcal{H}\mathcal{Q}|\psi_Q\rangle + \mathcal{Q}\mathcal{H}\mathcal{P}|\psi_P\rangle = E|\psi_Q\rangle \\ \Rightarrow |\psi_Q\rangle = (E\mathcal{I} - \mathcal{Q}\mathcal{H}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{H}\mathcal{P}|\psi_P\rangle\end{aligned} \tag{10b}$$

giving us the effective Hamiltonian acting on the P subspace

$$\mathcal{H}^{(P)}_{\text{eff}} = \mathcal{P}\mathcal{H}\mathcal{P} + \mathcal{P}\mathcal{H}\mathcal{Q}(E\mathcal{I} - \mathcal{Q}\mathcal{H}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{H}\mathcal{P} = \mathcal{P}\mathcal{H}\mathcal{Q}\frac{1}{E-U}\mathcal{Q}\mathcal{H}\mathcal{P} \tag{11}$$

$\mathcal{PHP} = 0$ since $\mathcal{H}$ brings a P state into the Q subspace and $\mathcal{P}$ annihilates it again. We have also replaced $(E\mathcal{I} - \mathcal{QHQ})^{-1}$ with the scalar value $(E-U)^{-1}$ since $\mathcal{Q}$ ensures only Q states are left, such that $\mathcal{QHQ}$ simply gives a factor of U.
Writing the Hubbard Hamiltonian $\mathcal{H} = \mathcal{T} + \mathcal{V}$, where $\mathcal{T}$ is the hopping term and $\mathcal{V}$ the potential term only $\mathcal{T}$ can bring a state $|\psi_P\rangle$ out of the P subspace. Thus the effective Hamiltonian can be rewritten

$$\mathcal{H}_{\text{eff}} = \mathcal{P}\left[\frac{1}{E-U}\mathcal{TQT}\right]\mathcal{P} \tag{12}$$

The effective Hamiltonian crucially begins and ends in the P subspace, allowing for transitions between states in this subspace (such as $|\uparrow\downarrow\rangle \to |\downarrow\uparrow\rangle$) along the way. Utilizing this and using the formalism of second quantization to write spin operators we reformulate the effective Hamiltonian as follows

$$S^z = \frac{1}{2}(c_\uparrow^\dagger c_\uparrow - c_\downarrow^\dagger c_\downarrow), \quad S^+ = c_\uparrow^\dagger c_\downarrow, \quad S^- = c_\downarrow^\dagger c_\uparrow \tag{13}$$

$$\begin{aligned}
\mathcal{H}_{\text{eff}} &= \mathcal{P}\Big[\sum_{<ij>}\frac{t^2}{E-U}\sum_{\sigma\sigma'}(c_{i\sigma}^\dagger c_{j\sigma} c_{j\sigma'}^\dagger c_{i\sigma'} + c_{j\sigma}^\dagger c_{i\sigma} c_{i\sigma'}^\dagger c_{j\sigma'})\Big]\mathcal{P} \\
&= \mathcal{P}\Big[\sum_{<ij>}\frac{t^2}{E-U}\sum_{\sigma\sigma'}\{\delta_{\sigma\sigma'}(c_{i\sigma}^\dagger c_{i\sigma'} + c_{j\sigma}^\dagger c_{j\sigma'}) - c_{i\sigma}^\dagger c_{i\sigma'} c_{j\sigma'}^\dagger c_{j\sigma} - c_{j\sigma}^\dagger c_{j\sigma'} c_{i\sigma'}^\dagger c_{i\sigma}\}\Big]\mathcal{P} \\
&= \mathcal{P}\left[\sum_{<ij>}\frac{2t^2}{E-U}\left(\frac{1}{2} - S_i^+ S_j^- - S_i^- S_j^+ - 2S_i^z S_j^z\right)\right]\mathcal{P} = -\frac{4t^2}{E-U}\sum_{<ij>}\left(\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j - \frac{1}{4}\right)
\end{aligned} \tag{14}$$

to take the familiar form of the Heisenberg Hamiltonian for a lattice in the P subspace. Like the Hubbard Hamiltonian, this is a nearest neighbor model. It is clear that for the two electron triplet state $|t\rangle$, $\mathcal{H}_{\text{eff}}|t\rangle = 0$. For the two electron singlet state $|s\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$,

$$\mathcal{H}_{\text{eff}}|s\rangle = \frac{4t^2}{E-U}|s\rangle = E|s\rangle$$

Defining the interaction $J = -4t^2/(E-U)$ we write the Hamiltonian

$$\mathcal{H}_{\text{eff}} = J\sum_{<ij>}\left(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{1}{4}\right) \tag{15}$$

It is clear that $J > 0$ ($U > E$) and thus the effective Hamiltonian has an antiferromagnetic ground state since opposite spins will minimize $\mathbf{S}_i\cdot\mathbf{S}_j - 1/4$.
As $\mathcal{H}_{\text{eff}}|s\rangle = -J|s\rangle$, nearest neighbor singlet bonds minimize the energy of a lattice. From Eq. 10a, $\mathcal{H}_{\text{eff}}|\psi_P\rangle = E|\psi_P\rangle$ and noting that $\mathcal{H}_{\text{eff}}$ itself is a function of E (Eq. 14) we conclude that its eigenvalues must be solved self-consistently to know the precise value of J. However, knowing that $J > 0$ is enough to know that we need to look for anti ferromagnetic coupling and we do not need to know its precise value.

Since the singlet state is the ground state ($E_s = -J < E_t = 0$) it is clearly preferable for two electrons to form a singlet bond and not a triplet bond. Therefore when studying

organic molecules we will look for the lowest spin state, i.e. the ones with as many nearest neighbor singlet bonds as possible – in the picture language developed in section 5.1 these are represented as double bonds.

4.2.1 From Hubbard to $\mathcal{H}_{\text{eff}}$

In section 2.1 we found the ground state of the two-electron Hubbard model to be a superposition of two singlet states – one with the electrons occupying separate atoms and one with them occupying the same atom, i.e., one belonging to the P subspace and one belonging to the Q subspace. The effective Hamiltonian was derived simply by multiplying both sides of $\mathcal{H}|\psi\rangle = E|\psi\rangle$ with $\mathcal{P}$ such that $|\psi_P\rangle$, the eigenstates of $\mathcal{H}_{\text{eff}}$ are merely the parts of the Hubbard Hamiltonian eigenstates belonging to the P subspace. The singlet $|s\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ is the ground state of the effective Hamiltonian so $\mathcal{H}_{\text{eff}}|s\rangle = 4t^2/(E-U) = E|s\rangle$ (Eq. 10a). Solving for E gives

$$E = \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2}$$

giving us the same ground state energy as in Eq. 5 for the Hubbard model.

5 Picture formalism and singlet projection

5.1 Picture formalism

In the preceding section we developed a model to analyze bonds between nearest neighbor atoms on a lattice. Any organic molecule could be modelled by such a lattice. Carbon is the building block of organic molecules and different bonds are formed in these molecules. These bonds can be represented by the skeletal formula [1] or picture formalism, where the placement of the majority of the atoms is implicit. As an example a chain of four Carbon atoms can be represented with this formula as seen in figure 3.

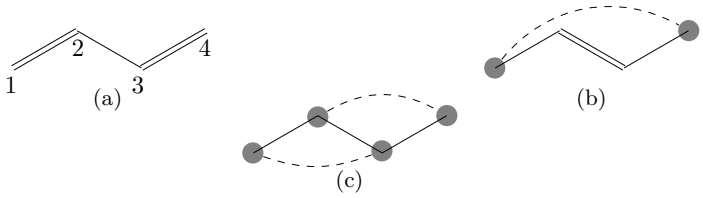
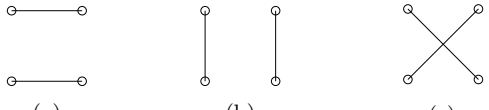


Figure 3: A chain of Carbon atoms with singlet bonds placed between different lattice sites. The dashed lines represent non-nearest neighbor singlet bonds.

Singlet bonds are represented as double bonds for nearest neighbors and single (sometimes dashed) lines between non nearest neighbor sites, such that the state in figure 3a has two nearest neighbor singlet bonds between sites 1 and 2 as well as between sites 3 and 4. The state in figure 3b has a nearest neighbor bond between sites 2 and 3 and a non nearest neighbor bond between sites 1 and 4. Introducing the singlet creation operator

$$S_{ij}^\dagger = \frac{1}{\sqrt{2}}(c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger - c_{i\downarrow}^\dagger c_{j\uparrow}^\dagger) \tag{16}$$

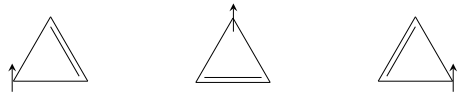


(a) (b) (c)

Figure 4: We cannot have crossed bonds on our real space lattice. Of the three possible ways of arranging two bonds onto four sites only the first two are allowed in the above picture.

we can using these find the quantum states of the configurations above exactly like for fermionic creation operators – note that not only is $S^\dagger_{ij} = S^\dagger_{ji}$, it is also a bosonic creation operator, such that when dealing with several singlet bonds the operators commute.

The states in figure 3 are not linearly independent and in fact sum to zero, $\psi_{3a} + \psi_{3b} + \psi_{3c} = 0$. Another important linear dependence is seen in figure 5 – both of these can be shown using the singlet creation operator in Eq. 16, noting that $[S^\dagger_{ij}, c^\dagger_{k\uparrow}] = 0$. For example, $|3a\rangle = S^\dagger_{12} S^\dagger_{34} |0\rangle$.



(a) (b) (c)

Figure 5: Like the states in figure 3, the states seen here are linearly dependent, $\psi_{5a} + \psi_{5b} + \psi_{5c} = 0$.

5.2 Singlet projection

Having shown that the effective Hamiltonian is the Heisenberg model and knowing that the energy of a nearest neighbor singlet bond is $-J$, $\mathcal{H}_{\text{eff}} |s\rangle = -J |s\rangle$, we now have the tools required to calculate the ground states of molecules of interest. The Hamiltonian is a nearest neighbor model so all required is to act on each nearest neighbor couple. However before we proceed any further we must know how the model acts on nearest neighbor couples that do not form a singlet bond – as an example we can act with $\mathbf{S}_2 \cdot \mathbf{S}_3 - \frac{1}{4}$ on the state in figure 3a:

$$\left[\mathbf{S}_2 \cdot \mathbf{S}_3 - \frac{1}{4}\right] \quad = \left[\mathbf{S}_2 \cdot \mathbf{S}_3 - \frac{1}{4}\right] \frac{1}{2} \left(|\uparrow\downarrow\uparrow\downarrow\rangle - |\uparrow\downarrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\downarrow\rangle + |\downarrow\uparrow\downarrow\uparrow\rangle\right)$$

$$\left[S^z_2 S^z_3 + \frac{1}{2}\left(S^+_2 S^-_3 + S^-_2 S^+_3\right)\right] \frac{1}{2} \left(|\uparrow\downarrow\uparrow\downarrow\rangle - |\uparrow\downarrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\downarrow\rangle + |\downarrow\uparrow\downarrow\uparrow\rangle\right)$$

$$\frac{1}{4} \left(|\uparrow\uparrow\downarrow\downarrow\rangle - |\uparrow\downarrow\uparrow\downarrow\rangle - |\downarrow\uparrow\downarrow\uparrow\rangle + |\downarrow\downarrow\uparrow\uparrow\rangle\right) = \frac{1}{2}$$

(17)

Evidently acting on a nearest neighbor pairing with the Heisenberg Hamiltonian where a singlet bond is not present creates one between those sites as well as an additional bond between the two adjacent sites (in this case site 1 and 4). Introducing the projection operator $\hat{p}_{ij} = -\left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}\right)$ that projects any state into one with a double bond between

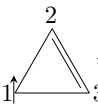
sites i and j (i and j are nearest neighbors as the Hamiltonian is a nearest neighbor model), we can once more rewrite the Hamiltonian as

$$\mathcal{H} = -J \sum_{<ij>} \hat{p}_{ij} \tag{18}$$

where J is the exchange interaction – note that we dropped the subscript on $\mathcal{H}_{\text{eff}}$ since for all intents and purposes this is the Hamiltonian.
Since two linearly independent singlet states are allowed for four sites, each singlet bond is unique to a specific state - i.e. $S^{\dagger}_{23}$ in ψ_{3b} and $S^{\dagger}_{12}$ in ψ_{3a} - thus projecting a state into one with nearest neighbor bond between two sites is the *same* as projecting the state into the only allowed state with that exact singlet bond. I.e. $\hat{p}_{23}$ is a projection into $|3b\rangle$ and as such can be written

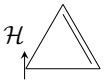
$$\hat{p}_{23} = |3b\rangle \langle 3b| \tag{19}$$

and therefore it is clear from this definition that $\hat{p}_{23}|3a\rangle = -\frac{1}{2}|3b\rangle$. $\langle 3b|3a\rangle = -\frac{1}{2}$, as seen from Eq. 17 where both states are written. Thus $\hat{p}_{ij}$ is a projection operator like any other. It can similarly be shown that acting on the states in figure 5 with the projection operator $\hat{p}_{ij}$ on a state where i or j carries the unpaired spin will create a singlet bond between i and j and move the unpaired spin to the (now) vacant site:

$$\left[\mathbf{S}_1 \cdot \mathbf{S}_2 - \frac{1}{4}\right]$$  $$= \left[\mathbf{S}_1 \cdot \mathbf{S}_2 - \frac{1}{4}\right] \frac{1}{\sqrt{2}} \left(|\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\uparrow\rangle\right)$$

$$= \frac{1}{2\sqrt{2}} \left(|\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle\right) = \frac{1}{2}$$  $$\Rightarrow \hat{p}_{12}$$  $$= -\frac{1}{2}$$  (20)

The factor of $-\frac{1}{2}$ can more simply be shown by utilizing the linear independences of both figure 3 and 5. For example, $\hat{p}_{12}(\psi_{3a} + \psi_{3b} + \psi_{3c}) = (1 + 2\alpha)\psi_{3a} = 0 \Rightarrow \alpha = -\frac{1}{2}$. In fact each triangle state is an eigenstate of the Hamiltonian with eigenvalue $-3J/2$. Since two of these are linearly independent the eigenstates are degenerate.

$$\mathcal{H}$$  $$= -J$$  $$+ \frac{1}{2}\left($$  $$+$$  $$\right) = -\frac{3}{2}J$$  (21)

Most interesting molecules have more than 3 or 4 lattice sites, but the above relations are still immensely useful and important; only a part of the molecule needs to have the configurations in figures 3 and 5 – when acting with the projection operator, $\hat{p}_{ij}$ on a larger molecule the non nearest neighbor sites of i and j can essentially be thought of as some factor of creation operators that commute with the projection operator and as such do not interfere with it. For a given lattice we look for the lowest spin state but this is different from an even number of lattice points to an odd number of lattice points. For n electrons the addition of spin angular momentum yields the following total spin states

$$\text{total spin, } s = \begin{cases} 0 \ldots \frac{n}{2} & \text{for } n \text{ even} \\ \frac{1}{2} \ldots \frac{n}{2} & \text{for } n \text{ odd} \end{cases}$$

Each spin state carries some degeneracy (there is a set of linearly independent states with spin s for n electrons) and the lowest spin state may have multiple configurations.

The degeneracy can be counted (see figure 6) for low enough numbers of electrons, but for many particles it becomes tedious and other methods are preferred.

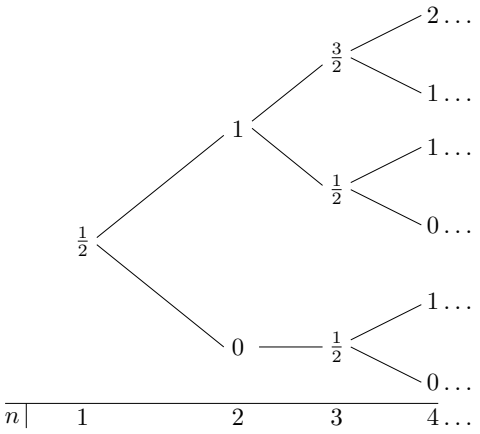


Figure 6: Adding an electron can either raise or lower (as long as $s > 0$) the total spin of the system by $\frac{1}{2}$ creating one (if $s = 0$) or two new states. From this we confirm that for three electrons two spin-$\frac{1}{2}$ doublets exist and for four electrons two singlets exist and thus the linear dependences from figure 3 and 5 must hold.

6 Ground state of organic molecules

From figure 6 we know the degeneracy of each spin state and thus the size of our basis. We know how the Hamiltonian acts on basis states so we can now write the matrix representation of the Hamiltonian and find the ground state looking for the lowest possible spin state.

6.1 Benzene

Benzene consists of bonds between six electrons – six spin-$\frac{1}{2}$ particles allow for 5 linearly independent singlet states. The singlet states are represented in the skeletal formula in figure 7.

Referring to the states in figure 7 (a)-(e) as $|A\rangle$, $|B\rangle$, $|c\rangle$, $|d\rangle$ and $|e\rangle$ respectively we can use this basis of singlet states to determine the Hamiltonian in matrix form and find the eigenvalues and eigenstates. The basis contains two low energy states with three double bonds ($|A\rangle$ and $|B\rangle$) as well as three slightly higher energy states the three Dewar states ($|c\rangle$, $|d\rangle$ and $|e\rangle$). These states contain a singlet bond between non nearest neighbor sites. It was stated above that the projection operator, $\hat{p}_{ij}$ is only relevant to sites i and j and their nearest neighbors. For example, $\hat{p}_{16}$ is a projection into either $|A\rangle$ or $|c\rangle$, depending on how the rest of the molecule the operator is acting on looks. E.g., acting on $|B\rangle$

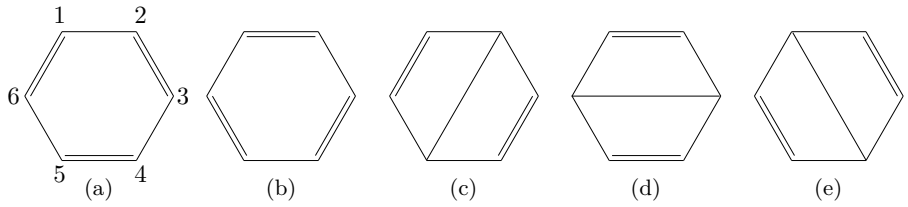
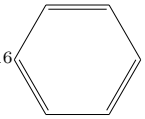
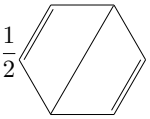


Figure 7: The five singlet states of Benzene.

$$\hat{p}_{16}$$  $$= |c\rangle \langle c|B\rangle = -\frac{1}{2}|c\rangle = -\frac{1}{2}$$  (22)

since $|B\rangle$ and $|c\rangle$ have the same singlet bond between sites 3 and 4. As $\langle c|B\rangle = -\frac{1}{2}$ (see Appendix A) the projection operator indeed yields the correct result . Clearly we do not need to do rigorous calculations to understand how the Hamiltonian acts on basis states as the picture formalism is more than adequate.

The Hamiltonian will project $|A\rangle$ and $|B\rangle$ into themselves (not each other) and into the three Dewar states (figure 7(c)-(e)) such that

$$\mathcal{H}|A\rangle = -3J|A\rangle + \frac{1}{2}J(|c\rangle + |d\rangle + |e\rangle), \quad \mathcal{H}|B\rangle = -3J|B\rangle + \frac{1}{2}J(|c\rangle + |d\rangle + |e\rangle) \tag{23a}$$

$$\mathcal{H}|i\rangle = -2J|i\rangle + J(|A\rangle + |B\rangle), \quad i = c,\, d,\, e \tag{23b}$$

giving us the 5×5 Hamiltonian of the form:

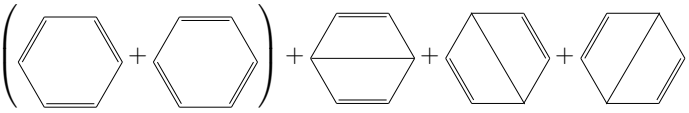
$$h = J\begin{bmatrix} -3 & 0 & 1 & 1 & 1 \\ 0 & -3 & 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & -2 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & -2 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & -2 \end{bmatrix} \tag{24}$$

The first thing to note about this is that the matrix representation of the Hamiltonian is not hermitian – this is due to the fact that the basis is not orthogonal as we specifically saw above for $|B\rangle$ and $|c\rangle$. If the basis had been orthonormal then all off diagonal elements would be zero as $|i\rangle \langle i|j\rangle = \delta_{ij}|i\rangle$, i.e. the Hamiltonian could not project basis states into others. Having expressed the Hamiltonian as a matrix, we can now find the eigenvalues and eigenstates of the Hamiltonian with ease. The ground state energy is

$$E_{\text{gs}} = -\frac{1}{2}\Big(5 + \sqrt{13}\Big)J \approx -4.30J \tag{25}$$

Not surprisingly it is lower than the lowest energy of the basis states. The ground state

is:

$$|gs\rangle = -2.3028$$  (26)

And again, not surprisingly the two low energy states weigh the most.

6.2 Pentagonal lattice

Looking at a similar molecule with five lattice sites instead of six, the lowest spin state is a spin-$\frac{1}{2}$ doublet. With five electrons there are five of these. Each doublet has two double bonds and the remaining lattice site carries an unpaired electron.

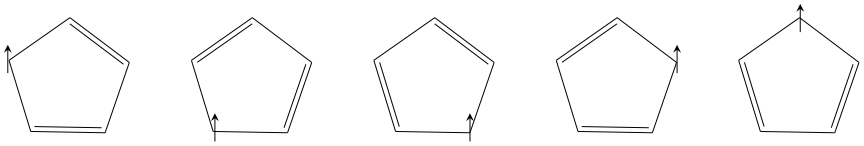
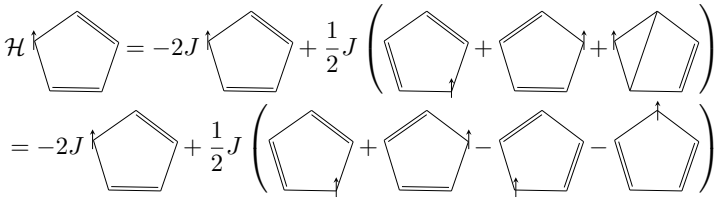


Figure 8: Five lattice sates arranged periodically with a period of 72° with one uncoupled electron.

Each state in this basis is the previous state rotated 72°, so naturally the the Hamiltonian works similarly for all of them.

$$\mathcal{H}$$  (27)

and generally, if $|n\rangle$ refers to the state with unpaired spin on the n^{th} site

$$\mathcal{H}\,|n\rangle = -2J\,|n\rangle + \frac{1}{2}\left(|n+2\rangle + |n-2\rangle - |n+1\rangle - |n-1\rangle\right) \tag{28}$$

for cyclical n. Clearly the basis states are not eigenstates of the Hamiltonian. However, since the valence electrons move in a periodic potential (we can essentially think of it as the unpaired spin moving around in a periodic potential) it would be appropriate to introduce Bloch states [2] $|k\rangle = \sum_n \mathrm{e}^{ikn}\,|n\rangle$, where $k = (2\pi/5)l$ (setting the lattice spacing $a = 1$) is the electron's wave number and l is an integer.

$$\mathcal{H}\,|k\rangle = \sum \mathrm{e}^{ikn}\Big(-2J\,|n\rangle + J\cos 2k\,|n\rangle - J\cos k\,|n\rangle\Big) = (-2J + J\cos 2k - J\cos k)\,|k\rangle$$

proving that Bloch states are indeed eigenstates of the Hamiltonian. Since $|k| \leq \pi$, the five values of k within the Brillouin zone are used ($l = -2, -1, 0, 1, 2$) to find the

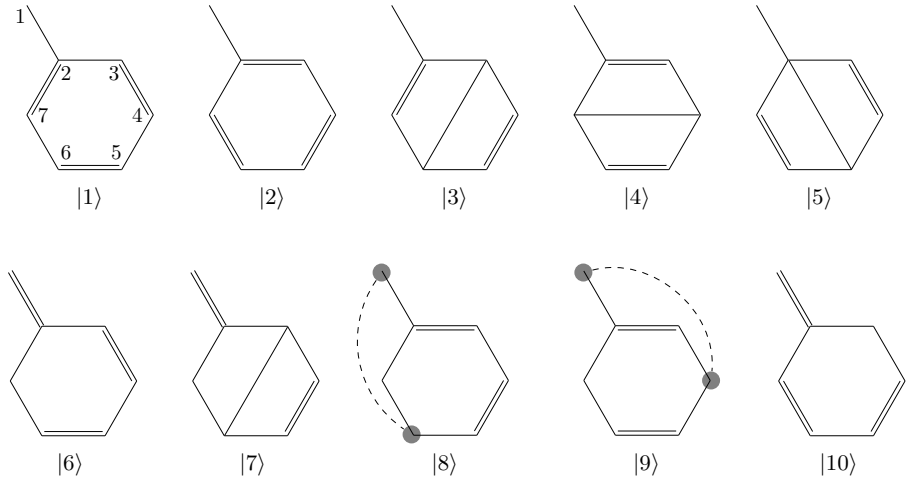
eigenvalues of the Hamiltonian which are found to be identical to the ones found from the 5×5 Hamiltonian constructed by the basis states in figure 8 using Eq. 28 (see Appendix B). Thus the ground state energy is found as

$$E_{\text{gs}} = -\frac{1}{2}\Big(4 + \sqrt{5}\Big)J$$

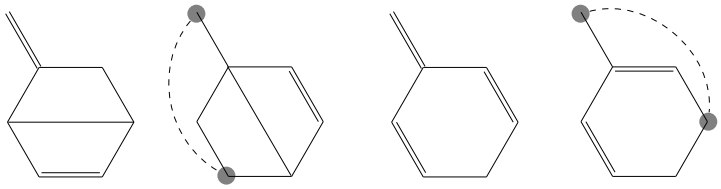
lowering the energy by $(\sqrt{5}/2)J \approx 1.18J$ compared to each basis state. We note that the ground state is doubly degenerate for $k = \pm 2\pi/5$. These two values of k correspond to the unpaired spin moving around the molecule with equal but opposite momentum. Not all too surprisingly these correspond to the same energy.

6.3 Benzyl

Molecules such as the pentagon and Benzene ring analyzed are not always found on their own. Benzene especially is often a small but vital part of a larger organic compound so it makes sense to study a molecule similar to Benzene but with an extra lattice site added outside one of the corners. This lattice is part of the benzyl group where an extra Carbon atom takes the place of one of the six Hydrogen atoms of Benzene and thus making room for more bonds and thereby a larger molecule. This seems like an innocuous change to the system, but actually makes quite a difference. As for odd numbers of electrons, the lowest spin state is a spin-$\frac{1}{2}$ doublet. For seven electrons fourteen possible spin-$\frac{1}{2}$ states are allowed with singlet bonds arranging themselves in all manners of different configurations and an unpaired spin placing itself at the remaining site. The fourteen doublet states are sketched below (note that five of them are the familiar Benzene singlets with the unpaired spin at site 1).

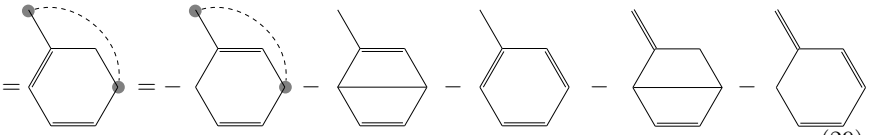


One noticeable thing about the basis is that the unpaired spin (now just symbolized by an unconnected site and not explicitly by an arrow) is always found on the odd numbered sites (see $|1\rangle$ for numeration) and all singlet bonds are between odd and even numbered sites, not just the nearest neighbor bonds. When acting on the basis states with the Hamiltonian, half of them are at least once (seemingly) brought out of the Hilbert space



$|11\rangle$ $|12\rangle$ $|13\rangle$ $|14\rangle$

but each of these new states can be shown to be linear combinations of the basis states using both linear linear dependences reviewed above – an example is provided below. We see that $\hat{p}_{72}\,|9\rangle$ creates the state below, which is the linear combination of basis states given in Eq. 29.

$-2\hat{p}_{72}\,|9\rangle =$  (29)

It is quite impressive that using just the two linear independences from figure 3 and 5 any singlet state can be expressed as linear combinations of our fourteen basis states. Having done this with all supposed out-of-basis states, the Hamiltonian can be expressed in matrix form (see Appendix C) and the ground state energy can be found as

$$E_{\text{gs}} = -4.7949J$$

thus lowering the energy slightly compared to the ground state of Benzene.
As for all lattices with odd-numbered sites there is an uncoupled spin. This motivates the question of spin density – i.e., what is the spin density of the benzyl ground state for a specific site? In each basis state one site carries the uncoupled spin, so naturally $S_i^z\,|j\rangle = 1/2\,|j\rangle$ if site i carries the uncoupled spin in $|j\rangle$, but for all other sites $|j\rangle$ is not an eigenstate of S_i^z. We want to answer the question: where *is* the spin in the ground state?

7 Ground state spin density

7.1 Benzyl spin density

The ground state is a linear combination of the fourteen basis states and each basis state carries the uncoupled spin at some fixed site but we want to know the weight with which each site carries the spin of the ground state, i.e. what is $\langle\psi_0|\,S_j^z\,|\psi_0\rangle$ for each site.

To begin with we only need to look at the states in figure 5 which provide a simple insight into how the spin operator works for larger radicals. For three sites two doublets and one quadruplet exist (see figure 6) – thus we have three states with total $S_z = \frac{1}{2}$:

$$|1/2,1/2\rangle^{(1)} = \frac{1}{\sqrt{2}}\left(|\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\uparrow\rangle\right), \quad |1/2,1/2\rangle^{(2)} = \frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\uparrow\rangle - |\uparrow\uparrow\downarrow\rangle\right) \tag{30a}$$

$$|3/2,1/2\rangle = S^- |\uparrow\uparrow\uparrow\rangle = \frac{1}{\sqrt{3}} \left(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle\right) \tag{30b}$$

We define the (unnormalized) state

$$|\psi\rangle = S_2^z \, |1/2,1/2\rangle^{(1)} = \frac{1}{2\sqrt{2}} \left(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle\right) \tag{31}$$

which can be written as a linear combination of the states in Eq. 30a and 30b

$$|\psi\rangle = \frac{1}{\sqrt{6}} \, |3/2,1/2\rangle - \frac{1}{6} \, |1/2,1/2\rangle^{(1)} - \frac{1}{3} \, |1/2,1/2\rangle^{(2)}$$

Measuring the spin of a site bound to another thus gives a quadruplet, the same doublet and another doublet – in the context of the Benzyl lattice studied above, if this other doublet carries the spin at an even numbered site we can write it as a linear combination of two allowed states – where the unpaired spin is at odd numbered sites. As not all basis states are eigenstates of S_j^z, the spin operators must be represented as matrices in the basis used for our Hamiltonian.
Calculating the spin density of each site in the ground state could be done with $\langle\psi_0| \, S_i^z \, |\psi_0\rangle$, but as our basis is not orthogonal we would prefer to calculate it without using the inner product (even normalizing the eigenstates requires using the inner product). Thus we need to derive an expression for the ground state expectation value of S_j^z. This can be done by considering the spin as a perturbation of the original Hamiltonian (i.e. if a magnetic field along the $\hat{z}$-axis were present).
We define α as a matrix where each is column is an (unnormalized) eigenstate of the Hamiltonian and β its inverse.

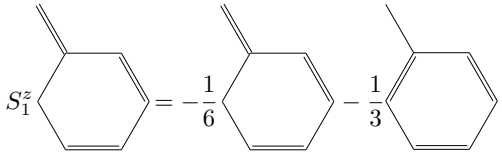
We know that $h\alpha_i = \varepsilon_i \alpha_i$ (ε_i is the eigenvalue corresponding to the i^{th} column, α_i and h is the matrix representation of the Hamiltonian in our basis) as well as $\beta_i h = \varepsilon_i \beta_i$ (an eigenvalue equation where h acts to the left), where β_i is the i^{th} *row* in β. If we now let $h \to h_0 + h_1$, where h_1 is the "perturbation", i.e. the matrix representation of S_j^z in the same basis, and $\alpha_i \to \alpha_i^{(0)} + \alpha_i^{(1)}$ and $\varepsilon_i \to \varepsilon_i^{(0)} + \varepsilon_i^{(1)}$, then to first order we get

$$h_0\alpha_i^{(1)} + h_1\alpha_i^{(0)} = \varepsilon_i^{(1)}\alpha_i^{(0)} + \varepsilon_i^{(0)}\alpha_i^{(1)} \Rightarrow \beta_i h_0 \alpha_i^{(1)} + \beta_i h_1 \alpha_i^{(0)} = \varepsilon_i^{(0)} \beta_i \alpha_i^{(1)} + \varepsilon_i^{(1)} \beta_i \alpha_i^{(0)}$$

The first term on each side cancels giving us the expression needed

$$\varepsilon_i^{(1)} = \langle\psi_i| \, S^z \, |\psi_i\rangle = \beta_i h_1 \alpha_i^{(0)} \tag{32}$$

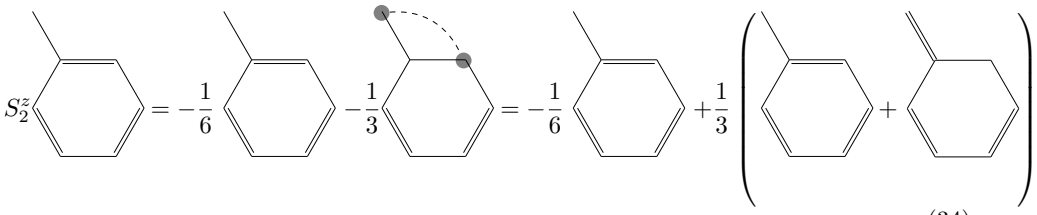
Equating how the spin operators act on the 3 site states above with how it acts on our basis is simple and two examples are given below – one where we measure the spin of an allowed (odd) site and on a forbidden (even) site.



(33)

Table 1

site	spin density
1	0.3254
2	−0.1614
3	0.2034
4	−0.1278
5	0.1849
6	−0.1278
7	0.2034



(34)

Knowing how the spin operators work on our basis states, we can write the matrix representation of S_j^z $(j = 1 \dots 7)$ and thereby, using Eq. 32, find the spin density of each site in the Benzyl ground state – the matrix representations are written in Appendix D. The results are given in table 1 and visualized in figure 12.

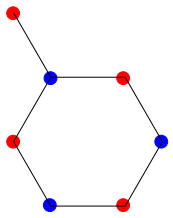
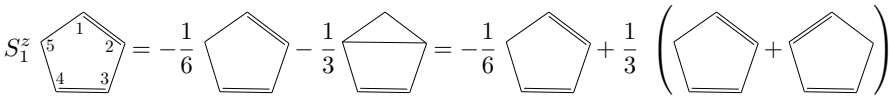


Figure 12: The sign of each site's spin density is here shown with either a red (+) or blue (-) dot.

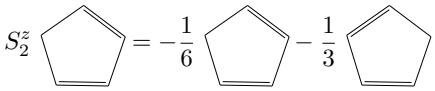
While the Hamiltonian in Eq. 15 clearly prefers an antiferromagnetic ground state, each Benzyl basis state only specifies that individual singlet bonds have opposite spins, not that every nearest neighbor couple has opposite spins. However these results confirm the antiferromagnetic coupling – on average, each site carries spin of opposite sign of its nearest neighbors' spin. This is possible due to the structure of the lattice – if site 1 had been placed among the rest of the sites, not each site would have opposite signed neighbors. For this reason it would be practical to return to the pentagonal lattice studied in section 6.2.

7.2 Pentagonal lattice spin density

The spin operators act on the basis states similarly



(35)



(36)

Eqs. 35 and 36 can be generalized as

$$S_n^z |n\rangle = \frac{1}{2} |n\rangle \tag{37a}$$

$$S_n^z |n \pm 1\rangle = \frac{1}{6} |n \pm 1\rangle + \frac{1}{3} |n \mp 1\rangle \tag{37b}$$

$$S_n^z |n \pm 2\rangle = -\frac{1}{6} |n \pm 2\rangle - \frac{1}{3} |n\rangle \tag{37c}$$

once again for cyclical n with $|n\rangle$ referring to the state with unpaired spin at site n. We calculate the spin density of each site of the two ground states using Eq. 32 and these are visualized in 13.

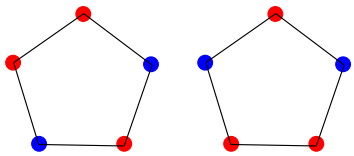


Figure 13: The sign of each site's spin density in the pentagonal lattice shown as before for the two ground states.

As suspected each ground state does not have perfect antiferromagnetic coupling. From the principle of superposition, any linear combination of the two ground states will naturally also be a ground state of the Hamiltonian.

7.2.1 The Jahn-Teller effect

The symmetry of a molecule such as the pentagonal lattice can be broken in order to reduce the energy of the system. The Jahn-Teller effect [3] states that any molecule with a degenerate groundstate will undergo a distortion that removes the degeneracy of the ground state. This corresponds to reducing the distance between two sites and thus the interaction J varies from nearest neighbor couple to nearest neighbor couple and the Hamiltonian becomes perturbed by the term

$$H' = -\Delta J \cos(n\Delta k + \phi) = -\Delta J \cos\left(\frac{4\pi}{5} n + \phi\right) \tag{38}$$

where $\Delta k = 4\pi/5$ is the difference between the two ground state Bloch waves of the unperturbed Hamiltonian and ϕ is a phase factor determining where this perturbation

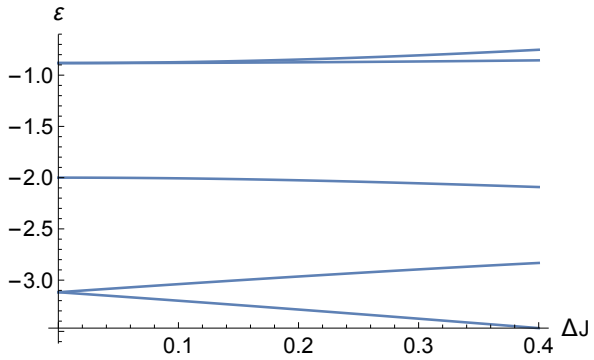


Figure 14: The perturbation of the eigenvalues of the Hamiltonian as a function of the parameter ΔJ.

starts. For $\phi = 0$ the perturbation is largest at $n = 5$ (whereever in the lattice that may be chosen to be). As seen in figure 14 the two ground state energies increase and decrease linearly with ΔJ.

J increases quadratically with t (which increases for smaller site-to-site separation) and for a given ΔJ the linearly decreasing perturbation and quadratically decreasing $-J$ will intersect at which point the minimum energy is found – this value of ΔJ is "chosen" by the molecule itself and the ground state is stable but not degenerate. The Jahn-Teller theorem states exactly this: stability and degeneracy of the ground state are not simultaneously possible.

8 Conclusion

In this thesis I have developed a model to analyze organic molecules using valence bond theory and a simple picture language. Having shown that the Hubbard model which acted on two subspaces of the Hilbert space could be reduced to two effective Hamiltonian's acting on each subspace, one of which was our primary focus. Using the formalism of second quantization and a neat method of counting the degeneracy of a spin state for a specific amount of electrons it was possible to set up two simple linear dependences of lattices with respectively three and four sites that were immensely useful in regards to larger compounds. The picture formalism gave us the means to understand how the Hamiltonian acts on basis states of different lattices and thus finding the ground state energies of three kinds of organic molecules. Using just a simple triangular lattice with three sites we understood how the spin operator S^z acts on free radicals allowing us to calculate the spin density of two of our lattices and understanding the kind of antiferromagnetic coupling existent in organic molecules.

9 References

[1] L. C. Pauling, *The Nature of the Chemical Bond.* Cornell University Press, 1960.
[2] C. Kittel, *Introduction to Solid State Physics.* John Wiley & Sons, 2014.

[3] S. Blundell, *Magnetism in Condensed Matter*. Oxford University Press, 2014.

Appendices

A Overlap of Benzene States

The quantum representation of the states in figure 7b and 7c are

$$\begin{aligned}|B\rangle &= S_{12}^{\dagger}S_{34}^{\dagger}S_{56}^{\dagger}\,|0\rangle \\ &= \frac{1}{\sqrt{8}}\left(|\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\rangle - |\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\uparrow\uparrow\downarrow\rangle - |\downarrow\uparrow\uparrow\downarrow\uparrow\downarrow\rangle + |\downarrow\uparrow\uparrow\downarrow\downarrow\uparrow\rangle - |\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\uparrow\downarrow\uparrow\rangle - |\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\rangle\right)\end{aligned} \tag{39}$$

$$\begin{aligned}|c\rangle &= S_{61}^{\dagger}S_{34}^{\dagger}S_{25}^{\dagger}\,|0\rangle \\ &= \frac{1}{\sqrt{8}}\left(|\downarrow\downarrow\uparrow\downarrow\uparrow\uparrow\rangle - |\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\rangle + |\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\downarrow\downarrow\uparrow\rangle + |\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\rangle + |\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\rangle - |\uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\rangle\right)\end{aligned} \tag{40}$$

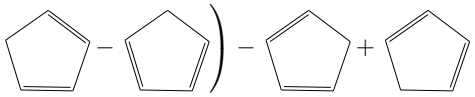
and indeed $\langle c|B\rangle = -\frac{1}{2}$

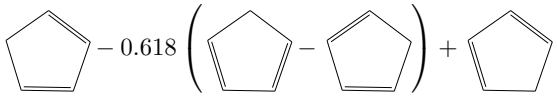
B Five-site Hamiltonian

The Hamiltonian matrix representation of the pentagonal lattice system is

$$h = J\begin{bmatrix} -2 & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -2 & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -2 & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -2 & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -2 \end{bmatrix} \tag{41}$$

In the picture formalism the (unnormalized) ground states can be presented as such

$|gs_1\rangle = 0.618$  (42)

$|gs_2\rangle = -$  (43)

C Benzyl Hamiltonian

Using the basis states for the Benzyl molecule the Hamiltonian can be expressed in matrix form:

$$h = J \begin{bmatrix}
-3 & 0 & 1 & 1 & 1 & \frac{1}{2} & 0 & 0 & -\frac{1}{2} & 0 & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\
0 & -3 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\frac{1}{2} & \frac{1}{2} & -2 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 \\
\frac{1}{2} & \frac{1}{2} & 0 & -2 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & 0 & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & 0 & 0 & 0 & 0 & -3 & 1 & 0 & \frac{1}{2} & 0 & 0 & \frac{1}{2} & 0 & 1 \\
0 & 0 & \frac{1}{2} & 0 & 0 & \frac{1}{2} & -2 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & \frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -5/2 & \frac{1}{2} & -\frac{1}{2} & 0 & 1 & 0 & \frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & \frac{1}{2} & -5/2 & 0 & -\frac{1}{2} & 0 & 0 & 1 \\
0 & \frac{1}{2} & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & -7/2 & 1 & 0 & \frac{1}{2} & \frac{1}{2} \\
0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{1}{2} & -5/2 & 0 & 0 & \frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & -3/2 & -\frac{1}{2} & \frac{1}{2} \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & \frac{1}{2} & 0 & -\frac{1}{2} & -7/2 & 3/2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & \frac{1}{2} & -2
\end{bmatrix} \tag{44}$$

and the (unnormalized) ground state is

$$\begin{aligned}
|\psi_0\rangle = &-5.36421\,|1\rangle - 2.84991\,|2\rangle + 2.534\,|3\rangle + 1.01969\,|4\rangle + 0.56151\,|5\rangle \\
&+1.73923\,|6\rangle - 0.182422\,|7\rangle + 1.51431\,|8\rangle - 1.51431\,|9\rangle + 4.25353\,|10\rangle \\
&-1.69673\,|11\rangle - |12\rangle - 4.07543\,|13\rangle + |14\rangle
\end{aligned} \tag{45}$$

D S^z Matrix Representation

The basis states are not eigenstates of all S^z operators, so in our calculation of each site's spin density we need to derive each site's spin operator's matrix representation.

$$s_1^z = \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} \\
0 & 0 & \frac{1}{2} & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & -\frac{1}{3} & 0 \\
0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6}
\end{bmatrix} \tag{46}$$

$$s_2^z = \begin{bmatrix}
\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & \frac{1}{3} & -\frac{1}{3} \\
\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} \\
0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & \frac{1}{3} & -\frac{1}{3} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6}
\end{bmatrix} \tag{47}$$

$$s_3^z = \begin{bmatrix}
\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & -\frac{1}{6} & \frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{2}{3} & 0 & \frac{1}{3} \\
0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
\frac{1}{3} & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} \\
\frac{1}{3} & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{6} & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\
0 & -\frac{1}{3} & \frac{1}{3} & 0 & \frac{1}{3} & 0 & -\frac{1}{3} & \frac{1}{3} & 0 & \frac{1}{2} & 0 & -\frac{1}{3} & -\frac{1}{3} & \frac{1}{3} \\
\frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & \frac{1}{3} & 0 & \frac{1}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{3} \\
0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{6}
\end{bmatrix} \tag{48}$$

$$s_4^z = \begin{bmatrix}
-\frac{1}{6} & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
0 & \frac{1}{6} & \frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{2}{3} & 0 & \frac{1}{3} \\
0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
-\frac{1}{3} & 0 & \frac{1}{3} & \frac{1}{6} & 0 & 0 & 0 & -\frac{1}{3} & \frac{1}{3} & 0 & 0 & \frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
-\frac{1}{3} & 0 & \frac{2}{3} & 0 & 0 & \frac{1}{6} & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & \frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
-\frac{1}{3} & 0 & \frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 & -\frac{1}{3} & \frac{1}{6} & 0 & 0 & \frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & \frac{1}{6} & 0 & \frac{1}{3} & \frac{1}{3} & 0 \\
-\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & \frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & \frac{1}{3} & 0 & \frac{1}{3} & \frac{1}{6} & 0 \\
0 & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & \frac{1}{6}
\end{bmatrix} \tag{49}$$

$$s_5^z = \begin{bmatrix}
\frac{1}{6} & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
0 & -\frac{1}{6} & -\frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} & \frac{1}{6} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{3} & 0 & -\frac{1}{3} & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
\frac{1}{3} & 0 & -\frac{2}{3} & 0 & 0 & -\frac{1}{6} & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & \frac{1}{3} & 0 & 0 \\
0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & -\frac{1}{6} & \frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 \\
\frac{1}{3} & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 \\
\frac{1}{3} & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & -\frac{1}{3} & \frac{1}{3} & 0 & 0 & -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} & \frac{1}{2} & 0 \\
0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{2}
\end{bmatrix} \tag{50}$$

$$s_6^z = \begin{bmatrix}
-\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{6} & -\frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 \\
-\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{3} & 0 \\
0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & \frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 \\
0 & \frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & \frac{1}{3} \\
0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & \frac{1}{6} & -\frac{1}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 \\
-\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 \\
-\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & \frac{1}{6} & 0 \\
0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{6}
\end{bmatrix} \tag{51}$$

$$s_7^z = \begin{bmatrix} -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & -\frac{1}{3} & 0 \\ 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & -\frac{1}{3} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} \end{bmatrix} \tag{52}$$