

Computation of Electronic Spectra of Molecules in Strong Magnetic Fields Using Linear Response of Hartree-Fock Theory

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requirements for the degree of

Master of Science

Declaration

I, **Rahul Raj K**(Roll No: 17MS202), hereby declare that this report entitled '**Computation of Electronic spectra of Molecules in Strong Magnetic Fields using Time-dependent Hartree-Fock Theory**' submitted to the Indian Institute of Science Education and Research Kolkata towards the partial requirement of **Master of Science in Chemical Sciences** is an original work carried out by me under the supervision of Dr.Sangita Sen and has not formed the basis for the award of any degree or diploma, in this or any other institution or university. I have sincerely tried to uphold academic ethics and honesty. Whenever any external information or statement, or result has been used, they have been duly acknowledged and cited.

Kolkata - 741246
May 2022

Rahul Raj K

CERTIFICATE

This is to certify that the thesis titled “Computation of Electronic Spectra of Molecules in Strong Magnetic Field using Linear Response of Hartree-Fock Theory”, submitted by Mr. Rahul Raj K (17MS202), a student of the Department of Chemical Sciences of the BS-MS Dual Degree Programme of IISER Kolkata is based upon his own research work under my supervision. I also certify, to the best of my knowledge, that neither the thesis nor any part of it has been submitted for any degree/diploma or any other academic award anywhere before. In my opinion, the thesis fulfills the requirement for the award of the degree of Master of Science.

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Dr.Sangita Sen

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Abstract

External magnetic fields can have an effect on the electronic structure of molecules when the field interaction strengths are comparable with Coulomb interactions. For small atoms/molecules, magnetic field strengths of around $235\text{ }kT$ or $1\text{ }au$ can alter the electronic spectra. In nature, white dwarfs and neutron stars have magnetic fields of this order. The observed electronic spectra available from white dwarf stars are strongly distorted by magnetic fields, and it is difficult to interpret them in connection with atomic and molecular structure. In this project, we compute the electronic spectra of molecules under a strong magnetic field using the random phase approximation (RPA), also known as the linear response of Hartree-Fock theory or time-dependent Hartree-Fock theory. Here our goal is not to accurately calculate the excitation energies but to understand the modification induced by the magnetic field compared to the zero-field case. The ground state is optimized in the presence of an external magnetic field, and the excited states are obtained via linear response. London atomic orbitals (LAOs) are employed to enforce gauge-origin invariance and accelerate basis set convergence. We also compute the spectral intensities in order to explore how the symmetric forbidden transitions become allowed in the presence of magnetic fields which lift this symmetry. We try to justify the changes in the electronic spectra at the level of orbital changes due to the magnetic field.

Chapter 1

Introduction

1.1 Electronic Structure Theory

Nature has always fascinated humans. This leads us to understand the universe. Since the discovery of the electron in 1896–1897 our great challenge was to understand the electronic structure of atoms/molecules in order to define the behavior of matter in the universe.

The fundamental basis for understanding materials and phenomena ultimately rests upon understanding the electronic structure, which means that we must deal with the interacting many-electron problem in diverse, realistic situations. The electronic structure of the hydrogen atom can be analytically solved. While the quantum theory is not necessary for all systems, it is the most fundamental approach we can adopt. Electronic structure theory describes the motion of electrons in atoms or molecules. For predicting the electronic structure of complex molecules, we use many approximation methods like Hartree-Fock(HF), density functional theory(DFT), coupled-cluster theory(CC), etc.,

The Hamiltonian for many-electron molecule in atomic units can be defined as

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.1)$$

Here M_A is the ratio of the mass of nucleus A to the mass of an electron, and Z_A is the atomic number of nucleus A. Laplacian operators ∇_i^2, ∇_A^2 involve differentiation with respect to the coordinates of the i^{th} electron and A^{th} nucleus. The first term in the equation. (1.1) is the operator for the kinetic energy of the electrons; the second term is the operator for the kinetic energy of nuclei; the third term represents the Coulomb attraction between electrons and nuclei; the fourth and fifth terms represent the repulsion between electrons and nuclei respectively.

Since electrons are so much lighter and therefore faster than nuclei, one can consider the electrons in a molecule to be moving in the field of fixed nuclei. This is known as the Born-Oppenheimer Approximation. So the term in equation (1.1), which represents the kinetic energy of the nuclei, is considered a constant, and adding a constant to the Hamiltonian operator only added to the eigenvalues and has no

effect on the eigenfunctions. The Electronic Hamiltonian describing the motion of N electrons in the field of M point charges can be defined as

$$\hat{H}_{elec} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (1.2)$$

The Schrodinger equation involving the electronic Hamiltonian,

$$\hat{H}_{elec} \Phi_{elec} = \epsilon_{elec} \Phi_{elec} \quad (1.3)$$

The approximations on the Hamiltonian, \hat{H}_{elec} and the wavefunction, Φ_{elec} necessary to make equation 1.3 solvable, albeit numerically, constitute the various electronic structure theories in use today. The electronic structure problem is then to solve. In this thesis, we have dealt with a simple orbital picture and thus used only the Hartree-Fock Theory.

1.1.1 Hartree-Fock Theory

In computational physics and chemistry, the Hartree–Fock (HF) method is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state. The Hartree–Fock method often assumes that the exact N-body wave function of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons) of N spin-orbitals. Spin orbitals are obtained by solving the Hartree-Fock equation(equation(1.4)), which involves an effective one-body operator called the Fock operator in lieu of the many-body Hamiltonian(equation(1.2)). By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree–Fock wave function and energy of the system.

Hartree-Fock equation is

$$f(x_1)X_i(x_1) = \epsilon_i X_i(x_1) \quad (1.4)$$

Where $f(x_1)$ is the fock operator. The Fock operator can be separated into a true-one electron part, $h(x_1)$ and effective one electron operator J (Coloumb) and K (Exchange)

$$f(x_1) = h(x_1) + \sum_j J_j(x_1) - K_j(x_1) \quad (1.5)$$

After expanding each spin orbital in a basis, the Hartree-Fock Roothan equation is obtained. And Hartree-Fock Roothan equation is defined as

$$\sum_{\nu} F_{\nu\mu} C_{\nu i} = \sum_i \sum_{\nu} S_{\nu\mu} C_{\nu i} \quad (1.6)$$

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (1.7)$$

where S is an overlap matrix of basis function, $C_{\nu i}$ are the basis coefficient of molecular orbital i and ϵ is the diagonal matrix of the orbital energy ϵ_i

Here we use Linear response of hartree-fock to calculate the excitation energies.

1.2 In the presence of a Magnetic Field

1.2.1 Electronic Hamiltonian in Magnetic Field

When a molecule is placed in an external magnetic field B associated with a vector potential A such that $\vec{B} = \vec{\nabla} \times \vec{A}$, the kinetic energy term is modified. In the presence of an additional scalar potential ϕ , we get

$$\hat{\mathcal{H}} = \frac{\pi^2}{2m} - e\phi \quad (1.8)$$

Where $\pi = p + eA$

$$p = -i\hbar\nabla + eA \quad (1.9)$$

Here we assume coloumb gauge

$$\nabla A = 0$$

Now proceeding,

$$\hat{\mathcal{H}}\Psi = \left\{ \frac{\pi^2}{2m} - e\phi \right\} \Psi \quad (1.10)$$

$$\pi^2\Psi = (p + eA)(p + eA)\Psi \quad (1.11)$$

$$= p^2\Psi + eAp\Psi + epA\Psi + e^2A^2\Psi \quad (1.12)$$

$$= p^2\Psi + eA(p\Psi) + e(pA)\Psi + eA.(p\Psi) + e^2A^2\Psi \quad (1.13)$$

$$= p^2\Psi + 2eA(P\Psi) + e(p.A)\Psi + e^2A^2\Psi \quad (1.14)$$

$$= p^2\Psi + 2e(A.p)\Psi + e^2A^2\Psi \quad (1.15)$$

Substituting equation (1.7) in (1.1) and including potential energy terms

$$\hat{\mathcal{H}} = \underbrace{\sum_{i=1}^{N_{el}} \frac{1}{2m} p_i^2}_1 - \underbrace{\frac{e^2}{4\pi\epsilon} \sum_{k,i} \frac{Z_k}{r_{ik}}}_2 + \underbrace{\frac{e^2}{4\pi\epsilon} \sum_{i>j} \sum_j \frac{1}{r_{ij}}}_3 - \underbrace{e \sum_i \phi_i}_4 + \underbrace{\sum_i \frac{e}{m} (A_i p_i)}_5 + \underbrace{\frac{e^2}{2m} \Psi_i A_i^2}_6 + \underbrace{B.S}_7 \quad (1.16)$$

Here this terms represents

$i, j \rightarrow$ electron index

$k \rightarrow$ Nuclei index

$r_{ik} \rightarrow$ electron i & nucleus k 's distance

$r_{ij} \rightarrow$ electron i & j 's distance

1 → Kinetic energy of electrons

2 → Electron nuclei attraction

3 → Electron-Electron repulsion

4 → Interaction of electron with scalar potential

5 → Electron interaction on the vector potential at it's own position.(That is why i on the vector potential also), i.e., paramagnetic interaction

6 → Interaction with electron with square of vector potential, i.e., diamagnetic interaction

7 → Interaction of electron spin and Magnetic field

Separating the magnetic terms we get:[6]

$$\hat{H} = \hat{H}_0 + \underbrace{\mathbf{A}_{tot}(\mathbf{r}) \cdot \hat{\mathbf{p}}}_{\text{Orbital Paramagnetic}} - \underbrace{\mathbf{B}_{tot}(\mathbf{r}) \cdot \hat{\mathbf{S}}}_{\text{Spin Paramagnetic}} + \underbrace{\frac{1}{2} A_{tot}(\mathbf{r})^2}_{\text{Diamagnetic}} \quad (1.17)$$

Here $\mathbf{B} \cdot \mathbf{S}$ represents the **spin-Zeeman** interaction and in the Coulomb gauge vector potential, $\mathbf{A}_{tot}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{g})$. Simplifying equation (1.18) only in Z-direction we get the final \hat{H} as equation(1.17). Here $\frac{1}{2}\mathbf{B} \cdot \mathbf{L}_0$ comes from $\mathbf{A}_{tot}(\mathbf{r}) \cdot \mathbf{p}$ and is called the **orbital-Zeeman** interaction, where \mathbf{L}_0 is orbital angular momentum.

Electrons interact with a magnetic field by virtue of their orbital motion, which is called the orbital-Zeeman effect, as well as due to their spin, which is called the spin-Zeeman effect. In this section, we focus on a one-electron system to highlight some crucial aspects of these interactions. The one-electron molecular Hamiltonian in the absence of a magnetic field (a.u.):

$$H_0 = \frac{1}{2}p^2 + V, \quad p = -i\nabla$$

In a magnetic field, $\mathbf{B} = \nabla \times \mathbf{A}$, the kinetic-energy operator is modified and spin added:

$$H = \frac{1}{2}(p + A) \cdot (p + A) - B \cdot S + V$$

For a uniform magnetic field in the z direction, expansion of the kinetic energy gives:

$$H = H_0 - \frac{1}{2}BL_z + BS_z + \frac{1}{8}B^2(x^2 + y^2) \quad (1.18)$$

where $L_z = xp_y - yp_x$ can be identified as the orbital angular momentum. The paramagnetic Zeeman terms BL_z and BS_z split three components of the energy levels depending on L_z and S_z values of the state. The Quadratic term in equation(1.17) is the diamagnetic term, which always raises the energy. To exist in the lowest energy state, $x^2 + y^2$ is minimized to reduce the energy. So atoms become squeezed in that plane. This can be seen in the He atom in figure 1.1, where figure 1.1a is the $1s$ orbital when the magnetic field is zero, and it is spherical. But when we are applying a magnetic field in the X-direction, the spherical orbital becomes elongated in the X-direction.

$$\hat{H} = \frac{1}{2}\hat{\pi}^2 - v(\mathbf{r}) + \frac{1}{r} + \mathbf{B}_{tot}(\mathbf{r}) \cdot \hat{\mathbf{S}}; \quad \hat{\pi} = \hat{\mathbf{p}} + \mathbf{A}_{tot}(\mathbf{r})$$

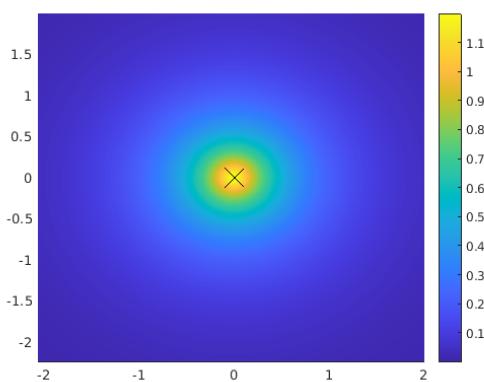
1.2.2 Gauge origin invariance

Non-relativistic molecular Hamiltonian in a magnetic field is defined as

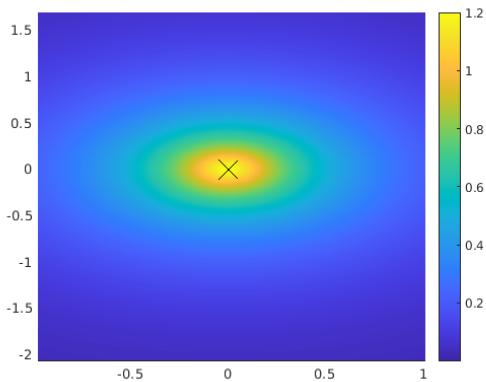
$$H = H_0 + \mathbf{A}(\mathbf{r}) \cdot \mathbf{p} + \mathbf{B}(\mathbf{r}) \cdot \mathbf{s} + \frac{1}{2}\mathbf{A}(\mathbf{r})^2$$

Now Vector potential of a uniform field, \mathbf{B} is given by:

$$\mathbf{B} = \nabla \times \mathbf{A} = const \Rightarrow \mathbf{A}_o(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_O$$



(a) He orbital $1s$ with $B=0$



(b) He orbital $1s$ with $B=0.1$ au along X-axis

Figure 1.1: He $1s$ orbital symmetry changes with applying magentic field along X-axis

The **gauge origin**, \mathbf{O} , is **arbitrary** ! A change of origin is a gauge transformation. A general gauge transformation can be written as:[1],[4]

$$\mathbf{A}' = \mathbf{A} + \nabla f, \quad \phi' = \phi - \frac{\partial f}{\partial t}$$

This is equivalent to a unitary transformation of $(H - i\partial/\partial t)$ and to continue to satisfy the Schrödinger equation, $\psi' \Rightarrow \psi$.

$$(H' - i\frac{\partial}{\partial t}) = e^{-if}(H - i\frac{\partial}{\partial t})e^{if}, \quad \psi' = e^{-if}\psi$$

From this transformation all **observables** remain unchanged.

London Atomic Orbital(LAO_s)

Since Gauge origin is arbitrary both energy and wavefunction is dependent on Gauge origin. in order to make this gauge invariant we can use London Atomic Orbitals. It is of the form [2][6]

$$W_{lm}(r_k, B, G) = e^{\frac{i}{2}[B \times (G - k)] \cdot r} \chi_{lm}(r_k)$$

Choices of gauge origin (\mathbf{O} or \mathbf{G}) for the external vector potential are related by gauge transformations:

$$\mathbf{A}_G(\mathbf{r}) = \mathbf{A}_O(\mathbf{r}) - \mathbf{A}_O(\mathbf{G}) = \mathbf{A}_O(\mathbf{r}) + \nabla f, \quad f(\mathbf{r}) = -\mathbf{A}_O(\mathbf{G}) \cdot \mathbf{r}$$

The exact wave-function transforms accordingly as:

$$\psi_G^{exact} = e^{-if(\mathbf{r})} \psi_O^{exact} = e^{i\mathbf{A}_O(\mathbf{G}) \cdot \mathbf{r}} \psi_O^{exact} = e^{i\frac{1}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{O}) \cdot \mathbf{r}} \psi_O^{exact}$$

This behaviour can be built into the atomic orbitals (AO)s. Each AO responds correctly to the applied magnetic field and this type of transformed **AOs** Called **London** orbitals or **GIAOs** (Gauge Including AOs)

1.2.3 Hartree-Fock theory in magnetic field

When the orbital becomes complex, if there is a uniform magnetic field, correct flavor would be to use Unrestricted Hartree-Fock (UHF). If this was done using Restricted Hartree-Fock (RHF), then we only get orbital-Zeeman interaction. If it's a non-uniform magnetic field, this was done by general Hartree-Fock (GHF). Each orbital is associated with mixed spin wavefunction.

RHF is used for closed-shell systems, and its common spatial orbital is associated with a pair of α and β spin functions. And it is not suitable for Spin-Zeeman interaction. For UHF, it is used for an open-shell system, and the spatial parts have the freedom to be different. There is spin breaking that occurs, so the operator S^2 is not conserved due to spurious spin breaking, whereas S_z conserved. This is suitable for the calculation of Spin-Zeeman in uniform \mathbf{B} . In the case of GHF, it's used when the system is open, and its Orbitals are not factorizable into spatial and spin parts. This is suitable for Spin-Zeeman in all \mathbf{B} .

Chapter 2

Electronic Excitation in a Magnetic Field

In this chapter, we use a simple methodology to compute singly excited states of closed-shell systems using linear response theory for a Hartree-Fock function. Linear response is a framework that is generally applied to compute the properties of a system. The simplest application of linear response is the computation of excitation energies which we shall use in our project. Our goal is to identify and understand the modulation of electronic excitation energies by a strong external magnetic field. While excitation energies are notoriously sensitive to electron correlation and require high levels of theory to reproduce accurately, the qualitative changes caused by the magnetic fields are relatively insensitive. We have thus chosen this simple approach for our initial exploration.

2.1 Linear Response of Hartree-Fock Theory

Here our goal is to calculate the properties of a system when there is a perturbation, whether time-independent or dependent. Perturbation theory is the most straightforward way to approach this problem. Response theory is a general approach equally applicable to classical and quantum systems that is closely related to perturbation theory but follows a different language rooted in classical mechanics as developed by Kubo (REF). When the external perturbation is small enough such that the change in the wavefunction of the system is linear with respect to the perturbation strength, the theory is called linear response theory. In the case of time-dependent perturbations, one may understand this in the frequency domain. If the system starts oscillating with frequency, ω under a perturbation of frequency ω - this would constitute a linear response of the system.

In this report, we use linear response theory to compute excitation energies which are basically the poles of the response function and independent of the strength of the perturbation. Thus, it is sufficient to restrict our theoretical development to a time-independent framework. While it is not the traditional way to derive linear response, the implementation we have used in our computations (REF) is based on the working equations derived herein.

Time independent formulation of Linear Response Theory

Let $|gs\rangle \rightarrow$ Exact ground state,

$\hat{X} \rightarrow$ Excitation Operator,
 $\hat{X}|gs\rangle \rightarrow$ Exact excited state
 $E_{ai} \rightarrow$ Excitation operator from state i to a

$$\hat{H}|gs\rangle = E_0|gs\rangle$$

$$\langle gs|\hat{H} = E_0\langle gs|$$

$$\langle gs|\hat{H}\hat{E}_{ai}|X\rangle = E_0\langle gs|\hat{H}|X\rangle \quad (2.1)$$

$$\hat{H}\hat{X}|gs\rangle = E_x\hat{X}|gs\rangle$$

$$\hat{H}|X\rangle = E_x|X\rangle$$

$$E_{ai}\hat{H}|X\rangle = E_xE_{ai}|X\rangle$$

$$\langle gs|\hat{E}_{ai}\hat{H}|X\rangle = E_x\langle gs|\hat{E}_{ai}|X\rangle \quad (2.2)$$

equation (2.2)-equation(2.1) \implies

$$\langle gs|[\hat{E}_{ai}, \hat{H}]|X\rangle = (E_x - E_0)\langle gs|\hat{E}_{ai}|X\rangle$$

$$\langle gs|[\hat{E}_{ai}, \hat{H}]|X\rangle = \omega\langle gs|\hat{E}_{ai}|X\rangle$$

where $\hbar = 1$

$$\langle gs|[\hat{E}_{ai}, \hat{H}]\hat{X}|gs\rangle = \omega\langle gs|\hat{E}_{ai}\hat{X}|gs\rangle$$

Now,

$$\langle gs|\hat{X} = \langle X^\dagger gs| = 0$$

\therefore subtracting $\langle gs|\hat{X}[\hat{E}_{ai}, \hat{H}]|gs\rangle$ from LHS and $\langle gs|\hat{X}\hat{E}_{ai}|gs\rangle$ from RHS we get,

$$\langle gs|[[\hat{E}_{ai}, \hat{H}], \hat{X}]|gs\rangle = \omega\langle gs|[\hat{E}_{ai}, \hat{X}]|gs\rangle \quad \forall a, i \quad (2.3)$$

Equation(2.3) can be regarded as the equation for computing the excitation energy w . To obtain the working equation for RPA we make the following approximations.

- Replace exact ground state with Hartree-Fock ground state
 $|gs\rangle \rightarrow |HF\rangle$
- \hat{X} as single excitation operator
 $\hat{X} \rightarrow \hat{Y} + \hat{Z}$
 where $\hat{Y} \rightarrow$ Single excitation operator & $\hat{Z} \rightarrow$ Single de-excitation operator
- If $\hat{X} = \hat{Y}$ Then this is called Tamm-Dancoff approximation (TDA)

2.2 Computation using London

2.2.1 Procedure

The HF linear response method, as outlined above, is implemented in the London program package(REF). London was the first (REF) quantum chemistry software developed for the direct computation of molecules in an external magnetic field. A sample input file is reproduced below. This particular input file initiates a UHF computation of H_2O ground state and the five lowest excitation energies. The HF computation is followed by a response calculation.

```
1 scf{
2     spin-symmetry-constraint = Restricted Hartree-Fock
3     linear-dependence-tol = 1e-10
4     uhf-spin-projection = 0
5     disable-spin-zeeman-in-fock-matrix = no
6     noisy-init-guess = no
7     min-scf-iterations = 0
8     max-scf-iterations = 160
9     use-density-fitting = no
10    use-admm = no
11    analyze-using-dft-grid = no
12
13    diis{
14        convergence-tolerance = 1e-10
15        subspace-dimension = 7
16        diagonalization-temperature = 0
17    }
18 }
19
20 rsp{
21     number-of-roots-requested = 5
22     root-selection-method = energy
23     excitation-basis = MObasis
24     starting-guess = UnitGuess
25     solver_choice = GenEig
26     precondition = false
27     initial-subspace-dimension = 100
28     maximum-subspace-dimension = 800
29     convergence-tolerance = 1e-10
30     max-rsp-iterations = 200
31 }
32
33
34 system{
35     molecular-charge = 0
36     correlation-model = rsp
37
38     hamiltonian{
39         electron-mass = 1
40         speed-of-light = 137.036
41         adiabatic-connection-lambda = 1
42         nuclear-charge-distribution = point charge
43
44         magnetic-field = (0, 0, 1.0)
45         gauge-origin = (0, 0, 0.1173)
46 }
```

```

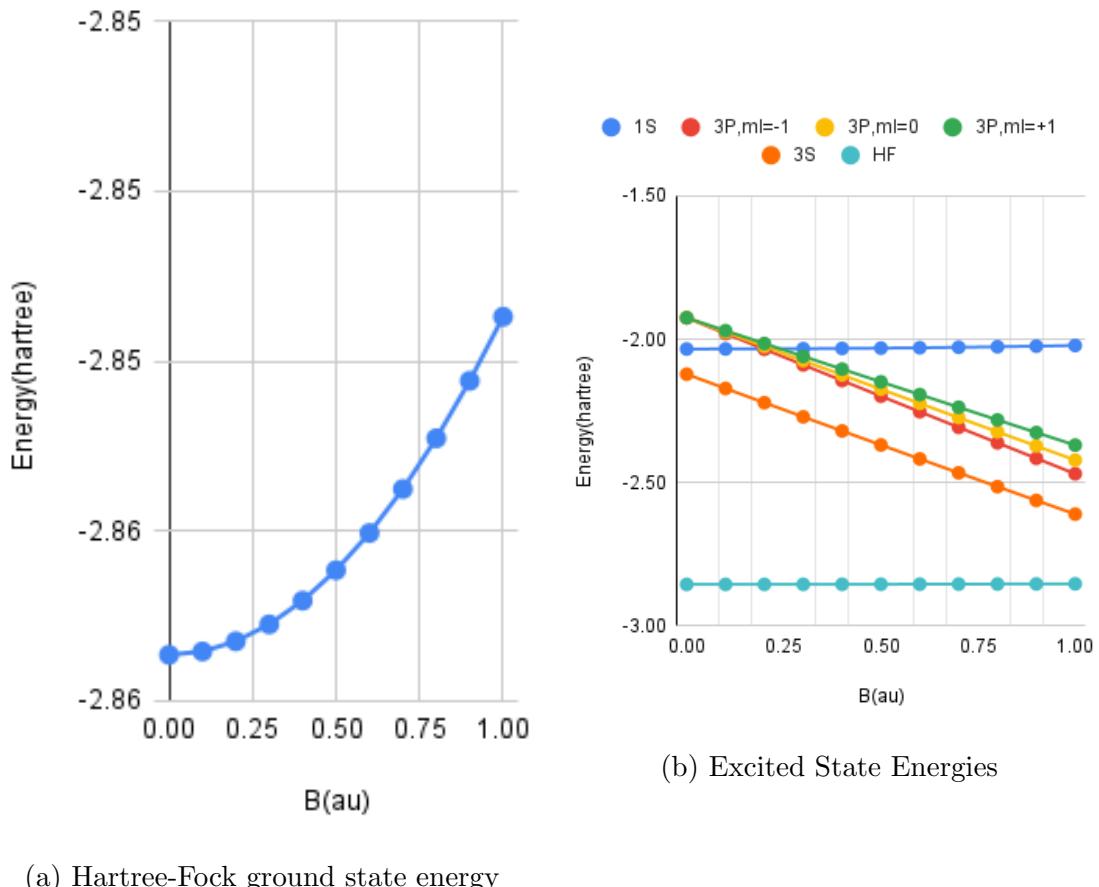
47     linear-magnetic-field = {(0.0, 0, 0), (0, 0, 0), (0, 0, 0)}
48     linear-magnetic-origin = (0, 0, 0)
49
50     electric-field = (0, 0, 0)
51     electric-origin = (0, 0, 0)
52     linear-electric-field = {(0, 0, 0), (0, 0, 0), (0, 0, 0)}
53
54
55 # data on state flags lost, output incomplete here
56 use-london-orbitals = yes
57 gto-contraction-type = normalized primitive
58 basis = aug-cc-pVDZ
59 # geometry
60 charge = 1.0
61 H 0.3707 0.0000 0.0000
62 H -0.3707 0.0000 0.0000
63 }
64 }
```

Listing 2.1: London input file of H_2 molecule with magnetic field

2.3 Results and Discussions

As discussed earlier, magnetic fields have multiple effects on electronic states depending on their L and S value, as well as the relative orientation of the field and the atom/molecule. We have chosen three representative systems with decreasing symmetry to elucidate these effects. In this chapter, we study the energy changes. The effects on the intensity of the excitation will be studied in chapter 3. We compute a few of the lowest singly excited states in each illustrative case using the HF linear response method as described in chapter 2.

2.3.1 He atom



(a) Hartree-Fock ground state energy

Figure 2.1: Variation of the electronic states of He atom placed in strong magnetic field

The *He* atom is the smallest closed-shell atom. We take it as an example of a spherically symmetric system. In this case, we carry out the unrestricted HF(UHF) ground state computation followed by a linear response. Due to the unrestricted nature of the excitation operators, we can access the singlet and triplet manifold of excited states. The aug-ccpVDZ basis is used. Since He is spherically symmetric, applying the magnetic field direction doesn't matter. Operationally we are considering the magnetic field along X direction with a strength range from 0 to 1 au. Since it is a two-electron system and electron nuclei interaction is more, we need

high magnetic field strength to perturb the system. That is why we use magnetic field strength up to 1 au. The figure 2.1a is the Hartree-Fock ground state energy varying with the strong magnetic field. Excited-state energies are computed by adding the computed excitation energy to the HF ground state value at each field strength. These are plotted in the figure 2.1b. 3S , the first excited state, which is singly degenerate and thus doesn't split under a strong magnetic field. Similarly, 1S is also not degenerate. The effect of the Spin-Zeeman term is clearly visible on the 3S state, which dips in the magnetic field and dominates the diamagnetic term. On the other hand, in the absence of any paramagnetic interaction 1S curves parabolically up under He quadratic diamagnetic term. For the case of $^3P, ml=-1, ^3P, ml=0, ^3P, ml=+1$ while $B=0$ their energies are same but on applying the magnetic field three different energies are obtained for $m_l = -1, 0, 1$ on account of He Orbital-Zeeman term. In addition to the Spin-Zeeman term lowering the energy of the three 3P states the Orbital-Zeeman term causes additional lowering of $^3P, ml=-1$, raises $^3P, ml=+1$ and doesn't affect $^3P, ml=0$. In figure 2.1b we can see that the energy of some states increase, including the initial ground state(HF) (Figure2.1a) and some decrease resulting in multiple crossings of the energy states with increasing magnetic field strength. In the figure 4.14which reproduces from (KEF) we see that after a while, one of the excited states with paramagnetic property will cross with the ground state and become the new ground state at a certain magnetic field. This crossing point is sensitive to the basis set and electron correlation. Our computations in figure (2.1) in aug-cc-pVDZ basis indicates a crossing at $B > 1$ au while similar computations in aug-cc-pCVQZ basis in figure 4.14 shows a crossing at $B \approx 0.48$ au.

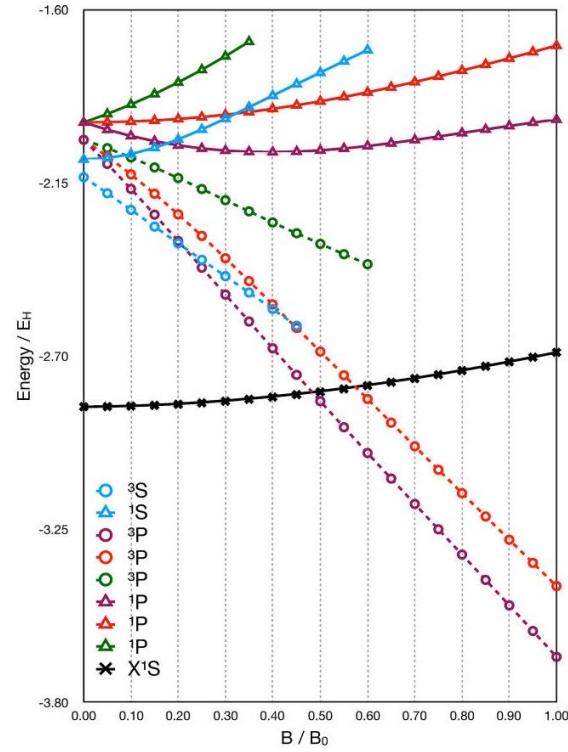


Figure 2.2: Spectrum of the He atom subject to uniform magnetic fields. The ground and excited states are computed using Hartree-Fock (GHF) and RPA, respectively, with the Luug-cc-pCVQZ basis [5]

2.3.2 H_2 Molecule

The H_2 molecule is taken as a representative molecule for homonuclear diatomics. The molecule has a centre of symmetry and belongs to the $D_{\infty h}$ point group. Two relative orientations of the field are possible - Parallel and perpendicular to the bond axis (taken as X-axis here).

We have carried out RHF calculations on H_2 followed by linear response using spin restricted/conserving excitation operators. Thus we have accessed only the singlet manifold of excited states subject only to the orbital-zeeman effect. For the case of H_2 molecule in figure 2.3 and figure 2.4, HF is the Hartree-Fock ground state. In the presence of strong magnetic field the state shows increase in energy. Beyond a certain value of magnetic field strength the ground state will cross with one of the excited state that excites state will become the new ground state. From the figure we can see that by applying the magnetic field irrespective of the direction in which it applied, the states becomes degenerate and formed two doubly degenerate state of H_2 molecule. When the field direction is in the X-axis (figure 2.3) is parallel to the bonds one of the doubly degenerate π states of Π_u symmetry initially decreases in energy and crosses two Σ states. $1\Sigma_g$ cross with $1\Sigma_u$ becomes the third excited state.

When the field direction is in Z-axis figure (2.4), the one of the doubly degenerate π state which is Π_u initially decrease in energy and cross with Σ_g state of H_2 molecule. With increasing magnetic field state energies of every level eventually starts increasing as the term quadratic in vector potential, A^2 , starts to dominate. This is called the quadratic Zeeman effect.

2.3.3 H_2O as an Illustrative case

Since H_2O is a larger molecule than the two previous examples, the effect of the magnetic field can be seen with weak fields. Here we take 10 points between [0,0,1] au. We carried out UHF calculations followed by the linear response with the excitation operator, which allows spin-flipping. Thus, a single excitation manifold involving both singlet and triplet states is obtained.

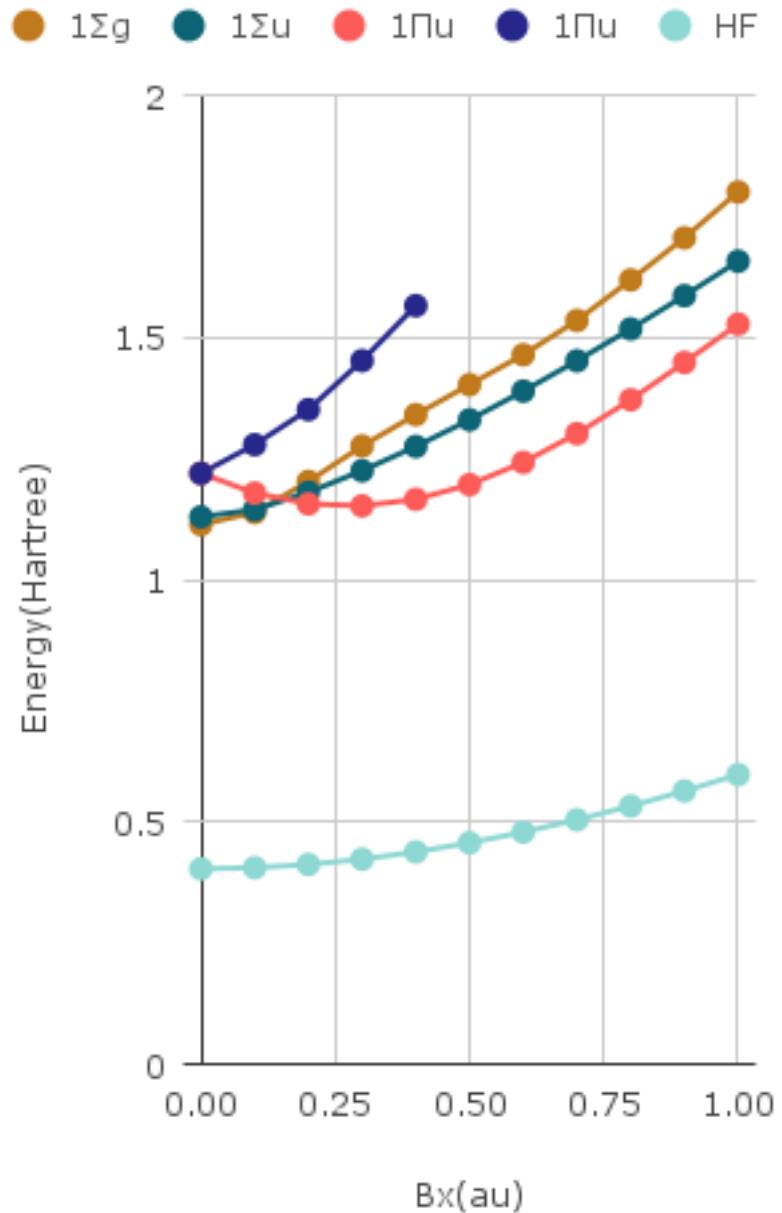


Figure 2.3: Spectrum of the H_2 molecule subject to uniform magnetic fields in X-direction parallel to the bond with the position coordinates of H atoms are in $(-0.1643, 0, 0), (0.1643, 0, 0)$. The ground and singlet excited states are computed using Hartree-Fock (RHF) and RPA respectively with the aug-cc-pVDZ basis

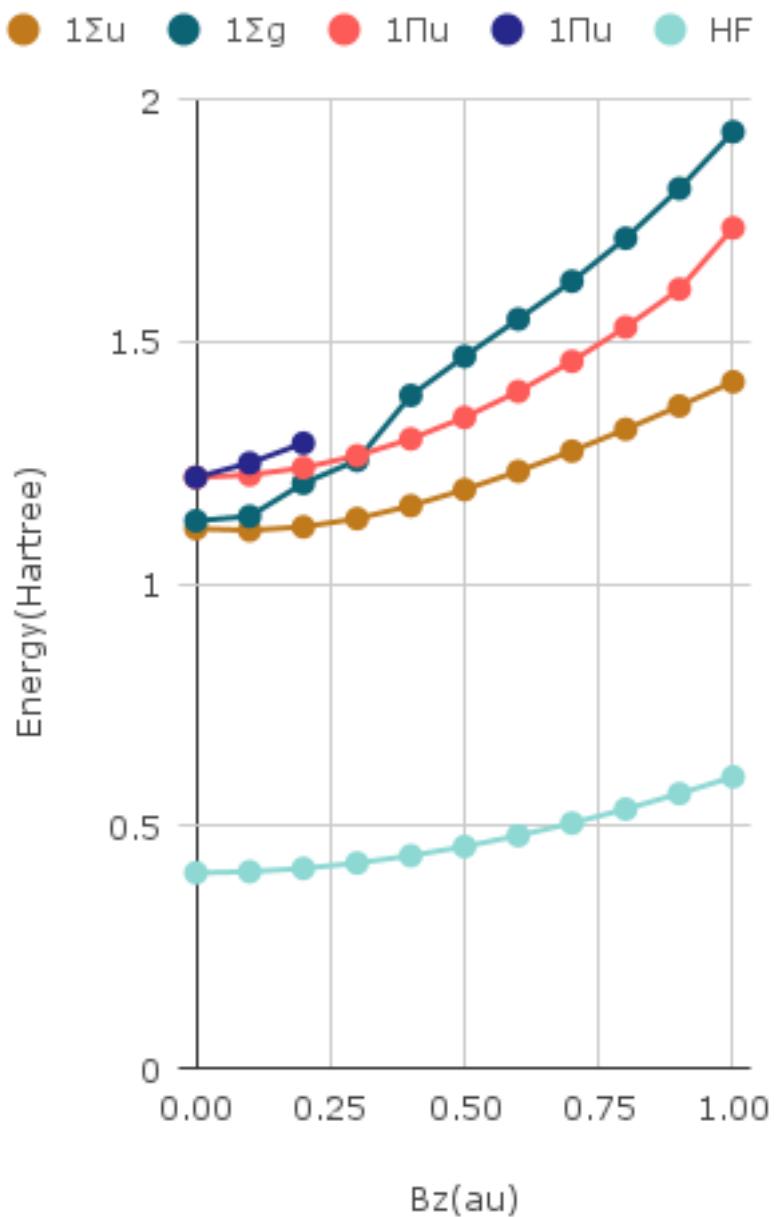


Figure 2.4: Spectrum of the H_2 molecule subject to uniform magnetic field in Z-direction perpendicular to the bond with the position coordinates of H atoms are at $(-0.1643, 0, 0), (0.1643, 0, 0)$. The ground and singlet excited states are computed using Hartree-Fock (RHF) and RPA respectively with the aug-cc-pVDZ basis

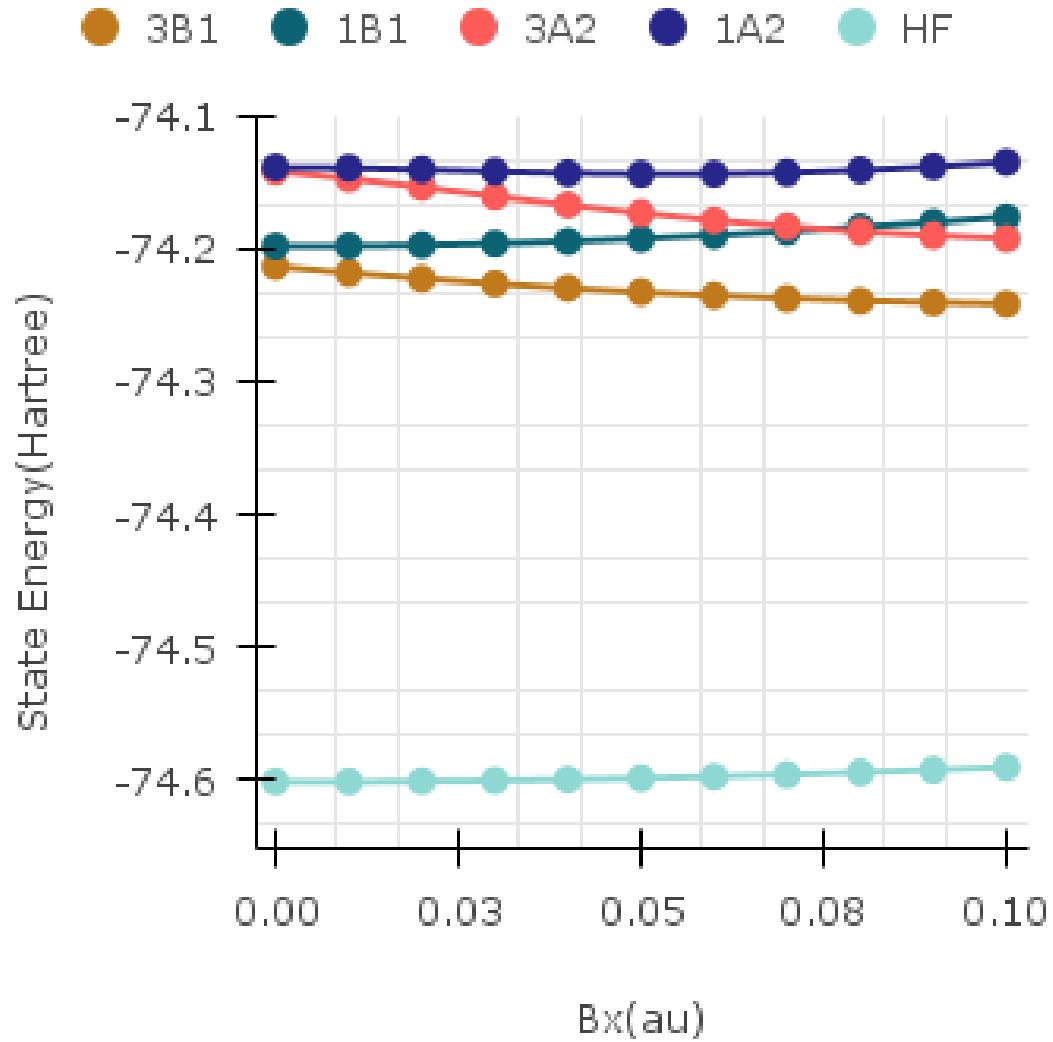


Figure 2.5: Four lowest state energies of H_2O Molecule in a YZ-plane and having Z-axis as C_{2v} axis of symmetry plotted against B_X using basis aug-cc-pVDZ. X-axis represents Magnetic field along the X-axis represents state Energy

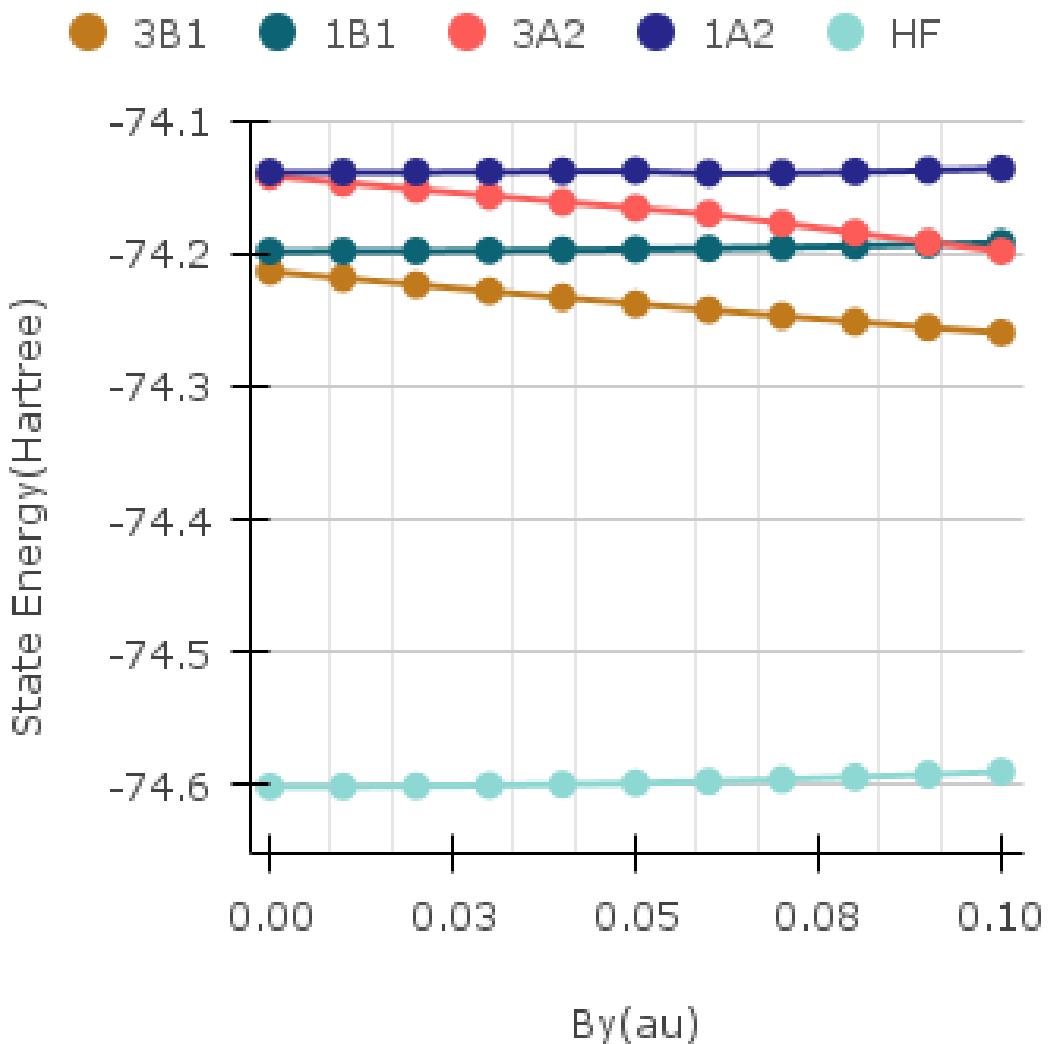


Figure 2.6: Four lowest state energies of H_2O Molecule in a YZ-plane and having Z-axis as C_{2v} axis of symmetry plotted against B_Y using basis aug-cc-pVDZ. X-axis represents Magnetic field along the Y-axis represents state Energy

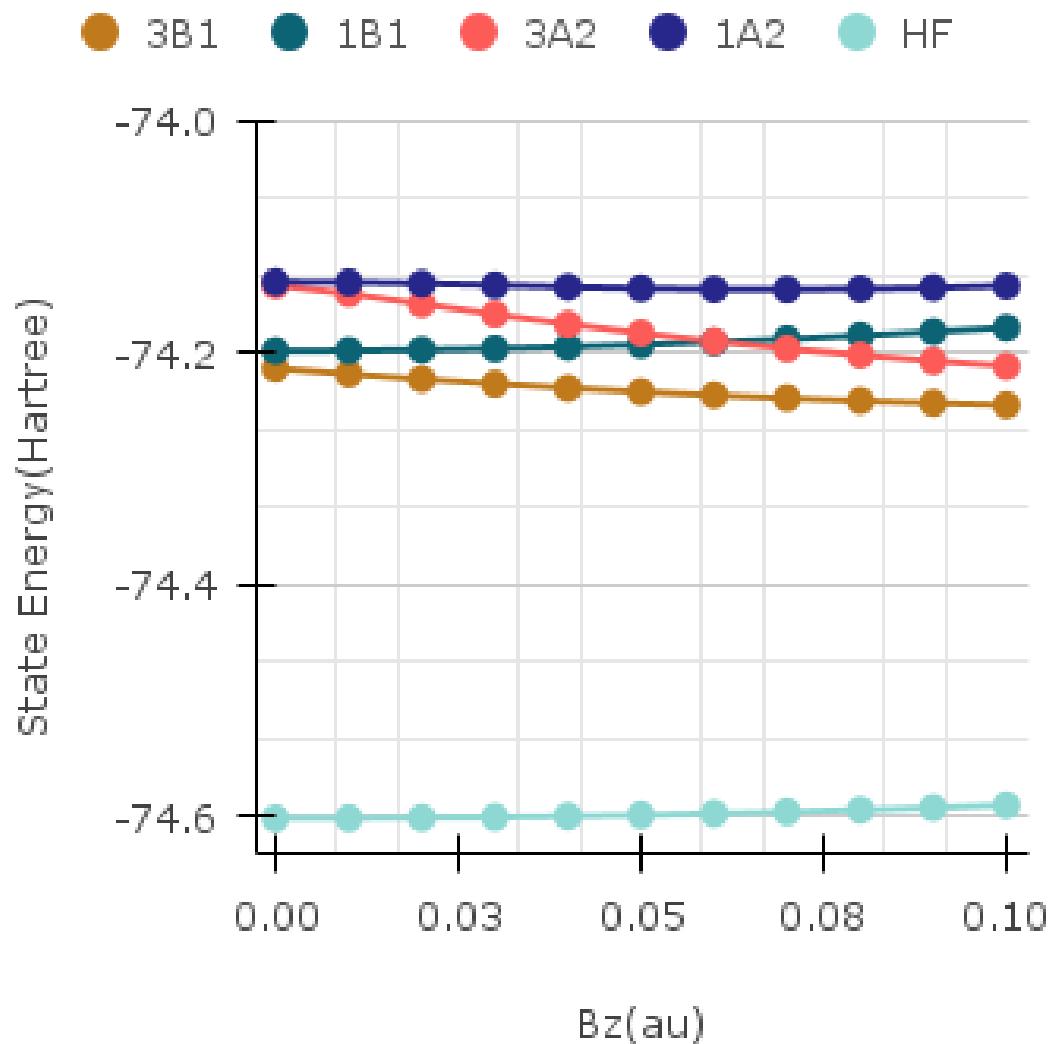


Figure 2.7: Four lowest state energies of H_2O Molecule in a YZ-plane and having Z-axis as C_{2v} axis of symmetry plotted against B_Z using basis aug-cc-pVDZ. X-axis represents Magnetic field along the Z-axis represents state Energy

H_2O is taken to have the σ_v plane as YZ-plane and Z-axis as the C_2 axis. We apply the magnetic field in three separate axes and determine the changes. All three directions are in-equivalent for H_2O . H_2O ground state is diamagnetic for all directions of the field but to different extents. Experiments typically yield vibrationally and rotationally averaged values that do not reflect directionality. The lowest singlet excited state, 1B_1 , is also diamagnetically for all directions of the field. The 1A_2 state shows interesting behavior. For all directions of the field, it shows an initial paramagnetic response that must arise from the orbital Zeeman interaction. Eventually, as discussed before, the quadratic Zeeman term causes it to become diamagnetic beyond a certain field strength. It is also this 1A_2 state, which is electric-dipole forbidden in zero field but gains in intensity when the field breaks the C_{2v} point group symmetry of the molecule, as we shall see in chapter 3. For the 3B_1 and 3A_2 states, the spin-Zeeman paramagnetic effect dominates initially, but the orbital diamagnetic effect gradually damps it out. The upturn towards diamagnetic behavior can already be anticipated from magnetic field range from 0 to 0.1 au plot.

2.4 Conclusions

Here from the graphs, we came to the conclusion that a strong magnetic field leads to the splitting of degenerate excited states due to the lowering of symmetry. The electronic state, which is the GS can change with changing field strength. With an increase in the magnetic field, a state of higher multiplicity rapidly comes down and becomes a new ground state. Also, we can see from the plots that the excited states were found to be more sensitive to the applied magnetic field.

Chapter 3

Spectral Intensity

3.1 Theory

Considering the light matter interaction a general Hamiltonian can be written as

$$H = H_{matter} + H_{Light} + H_{Light-Matter}$$

Representation of light in terms of a vector potential is

$$A(r, t) = A_0 \vec{\epsilon} \cdot \vec{p} \cdot e^{i(kr - wt)} - A_0 \vec{\epsilon} \cdot \vec{p} \cdot e^{-i(kr - wt)}$$

Where k is the wave vector and $\vec{\epsilon}$ is the polarization vector.

$$\begin{aligned} \hat{H} &= \sum_i \frac{1}{2m_i} (\hat{p} - q_i \vec{A})^2 \\ \hat{H} &= \hat{H}_0 - \sum_i \frac{q_i}{2m_i} (\vec{p}_i \cdot \vec{A} + \vec{A} \cdot \vec{p}_i) + \sum_i \frac{q_i}{2m_i} |\vec{A}|^2 \end{aligned}$$

where H_0 is the unperturbed Hamiltonian. Ignoring the quadratic term we get the Electric Dipole Hamiltonian

$$\hat{H} = \hat{H}_0 - \sum_i \frac{q_i}{2m_i} (\vec{p}_i \vec{A} + \vec{A} \vec{p}_i)$$

This can be concisely written as:

$$\begin{aligned} \hat{H} &= \hat{H}_0 + V(t) \\ V(t) &= \frac{q}{m} (A_0 \vec{\epsilon} \cdot \vec{p} \cdot e^{-iwt} - A_0 \vec{\epsilon} \cdot \vec{p} \cdot e^{iwt}) \end{aligned}$$

Under the long wavelength approximation $V(t)$ can be represented as

$$V(t) = \sum_i \frac{q_i}{m_i} (\epsilon \cdot p_i) \frac{E_0}{\omega} \sin(\omega t) V(t) = V_0 \sin(\omega t)$$

Here we assume that if wave length of light, $\lambda \gg$ molecular dimension, then

$$k = \frac{2\pi}{\lambda} \rightarrow 0$$

Rate of transition from $l \rightarrow k$ electronic states can be then derived via time-dependent perturbation theory and is given by

$$W_{kl} = \frac{\pi}{2\hbar} |V_{kl}|^2 [\delta(E_k - E_l - \hbar\omega) + \delta(E_k - E_l + \hbar\omega)]$$

where

$$V_{kl} = -iE_0 \frac{\omega_{lk}}{\omega} \langle k | \hat{e} \cdot \hat{\mu} | l \rangle$$

Where $\hat{\mu}$ being the electric dipole moment operator and the electronic transition occurs when $\hbar\omega = \Delta E_{kl}$. At this point the oscillator strength f for an electric dipole transition in dipole length approximation is : [5]

$$f_l = \frac{2}{3} \cdot \Delta E | \sum_{i=1}^N r_i |X_k > |^2 \quad (3.1)$$

and in velocity representation it is

$$f_v = \frac{2}{3\Delta E} | \sum_{i=1}^N \pi_i |X_k > |^2 \quad (3.2)$$

where $\pi = \hat{P} + A_{tot}$

f_l - Oscillator strength in the length gauge

f_v - Oscillator strength in the velocity gauge

The length and velocity expressions for oscillator strength are equivalent for exact eigenstates of the Hamiltonian. In principle, they are inequivalent for approximate methods and finite basis sets. For certain special cases such as Hartree-Fock, linear responses have been shown to be equivalent in the complete basis set limit. Their equivalence for complex orbitals, as in our case, has been numerically demonstrated in [3]

The oscillator strength is the theoretically computed quantity that indicates the intensity of absorption in electronic spectroscopy. The computation of oscillator strength in the context of electronic spectra computations in a magnetic field is especially interesting as it is a marker of symmetry breaking. Uniform magnetic fields can be placed in various directions relative to the symmetry axes and planes of the molecule to break its point group symmetry. This would result in formerly forbidden transitions becoming allowed. The degree to which it occurs depends greatly on the nature of the excited state, and this can be a beautiful indicator of the sensitivity of various states to magnetic interactions. Furthermore, although beyond the scope of this report, non-uniform magnetic fields can also make spin forbidden transitions progressively allowed with increasing non-uniformity in the field.

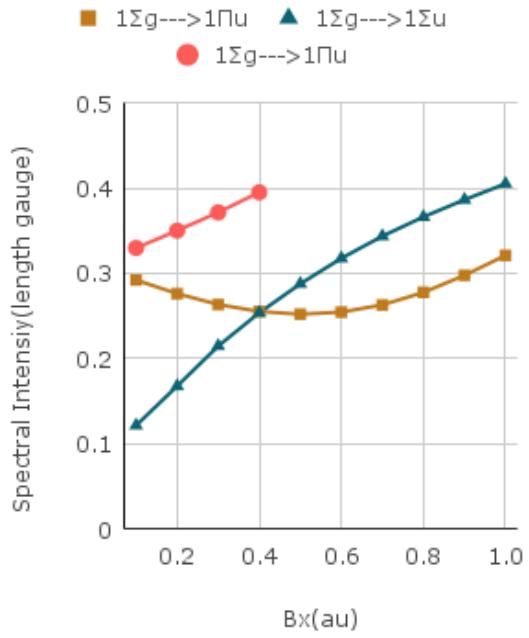
3.2 Computational Studies

The high atomic symmetry of the low-lying excited states of He atom can not be broken by uniform fields, so we do not present results for it here. The breaking of the center of symmetry is demonstrated in H_2 . H_2O is used as an example when all three directions of the field have inequivalent effects.

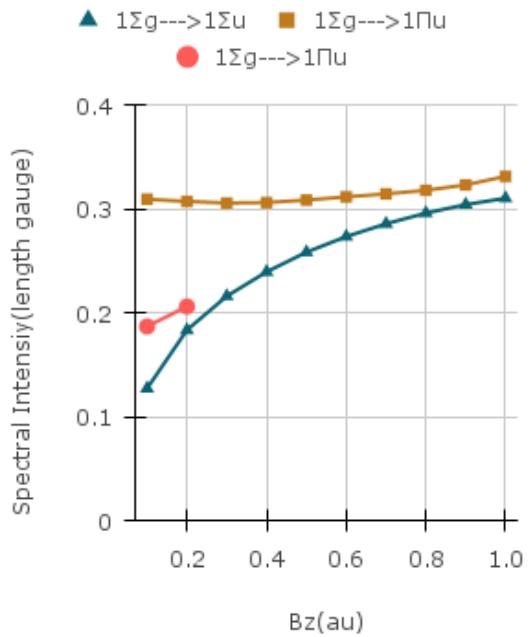
H_2 Molecule

H_2 molecule has a center of symmetry and belongs to $D_{\infty h}$ point group. As mentioned in the section 2.3.2 we are computing the RHF on H_2 followed by linear response using spin restricted/conserving excitation operator. Thus we only obtain the singlet states when applying the magnetic field along the bond axis(X-axis) and perpendicular(Z-axis).

When magnetic field along the bond axis, in figure 3.1a we observe three non-zero spectral intensities in length gauge from ground state, $^1\Sigma_g$ to excited states, $^1\Sigma_u$ and $^1\Pi_u$ (doubly degenerate) respectively and when magnetic field is perpendicular to the bond axis, in figure 3.2a. The spectral intensities in the velocity gauge when magnetic field along the bond axis and perpendicular to the bond axis are shown in figures (3.2a) and (3.2b), respectively. Although the g/u symmetry of H_2 is broken by the field - this effect is very small, at least up to $B=1$ au, and effects on the spectral intensities are insignificant.

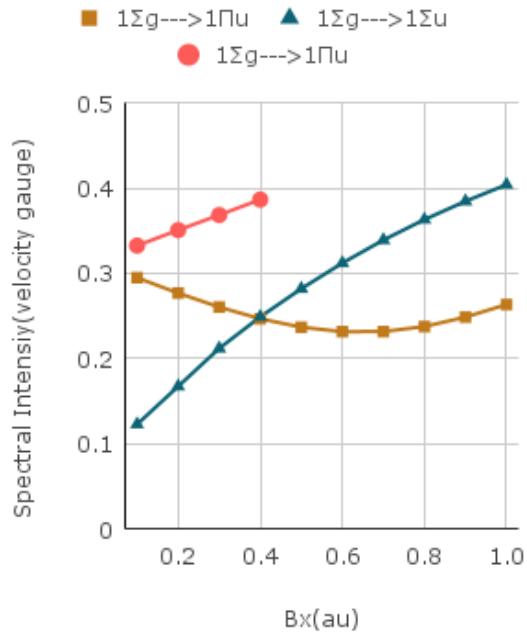


(a) Spectral Intensity in length gauge. Magnetic field along X-axis(Bond axis)

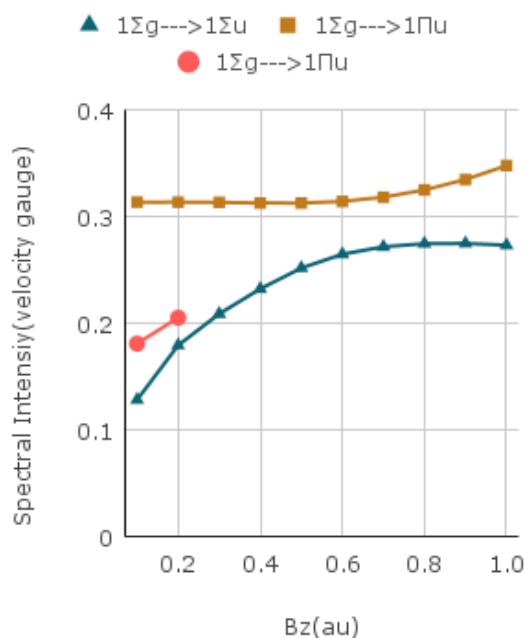


(b) Spectral Intensity in length gauge. Magnetic field along Z-axis(Perpendicular to the bond axis)

Figure 3.1: Spectral Intensity in length gauge B



(a) Spectral Intensity in velocity gauge. Magnetic field along X-axis(Bond axis)

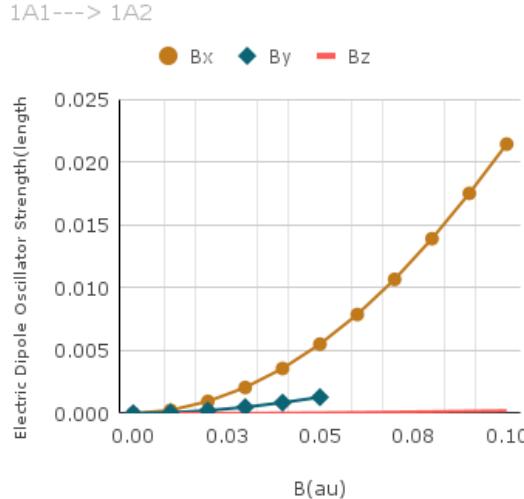


(b) Spectral Intensity in velocity gauge. Magnetic field along Z-axis(Perpendicular to the bond axis)

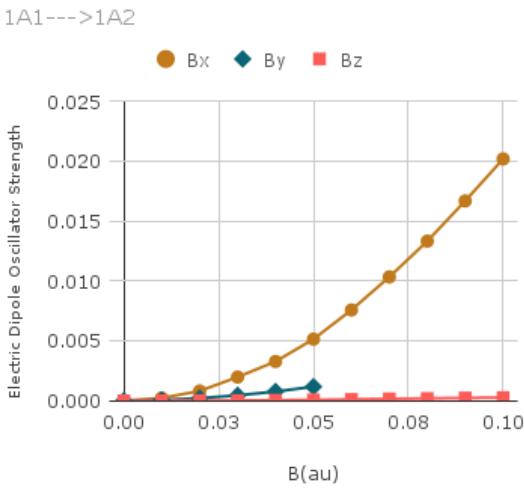
Figure 3.2: Spectral Intensity in velocity gauge

H_2O Molecule

For water molecule we already calculated the state energies of four excited states. Now we are computing the electric dipole oscillator strength of H_2O by applying field independently in each X,Y,& Z axes. The σ_v plane of H_2O molecule is YZ-plane and the Z-axis is the C_2 axis.



(a) Transition from 1A_1 to 1A_2 when oscillator strength is in length gauge



(b) Transition from 1A_1 to 1A_2 when oscillator strength is in velocity gauge

Spectral intensity changes with field for transition from ground state 1A_1 to excited state 1B_1 and to 1A_2 are shown in figure 3.4 and figure 3.3a. $^1A_1 \rightarrow ^1A_2$ is electric dipole forbidden. However, Figure(3.3b) shows the intensity growing with increasing field strength. This means there is a transition which wasn't allowed before is getting transitioned by applying a strong magnetic field.

From the plots, the transition moment change is more when the applied magnetic field direction is perpendicular to the σ_v plane of H_2O i.e, for the transition from $A_1 \rightarrow A_2$ is higher for magnetic field applied along the X-direction. This is because

the C_2 axis and one of the σ_V plane of symmetry are lost and $A_1 \rightarrow A_2$ transition becomes allowed. Even for the magnetic field in Y-direction, it shows transition, but the higher transition is for the magnetic field in the X-direction.

From the velocity gauge data shown in the figure 3.4 we obtain almost similar

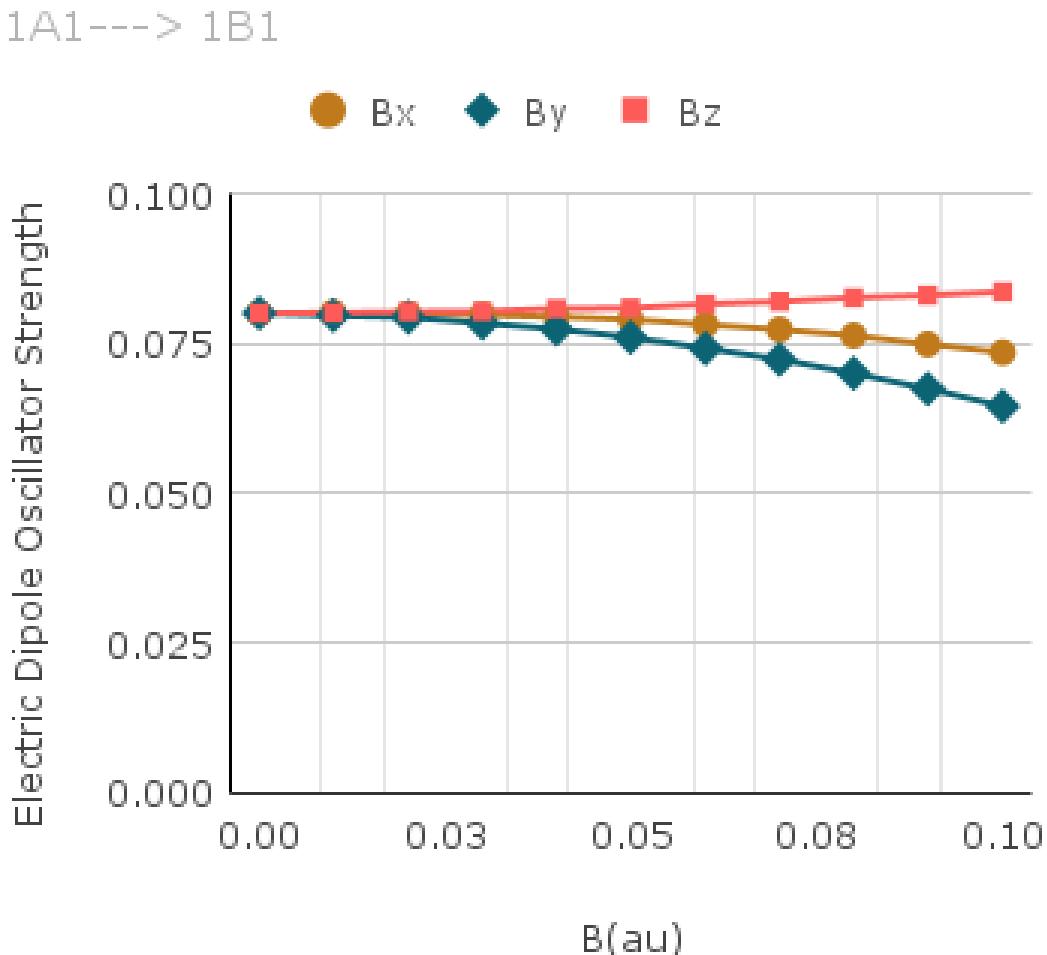


Figure 3.4: Transition from 1A_1 to 1B_1 when oscillator strength is in velocity gauge result as that from length gauge data. The value of intensities are different because

- We are using Finite basis
- Computing method is approximate

As going to the large basis set length and velocity gauges gives same result.

In conclusion, with the presence of a strong uniform magnetic field, there is a possibility of forbidden transition becoming allowed by the loss of symmetry.

Chapter 4

Orbital Analysis of Excitation Spectra

The intensity of an electronic excitation transition is governed by various factors. Primary among them is the Frank-Condon principle. Ground and excited states typically have different equilibrium geometries. However, since an electronic transition is too fast for the nuclei to rearrange, the transitions are vertical, and excited electrons go to whichever vibrational level is vertically available to them. It is this vertical excitation energy that we compute here. Moreover, peak widths and vibrational structure of the spectrum are not considered. While there are standard procedures to take these into account, we deemed it unnecessary to carry out these procedures for the purpose of this project because our motive here is not to construct accurate spectra but to understand the mechanisms through which magnetic fields affect spectra and establish the issues to be considered when trying to explain the spectral shifts induced by the fields. We have thus chosen the simplest possible systems and looked at the simplest excitations. Further improvements and studies of complex systems may be desirable, but our current understanding is insufficient to handle them. In the early chapters, we have computed peaks and intensities of electronic spectra and seen how the peak positions and heights change under a magnetic field. The goal of this chapter is to analyze the reason behind these changes at the orbital level. Recall that the orbitals, Φ are optimized via Hartree-Fock theory in the presence of an external field. The use of London orbitals to ensure gauge-origin invariance makes them complex. We will thus plot $\Phi_i^* \Phi_i$, the so-called orbital density, in all cases. We accept that the Frank-Condon overlap of the vibrational levels between which the transition is occurring will have an additional impact on the intensity and will be necessary to compare with an experimental spectrum in principle. Leaving this aside, the spectral intensity depends on the orbitals involved in the transition. The orbital picture is only a simple model and may well fail for highly correlated states, but it has been found to provide reasonable justification for low-lying purely valence excitations in the zero-field situation. We shall assume for the moment that this fact will continue to hold in the presence of a field.

4.1 Methodology for Plotting

The molecular orbitals are obtained on a customizable grid from the LONDON program. As the spatial extent of the orbitals is not known a priori, some amount of trial and error is involved. We have then developed a Matlab script to read the data for the complex orbitals Φ_i , compute $\Phi\Phi^*$ at each grid point, and plot the orbital densities as a color gradient. The orbitals are labeled with their zero-field names and symmetry labels, although their symmetry is reduced in the field for ease of reference. Three field strengths $B = 0$, $B = 0.1$ and $B = 1 \text{ au}$ are plotted. The weak field plots are necessary to correlate with the zero-field orbitals in terms of their energies as the orbital gets largely scrambled as the field increases.

It is important to note that in LONDON, the orbitals like p,d, etc which are complex in general, are not recombined to real functions. Thus the labelling used is p_{+1}, p_0, p_{-1} ,etc and they are randomly oriented in space. On the application of a magnetic field, they get oriented.

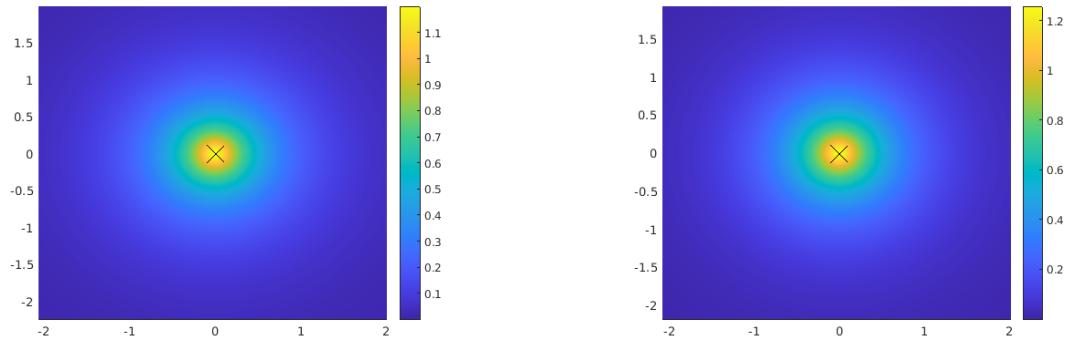
In this project, we have only studied these orbital density plots visually. However, to identify certain subtle effects and to quantitatively assess the changes, we plan on calculating some numerical quantities, such as overlap with zero-field orbitals, etc., in continuation of this work. This would also help us to study more complicated systems where visual analysis will not suffice. Even in these simple cases, the changes in some of the orbitals are not visually apparent.

4.2 Results and Conclusions

We have studied the simplest closed-shell atoms – He, Be, and Ne – and the simplest molecule – H_2 and plotted the orbital densities of the occupied orbitals and a few of the lowest virtual unoccupied orbitals in the following sections. The aug-ccpVDZ basis was used in all cases. The basis functions were taken to be uncontracted as the contraction coefficients are optimized for the zero-field optimization and would bias the results. The occupied orbitals are directly modified due to the presence of the magnetic field in their Fock operator, while the virtuals are modified due to the requirement of orthogonality of the orbitals.

4.2.1 Atomic Orbitals

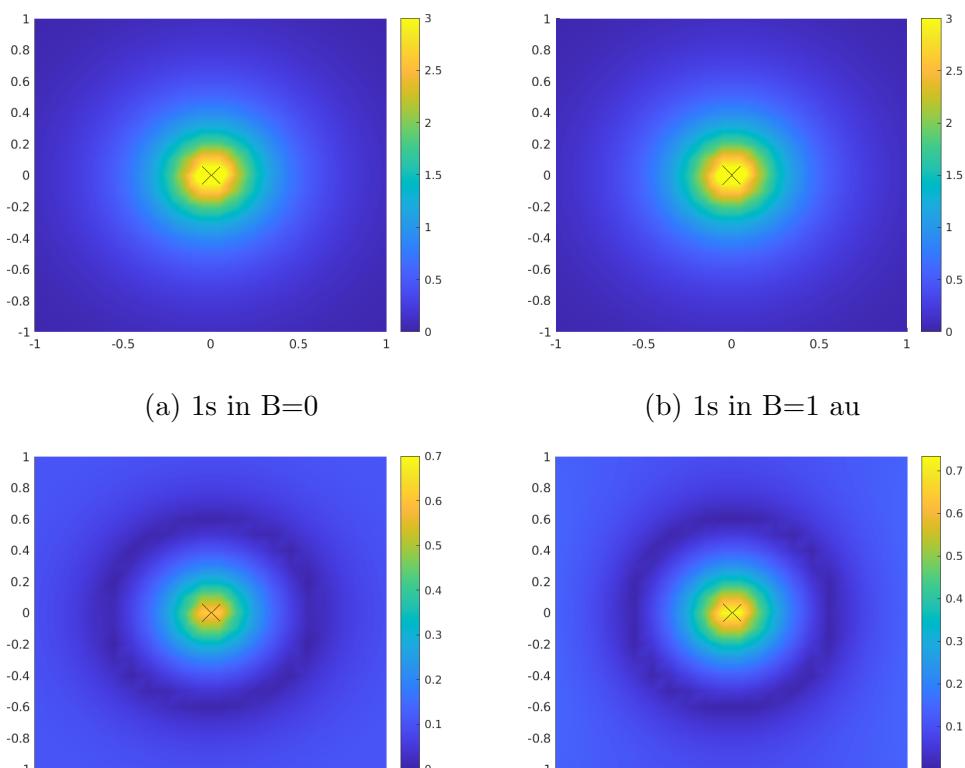
The s and p orbitals of three closed-shell atoms - He, Be, and Ne are plotted in Figs. 4.1a to 4.3f both without and with a strong magnetic field. Very little change is noted in the s orbitals except for a little contraction of density. Only the 2s orbital of Ne shows a large decrease in size. This could be a basis effect as the absence of basis functions of higher angular momentum for the core reduces the flexibility of the 1s orbitals to adapt to the field. We are currently investigating this aspect further. The $2p_{-1}$ orbital of Ne is randomly oriented when $B=0$ as seen in Fig. 4.3e but gets aligned along the field when $B=1 \text{ au}$ as seen in Fig. 4.3f.



(a) 1s in B=0

(b) 1s in B=1 au

Figure 4.1: He occupied orbitals



(a) 1s in B=0

(b) 1s in B=1 au

(c) 2s in B=0

(d) 2s in B=1 au

Figure 4.2: Be occupied orbitals

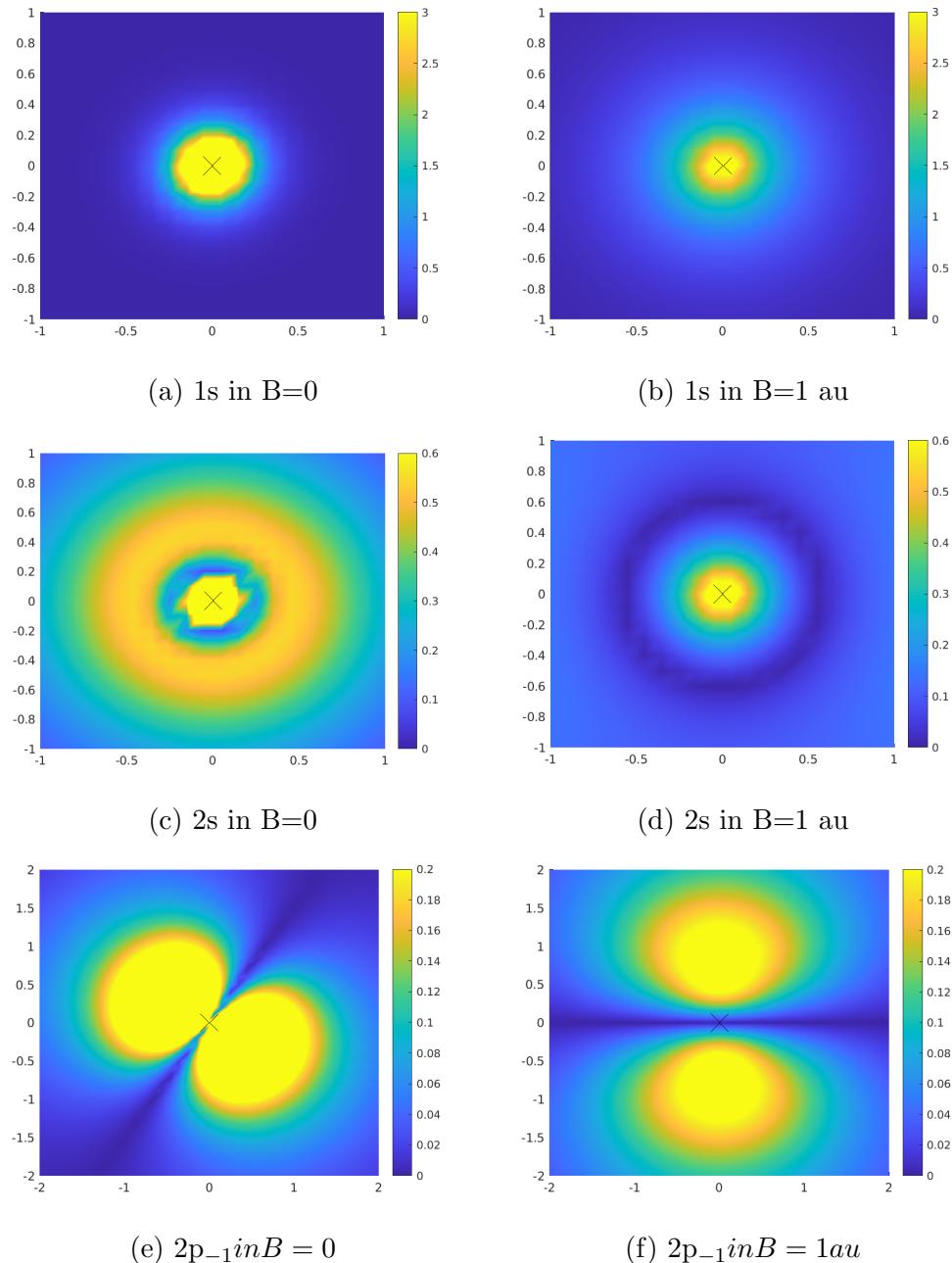


Figure 4.3: Ne occupied orbitals

4.2.2 He atom

The lowest singlet excited state of the He atom is 2^1S with dominant contribution from $1s \rightarrow 2s$ excitation. The excitation energy is found to increase with the increasing magnetic field. In Fig. 4.4, we see that due to only diamagnetic interaction, the energies of all the s-orbitals are raised. The $2s$ orbital energy rises more sharply than $1s$ and even crosses the $2p_{-1}$ and $2p_0$ orbitals at $B=1$ au. Since the orbital energy difference is the first approximation to the excitation energy, it is not surprising that the $1^1S \rightarrow 2^1S$ excitation energy increases. However, this is an electric dipole forbidden transition, so we do not obtain a spectral intensity plot. The 3S excited state is paramagnetic in $B=[0,1$ au] for He on account of the dominating spin-Zeeman term, and thus, the excitation energies decrease in spite of the diamagnetism of the s-orbitals. These transitions are spin-forbidden. The $1s$ orbital does not change much in a field, but we can see from Fig. ?? that the $2s$ orbital is significantly contracted at $B=1$ au vs $B=0$. Similarly, in Fig. 4.11b we see a contraction in the $3s$ orbital. We find a correlation between the shrinking of orbital density and the increase in energy of the s-orbitals.

The 3P excited states have a common spin-Zeeman term which decreases their energies. However, the dominant $1s \rightarrow 2p$ excitation involves p-orbitals with different m_l values in each case resulting in different rates of change of the state energy. The p_{+1} orbital rises rapidly due to diamagnetic linear and quadratic terms while p_0 rises only due to the quadratic term. The p_{-1} orbital is affected by a paramagnetic linear and diamagnetic quadratic term. In the interval $B=[0,1$ au], the linear term appears to dominate for He resulting in a net paramagnetic behavior.

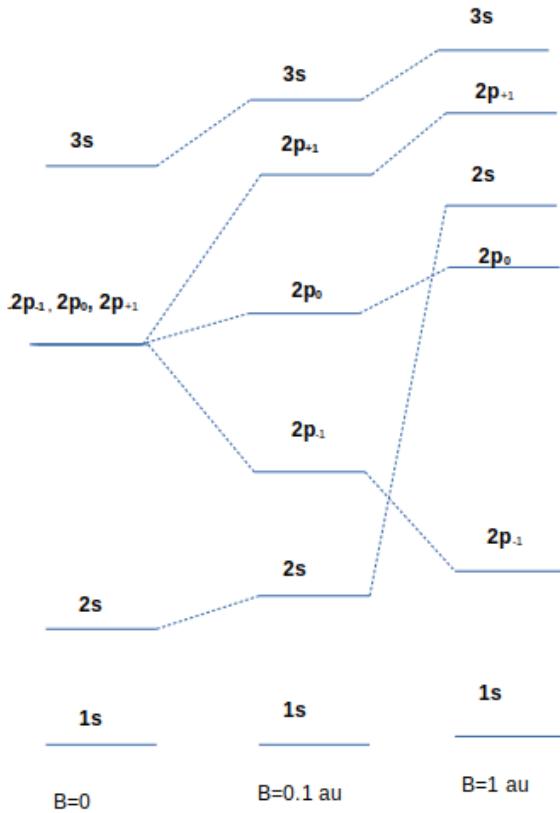


Figure 4.4: Orbital energies changing with magnetic field strength

4.2.3 H_2 Molecule

Only the singlet manifold of excited states has been computed for H_2 (Fig. 2.3 and 2.4) for the sake of simplicity. All the states except one of the $^1\Pi_u$ s are found to be diamagnetic, and their energies rise at a faster rate than the ground state. Excitation energies are consequently increasing with field strength. The $^1\Pi_u$ state shows orbital paramagnetism up to $B=0.3$ au, and then the quadratic-Zeeman term takes over. The corresponding excitation energy thus decreases first and then increases again.

The spectral intensities are seen in Figs. 3.1a-3.2b. The $^1\Sigma_g \rightarrow ^1\Sigma_u$ and $^1\Sigma_g \rightarrow ^1\Pi_u$ transitions show increase in spectral intensity with field strength for both B_x and B_z , ie. parallel and perpendicular to bond-axis (x-direction). For B_z , the intensity remains roughly constant after a point. This may also be a basis set effect, which we shall explore in the future. The intensity change for the orbital-paramagnetic $^1\Pi_u$ state follows the change of the excitation energy, although the turning points of the plots are different.

Although the H_2 molecule belongs to the $D_{\infty h}$ point group, we have labeled the orbitals using symmetry labels from one of its Abelian subgroups, namely D_{2h} . This helps us to track the orbitals when the symmetry of the system with the field is reduced. From the plots of the orbital densities in Figs. 4.11-4.16, we see that the apart from a change in size, a field parallel to the bond axis does not alter the orbitals qualitatively. The B_{3u} orbital involved the $^1\Sigma_g \rightarrow ^1\Pi_u$ transition, which shows a modulation of spectral intensity which goes through a minimum around $B_x=0.4-0.6$ au, shows an initial expansion with field followed by a contraction. The

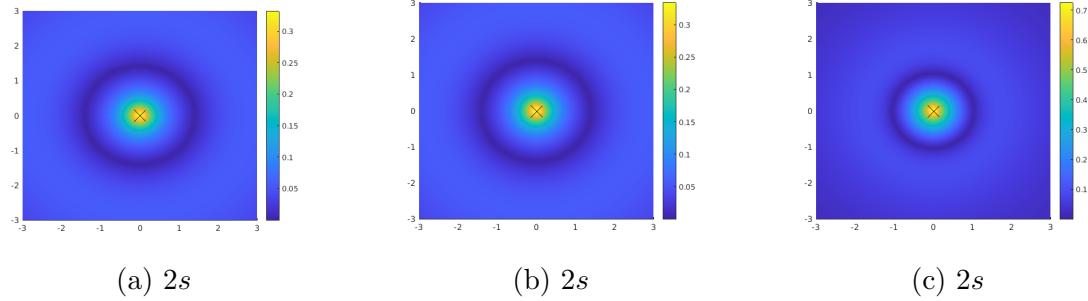


Figure 4.5: He 2s orbital in Zero Field(a), Weak field(b), Strong Field(c)

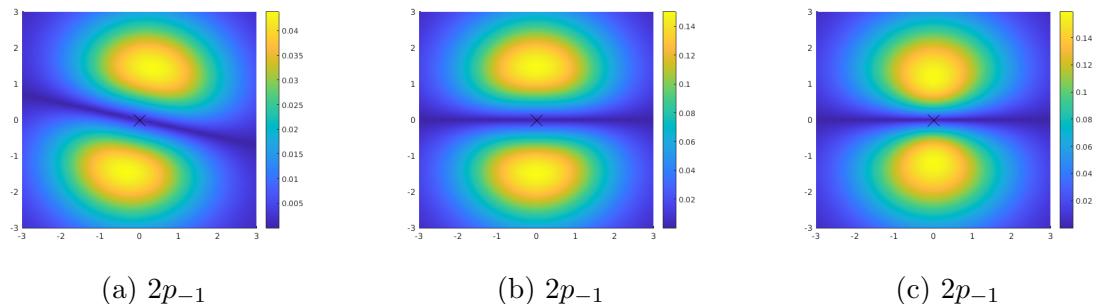


Figure 4.6: He 2p₋₁ orbital in Zero Field(a), Weak field(b), Strong Field(c)

expansion corresponds to a decrease in intensity as the overlap with the A_g orbital, which is smaller, is reduced, and the reverse happens when the orbital contracts again beyond a certain field. A quantitative analysis of this phenomenon in future studies will help us pin down the correlation. When a perpendicular field is applied, i.e., B_z , the orbitals show dramatic changes in size and shape. New nascent nodes are also observed in some cases. At this moment, we do not have a full understanding of their implication for the intensities. In Fig. 4.17, we present the total density of the H_2 molecule, which shows noticeable changes in the field, unlike the atomic systems.

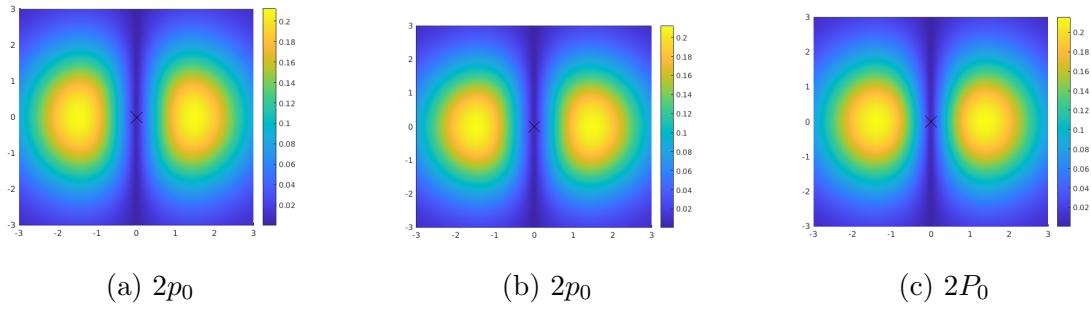


Figure 4.7: He $2p_0$ orbital in Zero Field(a), Weak field(b), Strong Field(c)

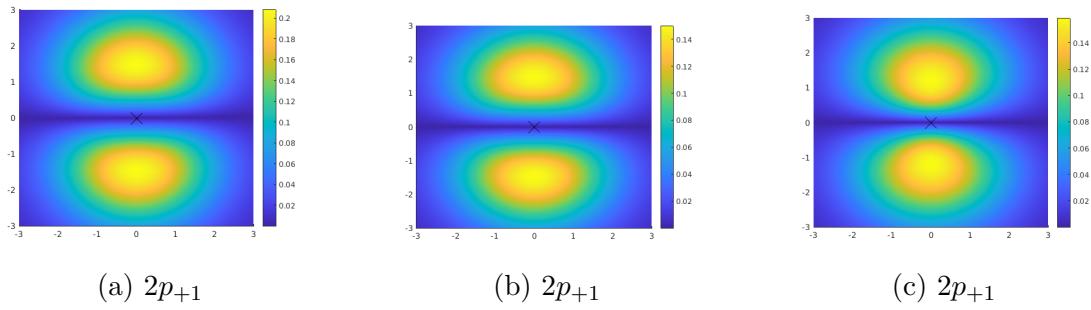


Figure 4.8: He $2p_{+1}$ orbital in Zero Field(a), Weak field(b), Strong Field(c)

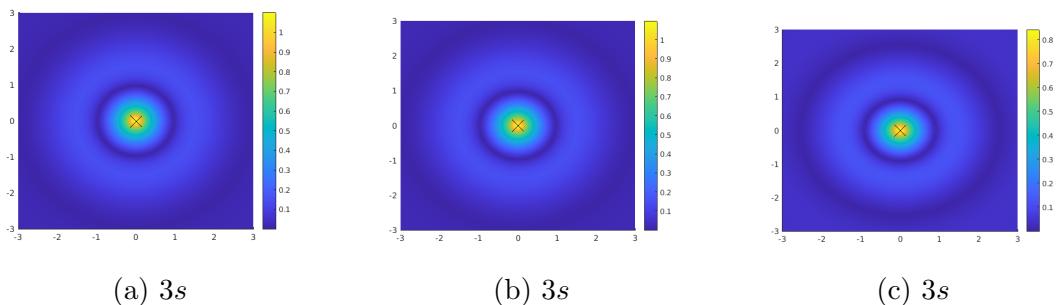


Figure 4.9: He $3s$ orbital in Zero Field(4.9a), Weak field(4.9b), Strong Field(4.9c)

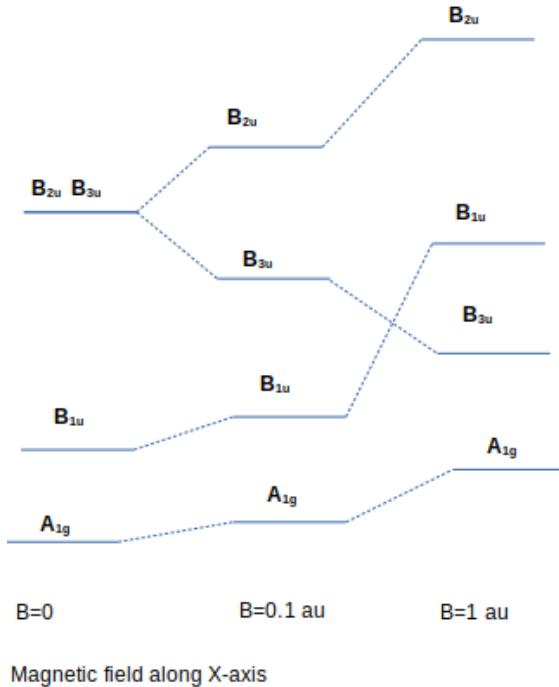


Figure 4.10: Change in orbital energy levels of H_2 molecule with magnetic field along bond axis

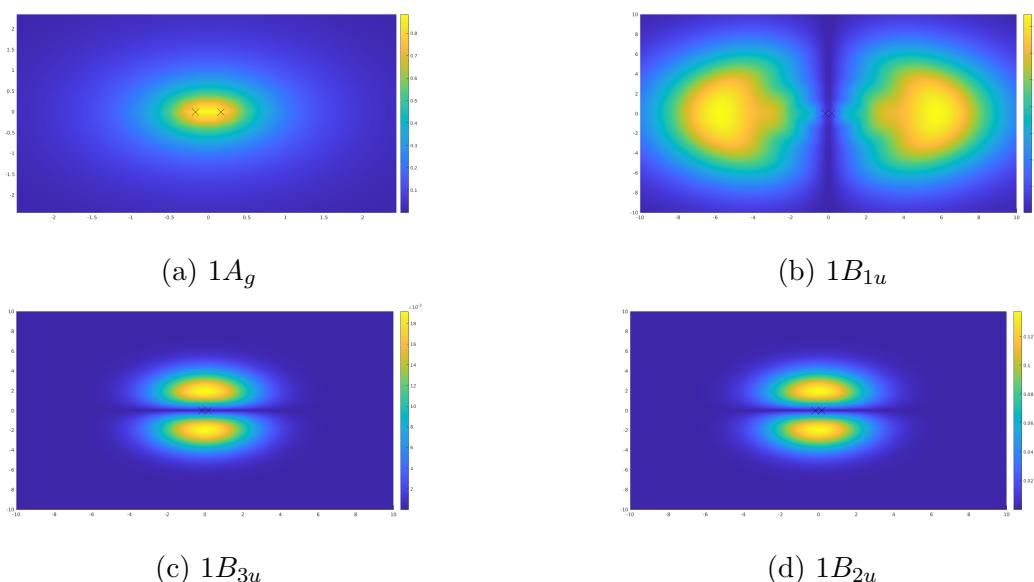


Figure 4.11: Orbital density plots of H_2 molecule placed in X-axis and viewing above the XY-plane, when $B=0$ using basis aug-cc-pVDZ

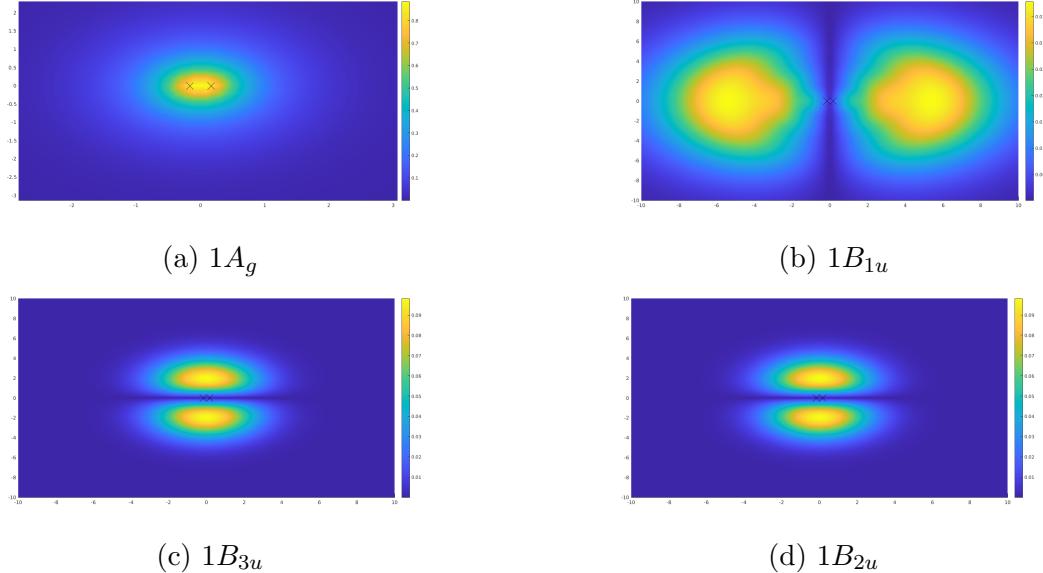


Figure 4.12: Orbital density plots of H_2 molecule placed in X-axis and viewing above the XY-plane, when $B=0.1$ along X-axis using basis aug-cc-pVDZ

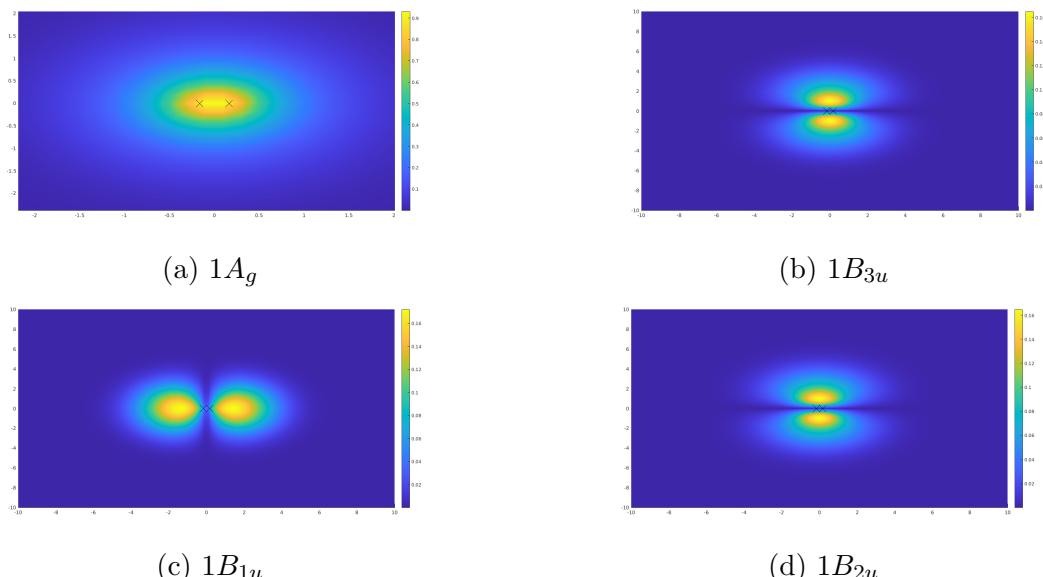


Figure 4.13: Orbital density plots for the H_2 molecule placed in X-axis and viewing above the XY-plane, when $B=1$ along X-axis, using basis aug-cc-pVDZ

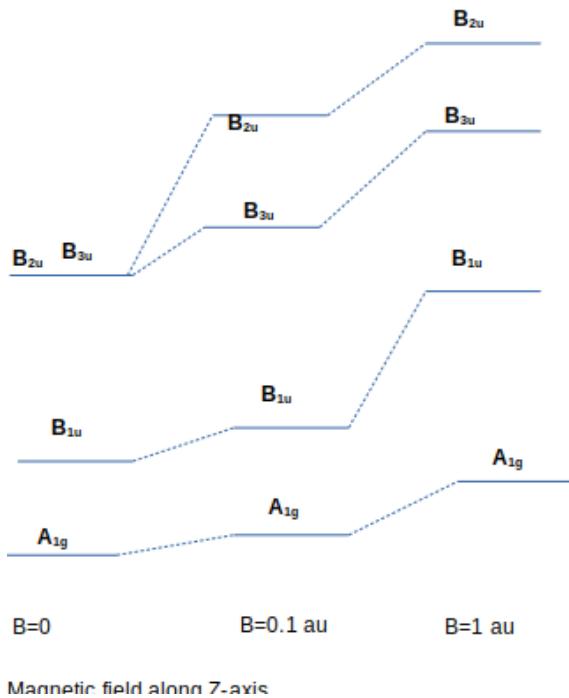


Figure 4.14: Changes in orbital energy levels of H_2 molecule with magnetic field perpendicular to bond axis

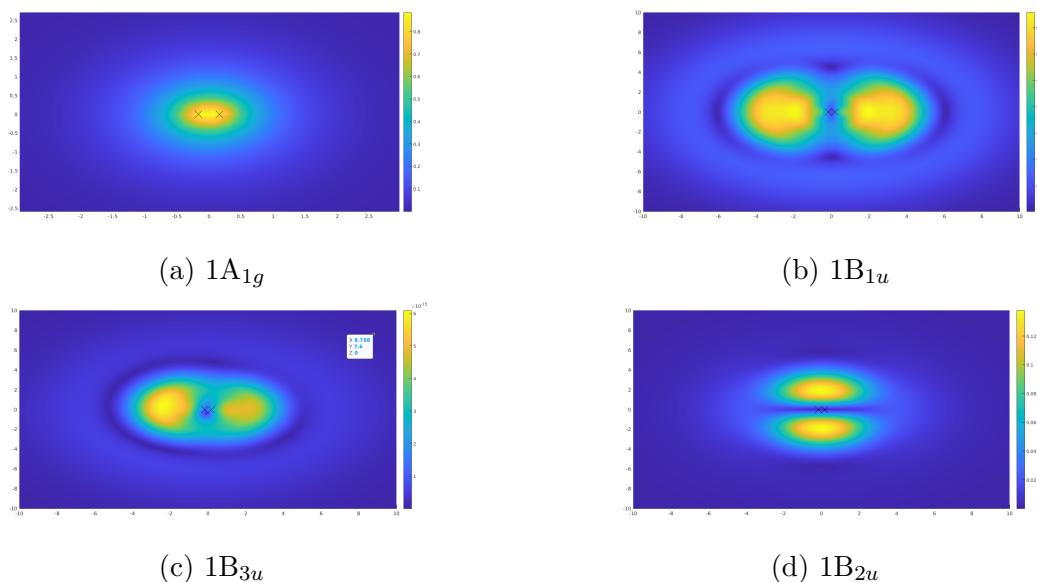


Figure 4.15: Orbital density plots for the H_2 molecule placed in X-axis and viewing above the XY-plane, when $B=0.1$ au along Z-axis, using basis aug-cc-pVDZ

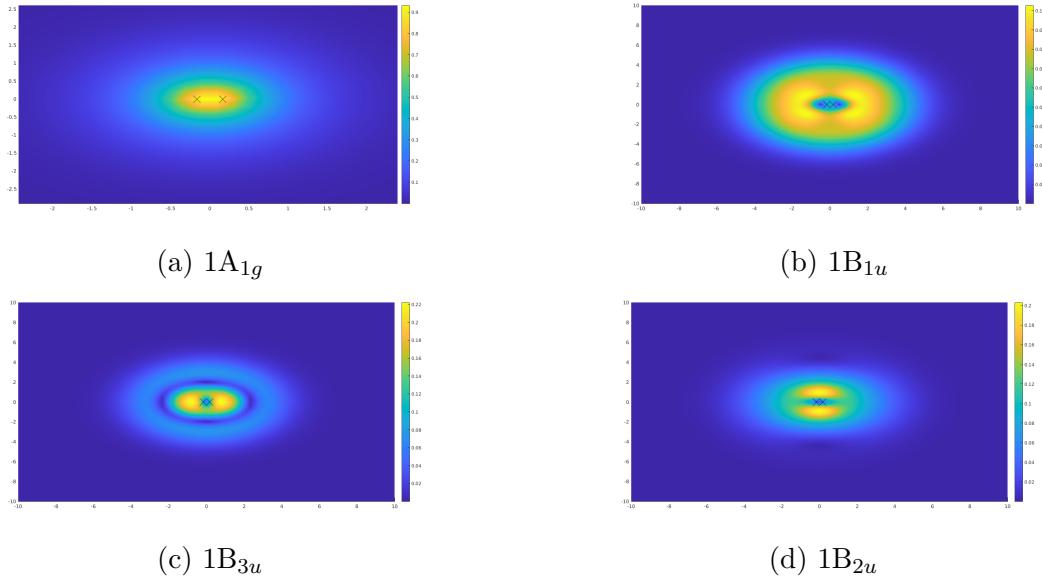


Figure 4.16: Orbital density plots for the H_2 molecule placed in X-axis and viewing above the XY-plane, when $B=1$ along Z- axis, using basis aug-cc-pVDZ

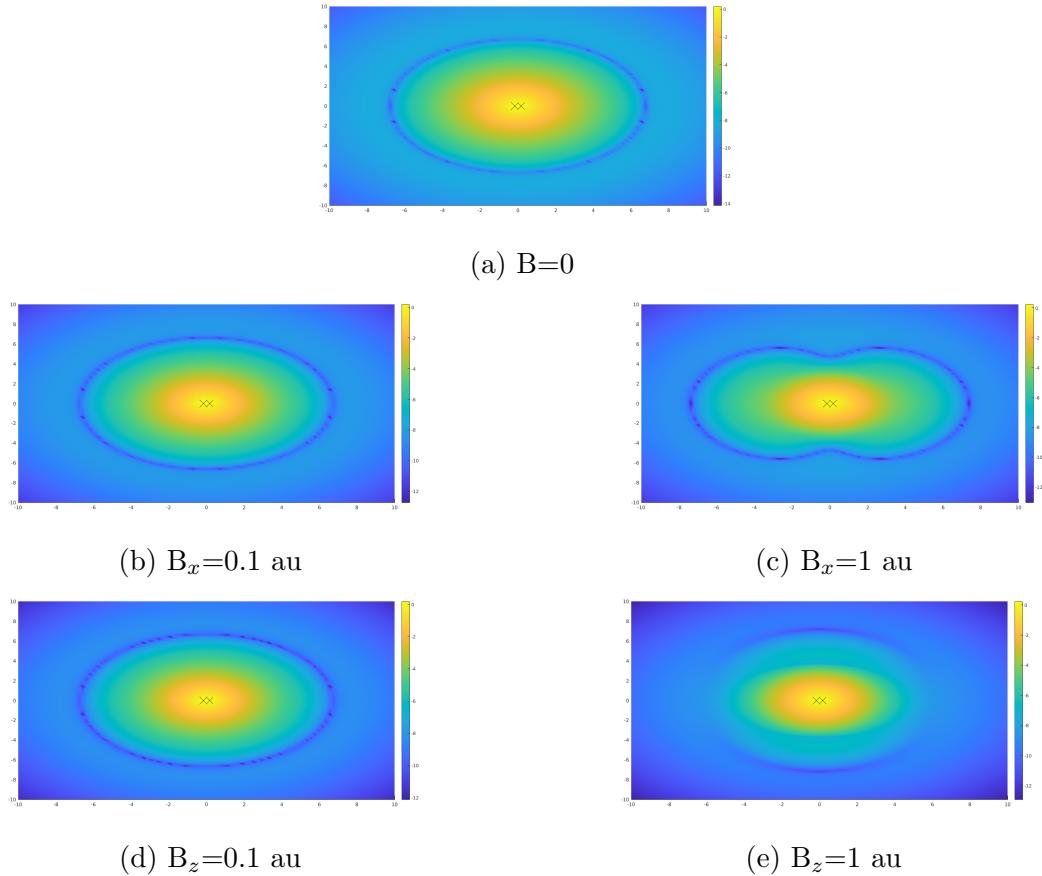


Figure 4.17: Total density of H_2 molecule for $B=0, 0.1, 1$ au along X-axis and Z-axis, using aug-cc-pVDZ basis

Chapter 5

Future Outlook

In this project, we have explored electronic spectra in strong magnetic fields in terms of peak shifts and intensities. A simple Hartree-Fock linear response method has been applied. We have computed transition moments in the electric dipole approximation. The most dramatic effects are in terms of symmetry-breaking of the molecule, which results in electric-dipole forbidden excitations becoming allowed. We have computationally demonstrated the orbital-Zeeman and spin-Zeeman effects for various electronic states and identified state crossings. Ground states also change under magnetic field effects. Moreover, the quadratic Zeeman effect, wherein all electronic states become diamagnetic after a certain system-dependent field strength, has also been demonstrated. This is seldom pointed out but is interesting to note. By using different flavors of the Hartree-Fock theory in terms of the spin constraints on the orbitals, we can isolate spatial and spin effects of the magnetic field, and this allows us to understand the changes better. We have analyzed the orbitals under a field to try to justify the changes in the electronic spectra.

This project was designed to initiate studies in this direction and has opened the way to a large number of possibilities. As is evident, we plan to arrive at a detailed understanding of the mechanism in which orbital changes by magnetic fields affect electronic spectra. Our current studies have indicated that an extensive study of basis set effects on all the significant observations made is required as our ability to computationally capture the response of various quantities to the external field critically depends on the functional space available to the variational procedure. Since magnetic fields offer a unique opportunity to continuously change the orbitals, we would hopefully find a correlation between orbital shapes and peak positions and intensities. Simultaneously, continuous breaking of symmetry is also possible, and exploration of these effects is also eminently possible. Another direction of future research would be to extend the investigations to non-uniform fields wherein spin-density changes of the orbitals will have to be addressed. In summary, this project tries to further our fundamental understanding of the electronic structure, and the exploration can be continued in various ways.

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Appendix

```
1 scf{
2     spin-symmetry-constraint = Restricted Hartree-Fock
3     linear-dependence-tol = 1e-10
4     uhf-spin-projection = 0
5     disable-spin-zeeman-in-fock-matrix = no
6     noisy-init-guess = no
7     # density-matrix-input-file = h2o.UHF.0.005.dmat
8     # density-matrix-output-file = plotxy15.csv
9     density-plot-data = {plotxyBz1.csv,(-10,-10,0),(20,0,0)
10    ,(0,20,0),(0,0,2),(100x101x1),precision=4,scolon=y,fields{rho,j
11    }}
12     molecular-orbitals-to-plot = (1,2,3,4,5,6,7,8)      min-scf-
13     iterations = 0
14     max-scf-iterations = 160
15     use-density-fitting = no
16     use-admm = no
17     analyze-using-dft-grid = no
18
19     diis{
20         convergence-tolerance = 1e-10
21         subspace-dimension = 7
22         diagonalization-temperature = 0
23     }
24
25 system{
26     molecular-charge = 0
27     correlation-model = Hartree-Fock
28
29     hamiltonian{
30         electron-mass = 1
31         speed-of-light = 137.036
32         adiabatic-connection-lambda = 1
33         nuclear-charge-distribution = point charge
34
35         magnetic-field = (0.000,0.000,1)
36         gauge-origin = (0, 0, 0.1173)
37
38         linear-magnetic-field = {(0.0, 0, 0), (0, 0, 0), (0, 0, 0)}
39         linear-magnetic-origin = (0, 0, 0)
40
41         electric-field = (0, 0, 0)
42         electric-origin = (0, 0, 0)
43         linear-electric-field = {(0, 0, 0), (0, 0, 0), (0, 0, 0)}
44         integral{
```

```

45     use-coulomb-integral-permutation-symmetry = yes
46     use-cauchy-schwarz-screening = yes
47     cauchy-schwarz-tol = 1e-15
48     boys-function-tol = 1e-17
49   }
50 }
51
52 # data on state flags lost, output incomplete here
53 use-london-orbitals = yes
54 gto-contraction-type = normalized primitive
55 basis = aug-cc-pVDZ
56 # geometry
57 charge = 1.0
58 H 0.1643 0.0000 0.0000
59 H -0.1643 0.0000 0.0000
60 }
61 }
```

Listing 5.1: London input file of H₂ molecule for orbital analysis

This is an london input file generates 8 orbitals of H₂ under B=1 au applied in Z-direction with aug-cc-pVDZ basis. Where these two H-atoms are positioned at (-0.1643,0,0) and (0.1643,0,0).

```

1 DATA = load('plotxyB0.csv');
2
3 MOLECULE = [
4   0.0000 0.0000 0.0000
5 ];
6
7 n1 = 101;
8 n2 = 100;
9 Xi = DATA(:,1);
10 Yi = DATA(:,2);
11 Zi = DATA(:,3);
12 Xm = reshape(Xi,n1,n2);
13 Ym = reshape(Yi,n1,n2);
14 Zm = reshape(Zi,n1,n2);
15 Rhoi = DATA(:,4);
16 Rhom = reshape(Rhoi,n1,n2);
17
18 figure('Name','RHFDensity','NumberTitle','off'); clf; hold on;
19
20 %contourf(Ym,Zm,log10(1e-20+Rhom),50);
21 pcolor(Xm,Ym,log10(1e-20+Rhom));
22 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
23 shading interp
24
25 DATA = load('plotxyB0.csv_orb');
26
27 n1 = 101;
28 n2 = 100;
29 Xi = DATA(:,1);
30 Yi = DATA(:,2);
31 Zi = DATA(:,3);
32 Xm = reshape(Xi,n1,n2);
33 Ym = reshape(Yi,n1,n2);
34 Zm = reshape(Zi,n1,n2);
```

```

36 HOMOi = DATA(:,4) + 1i*DATA(:,5);
37 HOMOm = reshape(HOMOi,n1,n2);
38
39 figure('Name','RHFOrb_1','NumberTitle','off'); clf; hold on;
40
41 %contourf(Ym,Zm,abs(HOMOm),50);
42 pcolor(Xm,Ym,abs(HOMOm));
43 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
44 shading interp
45
46
47 HOMOi = DATA(:,6) + 1i*DATA(:,7);
48 HOMOm = reshape(HOMOi,n1,n2);
49
50 figure('Name','RHFOrb_2','NumberTitle','off'); clf; hold on;
51
52 %contourf(Ym,Zm,abs(LUMOm),50);
53 pcolor(Xm,Ym,abs(HOMOm));
54 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
55 shading interp
56
57 LUMOi = DATA(:,8) + 1i*DATA(:,9);
58 LUMOm = reshape(LUMOi,n1,n2);
59
60 figure('Name','RHFOrb_3','NumberTitle','off'); clf; hold on;
61
62 %contourf(Ym,Zm,abs(LUMOm),50);
63 pcolor(Xm,Ym,abs(LUMOm));
64 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
65 shading interp
66
67
68 HOMOi = DATA(:,10) + 1i*DATA(:,11);
69 HOMOm = reshape(HOMOi,n1,n2);
70
71 figure('Name','RHFOrb_4','NumberTitle','off'); clf; hold on;
72
73 %contourf(Ym,Zm,abs(LUMOm),50);
74 pcolor(Xm,Ym,abs(HOMOm));
75 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
76 shading interp
77
78
79 HOMOi = DATA(:,12) + 1i*DATA(:,13);
80 HOMOm = reshape(HOMOi,n1,n2);
81
82 figure('Name','RHFOrb_5','NumberTitle','off'); clf; hold on;
83
84 %contourf(Ym,Zm,abs(LUMOm),50);
85 pcolor(Xm,Ym,abs(HOMOm));
86 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
87 shading interp
88
89
90 HOMOi = DATA(:,14) + 1i*DATA(:,15);
91 HOMOm = reshape(HOMOi,n1,n2);
92
93 figure('Name','RHFOrb_6','NumberTitle','off'); clf; hold on;

```

```

94 %contourf(Ym,Zm,abs(LUMOm),50);
95 pcolor(Xm,Ym,abs(HOMOm));
96 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
97 shading interp
98
99
100
101
102 HOMOi = DATA(:,16) + 1i*DATA(:,17);
103 HOMOm = reshape(HOMOi,n1,n2);
104
105 figure('Name','RHFOrb_7','NumberTitle','off'); clf; hold on;
106
107 %contourf(Ym,Zm,abs(LUMOm),50);
108 pcolor(Xm,Ym,abs(HOMOm));
109 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
110 shading interp
111
112 HOMOi = DATA(:,18) + 1i*DATA(:,19);
113 HOMOm = reshape(HOMOi,n1,n2);
114
115 figure('Name','RHFOrb_8','NumberTitle','off'); clf; hold on;
116
117 %contourf(Ym,Zm,abs(LUMOm),50);
118 pcolor(Xm,Ym,abs(HOMOm));
119 plot(MOLECULE(:,1),MOLECULE(:,2),'kx','MarkerSize',20);
120 shading interp

```

Listing 5.2: Matlab code for plotting complex orbitals

```

1 # This script is for Making multiple output file and running the
2     london program for every file
3 #Uncomment the tuple accordingly for B only in X direction , B only
4     in Y direction & only in Z direction
5 import os
6 import numpy as np
7 #For B only in X direction
8 t= tuple((np.around(i,2),0,0) for i in np.around(np.linspace
9     (0,0.1,10),2))
10
11
12 #Loading the given input file of H2O
13 f=open('h2o.UHF.0.000.inp')
14 script=open('h2o.sh')
15 with script as line:
16     scr=line.readlines()
17 with f as line:
18     #reading through the file
19     s=line.readlines()
20 #s will be as a list
21 for i in range(len(t)):
22     #I find out that line 102 ,that is here s[102] contains the
23         magnetic field value and Now change that value to our input
24         vlaues
25     s[102]=f'    magnetic-field = {str(t[i])}\n'
26
27 k=open("file_x"+str(i)+".inp","w")
28 #writting that input to a seperate file for every Magnetic
29 field value

```

```

24     #New input file created
25     for j in s:
26         k.write(j)
27     k.close()
28 #for script file update
29     scr[23]=f'/home/sangita.sen/packages/london/london.x file_x'+
30     str(i)+'.inp >file_x'+str(i)+'.out\n'
31     script1=open("h2o_x_"+str(i)+".sh","w")
32     for l in scr:
33         script1.write(l)
34     script1.close()
35
36     #Running the london with every file and save the output to a
37     #Give the london.x path according to your path variable (For me
38     #it is /home/rahul/Documents/london./london.x)
39     os.system("qsub h2o_x_"+str(i)+".sh")
40 f.close()

```

Listing 5.3: Python code for running london

```

1 #To extract the energies from the output file
2 import numpy as np
3 #running for every output file at once
4 for xx in range(10):
5     #opening the output file
6     #edit the file name string accordingly
7     l="file_x"+str(xx)+".out"
8     g=open(l,'r')
9
10    #reading through the output file
11    with g as line:
12        p=line.readlines()
13        #print(p)
14    j=0
15    for i in p:
16        j=j+1
17        #searching a specific string i from the file line p
18        if i=='The Final eigenvalues from the Davidson method\n':
19
20            #print(i)
21            #print(p[j+1])
22            #From the file p[j+1] will give us the string containing
23            #the energy values
24            v=p[j+1]
25            #print(type(v))
26            #print(v)
27
28            #splitting the v string with space
29            jj=v.split()
30            #print(jj)
31            c=[]
32            #extracting the energies only to o
33            o=jj[3::]
34            #print(o)
35            #float the numbers in the list and appending to c
36            for i in o:
37                c.append(float(i))
38            #print(c)

```

```

38
39     a=np.array(c)
40     #filename=input("filename is := ")
41     #can change the file name according to the magnetic field
42     #directions
43     n=open("arrayX.txt","a+")
44     #writting to file only with energy values
45     np.savetxt(n,a,newline="\n")
46
47     n.close()

```

Listing 5.4: Python code for extraction of energy

```

1 L=[]
2 for i in range(11):
3     with open('file_y'+str(i)+'.out') as line:
4         l=line.readlines()
5         L.append(float(l[591][33:51]))
6 import numpy as np
7 np.savetxt('xvalue.txt',np.array(L))

```

Listing 5.5: Python code for extraction of Hartree-energy

```

1 #!/bin/bash
2 # Parallel job submission script:
3 # Usage: qsub <this_script>
4 # The shell used to run the job
5 #\$ -S /bin/bash
6 #
7 # The name of the parallel queue to submit the job to
8 #
9 # Define the parallel runtime environment and number of nodes
10 # NB: number of nodes is one more than needed as one copy resides
11 #      on the master node
12 #\$ -pe mpi 1
13 # Use location that job was submitted as working directory
14 #\$ -cwd
15 #
16 # Export all environment variables to the slave jobs
17 #\$ -V
18 #
19 # Put stdout & stderr into the same file
20 #\$ -j y
21 #
22 # The name of the SGE logfile for this job
23 #\$ -o output.log
24 #mpexec -n $ NSLOTS ./heat
25 /home/sangita.sen/packages/london/london.x file_x+str(i)+.inp >
    file_x+str(i)+.out

```

Listing 5.6: bash file for cluster