

Project Report

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Arun Kantholi

Exploring Atomic and Molecular Electronic Excitation in Strong Magnetic Fields

Prof. Dr. Sangita Sen



Abstract

Magnetic features like moments, susceptibilities, and others are defined through perturbation. As a result, they are suitable for describing how a molecule responds to weak external magnetic fields, however, when the magnetic fields reach around 10^5 Tesla .

The electrical and magnetic interactions start to compete with each other and cannot be considered perturbations anymore. These types of fields are commonly found in highly magnetized white dwarfs and neutron stars, and studying the spectroscopic characteristics of atoms and molecules in such celestial bodies is essential for astrophysicists. Analyzing the spectra from magnetized white dwarfs is one practical application of this research. The complex electronic structures resulting from magnetic interactions make it difficult to form an intuitive understanding of the molecule and the resulting spectra, bonding, and reactivity. This project aims to examine the electronic structure of molecules in strong magnetic fields from these perspectives and also enhance our theoretical methods to address this extreme environment. Explore the electronic structure of molecules in the presence of strong magnetic fields within the framework of their electronic spectra, although there are many possible avenues of research. Our goal is to use Hartree-Fock linear response (equivalent to time-dependent Hartree-Fock or TDHF theory), also known as the Random Phase Approximation (RPA), and Tamm-Dancoff approximation (TDA) to calculate shifts in peak positions and intensities, and then explain these shifts in terms of electronic structure.

External magnetic fields that aren't uniform and act on molecules cause spin densities and break spin symmetry in a non-collinear manner. This requires a representation of a general two-component Pauli spinor. we present the implementation of a general Hartree-Fock method, without any restrictions on spin, for calculations with finite non-uniform fields that are non-perturbative. London atomic orbitals are used for faster convergence of the basis and to maintain invariance under constant magnetic vector potential gauge shifts. We have used this implementation to study the joint response of the orbital and spin to a field gradient, which is quantified by anapole moments, in a series of small molecules. The theoretical and computational analysis has revealed that spin effects are more robust in closed shell molecules, exhibiting a paramagnetic behavior, while orbital effects can have varying directions. We have also reported the convergence of the basis set and size effects of anapole susceptibility tensors. Additionally, the relationship between the mixed anapole susceptibility tensor and chirality is demonstrated.

This work computes exotic properties such as induced toroidal/anapole moments, and we aim to calculate excited state anapole moments, which has not been done before. This suggests that significant findings obtained from our research may be extrapolated to real experimental systems in the future.

1. Introduction

1.1 Literature Review

What is Electronic Structure Theory?

Properties Predicted by Electronic Structure Theory

According to one of the principles in quantum mechanics, if we know the wavefunction

$$\Psi(r, t)$$

of a given system, we can determine any property of that system, however, at least in principle. Obviously, if we use approximations in determining the wave function, then the properties obtained from that wavefunction will also be approximate. In the context of electronic structure theory, we typically only have access to the electronic wavefunction and not the complete wavefunction for electrons and nuclei, which means that certain properties related to nuclear motion might not be available. Nevertheless, by using the electronic structure results, we can obtain valuable information about a chemical reaction and perform subsequent dynamics calculations. Fortunately, many properties can be determined solely by examining the electronic problem. For instance, since the electronic energy represents the potential energy experienced by the nuclei, optimizing the electronic energy in relation to the nuclear coordinates gives us the equilibrium configuration of the molecule, which may be a global or local minimum.

The electronic wavefunction or its various derivatives are sufficient to determine the following properties:

- Geometrical structures (rotational spectra).
- Rovibrational energy levels (infrared and Raman spectra)
- Electronic energy levels (UV and visible spectra)
- Quantum Mechanics + Statistical Mechanics \rightarrow Thermochemistry ($\Delta H, \Delta S, \Delta G, C_v, C_p$)

primarily gas phase

- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics, this leads to reaction rates and mechanisms..
- Ionization potentials (photoelectron and X-ray spectra)
- Electron affinities
- Franck-Condon factors (transition probabilities, vibronic intensities)
- IR and Raman intensities
- Electron density maps and population analyses
- Dipole moments and Polarizabilities
- Magnetic shielding tensors \rightarrow NMR spectra

Hartree-Fock Molecular Orbital Theory

Hartree-Fock theory plays a fundamental role in electronic structure theory. It serves as the foundation for molecular orbital (MO) theory, which suggests that the movement of each electron can be described by a single-particle function (orbital) independent of the instantaneous motions of other electrons. You may have encountered Hückel MO theory, which builds upon Hartree-Fock MO theory and simplifies calculations by disregarding most terms. The widespread usage of orbital concepts in chemistry is a testament to the Hartree-Fock MO theory's predictive power and intuitive appeal. However, it is crucial to remember that these orbitals are mathematical constructs that only approximate reality. Only for the hydrogen atom (or other one-electron systems, like He^+) are the orbitals exact eigenfunctions of the complete electronic Hamiltonian. As long as we focus on molecules near their equilibrium geometry, Hartree-Fock theory often serves as a solid starting point for more advanced theoretical approaches that provide better approximations to the electronic Schrödinger equation (e.g., many-body perturbation theory, single-reference configuration interaction).

The Hartree-Fock (HF) method is a widely used approximation technique for calculating a quantum many-body system's wave function and energy in a stationary state. In computational physics and chemistry, this method assumes that the exact wave function of the system can be approximated by either a single Slater determinant (for fermions) or a single permanent (for bosons) of spin orbitals. These spin orbitals are determined by solving the Hartree-Fock equation, which involves an effective one-body operator known as the Fock operator instead of the many-body Hamiltonian. A set of coupled equations for the spin orbitals can be derived using the variational method. Solving these equations provides the Hartree-Fock wave function and energy for the system.

$$f(x_1)\chi_i(x_1) = \epsilon\chi_i(x_1)$$

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

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

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

$$\sum_v F_{v\mu} C v_i = \sum_i \sum_v S_{v\mu} C v_i$$

$$FC = SC_\epsilon$$

where S is an overlap matrix of basis function, C_i are the basis coefficient of molecular orbital i and ϵ is the diagonal matrix of the orbital energy i

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

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 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 B.

Electronic Excitation in a Magnetic Field

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.

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. 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 is based on the working equations derived herein.

Time independent formulation of Linear Response Theory

Let

$$|gs\rangle = \text{Exactgroundstate}$$

$$\hat{X} = \text{ExcitationOperator}$$

$$\hat{X}|gs\rangle = \text{Exactexcitedstate}$$

$$E_a i = \text{ExcitationOperator from state } i \text{ to } a$$

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

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

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

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

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

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

$$\langle gs|\hat{E}_{ai},\hat{H}|X\rangle = E_x\langle gs|E_{ai}|X\rangle$$

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

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

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

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

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

Equation(can be regarded as the equation for computing the excitation energy ω

To obtain the working equation for RPA we make the following approximations.

Replace exact ground state with Hartree-Fock ground state

$$|gs\rangle = |HF\rangle$$

$$\hat{X} \text{ as single excitation operator}$$

$$\hat{X} \rightarrow \hat{Y} + \hat{z}$$

where \rightarrow Single excitation operator \rightarrow Single de-excitation operator

- If

$$\hat{X} = \hat{Y}$$

Then this is called Tamm-Dancoff approximation (TDA)

Investigation of Anapole susceptibility

These assumptions include a uniform or dipole field, as well as the use of low-order perturbation theory. For many purposes, these assumptions are reasonable, given that laboratory magnetic fields are generally weaker than molecular energy scales. However, there are unexplored effects that go beyond these idealizations. Examples include the behavior of atoms and molecules in strong uniform magnetic fields and the response of molecular systems to magnetic field gradients. These responses can be divided into orbital and spin effects, both of which have been relatively underexplored. The only notable exception is the work by Lazzeretti and co-workers, who have developed a perturbative formalism for the orbital response due to field gradients. There have been a few computational studies at different levels, including the Hückel level, Hartree–Fock (HF) level, and correlated levels.

The perturbative method becomes difficult to manage for a higher-order magnetic response, especially when using London atomic orbitals (LAOs) to ensure gauge-origin invariance and speed up basis set convergence. When using ordinary Gaussians, very large basis sets are needed to approach gauge-origin invariance. In our approach, we combine LAOs with a non-perturbative (finite field) method. This requires implementing integral evaluation for the LAOs, which are hybrid functions of plane waves and Gaussians but does not require any additional modifications for higher-order properties. One advantage of this implementation is that only the one-electron part of the Hamiltonian is modified for different external fields, and no extra effort is needed to extend it to post-Hartree–Fock theories. Therefore, it offers the possibility of studying non-perturbative phenomena. Recently, a finite field procedure has been developed for both uniform and non-uniform magnetic fields involving LAOs. This has led to the discovery of a non-perturbative transition from closed-shell para- to diamagnetism and a new bonding mechanism in very strong magnetic fields.

A way to conveniently measure the response to magnetic field gradients is through the anapole moment. In the energy's multipole expansion, anapole moments are the moments that couple linearly to the curl of the magnetic field. They have been mostly ignored since they were first considered by Zeldovich in 1957, who also coined the term "anapole." These moments differ from the usual magnetic moments that arise from a perturbative expansion in the magnetic field. Instead, they can be visualized as resulting from the meridional currents in a toroidal charge distribution. Anapole moments are antisymmetric under both spatial

inversion and time reversal. Nuclear physicists have given attention to anapole moments due to their connection with parity violation in atoms and molecules. The first experimental evidence for anapole moments came from measurements on the Cs atom. Spaldin et al. have proposed experiments to measure anapole moments in ferrotoroidic materials. There have also been suggestions for experiments to measure permanent and induced electronic anapole moments. Only specific structures possess permanent anapole moments, such as molecular nanotoroids, ferroelectric nanostructures, ferromagnetic structures, and Dy clusters. Various groups have demonstrated anapole moments in metamaterials for potential sensor applications. In the presence of an external non-uniform field, toroidal spin and/or orbital currents are induced, resulting in anapole moments that can be computed through the corresponding susceptibilities. The induced anapolar current densities have been studied for conjugated cyclic acetylenes. Another study analyzed the topological characteristics of anapolar current densities in small molecules. Spin and orbital contributions to anapole moments have been examined in a simple analytical model of diatomics. Ab initio computational studies, both perturbative and non-perturbative, have estimated the orbital contribution to anapole susceptibilities in closed-shell molecules. Recent efforts have also focused on gaining a further understanding of the interactions between toroidal moments and external fields.

In this study, we investigate the combined effects of orbital and spin in a group of molecules under magnetic field gradients. Our focus is on transverse gradients and the resulting induced anapole moments. We numerically examine the relative significance of orbital and spin effects. Additionally, we offer theoretical findings on the direction and additivity of spin contributions to induced anapole moments..

1. When a magnetic field is applied to a molecule, one of the two things can happen
 - (a) the energy is lowered: molecular paramagnetism.
 - (b) the energy is raised: molecular diamagnetism.
1. Open-shell molecules are paramagnetic.
 - (a) permanent magnetic moments (unpaired spins).
 - (b) the molecule reorients itself and moves into the field.
 - (c) temperature dependent.
1. No permanent magnetic moment.
 - (a) induced magnetic dipole.
 - (b) induced currents oppose the external field (Lenz's law)
 - (c) temperature independent.
 - (d) much weaker than open-shell paramagnetism.

Hamiltonian in a Uniform magnetic field For the uniform magnetic field in the z direction, the hamiltonian can be written as,

$$H = H_0 + \underbrace{\frac{1}{2}\mathbf{B}\mathbf{L}_z}_{\text{Orbital Paramagnetic}} + \underbrace{\mathbf{B}\mathbf{S}_z}_{\text{Spin Paramagnetic}} + \underbrace{\frac{1}{8}\mathbf{B}^2(\mathbf{x}^2 + \mathbf{y}^2)}_{\text{Diamagnetic}}$$

Paramagnetic Zeeman terms split energy levels depending on L and S value of the state.

Diamagnetic terms always raise the energy.

Diamagnetism: To reduce energy, $x^2 + y^2$ is minimized, ie. atoms become squeezed.

Open-Shell: Initial lowering by paramagnetic Zeeman till the diamagnetic terms take over
→ Quadratic Zeeman effect

Closed Shell: $L_z = S_z = 0$ for ground state.

1 Hamiltonian and properties

In the following sections, we will examine electronic systems that are exposed to a magnetic field that varies linearly and is represented by the following form

$$\mathbf{B}_{\text{tot}}(\mathbf{r}) = \nabla \times \mathbf{A}_{\text{tot}} = \mathbf{B} + \mathbf{r}_h^T \mathbf{b} - \frac{1}{3} \mathbf{r}_h \text{Tr}(\mathbf{b})$$

The magnetic field with a uniform component \mathbf{B} , \mathbf{b} is a 3×3 matrix defining the field gradients, and

$$r_h = r - h$$

is the position relative to some reference point h . This type of magnetic field is most naturally viewed as arising from a Taylor expansion around $\mathbf{r} = h$, truncated at linear order. The corresponding vector potential can be written as

$$\begin{aligned} \mathbf{B}_{\text{tot}}(\mathbf{r}) &= \nabla \times \mathbf{A}_{\text{tot}} \\ &= \mathbf{B} + (\mathbf{r} - \mathbf{h})^T \mathbf{b} - \frac{1}{3} \mathbf{r} \text{Tr}(\mathbf{b}) \end{aligned}$$

In the context of the total vector potential given by

$$\mathbf{A}_{\text{tot}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r}_g) - \frac{1}{3} \mathbf{r}_h \times (\mathbf{r}_h^T \mathbf{b}),$$

In the context where $r_g = r - g$ with g as the gauge origin, it is established that $\mathbf{B}_{\text{tot}} = \nabla \times \mathbf{A}_{\text{tot}}$. The magnetic field maintains its divergence-free property ($\nabla \cdot \mathbf{B}_{\text{tot}} = 0$) even in the presence of a non-traceless \mathbf{b} due to the contribution of the term $\frac{1}{3} r_h \text{Tr}(\mathbf{b})$ in Eq. (1). Progressing further, focus shifts to the anti-symmetric part, $C_\alpha = (\nabla \times \mathbf{B}_{\text{tot}}(\mathbf{r}))_\alpha = \epsilon_{\alpha\beta\gamma} b_{\beta\gamma}$, of the matrix \mathbf{b} . Assuming the symmetric part vanishes ($\mathbf{b} = \mathbf{b}^T$), the analysis proceeds.

$$\mathbf{A}_{\text{tot}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}_g - \frac{1}{3} \mathbf{r}_h \times (\mathbf{C} \times \mathbf{r}_h) \quad (2)$$

The total magnetic field is given by

$$\mathbf{B}_{\text{tot}}(\mathbf{r}) = \mathbf{B} + \frac{1}{2} \mathbf{C} \times \mathbf{r}_h \quad (3)$$

Here, the gradients are represented in the 3×3 matrix \mathbf{b} .

$$b_{\mu\lambda} = b_{\mu\lambda}^{\text{sym}} + \frac{1}{2} \epsilon_{\mu\lambda\alpha} C_\alpha \quad (4)$$

The symmetric part of the gradient matrix is defined as

$$\mathbf{b}^{\text{sym}} = \frac{1}{2} (\mathbf{b} + \mathbf{b}^T) = 0 \quad (5)$$

Furthermore, the anti-symmetric part C_α is related to the total magnetic field gradient through

$$C_\alpha = (\nabla \times \mathbf{B}_{\text{tot}}(\mathbf{r}))_\alpha = \epsilon_{\alpha\beta\gamma} b_{\beta\gamma} \quad (6)$$

Furthermore, the constant vector encoding the anti-symmetric part of b equals the curl of the magnetic field, $\nabla \times \mathbf{B}_{\text{tot}} = \mathbf{C}$.

The non-relativistic Schrödinger–Pauli Hamiltonian is given by

$$\hat{H} = \frac{1}{2} \sum_l \hat{\pi}_l^2 - \sum_l v(r_l) + \sum_{k < l} \frac{1}{r_{kl}} + \sum_l \mathbf{B}_{\text{tot}}(r_l) \cdot \hat{\mathbf{S}}_l$$

In this context, the mechanical momentum operator is defined as $\hat{\pi}_l = -i\nabla_l + A_{\text{tot}}(r_l)$, where $A_{\text{tot}}(r_l)$ represents the total vector potential. Properties of the system can be alternatively viewed as expectation values $\langle \Psi | \hat{\Omega} | \Psi \rangle$ or as derivatives of the energy in terms of a Taylor expansion $E = \langle \Psi | \hat{H} | \Psi \rangle$. These properties are related to terms in a Taylor expansion, with the first-order properties including the orbital and spin magnetic dipole moments.

$$L_{\mathbf{q}} = \sum_l \langle \psi | \hat{L}_{\mathbf{q};l} | \psi \rangle, \quad \hat{L}_{\mathbf{q};l} = \mathbf{r}_{\mathbf{q};l} \times \hat{\pi}_l$$

$$S = \sum_l \langle \psi | \hat{S}_{\mathbf{l};l} | \psi \rangle$$

which combine to a total dipole moment $\mathbf{J}_{\mathbf{q}} = \mathbf{L}_{\mathbf{q}} + 2\mathbf{S}$. Here, \mathbf{q} is an arbitrary reference point. Given the form of the magnetic vector potential above, it is $\mathbf{L}_{\mathbf{g}}$, with the reference point at the gauge origin, which is the relevant magnetic dipole moment. The anapole moment is similarly given by

$$a = - \sum_l \langle \psi | r_{\mathbf{h};l} | \psi \rangle \times \left(\frac{1}{3} \hat{L}_{\mathbf{q};l+\hat{\mathbf{S}}_{\mathbf{l}} | \psi} \right)$$

The weighting of the orbital and spin contributions to these quantities is not arbitrary and takes a more intuitive form when they are expressed in terms of the total current density,

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= \frac{\partial E}{\partial \mathbf{A}_{\text{tot}}(\mathbf{r})} \\ &= \frac{1}{2} \sum_l \langle \psi | \delta(r_l - r) \hat{\pi}_l | \psi \rangle + \sum_l \langle \psi | \delta(r_l - r) \hat{S}_l | \psi \rangle \end{aligned}$$

where the first term is the orbital current density and the last term—the curl of the spin density—is the spin current density. The magnetic dipole moment and anapole moment can now be identified with linear and quadratic moments of the total current density,

$$\mathbf{j}(\mathbf{g}) = \int \mathbf{r}(\mathbf{g}) \times \mathbf{j}(\mathbf{r}) d\mathbf{r}$$

$$\mathbf{a} = -\frac{1}{3} \int \mathbf{r}(\mathbf{g}) \times \mathbf{j}(\mathbf{r}) d\mathbf{r}$$

$$\mathcal{M}'_{\alpha\beta} = \left. \frac{\partial L_g; \alpha(B, C)}{\partial C_\beta} \right|_{B=0, C=0}$$

$$\mathcal{M}''_{\alpha\beta} = \left. \frac{\partial \alpha\beta(B, C)}{\partial B_\beta} \right|_{B=0, C=0}$$

In the basis set limit, equivalence is restored, i.e., $\mathcal{A}' = \mathcal{A}'$ and $\mathcal{M} = \mathcal{M}' = \mathcal{M}''$. However, for finite LAO basis sets, numerical investigation of the basis set convergence is warranted.

2 The General Hartree-Fock model with an external non-uniform magnetic field

The magnetic field B is constant and aligned with the z -axis, the spin operators \hat{S}^2 and \hat{S}_z commute with the Hamiltonian, and each molecular orbital can be expressed as a product where a spatial function is multiplied by a constant spin part. Additionally, each spin part defines a spin that is either parallel or anti-parallel to B - the uniform field establishes a global spin quantization axis. However, in the presence of a non-uniform magnetic field, neither \hat{S}^2 nor any projection $\mathbf{u} \cdot \hat{\mathbf{S}}$ (on a fixed unit vector \mathbf{u}) necessarily produce good quantum numbers. This leads to the coupling of the spatial and spin parts of molecular orbitals, requiring a representation as 2-component Pauli spinors. Since the direction of the magnetic field changes with position, there is no natural global spin quantization axis, and the spin density becomes non-collinear. This setting is unique as it involves a non-relativistic Hamiltonian that necessitates a non-collinear, 2-component representation.

The Hartree-Fock (HF) models in the non-relativistic domain may be subdivided into Restricted HF (RHF), Unrestricted HF (UHF), Restricted Open-shell HF (ROHF), and General HF (GHF). The RHF model imposes singlet spin symmetry and is therefore oblivious to the spin-Zeeman term, making it a useful analysis tool for estimating the purely orbital contribution to the total magnetic field effect. The UHF and ROHF flavors impose a global spin quantization axis and are therefore not meaningful in combination with a position-dependent spin-Zeeman term. Nonetheless, we shall consider below UHF results obtained with the spin-Zeeman term disabled in order to isolate the purely orbital field effects in open-shell systems. In order to treat joint orbital and spin effects, the HF flavor can be no less than a complex GHF mode

In more detail, molecular orbitals $\phi_K(r)$ in the GHF model take the form of generic 2-component spinors,

$$\phi_K(r) = \sum_a C_{\uparrow}^{a,K} \chi^a(r) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sum_a C_{\downarrow}^{a,K} \chi^a(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Alternatively, the expression for $\phi_K(r)$ can be written as

$$\phi_K(r) = \sum_a \chi^a(r) \begin{pmatrix} C_{\uparrow}^{a,K} \\ C_{\downarrow}^{a,K} \end{pmatrix}$$

Where χ_a denotes a spin-free basis function. From now on, Ψ will denote a Slater determinant formed from such spinors. The spinors also define an associated 2×2 density matrix kernel,

$$\begin{aligned} D^2 \times^2 &= \sum_K^{OCC} \phi_K(r) \phi_K(r') \\ &= \sum_{ab} \chi_a(r) \begin{pmatrix} D_{ab}^{\uparrow\uparrow} & D_{ab}^{\uparrow\downarrow} \\ D_{ab}^{\downarrow\uparrow} & D_{ab}^{\downarrow\downarrow} \end{pmatrix} \chi_b(r') \end{aligned}$$

For given basis function indices a and b , the corresponding matrix elements are written as

$$D_{ab}^{\sigma\tau} = \sum_K C_K^a{}^{\sigma\tau*}, \quad \sigma, \tau \in \{\uparrow, \downarrow\}$$

The GHF electronic energy can be decomposed into kinetic, spin-Zeeman, electrostatic nuclear attraction, Coulomb repulsion, and exchange energy. Only the spin-Zeeman and exchange terms differ substantially from the standard RHF and UHF forms since only these terms involve the off-diagonal spin blocks of $D^2 \times^2$. When evaluating the spin-Zeeman term, it is convenient to introduce density matrix-like quantities obtained by letting the Pauli spin matrices act on $D^2 \times^2$ and tracing out the spin degrees of freedom,

$$\begin{aligned} M_x(r, r') &= \sum_{\tau} \langle \tau | \sigma_x D^2 \times^2(r, r') | \tau \rangle \\ &= \sum_{ab} \chi_a(r) \chi_b(r') (D_{ab}^{\downarrow\uparrow} + D_{ab}^{\uparrow\downarrow}) \end{aligned}$$

$$\begin{aligned} M_y(r, r') &= \sum_{\tau} \langle \tau | \sigma_y D^2 \times^2(r, r') | \tau \rangle \\ &= \sum_{ab} \chi_a(r) \chi_b(r')^* (D_{ab}^{\downarrow\uparrow} - D_{ab}^{\uparrow\downarrow}) \end{aligned}$$

$$\begin{aligned} M_z(r, r') &= \sum_{\tau} \langle \tau | \sigma_z D^2 \times^2(r, r') | \tau \rangle \\ &= \sum_{ab} \chi_a(r) \chi_b(r')^* (D_{ab}^{\uparrow\uparrow} - D_{ab}^{\downarrow\downarrow}) \end{aligned}$$

Letting $S_{ba} = \int \chi_b(r)^* \chi_a(r) dr$ denote an overlap integral and $\mu_{ba;\gamma} = \int r^\gamma \chi_b(r)^* \chi_a(r) dr$ a dipole moment integral, the spin-Zeeman term is given by

$$\begin{aligned}
 E_Z &= \sum_l \langle \Psi | B_{\text{tot}}(r_l) \cdot \hat{S} | \Psi \rangle \\
 &= \frac{1}{2} \int B_{\text{tot}}(r) \cdot M(r, r) dr \\
 &= \frac{1}{2} (B_x S_{ba} + \mathcal{M}_{ba;\gamma_x} (D_{ab}^{\downarrow\uparrow}, D_{ab}^{\uparrow\downarrow}) \\
 &\quad + \frac{1}{2} (B_y S_{ba} + \mathcal{M}_{ba;\gamma_y} (-i D_{ab}^{\downarrow\uparrow}, D_{ab}^{\uparrow\downarrow}) \\
 &\quad + \frac{1}{2} (B_z S_{ba} + \mathcal{M}_{ba;\gamma_z} (-i D_{ab}^{\downarrow\uparrow}, D_{ab}^{\uparrow\downarrow})
 \end{aligned}$$

With implicit summation over repeated indices and the notation $\tilde{b} = b - \frac{1}{3} \text{Tr}(b) I$ and $\tilde{B} = B - h^T \tilde{b}$. The contribution to the Fock matrix is obtained as the derivative.

With the compact notation $\tilde{B}_\pm = \tilde{B}_x \pm i \tilde{B}_y$ and $\tilde{b}_{\gamma,\pm} = \tilde{b}_{\gamma x} \pm i \tilde{b}_{\gamma y}$, the spin blocks are given by

$$F^{2 \times 2}_{Z;ba} = \begin{pmatrix} B_z S_{ba} + \mathcal{M}_{ba;\gamma_z} & B_- S_{ba} + \mathcal{M}_{ba;\gamma_-} \\ B_+ S_{ba} + \mathcal{M}_{ba;\gamma_+} & B_z S_{ba} + \mathcal{M}_{ba;\gamma_z} \end{pmatrix}$$

Turning to the exchange energy, we use Mulliken notation for the electron-electron repulsion integrals and write

$$E_X = \sum_{KL}^{OCC} (KL|LK) = -\frac{1}{2} D^{\sigma\tau:da} D^{\tau\sigma:bc} (ab|cd)$$

again with implicit summation over spin and basis function indices. The exchange contribution to the Fock matrix is obtained as

$$\frac{\partial E_x}{\partial D^{\sigma\tau:ef}} = -D^{\tau\sigma:bc} (eb|cf)$$

Alternatively, in a 2×2 component form,

$$K^{2 \times 2}_{fa} = - \begin{pmatrix} D^{\uparrow\uparrow bc} & D^{\uparrow\downarrow bc} \\ D^{\downarrow\uparrow bc} & D^{\downarrow\downarrow bc} \end{pmatrix}$$

3 WORK IS PROGRESSING.....