Generalized Hartree-Fock with a Non-perturbative Treatment of Strong Magnetic Fields: Application to Molecular Spin Phase Transitions

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Abstract

In this work, we present a framework of an *ab initio* variational approach to effectively explore electronic spin phase transitions in molecular systems inside a homogenous magnetic field. In order to capture this phenomenon, the Complex generalized Hartree-Fock ($\mathbb{C}$-GHF) method is used in the spinor formalism with London orbitals. Recursive algorithms for computing the one- and two-electron integrals of London orbitals are also provided. A Pauli matrix representation of the $\mathbb{C}$-GHF method is introduced to separate spin contributions from the scalar part of the Fock matrix. Next, spin phase transitions in two different molecular systems are investigated in the presence of a strong magnetic field. Non-collinear spin configurations are observed during the spin phase transitions in H_2 and a di-Chromium complex, $[(H_3N)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, with an increase in magnetic field strength. The competing driving forces of exchange coupling and the spin Zeeman effect have been shown to govern the spin phase transition and its transition rate. Additionally, the energetic contributions of the spin

Zeeman, orbital Zeeman, and diamagnetic terms to the potential energy surface are also analyzed.

1 Introduction

Electron spin is a fundamental physical property that is important to a wide array of science and technological applications such as energy storage, quantum computing, and chemical catalysis. An atomic or molecular system has a spin-dependent many-electron response that can be perturbed by an external electromagnetic field. Although effective model Hamiltonians with perturbative treatments of external fields[1–4] have their merits, they are limited in their description of spin-dependent processes in the strong perturbation limit. While molecular response to external electric fields has been a subject of extensive theoretical work, computational frameworks for modeling finite magnetic field effects have been lagging behind mainly due to three challenges; the gauge-origin problem, spin non-collinearity, and necessity of complex arithmetic.

For many-atom systems, electronic structure calculations in the presence of electromagnetic fields become dependent on the choice of the gauge-origin, mainly due to the basis set incompleteness of Gaussian type orbitals.[5–12] Among various approaches to correct for the gauge-origin problem, electronic structure methods using London type orbitals[13,14] provide the most satisfactory solution.[15–21] London orbitals are constructed from conventional atomic orbitals dressed by a complex phase factor that depends on the external vector potential, and are considered physically appropriate for modeling chemical systems in an external magnetic field.[5]

In the non-perturbative limit, such as in the presence of a strong magnetic field, variational treatment of the electronic structure using London orbitals is required.[22–24] For this purpose, Helgaker and coworkers have made algorithmic advances for evaluating one- and two-electron integrals using London orbitals, and applied a variational approach to study

molecules in strong magnetic fields within the spin collinear framework at the level of Hartree-Fock,[25,26] coupled cluster,[27] configuration interaction,[28] density functional theory, and current density functional theory.[29–31] While the electronic characteristics of spin states in a magnetic field can be obtained using a variational spin-collinear method, the spin phase transition process, *e.g.*, from singlet to triplet, driven by a static magnetic field requires a spin-noncollinear treatment.

It is well known that certain symmetry breaking, such as an external static magnetic field breaking time reversal symmetry and geometric frustration breaking continuous translation symmetry, will cause noncollinear spin configurations to arise.[32–36] Thus, a proper description of spin processes must come from a solution of the first-principles spin-dependent Hamiltonian that allows a variational treatment of non-collinear spin. The generalized Hartree-Fock (GHF) method removes the spin collinear constraint from conventional restricted and unrestricted Hartree-Fock (RHF and UHF) methods so that spins are allowed to rotate freely in a non-collinear framework. A detailed history of the early GHF method can be found in Reference 37 and we refer readers to a recent review[36] on non-collinear spin. The GHF approach has been shown to be a convenient and inexpensive computational platform to simulate spin dynamics of a single spin center in a static magnetic field[38] and in a dissociated reaction.[39]

In this work, we introduce a variational spin non-collinear approach using the complex GHF ($\mathbb{C}$-GHF) method with London orbitals in the presence of a strong magnetic field. The method implemented herein is able to model both spin-collinear and noncollinear phenomena as well as the processes underlying the magnetic field induced spin phase transition. Note that during the preparation of this manuscript, a variational GHF approach has been applied to studies of orbital and spin effects in molecules subject to non-uniform magnetic fields.[40]

2 Methodology

2.1 Spinor Formalism of Generalized Hartree-Fock with London Orbitals

In order to treat non-collinear spins in a non-perturbative magnetic field, one needs to retain the full vector form of the magnetization $\mathbf{m}(\mathbf{r})$ and allow each spin quantization axis to rotate. This is equivalent to writing the spin orbitals as a superposition of the spin-up and spin-down manifolds. For Hartree-Fock, this leads to the generalized Hartree-Fock (GHF) method,[32,34,36–38,41–43] which is similar in structure to the wave function used in two-component relativistic models.[44–53]

The spinor orbital is defined as

$$\psi_j(\mathbf{r}) = \begin{pmatrix} \phi_j^{\alpha}(\mathbf{r}) \\ \phi_j^{\beta}(\mathbf{r}) \end{pmatrix} \tag{1}$$

The spatial functions $\{\phi_j^{\alpha}(\mathbf{r}, \mathbf{k}_A)\}$, $\{\phi_j^{\beta}(\mathbf{r}, \mathbf{k}_A)\}$ are expanded in terms of a common set of complex London orbitals $\{\tilde{\chi}_{\mu}(\mathbf{r}, \mathbf{k}_A)\}$,

$$\phi_j^{\alpha}(\mathbf{r}, \mathbf{k}_A) = \sum_{\mu} C_{\mu j}^{\alpha} \tilde{\chi}_{\mu}(\mathbf{r}, \mathbf{k}_A) \tag{2}$$

$$\phi_j^{\beta}(\mathbf{r}, \mathbf{k}_A) = \sum_{\mu} C_{\mu j}^{\beta} \tilde{\chi}_{\mu}(\mathbf{r}, \mathbf{k}_A) \tag{3}$$

$$\tilde{\chi}_{\mu}(\mathbf{r}, \mathbf{k}_A) = \chi_{\mu}(\mathbf{r} - \mathbf{R}_A) e^{i\mathbf{k}_A \cdot (\mathbf{r} - \mathbf{R}_A)} \tag{4}$$

where $\{\chi_{\mu}(\mathbf{r} - \mathbf{R}_A)\}$ are real atomic orbital (AO) basis functions centered at $\mathbf{R}_A$. The exponential form of the London orbital phase factor defines the local gauge origin at each nuclear center in the presence of magnetic field with a plane wave vector described by $\mathbf{k}_A = \frac{\mathbf{R}_A \times \mathbf{B}}{2}$, where $\mathbf{B}$ is the external magnetic field.

In the spinor orbital basis defined in Eq. (1), the Fock matrix ($\mathbf{F}$) and the density matrix

($\mathbf{P}$ with $P^{\sigma\sigma'}_{\mu\nu} = \sum_j^{\text{occ}} C^{\sigma}_{\mu j} C^{\sigma' *}_{\nu j}$) have a spin-blocked form,[38] shown in Eq. (5)

$$\mathbf{X} = \begin{pmatrix} \mathbf{X}^{\alpha\alpha} & \mathbf{X}^{\alpha\beta} \\ \mathbf{X}^{\beta\alpha} & \mathbf{X}^{\beta\beta} \end{pmatrix}, \quad \mathbf{X} \in \{\mathbf{F}, \mathbf{P}\} \tag{5}$$

In the current implementation, we cast the rank-2 spin-blocked $\mathbf{F}$ and $\mathbf{P}$ matrices in the Pauli matrix basis,[53]

$$\mathbf{F} = \sum_{n=0}^{3} \mathbf{F}_n \otimes \boldsymbol{\sigma}_n \tag{6}$$

$$\mathbf{P} = \sum_{n=0}^{3} \mathbf{P}_n \otimes \boldsymbol{\sigma}_n \tag{7}$$

$$\boldsymbol{\sigma}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

where the scalar ($\mathbf{F}_0$) and spin part ($\mathbf{F}_1, \mathbf{F}_2, \mathbf{F}_3$) of Fock matrix are defined as[53]

$$\mathbf{F}_0 = \mathbf{h}_0 + \mathbf{J}[\mathbf{P}_0] - \mathbf{K}[\mathbf{P}_0], \tag{8}$$

$$\mathbf{F}_n = \mathbf{h}_n - \mathbf{K}[\mathbf{P}_n], \quad n = 1, 2, 3. \tag{9}$$

The Coulomb ($\mathbf{J}$) and exchange ($\mathbf{K}$) matrices are,

$$J_{\mu\nu}[\mathbf{P}_0] = \sum_{\lambda\kappa} (\mu\nu|\kappa\lambda) P_{0,\lambda\kappa} \tag{10}$$

$$K_{\mu\nu}[\mathbf{P}_n] = \sum_{\lambda\kappa} (\mu\lambda|\kappa\nu) P_{n,\lambda\kappa}, \quad n = 0, 1, 2, 3 \tag{11}$$

where

$$(\mu\nu|\kappa\lambda) = \int \mathrm{d}^3\mathbf{r}_1 \int \mathrm{d}^3\mathbf{r}_2 \frac{\tilde{\chi}^*_\mu(\mathbf{r}_1, \mathbf{k}_A) \tilde{\chi}_\nu(\mathbf{r}_1, \mathbf{k}_B) \tilde{\chi}^*_\kappa(\mathbf{r}_2, \mathbf{k}_C) \tilde{\chi}_\lambda(\mathbf{r}_2, \mathbf{k}_D)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{12}$$

are the electron repulsion integrals (ERIs). Note that since ERIs using London orbitals are complex valued, they only have a four-fold symmetry instead of eight, as in the case of real-valued ERIs,

$$(\mu\nu|\kappa\lambda) =(\kappa\lambda|\mu\nu) = (\nu\mu|\lambda\kappa)^* = (\lambda\kappa|\nu\mu)^* \tag{13}$$

2.2 The Non-Relativistic Hamiltonian in the Presence of a Static and Uniform Magnetic Field

In the non-relativistic framework, the interaction of an electron spin with external electromagnetic field is described by the Schrödinger-Pauli Hamiltonian:

$$\hat{h}^{\text{Pauli}} = \frac{1}{2}\left[\boldsymbol{\sigma}\cdot(\mathbf{p}+\mathbf{A})\right]^2 - \hat{U} \tag{14}$$

where $\mathbf{A}$ and $\hat{U}$ are the vector potential and scalar potential of the electromagnetic field, respectively. $\mathbf{p} = -i\boldsymbol{\nabla}$ is the momentum operator. Given the relationship between the vector potential and the magnetic field, $\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r}$, the one-electron Pauli Hamiltonian can be written as

$$h^{\text{Pauli}} = \hat{h}_0(\mathbf{r}) + \frac{1}{2}(\boldsymbol{\sigma} - i\mathbf{r}\times\boldsymbol{\nabla})\cdot\mathbf{B} + \frac{1}{8}(\mathbf{B}\times\mathbf{r})^2 \tag{15}$$

where $\hat{h}_0(\mathbf{r})$ is the field-free one-electron Hamiltonian. The second term includes spin and orbital Zeeman contributions. The third term is the diamagnetic contribution and is quadratic in the strength of magnetic field, which can be expanded as

$$\begin{aligned}(\mathbf{B}\times\mathbf{r})^2 =&(B_y^2+B_z^2)x^2 + (B_x^2+B_z^2)y^2 + (B_x^2+B_y^2)z^2 \\ &- 2B_xB_yxy - 2B_yB_zyz - 2B_xB_zxz\end{aligned} \tag{16}$$

The orbital Zeeman and the diamagnetic term do not directly contribute to the spin dynamics.[38] Although these two terms are relatively small, they are important contributions

in diamagnetism.[54–57] In the presence of a strong magnetic field, these two terms account for significant contributions to the interaction between the chemical system and the external field.[26]

Using the formalism of generalized Hartree-Fock in the Pauli matrix basis (Eq. (6)), spin contributions in Eq. (14) can be separated from the scalar part. The resulting scalar Fock matrix is

$$\begin{aligned}\mathbf{F}_0 =&\mathbf{h}_0 + \mathbf{J}[\mathbf{P}_0] - \mathbf{K}[\mathbf{P}_0] - \frac{i}{2}\mathbf{L}\cdot\mathbf{B} + \frac{1}{8}\big\{(B_y^2+B_z^2)\mathbf{q}_{xx} + (B_x^2+B_z^2)\mathbf{q}_{yy} + (B_x^2+B_y^2)\mathbf{q}_{zz} \\ &- 2B_xB_y\mathbf{q}_{xy} - 2B_yB_z\mathbf{q}_{yz} - 2B_xB_z\mathbf{q}_{xz}\big\} \end{aligned} \tag{17}$$

where $\mathbf{L}_{\mu\nu} = \langle\tilde{\chi}_\mu|\mathbf{r}\times\boldsymbol{\nabla}|\tilde{\chi}_\nu\rangle$ is the orbital-angular momentum integral , and $(\mathbf{q}_{nm})_{\mu\nu} = \langle\tilde{\chi}_\mu|\hat{r}_n\hat{r}_m|\tilde{\chi}_\nu\rangle$ is the electric quadrupole integral. After spin separation using the Pauli matrices, spin components of the Fock matrix are

$$\mathbf{F}_n = \frac{1}{2}B_n\mathbf{S} - \mathbf{K}[\mathbf{P}_n], \quad n = 1,2,3. \tag{18}$$

where $\mathbf{S}$ is the overlap matrix.

2.3 Electron Integrals using London Type Orbitals

The electronic structure method introduced in this work requires the computation of one- and two-electron integrals of London orbitals. Integrals are evaluated in complex arithmetic, and corresponding recursion relationships are presented in the Appendix. In the current work, one- and two-electron integrals of London orbitals and the complex generalized Hartree-Fock method are implemented in the Chronus Quantum software package.[58]

3 Results and Discussion

The formalism of generalized Hartree-Fock in the spinor basis allows for calculations of non-collinear spin states within the *ab initio* framework. With the atomic London orbitals and associated one- and two-electron integrals, wave functions of chemical systems with multi-spin-centers in the presence of a static magnetic field can be variationally optimized. In this current work, we study the spin noncollinearity and magnetic phase transition of molecular systems driven by static magnetic fields. All ℂ-GHF calculations are done using the Chronus Quantum software package.

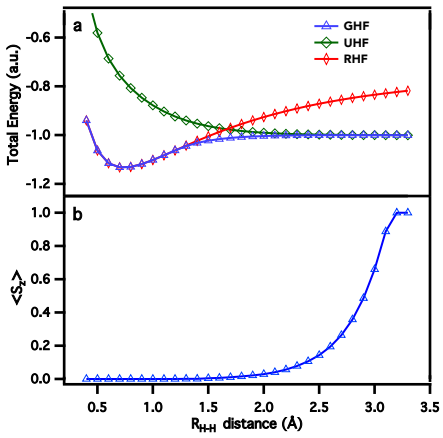

Figure 1. (**a**): The potential energy surface of an H_2 molecule in a homogenous magnetic field, $|B_z| = 0.001$ a.u. along the $-z$ direction. (**b**): The expectation value of S_z of the ℂ-GHF solution.

The first test case is a H_2 molecule in a uniform magnetic field. ℂ-GHF solutions in the presence of a static magnetic field were obtained with several different basis sets, including 6-31G, 6-31G(d,p), aug-cc-pVDZ, and aug-cc-pVTZ. Although differences in the absolute energy computed with different basis sets are noticeable, the expectation values of S_z at a given magnetic field only differ by less than 3%. In the following discussion, we will only present the results computed at the ℂ-GHF/aug-cc-pVTZ level of theory.[59] In this test system, the static magnetic field (1 a.u. $\approx 2.35 \times 10^5$ T, based on SI units for magnetic field) is aligned perpendicular to the molecular axis. Figure 1 plots the potential energy curve of an

H_2 molecule in a uniform magnetic field ($|B_z| = 0.001$ a.u. along the $-z$ direction) computed using the complex generalized Hartree-Fock (ℂ-GHF), complex unrestricted Hartree-Fock (ℂ-UHF), and complex restricted Hartree-Fock (ℂ-RHF) with London orbitals. ℂ-UHF and ℂ-RHF calculations are restricted to spin triplet ($S_z = 1$) and singlet ($S_z = 0$) states, respectively. The ℂ-GHF solution is not spin restricted. As a result, at all bond distances, the ℂ-GHF solution is always the lowest in energy.

From the equilibrium bond length toward the asymptotic dissociation limit, the change in $\langle S_z \rangle$ of the ℂ-GHF solution suggests that the system undergoes a spin phase transition from $\langle S_z \rangle = 0$ to 1. This spin phase transition is a result of the competing driving forces of the exchange coupling and paramagnetism. This can be understood from the perturbative and phenomenological spin Hamiltonian including both the spin exchange coupling and Zeeman effect,

$$H = -\frac{1}{2} J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2 - g\mu_B \mathbf{B} \cdot (\mathbf{S}_1 + \mathbf{S}_2) \tag{19}$$

$$= -\frac{1}{2} J_{12} |\mathbf{S}_1||\mathbf{S}_2| \cos(\theta) - g\mu_B B_z (S_{1z} + S_{2z}) \tag{20}$$

where J_{12} is the exchange coupling strength, g is the spin g-factor, and μ_B is the Bohr magneton. For a non-collinear spin alignment in the presence of a static magnetic field in the z direction depicted in Fig. 2, the spin Hamiltonian can be written as in Eq. (20), with the angle between the two spin vectors defined as θ. In the collinear spin electronic structure framework, such as RHF and UHF, θ can only be 0° or 180°. Without spin-orbit coupling, the exchange coupling is isotropic.

At the equilibrium bond distance, the exchange coupling is much stronger than the Zeeman term, giving rise to the antiparallel orientation of the two electrons, *i.e.*, a closed-shell configuration and $\theta = 180°$. As the bond length increases, the exchange coupling decreases exponentially, whereas the strength of the Zeeman effect remains constant. At certain bond lengths when the exchange coupling becomes weaker than the Zeeman term,

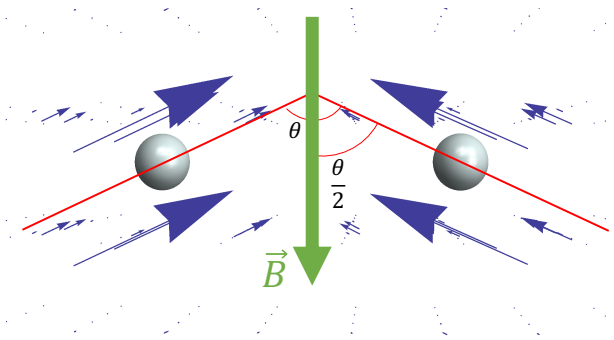

Figure 2. Illustration of non-collinearity of two spin vectors.

the electronic system undergoes a spin phase transition. This spin phase transition is a non-collinear process where θ can take on any value between 0° and 180°, and the non-collinear spin state has the lowest energy. In this regime, only the non-collinear $\mathbb{C}$-GHF can describe the electronic characteristics of the spin system.

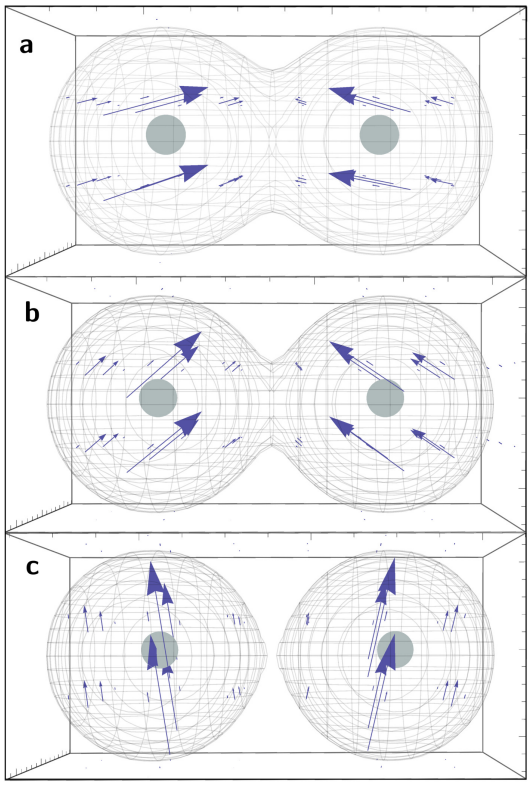

Figure 3. Spin magnetization vector at different H-H bond lengths. (**a**): R_{HH} = 2.6 Å, $\langle S_z \rangle$ =0.19428, (**b**): R_{HH} = 2.9 Å, $\langle S_z \rangle$ =0.48588, and (**c**): R_{HH} = 3.1 Å, $\langle S_z \rangle$ =0.88685. For all cases, the magnetic field strength is 0.001 a.u. along the $-z$ direction. The area enclosed by the mesh has a charge density > 0.002. The size of the 3D box is 550pm(W) × 300pm(H) × 300pm(D).

Figure 3 shows the progression of spin vectors during the spin phase transition when the bond length is stretched from 2.6 to 3.1 Å, while keeping the magnetic field strength constant, $|B_z| = 0.001$ a.u., along the $-z$ direction. When a non-zero $\langle S_z \rangle$ moment is obtained in the system, the overall spin vector is aligned opposite to the magnetic field arising from the spin Zeeman effect. As the spins undergo a phase transition, the angle between local spin vectors decreases from 180° to 0°. At $R_{HH} \sim 2.9$ Å (Fig. 3b) the two local spin vectors are nearly orthogonal, exhibiting a strong non-collinearity in the presence of a magnetic field. The UHF and RHF solutions are restricted by collinear spin configuration, and therefore, can not capture the progression of spin phase transition via the spin noncollinear configuration.

The framework of $\mathbb{C}$-GHF with London orbitals also allows for a variational exploration of critical magnetic field strengths that can induce a spin phase transition in molecular systems. Figure 4 plots the spin magnetization vector at different field strengths while keeping the bond length fixed at 2.6 Å. As the magnetic field gets stronger, the expectation value of S_z becomes greater, and a non-collinear spin phase transition is observed. In contrast to the phenomenon in Fig. 3 where bond stretching weakens the exchange coupling, the spin phase transition in Fig. 4 arises from the increasing strength of the spin Zeeman effect, due to the increase in magnetic field strength. At $|B_z| = 0.005$ a.u., the spin phase transition is already complete, and the triplet spin-collinear configuration is the lowest energy state.

Figure 5 plots the expectation value of S_z as a function of H-H bond length and magnetic field strength. Figure 5 suggests that the rate of the spin phase transition sensitively depends on the strength of exchange coupling and spin Zeeman terms. At near the equilibrium bond distance with the strongest magnetic field ($|B_z| = 0.3$ a.u.) considered here, the spin configuration switches almost immediately. In the weak field or weak exchange coupling regime, spins can be seen to undergo a much slower phase transition compared to those in the strong field or strong exchange coupling regime.

Although the orbital Zeeman and diamagnetic terms in Eq. (15) do not directly modify the spin interaction with the external magnetic field, they are important contributions to the

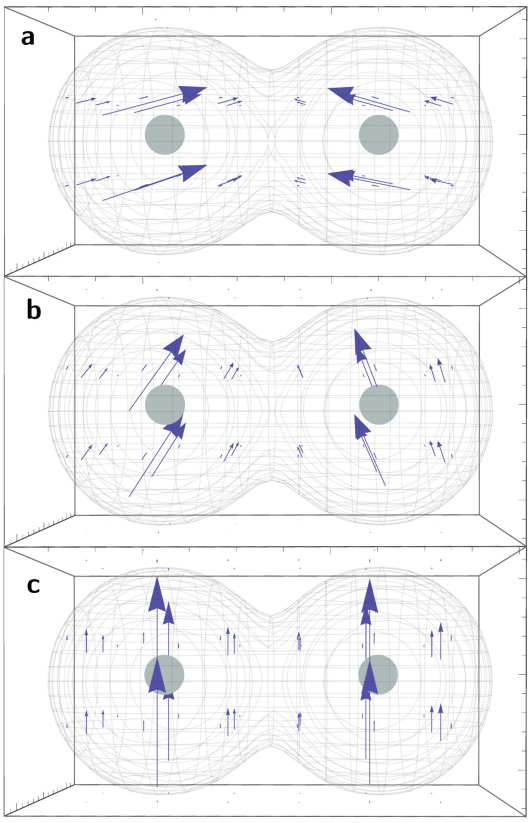

Figure 4. Spin magnetization vectors for H_2 at different field strengths. (**a**): $|B_z| = 0.001$ a.u., $\langle S_z \rangle$ =0.19428, (**b**): $|B_z| = 0.003$ a.u., $\langle S_z \rangle$ =0.59040, and (**c**): $|B_z| = 0.005$ a.u., $\langle S_z \rangle = 1.0000$. The H-H bond length is $R_{HH} = 2.6$ Å. The area enclosed by the mesh has a charge density > 0.002. The size of the 3D box is 550pm(W) $\times$ 300pm(H) $\times$ 300pm(D).

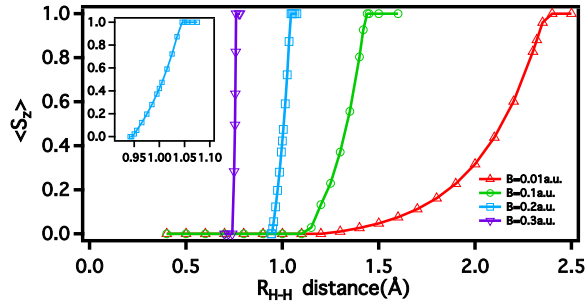

Figure 5. $\langle S_z \rangle$ as a function of H-H bond length and magnetic field strength.

stability of molecular system in magnetic field and can indirectly influence spin dynamics through perturbing the spatial extent and energetics of molecular orbitals.[28] Figure 6 shows the magnitudes of spin Zeeman, orbital Zeeman, and diamagnetic contributions to the total

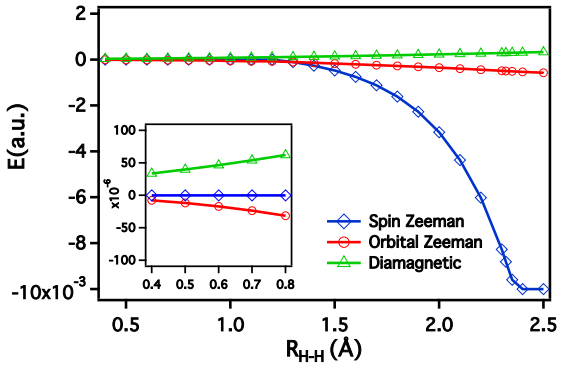

Figure 6. Energetic contributions of spin Zeeman, orbital Zeeman, and diamagnetic terms. $|B_z| = 0.01$ a.u.

potential energy. In the strong exchange couple regime ($R_{HH} \sim 0.4 - 0.6$ Å), the diamagnetic term has the largest contribution, followed by the orbital Zeeman term. These two terms are different in sign with the diamagnetic term destabilizing the system energy with respect to the field-free molecular system. In this regime, the system takes on a closed-shell configuration. As a result, the spin Zeeman contribution is zero. As the system undergoes a spin phase transition, the non-zero overall spin vector gives rise to an increasing spin Zeeman contribution that significantly stabilizes the molecular system. Analysis of Fig. 6 suggests that in a closed-shell configuration, orbital Zeeman and diamagnetic contributions are responsible for the interaction between the electronic system and the external magnetic field. In an open-shell system, the spin Zeeman is the dominant driving force underlying the system-magnetic-field interaction in the weak field regime. As the field strength increases, the diamagnetic term becomes non-negligible as it increases quadratically with respect to the field.

In order to probe the spin phase transition in a more complex magnetic molecular system, we study the spin characteristics of a di-chromium molecular complex, $[(H_3N)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, in a uniform magnetic field. Figure 7 illustrates the molecular structure and computational setup where the magnetic field is applied in $+z$ direction, perpendicular to the Cr-O-Cr-O plane. The molecular geometry was optimized[60] with the GAUSSIAN16 software package[61]

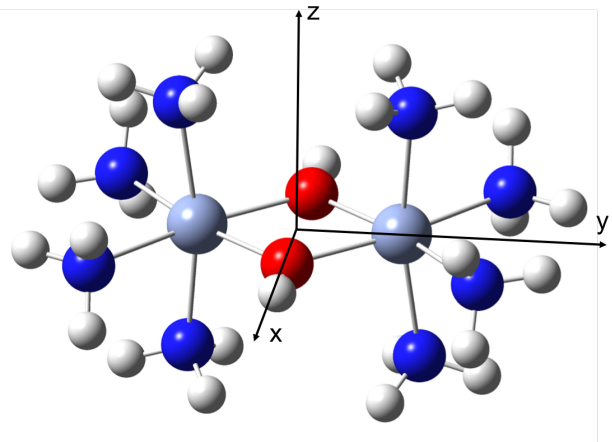

Figure 7. The molecular structure of a di-chromium molecular complex, $[(H_3N)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$ that has D_{2h} symmetry. Each Cr atom is in a distorted octahedral coordination environment. The magnetic field is applied in the $+z$ direction, perpendicular to the Cr-O-Cr-O plane.

at the B3LYP/6-31G level of theory.[62–65] The electronic structures in a magnetic field were calculated using ℂ-GHF with 6-31G London atomic orbitals in the Chronus Quantum software package.

In the di-Cr(III) molecular complex, the octahedral ligand field splits Cr d orbitals into e and t_2 sets where three unpaired electrons occupy the t_2 manifold (Fig. 8b). In contrast to the previous molecular H_2 system where the ground state at equilibrium bond length is in a non-magnetic closed-shell configuration, the ground state of the di-Cr(III) molecular complex exhibits a magnetic ℂ-GHF solution. Cr(III) cations in an octahedral coordination environment bridged by oxygen atoms are known to have antiferromagnetic super-exchange coupling.[66–68] The J constant in Eq. (20) for super-exchange coupling is negative in sign, favoring the antiferromagnetic spin alignment in the ground state ($\langle S_z \rangle = 0$, see Fig. 8b). The lack of electron correlation in Hartree-Fock calculation gives rise to an overestimation of the J constant magnitude because the correlation effect has an opposite contribution to the magnetism.[66] Nevertheless, qualitative characteristics and trends of spin phase transitions can still be captured by ℂ-GHF calculations with London atomic orbitals.

In the absence of an external magnetic field, the ground state wave function of the

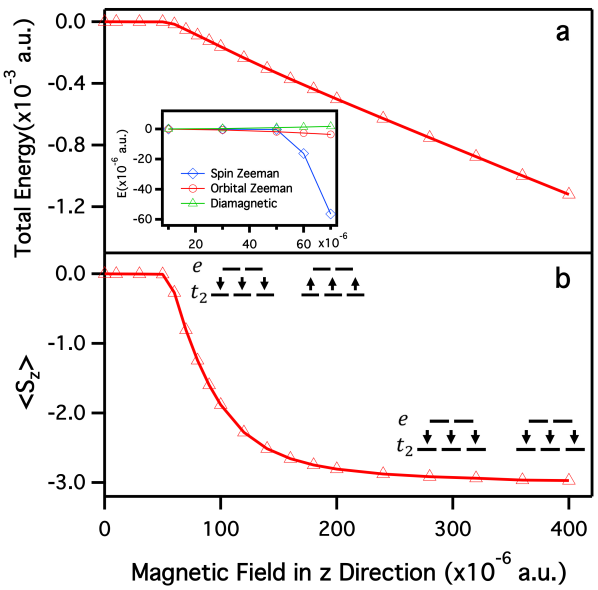

Figure 8. (**a**) Total energy of di-Cr(III) complex in a finite magnetic field. (**b**) The expectation value of S_z of the $\mathbb{C}$-GHF solution.

di-Cr(III) molecular complex obtained from the $\mathbb{C}$-GHF calculation is antiferromagnetic. Figure 8 plots the relative total energy compared to that in the absence of a magnetic field and the expectation value of S_z as a function of applied magnetic field strength. When the magnetic field is relatively weak, the system is in the antiferromagnetic state. In this region, the super-exchange coupling is constant and the small energy change is solely due to the orbital Zeeman and diamagnetic terms. As the magnetic field reaches a critical point ($\sim 60 \times 10^{-6}$ a.u.) where a small change in spin alignment can give rise to a spin Zeeman term strong enough to overcome the antiferromagnetic super-exchange coupling, the system starts to undergo a spin phase transition. As the magnetic field strength increases, the energy of the molecule decreases due to the increasing spin Zeeman contribution. The change of expectation value of S_z indicates that the spin state gradually switches from the antiferromagnetic $\langle S_z \rangle = 0$ to ferromagnetic $\langle S_z \rangle = -3$ configuration (Fig. 8b). This case study suggests that $\mathbb{C}$-GHF calculations with London atomic orbitals can be used to investigate magnetic phase transitions in transition metal complexes.

4 Conclusion

Presented in this article is a framework of *ab initio* variational approach using complex generalized Hartree-Fock (ℂ-GHF) with London orbitals to effectively explore the spin phase space in the presence of a homogenous magnetic field. We introduced the implementation of the ℂ-GHF approach within the spinor formalism. In order to account for gauge origin-independence in the self-consistent field, the ℂ-GHF is represented in the London orbital basis with a magnetic field complex phase factor. Recursive algorithms for computing one- and two-electron integrals of London orbitals are provided in the Appendix. Additionally, a Pauli matrix representation of the ℂ-GHF is introduced in this work that allows for the separation of spin contributions from the scalar part of the Fock matrix.

ℂ-GHF with London orbitals in the presence of a homogenous magnetic field has been applied to study the spin phase transition in a molecular H_2 system. Non-collinear spin configurations have been observed during the phase transition from a singlet to triplet state. The competing driving forces of exchange coupling and the spin Zeeman effect have been shown to govern the spin phase transition and its transition rate. In addition, energetic analysis suggests that in the presence of a static magnetic field, orbital Zeeman and diamagnetic terms are important contributions in a closed-shell configuration, while the spin Zeeman term is the dominant interaction driving force in an open-shell state.

The variational ℂ-GHF method with London orbitals can also be used to compute magnetic phase transitions in molecular complexes driven by an external magnetic field. Results show that there exists a critical point where the spin Zeeman is large enough to compete with the super-exchange coupling so that the spin phase transition takes place and drives the magnetic phase transition.

The method presented in this work is based on the single Slater determinant wave function ansatz which lacks important electron correlation effects. Future developments will use the variational ℂ-GHF reference for correlated electronic structure methods which will provide more accurate descriptions of spin and magnetic phase transitions.

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Appendix: Integral Evaluation

A London orbital is defined as

$$\tilde{\chi}(\mathbf{r}, \mathbf{k}_A) = \chi(\mathbf{r} - \mathbf{R}_A) e^{i\mathbf{k}_A \cdot (\mathbf{r} - \mathbf{R}_A)} \tag{21}$$

where $\{\chi\}$ are primary atom-centered Gaussian type orbitals,

$$\chi_a = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\zeta_a |\mathbf{r} - \mathbf{A}|} \tag{22}$$

$$|\mathbf{r} - \mathbf{A}| = \sqrt{(x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2} \tag{23}$$

$\mathbf{A} = \{A_x, A_y, A_z\}$ is the coordinate of the atom center and $\mathbf{a} = \{a_x, a_y, a_z\}$ is the angular momentum. ζ_a is the exponent of primary Gaussian type orbitals.

The London orbital defined in Eq. (21) has the following identity,

$$\tilde{\chi}^*_\mu(\mathbf{r}, \mathbf{k}_A) = \tilde{\chi}_\mu(\mathbf{r}, -\mathbf{k}_A) \tag{24}$$

The one-electron integral for any one-electron operator $\hat{O}_1$ can be defined as

$$(\mathbf{a}|\hat{O}_1|\mathbf{b}) = \int \mathrm{d}^3\mathbf{r} \tilde{\chi}^*(\mathbf{r}, \mathbf{k}_A)\, \hat{O}_1\, \tilde{\chi}(\mathbf{r}, \mathbf{k}_B) = \int \mathrm{d}^3\mathbf{r} \tilde{\chi}(\mathbf{r}, -\mathbf{k}_A)\, \hat{O}_1\, \tilde{\chi}(\mathbf{r}, \mathbf{k}_B) \tag{25}$$

and, for a two-electron operator $\hat{O}_2$, the integral is defined as

$$\begin{aligned}(\mathbf{ab}|\hat{O}_2|\mathbf{cd}) &= \int \mathrm{d}^3\mathbf{r}_1 \int \mathrm{d}^3\mathbf{r}_2\, \tilde{\chi}^*(\mathbf{r}_1, \mathbf{k}_A) \tilde{\chi}(\mathbf{r}_1, \mathbf{k}_B)\, \hat{O}_2\, \tilde{\chi}^*(\mathbf{r}_2, \mathbf{k}_C) \tilde{\chi}(\mathbf{r}_2, \mathbf{k}_D) \\ &= \int \mathrm{d}^3\mathbf{r}_1 \int \mathrm{d}^3\mathbf{r}_2\, \tilde{\chi}(\mathbf{r}_1, -\mathbf{k}_A) \tilde{\chi}(\mathbf{r}_1, \mathbf{k}_B)\, \hat{O}_2\, \tilde{\chi}(\mathbf{r}_2, -\mathbf{k}_C) \tilde{\chi}(\mathbf{r}_2, \mathbf{k}_D)\end{aligned} \tag{26}$$

General recursion relationships for one- and two-electron integrals using mixed plane-wave/Gaussian type orbitals were presented by Obara and coworkers,[69] and the application to London orbitals was developed by Helgaker and Teale.[25,70] In this work, we use a modified

Obara-Saika algorithm to calculate one- and two-electron integrals using London orbitals. As the derivations are similar to those in references 69 and 25, we only present the working equations used in this work without going through the detailed mathematics. Note that recursive algorithms presented herein can be used for evaluating integrals of mixed plane-wave/Gaussian orbitals with an arbitrary wave vector.

The following intermediate quantities are defined for integral recursion relationships used in this work,

$$\zeta = \zeta_a + \zeta_b \tag{27}$$

$$\eta = \zeta_c + \zeta_d \tag{28}$$

$$\xi = \frac{\zeta_a \zeta_b}{\zeta_a + \zeta_b} \tag{29}$$

$$\rho = \frac{\zeta \eta}{\zeta + \eta} \tag{30}$$

$$\mathbf{P} = \frac{\zeta_a A + \zeta_b B}{\zeta_a + \zeta_b} \tag{31}$$

$$\mathbf{Q} = \frac{\zeta_c C + \zeta_d D}{\zeta_c + \zeta_d} \tag{32}$$

$$\mathbf{W} = \frac{\zeta P + \eta Q}{\zeta + \eta} \tag{33}$$

$$\mathbf{k}_p = -\mathbf{k}_a + \mathbf{k}_b \tag{34}$$

$$\mathbf{k}_q = -\mathbf{k}_c + \mathbf{k}_d \tag{35}$$

A.1 Overlap Integral

The recursion for the overlap integral is

$$(\mathbf{a} + \mathbf{1}_\mu || \mathbf{b}) = \left(\mathbf{P} + \frac{i(-\mathbf{k}_A + \mathbf{k}_B)}{2\zeta} - \mathbf{A} \right)_\mu (\mathbf{a}||\mathbf{b}) + \frac{1}{2\zeta} \Big\{ N_\mu(\mathbf{a})(\mathbf{a} - \mathbf{1}_\mu || \mathbf{b}) + N_\mu(\mathbf{b})(\mathbf{a}||\mathbf{b} - \mathbf{1}_\mu) \Big\} \tag{36}$$

$$(\mathbf{0}_A||\mathbf{0}_B) = \left(\frac{\pi}{\zeta} \right)^{3/2} e^{-\xi(\mathbf{A}-\mathbf{B})^2} e^{-\frac{(-\mathbf{k}_a + \mathbf{k}_b)^2}{4\zeta}} e^{i\{(-\mathbf{k}_a)\cdot(\mathbf{P}-\mathbf{A}) + \mathbf{k}_b \cdot (\mathbf{P}-\mathbf{B})\}} \tag{37}$$

where $N_\mu(\mathbf{a})$ is the μ component of the angular momentum $\mathbf{a}$. $\mathbf{a} \pm \mathbf{1}_\mu$ means that the μ component of the angular momentum $\mathbf{a}$ is raised/lowered by one.

A.2 Kinetic Energy Integral

Kinetic integral is the second derivatives of overlap integrals,

$$(\mathbf{a}|\mathscr{T}|\mathbf{b}) = -\frac{1}{2}\sum_{\nu=x,y,z}(\mathbf{a}||\partial_\nu^2\mathbf{b}) \tag{38}$$

The recursion relationship for the kinetic energy integral is

$$\begin{aligned}-\frac{1}{2}(\mathbf{a}||\partial_\nu^2\mathbf{b}) =& -2{\zeta_b}^2(\mathbf{a}||\mathbf{b}+\mathbf{2}_\nu) + 2i\zeta_b k_{b\mu}(\mathbf{a}||\mathbf{b}+\mathbf{1}_\nu) + \left(2\zeta_b N_\nu(\mathbf{b})\zeta_b + \frac{1}{2}\mathbf{k}_b^2\right)(\mathbf{a}||\mathbf{b}) \\ & - iN_\nu(\mathbf{b})k_{b\nu}(\mathbf{a}||\mathbf{b}-\mathbf{1}_\nu) - \frac{1}{2}N_\nu(\mathbf{b})(N_\nu(\mathbf{b})-1)(\mathbf{a}||\mathbf{b}-\mathbf{2}_\nu)\end{aligned} \tag{39}$$

where $k_{b\mu}$ is the μ component of the wave vector $\mathbf{k}_b$.

4.1 Angular Momentum Integral

Angular momentum integral is defined as

$$\begin{aligned}(\mathbf{a}|\mathbf{r}\times\boldsymbol{\nabla}|\mathbf{b}) &= \hat{\mathbf{x}}\,(\mathbf{a}|r_y\partial_z - r_z\partial_y|\mathbf{b}) + \hat{\mathbf{y}}\,(\mathbf{a}|r_z\partial_x - r_x\partial_z|\mathbf{b}) + \hat{\mathbf{z}}\,(\mathbf{a}|r_x\partial_y - r_y\partial_x|\mathbf{b}) \\ &= -\hat{\mathbf{x}}\,(\mathbf{a}|r_y\partial_{B_z} - r_z\partial_{B_y}|\mathbf{b}) - \hat{\mathbf{y}}\,(\mathbf{a}|r_z\partial_{B_x} - r_x\partial_{B_z}|\mathbf{b}) - \hat{\mathbf{z}}\,(\mathbf{a}|r_x\partial_{B_y} - r_y\partial_{B_x}|\mathbf{b})\end{aligned} \tag{40}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are unit vectors in the x, y, z directions. ∂_{B_μ} is the partial derivative with respect to nuclear coordinates at atom center B. The integral of the type $(\mathbf{a}|r_\mu\partial_\nu|\mathbf{b})$ where

$\mu, \nu = x, y, z$ can be evaluated as linear combinations of overlap integrals:

$$\begin{aligned}(\mathbf{a}|r_\mu \partial_\nu|\mathbf{b}) = &-\left\{2\zeta_b(\mathbf{a}+\mathbf{1}_\mu||\mathbf{b}+\mathbf{1}_\nu) - N_\nu(\mathbf{b})(\mathbf{a}+\mathbf{1}_\mu||\mathbf{b}-\mathbf{1}_\nu) - ik_{b\nu}(\mathbf{a}+\mathbf{1}_\mu||\mathbf{b})\right\} \\ &- A_\mu\left\{2\zeta_b(\mathbf{a}||\mathbf{b}+\mathbf{1}\nu) - N_\nu(\mathbf{b})(\mathbf{a}||\mathbf{b}-\mathbf{1}_\nu) - ik_{b\nu}(\mathbf{a}||\mathbf{b})\right\} \end{aligned} \tag{41}$$

A.3 Electric Quadrupole Integral

The recursion relationship for the electric quadrupole integral is

$$(\mathbf{a}|r_\mu r_\nu|\mathbf{b}) = (\mathbf{a}+\mathbf{1}_\mu||\mathbf{b}+\mathbf{1}_\nu) + A_\mu(\mathbf{a}||\mathbf{b}+\mathbf{1}_\nu) + B_\nu(\mathbf{a}+\mathbf{1}_\mu||\mathbf{b}) + A_\mu B_\nu(\mathbf{a}||\mathbf{b}) \tag{42}$$

A.4 Nuclear Attraction Integral

Define the operator

$$V = \frac{1}{|\mathbf{r}-\mathbf{C}|} \tag{43}$$

where $\mathbf{C}$ is the nuclear coordinate. The recursion for nuclear attraction integral is

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_\mu|V|\mathbf{b})^{(m)} =&(\mathbf{P}+\frac{i\mathbf{k}_{p\mu}}{2\zeta}-\mathbf{A})_\mu(\mathbf{a}|V|\mathbf{b})^{(m)} - (\mathbf{P}+\frac{i\mathbf{k}_{p\mu}}{2\zeta}-\mathbf{C})_\mu(\mathbf{a}|V|\mathbf{b})^{(m+1)} \\ &+\frac{1}{2\zeta}N_\mu(\mathbf{a})\left\{(\mathbf{a}-\mathbf{1}_\mu|V|\mathbf{b})^{(m)} - (\mathbf{a}-\mathbf{1}_\mu|V|\mathbf{b})^{(m+1)}\right\} \\ &+\frac{1}{2\zeta}N_\mu(\mathbf{b})\left\{(\mathbf{a}|V|\mathbf{b}-\mathbf{1}_\mu)^{(m)} - (\mathbf{a}|V|\mathbf{b}-\mathbf{1}_\mu)^{(m+1)}\right\} \end{aligned} \tag{44}$$

$$(\mathbf{0}_A|V|\mathbf{0}_B)^{(m)} = 2\left(\frac{\zeta}{\pi}\right)^{1/2}(\mathbf{0}_A||\mathbf{0}_B)\ F_m(T) \tag{45}$$

$$T = \zeta\left(\mathbf{P}-\mathbf{C}+i\frac{\mathbf{k}_a+\mathbf{k}_b}{2\zeta}\right)^2 \tag{46}$$

A.5 Electron Repulsion Integral

The recursion for electron repulsion integral is

$$\begin{aligned}((\mathbf{a}+\mathbf{1}_\mu)\mathbf{b}|\mathbf{cd})^{(m)} =& \left(\mathbf{P}-\mathbf{A}+\frac{i\mathbf{k}_{p\mu}}{2\zeta}\right)_\mu (\mathbf{ab}|\mathbf{cd})^{(m)} \\ &+\left(\mathbf{W}-\mathbf{P}-\frac{i\rho(\mathbf{k}_a+\mathbf{k}_b)_\mu}{2\zeta^2}+\frac{i(\mathbf{k}_c+\mathbf{k}_d)_\mu}{2(\zeta+\eta)}\right)_\mu (\mathbf{ab}|\mathbf{cd})^{(m+1)} \\ &+\frac{1}{2\zeta}N_\mu(\mathbf{a})\left\{((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{cd})^{(m)}-\frac{\rho}{\zeta}((\mathbf{a}-\mathbf{1}_\mu)\mathbf{b}|\mathbf{cd})^{(m+1)}\right\} \\ &+\frac{1}{2\zeta}N_\mu(\mathbf{b})\left\{(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{cd})^{(m)}-\frac{\rho}{\zeta}(\mathbf{a}(\mathbf{b}-\mathbf{1}_\mu)|\mathbf{cd})^{(m+1)}\right\} \\ &+\frac{1}{2(\zeta+\eta)}\left\{N_\mu(\mathbf{c})(\mathbf{ab}|(\mathbf{c}-\mathbf{1}_\mu)\mathbf{d})^{(m+1)}+N_\mu(\mathbf{d})(\mathbf{ab}|\mathbf{c}(\mathbf{d}-\mathbf{1}_\mu))^{(m+1)}\right\}\end{aligned} \tag{47}$$

$$(\mathbf{00}|\mathbf{00})^{(m)} = 2\left(\frac{\rho}{\pi}\right)^{1/2}(\mathbf{0}_A||\mathbf{0}_B)(\mathbf{0}_C||\mathbf{0}_D)\ F_m(T) \tag{48}$$

$$T = \rho\left[\left(\mathbf{P}+i\frac{\mathbf{k}_1}{2\zeta}\right)-\left(\mathbf{Q}+i\frac{\mathbf{k}_2}{2\eta}\right)\right]^2 \tag{49}$$

where F_m is the Boys function. The horizontal recursion can be derived from Eq. (47) easily.[71]

$$(\mathbf{a}(\mathbf{b}+\mathbf{1}_\mu)|\mathbf{cd})^{(m)} = ((\mathbf{a}+\mathbf{1}_\mu)\mathbf{b}|\mathbf{cd})^{(m)} + (\mathbf{A}-\mathbf{B})_\nu(\mathbf{ab}|\mathbf{cd})^{(m)} \tag{50}$$

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Graphical TOC Entry