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## Embedding non-collinear two-component electronic structure in a collinear quantum environment

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### ABSTRACT

Spin-containing materials are important for spintronic applications. In this work, we present a computational framework to embed nonrelativistic, two-component calculations in a one-component environment. In this framework, both embedding scalar potential and magnetic field can be included to describe the interaction between quantum subsystems. In this current development, a generalized Kohn-Sham density functional theory electronic structure is embedded in unrestricted Kohn-Sham density functional theory. Two test systems are studied: a Li<sub>3</sub> on a closed-shell He lattice and a Li<sub>3</sub> on a He lattice containing a Li atom defect. The noncollinearity of Li<sub>3</sub> is unaffected upon embedding in a closed-shell environment through the scalar potential embedding. However, the open-shell nature of the Li atom defect introduces an effective magnetic field that couples to the magnetic components of the generalized Kohn-Sham Hamiltonian. These results show that noncollinear quantum embedding in an open-shell collinear environment may modify the spin structure of the embedded system. The formalism developed herein may serve as a useful tool in the modeling of inhomogeneous magnetic fields in two-component calculations.

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### I. INTRODUCTION

Spin-containing materials have picked up interest due to their relevance for spintronic applications.<sup>1</sup> For magnetic and spin phenomena, noncollinear electronic structure theory is the natural choice on account of spin-symmetry breaking terms in the Hamiltonian (spin-orbit and external magnetic fields).<sup>2</sup> Due to the number and types of atoms in these materials, a computational prescription capable of treating noncollinear spin at a reasonable cost is needed. For large molecular or material systems, one often has to make significant compromises in accuracy by going to a less computationally expensive method. This has opened the door for quantum embedding schemes to find use, where a system is separated into quantum subsystems that can be treated at different levels of theory. Until a single electronic structure method is capable of such a daunting task, quantum embedding provides a pragmatic alternative in the meantime.

Quantum embedding is a useful tool when one wishes to study local phenomena of an extended system. The total system is separated into subsystems, where different electronic structure methods can be used for the subsystems. For the purposes of this article, we will only consider two quantum subsystems: (A) the cluster, where a more accurate electronic structure (high level of theory) is desired, and (B) the environment, where a less accurate electronic structure method (low level of theory) is suitable. However, the embedding formalism is applicable to a general number of quantum subsystems.

There are a number of quantum embedding approaches in the literature. In this work, we focus on density-based embedding<sup>3–20</sup> and use the density functional embedding theory.<sup>21,22</sup> The clusterenvironment interaction is handled by the embedding perturbations, which account for the environment in the cluster calculation and vice versa, under the condition that the subsystem densities from density functional embedding theory sum to the total density of the interacting system. Satisfying this condition is desirable for the computation of density-dependent properties.

In this work, we introduce an approach for embedding noncollinear two-component, nonrelativistic calculations in a collinear, nonrelativistic environment within the density functional embedding framework. Closed-shell subsystems will generate a scalar embedding potential, whereas spin-polarized open-shell systems can give rise to a scalar potential and an effective magnetic field. There have been successful developments that embed two- or fourcomponent relativistic methods, focusing only on the scalar potential embedding scheme.<sup>23–27</sup> In this paper, we generalized the twocomponent noncollinear embedding scheme to both open- and closed-shell cases within a spin-separated embedding scheme that can handle both the scalar embedding potential and the effective magnetic field generated from the environment.

### **II. METHODOLOGY**

Atomic units are used throughout. In the following discussion, we use tilde notations, e.g.,  $\tilde{\rho}$  and  $\tilde{m}$ , for quantities computed at low levels, and primed notations, e.g., V' and F', for perturbing potentials or perturbed Hamiltonians.

#### A. Embedding potential and embedding magnetic field

Embedding calculations for nonspin-polarized systems using density functional embedding theory were discussed in detail in Ref. 21. Here, we briefly review density functional embedding theory for collinear spin-polarized systems.

The Kohn-Sham (KS) energies of the cluster and environment are

 $E_{\rm clu}[\tilde{\rho}_{\rm clu}, \tilde{m}_{\rm clu}]$ 

$$= -\sum_{\sigma,j} f_{\sigma,j}^{\text{clu}} \int d^3 r \, \phi_{\sigma,j}^{\text{clu}}(\mathbf{r}) \frac{\nabla^2}{2} \phi_{\sigma,j}^{\text{clu}}(\mathbf{r}) + J[\tilde{\rho}_{\text{clu}}] + \int d^3 r \, v_{ext}^{\text{clu}}(\mathbf{r}) \tilde{\rho}_{\text{clu}}(\mathbf{r}) + E_{xc}[\tilde{\rho}_{\text{clu}}, \tilde{m}_{\text{clu}}] + \int d^3 r \, \tilde{\rho}_{\text{clu}}(\mathbf{r}) V'(\mathbf{r}) + \mu_B \int d^3 r \, \tilde{\mathbf{m}}_{\text{clu}}(\mathbf{r}) \cdot \mathbf{B}'(\mathbf{r}) - TS_{\text{clu}}, \quad (1)$$

 $E_{\rm env}[\tilde{\rho}_{\rm env}, \tilde{m}_{\rm env}]$ 

$$= -\sum_{\sigma,j} f_{\sigma,j}^{\text{env}} \int d^3 r \, \phi_{\sigma,j}^{\text{env}}(\mathbf{r}) \frac{\nabla^2}{2} \phi_{\sigma,j}^{\text{env}}(\mathbf{r}) + J[\tilde{\rho}_{\text{env}}] + \int d^3 r \, v_{ext}^{\text{env}}(\mathbf{r}) \tilde{\rho}_{\text{env}}(\mathbf{r}) + E_{xc}[\tilde{\rho}_{\text{env}}, \tilde{m}_{\text{env}}] + \int d^3 r \, \tilde{\rho}_{\text{env}}(\mathbf{r}) V'(\mathbf{r}) + \mu_B \int d^3 r \, \tilde{\mathbf{m}}_{\text{env}}(\mathbf{r}) \cdot \mathbf{B}'(\mathbf{r}) - TS_{\text{env}},$$
(2)

where  $\phi_{\sigma,j}^{\text{clu}}$  and  $\phi_{\sigma,j}^{\text{env}}$  are the *j*th KS orbital of the cluster and environment for the spin index  $\sigma$ , respectively. The cluster and environment's ionic potentials are  $v_{ext}^{\text{clu}}(\mathbf{r}) = \sum_{j} v_{ext,j}(\mathbf{r})$  and  $v_{ext}^{\text{env}}(\mathbf{r}) = \sum_{k} v_{ext,k}(\mathbf{r})$ , respectively, where  $v_{ext,j}(\mathbf{r})$  is the ionic potential of atom *j* with indices *j* and *k* running over the atoms in the cluster and environment, respectively.  $\tilde{\rho}_{\text{clu}}$  ( $\tilde{\rho}_{\text{env}}$ ) and  $\tilde{\mathbf{m}}_{\text{clu}}$  ( $\tilde{\mathbf{m}}_{\text{env}}$ ) are the

charge density and the magnetization density vector, respectively, of the cluster (environment). { $f_{\sigma,j}$ } are the occupation numbers and are assigned according to the Fermi-Dirac statistics with the smearing temperature T.  $\mu_B$  is the Bohr magneton.  $S_{clu}$  and  $S_{env}$  are the electronic entropies, for the cluster and environment, respectively, e.g., for cluster  $S_{clu} = -k_B \sum_{\sigma,j} (f_{\sigma,j}^{clu} \ln f_{\sigma,j}^{clu} + (1 - f_{\sigma,j}^{clu}) \ln (1 - f_{\sigma,j}^{clu}))$ .  $J[\tilde{\rho}_{clu}]$  and  $J[\tilde{\rho}_{env}]$  are the Hartree energies of the cluster and environment, respectively.

The cluster and environment share a common embedding potential  $[V'(\mathbf{r})]$  and embedding magnetic field  $[\mathbf{B}'(\mathbf{r})]$  in density functional embedding theory.<sup>9,21</sup> Embedding potential and embedding magnetic field V' and  $\mathbf{B}'$  "glue" the cluster and environment together such that  $\tilde{\rho}_{clu}(\mathbf{r}) + \tilde{\rho}_{env}(\mathbf{r}) = \tilde{\rho}_T(\mathbf{r})$  and  $\tilde{\mathbf{m}}_{clu}(\mathbf{r}) + \tilde{\mathbf{m}}_{env}(\mathbf{r})$  $= \tilde{\mathbf{m}}_T(\mathbf{r})$ .  $\tilde{\rho}_T$  and  $\tilde{\mathbf{m}}_T$  are the total charge density and magnetization density vector, respectively. After partitioning the system's electron density, the system's energy *E* is formally partitioned as

$$E[\tilde{\rho}_T, \tilde{\mathbf{m}}_T] = E_{clu}[\tilde{\rho}_{clu}, \tilde{\mathbf{m}}_{clu}] + E_{env}[\tilde{\rho}_{env}, \tilde{\mathbf{m}}_{env}] + E_{int}[\tilde{\rho}_{clu}, \tilde{\mathbf{m}}_{clu}, \tilde{\rho}_{env}, \tilde{\mathbf{m}}_{env}].$$
(3)

 $E_{\rm int}$  is the cluster-environment interaction energy and is formally defined as  $E_{\rm int} = E - E_{\rm clu} - E_{\rm env}$ . For fixed  $\tilde{\rho}_T$  and  $\tilde{\mathbf{m}}_T$ ,  $E_{\rm int}$  is, therefore, a functional of  $\tilde{\rho}_{\rm clu}$  and  $\tilde{\mathbf{m}}_{\rm clu}$ . The embedding potential and embedding magnetic field that the environment exerts on the cluster are formally defined as

$$V'(\mathbf{r}) = \frac{\delta E_{\text{int}}}{\delta \tilde{\rho}_{\text{clu}}(\mathbf{r})},\tag{4}$$

$$\mathbf{B}'(\mathbf{r}) = \frac{\delta E_{\text{int}}}{\delta \tilde{\mathbf{m}}_{\text{clu}}(\mathbf{r})}.$$
 (5)

In this work,  $V'(\mathbf{r})$  and  $\mathbf{B}'(\mathbf{r})$  are obtained via a Wu-Yang optimized effective potential (OEP) method<sup>21,28</sup>

$$W[V', \mathbf{B}'] = E_{clu}[V', \mathbf{B}'] + E_{env}[V', \mathbf{B}'] - \int V'(\mathbf{r})\tilde{\rho}_T(\mathbf{r})d^3r$$
$$-\mu_B \int \mathbf{B}'(\mathbf{r}) \cdot \tilde{\mathbf{m}}_T(\mathbf{r})d^3r.$$
(6)

For trial V' and  $\mathbf{B}'$ , the KS systems defined in Eqs. (1) and (2) are solved. The cluster and environment's electron and magnetization densities are then used to compute W. Thus, W is a functional of V' and  $\mathbf{B}'$ .

In a one-component density functional embedding framework, quantities obtained from the Wu-Yang OEP approach are spin-up and spin-down embedding potentials,  $V_{\uparrow}$  and  $V_{\downarrow}$ , up to some constants,  $\lambda_{\uparrow}$  and  $\lambda_{\downarrow}$ .<sup>22</sup> In one-component electronic structure methods, due to spin collinearity, only one of the magnetization densities can be nonzero,<sup>29,30</sup> which is conveniently chosen to be the *z*-component of the magnetization density vector. A simple mathematical procedure using the Pauli spin matrices [Eq. (7)]

$$\boldsymbol{\sigma}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
(7)

leads to the following relationship:

$$V'(\mathbf{r}) = \frac{1}{2} (V_{\uparrow}(\mathbf{r}) + \lambda_{\uparrow} + V_{\downarrow}(\mathbf{r}) + \lambda_{\downarrow}), \qquad (8)$$

$$B'_{z}(\mathbf{r}) = \frac{1}{2\mu_{B}} (V_{\uparrow}(\mathbf{r}) + \lambda_{\uparrow} - V_{\downarrow}(\mathbf{r}) - \lambda_{\downarrow}), \qquad (9)$$

which are used to compute the embedding potential and embedding magnetic field. Note that the *z*-component of the magnetization density vector is also defined as the  $\sigma_3$  component of the Pauli matrix. The solutions of two-component Kohn-Sham density functional theory (KS-DFT) depend on  $\lambda_{\uparrow} - \lambda_{\downarrow}$  in  $B'_z(\mathbf{r})$ .  $\lambda_{\uparrow} - \lambda_{\downarrow}$  is determined based on the condition that the Fermi levels of the spin-up and spin-down electrons are equal in the embedded cluster.

## B. Embedding two-component noncollinear electronic structure

In this work,  $E_{clu}$  and  $E_{env}$  are solved in the collinear case (the low-level theory), and the noncollinear embedded cluster calculations are considered as the high-level calculations. In this section, we discuss a strategy to introduce the embedding potential V' and embedding magnetic field **B**' to the noncollinear high-level calculations.

We choose to use single-reference, nonrelativistic twocomponent (2c) calculations to model noncollinear electronic structure in this work. The working equations below are equally applicable to Hartree-Fock (HF) and Kohn-Sham density functional theory (KS-DFT), where we consider a general Fock operator. Note that 2c versions of nonrelativistic HF and KS-DFT are often referred to as generalized variants in the literature.<sup>31–40</sup> We will adopt this nomenclature and refer to 2c KS-DFT as generalized KS-DFT (GKS).

In a 2c formalism, one works in a basis of one-electron spinors

$$\phi_p(\mathbf{x}) = \begin{pmatrix} \phi_p^{\alpha}(\mathbf{r}) \\ \phi_p^{\beta}(\mathbf{r}) \end{pmatrix}, \tag{10}$$

$$\phi_p^{\sigma}(\mathbf{r}) = \sum_{\mu} c_{p\mu}^{\sigma} \chi_{\mu}(\mathbf{r}), \quad \sigma \in \{\alpha, \beta\},$$
(11)

where **x** is the electronic spatial and spin coordinate, **r** is a spatial coordinate,  $c_{\rho\mu}^{\sigma}$  is a molecular orbital (MO) coefficient, and  $\chi_{\mu}$  is an atom-centered basis function. Electronic structure methods based on the spinor basis allow for spin rotations and noncollinear spin arrangements.

The spin-blocked 2c working equation in an atomic orbital basis  $\mathrm{is}^2$ 

$$\begin{bmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha} \\ \mathbf{c}^{\beta} \end{bmatrix} = \begin{bmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{\alpha} \\ \mathbf{c}^{\beta} \end{bmatrix} \boldsymbol{\epsilon}, \qquad (12)$$

where  $\mathbf{F}^{\sigma\tau}$  is the spin-blocked Fock matrix, **S** is the overlap matrix, and  $\epsilon$  are the eigenvalues. The density matrix (**P** with  $P^{\sigma\tau}_{\mu\nu} = \sum_{i}^{occ} c^{\sigma}_{\mu j} c^{\tau*}_{\nu j}$ ) also has a spin-blocked form.

We can cast the rank-2 spin-blocked **F** and **P** matrices in the Pauli matrix basis,  $30^{30}$ 

$$\mathbf{F} = \sum_{n=0}^{3} \mathbf{F}_n \otimes \boldsymbol{\sigma}_n, \tag{13}$$

$$\mathbf{P} = \sum_{n=0}^{3} \mathbf{P}_n \otimes \boldsymbol{\sigma}_n, \tag{14}$$

where the scalar ( $\mathbf{F}_0$ ) and spin parts ( $\mathbf{F}_1$ ,  $\mathbf{F}_2$ ,  $\mathbf{F}_3$ ) of the Fock matrix are defined as<sup>30</sup>

$$\mathbf{F}_0 = \mathbf{h}_0 + \mathbf{J}[\mathbf{P}_0] - \zeta \mathbf{K}[\mathbf{P}_0] + \mathbf{V}^{\mathrm{xc}}[\mathbf{P}_0], \qquad (15)$$

$$\mathbf{F}_n = \mathbf{h}_n - \zeta \mathbf{K} [\mathbf{P}_n] + \mathbf{V}^{\mathrm{xc}} [\mathbf{P}_n], \quad n = 1, 2, 3, \tag{16}$$

where **h** is the core Hamiltonian, **J** and **K** are the Coulomb and exchange matrices, respectively,  $\zeta$  is the coefficient of the exact exchange in hybrid density functional theory, and **V**<sup>xc</sup> is the torque-free noncollinear density functional kernel. In the case of HF, **V**<sup>xc</sup> = 0 and  $\zeta = 1$ . For details regarding the implementation of noncollinear density functional theory, we refer the readers to Ref. 30. Note that in restricted collinear formalisms, only the scalar part  $\sigma_0$  is nonzero and in unrestricted collinear formalisms the scalar  $\sigma_0$  and magnetization  $\sigma_3$  terms are nonzero.

With the Pauli-spin-separated form of the generalized Fock matrix [Eq. (13)], the embedding potential V' and embedding magnetic field **B**' can be introduced as perturbations. The embedded Fock matrix **F**' for the high-level subsystem is

$$\mathbf{F}' = (\mathbf{F}_0 + \mathbf{V}') \otimes \boldsymbol{\sigma}_0 + \sum_n (\mathbf{F}_n + \mu_B \mathbf{B}'_n) \otimes \boldsymbol{\sigma}_n, \qquad (17)$$

$$V'_{\mu\nu} = \int \chi_{\mu}(\mathbf{r}) V'(\mathbf{r}) \chi_{\nu}^{*}(\mathbf{r}) d\mathbf{r}, \qquad (18)$$

$$B'_{n,\mu\nu} = \int \chi_{\mu}(\mathbf{r}) B'_{n}(\mathbf{r}) \chi_{\nu}^{*}(\mathbf{r}) d\mathbf{r}, \qquad (19)$$

where  $\mathbf{V}'$  is the embedding potential and  $\mathbf{B}'_n$  is the embedding magnetic field polarized along the *n* direction. In this article, we will assume the spin-Zeeman contribution from the interaction energy is dominant and ignore other effects due to the embedding magnetic field (e.g., orbital Zeeman and diamagnetic terms).<sup>41,40</sup> Since the low level is treated in a collinear framework in which spin orientation is arbitrary, one first needs to define a proper spin-frame. In this work, we choose to align the collinear spin orientation in the low-level calculation with the  $\mathbf{P}_3$  component of the noncollinear high level subsystem. This treatment gives rise to a spin-Zeeman term acting on the high-level quantum subsystem.<sup>42,43,29</sup>

### C. Representation transformation of embedding potential and embedding magnetic field

In this work, the embedding potential and embedding magnetic field are resolved from periodic plane-wave calculations and represented in real-space which is suitable for describing delocalized systems. However, the wave function of the high-level subsystem is expanded in an atom-centered basis set which is ideal for localized properties. Due to nonuniformity, evaluations of Eqs. (18) and (19) require a numerical integration over basis functions that expand the wave function of the high-level subsystem. A transformation of representation is needed to map the embedding potential and embedding magnetic field generated in real-space onto the

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numerical grid used for atom-center basis functions. In the current implementation, the grid points of each atoms in the high-level subsystem are arranged in Lebedev spheres of several Euler-Maclaurin radii. We use a linear interpolation scheme to map the numerical values of embedding potential and embedding magnetic field at Euler-Maclaurin-Lebedev grid points.

### **III. RESULTS AND DISCUSSION**

We consider two test systems: noncollinear Li<sub>3</sub> interacting with (1) a closed-shell periodic He atom lattice and (2) a periodic He atom lattice with a Li atom defect. The first system describes embedding subsystems that are coupled through a scalar embedding potential, whereas an additional magnetic coupling field is introduced in the second model system. We chose He atoms due to their closed-shell electronic structure, and the Li atom was chosen as a model open-shell environment due to its single unpaired electron. Li<sub>3</sub> was selected due to its 2-component instability, which exhibits a noncollinear electronic structure where net magnetization is zero (Fig. 1).<sup>2,38,39</sup>

The "low-level" of theory used in this work is unrestricted collinear KS-DFT with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.44 The unrestricted PBE calculations on the total system were performed with the ABINIT<sup>45</sup> software package. To avoid producing embedding perturbations that are reflective of the inadequate treatment of Li3 with a collinear reference, we replaced Li3 with Be3 in the calculations that generate the embedding potential and embedding magnetic field. The Be3 geometry is an equilateral triangle with bond lengths of 4 Å and placed 3 Å above a lattice of He atoms with a 2 Å spacing. In the case of the Li-atom defect in the periodic He lattice, we replaced the He atom at the center of the unit cell with a Li atom. The unit cell was 14 Å, 14 Å, and 15 Å in x, y, and z, respectively, where the trimer and lattice were placed in the xy plane. We used a 600 eV kinetic energy cutoff for the plane-wave one-particle basis and norm-conserving pseudopotentials were generated with the fhi98pp<sup>46</sup> program. KS orbitals are occupied following the Fermi-Dirac statistics with a smearing temperature of 10<sup>-6</sup> eV. Subsystem and embedding potential calculations were performed with a locally modified version of the software presented in Ref. 21. Upon maximization of Eq. (6), we obtained embedding perturbations on a uniform grid in position space. The VESTA (visualization for electronic and structural analysis) software was used to generate plots.4

The "high-level" calculation is complex two-component PBE0<sup>48</sup> (2c-PBE0 or  $\mathbb{C}$ -GPBE0), a hybrid density functional, with a cc-pVDZ basis set.<sup>49</sup> The embedding scheme introduced in this



**FIG. 1**. Depiction of stable  $\mathbb{C}$ -GPBE0 solution of Li<sub>3</sub> with no embedding perturbations: (left) top view and (right) 3D view. Li nuclei are in blue, and magnetization vectors are denoted by red arrows.



**FIG. 2.** (Left) Charge density of Be<sub>3</sub> on a He lattice computed with unrestricted PBE. (Right) Embedding potential for Be<sub>3</sub> interacting with the He lattice. Be atoms are in green, He atoms are in silver, turquoise denotes negative values, and yellow denotes positive values. Isosurface values of 0.001 a.u. and 0.026 a.u. were used for the charge density and embedding potential, respectively.

work allows for practical applications with hybrid functionals without incurring increased cost compared to working in the plane wave basis. Note the "high-level" label designation is in reference to the noncollinearity as opposed to the quality of one- or *N*-electron bases. The Li<sub>3</sub> geometry used in this work is that of an equilateral triangle with bond lengths of 4 Å. A stable solution for gas-phase Li<sub>3</sub> was obtained using the development version of Gaussian<sup>50</sup> with stability checks and optimizations of complex 2-component wave functions.<sup>38,51</sup> We used real basis functions and complex MO coefficients. Embedded Li<sub>3</sub> calculations were performed in a locally modified version of Chronus Quantum<sup>52</sup> using the stable solution from Gaussian.

### A. Embedding via scalar potential

Figure 1 shows the magnetization vectors of the stable  $\mathbb{C}$ -GPBE0 solution for a Li<sub>3</sub>. Because such a noncollinear solution cannot be obtained using collinear electronic structure methods, the embedding perturbations were computed using Be<sub>3</sub> instead of Li<sub>3</sub> to avoid unphysical spin polarizations arising from spin collinear calculations of Li<sub>3</sub>. The charge density and resulting embedding potential of Be<sub>3</sub> interacting with the He atom lattice are shown in Fig. 2. The embedding magnetic field is zero due to the closed-shell nature of the subsystems. The attractive region of the embedding potential is around the Be atoms, reflecting how the density is pulled down toward the He lattice upon interaction, and the repulsive region near the He lattice surface prevents the Be<sub>3</sub> density from getting too close to the He atoms.

Upon embedding the  $\mathbb{C}$ -GPBE0 Li<sub>3</sub> solution (Fig. 1) using the Be<sub>3</sub>/He embedding potential, the magnetization density is unchanged, resulting in the similar solution depicted in Fig. 1. Although the embedding potential only enters the scalar part of the two-component Hamiltonian in Eq. (17), it can indirectly modify the magnetic moments by altering the electron density distribution. In this weak interaction scenario, embedding a noncollinear system



FIG. 3. Magnetization density of the He lattice with a Li atom defect computed with unrestricted PBE. Li atom is purple, and He atoms are silver. An isosurface value of 0.001 a.u. was used.



**FIG. 4**. (Left) Charge density of Be<sub>3</sub>/HeLi computed with unrestricted PBE. (Right) Embedding magnetic field for Be<sub>3</sub>/HeLi. Be atoms are in green, He atoms are in silver, Li atom is purple, turquoise denotes negative values, and yellow denotes positive values. Isosurface values of 0.001 a.u. and 0.072 a.u. were used for the charge density and embedding magnetic field, respectively.

in a closed-shell environment leaves the overall spin structure of the embedded system nearly unaffected.

### B. Embedding via scalar potential and magnetic field

To model the effect of an embedding magnetic field, a Li defect is introduced to the He lattice. The magnetization density at the low level is nonzero as shown in Fig. 3, which gives rise to a nonzero embedding magnetic field. The charge density of the total Be<sub>3</sub>/HeLi system and the resulting embedding magnetic field are shown in Fig. 4. In the nonrelativistic and one-component electronic structure framework, the spin orientation is not a welldefined quantity in real-space. As a result, the embedding magnetic field must be prealigned with respect to the magnetization axes in the two-component framework. In other words, the spin frames of low-level and high-level subsystems must be aligned. In this work, we make the choice to align the embedding magnetic field with the  $P_3$  component of the magnetization vector for Li<sub>3</sub>. As noted in Sec. II B, this alignment gives rise to the spin-Zeeman effect along the z-axis defined perpendicular to the plane of the He lattice.

The effect of the embedding potential and magnetic field on noncollinear Li<sub>3</sub> is depicted in Fig. 5. Due to the embedding magnetic field, the Li<sub>3</sub> is now collinear where the magnetization vectors have aligned along the embedding magnetic field (the  $P_3$  component is defined along the *z* axis). Although the two subsystems are 3 Å apart, the embedding magnetic field is strong enough to align spins in Li<sub>3</sub>, resulting in a quartet collinear configuration for the high-level subsystem. This indicates that our embedding formalism may be useful in modeling spin-phase transitions in different environments.<sup>40</sup>



FIG. 5. Depiction of ℂ-GPBE0 solution of Li<sub>3</sub> embedded with the Be<sub>3</sub>/HeLi embedding potential and embedding magnetic field: (left) side view and (right) 3D view. Li nuclei are in blue, and magnetization vectors are denoted by red arrows.

#### **IV. CONCLUSION**

In this work, we have developed a framework for performing single-reference two-component quantum embedding with a nonrelativistic Hamiltonian. The two-component electronic structure is formulated in the Pauli matrix basis which separates spin and scalar components. In this formalism, embedding scalar potential and magnetic field can be introduced to couple different quantum subsystems.

We investigated the effects of scalar potential embedding and magnetic field embedding on the noncollinear spin characteristics of a Li<sub>3</sub> system. When the environment introduces only a scalar embedding potential (e.g., a closed-shell subsystem), the noncollinearity of Li<sub>3</sub> was unaffected. When a magnetic defect introduces an additional embedding magnetic field, it can alter the spin structure of the high-level system.

The result from this two-component embedding scheme is important to consider when one wishes to embed a noncollinear spin system in an environment and to study how magnetic environment affects the electronic characteristics of a molecular system. Because the relativistic two-component Hamiltonian has a similar matrix structure, this work marks an important first step toward two-component relativistic quantum embedding.

In this work, we assume that all spin noncollinearity resides within the high-level subsystem. The embedding method introduced here will be inadequate when there is a significant noncollinear spin transfer from the high-level to the environment. In addition, using a closed-shell model system, e.g., Be<sub>3</sub>, in the computation of embedding perturbations has an advantage of removing unphysical spin polarization due to the spin collinear constraint in low-level calculations, but it also ignores the mutual spin polarization of subsystems. A future development will consider the construction of a full vector form of the embedding magnetic field, which may be capable of tackling such challenging problems.

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