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# Valence-dependent analytic bond-order potential for magnetic transition metals

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We extend the analytic bond-order potentials for transition metals [Phys. Rev. B **74**, 174117 (2006)] to include ferro, antiferro, and noncollinear magnetism and charge transfer. This is achieved by first deriving a suitable tight-binding model through the expansion of the spin-density energy functional to second order with respect to magnetic and charge fluctuations. The tight-binding model is then approximated locally by the bond-order potential expansion, where the variational property of the bond-order potential expansion allows us to derive analytic expressions for the forces and torques on the atoms. From the bond-order potentials we then extract a hierarchy of multispin interactions beyond the conventional Heisenberg model. The explicit valence dependence of the bond-order potentials enables us to characterize the magnetic properties of the $3d$ transition metals and to reproduce the trend from antiferromagnetic spin ordering close to the center of the $d$ band through noncollinear spin configurations to ferromagnetic ordering toward the edges of the $d$ band. The analytic representation of the energy within the bond-order potentials is then further expanded in the form of a Ginzburg-Landau expansion, deriving the prefactors explicitly from tight-binding and bond-order potentials. Thus, in this paper we present a coherent simplification from fundamental to empirical models of magnetism through coarse graining the electronic structure from spin-density functional theory to tight binding to bond-order potentials to the Ginzburg-Landau expansion.

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## I. INTRODUCTION

While the nonmagnetic isovalent $4d$ and $5d$ transition metal elements ruthenium and osmium take a hexagonal close-packed structure, the magnetic $3d$ transition metal iron takes the bcc $\alpha$ phase as its ground state. This stability of the bcc phase of iron is due to a magnetic contribution to the binding energy of the bcc structure of 0.5 eV/atom[1] compared to only small magnetic contributions for the energy of the close-packed fcc and hcp structures. The sensitivity of magnetism to the crystal structure and local environment manifests itself in other properties of Fe: the $\langle 110\rangle$ dumbbell self-interstitial defect in iron carries a spin that is suppressed by 90% and antiferromagnetic to the host lattice,[2,3] similarly to the magnetic behavior of the close-packed $\gamma$ phase of iron.

The microstructure of iron is driven by magnetism through the stabilization of grain boundary structures[4] or the modified behavior of nanocrystalline iron compared to crystalline iron.[5] The structural dependence of the magnetic free energy also governs the iron phase diagram.[6] Unlike Ni and Co, whose atomic magnetic moments collapse in the magnetically disordered state, the atomic moments in Fe contribute to the free energy also in the disordered state.[7,8]

Electronic structure methods such as density functional theory or the tight-binding (TB) method are able to capture the magnetic behavior across the $3d$ transition metal series. A robust tight-binding bond model of magnetism in Fe[9–11] within the framework of numerical bond-order potentials has been developed only recently,[12] where the numerical bond-order potentials are an O(N) approximation to tight binding.[13,14] Although the numerical bond-order potentials provide an analytic representation of the Green's function, a numerical integration of the density of states is required for the evaluation of the bond energy such that no explicit magnetic interatomic potential may be obtained. Possibly for this reason, until recently, studies of interatomic potentials have tried to capture magnetism *implicitly* by fitting equilibrium properties that included magnetic contributions[15,16] and only Dudarev and Derlet have proposed a second-moment potential that *explicitly* accounted for magnetism.[17] While this potential takes into account the ferromagnetic energy in a reference structure such as bcc $\alpha$ iron explicitly and is suitable for large-scale atomistic simulations due to its computational efficiency, it is unable to describe the subtle structural dependence of the magnetic energy that is driven by higher-moment contributions. The latter, fourth, fifth, sixth, and so on, moment contributions to the local density of states are important for modeling defect energies as well as the phase diagram of iron.[6,18,19]

In 2006 the present authors[20] presented an analytic interatomic bond-order potential (BOP) that predicted the ferromagnetic moments of different structures in iron in good agreement with tight-binding calculations.[18,21,22] While the numerical and the analytic BOPs provide a representation of the energy that is of the same quality for close-packed transition metals,[23] the analytic BOPs[20] also provide an explicit, analytic representation of the energy. This allows for a direct interpretation of the structural energy in terms of band-filling-dependent many-body interactions.[24] In addition, the gradients of the energy may also be calculated analytically such that large-scale molecular dynamics (MD) simulations become possible while the approximate Hellmann-Feynman-type forces of the numerical BOPs are not sufficient in accuracy for MD at low-moment expansions.[14]

In this paper we extend the analytic bond-order potential developed in Ref. 20 to take into account antiferromagnetic (AFM) and noncollinear (NCM) spin configurations in addition to ferromagnetic (FM) states. The resulting analytic BOPs allow direct contact to be made to classical models of magnetism such as the Heisenberg model or the Ginzburg-Landau expansion.

The approximation introduced by the BOP expansion means that the usual self-consistent solution to the Kohn-Sham equations does not correspond to a stationary point of the total energy functional. Therefore, an approach for optimizing the energy that differs from the usual self-consistency has to be used. We will therefore review the derivation of the TB approximation from spin-density functional theory (SDFT) in view of a direct optimization of the total energy that does not rely on the self-consistent iteration of the charge density. This will also lead to the extension of the tight-binding bond model to include noncollinear magnetism and charge transfer as well as nonorthogonal basis functions.

The outline of the paper is as follows. In Sec. II the second-order expansion of spin-density functional theory is reviewed. Detailed literature exists on this topic,[11,25–33] so here only the aspects necessary for the development of the analytic bond-order potentials are presented. In particular, a functional form for the total energy of the tight-binding model is derived, which is suitable for a subsequent BOP expansion. In Sec. III TB models are linked directly to the second-order expansion of SDFT. In particular, a TB model suitable for noncollinear magnetism is obtained that is of similar format to the TB models presented in Refs. 27 and 34. This TB model is then cast in the form of a TB bond model that is suitable for the BOP expansion in the following section. In Sec. IV the BOP expansion of the TB bond model is carried out and extended to include magnetism and charge transfer. The analytic forces and the gradients required for the minimization of the energy functional are discussed. In Sec. V the hierarchy of multispin interactions is discussed and shown in its simplest form to approximate the Heisenberg model. In Sec. VI the analytic magnetic BOP is used to discuss trends in magnetic stability across the $3d$ transition metal series, thereby making contact with the Ginzburg-Landau expansion of the magnetic energy. In Sec. VII we conclude.

## II. SECOND-ORDER EXPANSION OF SPIN-DENSITY FUNCTIONAL THEORY

### A. Overview

In this section we briefly summarize as much as required of SDFT[35–37] in order to carry out the second-order expansion with respect to charge and magnetic fluctuations in a basis of localized orbitals. This will lead us directly to a TB model that forms a suitable framework for the magnetic BOPs.

In spin-density functional theory the effective one-particle eigenstates are written as two component spinors

$$\psi_n(\boldsymbol{r}) = \begin{bmatrix} \psi_{n\uparrow}(\boldsymbol{r}) \\ \psi_{n\downarrow}(\boldsymbol{r}) \end{bmatrix}. \tag{1}$$

The 2 × 2 spin density is obtained from the sum of the products of the spinors

$$\rho_{\mu\nu}(\boldsymbol{r}) = \sum_n^{\text{occ}} \psi^*_{n\mu}(\boldsymbol{r})\psi_{n\nu}(\boldsymbol{r}), \tag{2}$$

where the sum is taken over all occupied eigenstates $n$. The components of the spin density are calculated from the spinors by projecting on the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x,\sigma_y,\sigma_z)$

$$\boldsymbol{m}(\boldsymbol{r}) = \sum_n^{\text{occ}} \sum_{\mu\nu} \psi^*_{n\mu}(\boldsymbol{r})\boldsymbol{\sigma}_{\mu\nu}\psi_{n\nu}(\boldsymbol{r}). \tag{3}$$

The charge density is given by

$$n(\boldsymbol{r}) = \rho_{\uparrow\uparrow} + \rho_{\downarrow\downarrow} = \text{Tr}(\boldsymbol{\rho}), \tag{4}$$

such that the spin-density matrix may be written as a function of charge density $n$ and spin density $\boldsymbol{m}$

$$\boldsymbol{\rho}(\boldsymbol{r}) = \tfrac{1}{2}n(\boldsymbol{r})\boldsymbol{1} + \tfrac{1}{2}\boldsymbol{m}(\boldsymbol{r})\boldsymbol{\sigma}, \tag{5}$$

where $\boldsymbol{m}\boldsymbol{\sigma} = m_x\sigma_x + m_y\sigma_y + m_z\sigma_z$. The total energy in SDFT may be written as

$$U[\boldsymbol{\rho}] = T^{\text{KS}}[\boldsymbol{\rho}] + U_H[n] + U_{XC}[\boldsymbol{\rho}] + U_{\text{ext}} + U_{\text{nuc}}, \tag{6}$$

with the Kohn-Sham kinetic energy of the noninteracting electrons

$$T^{\text{KS}}[\boldsymbol{\rho}] = \sum_n^{\text{occ}} \langle\psi_n| - \frac{\hbar^2}{2m}\Delta|\psi_n\rangle. \tag{7}$$

In the presence of a magnetic field $\boldsymbol{B}$ the external potential is given by

$$\boldsymbol{W}_{\text{ext}} = V(\boldsymbol{r})\boldsymbol{1} + \mu_B\boldsymbol{B}(\boldsymbol{r})\boldsymbol{\sigma}, \tag{8}$$

so the external potential energy takes the form

$$\begin{aligned} U_{\text{ext}} &= \int \text{Tr}(\boldsymbol{\rho}\boldsymbol{W})\,d\Omega \\ &= \int [n(\boldsymbol{r})V(\boldsymbol{r}) + \mu_B\boldsymbol{m}(\boldsymbol{r})\boldsymbol{B}(\boldsymbol{r})]d\Omega, \end{aligned} \tag{9}$$

where the Hartree energy is denoted by $U_H[n]$ and $U_{XC}[\boldsymbol{\rho}]$ stands for the exchange-correlation energy and $U_{\text{nuc}}$ is the electrostatic interaction between the nuclei.

The ground-state energy is obtained by minimizing the SDFT total energy with respect to the spin-density matrix

$$\delta_{\boldsymbol{\rho}}\left[U[\boldsymbol{\rho}] - \mu\int \text{Tr}(\boldsymbol{\rho})\,d\Omega\right] = 0, \tag{10}$$

where charge conservation is taken into account with the Lagrange multiplier $\mu$. Variation of the energy leads to an effective one-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta + \boldsymbol{W}_{\text{eff}}(\boldsymbol{r})\right]\psi_n(\boldsymbol{r}) = \epsilon_n\psi_n(\boldsymbol{r}), \tag{11}$$

with the effective potential matrix

$$\boldsymbol{W}_{\text{eff}}(\boldsymbol{r}) = V_H(\boldsymbol{r})\boldsymbol{1} + \boldsymbol{W}_{XC}(\boldsymbol{r}) + \boldsymbol{W}_{\text{ext}}(\boldsymbol{r}), \tag{12}$$

where the Hartree potential is $V_H$ and the exchange-correlation potential is given by

$$\boldsymbol{W}_{XC}(\boldsymbol{r}) = \frac{\delta U_{XC}}{\delta\boldsymbol{\rho}}. \tag{13}$$

### B. Second-order expansion of the exchange-correlation energy

The exchange-correlation energy $U_{XC}$ must be invariant with respect to unitary transformations of the spin-density matrix. As $\boldsymbol{\rho}$ is a 2 × 2 matrix, its eigenvalues are fully characterized by its trace $\text{Tr}[\boldsymbol{\rho}]$ and determinant $\text{Det}[\boldsymbol{\rho}]$. A second-order expansion of the energy with respect to $\boldsymbol{m}$ and $n$ must also be obtained from invariants of $\boldsymbol{\rho}$ or invariants of products of $\boldsymbol{\rho}$. The only contributions that are of second order with respect to $\boldsymbol{m}$ and $n$ are

$$\mathrm{Tr}[\boldsymbol{\rho}] = n, \tag{14}$$

$$\mathrm{Det}[\boldsymbol{\rho}] = \tfrac{1}{4}[n^2 - \boldsymbol{m}^2], \tag{15}$$

$$\mathrm{Tr}[\boldsymbol{\rho}(\boldsymbol{r})\boldsymbol{\rho}(\boldsymbol{r}')] = \tfrac{1}{2}[n(\boldsymbol{r})n(\boldsymbol{r}') + \boldsymbol{m}(\boldsymbol{r})\boldsymbol{m}(\boldsymbol{r}')]. \tag{16}$$

If we assume a local approximation to correlation and exchange and neglect gradient terms with respect to the spin-density matrix, then the second-order approximation of $U_{XC}$ is given by

$$\begin{aligned} U_{XC}^{(2)} = & \int K_{XC}(\boldsymbol{r})n(\boldsymbol{r})d\Omega \\ & + \frac{1}{2}\int\int J_{XC}(\boldsymbol{r},\boldsymbol{r}')n(\boldsymbol{r})n(\boldsymbol{r}')d\Omega d\Omega' \\ & - \frac{1}{4}\int\int I_{XC}(\boldsymbol{r},\boldsymbol{r}')\boldsymbol{m}(\boldsymbol{r})\boldsymbol{m}(\boldsymbol{r}')d\Omega d\Omega', \end{aligned} \tag{17}$$

where $K_{XC}$, $J_{XC}$, and $I_{XC}$ are the expansion coefficients such that for $\boldsymbol{r} \neq \boldsymbol{r}'$, $I_{XC}(\boldsymbol{r},\boldsymbol{r}') = -2J_{XC}(\boldsymbol{r},\boldsymbol{r}')$ to satisfy Eq. (16) and where the factor of $-2$ between $I_{XC}$ and $J_{XC}$ was chosen in order to arrive at the usual Stoner representation of the exchange energy. For the homogenous electron gas Eq. (17) would simplify to $U_{XC} = \bar{K}_{XC}n + \frac{1}{2}\bar{J}_{XC}n^2 - \frac{1}{4}\bar{I}_{XC}\boldsymbol{m}^2$, where $\bar{K}_{XC}$, $\bar{J}_{XC}$, and $\bar{I}_{XC}$ are obtained from the integration of $K_{XC}$, $J_{XC}$, and $I_{XC}$.

Unsurprisingly, the spin density only contributes in invariant terms of the order of $\boldsymbol{m}^2$, $\boldsymbol{m}^4$, and so on, which means that the lowest-order term that explicitly relates the charge and the spin density $n \times \boldsymbol{m}^2$ is of third order.

### C. Expansion in a basis

In order to make contact to tight-binding theory, in the following we rewrite the SDFT with respect to a set of basis functions $\{|\varphi_{i\nu}\rangle\}$ with the two-component basis spinors

$$\varphi_{i\uparrow} = \begin{pmatrix} \varphi_i \\ 0 \end{pmatrix}; \quad \varphi_{i\downarrow} = \begin{pmatrix} 0 \\ \varphi_i \end{pmatrix}. \tag{18}$$

The basis spinors are orthogonal in spin space but not necessarily orthogonal in real space

$$\langle\varphi_{j\mu}|\varphi_{i\nu}\rangle = S_{ij}\delta_{\mu\nu}, \tag{19}$$

where for a linear combination of atomic orbitals (LCAO) the index $i$ combines atom and orbital index. In the following a nonorthogonal basis set is used in the same way as an orthogonal basis set by employing covariant and contravariant basis functions[38]

$$\left|\varphi_\mu^j\right\rangle = \sum_i |\varphi_{i\mu}\rangle(S^{-1})_{ij} \tag{20}$$

because

$$\left\langle\varphi_{j\mu}\middle|\varphi_\mu^k\right\rangle = \sum_i \langle\varphi_{j\mu}|\varphi_{i\mu}\rangle(S^{-1})_{ik} = \delta_{kj}. \tag{21}$$

The eigenspinors may be expanded in this basis

$$\psi_n(\boldsymbol{r}) = \sum_{i\mu} c_{i\mu}^{(n)}\varphi_\mu^i(\boldsymbol{r}) = \sum_{i\mu} c_\mu^{(n)i}\varphi_{i\mu}(\boldsymbol{r}), \tag{22}$$

with the expansion coeffcients

$$c_{i\mu}^{(n)} = \langle\varphi_{i\mu}|\psi_n\rangle, \quad c_\mu^{(n)i} = \left\langle\varphi_\mu^i\middle|\psi_n\right\rangle \tag{23}$$

and

$$c_{i\mu}^{(n)} = \sum_j S_{ij}c_\mu^{(n)j}. \tag{24}$$

In the basis, the charge and spin density are written as

$$n(\boldsymbol{r}) = \sum_{ij} n_i^j\chi_j^i, \tag{25}$$

$$\boldsymbol{m}(\boldsymbol{r}) = \sum_{ij} \boldsymbol{m}_i^j\chi_j^i, \tag{26}$$

with

$$\chi_j^i = \varphi^{i*}(\boldsymbol{r})\varphi_j(\boldsymbol{r}). \tag{27}$$

The expansion coefficients of the spin-density matrix

$$\rho_{i\mu\nu}^j = \sum_n^{\mathrm{occ}} c_{i\mu}^{*(n)}c_\nu^{(n)j}, \tag{28}$$

determine the coefficients of the charge and spin density through

$$n_i^j = \rho_{i\uparrow\uparrow}^j + \rho_{i\downarrow\downarrow}^j, \tag{29}$$

$$\boldsymbol{m}_i^j = \sum_{\mu\nu}\rho_{i\mu\nu}^j\boldsymbol{\sigma}_{\mu\nu}. \tag{30}$$

The total energy Eq. (6) may now be expanded to second order using the expansion of the exchange-correlation functional Eq. (17),

$$\begin{aligned} U = & \sum_{ij} n_i^j T_j^i + \sum_{ij} n_i^j V_j^i + \sum_{ij} n_i^j K_j^i + \sum_{ij} \boldsymbol{m}_i^j \boldsymbol{B}_j^i \\ & + \frac{1}{2}\sum_{ij}\sum_{i'j'} J_{ii'}^{jj'} n_j^i n_{j'}^{i'} - \frac{1}{4}\sum_{iji'j'} I_{jj'}^{ii'}\boldsymbol{m}_i^j\boldsymbol{m}_{i'}^{j'} + U_{\mathrm{nuc}}. \end{aligned} \tag{31}$$

The matrix elements of the kinetic energy are given by

$$T_j^i = \langle\varphi^i|\hat{T}^{\mathrm{KS}}|\varphi_j\rangle, \tag{32}$$

and the Hartree energy

$$\begin{aligned} U_H &= \frac{e^2}{2}\int\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\Omega d\Omega' \\ &= \sum_{ij}\sum_{i'j'}\frac{1}{2}n_i^j n_{i'}^{j'} J_{Hii'}^{jj'}, \end{aligned} \tag{33}$$

with

$$J_{Hii'}^{jj'} = e^2\int\frac{\chi_i^j(\boldsymbol{r})\chi_{i'}^{j'}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\Omega d\Omega'. \tag{34}$$

The expansion coefficient $J_{Hii'}^{jj'}$ is grouped with the second-order contribution from the exchange-correlation functional

$$J_{ii'}^{jj'} = J_{Hii'}^{jj'} + J_{XCii'}^{jj'}. \tag{35}$$

For simplicity in the following we will refer to $J_{ii'}^{jj'}$ as the Coulomb integral rather than the screened Coulomb integral and to the energy associated with $J_{ii'}^{jj'}$ as the Coulomb energy.

Similarly, we will refer to $I_{ii'}^{jj'} = I_{XCii'}^{jj'}$ as the exchange integral and the associated exchange energy. The complete expressions for the matrix elements are summarized in Appendix A.

The matrix elements of the Hamiltonian are obtained from the derivative of the energy with respect to the spin-density matrix

$$H_{j\mu\nu}^{i} = \frac{\partial U}{\partial \rho_{i\mu\nu}^{j}}. \tag{36}$$

From Eq. (31) the Hamiltonian matrix elements are given by

$$\begin{aligned} H_{j\mu\nu}^{i} = {} & \left(T_j^i + V_j^i + K_j^i\right)\delta_{\mu\nu} + \boldsymbol{B}_j^i \boldsymbol{\sigma}_{\mu\nu} \\ & + \sum_{i'j'} J_{jj'}^{ii'} n_{i'}^{j'} \delta_{\mu\nu} - \sum_{i'j'} \frac{1}{2} I_{jj'}^{ii'} \boldsymbol{m}_{i'}^{j'} \boldsymbol{\sigma}_{\mu\nu}. \end{aligned} \tag{37}$$

By making use of the Hamiltonian matrix elements, the energy Eq. (31) may be rewritten in the usual form[29] as the sum of the band energy

$$U_{\text{band}} = \sum_{ij} \sum_{\mu\nu} H_{j\mu\nu}^{i} \rho_{j\mu\nu}^{i} \tag{38}$$

and double counting terms

$$\begin{aligned} U = {} & U_{\text{band}} - \frac{1}{2} \sum_{ij} \sum_{i'j'} J_{jj'}^{ii'} n_{i'}^{j'} n_i^j \\ & + \frac{1}{4} \sum_{ij} \sum_{i'j'} I_{jj'}^{ii'} \boldsymbol{m}_{i'}^{j'} \boldsymbol{m}_i^j + U_{\text{nuc}}. \end{aligned} \tag{39}$$

### D. Variational properties and self-consistent solution

In the following the matrix indices are dropped and mixed co- and contravariant matrix elements are assumed everywhere. The variational optimization of the energy Eq. (10) may be written as

$$0 = \frac{\partial}{\partial c^{*(n)}} \left[ U - \sum_{n}^{\text{occ}} \epsilon_n \left(c^{*(n)} c^{(n)}\right) \right] = (H - \epsilon_n)\, c^{(n)}, \tag{40}$$

where the Lagrange multipliers $\epsilon_n$ ensure that the one-particle wave functions are normalized and we made use of Eq. (37).

Often the optimization of the total energy with respect to charge and magnetic density is not carried out directly but in an iterative, self-consistent way.[37] To this end, one generates a suitable trial spin density $\rho^{(\text{out})}$ for the evaluation of the energy $U^{(\text{out})} = U[\rho^{(\text{out})}]$. The trial spin density is obtained according to Eq. (2) from wave functions that diagonalize the Hamiltonian $\hat{H}^{(\text{in})}$ and, therefore, $\rho^{(\text{out})} = \rho^{(\text{out})}[\hat{H}^{(\text{in})}]$. Through the variational principle of SDFT, the ground-state energy $U_0$ is lower than $U^{(\text{out})}$,

$$U^{(\text{out})} \geqslant U_0. \tag{41}$$

We use Eq. (37) for $\hat{H}^{(\text{in})}$,

$$H^{(\text{in})} = (T + V + K) + \boldsymbol{B\sigma} + J n^{(\text{in})} - \tfrac{1}{2} I \boldsymbol{m}^{(\text{in})} \boldsymbol{\sigma}, \tag{42}$$

where $n^{(\text{in})}$ and $\boldsymbol{m}^{(\text{in})}$ are obtained from a suitably chosen trial spin density $\rho^{(\text{in})}$. Clearly, the diagonalization of $H^{(\text{in})}$ results in a spin-density matrix $\rho^{(\text{out})} = \rho_0$ that fulfills Eq. (40) if

$$\rho^{(\text{out})} = \rho^{(\text{in})}, \tag{43}$$

i.e., the variational state corresponds to the self-consistent solution.

The energy Eq. (31) obtained from $\rho^{(\text{out})}$ is given by

$$\begin{aligned} U^{(\text{out})} = {} & (T + V + K) n^{(\text{out})} + \boldsymbol{B m}^{(\text{out})} + \tfrac{1}{2} J n^{(\text{out})} n^{(\text{out})} \\ & - \tfrac{1}{4} I \boldsymbol{m}^{(\text{out})} \boldsymbol{m}^{(\text{out})} + U_{\text{nuc}}. \end{aligned} \tag{44}$$

Using the Hamiltonian matrix $H^{(\text{in})}$, the trial energy is written as

$$\begin{aligned} U^{(\text{out})} = {} & H^{(\text{in})} \rho^{(\text{out})} + \tfrac{1}{2} J [n^{(\text{out})} n^{(\text{out})} - 2 n^{(\text{in})} n^{(\text{out})}] \\ & - \tfrac{1}{4} I [\boldsymbol{m}^{(\text{out})} \boldsymbol{m}^{(\text{out})} - 2 \boldsymbol{m}^{(\text{in})} \boldsymbol{m}^{(\text{out})}] + U_{\text{nuc}}. \end{aligned} \tag{45}$$

This form of $U^{(\text{out})}$ is not satisfactory, as the (in) and (out) spin-density matrix elements are used simultaneously.[25] By expanding around a reference charge density $n^{(0)}$ and spin density $\boldsymbol{m}^{(0)}$

$$n^{(\text{in})} = n^{(0)} + \delta n^{(\text{in})}, \quad n^{(\text{out})} = n^{(0)} + \delta n^{(\text{out})}, \tag{46}$$

$$\boldsymbol{m}^{(\text{in})} = \boldsymbol{m}^{(0)} + \delta \boldsymbol{m}^{(\text{in})}, \quad \boldsymbol{m}^{(\text{out})} = \boldsymbol{m}^{(0)} + \delta \boldsymbol{m}^{(\text{out})}, \tag{47}$$

and splitting $H^{(\text{in})}$ accordingly

$$H^{(\text{in})} = H^{(0)} + V + \boldsymbol{B\sigma} + J \delta n^{(\text{in})} - \tfrac{1}{2} I \delta \boldsymbol{m}^{(\text{in})} \boldsymbol{\sigma}, \tag{48}$$

a more useful expression for $U^{(\text{out})}$ is obtained

$$\begin{aligned} U^{(\text{out})} = {} & H^{(0)} \rho^{(\text{out})} + \tfrac{1}{2} J \delta n^{(\text{out})} \delta n^{(\text{out})} - \tfrac{1}{4} I \delta \boldsymbol{m}^{(\text{out})} \delta \boldsymbol{m}^{(\text{out})} \\ & + V n^{(\text{out})} + \boldsymbol{B m}^{(\text{out})} - \tfrac{1}{2} J n^{(0)} n^{(0)} \\ & + \tfrac{1}{4} I \boldsymbol{m}^{(0)} \boldsymbol{m}^{(0)} + U_{\text{nuc}}. \end{aligned} \tag{49}$$

Similar expressions for the energy were obtained in Refs. 25, 27, and 29. As $U^{(\text{out})}$ may be written as a functional of (out) quantities alone, any valid spin-density matrix $\rho^{(\text{out})}$ may be used in a variational optimization of $U^{(\text{out})}$. Therefore, we may view $\delta n^{(\text{in})}$ and $\delta \boldsymbol{m}^{(\text{in})}$, or, equivalently, $\rho^{(\text{in})}$, as parameters that may be used to generate suitable trial spin densities $\rho^{(\text{out})} = \rho^{(\text{out})}[H^{(\text{in})}]$ from Eq. (48). The direct minimization of the energy $U^{(\text{out})}$ with respect to $\rho^{(\text{in})}$,

$$\frac{\partial U^{(\text{out})}}{\partial \rho^{(\text{in})}} = \frac{\partial U^{(\text{out})}}{\partial H^{(\text{in})}} \frac{\partial H^{(\text{in})}}{\partial \rho^{(\text{in})}} = 0, \tag{50}$$

is therefore equivalent to solving Eq. (40) or the self-consistent solution Eq. (43). As we will see in Sec. IV, for working with bond-order potentials, it is most convenient to use Eq. (50) because the approximate representation of the electronic structure within bond-order potentials breaks the equivalence between the variational optimization of Eq. (40) and the self-consistent solution of the Kohn-Sham equations, Eq. (43), such that the self-consistent solution within the BOP approximation does not correspond to a stationary point of the total energy.

## III. MAGNETIC TIGHT BINDING

### A. From spin-density functional theory to the tight-binding approximation

The tight-binding approximation to the energy is obtained from Eq. (49) by choosing an atomiclike minimal basis $\{|\phi_{i\alpha\mu}\rangle\}$ for the expansion of the one-electron wave functions and by identifying $n^{(0)}$ as the charge density of overlapping free atomlike charge densities. The basis function $|\phi_{i\alpha\mu}\rangle$ is centered on atom $i$, the different orbitals on atom $i$ are labeled by $\alpha$, and $\mu$ indicates the spin-up $\uparrow$ or spin-down $\downarrow$ character of the basis function.

Typically, one assumes that the reference spin-density is zero, $\boldsymbol{m} = 0$, such that $\delta \boldsymbol{m}$ corresponds to the full spin density. If we drop the (out) indices from Eq. (49) with the understanding that the energy is written in terms of (out) quantities only, then the energy of the TB model may be written as

$$U = H^{(0)}n + \tfrac{1}{2}J\delta n\delta n - \tfrac{1}{4}\boldsymbol{Imm} + Vn + \boldsymbol{Bm} - \tfrac{1}{2}Jn^{(0)}n^{(0)} + U_{\text{nuc}}, \tag{51}$$

while the reference Hamiltonian is nonmagnetic,

$$H^{(0)} = (T + K)n^{(0)} + Jn^{(0)}. \tag{52}$$

Because $n^{(0)}$ is given by overlapping free atomlike charge densities, $H^{(0)}$ is obtained from the corresponding overlapping free atomlike potentials.

For many practical applications of TB Eq. (51) is further simplified. Writing all indices explicitly, the second-order term of the Coulomb and exchange energies are given by

$$U_C = \frac{1}{2}J\delta n\delta n = \frac{1}{2}\sum_{i\alpha,i'\alpha'} J_{i\alpha i'\alpha'}^{i\alpha i'\alpha'}\delta n_{i'\alpha'}^{i'\alpha'}\delta n_{i\alpha}^{i\alpha} + \frac{1}{2}\sum_{i\alpha,i'\alpha',j\beta,j'\beta'}^{i\alpha\neq j\beta,i'\alpha'\neq j'\beta'} J_{j\beta j'\beta'}^{i\alpha i'\alpha'}\delta n_{i'\alpha'}^{j'\beta'}\delta n_{i\alpha}^{j\beta}, \tag{53}$$

$$U_X = -\frac{1}{4}\boldsymbol{Imm} = -\frac{1}{4}\sum_{i\alpha,i'\alpha'} I_{i\alpha i'\alpha'}^{i\alpha i'\alpha'}\boldsymbol{m}_{i'\alpha'}^{i'\alpha'}\boldsymbol{m}_{i\alpha}^{i\alpha} - \frac{1}{4}\sum_{i\alpha,i'\alpha',j\beta,j'\beta'}^{i\alpha\neq j\beta,i'\alpha'\neq j'\beta'} I_{j\beta j'\beta'}^{i\alpha i'\alpha'}\boldsymbol{m}_{i'\alpha'}^{j'\beta'}\boldsymbol{m}_{i\alpha}^{j\beta}, \tag{54}$$

where we separated the diagonal contributions $\delta n_{i\alpha}^{i\alpha}$ from the off-diagonal contributions $\delta n_{i\alpha}^{j\beta}$. As a first simplification it is often assumed that the contribution of the bond charge[19] to the Coulomb and exchange energies, which is associated with the off-diagonal contributions $\delta n_{i\alpha}^{j\beta}$, may be neglected, such that

$$J_{j\beta,j'\beta'}^{i\alpha i'\alpha'} = J_{j\beta j'\beta'}\delta_{i\alpha,j\beta}\delta_{i'\alpha',j'\beta'}, \tag{55}$$

$$I_{j\beta,j'\beta'}^{i\alpha i'\alpha'} = I_{j\beta j'\beta'}\delta_{i\alpha,j\beta}\delta_{i'\alpha',j'\beta'}. \tag{56}$$

By noting that the diagonal element $\delta n_{i\alpha}^{i\alpha}$ corresponds to the Mulliken charge of orbital $|i\alpha\rangle$,

$$q_{i\alpha} = \delta n_{i\alpha}^{i\alpha} = \sum_{j\beta} S_{i\alpha j\beta}\delta n^{j\beta i\alpha}, \tag{57}$$

and a similar definition for the atomic magnetic moments

$$\boldsymbol{m}_{i\alpha} = \boldsymbol{m}_{i\alpha}^{i\alpha} = \sum_{j\beta} S_{i\alpha j\beta}\boldsymbol{m}^{j\beta i\alpha}, \tag{58}$$

the Coulomb and exchange energies take a much simpler form,

$$U_C = \frac{1}{2}\sum_{i\alpha,j\beta} J_{i\alpha j\beta}q_{j\beta}q_{i\alpha}, \tag{59}$$

$$U_X = -\frac{1}{4}\sum_{i\alpha,j\beta} I_{i\alpha j\beta}\boldsymbol{m}_{j\beta}\boldsymbol{m}_{i\alpha}. \tag{60}$$

At this level of approximation, different orbitals that belong to the same angular momentum quantum number may be populated with different numbers of electrons. For example, the five $d$ orbitals on an atom or the three $p$ orbitals on an atom may all carry different Mulliken charges. Therefore, the charge distribution on an atom will, in general, not be spherical but will in essence correspond to a multipole expansion of the charge density.[39]

Finally, the simplest approximation to the Coulomb and exchange energies assumes that only the total charges and magnetic moments are relevant and, therefore,

$$U_C = \frac{1}{2}\sum_{ij} J_{ij}q_jq_i, \tag{61}$$

$$U_X = -\frac{1}{4}\sum_{ij} I_{ij}\boldsymbol{m}_j\boldsymbol{m}_i, \tag{62}$$

with

$$q_i = \sum_{\alpha} q_{i\alpha}, \quad \boldsymbol{m}_i = \sum_{\alpha}\boldsymbol{m}_{i\alpha}. \tag{63}$$

It is then sometimes further assumed that this approximation also implies a spherical distribution of the charge on each atom.[27,34]

In the following we will work with the Coulomb and exchange energies in the form of Eqs. (59) and (60), such that the energy is simplified to

$$U = \sum_{i\alpha j\beta} H_{j\beta}^{(0)i\alpha}n_{i\alpha}^{j\beta} + \frac{1}{2}\sum_{i\alpha,j\beta} J_{i\alpha j\beta}q_{i\alpha}q_{j\beta} - \frac{1}{4}\sum_{i\alpha,j\beta} I_{i\alpha j\beta}\boldsymbol{m}_{i\alpha}\boldsymbol{m}_{j\beta} + \sum_{i\alpha} V_{i\alpha}N_{i\alpha} + \sum_{i\alpha}\boldsymbol{B}_{i\alpha}\boldsymbol{m}_{i\alpha} - \frac{1}{2}\sum_{i\alpha,j\beta} J_{i\alpha j\beta}N_{i\alpha}^{(0)}N_{j\beta}^{(0)} + U_{\text{nuc}}, \tag{64}$$

where we assumed

$$V_{i\alpha}^{i'\alpha'} = V_{i\alpha}\delta_{i\alpha i'\alpha'}, \tag{65}$$

$$\boldsymbol{B}_{i\alpha}^{i'\alpha'} = \boldsymbol{B}_{i\alpha}\delta_{i\alpha i'\alpha'}, \tag{66}$$

and write the number of electrons in orbital $\alpha$ on atom $i$ as the sum of the orbital Mulliken charges and the number of electrons in orbital $\alpha$ in the reference charge density $n^{(0)}$

$$N_{i\alpha} = q_{i\alpha} + N_{i\alpha}^{(0)}. \tag{67}$$

From Eq. (48) the corresponding Hamiltonian matrix is given by

$$H_{i\alpha\mu\nu}^{j\beta} = H_{i\alpha}^{(0)j\beta}\delta_{\mu\nu} + \left(\sum_{k\gamma} J_{i\alpha k\gamma}q_{k\gamma}\delta_{\mu\nu} - \frac{1}{2}\sum_{k\gamma} I_{i\alpha k\gamma}\boldsymbol{m}_{k\gamma}\boldsymbol{\sigma}_{\mu\nu} + V_{i\alpha}\delta_{\mu\nu} + \boldsymbol{B}_{i\alpha}\boldsymbol{\sigma}_{\mu\nu}\right)\delta_{i\alpha j\beta}. \tag{68}$$

The approximation that the bond charge does not enter the Coulomb and exchange energies Eqs. (59) and (60) means that only the diagonal elements of the Hamiltonian are modified by charge and magnetism

$$E_{i\alpha\mu\nu} = H^{i\alpha}_{i\alpha\mu\nu} = E^{(0)}_{i\alpha}\delta_{\mu\nu} + \sum_{k\gamma} J_{i\alpha k\gamma} q_{k\gamma}\delta_{\mu\nu} - \frac{1}{2}\sum_{k\gamma} I_{i\alpha k\gamma}\boldsymbol{m}_{k\gamma}\boldsymbol{\sigma}_{\mu\nu} + V_{i\alpha}\delta_{\mu\nu} + \boldsymbol{B}_{i\alpha}\boldsymbol{\sigma}_{\mu\nu}, \tag{69}$$

where $E^{(0)}_{i\alpha} = H^{(0)i\alpha}_{i\alpha}$. Equations (64) and (69) are given in mixed covariant and contravariant matrix elements. When transformed to contravariant indices with the help of Eqs. (20), (64) and (69) correspond to an extension of the expressions obtained in Refs. 27 and 34 to include noncollinear magnetism. This is discussed in more detail in Appendix B.

The tight-binding model [Eq. (64)] differs from traditional tight-binding band models that represent the energy as the sum of the band energy and an empirical potential, the repulsive energy.[25,40] It is evident that such a representation of the tight-binding energy is not amenable to the optimization of the energy as the energy does not fulfill any variational principle. Therefore, in contrast to the tight-binding model [Eq. (64)], the traditional, empirical tight-binding band models do not fulfill the force theorem.[11,41,42]

## B. Tight-binding bond model

### 1. *Intersite representation of the bond energy*

The tight-binding bond model[9,11] allows for an intuitive and transparent decomposition of the energy into various contributions relevant to the formation of the intersite chemical bonds and the associated binding energy. Here we show how the tight-binding model [Eq. (64)] may be written in the form of a tight-binding bond model, thereby extending the tight-binding bond model to include charge transfer and noncollinear magnetism as well as nonorthogonal basis functions.

We start by introducing the bond energy as

$$U_{\text{bond}} = \sum_{i\alpha\mu j\beta\nu} H^{j\beta}_{i\alpha\mu\nu}\rho^{i\alpha}_{j\beta\nu\mu} - \sum_{i\alpha\mu\nu} E_{i\alpha\mu\nu}\rho^{i\alpha}_{i\alpha\mu\nu}, \tag{70}$$

where we subtract the diagonal elements from the band energy, Eq. (38), which guarantees that the bond energy is independent of the choice of the zero of the energy axis.

Because only the diagonal elements of the Hamiltonian in Eq. (69) are modified by charge transfer and magnetism, the bond energy [Eq. (70)] in the *intersite* representation may be written as

$$\begin{aligned} U_{\text{bond}} &= \sum_{i\alpha j\beta} H^{(0)i\alpha}_{j\beta} n^{j\beta}_{i\alpha} - \sum_{i\alpha} E^{(0)}_{i\alpha} N_{i\alpha} \\ &= \sum_{i\alpha j\beta}^{i\neq j} H^{(0)i\alpha}_{j\beta} n^{j\beta}_{i\alpha} + \sum_{i\alpha\beta}^{\alpha\neq\beta} H^{(0)i\alpha}_{i\beta} n^{i\beta}_{i\alpha}, \end{aligned} \tag{71}$$

where we made use of Eq. (29). The second term of the right-hand-side equation is sometimes separated from the first as it relates two orbitals on the same atom and is, therefore, not strictly related to the formation of bonds between atoms,[29,43] but we keep this term formally with the bond energy as this is required for the transformation of the bond energy in the *onsite* representation that will be discussed in Sec. III B 3. Also, in most tight-binding parametrizations, the off-diagonal terms of the onsite matrix elements are neglected such that $H^{(0)i\alpha}_{i\beta} = E^{(0)}_{i\alpha}\delta_{\alpha\beta}$ and the last term on the right-hand side vanishes.

We further introduce the electron transfer energy as the energy that is associated to the transfer of electrons from their reference distribution of the nonmagnetic free atom to their actual occupation numbers with respect to the reference levels $E^{(0)}_{i\alpha}$,

$$U_{\text{trans}} = \sum_{i\alpha} E^{(0)}_{i\alpha} q_{i\alpha}. \tag{72}$$

For neutral systems this contribution corresponds to the usual promotion energy that is required to create $sp^3$ hybrid orbitals from $s^2p^2$ free atomic states, for example. For nondegenerate ionic systems, such as an $AB$ $s$-valent alloy, this term corresponds to the negative linear driving term for charge flow from the higher- to lower-level sites. We have also defined the preparation energy as

$$U_{\text{prep}} = \sum_{i\alpha}\left(E^{(0)}_{i\alpha} - E^{(\text{at})}_{i\alpha}\right)N^{(0)}_{i\alpha}, \tag{73}$$

with the energy levels $E^{(\text{at})}_{i\alpha}$ of nonmagnetic free atoms and the occupation of these levels with $N^{(0)}_{i\alpha}$ electrons. The shift of the atomic levels from $E^{(\text{at})}_{i\alpha}$ to $E^{(0)}_{i\alpha}$ is driven by different contributions. Typically, the main contribution is due to the overlap of the atomic orbitals which introduces repulsive upward shifts of the atomic levels. The overlapping atomic potentials also lead to the splitting of the degenerate atomic levels by crystal field effects, associated with a typically small and negative crystal field energy. There is also a sizable shift due to the renormalization of the atomiclike local orbitals.[21,44] The latter is due to the increase in kinetic energy of the atomiclike orbitals that have to contract under compression in order to satisfy the virial theorem. In particular, for transition metals the $d$-overlap contribution to the shift of the atomic levels is much smaller than the shift associated with the contraction of the atomiclike orbitals as the overlap of the $d$ orbitals is small.

We see immediately that the sum

$$U_{\text{bond}} + U_{\text{trans}} + U_{\text{prep}} = \sum_{i\alpha j\beta} H^{(0)i\alpha}_{j\beta} n^{j\beta}_{i\alpha} - \sum_{i\alpha} E^{(\text{at})}_{i\alpha} N^{(0)}_{i\alpha} \tag{74}$$

equals the difference between the first term of Eq. (64) and the band energy of nonmagnetic free atoms.

The *binding* energy $U_B$ is defined with respect to nonmagnetic free atoms, whose energy is given by

$$U_{\text{atoms}} = \sum_{i\alpha} E^{(\text{at})}_{i\alpha} N^{(0)}_{i\alpha} - \frac{1}{2}\sum_{i\alpha\beta} J_{i\alpha i\beta} N^{(0)}_{i\alpha} N^{(0)}_{i\beta}, \tag{75}$$

where the latter contribution is the double-counting Coulomb energy of the free atom. It follows from Eq. (64) that the binding energy $U_B = U - U_{\text{atoms}}$ may be written as

$$U_B = U_{\text{bond}} + U_{\text{trans}} + U_{\text{rep}} + U_C + U_X + U_{\text{ext}}, \tag{76}$$

where the bond, electron transfer, Coulomb, and exchange energies are given by Eqs. (70), (72), (73), (59), and (60), respectively. The repulsive energy is defined by

$$U_{\mathrm{rep}} = -\frac{1}{2}\sum_{i\alpha j\beta}^{i\neq j} J_{i\alpha j\beta} N_{i\alpha}^{(0)} N_{j\beta}^{(0)} + U_{\mathrm{prep}} + U_{\mathrm{nuc}}, \tag{77}$$

where the preparation energy term $U_{\mathrm{prep}}$ has been grouped into the repulsive energy as in the original TB bond model.[11] In the absence of nonorthogonality contributions, $U_{\mathrm{rep}}$ would thus correspond to the physical Coulomb interaction between the frozen free atoms arranged on the bulk sites. Including the overlap contribution $(HS)_{ii}$ in the preparation energy ensures that $U_{\mathrm{rep}}$ is positive (apart from a small attractive contribution at large interatomic separation) and decays monotonically as a function of distance between the atoms.[44,45] Further, we see that the repulsive energy is independent of the electron transfer $q_{i\alpha}$ or the magnetic moments $\boldsymbol{m}_{i\alpha}$ and therefore independent of the electronic state of the system. Therefore, it may be parameterized as a function of the interatomic positions. In most practical TB simulations $U_{\mathrm{rep}}$ is approximated by a simple pairwise potential.

The external energy is given by

$$U_{\mathrm{ext}} = \sum_{i\alpha} V_{i\alpha} N_{i\alpha} + \sum_{i\alpha} \boldsymbol{B}_{i\alpha}\boldsymbol{m}_{i\alpha}. \tag{78}$$

The binding energy $U_B$, Eq. (76), is independent of the energy of the free atoms because every term in Eq. (76) vanishes individually when the atoms of a molecule or a solid are separated into uncharged and nonmagnetic free atoms. Therefore, in practical TB calculations, each of the contributions to Eq. (76) may be analyzed separately regarding its role in the formation of chemical bonds.

Furthermore, by writing the contributions of the tight-binding bond model in mixed covariant and contravariant notation, an extension of the tight-binding bond model to nonorthogonal basis functions has been achieved. A simple transformation inverse to Eq. (20), i.e., the multiplication with the overlap matrix $S$, leads to an explicitly nonorthogonal generalization of the density of states, the bond energy, and the remaining contributions to the binding energy. We give the explicitly nonorthogonal representation of the TB bond model in Appendix B, where the resulting formulas are also compared to the expressions obtained by Fähnle and coworkers,[43,46] Finnis[29] and Paxton.[30]

### 2. *The binding energy in the tight-binding bond model*

In the following we will illustrate the bond formation among atoms within the TB bond model with three exemplary cases: a nonmagnetic system where charge transfer may be neglected, a system where ionic contributions are important for the binding energy, and, finally, a magnetic system.

(*a*) *Local charge neutrality.* Many metals and alloys are well described by assuming that the atoms remain charge neutral, such that for the simplest model of the Coulomb energy $U_C = 0$ from Eq. (61). If the system at hand is also nonmagnetic, then $U_X = 0$, and we may drop the magnetic indices $\mu,\nu$ in the following. The onsite levels $E_{i\alpha}$ are adjusted to fulfill the condition of local charge neutrality.[14] The bond energy in this system may be written as

$$U_{\mathrm{bond}} = \sum_{i\alpha j\beta} \beta_{j\beta i\alpha}\Theta_{i\alpha j\beta}, \tag{79}$$

with the bond order $\Theta$ and the bond integrals[19]

$$\beta_{i\alpha j\beta} = H_{i\alpha j\beta} - \tfrac{1}{2}(E_{i\alpha} + E_{j\beta})S_{i\alpha j\beta}, \tag{80}$$

as given by Eq. (B10) in Appendix B. If the TB basis functions are orthogonal, then the bond energy $U_{\mathrm{bond}}$ coincides with the definition of the covalent bond energy $U_{\mathrm{cov}}$ in the TB bond model.[11] The electron transfer energy $U_{\mathrm{trans}}$ reduces to the conventional promotion energy, i.e., the repopulation of the atomic levels by electron transfer between the atomic states

$$U_{\mathrm{prom}} = \sum_{i\alpha} E_{i\alpha}^{(0)} q_{i\alpha}, \tag{81}$$

with $\sum_\alpha q_{i\alpha} = 0$ for all atoms $i$. As the occupation of the atomic levels in the free atom corresponds to the minimum of the energy, the modification of the population of the levels increases the energy and $U_{\mathrm{prom}} \geqslant 0$. The promotion energy corresponds to the energy required to create hybrid orbitals. The complete binding energy for the locally charge-neutral system is given by

$$U_B^{(\mathrm{LCN})} = U_{\mathrm{bond}} + U_{\mathrm{prom}} + U_{\mathrm{rep}}. \tag{82}$$

Because both the promotion energy and the repulsive energy are positive, the attraction between the atoms is due to the bond energy.

(*b*) *Including charge transfer.* The electron transfer energy may be decomposed into two contributions, the energy associated with the flow of the charge $q_i = \sum_\alpha q_{i\alpha}$ to or from atom $i$ that drives the formation of ions and the promotion energy associated with the formation of hybrid orbitals. The charge $q_i$ that is transferred from or to the atom is taken from or placed on the neutral atom in such a way that the energy of the atom is modified as little as possible, which means that the charge $q_i$ is taken out of the highest occupied states or placed in the lowest partly or unoccupied states. Hence, if we break the electron transfer energy into two steps, in the first step the occupation numbers of the charge-neutral atom are changed by an amount $\Delta q_{i\alpha}$ with $q_i = \sum_\alpha \Delta q_{i\alpha}$ in such a way that the associated energy is minimal. In the second step the remaining electrons are exchanged between the atomic levels in such a way that the charge of the atom remains constant. The electron transfer energy may be written accordingly as

$$U_{\mathrm{trans}} = \sum_i \bar{E}_i q_i + U_{\mathrm{prom}}, \tag{83}$$

with

$$\bar{E}_i = \frac{\sum_\alpha E_{i\alpha}^{(0)} \Delta q_{i\alpha}}{q_i}, \tag{84}$$

and the modified expression for the promotion energy

$$U_{\mathrm{prom}} = \sum_{i\alpha} E_{i\alpha}^{(0)} (q_{i\alpha} - \Delta q_{i\alpha}). \tag{85}$$

As $\sum_\alpha (q_{i\alpha} - \Delta q_{i\alpha}) = 0$, we may view the promotion energy as the energy associated with the repopulation of the atomic levels in the charged atom, from which we also conclude that $U_{\text{prom}} \geqslant 0$. On the other hand, the Coulomb contribution $U_C$ to the binding energy may be split in an onsite term and an intersite term

$$U_C = \frac{1}{2}\sum_i J_{ii}q_i^2 + \frac{1}{2}\sum_{ij}^{i\neq j} J_{ij}q_iq_j, \tag{86}$$

where the first, self-energy, term is strictly positive and the second, Madelung-type, term in general will be negative. For simplicity, we adopt the approximation that only the total atomic charges are relevant for the energy as in Eq. (61).

The final expression for the binding energy [Eq. (76)] now becomes

$$U_B = U_{\text{bond}} + U_{\text{prom}} + U_{\text{rep}} + \sum_i \left(\bar{E}_i q_i + \frac{1}{2}J_{ii}q_i^2\right) + \frac{1}{2}\sum_{ij}^{i\neq j} J_{ij}q_iq_j + U_{\text{ext}}. \tag{87}$$

Therefore, including charge transfer in the expression for the binding energy of the locally charge-neutral atoms, Eq. (82), modifies the expression for the binding energy in two ways. First, the charging of the atoms leads to a parabolic change of the energy. While the term $\bar{E}_i q_i$ will contribute to drive the charge transfer in multicomponent systems similarly to an effective electronegativity difference between the atoms, the second term $1/2 J_{ii}q_i^2$ will counteract the charge transfer from or to the atom and is referred to as the chemical hardness, such that the sum and difference of the two terms may be related to the electron affinity or ionization potential, respectively [see, for example, Eqs. (103) and (104) of Ref. 47]. We therefore denote this term as the energy to form ions,

$$U_{\text{ion}} = \sum_i \left(\bar{E}_i q_i + \frac{1}{2}J_{ii}q_i^2\right). \tag{88}$$

Second, the term $1/2 J_{ij}q_iq_j$ associated to the electrostatic energy will usually be negative and, hence, contribute to a lowering of the binding energy. It will be denoted as the electrostatic energy,

$$U_{\text{es}} = \frac{1}{2}\sum_{ij}^{i\neq j} J_{ij}q_iq_j. \tag{89}$$

For the approximation that $J_{ij}$ falls off as $1/R$ this term (normalized by the number of ion pairs in the system) reduces to the well-known Madelung energy.

It should be noted that, in general, charge transfer will affect the density matrix/bond order. For the simplest case of an $s$-valent heteronuclear dimer, the stronger the degree of ionicity, the weaker the degree of covalency and vice versa (see, for example, Sec. 3.2 of Ref. 19).

(*c*) *Including magnetism.* The exchange contribution to the energy $U_X$ is typically dominated by the onsite contribution $-\frac{1}{4}I_{ii}m_i^2$ while the intersite terms $-\frac{1}{4}I_{ij}\boldsymbol{m}_i\boldsymbol{m}_j$ are small. Therefore, if we approximate the exchange contribution to the energy as

$$U_X = -\frac{1}{4}\sum_i I_{ii}m_i^2, \tag{90}$$

we see that an increase of the magnetic moments may contribute to lowering the binding energy, which now is given by

$$U_B = U_{\text{bond}} + U_{\text{prom}} + U_{\text{rep}} + U_{\text{ion}} + U_{\text{es}} + U_X + U_{\text{ext}}. \tag{91}$$

The lowering of the energy by the exchange energy is counterbalanced by an increase in the bond energy as the chemical bonds between the atoms are weakened when the magnetic moments increase because of the associated increase of the kinetic energy of the electrons. Therefore, the magnetic energy contains negative contributions from the exchange energy and positive contributions from the increase of the bond energy. The balance between the exchange energy and the increase of the bond energy determines whether stable magnetic moments are formed. If the sum of the two contributions is negative, a magnetic state will be favored, otherwise, the material will be nonmagnetic. As will be discussed in detail in Secs. V and VI, the bond energy depends on the relative direction of the magnetic moments and induces an interatomic spin interaction even if the exchange energy contains only onsite terms[48] as in Eq. (90).

The increase of the bond energy on formation of a magnetic moment may be understood directly from the onsite representation of the bond energy that is discussed in the next section.

### 3. *Onsite representation of the bond energy*

The bond energy [Eq. (70)] may alternatively be written in an *onsite* form by subtracting off the diagonal elements of the Hamiltonian from the band energy $U_{\text{band}}$. This onsite representation of the bond energy forms the basis for the bond-order potential expansion of the bond energy in the next section and therefore will be briefly introduced here. To obtain the onsite representation we start with the band energy Eq. (38)

$$U_{\text{band}} = \sum_{i\alpha\mu j\beta\nu} H_{i\alpha\mu\nu}^{j\beta}\rho_{j\beta\nu\mu}^{i\alpha}.$$

Diagonalization of the Hamiltonian matrix results in the eigenvalues $\epsilon_n$ and the expansion coefficients of the eigenspinors [Eq. (22)]. By using the normalization of the eigenspinors $\sum_{i\alpha\nu}(c_{i\alpha\nu}^{(n)})^* c^{(n)i\alpha\nu} = 1$, a local decomposition of the band energy may be achieved,

$$U_{\text{band}} = \sum_n^{\text{occ}} \epsilon_n = \sum_{i\alpha\nu}\int^{E_F} E\, n_{i\alpha\nu}(E)\, dE, \tag{92}$$

where the summation in the first equation runs over all occupied states and $E_F$ is the Fermi energy. The local density of states is given by

$$n_{i\alpha\nu}(E) = \sum_n \left(c_{i\alpha\nu}^{(n)}\right)^* c_\nu^{(n)i\alpha}\delta(E-\epsilon_n), \tag{93}$$

and the number of electrons associated with orbital $|i\alpha\nu\rangle$ is obtained from

$$N_{i\alpha\nu} = \int^{E_F} n_{i\alpha\nu}(E)\, dE. \tag{94}$$

By choosing a local coordinate system for each atom and orbital parallel to the direction of the magnetic moment $\boldsymbol{e}_z = \boldsymbol{s}_{i\alpha}$ with

$$\boldsymbol{s}_{i\alpha} = \frac{\boldsymbol{m}_{i\alpha}}{m_{i\alpha}}, \tag{95}$$

from Eq. (5) the matrix elements of the spin density $\rho^{i\alpha}_{i\alpha\nu\mu}$ are diagonal such that

$$N_{i\alpha\uparrow} = \rho^{i\alpha}_{i\alpha\uparrow\uparrow}, \quad N_{i\alpha\downarrow} = \rho^{i\alpha}_{i\alpha\downarrow\downarrow}, \tag{96}$$

and

$$\rho^{i\alpha}_{i\alpha\uparrow\downarrow} = \rho^{i\alpha}_{i\alpha\downarrow\uparrow} = 0. \tag{97}$$

In this coordinate system the charge and magnetic moment may be obtained from the local density of states as

$$q_{i\alpha} = (N_{i\alpha\uparrow} + N_{i\alpha\downarrow}) - N^{(0)}_{i\alpha}, \tag{98}$$

$$\boldsymbol{m}_{i\alpha} = (N_{i\alpha\uparrow} - N_{i\alpha\downarrow})\boldsymbol{s}_{i\alpha} = m_{i\alpha}\boldsymbol{s}_{i\alpha}, \tag{99}$$

and the bond energy Eq. (70) may now be given in the *onsite* representation

$$U_{\text{bond}} = \sum_{i\alpha} \int^{E_F} (E - E_{i\alpha\uparrow}) n_{i\alpha\uparrow}(E)\, dE + \sum_{i\alpha} \int^{E_F} (E - E_{i\alpha\downarrow}) n_{i\alpha\downarrow}(E)\, dE, \tag{100}$$

with $E_{i\alpha\uparrow} = E_{i\alpha\uparrow\uparrow}$ and $E_{i\alpha\downarrow} = E_{i\alpha\downarrow\downarrow}$.

As the tight-binding bond model [Eq. (76)] is derived from the second-order expansion of the spin-density functional energy, the variational property in the form of Eq. (50) may be used for the optimization of the energy and for the evaluation of the binding energy. Because from Eq. (69) only the diagonal matrix elements of $H^{(\text{in})}$ vary, this means that Eq. (50) may be slightly modified and the binding energy $U_B$ for a set of given spin directions $\{\boldsymbol{s}_i\}$ may be obtained by minimizing Eq. (76) with respect to the onsite levels $E_{i\alpha\uparrow}$ and $E_{i\alpha\downarrow}$,

$$\frac{\partial U_B}{\partial E_{i\alpha\nu}} = 0. \tag{101}$$

Therefore, within the approximation of Eqs. (59) and (60), the onsite levels may be viewed as free parameters with respect to which the energy is minimized. We will use Eq. (101) for the optimization of the binding energy within the bond-order potential approximation in Sec. IV C. But, first, we will briefly review the analytic bond-order potentials and discuss their extension to include magnetism and charge transfer.

## IV. MAGNETIC BOND-ORDER POTENTIALS

### A. Summary of nonmagnetic bond-order potentials

In Ref. 20 we developed an expansion that allowed us to approximate the local density of states and to integrate the bond energy analytically. In this section we briefly summarize the theory developed in Ref. 20 before extending it to include magnetism. The moments of the local density of states

$$\mu^{(n)}_{i\alpha} = \int E^n n_{i\alpha}(E)\, dE, \tag{102}$$

may be evaluated without explicit knowledge of the density of states by relating the moment of order $n$ to the self-returning hopping paths of length $n$ that start and end on orbital $|i\alpha\rangle$,[49,50]

$$\mu^{(n)}_{i\alpha} = \sum_{i_1\alpha_1, i_2\alpha_2, \ldots, i_{n-1}\alpha_{n-1}} \langle i\alpha|\hat{H}|i_1\alpha_1\rangle\langle i_1\alpha_1|\hat{H}|i_2\alpha_2\rangle \times \cdots \langle i_{n-1}\alpha_{n-1}|\hat{H}|i\alpha\rangle, \tag{103}$$

where we assumed that the basis functions are orthonormal.

Closely related to the evaluation of the moments in terms of hopping paths is the representation of a Hamiltonian in the form of a semi-infinite one-dimensional chain with onsite matrix elements $a_n$ and nearest-neighbor hopping matrix elements $b_n$; see, for example, Eqs. (13) and (14) in Ref. 20. Any Hamiltonian may be mapped onto the form of a semi-infinite $1d$ chain by using the Lanczos recursion algorithm.[51] The Lanczos recursion algorithm also generates associated polynomials that form an orthogonal and complete set if the density of states is used as a weight function in the definition of the scalar product.[51] Hence, if the density of states of a reference Hamiltonian is known, the associated polynomials may be used for expanding the density of states of a different Hamiltonian.

A particular attractive reference Hamiltonian is provided by the semi-infinite chain with constant matrix elements $a_n = a^{(\infty)}_{i\alpha}$, $b_n = b^{(\infty)}_{i\alpha}$ (see section 12 of Ref. 51). The resulting semielliptic density of states,

$$n_{i\alpha 0}(\epsilon) = \frac{2}{\pi}\sqrt{1 - \epsilon^2}, \tag{104}$$

represents a single band of states between $\epsilon = \pm 1$, where $\epsilon = (E - a^{(\infty)}_{i\alpha})/(2b^{(\infty)}_{i\alpha})$. Correspondingly, $n_{i\alpha 0}(E) = n_{i\alpha 0}(\epsilon)/(2b^{(\infty)}_{i\alpha})$ between $E = a^{(\infty)}_{i\alpha} \pm 2b^{(\infty)}_{i\alpha}$. The Finnis-Sinclair second-moment interatomic potential[52] corresponds to taking $a^{(\infty)}_{i\alpha} = a_{i\alpha 0}$, $b^{(\infty)}_{i\alpha} = b_{i\alpha 1}$, so the resultant bond energy is proportional to $b_{i\alpha 1} = \sqrt{\mu^{(2)}_{i\alpha}}$, the square root of the second moment about site $i$.

We have generalized the second-moment approximation for a nonmagnetic system by writing the local density of states in the form[20,51,53]

$$n_{i\alpha}(\epsilon) = n_{i\alpha 0}(\epsilon) + \delta n_{i\alpha}(\epsilon). \tag{105}$$

The semielliptic form of $n_{i\alpha 0}(\epsilon)$ suggests expanding $\delta n_{i\alpha}(\epsilon)$ in terms of Chebyshev polynomials of the second kind,[54] $P_n(\epsilon)$, since they are the polynomial eigenstates of the semi-infinite constant chain and are, thus, orthonormal with respect to the weight function $\frac{2}{\pi}\sqrt{1 - \epsilon^2}$,

$$\frac{2}{\pi}\int_{-1}^{1} P_n(\epsilon) P_m(\epsilon)\sqrt{1 - \epsilon^2} d\epsilon = \delta_{nm}, \tag{106}$$

and, therefore,

$$n_{i\alpha}(\epsilon) = \frac{2}{\pi}\sqrt{1 - \epsilon^2}\left[\sum_{m=0} \sigma^{(m)}_{i\alpha} P_m(\epsilon)\right]. \tag{107}$$

Approximate representations of the density of states may be obtained by terminating the expansion at a maximum $n_{\max}$,

$$n^{(n_{\max})}_{i\alpha}(\epsilon) = \frac{2}{\pi}\sqrt{1 - \epsilon^2}\left[\sum_{m=0}^{n_{\max}} \sigma^{(m)}_{i\alpha} P_m(\epsilon)\right]. \tag{108}$$

The expansion coefficients $\sigma_{i\alpha}^{(m)}$ may be evaluated from[20]

$$\sigma_{i\alpha}^{(m)} = \sum_{n=0}^{m} p_{mn} \hat{\mu}_{i\alpha}^{(n)} \tag{109}$$

which follows from expanding the Chebyshev polynomials of the second kind explicitly as

$$P_m(\epsilon) = \sum_{n=0}^{m} p_{mn} \epsilon^n. \tag{110}$$

The dimensionless moments $\hat{\mu}_{i\alpha}^{(n)}$ may be obtained directly from the moments $\mu_{i\alpha}^{(n)}$ of the local density of states $n_{i\alpha}(\epsilon)$. Substituting $\epsilon = (E - a_{i\alpha}^{(\infty)})/(2b_{i\alpha}^{(\infty)})$ into Eq. (102) and performing the binomial expansion, one arrives at

$$\hat{\mu}_{i\alpha}^{(n)} = \frac{1}{\left(2b_{i\alpha}^{(\infty)}\right)^n} \sum_{l=0}^{n} \binom{n}{l} (-1)^l \left(a_{i\alpha}^{(\infty)}\right)^l \mu_{i\alpha}^{(n-l)}. \tag{111}$$

The expansion of the density of states Eq. (108) may be integrated analytically. In particular, one finds for the number of electrons in orbital $|i\alpha\rangle$ in a nonmagnetic material

$$N_{i\alpha}^{(n_{\max})} = 2\int^{E_F} n_{i\alpha}^{(n_{\max})} dE = 2\sum_{m=0}^{n_{\max}} \sigma_{i\alpha}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha}), \tag{112}$$

where the Fermi phase is given by $\phi_{F,i\alpha} = \cos^{-1}[(E_F - a_{i\alpha}^{(\infty)})/(2b_{i\alpha}^{(\infty)})]$ and

$$\hat{\chi}_1 = 1 - \frac{\phi_F}{\pi} + \frac{1}{2\pi}\sin(2\phi_F), \tag{113}$$

and for $n \geqslant 2$ the dimensionless response functions take the canonical form

$$\hat{\chi}_n(\phi_F) = \frac{1}{\pi}\left[\frac{\sin(n+1)\phi_F}{n+1} - \frac{\sin(n-1)\phi_F}{n-1}\right]. \tag{114}$$

Similarly, the nonmagnetic bond energy may expanded as

$$U_{i\alpha,\mathrm{bond}}^{(n_{\max})} = 2b_{i\alpha}^{(\infty)} \sum_{m=0}^{n_{\max}} \sigma_{i\alpha}^{(m)} [\hat{\chi}_{m+2}(\phi_{F,i\alpha}) - \gamma_{0i\alpha}\hat{\chi}_{m+1}(\phi_{F,i\alpha}) + \hat{\chi}_m(\phi_{F,i\alpha})], \tag{115}$$

with $\gamma_{0i\alpha} = (E_{i\alpha} - a_{i\alpha}^{(\infty)})/b_{i\alpha}^{(\infty)}$ and $\hat{\chi}_0 = 0$.

### B. Magnetic bond-order potentials with charge transfer

Charge transfer and magnetism modifies the local moments of the density of states. As in Eq. (100), we assume that the local coordinate system on atom $i$ and orbital $\alpha$ has been rotated so the $z$ axis is parallel to the local moment. Therefore, we need to characterize the up- and down-spin density of states only, for which the evaluation of the $\uparrow\uparrow$ and $\downarrow\downarrow$ matrix elements of the moments of the total Hamiltonian is sufficient, namely

$$\mu_{i\alpha\nu}^{(n)} = \int E^n n(E)_{i\alpha\nu} dE = \langle i\alpha\nu|\hat{H}^n|i\alpha\nu\rangle. \tag{116}$$

By adapting Eq. (108) to up- and down-spin channels, the bond energy [Eq. (115)] for a magnetic system may be calculated from

$$U_{\mathrm{bond}} = \sum_{i\alpha}\sum_{\nu=\uparrow,\downarrow} U_{\mathrm{bond},i\alpha\nu}, \tag{117}$$

where

$$\begin{aligned} U_{\mathrm{bond},i\alpha\nu} &= \int^{E_F} (E - E_{i\alpha\nu}) n_{i\alpha\nu}(E)\, dE \\ &= b_{i\alpha\nu}^{(\infty)} \sum_{m=0}^{n_{\max}} \sigma_{i\alpha\nu}^{(m)} [\hat{\chi}_{m+2}(\phi_{F,i\alpha\nu}) - \gamma_{0i\alpha\nu}\hat{\chi}_{m+1}(\phi_{F,i\alpha\nu}) \\ &\quad + \hat{\chi}_m(\phi_{F,i\alpha\nu})] \end{aligned} \tag{118}$$

with

$$\gamma_{0i\alpha\nu} = \left(E_{i\alpha\nu} - a_{i\alpha\nu}^{(\infty)}\right)/b_{i\alpha\nu}^{(\infty)}. \tag{119}$$

The local magnetic Fermi phase is given by

$$\phi_{F,i\alpha\nu} = \cos^{-1}\left[\left(E_F - a_{i\alpha\nu}^{(\infty)}\right)/\left(2b_{i\alpha\nu}^{(\infty)}\right)\right], \tag{120}$$

and the magnetic expansion coefficients by

$$\sigma_{i\alpha\nu}^{(m)} = \sum_{n=0}^{m} p_{mn} \hat{\mu}_{i\alpha\nu}^{(n)}. \tag{121}$$

The reduced moments take the form,

$$\hat{\mu}_{i\alpha\nu}^{(n)} = \frac{1}{\left(2b_{i\alpha\nu}^{(\infty)}\right)^n} \sum_{l=0}^{n} \binom{n}{l} (-1)^l \left(a_{i\alpha\nu}^{(\infty)}\right)^l \mu_{i\alpha\nu}^{(n-l)}, \tag{122}$$

where, in general, $a_{i\alpha\nu}^{(\infty)}$ and $b_{i\alpha\nu}^{(\infty)}$ depend on the spin state and the environment of atom $i$. Expressions for the magnetic moment and charge on atom $i$ are obtained by integrating the up- and down-spin density of states,

$$N_{i\alpha\nu} = \int^{E_F} n_{i\alpha\nu}(E)\, dE = \sum_{m=0}^{n_{\max}} \sigma_{i\alpha\nu}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha\nu}). \tag{123}$$

### C. Binding energy, forces, and torques

The binding energy, equilibrium charges, and magnetic moments are obtained by minimizing the energy with respect to the onsite levels according to Eq. (101). In the following, we derive the expressions for the gradient of the energy with respect to the onsite levels that are required for the optimization of the total energy. As these expressions are similar to the expressions for the evaluation of the forces and torques, we first discuss the derivative of the energy with respect to an abstract parameter. In the following, we assume that the energy depends on the parameter $\Lambda$ and develop the expressions for the derivative of the binding energy with respect to $\Lambda$. Later, we will then replace $\frac{d}{d\Lambda}$ with the derivative with respect to an onsite level $\frac{d}{dE_{j\beta\mu}}$ or the gradient $\nabla_j$ with respect to the displacement of atom $j$ or the derivative with respect to spin rotation $\frac{d}{d\boldsymbol{s}_{j\alpha}}$.

In the following, we will obtain the derivative $\frac{dU_B}{d\Lambda}$ of the binding energy [Eq. (76)] by discussing the derivatives of the individual contributions to $U_B$. The derivative of the *bond* energy in the onsite representation [Eq. (100)] with respect to $\Lambda$ may be written as

$$\frac{dU_{\mathrm{bond},i\alpha\nu}}{d\Lambda} = (E_F - E_{i\alpha\nu})n_{i\alpha\nu}(E_F)\frac{dE_F}{d\Lambda} + \int^{E_F}(E-E_{i\alpha\nu})\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE - N_{i\alpha\nu}\frac{dE_{i\alpha\nu}}{d\Lambda}. \tag{124}$$

Similarly, the derivative of the number of electrons associated with orbital $|i\alpha\nu\rangle$ may be written from Eq. (94) as

$$\frac{dN_{i\alpha\nu}}{d\Lambda} = n_{i\alpha\nu}(E_F)\frac{dE_F}{d\Lambda} + \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE. \tag{125}$$

The derivative of the Fermi energy that is required in the two previous equations may be worked out by using charge conservation,

$$0 = \frac{dN}{d\Lambda} = \sum_{i\alpha\nu}\frac{dN_{i\alpha\nu}}{d\Lambda}, \tag{126}$$

once we have an expression for $\int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE$, which will be obtained in the next section from the analytic bond-order potentials. It thus follows from Eqs. (125) and (126) that the derivative of the *band* energy $U_{\mathrm{band}} = \sum_{i\alpha\nu}\int^{E_F}En_{i\alpha\nu}(E)dE$ may be written as

$$\frac{dU_{\mathrm{band}}}{d\Lambda} = \sum_{i\alpha\nu}\int^{E_F}(E - E_F)\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE. \tag{127}$$

The gradient of the *binding* energy requires the derivative of functions of the type $\sum_{i\alpha\nu} f_{i\alpha\nu}N_{i\alpha\nu}$ with constant factors $f_{i\alpha\nu}$. Using charge conservation leads to the following identity:

$$\sum_{i\alpha\nu} f_{i\alpha\nu}\frac{dN_{i\alpha\nu}}{d\Lambda} = \sum_{i\alpha\nu}\left[f_{i\alpha\nu} - \frac{\sum_{j\beta\mu} f_{j\beta\mu}n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)}\right] \times \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE. \tag{128}$$

The gradient of the bond energy Eq. (124) may now be written as

$$\frac{dU_{\mathrm{bond}}}{d\Lambda} = \sum_{i\alpha\nu}\int^{E_F}(E - E_F)\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE - \sum_{i\alpha\nu}\left[E_{i\alpha\nu} - \frac{\sum_{j\beta\mu} E_{j\beta\mu}n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)}\right] \times \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda} - \sum_{i\alpha\nu} N_{i\alpha\nu}\frac{dE_{i\alpha\nu}}{d\Lambda}. \tag{129}$$

The derivative of the electron transfer energy Eq. (72) is obtained as

$$\frac{dU_{\mathrm{trans}}}{d\Lambda} = \sum_{i\alpha\nu}\left[E^{(0)}_{i\alpha} - \frac{\sum_{j\beta\mu} E^{(0)}_{j\beta}n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)}\right] \times \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE, \tag{130}$$

the derivative of the Coulomb energy Eq. (59) is obtained as

$$\frac{dU_C}{d\Lambda} = \sum_{i\alpha\nu}\left[\sum_{k\gamma} J_{k\gamma i\alpha}q_{k\gamma} - \frac{\sum_{j\beta k\gamma} J_{k\gamma j\beta}q_{k\gamma}\sum_{\mu} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)}\right] \times \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE + \frac{1}{2}\sum_{i\alpha j\beta}\frac{dJ_{i\alpha j\beta}}{d\Lambda}q_{j\beta}q_{i\alpha}, \tag{131}$$

and the derivative of the exchange energy Eq. (60) is written as

$$\frac{dU_X}{d\Lambda} = -\frac{1}{2}\sum_{i\alpha\nu}\left[(-1)^{\nu}\sum_{k\gamma} I_{k\gamma i\alpha}\boldsymbol{m}_{k\gamma}\boldsymbol{s}_{i\alpha} - \frac{\sum_{j\beta\mu}(-1)^{\mu}\sum_{k\gamma} I_{k\gamma j\beta}\boldsymbol{m}_{k\gamma}\boldsymbol{s}_{j\beta}n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)}\right] \times \int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE - \frac{1}{2}\sum_{i\alpha j\beta} I_{i\alpha j\beta}\boldsymbol{m}_{j\beta}m_{i\alpha}\frac{d\boldsymbol{s}_{i\alpha}}{d\Lambda} - \frac{1}{4}\sum_{i\alpha j\beta}\frac{dI_{i\alpha j\beta}}{d\Lambda}\boldsymbol{m}_{j\beta}\boldsymbol{m}_{i\alpha}, \tag{132}$$

where, in the evaluation for the derivative of $U_X$, we took $\nu = 0$ for the up-spin ↑ component and $\nu = 1$ for the down-spin ↓ component. The derivatives of the external energy $U_{\mathrm{ext}}$ follow along the same lines.

We see above that the evaluation of the gradient of the binding energy [Eq. (76)] requires expressions of the type $\int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE$ to be evaluated. By using the analytic BOP expansion [Eq. (123)], the gradients may be written as

$$\sum_{i\alpha\nu} g_{i\alpha\nu}\int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE = \sum_{i\alpha\nu} g_{i\alpha\nu}\frac{d}{d\Lambda}\sum_{m=0}^{n_{\max}}\sigma^{(m)}_{i\alpha\nu}\hat{\chi}_{m+1}(\phi_{F,i\alpha\nu}) = \sum_{i\alpha\nu} g_{i\alpha\nu}\sum_{m=0}^{n_{\max}}\sum_{n=0}^{n_{\max}}\left(\frac{\partial\sigma^{(m)}_{i\alpha\nu}}{\partial\mu^{(n)}_{i\alpha\nu}}\hat{\chi}_{m+1} + \sigma^{(m)}_{i\alpha\nu}\frac{\partial\hat{\chi}_{m+1}}{\partial\mu^{(n)}_{i\alpha\nu}}\right)\frac{d\mu^{(n)}_{i\alpha\nu}}{d\Lambda}, \tag{133}$$

where $g_{i\alpha\nu}$ are the prefactors of $\int^{E_F}\frac{dn_{i\alpha\nu}(E)}{d\Lambda}dE$ in Eqs. (129)–(132). Note that the response functions $\hat{\chi}_{m+1}$ depend on the local moments $\mu^{(n)}_{i\alpha\nu}$ through the dependence of the Fermi phase Eq. (120) on $a^{(\infty)}_{i\alpha\nu}$ and $b^{(\infty)}_{i\alpha\nu}$. Therefore, by using the analytic BOP expansion explicit analytic expressions for the gradients $\frac{\partial\sigma^{(m)}_{i\alpha\nu}}{\partial\mu^{(n)}_{i\alpha\nu}}$ and $\frac{\partial\hat{\chi}_{m+1}}{\partial\mu^{(n)}_{i\alpha\nu}}$ may be obtained. The total gradient of the binding energy, thus, may be calculated analytically.

The first line of Eq. (129) may be written in a similar way as a gradient with respect to the local moments $\mu^{(n)}_{i\alpha\nu}$, such that the total gradient of the binding energy may be written in the form

$$\frac{dU_B}{d\Lambda} = \sum_{i\alpha\nu}\sum_{n=0}^{n_{\max}} w^{(n)}_{i\alpha\nu}\frac{d\mu^{(n)}_{i\alpha\nu}}{d\Lambda} - \sum_{i\alpha\nu} N_{i\alpha\nu}\frac{dE_{i\alpha\nu}}{d\Lambda} + \frac{1}{2}\sum_{i\alpha j\beta}\frac{dJ_{i\alpha j\beta}}{d\Lambda}q_{j\beta}q_{i\alpha}$$

$$-\frac{1}{2}\sum_{i\alpha j\beta} I_{i\alpha j\beta}\boldsymbol{m}_{j\beta}m_{i\alpha}\frac{d\boldsymbol{s}_{i\alpha}}{d\Lambda}-\frac{1}{4}\sum_{i\alpha j\beta}\frac{dI_{i\alpha j\beta}}{d\Lambda}\boldsymbol{m}_{j\beta}\boldsymbol{m}_{i\alpha}+\frac{dU_{\text{rep}}}{d\Lambda}, \tag{134}$$

and where the prefactors $w_{i\alpha\nu}^{(n)}$ are obtained from the analytic BOP expansion. They are given explicitly in the accompanying paper where it will be shown that the analytic forces are identical to the numerical forces obtained from small displacements of the atoms and the numerical efficiency of the analytical forces compared to the numerical forces will be demonstrated.[55]

In essence the gradient of the binding energy Eq. (76) therefore has been reduced to finding the gradients of the local moments $\frac{d\mu_{i\alpha\nu}^{(n)}}{d\Lambda}$ weighted by the factors $w_{i\alpha\nu}^{(n)}$. Before Eq. (134) may be applied to the calculation of the equilibrium binding energy, charges, and magnetic moments, as well as the forces and torques, an efficient evaluation of the gradient of the local moments of the density of states is still required. This will be addressed in the next section, where also explicit expressions for the calculation of forces and torques will be given.

### D. Hellmann-Feynman-type forces

For the evaluation of forces and torques the derivatives $\frac{d\mu_{i\alpha\nu}^{(n)}}{d\Lambda}$ need to be evaluated in a numerically efficient way. This is achieved by writing the moments explicitly in terms of self-returning products of the Hamiltonian matrix elements, so the first contribution on the right-hand side of Eq. (134) becomes

$$\begin{aligned}\frac{dU_b}{d\Lambda} &= \sum_{n=0}^{n_{\max}}\sum_{i_1\alpha_1\nu_1} w_{i_1\alpha_1\nu_1}^{(n)}\frac{d\mu_{i_1\alpha_1\nu_1}^{(n)}}{d\Lambda} = \sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} w_{i_1\alpha_1\nu_1}^{(n)}\frac{dH_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}}{d\Lambda}H_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots H_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}\\ &\quad+\sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} w_{i_1\alpha_1\nu_1}^{(n)}H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}\frac{dH_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}}{d\Lambda}\ldots H_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}\\ &\quad+\cdots+\sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} w_{i_1\alpha_1\nu_1}^{(n)}H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}H_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots\frac{dH_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}}{d\Lambda},\end{aligned} \tag{135}$$

using the product rule for evaluating the derivatives with respect to $\Lambda$. As each of the sums is taken over all orbitals $|i\alpha\nu\rangle$ in the system, we may rearrange the summations in a more suitable way

$$\begin{aligned}\frac{dU_b}{d\Lambda} &= \sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}H_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots w_{i_n\alpha_n\nu_n}^{(n)}\frac{dH_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}}{d\Lambda}\\ &\quad+\cdots+\sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}w_{i_2\alpha_2\nu_2}^{(n)}H_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots\frac{dH_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}}{d\Lambda}\\ &\quad+\sum_{n=0}^{n_{\max}}\sum_{i_1i_2\ldots i_n}\sum_{\alpha_1\alpha_2\ldots\alpha_n}\sum_{\nu_1\nu_2\ldots\nu_n} w_{i_1\alpha_1\nu_1}^{(n)}H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}H_{i_2\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots\frac{dH_{i_n\alpha_n\nu_ni_1\alpha_1\nu_1}}{d\Lambda}.\end{aligned} \tag{136}$$

Therefore, instead of taking the gradient of the Hamiltonian matrix elements from left to right as in Eq. (135), we shift the weights $w_{i\alpha\nu}^{(n)}$ from right to left. This may be written in a more compact form by introducing

$$\Xi_{i_1\alpha_1\nu_1i_n\alpha_n\nu_n}^{(n-1,m)} = \sum_{i_2i_3\ldots i_{n-1}}\sum_{\alpha_2\alpha_3\ldots\alpha_{n-1}}\sum_{\nu_2\nu_3\ldots\nu_{n-1}}\left(\sum_{l=1}^{n} w_{i_l\alpha_l\nu_l}^{(m)}\right)H_{i_1\alpha_1\nu_1i_2\alpha_2\nu_2}H_{i_3\alpha_2\nu_2i_3\alpha_3\nu_3}\ldots H_{i_{n-1}\alpha_{n-1}\nu_{n-1}i_n\alpha_n\nu_n}. \tag{137}$$

The gradients may be written in the form of Hellmann-Feynman-type forces

$$\frac{dU_b}{d\Lambda} = \sum_{i\alpha\nu j\beta\mu}\tilde{\Theta}_{i\alpha\nu j\beta\mu}\frac{dH_{j\beta\mu i\alpha\nu}}{d\Lambda}, \tag{138}$$

where we defined a bond-order type term

$$\tilde{\Theta}_{i\alpha\nu j\beta\mu} = \sum_{n=1}^{n_{\max}}\Xi_{i\alpha\nu j\beta\mu}^{(n-1,n)}. \tag{139}$$

If $n_{\max}\to\infty$ and the bond-order expansion of $U_B$ approaches the TB energy, $\tilde{\Theta}_{i\alpha j\beta}$ becomes the usual bond order and Eq. (138) corresponds to the normal expression for the Hellman-Feynman gradients.[56,57]

By making use of Eq. (138) the expressions for the forces and torques now may be further simplified. From Eq. (134) the gradient of the energy with respect to the onsite levels is obtained by replacing $\Lambda$ with $E_{j\beta\mu}$ and by dropping all contributions that do not depend on the onsite levels. This leads to a more intuitive formula for the gradients

$$\frac{\partial U_B}{\partial E_{j\beta\mu}} = \tilde{\Theta}_{j\beta\mu j\beta\mu} - N_{j\beta\mu}, \tag{140}$$

such that in equilibrium from Eq. (101) $N_{j\beta\mu} = \tilde{\Theta}_{j\beta\mu j\beta\mu}$. In a similar way, the expression for the forces is obtained by replacing $\frac{d}{d\Lambda}$ with $\nabla_k$ in Eq. (134), which in equilibrium [Eq. (101)] leads to

$$\nabla_k U_B = \sum_{i\alpha\nu j\beta\mu}^{i\alpha\neq j\beta} \tilde{\Theta}_{i\alpha\nu j\beta\mu} \nabla_k H_{j\beta\mu i\alpha\nu} + \frac{1}{2} \sum_{i\alpha j\beta} (\nabla_k J_{i\alpha j\beta}) q_{j\beta} q_{i\alpha} - \frac{1}{4} \sum_{i\alpha j\beta} (\nabla_k I_{i\alpha j\beta}) \boldsymbol{m}_{j\beta} \boldsymbol{m}_{i\alpha} + \nabla_k U_{\text{rep}}. \tag{141}$$

The torques are obtained along the same lines and are given by

$$\frac{dU_B}{d\boldsymbol{s}_{k\gamma}} = \frac{1}{2} \left( \sum_{\nu\mu} \tilde{\Theta}_{k\gamma\nu k\gamma\mu} \boldsymbol{\sigma}_{\mu\nu} \Delta_{k\gamma} - \sum_{i\alpha} I_{i\alpha k\gamma} \boldsymbol{m}_{i\alpha} m_{k\gamma} \right), \tag{142}$$

with $\Delta_{k\gamma} = E_{k\gamma\uparrow} - E_{k\gamma\downarrow}$ and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$.

The bond-order $\tilde{\Theta}_{i\alpha\nu j\beta\mu}$ may be evaluated recursively in a similar way to the calculation of interference paths[20]

$$\xi^{(n)}_{i\alpha\nu j\beta\mu} = \langle i\alpha\nu | \hat{H}^{(n)} | j\beta\mu \rangle = \sum_{k\gamma\tau} H_{i\alpha\nu k\gamma\tau} \xi^{(n-1)}_{k\gamma\tau j\beta\mu}. \tag{143}$$

This is trivially rearranged to

$$\xi^{(n)}_{i\alpha\nu j\beta\mu} = \sum_{k\gamma\tau} \xi^{(l)}_{i\alpha\nu k\gamma\tau} \xi^{(n-l)}_{k\gamma\tau j\beta\mu}, \tag{144}$$

with $n \geqslant l \geqslant 0$. To illustrate the recursive evaluation of the forces, we introduce the transfer matrices

$$T^{(n-1,m)}_{i\alpha\nu j\beta\mu} = \Xi^{(n-1,m)}_{i\alpha\nu j\beta\mu} - w^{(m)}_{i\alpha\nu} \xi^{(n-1)}_{i\alpha\nu j\beta\mu}. \tag{145}$$

Similarly to the interference paths [Eq. (143)], the transfer matrices may be calculated iteratively,

$$T^{(n,m)}_{i\alpha\nu j\beta\mu} = \sum_{k\gamma\tau} H_{i\alpha\nu k\gamma\tau} T^{(n-1,m)}_{k\gamma\tau j\beta\mu} + w^{(m)}_{i\alpha\nu} \xi^{(n)}_{i\alpha\nu j\beta\mu}, \tag{146}$$

and a product rule similar to that of Eq. (144) also holds,

$$T^{(n-1,m)}_{i\alpha\nu j\beta\mu} = \sum_{k\gamma\tau} T^{(l-1,m)}_{i\alpha\nu k\gamma\tau} \xi^{(n-l)}_{k\gamma\tau j\beta\mu} + \sum_{k\gamma\tau} \xi^{(l-1)}_{i\alpha\nu k\gamma\tau} T^{(n-l,m)}_{k\gamma\tau j\beta\mu}. \tag{147}$$

With the help of Eqs. (146) and (147), a numerically efficient implementation of the gradients of Eq. (138) becomes possible, as will be demonstrated in Ref. 55 for the gradients and forces.

## V. BEYOND THE HEISENBERG INTERACTION

In this section we will establish a hierarchy of multispin interactions beyond the classical Heisenberg model through the BOP expansion of the binding energy [Eq. (76)]. In order to separate geometrical interactions of the atomic magnetic moments from the contributions due to changes in the magnitude of the moments during spin rotation, we initially discuss a material where we may assume that the magnetic moments maintain constant values while the spins are rotated (and that the number of electrons in each orbital $N_{i\alpha\nu}$ remains constant). The change of the bond energy [Eq. (100)] on spin rotation then is given by the change of the band energy alone as, through Eq. (69), the onsite levels also remain unchanged, so

$$\Delta U_{\text{bond}} = \Delta U_{\text{band}}\,. \tag{148}$$

Because the band energy may be written as a function of the average local density of states, $n_{i\alpha}(E) = n_{i\alpha\uparrow}(E) + n_{i\alpha\downarrow}(E)$, Eq. (92),

$$U_{\text{band},i\alpha} = \int^{E_F} E[n_{i\alpha\uparrow}(E) + n_{i\alpha\downarrow}(E)]\, dE,$$

the band energy may be obtained from the moments of the average local density of states,

$$\mu^{(n)}_{i\alpha} = \mu^{(n)}_{i\alpha\uparrow} + \mu^{(n)}_{i\alpha\downarrow} = \int E^n [n_{i\alpha\uparrow}(E) + n_{i\alpha\downarrow}(E)]\, dE, \tag{149}$$

using the relation between the band energy and the bond energy in Eq. (70) and the BOP expansion for the bond energy in Eq. (115) from Sec. IV. Furthermore, as the BOP expansion [Eq. (115)] is a linear function of the local moments of the density of states for constant values of $a^{(\infty)}_{i\alpha\nu}$ and $b^{(\infty)}_{i\alpha\nu}$, the modification of the average local moments on spin rotation contributes directly to the energy change when the spins are rotated. Therefore, an analysis of the local moments of the density of states that enter the analytic BOP expansion allows us to extract the nature of the multispin interactions in the tight-binding bond model.

The analysis of the local moments of the density of states is simplified by noting that, from Eq. (69), only the onsite elements of the Hamiltonian are modified by electron transfer and magnetism. We next separate the magnetic from the nonmagnetic contributions in the onsite levels by rewriting Eq. (69) in the form of a 2×2 matrix in spin space

$$\boldsymbol{E}_{i\alpha} = \Lambda^{(\text{nm})}_{i\alpha} \mathbf{1} + \Lambda^{(m)}_{i\alpha} (\boldsymbol{s}_{i\alpha} \boldsymbol{\sigma}). \tag{150}$$

The coefficient $\Lambda^{(\text{nm})}_{i\alpha}$ comprises all contributions to the onsite levels that are independent of magnetism, while $\Lambda^{(m)}_{i\alpha}$ summarizes the contributions that depend on magnetism. As the Hamiltonian matrix elements between different atoms are diagonal in spin space, $\boldsymbol{H}_{i\alpha j\beta} = H_{i\alpha j\beta} \mathbf{1}$, the spin-space products of $\boldsymbol{H}_{i\alpha j\beta}$ and $\boldsymbol{E}_{i\alpha}$ commute and the products of the type $\boldsymbol{E}_{i\alpha} \boldsymbol{E}_{j\beta}$ may be analyzed separately.

Because for the evaluation of the band energy only the average moments of the spin-up and -down densities of states is required, it is sufficient to characterize the sum of the up- and down-spin contributions together. The trace of the 2×2 spin-space matrices for the first four products is given by

$$\mathrm{Tr}[\boldsymbol{E}_{i\alpha}]/2 = \Lambda^{(\mathrm{nm})}_{i\alpha}, \tag{151}$$

$$\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}]/2 = \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{j\beta} + \Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{j\beta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}), \tag{152}$$

$$\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}]/2 = \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(\mathrm{nm})}_{k\gamma} + \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(m)}_{j\beta}\Lambda^{(m)}_{k\gamma}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) + \Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(m)}_{k\gamma}\Lambda^{(m)}_{i\alpha}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{i\alpha}) + \Lambda^{(\mathrm{nm})}_{k\gamma}\Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{j\beta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}), \tag{153}$$

$$\begin{aligned}\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}\boldsymbol{E}_{l\delta}]/2 = {} & \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(\mathrm{nm})}_{k\gamma}\Lambda^{(\mathrm{nm})}_{l\delta} + \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(m)}_{k\gamma}\Lambda^{(m)}_{l\delta}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) + \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{k\gamma}\Lambda^{(m)}_{j\beta}\Lambda^{(m)}_{l\delta}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta}) \\ & + \Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(\mathrm{nm})}_{k\gamma}\Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{l\delta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta}) + \Lambda^{(\mathrm{nm})}_{i\alpha}\Lambda^{(\mathrm{nm})}_{l\delta}\Lambda^{(m)}_{j\beta}\Lambda^{(m)}_{k\gamma}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) + \Lambda^{(\mathrm{nm})}_{j\beta}\Lambda^{(\mathrm{nm})}_{l\delta}\Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{k\gamma}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma}) \\ & + \Lambda^{(\mathrm{nm})}_{k\gamma}\Lambda^{(\mathrm{nm})}_{l\delta}\Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{j\beta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}) + \Lambda^{(m)}_{i\alpha}\Lambda^{(m)}_{j\beta}\Lambda^{(m)}_{k\gamma}\Lambda^{(m)}_{l\delta}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) \\ & + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) - (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})].\end{aligned} \tag{154}$$

For the particular case that $\Lambda^{(\mathrm{nm})}$ and $\Lambda^{(m)}$ are identical for all atoms and orbitals, the expressions for the three and four-spin products are simplified considerably. We give these expressions explicitly as the structure of the products becomes clearer in this simplified case,

$$\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}]/2 = \Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})} + \Lambda^{(\mathrm{nm})}\Lambda^{(m)}\Lambda^{(m)}[(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) + (\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{i\alpha}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})], \tag{155}$$

$$\begin{aligned}\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}\boldsymbol{E}_{l\delta}]/2 = {} & \Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})} \\ & + \Lambda^{(\mathrm{nm})}\Lambda^{(\mathrm{nm})}\Lambda^{(m)}\Lambda^{(m)}[(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) + (\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta}) + (\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})] \\ & + \Lambda^{(m)}\Lambda^{(m)}\Lambda^{(m)}\Lambda^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) - (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})].\end{aligned} \tag{156}$$

The products [Eqs. (152)–(154)] are obtained by making use of the following properties of the Pauli matrices:

$$\mathrm{Tr}[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})]/2 = (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}), \tag{157}$$

$$\mathrm{Tr}[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})]/2 = 0, \tag{158}$$

$$\begin{aligned}&\mathrm{Tr}[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})]/2 \\ &\quad = (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma}) \\ &\qquad - (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta}),\end{aligned} \tag{159}$$

where, on the right-hand side, we left out the contributions that are canceled if the products are carried out in reverse order. A detailed derivation of the expressions for the products of the Pauli matrices and the onsite matrix elements is given in Appendix C.

It is obvious from Eq. (152) that only moments that involve a minimum of two onsite hops may contribute to a direct geometrical interaction between the spins. The shortest possible self-returning paths that fulfill this condition are part of the fourth moment

$$\begin{aligned}\mu^{(4)}_{i\alpha} = \mu^{(4)}_{i\alpha\uparrow} + \mu^{(4)}_{i\alpha\downarrow} = {} & \sum_{j\beta}\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{H}_{i\alpha j\beta}\boldsymbol{E}_{j\beta}\boldsymbol{H}_{j\beta i\alpha}] \\ & + \sum_{j\beta}\mathrm{Tr}[\boldsymbol{H}_{i\alpha j\beta}\boldsymbol{E}_{j\beta}\boldsymbol{H}_{j\beta i\alpha}\boldsymbol{E}_{i\alpha}] + \mu^{(4,nm)}_{i\alpha},\end{aligned} \tag{160}$$

where the contributions to the fourth moment that are independent of magnetism $\mu^{(4,nm)}_{i\alpha}$ have not been given explicitly here. Therefore, from Eq. (152), the change of the fourth moment as a function of spin direction is given by a Heisenberg-type $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}) \propto \cos\theta$ dependence. If the magnitude of the local magnetic moments remains unchanged when the spins are rotated, then from the BOP expansion we know that the dependence of the moment on the spin directions translates directly into the dependence of the energy on the spin directions. Thus, to lowest order, the interaction induced through the Stoner term leads to a Heisenberg interaction between the spins. This is graphically illustrated in Fig. 1.

The lowest moment that potentially could contribute to three-spin interactions is the sixth moment, with terms of the type $\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{H}_{i\alpha j\beta}\boldsymbol{E}_{j\beta}\boldsymbol{H}_{j\beta k\gamma}\boldsymbol{E}_{k\gamma}\boldsymbol{H}_{k\gamma i\alpha}]$. From Eq. (153), however, it is clear that there are no direct three-spin interactions from the product of three onsite levels as the product of three onsite levels may be represented as the sum of pairwise Heisenberg-like $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})$ terms. If $\Lambda^{(\mathrm{nm})} = 0$ in a system where all atoms are equivalent, then, according to Eq. (155), the product of three spins vanishes and cannot contribute anything to the interaction of the spins.

In fact, from Eq. (154), the lowest moment that may contribute to a direct geometrical interaction of more than two spins, namely four spins, must contain four onsite hops. In addition to the four onsite hops, a minimum of four intersite hops are required to reach four different atoms. Therefore, the lowest moment that contributes to a direct four-spin

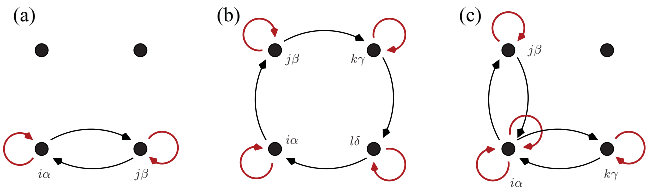

FIG. 1. (Color online) Illustration of spin interactions: (a) the fourth-moment contribution leads to Heisenberg $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})$ interactions between spins. (b) The eighth-moment interaction is the lowest moment to contribute to four-spin interactions of type $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})$. (c) Eighth-moment contributions that hop through the same atom twice contribute to three-spin interactions of type $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})$. These diagrams are the analogous spin interactions to cluster interactions in nonmagnetic binary alloys.[58–60]

interaction is given by the eighth moment with terms of the form $\mathrm{Tr}[\boldsymbol{E}_{i\alpha}\boldsymbol{H}_{i\alpha j\beta}\boldsymbol{E}_{j\beta}\boldsymbol{H}_{j\beta k\gamma}\boldsymbol{E}_{k\gamma}\boldsymbol{H}_{k\gamma l\delta}\boldsymbol{E}_{l\delta}\boldsymbol{H}_{l\delta i\alpha}]$. As can be seen from Eq. (154), the four-spin interaction is of the form $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})$.

The four-spin interaction also includes direct three-spin interactions that are generated by visiting one atom twice and that are part of the eighth moment. From Eq. (154) if an orbital is visited twice, the contribution to the energy is of the form $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})$. The three-spin interactions are schematically illustrated in Fig. 1(c).

Thus, our analysis of the magnetic interaction results in a magnetic extension of the cluster expansion for nonmagnetic alloys[58,61,62] with spin interactions of the form[63]

$$\Delta U = \sum_{i\alpha j\beta} K_{i\alpha j\beta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}) + \sum_{i\alpha j\beta k\gamma} K_{i\alpha j\beta k\gamma}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma}) + \sum_{i\alpha j\beta k\gamma l\delta} K_{i\alpha j\beta k\gamma l\delta}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta}) + \cdots, \tag{161}$$

where we have shown that the expansion coefficients $K$ are given by the BOP expansion. Because the expansion coefficients depend on the Fermi level and bandfilling through the oscillatory response functions $\hat{\chi}_n$, Eq. (114), it is, however, difficult to make general statements about the relative strength of the two-, three-, and four-spin expansion coefficients. As, however, the lowest moment that contributes to the four-spin interactions is the eighth moment, and as the energy that is typically associated with the eighth moment is much smaller than the energy associated with the fourth moment, one could expect that for systems where the magnitude of the moments remains constant on rotation of the spins, the interaction between the spins is dominated by the Heisenberg interaction and that the magnitude of the four-spin interactions is significantly smaller. As the three-spin interaction coefficients are obtained from subsets of hopping paths that contribute to the four-spin interactions, one could further assume that the three-spin interactions are smaller than the four-spin interactions, although one has to be careful with such simplified arguments as the angular dependence of the hopping paths may change the sign of the individual contributions to the moments. The hierarchy of the multispin interactions expected from these simplified considerations has recently been found by a spin-cluster expansion of *ab initio* data for bcc and fcc iron.[64]

However, as we will see in the next section, the approximation of a constant atomic magnetic moment on spin rotation is rarely valid. Typically, the number of up- and down-spin electrons are modified when the spins are rotated. This then changes the onsite levels and, in general, affects the up- and down-spin density of states in different ways. The modification of the energy of Eq. (76) has to be calculated from the bond energy of Eq. (118), where the moments of the up- and down-spin density of states $\mu_{i\alpha\uparrow}^{(n)}$ and $\mu_{i\alpha\downarrow}^{(n)}$ have to be handled *individually*. The relevant expressions for the evaluation of the multispin interactions are given in Appendix C. These expressions are more complicated and cumbersome to analyze than the trace of the moments. We will therefore, in the next section, discuss the simplest situation, namely the self-consistent fourth-moment approximation. This approximation suffices to show clearly that in situations where the magnitude of the spin changes on rotation, the Heisenberg model is not a valid approximation, but terms of the type $(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})^2$ and multispin interactions can play a dominant role.

## VI. GINZBURG-LANDAU EXPANSION

In this section we derive a Ginzburg-Landau (GL) expansion[65,66] for the magnetic energy of $3d$-valent transition metals within the fourth-moment approximation. We work with the averaged density of states $n_i(E) = (\sum_{\alpha=1}^{5} n_{i\alpha})/5$ of the $d$ valence, use local charge neutrality, and assume that the Stoner exchange parameter is diagonal $I_{ij} = I_i\delta_{ij}$, which is a good approximation for the $3d$ metals, such that the binding energy Eq. (76) reduces to

$$U_B(\boldsymbol{\Delta}) = U_{\mathrm{bond}} - \frac{1}{4}\sum_i I_i m_i^2 + U_{\mathrm{rep}}. \tag{162}$$

From Eq. (101) for a given set of spin directions $\boldsymbol{s}_i$ the equilibrium magnetic moments and the energy are obtained by minimizing the energy with respect to $\Delta_i = E_{i\uparrow} - E_{i\downarrow}$ for every atom $i$ while the average onsite level $(E_i^{\uparrow} + E_i^{\downarrow})/2$ is varied to ensure local charge neutrality. We normalize the energy $\epsilon = (E - a_\infty)/(2b_\infty)$ by half the bandwidth $W/2 = 2b_\infty$ and center it on $a_\infty$ independent of the spin channel, so the BOP expansion [Eq. (118)] leads to the following expression for the atomic bond energy and magnitude of the atomic moment:

$$U_{\mathrm{bond}} = \frac{b_\infty}{2}\sum_{n=0}\sigma_{n\uparrow}(\chi_{n+2} - \gamma_{0\uparrow}\chi_{n+1} + \chi_n) + \frac{b_\infty}{2}\sum_{n=0}\sigma_{n\downarrow}(\chi_{n+2} - \gamma_{0\downarrow}\chi_{n+1} + \chi_n), \tag{163}$$

$$m = \sum_{n=0}(\sigma_{n\uparrow} - \sigma_{n\downarrow})\chi_{n+1}, \tag{164}$$

where $\gamma_{0\uparrow} = (E_\uparrow - a_\infty)/b_\infty$. We have dropped the atom index $i$ as in the following we will assume that all atoms are crystallographically equivalent, as, for example, in an unfrustrated, magnetically ordered crystal where the spins on the two sublattices point in different directions $\boldsymbol{s}_A$ and $\boldsymbol{s}_B$ such that $\cos\theta = (\boldsymbol{s}_A\boldsymbol{s}_B)$ between all neighboring atoms. If the expansion [Eq. (163)] is taken up to the second moment $n = 2$, the expansion leads to the square-root embedding term of the Finnis-Sinclair potential[52] as $\sigma^{(1)} = \sigma^{(2)} = 0$. The fourth-moment expansion with maximum $n = 4$ is the lowest order of approximation that is able to differentiate between bcc and the close-packed fcc and hcp structure types, while the sixth-moment expansion resolves the small energy differences between the fcc and hcp phases.[19,20] In this section we use the fourth-moment model as the basis for the GL expansion of the magnetic energy as a minimum of four moments are required to distinguish among ferromagnetic FM, noncollinear magnetic NCM, and antiferromagnetic AFM configurations. The GL expansion discussed in the following paragraphs may, however, in principle, be applied to an arbitrary number of moments.

We analyze an elemental crystal with equivalent positions that provides no three-member ring contributions such that the third moment of the density of states vanishes through

Eq. (103) and the first four moments of the nonmagnetic density of states are given by

$$\mu^{(0)} = 1, \quad \mu^{(1)} = 0, \quad \mu^{(2)} = b_1^2, \\ \mu^{(3)} = 0, \quad \mu^{(4)} = (1+s)b_1^4, \tag{165}$$

where $s$ is the bimodal shape parameter $s = \mu^{(4)}/(\mu^{(2)})^2 - 1$. In the magnetic state the up- and down-spin levels split by $\pm\hat{\Delta} = \pm\Delta/(2b_1)$ and the moments of the density of states become

$$\mu^{(0)} = 1, \tag{166}$$

$$\mu^{(1)}/b_1 = \pm\hat{\Delta}, \tag{167}$$

$$\mu^{(2)}/b_1^2 = 1 + \hat{\Delta}^2, \tag{168}$$

$$\mu^{(3)}/b_1^3 = \pm[(2+\cos\theta)\hat{\Delta} + \hat{\Delta}^3], \tag{169}$$

$$\mu^{(4)}/b_1^4 = (1+s) + 2(2+\cos\theta)\hat{\Delta}^2 + \hat{\Delta}^4, \tag{170}$$

where $\theta$ is the angle included between the atomic magnetic moments on two neighboring atoms $i$ and $j$, $\cos\theta = (\boldsymbol{s}_i \boldsymbol{s}_j)$. By choosing $a_\infty = 0$ and $b_\infty = \sqrt{\mu^{(2)}} = b_1(1+\hat{\Delta}^2)$ this leads to a straightforward expression for the bond energy

$$U_{\text{bond}}/b_1 = \frac{1}{\sqrt{(1+\hat{\Delta}^2)^3}}[(1+\hat{\Delta})^2\chi_2 - (1 - s - \cos\theta\,\hat{\Delta}^2)\chi_4 \\ -(1 - s - 2\cos\theta\,\hat{\Delta}^2 + \hat{\Delta}^4)\chi_6] \tag{171}$$

and the magnitude of the magnetic moment

$$m = \frac{2\hat{\Delta}}{\sqrt{(1+\hat{\Delta}^2)^3}}[(1+\hat{\Delta}^2)\chi_2 - (\hat{\Delta}^2 - \cos\theta)\chi_4]. \tag{172}$$

As expected from the discussion in the previous section, the fourth moment leads to a $\cos\theta$ interaction between the spins in $U_{\text{bond}}$. Furthermore, $U_{\text{bond}}$ is a symmetric function of $\Delta$, such that $U_{\text{bond}}(\Delta) = U_{\text{bond}}(-\Delta)$ while the magnetic moment changes sign with the exchange-level splitting, $m(-\Delta) = -m(\Delta)$. The Fermi level $E_F$ that is required for the evaluation of the response functions in the bond energy and the magnetic moment depends on the magnetic state because the modification of the onsite levels through $\hat{\Delta}$ leads to a deformation of the density of states. The modification of the Fermi energy $E_F$ on spin rotation may be obtained by taking into account charge conservation

$$N = 2\chi_1 - \frac{1 - s - 2\cos\theta\,\hat{\Delta}^2 + \hat{\Delta}^4}{(1+\hat{\Delta}^2)^2}\chi_5\,. \tag{173}$$

In Fig. 2 the most stable phase obtained from Eq. (162) with the BOP expansion [Eqs. (171) and (172)] is displayed as a function of the number of valence electrons $N$ and the Stoner exchange parameter $I$. Compared are the nonmagnetic (NM), FM, and AFM phases and NCM spin configurations with $\cos\theta$ varying in steps of $1/4$ between FM and AFM. The lines correspond to the onset of magnetism for the FM, AFM, and disordered (DIS, $\cos\theta = 0$) phases. As the diagram is symmetric about $N = 5$, only the region from five to nine valence electrons is shown. A shape factor $s = 1$ was used for the evaluation of the diagram and the exchange splitting was limited to values $|\hat{\Delta}| < 1/2$ to avoid unphysically large distortions of the single-banded density of states.

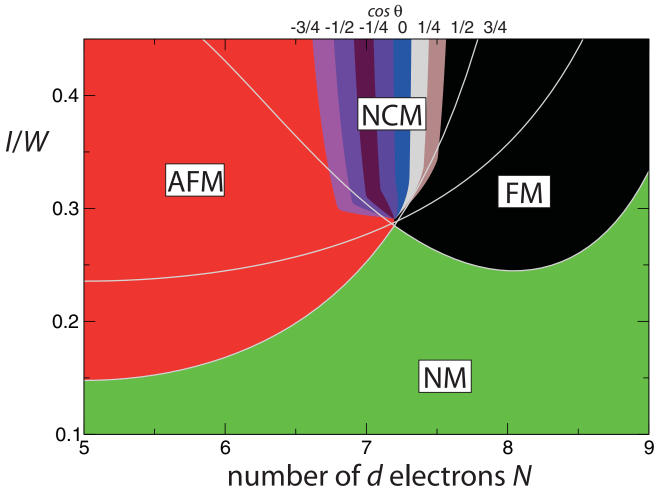

FIG. 2. (Color online) Phase stability diagram showing the most stable phase as a function of the number of valence electrons $N$ and the Stoner exchange integral $I$ (NM, green; AFM, red; FM, black; NCM, $\cos\theta$ in steps of $1/4$). The lines show the onset of magnetism for the AFM, FM, and disordered magnetic configurations according to $A = 0$ [Eq. (179)].

The stability diagram agrees qualitatively with an earlier diagram obtained by of one of us,[7] where the density of states was explicitly approximated by a (skewed) rectangular band model. The Stoner exchange parameter required to stabilize the AFM or DIS magnetic phase increases from the center of the band outward. Heine and Samson noted that a suitable fourth-moment response function must have two nodes in order to drive the stability from AFM in the center of the band to FM toward the band edges.[67] As displayed in Fig. 2, the analytic fourth-moment response function $\hat{\chi}_4$, Eq. (114), behaves in exactly this manner and by coupling to $\cos\theta$ in Eq. (171) changes the stability from AFM ordering at half-full band to FM ordering at nearly full band.

Between the AFM and FM stability at a valence electron count of approximately 7, noncollinear spin configurations are more stable than either the FM or AFM ordering. In our simple model the noncollinear spin configurations cannot be stabilized by a simple Heisenberg-type $\cos\theta$ dependence, as a linear dependence of the energy on $\cos\theta$ would mean that the minimum of the energy would be at the extrema of the cosine function and therefore correspond either to FM or to AFM ordering. Hence, the noncollinear states are stabilized by non-Heisenberg interactions of the type $\cos^2\theta$. These non-Heisenberg interactions are induced by changes in the magnetic moment as a function of $\theta$ that have their origin in deformations of the density of states that differ for the up and down density of states. This leads from Eq. (172) to a $\cos^2\theta$ contribution in the magnetic exchange energy in Eq. (163).

The behavior between 7 and 8 valence electrons is shown in more detail in Fig. 3. At $N = 7$ the parallel alignment of the FM phase has a larger energy than any other rotation angle $\theta$. The minimum of the energy is found at $\theta \approx 6/10\pi$. On increasing the valence electron count, the minima of the energy shifts toward smaller angles $\theta$ and turns to FM ordering at

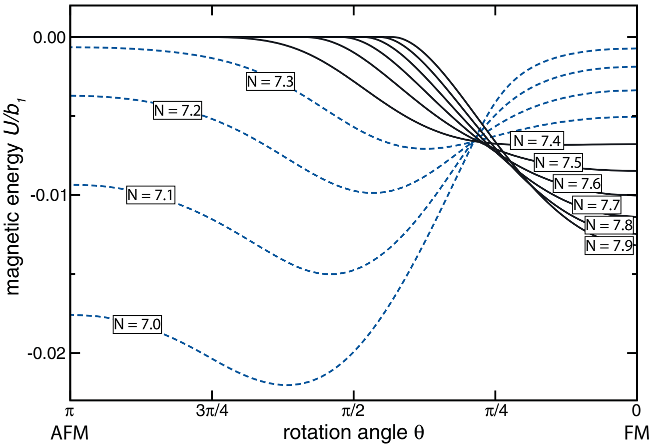

FIG. 3. (Color online) Magnetic contribution to the energy as a function of the angle $\theta$ between spins on neighboring atoms. The graph shows the energy at a number of valence electrons between $N = 7$ and $N = 8$. It was evaluated for $I/b_1 = 0.32$. Valence electron numbers for which the FM state is the most stable configuration are indicated by a solid line.

$N \approx 7.4$. At this electron count, the AFM phase can no longer be stabilized and the magnetic moment collapses such that the magnetic energy vanishes. This behavior is well established for Ni, where the magnetic moments practically collapse in antiferromagnetic spin orientation.[68]

The non-Heisenberg spin interactions may also be discussed in the view of the Ginzburg-Landau expansion, which we will derive from the fourth-moment BOP model next. The magnetic contribution to the energy Eq. (162) may be parameterized as a function of the $d$-onsite energy splitting $\Delta$. For $\Delta = 0$ the material is nonmagnetic, so we may use $\hat{\Delta} = \Delta/(2b_1)$ as the order parameter in the GL expansion

$$U^{(\mathrm{GL})}/b_1 = U^{(0)}/b_1 + A\hat{\Delta}^2 + B\hat{\Delta}^4, \tag{174}$$

where $U^{(0)}$ corresponds to the nonmagnetic energy. As a first step to obtaining the expansion coefficients $A$ and $B$, the fourth-moment BOP expansion of the binding energy Eq. (171) is expanded with respect to $\hat{\Delta}$, resulting in

$$\begin{aligned} A^{(0)} = {} & \tfrac{1}{2}[-\chi_2 + (3(1-s) + 2\cos\theta)\chi_4 \\ & + (3(1-s) + 4\cos\theta)\chi_6] - I(\chi_2 + \cos\theta\,\chi_4)^2, \end{aligned} \tag{175}$$

$$\begin{aligned} B^{(0)} = {} & \tfrac{1}{8}[3\chi_2 - (15(1-s) + 12\cos\theta)\chi_4 \\ & - (23 - 15s + 24\cos\theta)\chi_6] \\ & + I(\chi_2 + \cos\theta\,\chi_4)(\chi_2 + (2 + 3\cos\theta)\chi_4), \end{aligned} \tag{176}$$

where the superscript (0) indicates that the expansion was carried out at the Fermi level of the nonmagnetic state. The expansion coefficient $A^{(0)}$ is a quadratic function of $\cos\theta$; therefore, the condition for the onset of magnetism $A^{(0)} = 0$ may be reached by a noncollinear spin configuration at a lower energy than an FM or AFM spin configuration. Differing from the usual GL expansion, where the magnetic moment is used as the order parameter, the fourth-order expansion coefficient $B^{(0)}$ depends on the Stoner exchange parameter $I$ because of the nonlinear dependence of the magnetic moment Eq. (172) on $\Delta$.

The dependence of the Fermi phase $\phi_F$ on the magnetic state $\hat{\Delta}$ may be established to fourth order

$$\phi_F = \phi_F^{(0)} + a\hat{\Delta}^2 + b\hat{\Delta}^4, \tag{177}$$

where $\phi_F^{(0)}$ is the Fermi phase of the nonmagnetic state. Analytic expressions for $a$ and $b$ may be obtained from Eq. (173), the expression for $a$ is given by

$$a = \frac{(1 - s + \cos\theta)\big(3\sin 4\phi_F^{(0)} - 2\sin 6\phi_F^{(0)}\big)}{6\big(-1 + \cos 2\phi_F^{(0)} + (1-s)\big(\cos 4\phi_F^{(0)} - \cos 6\phi_F^{(0)}\big)\big)}. \tag{178}$$

By inserting the expansion of the Fermi energy Eq. (177) into $A^{(0)}$ and $B^{(0)}$ and expanding the resulting expressions to fourth order in $\hat{\Delta}$, the GL expansion for the magnetic energy is completed.

As for $A^{(0)}$, the dependence of $A$ on $\theta$ does not follow a simple Heisenberg interaction but includes quadratic terms $\cos^2\theta$

$$\begin{aligned} A = {} & \frac{2\sin^3\varphi}{1575\pi}\{1200 - 675s + 1200(1-s)\cos 2\varphi + 750(1-s)\cos 4\varphi + \cos\theta(690 + 1110\cos 2\varphi + 300\cos 4\varphi) \\ & - I[1050\sin\varphi - 350\sin 3\varphi + \cos\theta(700\sin 3\varphi - 420\sin 5\varphi) + \cos^2\theta(210\sin\varphi + 154\sin 3\varphi + 42\sin 5\varphi - 126\sin 7\varphi)]\}. \end{aligned} \tag{179}$$

Nonlinear terms in $\cos\theta$ are also observed in $B$. The critical value of $I$ for the onset of magnetism evaluated from $A = 0$ is shown in Fig. 2 for the onset of the ferromagnetic, the antiferromagnetic and disordered magnetic state.

As expected the GL expansion Eq. (174) is only valid for small values of $\hat{\Delta} \ll 1$. This is seen in Fig. 4 and leads to the inability of the GL expansion to predict the complete phase diagram of Fig. 2 as the expansion predicts the wrong sequence of magnetic ordering for large values of $\hat{\Delta}$. In Fig. 4 the deviations of the GL expansion from the BOP reference are illustrated. While the overall behavior remains intact even for relatively large values of $\hat{\Delta}$, the equilibrium values of the magnetic energy are predicted incorrectly as compared to the BOP reference.

This is the first time that the prefactors $A$ and $B$ for a magnetic GL expansion have been predicted from first principles. Even though the dependence of the fourth moment on the spin directions follows a simple Heisenberg interaction, because of the relaxation of the magnitude of the magnetic moment as a function of angle between the spins, both $A$ and $B$ depend

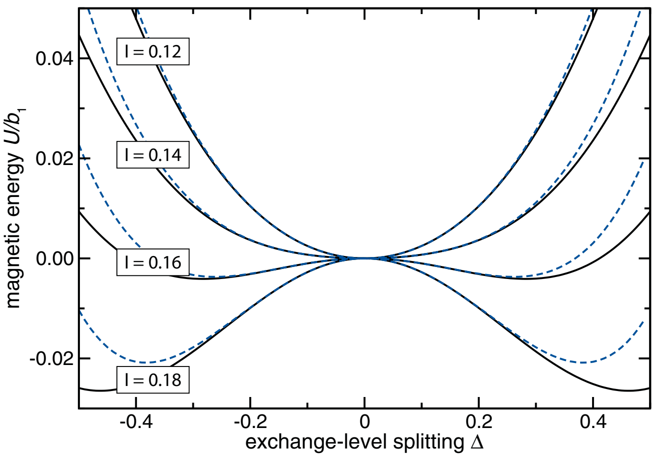

FIG. 4. (Color online) Magnetic contribution to the energy as a function of the exchange-level splitting $\hat{\Delta}$ for different values of the Stoner exchange integral. The graph shows the energy at $N = 5$ electrons and AFM spin orientation. The black lines correspond to the fourth-moment analytic BOP expansion of the energy [Eq. (162)], and the dashed lines correspond to the fourth-order GL expansion [Eq. (174)].

on $\cos^2\theta$. Therefore, a Heisenberg model cannot describe the energy correctly. In fact, in our unfrustrated nearest-neighbor model the Heisenberg interaction alone is unable to stabilize noncollinear spin configurations, the stability of the NCM phase depends critically on the non-Heisenberg $\cos^2\theta$ term. Because of the O(4) expansion of the Ginzburg-Landau model, it is unable to reproduce the fourth-moment BOP expansion for stable, saturated magnetic moments that do not fulfill $\hat{\Delta} \ll 1$, such that the GL expansion is unable to model the stability of competing magnetic phases in iron, for example. Thus, although the maximum and minimum DFT energy values as a function of $\Delta$ can be fitted by a fourth-order GL expansion, the curvatures are wrong due to the neglect of higher-order contributions (see, e.g., Fig. 3 in Ref. 69).

## VII. SUMMARY

From a second-order expansion of the DFT energy functional an extension of the tight-binding bond model to include noncollinear magnetism and charge transfer was derived. Within the framework of bond-order potentials, an analytic approximation of the magnetic TB energy was developed and the necessary gradients for self-consistency, forces, and torques were established. A discussion of the moments expansion then showed that atomic magnetic moments with a fixed length are expected to interact with a Heisenberg-type interaction, while four-spin interactions are introduced only by the eighth and higher moments. We, furthermore, showed that the GL expansion of the magnetic energy may be obtained analytically from the TB and BOP representation of the electronic structure. At the fourth-moment level, the analytic magnetic bond-order potential predicts the correct sequence of magnetic ordering in agreement with earlier work. The GL expansion reproduces the BOP predictions for small values of $\hat{\Delta}$ but deviates significantly for larger values and is therefore not suitable for the comparison of the stability of different magnetic phases. From our expansion we also predict that Heisenberg interactions of the type $(\boldsymbol{s}_i\boldsymbol{s}_j)$ are not adequate for the description of spin interactions if the magnitude of the atomic magnetic moments is altered significantly when the spins are rotated.

## APPENDIX A: MATRIX ELEMENTS OF THE SDFT ENERGY

The second-order expansion of Eqs. (6) and (31),

$$U = \sum_{ij} n_i^j T_j^i + \sum_{ij} n_i^j V_j^i + \sum_{ij} n_i^j K_j^i + \sum_{ij} \boldsymbol{m}_i^j \boldsymbol{B}_j^i + \frac{1}{2}\sum_{ij}\sum_{i'j'} J_{ii'}^{jj'} n_j^i n_{j'}^{i'} - \frac{1}{4}\sum_{iji'j'} I_{jj'}^{ii'} \boldsymbol{m}_i^j \boldsymbol{m}_{i'}^{j'},$$

contains the following matrix elements. The kinetic energy Eq. (7) is given by

$$T^{\mathrm{KS}} = \sum_{ij} n_i^j T_j^i, \tag{A1}$$

with

$$T_j^i = \langle \varphi^i | \hat{T}^{\mathrm{KS}} | \varphi_j \rangle. \tag{A2}$$

The external energy is given by

$$\begin{aligned} U_{\mathrm{ext}} &= \int \mathrm{Tr}(\boldsymbol{\rho}(\boldsymbol{r})\boldsymbol{W}(\boldsymbol{r}))d\Omega \\ &= \int n(\boldsymbol{r})V(\boldsymbol{r})d\Omega + \int \mu_B \boldsymbol{B}\boldsymbol{m}d\Omega \\ &= \sum_{ij} n_i^j \int V_j^i d\Omega + \mu_B \sum_{ij} \boldsymbol{m}_i^j \int \boldsymbol{B}\chi_j^i d\Omega \\ &= \sum_{ij} n_i^j V_j^i + \sum_{ij} \boldsymbol{m}_i^j \boldsymbol{B}_j^i, \end{aligned} \tag{A3}$$

with

$$V_j^i = \int \chi_j^i V(\boldsymbol{r}) d\Omega \tag{A4}$$

and

$$\boldsymbol{B}_j^i = \mu_B \int \chi_j^i \boldsymbol{B}(\boldsymbol{r}) d\Omega, \tag{A5}$$

and the Hartree energy by

$$U_H = \frac{e^2}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\Omega d\Omega' = \sum_{ij}\sum_{i'j'} \frac{1}{2} n_i^j n_{i'}^{j'} J_{Hii'}^{jj'}, \tag{A6}$$

with

$$J_{Hii'}^{jj'} = e^2 \int \frac{\chi_j^i(\boldsymbol{r})\chi_{j'}^{i'}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\Omega d\Omega'. \tag{A7}$$

The second-order expansion of the exchange-correlation energy is written as

$$U_{XC}^{(2)} = \sum_{ij} n_i^j K_j^i + \frac{1}{2}\sum_{iji'j'} n_i^j n_{i'}^{j'} J_{XCjj'}^{ii'} - \frac{1}{4}\sum_{iji'j'} m_i^j m_{i'}^j I_{jj'}^{ii'}, \tag{A8}$$

with

$$K_j^i = \int \chi_j^i K_{XC}(\boldsymbol{r})d\Omega, \tag{A9}$$

$$J_{XCjj'}^{ii'} = \int \chi_j^i(\boldsymbol{r})\chi_{j'}^{i'}(\boldsymbol{r}')J_{XC}(\boldsymbol{r},\boldsymbol{r}')d\Omega, \tag{A10}$$

$$I_{jj'}^{ii'} = \int \chi_j^i(\boldsymbol{r})\chi_{j'}^{i'}(\boldsymbol{r}')I_{XC}(\boldsymbol{r},\boldsymbol{r}')d\Omega. \tag{A11}$$

## APPENDIX B: EXPLICITLY NONORTHOGONAL TIGHT-BINDING BOND MODEL

In Sec. III B we provide the contributions to the binding energy in the tight-binding bond model in mixed co- and contravariant notation, which looks very similar to an orthogonal TB model. Here we list the expressions for the equivalent but explicitly nonorthogonal representation of the TB bond model, starting from the expressions for the Mulliken charges and the local magnetic moments, Eqs. (57) and (58),

$$q_{i\alpha} = \delta n_{i\alpha}^{i\alpha} = \sum_{j\beta} S_{i\alpha j\beta}\delta n^{j\beta i\alpha},$$

$$\boldsymbol{m}_{i\alpha} = \boldsymbol{m}_{i\alpha}^{i\alpha} = \sum_{j\beta} S_{i\alpha j\beta}\boldsymbol{m}^{j\beta i\alpha}.$$

From this the expressions for the Coulomb and exchange energy, Eqs. (59) and (60), are given by

$$U_C = \frac{1}{2}\sum_{i\alpha,j\beta} J_{i\alpha j\beta}\sum_{k\gamma} S_{i\alpha k\gamma}\delta n^{k\gamma i\alpha}\sum_{l\delta} S_{j\beta l\delta}\delta n^{l\delta j\beta}, \tag{B1}$$

$$U_X = -\frac{1}{4}\sum_{i\alpha,j\beta} I_{i\alpha j\beta}\sum_{k\gamma} S_{i\alpha k\gamma}\boldsymbol{m}^{k\gamma i\alpha}\sum_{l\delta} S_{j\beta l\delta}\boldsymbol{m}^{l\delta j\beta}. \tag{B2}$$

The Hamiltonian [Eq. (68)] is given by

$$H_{i\alpha\mu j\beta\nu} = H_{i\alpha j\beta}^{(0)}\delta_{\mu\nu} + \left[\sum_{l\delta} S_{k\gamma l\delta}\left(\sum_{k\gamma} J_{i\alpha k\gamma}\delta n^{l\delta k\gamma}\delta_{\mu\nu} - \frac{1}{2}\sum_{k\gamma} I_{i\alpha k\gamma}\boldsymbol{m}^{l\delta k\gamma}\boldsymbol{\sigma}_{\mu\nu}\right) + V_{i\alpha}\delta_{\mu\nu} + \boldsymbol{B}_{i\alpha}\boldsymbol{\sigma}_{\mu\nu}\right] S_{i\alpha j\beta}, \tag{B3}$$

similarly to the expression obtained in Ref. 34. Differing from the mixed co- and contravariant notation, the modification of the Hamiltonian by electron transfer, magnetism, or external fields is no longer diagonal but proportional to the overlap matrix $S_{i\alpha j\beta}$.

The intersite representation of the bond energy Eq. (70) is given by

$$U_{\text{bond}} = \sum_{i\alpha\mu j\beta\nu} (H_{i\alpha\mu j\beta\nu} - E_{i\alpha\mu\nu}S_{i\alpha j\beta})\rho_{\nu\mu}^{j\beta i\alpha}. \tag{B4}$$

The electron transfer energy Eq. (72) may be represented as

$$U_{\text{trans}} = \sum_{i\alpha j\beta} E_{i\alpha}^{(0)} S_{i\alpha j\beta}\delta n^{j\beta i\alpha} \tag{B5}$$

and the preparation energy is given by Eq. (73) as

$$U_{\text{prep}} = \sum_{i\alpha} \left(E_{i\alpha}^{(0)} - E_{i\alpha}^{(\text{at})}\right)N_{i\alpha}^{(0)},$$

where we used $S_{i\alpha i\alpha} = 1$ and the fact that the reference density matrix is diagonal,

$$n^{(0)j\beta i\alpha} = N_{i\alpha}^{(0)}\delta_{j\beta i\alpha}. \tag{B6}$$

The sum of the bond energy, electron transfer energy, and preparation energy adds up to

$$U_{\text{bond}} + U_{\text{trans}} + U_{\text{prep}} = \sum_{i\alpha j\beta} H_{j\beta i\alpha}^{(0)} n^{i\alpha j\beta} - \sum_{i\alpha} E_{i\alpha}^{(\text{at})} N_{i\alpha}^{(0)}.$$

The expressions for the energy of free atoms and the repulsive energy, Eqs. (75) and (77), remain as they are, while the expressions for the external energy $U_{\text{ext}}$ follow from the transformations of $q_{i\alpha}$ and $\boldsymbol{m}_{i\alpha}$.

The onsite representation of the bond energy may also be given in a nonorthogonal basis. The spectrally resolved density matrix[20]

$$n_{\nu\nu}^{j\beta i\alpha}(E) = \sum_n \left(c_\nu^{(n)j\beta}\right)^* c_\nu^{(n)i\alpha}\delta(E - \epsilon_n), \tag{B7}$$

may be related to the density of states[30]

$$n_{i\alpha\nu}(E) = \sum_n \sum_{j\beta} S_{i\alpha j\beta}\left(c_\nu^{(n)j\beta}\right)^* c_\nu^{(n)i\alpha}\delta(E - \epsilon_n). \tag{B8}$$

The number of electrons associated with orbital $|i\alpha\nu\rangle$ is obtained from

$$N_{i\alpha\nu} = \int^{E_F} n_{i\alpha\nu}(E)\,dE\,,$$

and the bond energy Eq. (B4) in the *onsite* representation is given by Eq. (100),

$$U_{\text{bond}} = \sum_{i\alpha}\int^{E_F}(E - E_{i\alpha\uparrow})n_{i\alpha\uparrow}(E)\,dE + \sum_{i\alpha}\int^{E_F}(E - E_{i\alpha\downarrow})n_{i\alpha\downarrow}(E)\,dE\,.$$

### 1. Expressions used in Refs. 46 and 43

While from Eq. (70) a generalization of the bond energy of orbital $|i\alpha\nu\rangle$ would read

$$U_{\text{bond},i\alpha\nu} = \sum_{j\beta\nu}(H_{i\alpha\mu j\beta\nu} - E_{i\alpha\mu\nu}S_{i\alpha j\beta})\rho_{\nu\mu}^{j\beta i\alpha}, \tag{B9}$$

one may prefer an explicitly symmetric separation of the bond energy. This is known as a the covalent bond energy,[43,46] which we give in a magnetic generalization as follows:

$$U_{\mathrm{cov},i\alpha\nu j\beta\mu} = \left[H_{i\alpha\mu j\beta\nu} - \tfrac{1}{2}(E_{i\alpha\mu\nu} + E_{j\beta\mu\nu})S_{i\alpha j\beta}\right]\rho_{\nu\mu}^{j\beta i\alpha}. \tag{B10}$$

Bester and Fähnle, in Ref. 43, refer to the diagonal terms $i = j$ as the polarization energy $U_{\mathrm{polar},i\alpha\nu i\beta\mu} = U_{\mathrm{cov},i\alpha\nu i\beta\mu}$. Clearly, if one takes the sum over all bonds, the sum of the covalent bond energy and the polarization energy corresponds to the bond energy,

$$U_{\mathrm{bond}} = \sum_{i\alpha\nu j\beta\mu}^{i\neq j} U_{\mathrm{cov},i\alpha\nu j\beta\mu} + \sum_{i\alpha\nu\beta\mu} U_{\mathrm{polar},i\alpha\nu i\beta\mu}. \tag{B11}$$

The electron transfer energy Eq. (72) is identical to the expression given for the promotion energy in Ref. 43 if one makes the approximation that the reference atomic levels $E_{i\alpha}^{(0)}$ coincide with the atomic energy levels $E_{i\alpha}^{(\mathrm{at})}$ such that the preparation energy is zero.

### 2. Expressions used in Refs. 29 and 30

In his book Finnis[29] follows the definition of the promotion energy given in Ref. 43. Eq. (7.37) of Ref. 29 reads

$$U_{\mathrm{prom}}^{(7.37)} = \sum_{i\alpha} E_{i\alpha}^{(\mathrm{at})} q_{i\alpha}, \tag{B12}$$

which coincides with our definition of the electron transfer energy Eq. (72),

$$U_{\mathrm{trans}} = \sum_{i\alpha} E_{i\alpha}^{(0)} q_{i\alpha},$$

if $E_{i\alpha}^{(\mathrm{at})} = E_{i\alpha}^{(0)}$ such that the preparation energy contribution is zero as discussed above and where one has to be careful with the comparison as Finnis defines $q_{i\alpha}$ as the total number of electrons $N_{i\alpha}$ in orbital $|i\alpha\rangle$, while we use the charges as the difference between the number of electrons in an orbital to the number of electrons of a free atom in the same orbital, $q_{i\alpha} = N_{i\alpha} - N_{i\alpha}^{(0)}$. Paxton[30] uses the same definition of the promotion energy.

However, Finnis then introduces a modification of this expression, given in Eq. (7.39) of Ref. 29, that includes the preparation energy. In our notation this reads

$$U_{\mathrm{prom}}^{(7.39)} = \sum_{i\alpha\beta} \left(H_{i\alpha i\beta}^{(0)} n^{i\alpha i\beta} - E_{i\alpha}^{(\mathrm{at})} N_{i\alpha}^{(0)}\right), \tag{B13}$$

and may be identified as

$$U_{\mathrm{prom}}^{(7.39)} = U_{\mathrm{prep}} + U_{\mathrm{trans}} + \sum_{i\alpha\beta}^{\alpha\neq\beta} H_{i\beta}^{(0)i\alpha} n_{i\alpha}^{i\beta}, \tag{B14}$$

where the last term on the right-hand side corresponds to the atom-diagonal contribution of the bond energy, Eq. (71).

As Finnis in Eq. (7.14) and also Paxton introduce the bond energy as strictly defined between two different atoms

$$U_{\mathrm{bond}}^{(7.14)} = \sum_{i\alpha j\beta}^{i\neq j} H_{i\alpha j\beta}^{(0)} n^{i\alpha j\beta}, \tag{B15}$$

we recover

$$\begin{aligned} U_{\mathrm{bond}}^{(7.14)} + U_{\mathrm{prom}}^{(7.39)} &= U_{\mathrm{bond}} + U_{\mathrm{trans}} + U_{\mathrm{prep}} \\ &= \sum_{i\alpha j\beta} H_{j\beta i\alpha}^{(0)} n^{i\alpha j\beta} - \sum_{i\alpha} E_{i\alpha}^{(\mathrm{at})} N_{i\alpha}^{(0)}, \end{aligned} \tag{B16}$$

such that the sum of the contributions is identical to our expressions. Finnis then continues to modify the expression for the energy in Sec. 7.5.3 of Ref. 29. Thereby he uses a modification of the covalent bond energy and changes the separation of the energy in different terms. He explicitly defines a crystal field term $U_{\mathrm{cfs}}$ and a term $U_{Mq}$ that is closely related to our definition of the electron transfer energy. These two terms are then integrated into the repulsive energy. In this way the repulsive energy becomes dependent on the charge and density matrix, which is in contrast to the usual parametrization of the repulsive energy as a potential function. Finnis is aware of this and argues that the relevant terms are small.

## APPENDIX C: MULTIPLICATION OF ONSITE MATRICES

The evaluation of the local moments may be simplified by exploiting that the magnetic contribution to the Hamiltonian is diagonal in real space and off-diagonal in spin space, Eq. (69), while the nonmagnetic contributions are off-diagonal in real space and diagonal in spin space. As the onsite matrix elements are given as linear combination of Pauli matrices, we start by analyzing the products of multiple Pauli matrices.

The multiplication of up to four Paul matrices may be simplified by using the following identities:

$$\boldsymbol{\sigma}_{n_1}\boldsymbol{\sigma}_{n_2} = \delta_{n_1n_2}\mathbf{1} + \sqrt{-1}\epsilon_{n_1n_2n_3}\boldsymbol{\sigma}_{n_3}, \tag{C1}$$

$$\boldsymbol{\sigma}_{n_1}\boldsymbol{\sigma}_{n_2}\boldsymbol{\sigma}_{n_3} = \sqrt{-1}\epsilon_{n_1n_2n_3}\mathbf{1} + \delta_{n_1n_2}\boldsymbol{\sigma}_{n_3} + \delta_{n_2n_3}\boldsymbol{\sigma}_{n_1} - \delta_{n_1n_3}\boldsymbol{\sigma}_{n_2}, \tag{C2}$$

$$\begin{aligned} \boldsymbol{\sigma}_{n_1}\boldsymbol{\sigma}_{n_2}\boldsymbol{\sigma}_{n_3}\boldsymbol{\sigma}_{n_4} &= \left(\delta_{n_1n_2}\delta_{n_3n_4} - \delta_{n_1n_3}\delta_{n_2n_4} + \delta_{n_1n_4}\delta_{n_2n_3}\right)\mathbf{1} + \sqrt{-1}\left(\delta_{n_1n_2}\epsilon_{n_3n_4n_5} + \delta_{n_3n_4}\epsilon_{n_1n_2n_5}\right)\boldsymbol{\sigma}_{n_5} \\ &\quad - \frac{\sqrt{-1}}{2}\left(\epsilon_{n_2n_3n_4}\boldsymbol{\sigma}_{n_1} - \epsilon_{n_1n_3n_4}\boldsymbol{\sigma}_{n_2} + \epsilon_{n_1n_2n_4}\boldsymbol{\sigma}_{n_3} - \epsilon_{n_1n_2n_3}\boldsymbol{\sigma}_{n_4}\right), \end{aligned} \tag{C3}$$

where we used the Einstein summation convention. Using these relations, the products of the form $(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})\cdots$ that are required for the evaluation of the moments become

$$(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma}) = (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})\mathbf{1} + \sqrt{-1}(\boldsymbol{s}_{i\alpha} \times \boldsymbol{s}_{j\beta})\boldsymbol{\sigma}, \tag{C4}$$

$$(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma}) = \sqrt{-1}[\boldsymbol{s}_{i\alpha},\boldsymbol{s}_{j\beta},\boldsymbol{s}_{k\gamma}]\mathbf{1} + (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma}) + (\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma}) - (\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma}), \tag{C5}$$

$$\begin{aligned}&(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})\\&\quad=[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})+(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})]\mathbf{1}+\sqrt{-1}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\times\boldsymbol{s}_{l\delta})\boldsymbol{\sigma}+(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{i\alpha}\times\boldsymbol{s}_{j\beta})\boldsymbol{\sigma}]\\&\qquad-\frac{\sqrt{-1}}{2}\{(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})[\boldsymbol{s}_{j\beta},\boldsymbol{s}_{k\gamma},\boldsymbol{s}_{l\delta}]-(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})[\boldsymbol{s}_{i\alpha},\boldsymbol{s}_{k\gamma},\boldsymbol{s}_{l\delta}]+(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})[\boldsymbol{s}_{i\alpha},\boldsymbol{s}_{j\beta},\boldsymbol{s}_{l\delta}]-(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})[\boldsymbol{s}_{i\alpha},\boldsymbol{s}_{j\beta},\boldsymbol{s}_{k\gamma}]\},\end{aligned}\tag{C6}$$

where $[\boldsymbol{s}_{i\alpha},\boldsymbol{s}_{j\beta},\boldsymbol{s}_{k\gamma}]$ is the determinant and Eq. (C4) is a well-known property of Pauli matrices. The above products are complex. However, for the evaluation of the moments, each hopping path is evaluated in forward and backward directions. For example, if a path contains the product $(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})$, then the equivalent backward path will contain the product $(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})$. This means that for the further evaluation of the moments we may drop all contributions of the above products that add up to zero when a given product of Hamiltonian matrix elements is calculated in forward and backward directions. For example,

$$(\boldsymbol{s}_{i\alpha}\times\boldsymbol{s}_{j\beta})+(\boldsymbol{s}_{j\beta}\times\boldsymbol{s}_{i\alpha})=0\,,\tag{C7}$$

and, therefore, contributions from cross products or determinants do not need to be taken into account. We see that all contributions that are premultiplied by $\sqrt{-1}$ drop out, so, as expected, we are left with only real contributions. Thus, we obtain the much simplified expressions

$$[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})+(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})]/2=(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})\mathbf{1},\tag{C8}$$

$$\begin{aligned}&[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})+(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})]/2\\&\quad=(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})+(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma}),\end{aligned}\tag{C9}$$

$$\begin{aligned}&[(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})+(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\sigma}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})]/2\\&\quad=[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})+(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})]\mathbf{1}.\end{aligned}\tag{C10}$$

Equations (157)–(159) follow directly as $\mathrm{Tr}[\sigma_i]=0$ for all Pauli matrices $i=x,y,z$ and where, for simplicity of notation, we did not write down the backward path explicitly on the left-hand side. We do this from now on, whereby the left-hand side of the following equations implicitly corresponds to the average of the forward and the backward products.

Because we are only interested in the $\uparrow\uparrow$ and $\downarrow\downarrow$ matrix elements for the calculation of the moments on atom $n$ and orbital $\kappa$, only the Pauli matrix $\boldsymbol{\sigma}_z$ can contribute. By denoting the $z$ axis on orbital $|n\kappa\rangle$ as $\boldsymbol{s}_{n\kappa}=\boldsymbol{e}_z$, we arrive at the following expressions, where $\nu=\uparrow=+$ and $\nu=\downarrow=-$,

$$\langle n\kappa\nu|(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})|n\kappa\nu\rangle=(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}),\tag{C11}$$

$$\langle n\kappa\nu|(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})|n\kappa\nu\rangle=\pm[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})+(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})],\tag{C12}$$

$$\langle n\kappa\nu|(\boldsymbol{s}_{i\alpha}\boldsymbol{\sigma})(\boldsymbol{s}_{j\beta}\boldsymbol{\sigma})(\boldsymbol{s}_{k\gamma}\boldsymbol{\sigma})(\boldsymbol{s}_{l\delta}\boldsymbol{\sigma})|n\kappa\nu\rangle=(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})+(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta}).\tag{C13}$$

With the decomposition of the onsite Hamiltonian according to Eq. (150) we next write down the expressions for the products of the onsite matrix elements. Spin-space products of the onsite Hamiltonian yield the following for up- and down-spin channels with respect to the coordinate system on orbital $|n\kappa\rangle$

$$\left[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\right]_{\nu\nu}=\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})\pm\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})+\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta}),\tag{C14}$$

$$\begin{aligned}[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}]_{\nu\nu}=&\;\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(m)}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})\pm\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})\pm\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})\\&+\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})+\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(m)}\Lambda_{i\alpha}^{(m)}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{i\alpha})+\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})\\&\pm\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})+(\boldsymbol{s}_{j\alpha}\boldsymbol{s}_{k\beta})(\boldsymbol{s}_{i\gamma}\boldsymbol{s}_{n\kappa})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\beta})(\boldsymbol{s}_{j\gamma}\boldsymbol{s}_{n\kappa})],\end{aligned}\tag{C15}$$

$$\begin{aligned}\left[\boldsymbol{E}_{i\alpha}\boldsymbol{E}_{j\beta}\boldsymbol{E}_{k\gamma}\boldsymbol{E}_{l\delta}\right]_{\nu\nu}=&\;\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(m)}(\boldsymbol{s}_{l\delta}\boldsymbol{s}_{n\kappa})\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(m)}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})\\&\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})\pm\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})+\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(m)}\Lambda_{l\delta}^{(m)}(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})\\&+\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}\Lambda_{l\delta}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})+\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}\Lambda_{l\delta}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})+\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})\\&+\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}\Lambda_{k\gamma}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})+\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})\pm\Lambda_{i\alpha}^{(\mathrm{nm})}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}\Lambda_{l\delta}^{(m)}[(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{l\delta}\boldsymbol{s}_{n\kappa})\\&+(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})-(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})]\pm\Lambda_{l\delta}^{(\mathrm{nm})}\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})+(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})\\&-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})]\pm\Lambda_{k\gamma}^{(\mathrm{nm})}\Lambda_{l\delta}^{(m)}\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{l\delta}\boldsymbol{s}_{n\kappa})+(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{n\kappa})]\\&\pm\Lambda_{j\beta}^{(\mathrm{nm})}\Lambda_{k\gamma}^{(m)}\Lambda_{l\delta}^{(m)}\Lambda_{i\alpha}^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{l\delta}\boldsymbol{s}_{n\kappa})+(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{n\kappa})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{n\kappa})]\\&+\Lambda_{i\alpha}^{(m)}\Lambda_{j\beta}^{(m)}\Lambda_{k\gamma}^{(m)}\Lambda_{l\delta}^{(m)}[(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{j\beta})(\boldsymbol{s}_{k\gamma}\boldsymbol{s}_{l\delta})+(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{l\delta})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{k\gamma})-(\boldsymbol{s}_{i\alpha}\boldsymbol{s}_{k\gamma})(\boldsymbol{s}_{j\beta}\boldsymbol{s}_{l\delta})].\end{aligned}\tag{C16}$$

The moments of the density of states may now be obtained by multiplying the onsite matrix elements with intersite Hamiltonian matrix elements.

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