.

Effective Hamiltonians for correlated narrow energy band systems and magnetic insulators: Role of spin-orbit interactions in metal-insulator transitions and magnetic phase transitions

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Effective Hamiltonians for correlated narrow energy band systems and magnetic insulators: Role of spin-orbit interactions in metal-insulator transitions and magnetic phase transitions

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Using a second-quantized many-electron Hamiltonian, we obtain (a) an effective Hamiltonian suitable for materials whose electronic properties are governed by a set of strongly correlated bands in a narrow energy range and (b) an effective spin-only Hamiltonian for magnetic materials. The present Hamiltonians faithfully include phonon and spin-related interactions as well as the external fields to study the electromagnetic response properties of complex materials and they, in appropriate limits, reduce to the model Hamiltonians due to Hubbard and Heisenberg. With the Hamiltonian for narrow-band strongly correlated materials, we show that the spin-orbit interaction provides a mechanism for metal-insulator transition, which is distinct from the Mott-Hubbard (driven by the electron correlation) and the Anderson mechanism (driven by the disorder). Next, with the spin-only Hamiltonian, we demonstrate the spin-orbit interaction to be a reason for the existence of antiferromagnetic phase in materials which are characterized by a positive isotropic spin-exchange energy. This is distinct from the Néel-VanVleck-Anderson paradigm which posits a negative spin-exchange for the existence of antiferromagnetism. We also find that the Néel temperature increases as the absolute value of the spin-orbit coupling increases. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4945705]

I. INTRODUCTION

To study the electromagnetic response properties of complex materials, it is frequently useful to employ effective Hamiltonians,[1–19] notable examples of which are the Hubbard's model for strongly correlated electrons[1–3] and the Heisenberg's spin-only model for magnetic materials.[4–7] What remains mostly absent in the contemporary discourse on effective Hamiltonian based theory of correlated electrons, notwithstanding a number of studies in the past,[10–25] is a systematic account of various spin-related interactions. In fact, it is not very obvious as to how one may systematically improve starting from the model Hamiltonians such as those of Heisenberg, Hubbard and others that faithfully takes into consideration a variety of spin-related interactions. The objective of the present work is to bridge this significant gap. Why is this important? To be specific, it is today urgent to fully understand the detailed nature and the exact mathematical expressions for interactions involving the spin angular momentum of electrons such as the spin-orbit, spin-phonon, and the spin exchange couplings among others, for they herald a rich variety of physical processes within the complex material which are amenable to external control (mechanical as well as electromagnetic) and a complete understanding of which would unravel the necessary mechanistic paths for designing smart materials of well-defined functionalities, as recent works on quantum magnetism, spintronics, and other research areas have revealed.[26–40] The importance of spin-orbit interactions has also been emphasized in condensed matter wherein such interactions lead to exotic topological insulating electronic phases observed in real materials.[41–43] To fulfil the objective, therefore, we systematically reduce the many-electron Hamiltonian in the frequency-specific Lorentz gauge to advance a variety of effective Hamiltonians suitable for complex materials that include important spin-related interactions in a rigorous fashion. To this end, we have followed the minimalist program of Hubbard[1] and Heisenberg[4] among others,[2,3,5–7,44,45] but with a number of significantly new ideas. We first use, following the works of Hubbard[1] and Anderson,[6] a complete set of one-particle Wannier states and obtain the Hamiltonian in the second-quantized form. To reduce the dimensionality of the Hilbert space, we follow two distinct lines of approaches keeping in view the present day interests on complex materials. In the first, following Hubbard and others,[1–3,9–12] we specialize in materials for which interacting electrons form a disjoint set of strongly correlated narrow energy bands and, through a sequence of well-defined approximations, we finally obtain an effective Hamiltonian, especially suitable for insulators and poor conductors, that rigorously includes important spin and phonon related interactions. Next, we reduce the second-quantized Hamiltonian to obtain an effective spin-only Hamiltonian, akin to the Heisenberg model,[4–7] that faithfully includes the effects of spin-orbit and spin-phonon interactions. By definition, the effective Hamiltonians obtained here, in appropriate limits, recover the Heisenberg, Hubbard, and related Hamiltonians that are in frequent use today.[1–7,9–19]

As immediate applications of the effective Hamiltonians advanced here, we address two important classes of problems in complex materials. First, we use the Hamiltonian for strongly correlated narrow energy bands and ask: Does

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the spin-orbit interaction play a role in metal–insulator transitions? As the present work reveals, the spin-orbit interaction tends to favour the material to be insulating in character and therefore it provides a mechanism for metal–insulator transitions, which is distinct from the well-known Mott-Hubbard (driven by the strong electron correlations of electrostatic origin)[1,46] and the Anderson mechanism (driven by the disorder).[47] Next, we use the effective spin-only Hamiltonian and address the question: Does the antiferromagnetic phase exist in a magnetic material that is characterized by a positive-definite spin-exchange coupling between the nearest neighbour lattice sites? As we will see presently, the answer is in the affirmative and it is the spin-orbit interaction that provides the necessary mechanism for the existence of the antiferromagnetic phase in magnetic systems if the exchange couplings are positive. This is significant for it has long been believed, through the works of Néel,[48] Van Vleck,[49] and Anderson,[6] that the exchange coupling parameter in the standard Heisenberg model must be negative for the existence of the antiferromagnetic phase. The paper is organized as follows. In Section II, we introduce a many-electron Hamiltonian that includes electron-phonon interaction. In Section III, we construct effective one-electron states (delocalized as well localized) for periodic crystalline lattices and use the set of localized states to obtain a second-quantization form of the many-electron Hamiltonian, which is specially suitable for insulators. In Section IV, we obtain a variety of effective Hamiltonians for complex materials. In Section V, we use the effective Hamiltonians to study the role of spin-orbit interaction in metal-insulator transitions and magnetic phase transitions. Finally, we close the paper with a brief discussion on the future outlook.

II. MANY-ELECTRON HAMILTONIAN

To obtain the Hamiltonian for a system consisting of N electrons and M nuclei (spin 1/2) in the presence of external electromagnetic fields, we begin with the one-particle Dirac-Pauli equation which reads as follows (see supplementary material, Section I for the derivation of semi-relativistic Hamiltonian[50]):

$$\hat{H} = \frac{1}{2m_0}\left[\left(\vec{p} - q\vec{A}\right)^2 - q\hbar\left(\vec{\sigma}\cdot\vec{B}\right)\right] + q\phi$$
$$+ \frac{\hbar q}{4m_0^2 c^2}\vec{\sigma}\cdot\left[\vec{\nabla}\phi \times \left(\vec{p} - q\vec{A}\right)\right]. \tag{1}$$

We now decompose the scalar and vector potentials as follows: $\phi(\vec{r}) = \phi^{(\mathrm{ext})}(\vec{r}) + \phi^{(\mathrm{int})}(\vec{r})$ and $\vec{A}(\vec{r}) = \vec{A}^{(\mathrm{ext})}(\vec{r}) + \vec{A}^{(\mathrm{int})}(\vec{r}) = \vec{A}^{(\mathrm{ext})}(\vec{r}) + \vec{A}^{(\mathrm{int})}_{\mathrm{space}}(\vec{r}) + \vec{A}^{(\mathrm{int})}_{\mathrm{spin}}(\vec{r})$, where $\phi^{(\mathrm{ext})}(\vec{r})$ and $\vec{A}^{(\mathrm{ext})}(\vec{r})$, respectively, are the scalar and vector potentials due to the external electromagnetic fields. $\phi^{(\mathrm{int})}(\vec{r})$ is the scalar potential, and $\vec{A}^{(\mathrm{int})}_{\mathrm{space}}(\vec{r})$ and $\vec{A}^{(\mathrm{int})}_{\mathrm{spin}}(\vec{r})$ stand, respectively, for the vector potentials due to the spatial and spin degrees of freedom of the dynamic charged particles, the explicit expressions of which, in the frequency-specific Lorentz gauge $(\vec{\nabla}\cdot\vec{A}(\vec{r},\omega) - (i\omega/c^2)\phi(\vec{r},\omega) = 0)$, are as given below (see supplementary material, Section VII for electromagnetic potentials in the Lorentz gauge[50])

$$\phi^{(\mathrm{int})}(\vec{r}) = \sum_{j=1}^{N+M} \frac{q_j}{4\pi\epsilon_0}\frac{\cos\left(\frac{\omega}{c}|\vec{r}-\vec{r}_j|\right)}{|\vec{r}-\vec{r}_j|}, \tag{2}$$

$$\vec{A}^{(\mathrm{int})}_{\mathrm{space}}(\vec{r}) = \frac{\mu_0}{4\pi}\sum_{j=1}^{N+M} \frac{q_j}{m_j}\frac{\cos\left(\frac{\omega}{c}|\vec{r}-\vec{r}_j|\right)}{|\vec{r}-\vec{r}_j|}\vec{p}_j, \tag{3}$$

$$\vec{A}^{(\mathrm{int})}_{\mathrm{spin}}(\vec{r}) = \frac{\mu_0}{4\pi}\sum_{j=1}^{N+M} \cos\left(\frac{\omega}{c}|\vec{r}-\vec{r}_j|\right)\frac{\vec{m}^{(\mathrm{spin})}_j \times (\vec{r}-\vec{r}_j)}{|\vec{r}-\vec{r}_j|^3}. \tag{4}$$

We now use the Lorentz gauge to evaluate the kinetic energy operator as $(\vec{p} - q\vec{A})^2 = p^2 - q(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + q^2A^2 = p^2 - i\hbar(\vec{\nabla}\cdot\vec{A}) + 2\vec{A}\cdot\vec{p} + q^2A^2 = p^2 - (q\hbar\omega/c^2)\phi - 2q\vec{A}\cdot\vec{p} + q^2A^2$ and express the total Hamiltonian as a sum of one-particle Hamiltonians in Eq. (1) as follows:

$$\hat{H} = \sum_{i=1}^{N+M} \frac{p_i^2}{2m_i} - \sum_{i=1}^{N+M} \frac{q_i}{m_i}\vec{A}^{(\mathrm{ext})}(\vec{r}_i)\cdot\vec{p}_i + \sum_{i=1}^{N+M} \frac{q_i^2}{2m_i}\left(\vec{A}^{(\mathrm{ext})}(\vec{r}_i) + \vec{A}^{(\mathrm{int})}(\vec{r}_i)\right)^2$$
$$- \sum_{i=1}^{N+M} \frac{\hbar q_i}{2m_i}\vec{\sigma}_i\cdot\vec{B}^{(\mathrm{ext})}(\vec{r}_i) + \sum_{i=1}^{N+M} q_i\phi^{(\mathrm{ext})}(\vec{r}_i) + \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{ext})}(\vec{r}_i)\times\vec{p}_i\right]$$
$$+ \sum_{i=1}^{N+M} q_i\phi^{(\mathrm{int})}(\vec{r}_i) + \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{int})}(\vec{r}_i)\times\vec{p}_i\right] - \sum_{i=1}^{N+M} \frac{q_i}{m_i}\vec{A}^{(\mathrm{int})}(\vec{r}_i)\cdot\vec{p}_i - \sum_{i=1}^{N+M} \frac{\hbar q_i}{2m_i}\vec{\sigma}_i\cdot\vec{B}^{(\mathrm{int})}(\vec{r}_i)$$
$$- \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{int})}(\vec{r}_i)\times q_i\vec{A}^{(\mathrm{int})}(\vec{r}_i)\right] - \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{ext})}(\vec{r}_i)\times q_i\vec{A}^{(\mathrm{int})}(\vec{r}_i)\right]$$
$$- \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{int})}(\vec{r}_i)\times q_i\vec{A}^{(\mathrm{ext})}(\vec{r}_i)\right] - \sum_{i=1}^{N+M} \frac{\hbar q_i}{4m_i^2 c^2}\vec{\sigma}_i\cdot\left[\vec{\nabla}\phi^{(\mathrm{ext})}(\vec{r}_i)\times q_i\vec{A}^{(\mathrm{ext})}(\vec{r}_i)\right]. \tag{5}$$

Eq. (5) is the complete many-body Hamiltonian for a collection of spin-1/2 charged particles in the presence of external electromagnetic fields. As it stands, Eq. (5) is too general and complex, and therefore it is important to identify terms that may be frequently useful for a variety of materials of interest. For example, the 3rd term in Eq. (5) is quadratic

in the vector potential whereas the 10th–12th terms are a product of spin angular momentum and spin/orbital angular momentum. These quadratic terms may safely be ignored in the first approximation. In 13th–14th terms, the external vector potential $\vec{A}^{(\text{ext})}(\vec{r})$, which is expected to be small in magnitude under the weak-field limit, interacts with the spin via the gradient of the scalar potentials, which is also expected to be small for slowly varying fields, and hence we ignore them here.

As we are here concerned with problems involving electrons, we now substitute the expression for the scalar and vector potentials due to the dynamic electrons from Eqs. (2)–(4) in Eq. (5) and ignore the nuclear kinetic energy (justified under the Born-Oppenheimer scheme) and the nuclear-nuclear repulsion energy which is just a constant number for electronic problems. The simplified operator for correlated electrons is then given as follows:

$$
\begin{aligned}
\hat{H} = \sum_{i=1}^{N} \Bigg\{ & \frac{p_i^2}{2m} - \left(\sum_{j=1}^{M} \frac{z_j a_u^{(1)} \cos\left[\frac{\omega}{c} |\vec{r}_i - \vec{R}_j| \right]}{|\vec{r}_i - \vec{R}_j|} \right) \\
& - e\, \phi^{(\text{ext})}(\vec{r}_i) + \frac{e}{m} \vec{A}^{(\text{ext})}(\vec{r}_i) \cdot \vec{p}_i + 2\mu_B \vec{s}^{(i)} \cdot \vec{B}^{(\text{ext})}(\vec{r}_i) - \frac{e a_u^{(2)}}{2} \vec{s}^{(i)} \cdot \left[\left\{ \vec{\nabla} \phi^{(\text{ext})}(\vec{r}_i) \right\} \times \vec{p}_i \right] \\
& + \left(\sum_{j=1}^{M} \frac{z_j a_u^{(1)} a_u^{(2)}}{2} f(\vec{r}_i, \vec{R}_j) \vec{s}^{(i)} \cdot \left[(\vec{r}_i - \vec{R}_j) \times \vec{p}_i \right] \right) \Bigg\} + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \Bigg\{ \frac{a_u^{(1)}}{2} \frac{\cos\left[\frac{\omega}{c} |\vec{r}_i - \vec{r}_j| \right]}{|\vec{r}_i - \vec{r}_j|} \\
& - \frac{a_u}{4} \left[f(\vec{r}_i, \vec{r}_j) \vec{s}^{(i)} \cdot \left\{ (\vec{r}_i - \vec{r}_j) \times \vec{p}_i \right\} + f(\vec{r}_j, \vec{r}_i) \vec{s}^{(j)} \cdot \left\{ (\vec{r}_j - \vec{r}_i) \times \vec{p}_j \right\} \right] \\
& + \frac{a_u}{2} \frac{\cos\left[\frac{\omega}{c} |\vec{r}_i - \vec{r}_j| \right]}{|\vec{r}_i - \vec{r}_j|^3} \left[\vec{s}^{(i)} \cdot \left\{ (\vec{r}_i - \vec{r}_j) \times \vec{p}_j \right\} + \vec{s}^{(j)} \cdot \left\{ (\vec{r}_j - \vec{r}_i) \times \vec{p}_i \right\} \right] \Bigg\},
\end{aligned}
\tag{6}
$$

where

$$
f(\vec{r}_i, \vec{r}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|^2} \left[\frac{\cos\left(\frac{\omega}{c} |\vec{r}_i - \vec{r}_j| \right)}{|\vec{r}_i - \vec{r}_j|} + \frac{\omega}{c} \sin\left(\frac{\omega}{c} |\vec{r}_i - \vec{r}_j| \right) \right].
$$

Here, $a_u^{(1)} = \frac{e^2}{4\pi\epsilon_0}$, $a_u^{(2)} = \frac{\hbar}{m^2 c^2}$, and $a_u = a_u^{(1)} \times a_u^{(2)}$ (the Planck constant, $h = 2\pi\hbar$; $m = $ the rest mass of the electron, $e = $ the modulus of the electronic charge, $c = $ the speed of light in vacuum, $\mu_B = \frac{e\hbar}{2m} = $ the Bohr magneton, and $\epsilon_0 = $ the dielectric constant in vacuum). In Eq. (6), we have dropped the many-body momentum correlation that arises due to $\vec{A}_{\text{space}}^{(\text{int})}(\vec{r})$ as given in Eq. (3), which may be of importance for diamagnetic materials. The first seven terms in Eq. (6) are one-electron operators and they, respectively, represent the kinetic energy, electron-nucleus attraction (at finite frequency), interaction of electrons with the external scalar potential, interaction of the electronic momentum with the external vector potential, interaction of electron spin with the external magnetic field, the coupling of electronic spin with the linear momentum of the electron that is mediated by the external scalar potential, and the spin-orbit coupling (SOC) in which the spatial angular momentum refers to the axis formed by the coordinate of the electron relative to the coordinate of the nucleus. Other physically distinct mechanisms of SOC are given by the last two terms of Eq. (6) wherein the spatial angular momentum refers to the axis formed by the coordinate of the electron relative to the coordinates of other electrons and therefore these SOCs are in essence mediated by the electron correlations which are expected to be significant particularly for strongly correlated materials. We parenthetically note that the last two terms of the Hamiltonian in Eq. (6), respectively, give rise to the idea of what is frequently known as the spin-own-orbit and spin-other-orbit interactions. Finally, the eighth term of Eq. (6) is the

repulsion between electron-pairs, which is a finite frequency extension of the Coulomb's law of electrostatics. To account for the dynamical nature of the lattice, we follow Bardeen and co-workers[44,45] and introduce a mechanism of the electron-phonon interaction, the final expression of which, in terms of phonon annihilation $\left(b_{\vec{g}\lambda} \right)$ and creation operator $\left(b_{-\vec{g}\lambda}^{\dagger} \right)$, is given as follows (see supplementary material, Section III for the derivation of electron-phonon interactions[50]):

$$
\hat{H}_{\text{electron–phonon}} = \sum_{i=1}^{N} \sum_{\vec{g}, \lambda} \left[\hat{H}_{\{i, \vec{g}, \lambda\}}^{(e-p;a)} + \hat{H}_{\{i, \vec{g}, \lambda\}}^{(e-p;b)} \right] \left(b_{\vec{g}\lambda} + b_{-\vec{g}\lambda}^{\dagger} \right).
\tag{7}
$$

Finally, we add Eq. (7) in Eq. (6) to obtain the complete many-electron Hamiltonian that recognizes the non-adiabatic phonon-related electronic processes in the material.

III. BASE KETS AND SECOND QUANTIZATION

To obtain a second-quantized form of the Hamiltonian, one must first choose a complete set of one-particle base kets and such a choice in a many-electron theory is often dictated by the physical problem at hand. For example, it is frequently convenient to use localized functions (Wannier construction,[51,52] for example) to describe the insulators and poor conductors, whereas the delocalized Bloch waves are generally found useful for conducting materials. In other situations, one may also use a mixed set of kets that include both localized and delocalized functions. We here discuss the explicit construction of a set of effective one-electron quantum states (both localized and delocalized) for a periodic crystalline material, to be used in the second quantization framework. As it is well-known, effective one-electron states

for a periodic lattice take the Bloch's form as follows:

$$\psi_n\left(\vec{r}, \vec{k}\right) = e^{i\vec{k}\cdot\vec{r}} e^{i\phi(\vec{k})} \eta_n\left(\vec{r}, \vec{k}\right), \quad (8)$$

where $\vec{k}$ stands for the Bloch wave vector (real-valued), spanning the first Brillouin zone (FBZ) and $\eta_n(\vec{r}, \vec{k})$ satisfies the periodicity of the lattice, that is, $\eta_n(\vec{r} + \vec{d}, \vec{k}) = \eta_n(\vec{r}, \vec{k})$ where $\vec{d}$ is a lattice vector. $\phi(\vec{k})$ is a phase (real-valued) associated with the kth Bloch state and the integer n stands for a triplet of quantum numbers, defining the energy band. We here adopt the orthonormality condition: $\langle\psi_{n'}(\vec{k}')|\psi_n(\vec{k})\rangle = \delta(\vec{k} - \vec{k}')\,\delta_{nn'}$, which implies $(2\pi)^3\langle\eta_{n'}(\vec{k})|\eta_n(\vec{k})\rangle_V = V\delta_{nn'}$, the integration over the primitive unit cell volume, V. For a particular $\vec{k}$, $\eta_n(\vec{r}, \vec{k})$ is the solution of the following effective one-electron equation:

$$\left[\frac{\hbar^2}{2m}\left(\vec{\nabla} + i\vec{k}\right)^2 + E_n\left(\vec{k}\right) - V_{\text{eff}}\left(\vec{r}\right)\right]\eta_n\left(\vec{r}, \vec{k}\right) = 0, \quad (9)$$

where m is the mass of the electron and $E_n(\vec{k})$ is the allowed electronic band energy. $V_{\text{eff}}(\vec{r})$ in Eq. (9) is the effective potential energy, which may be taken as the sum of electron-nucleus attraction, nucleus-nucleus repulsion and the (non-linear) Hartree-Fock potential, $V_{\text{HF}}(\vec{r})$ or a Kohn-Sham potential of the density functional theory. As one can easily show, $V_{\text{HF}}(\vec{r})$ satisfies the periodicity of the lattice. To solve Eq. (9) algebraically, we expand $|\eta_n(\vec{k})\rangle$ as follows: $|\eta_n(\vec{k})\rangle = \sum_{m=1}^{N} C_{nm}(\vec{k})|\chi_m\rangle$ where the ket $|\chi_m\rangle$ must satisfy the periodicity of the lattice, that is, $\chi_m(\vec{r} + \vec{d}) = \chi_m(\vec{r})$. Assuming orthonormality over the primitive unit cell volume, it is convenient to choose $\langle\vec{r}|\chi_m\rangle = V^{-1/2}\exp(i\vec{g}_m\cdot\vec{r})$, where $\vec{g}_m$ is the reciprocal lattice vector (real-valued). Using $|\chi_m\rangle$ as a basis, we now diagonalize Eq. (9) to obtain the eigenvalues $E_n(\vec{k})$ and the eigenvector elements $C_{nm}(\vec{k})$, and therefore Eq. (8) takes the following form:

$$\psi_n\left(\vec{r}, \vec{k}\right) = V^{-1/2}\sum_{m=1}^{N} C_{nm}\left(\vec{k}\right) e^{i\phi(\vec{k})} e^{i(\vec{k}+\vec{g}_m)\cdot\vec{r}}. \quad (10)$$

Following Wannier,[51] we now construct a linear combination of Eq. (10) as follows:

$$\Phi_{\vec{d}n}(\vec{r}) = \sum_{m=1}^{N} f_{nm}\left(\vec{r} - \vec{d}\right) e^{i\vec{g}_m\cdot\vec{r}}, \quad (11)$$

where

$$f_{nm}\left(\vec{r} - \vec{d}\right) = \frac{1}{(2\pi)^{3/2}}\int_{\text{FBZ}} d^3k\; e^{i\vec{k}\cdot(\vec{r}-\vec{d})} e^{i\phi(\vec{k})} C_{nm}\left(\vec{k}\right), \quad (12)$$

where the vector $\vec{d}$ locates the lattice point at which $\Phi_{\vec{d}n}(\vec{r})$ is centred. Also, the set $\Phi_{\vec{d}n}(\vec{r})$ is ortho-normal over the energy bands as well as the lattice vectors, that is, $\langle\Phi_{\vec{d}'n'}|\Phi_{\vec{d}n}\rangle = \delta_{nn'}\delta_{\vec{d}\vec{d}'}$. Evidently, it is the quantity $C_{nm}(\vec{k})$, and hence $V_{\text{eff}}(\vec{r})$ in Eq. (9) that finally determines the extent to which the function $\Phi_{\vec{d}n}(\vec{r})$ will be localized in the region around $\vec{r} = \vec{d}$. Let us suppose that $\phi(\vec{k}) = 0$ and $C_{nm}(\vec{k})$ is a constant, say, $(2\pi)^{3/2}$, in which case Eqs. (11) and (12) yield: $\Phi_{\vec{d}n}(\vec{r}) = \text{Sinc}(x - d_x)\text{Sinc}(y - d_y)\text{Sinc}(z - d_z)$, where $\pi(x - d_x)\text{Sinc}(x - d_x) = \sin[(2N + 1)\pi(x - d_x)/a_x]$ and a_x is the length of the primitive unit

cell in the Cartesian x-direction. For a general situation, when $C_{nm}(\vec{k})$ is not a constant, $|\Phi_{\vec{d}n}\rangle$ will fundamentally inherit the oscillatory and simultaneously decaying feature of the tail of the Sinc function, albeit in a subtle form, and this, in fact, is necessary to ensure that the set $|\Phi_{\vec{d}n}\rangle$ remains orthogonal over the lattice vectors.[53] In any event, Eqs. (10) and (11), respectively, represent a complete set of delocalized and localized effective one-electron quantum states, which may be used, within the second-quantization framework, to study the electronic properties of metals and insulators, respectively.

As we have noted above, the function $\Phi_{\vec{d}n}(\vec{r})$ in Eq. (11) may exhibit, for a given $V_{\text{eff}}(\vec{r})$ in Eq. (9), an oscillatory and simultaneously decaying feature, away from the lattice point $\vec{r} = \vec{d}$. In a specific application, it may be desirable to suppress this oscillation, particularly in the region beyond the individual primitive unit cell volume. Such a localization, as we discuss below, may be achieved by using an appropriate filter in Eq. (12). An ideal filter, in the present context, would produce a new set of one-electron states, all well-confined in the real space within the primitive unit cells located at various lattice sites. However, a necessary consequence of the filter is that the new set of states will no longer be orthogonal over the lattice vectors $\vec{d}$. If so desired, then, one may use the method of symmetric orthogonalization due to Lowdin[54] and transform the new set to yet another new set of states that are orthonormal over the lattice vectors, $\vec{d}$, as well as the band indices, n. Let us now introduce a filter $\Gamma_{nm}(\vec{k}; \vec{\epsilon})$ and redefine Eq. (12) as shown below

$$\tilde{f}_{nm}\left(\vec{r} - \vec{d}; \Gamma\right) = \frac{1}{(2\pi)^{3/2}}\int_{\text{FBZ}} d^3k\; e^{i\vec{k}\cdot(\vec{r}-\vec{d})}$$
$$\times \Gamma_{nm}\left(\vec{k}; \vec{\epsilon}\right) e^{i\phi(\vec{k})} C_{nm}\left(\vec{k}\right). \quad (13)$$

That is, the essential effect of a filter is to rescale the elements $C_{nm}(\vec{k})$ of Eq. (10), such that the resulting function $\tilde{f}_{nm}(\vec{r} - \vec{d}; \Gamma)$ will have the structure of the Sinc function centred at $\vec{r} = \vec{d}$, superimposed with an envelope, which is decaying with a characteristic length scale as defined by the damping variable $\vec{\epsilon}$ of the filter function, $\Gamma_{nm}(\vec{k}; \vec{\epsilon})$. With $\tilde{f}_{nm}(\vec{r} - \vec{d}; \Gamma)$ in Eq. (13), Eq. (11) produces a non-orthogonal set of one-electron states $\tilde{\Phi}_{\vec{d}n}(\vec{r}; \Gamma)$, which, upon symmetric orthogonalization, defines a new set of one-electron states as follows:

$$\Phi_{\vec{d}n}^{(\text{new})}(\vec{r}; \Gamma) = \sum_{\vec{d}'}(S_n^{-1/2})_{\vec{d}\vec{d}'}\,\tilde{\Phi}_{\vec{d}'n}(\vec{r}; \Gamma), \quad (14)$$

where

$$(S_n)_{\vec{d}\vec{d}'} = \langle\tilde{\Phi}_{\vec{d}n}(\Gamma)|\tilde{\Phi}_{\vec{d}'n}(\Gamma)\rangle. \quad (15)$$

It is easy to verify that $\langle\Phi_{\vec{d}'n'}^{(\text{new})}(\Gamma)|\Phi_{\vec{d}n}^{(\text{new})}(\Gamma)\rangle = \delta_{nn'}\delta_{\vec{d}\vec{d}'}$. We may now use one-electron states in Eq. (14) as a basis to construct a second-quantized form of the many electron Hamiltonian, suitable particularly for insulators. For the symmetric orthogonalization process in Eq. (14) to succeed, we note, the overlap matrix in Eq. (15), if required, must be made non-singular, using, for example, the method of singular value decomposition. The nature of the overlap matrix in Eq. (15) and the consequent localization characteristics of the resulting one-electron states $|\Phi_{\vec{d}n}^{(\text{new})}(\Gamma)\rangle$ in Eq. (14) are

critically dependent upon the choice of the filter function $\Gamma_{nm}(\vec{k}; \vec{\epsilon})$. In what follows, we discuss the possible choices for the filter function that one may introduce in a specific application.

We first note that the filter, beside the damping parameter $\vec{\epsilon}$, is a function of the Bloch wave vector $\vec{k}$ and the indices n and m, as displayed in Eq. (13). In the first approximation, we may consider the filter to be the same for all n and m, that is, $\Gamma_{nm}(\vec{k}; \vec{\epsilon}) = \Gamma(\vec{k}; \vec{\epsilon}) = \exp(\ln[\Gamma(\vec{k}; \vec{\epsilon})])$. Formally, therefore, this filter results by simply adding an imaginary quantity, $-i \ln[\Gamma(\vec{k}; \vec{\epsilon})]$, to the real-valued phase, $\phi(\vec{k})$, of the Bloch states in Eq. (10). For example, the choice $\ln[\Gamma(\vec{k}; \vec{\epsilon})] = -(\epsilon_x^2 k_x^2 + \epsilon_y^2 k_y^2 + \epsilon_z^2 k_z^2)$ amounts to a filter function that is Gaussian in nature. Accordingly, $\tilde{f}_{nm}(\vec{r} - \vec{d})$ in Eq. (13) will exhibit a curve that is centred at $\vec{r} = \vec{d}$ with a Gaussian-like profile, and therefore $|\tilde{\Phi}_{\vec{d}n}\rangle$, resulting from Eq. (11), would be localized like a Gaussian, within the primitive unit cell, located at the lattice point $\vec{d}$. We may now use this $|\tilde{\Phi}_{\vec{d}n}\rangle$ in Eq. (14) to obtain a new set of orthogonal one-electron states.

As an alternative, let us choose an arbitrary function, $h_n(\vec{r})$, which is localized within a primitive unit cell, located at the lattice point $\vec{d}$. Let us now obtain the filter, using the information available in Eq. (10), as defined below

$$\Gamma_{nm}(\vec{k}) = \sum_{p=1}^{N} \frac{C_{pm}(\vec{k})}{C_{nm}(\vec{k})} \langle \psi_P(\vec{k}) | h_n \rangle. \quad (16)$$

As we have noted above, the effect of the filter is to simply rescale $C_{nm}(\vec{k})$ of Eq. (10) and therefore we have the following expression for a non-orthogonal one-electron states of the Bloch class, emerging from Eq. (10)

$$\tilde{\psi}_n(\vec{r}, \vec{k}) = V^{-1/2} \sum_{m=1}^{N} \Gamma_{nm}(\vec{k}) C_{nm}(\vec{k}) e^{i\phi(\vec{k})} e^{i(\vec{k}+\vec{g}_m)\cdot\vec{r}}. \quad (17)$$

With Eq. (16), Eq. (17) takes the following form:

$$\tilde{\psi}_n(\vec{r}, \vec{k}) = \sum_{p=1}^{N} a_{np}(\vec{k}) \psi_P(\vec{r}, \vec{k}), \quad (18)$$

where $a_{np}(\vec{k}) = \langle \psi_p(\vec{k}) | h_n \rangle$. As Eq. (18) reveals, the effect of the filter as given in Eq. (16) is to linearly transform the orthogonal set of Bloch states in Eq. (10) to a non-orthogonal set of the same Bloch class. We now use the method of symmetric orthogonalization[54] to obtain, using $\tilde{\psi}_n(\vec{r}, \vec{k})$ in Eq. (18), a new set of orthogonal states of the Bloch class as follows:

$$\psi_n^{(\text{new})}(\vec{r}, \vec{k}) = \sum_{p=1}^{N} (S_{\vec{k}}^{-1/2})_{np} \tilde{\psi}_P(\vec{r}, \vec{k}), \quad (19)$$

where

$$(S_{\vec{k}})_{np} = \langle \tilde{\psi}_n(\vec{k}) | \tilde{\psi}_P(\vec{k}) \rangle. \quad (20)$$

Finally, we use Eq. (19) to construct the Wannier-like one-electron states, localized at the lattice point $\vec{d}$, as given below

$$\Phi_{\vec{d}n}^{(\text{new})}(\vec{r}) = \int_{\text{FBZ}} d^3k \, e^{-i\vec{k}\cdot\vec{d}} \psi_n^{(\text{new})}(\vec{r}, \vec{k}). \quad (21)$$

We may now use $|\Phi_{\vec{d}n}^{(\text{new})}\rangle$ in Eq. (21) as a basis to construct a second-quantized form of the many electron Hamiltonian. Now, if we restrict the summation in Eqs. (16), (18), and (19) to a subset, J, of the energy bands (that is, $p = 1, J$), where J is less than N, and accordingly the index n in Eqs. (18) and (19) is restricted to the number J, then we will obtain the class of localized Wannier-like states, as advanced by Vanderbilt and co-workers.[52] It should, however, be noted that the symmetric orthogonalization process for a subset J of the energy bands, as shown in Eq. (19), may sometimes fail due to the presence of singularities in the overlap matrix in Eq. (20). A notable example of the occurrence of such singular overlap is the topological insulator.[52,55] In such circumstances, the filter function as given in Eq. (16) may not be optimal. As yet another alternative, one may use other filter techniques such as those based on distributed approximating functionals, as pioneered by Kouri and co-workers,[56,57] to obtain a set of orthonormal one-electron states, which are well-localized within the primitive unit cell. We parenthetically note that the use of filters to suppress the oscillatory behaviour and localize the Wannier-like one-electron base kets completely within the volume of the unit cell, located at various lattice sites, is not essential, though it may be desirable in specific instances. In any event, the complete set of orthonormal one-electron base kets as given in Eq. (11), the localization features of which are determined, if the phase $\phi(\vec{k})$ is zero, solely by the coefficients, $C_{nm}(\vec{k})$, which are the eigenvector elements of Eq. (9), would, in general, continue to serve the purpose, *we stress*.

Finally, assuming Eq. (11) or Eq. (14) or Eq. (21) as a basis, we obtain the second-quantized form of the Hamiltonian in Eqs. (6) and (7), which is suitable, in particular, for insulators. The details of the second quantization are presented in the supplementary material (see supplementary material, Section IV for the derivation of the second-quantized Hamiltonian[50]) and the final results are summarized in Tables I and II.

IV. EFFECTIVE HAMILTONIANS

The Hamiltonian as given in Tables I and II is still too complex and it may not be necessary to include all the terms in a specific application. In the following, we outline a set of approximations for the Hamiltonian in Tables I and II, reduce the Hilbert space and finally derive a number of effective Hamiltonians suitable for a variety of materials.

A. Strongly correlated narrow energy band systems

We here advance, in the spirit of the classic works of Hubbard[1] and others,[2,3,6,9] a simplification scheme for the Hamiltonian in Tables I and II which may be suitable for materials that display strong electron correlations among a set of bands within a narrow energy range. Let us first consider the one electron operators in Table I. The 1st term represents a combination of the kinetic energy, electron-nucleus attraction, the coupling of electronic momentum with

TABLE I. One-electron operators of the total Hamiltonian.

S.No.	Terms of the Hamiltonian	Remark[a]
1	$\sum_{\vec{d}_1, n_1} t^{(1)}_{\vec{d}_1 n_1} \, \hat{n}_{\vec{d}_1 n_1}$	$\hat{H}_{\text{Diag}}$
2	$\sum_{\substack{\vec{d}_1, \sigma_1, \\ n_1 \neq n_2}} t^{(2)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_1 n_2\}} c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_1 \sigma_1; n_2}$	$\hat{H}_{\text{BT}}$
3	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2, \sigma_1}} t^{(3)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\}} c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_1; n_2}$	$\hat{H}_{\text{Hopping}}$
4	$\sum_{\vec{d}_1, n_1} t^{(4)}_{\vec{d}_1 n_1} \, s^z_{\vec{d}_1 n_1}$	$\hat{H}_{\text{Zeeman}}$
5	$\sum_{\vec{d}_1, n_1 \neq n_2} t^{(5)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_1 n_2\}} \left(c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_1 \alpha; n_2} - c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_1 \beta; n_2} \right)$	
6	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2,}} t^{(6)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\}} \left(c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_2 \alpha; n_2} - c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_2 \beta; n_2} \right)$	
7	$\sum_{\vec{d}_1, n_1} t^{(7)}_{\vec{d}_1 n_1} \, s^z_{\vec{d}_1 n_1}$	$\hat{H}_{\text{SOC1}}$
8	$\sum_{\vec{d}_1, n_1} t^{(8)}_{\vec{d}_1 n_1} \, s^+_{\vec{d}_1 n_1}$	
9	$\sum_{\vec{d}_1, n_1} t^{(9)}_{\vec{d}_1 n_1} \, s^-_{\vec{d}_1 n_1}$	
10	$\sum_{\vec{d}_1, n_1 \neq n_2} t^{(10)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_1 n_2\}} \left(c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_1 \alpha; n_2} - c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_1 \beta; n_2} \right)$	
11	$\sum_{\vec{d}_1, n_1 \neq n_2} t^{(11)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_1 n_2\}} c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_1 \beta; n_2}$	
12	$\sum_{\vec{d}_1, n_1 \neq n_2} t^{(12)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_1 n_2\}} c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_1 \alpha; n_2}$	
13	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} t^{(13)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\}} \left(c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_2 \alpha; n_2} - c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_2 \beta; n_2} \right)$	
14	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} t^{(14)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\}} c^{\dagger}_{\vec{d}_1 \alpha; n_1} c_{\vec{d}_2 \beta; n_2}$	
15	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} t^{(15)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\}} c^{\dagger}_{\vec{d}_1 \beta; n_1} c_{\vec{d}_2 \alpha; n_2}$	
16	$\sum_{\substack{\vec{d}_1, \vec{d}_2, \\ n_1, n_2, \\ \sigma_1}} \sum_{\vec{g}, \lambda} w^{(8)}_{\{\vec{d}_1 n_1\} \mid \{\vec{d}_2 n_2\} \mid \mid \{\vec{g} \lambda\}} \left(b_{\vec{g} \lambda} + b^{\dagger}_{\vec{g} \lambda} \right) c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_1; n_2}$	$\hat{H}_{\text{EP}}$
17	$\sum_{\substack{\vec{d}_1, \vec{d}_2, \\ n_1, n_2, \\ \sigma_1, \sigma_2}} \sum_{\vec{g}, \lambda} w^{(9)}_{\{\vec{d}_1 \sigma_1; n_1\} \mid \{\vec{d}_2 \sigma_2; n_2\} \mid \mid \{\vec{g} \lambda\}} \left(b_{\vec{g} \lambda} + b^{\dagger}_{\vec{g} \lambda} \right) c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_2; n_2}$	$\hat{H}_{\text{SP}}$

[a] $\hat{H}_{\text{Diag}}$ = diagonal energy, $\hat{H}_{\text{BT}}$ = electronic band transition at a lattice site,
$\hat{H}_{\text{Hopping}}$ = electron hoping among the lattice sites, $\hat{H}_{\text{SOC1}}$ = spin-orbit coupling
$\hat{H}_{\text{Zeeman}}$ = interactions of electron spin with the external magnetic field,
$\hat{H}_{\text{EP}}$ = electron-phonon interaction and $\hat{H}_{\text{SP}}$ = spin-phonon interactions.
$\vec{d}$ = lattice vector, n = band index and σ = spin.

the external vector potential and the acceleration of electron due to the external scalar potential. As the bands belong to a narrow energy range, the term $t^{(1)}_{\vec{d}_1 n_1}$ in the 1st term is not expected to vary appreciably when the lattice vector $\vec{d}_1$ and the band n_1 change and therefore it may be approximated as a constant. With a constant $t^{(1)}_{\vec{d}_1 n_1}$, the number operator $\hat{n}_{\vec{d}_1 n_1}$, when summed over $\vec{d}_1$ and n_1, measures the total number of electrons within the narrow energy range. Consequently, the 1st term would effectively give a constant energy contribution to the total Hamiltonian which we can safely ignore from further considerations. Physically, this means that there is no escape for electrons from the band belonging to the narrow energy range. The 2nd and 3rd terms, respectively, stand for the inter-band electronic transitions (within the narrow energy range under study) at the same lattice point (a non-adiabatic process) and the electron hopping from one lattice point to the other, both are mediated by a number of sources such as the electron-nucleus attraction, the external scalar potential,

and the external vector potential (see supplementary material, Section IV for the detailed expression[50]). The 2nd term may be ignored if we consider only adiabatic processes in the material, whereas the hopping term gets simplified if there is no external electromagnetic field. Terms 4th, 5th, and 6th in Table I display the interactions of external magnetic field with the spin angular momentum of electrons; of these the 5th and 6th terms are non-vanishing only when the external magnetic field is spatially dispersive (see supplementary material, Section IV for the detailed expression[50]). And therefore, in the first approximation, we may assume the external magnetic field to be spatially non-dispersive ($t^{(4)}$ is then simply equal to $2\mu_B B^{(\text{ext})}$) and accordingly we retain only the 4th term. Terms from 7th to 15th stand for a variety of physical processes that arise due to the interaction of spin with the spatial motion of electrons. Of these, the 7th-9th terms refer to the Thomas precession of the individual spins interacting with the internal magnetic field originating from the orbital motion of the charged particles and they are therefore analogous to the

TABLE II. Two-electron operators of the total Hamiltonian.

S.No.	Terms of the Hamiltonian	Remark[a]
1	$\sum_{\vec{d}_1 n_1} u^{(1)}_{\vec{d}_1 n_1} \hat{n}_{\vec{d}_1 \alpha; n_1} \hat{n}_{\vec{d}_1 \beta; n_1}$	$\hat{H}_{\text{Corr}}$
2	$\sum_{\substack{\vec{d}_1, \sigma_1, \sigma_2, \\ n_1 \neq n_2}} u^{(2)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_1 n_2\}} \hat{n}_{\vec{d}_1 \sigma_1; n_1} \hat{n}_{\vec{d}_1 \sigma_2; n_2}$	
3	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2 \\ \sigma_1, \sigma_2}} u^{(3)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} \hat{n}_{\vec{d}_1 \sigma_1; n_1} \hat{n}_{\vec{d}_2 \sigma_2; n_2}$	
4	$-\sum_{\substack{\vec{d}_1, \sigma_1, \sigma_2, \\ n_1 \neq n_2,}} u^{(4)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_1 n_2\}} c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_1 \sigma_2; n_1} c^{\dagger}_{\vec{d}_1 \sigma_2; n_2} c_{\vec{d}_1 \sigma_1; n_2}$	
5	$-\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2 \\ \sigma_1, \sigma_2}} u^{(5)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_1 \sigma_2; n_1} c^{\dagger}_{\vec{d}_2 \sigma_2; n_2} c_{\vec{d}_2 \sigma_1; n_2}$	
6	$\sum_{\vec{d}_1, n_1 \neq n_2} \left(u^{(6)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_1 n_2\}} + u^{(7)}_{\{\vec{d}_1 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_1 n_2} s^{z}_{\vec{d}_1 n_1}$	$\hat{H}_{\text{SOC2}}$
7	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} \left(u^{(8)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} + u^{(9)}_{\{\vec{d}_2 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_2 n_2} s^{z}_{\vec{d}_1 n_1}$	
8	$\sum_{\vec{d}_1, n_1 \neq n_2} \left(u^{(10)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_1 n_2\}} + u^{(11)}_{\{\vec{d}_1 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_1 n_2} s^{+}_{\vec{d}_1 n_1}$	
9	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} \left(u^{(12)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} + u^{(13)}_{\{\vec{d}_2 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_2 n_2} s^{+}_{\vec{d}_1 n_1}$	
10	$\sum_{\vec{d}_1, n_1 \neq n_2} \left(u^{(14)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_1 n_2\}} + u^{(15)}_{\{\vec{d}_1 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_1 n_2} s^{-}_{\vec{d}_1 n_1}$	
11	$\sum_{\substack{\vec{d}_1 \neq \vec{d}_2, \\ n_1, n_2}} \left(u^{(16)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} + u^{(17)}_{\{\vec{d}_2 n_2\}|\{\vec{d}_1 n_1\}} \right) \hat{n}_{\vec{d}_2 n_2} s^{-}_{\vec{d}_1 n_1}$	

[a] $\hat{H}_{\text{Corr}}$ = electron-pair repulsion and $\hat{H}_{\text{SOC2}}$ = spin-orbit interaction.
$\vec{d}$ = lattice vector, n = band index and σ = spin.

standard $\vec{l} \cdot \vec{s}$ coupling in the atomic system. We must retain these terms to study the effects of the interaction between the spatial and spin angular momenta on material properties. Analogous to the 3rd term, 10th-12th terms describe the inter-band transitions (nonadiabatic) involving spins ($\alpha \to \alpha$, $\beta \to \beta$, $\beta \to \alpha$ and $\alpha \to \beta$) occurring at a given lattice point and hence may be ignored in the first approximation. The 13th-15th terms give a further mechanism of hopping from one lattice point to another with and without spin-flip processes that are mediated by the spin-orbit coupling, which we ignore here. Finally, 16th and 17th terms, respectively, provide the mechanism of electron-phonon and spin-phonon couplings, of which the former plays an important role in the charge

transport processes and the latter is significant for magnetic properties of matter and therefore we consider them here in the Hamiltonian. We next consider the terms that involve the coordinates of two-electron as given in Table II. In general, we intuitively expect the repulsion among electrons belonging to the same lattice site and the same band, which the 1st term in Table II represents, to be much more profound in comparison to other processes involving two-electrons. And hence, we may neglect Table II, except the 1st term, completely. Finally, the Hamiltonian may be further simplified if we consider the interactions only between the neighbouring lattice points. With the series of approximations outlined above, a much simpler effective Hamiltonian is given below

$$
\hat{H} = \sum_{\substack{\langle \vec{d}_1, \vec{d}_2 \rangle \\ n_1, n_2, \sigma_1}} t_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}} c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_1; n_2} + \sum_{\vec{d}_1 n_1} u_{\vec{d}_1 n_1} \hat{n}_{\vec{d}_1 \alpha; n_1} \hat{n}_{\vec{d}_1 \beta; n_1} + 2\mu_B B^{(\text{ext})} \sum_{\vec{d}_1, n_1} s^{z}_{\vec{d}_1 n_1} + \sum_{\vec{d}_1, n_1} \Lambda^{(z)}_{\vec{d}_1 n_1} s^{z}_{\vec{d}_1 n_1}
$$

$$
+ \sum_{\vec{d}_1, n_1} \Lambda_{\vec{d}_1 n_1} s^{+}_{\vec{d}_1 n_1} + \sum_{\vec{d}_1, n_1} \Lambda^{*}_{\vec{d}_1 n_1} s^{-}_{\vec{d}_1 n_1} + \sum_{\substack{\vec{d}_1, \vec{d}_2, \\ n_1, n_2, \\ \sigma_1}} \sum_{\vec{g}, \lambda} \epsilon^{(ep)}_{\{\vec{d}_1 n_1\}|\{\vec{d}_2 n_2\}\|\{\vec{g} \lambda\}} \left(b_{\vec{g} \lambda} + b^{\dagger}_{\vec{g} \lambda} \right) c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_1; n_2}
$$

$$
+ \sum_{\substack{\vec{d}_1, \vec{d}_2, \\ n_1, n_2, \\ \sigma_1, \sigma_2}} \sum_{\vec{g}, \lambda} \Lambda^{(ep)}_{\{\vec{d}_1 \sigma_1; n_1\}|\{\vec{d}_2 \sigma_2; n_2\}\|\{\vec{g} \lambda\}} \left(b_{\vec{g} \lambda} + b^{\dagger}_{\vec{g} \lambda} \right) c^{\dagger}_{\vec{d}_1 \sigma_1; n_1} c_{\vec{d}_2 \sigma_2; n_2},
\tag{22}
$$

where the symbol $\langle \vec{d}_1, \vec{d}_2 \rangle$ in Eq. (22) means that the inter-site hopping takes place only between the neighbouring lattice points. To be consistent with the standard notation in the literature, we have changed the symbols while writing Eq. (22)

as follows: (a) $t^{(3)} = t$, (b) $u^{(1)} = u$, (c) $t^{(4)} = 2\mu_B B^{(\text{ext})}$, (d) $t^{(7)} = \Lambda^{(z)}$, (e) $t^{(8)} = \Lambda$, (f) $t^{(9)} = \Lambda^{*}$, (g) $w^{(8)} = \epsilon^{(ep)}$, and (h) $w^{(9)} = \Lambda^{(ep)}$. Λ^{*} is the complex conjugate of Λ. We note that the Hamiltonian in Eq. (22), in the absence of phonons

and spin-orbit couplings, reduces to the Hubbard model for strongly correlated electrons where the symbols t and u, respectively, stand for the hopping and electron repulsion.[1] Eq. (22) thus represents a minimal extension of the Hubbard model,[1] which may be fruitfully utilized for practical studies on complex materials.

B. Effective spin-only Hamiltonian

To study the magnetic properties of complex materials, it is frequently desired to have a Hamiltonian that involves only the spin degree of freedom of electrons (or quasi-particles), and that, at the same time, includes other essential physical processes of interest in magnetism. We implement such a program here by a systematic reduction of the Hamiltonian in Tables I and II. The reduction program, in essence, follows the classic works of Heisenberg and others,[4–7,58] but it differs in the detailed physical content of the Hamiltonian we advance here. As detailed in the supplementary material (see supplementary material, Section V for the derivation of the spin-only Hamiltonian[50]), the final expression for the effective spin-only Hamiltonian takes the following form:

$$
\hat{H}_{\text{spin}}^{(\text{eff})} = - \sum_{\vec{d}_1 \neq \vec{d}_2} \sum_{i \in x, y, z} J_{\vec{d}_1 \vec{d}_2}^{(i)} S_{\vec{d}_1}^i S_{\vec{d}_2}^i + \sum_{\vec{d}_1} \left[\vec{\Lambda}_{\vec{d}_1} + 2\mu_B \, \vec{B}^{(\text{ext})} + \left\{ \sum_{\vec{g}\lambda} \vec{\Omega}_{\vec{d}_1 \vec{g}\lambda} \left(b_{\vec{g}\lambda} + b_{\vec{g}\lambda}^{\dagger} \right) \right\} \right] \cdot \vec{S}_{\vec{d}_1}
$$
$$
+ \sum_{\vec{d}_1 \neq \vec{d}_2} \vec{D}_{\vec{d}_1 \vec{d}_2} \cdot \left[\vec{S}_{\vec{d}_1} \times \vec{S}_{\vec{d}_2} \right] + \sum_{i \neq j \in x, y, z} \sum_{\vec{d}_1 \neq \vec{d}_2} \Gamma_{\vec{d}_1 \vec{d}_2}^{i,j} S_{\vec{d}_1}^i S_{\vec{d}_2}^j, \tag{23}
$$

where $J_{\vec{d}_1 \vec{d}_2}^{(i)} = J_{\vec{d}_1 \vec{d}_2}^{(\text{dir})} - J_{\vec{d}_1 \vec{d}_2}^{(\text{ind})} - \Gamma_{\vec{d}_1 \vec{d}_2}^{i,i}$. $\vec{D}_{\vec{d}_1 \vec{d}_2}$ and $\Gamma_{\vec{d}_1 \vec{d}_2}^{i,j}$, respectively, are the antisymmetric and symmetric anisotropic spin exchange involving a pair of lattice sites.[7,58,59] $\vec{B}^{(\text{ext})}$ is the external magnetic field and $\vec{\Omega}_{\vec{d}_1 \vec{g}\lambda}$ stands for the spin-phonon coupling energy. The term $\vec{\Lambda}_{\vec{d}_1} \cdot \vec{S}_{\vec{d}_1}$ in Eq. (23) arises due to the Thomas precession of the individual spins interacting with the internal magnetic field originating from the orbital motion of the charged particles and therefore $\vec{\Lambda}_{\vec{d}_1}$ is analogous to the standard spin-orbit coupling energy of the atomic system. To our knowledge, the importance of $\vec{\Lambda}_{\vec{d}_1} \cdot \vec{S}_{\vec{d}_1}$ has not been fully recognized in the literature. Eq. (23) represents a generic spin-only Hamiltonian that may fruitfully be utilized in a practical study on magnetic materials. A remark on the sign of $J_{\vec{d}_1 \vec{d}_2}$ in Eq. (23) is in order here. $J_{\vec{d}_1 \vec{d}_2}^{(\text{dir})}$ is related to $w_{\{\vec{d}_1 n_1\}\{\vec{d}_2 n_2\}|\{\vec{d}_1 n_1\}\{\vec{d}_2 n_2\}}^{(10)}$ (see supplementary material, Eqs. (66), (86), and (94)[50]) which is given as follows:

$$
w^{(10)} = \left\langle \{\vec{d}_1 n_1\}^{(i)} \{\vec{d}_2 n_2\}^{(j)} \left| \frac{a_u^{(1)}}{2} \frac{\cos\left[\frac{\omega}{c}|\vec{r}_i - \vec{r}_j|\right]}{|\vec{r}_i - \vec{r}_j|} \right| \right.
$$
$$
\left. \times \{\vec{d}_1 n_1\}^{(j)} \{\vec{d}_2 n_2\}^{(i)} \right\rangle. \tag{24}
$$

The one-particle Wannier state $\left|\vec{d}n\right\rangle$ appearing in Eq. (24) is expected to be strongly localized at the lattice point $\vec{d}$. As an example of a localized state, let us consider the sinc function, which in one dimension reads as $e^{i\theta} \frac{1}{|d^{(x)} - x_i|} \sin\left(\frac{|d^{(x)} - x_i|}{L_x}\right)$ where $d^{(x)}$ is the x-component of the lattice vector $\vec{d}$, x_i is the x-coordinate of the ith electron and L_x is much less than the lattice constant. In fact, $L_x \to 0$ limit will yield the ideal localization. It is then clear that the dominant contribution to the integral in Eq. (24) will come from the values of the integrand in the small region surrounding the lattice points, and in this small region the frequency-modulated Coulomb repulsion and the product of four sinc functions, for example, should be positive definite. As a result, $w^{(10)}$ in Eq. (24) and hence $J_{\vec{d}_1 \vec{d}_2}^{(\text{dir})}$ is expected to be a positive quantity.

Furthermore, the indirect exchange coupling $J_{\vec{d}_1 \vec{d}_2}^{(\text{ind})}$ here arises from the second-order perturbation correction and therefore the magnitude of $J_{\vec{d}_1 \vec{d}_2}^{(\text{ind})}$ is expected to be smaller than the magnitude of $J_{\vec{d}_1 \vec{d}_2}^{(\text{dir})}$, at least for insulators and poor conductors. That means, the total exchange coupling $J_{\vec{d}_1 \vec{d}_2} = J_{\vec{d}_1 \vec{d}_2}^{(\text{dir})} - J_{\vec{d}_1 \vec{d}_2}^{(\text{ind})}$ is expected to be a positive quantity. This is in contrast to the interpretation of $J_{\vec{d}_1 \vec{d}_2}$ in the Heisenberg model[4,5] where it is treated both as a positive entity and a negative entity. We finally note that Eq. (23), in the absence of spin-orbit and spin-phonon couplings, reduces to the Heisenberg model for magnetic materials.[4–6]

V. APPLICATIONS

As definite applications of effective Hamiltonians presented above, we now consider two simple problems of complex materials wherein the role of spin-orbit interactions is manifestly distinct and non-trivial. In Section V A below, we study a simplified one-dimensional form of the Hamiltonian for strongly correlated materials as given in Eq. (22) and address the question if the spin-orbit interaction provides a possible route for metal-insulator transition. In Section V B, we use a simplified one-dimensional form of the spin-only Hamiltonian as given in Eq. (23) and demonstrate the spin-orbit interaction to be a reason for the existence of the antiferromagnetic phase in materials that are characterized by a positive spin-exchange couplings between the nearest neighbour lattice points.

A. Spin-orbit interaction: Metal-insulator transition

We consider an one-dimensional from of the Hamiltonian in Eq. (22) with nearest neighbour hopping interaction wherein the system is half-filled (that is, the number of lattice points is equal to the number of unpaired electrons) and the phonon-related processes are absent. In such

a situation, the Hamiltonian takes the following simple form:

$$\hat{H} = t \sum_{m=1}^{N} \sum_{\sigma} c_{m\sigma}^{\dagger} c_{m+1\sigma}$$
$$+ t^* \sum_{m=1}^{N} \sum_{\sigma} c_{m+1\sigma}^{\dagger} c_{m\sigma} + u \sum_{m=1}^{N} \hat{n}_{m\alpha} \hat{n}_{m\beta}$$
$$+ \left(\frac{\Lambda^{(z)}}{2} + \mu_B B^{(ext)} \right) \sum_{m=1}^{N} \left(c_{m\alpha}^{\dagger} c_{m\alpha} - c_{m\beta}^{\dagger} c_{m\beta} \right)$$
$$+ \Lambda \sum_{m=1}^{N} c_{m\alpha}^{\dagger} c_{m\beta} + \Lambda^* \sum_{m=1}^{N} c_{m\beta}^{\dagger} c_{m\alpha}. \tag{25}$$

Notably, the Hamiltonian in Eq. (25) carries a simplified treatment of SOC (represented by the symbol Λ), in the absence of which it reduces to the standard one-dimensional Hubbard model in the presence of the external magnetic field.[1] To get an insight into the nature of metal-insulator transition, we compute the electronic band-gap as a function of a dimensionless variable that depends upon the spin-orbit coupling. The third term of the Hamiltonian in Eq. (25), which represents the electron pair repulsion at a lattice point, is quadratic in the one-particle density operator and this

makes the exact diagonalization of the Hamiltonian a difficult mathematical task. To circumvent this, we here use the mean field approximation as explained below. Let us first consider the following operator identity involving the product of two number operators:

$$\hat{n}_{m\alpha} \hat{n}_{m\beta} = \hat{n}_{m\alpha} \langle \hat{n}_{m\beta} \rangle + \hat{n}_{m\beta} \langle \hat{n}_{m\alpha} \rangle - \langle \hat{n}_{m\alpha} \rangle \langle \hat{n}_{m\beta} \rangle$$
$$+ [\langle \hat{n}_{m\alpha} \rangle - \hat{n}_{m\alpha}][\langle \hat{n}_{m\beta} \rangle - \hat{n}_{m\beta}]. \tag{26}$$

In the mean field approximation, the last term that represents a product of fluctuations in the densities is negligible.[1] We also assume $\langle \hat{n}_{m\sigma} \rangle = n_{\sigma}$ for all lattice indices m. Next, we introduce the Fourier transformation of the fermionic operators as below

$$c_{m\sigma}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{k \in B.Z.} c_{k\sigma}^{\dagger} e^{-ikd_m}$$

and

$$c_{m\sigma} = \frac{1}{\sqrt{N}} \sum_{k \in B.Z.} c_{k\sigma} e^{ikd_m} \tag{27}$$

where $d_m = ma$ with m = integer and a = lattice constant. We now substitute Eqs. (26) and (27) in Eq. (25) and use the definition of the number operator $\hat{n}_{k\sigma} = c_{k\sigma}^{\dagger} c_{k\sigma}$ to obtain the Hamiltonian in Eq. (25) in the following form:

$$\hat{H} = \sum_{k \in B.Z.} \sum_{\sigma} \left(te^{ika} + t^* e^{-ika} \right) \hat{n}_{ka} + un_{\alpha} \sum_{k \in B.Z.} \hat{n}_{k\beta} + un_{\beta} \sum_{k \in B.Z.} \hat{n}_{k\alpha} - D(T)$$
$$+ \left(\frac{\Lambda^{(z)}}{2} + \mu_B B^{(ext)} \right) \sum_{k \in B.Z.} \left(\hat{n}_{k\alpha} - \hat{n}_{k\beta} \right) + \Lambda \sum_{k \in B.Z.} c_{k\alpha}^{\dagger} c_{k\beta} + \Lambda^* \sum_{k \in B.Z.} c_{k\beta}^{\dagger} c_{k\alpha} \tag{28}$$
$$= \sum_{k \in B.Z.} \left[te^{ika} + t^* e^{-ika} + \frac{\Lambda^{(z)}}{2} + \mu_B B^{(ext)} + u\frac{n}{2} + u\frac{m}{2} \right] \hat{n}_{k\alpha}$$
$$+ \sum_{k \in B.Z.} \left[te^{ika} + t^* e^{-ika} - \frac{\Lambda^{(z)}}{2} - \mu_B B^{(ext)} + u\frac{n}{2} - u\frac{m}{2} \right] \hat{n}_{k\beta} + \Lambda \sum_{k \in B.Z.} c_{k\alpha}^{\dagger} c_{k\beta} + \Lambda^* \sum_{k \in B.Z.} c_{k\beta}^{\dagger} c_{k\alpha}. \tag{29}$$

In Eq. (28), $D(T) = u \sum_{m=1}^{N} \langle \hat{n}_{m\alpha} \rangle \langle \hat{n}_{m\beta} \rangle$ may be considered as a constant energy term and hence we have neglected it completely. To go from Eq. (28) to Eq. (29), we have introduced $n_{\alpha} + n_{\beta} = n$ and $n_{\beta} - n_{\alpha} = m = -2 \langle s^z \rangle$, where n and m represent the average number of electrons at each lattice site and the effective spin magnetic moment (dimensionless) along the z direction at each lattice site, respectively. The term t in Eq. (29) is related to the hopping probability amplitude which, in general, is a complex number $(t_R + it_I)$ and hence we write $te^{ika} + t^* e^{-ika} = 2 \times (t_R \cos ka - t_I \sin ka)$ and simplify Eq. (29) as follows:

$$\hat{H} = \sum_{k \in B.Z.} A_k \hat{n}_{k\alpha} + \sum_{k \in B.Z.} B_k \hat{n}_{k\beta} + \Lambda \sum_{k \in B.Z.} c_{k\alpha}^{\dagger} c_{k\beta} + \Lambda^* \sum_{k \in B.Z.} c_{k\beta}^{\dagger} c_{k\alpha}, \tag{30}$$

$$\text{with} \quad A_k = \left[2 \times (t_R \cos ka - t_I \sin ka) + \frac{\Lambda^{(z)}}{2} + \mu_B B^{(ext)} + u\frac{n}{2} + u\frac{m}{2} \right], \tag{31}$$

and

$$B_k = \left[2 \times (t_R \cos ka - t_I \sin ka) - \frac{\Lambda^{(z)}}{2} - \mu_B B^{(ext)} + u\frac{n}{2} - u\frac{m}{2} \right]. \tag{32}$$

We note that the Hamiltonian in Eq. (30) is now fully decoupled in the k-space. To diagonalize Eq. (30) for a given wave vector k, we choose the base kets to be $c_{k\alpha}^{\dagger} |vac\rangle$ and $c_{k\beta}^{\dagger} |vac\rangle$ and consequently the Hamiltonian in Eq. (30) takes the form of a 2×2 matrix whose eigenvalues are as given below

$$\lambda_k^{\pm} = \frac{1}{2}\left[(A_k + B_k) \pm \sqrt{(A_k + B_k)^2 - 4\left(A_k B_k - |\Lambda|^2\right)} \right],$$ (33)

$$\implies \epsilon_k^{\pm} = 2 \times (\tilde{t}_R \cos ka - \tilde{t}_I \sin ka) + \frac{1}{2}n \pm \sqrt{\left(\tilde{\Lambda}^{(z)} + \tilde{B} + \frac{m}{2}\right)^2 + \tilde{\Lambda}^2},$$ (34)

where $\epsilon_k^{\pm} = \lambda_k^{\pm}/u$, $\tilde{t}_R = t_R/u$, $\tilde{t}_I = t_I/u$, $\tilde{\Lambda}^{(z)} = \Lambda^{(z)}/2u$, $\tilde{B} = \mu_B B^{(\text{ext})}/u$, and $\tilde{\Lambda} = |\Lambda|/u$. We now compute the band gap to ascertain if the spin-orbit coupling can lead to the metal-insulator transition. It is clear from Eq. (34) that $\epsilon_k^+ > \epsilon_k^-$; that is, ϵ_k^+ and ϵ_k^-, respectively, refer to the energies of the upper and lower bands. The band gap will then be given by the difference of the minimum of ϵ_k^+ and the maximum of ϵ_k^-. Upon differentiating Eq. (34) with respect to (ka) and equating to zero, we find the extrema to be of following types.

Type-1: If $\tilde{t}_R > 0$ and $\tilde{t}_I > 0$ and if $\tilde{t}_R > 0$ and $\tilde{t}_I < 0$, then we have the following solutions for the extrema (l = integer):

$$ka = l\pi + \sin^{-1}\left(-\frac{\tilde{t}_I}{\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2}}\right) = l\pi + \cos^{-1}\left(\frac{\tilde{t}_R}{\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2}}\right).$$

The second derivative of $\epsilon_k^{\pm}$ then determines that both ϵ_k^+ and ϵ_k^- have a maximum when $l = 0$ and minima when $l = \pm 1$.

Type-2: If $\tilde{t}_R < 0$ and $\tilde{t}_I < 0$ and if $\tilde{t}_R < 0$ and $\tilde{t}_I > 0$, then we have the following solutions for the extrema (l = integer):

$$ka = l\pi + \sin^{-1}\left(\frac{\tilde{t}_I}{\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2}}\right) = l\pi + \cos^{-1}\left(-\frac{\tilde{t}_R}{\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2}}\right).$$

The second derivative of $\epsilon_k^{\pm}$ then determines that both ϵ_k^+ and ϵ_k^- have a minimum when $l = 0$ and maxima when $l = \pm 1$.

In both situations, within the first Brillouin zone, we thus find that the minimum value of ϵ_k^+ is $-2\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2} + \sqrt{\left(\tilde{\Lambda}^{(z)} + \tilde{B} + \frac{m}{2}\right)^2 + \tilde{\Lambda}^2}$ and the maximum value of ϵ_k^- is $2\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2} - \sqrt{\left(\tilde{\Lambda}^{(z)} + \tilde{B} + \frac{m}{2}\right)^2 + \tilde{\Lambda}^2}$. The band gap, $\epsilon_k^+|_{\min} - \epsilon_k^-|_{\max}$, is then equal to $-4\sqrt{\tilde{t}_R^2 + \tilde{t}_I^2} + 2\sqrt{\left(\tilde{\Lambda}^{(z)} + \tilde{B} + \frac{m}{2}\right)^2 + \tilde{\Lambda}^2}$. We recall that the model Hamiltonian being studied here defines a material system that is half-filled and therefore we expect the system to be an insulator if the band gap is positive. On the other hand, if the bands are overlapping (the gap being negative) then we expect the system to be a metal. For the materials to behave as an insulator, then, the band gap measure, M_{bg}, must be greater than unity, where

$$M_{bg} = \left[\left(\tilde{\Lambda}^{(z)} + \tilde{B} + \frac{m}{2}\right)^2 + \tilde{\Lambda}^2\right]/4\left(\tilde{t}_R^2 + \tilde{t}_I^2\right).$$ (35)

In Fig. 1, we schematically show the regions of metal and insulator as a function of the band gap measure. It is evident from Eq. (35) that the spin-orbit interaction favours the material to be insulating in character and this is certainly so if the effective magnetic moment m is zero and there is no external magnetic field. The present finding is consistent with a recent study on Mott physics which predicts electrons to be in metallic and topological band insulator phases at weak and

strong spin-orbit interaction, respectively.[60] To conclude, the spin-orbit interaction provides a viable mechanism of metal-insulator transition, which is distinct from the well-known Mott-Hubbard (driven by the strong electron correlations of electrostatic origin)[1,46] and the Anderson mechanism (driven by the disorder).[47] This may be further verified in experiments.

B. Spin-orbit interaction: Magnetic phase transition

Here we study the spin-only Hamiltonian in Eq. (23) for an one-dimensional spin-S chain with N lattice points in the presence of external magnetic field which is directed along the z direction with nearest neighbour exchange interactions, to understand the significance of spin-orbit interaction in magnetic phase transitions. It is to be noted that the exchange parameters J in Eq. (23) is greater than zero. Let us first consider the situation when the SOC parameter Λ is greater than zero, in which case the Hamiltonian simplifies as follows:

$$\hat{H}_{\text{spin}}^{(\text{eff})} = -2J \sum_{m=1}^{N} \vec{S}_m \cdot \vec{S}_{m+1} + \Lambda^{(z)} \sum_{m=1}^{N} S_m^z$$

$$+ 2\mu_B B^{(\text{ext})} \sum_{m=1}^{N} S_m^z.$$ (36)

To diagonalize the Hamiltonian in Eq. (36), we first introduce the Holstein-Primakoff approximation for the spin angular momentum operators as follows:[61]

$$S_m^z = -S + \frac{1}{2}(\hat{p}_m^2 + \hat{q}_m^2 - 1),$$
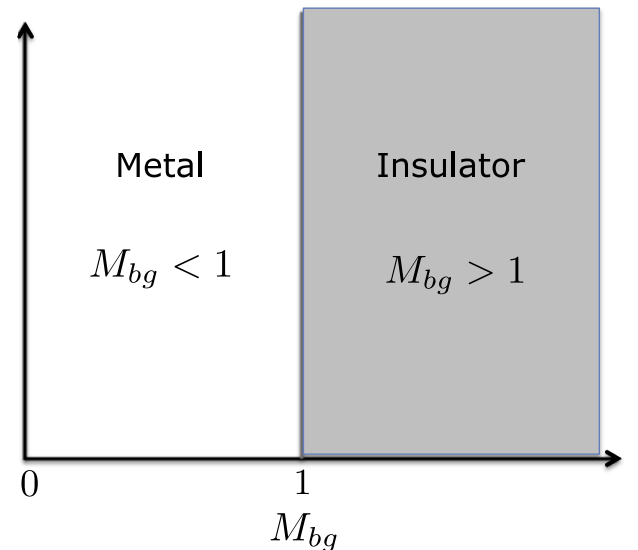$$S_m^x = \sqrt{S}\hat{q}_m, \text{ and } S_m^y = -\sqrt{S}\hat{p}_m,$$ (37)

FIG. 1. Metal-Insulator phase transition. M_{bg} is the band gap measure, see Eq. (35).

where the operators $\hat{q}_m$ and $\hat{p}_m$ satisfy the following commutation relations: $[\hat{q}_m, \hat{p}_n] = i\delta_{mn}$, $[\hat{q}_m, \hat{q}_n] = 0$ and $[\hat{p}_m, \hat{p}_n] = 0$. The first term of the Hamiltonian in Eq. (36) is manifestly quadratic, the z-component of which we linearize using Eq. (37) as shown below

$$S_m^z S_{m+1}^z = \left[-S + \frac{1}{2}(\hat{p}_m^2 + \hat{q}_m^2 - 1) \right]$$
$$\times \left[-S + \frac{1}{2}(\hat{p}_{m+1}^2 + \hat{q}_{m+1}^2 - 1) \right]$$
$$\approx S^2 - \frac{S}{2}(\hat{p}_m^2 + \hat{q}_m^2 - 1) - \frac{S}{2}(\hat{p}_{m+1}^2 + \hat{q}_{m+1}^2 - 1). \quad (38)$$

We next use the periodic boundary condition on the one-dimensional lattice with $\vec{S}_{N+1} = \vec{S}_1$ and express the operators $\hat{q}_m$ and $\hat{p}_m$ in the Fourier series as shown below[61]

$$\hat{q}_m = \frac{1}{\sqrt{N}} \sum_k e^{ikma} \hat{Q}_k \text{ and } \hat{p}_m = \frac{1}{\sqrt{N}} \sum_k e^{-ikma} \hat{P}_k, \quad (39)$$

where the k's lie within the first Brillouin zone and a is the lattice constant. Notably, the operators $\hat{P}_k$ and $\hat{Q}_k$

satisfy the following commutation relations: $[\hat{Q}_k, \hat{P}_{k'}] = i\delta_{kk'}$, $[\hat{Q}_k, \hat{Q}_{k'}] = 0$ and $[\hat{P}_k, \hat{P}_{k'}] = 0$. We now use Eqs. (37)-(39) to transform the Hamiltonian in Eq. (36) to the following form:

$$\hat{H}_{\text{spin}}^{(\text{eff})} = -2JNS^2 - (2\mu_B B^{(\text{ext})} + \Lambda^{(z)})NS$$
$$+ (4JS + 2\mu_B B^{(\text{ext})} + \Lambda^{(z)})$$
$$\times \sum_k \frac{1}{2}(\hat{P}_k \hat{P}_{-k} + \hat{Q}_k \hat{Q}_{-k} - 1)$$
$$- 2JS \sum_k (\hat{P}_k \hat{P}_{-k} + \hat{Q}_k \hat{Q}_{-k}). \quad (40)$$

We next introduce the magnon creation ($a_k^\dagger$) and annihilation (a_k) operators as shown below

$$\hat{Q}_k = \frac{1}{\sqrt{2}}(a_k + a_{-k}^\dagger) \text{ and } \hat{P}_k = -\frac{i}{\sqrt{2}}(a_{-k} - a_k^\dagger). \quad (41)$$

They are manifestly bosonic in character for they satisfy the commutation relations: $[a_k, a_{k'}^\dagger] = \delta_{kk'}$, $[a_k, a_{k'}] = 0$, and $[a_k^\dagger, a_{k'}^\dagger] = 0$. In terms of the magnon operators, the Hamiltonian in Eq. (40) assumes the following form:[61]

$$\hat{H}_{\text{spin}}^{(\text{eff})} = -2JNS^2 - (2\mu_B B^{(\text{ext})} + \Lambda^{(z)})NS - 2JS \sum_k \cos ka$$

$$+ \sum_k \left[4JS(1 - \cos ka) + 2\mu_B B^{(\text{ext})} + \Lambda^{(z)} \right] a_k^\dagger a_k = A + \sum_k E_k a_k^\dagger a_k, \quad (42)$$

$$\text{with } E_k = \left[4JS(1 - \cos ka) + 2\mu_B B^{(\text{ext})} + \Lambda^{(z)} \right] \approx 2JSk^2 a^2 + 2\mu_B B^{(\text{ext})} + \Lambda^{(z)}, \quad (43)$$

where $A = -2JNS^2 - (2\mu_B B^{(\text{ext})} + \Lambda^{(z)})NS - 2JS \sum_k \cos ka$, which is just a constant energy and hence we ignore here. Eq. (43) provides the necessary expression of the energy for computing the thermal properties of the spin system. The total spin angular momentum operator of the system along the z direction, using Eq. (37), can be written as follows:

$$S_{\text{total}}^z = \sum_{m=1}^N S_m^z = -NS + \sum_{m=1}^N \frac{1}{2}(\hat{p}_m^2 + \hat{q}_m^2 - 1)$$
$$= -NS + \sum_k a_k^\dagger a_k. \quad (44)$$

Hence the total spin angular momentum of the system at a finite temperature is computed as shown below.

$$\langle S_{\text{total}}^z \rangle = -NS + \sum_k \langle a_k^\dagger a_k \rangle$$
$$= -NS + \sum_k [\exp(E_k/k_B T) - 1]^{-1}, \quad (45)$$

where k_B = Boltzmann constant. We note that $\exp(E_k/k_B T)$, in the low temperature limit, is greater than unity and therefore $[\exp(E_k/k_B T) - 1]^{-1}$ may be approximated as a $\exp(-E_k/k_B T)$. Consequently, $\langle S_{\text{total}}^z \rangle$, in the low temperature limit, takes the following simple form:

$$\langle S_{\text{total}}^z \rangle = -NS + \sum_k \exp(-E_k/k_B T). \quad (46)$$

We now substitute the expression for the energy E_k from Eq. (43) in Eq. (46) and compute the total magnetic moment, $M_{\text{total}}^z = -2\mu_B \langle S_{\text{total}}^z \rangle$, as given below

$$M_{\text{total}}^z = 2N\mu_B S - \frac{\mu_B(N-1)a}{\pi} \sqrt{\frac{\pi k_B T}{2JSa^2}}$$
$$\times \exp\left[-\frac{2\mu_B B^{(\text{ext})} + \Lambda^{(z)}}{k_B T} \right]. \quad (47)$$

The change in total magnetic moment due to the external magnetic field is an observable quantity which is easily obtained with Eq. (47) as follows: $\Delta M_{\text{total}}^z = M_{\text{total}}^z(B^{(\text{ext})}) - M_{\text{total}}^z(B^{(\text{ext})} = 0)$. Finally, the magnetic susceptibility of the spin system as a function of temperature is computed as shown below.

$$\chi(T)|_{B^{(\text{ext})}=0} = \frac{\mu_0}{\text{volume of the material}} \lim_{B^{(\text{ext})} \to 0} \frac{\Delta M_{\text{total}}^z}{B^{(\text{ext})}}$$
$$= \frac{\mu_B^2 \mu_0 (N-1)}{\text{volume of the material}}$$
$$\times \sqrt{\frac{2}{\pi JS k_B T}} \exp\left(-\frac{\Lambda^{(z)}}{k_B T} \right). \quad (48)$$

As Eq. (48) reveals, $\chi(T)$ has a maximum at $T = T_{\text{critical}}$ which we compute as follows:

$$\frac{\partial \chi(T)|_{B^{(\text{ext})}=0}}{\partial T} = 0 \implies T = 2\frac{\Lambda^{(z)}}{k_B} = T_{\text{critical}}. \quad (49)$$
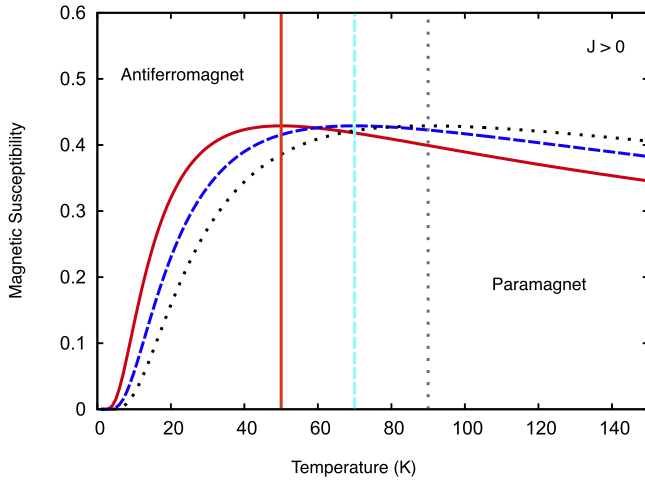
FIG. 2. The magnetic susceptibility, $\chi(T)$ multiplied by $\frac{\text{volume of the material}}{4\mu_B^2 \mu_0 (N-1)}$ $\sqrt{8\pi J S \Lambda^{(z)}}$ as a function of the temperature (K). The solid line (red), the dashed line (blue), and the dotted line (black) curves are for $\frac{\Lambda^{(z)}}{k_B} = 25$ K, 35 K, and 45 K, respectively. The Néel temperature (T_{critical}) for the curves is indicated by the vertical lines at 50 K, 70 K, and 90 K, respectively.

In Fig. 2, we show the magnetic susceptibility, for a given J and S, as a function of the temperature for different values of spin-orbit coupling strengths. It is evident from Fig. 2 that the susceptibility first increases with the temperature and this demonstrates the existence of the antiferromagnetic phase. Beyond a certain temperature which is determined by the spin-orbit coupling strength, the susceptibility falls as the temperature increases and this signals the onset of a paramagnetic phase. The temperature at which the $\chi(T)$ curves in Fig. 2 assume a maximum value is known as the Néel temperature which, as also evident from Eq. (49), is a function of the spin-orbit coupling strength. We note that the antiferromagnetic phase depicted in Fig. 2 ceases to exist if the spin-orbit coupling is zero. This result is understandable as the Hamiltonian in Eq. (36), in the absence of spin-orbit coupling ($\Lambda^{(z)} = 0$), simply reduces to the standard Heisenberg model with a positive exchange coupling (J) and this model is known to admit only the ferromagnetic or paramagnetic phase. The present study thus demonstrates the possibility of an antiferromagnetic to paramagnetic or ferromagnetic phase transition that is driven by the spin-orbit interaction. This is distinct from the Néel-VanVleck-Anderson paradigm,[6,48,49] which posits a negative spin-exchange for the existence of antiferromagnetic phase in the material.

VI. CONCLUDING REMARKS

We now briefly discuss how the present theory of correlated electrons may be further extended and utilized to study the structure and various electromagnetic properties of complex materials. We first note that the many-electron Hamiltonian in Eq. (5) contains all possible interactions, within the semi-relativistic regime of quantum electrodynamics, for a collection of dynamic spin-1/2 charged particles in the presence of external electromagnetic fields and hence it is formally complete. In the present study, we have used Eq. (5) as a starting point to devise, through a

series of simplifying approximations, effective Hamiltonians that are expected to be useful for studying strongly correlated materials and interacting quantum spin systems. The model Hamiltonians that we have presented in Eqs. (22) and (23) are relatively simple, yet rich in physical content and they go beyond the models that are frequently being used in the present day discourse on this subject and therefore we expect the models in Eqs. (22) and (23) to be useful in addressing a range of research problems related to the magnetic and electron transport properties of complex materials, beyond what may be possible now. For applications here, we have used simple analytical methods such as the mean-field approximation to diagonalize the Hamiltonian in Eq. (22) and the spin wave theory while using Eq. (23) to compute the magnetic susceptibility. For more accurate studies, it would be necessary to develop sophisticated analytical tools such as those based on Green's functions,[62] Bethe ansatz,[63] and so forth. It would also be important to develop accurate numerical techniques such as matrix diagonalization, time propagation, Monte Carlo, and so forth involving the model Hamiltonians in Eqs. (22) and (23) to study large systems. We envisage further applications of the many-electron Hamiltonian in Eq. (5) in the following manner. For example, one may choose a number of necessary terms from Eq. (5) that are expected to be involved in the physical processes of interest and construct a variety of model Hamiltonians to study specific classes of phenomena in complex materials, either by analytical or numerical means. Model Hamiltonians and their applications in the present study have been confined mostly to insulators and poor conductors. It would be of interest to extend the present theoretical approach to study the dynamics of correlated electrons in metals. We will report such studies in future. In conclusion, we have presented a complete quantum mechanical structure that would be useful to study various electromagnetic response properties of complex materials.

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