Magnetic transitions in strong coupling expansions for nearly degenerate states

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A strong coupling expansion for a two-band Hubbard model on two sites with nearly degenerate states is considered. A comparative analysis is performed for different schemes of perturbation theory which are applicable to systems with nearly degenerate states. A fourth order approach which builds on a four-dimensional low-energy subspace with nearly degenerate states captures accurately the transition from an antiferromagnetic to a ferromagnetic ground state at large on-site Coulomb interaction.

1 Introduction

The emergence and antagonism of ferromagnetic and antiferromagnetic ground states in strongly correlated electron systems has always been considered to be of prime importance for a thorough understanding of the magnetic states in narrow band systems such as the transition metal oxides. In a large number of cases the nature of the magnetic coupling is successfully predicted by appropriate spin-orbital models. Formally the magnetic coupling results from second order expansion in some hopping amplitude parameter \( t \), and therefore applies to systems in the strong coupling regime with strong on-site Coulomb interaction \( U \) (with respect to the kinetic energy \( t \), i.e., \( t \ll U \)). In that case spin-orbital models provide a framework to analyze a wealth of properties (for a recent reference see Oleś \textit{et al}. [1] and references therein). Nevertheless, many systems are rather tracked down to be in the intermediate coupling regime, where, for example, phase transitions between ferromagnetic and antiferromagnetic phases can take place (see, e.g., [2]). Such situations are not covered by the standard spin-orbital models, and higher orders in the expansion in \( t \) are needed. Unfortunately this often implies to take nearly degenerate states into account. In fact, the determination of the magnetic coupling of nearly degenerate states beyond second order perturbation theory has been rarely addressed in solid state physics. Our paper aims at filling this gap.

Whereas small clusters with few electronic states can be exactly diagonalized to characterize the electronic state, larger clusters with millions of states require different approaches. Already a cluster of three transition metal ions (with six \( d \) electrons per site) and two oxygen ions provides more than 600 thousand low energy states which are nearly degenerate. To be explicit, this challenge is encountered in the quasi-1D Mott-insulator \( \text{Ca}_3\text{Co}_2\text{O}_6 \), when effective interaction parameters are calculated from a minimal cluster of three Co sites (only counting the 3\( d \) states) and two O ligand sites (exclusively considering 2\( p \) states), and a microscopic analysis of the dominant ferromagnetic coupling between high-spin next-nearest neighbor Co\(^{3+}\) sites has not yet included all low-energy states. In such a system one would have to implement a perturbation theory of at least 5\(^{th}\) order (due to the necessity to include ring exchange). Moreover, an adequate perturbation theory should be fully qualified to cope with a large number of nearly degenerate states in the...
low energy sector. Such a situation with several or many nearly degenerate low energy states, which are separated by a large energy scale $U$ from the high energy sector, is typical for multi-band transition metal oxides and the question arises if well established perturbation theories are available with which electronic systems with almost or nearly degenerate ground states can be reliably handled [3].

Schemes for the implementation of a perturbation theory with degenerate states in the low energy sector have been known for a long time and are well presented in textbooks on quantum mechanics and review articles (e.g., see the Refs. [4–11]). The extension to almost degenerate states seems to be straightforward with either of two alternative procedures: (i) one formally assigns a degenerate “unperturbed” Hamiltonian to those eigenstates which are nearly degenerate [5, 7]. The perturbation expansion is then set up with respect to this artificially constructed, unperturbed degenerate Hamiltonian with the perturbation being comprised of the terms which lift the degeneracy and the original perturbation terms which connect to the high energy sector. This scheme, which introduces an artificial degeneracy, is in general not physically motivated and may produce inferior convergence as we will demonstrate in Sec. 3. (ii) Alternatively, one first diagonalizes the unperturbed Hamiltonian jointly with that part of the perturbation which can be projected onto the low energy sector of the Hilbert space (in which the degenerate and almost degenerate states live). The part of the perturbation which connects to the high energy sector can then be treated in standard perturbation theory [6]. However this latter scheme is valid only up to third order where intermediate states in this scheme are exclusively states from the high energy sector. In fourth order, this scheme breaks down because intermediate states are then in turn allowed to be taken from the low energy sector. We will shortly introduce this procedure in the following section. The standard argument implicates the expectation that the degeneracy or near degeneracy is lifted in second order of perturbation theory. However this is extremely implausible for thousands of nearly degenerate states.

A generalization of scheme (ii) actually exists which extends its validity to all orders of the perturbation theory. This generalization, introduced by Brandow in a review article [12], is a Brillouin-Wigner (BW) type of perturbation theory, which requires to calculate the system energies self-consistently [13]. This self-consistency implies that BW expansions do not scale properly with the particle number in any finite order which can impede their use in solid state physics.

A considerable number of perturbation techniques for nearly degenerate states were developed for purposes specific to quantum chemistry. Here we focus on a perturbation expansion which was developed by Lindgren [14]. It is of Rayleigh-Schrödinger (RS) type and can handle multi-particle problems with nearly degenerate ground states. From the formal structure it is more demanding than a BW expansion but it obeys the linked cluster theorem [15] and the correct particle number scaling without adjustments.

To our knowledge, neither the BW-scheme of Brandow nor the RS-scheme of Lindgren were used extensively in solid state physics in order to solve electronic problems with nearly degenerate states. In this context, it is of particular interest if these schemes can be employed effectively to investigate magnetic states of strongly correlated electron systems. Especially, can we reliably gain magnetic coupling constants if there is a competition between ferromagnetic and antiferromagnetic correlations and only higher orders in perturbation theory can settle the sign of the coupling?

In the following section (Sec. 2), we first introduce the concept of “nearly degenerate perturbation theory” and then present the schemes of Brandow and Lindgren for the generalization of BW and RS perturbation theory, respectively. As already mentioned, these schemes were little used in solid state physics and it is worthwhile to review the basics. In order to reassess their applicability in this context, we employ in Sec. 3 the different perturbation expansions to a two-site cluster with two orbitals and the standard set of local interactions, kinetic transfer of electrons, amended by a crystal field term acting in the two-orbital subspace. Such a term arises due to small deviations from the cubic symmetry, generically observed in the perovskites of transition metal oxides. In the Fock space with two electrons, this system may display a transition from a singlet to a triplet state for intermediate to large on-site Coulomb interaction $U$. This transition to a spin-orbital entangled state is not expected from conventional reasoning as it cannot be identified in standard second-order perturbation theory [16]. We investigate the quality of the different perturbation schemes by comparing the 4th order result to the exact solution. We summarize our analysis in the last section.
2 Formalism

We consider the time-independent Hamiltonian problem

$$H |\Psi_n\rangle = E_n |\Psi_n\rangle$$

(1)

where $H$ is in the Schrödinger representation. The eigenvalues $E_n$ and the eigenfunctions $\Psi_n$ are labeled by $n$. We assume that the Hamiltonian $H$ can be separated into

$$H = H_0 + H_1,$$

(2)

where $H_0$ is the unperturbed Hamiltonian which defines an exactly solvable problem and $H_1$ is the perturbation. Accordingly, we assume that $H_0$ can be diagonalized, and consider the energy corrections to the eigenenergy $E_n^{(0)}$ corresponding to the eigenstate $|n\rangle$ of $H_0$. The eigenenergy with corrections up to an appropriate order $k$ will be denoted as $E_n^{(k)}$ and, to infinite order, $E_n$ represents the exact eigenenergy of $H$.

![Hilbert Space Structure](image)

Fig. 1 (Color online) Structure of the Hilbert space representative for the almost degenerate perturbation theory. It is comprised of a low-energy subspace $\mathcal{D}$ and a high-energy sector $\mathcal{H}/\mathcal{D}$. They are separated by an energy gap which is sufficiently large to allow a perturbative expansion in an “interaction” which relates states in $\mathcal{D}$ and $\mathcal{H}/\mathcal{D}$. The projection operators $\mathcal{P}$ and $\mathcal{Q}$ allow to project general state vectors onto $\mathcal{D}$ and $\mathcal{H}/\mathcal{D}$, respectively. The state indexed by $n$ is the reference state for which we consider the perturbation expansion; it is always in $\mathcal{D}$.

Moreover, we suppose that the eigenstates of both, the total Hamiltonian $H$ and the unperturbed Hamiltonian $H_0$, can be assigned to either of the two sectors of the Hilbert space $\mathcal{H}$: a low energy sector $\mathcal{D}$ of dimension $d$ and a high energy sector $\mathcal{H}/\mathcal{D}$ which is the orthogonal space of $\mathcal{D}$ (see Fig. 1). We note, that the subspace $\mathcal{D}$ is often referred to as the “model space” (see, e.g., Ref. [7]). We assume that the states in $\mathcal{D}$ are all degenerate or nearly degenerate— with near degeneracy implying that the energy difference of the states in $\mathcal{D}$ is smaller than the difference to any of the states in $\mathcal{H}/\mathcal{D}$. This decomposition allows to devise a well-defined perturbation expansion if the perturbative part $H_1$ of the Hamiltonian has matrix elements smaller than the gap between low energy and high energy states.

The projection operators which are associated with the two complementary subspaces are:

$$\mathcal{P} = \sum_{p \in \mathcal{D}} |p\rangle \langle p|$$

$$\mathcal{Q} = \sum_{q \in \mathcal{H}/\mathcal{D}} |q\rangle \langle q| = 1 - \mathcal{P}$$

(3)

where the index $p$ ($q$) refers to orthonormalized eigenstates $|p\rangle$ ($|q\rangle$) of $H_0$ in the low (high) energy sector of the Hilbert space. The projections of the eigenvectors of $H$ into the low energy sector are denoted by $|\Psi_p\rangle = \mathcal{P}|\Psi_p\rangle$. This notation will be kept for the rest of the paper. We use the normalization with $\langle \Psi_p | \Psi_p \rangle = 1$. 

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2.1 Third order perturbation theory for nearly degenerate states

We rewrite the Hamiltonian:

\[ H = H_0 + (\mathcal{P} + \mathcal{Q})H_1(\mathcal{P} + \mathcal{Q}) = H_0 + \mathcal{P} H_1 \mathcal{P} + \mathcal{Q} H_1 \mathcal{P} + \mathcal{P} H_1 \mathcal{Q} + \mathcal{Q} H_1 \mathcal{Q}. \]  
(4)

At this point we will simply redefine the unperturbed part of the Hamiltonian and the perturbation. With the definitions:

\[ H_0 \equiv H_0 + \mathcal{P} H_1 \mathcal{P}, \]
\[ H_1 \equiv \mathcal{P} H_1 \mathcal{Q} + \mathcal{Q} H_1 \mathcal{P} + \mathcal{Q} H_1 \mathcal{Q}, \]
(5)

the perturbative problem is restated in an adequate fashion for nearly degenerate cases \[6\]: \( H_0 \) is to be diagonalized in the \( d \) dimensional subspace \( \mathbb{D} \) and \( H_1 \) constitutes the perturbation of these “zero order” states with energies \( E_n^{(0)} \equiv \langle p|H_0|p \rangle \). This reformulation of the problem has an irrefutably beneficial effect: all matrix elements of \( H_1 \) connecting two states in \( \mathbb{D} \) are zero by construction; therefore only states in the complement \( \mathbb{H}/\mathbb{D} \) can be intermediate states in the perturbation expansion up to third order. We present the textbook formulae of non-degenerate perturbation theory for the new perturbation Hamiltonian \( H_1 \) to find for a state \( n \in \mathbb{D} \)

\[ E_n^{(1)} - E_n^{(0)} = \sum_q \frac{H_{1n}^{0q} H_{1n}^{0q}}{\Delta E_q} + \sum_{q_1,q_2} \frac{H_{1n}^{0q_1} H_{1n}^{0q_2} H_{1n}^{0q_2}}{\Delta E_{q_1} \Delta E_{q_2}} \]
(6)

where we use the short hand notation \( \Delta E_q \equiv E_n^{(0)} - E_q^{(0)} \) and \( H_{1n}^{0q_1 q_2} = \langle q_1|H_1|q_2 \rangle \), and \( q_1, q_2 \) are indices for states in \( \mathbb{H}/\mathbb{D} \), exclusively. The first order energy correction \( \langle n|H_1|n \rangle \) vanishes identically by construction because the state \( n \) belongs to the subspace \( \mathbb{D} \). The first order is already encoded in the setup of \( H_0 \), and the suppression of the first order in the subsequent perturbation expansion also simplifies the third order term to the form presented in Eq. (6). Beyond third order, intermediate states \( p \in \mathbb{D} \) intrude and spoil the expansion due to the smallness of \( \Delta E_q \) in the denominators.

In order to overcome this difficulty, one has to recast the perturbation expansion into a form that allows to separate the virtual excitations into the high energy states from the low energy processes in such a way that virtual excitations into intermediate low energy states are excluded. Such a reformulation exists for the Brillouin-Wigner perturbation theory as well as for the Rayleigh-Schrödinger perturbation theory. For the first (BW) we refer to Brandow’s approach \[12\] and for the second (RS) to Lindgren’s treatment \[14\].

2.2 Brandow’s generalized Brillouin-Wigner perturbation theory

The Brillouin-Wigner perturbation theory is straightforwardly generalized to account for a low energy subspace \( \mathbb{D} \) of dimension \( d \) with nearly degenerate or exactly degenerate states: the states of the model space \( \mathbb{H} \) are excluded from the intermediate summations in the perturbation series. In fact, this procedure is an exact resummation as shown in Sec. II of Brandow’s review \[12\] and in Ref. \[14\]. For convenience we label this procedure by BBW (Brandow Brillouin-Wigner) as Brandow seems to have been the first to make this approach explicit for a “quasi-degenerate” model space (see also Refs. \[9,17,18\]).

In the standard BW approach the energy eigenvalues in \( \mathbb{D} \) are found self-consistently from

\[ E_n = E_n^{(0)} + H_{1n}^{nn} + \sum_{q \in \mathbb{H}/\mathbb{D}} \frac{H_{1n}^{0q} H_{1n}^{0q}}{E_n - E_q^{(0)}} + \sum_{q_1, q_2 \in \mathbb{H}/\mathbb{D}} \frac{H_{1n}^{0q_1} H_{1n}^{0q_2} H_{1n}^{0q_2}}{(E_n - E_q^{(0)})(E_n - E_q^{(0)})} + \cdots \]
(7)

if \( \mathbb{D} \) consists of a single state. Here, we use the short hand notation \( H_{1n}^{0q_1 q_2} = \langle q_1|H_1|q_2 \rangle \).

For the BBW scheme with a \( d \)-dimensional model space \( \mathbb{D} \), an effective Hamiltonian \[14\] is introduced for each eigenvalue \( E_n \)

\[ H_{\text{eff}} = \mathcal{P} H_0 \mathcal{P} + \mathcal{P} W^n \]
(8)

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where the effective interaction $\mathcal{P} W^n$ in the low energy sector is found from

$$W^n = H_1 \mathcal{P} + H_1 T^n W^n$$

with the resolvent [19]

$$T^n = \sum_{q \in \mathbb{H}/\mathbb{D}} \frac{|q\rangle\langle q|}{E_n - E_q^{(0)}}$$

which is exclusively defined in the high energy sector $\mathbb{H}/\mathbb{D}$. Eq. (9) allows to write the eigenvalue equations

$$H_{\text{eff}}^n |\Psi_n^D\rangle = E_n |\Psi_n^D\rangle.$$  

We emphasize that the states $|q\rangle$ are the unperturbed states of the complementary space $\mathbb{H}/\mathbb{D}$ and they specify the effective Hamiltonian through the sum in $T^n$ over the high-energy sector. The $E_n$ denote the perturbed eigenvalues in the low-energy sector which is spanned by the corresponding eigenvectors $|\Psi_n^D\rangle$.

The perturbed eigenstates $|\Psi_n^D\rangle$ are identified through

$$|\Psi_n^D\rangle = (1 + T^n W^n) |n\rangle$$

Again, we stress that the resolvent $T^n$ and the effective Hamiltonian $H_{\text{eff}}^n$ depends on the perturbed energies $E_n$: There is an effective Hamiltonian $H_{\text{eff}}^n$ for each $E_n$, and the eigenvalue equation Eq. (11) has to be solved self-consistently for each $E_n$ with the corresponding $H_{\text{eff}}^n$.

As the states of the model space $\mathbb{D}$ are excluded from the intermediate summations in the perturbation series, it is obvious that infinitely many terms are missing in the BBW summations with respect to the standard BW approach. However their respective contribution is generated through the initial diagonalization in the enlarged model space $\mathbb{D}$. If $\mathbb{D}$ consists of a single state, BBW reduces to Brillouin-Wigner perturbation theory and if $\mathbb{D}$ covers the entire Hilbert space $\mathbb{H}$, the diagonalization already solves the problem and the perturbation expansion collapses to the zeroth order term. In sec. 3 we will present a model where an appropriately chosen $\mathbb{D}$ reduces the full perturbation expansion to the second order term. In such a case no further higher order processes can be produced which relate states in the high energy sector $\mathbb{H}/\mathbb{D}$: due to the restriction to states in $\mathbb{H}/\mathbb{D}$ on the summations, the second order term already induces the exact solution.

Albeit the simplicity of the Brillouin-Wigner and BBW schemes, a formal disadvantage has to be faced: The linked cluster theorem does not apply [12], which implies an incorrect scaling with the number of particles term by term in the perturbation theory. This inconsistency is only lifted in infinite order.

2.3 Lindgren’s nearly degenerate Rayleigh-Schrödinger perturbation theory

Rayleigh-Schrödinger perturbation theory cannot be generalized for a problem with almost degenerate states in the model space $\mathbb{D}$ by excluding straightforwardly the states of $\mathbb{D}$ from the intermediate summations in the perturbation series. Such an approach would be correct if the $d$ states of $\mathbb{D}$ were completely degenerate. However we want to address the case with $d$ almost degenerate states, where the degenerate subspaces of $\mathbb{D}$ may have the dimensions $d_\alpha$, with $1 \leq d_\alpha \leq d$ and $\sum_\alpha d_\alpha = d$.

In this situation it is convenient to introduce the wave operator $\Omega$ [20,21], which transforms all unperturbed states in $\mathbb{D}$ into the exact eigenfunctions of $H$, and expand $\Omega$ order by order [14]. This yields the set of the desired $d$ eigenenergies and eigenstates [22] to the appropriate order. As the approach traces back to the Rayleigh-Schrödinger perturbation theory, it does not suffer from a lack of extensivity, in contrast to Brillouin-Wigner perturbation theory.

One introduces the wave operator $\Omega$ through

$$|\Psi_p\rangle = \Omega |\Psi_n^D\rangle$$

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satisfying $|\Psi_p\rangle = \Omega P|\Psi_p\rangle$ and

$$\Omega Q = 0.$$  \quad (14)

Namely, if one projects any of the $d$ low energy exact eigenstates $|\Psi_q\rangle$ of the full Hamiltonian onto the low energy Hilbert space $\mathcal{D}$, the wave operator takes care of restoring the “out-projected” part of the eigenstate, while $\Omega$ yields a null result when operating on the complementary subspace.

To zeroth order the wave operator is simply the projection operator onto $\mathcal{D}$:

$$\Omega^{(0)} = P$$ \quad (15)

Once $\Omega^{(i)}$ is obtained to order $i - 1$, the effective Hamiltonian $H^{(i)}_{\text{eff}}$ acting on $\mathcal{D}$ takes the form [14]:

$$H^{(i)}_{\text{eff}} = P H_0 P + P H_1 \left( \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + \ldots + \Omega^{(i-1)} \right)$$ \quad (16)

The solution of the eigenvalue problem

$$H^{(i)}_{\text{eff}} |\Psi^{(i)}_n\rangle = E^{(i)}_n |\Psi^{(i)}_n\rangle$$ \quad (17)

yields the exact eigenenergies $E^{(i)}_n$ (to order $i$) in the low energy space, even though it operates on the eigenstates $|n\rangle$ of $H_0$ in $\mathcal{D}$. As the wave operator is unique for the entire low-energy Hilbert space, also the effective Hamiltonian is independent of the state $n$, in contrast to that of the Brillouin-Wigner type Hamiltonian in Sec. 2.2.

Starting from Schrödinger’s equation, Lindgren obtained a recursion formula for $\Omega^{(i)}$:

$$\left[ \Omega^{(i)} , H_0 \right] = \mathcal{Q} H_1 \Omega^{(i-1)} - \sum_{m=1}^{i-1} \Omega^{(i-m)} H_1 \Omega^{(m-1)}$$ \quad (18)

The lowest orders are then explicitly obtained as:

$$\begin{align*}
\Omega^{(1)} &= \sum_{q\in\mathcal{D}/p\in\mathcal{D}} |q\rangle \langle p| \frac{\langle q | H_1 | p \rangle}{E^{(0)}_p - E^{(0)}_q} \\
\Omega^{(2)} &= \sum_{q\in\mathcal{D}/p\in\mathcal{D}} \sum_{m\in\mathcal{D}} |q\rangle \langle p| \frac{\langle q | H_1 \Omega^{(1)} - \Omega^{(1)} H_1 | p \rangle}{E^{(0)}_p - E^{(0)}_q} \\
\Omega^{(3)} &= \sum_{q\in\mathcal{D}/p\in\mathcal{D}} \sum_{m\in\mathcal{D}} |q\rangle \langle p| \frac{\langle q | H_1 \Omega^{(2)} - \Omega^{(1)} H_1 \Omega^{(1)} - \Omega^{(2)} H_1 | p \rangle}{E^{(0)}_p - E^{(0)}_q} \\
\Omega^{(4)} &= \sum_{q\in\mathcal{D}/p\in\mathcal{D}} \sum_{m\in\mathcal{D}} |q\rangle \langle p| \frac{\langle q | H_1 \Omega^{(3)} - \Omega^{(1)} H_1 \Omega^{(2)} - \Omega^{(2)} H_1 \Omega^{(1)} - \Omega^{(3)} H_1 | p \rangle}{E^{(0)}_p - E^{(0)}_q}
\end{align*}$$ \quad (19)

With the knowledge of $\Omega^{(1)}$, up to the appropriate order $i - 1$, one identifies the effective Hamiltonian $H^{(i)}_{\text{eff}}$, Eq. (16), and determines the eigenvalues $E^{(i)}_n$ in the low-energy sector $\mathcal{D}$ through Eq. (17).

Whereas the conventional approach of Sec. 2.1 is a straightforward Rayleigh-Schrödinger perturbation expansion of the eigenenergies to the appropriate order in $H_1$ (see Eqs. (5) and (6)), the Lindgren approach is an expansion of the effective Hamiltonian $H^{(i)}_{\text{eff}}$ to order $i$ in $H_1$. The diagonalization of $H^{(i)}_{\text{eff}}$ then introduces higher orders beyond $i$ into the respective eigenenergies $E^{(i)}_n$. 

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3 A two-site model to test perturbation theories

It is now compelling to put the theoretical presentation into practical terms. A comparative analysis of the different perturbational schemes is realized for a basic model for which an exact solution is known: the two-band Hubbard Hamiltonian for interacting $e_g$ electrons on a two-site molecule. Such a model may be written as follows

$$H = H_{\text{kin}} + H_{\text{int}} + H_{\text{CF}}.$$  \hspace{1cm} (20)

For $e_g$ electrons there are two orbital flavors: $|x\rangle \sim x^2 - y^2$ and $|z\rangle \sim 3z^2 - r^2$ forming a basis in the orbital space. Accordingly, the kinetic energy for hopping in $y$-direction is parameterized by

$$H_{\text{kin}} = \sum_{\rho \rho'} t_{\rho \rho'} (c_{i \rho \uparrow}^{\dagger} c_{2 \rho' \sigma} + \text{h.c.}), \quad t_{\rho \rho'} = -\frac{t}{4} \left( \begin{array}{cc} 3 & \sqrt{3} \\ \sqrt{3} & 1 \end{array} \right).$$  \hspace{1cm} (21)

Here $t$ is an effective $(dd \sigma)$ hopping matrix element, $\rho$ is a band index with entries $\rho = x$ or $z$, while $\sigma$ labels the spin states. The electron-electron interactions are described by the on-site terms, which we write in the following form \[23\]

$$H_{\text{int}} = U \sum_i (n_{ix \uparrow} n_{ix \downarrow} + n_{iz \uparrow} n_{iz \downarrow}) + \left(U - \frac{5}{2} J_H \right) \sum_i n_{ix} n_{ix}$$

$$- 2 J_H \sum_i S_{ix} \cdot S_{iz} + J_H \sum_i (c_{ix \uparrow}^{\dagger} c_{ix \downarrow} c_{iz \downarrow} c_{iz \uparrow} + c_{iz \uparrow}^{\dagger} c_{iz \downarrow} c_{ix \downarrow} c_{ix \uparrow}).$$  \hspace{1cm} (22)

Here $U$ and $J_H$ denote the intra-orbital Coulomb and Hund’s exchange elements, whereas $n_{i \rho} = \sum_\sigma n_{i \rho \sigma}$ is the electron density at site $i$ in the $\rho = x, z$ orbital state. The term $H_{\text{CF}}$ represents the uniform crystal-field splitting

$$H_{\text{CF}} = \frac{1}{2} E_{\text{CF}} \sum_{i \sigma} (n_{ix \sigma} - n_{iz \sigma})$$  \hspace{1cm} (23)

resulting from, for example, a uni-axial pressure along the $z$-axis.

Considerable interest in models with orbital degeneracy has been fueled by the investigation of the Mott transitions and their understanding (see, for example, Ref. \[24\]). As concerns the lattice version of this particular model, the surprising richness of its phase diagram is instructive, especially in connection with the CMR manganites (for a review see \[25\]). For instance, several antiferromagnetic phases and ferromagnetic phases have been studied in mean-field approximation on the square lattice \[26\], or by exact diagonalization \[27\] and DMFT studies \[28\]. The model is also believed to be a minimal model for the striped nickelates \[29, 30\], and striped phases have been studied in a number of ways (e. g. Refs. \[31, 32\]).

In the following we consider

$$H_1 = H_{\text{kin}}$$  \hspace{1cm} (24)

as a perturbation of the local Hamiltonian

$$H_0 = H_{\text{int}} + H_{\text{CF}}.$$  \hspace{1cm} (25)

With the proper perturbational expressions for the energy corrections, we can investigate the conditions under which the ground state of the model \[20\] is ferromagnetic. In order to study this transition within the introduced perturbational schemes, one first needs to determine the set of states forming the subspace $D$. There are four subspaces, corresponding to states with either spin $0$ (one subspace), or spin $1$ (three subspaces). Let us first focus on the triplet states, restricting ourselves to the ones with $S_z = 1$. A basis
Fig. 2 (Color online) Energy of the lowest singlet and triplet states of the two-band Hubbard model for 2 sites with $J_H/U = 0.2$, $E_{CF}/t = 0.5$. The results for the Lindgren Rayleigh-Schrödinger scheme were generated with four nearly degenerate states in the low-energy subspace $\mathcal{D}$. The upper two dashed curves display the result to fourth order, the lower two to second order.

of the four-dimensional subspace $\mathcal{D}$ is given in Appendix A, and it is easily verified that these basis states are eigenstates of $H_0$. A basis of the two-dimensional complementary subspace $\mathbb{H}/\mathcal{D}$ is also given in Appendix A. These states are eigenstates of $H_0$ as well. We form the $2 \times 4$ matrix $\langle q | H_1 | p \rangle$. It reads

$$\langle q | H_1 | p \rangle = \frac{t}{4} \begin{pmatrix} 0 & 0 & -4 & 0 \\ \sqrt{6} & 2 & 0 & -\sqrt{6} \end{pmatrix}.$$  \hspace{1cm} (26)

One can then easily evaluate Eq. (19) and solve Eq. (17). If we now consider the singlet states, the calculation runs in an analogous fashion. The subspace $\mathcal{D}$ is again four-dimensional, while the subspace $\mathbb{H}/\mathcal{D}$ is now six-dimensional. Using the basis given in Appendix B, we obtain the $6 \times 4$ matrix $\langle q | H_1 | p \rangle$ as:

$$\langle q | H_1 | p \rangle = \frac{t}{4} \begin{pmatrix} -\sqrt{2} & -2\sqrt{3} & 0 & -3\sqrt{2} \\ -\sqrt{2} & 0 & 0 & 3\sqrt{2} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{3} & 0 \\ -\sqrt{6} & -4 & 0 & -\sqrt{6} \\ 0 & 0 & 2 & 0 \end{pmatrix}.$$  \hspace{1cm} (27)
Fig. 3 (Color online) Results for the standard Rayleigh-Schrödinger and Brillouin-Wigner perturbative expansions for the two-band Hubbard model for 2 sites with $J_H/U = 0.2$, $E_{CF}/t = 0.5$. These evaluations use a one-dimensional low-energy subspace.

Note that the states $|q\rangle$, which enter Eq. (27), are not eigenstates of $H_0$, and one further diagonalization step is necessary in order to obtain the desired $⟨q|H_1|p⟩ = ∑_{M=1}^{N} ⟨q|H_1|\varphi^M⟩⟨\varphi^M|p⟩$. This is described in Appendix B. Once these steps are worked out, the desired energy for eigenstate $n$ to perturbative order $i$, viz. $E_{i}^{(n)}|n⟩$, can be evaluated. The higher order terms of the wave operator in the Lindgren Rayleigh-Schrödinger technique simplify substantially: $Ω^{(2)} = 0 = Ω^{(4)}$ and $Ω^{(3)} = −∑_{q\in H/D} ∑_{p\in D} |q⟩⟨p| ⟨q|Ω^{(1)}H_1Ω^{(1)}|p⟩/(E^{(0)}_p − E^{(0)}_q)$ due to the suppression of high-energy hopping processes.

The result of this evaluation for both singlet and triplet states is shown in Fig. 2. Remarkably, the transition from the large $U$ ferromagnetic to the intermediate $U$ antiferromagnetic ground state that occurs at $U_c/t = 9.6$ in the exact diagonalization calculation [16] (see vertical arrow in Fig. 2) is reproduced in the perturbative treatment, i.e., in Lindgren’s Rayleigh-Schrödinger type perturbation theory. It occurs here to fourth order perturbation theory at $U_c^{Lindgren}/t = 9.75$ for four nearly degenerate states in the low energy sector $D$. These states in $D$ are identified by Eqs. (30) and (28) for the singlet and triplet spaces, respectively. For second order perturbation theory with four nearly degenerate states $U_c^{Lindgren}/t = 8.9$ (see Fig. 4). The success of the perturbative evaluation derives from the correct identification of the (four-dimensional) low-energy space and the inclusion of the fourth order term, i.e. $Ω^{(3)}$.

Within non-degenerate Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory there seems to be no transition for the chosen parameter set (see Fig. 3 for fourth order perturbation theory). As expected,
these results are inferior due to the inappropriately chosen (one-dimensional) subspace $\mathcal{D}$ (cf. to the four-state Lindgren scheme and the exact result in Figs. 4 and 5). An exception is the evaluation of the triplet state within non-degenerate Brillouin-Wigner.

The conventional approach [6], which was briefly presented in Sec. 2.1, reduces to the Rayleigh-Schrödinger perturbation theory for this specific model, as $H_0 = H_0$ in Eq. (5): there are no states in the low-energy sector which may be hybridized through $\mathcal{P} H_1 \mathcal{P}$. Consequently, the conventional approach compares poorly with the Lindgren approach, even in second order (see Fig. 6).

The implementation of degenerate perturbation theory, for example, by setting $E_{CF}$ to zero and perturbing the four-fold singlet state with respect to $U$ and $E_{CF}$, which then lifts the degeneracy, has often been suggested. However, the artificial introduction of the zeroth-order degeneracy does not lead to adequate results, as seen in Fig. 5 for the evaluation up to fourth order.

As the matrix elements obey $\langle q | H_1 | q' \rangle = 0$ for the considered model, the Brandow Brillouin-Wigner technique becomes exact for the four nearly degenerate states in the low energy sector $\mathcal{D}$ (given by Eqs. (30) and (23)) already in second order. This is a special property of the chosen model and not generic for larger systems.

Fig. 4 (Color online) Energy of the lowest triplet state of the 2-band Hubbard model for 2 sites with $J_H/U = 0.2$, $E_{CF}/t = 0.5$. The Lindgren approach uses a 4-dimensional low-energy subspace $\mathcal{D}$. In contrast, the displayed results for the standard Rayleigh-Schrödinger and Brillouin-Wigner perturbative expansions build on a one-dimensional $\mathcal{D}$. The three perturbative approaches have been performed up to 4th order.
4 Summary

Perturbation theory for atomic clusters is, for typically thousands of low energy states, generically a perturbation expansion with a large number of almost degenerate states. Moreover, third or fourth order evaluations are often necessary to attain the required accuracy or include new qualitative effects such as electronic ring exchanges. Consequently, a perturbation-theory scheme for almost degenerate states is an essential tool in theoretical physics. Almost degenerate perturbation theory has been elaborately investigated in quantum chemistry but, to our knowledge, these approaches have had little impact on solid state modeling. In fact, second or third order theory is well established [6], but it cannot be straightforwardly extended to fourth order and beyond (see Sec. 2.1) due to intruding low-energy states as intermediate states. A much cited technique is to start with the corresponding degenerate problem and then introduce the deviation from the degenerate case as perturbation; such an approach could benefit from the commonly accepted schemes for highly degenerate perturbation theory. However, this approach leads to unsatisfying results in higher order, on account of systematically inaccurate energy denominators—this shortcoming is confirmed for the investigated model (see the result for “degenerate perturbation theory” in Fig. 5).
A suitable perturbation theory has to start from unperturbed low- and high-energy states which are diagonalized in the respective subspaces. One then has to devise a scheme in which the low-energy subspace is not retraced in the “string” of virtual excitation processes induced by the perturbation, otherwise small energy denominators spoil the evaluation. This is achieved in Lindgren’s scheme [14] for a perturbation theory of Rayleigh-Schrödinger type (see Sec. 2.3). In this scheme, an effective Hamiltonian is to be identified through appropriate traces over high-energy states, and the eigenvalue problem for the effective Hamiltonian provides the perturbed eigenenergies and states in the low-energy space. For a Brillouin-Wigner type perturbation theory the approach is methodically very simple: the low energy intermediate states are excluded in the perturbation-theory summations, as originally presented by Brandow (see Sec. 2.2). The Lindgren scheme can be derived from the Brandow Brillouin-Wigner expressions through expansion [12]. The schemes were introduced in nuclear physics and quantum chemistry but have not received much attention in solid state physics.

For the basic example of a two-site two-orbital Hubbard model we presented a comparative analysis of the most prominent perturbative approaches and examined them against a singlet-triplet transition for strong electronic correlations which is known from the exact diagonalization. The Lindgren approach reproduces this transition even quantitatively (in fourth order). The Brandow scheme becomes exact in second order if the subspace of low-energy states \( \mathcal{D} \) is appropriately chosen. However, this property of the Brandow perturbation expansion is particular for the considered model and will generally not persist for larger systems. As to the formal structure, the Lindgren Rayleigh-Schrödinger expansion is more...
demanding but it obeys the linked cluster theorem in each order of the expansion which implies the correct particle-number scaling.

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A Basis of \( \mathcal{D} \) in the triplet subspace

When considering triplet states (with \( S_z = 1 \)), a convenient basis for the subspace \( \mathcal{D} \) is given by \( \{ |p\rangle_T, 1 \leq p \leq 4 \} \), with:

\[
|1\rangle_T = c_{1,z,\uparrow}^\dagger c_{2,z,\uparrow}^\dagger |0\rangle \\
|2\rangle_T = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{2,z,\uparrow}^\dagger + c_{1,z,\uparrow}^\dagger c_{2,x,\uparrow}^\dagger \right) |0\rangle \\
|3\rangle_T = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{2,z,\uparrow}^\dagger - c_{1,z,\uparrow}^\dagger c_{2,x,\uparrow}^\dagger \right) |0\rangle \\
|4\rangle_T = c_{1,x,\uparrow}^\dagger c_{2,x,\uparrow}^\dagger |0\rangle.
\]

These states are clearly eigenstates of \( H_0 \), with eigenvalues \( E_1^{(0)} = -E_{CF} \), \( E_2^{(0)} = E_3^{(0)} = 0 \), and \( E_4^{(0)} = E_{CF} \). As for the complementary space \( \mathcal{H}/\mathcal{D} \), we use the basis \( \{ |q\rangle_T, 1 \leq q \leq 2 \} \) given by:

\[
|I\rangle_T = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{1,z,\uparrow}^\dagger + c_{2,z,\uparrow}^\dagger c_{1,z,\downarrow}^\dagger \right) |0\rangle \\
|II\rangle_T = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{1,z,\uparrow}^\dagger - c_{2,z,\uparrow}^\dagger c_{1,z,\downarrow}^\dagger \right) |0\rangle.
\]

Both are eigenstates of \( H_0 \), with eigenvalues \( U - 3J_H \).

B Basis of \( \mathcal{D} \) in the singlet subspace

When considering singlet states, a convenient basis for the subspace \( \mathcal{D} \) is given by \( \{ |p\rangle_S, 1 \leq p \leq 4 \} \), with:

\[
|1\rangle_S = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{2,z,\downarrow}^\dagger - c_{1,z,\downarrow}^\dagger c_{2,x,\uparrow}^\dagger \right) |0\rangle \\
|2\rangle_S = \frac{1}{2} \left( c_{1,x,\uparrow}^\dagger c_{2,z,\downarrow}^\dagger - c_{1,x,\downarrow}^\dagger c_{2,z,\uparrow}^\dagger + c_{1,z,\uparrow}^\dagger c_{2,x,\downarrow}^\dagger - c_{1,z,\downarrow}^\dagger c_{2,x,\uparrow}^\dagger \right) |0\rangle \\
|3\rangle_S = \frac{1}{2} \left( c_{1,x,\uparrow}^\dagger c_{2,z,\downarrow}^\dagger - c_{1,x,\downarrow}^\dagger c_{2,z,\uparrow}^\dagger - c_{1,z,\uparrow}^\dagger c_{2,x,\downarrow}^\dagger + c_{1,z,\downarrow}^\dagger c_{2,x,\uparrow}^\dagger \right) |0\rangle \\
|4\rangle_S = \frac{1}{\sqrt{2}} \left( c_{1,x,\uparrow}^\dagger c_{2,x,\uparrow}^\dagger - c_{1,x,\downarrow}^\dagger c_{2,x,\downarrow}^\dagger \right) |0\rangle.
\]
These states are eigenstates of $H_0$, with eigenvalues $E_1^{(0)} = -E_{CF}$, $E_2^{(0)} = E_3^{(0)} = 0$, and $E_4^{(0)} = E_{CF}$. As for the complementary space $\mathbb{H}/D$, we start with the basis $\{|q\rangle_S, 1 \leq q \leq 6\}$ given by:

$$
|I\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{1,z,\uparrow}^\dagger + c_{1,x,1}^\dagger c_{1,x,\uparrow}^\dagger + c_{2,z,1}^\dagger c_{2,z,\uparrow}^\dagger + c_{2,x,1}^\dagger c_{2,x,\uparrow}^\dagger) |0\rangle
$$

$$
|II\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{2,z,\uparrow}^\dagger - c_{1,x,1}^\dagger c_{2,x,\uparrow}^\dagger + c_{2,z,1}^\dagger c_{2,x,\uparrow}^\dagger - c_{2,x,1}^\dagger c_{2,z,\uparrow}^\dagger) |0\rangle
$$

$$
|III\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{2,z,\uparrow}^\dagger + c_{1,x,1}^\dagger c_{2,x,\uparrow}^\dagger - c_{2,z,1}^\dagger c_{2,x,\uparrow}^\dagger - c_{2,x,1}^\dagger c_{2,z,\uparrow}^\dagger) |0\rangle
$$

$$
|IV\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{1,z,\uparrow}^\dagger - c_{1,x,1}^\dagger c_{1,x,\uparrow}^\dagger - c_{2,z,1}^\dagger c_{2,z,\uparrow}^\dagger + c_{2,x,1}^\dagger c_{2,x,\uparrow}^\dagger) |0\rangle
$$

$$
|V\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{1,z,\uparrow}^\dagger + c_{1,x,1}^\dagger c_{1,x,\uparrow}^\dagger + c_{2,z,1}^\dagger c_{2,z,\uparrow}^\dagger + c_{2,x,1}^\dagger c_{2,x,\uparrow}^\dagger) |0\rangle
$$

$$
|VI\rangle_S = \frac{1}{2} (c_{1,z,1}^\dagger c_{1,z,\uparrow}^\dagger + c_{1,x,1}^\dagger c_{1,x,\uparrow}^\dagger - c_{2,z,1}^\dagger c_{2,z,\uparrow}^\dagger - c_{2,x,1}^\dagger c_{2,x,\uparrow}^\dagger) |0\rangle
$$

Unfortunately these eigenstates of $H_{int}$ are not eigenstates of $H_0$, as $\langle I|H_0|II\rangle_S = \langle III|H_0|IV\rangle_S = -E_{CF}$, but the resulting $2 \times 2$ blocs are most easily diagonalized. As a result we obtain the eigenvalues of the unperturbed Hamiltonian as $E^{(0)}_I = E^{(0)}_{II} = U - \sqrt{J_R^2 + E_{CF}^2}$, $E^{(0)}_{III} = E^{(0)}_{IV} = U + \sqrt{J_R^2 + E_{CF}^2}$, and $E^{(0)}_{V} = E^{(0)}_{VI} = U - J_H$.

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