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Self-consistent perturbative evaluation of ground-state energies: Application to cohesive energies of spin lattices

Mohamad Al Hajj and Jean-Paul Malrieu
Laboratoire de Physique Quantique, IRSAMC/UMR5626, Université Paul Sabatier, 118 Route de Narbonne, F-31062 Toulouse Cedex 4, France

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This work presents a simple formalism which proposes an estimate of the ground-state energy from a single reference function. It is based on a perturbative expansion but leads to nonlinear coupled equations. It can be viewed as well as a modified coupled cluster formulation. Applied to a series of spin lattices governed by model Hamiltonians the method leads to simple analytic solutions. The so-calculated cohesive energies are surprisingly accurate. Two examples illustrate its applicability to locate phase transition.

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I. INTRODUCTION

The quantum many-body problem has been perfectly clarified a long time ago for the single-reference approaches. Its logics is given by the linked cluster theorem,[1–3] which relies on a perturbative expansion and its diagrammatic representation. A panoply of computational methods satisfying the basic size-consistency requirements are available. One of them is the Möller-Plesset order-by-order perturbative expansion[4] which suffers from its slow convergence (and in some cases high-order divergences[5]). Other methods lead to nonlinear equations coupling the coefficients of the vectors which are singly or doubly excited with respect to the single reference Φ_0. Among them one may quote the coupled electron pair approximation (CEPA) formalism[6–8] which eliminates unlinked diagrams from a singles and doubles configuration interaction (SDCI) and introduces part of [in CEPA-2 (Refs. 7 and 8)] or all [in the self-consistent size-consistent $(\mathrm{SC})^2$ SDCI version (Ref. 9)] of the exclusion principle violating (EPV) diagrams. The coupled cluster method [CCM (Refs. 10–12)] has a better standard since it is an elegant and generalizable formalism. This method gives an exponential structure to the wave operator Ω which transforms a reference function Φ_0 in the exact solution Ψ_0, $\Psi_0=\Omega\Phi_0$, $\Omega=\exp(S)$. In practice, S is limited to a certain set of excitations. The simplest version, called (CCSD), introduces single and double excitations on the top of Φ_0 and takes into account the connected effect of the quadruples. It does not correctly treat the effect of the triples, which has to be incorporated perturbatively in the CCSD(T) formalism.[13,14]

The present work returns to a low-order semiperturbative development from Φ_0. It leads to a system of equations fixing the coefficients of the singly and doubly excited vectors, which

(i) Does not require to assume an exponential structure of the wave operator,

(ii) Introduces the effect of deviations from additivity of excitation energies (deviations which is implicitly supposed to be negligible in CCSD), and

(iii) Introduces some high-order effects through EPV corrections to the excitation energies.

The method is applied to a few infinite periodic spin lattices governed by Heisenberg Hamiltonians which only consider interactions between nearest neighbors. In these problems if all bonds are identical, the solutions of our self-consistent perturbative (SCP) method lead to simple polynomial equations. The results, compared to the exact solutions, are of surprising quality. The method is then employed to identify phase transitions in two different two-dimensional (2D) problems.

II. FORMALISM

A. Generalities

Let us call Φ_0 a suitable single reference supposed to be a relevant approximation to the ground state of the system governed by an Hamiltonian H and Φ_m vectors orthogonal to Φ_0. In the intermediate normalization

$$\Psi_0 = \Phi_0 + \sum_m C_m \Phi_m, \tag{1}$$

the exact energy is given by the eigenequation relative to Φ_0, $\langle\Phi_0|H-E|\Psi_0\rangle=0$

$$E = H_{00} + \sum_k H_{0k} C_k, \tag{2}$$

where $H_{ij}=\langle\Phi_i|H|\Phi_j\rangle$. The Hamiltonians are at most bielectronic. One may call h_1 and h_2 the monoelectronic and bielectronic parts of the Hamiltonian $H=h_1+h_2$. One may label $m,n\ldots$ (holes) the monoelectronic function occupied in Φ_0 and $r,s\ldots$ (particles) those which are not occupied in Φ_0.

In the following we shall refer to an Epstein-Nesbet[15–17] zero-order Hamiltonian which is the diagonal part of the Hamiltonian in the basis of the N-electronic vectors $\{\Phi_0,..\Phi_m..\}$

$$H_0 = \sum_m |\Phi_m\rangle\langle\Phi_m|H|\Phi_m\rangle\langle\Phi_m|. \tag{3}$$

The perturbation operator V

$$V = H - H_0 \tag{4}$$

is zero diagonal in this basis

$$V = \sum_i \sum_j{}' |\Phi_i\rangle\langle\Phi_i|H|\Phi_j\rangle\langle\Phi_j|. \tag{5}$$

The Hamiltonian being at most bielectronic, it appears from Eq. (2) that the knowledge of the coefficient of the singly and doubly excited vectors which interact with Φ_0 is sufficient to give the ground-state energy. We shall call first generation S_1 the set of vectors Φ_i interacting with Φ_0,

$$S_1 = \{\Phi_i\}, \;\; \langle\Phi_i|H|\Phi_0\rangle \neq 0,$$

and T_i^+ the operators creating the vectors Φ_i from Φ_0,

$$\Phi_i = T_i^+\Phi_0.$$

These operators may be written as

$$T_i^+ = a_r^+ a_a[1 - \delta(\langle r|h_1|a\rangle)] \tag{6}$$

or

$$T_k^+ = a_r^+ a_s^+ a_b a_a[1 - \delta(\langle rs|h_2|ab\rangle)], \tag{7}$$

where δ is the Kroneker symbol. The coefficients of the first generation vectors can be estimated from the eigenequations relative to them. For Φ_i the equation $\langle\Phi_i|H-E|\Psi_0\rangle = 0$ can be written using Eq. (2) as

$$\Big(H_{ii} - H_{00} - \sum_k H_{0k}C_k\Big)C_i + H_{i0} + \sum_{j\in S_1} H_{ij}C_j + \sum_{\alpha\notin S_1} H_{i\alpha}C_\alpha = 0. \tag{8}$$

To determine the coefficients C_i of the first generation vectors, it is sufficient to have an estimate of the coefficient of vectors Φ_α of the second generation, i.e., those which interact with the vectors of S_1. Among the vectors Φ_α belonging to the second generation one may distinguish those which are obtained from Φ_i by the actions of operators T_k^+ possible on Φ_0 (type 1), and the others which are obtained from Φ_i by operators R_m^+ different from the $T_s'^+$ (type 2).

If one calls T the sum of the operators T_k^+ and of their adjoints

$$T = \sum_k (T_k^+ + T_k^{+\perp}) \tag{9}$$

the operators R

$$R = 1 - \sum_l |\Phi_l\rangle\langle\Phi_l| - T, \tag{10}$$

is the sum of all the operators changing one or two monoelectronic functions which are different from T_k^+ operators. Notice that $\langle R_m^+\Phi_0|H|\Phi_0\rangle = 0$. With the Hamiltonians considered hereafter the second generation vectors Φ_α are either of type 1 or of type 2, i.e., are generated either as

$$\Phi_\alpha = T_l^+ T_k^+ \Phi_0 \text{ (type 1)}$$

or as

$$\Phi_\alpha = R_m^+ T_k^+ \Phi_0 \text{ (type 2)}$$

as pictured in Fig. 1.

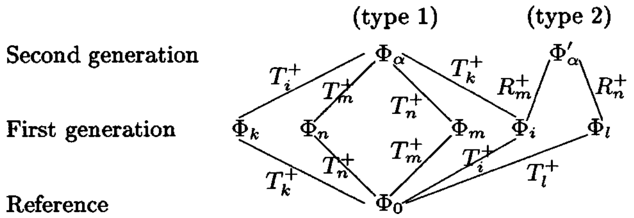


FIG. 1. Illustration of the genealogic generation of Ψ_0 from the reference function Φ_0.

B. Evaluation of the coefficients of second generation vectors

Regarding the *vectors of type 1*, the operators T_k^+ are in general possible on Φ_i, but some of them are impossible ($T_k^+\Phi_i = 0$). Let us call EPV(i) (exclusion principle violating correction) the quantity[9]

$$\mathrm{EPV}(i) = \sum_{\substack{k \\ T_k^+\Phi_i = 0}} H_{0k}C_k. \tag{11}$$

Noting that if $\Phi_\alpha = T_k^+\Phi_i$, and if T_k^+ is a double excitation $H_{i\alpha} = H_{0k}$. Introducing Eq. (11), Eq. (8) can be written

$$\begin{aligned}[H_{ii} - H_{00} - \mathrm{EPV}(i)]C_i + H_{i0} + \sum_{j\in S_1} H_{ij}C_j \\ + \sum_{\substack{k \\ T_k^+\Phi_i \neq 0}} H_{0k}(C_{T_k^+\Phi_i} - C_iC_k) \\ + \sum_{\substack{m \\ R_m^+\Phi_i \notin S_1}} \langle\Phi_i|H|R_m^+\Phi_i\rangle C_{R_m^+\Phi_i} = 0.\end{aligned} \tag{12}$$

A first-order evaluation of C_i is of course the Epstein-Nesbet[15–17] one

$$C_i = H_{i0}/(H_{00} - H_{ii}). \tag{13}$$

Introducing EPV corrections in the energy denominator

$$C_i = H_{i0}/[H_{00} - H_{ii} + \mathrm{EPV}(i)], \tag{14}$$

incorporates an infinite summation of diagrams.[18,19] One may use a second-order perturbation theory to evaluate the coefficients $C_{T_k^+\Phi_i}$ and $C_{R_m^+\Phi_i}$.

The vector of type 1 $T_k^+\Phi_i = T_i^+\Phi_k = T_k^+T_i^+\Phi_0$ can also be reached from Φ_0 by other sets of excitations $T_m^+T_n^+\Phi_0$ (cf. Fig. 1). The second-order expansion of the wave function tells us

$$C_{T_k^+\Phi_i} = \frac{H_{0k}C_i + H_{0i}C_k}{H_{00} - H_{i+k,i+k}} + \frac{\sum'_{\langle m,n\rangle}(H_{0m}C_n + H_{0n}C_m)}{H_{00} - H_{i+k,i+k}}, \tag{15}$$

where $H_{i+k,i+k} = \langle\Phi_{T_k^+\Phi_i}|H|\Phi_{T_k^+\Phi_i}\rangle$ and $\Sigma'_{\langle m,n\rangle}$ runs on the couples $T_m^+T_n^+\Phi_0 = T_k^+T_i^+\Phi_0$ but different from the couple ik.

An infinite summation of diagrams would lead to the introduction of an EPV correction in the energy denominator

$$\mathrm{EPV}(i+k) = \sum_{\substack{l \\ T_l^+ T_k^+ \Phi_i = 0}} H_{0l} C_l, \tag{16}$$

and to replace $H_{00} - H_{i+k,i+k}$ by $H_{00} - H_{i+k,i+k} + \mathrm{EPV}(i+k)$.

$$C_{T_k^+\Phi_i} = \frac{H_{0k}C_i + H_{0i}C_k + \sum'_{\langle m,n\rangle}(H_{0m}C_n + H_{0n}C_m)}{H_{00} - H_{i+k,i+k} + \mathrm{EPV}(i+k)}. \tag{17}$$

Now taking benefit of [Eq. (14)] i.e., replacing H_{0i} (and H_{0k}) by products $C_i[H_{00} - H_{ii} + \mathrm{EPV}(i)]$ in Eq. (17) one obtains an expression closer to the CC expansion

$$C_{T_k^+\Phi_i} = C_i C_k \left(\frac{H_{00} - H_{ii} + \mathrm{EPV}(i) + H_{00} - H_{kk} + \mathrm{EPV}(k)}{H_{00} - H_{i+k,i+k} + \mathrm{EPV}(i+k)} \right) + \sum_{\langle m,n\rangle}{}' C_m C_n \left(\frac{H_{00} - H_{mm} + \mathrm{EPV}(m) + H_{00} - H_{nn} + \mathrm{EPV}(n)}{H_{00} - H_{i+k,i+k} + \mathrm{EPV}(i+k)} \right). \tag{18}$$

The CC theory writes

$$C_{T_k^+\Phi_i} = C_i C_k + \sum_{\langle m,n\rangle}{}' C_m C_n, \tag{19}$$

which ignores the possible deviation of the energy denominators from additivity, i.e., assumes $H_{00} - H_{i+k,i+k} = H_{00} - H_{ii} + H_{00} - H_{kk}$. Using the compact notation $\Delta_i = -H_{00} + H_{ii}$, $\Delta_{i+k} = -H_{00} + H_{i+k,i+k}$, one obtains

$$C_{T_k^+\Phi_i} - C_i C_k = C_i C_k \left(\frac{-\Delta_i + \mathrm{EPV}(i) - \Delta_k + \mathrm{EPV}(k)}{-\Delta_{i+k} + \mathrm{EPV}(i+k)} - 1 \right) + \sum_{\substack{\langle m,n\rangle \\ T_m^+ T_n^+ \Phi_0 = T_k^+ T_i^+ \Phi_0}}{}' C_m C_n \left(\frac{-\Delta_m + \mathrm{EPV}(m) - \Delta_n + \mathrm{EPV}(n)}{-\Delta_{i+k} + \mathrm{EPV}(i+k)} \right). \tag{20}$$

Notice that if there is only one route to create $\Phi_\alpha = \Phi_{i+k}$ from Φ_0 the last sum disappears. If the excitation energies (eventually including EPV's) are additive, the full term vanishes in agreement with the cancellation of disconnected diagrams. This will be the case in the applications to spin lattices with nearest-neighbor interactions when excitations T_i^+ and T_k^+ will concern remote bonds.

Regarding the *vectors of type2*, the operators $R_m^+ (\neq T^+)$ which lead from Φ_i to $R_m^+\Phi_i$ have to be treated perturbatively as follows. Analogous to Eq. (17) one obtains

$$C_{R_m^+\Phi_i} = \frac{H_{i,R_m^+ i} C_i}{-\Delta_{R_m^+ i} + \mathrm{EPV}(R_m^+ i)} + \sum_{\substack{\langle n,l\rangle \\ R_n^+ \Phi_l = R_m^+ \Phi_i}}{}' \frac{H_{l,R_n^+ l} C_l}{-\Delta_{R_m^+ i} + \mathrm{EPV}(R_m^+ i)}. \tag{21}$$

C. Final equations and comments

If R_m^+ is a bielectronic operator, $H_{i,R_m^+ i} = H_m$ and the eigenequation relative to Φ_i will be

$$\begin{aligned}
&[\Delta_i - \mathrm{EPV}(i)]C_i + H_{i0} + \sum_{j \in S_1} H_{ij} C_j \\
&\quad + \sum_{\substack{k \\ T_k^+ \Phi_i \neq 0}} H_{0k} C_k C_i \left(\frac{\Delta_i - \mathrm{EPV}(i) + \Delta_k - \mathrm{EPV}(k)}{\Delta_{i+k} - \mathrm{EPV}(i+k)} - 1 \right) \\
&\quad + \sum_{\substack{\langle m,n\rangle \\ T_m^+ T_n^+ \Phi_0 = T_k^+ T_i^+ \Phi_0}}{}' H_{0k} C_m C_n \\
&\quad \times \left(\frac{\Delta_m - \mathrm{EPV}(m) + \Delta_n - \mathrm{EPV}(n)}{\Delta_{i+k} - \mathrm{EPV}(i+k)} \right) \\
&\quad + \sum_{\substack{m \\ R_m^+ \Phi_0 = 0}} \frac{H_m^2 C_i}{-\Delta_{R_m^+ i} + \mathrm{EPV}(R_m^+ i)} \\
&\quad + \sum_{\substack{\langle n,l\rangle \\ R_n^+ T_l^+ \Phi_0 = R_m^+ T_i^+ \Phi_0}}{}' \frac{H_m H_n C_l}{-\Delta_{R_m^+ i} + \mathrm{EPV}(R_m^+ i)} = 0.
\end{aligned} \tag{22}$$

This will be our basic equation. It is somewhat related to the usual coupled cluster equations. The similarity and differences appear clearly if ones considers the case of a self-consistent field Φ_0. Then the vectors of the first generation are all the Doubles, hence the method should be compared to a coupled clustered Doubles (CCD) expansion. The differences are the following:

(i) The effect of the quadruples in CCD does not take care of possible deviations from the additivity of the denominators and the sum over k reduces to

$$\sum_{\substack{k \\ T_k^+\Phi_i\neq 0}} C_k C_i + \sum_{\substack{\langle m,n\rangle \\ T_m^+T_n^+\Phi_0=T_k^+T_i^+\Phi_0}}{}' C_m C_n. \tag{23}$$

We take into account the deviation from additivity of energy denominators.

(ii) We take care of the coupling with the Singles and Triples through the last summation. Hence our method would be similar to a CCD(S,T).

(iii) Our (semi) perturbative treatment of the Singles and Triples includes EPV corrections in the energy denominators. These corrections also appear in the effect of deviations from additivity of multiple excitation energies. Most of these effects were considered in previous works,[20,21] which were expressed in an intermediate Hamiltonian formalism, requiring an iterative dressing of small matrices. The set of coupled nonlinear equations [Eq. (22)] is much clearer.

III. APPLICATIONS TO PERIODIC 1D AND 2D SPIN LATTICES

As will be shown in this section the method is of an extreme simplicity when applied

(i) To periodic lattices of spins (and electrons[22,23]),

(ii) Ruled by model Hamiltonians which only introduce short range interactions (usually between nearest-neighbor atoms),

(iii) Provided that one starts from a strongly localized wave function, product of atomic or bond orbitals.

The usual implementation of the coupled cluster method are governed by a hierarchy of excitations. They introduce for instance all single and double excitations. Here we adopt a different strategy, since we follow the genealogy of the generation of Ψ_0 from Φ_0 under the successive applications of H. Due to the localized character of Φ_0 and the short range nature of the operator in H, the first-generation vectors will involve short range excitations only, and in periodic systems one has a limited number of types of first-generation excitations. Under these conditions the number of coefficients to determine is extremely reduced, and their values are obtained by solving a set of coupled polynomial equations, which may be done on a pocket calculator. We shall take a few examples illustrating the method and its performances, comparing the so-calculated values to the exact (or highly accurate) ones. Section III A will illustrate the derivation of the SCP equations for simple lattices, and will compare the resulting cohesive energies to benchmarks values. Section II B will employ the SCP method to study two phase transition phenomena taking place in 2D lattices.

A. Cohesive energy of simple spin lattices

The ruling Hamiltonian will introduce only nearest-neighbor interactions

$$H = \sum_{\langle i,j\rangle} 2J(S_iS_j - 1/4), \tag{24}$$

between adjacent atoms. This Hamiltonian puts to zero the energy of the upper multiplet

1. 1D chain from Néel

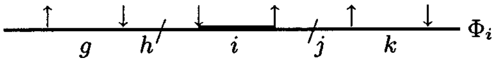
If all bonds are equal, taking Φ_0 as the Néel function (spin alternation between adjacent atoms), the zero order energy per atom is $E_{\text{coh}}^{(0)}=-J$. There is only one type of vectors in S_1, the one obtained from a spin exchange T_i^+ on a bond i, of coefficient C, coupled by J with $\Phi_0(H_{i0}=J)$ hence

$$E_{\text{coh}} = -J(1-C),$$

$$H_{ii} - H_{00} = \Delta_i = 2J,$$

$$\text{EPV}(i) = 3CJ. \tag{25}$$

A simple second-order estimate of the energy would lead to $C=-1/2$, $E_{\text{coh}}^{(2)}=-1.5J$, much larger than the exact value $E_{\text{coh}}^{\text{exact}}=-2J\ln 2=-1.386J$. Including the EVP's in the denominator would give



$$(2J-3CJ)C+J=0,$$

$$3C^2-2C-1=0,$$

$$C=-1/3,$$

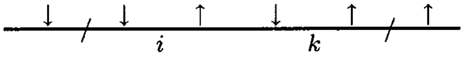
$$E'^{(2)}_{\text{coh}} = -1.333J, \tag{26}$$

which is already a better estimate. There is no coupling between the vectors Φ_i and $\Phi_j \in S_1$. The second generation vectors are obtained by two spin exchanges on bonds i and k. If the bonds i and k are far the doubly excited vectors $T_k^+T_i^+\Phi_0$ have a coefficient $C_{i+k}=C_iC_k$ since

(i) There is no other couple of first-generation excitation $T_m^+T_n^+\Phi_0=T_k^+T_i^+\Phi_0$,

(ii) The excitation energies are additive.

The only exceptions concern the double exchanges $T_h^+T_i^+$ and $T_i^+T_k^+$, on second-neighbor bonds. For them $\Delta_{i+k}=2J$, EVP$(i+k)=5CJ$. Their coefficient can be evaluated according to [Eq. (18)] as



$$C_{i+k} = 2C^2\left(\frac{2J - 3CJ}{2J - 5CJ}\right), \qquad (27)$$

and the final equation is

$$(2 - 3C)C + 1 + 2C^2\left(\frac{4 - 6C - 2 + 5C}{2 - 5C}\right) = 0,$$

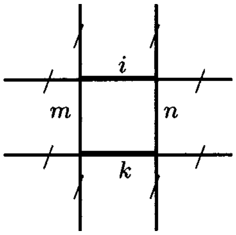
$$- 3C^2 + 2C + 1 + 2C^2\left(\frac{2 - C}{2 - 5C}\right) = 0. \qquad (28)$$

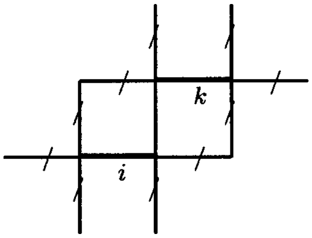
Its solution is $C=-0.3751$ hence $E_{\mathrm{coh}}=-1.3751J$, which deviates by 0.8% from the exact value $-1.3862J=2J\ln 2$.

2. 2D square lattice from Néel

Here, $E_{\mathrm{coh}}^{(0)}=-2J$, $E_{\mathrm{coh}}=-2J(1+C)$, where C is the coefficient relative to a spin exchange on a bond. Here $\Delta_i=H_{ii}-H_{00}=6J$, EPV$(i)=7CJ$. The coefficients of the doubly spin exchanged vectors are C_kC_i, except for the following:

(i) Spin exchanges on the same plaquette. There are two such double excitations for a bond i.





(ii) Spin exchanges on other second-neighbor bonds [the number of which is 14 for a given bond (5)i].

The final equation is

$$(6 - 7C)C + 1 + 2C^2\left(\frac{16 - 16C}{8 - 12C}\right) + 14C^2\left(\frac{2 - C}{10 - 13C}\right) = 0, \qquad (29)$$

the solution of which is $C=-0.16327$, $E_{\mathrm{coh}}=-2.3265J$ to be compared with the best Monte Carlo estimate $-2.3386J$. The error is 0.51%. Our estimate may be compared with classical CC evaluations[24,25] which give

$-2.2970J$ with two-body operators,

$-2.3274J$ with four-body operators,

$-2.3340J$ with six-body operators,

$-2.3364J$ with eighth-body operators.

The use of many-body operators makes the algorithm much more complex. Our results is a modified two-body method, which provides the same accuracy as handling four-body operators. The same accuracy is obtained for anisotropic Hamiltonian.

B. Identification of phase transitions

This section illustrates the ability of the (SCPE) method to locate the critical values of physical interactions at which phase transition occurs. Two examples will be considered, both concerning 2D lattices. In all cases a relevant reference function Φ_0 is selected for each phase, from physical arguments. The SCP equations are established, leading to an evaluation of the cohesive energy for the corresponding phase. The step-by-step derivation of these equations in not given, and the equations are reported in the Appendix. The intersection of the cohesive energy curves as functions of the structural parameter enables us to give a reasonable estimate of the critical value of the parameters.

1. Anisotropic Heisenberg Hamiltonian for the 2D square lattice

The anisotropic Hamiltonian may be written as

$$H = \sum_{\langle i,j\rangle} J(\lambda S_z^i S_z^j + S_x^i S_x^j + S_y^i S_y^j). \qquad (30)$$

For a 2D square lattice and for $\lambda<-1$ the ground state is ferromagnetic, all sites bearing parallel spins. For $\lambda=-1$ the ferromagnetic state is degenerate with the pure XY solution, in which the bonded atoms bear alternatively $(\alpha+\beta)$ and $(\alpha-\beta)$ spins. This distribution defines a reference function Φ_0 which will be relevant for the $-1\leqslant\lambda\leqslant 1$ domain. For $\lambda\geqslant 1$ the wave function can be generated from the Néel function Φ_0' in which adjacent atoms bear different spins. When λ tends to infinity the system becomes Ising $(\Psi_0\rightarrow\Phi_0')$. The phase transition between the XY supported and the Néel supported phase takes place for the isotropic lattice $(\lambda=1)$. Besides analytic series expansions[26–29] accurate calculations on this problem have been performed according to various techniques, among which one may quote

(i) Quantum Monte Carlo calculations,[30–38]

(ii) Real space renormalization group with effective interactions,[39]

(iii) Coupled cluster expansions,[24,25]

(iv) Dressed cluster method (DCM).[39]

The two first techniques do not introduce any reference function Φ_0. The two last ones imply a choice of such reference functions either as a zero-order function for the coupled cluster method, or as a bath in which a finite cluster is embedded in the DCM. Our approach belongs to the same family. The equations derived from $\Phi_0=\Phi_0^{XY}$ or from $\Phi_0'=\Phi_0^{\text{Néel}}$ are given in Appendix A. One may see that they coincide for $\lambda=1$, which appears as the critical value of the parameter. Figure 2 and Table I give the evolution of the cohesive energy E_0 and E_0' calculated from both references and a comparison with the most accurate results. One sees

(i) That the derivatives of the energies in $\lambda=1$ are not identical

$$\left(\frac{\partial E}{\partial\lambda}\right)^-_{\lambda\rightarrow 1} = \left(\frac{\partial E_0}{\partial\lambda}\right)_{\lambda=1} \neq \left(\frac{\partial E_0'}{\partial\lambda}\right)_{\lambda=1} = \left(\frac{\partial E}{\partial\lambda}\right)^+_{1\leftarrow\lambda}, \qquad (31)$$

which confirms the first-order character of the phase transition,

(ii) The agreement of the here-calculated cohesive energies with the best (QMC) calculations in good, the error

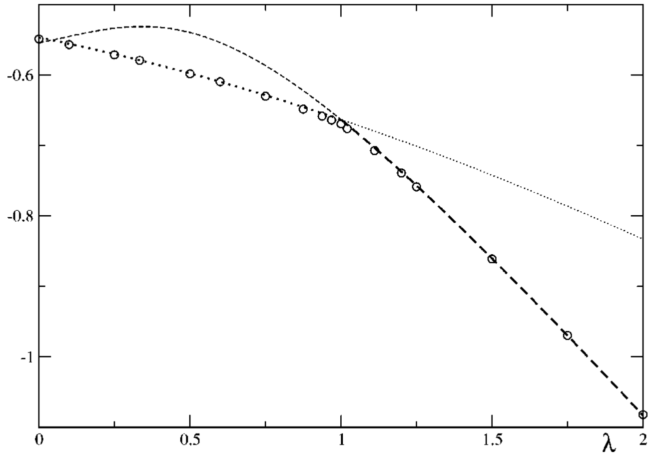


FIG. 2. 2D square anisotropic spin lattice, evolution of the cohesive energy as a function of the anisotropy parameter λ. (○) QMC (Ref. 38), SCP results: (…) from XY Φ_0, (-) from Néel Φ_0'. The thick symbols identify the relevant domains from Φ_0 and Φ_0', respectively.

being lower than 1% in the $-1<\lambda<\infty$ domain.

TABLE I. Cohesive energy of the anisotropic 2D lattice.

λ	SCP(XY)	SCP(Néel)	QMC (Ref. 38)
0	−0.54672		−0.54882
0.1	−0.55564		−0.55681
0.25	−0.57024		−0.57142
0.33333	−0.57892		−0.57926
0.5	−0.59777		−0.59832
0.6	−0.60965		−0.60958
0.75	−0.62885		−0.63017
0.875	−0.64557		−0.64848
0.9375	−0.64196		−0.65846
0.96875	−0.65264		−0.66396
1	−0.66327	−0.66327	−0.66944
1.02040		−0.67061	−0.67612
1.11111		−0.70330	−0.70722
1.2		−0.73727	−0.73920
1.25		−0.75696	−0.75862
1.5		−0.86046	−0.86100
1.75		−0.96989	−0.96965
2		−1.08314	−1.08220

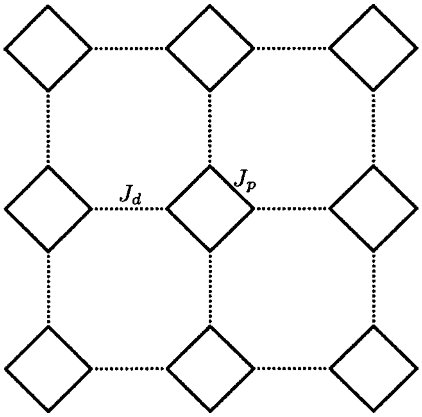


FIG. 3. The 1/5-depleted 2D square lattice.

2. 1/5-*depleted square lattice*

The 1/5-depleted square lattice has received interest in the context of the study of a real material, namely, the CaV_2O_4 lattice. Precise studies of that material indicated that second-neighbor interactions have to be considered. Nevertheless the physics of the simple lattice, built of plaquettes and octogons, or of plaquettes connected by bonds (cf. Fig. 3), appeared interesting by itself. There are two types of spin interactions, namely, in the plaquette (J_p) and in the bonds between the plaquettes (J_d). Early studies did not give evidence of phase transitions, but perturbative expansions[40] and quantum Monte Carlo calculations[41] indicate the existence of three phases, namely, a gapped plaquette phase for $J_p/J_d>1.05-1.10$, a gapped dimer phase for $J_p/J_d<0.65$ and a gapless Néel-type phase in the intermediate regime. We have reexamined this problem with the SCP equations starting from three different references Φ_0, namely,

(i) A product of bond singlets on the interplaquette bonds which is expected to be relevant in the $J_p/J_d<1$ regime,

(ii) The Néel function, which should be valid in the $J_p\sim J_d$ region,

(iii) A product of bond Singlets on intraplaquette bonds, relevant in the $J_p>J_d$ regime.

The corresponding equations are given in Appendix B. The results appear in Fig. 4. One should remark that our SCP equations never diverge, even when applied in paradoxical regimes, for instance when one enters in the $J_p\ll J_d$ regime from interplaquette bonds. The expansion from Néel tends to

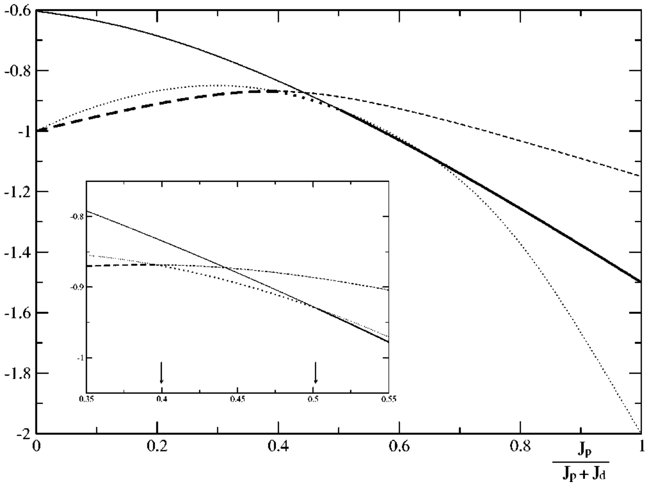


FIG. 4. 1/5-depleted 2D square lattice. Evolution of the cohesive energy as a function of the $J_p/(J_p+J_d)$ ratio according to the SCP method. (--) from interplaquette bond Singlets Φ_0, (…) from Néel Φ_0', and (—) from plaquette Singlets Φ_0''. The thick symbols identify the relevant domains from the various reference functions. The arrows indicate the phase transition critical values.

an erroneous ($-2J$ instead of $-1.5J$) value for $J_d=0$ (isolated plaquettes). Using the perturbative evaluation of the coefficient of the doubly permuted vectors [Eq. (17) instead of Eq. (18)], one reaches the correct asymptotic value for $J_d=0$. One must concentrate on the estimates of the cohesive energy in the relevant domains. As seen from Fig. 4 one notices the existence of three phases:

(i) A dimer phase for $J_p/J_d < 0.6563$,
(ii) A Néel-order phase for $0.65 < J_p/J_d < 1.0105$,
(iii) A plaquette phase for $J_p/J_d > 1.0105$.

Using Eq. (17) instead of Eq. (18), the critical ratios remain almost identical. The method confirms the existence of these three phases and the calculated critical values of the J_p/J_d ratios are in good agreement with previously mentioned estimates.

IV. DISCUSSION AND CONCLUSION

The here presented method is based on perturbative expansion of the wave function but it is not strictly perturbative. It is perturbative in the sense that it follows a genealogic generation of the wave function and that it uses (or refers to) pertubative estimates of the coefficients of the second generation vectors.

But it is not perturbative in the sense that the coefficients of the first generation vectors are obtained by solving a set of coupled polynomial equations. It may compared to the coupled cluster method [and in particular to a CCD(S,T) version] from which it differs by the consideration of possible deviations from additivity of multiple-excitation energies and by the introduction of EPV corrections in energy denominators.

Although perfectly applicable to *ab initio* calculations, the method has been essentially designed for the study of periodic lattices and model Hamiltonians. In such cases, starting from strongly localized zero-order pictures, the method is analytical, it leads to simple polynomial expressions, introducing a very limited number of variables (one per type of bond in most cases), which can be solved on a pocket calculator. The accuracy of such a simple method is surprising, as illustrated above. It provides an elegant exploratory tool for the study of spin periodic lattices. The present work has shown that the method may be employed to identify phase transitions. The method is of course applicable to Hubbard Hamiltonians, whose exact solutions are not known (except for the 1D regular chain) and to 2D or 3D lattices. Since the method only explores the physics around a given bond (up to six bonds in each direction) it may lead to some stimulating qualitative discussions to assess what is local, regional, and properly collective in the cohesive energy of delocalized systems.[22,23] Further work will study the spin-Peierls distortions. The present method essentially furnishes an estimate of the ground-state energy. It may also provide short range correlation functions. The localized character of Φ_0 and the fact that the excitation processes playing a role in the low-order processes only concern a few bonds prevent to give estimates of the correlation beyond this limit. The related coupled cluster formalism has led to specific methods for the evaluation of spectra, namely, the equation of motion coupled cluster algorithm.[42] Future works will analyze the possibility of such an extension in the frame of our development.

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APPENDIX A

SCP equations for the anisotropic 2D square lattice [Eq. (30)]

(1) Equation from Néel

$$(6\lambda J - 7JC)C + J + 2J\left[2\left(\frac{12\lambda J - 14JC}{8\lambda J - 12JC}\right) - 1\right]C^2 + 14J\left[\frac{12\lambda J - 14JC}{10\lambda J - 13JC} - 1\right]C^2 = 0, \tag{A1}$$

$$E_{\mathrm{coh}} = J\left(C - \frac{\lambda}{2}\right). \tag{A2}$$

(2) Equation from *XY*

$$\left[6J - \frac{7J}{2}(1+\lambda)C\right]C + \frac{J}{2}(1+\lambda) + 2J\left[2\left(\frac{12J - 7J(1+\lambda)C}{8J - 6J(1+\lambda)C}\right) - 1\right]C^2 + 14J\left[\frac{12J - 7J(1+\lambda)C}{10J - \frac{13J}{2}(1+\lambda)C} - 1\right]C^2 - \frac{J^2(1-\lambda)^2 C}{2\left[J - \frac{J}{2}(1+\lambda)C\right]} - \frac{J^2(1-\lambda)^2 C}{8\left[J - \frac{J}{2}(1+\lambda)C\right]} = 0, \tag{A3}$$

$$E_{\mathrm{coh}} = \frac{J}{2}[(1+\lambda)C - 1]. \tag{A4}$$

APPENDIX B

SCP equations for the 1/5-depleted 2D square lattice with $J_p=(1+\delta)$ and $J_d=(1-\delta)$

(1) Equation from interplaquette bond singlets

$$\left[4(1-\delta)-\frac{5}{6}(1+\delta)-\frac{7\sqrt{3}}{2}(1+\delta)C\right]C+\frac{\sqrt{3}}{2}(1+\delta)-\frac{15(1+\delta)^2C}{4(1-\delta)-\frac{9\sqrt{3}}{2}(1+\delta)C}=0, \tag{B1}$$

$$E_{\text{coh}}=\frac{1}{2}\left[-\frac{3}{2}+\frac{\delta}{2}+\frac{\sqrt{3}}{2}(1+\delta)C\right]. \tag{B2}$$

(2) Equations from Néel function. The coefficient C (resp. C') is relative to the spin exchange in the plaquette (resp. between the plaquettes)

$$\begin{aligned}&[4-3(1+\delta)C-2(1-\delta)C']C+(1+\delta)+(1+\delta)\\&\quad\times\left[2\frac{8-6(1+\delta)C-4(1-\delta)C'}{4(1-\delta)-4(1-\delta)C'-4(1+\delta)C}-1\right]\\&\quad\times C^2 4(1-\delta)\left[\frac{8-6(1+\delta)C-4(1-\delta)C'}{4(1+\delta)+2(1-\delta)-4(1+\delta)C-3(1-\delta)C'}-1\right]C^2+2(1+\delta)\\&\quad\times\left[\frac{4+4(1+\delta)-7(1+\delta)C-3(1-\delta)C'}{4(1+\delta)+2(1-\delta)-4(1+\delta)C-3(1-\delta)C'}-1\right]CC'=0,\end{aligned} \tag{B3}$$

$$\begin{aligned}&[4(1+\delta)-4(1+\delta)C-(1-\delta)C']C'+(1-\delta)+4(1+\delta)\left[\frac{4+4(1+\delta)-7(1+\delta)C-3(1-\delta)C'}{4(1+\delta)+2(1-\delta)-4(1+\delta)C-3(1-\delta)C'}-1\right]\\&\quad\times CC'4(1+\delta)\left[\frac{8(1+\delta)-8(1+\delta)C-2(1-\delta)C'}{6(1+\delta)-6(1+\delta)C-2(1-\delta)C'}-1\right]C'^2=0,\end{aligned} \tag{B4}$$

$$E_{\text{coh}}=\frac{1}{2}\left[-\frac{3}{2}-\frac{\delta}{2}+(1+\delta)C+\frac{1}{2}(1-\delta)C'\right]. \tag{B5}$$

(3) Equations from intraplaquette bond Singlets. C and C' concern, respectively, intra- and inter-plaquette diexcitations

$$\left[2(1+\delta)-2\sqrt{3}(1-\delta)C'+(1+\delta)C\right]C+\sqrt{3}(1+\delta)+\frac{2\sqrt{3}(1-\delta)\left[\frac{\sqrt{3}}{2}(1-\delta)C+\sqrt{3}(1+\delta)C'\right]}{-4(1+\delta)+2\sqrt{3}[(1-\delta)C'+(1+\delta)C]}=0, \tag{B6}$$

$$\begin{aligned}&\left[\frac{19}{6}(1+\delta)-\frac{3\sqrt{3}}{2}(1-\delta)C'-2\sqrt{3}(1+\delta)C\right]C'+\frac{\sqrt{3}}{2}(1-\delta)+\frac{3(1-\delta)^2C'+2\sqrt{3}(1+\delta)\left[\frac{\sqrt{3}}{2}(1-\delta)C+\sqrt{3}(1+\delta)C'\right]}{-4(1+\delta)+2\sqrt{3}[(1-\delta)C'+(1+\delta)C]}\\&\quad=0,\end{aligned} \tag{B7}$$

$$E_{\text{coh}}=\frac{1}{2}\left[-\frac{3}{2}-\delta+\frac{\sqrt{3}}{4}[(1+\delta)C+(1-\delta)C']\right]. \tag{B8}$$

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