



# Single reference Coupled Cluster treatment of nearly degenerate problems: Cohesive energy of antiferromagnetic lattices of spin 1 centers

Jean-Paul Malrieu \*

Laboratoire de Chimie et Physique Quantiques, (CNRS UMR 562), IRSAMC University of Toulouse 3, 118 Rte de Narbonne, 31062 Toulouse Cedex, France

## ARTICLE INFO

### Article history:

Available online 12 November 2011

### Keywords:

Coupled Cluster  
Perturbation Theory  
Magnetic lattices  
Heisenberg Hamiltonians

## ABSTRACT

Lattices of antiferromagnetically coupled spins, ruled by Heisenberg Hamiltonians, are intrinsically highly degenerate systems. The present work tries to estimate the ground state energy of regular bipartite spin lattices of  $S = 1$  sites from a single reference Coupled Cluster expansion starting from a Néel function, taken as reference. The simultaneous changes of spin momentum on adjacent sites play the role of the double excitations in molecular electronic problems. Propagation of the spin changes plays the same role as the triple excitations. The treatment takes care of the deviation of multiple excitation energies from additivity. Specific difficulties appear for 1D chains, which are not due to a near degeneracy between the reference and the vectors which directly interact with it but to the complexity of the processes which lead to the low energy configurations where a consistent reversed-Néel domain is created inside the Néel starting spin wave. Despite these difficulties a reasonable value of the cohesive energy is obtained.

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## 1. Introduction

The Coupled Cluster method was originally proposed by nuclear physicists [1,2]. The domain where it has received its major success definitely is the treatment of the electronic correlation in molecular physics or quantum chemistry [3,4]. In this domain the Coupled Cluster formalism is considered, at various levels of sophistication, as a standard method, at least for the study of systems where a relevant single determinant, usually obtained from mean field calculations, may be constructed and used as reference function for a single-reference Coupled Cluster (CC) expansion. The limits of the method are well documented, they concern the situations where the largest components of the wave functions are developed on several determinants with equal or nearly equal coefficients. This situation occurs in the breaking of covalent bonds and in most of the excited states. The generalization of CC approaches to multireference situations has been the subject of numerous efforts which we shall not recall here, but where Mukerjee has taken a major part [5,6]. The most satisfactory developments (from both the logical criterions and the accuracy) lead to significantly more complex formalisms.

Surprisingly enough the CC method has not received a similar audience in the field of Solid State Theory. In principle its application to systems which imply covalent bonds, or ionic solids, should not present any difficulty since the mean-field calculation of the ground state delivers a relevant single determinantal reference

and the existence of a gap at the Fermi level avoids any near-degeneracy problem. In such cases practical calculations of course require to transform the delocalized Bloch functions into localized equivalent Wannier functions. Then the calculation of the correlation energy per cell is as easy as that of finite molecular systems, one should only consider as independent variables the amplitudes of the double excitations which involve at least one electron (or occupied orbital) of the reference cell. The summation necessarily runs only on the MOs of the neighbor cells. The problems arise for two opposite limits of the electron repulsion versus electron delocalization ratio, illustrated by the  $U/t$  ratio in the Hubbard model Hamiltonian. The first one is the metallic case, where a near degeneracy between the highest occupied and lowest empty orbital energies takes place. Double excitations around the Fermi level take larger and larger amplitudes when the size of the cluster increases, as illustrated in the fascinating work by Chan and coworkers [7] on polyacenes of increasing lengths. Some collective correlation effects are manifest, at least on the wave function if not on the correlation energy. The problem of a relevant method for the calculation of the correlation energy in metallic or quasi-metallic systems remains an open challenge.

On the other extreme of the  $U/|t|$  ratio for half-filled band systems one finds the magnetic regime. In this limit one may consider the delocalization as a perturbation and define model spaces where each site is supposed to be neutral. The mixing between the neutral and ionic structures will be treated as a perturbation. This is the foundation of Heisenberg model Hamiltonians, which simply play with the spin distributions. They appear as effective Hamiltonians, in the sense of Bloch [8] or des Cloizeaux [9], and

\* Corresponding author. Tel.: +33 561556047; fax: +33 561556065.

E-mail address: [malrieu@irsamc.ups-tlse.fr](mailto:malrieu@irsamc.ups-tlse.fr)

Quasi-degenerate Perturbation Theory may be used to define their form and to estimate the amplitude of the effective spin–spin interactions. The simplest case concerns the systems where each site brings one electron in one orbital, which constitutes a half-filled band system. The model space for a several-site problem is defined by the determinants where each of these orbitals bears one and only one electron, i.e. the neutral Valence Bond distributions. The leading second-order treatment produces the bilinear Heisenberg Hamiltonian. In such a case the spins are spin  $\frac{1}{2}$  and if the ferromagnetic state energy is taken as zero of energy the resulting effective Hamiltonian is the Heisenberg Hamiltonian

$$H^H = \sum_{\langle ij \rangle} J_{ij} (\vec{S}_i \vec{S}_j - I/4)$$

where  $I$  is the identity operator. To the second order of Perturbation Theory the expression of the effective exchange integral is

$$-J_{ij} = 2K_{ij} - 4 \frac{t_{ij}^2}{U}$$

where  $K_{ij}$  is the direct exchange integral (always positive) and the second term is the so called kinetic exchange (always negative) reflecting the impact of the local ionic VB structure, which stabilize the low spin states.  $U$  is the energy difference between the ionic ( $I^+J^-$  or  $I^-J^+$ ) and neutral VB structure and  $t_{ij}$  is the inter-site hopping integral coupling neutral and ionic determinants. Usually, due to the rapid decrease of the inter-site differential overlap between the magnetic orbitals, the nonnegligible effective exchange integrals only concern the couples of nearest-neighbor (NN) sites. Four-spin operators may be considered, especially in plaquette containing lattices, but they appear at fourth order only.

The estimation of the ground state energy of a regular bipartite lattice of spin  $\frac{1}{2}$  has been the subject of theoretical works. All bonds are identical, and have the same magnetic coupling,  $J$ . The Heisenberg Hamiltonian considers all spin distributions of  $n$  electrons on  $n$  sites, their mean energies and their interactions. The diagonal energies of these spin distributions are not equal. In antiferromagnetic systems ( $J > 0$ ) and bipartite (or alternant) lattices the determinant of lowest energy is the so-called Néel function where each site of a given spin is surrounded by NN sites of opposite spin. Each bond contributes by a quantity  $-J/2$  to its energy. The Néel function is unique if the number of sites is odd, there are two Néel functions if this number is even, but of course for a very large number of sites the energy per site or per bond does not depend on this parity and the simpler case of a single Néel function may be considered. This may of course be seen as a symmetry-broken approach. The spin-frustrated graphs are not tractable in this manner in the absence of a candidate vector to be considered as a valuable reference function. Starting from the Néel function, the action of the Hamiltonian may reverse two adjacent spins, for instance between sites  $J$  and  $K$ . The Néel function is coupled with all the determinants which are obtained by such adjacent spins permutation. The energies of these determinants are higher than that of the Néel function since the bonds adjacent to the permuted spins, i.e. the bonds  $IJ$  and  $KL$ , are now frustrated. Being the function of lowest energy with the largest number of off-diagonal matrix elements the Néel function is the one of largest coefficient in the ground state eigenfunction. It is tempting to consider this function as a reference function, as we typically do in the electron correlation problem with the Hartree–Fock single determinant, and to apply one of the familiar single reference tools developed in Quantum Chemistry to this problem. The difficulty comes from the ratio between the off-diagonal elements and the diagonal energy differences, which scales as the  $(2Nv - 2)^{-1}$ , where  $Nv$  is the number of bonds in which each site is engaged (or the number of NN sites). This ratio is as large as  $\frac{1}{2}$  for a one-

dimensional (1D) chain, which prevents a perturbative approach to be considered. The difficulty becomes less dramatic when the number  $Nv$  increases and of course in 2D or 3D systems of various topologies, but spin systems may be considered as nearly degenerate problems.

Among the non-perturbative methods one may quote Coupled Cluster expansions. The applications of this approach to such problems are not numerous. One may quote the works of the author and coworkers [10–14] and those of Bishop et al. [15–18]. These last authors have introduced many-body operators (up to 10-body ones) despite the fact that the reference is only coupled to a single type of spin distributions, namely those obtained by spin exchanges between adjacent sites. Our strategy stays with these elementary excitations in the Coupled Cluster expansion but takes into account perturbatively the lacking fourth-order processes (as done for the triples in CCSD(T) methods) and the deviation of multiple excitation energies from additivity of the excitation energies. The principles of the method, developed in Refs. [10,13], will be briefly recalled. Applied to spin  $\frac{1}{2}$  bipartite antiferromagnetic lattices it gave very accurate estimates of the ground state energy per bond. One advantage is its simplicity, the results are practically analytical. The present paper would like to extend this strategy to spin  $S = 1$  periodic antiferromagnetic lattices.

## 2. The Hamiltonian

If one considers magnetic sites with 2 electrons in 2 orbitals,  $a_i$  and  $b_i$  on site  $I$ , the ground state of the site is a triplet according to the Hund's rule, with 3 possible  $M_s = +1, 0$  or  $-1$  components,

$$\begin{aligned} T_i^+ &= |a_i b_i| \\ T_i^0 &= (|a_i \bar{b}_i| + |\bar{a}_i b_i|) / \sqrt{2} \\ T_i^- &= |\bar{a}_i \bar{b}_i| \end{aligned} \quad (1)$$

The open-shell singlet state  $S_i^0 = (|a_i \bar{b}_i| - |\bar{a}_i b_i|) / \sqrt{2}$  lies at an energy  $2K_{a_i b_i}$  above the triplet configuration, and it will be omitted in the modelization, assuming that this intra-site exchange integral is much larger than the inter-site effective exchanges  $K \gg |J|$ . The working space will actually be defined by all possible products of on-site triplet states. The Heisenberg Hamiltonian may be written as

$$H^H = \sum_{\langle ij \rangle} J_{ij} (\vec{S}_i \vec{S}_j + I) \quad (2)$$

where the identity operator  $I$  insures that the ferromagnetic state energy is taken as the zero of energy. The amplitude of the hereafter supposed antiferromagnetic coupling is now

$$-J_{ij} = \sum_{a_i b_j} K_{a_i b_j} - 2t_{a_i b_j}^2 / U \quad (3)$$

where  $a_i$  and  $b_j$  are magnetic orbitals on sites  $I$  and  $J$ .

The inter-site coupling constants  $J_{ij}$  reflect the mixing with ionic VB determinants, which stabilize the spin alternant distributions and introduce inter-site spin exchanges. Let us recall the main couplings of a spin  $S = 1$  Heisenberg Hamiltonian between two sites, for the diagonal elements,

$$\langle T_A^+ T_B^+ | H | T_A^+ T_B^+ \rangle = \langle T_A^- T_B^- | H | T_A^- T_B^- \rangle = 0 \quad (4a)$$

$$\langle T_A^+ T_B^- | H | T_A^+ T_B^- \rangle = \langle T_A^- T_B^+ | H | T_A^- T_B^+ \rangle = -2J \quad (4b)$$

$$\langle T_A^+ T_B^0 | H | T_A^+ T_B^0 \rangle = \langle T_A^- T_B^0 | H | T_A^- T_B^0 \rangle = \langle T_A^0 T_B^0 | H | T_A^0 T_B^0 \rangle = -J, \quad (4c)$$

according to the  $J(S_z^A S_z^B - 1)$  diagonal part of the spin Hamiltonian.

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