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Encapsulated spin function for periodic lattices

F. Pétuaud-Létang, A. Fritsch, G. Bignonneau, L. Ducasse

Laboratoire de Physico-Chimie Moléculaire, Université Bordeaux I, F-33405 Talence Cédex, France

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Abstract. An approximate spin function for infinite periodic spin lattices is introduced. The "encapsulated spin function" is built from spin blocks variationally determined on open clusters. It gives a zeroth-order description of the short-range spin correlation while insuring a proper translational symmetry with an appropriate projection of the local spin function over the entire lattice. A recursion expression is derived that removes the normalization difficulty that arises in the projection. The one-dimensional Heisenberg regular Hamiltonian is tested in the present paper but the model allows for more complicated topologies of the interactions, including long-range exchange and three-spin exchange.

Key words: Infinite periodic spin lattices – Spin function – Spin blocks – Heisenberg Hamiltonian – Valence bond

1 Introduction

In the field of strongly correlated electronic and magnetic materials quantum chemistry contributes by a quantitative evaluation of magnetic interactions which are obviously linked to the intimate electronic structure of the magnetic units, but also to their mutual interactions. Valence bond (VB) theory in its modern formulation [1, 2] teaches us that most electronic assemblies in molecules and more extended entities may be very accurately described in terms of a local orbital model. Magnetic spin half insulators, are manifestly the kind of electronic ensembles that may be ideally suited for a VB description consisting of a collection of equivalent non-orthogonal "site" orbitals, singly occupied, and an attached spin function that accounts for the fluctuating spin coupling schemes. The wavefunction "natural" approximation obeys the spin-coupled (SC) formulation (for Ne electrons) [1]:

$$\Psi_{SM}^{N} = \sqrt{Ne!}\mathscr{A}\{\phi_1(r_1)\phi_2(r_2)\ldots\phi_{Ne}(r_{Ne})\Theta_{SM}^{Ne}(\sigma_1\ldots\sigma_{Ne})\} \ ,$$

where the ϕ_i are singly occupied orbitals and Θ_{SM}^{Ne} is the global spin function. $\mathscr{A}$ is the antisymmetrizer that involves all permutations of the electrons space and spin coordinates. Such a wavefunction, when the orbitals and the spin function are fully optimized without any orthogonality constraint, provides the best possible single configuration wavefunction, accounting for a large part of the correlation energy. The release of the orthogonality constraints usually leads to local and non-orthogonal orbitals. Typically, the overlap between optimized orbitals located across a chemical bond allows the inclusion of the essential part of the left-right correlation between bonding electrons, being almost equivalent to the variational mixing of covalent and ionic structures [3]. Therefore, the SC wavefunction incorporates by construction much more electron correlation than the standard Hartree-Fock wavefunction. The SC orbitals are fundamentally different from localized molecular orbitals and reflect the impact of electron repulsion.

When the SC orbitals are weakly overlapping, such a wavefunction may be used in order to provide an effective spin Hamiltonian [4, 5] relating the magnetic coupling constants to the orbitals shape [6] through the one-and two-electron integrals involving orbitals within a certain range. The electronic energy may then be written as:

$$E = \frac{\langle \Psi_{SM}^{Ne} | \hat{H} | \Psi_{SM}^{Ne} \rangle}{\langle \Psi_{SM}^{Ne} | \Psi_{SM}^{Ne} \rangle} \cong \langle \Theta_{SM}^{Ne} | \hat{H}_{spin} | \Theta_{SM}^{Ne} \rangle \ .$$

The spin Hamiltonian in its most simplified form may be expressed in terms of the two-spin exchange operators $\hat{P}_{ij}$ for any spin pair (i, j):

$$\hat{H}_{spin}(\{\phi_i\}) = E_0(\{\phi_i\}) + \sum_{(i,j)}^{Ne} \mathscr{J}_{ij}(\{\phi_i\})\hat{P}_{ij} \ .$$

E_0 is the "Hartree energy" that does not take into account the antisymmetry of the wavefunction. The $\mathscr{J}_{ij}$

Correspondence to: L. Ducasse

values depend on the shape of the orbitals. With such a functional, the variationally calculated orbitals and magnetic constants are intimately linked to the competition between Coulomb interactions, quantum exchange and delocalization forces that are themselves dependent on the nature of the spin correlation around each spin. This is far more subtle than dimer calculations of the singlet-triplet gap, but also more demanding since it is necessary to give a proper account of these interactions within a reasonable range. The dilemma that is encountered here is linked to the fact that in magnetic insulators, the range of exchange interactions is much shorter than that of the Coulomb potential, but both have to be incorporated for the final electronic wavefunction to be faithful enough to provide a reliable picture. In these respects, calculations based on finite size clusters are not suited for obtaining the correct picture of the magnetic interactions:

1. Open clusters show considerable boundary effects, either in the evolution of spin correlation throughout the cluster, or in the polarization of the electronic cloud. The symmetry of such clusters is also far from the actual symmetry encountered in periodic systems.

2. Finite size clusters with imposed cyclic boundary conditions may be an alternate way to mimic the crystal symmetry, but this is only true with specific model electronic Hamiltonians such as the Hubbard Hamiltonian [7] restricted to close neighbours. With any long-range potential, the adequacy of such clusters is subject to caution. In other words, a Hubbard ring may be representative of a chain, but a Pariser-Parr-Pople (PPP) [8] ring includes interactions that are absent from the infinite PPP chain and thus should be used with great care.

On the other hand, performing explicit SC calculations on a very large to infinite number of local electrons is a daunting task. Apart from the non-orthogonality difficulty that may be avoided for weakly overlapping SC orbitals following [4–6], there is a crucial need for a sufficiently flexible spin function so that we may consider that spin correlation is properly accounted for at least locally.

We may conclude from these considerations that what is crucially needed for performing SC calculations on extended periodic systems with a long-range electrostatic potential and a correct picture of the spin state locally, is an in situ technique. The technique should allow each spin to feel the same exchange interactions as its symmetry equivalent neighbours and should be reliable in terms of the rendering of the short to medium-range magnetic order, but also as simple as possible so as to be employed within a quantum electronic wavefunction in the SC spirit.

The behaviour of spin correlation is usually regulated through the use of a formal spin Hamiltonian in its quantum Heisenberg guise or a more classical one such as the "Ising" model. The exact solutions of these apparently simple models are not known; apart from the regular one-dimensional (1D) system for which the Bethe ansatz provides the exact result for regular Heisenberg chains [9]. The well-known Lanczos technique [10] provides exact information on finite size clusters but limitations of the computer memory severely restricts the maximum size: for the two-dimensional (2D) Heisenberg model on a square lattice, a maximum number of 36 spins may be handled exactly [11]. Several authors proposed to bypass this limitation by means of exact diagonalizations in reduced Hilbert spaces [12–15]. In order to bypass the severe limitations of finite size calculations, the usage of good embedding techniques provides quite accurate results on 1D and 2D periodic systems [16]. The recently proposed density matrix renormalization group [17, 18] provides an optimized basis truncation in quasi-1D systems; it provides very accurate results for very large systems but the study of momentum dependence of observables is complicated by the use of open boundary conditions. Cyclic boundary conditions may be employed but are computationally much more demanding. The cumulant technique of Becker and Vojta [19] provides accurate results for spin half 2D antiferromagnets. Recent quantum Monte Carlo calculations by Sandvik et al. [20] achieve a relative accuracy of 10^{-5} on the $S = 1/2$ t-J model. The previously mentioned many-body techniques represent the state of the art in the study of strongly correlated electrons. Let us mention the use of cluster expanded wavefunctions that have been investigated by Klein and Garcia-Bach [21].

Calculating the optimized spin state for infinite periodic systems is nevertheless far from being trivial. The question also arises whether it is of any relevance when one is more interested in the nature of the spin-correlation functions within a medium range than in obtaining the "exact" energy for the infinite system. In this paper, we introduce an encapsulated spin function (ESF) which, from periodically replicated finite size clusters, builds up a spin function that preserves translational symmetry, while retaining some extensive spin resonance within a certain range. The main purpose of this work is to provide a simple and tractable scheme for future use in approximate non-orthogonal SC calculations on periodic systems so as to assess the possibility of calculating in situ optimized magnetic coupling interactions

2 Model

In this paper for the sake of simplicity, we only treat periodic 1D chains with one spin per unit cell. The 1D character is not essential for what follows. Extension to 2D or 3D lattices is not difficult, apart from the computational effort required to give a proper account of the spin function in a spin block that should be as large as possible.

The 1D chain has unit cell parameter a. It is divided into supercells containing P spins each with supercell parameter $\vec{R}_P = P\vec{a}$. We call such a supercell a spin window (SW). There are P ways for partitioning the chain into SWs of P spins. If we start from an arbitrary "reference partition" called partition 0, all other partitions may be deduced from the reference by a translation of $1, 2, \ldots, P-1$ elementary translations. In Fig. 1, $\vec{R}_P = 4\vec{a}$ and the SW contains four spins. Figure 2 shows distinct partitions for $P = 4$.

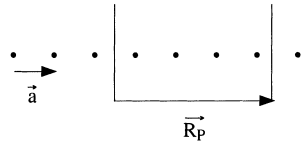

Fig. 1. P = 4-spin window in a regular 1D chain

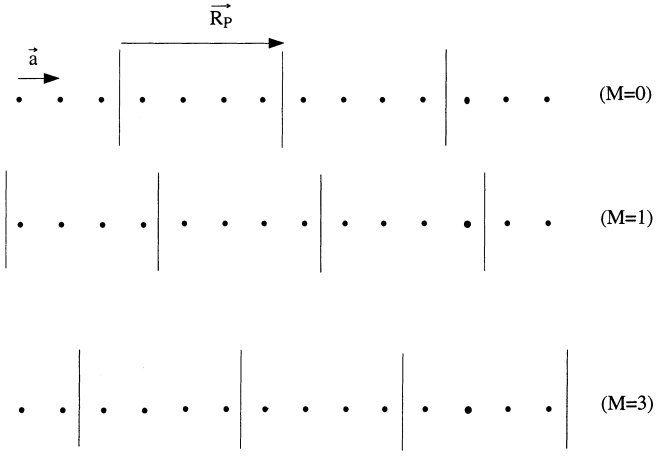

Fig. 2. Three among the four partitions for P = 4

3 The encapsulated spin function (ESF)

The normalized spin function for the i^{th} SW in partition M is Θ^i_M. All SWs are described by the same function which may be developed into any convenient basis $\{\delta_k\}$ of spin functions. We assume it is a spin eigenfunction with S = M = 0 for an even number of electrons.

$$\Theta^i_M(P^*(i-1)+1,\ldots,P^*i) = \sum_k C_k \delta_k(P^*(i-1)+1,\ldots,P^*i) \ .$$

We then build the normalized product of these spin functions for N windows:

$$\Theta_{M;N} = \prod_{i=1}^{N} \Theta^i_M \ .$$

$\Theta_{M;N}$ is not a proper spin function because it does not have the proper translational symmetry. In order to restore this symmetry, we project $\Theta_{M;N}$ using the "translation" operators $\hat{T}^n$ where $\hat{T}^1$ is the elementary translation with unit cell vector $\vec{a}$. $\hat{T}^1$ may also be considered as the cyclic permutation of the spin indices of rank 1. Such translations generate new partitions of the chain:

$$\hat{T}^n \Theta_{M;N} = \Theta_{M+n;N} \ .$$

In $\hat{T}^1 \Theta_{0;N} = \Theta_{1;N}$ for example, the first spin of the first window has the label "2".

The fully symmetric unnormalized ESF is thus:

$$\Theta = \sum_{n=0}^{P-1} \Theta_{M+n;N} \ .$$

The evaluation of the energy integral for the symmetry-adapted spin function requires the calculation of all $\langle \Theta_{M;N}|\hat{H}|\Theta_{L;N}\rangle$ and overlaps $\langle \Theta_{M;N}|\Theta_{L;N}\rangle$. These are integrals over all spin coordinates between non-orthogonal functions, similar in form, but expressed in partitions that do not coincide. With

$$\langle \Theta|\hat{H}|\Theta\rangle = \left[\sum_{n=0}^{P-1}\sum_{m=0}^{P-1}\langle \Theta_{M+n;N}|\hat{H}|\Theta_{M+m;N}\rangle\right]$$

and

$$\langle \Theta|\Theta\rangle = \left[\sum_{n=0}^{P-1}\sum_{m=0}^{P-1}\langle \Theta_{M+n;N}|\Theta_{M+m;N}\rangle\right] \ ,$$

the normalized energy becomes

$$E = \frac{\sum_{n=0}^{P-1}\langle \Theta_{M;N}|\hat{H}|\Theta_{M+n;N}\rangle}{\sum_{n=0}^{P-1}\langle \Theta_{M;N}|\Theta_{M+n;N}\rangle} \ .$$

4 The spin Hamiltonian

The Heisenberg Hamiltonian or Dirac vector model may be cast in the following form:

$$\hat{H} = \sum_{r<s}^{P^*N} J_{rs}\hat{P}_{rs} \ ,$$

where the $\hat{P}_{rs}$ are the elementary transpositions of spin indices r and s. For simplicity we set

$$J_{rs} = J \qquad \text{for } s = r+1,$$
$$J_{rs} = 0 \qquad \text{otherwise} \ ,$$

with implicit cyclic boundary conditions. This yields the standard first neighbour Heisenberg model.

The Hamiltonian is divided into an intra-SW part $\hat{H}_I$ and an inter-SW part $\hat{H}_{II}$:

$$\hat{H}_I = \sum_{i=1}^{N}\hat{H}^i_I = J\sum_{i=0}^{N-1}\sum_{p=1}^{P-1}\hat{P}_{P^*i+p,\,P^*i+p+1} \ ,$$

$$\hat{H}_{II} = \sum_{i=1}^{N}\hat{H}^{i,i+1}_{II} = J\sum_{i=1}^{N}\hat{P}_{P^*i,\,P^*i+1} \ .$$

Spin P*i is the last spin of SW i, spin P*i + 1 is the first of SW i + 1. The last spin of the last SW in the chain is connected with the first spin of the first SW.

5 Diagonal matrix elements

The expectation value of $\hat{H}_I$ gives:

$$\langle \Theta_{M;N}|\hat{H}_I|\Theta_{M;N}\rangle = \sum_{i=1}^{N}\langle \Theta^i_M|\hat{H}^i_I|\Theta^i_M\rangle = N\langle \Theta^i_M|\hat{H}^1_I|\Theta^i_M\rangle = N E_I \ .$$

As expected, the intra-SW terms give an extensive contribution to the energy. If we choose Θ^i_M as the lowest eigenvector of $\hat{H}^i_I$ with eigenvalue ε, we get:

$$\langle \Theta_{M;N}|\hat{H}_I|\Theta_{M;N}\rangle = N\,\varepsilon \ .$$

The expectation value of $\hat{H}_{II}$ gives:

$$\langle \Theta_{M;N}|\hat{H}_{II}|\Theta_{M;N}\rangle = \sum_{j=1}^{N}\langle \Theta_M^j \Theta_M^{j+1}|\hat{H}_{II}^{j,j+1}|\Theta_M^j \Theta_M^{j+1}\rangle$$
$$= N\,E_{II} \ .$$

The inter-SW contribution is also extensive. Calculating E_I and E_{II} only requires the spin coupling coefficients C_n. In the case of the first neighbour Heisenberg Hamiltonian, E_{II} may be simplified, due to the factorized form of our spin function. Let us consider the decomposition of the product $\Theta_M^j \Theta_M^{j+1}$ in terms of Rumer spin functions $\{\delta_p\}$ [22], the Pauling superposition pattern [11] for $\langle \delta_p^j \delta_q^{j+1}|\delta_r^j \delta_s^{j+1}\rangle$ is made of two disconnected sets. When evaluating the superposition pattern for $\langle \delta_p^j \delta_q^{j+1}|\hat{H}_{II}^{j,j+1}|\delta_r^j \delta_s^{j+1}\rangle$, it turns out that the number of Pauling islands is always decreased by one and the number of arrow reversals is even; therefore one gets [23]:

$$\langle \delta_p^j \delta_p^{j+1}|\hat{H}_{II}^{j,j+1}|\delta_r^j \delta_s^{j+1}\rangle = \frac{J}{2}\langle \delta_p^j \delta_q^{j+1}|\delta_r^j \delta_s^{j+1}\rangle \ ,$$

$$\langle \Theta_{M;N}|\hat{H}_{II}^{j,j+1}|\Theta_{M;N}\rangle = \frac{J}{2}\sum_{p,q,r,s} C_p\,C_q\,C_r\,C_s\langle \delta_p^j \delta_q^{j+1}|\delta_r^j \delta_s^{j+1}\rangle$$
$$= \frac{J}{2}\langle \Theta_{M;N}|\Theta_{M;N}\rangle = \frac{J}{2} \ .$$

6 Off-diagonal matrix elements

There are only $P(P-1)/2$ distinct overlap terms to calculate that may be obtained recursively. Let us consider one of these terms involving partitions differing by a translation of n cells. If we superpose the two partitions, we can identify a common coinciding subpartition for $\Theta_{M;N}$ and $\Theta_{M+n;N}$. We divide each SW of partition M in two subwindows; the first containing the first n spins, the second describing the remaining $P-n$ spins. On the other hand the first subwindow in partition $M+n$ contains $P-n$ spins and the last one n spins, as illustrated in Fig. 3.

We then proceed as follows: the spin function of a SW in partition M is decomposed in the direct product basis of the two subwindows:

$$\Theta_M^i = \sum_{p}^{2^n}\sum_{q}^{2^{P-n}} C_{pq}\,\gamma_{M,p}^i\,\bar{\gamma}_{M,q}^i$$

and we do the same for partition $M+n$

$$\Theta_{M+n}^j = \sum_{r}^{2^{P-n}}\sum_{s}^{2^n} D_{rs}\,\bar{\gamma}_{M+n,r}^j\,\gamma_{M+n,s}^j \ .$$

The basis functions in the subwindows may have all possible S_z values. In practice, the $\gamma_{M,p}^i$ are simple spin products for n spins whilst the $\bar{\gamma}_{M,p}^i$ are spin products for $P-n$ spins. The coefficients for non-compatible products are just set to zero. In practical computations,

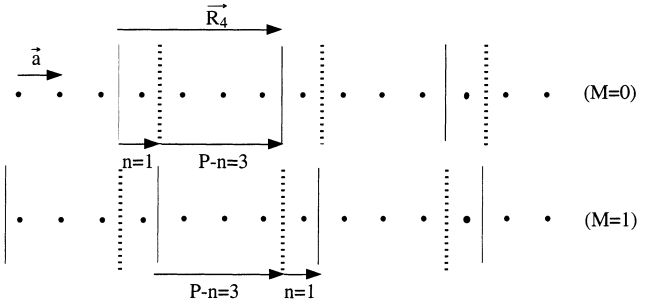

Fig. 3. Common subdivision of partitions 0 and 1, for $P = 4$

however, the **C** and **D** matrices may actually be compressed, since they contain nothing more than the eigenvector of $\hat{H}_I$.

In an ordered sequence of the spins along the chain, $\Theta_{M;N}$ components start with a $\gamma_{M,p}^1$ function acting on spins $1, 2, \ldots, n$, whilst $\Theta_{M+n;N}$ components start with a $\gamma_{M+n,s}^N$ function acting on spins $1, 2, \ldots, n$.

We now introduce the $T^{(N)}$ matrix with elements:

$$T_{as}^{(N)} = \langle \Theta_{M;N}|\gamma_{M+n,s}^N\,\Theta_{M+n;N-1}\bar{\gamma}_{M+n,a}^N\rangle \ .$$

It is implicit that the spin indices coincide in the bra and the ket. We drop the superscripts on the γ functions hereafter. It can be shown (cf. Appendix) that a recursion formula stands for the T matrices that links matrices for $N-1$ and N windows:

$$T_{as}^{(N)} = \sum_{p}^{2^n}\sum_{r}^{2^{P-n}} C_{pa}\,D_{rp}\,T_{rs}^{(N-1)} \ ,$$

$$T_{as}^{(N)} = \sum_{r}^{2^{P-n}}\left[\sum_{p}^{2^n} C_{pa}\,D_{rp}\right]T_{rs}^{(N-1)} = \sum_{r}^{2^{P-n}}(DC)_{ra}\,T_{rs}^{(N-1)} \ ,$$

$$T_{as}^{(N)} = \sum_{r}^{2^{P-n}}(DC)_{ar}^{\top}\,T_{rs}^{(N-1)} = \left[(DC)^{\top}\,T^{(N-1)}\right]_{as} \ ,$$

$$T^N = (DC)^{\top}\,T^{(N-1)}$$

with, for a single window: $T^{(1)} = C^{\top}$. The $T^{(N)}$ are rectangular $(2^{P-n} * 2^n)$ matrices.

The T matrices are thus elements of a (geometrical) suite and we finally get:

$$T^N = \left[(DC)^{\top}\right]^{(N-1)}T^{(1)} \ .$$

The overlap integral between the two functions $\Theta_{M;N}$ and $\Theta_{M+n;N}$ may then easily be expressed in terms of the T matrix:

$$\langle \Theta_{M;N}|\Theta_{M+n;N}\rangle$$
$$= \sum_{i}^{2^{P-n}}\sum_{j}^{2^n} D_{ij}\langle \Theta_{M;N}|\gamma_{M+n;j}\,\Theta_{M+n;N-1}\bar{\gamma}_{M+n;i}\rangle$$
$$= \sum_{i}^{2^{P-n}}\sum_{j}^{2^n} D_{ij}\,T_{ij}^{(N)} \ .$$

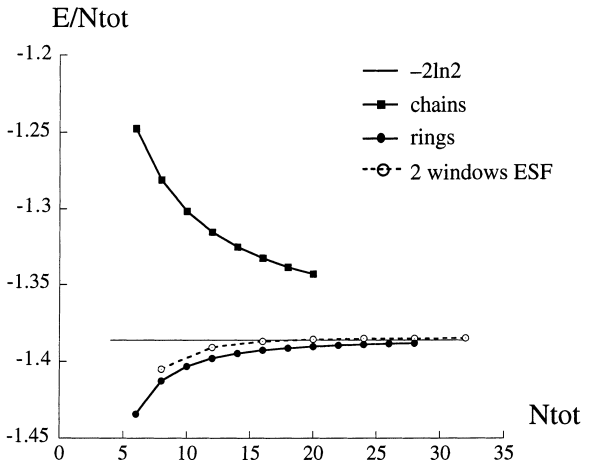

Fig. 4. Energy per spin for finite rings, finite chains and the two-window ESF (Ntot is the total number of spins = N*P). The exact Bethe result is −2Ln 2

Off-diagonal Hamiltonian matrix elements may be obtained in a similar way. If we consider the eigenvector Θ^i_{M+n} of the intra-window Hamiltonian $\hat{H}^i_I$:

$$\hat{H}^i_I|\Theta^i_{M+n}\rangle = \varepsilon|\Theta^i_{M+n}\rangle \ .$$

We easily get (cf. Appendix):

$$\langle\Theta_{M;N}|\hat{H}^i_I|\Theta_{M+n;N}\rangle = \varepsilon\langle\Theta_{M;N}|\Theta_{M+n;N}\rangle = \varepsilon\sum_r^{2^{P-n}}\sum_s^{2^n} D_{rs}\, T^{(N)}_{rs} \ .$$

For the inter-window contribution, one obtains (cf. Appendix):

$$\langle\Theta_{M;N}|\hat{H}^i_{II}|\Theta_{M+n;N}\rangle = N\,J\sum_p^{2^{P-n}}\sum_q^{2^n}\sum_r^{2^{P-n}}\sum_s^{2^n} D_{pq}\, D_{rs}\, C_{ab}\, T^{(N-1)}_{ps}$$

where indices a and b are such that

$$\hat{P}_{n,n+1}|\gamma_{M+n,q}\,\bar{\gamma}_{M+n,r}\rangle = |\gamma_{M+n,a}\,\bar{\gamma}_{M+n,b}\rangle \ .$$

These expressions are applicable to a Heisenberg Hamiltonian involving any number of neighbours ; the unique J magnetic exchange constant being replaced by the relevant J_{ij}'s.

7 Results for the regular 1D Heisenberg model

We performed calculations on 1D spin half chains, using the first neighbour Heisenberg Hamiltonian:

$$\hat{H} = \sum_r^{P^*N} 2J\left(\hat{\vec{S}}_r \cdot \hat{\vec{S}}_{r+1} - \frac{1}{4}\right) = \sum_r^{P^*N} J\left(\hat{P}_{r,r+1} - 1\right) \ .$$

In the calculations, the J value is taken equal to 1.0. The Bethe ansatz gives the asymptotic value −2 Ln 2 for the infinite. We carried out exact diagonalizations for finite size rings, finite size opened chains and partitioned rings of different sizes, and different window sizes.

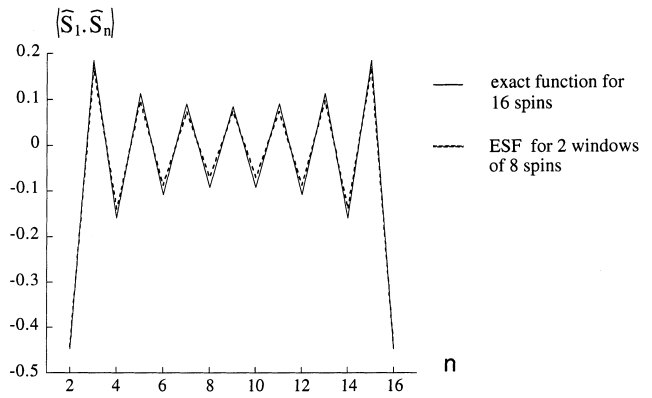

Fig. 5. Spin correlation functions for the 16-site ring and the corresponding 2-window ESF

7.1 Two-window rings

Our calculation on two-window rings may be compared to exact diagonalizations on chains and rings with the same overall number of spins. Figure 4 shows, as a function of the total number of spins Ntot, the energy per spin obtained from exact diagonalization on finite size rings (filled circles), finite size opened chains (filled squares) and the two-window results (empty circles), using the exact eigenvector for the Ntot/2 chains.

All three curves converge towards the exact result of Bethe, with the chain exact calculations showing a positive convergence whilst the ring results show a negative convergence due to the fact that there is one more exchange interaction in the ring.

The ESF results shown in Fig. 4 are obtained with only two windows. They are based on the eigenvector of the Ntot/2 sites open chain but included in a ring with Ntot sites. The resulting energy is thus closer to the ring result. The energy per spin actually shows a positive convergence although it is below the Bethe ansatz for Ntot $\leq$ 20. For Ntot = 24, 28 and 32 spins, the energy per site in unit of J is −1.38530, −1.38511 and −1.38507, respectively.

In order to compare the ESF and the exact result on a ring, it is also interesting to look at the spin correlation function:

$$\langle\vec{S}_i \cdot \vec{S}_{i+1}\rangle = \frac{1}{2}\langle\hat{P}_{i,i+n}\rangle - \frac{1}{4} \ .$$

This is plotted in Fig. 5 for a 16-site ring from the exact eigenvector and the corresponding 2-window ESF.

The exact eigenvector shows an oscillating and vanishing correlation function with the separation between spins. This is the manifestation of the "spin liquid" nature of the spin state. The ESF almost perfectly reproduces the results. With this rather large window size, the degradation due to the inter-SW effects in the diagonal contribution are almost perfectly balanced by the off-diagonal terms. The two-window ESF thus appears to be a very faithful approximation of a ring with a doubled size. Obviously, for larger window sizes, results would get even better, allowing, in the present state of the art, for a 48-site ring to be described from a spin chain containing only 24 spins.

7.2 Infinite rings

In the limit of an infinite number of windows, the $T^{(N)}$ matrices vanish, and therefore the $\Theta_{M;N}$ functions become uncoupled. One is left with a superposition of orthogonal and non-interacting states and the expectation values obtained from the symmetrized state are thus just directly obtained from the diagonal terms. The energy becomes:

$$E_\infty = \frac{\sum_{M=1}^{P}\sum_{l=1}^{P}\delta_{M\,M+1}\langle\Theta_{M;\infty}|\hat{H}|\Theta_{M+l;\infty}\rangle}{\sum_{M=1}^{P}\sum_{l=1}^{P}\delta_{M\,M+1}\langle\Theta_{M;\infty}|\Theta_{M+l;\infty}\rangle} \quad ,$$

$$E_\infty = \frac{1}{P}\sum_{M=1}^{P}\langle\Theta_{M;\infty}|\hat{H}|\Theta_{M;\infty}\rangle = \langle\Theta_{1;\infty}|\hat{H}|\Theta_{1;\infty}\rangle$$

and the energy per spin takes the somehow delusively simple form:

$$e_\infty = \frac{E_\infty}{N^*P} = \frac{1}{P}\left(\varepsilon + \frac{J}{2}\right) \quad .$$

The ESF energy per spin therefore converges slightly above the finite chain result. Figure 6 shows the energy per spin as a function of the number of windows, for 8 to 16-spin partitioning. The position of the asymptote depends on the window's size. With larger windows, the relative weight of the constant inter-SW contribution decreases while the window energy decreases.

The correlation function $\langle\hat{P}_{i,i+n}\rangle$ reduces to a mean value over the different partitions:

$$\langle\hat{P}_{i,i+n}\rangle = \frac{1}{P}\sum_{M=1}^{P}\langle\Theta_{M;\infty}|\hat{P}_{i,i+n}|\Theta_{M;\infty}\rangle \quad ,$$

using the translational symmetry relation

$$\langle\Theta_{M-l;\infty}|\hat{P}_{i,i+n}|\Theta_{M-l;\infty}\rangle = \langle\Theta_{M;\infty}|\hat{P}_{i+l,i+n+l}|\Theta_{M;\infty}\rangle$$

one gets

$$\langle\hat{P}_{i,i+n}\rangle = \frac{1}{P}\sum_{l=1}^{P}\langle\Theta_{M;\infty}|\hat{P}_{i+l,i+n+l}|\Theta_{M;\infty}\rangle \quad ,$$

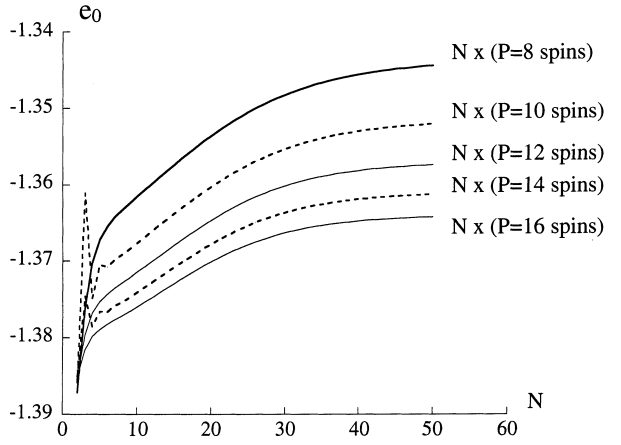

Fig. 6. Energy per spin as a function of the number of windows N, for various window sizes P

obtained in a single partition. The correlation function for n^{th} neighbours is thus just the mean value of all similar pairs in one single partition. Two cases arise:

$$\langle\Theta_{M;\infty}|\hat{P}_{i,i+n}|\Theta_{M;\infty}\rangle$$
$$= \langle\Theta^a_M|\hat{P}_{i,i+n}|\Theta^a_M\rangle \text{ when i and i + n belong to window a}$$

$$\langle\Theta_{M;\infty}|\hat{P}_{i,i+n}|\Theta_{M;\infty}\rangle$$
$$= \frac{1}{2} \text{ when i and i + n do not belong to the same window}$$

In Fig. 7, the correlation function is given for 20-spin windows and compared to the exact correlation function in a 24-spin ring. When the neighbouring range extends beyond the size of the window, the correlation function becomes equal to 1/2, which corresponds to $\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle = 0$: the spins are uncorrelated. The degradation of the energy compared to the exact result is due to this imposed uncorrelation outside the window. Note that even for pairs within the window range, there are some partitions for which the two spins are in distinct windows. Therefore, a contamination of the short-range correlation occurs that originates in the imposed partitioning of the spin function. The longer the range, the higher the degree of contamination. In this respect it is useful to use the largest possible window to ensure a good description of short to medium-range spin correlation.

The symmetry adapted ESF insures that all $\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle$ are independent of the spin position i. A comparison for the first neighbour correlation $\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle$ was made with the embedded result of Miguel et al. [16]. The 20-spin ESF gives -0.43413; the embedding technique based on 18-spins chains gives first neigbour values oscillating between -0.4434 and -0.4406 whilst the exact Bethe result is -0.4431. It is therefore clear that the ESF should only be considered as a convenient zeroth-order model spin function.

8 Extension to three-spin exchange

Three-spin exchange terms in the Hamiltonian take the form:

$$J_{pqr}\,\hat{P}^{qrp}_{pqr} \quad \text{and} \quad J_{pqr}\,\hat{P}^{rpq}_{pqr} \quad .$$

We write the Hamiltonian as:

$$\hat{H} = \sum_{(p,q)}^{P^*N} J_{pq}\,\hat{P}_{pq} + \sum_{(p,q,r)}^{P^*N} J_{pqr}\left(\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}\right)$$

where summations are now over distinct spins only.

For three-spin exchange interactions involving spins that belong to different windows, these permutations may be decomposed to:

$$\hat{P}^{qrp}_{pqr} = \hat{P}_{pq}\hat{P}_{qr} = \hat{P}_{pr}\hat{P}_{pq} = \hat{P}_{qr}\hat{P}_{pr}$$

and

$$\hat{P}^{rpq}_{pqr} = \hat{P}_{pr}\hat{P}_{qr} = \hat{P}_{qr}\hat{P}_{pq} = \hat{P}_{pq}\hat{P}_{pr} \quad .$$

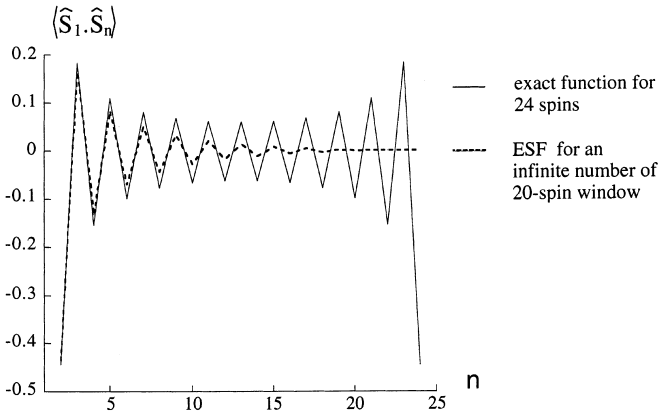

Fig. 7. Spin correlation functions for an infinite ring partitioned into P = 20-spin windows, compared to the exact result for a 24-spin ring

Evaluation of the expectation values in a given partition, using the appropriate decomposition, yields the following cases:

1. Spins p, q and r belong to the same window i:

$$J_{pqr}\langle\Theta_{M;N}|\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}|\Theta_{M;N}\rangle = J_{pqr}\langle\Theta^i_M|\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}|\Theta^i_M\rangle \ .$$

2. Spins p and q belong to the same window i, spin r to another window:

$$J_{pqr}\langle\Theta_{M;N}|\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}|\Theta_{M;N}\rangle = J_{pqr}\langle\Theta^i_M|\hat{P}_{pq}|\Theta^i_M\rangle \ .$$

3. Spins p, q and r belong to distinct windows:

$$J_{pqr}\langle\Theta_{M;N}|\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}|\Theta_{M;N}\rangle = \frac{J_{pqr}}{2} \ .$$

For a given partition, the magnetic energy per window may be cast in the following form that distinguishes between an intra-SW contribution and an inter-SW constant contribution:

$$E_{intra} = \sum_{(p,q)\in i}^{P} J_{pq}\langle\hat{P}_{pq}\rangle + \sum_{(p,q,r)\in i}^{P} J_{pqr}\langle\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}\rangle + \sum_{(p,q)\in i}^{P}\sum_{r\ \text{external}} 3J_{pqr}\langle\hat{P}_{pq}\rangle \ ,$$

$$E_{inter} = \sum_{p}^{P}\sum_{q\ \text{external}}\frac{J_{pq}}{2} + \sum_{p}^{P}\sum_{q\ \text{external}}\sum_{r\ \text{external}}\frac{J_{pqr}}{2}$$

with, in the last sum, p, q and r belonging to three distinct windows.

Calculation of the off-diagonal terms may be carried out in the same way as for the simple Heisenberg Hamiltonian. Such matrix elements also vanish for an infinite number of windows and the asymptotic value of the energy per window is thus:

$$E_\infty = E(\Theta_{(M;\infty)}) = E_{intra} + E_{inter} \qquad \forall\ M \ .$$

9 Optimization of the SW function

The energy expression for the infinite chain may be used for the variational optimization of the function Θ^i_M. We define the intra-SW Hamiltonian for a given window:

$$\hat{H}^i_{intra} = \sum_{(p,q)\in i}^{P} J_{pq}\hat{P}_{pq} + \sum_{(p,q,r)\in i}^{P} J_{pqr}\left(\hat{P}^{qrp}_{pqr} + \hat{P}^{rpq}_{pqr}\right) + \sum_{(p,q)\in i}^{P}\sum_{r\ \text{external}} 3J_{pqr}\hat{P}_{pq}$$

and the inter-SW Hamiltonian (constant) as

$$\hat{H}^i_{inter} = \sum_{p\in i}^{P}\sum_{q\ \text{external}}\frac{J_{pq}}{2} + \sum_{p\in i}^{P}\sum_{q\ \text{external}}\sum_{r\ \text{external}}\frac{J_{pqr}}{2} \ .$$

The expectation value of $\hat{H}_{intra}$ gives E_{intra}.
The expectation value of $\hat{H}^i_{inter}$ gives E_{inter}.
The norm of Θ^i_M is:

$$\Delta = \langle\Theta^i_M|\Theta^i_M\rangle .$$

Differentiating with respect to the spin function Θ^i_M, we get:

$$\delta\Delta = \langle\delta\Theta^i_M|\Theta^i_M\rangle + \langle\Theta^i_M|\delta\Theta^i_M\rangle \ ,$$

$$\delta E_{intra} = \langle\delta\Theta^i_M|\hat{H}^i_{intra}|\Theta_M\rangle + \langle\Theta^i_M|\hat{H}^i_{intra}|\delta\Theta^i_M\rangle \ ,$$

$$\delta E_{inter} = 0 \ .$$

Setting the differential of the Lagrangian $L = E_{intra} + E_{inter} - \varepsilon(\Delta - 1)$ to zero leads to the operator equation:

$$\hat{H}^i_{intra}|\Theta^i_M\rangle = \varepsilon|\Theta^i_M\rangle \ .$$

In this case, the contribution of three-spin inter-SW exchange to the intra-SW Hamiltonian produces an eigenvalue equation that differs from the the equation for the isolated open chain. In the case of the Heisenberg Hamiltonian restricted to two-spin exchange, the two equations would be identical.

10 Conclusion

Although it does not account for long-range correlation, the ESF main quality lies in its ability to provide a flexible symmetry-adapted spin function that may correctly approximate the short-range spin fluctuations. The optimized window function is an eigenvector of a finite size problem with open boundaries, but the resulting ESF is symmetry adapted by combining the translationally equivalent ways of partitioning the lattice. In comparison to exact spin functions calculated for isolated open clusters, all symmetry equivalent spins are equally treated in terms of the interactions with their neighbourhood.

Exact results obtained on finite rings may be extremely well reproduced by a two-window ESF built from half-size open chains, with a drastic reduction in the computational size of the variational problem. Infi-

nite ESFs, with sufficiently large windows, correctly reproduce the short-range correlation among close neighbours that is chemically relevant. However, the main advantage lies in the possibility of using the ESF in VB calculations, so as to properly account for the exchange component of the electronic energy, without the arbitrariness of a posteriori spin projection technique. Assuming that the underlying electronic structure may be built from symmetry equivalent local orbitals, approximate SC calculations may be carried out even with the inclusion of a long-range Coulombic potential. The ESF procedure allows for the evaluation of the exchange and electrostatic interactions to which the electrons in a reference window are exposed; these interactions originate from the whole infinite lattice. In finite size clusters with periodic boundary conditions, they would not reproduce what actually occurs in a crystal. PPP semiempirical or even ab-initio potentials may be used. Applications to electronic SC calculations within the framework of the Hubbard and PPP Hamiltonians will be published elsewhere.

The sensitive point is obviously linked to the size of the window. This is critical because the size of the spin basis set explodes with the number of spins. The state of the art in terms of exact diagonalization of the Heisenberg problem lies around 30 spins. For a 2D ESF, the largest partitioning would be made of 6×6-spin windows only, which would affect the short-range correlation more effectively than in 1D. Nevertheless, the method may accomodate any approximate spin function calculated on larger windows.

The ESF may then be considered as a zeroth-order function that may be improved on two major points.

1. A better connection of the windows, treating in a more thorough way the inter-window interactions; density matrix renormalization group techniques may then be useful [17, 18], as well as the Hamiltonian dressing techniques [15, 16], that allow for the description of the inter-window couplings with a truncated configuration interaction incorporating the external space in an effective way.

2. One may also follow the size-consistent coupled cluster techniques [24] such as found in the work of Klein and Garcia-Bach [21] based on a cluster expansion of the wavefunction itself, that allows for the proper account of independent spin excitations. Besides, the more general cumulant approach [19, 25] with an exponential ansatz should provide an effective way for treating 2D or 3D lattices.

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Appendix

Recurrence on the T matrices

The window function writes:

$$\Theta_M^i = \sum_k C_k \delta_k \ .$$

It is developed as a combination of spin products $\gamma_{M,p}^i$ and $\bar{\gamma}_{M,q}^i$ which describe the subpartitions containing n and $P-n$ spins, respectively:

$$\Theta_M^i = \sum_p^{2^n} \sum_q^{2^{P-n}} C_{pq}\ \gamma_{M,p}^i\ \bar{\gamma}_{M,q}^i \ .$$

The subpartitions which coincide in both partitions are inverse to one another. We can develop the SW function in the ket partition:

$$\Theta_{M+n}^j = \sum_r^{2^{P-n}} \sum_s^{2^n} D_{rs}\ \bar{\gamma}_{M+n,\,r}^j\ \gamma_{M+n,\,s}^j \ .$$

The $T^{(N)}$ matrix is defined as:

$$T_{as}^{(N)} = \langle \Theta_{M;N} | \gamma_{M+n,\,s}^N \Theta_{M+n;\,N-1} \bar{\gamma}_{M+n,\,a}^N \rangle$$

where $\Theta_{M;N} = \Theta_M$ for N windows in partition M, $\Theta_{M+n;N-1} = \Theta_{M+n}$ for $N-1$ windows in partition $M+n$.

Upper indices are suppressed hereafter. We impose that the ordrering of the spin indices is the same in the bra and the ket.

$$T_{as}^{(N)} = \langle \Theta_{M;N} | \gamma_{M+n,\,s^{(1,2,\ldots,n)}} \Theta_{M+n;\,N-1} \bar{\gamma}_{M+n,\,a^{((N-1)P_{+n+1},\ldots,NP)}} \rangle$$

is then written as:

$$T_{as}^{(N)} = \langle \Theta_{M;N} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \bar{\gamma}_{M+n,\,a} \rangle$$

when decomposing the last window in the bra:

$$T^{(N)}_{as} = \left\langle \Theta_{M;N-1} \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \gamma_{M,p} \bar{\gamma}_{M,q} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \bar{\gamma}_{M+n,\,a} \right\rangle \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \langle \Theta_{M;N-1} \gamma_{M,p} \bar{\gamma}_{M,q} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \bar{\gamma}_{M+n,\,a} \rangle \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \langle \Theta_{M;N-1} \gamma_{M,p} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \rangle \langle \bar{\gamma}_{M,q} | \bar{\gamma}_{M+n,\,a} \rangle \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \langle \Theta_{M;N-1} \gamma_{M,p} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \rangle \delta_{qa} \ ,$$

$$T^{(N)}_{as} = \sum_{q}^{2^n} C_{pa} \langle \Theta_{M;N-1} \gamma_{M,p} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-1} \rangle \ .$$

The last window in the ket is decomposed to:

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} \sum_{t}^{2^n} C_{pa} D_{rt} \langle \Theta_{M;N-1} \gamma_{M,p} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-2} \bar{\gamma}_{M+n,\,r} \gamma_{M+n,\,t} \rangle \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} \sum_{t}^{2^n} C_{pa} D_{rt} \langle \Theta_{M;N-1} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-2} \bar{\gamma}_{M+n,\,r} \rangle \langle \gamma_{M,\,p} | \gamma_{M+n,\,t} \rangle \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} \sum_{t}^{2^n} C_{pa} D_{rt} \langle \Theta_{M;N-1} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-2} \bar{\gamma}_{M+n,\,r} \rangle \delta_{pt} \ ,$$

$$T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} C_{pa} D_{rp} \langle \Theta_{M;N-1} | \gamma_{M+n,\,s} \Theta_{M+n;\,N-2} \bar{\gamma}_{M+n,\,r} \rangle \ .$$

We eventually get: $T^{(N)}_{as} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} C_{pa} D_{rp} T^{(N-1)}_{rs}$.

Overlap integrals

The overlap integral between two spin functions defined in two distinct partitions is then easily calculated:

$$\langle \Theta_{M;n} | \Theta_{M+n;N} \rangle = \sum_{i}^{2^{P-n}} \sum_{j}^{2^n} D_{ij} \langle \Theta_{M:N} | \gamma_{M+n;j} \Theta_{M+n;N-1} \bar{\gamma}_{M+n;i} \rangle$$
$$= \sum_{i}^{2^{P-n}} \sum_{j}^{2^n} D_{ij} \ T^{(N)}_{ij}$$

with $T^{(N)}_{ij} = \sum_{p}^{2^n} \sum_{r}^{2^{P-n}} C_{pi} D_{rp} T^{(N-1)}_{rj}$.

The first term in the recurrence is:

$$T^{(1)}_{rj} = \langle \Theta_{M;1} | \gamma_{M+n,\,j} \bar{\gamma}_{M+n,\,r} \rangle \ ,$$

$$T^{(1)}_{rj} = \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \langle \gamma_{M,p} \bar{\gamma}_{m,q} | \gamma_{M+n,\,j} \bar{\gamma}_{M+n,\,r} \rangle \ ,$$

$$T^{(1)}_{rj} = \sum_{p}^{2^n} \sum_{q}^{2^{P-n}} C_{pq} \delta_{pj} \delta_{qr} = C_{jr} \ .$$

Intra-window matrix element

The intra-window Hamiltonian $\hat{H}^i_I$ only acts on the spins belonging to window i:

$$\hat{H}^i_I | \Theta_{M+n;N} \rangle = \hat{H}^i_I | \prod_{p}^{N} \Theta^p_{M+n} \rangle = \left(\prod_{p \neq i} \Theta^p_{M+n} \right) \hat{H}^i_I | \Theta^i_{M+n} \rangle \ .$$

If Θ^i_{M+n} is an eigenfunction of $\hat{H}^i_I$ with eigenvalue ε : $\hat{H}^i_I | \Theta^i_{M+n} \rangle = \varepsilon | \Theta^i_{M+n} \rangle$ we get:

$$\langle \Theta_{M;N} | \hat{H}^i_I | \Theta_{M+n;N} \rangle = \varepsilon \left\langle \Theta_{M;N} | \left(\prod_{p \neq i} \Theta^p_{M+n} \right) \Theta^i_{M+n} \right\rangle \ .$$

We decompose Θ^i_{M+n} : $\Theta^i_{M+n} = \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \bar{\gamma}_{M+n,\,r} \gamma_{M+n,\,s}$

$$\langle \Theta_{M;N} | \hat{H}^i_I | \Theta_{M+n;N} \rangle = \varepsilon \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \left\langle \Theta_{M;N} | \left(\prod_{p \neq i} \Theta^p_{M+n} \right) \bar{\gamma}_{M+n,\,r} \gamma_{M+n,\,s} \right\rangle \ .$$

One may label the spins so that $\Theta_{M+n;N}$ depends on spins 1, 2, ... , n, in the same order from left to right than $\Theta_{M;N}$.

$$\langle \Theta_{M;N} | \hat{H}^i_I | \Theta_{M+n;N} \rangle = \varepsilon \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \left\langle \Theta_{M;N} | \gamma_{M+n,\,s} \left(\prod_{p \neq i} \Theta^p_{M+n} \right) \bar{\gamma}_{M+n,\,r} \right\rangle \ ,$$

$$\langle \Theta_{M;N} | \hat{H}^i_I | \Theta_{M+n;N} \rangle = \varepsilon \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \langle \Theta_{M;N} | \gamma_{M+n,\,s} \ \Theta_{M+n\,;N-1} \ \bar{\gamma}_{M+n,\,r} \rangle \ ,$$

$$\langle \Theta_{M;N} | \hat{H}^i_I | \Theta_{M+n;N} \rangle = \varepsilon \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \ T^{(N)}_{rs} \ ,$$

$$\langle \Theta_{M;N} | \hat{H}_I | \Theta_{M+n;N} \rangle = N\varepsilon \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{rs} \ T^{(N)}_{rs} \ .$$

Inter-window matrix element

$$\langle \Theta_{M;N} | \hat{H}_{II} | \Theta_{M+n;N} \rangle = \sum_{i=1}^{N} \langle \Theta_{M;N} | \hat{H}^{i,i+1}_{II} | \Theta_{M+n;N} \rangle \ ,$$

$$\hat{H}^{i,i+1}_{II} | \Theta_{M+n;N} \rangle = \left(\prod_{j \neq i;\, j \neq i+1} \Theta^j_{M+n} \right) \hat{H}^{i,i+1}_{II} | \Theta^i_{M+n} \Theta^{i+1}_{M+n} \rangle \ ,$$

$\Theta^i_{M+n} \Theta^{i+1}_{M+n}$ is decomposed in the sub-window partition:

$$| \Theta^i_{M+n} \Theta^{i+1}_{M+n} \rangle = \sum_{p}^{2^{P-n}} \sum_{q}^{2^n} \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{pq} D_{rs} | \bar{\gamma}_{M+n,\,p} \ \gamma_{M+n,\,q} \ \bar{\gamma}_{M+n,\,r} \ \gamma_{M+n,\,s} \rangle \ ,$$

$$\hat{H}^{i,i+1}_{II} | \Theta^i_{M+n} \Theta^{i+1}_{M+n} \Theta_{M+n;\,N-2} \rangle = \sum_{p}^{2^{P-n}} \sum_{q}^{2^n} \sum_{r}^{2^{P-n}} \sum_{s}^{2^n} D_{pq} D_{rs} \hat{H}^{i,i+1}_{II} \times | \bar{\gamma}_{M+n,\,p} \ \gamma_{M+n,\,q} \ \bar{\gamma}_{M+n,\,r} \ \gamma_{M+n,\,s} \ \Theta_{M+n;N-2} \rangle \ .$$

Exchange occurs between the internal sub-windows. These two sub-windows build up window i + 1 in partition M. One may decompose the corresponding spin function in the bra.

$$\Theta_M^{i+1} = \sum_a^{2^n} \sum_b^{2^{P-n}} C_{ab} \gamma_{M,a}\ \bar{\gamma}_{M,b}$$

$$\langle \Theta_M^{i+1}\, \Theta_{M;N-1} | \hat{H}_{II}^{i,i+1} | \Theta_{M+n}^{i}\, \Theta_{M+n}^{i+1}\, \Theta_{M+n;N-2} \rangle$$
$$= \sum_a^{2^n} \sum_b^{2^{P-n}} \sum_p^{2^{P-n}} \sum_q^{2^n} \sum_r^{2^{P-n}} \sum_s^{2^n} D_{pq}\, D_{rs} C_{ab}\, T_{ps}^{(N-1)}$$
$$\times \langle \gamma_{M,a} \bar{\gamma}_{M,b} | \hat{H}_{II}^{i,i+1} | \gamma_{M+n,q}\, \bar{\gamma}_{M+n,r} \rangle\ .$$

In the orthogonal basis of spin products, exchange acting upon $\gamma_{M+n,q}\ \bar{\gamma}_{M+n,r}$ gives a contribution only when it produces $\gamma_{M,a}\ \bar{\gamma}_{M,b}$. The summation reduces to a quadruple sum:

$$\langle \Theta_{M;N} | \hat{H}_{II}^{i,i+1} | \Theta_{M+n;N} \rangle = J \sum_p^{2^{P-n}} \sum_q^{2^n} \sum_r^{2^{P-n}} \sum_s^{2^n} D_{pq}\ D_{rs}\ C_{ab}\ T_{ps}^{(N-1)}$$

when the condition $\hat{H}_{II}^{i,i+1}\ |\gamma_{M+n,q} \bar{\gamma}_{M+n,r}\rangle = |\gamma_{M+n,a}\ \bar{\gamma}_{M+n,b}\rangle$ is fulfilled.