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Combining coupled-cluster and perturbative expansions through intermediate Hamiltonians: Theory and application to 1D and 2D spin lattices

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Using the perturbative expansion of the wave function from a single determinantal reference, it is possible to define a genealogical hierarchy of model spaces. The corresponding configuration-interaction matrices are dressed in the frame of intermediate Hamiltonian theory from estimates of the coefficients of the outer space determinants, which may take a coupled cluster (CC) or a perturbative form. The deviations from the additivity of transition energies are taken into account as a modification of coupled-cluster amplitudes, and higher-order exclusion-principle-violating corrections are introduced. The resulting equations relative to the first and second generations are applied to anisotropic Heisenberg Hamiltonians for one-dimensional and square two-dimensional spin lattices. The results show the efficiency of the method, which gives as accurate results with adjacent two-body operators as the traditional CC expansion with local four-body operators. With local four-body operators we obtain results comparable to those obtained with local six-body operators in normal CC treatments. [S0163-1829(96)06127-9]

I. INTRODUCTION

The coupled-cluster (CC) formalism has been initially proposed for the treatment of the nuclear many-body problem.[1] It first assumes that for the state of concern (usually the ground state) one can recognize a single determinantal approximation ϕ_0 having the largest coefficient in the configuration-interaction (CI) development of the exact wave function. In the intermediate normalization, ψ is written

$$\psi=\phi_0+\sum_i c_i\phi_i , \tag{1}$$

$$|c_i|<1, \quad \forall i \tag{2}$$

The main idea consists of imposing an exponential structure on the wave operator Ω,

$$\psi=\Omega\phi_0 , \tag{3}$$

$$\Omega=\exp(S), \tag{4}$$

and to truncate the operator S to a low degree of complexity, introducing, for instance, only single- and double-excitations (SD) operators in S,

$$S=T_1+T_2 , \tag{5}$$

Thus one obtains the CC-SD approximation,[2] which is now a standard method in molecular physics for the treatment of the electronic correlation in the ground state of atoms and molecules.[3] It is both formally satisfactory (size consistent) and accurate, since it incorporates most of the fourth-order corrections to the energy of the standard many-body perturbation theory (MBPT) expansion, and has a larger radius of reliability than perturbation.

There have been few applications in solid-state physics[4–9] for the treatment of periodic electronic systems with model Hamiltonians. Most of them concern the treatment of Heisenberg Hamiltonians on spin lattices. The numerical results indicate that, contrary to what happens in molecular physics, a satisfying accuracy requires introducing many-body (at least four-body) operators in the S operator. The present paper will trace this need for many-body operators in terms of deviations of the additivity of transition energies. Section II recalls that the exponential form of Ω is valid only when the coefficients of multiple excitations can be seen as products of the coefficients of elementary excitations, and assumes this additivity of excitation energies. It is possible to take into account the effect of deviations from additivity without introducing many-body operators. Several approximations will be derived in this section which revise the CC formulation through perturbative arguments, and make use of the intermediate Hamiltonian theory.[10]

Section III will present results for bipartite spin lattices, namely linear one-dimensional (1D) chain and 2D square lattices, treated with an anisotropic Hamiltonian, taking the Néel state as a reference function ϕ_0. The results will be compared to the exact solution for 1D, and with accurate numerical computations using either CC or other formalisms. It will be shown that one may reach the same type of accuracy with our corrected two-body (four-body) formalism than with traditional CC involving four-body (six-body) operators. For values of the diagonal ansiotropy parameter $\lambda<1$, it becomes rational to use another reference function, which is polarized in the XY plane. The results obtained from this second reference are better, especially for the 2D square lattice, where the phase transition at $\lambda=1$ appears very clearly.

II. METHOD

A. Intermediate Hamiltonian formulation

Let us consider a zero-order single-determinantal description $|\phi_0\rangle$ of the ground-state wave function $|\psi_0\rangle$. ϕ_0 will represent our reference or main-model space. Then consider a set of determinants $|\phi_i\rangle$, coupled directly or indirectly to $|\phi_0\rangle$, which with ϕ_0 constitute the total model space S of projector P_S. We shall suppose that S contains all the determinants which interact with $|\phi_0\rangle$ (i.e., $\langle\phi_i|H|\phi_0\rangle = H_{i0}\neq 0$). Let us call ϕ_α the other determinants, which do not belong to the model space. They consider the intermediate normalization of the wave function

$$\psi_0=\phi_0+\sum_i c_i\phi_i+\sum_{\alpha\notin S} d_\alpha\phi_\alpha , \tag{6}$$

$$H\psi_0=E_0\psi_0 . \tag{7}$$

The eigenequation relative to the ϕ_0 line is

$$E=H_{00}+\sum_i H_{i0}c_i , \tag{8}$$

so that a knowledge of the coefficients of the determinants interacting with ϕ_0 is sufficient to calculate the energy. To know the coefficient c_i, one should consider the eigenequation relative to the ϕ_i line:

$$\sum_{j\in S} H_{ij}c_j+(H_{ii}-E)c_i+\sum_{\alpha\notin S} H_{i\alpha}d_\alpha=0, \tag{9}$$

Then, if one has a procedure to evaluate the coefficients d_α of the outer-space determinants from the quantities $H_{i\alpha}$ and the c_i's, it become possible to define a dressed CI matrix $P_S(H+\Delta)P_S$ such that its eigenvalue is exact and its eigenvector is the projection of the exact eigenvector on the model space. Actually if one defines, for instance, a diagonal dressing operator[11]

$$\langle\phi_i|\Delta|\phi_j\rangle=\Delta_{ij}=0 \quad \text{if } i\neq j,$$

such that

$$\Delta_{ii}=\left(\sum_\alpha H_{i\alpha}d_\alpha\right)c_i^{-1}, \tag{10}$$

it is clear that

$$P_S(H+\Delta)P_S|P_S\psi_0\rangle=E_0|P_S\psi_0\rangle. \tag{11}$$

This is the basic idea of self-consistent state specific intermediate Hamiltonians[11,12] which our group introduced in molecular physics with a noticeable success. Reference 12 in particular has shown that CC methods may be formulated as self-consistently dressed CI problems. The same idea will be followed hereafter. We shall successively consider as model space the determinants which enter in the first-order-corrected wave function $\psi_0+\psi^{(1)}$, then those which enter into the second-order-corrected wave function $\psi_0+\psi^{(1)}+\psi^{(2)}$. In both cases we shall use perturbative arguments to find reasonable estimates of the coefficients d_α of the outer-space determinants coupled to the model-space determinants, i.e., which enter into $\psi^{(2)}$ in the first case, and into $\psi^{(3)}$ in the second case.

B. First-generation approximation

Hereafer we shall refer to a perturbative expansion of the wave operator Ω,

$$\Omega=1+\Omega^{(1)}+\Omega^{(2)}+\cdots, \tag{12}$$

using a development in powers of $V=H-H_0$, where H_0 is the diagonal part of the Hamiltonian[13]

$$H_0=\sum_i |\phi_i\rangle\langle\phi_i|H|\phi_i\rangle\langle\phi_i|.$$

This expansion will be used twice, (i) to fix the model space of the intermediate Hamiltonian and the operatorial form of S, and (ii) to suggest evaluations the coefficients d_α of the outer-space determinants.

For the sake of simplicity we shall assume that V is purely bielectronic [case (a)] or purely monoelectronic [case (b)] in our basis of determinants. So that the excitation operators T appearing in $\Omega^{(1)}$

$$\Omega^{(1)}=\sum_i c_i^{(1)}T_i=\sum_i \frac{H_{0i}}{\Delta E_i}T_i , \tag{13}$$

are either double [case (a)] or single [case (b)] excitations. The model space will be limited to the determinants appearing in $\psi^{(1)}$,

$$P_S=\sum_{i,H_{i0}\neq 0} |\phi_i\rangle\langle\phi_i|. \tag{14}$$

From a coupled-cluster point of view the operator S will be limited to the operators T_i appearing in $\Omega^{(1)}$,

$$S=\sum_i t_iT_i , \tag{15}$$

If we write $c_i=\langle\phi_i|\exp(S)|\phi_0\rangle$, we obtain

$$c_i=t_i \tag{16}$$

Notice that c_i (or t_i) is different from $c_i^{(1)}$ [Eq. (13)] due to the inclusion of higher-order effects.

It will be useful hereafter to partition the operator V into two parts:

$$V=V_1+V_2, \tag{17}$$

with

$$V_1=\sum_i V_{i0}T_i . \tag{18}$$

V_1 involves only the excitation operators appearing in T (i.e., in $\Omega^{(1)}$).

In order to dress the P_SHP_S matrix, we need to calculate the coefficients d_α on the outer-space determinants coupled to the ϕ_i's. Let us call Q_S the corresponding projector complementary to P_S,

$$Q_S=\sum_{\alpha\notin S} |\phi_\alpha\rangle\langle\phi_\alpha|. \tag{19}$$

In order to evaluate these coefficients, we shall turn to the expression for the second-order wave function. Since $\langle\phi_0|V|\phi_0\rangle=0$,

$$|\psi^{(2)}\rangle=\sum_{r\neq 0}\frac{|\phi_r\rangle\langle\phi_r|V|\psi^{(1)}\rangle}{\Delta E_r}. \tag{20}$$

We only want to calculate $Q_S\psi^{(2)}$,

$$Q_S|\psi^{(2)}\rangle=\sum_{\substack{\alpha\notin S\\ H_{i\alpha}\neq 0}}\frac{|\phi_\alpha\rangle\langle\phi_a|V|\psi^{(1)}\rangle}{\Delta E_\alpha}. \tag{21}$$

Now we shall replace $\psi^{(1)}$ by $\Sigma_i c_i\phi_i$ in the right ket, in order to add higher-order terms, and write

$$Q_s|\psi^{(2+\infty)}\rangle=\sum_{\substack{\alpha\notin S\\ H_{i\alpha}\neq 0}}\frac{|\phi_\alpha\rangle\left\langle\phi_\alpha\middle|V_1+V_2\middle|\sum_{i\notin S}c_i\phi_i\right\rangle}{\Delta E_\alpha}. \tag{22}$$

Using Eq. (18), one obtains

$$\begin{aligned}Q_S|\psi^{(2+\infty)}\rangle&=\sum_{j\in S}\sum_{i\in S}\frac{|T_jT_i\phi_0\rangle}{\Delta E_{ij}}F_{j0}c_i\\&\quad+\sum_{\substack{\alpha\notin S\\ H_{i\alpha}\neq 0}}\sum_i\frac{|\phi_\alpha\rangle\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha}c_i.\end{aligned} \tag{23}$$

In the first summation one generates the determinants

$$\phi_{ji}=T_jT_i|\phi_o\rangle \tag{24}$$

obtained by the product of two elementary excitations belonging to S; they are quadruples in case (a), doubles in case (b). The first summation is closely related to the second power of S in $\exp(S)$, which is supposed to treat the action of V_1^2. Actually,

$$\exp(S)=1+S+\frac{S^2}{2}+\cdots, \tag{25}$$

$$\tfrac{1}{2}S^2=\tfrac{1}{2}\sum_{j\in S}\sum_{i\in S}c_jc_iT_jT_i. \tag{26}$$

Replacing V_{j0} by $c_j\Delta E_j$ in the first term of Eq. (23), one obtains

$$C_{|T_iT_j\phi_0\rangle}=c_ic_j\frac{\Delta E_i+\Delta E_j}{\Delta E_{ij}}, \tag{27}$$

which reduces to c_ic_j if

$$\Delta E_i+\Delta E_j=\Delta E_{ij}. \tag{28}$$

Hence the coupled-cluster approximation appears valid for couples of excitations for which the transition energies are additive. Otherwise one obtains a modification of the term S^2 and may write

$$\tfrac{1}{2}S^2_{\mathrm{mod}}=\tfrac{1}{2}\sum_{j\in S}\sum_{i\in S}c_jc_iT_jT_i\frac{\Delta E_i+\Delta E_j}{\Delta E_{ij}}. \tag{29}$$

Finally we may write an approximation of Eq. (23),

$$Q_S'|\psi^{(2+\infty)}\rangle=\tfrac{1}{2}S^2_{\mathrm{mod}}|\phi_0\rangle+\sum_{\alpha\notin S}\sum_i\frac{|\phi_\alpha\rangle\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha}c_i. \tag{30}$$

The coefficient d_α of a determinant ϕ_α is then

$$\begin{aligned}d_\alpha&=\langle\phi_\alpha|\tfrac{1}{2}S^2_{\mathrm{mod}}\phi_0\rangle+\sum_i\frac{\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha}c_i\\&=\sum_{\substack{(i,j)\\ \phi_\alpha=T_iT_j\phi_0}}c_ic_j\frac{\Delta E_i+\Delta E_j}{\Delta E_\alpha}+\sum_i\frac{\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha}c_i,\end{aligned} \tag{31}$$

where (i,j) represents a pair of excitations.

Now it may be useful to compare our expression with the traditional CC procedures of molecular physics. If V_1 is purely bielectronic (for instance, when ϕ_0 is a Hartree-Fock determinant), one is in case (a), then S involves *only* double excitations but *all* double excitations in the *ab initio* problem. If one considers that

$$\Delta E_{ij}=\Delta E_i+\Delta E_j,$$

then

$$S^2_{\mathrm{mod}}=S^2.$$

If one omits the last sums in Eq. (31) or (30), one obtains the classical CC-*D* approximation. If one adds the second sum, ϕ_α may be a single or triple, and one would have the CC-*D*-[*ST*-1*a*] approximation, analogous to the CC-SD-[T_1]*a* first proposed by Urban *et al.*[14] and reformulated recently in the intermediate Hamiltonian formalism.[12]

It is known that a partial infinite summation of diagrams,[15] called the EPV (exclusion principle violating) diagrams, provides a better evaluation of c_i than the first-order perturbative ratio $H_{i0}/\Delta E_i$,

$$c_i=\frac{H_{i0}}{\Delta E_i+\mathcal{E}_i}, \tag{32}$$

where $\mathcal{E}$ represents EPV and where

$$\mathcal{E}_i=\sum_{\substack{j\\ T_j\phi_i=0}}H_{0j}c_j \tag{33}$$

represents the contribution of the excitations which cannot be applied to ϕ_i (since they involve either a hole or a particle already created in ϕ_i). Similarly, it is possible to replace ΔE_{ij} and ΔE_α by $\Delta E_{ij}+\mathcal{E}_{ij}$ and $\Delta E_\alpha+\mathcal{E}_\alpha$ in Eq. (31) by an appropriate infinite summation of diagrams, and to write

$$\begin{aligned}d_\alpha&=\sum_{\substack{(i,j)\\ T_iT_j\phi_0=\phi_\infty}}c_ic_j\frac{\Delta E_i+\Delta E_j+\mathcal{E}_i+\mathcal{E}_j}{\Delta E_\alpha+\mathcal{E}_\alpha}\\&\quad+\sum_i\frac{\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha+\mathcal{E}_\alpha}c_i,\end{aligned} \tag{34}$$

which will be our first working approximation 1G-*a* (first-generation-*a*).[16]

A more complex equation has been derived in a preceding work,[16] for the case where $\langle\phi_\alpha|V_2|\phi_i\rangle=0\;\forall i$, by considering the limited CI matrix concerning ϕ_0 and ϕ_α and all the doubles which are part of the quadruple ϕ_α (i.e., all $T_i\phi_0$ such that $\phi_\alpha=T_jT_i\phi_0$). One has introduced two types of $\mathcal{E}$ terms. Let us call S_α the set of double excitations which are part of the quadruple excitation leading to ϕ_α. We define

$$\mathcal{E}^1_\alpha=\sum_{j\in S_\alpha} H_{0j}c_j\,, \tag{35}$$

and $\mathcal{E}^2_\alpha=\mathcal{E}_\alpha-\mathcal{E}^1_\alpha$.

We have also introduced the quantity

$$\mathcal{E}^2_{i\alpha}=\sum_{\substack{m\\ T_m\phi_0\notin S_\alpha,\\ T_m\phi_i=0,}} H_{0m}c_m\,, \tag{36}$$

and have derived a second working equation

$$d_\alpha=\sum_{\substack{(i,j)\\ T_iT_j\phi_0=\phi_\alpha}} c_ic_j\,\frac{\Delta E_i+\Delta E_j+\mathcal{E}^2_{i\alpha}+\mathcal{E}^2_{j\alpha}+2\mathcal{E}^1_\alpha}{\Delta E_\alpha+2\mathcal{E}^1_\alpha+\mathcal{E}^2_\alpha}+\sum_i \frac{\langle\phi_\alpha|V_2|\phi_i\rangle}{\Delta E_\alpha+\mathcal{E}_\alpha}\,c_i\,, \tag{37}$$

which we shall call approximation 1G-*b*. It is important to verify whether approximations 1G-*a* [Eq. (34)] and 1G-*b* [Eq. (37)] satisfy the separability condition. One may consider the problem of an *A . . . B* supersystem, where *A* and *B* do not interact. The elementary excitations of nonzero amplitudes are localized on *A* or *B*,

$$T_1=T_1^A+T_1^B=\sum_{i_A} t_{i_A}T_{i_A}+\sum_{j_B} t_{h_B}T_{j_B}.$$

It is clear that for an intersystem composite excitation,

$$|\phi_{\alpha_{AB}}\rangle T_{i_A}T_{j_B}|\phi_0\rangle$$

can only be created by the successive actions of V_{1_A} and V_{1_B} (or reverse). It is also clear that

$$\Delta E_\alpha=\Delta E_{i_A}+\Delta E_{j_B},$$

$$\mathcal{E}_{i_\alpha}=\mathcal{E}_{i_A}+\mathcal{E}_{j_B};$$

hence Eq. (37) ensures

$$d_{\alpha_{AB}}=c_{i_A}c_{i_B}.$$

One also may check that $d_{\alpha_{AOB}}=d_{\alpha_A}$ for any intramolecular excitation appearing in $\phi^{(2)}$. As demonstrated elsewhere,[17] these conditions ensure that strict separability.

C. Second-generation approximation

Now we shall include in the model space, beyond ϕ_0 and the ϕ_i's appearing in $\psi^{(1)}$, the determinants which appear in $\psi^{(2)}$, the coefficients of which are not obtained as simple products of the elementary first-generation coefficients. This means that we add both (i) the determinants which do not satisfy the additivity of the transition energy, and for which one had to use S^2_{mod}; and (ii) those which are created from the determinants ϕ_i of $\psi^{(1)}$ by the action of V_2.

Let us call ϕ_m and ϕ_n these ''problematic'' determinants of the second generation, and d_m and d_n their coefficients. The eigenequation for them involves their interaction with determinants ϕ_α of the third generation, the coefficients e_α of which must be estimated. Turning again to perturbation theory, at third order now, one may see that

$$e_\alpha^{(3)}=\sum_m d_m^{(2)}\,\frac{V_{\alpha m}}{\Delta E_\alpha}\,. \tag{38}$$

Decomposing *V* into its two parts, one notices that

$$V_{\alpha m}=V_{i0}\quad \text{if}\quad \phi_\alpha=T_i\phi_m\,,$$

and replacing V_{i0} by $c_i\Delta E_i$, one obtains

$$e_\alpha^{(3)}=\sum_{\substack{(m,i)\\ \phi_\alpha=T_i\phi_m}} d_mc_i\,\frac{\Delta E_i}{\Delta E_\alpha}+\sum_m d_m\,\frac{\langle\phi_\alpha|V_2|\phi_m\rangle}{\Delta E_\alpha}\,. \tag{39}$$

Incorporating $\mathcal{E}$ corrections, one obtains the third working equation (approximation 2G-*a*)

$$e_\alpha=\sum_{\substack{(m,i)\\ \phi_\alpha=T_i\phi_m}} d_m\left[\frac{c_i(\Delta E_i+\mathcal{E}_i)+\langle\phi_\alpha|V_2|\phi_m\rangle}{\Delta E_\alpha+\mathcal{E}_\alpha}\right]. \tag{40}$$

An alternative formulation may be obtained by moving back to the CC formulation. Saying that one introduces independent coefficients d_m for the ''problematic'' second-generation determinants means that one introduces the corresponding many-body operators *U* in *S*,

$$S=T+U, \tag{41}$$

where

$$U=\sum_m u_mU_m\,,$$

The amplitudes of the T_i operators are equal to c_i,

$$t_i=c_i\,, \tag{42}$$

while for the U_m operator one has

$$d_m=\tfrac{1}{2}\sum_{\substack{(i,j)\\ \phi_m=T_iT_j\phi_0}} c_ic_j+u_m\,. \tag{43}$$

The *U* operator incorporates both the deviations to factorization of the coefficients for the T^2 part and the contribution from V_2V_1 products acting on ϕ_0.

The determinants of the third generation are obtained from the action of V_1 or V_2 on those of the second generation. The part coming from V_1 can be obtained through the cluster expansion.

$$\tfrac{1}{6}T^3+\tfrac{1}{2}(TU+UT) \tag{44}$$

and the part coming from the action of V_2 should be written perturbatively as above:

$$d_m \frac{\langle \phi_\alpha | V_2 | \phi_m \rangle}{\Delta E_\alpha} .$$

However, the action of T_i on ϕ_m can lead to a state ϕ_α, such that

$$\Delta E_\alpha \neq \Delta E_i + \Delta E_m$$

(an additional violation of the additivity of transition energies), and in such a case one should again introduce an energy correction

$$e_\alpha = \left\langle \phi_\alpha \middle| \tfrac{1}{6} \sum_i \sum_j \sum_k T_i T_j T_k \middle| \phi_0 \right\rangle c_i c_j c_k + \left\langle \phi_\alpha \middle| \tfrac{1}{2} \sum_i \sum_m (T_i U_m + U_m T_i) \middle| \phi_0 \right\rangle c_i u_m \frac{\Delta E_i + \mathcal{E}_i + \Delta E_m + \mathcal{E}_m}{\Delta E_\alpha + \mathcal{E}_\alpha} + \sum_m \frac{\langle \phi_\alpha | V_2 | \phi_m \rangle}{\Delta E_\alpha + \mathcal{E}_\alpha} d_m . \tag{45}$$

In the above expression, hereafter called the 2G-*b* approximation, one has again added the $\mathcal{E}$ terms in all transition energies ΔE_i, ΔE_m, and ΔE_α.

It is easy to verify that with such an expression of e_α the composite excitations on two interacting subsystems factorize, insuring the separability.

III. APPLICATION TO SPIN LATTICES

A. Generalities

We shall consider a Heisenberg Hamiltonian

$$H = \tfrac{1}{2} \sum_{\substack{r,s \\ \text{adjacent}}} S_r^x S_s^x + S_r^y S_s^y + \lambda S_r^z S_s^z , \tag{46}$$

where *r* and *s* are bonded atomic sites; S_r^x, S_r^y, and S_r^z are the components of the local spin momentum and λ an anisotropy parameter. The interactions are equal, and only concern first neighbors. The lattices considered in this work are bipartite, i.e., they accept a Néel function (perfect spin alternation between nearest neighbors). As far as λ is positive, the Néel function is the spin distribution of lowest energy, and it will be taken as our reference function ϕ_0. Notice that it is also the single determinant which is coupled to the largest number of determinants ϕ_i, since spin exchanges are possible on all bonds. This is true even when λ is negative. ϕ_0 only interacts with the determinants obtained by spin exchanges T_p between adjacent atoms, so that the energy is

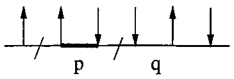
$$E = \langle \phi_0 | H | \phi_0 \rangle + \sum_p \langle \phi_0 | H | T_p \phi_0 \rangle C_{|T_p \phi_0\rangle} .$$

If all bonds are equivalent, all coefficients $C_{|T_p \phi_0\rangle}$ are equal, and the energy per bond brought by the configuration interaction in simply $c_p = c$. The final energy per bond is

$$E_p = -\frac{\lambda}{2} + c . \tag{47}$$

As an important remark, one should analyze the deviation of the additivity of transition energies. Consider, for instance, a 1D chain. Starting from the Néel state, the spin exchange between two adjacent atoms creates two spin frustrations on the adjacent bonds, so that

$$\Delta E_p = -2\lambda$$



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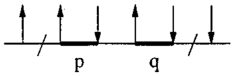
Now if one proceeds to a second spin exchange on a second-neighbor bond *q*, one obtains a determinant ϕ_{pq} with again two spin frustrations, despite the fact that it has been reached by two spin exchanges on bonds *p* and *q*,

$$\Delta E_{p\,q} = -2\lambda$$



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hence $(\Delta E_p + \Delta E_q)/\Delta E_{pq} = 2$, so that one may expect that the coefficient of this determinant of the second generation will be significantly larger than c^2. The CC-*D* method (called LSUB-2 in Ref. 7) will therefore underestimate *c* and the cohesive energy, and it will be necessary to go to four-body operators to take into account the effect of the deviations to additivity of transition energies in traditional CC expansions.

For values of λ smaller than 1 (and larger than -1, where the ground state becomes ferromagnetic), it seems reasonable to consider another reference function, namely an *XY*-polarized function

$$\phi_0' = \prod_i (2i + \overline{2i})[(2i+1) - \overline{(2i+1)}].$$

Its energy per bond is $-[(\lambda+1)/2]g$, which has to be compared with the energy per bond $(-\lambda_g)$ of the Néel function (taking the ferromagnetic state as zero of energy). It is clear that for $\lambda < 1$ the energy of ϕ_0' is lower than that of ϕ_0. One may construct a development from ϕ_0'. Since the algebra is a bit more complex, we have restricted our calculations to the 1G-*a* approximation.

B. First-generation approximation

Another remark concerns the periodicity. For equal interactions on all bonds all coefficients of the first generation are identical. Thus one may reduce the model space to ϕ_0 and a given determinant of the first generation, obtained by a spin exchange on bond p,

$$\phi_p = T_p \phi_0 ,$$

$$S = \{\phi_0 , \phi_p\}.$$

The dressing technique will follow the same principle as in the Sec. III A [i.e., obey Eqs. (10)], ϕ_0 being dressed by its interaction with the other determinants of the first-generation $\phi_q \neq \phi_p$.

The bare CI matrix is

$$\begin{array}{c} \phi_0 \\ \phi_p \end{array} \begin{vmatrix} 0 & 1, \\ 1 & -\Delta E_p \end{vmatrix} ,$$

where $\Delta E_p = -\lambda n_v$, n_v being the number of bonds adjacent to the bond p. If n_c is the number of neighbors of each atom, $n_v = 2(n_c - 1)$. Now one must proceed to the dressing.

For ϕ_0,

$$\Delta_{00} = \sum_{q \neq p} c_q , \tag{48}$$

since T_q is always possible on the Néel state. In this spin problem there is no interaction between the determinants of the first generation ($V_{pq} = 0$), and ϕ_p only interacts with the determinants $\phi_{pq} = T_q \phi_p$,

$$\Delta_{pp} = \left(\sum_{q \neq p} \langle \phi_p | H | \phi_{pq} \rangle C_{qp} \right) c_p^{-1} . \tag{49}$$

Most of the excitations T_q on ϕ_p are such that

$$\Delta E_\alpha = \Delta E_q + \Delta E_p ,$$

so that $c_{qp} = c_q c_p$. Such excitations T_q make the same contributions to the dressings Δ_{00} and Δ_{pp}, and have no influence on the determination of c_p. They may be omitted and one may restrict both summations to two types of excitations: (i) those which are possible on ϕ_0 and impossible on ϕ_p due to the spin frustrations of the bonds adjacent to p, and (ii) those which violate the transition energy additivity, i.e., those for which

$$\Delta E_\alpha \neq 2 \Delta E_p .$$

These excitations only concern the bonds q which are second neighbors of the bond p. For these on must estimate c_{pq} using Eqs. (34) or (37). Finally,

$$\Delta_{00} = c(n_1 + n_2), \tag{50}$$

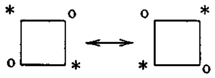
where n_1 and n_2, respectively, are the number of adjacent and second-neighbor bonds, and

$$\Delta_{pp} = \left(\sum_{\substack{q \\ \text{second neighbors}}} c_{qp} \right) c_p^{-1} . \tag{51}$$

C. Second-generation approximation

As explained previously we restrict the research of the second-generation coefficients d_m (and corresponding u_m amplitudes) to those of the quadruples which violate the transition energy additivity. As seen previously these determinants are obtained by spin exchanges on second-neighbor bonds.

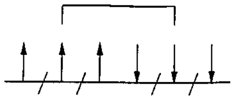
For a 1D chain there is only one such quadruple. The model space to define its amplitude has a dimension 4. For a 2D square lattice, one must distinguish four types of second-neighbor quadruples. For one of these, corresponding to a full spin exchange in a square,



the size of the model space is 6. For all others the corresponding size is 4. The method proceeds as before by a dressing of all diagonal elements of the corresponding remote bonds make the same dressing contribution to all determinants of these model spaces, and one has only to consider spin exchanges on the bonds which are adjacent or second neighbor to the bonds involved in the model space. For the 2D problem, the dressing of the various matrices couple them.

For the first time the operator V_2 begins to play a role at the second-generation approximation for the determinants ϕ_α of third generation which represent spin exchange through three bonds (i.e., which are obtained from ϕ_0 by two-body operators)

$\phi_\alpha =$



.

They interact with the second generation determinant ϕ_m,

$\phi_m =$

,

by a spin exchange on the central bond, which does not belong to the T operators since it changes (β,α) into (α,β), while the T operation changes (β,α) into (α,β). Its coefficient is therefore calculated perturbatively.

One should compare our approximations to those introduced by Bishop, Parkinson, and Xian[7] in a strict CC orthodoxy. Our first-generation approximations consider only one unknown variable, the amplitude of the spin exchange between adjacent atoms as does their SUB2-2 (or LSUB-2) approximation. Our second-generation approximations consider as variable the four-body processes which are included in their LSUB4 approximation. Our procedure differs by the evaluation of the outer-space coefficients, which may deviate from the simple exponential form, and by the perturbative evaluation of some third-order two-body operators amplitudes.

D. Results for the 1D spin-$\frac{1}{2}$ lattice

For a 1D spin-$\frac{1}{2}$ anisotropic Heisenberg Hamiltonian, the exact energy is known,[18] and one may distringuish (i) the ferromagnetic regime $\lambda \leqslant -1$, (ii) the critical antiferromagnetic phase $-1 \leqslant \lambda \leqslant 1$, and (iii) the Ising-like region $\lambda > 1$. The isotropic Heisenberg Hamiltonian has been widely studied. Taking the Néel state as the reference one, the c_i coefficient of the double excitation has been calculated with dif-

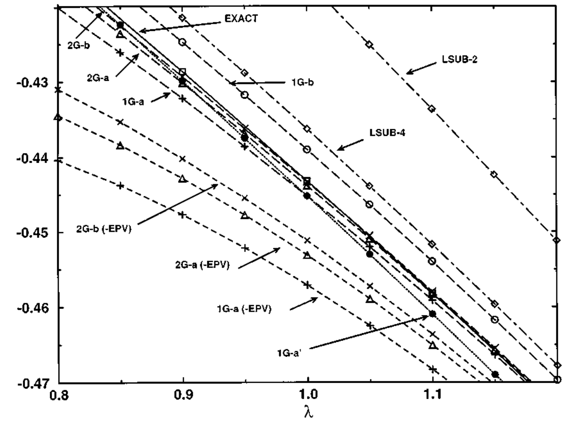


FIG. 1. Energy per bond for the 1D spin-lattice as a function of the anisotropy parameter λ in the weakly anisotropic region. LSUB-2 and LSUB-4 are CC values from Ref. 7. 1G-*a*, 1G-*b*, 2G-*a*, and 2G-*b* refer to the present work. The three lower curves present the results obtained from these approximations when neglecting the $\mathscr{E}$ corrections. 1G-a' is obtained from the *XY*-polarized reference function, all others are obtained from the Néel function. The exact energy is the full line.

ferent theoretical approaches. The exact Bethe-ansatz resolution of this Hamiltonian gives a coefficient of $-0.386\,29$. In the CC theory[7] when introducing in S the two-body operator between adjacent neighbor atoms, the coefficient obtained is $-0.333\,33$. This is the LSUB-2 CC approximation. When all the nonadjacent two-body operators are included (that is labelled the SUB2-∞ scheme) a fifth-order correction to the energy is included and the value of c, $-0.337\,20$, does not improve significantly. Our 1G-*a* and 1G-*b* approximations introduce the nonadditivity of transitions energies in the amplitudes of the two-body operators for neighbor atoms, that is equivalent to take into account the connected four-body diagrams. The coefficients obtained, $C_{1\text{G-}a}=-0.390\,39$ and $C_{1\text{G-}b}=-0.377\,96$, present a much lower error than the CC results.

The inclusion of some of the four-body operators in the CC exponential expansion (LSUB-4 approximation[7]), gives $C=-0.372\,54$ (slightly poorer than our 1G-*a* and 1G-*b* results). Taking into account the deviations to additivity for up to four-body operators (which includes six-body effects in an effective manner) one obtains $C_{2\text{G-}a}=0.387\,64$ and $C_{2\text{G-}b}=-0.386\,59$, which are values with errors of -1×10^{-3} and -3×10^{-4}. The more sophisticated CC calculation for the 1D spin-$\frac{1}{2}$ lattice is the LSUB-10 scheme, that includes some of the ten-body operators. This approximation gives a c of -0.3840, that still has an error of 2×10^{-3}. Only an extrapolation with the LSUB-n, where $n=4$, 6, 8, or 10, gives a coefficient of -0.3862. The coefficient of our 2G-*B* approximation has a lower error than the one obtained in the extrapolation of a numerical real-space renormalization-group approach[19] (7×10^{-4}), $c=-0.385\,57$.

In Fig. 1 are presented the energies obtained with the proposed first- and second-generation equations around $\lambda=1$. In order to compare our results with the previous ones of Bishop, Parkinson, Xian,[7] we have plotted their energies for LSUB-2 and LSUB-4 approximations. In the considered region ($0.8\leqslant\lambda\leqslant1.2$) our four proposed equations give more accurate values for the energy than the LSUB-2 and LSUB-4 CC approximations.

In order to study the contribution of EPV's to the deviation of the additivity of transition energies, we have included in Fig. 1 the corresponding results of approximations 1G, 2G-*a*, and 2G-*b* without $\mathcal{E}$ corrections. [Notice that when EPV's are removed, Eqs. (34) and (37) become identical, 1G-$b\equiv$1G-a.] From Fig. 1 one may conclude that around $\lambda=1$ the equations without EPV contributions give much poorer results than the corresponding equations with $\mathcal{E}$'s.

For analyzing the behavior of the equations proposed in this paper in the three different regions defined by the anisotropic parameter, several values of the first-generation coefficient c are calculated, and exact values at various points of λ are given in Table I, also, the energies have been plotted in Fig. 2 for $-1\leqslant\lambda\leqslant1$. Results show that in the Ising-like re-

TABLE I. Coefficients of the spin exchange between neighboring atoms for 1D spin lattices.

λ	1.5	1.0	0.5	0.0	−0.5
Exact[a]	−0.2969	−0.3863	−0.5000	−0.6366	−0.7990
LSub-2[b]	−0.2638	−0.3333	−0.4343	−0.5773	−0.7676
LSub-4[b]	−0.2890	−0.3725	−0.4884		
This work					
from Néel function					
1G-*a*	−0.2959	−0.3904	−0.5294	−0.7071	−0.8887
1G-*a* (without EPV)	−0.3028	−0.4142	−0.6180	−1.0000	
1G-*b*	−0.2912	−0.3780	−0.5000	−0.6546	−0.8273
2G-*a*	−0.2959	−0.3876	−0.5145	−0.6664	−0.8262
2G-*a* (without EPV)	−0.3001	−0.4062			
2G-*b*	−0.2959	−0.3866	−0.5075	−0.6457	−0.7976
2G-*b* (without EPV)	−0.2992	−0.4024			
from *XY*-polarized function					
1G-a'	−0.3062	−0.3904	−0.4969	−0.6292	−0.7915

[a] Reference 18.

[b] Reference 7.

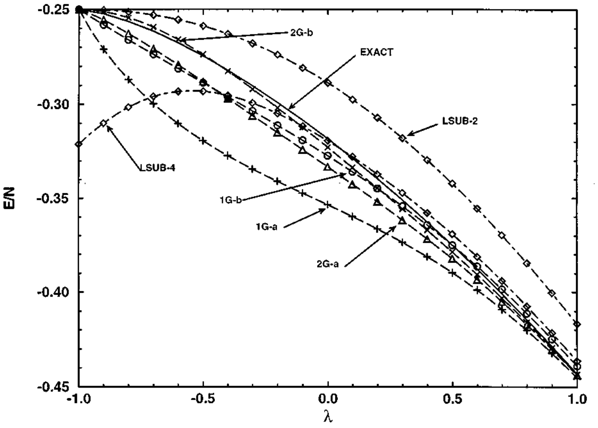


FIG. 2. Energy per bond for the 1D spin lattice as a function of the anisotropy parameter in the critical antiferromagnetic domain ($-1<\lambda<1$) when starting from the Néel function. Same comments as in Fig. 1.

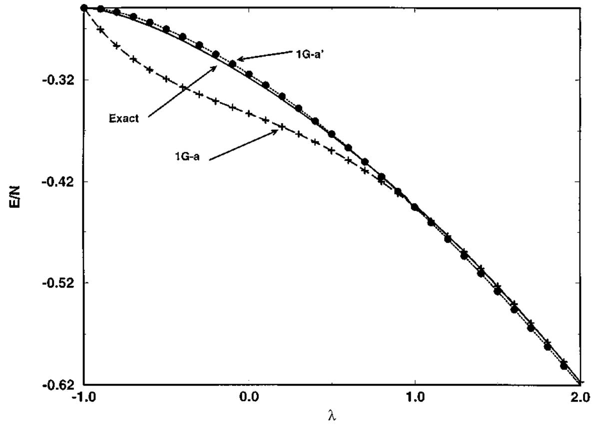


FIG. 3. Energy per bond of the 1D spin lattice as function of the anisotropy parameter λ. Comparison of the 1G-*a* approximation from the Néel state and the *XY* polarized function (1G-*a*′) with the exact values (full line).

gion ($\lambda>1$) our four equations tend to the exact value properly, as well as CC approximations.

At $\lambda=0$ the anisotropic Heisenberg Hamiltonian corresponds to the so-called *XY* model or a Hückel Hamiltonian, due to the fact that in the Hamiltonian matrix all the diagonal elements are zero, producing a complete degeneration between the Néel state and all the possible double, quadruple, etc. excitations. Therefore at $\lambda=0$ the correction to the CC products $c_i c_j$ introduced in our equations comes only from the nonadditivity of the EPV's. The c's obtained with our four equations have an error equal (approximation 1G-*a*) to or lower (1G-*b*, 2G-*a*, and 2G-*b*) than the LSUB-4 one. These results confirm that the EPV's make a great contribution to the treatment of the deviation of the additivity of transition energies. Moreover, EPV contributions are responsible for the unexpectedly good behavior in the critical antiferromagnetic region. Our approximation 1G-*a* without EPV's at $\lambda=0$ gives *a* value of c equal to -1.0 (see Table I) which is the exact value of c for $\lambda=-1$, and for the approximations 2G-*a* and 2G-*b* the coefficient of the considered quadruple excitation becomes greater than the c coefficient around $\lambda=0.7$–0.8. EPV's therefore play a crucial role.

In the region $-1<\lambda<0$ the Néel state becomes the determinant of higher energy, but it still remains a good function of reference because it is coupled with the N possible double excitations ϕ_i, produced by a spin exchange between two adjacent atoms, and its coefficient remains the largest one in the function. Results of Table I show that for this region the coefficients obtained from the second-generation approximation are nearer to the exact value than LSUB-4 ones. However, for the first generation, approximation 1G-*b* achieves the same accuracy as the two- and four-body CC approximations, approximation 1G-*b* giving the poorest result. Our best 2G-*b* approximation is surprisingly accurate in this paradoxical region.

The LSUB-2 approximation reaches the exact Bethe-ansatz energy at $\lambda=-1$, where one enters into the ferromagnetic regime; however, the LSUB-4 energy does not behave properly around $\lambda=-1$. All equations proposed here give the correct c coefficient at this point ($c=-1.0$). Notice that for $\lambda<-1$ our expressions have no validity, since the ratio $c_0/|c|$ becomes lower than 1, and the Néel function does not remain a good function of reference.

As mentioned in Sec. III A, for $-1<\lambda<1$, it is better to start from an *XY*-polarized reference function ϕ_0', which becomes of lower energy than the Néel function. The overall behavior of the result of the 1G-*a* approximation from this reference function (labeled 1G-*a*′) appears in Fig. 3, where it is compared with the exact solution and the result of the same approximation starting from the Néel function. The 1G-*a*′ results are excellent in the critical region ($-1<\lambda<1$), and remain surprisingly reasonable in the $\lambda>1$ region where the Néel function becomes more relevant. The zoom of Fig. 1 around $\lambda=1$ shows that 1G-*a* and 1G-*a*′ cross at $\lambda=1$, but at a very small angle, as compatible with the fact that this is not a real phase transition.[20]

E. Results for 2D spin-$\frac{1}{2}$ square lattice

Although this problem has not been solved exactly, some numerical Green's-function Monte Carlo (GFMC) (Ref. 22) and spin-wave function[23] calculations have been published. The energy given by the GFMC model for $\lambda=1$ (-0.669 a.u.) is usually chosen for making comparisons, due to its estimated error, and is in good agreement with other later published results. Bishop and co-workers[7,8] have treated this system with different CC approximations, mainly LSUB-*n* schemes. When they consider two-body nearest-neighbor operators (LSUB-2), the energy obtained is -0.648. The inclusion of all two-body operators causes a decrease of only 0.003. Their LSUB-4 scheme, that includes seven independent coefficients, gives an energy of -0.664 and their most satisfactory LSUB-6, with 72 coefficients for this system, achieves a value of -0.667.

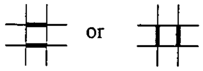
In second-generation calculations for the 2D spin lattice, we have considered five independent coefficients, c and the four quadruple excitations over the Néel state that violate the addivitity of transition energies. These four coefficients con-

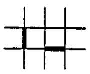
TABLE II. Coefficients of the spin exchange between neighboring atoms for 2D spin square lattices.

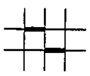
$\lambda=1$		c_i
CC[a]	LSUB-2	-0.148
	SUB2-∞	-0.151
	LSUB-4	-0.164
	LSUB-6	-0.167
GFMC[b]		-0.169
SWT[c]		-0.158
This work	1G-*a*=1G-*a*′	-0.164
	1G-*b*	-0.163
	2G-*a*	-0.165
	2G-*b*	-0.166

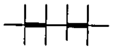
[a] Reference 18.
[b] Reference 22.
[c] Reference 23.

cern the following processes:







 .

The CC estimates of the *c*'s and the ones obtained with the four equations proposed in this work are presented in Table II. As in the 1D $\frac{1}{2}$-spin-lattice treatment, the consideration of the nonadditivity of transition energies and the inclusion of EPVs allow us to obtain results for the first-generation (second generation) comparable to the LSUB-4 (LSUB-6) approximation with a much smaller number of independent coefficients, our best estimate of the energy being $E=0.666$, rather close to the Monte Carlo extrapolation -0.669.

Regarding the dependence of the energy on the anisotropy parameter λ, it is clear that when λ is larger than 1, the weight of the Néel state in the wave function increases, and all methods agree (even a second-order perturbative evaluation). The coupled-cluster estimates for $\lambda<1$ are in good agreement between themselves (i.e., our two-body 1G level $\simeq$LSUB-4, our four-body 2G level $\simeq$LSUB-6). The LSUB-4 and LSUB-6 curves present a terminating point close to $\lambda=0.6$ and 0.75, respectively, which do not appear in our methods. In our expansions the largest coefficient for the quadruply excited determinants concerns the full spin flip on a square. This becomes larger than the coefficient of the first-generation determinant for $\lambda=0.304$ for 2G-*a*, and $\lambda=0.336$ for 2G-*b*. This is a signal of the breakdown of the generalogical hierarchy, and we have not plotted the energies for smaller values of λ in Fig. 3.

It is noticeable that the deviation between all coupled-cluster values and the Monte Carlo estimates increases when λ decreases. The analysis of the Monte Carlo calculations indicate a phase transition at $\lambda=1$, with a rapid change of the slope $E(\lambda)$, which is missed by the coupled-cluster expansion from the Néel state with up to six-body operators.

Indeed for $-1<\lambda<1$, one must change the reference function to start from the *XY*-polarized function. The results of the corresponding 1G-*a*′ approximation appear in Fig. 4. The curve $E(\lambda)$ parallels the few results of the Monte Carlo calculation below $\lambda=-0.9$. The two curves 1G-*a* from Néel and 1G-*a*′ from the *XY*-polarized function cross at $\lambda=1$. Contrary to what happened for the 1D lattice the crossing is well marked. For negative values of λ the energy goes to the correct terminal value (-0.5) at $\lambda=-1.0$, with a parabolic behavior.

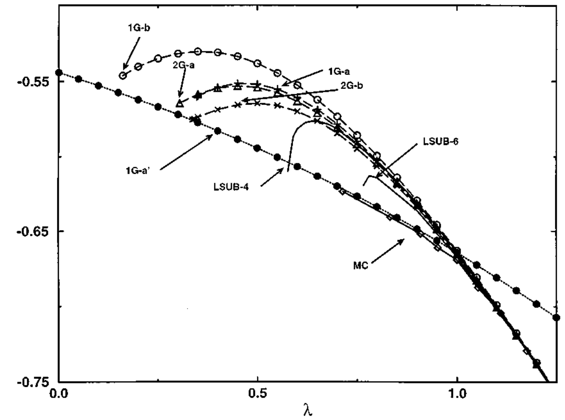


FIG. 4. Energy per bond for the square 2D spin lattice as a function of the anisotropy parameter in the domain $0<\lambda<1.2$. LSUB-4 and LSUB-6 are CC values from Refs. 7 and 8. MC are Monte Carlo results from Ref. 20. Approximation 1G-*a*, 1G-*b*, 2G-*a*, and 2G-*b* refer to the present work, starting from the Néel function, 1G-*a*′ concerns the 1G-*a* approximation starting from the *XY*-polarized function.

IV. CONCLUSION

We have developed a combination of coupled-cluster and perturbative expansions for the calculation of the energy of a ground state from a single-determinational zero-order description. The method proceeds through a choice of a model space and the dressing of the corresponding CI matrix under the effect of the interaction with the outer-space determinants, according to the strategy of state-specific intermediate Hamiltonians. The coefficients of these outer-space determinants are evaluated from products of coefficients of the inner-space determinants when possible, or from perturbative ratios. The possible deviations of the transition energies additivity result in corrections of the products of amplitudes, and in all cases the higher-order EPV corrections are taken into account through shifts of the transition energies.

The methodology presented here is applicable to molecular physics or to finite clusters, but its application to periodic systems treated through model Hamiltonians is especially simple, due to the translational invariance and to the nearest-neighbor restrictions of the interactions. As a first test we have studied 1D and square 2D spin lattices using an anisotropic Heisenberg Hamiltonian.

The results are very convincing. One achieves the same accuracy with one two-body operator than with the LSUB-4 CC developments which respectively involve three (1D) or seven (2D) independent operators. Introducing one four-body operator in 1D we obtain better accuracy than with LSUB-6 (seven operators) and for 2D with our four four-body operators one reaches the same accuracy as the LSUB-6 CC approximation (72 operators). The method is extremely resistant to degeneracy; for a 1D spin chain it is not only able to treat correctly the case of full degeneracy

(*XY* Hamiltonian) but also the paradoxical region ($-1 < \lambda < 0$) where the Néel state is the determinant of highest energy. Our equations correctly predict the phase transition to the ferromagnetic regime at $\lambda = -1$. The reading of the inner- and outer-space coefficients gives some control on the domain of validity of the approach. The phase transition occurring at $\lambda = 1$ for the 2D lattice is correctly reproduced by changing the reference function from the Néel state for $\lambda \geqslant 1$ to the *XY*-polarized function for $\lambda \leqslant 1$.

Starting from localized reference functions, the coupled-cluster development only introduces short-range operators and handles only a small section of the wave function, which are sufficient to produce good evaluations of the energy. It is less adapted to a determination of other observables, for instance long-range correlation factors, although the exponential wave operator furnishes an approximation of the whole wave function which may be used for such properties.

In the near future we shall apply the method to a series of problems, namely (i) the dimerization of polyacetylene treated as a spin Peierls problem through a geometry-dependent Heisenberg Hamiltonian,[21] (ii) the 1D spin-frustrated problem (J' between second-neighbor atoms), and (iii) the 1D Hubbard Hamiltonian starting from either the Néel state or products of bond singlets.

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[1] F. Coester, Nucl. Phys. **7**, 421 (1958); F. Coester and H. Kummel, *ibid.* **17**, 477 (1960).

[2] J. Cizek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969); R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989).

[3] R. J. Bartlett, Ann. Rev. Phys. Chem. **32**, 359 (1981); A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, J. Chem. Phys. **87**, 5361 (1987).

[4] D. J. Klein and M. A. Garcia-Bach, Int. J. Quantum Chem. **12**, 273 (1977); D. J. Klein, Phys. Rev. B **19**, 870 (1979); D. J. Klein and M. A. Garcia-Bach, *ibid.* **19**, 877 (1979).

[5] M. Roger and J. H. Hetherington, Phys. Rev. B **41**, 200 (1990); Europhys. Lett. **11**, 255 (1990).

[6] F. Harris, Phys. Rev. B **47**, 7903 (1993).

[7] R. F. Bishop, J. B. Parkinson, and Y. Xian, Phys. Rev. B **43**, 13 782 (1991); **44**, 9425 (1991).

[8] R. F. Bishop, R. G. Hale, and Y. Xian, Phys. Rev. Lett. **73**, 3157 (1994).

[9] F. Cornu, T. Jolicoeur, and J. C. LeGuillou, Phys. Rev. B **49**, 9548 (1994).

[10] J. P. Malrieu, Ph. Durand, and J. P. Daudey, J. Phys. A **18**, 809 (1985).

[11] J. P. Malrieu, I. Nebot-Gil, and J. Sanchez-Marin, J. Chem. Phys. **100**, 1440 (1994); J. L. Heully and J. P. Malrieu, Chem. Phys. Lett. **199**, 545 (1992); J. P. Daudey, J. L. Heully, and J. P. Malrieu, J. Chem. Phys. **99**, 1240 (1993).

[12] I. Nebot-Gil, J. Sanchez-Marin, J. L. Heully, J. P. Malrieu, and D. Maynau, Chem. Phys. Lett. **234**, 45 (1995); I. Nebot-Gil, J. Sanchez-Marin, J. P. Malrieu, J. L. Heully, and D. Maynau, J. Chem. Phys. **103**, 2576 (1995).

[13] R. S. Epstein, Phys. Rev. **28**, 695 (1926); R. K. Nesbet, Proc. R. Soc. London Ser. A **230**, 312 (1955); P. Claverie, S. Diner, and J. P. Malrieu, Int. J. Quantum Chem. **1**, 751 (1967).

[14] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).

[15] H. P. Kelly, Adv. Chem. Phys. **14**, 142 (1966); M. B. Lepetit and J. P. Malrieu, J. Chem. Phys. **87**, 5937 (1987).

[16] B. Miguel, J. P. Malrieu, and A. Pellegatti, Int. J. Quantum Chem. **S29** 245 (1995).

[17] J. Meller, J. P. Malrieu, and R. Caballol, J. Chem. Phys. **104**, 4068 (1996).

[18] M. A. Bethe, Z. Phys. **71**, 205 (1931); L. Hulthen, Ark. Mat. Astron. Fys. A **26**, 11 (1938).

[19] M. B. Lepetit and E. Manousakis, Phys. Rev. B **48**, 1028 (1993).

[20] T. Barnes, D. Kotchan, and E. S. Swanson, Phys. Rev. B **39**, 4357 (1989).

[21] M. A. Garcia-Bach, P. Blaise, and J. P. Malrieu, Phys. Rev. B **46**, 15 645 (1992).

[22] J. Carlson, Phys. Rev. B **40**, 846 (1986); N. Trivedi and D. M. Ceperley, *ibid.* **41**, 4552 (1990).

[23] P. W. Anderson, Phys. Rev. **86**, 694 (1952); T. Oguchi, *ibid.* **117**, 117 (1960).